INTERNATIONAL ATOMIC ENERGY AGENCY

Prospects and Challenges in Application of Radiation for Treating Exhaust Gases

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FOREWORD

Strategies to tackle environmental pollution are receiving increasing attention throughout the world in recent years. Besides improving conventional technologies, new ones are still being developed. Among them technologies for multipollutant control are of great interest.

The electron beam flue gas treatment technology (EBFGT) is one of the most promising technologies for simultaneous removal of multiple pollutants. The process was originally invented in Japan in 1970's. Later on, the process was investigated at the pilot scale plants in USA, Germany, Japan, China, Republic of Korea and Poland. This resulted in construction of commercial scale installation in Poland treating approximately 270,000 Nm$^3$/h of flue gases with the efficiency reaching up to 95% for SO$_x$ and up to 70% for NO$_x$. The by-product of the process is a high quality fertilizer. The advantages of the technology has been clearly demonstrated both from technological and economical points of view.

Recently an important research program has been realized in Maritza East 2 pilot plant in Bulgaria and another one considering application of electron beam technology for treatment of flue gas from heavy oils burning has been undertaken in Saudi Arabia. Apart of the research programs, new industrial plants are concerned. Another implementation of the EBFGT technology of industrial scale is the plant that is being constructed in Jingfeng Power Plant in Beijing (China) and should be put into operation soon. Another commercial plant (Sviloza Thermal Power plant in Svishtov, Bulgaria) is in the design phase.

The IAEA has been supporting the activities by establishing the Technical Cooperation Projects (e.g. POL/8/014, BUL/8/014) and through organizing Advisory Group Meetings, Consultants Meeting, Symposium, Technical Meetings, and Coordinated Research Projects. The Technical Meeting on “Prospects and Challenges in Application of Radiation for Treating Exhaust Gases” held on 14 - 18 May 2007 in Warsaw, Poland was one of the most important ones.

Over 26 participants from different countries have presented papers on the EBFGT process development. These papers contained three main fields of interest: EBFGT technology state of art and development directions, Volatile Organic Compounds (VOCs) treatment by electron beam technology and high power accelerators for electron beam flue gas treatment.

This publication describes the most important results and achievements of the participating groups during the course of this Technical Meeting. The results of the conference may prove to be valuable material for research groups working in the field of radiation technologies for flue gas treatment and may serve as a basis for both pre-feasibility study and technology implementation.

The IAEA wishes to thank all the participants for their valuable contributions and to Mr. A. Pawelec for the compiling of this TECDOC. The IAEA officer responsible for the Technical Meeting and this publication was Ms. Maria Helena de Oliveira Sampa of the Division of Physical and Chemical Sciences.
CONTENTS

SUMMARY ...........................................................................................................7

1. INTRODUCTION ..............................................................................................7

2. PRESENT STATUS AND DEVELOPMENT TRENDS IN EBFGT TECHNOLOGY .................................................................................................8

3. PURPOSE OF THE MEETING AND DISCUSSION TOPICS .........................9

4. MEETING CONCLUSIONS ...............................................................................9

PRESENTATIONS ..................................................................................................14

NATIONAL POLLUTANTS EMISSION LIMITS ..................................................15
A.G. Chmielewski, A. Pawelec

POLLUTANTS EMISSION IN POWER SECTOR ..................................................26
A.G. Chmielewski

JAPAN’S EXPERIENCE OF FLUE GAS TREATMENT BY ELECTRON BEAMS ....35
S. Machi

EXPERIENCES FROM OPERATION OF POMORZANY EBFGT PLANT AND DIRECTIONS OF TECHNOLOGY DEVELOPMENT ......................................43
A. Pawelec, A.G. Chmielewski, B. Tyminski, Z. Zimek, J. Licki, L. Sobolewski,
R. Kostrzewski, J. Mazurek

OPERATIONAL EXPERIENCE OF ELECTRON BEAM FLUE GASES TREATMENT PILOT INSTALLATION AT THE MARITSA EAST 2 THERMAL POWER PLANT .55
N. Dutskinov

POSSIBILITY FOR IMPLEMENTATION OF E-BEAM TECHNOLOGY IN TPS SVILOZA .................................................................................................69
N. Dutskinov, Y. Pelovski, K. Nikolov, L. Stamatov

OVERVIEW OF FLUE GAS TREATMENT IN BRAZIL ......................................76
W.A.P. Calvo, D.C.R. Poli, C.L. Duarte, N.M. Omi, W. Lima

OVERVIEW OF THE EBFGT INSTALLATION SOLUTIONS APPLICABLE FOR FLUE GASES FROM VARIOUS FUELS COMBUSTION .................................92
A.G. Chmielewski, B. Tyminski, A. Pawelec, Z. Zimek, J. Licki

ECONOMIC FEASIBILITY OF EBFGT TECHNOLOGY FOR REMOVAL OF POLLUTANTS FROM COMBUSTION OF LIQUID FUELS ..............................106
A. A. Basfar, O.I. Fageeha, N. Kunnunmal, S. Al-Ghamdi, A. Pawelec, A.G. Chmielewski,
B. Tyminski, Z. Zimek, J. Licki

PROPERTIES AND POSSIBILITIES TO USE BY-PRODUCT FROM E-BEAM INSTALLATIONS FOR PARTIAL RECYCLING OF AMMONIA ..........................118
Y. Pelovski
COLD PLASMA AND ITS APPLICATION FOR EMISSION CONTROL IN POWER PLANTS…………………………………………………………………………………………………139
R.R. Sonde

PROCESSING OF VOLATILE ORGANIC COMPOUNDS BY MICROWAVE PLASMAS...153
J. Mizeraczyk, M. Jasiński, M. Dors, Z. Zakrzewski

THE REMOVAL OF VOC FROM AIR USING EB, MW AND CATALYST – LAPORATOY PLANT RESULTS…………………………………………………………………………………………………163
I. Calinescu, D. Ighigeanu, D. Martin

COMPARISON OF DECOMPOSITION CHARACTERISTICS BETWEEN AROMATIC AND ALIPHATIC VOCS USING ELECTRON BEAM……………………………………………………………………………………………………………..178
Jo-Chun Kim

REMOVAL OF CHLORINATED ORGANIC COMPOUNDS FROM GAS PHASE USING ELECTRON BEAM TECHNOLOGY……………………………………………………………………………………………………………..186
Y. Sun, A.G. Chmielewski, S. Bulka, Z. Zimek

RADIATION-INDUCED DESTRUCTION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS BY DUAL OXIDATION/REDUCTION MECHANISM……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………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SUMMARY

1. INTRODUCTION

The municipal and industrial activities of man lead to environment degradation. The pollutants are emitted to the atmosphere with off-gases from industry, power stations, residential heating systems and vehicles. Fossil fuels, which include coal, natural gas, petroleum, shale oil and bitumen, are the main source of heat and electrical energy. Together with the emission of greenhouse effect gases, it is one of the most important issues regarding environment protection in the region. However, for the next 30 years fossil fuels will be still the dominant energy source in Europe. [1]

All these fuels contain major constituents (carbon, hydrogen, oxygen) as well as other materials, such as metal, sulphur and nitrogen compounds. During the combustion process different pollutants as fly ash, sulphur oxides (SO$_2$ and SO$_3$), nitrogen oxides (NO$_x$ = NO$_2$ + NO) and volatile organic compounds (VOC) are emitted. Fly ash contains different trace elements (heavy metals). These pollutants are present in the atmosphere in such conditions that they can affect man and his environment. Air pollution, caused by a particulate matter and other pollutants, not only affects directly on environment, but also contaminates water and soil and leads to their degradation. Wet and dry deposition of inorganic pollutants leads to acidification of the environment. These phenomena affect human health, increase corrosion and destroy plants and forests. Widespread forest damages have been reported in Europe and North America. Many cultivated plants are not resistant to these pollutants either, especially in the early period of vegetation. Mechanisms of pollutants transformation in atmosphere are described by environmental chemistry. Photochemistry plays an important role in these transformations. SO$_2$ and NO$_x$ are oxidized and sulphuric and nitric acids are thus formed in presence of water vapor, fog and droplets. Another problem caused by human activities is emission of volatile organic compounds to the atmosphere. These emissions cause stratospheric ozone layer depletion, ground level photochemical ozone formation, and toxic or carcinogenic human health effects, contribute to the global greenhouse effect, accumulate and persist in environment.

All these problems are seriously considered and new emission standards are being introduced or prepared both for already limited (SO$_x$, NO$_x$ etc.) and new (eq. VOC, Hg, CO$_2$) pollutants. Desulfurization and denitrification processes are mostly based on lime/limestone flue gas desulphurization (FGD) or selective catalytic reduction (SCR). However, new generation technologies are being developed as well [2]. VOC are removed mostly by the adsorption on the activated carbon process, but this process is rarely used for lean hydrocarbon concentrations up to now. A CO$_2$ sequestration scheme involves three distinct components: *capture of the emitted CO$_2$ from the source followed by compression and dehydration, transportation to the storage site and injection and storage of the CO$_2$ in the geological reservoir. One of the key barriers to the introduction of CO$_2$ sequestration technology is the cost associated with CO$_2$ capture. All these technologies are costly and complicated when used for complex pollutants removal. Therefore, new and more efficient technologies of multipollutant emission control are still developed. One of the most promising technologies and the only one that was already implemented in the industrial scale is electron beam flue gas treatment (EBFGT) technology.

Over the last few decades, extensive work has been carried out in utilizing radiation technology for environmental remediation. This includes application of radiation technology for simultaneous removal of sulphur dioxide and oxides of nitrogen from flue gases, purification of drinking water, wastewater purification and hygienization of sewage sludge for use in agriculture. Some R&D works regard application of radiation technology for conversion of greenhouse effect gases into the marketable products.
2. PRESENT STATUS AND DEVELOPMENT TRENDS IN EBFGT TECHNOLOGY

The electron beam technology for flue gas treatment was developed in Japan in the early 1970's [3]. Japanese scientists demonstrated the removal of SO$_2$ using an electron from a linear accelerator (2 – 12 MeV, 1.2 kW). A dose of 50 kGy at 100°C led the conversion of SO$_2$ to an aerosol of sulfuric acid droplets, which were easily removed.

Ebara Co. used an electron accelerator (0.75 MeV, 45 kW) to convert SO$_2$ and NO$_X$ into a dry product containing (NH$_4$)$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$·NH$_4$NO$_3$ which could be used as a fertilizer. Using the "Ebara process", two larger, pilot scale plants were constructed in Indianapolis, USA and Karlsruhe, Germany. The Indianapolis plant was equipped with two electron beam accelerators (0.8 MeV, 160 kW) and had a capacity of 1.6 - 3.2x10$^4$ m$^3$/h with gas containing 1000 ppm SO$_2$ and 400 ppm NO$_X$. In Karlsruhe, two electron accelerators (0.3 MeV, total power 180 kW) were used to treat 1 – 2x10$^4$ m$^3$/h flue gas containing 50 - 500 ppm SO$_2$ and 300 - 500 ppm NO$_X$.

However the final engineering design technology for industrial applications was achieved at the pilot plants being operated in Nagoya, Japan and Kaweczyn, Poland. The last facility could treat up to 20 000 Nm$^3$/h of flue gas using two accelerators (50 kW, 700 keV each) [4]. In this case new engineering solutions were applied: double – longitudinal gas irradiation, air curtain separating secondary window from corrosive flue gases and modifications of humidification/ammonia system (high enthalpy water or steam injection, ammonia water injection) and others.

As a next step, Ebara Corporation has constructed full scale plant in Chengdu, China mostly for SO$_X$ removal (NO$_x$ removal was assumed to be >10%), therefore the power of accelerators applied is 320 kW for treatment of 270 000 cubic meters per hour of the flue gas. Reported efficiency was over 80% for SO$_X$ [5]. Another similar plant was constructed in Hangzhou, China.

The most successful implementation of the technology was construction of demonstrational, industrial electron beam flue gas treatment plant in coal-fired power plant in Poland. The installation, located in EPS Pomorzany in Szczecin in the north of Poland, purifies flue gases from two Benson boilers of 65 MW$_{th}$ and 100 MW$_{th}$ each. The maximum flow rate of the gases is 270 000 Nm$^3$/h and the total beam power exceeds 1MW. Since the power of accelerators installed at the Polish plant is greater than 1 MW, it is the largest irradiation facility ever built. High efficiency of SO$_X$ and NO$_X$ removal was achieved (up to 95% for SO$_X$ and up to 70% for NO$_X$), and the by-product is a high quality fertilizer [6].

Another implementation of the EBFGT technology in the industrial scale is the plant that is constructed in Jingfeng Power Plant in Beijing, China. The plant is designed for treatment of 630 000 Nm$^3$/h of flue gas with removal efficiency 90% for SO$_2$ and 20% for NO$_X$ [7].

Recently, another pilot plant was tested (flow 10 000 Nm$^3$/h; 3x30 kW, 800 keV) in Bulgaria to treat high humidity, high SO$_X$ gases from combustion of low-grade lignite. The plant has achieved very good pollutant removal ranges from 87 to 97% for SO$_X$ and 85-90% for NO$_X$. The obtained by-product is of good quality with moisture content less than 1% and nitrogen content approximately 21% and higher (recommended value for use in commercial fertilizer is 21%). Full scale industrial plant is going to be constructed in this country.

There can be observed three ways of EBFGT technology development:

- improvement of the technology for SO$_X$ and NO$_X$ removal and new fields of technology application,
- research on VOC and other pollutants removal,
- development in high power electron accelerators.

All these topics were discussed during the meeting.
3. PURPOSE OF THE MEETING AND DISCUSSION TOPICS

The Technical Meeting on “Prospects and Challenges in Application of Radiation for Treating Exhaust Gases” was held on 14 to 18 May 2007 in Warsaw, Poland. The purpose of this meeting was to review the present status of the technology development focusing:

a) general problems concerning air pollution control,

b) flue gases treatment using electron beam,

c) recent developments of electron beam machines for treatment of flue gases, VOCs., etc.

The participants have discussed observed trends in EBFGT development. Status and possibility of commercialization of EBFGT technology and/or products were reviewed. The opportunities of radiation technology applications, based on needs and advantages of the technique, was reviewed as well.

4. MEETING CONCLUSIONS

4.1. General remarks- review on new trends in EBFGT process

The electron beam flue gas treatment technology is very attractive. The process allows for effective simultaneous removal of SO$_2$ and NO$_x$, and other pollutants (VOC, dioxins), that makes it universal multipollution control system with wide spectrum of potential applications. Process idea as well as facility construction is simple and most of apparatus are routinely used in the industry. This makes easy retrofitting and unification of the EBFGT facility with the power plant. With its high flexibility, the installation may be used in different modes (ex. winter and summer operation of thermal power plant) and may be easily upgraded for future modernizations. Not less important is the by-product, which is fully usable, very clean fertilizer. Also preliminary economical calculations indicate for competitiveness of the EBFGT process comparing to set of wet-FGD and SCR processes.

Research on market status of by-product confirmed, that there is real demand for such kind of fertilizer. In this way operational costs of the plant might be partially reduced by by-product selling. It is worth to notice that commercial value of by-product varies from 30 to 130 USD/tone according local market prices in various countries.

Fossil fuel especially carbon is still the most often used source of energy. Due to great importance of CO$_2$ emission limitation, focus on ‘Carbon Capture & Sequestration’ is gradually increasing. Today, it is imperative for the ‘Emission Control Technologies’ for SPM, NO$_x$ and SO$_x$ to be compliant with the ‘Carbon Capture Technologies’. Almost all known routes of carbon capture demands for total removal of SO$_x$. Electron beam flue gas treatment technology allows for very high level of SO$_x$ removal efficiency. Also it removes NO$_x$, particulates and other pollutants. In this way this technology may be used for preparation of flue gas for CO$_2$ capture.

However there are many advantages of the EBFGT technology, there are still some weak points that halt the process implementation in the industry. The most important is the high power accelerators state-of-art. The power of existing accelerators allows for construction of flue gas treatment facilities for low and medium size power generation units. On the other hand, the reliability of such big machines is still regarded as not satisfactory (over 8500 hours of operation per year is required) and the price of this apparatus is very high.

The second point is high investment risk of such enterprise. At this moment there is only one reference facility in the world – installation constructed at Pomorzany Electric Power Plant in Poland. Also no company in the world can offer key ready EBFGT facility. On the other hand wet-FGD process is the most popular desulphurization process and most of power plants in the industrialized countries are already equipped in such installations. In this case there is no point to double SO$_2$ removal system.

The breaking point of the technology development may be its commercialization. The first step of the whole process development is development of the crucial element of the chain – the
accelerators. Higher power and more reliable accelerators will allow for further implementations of the technology. With the increase of the implementations of the technology the demand for accelerators will increase that should result in reducing of the accelerators' price.

Another element is reducing the investment risk of new facilities. There success of projects in China, Bulgaria and Saudi Arabia may be an impulse for the investors. Of course the market in Europe, United States and other industrialized parts of the world according to power plants is already saturated by conventional desulphurization methods. Therefore new regions and new fields of application should be sought. EBFGT technology may be applied in the regions of the world, where emission control regulations were introduced recently. The second direction is application for the processes different then coal combustion. As the technology may be applied for more then two main pollutants it can be used in different branches of industry (eg. ore sintering off gases, waste incineration plants etc). The recent research also indicates that it can be used for treatment of the gas from combustion of fuels other then coal. New plants and processes, where no emission control method is used may be the chance for application of EBFGT technology.

The last, but not least problem is economy of the process. It seems that the process is economically attractive in the case of both pollutants removal and the market status of by-product is crucial for the operational costs of the plant. However the data available at the moment are not enough convincing for the investors. Therefore further studies on the process economy are welcome.

4.2. Electron beam VOCs treatment

The other possible application of the technology is VOC primarily and polycyclic aromatic hydrocarbons (PAH) removal, e.g. in flue gas treatment facilities for municipal waste incinera

The EB technology as potential process for volatile organic compounds (VOC) removal from flue gas has been investigated since 1990'. The applicability of EB technology to control the emission of VOCs has been studied in laboratory scale for wide range of aromatic (e.g.: benzene, toluene, xylene, styrene, ethylbenzene, diphenylether, etc.); aliphatic (pentene, hexane, heptane, cyclohexane, methanol, formaldehyde, etc.) and chlorinated hydrocarbons (dichloromethane, tetrachloromethane, dichloroethane, trichloroethylene, etc.). The removal process is based on oxidation by active species like OH radicals, O atoms and O\(_3\) produced in irradiated gas. The oxidation pathway is similar to atmospheric chemistry, but EB process decomposition is more rapid as the flue gas molecules are transformed into active oxidizing species with concentration much higher than in the atmosphere causing fast VOC decomposition. In the case of chlorinated organic compounds secondary thermalized electrons play also important role in the initialization of decomposition processes and this process is characteristic for non-thermal plasma treatment.

The EB treatment of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans PCDD/F was performed in Japan at the Takahama municipal waste incineration unit. Decomposition ratio obtained at 15 kGy was 90% or higher, initial PCDD/F concentration was reduced below the regulation limits set up in EU, US and Japan.

The effectiveness of electron beam irradiation on 16 Polycyclic Aromatic Hydrocarbons (PAH), present in the flue gas from coal combustion process, has been investigated in pilot scale in Poland. The results of performed work demonstrated that simultaneously with EB DeSO\(_x\) and DeNO\(_x\) process, total initial concentration of 16 PAH ~10\(^{-3}\) ppmv was reduced to ~10\(^{-4}\) ppmv at the dose of 8 kGy resulting in the flue gas global toxicity decrease.
4.3. High power accelerators for EBFGT

The basic principle of any accelerator is that the electric field acts on electrons as charged particles and gives the energy equal to the voltage difference across the acceleration gap. The electric field comes directly from high voltage electrodes or indirectly from the electromagnetic field.

Although there are many accelerator manufacturers offering a wide range of accelerators performance ratings, only few would be suitable for particular application. The availability of reliable well constructed accelerators which may operate in harsh industrial conditions is the key factor for further technology implementation. The lessons learned during the operation of Chinese and Polish industrial plants have demonstrated that the accelerators applied there do not meet these criteria and have to be replenished. Radiation facility should be designed with possibly:

- Low electron energy to reduce investment and unit operation costs,
- High beam power to increase productivity and reduce unit operation cost,
- High accelerator electrical efficiency to reduce exploitation and unit operation costs,
- High beam utilization to increase productivity and reduce unit operation cost.

High power accelerators have been developed to meet specific demands of environmental application and high throughput processes to increase the capacity and reduced unit cost of operation. Such accelerator construction must be compromise between size, efficiency and cost in respect to the field of its application. The most important feature of radiation processing is relatively high capital cost of an irradiation facility. This means that capital amortization is a major item in the operating cost. Appropriate accelerator selection should be performed to meet all technical and economical conditions for successful process implementation. The unit costs tend to decrease as the throughputs increase. Optimization of electron beam utilization by proper arrangement of irradiation unit increases productivity and reduces unit operation cost. Significant unit cost reduction can be obtained for implementation lower dose level.

4.3.1. Brief characterization of accelerators' constructions

The major difference between different accelerators applied in radiation processing is the method by which electric field is generated. Due to energy range and beam power level the most common constructions for radiation processing are direct accelerators, single cavity resonant accelerators and microwave linacs. The most suitable high power accelerator constructions for industrial scale flue gas treatment process are at present direct power line transformer accelerators. Different constructions of high power accelerators have been described in literature. Some of them could be selected for flue gas treatment process if their manufactures would be able to fulfill all requirements regarding electron energy, beam power, electrical efficiency, reliability/availability according to industrial practice and low price related to beam power.

**CW Linear accelerator**

The family of compact modular continuous wave (cw) linear electron accelerator has been designed and tested. The accelerator modules are now capable to accelerate 50 mA average beam current with electron energy increments 600 keV what corresponds to 30 kW beam power. Klystron operated at frequency 2.45 GHz was used. Electrical efficiency of the accelerator based on designed modules amounts 40%. Although high power microwave sources are now available, presented construction does not fit requirements of flue gas treatment process due to relatively low average current and low electrical efficiency.

**Single cavity resonance accelerator**

TT 1000 Rhodotron capable to deliver 5 and 7 MeV electron beams with average current intensity of 100 mA has been designed and tested. The electron accelerating concept is based on single cavity which is crossed several times by recirculation electron beam. Beam power up to 700 kW has
Working Material

been obtained with maximum electrical efficiency 55%. Several beams passing the same cavity concept is under consideration to increase average beam current and maintain high beam power with lower electron energy level. This conceptual design has not been tested yet.

High power compact transformer electron accelerator

High power compact transformer electron accelerator has been designed and tested at Institute of Nuclear Physics in Novosibirsk, Russia in connection to development of accelerating unit for experiments in the field of high energy physics. Compact power supply operated at 1 MV voltage with power 300 kW and outside diameter 1.2 m was used. The size of power unit was reduced due to applied 1 kHz power line frequency and SF₆ gas isolation. Power supply electrical efficiency of 95% has been achieved. The power supply was connected to accelerating section by HV feeder with gas isolation. Unfortunately this very promising construction has not been commercialized and there is no evidence about its exploitation performances.

High repetition pulsed accelerator

Design of the multi-beam accelerator was reported by Dolbilov et al. from JINR, Dubna, Russia. The parameters of the accelerator are as follows: energy 600 - 700 kV, beam power up to 300 - 350 kW, pulse current 5 A, pulse duration 10-20 µs, frequency 10 - 20 kHz, high efficiency 95%, low energy losses in extraction window. A coaxial spiral-line resonator serves as a high voltage power supply. Electron beams are generated by a mosaic cold cathode with threshold emission. Cold pyrolitic cathodes are located in such way that electrons emitted from a given cathode go to corresponding window. Threshold level is close to max. voltage and the electron energy dispersion are smaller than 15%. High beam current, high beam power, low cost, high reliability are expected. Unfortunately there is no evidence about industrial application of this interesting construction.

Induction accelerator

Induction accelerators are capable to deliver high power electron beams at energies of 1 - 10 MeV. Induction accelerator based on all-solid-state technology (modulator efficiency 85%) is in operation at Science Research Laboratory, Somerville, U.S.A. The following parameters have been obtained: electron energy 1.5 MeV, pulse duration 50 ns, pulse beam current 500 A, repetition rate 5 kHz, beam power up to 500 kW, efficiency >50%. Series of experiments were performed at SRL to demonstrate the capabilities of induction linacs for industrial applications. In spite of shown promise there is no commercial proposals regarding to high power industrial induction accelerator with confirmed performances including reliability.

Coupled-Multiplier Accelerator

A new approach to efficient high voltage generation at MV level has been recently demonstrated. High voltage is produced by a series of modules, each of which consists of a high-power alternator, step-up transformer, and 3-phase multiplier circuit. The alternators are connected mechanically along a rotating shaft driven by electrical motor. Relatively low cost and efficiency 67% have been reported. The first 1 MV and 100 kW of the coupled multiplier accelerator will be installed at a petrochemical plant and used to treat industrial wastewater. 2 MeV and 200 kW accelerating unit has been designed.

4.3.2. Accelerators for flue gas treatment

The principal parameters to be achieved for accelerators applied for flue gas treatment in pilot and industrial facility are as follows:

- **Electron energy**: 0.8 – 1.5 MeV
- **Beam power**: 100 – 500 kW
- **High reliability for long time operation**: (6000 h/y), >95 %,
- **Availability**: >95 %,
- **Electron beam cost**: ~2.5 $/W,
• Electrical efficiency $>80\%$,
• High current density, low level losses windows,
• Fault protection systems.

Manufacturers of high power transformer accelerators who are interested and capable to participate in practical implementation flue gas treatment technology are listed below:
• RDI - Radiation Dynamics, USA (power line frequency transformer),
• Wasik Associates, USA (power line frequency transformer),
• NIIIEFA - Sci. Inst. of Electrophysical Apparatus, Russia (power line frequency transformer),
• BINP - Institute of Nuclear Physic, Russia (coreless transformer),
• Vivirad, France (ICT transformer).

There is a great role of the International Atomic Energy Agency in the process of electron beam flue gas treatment technology development. IAEA was involved from very beginning in the technology promotion. TC projects have been implemented in Poland, Bulgaria and Ukraine. The new TC project is being implemented in Saudi Arabia. The Agency is coordinating CRP on VOC electron beam treatment as well. The future success of the technology will be common success of scientists, engineers and IAEA.

REFERENCES

PRESENTATIONS
NATIONAL POLLUTANTS EMISSION LIMITS

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Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Abstract

Fossil fuels are the main energy sources. Unfortunately the vast quantities of pollutants are emitted to the atmosphere during their combustion. These emissions lead to the environment degradation and affect human health. Therefore most of the countries have introduced the standards concerning emission control. These regulations for some countries are presented in the paper.

Key words; fossil fuel combustion, SO$\textsubscript{x}$, NO$\textsubscript{x}$, emission limits

1. INTRODUCTION

The problems of environmental damage and degradation of natural resources are receiving increasing attention throughout the world in recent years. The increasing population, higher living standards, increasing urbanization and enhanced industrial activities of mankind are all leading to degradation of environment. For example, fossil fuels, which include coal, natural gas, petroleum, shale oil and bitumen, are the main primary source of heat and electrical energy production, are responsible for emitting a large number of pollutants into the atmosphere with off-gases from industries, power stations, residential heating systems and vehicles. All these fuels contain major constituents (carbon, hydrogen, oxygen) as well as other materials, such as metal, sulphur and nitrogen compounds. During the combustion process different pollutants like fly ash, sulphur oxides (SO$\textsubscript{2}$ and SO$\textsubscript{3}$), nitrogen oxides (NO$\textsubscript{x}$ = NO$\textsubscript{2}$ + NO) and volatile organic compounds are emitted. Fly ash contains different trace elements (heavy metals). Air pollution, caused by a particulate matter and other pollutants, not only affects directly on environment, but also contaminate water and soil and leads to their degradation. Wet and dry deposition of inorganic pollutants leads to acidification of environment. These phenomena affect human health, increase corrosion, and destroy plants and forests. Widespread forest damages have been reported. Many cultivated plants are not resistant to these pollutants either, especially in the early period of vegetation. Mechanisms of pollutants transformation in atmosphere are described by environmental chemistry. Photochemistry plays an important role in these transformations. SO$\textsubscript{2}$ and NO$\textsubscript{x}$ are oxidized, sulphuric and nitric acids, which are formed in presence of water vapour, fog and droplets result in so called “acid rain” precipitation. In recent years, the knowledge that emission of volatile organic compounds to the atmosphere can cause stratospheric ozone layer depletion, ground level photochemical ozone formation, and toxic or carcinogenic human health effects and contribute to the global greenhouse effect has added a new dimension to the environmental degradation as a result of burning of fossil fuels. Ironically, coal and high sulphur oil the dirtiest fuels among hydrocarbons, is expected to remain the main fossil fuels for the next two centuries. How so ever one may wish, the necessity of increasing use of the fossil fuels will continue to meet the increasing demands of the developed and developing countries. Thus, there exists an urgent need develop technologies that reduce or minimize the pollution associated with this unavoidable necessity. However these technologies are being applied only in the countries which have introduced pollutions emission limits.

2. EMISSION LIMITS FOR SELECTED COUNTRIES

In most European countries, the emission limits are correlated with European Union directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants. The document regulates the emission of SO$\textsubscript{2}$, NO$\textsubscript{x}$ and dust which are the major problems in the case of fuel combustion. According to this document, emission limits are determined based on type of fuel and thermal input of the plant. Pollutants concentrations in flue gases are standardized for normal conditions, dry gases and oxygen content 6% for solid fuels and 3% liquid fuels. The values of the limits of SO$\textsubscript{2}$, NO$\textsubscript{x}$ and dust for existing and new plants are presented in Table I and II.
### TABLE I. EMISSION LIMIT VALUES FOR EXISTING PLANTS ACCORDING TO DIRECTIVE 2001/80/EC.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Fuel type</th>
<th>Emission limit values [mg/Nm³]</th>
<th>50 to 100 MW_{th}</th>
<th>100 to 300 MW_{th}</th>
<th>300 to 500 MW_{th}</th>
<th>&gt; 500 MW_{th}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Solid</td>
<td></td>
<td>2000</td>
<td>2000 to 400</td>
<td>1700</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td>1700 to 400</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Gaseous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35            (general case)</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Solid</td>
<td></td>
<td></td>
<td>600</td>
<td></td>
<td>500           (200 from 1.01.2016)</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td></td>
<td>450</td>
<td></td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Gaseous</td>
<td></td>
<td></td>
<td>300</td>
<td></td>
<td>200</td>
</tr>
<tr>
<td>Dust</td>
<td>Solid</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gaseous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5             (general case)</td>
</tr>
</tbody>
</table>

The directive also regulates emission ceilings that are to be attained by 2010 according to Gothenburg Protocol. The emission ceilings for SO₂ and NOₓ for selected European countries are given in Table III.

### TABLE II. EMISSION LIMIT VALUES FOR NEW PLANTS ACCORDING TO DIRECTIVE 2001/80/EC.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Fuel type</th>
<th>Emission limit values [mg/Nm³]</th>
<th>50 to 100 MW_{th}</th>
<th>300 to 500 MW_{th}</th>
<th>&gt; 500 MW_{th}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>Solid (general case)</td>
<td></td>
<td>850</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td>850</td>
<td>400 to 200</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Gaseous</td>
<td></td>
<td></td>
<td></td>
<td>35            (general case)</td>
</tr>
<tr>
<td>NOₓ</td>
<td>Solid (general case)</td>
<td></td>
<td>400</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td>400</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Gaseous (natural gas)</td>
<td></td>
<td></td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>Dust</td>
<td>Solid</td>
<td></td>
<td>50</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
<td>50</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>Gaseous</td>
<td></td>
<td></td>
<td></td>
<td>5             (general case)</td>
</tr>
</tbody>
</table>
TABLE III. NATIONAL SO₂ AND NOₓ EMISSION CEILINGS FOR SELECTED EUROPEAN COUNTRIES.

<table>
<thead>
<tr>
<th>Country</th>
<th>National emission ceilings in 1000 tons</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO₂</td>
<td>NOₓ</td>
</tr>
<tr>
<td>Austria</td>
<td>39</td>
<td>103</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>265</td>
<td>286</td>
</tr>
<tr>
<td>Finland</td>
<td>110</td>
<td>170</td>
</tr>
<tr>
<td>France</td>
<td>375</td>
<td>810</td>
</tr>
<tr>
<td>Germany</td>
<td>520</td>
<td>1051</td>
</tr>
<tr>
<td>Greece</td>
<td>523</td>
<td>344</td>
</tr>
<tr>
<td>Hungary</td>
<td>500</td>
<td>198</td>
</tr>
<tr>
<td>Lithuania</td>
<td>145</td>
<td>110</td>
</tr>
<tr>
<td>Poland</td>
<td>1397</td>
<td>879</td>
</tr>
<tr>
<td>Slovakia</td>
<td>110</td>
<td>130</td>
</tr>
<tr>
<td>Spain</td>
<td>746</td>
<td>847</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>585</td>
<td>1167</td>
</tr>
</tbody>
</table>

On the basis of the above regulations, more detailed national emission standards are elaborated. Polish emission standards are given in Minister of Environment Order from 20 December 2005. This act regulates emission of air contaminating substances from various technological processes in complex. Emission standards for SO₂ and NOₓ are set different according to fuel type, heat input of the source and operation period. Polish emission standards of SO₂ and NOₓ for existing plants and selected fuels are presented in Table IV and V. Pollutants’ concentrations are standardized for dry gas, normal conditions and oxygen content 6% for solid fuels and 3% for liquid fuels.
TABLE IV.  SO$_2$ EMISSION STANDARDS IN POLAND FOR EXISTING PLANTS AND SELECTED FUELS.

<table>
<thead>
<tr>
<th>Heat input of the source [MW]</th>
<th>Emission limits [mg/Nm$^3$]</th>
<th>Plants constructed before 29.03.1990</th>
<th>Plants constructed after 28.03.1990</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Until 31.12.2007</td>
<td>From 1.01.2008</td>
</tr>
<tr>
<td><strong>Hard coal combustion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;5</td>
<td>2000</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>5 to 50</td>
<td>2000</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>50 to 100</td>
<td>2000</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>100 to 225</td>
<td>2350</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>225 to 500</td>
<td>2350</td>
<td>1500 to 400 (linear decrease)</td>
<td></td>
</tr>
<tr>
<td>&gt;500</td>
<td>2350</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td><strong>Lignite combustion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 50</td>
<td>2500</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>50 to 100</td>
<td>2500</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>100 to 225</td>
<td>2500</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>225 to 500</td>
<td>2500</td>
<td>1500 to 400 (linear decrease)</td>
<td></td>
</tr>
<tr>
<td>&gt;500</td>
<td>2500</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td><strong>Liquid fuels combustion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;5</td>
<td>4375</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td>5 to 50</td>
<td>4375</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td>50 to 300</td>
<td>3500</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td>300 to 500</td>
<td>3500</td>
<td>1700 to 400 (linear decrease)</td>
<td></td>
</tr>
<tr>
<td>&gt;500</td>
<td>3500</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>
**TABLE V.** NO<sub>x</sub> EMISSION STANDARDS IN POLAND FOR EXISTING PLANTS AND SELECTED FUELS.

<table>
<thead>
<tr>
<th>Heat input of the source [MW]</th>
<th>Emission limits [mg/Nm&lt;sup&gt;3&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plants constructed before 29.03.1990</td>
</tr>
<tr>
<td></td>
<td>From 1.01.2016</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard coal combustion</td>
<td></td>
</tr>
<tr>
<td>&lt;50</td>
<td>400</td>
</tr>
<tr>
<td>50 to 50</td>
<td>600</td>
</tr>
<tr>
<td>&gt;500</td>
<td>540</td>
</tr>
<tr>
<td>Lignite combustion</td>
<td></td>
</tr>
<tr>
<td>&lt;500</td>
<td>500</td>
</tr>
<tr>
<td>&gt;500</td>
<td>500</td>
</tr>
<tr>
<td>Liquid fuels combustion</td>
<td></td>
</tr>
<tr>
<td>&lt;50</td>
<td>450</td>
</tr>
<tr>
<td>50 to 50</td>
<td>630</td>
</tr>
<tr>
<td>&gt;500</td>
<td>630</td>
</tr>
</tbody>
</table>

Facilities constructed after 27 November 2003 are considered as new plants. Table VI gives the emission standards for new plants in Poland (general case).

**TABLE VI.** GENERAL CASE SO<sub>2</sub> AND NO<sub>x</sub> EMISSION STANDARDS FOR NEW PLANTS IN POLAND

<table>
<thead>
<tr>
<th>Heat input of the source [MW]</th>
<th>Emission limits [mg/Nm&lt;sup&gt;3&lt;/sup&gt;]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>Solid fuels</td>
</tr>
<tr>
<td>&lt;5</td>
<td>1500</td>
</tr>
<tr>
<td>5 to 50</td>
<td>1300</td>
</tr>
<tr>
<td>50 to 100</td>
<td>850</td>
</tr>
<tr>
<td>100 to 300</td>
<td>200</td>
</tr>
<tr>
<td>&gt;300</td>
<td>200</td>
</tr>
</tbody>
</table>

In the United States of America, sulfur dioxide (SO2) emissions are restricted under the Clean Air Act Amendments of 1990. The CAAA established the Acid Rain Program, under Title IV, which requires major reductions of SO2 (and NOx) emissions in two phases. A nationwide cap-and-trade program was created to promote the most cost-effective compliance. Fuel switching to lower sulfur fuels and installation of flue gas desulfurization (FGD) systems (also referred to as scrubbers) have been used to comply with the SO2 limits. As the nationwide SO2 cap is reduced in 2010 as specified in the CAAA, additional SO2 control equipment will be needed for continued compliance.
The goal of this act was to reduce SO2 emission by 10 million tons below 1980 level and NOx emission by 2 million tons by 2000. It also established SO2 emission trading system (cap and trade), which is a base of SO2 emission management in USA. The national emission cap for SO2 was set to 8.95 million tons.

In March 2005, the U.S. Environmental Protection Agency promulgated the Clean Air Interstate Rule (CAIR). The CAIR limits SO2 and NOx emissions in the Eastern U.S. In contrast to the Acid Rain Program, which set a nationwide cap on SO2 emissions, the CAIR sets region-wide emission caps for SO2. Emission reductions are to be achieved in two phases (2010 and 2015). When fully implemented, the CAIR will reduce SO2 emissions in 28 Eastern states and the District of Columbia by over 70%. The CAIR applies to fossil fuel burning, electric generating units in the region that are greater than 25 MW.

An allowance authorizes a utility or industrial source to emit certain amount of SO2 during a given year or any year thereafter. EPA allocated allowances at an emission rate of 2.5 pounds of SO2/mmBtu (million British thermal units) of heat input, multiplied by the unit’s baseline mmBtu (the average fossil fuel consumed from 1985 through 1987). At the end of each year, the source must hold an amount of allowances at least equal to its annual emissions, i.e., a source that emits 5000 tons of SO2 must hold at least 5,000 allowances that are usable in that year. Allowances are fully marketable commodities. Once allocated, allowances may be bought, sold, traded, or banked for use in future years. Allowances may not be used for compliance prior to the calendar year for which they are allocated. SO2 cap and trade system was introduced in 1995.

Beside Clean Air Act, that is basic federal level law regulation, NOx emission is covered by NOx State Implementation Plans (SIP) Call of 24 September 1998. This state level act allowed to introduce NOx emission trading system by allocating state emission limit. NOx cap and trade system was introduced in 2003.

However, regardless of how many allowances a source holds, it is never entitled to exceed the limits set under Title I of Clean Air Act to protect public health. The emission limits can be found under New Source Performance Standards (NSPS) on the regulation of emissions from various types of industrial facilities, Code of Federal Regulations (SFR), Title 40 Protection of Environment, Part 60 Standards and Performances for New Stationary Sources. Apart from fulfilling the emission standards it is required to install Best Available Control Technology (BACT, BAT) during construction phase. Next, standards for two main groups of stationary sources: electric utility steam generating units and industrial steam generating units are presented.

The sulfur dioxide emission standards of performance for electric utility steam generating units for which construction is commenced after September 18, 1978 are written with consideration of type of fuel and year of construction or modification of the plant.

For the plants constructed or modernized before 28 February 2005 which combust solid or solid derived fuels, SO2 emission limit is:

- 520 ng/J (1.20 lb/million BTU) heat input and or 10% of potential combustion concentration (90% reduction), or
- 30% of potential combustion concentration (70% reduction) when emission is less than 260 ng/J (0.60 lb/million BTU) heat input.

For the plants constructed or modernized before 28 February 2005 which combust liquid or gaseous fuels, SO2 emission limit is:

- 340 ng/J (0.80 lb/million BTU) heat input and or 10% of potential combustion concentration (90% reduction), or
- 100% of potential combustion concentration (0% reduction) when emission is less than 86 ng/J (0.20 lb/million BTU) heat input.

When different fuels are combusted simultaneously, the emission standards are determined by the following formulas:
Working Material

- for sulfur dioxide emission greater than 260 ng/J (0.60 lb/million BTU) heat input
  \[ E_s = \frac{(340 \times x + 520 \times y)}{100} \text{ and } \%P_s = 10 \]

- for sulfur dioxide emission less then 260 ng/J (0.60 lb/million BTU) heat input
  \[ E_s = \frac{(340 \times x + 520 \times y)}{100} \text{ and } \%P_s = \frac{(10 \times x + 30 \times y)}{100}, \text{ where} \]

\( E_s \) is sulfur dioxide emission limit in ng/J,
\( \%P_s \) is the percentage of potential SO\(_2\) emission allowed,
\( x \) is the percentage of total heat input derived from combustion of liquid or gaseous fuels
\( y \) is the percentage of total heat input derived from combustion of solid or solid derived fuels.

In the case of new plants (constructed, reconstructed or modified after 28 February 2005) the following emission regulations are to be used:

- for facilities, which construction commenced after 28 February 2005
  180 ng/J (1.4 lb/million BTU) gross energy output on a 30-day rolling average basis, or
  5% of the potential combustion concentration (95% reduction) on a 30-day rolling average basis;

- for facilities, which reconstruction commenced after 28 February 2005
  180 ng/J (1.4 lb/million BTU) gross energy output on a 30-day rolling average basis, or
  65 ng/J (0.15 lb/million BTU) heat input on a 30-day rolling average basis, or
  5% of the potential combustion concentration (95% reduction) on a 30-day rolling average basis;

- for facilities, which modification commenced after 28 February 2005
  180 ng/J (1.4 lb/million BTU) gross energy output on a 30-day rolling average basis, or
  65 ng/J (0.15 lb/million BTU) heat input on a 30-day rolling average basis, or
  10% of the potential combustion concentration (90% reduction) on a 30-day rolling average basis.

The standards of performance for industrial-commercial-institutional steam generating units set, that in general case, SO\(_2\) emission limit for the plants constructed or modified before 28 February 2005 must not exceed 87 ng/J (0.20 lb/mmBTU) not regarding the fuel type or 10% of potential sulfur dioxide emission rate (90% reduction) must be achieved. In this case the emission limit is determined according to the formula:

\[ E_s = \frac{(K_a H_a = K_b H_b)}{(H_a+H_b)}, \text{ where} \]

\( E_s \) is sulfur dioxide emission limit given in ng/J or lb/million BTU heat input,
\( K_a \) is 520 ng/J (or 1.2 lb/million BTU),
\( K_b \) is 340 ng/J (or 0.80 lb/million BTU),
\( H_a \) is the heat input from the combustion of coal given in J (million Btu),
\( H_b \) is the heat input from the combustion of oil given in J (million Btu).

For the combustion of coal refuse alone in fluidized bed combustion steam generating unit the emission limit is 87 ng/J (0.20 lb/mmBTU) or 20% of potential sulfur dioxide emission rate (80% reduction) must be achieved. If coal refuse is combined with any other fuel general rules must be applied.

In the case of application of emerging technology for the sulfur dioxide emission control, the only rule is 50% reduction of the potential sulfur dioxide emission rate, but the emission limit is calculated using different emission factors. The formula for calculation of SO\(_2\) emission limit in this case is following:

\[ E_s = \frac{(K_c H_c = K_d H_d)}{(H_c+H_d)}, \text{ where} \]

\( E_s \) is sulfur dioxide emission limit given in ng/J or lb/million BTU heat input,
\( K_c \) is 260 ng/J (or 0.60 lb/million BTU),
\( K_d \) is 170 ng/J (or 0.40 lb/million BTU),
\( H_c \) is the heat input from the combustion of coal given in J (million Btu),
\( H_d \) is the heat input from the combustion of oil given in J (million Btu).
H₂ is the heat input from the combustion of oil given in J (million Btu).

New sources (constructed or modified after 28 February 2005) are obliged not to exceed 87 ng/J (0.20 lb/mmBTU) or 8% of potential sulfur dioxide emission rate (92% reduction) for 520 ng/J (1.2 lb/million Btu) must be achieved regardless the type of fuel.

The nitrogen oxides (expressed as NOₓ) emission standards of performance for electric utility steam generating units for which construction is commenced after September 18, 1978 and NOₓ reduction requirements are given in Table VII.

**TABLE VII. NOₓ EMISSION LIMITS AND REDUCTION REQUIREMENTS FOR ELECTRIC UTILITY STEAM GENERATION UNITS IN THE USA.**

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Emission limit for heat input</th>
<th>Percent reduction of potential combustion concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng/J</td>
<td>lb/million Btu</td>
</tr>
<tr>
<td>Gaseous fuels:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coal derived fuels</td>
<td>210</td>
<td>0.50</td>
</tr>
<tr>
<td>all other fuels</td>
<td>86</td>
<td>0.20</td>
</tr>
<tr>
<td>Liquid fuels:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coal derived fuels</td>
<td>210</td>
<td>0.50</td>
</tr>
<tr>
<td>shale oil</td>
<td>210</td>
<td>0.50</td>
</tr>
<tr>
<td>all other fuels</td>
<td>130</td>
<td>0.30</td>
</tr>
<tr>
<td>Solid fuels:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coal derived fuels</td>
<td>210</td>
<td>0.50</td>
</tr>
<tr>
<td>fuels containing more than 25% lignite</td>
<td>340</td>
<td>0.80</td>
</tr>
<tr>
<td>subbituminous coal</td>
<td>210</td>
<td>0.50</td>
</tr>
<tr>
<td>bituminous coal</td>
<td>260</td>
<td>0.60</td>
</tr>
<tr>
<td>anthracite coal</td>
<td>260</td>
<td>0.60</td>
</tr>
<tr>
<td>all other fuels</td>
<td>260</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case, when two or more fuels are combusted simultaneously the appropriate emission standard is calculated according to formula:

\[ E_{\text{n}} = \frac{(86 \times w + 130 \times x + 210 \times y + 260 \times z + 340 \times v)}{100} \]

where \( E_{\text{n}} \) is applicable NOₓ emission limit expressed in ng/J heat input, \( w, x, y, z, v \) are the percentages of total heat input derived from the combustion of fuels subject to respectively 86, 130, 210, 260 and 340 ng/J heat input standard.

In the case of new plants (constructed, reconstructed or modified after 28 February 2005) the following emission limits are set:

- for facilities, which construction commenced after 28 February 2005
  130 ng/J (1.0 lb/million BTU) gross energy output on a 30-day rolling average basis;
for facilities, which reconstruction commenced after 28 February 2005
130 ng/J (1.0 lb/million BTU) gross energy output on a 30-day rolling average basis, or
47 ng/J (0.11 lb/million BTU) heat input on a 30-day rolling average basis;

for facilities, which modification commenced after 28 February 2005
180 ng/J (1.4 lb/million BTU) gross energy output on a 30-day rolling average basis, or
65 ng/J (0.15 lb/million BTU) heat input on a 30-day rolling average basis.

The standards of performance for industrial-commercial-institutional steam generating units in
general case are given in Table VIII.

<table>
<thead>
<tr>
<th>Fuel/Steam generating unit type</th>
<th>Emission limit (expressed as NOₓ) for heat input</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ng/J</td>
</tr>
<tr>
<td>Natural gas and distillate oil:</td>
<td></td>
</tr>
<tr>
<td>low heat release rate</td>
<td>43</td>
</tr>
<tr>
<td>high heat release rate</td>
<td>86</td>
</tr>
<tr>
<td>Residual oil:</td>
<td></td>
</tr>
<tr>
<td>low heat release rate</td>
<td>130</td>
</tr>
<tr>
<td>high heat release rate</td>
<td>170</td>
</tr>
<tr>
<td>Coal:</td>
<td></td>
</tr>
<tr>
<td>mass-feed stoker</td>
<td>210</td>
</tr>
<tr>
<td>spreader stoker, fluidized bed combustion</td>
<td>260</td>
</tr>
<tr>
<td>pulverized coal</td>
<td>300</td>
</tr>
<tr>
<td>lignite</td>
<td>260</td>
</tr>
<tr>
<td>coal derived synthetic fuels</td>
<td>210</td>
</tr>
</tbody>
</table>

In the case of simultaneous combustion of two more fuel the following formula is used for
determination of NOₓ emission limit:

\[ E_n = \frac{\sum_{i=1}^{k} EL_i H_i}{\sum_{i=1}^{k} H_i} \], where

\( E_n \) is applicable NOₓ emission limit expressed in ng/J (lb/million Btu) heat input,
\( EL_i \) is appropriate emission limit for the successive fuel
\( H_i \) is heat input from combustion of the successive fuel

The countries outside of Europe and North America continents are introducing the emission
limits as well. The good example is the Kingdom of Saudi Arabia.

The Presidency of Meteorology and Environment of the Kingdom of Saudi Arabia is
responsible for regulation of the standards of ambient air quality as well as emission limits for
stationary combustion sources. The actual environmental protection standards are contained in General
Environmental Regulations and Rules for Implementation, Document NO. 1409-01 issued 15 October
According to this document all fossil fuel fired boilers and furnaces having a heat input capacity equal to or greater than 30 MW (100 MBTU/hour) shall utilize appropriate gas cleaning equipment to limit emissions to the following rates:

1. 43 ng/J (0.1 lb/MBTU) of total particulates.
2. 1 microgram/J (2.3 lb/MBTU) of sulfur dioxide.
3. 130 ng/J (0.3 lb/MBTU) of NO$_x$ for oil fired facilities.
4. 86 ng/J (0.2 lb/MBTU) of NO$_x$ for gas fired facilities.

Apart of general rules in Saudi Arabia there are special emission limits for two industrial cities – Jubail and Yanbu, set by The Royal Commission of Jubail and Yanbu (the governmental agency which is in charge of supervising Industrial Cities in both Jubail and Yanbu city). For SO$_2$ emission these regulations are stricter than given by the Presidency of Meteorology and Environment. In this case the SO$_2$ emission is limited to 340ng/J.

3. CONCLUSIONS

The fossil fuels are the main primary energy sources. The combustion of coal, gas and oil leads to the emission of vast quantities of pollutants. Fly ash, especially PM2.5 has adverse effects on human health and leads to life span reduction by several months in some regions. SO$_x$ and NO$_x$ lead to formation of acidic rains. CO$_2$, N$_2$O, VOC and others are the greenhouse effect gases. Therefore most of the countries are introducing the emission limits. The number of the countries which have such standards in place is growing and includes so called developing countries. The actions regarding air pollution control are the must nowadays.

ACKNOWLEDGMENT. This work was financed by Polish Ministry of Science and High Education – Project No PBZ-MEiN-3/2/2006 “Engineering of processes for emission control and utilization of hazardous and greenhouse effect gases” (PZ “Inżynieria procesów ograniczania emisji oraz utylizacji gazów szkodliwych i cieplarnianych”).
POLLUTANTS EMISSION IN POWER SECTOR

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Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Abstract

Fossil fuels, including coal, natural gas, petroleum, shale oil and bitumen, are the primary source of heat and electrical energy production and are responsible for emitting a large number and amount of pollutants into the atmosphere via exhaust gases from industry, power stations, residential heating systems and vehicles. During the combustion process, different pollutants such as CO\textsubscript{2}, SO\textsubscript{X} (including SO\textsubscript{2} and SO\textsubscript{3}), NO\textsubscript{X} (including NO\textsubscript{2}, NO and N\textsubscript{2}O), fly ash, VOCs and mercury are emitted. These emissions cause big environmental and human health hazard. CO\textsubscript{2}, N\textsubscript{2}O, some VOCs, CH\textsubscript{4} contribute to the global greenhouse effect, adding a new dimension to the environmental degradation resulting from the burning of fossil fuels. These problems regarding emissions inventory, their impact on the environment and human health, air pollution control technologies and costs, periods of fossil fuels depletion, role of renewable and nuclear energy in the further civilization development are briefly discussed.

Key words: fossil fuels, power generation, environment degradation.

1. INTRODUCTION

The population of the world exceeds six billion people. Since 1800 – 1850, when this number reached one billion, curve representing this increase versus time is almost exponential. Industrialization accompanied this rise in the number of inhabitants of our globe. The people would like to leave in the better conditions and this is connected with a big energy consumption. Population growth, higher standards of living, increased urbanization and enhanced industrial activities all contribute to the degradation of the environment. The problems of environmental damage and depletion of natural resources have received increasing attention throughout the world in the recent years. For example, fossil fuels, including coal, natural gas, petroleum, shale oil and bitumen, are the primary source of heat and electrical energy production and are responsible for emitting a large number and amount of pollutants into the atmosphere via exhaust gases from industry, power stations, residential heating systems and vehicles.

During the combustion process, different pollutants such as CO\textsubscript{2}, SO\textsubscript{X} (including SO\textsubscript{2} and SO\textsubscript{3}), NO\textsubscript{X} (including NO\textsubscript{2}, NO and N\textsubscript{2}O), fly ash, VOCs and mercury are emitted. Mechanisms of pollutant transformation in the atmosphere are described by the environmental chemistry. In the presence of water vapor, SO\textsubscript{X} and NO\textsubscript{X} are oxidized, forming sulphuric and nitric acids, respectively. Fog and droplets result in so-called acid rain (i.e. acid precipitation). Since they can be carried on many hundreds of kilometres by winds, acid pollutants emitted in one country may be deposited as acid rain in other countries. As industrialisation expanded across Europe during the 1970 and 1980’s, with the use of tall chimneys in industry and power generation increasing, acid deposition became a particularly prevalent problem. In a response to clean up Europe’s air, in 1979 the United Nations Economic Commission for Europe (UNECE) implemented the Convention on Long Range Transboundary Pollution, with the aim of reducing acidic emissions. Acid rain in Europe continues to be a problem in Europe until these emissions can be dramatically reduced. In recent years, investigations have shown that VOC emissions to the atmosphere can cause stratospheric ozone layer depletion and ground level photochemical ozone formation, and can have toxic or carcinogenic effects on human health. These emissions contribute to the global greenhouse effect, adding a new dimension to the environmental degradation resulting from the burning of fossil fuels. Small fly ash particles and aerosol particles being a result of chemical pollutants transformation contribute to so called PM 2.5 fractions (particles equal or smaller than 2.5 microns). When they reach respiratory system they dramatically affect human health. Unfortunately the estimations for the near future show that the fossil fuels will be still biggest primary sources of power generation, till the moment when they will be depleted globally [1].
2. ENERGY PRODUCTION AND DEMAND

Energy demand and primary energy sources are listed in Table I [2]. The share of transport rose from 24.2% in 1973 to just fewer than 30% in 2001. World energy demand has continued to increase even while the efficiency of many vehicles and energy-using appliances has improved. Both developed and developing countries are responsible for the growth. Improvements in energy efficiency in developed countries over the recent past did not lead to decreases in energy demand, because higher living standards have resulted in higher consumer expectations. In developing countries, rural and urban electrification programmes, together with the development of transport and industrialization, led to a strong increase in energy demand. The increase in demand was often faster than the growth in population. However, still some 2.4 billion people rely on traditional biomass for cooking and heating. That number will increase to 2.6 billion by 2030. In developing countries, biomass use will still represent over half of residential energy consumption in 30 years. Without policy changes, world energy demand is projected to increase steadily at 1.7% per year through 2030, less than the 2.1% annual growth over the past 30 years. In that event, fossil fuels will remain the primary sources of energy and will meet 90% of the increase in demand to 2030.

<table>
<thead>
<tr>
<th></th>
<th>1971</th>
<th>2002</th>
<th>2010</th>
<th>2020</th>
<th>2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>1 407</td>
<td>2 389</td>
<td>2 763</td>
<td>3 193</td>
<td>3 601</td>
</tr>
<tr>
<td>Oil</td>
<td>2 413</td>
<td>3 676</td>
<td>4 308</td>
<td>5 074</td>
<td>5 766</td>
</tr>
<tr>
<td>Gas</td>
<td>892</td>
<td>2 190</td>
<td>2 703</td>
<td>3 451</td>
<td>4 130</td>
</tr>
<tr>
<td>Nuclear</td>
<td>29</td>
<td>692</td>
<td>778</td>
<td>776</td>
<td>764</td>
</tr>
<tr>
<td>Hydro</td>
<td>104</td>
<td>224</td>
<td>276</td>
<td>321</td>
<td>365</td>
</tr>
<tr>
<td>Biomass and waste</td>
<td>687</td>
<td>1 119</td>
<td>1 264</td>
<td>1 428</td>
<td>1 605</td>
</tr>
<tr>
<td>Other renewables</td>
<td>4</td>
<td>55</td>
<td>101</td>
<td>162</td>
<td>256</td>
</tr>
<tr>
<td>Total</td>
<td>5 536</td>
<td>10 345</td>
<td>12 194</td>
<td>14 404</td>
<td>16 487</td>
</tr>
</tbody>
</table>

3. MAIN PRIMARY ELECTRICITY GENERATION SOURCES

Special attention should be put on electricity production, since all over the world a big percentage of population lives in the mega cites and in this case huge electricity generation power plants are required. The second reason is that in some cases power stations are located close to open mouth mines like Belchatów and Turów in Poland. Therefore their impact on the environment is meaningful.

The installed electricity generation capacity by the primary energy source category is presented for selected countries in Table II. Table III gives the general numbers for the world. Some 1.6 billion people – one-quarter of world population - have no access to electricity. About 80% of these people are located in India and sub-Saharan Africa.
### TABLE II. ELECTRICITY PRODUCTION [GWh] IN SELECTED COUNTRIES IN THE WORLD AFTER IEA ENERGY STATISTICS

<table>
<thead>
<tr>
<th>Country</th>
<th>USA</th>
<th>D</th>
<th>F</th>
<th>PL</th>
<th>ChRL</th>
<th>Ind</th>
<th>Iran</th>
<th>SAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>2 082</td>
<td>314 209</td>
<td>29 744</td>
<td>142 592</td>
<td>1 514</td>
<td>432</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Oil</td>
<td>137 560</td>
<td>4712</td>
<td>8673</td>
<td>2456</td>
<td>57 417</td>
<td>29 084</td>
<td>24 415</td>
<td>82 021</td>
</tr>
<tr>
<td>Gas</td>
<td>670 191</td>
<td>58 505</td>
<td>17 143</td>
<td>2425</td>
<td>5575</td>
<td>72 802</td>
<td>117 056</td>
<td>70 979</td>
</tr>
<tr>
<td>Biomass</td>
<td>46 029</td>
<td>4468</td>
<td>1760</td>
<td>454</td>
<td>2472</td>
<td>1877</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Waste</td>
<td>24 644</td>
<td>8884</td>
<td>3285</td>
<td>286</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nuclear</td>
<td>787 818</td>
<td>165 060</td>
<td>441 070</td>
<td>0</td>
<td>43 342</td>
<td>17 780</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydro</td>
<td>305 724</td>
<td>24 440</td>
<td>64 338</td>
<td>3294</td>
<td>283 681</td>
<td>75 339</td>
<td>11 098</td>
<td>0</td>
</tr>
<tr>
<td>Geothermal</td>
<td>14 870</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Solar PV</td>
<td>2</td>
<td>333</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Solar thermal</td>
<td>548</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Other sources</td>
<td>11 300</td>
<td>18 859</td>
<td>881</td>
<td>124</td>
<td>0</td>
<td>3590</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>4 081 468</td>
<td>599 470</td>
<td>566 902</td>
<td>151 631</td>
<td>1907 384</td>
<td>633 275</td>
<td>152 569</td>
<td>153 000</td>
</tr>
</tbody>
</table>

### TABLE III. ELECTRICITY GENERATION CAPACITY INSTALLED BY SOURCES.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Installed in 1995</th>
<th>Estimated for 2020</th>
<th>Net increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>870</td>
<td>1836</td>
<td>966</td>
</tr>
<tr>
<td>Gas</td>
<td>435</td>
<td>1296</td>
<td>861</td>
</tr>
<tr>
<td>Oil</td>
<td>435</td>
<td>648</td>
<td>213</td>
</tr>
<tr>
<td>Hydro</td>
<td>667</td>
<td>1026</td>
<td>359</td>
</tr>
<tr>
<td>Nuclear</td>
<td>348</td>
<td>378</td>
<td>30</td>
</tr>
<tr>
<td>Other</td>
<td>145</td>
<td>216</td>
<td>71</td>
</tr>
<tr>
<td>Total</td>
<td>2900</td>
<td>5400</td>
<td>2500</td>
</tr>
</tbody>
</table>
4. GASOUS AND PARTICULATE MATTER POLLUTANTS EMISSIONS

Carbon dioxide is the most important anthropogenic greenhouse gas. Global emissions of carbon dioxide have risen by 68% since 1971. Global energy-related carbon-dioxide emissions increase by 55% between 2004 and 2030, or 1.7% per year, according to the IEA Reference Scenario [2]. They reach 40 gigatonnes in 2030, an increase of 13 - 14 Gt over the 2004 level (Table IV). Power generation, which currently accounts for around 40 – 50 % of emissions will contribute almost half the increase (or 7 billion tonnes) in global emissions between 2000 and 2030. Transport will account for more than a quarter, residential, commercial and industrial sectors for the rest. Emissions are projected to grow slightly faster than primary energy demand – reversing the trend of the last two-and-a-half decades – because the average carbon content of primary energy consumption increases. Under this scenario, emissions are projected to grow by 69%, slightly more than the growth of 66% in energy supply. Fossil fuel shares in overall emissions changed slightly during the period. The relative weight of coal in global emissions has remained at approximately 40% since the early 1970s. The share of natural gas has increased from 14% in 1973 to 20% in 2001. Oil’s share decreased from 51% to 42%. Projections through the year 2030 show a continuing increase in global carbon dioxide emissions; if no new policies and measures are put in place. The average carbon content of energy – CO$_2$ emissions per unit of aggregate primary energy consumption – will increase over the next 30 years. The main cause of this reversal will be the declining share of nuclear and hydro power in the global energy mix.

<table>
<thead>
<tr>
<th>TABLE IV.</th>
<th>WORLD CARBON DIOXIDE EMISSIONS FROM COMBUSTION OF FOSSIL FUELS.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Million Tonns)</td>
<td></td>
</tr>
<tr>
<td>18 333.26</td>
<td>21 426.12</td>
</tr>
</tbody>
</table>

The global atmospheric concentration of carbon dioxide has increased from a pre-industrial value of about 280 ppm to 379 ppm in 2005. The atmospheric concentration of carbon dioxide in 2005 exceeds by far the natural range over the last 650,000 years (180 to 300 ppm) as determined from ice cores. The annual carbon dioxide concentration growth-rate was larger during the last 10 years (1995 – 2005 average: 1.9 ppm per year), than it has been since the beginning of continuous direct atmospheric measurements (1960 – 2005 average: 1.4 ppm per year) although there is year-to-year variability in growth rates [3].

Other two pollutants SO$_2$ and NO$_x$, responsible for acidic rain, mostly are emitted during coal and heavy oil combustion. These pollutants emissions are tremendous and data for selected countries are presented in Tables V and VI. The problem concerns especially countries like Poland where coal is a main fuel for electricity and heat production.

<table>
<thead>
<tr>
<th>TABLE V.</th>
<th>SO$_2$ EMISSION INVENTORY IN SELECTED COUNTRIES IN THE WORLD IN 2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>Country</td>
<td>SO$_2$ [1000 t]</td>
</tr>
<tr>
<td>USA</td>
<td>10 646</td>
</tr>
<tr>
<td>Germany</td>
<td>616</td>
</tr>
<tr>
<td>France</td>
<td>492</td>
</tr>
</tbody>
</table>
TABLE VI. NO\textsubscript{x} EMISSION INVENTORY IN SELECTED COUNTRIES IN THE WORLD IN 2003

<table>
<thead>
<tr>
<th>Country</th>
<th>NO\textsubscript{x} [1000 t]</th>
<th>Country</th>
<th>NO\textsubscript{x} [1000 t]</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>4532</td>
<td>Poland</td>
<td>1220</td>
</tr>
<tr>
<td>Germany</td>
<td>1428</td>
<td>Turkey</td>
<td>951</td>
</tr>
<tr>
<td>France</td>
<td>805</td>
<td>EU-15</td>
<td>9269</td>
</tr>
</tbody>
</table>

Recently recognized problem is connected with the health effects of PM 2.5. In the early years of air pollution standards establishment the mass load of particulate emission was considered, nowadays the limits concerning PM 2.5 emissions are being introduced.

Other problems is the emission of mercury during fossil fuel combustion, even quantities are not too big. Trace amounts of mercury can exist in coal and other fossil fuels. When these fuels burn, mercury vapor can be released to the atmosphere where it may drift for a year or more, spreading with air currents over vast regions of the globe. In 1995, an estimated 5500 tons of mercury was emitted globally from both natural and human sources. Coal-fired power plants contribute only a small part of the total worldwide emissions of mercury. The estimated 48 tons of mercury they emit in the US annually is about one-third of the total amount of mercury released annually by human activities in this country [4]. Never less it is a big concern due to the fact that mercury easily incorporates in the food chain.

Finally a new problem is connected with Volatile Organic Compounds (VOC) emission in thermal processes. These pollutants, which belong to Non Methane Organic Carbon (NMOC), fall in the categories of Polyaromatic Hydrocarbons (PAH), Persistent Organic Pollutants (POP) with the long live time in the environment etc. EPA listed 18 of these compounds as potential carcinogenic and WHO published similar list [5].

According to the German data losses linked to emission of one tonne of SO\textsubscript{2}, NO\textsubscript{x} and particulate were respectively 6000; 5000 and 13000 USD (1990). Total loses of EU-15 (1990) due to the greenhouse effect were estimated as 4.6x10\textsuperscript{9} – 1.7x10\textsuperscript{11} USD. In the Netherlands death rate caused by PM10 is bigger that caused by car accidents [6]. The map published at EU site [7] presents the regions where life time expectation is shorter by 12 months due to high PM2.5 concentrations. These are silent Charnobyls with the much higher tragic effects in comparison to this 1986’s accident.

5. EMISSION CONTROL TECHNOLOGIES

Quite big difference exists regarding pollution control technologies for SO\textsubscript{2}, NO\textsubscript{x} and fly ash removal, VOC and Hg treatment and finally CO\textsubscript{2} mitigation. Desulfurization and denitrification processes are mostly based on lime/limestone FGD or SCR. However, new generation technologies are being developed as well [8]. The add-on technologies to reduce regional air pollution remain necessary throughout the century. The costs to reach the NO\textsubscript{x} emission reduction targets in Europe are about three times as high as for SO\textsubscript{2}. The total annual costs are in the order of 1 or 2% of the present GDP, depending on the scenario [9].

A CO\textsubscript{2} sequestration scheme involves three distinct components: capture of the emitted CO\textsubscript{2} from the source followed by compression and dehydration, transportation to the storage site and injection and storage of the CO\textsubscript{2} in the geological reservoir. One of the key barriers to the introduction of CO\textsubscript{2} sequestration technology is the cost associated with CO\textsubscript{2} capture. Most CO\textsubscript{2} point sources considered to supply CO\textsubscript{2} (industrial and electricity plants) generally emit diluted CO\textsubscript{2} streams. Typical cost ranges for CO\textsubscript{2} removal from the exhaust gas of power plants with amines (state of the art technology) are in the range of 40–60 Euro/t [10].

Mercury emission control technologies are based on sorption mostly and are placebo type methods, just to demonstrate willing to solve the problem. VOC are emitted in very small quantities and on line monitoring methods are not developed yet. Sampling and GS/MS analytical methods are
applied to estimate emissions [11]. Therefore the control has been introduced in the dioxin abatement in municipal waste incinerators.

6. FOSSIL FUELS RESERVES

The fossil fuel reserves are limited [12]. Oil reserves according to the data available of 1 January 1997 were 1018.5-1160.1 billion barrels (7.1x10²¹ Joules). Average consumption in 1998 was 74.9 million barrels per day (457x10¹⁵ Joules per day, 167x10¹⁸ Joules per year). For these assumptions the oil reserves were left for 42.5 years. Oil Reserves as of 1 January 1999 were 967.5-1033.2 billion barrels and average consumption in 1998 was 73.643 million barrels per day. In this case the time left was 38.4 years. World Natural Gas Reserves as of January 1, 1997 was 140 - 146 Trillion Cubic Meters (5.37x10²¹ Joules). Natural gas consumption in 1996 was (81.9 x 10¹⁸ joules) per year. Natural gas lifetime appeared to be 65.5 years. Since that time the situation didn’t change too much (Table VII). Over 68% of oil and 67% of gas reserves are concentrated in the Middle East and Russia.

Coal resources are available in almost every country worldwide, with recoverable reserves in around 70 countries (Table VIII) [13]. At current production levels, proven coal reserves are estimated to last 155 years.

<table>
<thead>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>Billion barrels</td>
<td>1018 -1160</td>
<td>967 - 1033</td>
<td>1119 -1201</td>
<td>1317</td>
</tr>
<tr>
<td>Gas</td>
<td>Trillion, m³³</td>
<td>140 - 146</td>
<td>176 - 180</td>
<td>181</td>
<td>175</td>
</tr>
</tbody>
</table>

7. RAW MATERIALS PRESERVATION ASPECTS

Usage of oil and gas in big power plants is not acceptable at all. These applications should be prohibited by law. Fossil hydrocarbons are the main raw materials for chemical industries (like petrochemical – polymers, inorganic industry – ammonia, which is main reagent for fertilizers production etc.), fuels for transport and home applications. The Hubbert peak theory posits that for any given geographical area, from an individual oil field to the planet as a whole, the rate of petroleum production tends to follow a bell-shaped curve. It also shows how to calculate the point of maximum production in advance based on discovery rates, production rates and cumulative production. Early in the curve (pre-peak), the production rate increases due to the discovery rate and the addition of infrastructure. Late in the curve (post-peak), production declines due to resource depletion. Association for the Study of Peak Oil and Gas (ASPO) has suggested that the global production of conventional oil peaked in the spring of 2004 albeit at a rate of 23-GB/yr, not Hubbert's 13-GB/yr.

During 2004, approximately 24 billion barrels of conventional oil was produced out of the total of 30 billion barrels of oil; the remaining 6 billion barrels coming from heavy oil and tar sands, deep water oil fields, and natural gas liquids. In 2005, the ASPO revised its prediction for the peak in world
oil production, from both conventional and nonconventional sources, to the year 2010. Sing oil and gas demand, if unchecked, would accentuate the consuming countries vulnerability to a severe supply disruption and resulting price shock [14]. Unfortunately politicians put too big stress on political and economical problems, so called energy safety and they pay less attention to the environmental and raw materials depletion scenarios [15].

8. RENEWABLES

The big expectations were devoted to the development of renewables. However, the market penetration of renewables is slower than was hoped and improvements in energy efficiency in general have not offset the increasing demand for energy due to economic development. Some aspects limitations their applications are listed in Table IX. The real role in further development will play hydroenergy and biomass. The first is almost exploited in 100% of possible rivers potential energy in some countries. The share of renewable energies (including hydro) remained around 6%.

TABLE IX. PRESENT STATUS OF RENEWABLE ENERGY

<table>
<thead>
<tr>
<th></th>
<th>Photovoltaic</th>
<th>Wind Power</th>
<th>Nuclear Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area</td>
<td>20 m²/kW</td>
<td>500 m² for two 250 kW class unit (Height 30 m, diameter of vane 28 m)</td>
<td>0.4 km²/1000MW</td>
</tr>
<tr>
<td></td>
<td>130 km²/1000 MW</td>
<td>Wind velocity &gt; 6 m/s</td>
<td></td>
</tr>
<tr>
<td>Operation rate</td>
<td>Annual Capacity Factor ca.12%</td>
<td>Annual Capacity Factor 20 – 25%</td>
<td>Wind velocity &gt; 6 m/s</td>
</tr>
<tr>
<td></td>
<td>No generation during nighttime</td>
<td></td>
<td>Annual Capacity Factor ca.80%</td>
</tr>
</tbody>
</table>

Sustainable development is not an easy task nowadays. Recently the associations of the European Union food producers spoke out against the setting of a mandatory target for biofuels, saying it will damage the food industry by leading to a "serious" shortage of raw materials and price hikes. Rapeseed oil price doubled over the last five years and the price of cereals, starches, and glucose recently increased by about 20 per cent. They blame governments and the European Commission for promoting biofuels through tax incentives. High crude oil prices have also stimulated production. The result has been a growing conflict between the food and the energy industry for supplies [16]

9. CONCLUSIONS

The general public, policy makers and big business should treat the problems concerning power generation and connected with this activity environment degradation seriously. This industry development so important for civilization development holds responsibility for environment and human health decline, raw materials depletion. Since the fossil fuels are and will be the main energy sources the air pollution control technologies should be introduced widely in power industry.

ACKNOWLEDGMENTS

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32
REFERENCES


JAPAN’S EXPERIENCE OF FLUE GAS TREATMENT BY ELECTRON BEAMS

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Senior Advisor to JAEA

Abstract

The electron beam flue gas treatment technology was invented in Japan in 1970's. The paper presents the outlook of the Japanese activities on the development and present state of EBFGT technology.

1. INTRODUCTION

This year, in 2007, IAEA is celebrating its 50th anniversary. IAEA was established in 1957 on the basis of President Eisenhower’s speech of “Atoms for Peace” in UN General Assembly in 1953. The Statute of IAEA states “The Agency shall seek to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world”. Promotion of radiation and isotope applications in health-care, agriculture, environmental protection and industry is one of the most important pillars of the Agency activities. It is noted that the Polish government hosted the first Agency conference on isotope and radiation application in 1959.

FIG. 1. Photo from first IAEA conference in Warsaw, Poland

This IAEA Technical Meeting in Warsaw on environmental protection by using radiation is organized harmonizing very well with the Statute and timely as environmental degradation is seriously concerned worldwide.
2. NEEDS OF CLEANING COAL BURNING FLUE-GASES FOR ENVIRONMENTAL PROTECTION

OECD’s ‘World Energy Outlook 2006’ projected the world electricity demand will be doubled by 2030, and China as well as India see the fastest growth in demand. Coal fired power generation has the largest share of 40%, while nuclear 16%, and will further increase to 44% in 2030. In China power demand is increasing at high rate of 15% per year, and 65% of power is generated by coal polluting environment by SO$_2$, NO$_x$ and ashes. In India per capita consumption of power is still very low of 600kW for a year increasing at high rate of 7% per year, and coal-fired power shares about 65% high.

![IEA Power Generation Outlook 2006](image)

According to the report of World Bank, world total emission of SO$_2$ per year will be increasing to 80 million tons per year in 2020 which may cause serious environmental pollution. Therefore, clean coal technology (CCT) development is of great importance. Electron beam technology for removing both SO$_2$ and NO$_x$ from coal fired power plants is one of promising candidates of CCT.

3. ELECTRON ACCELERATOR APPLICATION GROWING IN INDUSTRY IN JAPAN

In Japan more than 250 electron accelerators are used in industry for production of value added polymer materials, sterilization of medical products and food packaging, and curing of surface coatings/printing. About 90% of automobile tires are produced by the use of electron beams, and most of heat resistant wires are made by using electron beam crosslinking. Radiation grafting of monomers to polymeric materials are used for the production of polymer membrane for battery separator and deodorant. More recently in 2004 new hydrogel wound dressing production by using low energy (300keV) accelerator has been penetrated in commercial market, which achieves faster healing rate of
wounds. In Japan, however, these applications of radiation technology benefiting society are not widely known by the public.

![Electron Beam Application in Japan](image)

**FIG. 3. Application of electron accelerators in the industry in Japan.**

4. DEVELOPMENT OF ELECTRON BEAM TECHNOLOGY FOR CLEANING FLUE GASES OF COAL AND OIL BURNING POWER STATION

In 1972 JAEA, former JAERI, Takasaki Radiation Chemistry Research Establishment first demonstrated electron beam process using small continuous flow type plant of 60 Nm³/h that 600-900 ppm of SO₂ and 80ppm NOₓ were removed by 80% and 90%, respectively with absorbed dose of 40 kGy. Following the demonstration, extensive basic research was conducted to elucidate reaction mechanism of SO₂ and NOₓ removals by radiation.

After 1975 Ebara Corporation and JAEA Takasaki demonstrated how to convert SO₂ and NOₓ to dry powder of ammonium sulphates and ammonium nitrates which are collected by ESP and can be used as agricultural fertilizer. The pilot plant of cleaning flue gas from steel sintering furnace was successfully operated to remove 95% of SO₂ and 80% of NOₓ at a capacity of 3000 m³/h.

In 1993 collaboration of Ebara Corporation, JAEA Takasaki and Chubu Power Co. have successfully demonstrated in large scale pilot plant of 12 000 m³/h removing 94% of SO₂ and 80% of NOₓ in exhaust gases from high sulphur heavy oil burning power station.

Economic analysis of the results indicated that construction and operation cost of treatment plant of flue gas using accelerator was 20% less than that of combination of conventional FGD and SCR. In 1997 Ebara Corporation then constructed a commercial scale plant in Chengdu in China to remove SO₂ and NOₓ with capacity of 300 000 m³/h flue gas containing 1800 ppm SO₂ and 400 ppm NOₓ from coal burning power station of 90 MW (Fig. 3).
Two units of electron accelerator of 800 keV x 400 mA were used. The plant was successfully operated to achieve its design performance to remove 80% and 20% at the absorbed dose of 4 kGy. The by-products of agricultural fertilizer of 7700 tons were produced for 5 year operation by 2002. The quality and composition of products were carefully compared with commercial chemical fertilizer to be found comparable with them. Economic analysis by Ebara and Chengdu group indicates that construction cost of the plant is about US$ 108 per kW of power plant capacity and running cost is US$ 0.001 per 1 kWh production which seems reasonable and competitive.

Ebara Corporation constructed commercial plant for cleaning exhaust gas from high sulphur oil burning power station of 220 MW of Chubu Power Co. in 1998 to clean 620 000 Nm$^3$/h of flue gas (Fig. 5). During test operation of the plant, Ebara faced serious problems of continuous operation of 6 large capacity electron accelerators of 800 keV x 500 mA due to break down of power-supply of 800 keV x 1 A. The Accelerator manufacture could not make appropriate improvement limited in duration of time to assure continuous operation for one year without break down of power-supply at 800 keV. The contract of Ebara with Chubu Power Company was finally cancelled due to time constraint for starting operation of the power plant. Similar power source break down happened in Poland for the plant in Pomorzany power station, but solved by reducing energy from 800 keV to 700 keV.
Major issues for design and installation of industrial scale plant have been well described by Prof. Chmielewski in the recent IAEA publication entitled with ‘Radiation Processing: Environmental Protection’. Experience in Japan indicates the sensitive components of plant are electron accelerator and ESP for continuous operation of industrial plant for appropriate period of time without breakdown. Manufacturing large capacity ranging from 500 to 1000 kW and reliable accelerator at reasonable cost is the most crucial challenge for future expansion of this technology in industrial use.

There are not many manufactures of electron accelerator of this kind worldwide. It is desirable that the Agency will take initiative to encourage manufactures to share information and cooperate to develop new design of accelerator to meet these needs. In view of important advantages of the technology and situation of several countries planning industrial scale plants installation such as Indonesia, Bulgaria, Saudi Arabia and Malaysia, further improvement of reliability of accelerator is urgently required.

In Poland industrial scale electron beam flue gas treatment plant is being operated at the Pomorzany power station to clean 270 000 Nm$^3$/h for 7 years by overcoming several troubles with accelerators and ESP by tireless efforts of relevant engineers and staff including IAEA. Experiences with the plant should be shared with the Agency’s member states. It should be also noted that this world first industrial scale plant has been achieved by effort and collaboration between Poland, IAEA and Japan among scientists, engineers, administrators and diplomats, and their financial supports. This Agency Technical Cooperation Project has demonstrated one of the most remarkable socio-economic benefits in application of nuclear technology for environmental protection.

In China two industrial scale exhaust gas treatment plants have been constructed by cooperation of the government, power companies and Ebara Corporation. A new industrial scale treatment plant is under construction at Jinfeng Power Station near Beijing.

For Bulgaria, the Agency and Government of Japan through JAERI have supported installation of pilot scale plant of 10,000 Nm$^3$/h at the Maritsa East 2 power plant to treat exhaust gas containing high SO$_2$ of 5000 ppm from burning high sulphur lignite coal. Three electron accelerators with one power supply were donated from JAERI Takasaki. The plant has been well operated to achieve SO$_2$...
removal of 87 to 97% and NO\textsubscript{x} removal of 85 to 90%. By-product was found to be a good quality fertilizer.

5. DISTINCT ADVANTAGES OF ELECTRON BEAM FLUE GAS TREATMENT FOR THERMAL POWER PLANT

   Followings are advantages proven by demonstration plants operation.
   
   - Dry process: Conventional FGD (flue gas desulphurization) needs large amount of fresh water scrubbing flue gases and following treatment of waste water, while EB process is essentially dry.
   
   - Simultaneous removals of SO\textsubscript{2} and NO\textsubscript{x}: Simpler than conventional FDG combined with SCR (selective catalytic reduction) for NO\textsubscript{x} removal,
   
   - Usable by-product as agricultural fertilizer: By-product of conventional FGD is gypsum which is not usable in some countries but wastes.

6. REMOVALS OF DIOXIN FROM MUNICIPAL WASTE INCINERATOR PLANT FLUE GAS IN JAPAN

   In Japan control of dioxin content in waste incineration plant flue gas has changed to be much stricter (from 80 ng/m\textsuperscript{3} to 1 ng/m\textsuperscript{3}) in 2002. The pilot plant of 1000 m\textsuperscript{3}/h was installed in the city of Takasaki for treatment of flue gas from municipal waste incineration plant. Using one self-shielded electron accelerator of 300 keV x 40 mA, 90% dioxin could be decomposed with 14 kGy. However this electron beam technology was not practically used because of delay in establishing the technology for the transfer to industrial application (Fig 6).

   ![FIG. 6. EBFGT pilot plant of waste incineration flue gas treatment](image)
7. REMOVALS OF VOC BY ELECTRON BEAMS IN JAPAN

Some volatile organic compounds (VOC) such as benzene, formaldehyde and trichloro-ethylene are hazardous for human and environment. JAEA Takasaki group has found that trichloro-ethylene of 200 - 300 ppm in air can be decomposed nearly 100% with absorbed dose less than 5 kGy, and formaldehyde of 1500 ppm in air can be effectively decomposed in much shorter time than that by catalytic thermal decomposition. Ground water in some areas is contaminated by trichloroethylene. The contaminated water is bubbled by air to remove trichloroethylene, which is absorbed by active carbon. This active carbon treatment is not efficient because absorbed trichloroethylene is to be decomposed by additional steps. Self-shielded electron accelerator of low energy should be used for VOC removals improving economic competitiveness (Fig. 7).

Aromatic VOC such as benzene and xylene are stable against radiation and not easily decomposed. The JAEA group reported 90% of 10 ppm xylene in flue gas is decomposed with 10 kGy.
EXPERIENCES FROM OPERATION OF POMORZANY EBFGT PLANT AND DIRECTIONS OF TECHNOLOGY DEVELOPMENT

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Abstract

Electron beam flue gas treatment technology is one of the most advanced technologies among new generation air pollution control processes. It is the only one process for simultaneous removal of \( \text{SO}_2 \) and \( \text{NO}_x \), applied in the industrial scale. Moreover other pollutants as acidic compounds, VOC and dioxins can be removed in one step. Among the other advantages a fully usable by-product – a fertilizer is created in the process. The industrial demonstrational plant was constructed in EPS Pomorzany in Szczecin (Poland). The facility treats the flue gases of maximum flow of 270,000 Nm\(^3\)/h, which are irradiated by four accelerators of 700 keV electron energy and 260 kW beam power each. The removal efficiency of \( \text{SO}_2 \) in this installation may reach 95%, while removal efficiency of \( \text{NO}_x \) – 70%. Apart of technical analysis also economical calculations of investment and operational costs of EBFGT installations, based on the data obtained on the Polish installation, was performed. The results show that in the case of multi-pollutant control the electron beam technology is strongly competitive to conventional technologies. Description of the experiences obtained during the operation of the plant and further possibilities of the technology development are presented in this paper.

1. INTRODUCTION

Emission of harmful compounds to the atmosphere is no more local problem due to relatively long residence time of pollutants in the air which results in long range transport of these substances. Therefore several international initiatives were undertaken in order to prevent pollutants proliferation in the environment.

Basic document regulating problems of \( \text{SO}_2 \) and \( \text{NO}_x \) emission to the atmosphere is the Geneva Convention on Long-range Trans-boundary Air Pollution signed in 1979 under auspices of United Nations Economic Commission for Europe, (UNECE). The Convention on Long-range Trans-boundary Air Pollution entered into force in 1983. The convention has been extended by eight specific protocols, among them five relate to the problem of \( \text{SO}_2 \) and \( \text{NO}_x \) emission: Geneva Protocol (1984), Helsinki Protocol (1985), Sofia Protocol (1988), Oslo Protocol (1994) and Gothenburg Protocol (1999). Following these agreements local emission limits were introduced in almost every country in the world.

The international and national emission limits regulations induce the development of emission control technologies. As the regulation became more strict new technologies are being developed. Among the others electron beam flue gas treatment technology as an example of multi-pollution control methods is the most promising.

Electron beam flue gas treatment process was invented in Japan. Preliminary research was conducted during 1970's by Japan Atomic Energy Research Institute (JAERI), Ebara Corporation and University of Tokyo. The process was initially dedicated for purification of flue gases from iron ore sintering plants [1]. Unfortunately steel crisis in the end of 1970's stopped the development of the process.

The next step of technology development was construction of laboratory and pilot plant EBFGT facilities in such countries as USA, Germany Japan and Poland. The research was carried out during 1980's and 1990's. The experiences gathered on these plants allowed for construction of demonstrational, industrial plants in China (Chengdu and Hangzhou power plants) and Poland (Pomorzany Power Plant in Szczecin). It has proved that the technology is ready for full scale industrial implementation.
At the moment only Polish Pomorzany industrial EBFGT plant is running, but new possibilities of technology implementation are still sought. There is big industrial installation under construction in Jingfeng Power Plant in Beijing (China) and another project (Sviloza Thermal Power plant in Svishtov, Bulgaria) is in design phase. An important research program has been recently realized in Maritza East 2 pilot plant in Bulgaria and another one considering application of electron beam technology for treatment of flue gas from heavy oils burning has been undertaken in Saudi Arabia. Other fields of application of the technology are still under research, so still the electron beam flue gas treatment is a promising emission control process.

Among the other advantages of the process the most important are:

– simultaneous removal of SO$_2$, NO$_x$ in one step, moreover the process may be applied for VOC decomposition and other pollutants removal,
– high effectiveness of the process,
– dry process, lack of problematic wastewaters,
– no wastes generation with agricultural use of by-product,
– simplicity of the construction and operation of the facility, that makes easy retrofitting.

All of this makes the EBFGT technology attractive from the technological point of view. Moreover the cost calculations indicate that the technology may be economically competitive to conventional ones.

As the Pomorzany EBFGT facility is a key reference plant at this stage of technology development, the operational experiences has been carefully analysed in order to find the possibilities of further improvement of the technology itself and make it more competitive to conventional ones.

2. EBFGT PROCESS AND PLANT CONSTRUCTION

The electron beam flue gas treatment process idea consists in oxidation of SO$_2$ and NO and creation of ammonium sulphate and ammonium nitrate in reaction with water vapour and ammonia. The process course was described in details elsewhere [2, 3, 4] and only general idea of the process, that impact on the process optimization, will be presented. NO$_x$ is being removed by interaction with oxidizing radicals, while in the case of SO$_2$ two ways of ammonium sulphate creation may be distinguished one similar to NOx removal (radiochemical reactions), while the second way goes thru creation of adduct (NH$_3$)$_2$SO$_2$ and its further oxidation (thermal reactions). It results in different set of parameters being responsible for SO$_2$ and NO$_x$ removal efficiency. Due to high impact of thermal reactions on total SO$_2$ removal efficiency, in this pollutant case, the most important parameters are temperature, humidity and ammonia stoichiometry. Dose is less important parameter. Opposite the main parameter in NO$_x$ removal process is the dose due to radical oxidation way of NO. The second one is inlet NO$_x$ concentration. The rest of parameters as ammonia stoichiometry and temperature play minor role in the process. Figure 1 presents the most important reaction ways of SO$_2$ and NO$_x$ removal.
The decision about construction of Pomorzany electron beam flue gas treatment plant was undertaken after completion of Feasibility Study in 1994. Design works were completed in 1996. The general investor was Dolna Odra Group – the owner of the power plant. The project was realized by Polish specialists under supervision of Institute of Nuclear Chemistry and Technology, Warsaw – the author of the technology. The project was also performed with participation of the International Atomic Energy Agency and was partially granted by IAEA (project POL 8014). Construction of the facility started in April 1999 and the installation was completed in October 2000. The startup works and trials were finished in April 2003 and the installation was put to exploitation.

The facility purifies 100 000 to 270 000 Nm$^3$/h of flue gas – half of the total flue gas amount emitted from two hard coal fired Benson boilers of 65 MW$_e$ each. The rest is bypassed and mixed with the treated part before stack. The temperature of the gas after economizer is up to 140°C and inlet concentration of pollutants about 1500 – 2000 mg/Nm$^3$ of SO$_2$ and 400 – 600 mg/Nm$^3$ of NO$_x$. Fly ash is removed by electrostatic precipitators before installation inlet. The scheme of the installation is presented in Figure 2.
FIG. 2. The scheme of Pomorzany electron beam flue gas treatment plant.

The overall construction of the facility is similar in all installations of this kind, but the solutions applied were previously tested in Polish EBFGT pilot plant in Kaweczyn near Warsaw [5]. According to constructional and functional point of view the installation may be divided in four main parts:

– Cooling and humidification of flue gases,
– Ammonia supply system,
– Reaction unit,
– By-product filtration and storage.

The first operation is realized in a cooling and humidification column by water spraying direct to the gases. Evaporation of water results in both lowering the temperature and rising the humidity of the gas to optimal values (temperature 60 to 75°C and humidity 12 to 14% vol.). For the above described conditions the dry bottom (complete evaporation) cooling tower has been chosen. This solution is appropriate for medium inlet temperatures and low dust concentration. Although it requires very careful water atomization it is simple and very useful construction.

Opposite to other EBFGT facilities, ammonia, the main reagent of the process, is stored in the form of ammonia water (25% ammonia solution in the water). Depending on the process conditions the ammonia water consumption is in the range of 150 to 600 kg/h. It may be dosed to the installation in two ways:

• Gaseous ammonia after the evaporation may be injected upstream the irradiation chamber (variant I).
• Ammonia water may be sprayed straight to the spray cooler using the separate system of nozzles (variant II).
Ammonia may be also dosed both in the form of ammonia water to spray cooler and gaseous ammonia before the irradiation chamber (mixed variant). It was noticed during operation of Pomorzany EBFGT plant, that the way of ammonia adding affects the pollutants (especially SO$_2$) removal efficiency.

The reaction unit is the most advanced part of the facility. It covers reaction chamber, accelerators with auxiliaries (power suppliers, accelerators cooling system, windows with window cooling system etc.), radiation shielding with ventilation system and other components.

High power accelerators being able to apply required dose of energy are the most important and the most technologically advanced components in EBFGT technology. The reliability of the whole installation depends on the reliability of the accelerators. The power of accelerator is proportional to mass flow of flue gas and the dose, that is necessary for removal of SO$_2$ and NO$_x$. Generally the doses of 8 to 12 kGy are used in the described plant.

The reaction unit in Pomorzany Power Plant consists of two parallel, cylindrical reaction vessels. Each vessel is equipped in two electron accelerators (700 keV, 260 kW) installed in series. Double window system with air curtain [6] was applied. Such a solution ensures the proper irradiation of flue gas.

The by-product being created during the process is collected in electrostatic precipitator and after granulation and storage is shipped to the fertilizer production plant. The by-product yield is up to 300 kg/h. For protection from the condensation of water the ESP with electrically heated bottom is used.

The flue gases after purification are taken back to the stack. After mixing with the unpurified part of the gas, the temperature in the stack inlet is above 110°C which reduces the problems with stack corrosion. In order to compensate pressure drops in installation, a draft fan has been installed.

3. OPERATIONAL EXPERIENCES

The operational experiences gathered on the Polish EBFGT industrial installation has proved the idea of process application in the industrial scale. During the start-up trials and operation of the industrial EBFGT installation the solutions applied in the facility was tested and demonstrated the suitability for use in this technology. The installation runs smoothly and removal efficiencies are kept at the required levels as it was proved by independent measurements.

As it was previously described different set of parameters is responsible for efficiency of SO$_2$ and NO$_x$ removal process. The same dependences were observed in the industrial facility [7]. Knowledge of the impact of process parameters on the process efficiency allows for the optimization of installation operation according to actual needs, this results in the reduction of operational costs of the plant.

The industrial installation highest pollutants removal efficiency may reach 95% for SO$_2$ and 70% for NO$_x$ (see Figure 3). Such results were obtained for low temperature (under 70°C) and high humidity of flue gases. In certain conditions these numbers might be even higher. For the temperature about 65°C and humidity 14% vol. as high as 98% of SO$_2$ removal was observed. 95% SO$_2$ removal and 70% NO$_x$ removal efficiencies correlates with previous pilot plant experiments, so it might be considered as reliable for this technology. The installation was tested for flue gas flow rates from 100 000 to 270 000 Nm$^3$/h and no impact of this parameter for the pollutants' removal ability was found. Such flexibility according to gas flow rate and other parameters (inlet pollutants' concentrations, required removal rates etc.) is characteristic for this technology.
As it was already reported, dose is the most important and the easiest to control parameter influencing NO\textsubscript{x} removal. The impact of dose on NO\textsubscript{x} removal in industrial EBFGT installation was illustrated in Figure 3. Two more parameters are also described in the literature - NO\textsubscript{x} inlet concentration and ammonia stoichiometry. Figure 4 presents the impact of NO\textsubscript{x} inlet concentration on NO\textsubscript{x} removal efficiency calculated by use of the empirical models, based on the multi-dimensional regression method, elaborated for this installation. The results point on very slight ammonia stoichiometry effect for NO\textsubscript{x} removal process. As the dose is the most important parameter from nitrogen oxides removal point of view, this parameter must be especially carefully optimized in order to minimize energy consumption by the accelerators, which results in lowering of the operational costs of the plant.
In the case of SO$_2$ removal, more parameters have impact on the removal efficiency due to process mechanism. The most important parameter is temperature of the gases at the reaction vessel inlet because of the thermal reactions pathway. SO$_2$ removal efficiency decreases rapidly with the temperature increase. Humidity is the second parameter, that impact on the process efficiency; however it is hard to observe it because of the strong correlation between the humidity and the temperature of the process caused by the simultaneous cooling and humidification process in the cooling tower. Nevertheless improvement of the removal efficiency was observed when humidity was increased by adding a steam into the cooling tower. Maximum SO$_2$ removal efficiency (98%) required increasing the humidity up to 14% vol.

During simultaneous removal of SO$_2$ and NO$_x$, the impact of ammonia stoichiometry on SO$_2$ removal is much higher than on NO$_x$ removal. This phenomenon is illustrated in Figure 5. As it was previously found during laboratory and pilot plant research, the dose (Figure 3) plays rather moderate role in this process and with low temperature and high humidity, low dose is required to obtain high removal efficiency.
Interesting phenomenon is the impact of ammonia injection pathway on SO₂ removal efficiency (see Figure 6). It is shown that adding at least 50% of total ammonia water amount straight to the cooling tower increases SO₂ removal efficiency considerably. The other factors as flue gas flow rate and inlet concentration has much less impact on SO₂ removal efficiency.

FIG. 5. SO₂ and NOₓ removal efficiency vs. ammonia stoichiometry.

FIG. 6. SO₂ removal efficiency vs. ammonia dosing way in Pomorzany, Poland.
The by-product output is usually in the range of 200 – 300 kg/h depending on the flue gas flow rate, and pollutants concentration. The by-product contents mainly ammonium sulphate (45 – 60%), ammonium nitrate (22 – 30%). The most important impurity is ammonium chloride (10 – 20%) that is a result of high concentration of sodium chloride in Polish coal. The insoluble matter content is in the range 0.5 – 2% and it consists mostly of residuals of fly ash and some rust, so the heavy metals occur only in traces. The total nitrogen content is up to 27% compared to 21% in ammonium sulphate. The whole amount of generated by-product is sold to the local fertilizer production plant, and the incomes lower the overall operational costs of the plant.

The most important problems during operation of the plant were connected with the accelerators produced by Nissin High Voltage (Japan). In the beginning of the start-up trials, a high voltage supplier malfunction occurred and the electron energy had to be lowered from 800 keV to 700 keV. Lowering the energy of electrons resulted in reduction beam penetration in the gas, so some part of the gas remained not irradiated. In order to correct this problem the construction of bottom of the reaction vessel had to be rearranged. Also availability of the accelerators was not satisfactory due to planned maintenance (window foil and cathode exchange) and frequent malfunctions. As all the problems with other parts of the facility were successfully solved, the proper selection of accelerators is crucial for reliability of the whole installation and further development of the technology.

The second problem that needs to be especially carefully considered is the corrosion. The corrosive conditions are inside the installation, especially inside and after the reaction vessel. The quality of materials used for the construction and anticorrosion coatings application is crucial for long life of the installation.

Apart of the technical advantages of EBFGT technology, the economical side of the investment is very important for the future investors. In the world, the most often used is a combination of wet flue gas desulphurisation and selective catalytic reduction systems. Therefore the trial of comparison of investment and operational costs between electron beam flue gas treatment method and wet FGD + SCR method was undertaken [8]. The comparison of the costs of various emission control methods for a 120 MW_e unit is presented in Table I.

<table>
<thead>
<tr>
<th>Emission control method</th>
<th>Investment cost (USD/kW_e)</th>
<th>Annual operational cost (USD/MW_e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet flue gas desulphurisation</td>
<td>120</td>
<td>3000</td>
</tr>
<tr>
<td>Selective catalytic reduction</td>
<td>110</td>
<td>4600</td>
</tr>
<tr>
<td>Wet FGD + SCR</td>
<td>230</td>
<td>7600</td>
</tr>
<tr>
<td>Electron beam FGT</td>
<td>160</td>
<td>7350</td>
</tr>
</tbody>
</table>

The above calculations indicate that the method is attractive in the case of both pollutants removal. Please notice that the calculations were made for high NO_x removal case. In the case of low NO_x removal both investment and operational costs will be considerably reduced. In the future it is expected to obtain the costs of EBFGT method at the level of wet-FGD costs.
4. PERSPECTIVES OF TECHNOLOGY DEVELOPMENT

The electron beam flue gas treatment technology is very attractive. The process allows for effective simultaneous removal of SO$_2$ and NO$_x$, and other pollutants (VOC, dioxins), that makes it universal multi-pollution control system with wide spectrum of potential applications. Process idea as well as facility construction is simple and most of apparatus are routinely used in the industry. This makes easy retrofitting and unification of the EBFGT facility with the power plant. With its high flexibility, the installation may be used in different modes (ex. winter and summer operation of thermal power plant) and may be easily upgraded for future modernizations. Not less important is the by-product, which is fully usable, very clean fertilizer. Also preliminary economical calculations indicate for competitiveness of the EBFGT process comparing to set of wet-FGD and SCR processes.

However there are many advantages of the EBFGT technology, there are still some weak points, that halt the process implementation in the industry. The most important is the high power accelerators state of art. The power of existing accelerators allows for construction of flue gas treatment facilities for low and medium size power generation units. On the other hand the reliability of such big machines is still regarded as not satisfactory (over 8500 hours of operation per year is required) and the price of this apparatus is very high.

The second point is high investment risk of such enterprise. At this moment there is only one reference facility in the world – installation constructed at Pomorzany Electric Power Plant in Poland. Also no company in the world can offer key ready EBFGT facility. On the other hand wet-FGD process is the most popular desulphurization process and most of power plants in the industrialized countries are already equipped in such installations. In this case there is no point to double SO$_2$ removal system.

The breaking point of the technology development may be its commercialization. The first step of the whole process development is development of the crucial element of the chain – the accelerators. Higher power and more reliable accelerators will allow for further implementations of the technology. With the increase of the implementations of the technology the demand for accelerators will increase that should result in reducing of the accelerators price.

Another element is reducing the investment risk of new facilities. There success of projects in China, Bulgaria and Saudi Arabia may be an impulse for the investors. Of course the market in Europe, United States and other industrialized parts of the world according to power plants is already saturated by conventional desulphurization methods. Therefore new regions and new fields of application should be sought. EBFGT technology may be applied in the regions of the world, where emission control regulations were introduced recently. The second direction is application for the processes different then coal combustion. As the technology may be applied for more then two main pollutants it can be used in different branches of industry (eg. ore sintering off gases, waste incineration plants etc.). The recent research also indicates that it can be used for treatment of the gas from combustion of fuels other than coal. New plants and processes, where no emission control method is used may be the chance for application of EBFGT technology.

The last, but not least problem is economy of the process. It seems that the process is economically attractive in the case of both pollutants removal and the market status of by-product is crucial for the operational costs of the plant. However the data available at the moment are not enough convincing for the investors. Therefore further studies on the process economy are welcome.

The electron beam flue gas treatment technology proved its ability for application in the industry. Intensive promotion of the method together with breaking up the last technological and marketing barriers will allow for creating the good engineering company being able to offer this technology in the international market. Success of such enterprise will be the success of international team working on different aspects of electron beam flue gas treatment.
5. CONCLUSIONS

1. The industrial EB plant has proven the ability of the technology for efficient removal of SO₂ and NOₓ from flue gases from coal combustion processes.

2. The solutions applied to main devices of this facility were correct. Most of the problems that were observed in the previous stage of operation were solved.

3. The by-product is a high quality fertilizer component and is well accepted by Fertilizer Company.

4. The experiences gathered during the erection and operation of Pomorzany EB plant can be used during the design and construction of new facilities.

5. EBF GT installation needs further development. The most important is development of the accelerators to assure high availability of the facility. Also further development of the technology itself will enable using it for treatment of flue gases from various combustion processes.

6. The EB technology is one of the most promising multi-pollution control systems. In the near future the commercialization of the technology should take place.

REFERENCES


OPERATIONAL EXPERIENCE OF ELECTRON BEAM FLUE GASES TREATMENT PILOT INSTALLATION AT THE MARITSA EAST 2 THERMAL POWER PLANT

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Manager of EB projects for Bulgaria, NEK-EAD, Bulgaria

Abstract

The electron beam flue gases treatment process is very versatile and effective technology for simultaneous removal of acidic pollutants i.e. sulfur dioxide ($SO_2$) and nitrogen oxide ($NO_x$) from the flue gas produced in the combustion of fossil fuel. The technology allows decomposition of VOC (volatile organic compound) such as polycyclic aromatic compound (PAC) and persistent organic pollutants (POP). The electron beam flue gases treatment technology for combustion flue gases purification was applied in Maritsa-East 2 Thermal Power Plant. The decision for construction of Electron Beam Pilot Plant at Maritsa-East 2 TPP was taken at the technical meeting in IAEA Vienna, November 1998. The flue gases of 10 000 nm³/h are irradiated by three high energy electron accelerators of 800 keV and 35 kW beam power each. The plant has been operated since November 2003. The removal efficiency 90 - 99 % for $SO_2$ and 85 - 90 % for $NO_x$ was observed. The quality of coals are characterised with high ash content up to 45%, high moisture up to 57%, low calorific value from 1196 kcal/kg up to 1603 kcal/kg and high concentration of sulphur. The Bulgarian lignite coals are unique in their usage as fuel for the thermal power plants in Maritsa East region.

1. INTRODUCTION

Power generation using fossil fuels, such as coal, natural gas and petroleum is responsible for the release of different pollutants into atmosphere along with the off-gases from industries, power stations, residential heating system and vehicles. During the combustion process various pollutants such as fly ash, sulphur oxides ($SO_2$ and $SO_3$), nitrogen oxides ($NO_x = NO_2 + NO$) and volatile organic compounds (VOC) are emitted. There are different methods and technologies worldwide for industrial flue gases cleaning. The choice of the best and most efficient method and technology depend on a long series of criteria, part of which are about the simultaneous purification of sulfur dioxide ($SO_2$) and nitrogen oxides ($NO_x$), the presence of a secondary pollution, the type of the by-products, the possibility for partial investments return, raw materials supply etc. The most widely applied systems for coal fired boilers are wet flue gas desulphurization (FGD) using limestone as reagent for $SO_2$ removal and selective catalytic reduction (SCR) for $NO_x$ reduction. All these technologies are complex chemical processes and generating waste like, waste water, gypsum and spent catalyst.

Radiation processing using electron beam accelerators has shown very promising result in this regards. The electron beam technology is a dry method for simultaneous purification of sulfur and nitrogen oxides in flue gases, without any waste products or water. The mix of nitrogen sulfate and nitrogen nitrate obtained as a by-product can be used directly as fertilizer or as component for mixed fertilizers used in agriculture. This technology has shown very good results when treating gases with high concentration of $SO_2$, as flue gases in the thermal power plants at the Maritsa East region.

2. IMPLEMENTATION OF THE PROJECT

The installation uses the Electron Beam Technology, developed jointly by JAERI and the Japanese company Ebara. According to the three parties Contract, the sides were responsible respectively for:

**NEK EAD** has provided for the financing of the operational design; the elaboration of the reactor and the spray cooler; the local production equipment supply; the Pilot Installation construction, erection and commissioning; the elaboration of a research study and report about the possibilities for applying the electron beam technology for flue gases treatment in Bulgaria.

**IAEA** participated in the project financing for part of the main equipment supply and for personnel training at the Pilot Installation.

**JAERI** has donated three accelerators and the entire electrical DC supply for them through IAEA to NEK EAD.
The project is of major importance from environmental point of view and it is monitored by IAEA in Vienna, the Bulgarian authorities, namely the Ministry of Environment and Waters, the Nuclear Regulatory Agency and the Ministry of Economy and Energy. Nuclear Regulatory Agency (NRA) monitors the activities concerning the industrial usage of Ionizing Radiation Sources (IRS).

3. PLANT DESCRIPTION

The EB Pilot Plant consists of six major equipments (Table I)

<table>
<thead>
<tr>
<th>Table I. SUMMARY OF MAJOR EQUIPMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong> Spray cooler</td>
</tr>
<tr>
<td>Number 1 unit</td>
</tr>
<tr>
<td><strong>Type</strong> Vertical and parallel flow, cooling water recycling</td>
</tr>
<tr>
<td><strong>Dimensions</strong> D = 1.0 m  H = 8.4 m</td>
</tr>
<tr>
<td><strong>Main components</strong> Spray column equipped with spray nozzles, recirculation pump with water filtration</td>
</tr>
<tr>
<td><strong>2</strong> Process vessel</td>
</tr>
<tr>
<td>Number 1 unit</td>
</tr>
<tr>
<td><strong>Type</strong> Horizontal flow, sideward irrigation, 3 h3ads</td>
</tr>
<tr>
<td><strong>Dimensions</strong> L = 11.0 m  W = 2.4 m  H = 2.4 m, Rectangular section</td>
</tr>
<tr>
<td><strong>Main components</strong> Process vessel with injection nozzles for water and ammonia, flashing nozzles for deposit discharge</td>
</tr>
<tr>
<td><strong>3</strong> E – beam system</td>
</tr>
<tr>
<td>Number 1 unit (x 3 accelerators of unit)</td>
</tr>
<tr>
<td><strong>Type</strong> Scanning (accelerators), transformer (power supply)</td>
</tr>
<tr>
<td><strong>Dimensions</strong> 800 kV x 45 mA x 3 heads</td>
</tr>
<tr>
<td><strong>Main components</strong> Accelerators, power supply, distributor, connecting cables</td>
</tr>
<tr>
<td><strong>4</strong> By-product collector</td>
</tr>
<tr>
<td>Number 1 unit</td>
</tr>
<tr>
<td><strong>Type</strong> Dry type electrostatic precipitator, horizontal flow</td>
</tr>
<tr>
<td><strong>Dimensions</strong> L = 16 m  W = 2.4 m  H = 8.0 m (total height)</td>
</tr>
<tr>
<td><strong>Main components</strong> ESP with by-product conveyor and discharge airlock</td>
</tr>
<tr>
<td><strong>5</strong> By-product handling System</td>
</tr>
<tr>
<td>Number 1 unit</td>
</tr>
<tr>
<td><strong>Type</strong> Rolling press with crusher</td>
</tr>
<tr>
<td><strong>Dimensions</strong> L = 1.2 m  W = 0.8 m  H = 1.5 m (only roll press)</td>
</tr>
<tr>
<td><strong>Main components</strong></td>
</tr>
<tr>
<td><strong>6</strong> Ammonia facility</td>
</tr>
<tr>
<td>Number 1 unit</td>
</tr>
<tr>
<td><strong>Type</strong> Liquid ammonia tank</td>
</tr>
<tr>
<td><strong>Dimensions</strong> D = 2.5 m  L = 8 m</td>
</tr>
<tr>
<td><strong>Main components</strong> 40 m³ tank, transfer pump, vaporizer, buffer tank</td>
</tr>
</tbody>
</table>

3.1. Spray cooler

The first operation unit is spray cooler (Fig. 1). It has the following dimensions: diameter 1.0 m and height 8.4 m. The spray column is equipped with spray nozzles and recirculation pump with water filtration unit. The flue gas from combustion process normally has too high temperature and too low humidity for optimal reduction of SO2 and NOx. Flue gases generated in Maritsa East 2 TPS from the boilers 1 and 7 of an amount of 10 000 nm³/h, with the temperature of 130 – 140°C are passing through spray cooler. The optimal temperature after spray cooler should be from 60 to 75°C and optimal humidity 12 to 14% vol. The spray cooler of wet bottom and circulation water type is used in EB flue gas treatment Pilot Plant located at TPS Maritsa East 2. This wet bottom type of spray cooler was tested first at Nagoya - Japan, Kaweczyn - Poland and Maritsa East 2, EBFGT Pilot Plant.
In the operation period there was a problem with spray nozzles. Because of high SO$_2$ content in the flue gas the rust is formed in the ducks and small bit portion come to spray cooler. After recirculation of the polluted water from the bottom of spray cooler, the small bits are coming into the nozzles and plug them. The nozzles were drilled from 4 mm to 6 mm diameter and the polluted water was sent to water treatment system and to spray nozzles. The holder tube was changed from welded stainless steel to polypropylene for better performance.

3.2. Process vessel (Reactor)

Flue gas after cooling at spray cooler is going thought process vessel – reactor (Fig. 2). The process vessel is rectangular cross section type. During the assembling fist process vessel (reactor) was installed and after that was leveling, to be higher in the inlet side and lower in outlet side of flue gas. This alignment was done because the deposits on the reactor bottom are washed with water, which together with the condensate is going by gravity through the outlet protection labyrinth and is taken to a drain basin, from where goes to the water treatment system for purification. The front and back labyrinths are welded to the reactor (see Fig. 2). In the process vessel gaseous ammonia mixed with water are put into reaction chamber, through special two way nozzles. After irradiation many
Working Material

different chemical reactions are going and creation of by-product is observed. The by-product is ammonium sulfate and nitrate which are fertilizers and may be used in agriculture sector.

In order to provide the necessary radiation protection, the reactor is installed in a room with reinforced concrete walls of 1.3 m thick, and metal labyrinths are erected at the inlet and outlet of flue gas for reducing the radiation to the admissible rates. In consequence of the radiation, ozone is produced in the process vessel room, so it is then taken away by ventilation fans.

In the operation period it was observed medium deposit from ammonium sulfate and nitrate on the reactor walls and on the accelerators outside foils. When the velocity of flue gas in the reactor is bigger the deposition of walls and foils is smaller.

3.3. Electron beam system

The accelerators are the most important and the most technological advanced apparatus in EB technology. There are three high energy scanning accelerators, transformer type power supply, with high voltage of 800 kV and beam current 45 mA with 35 kW beam power each. They are assembled with reactor by special flanges. The three accelerators are assembled horizontal in front of reactor vessel (see Fig. 3). The reactor is separated from the accelerators by two layers of titanium foil of the scanner windows, through which the high-energy electrons pass. When high-energy electrons react
with the substance a secondary X radiation is produced. Its intensity is 175 Sv/h. The scanner windows of accelerators have water cooling system and air cooling system. In the accelerator chamber, each Accelerator are radiation protected though lead screen.

In the operation period water cooling system and air cooling of windows of the accelerators were working properly. Parches air for cleaning deposits from windows' foils was working normally. Ozone is generated from this parches air after irradiation. It is removed to the atmosphere by ventilation system.

FIG. 3. Drawing of Process Vessel and Electrostatic Precipitator

3.4. By-product collector – Electrostatic precipitator (ESP)

The by-product obtained after reaction is captured in an electrostatic precipitator. The electrostatic precipitator is dry type with horizontal flow. It has four electrostatic stages. By-product precipitated in ESP is hygroscopic and the corrosion may occur if it is wet. For protection from the condensation of water the walls and bottom of ESP are steam heated. By-product is removed from electrodes with special hammers mounting inside in ESP and falls down where longitudinal conveyor is installed. ESP has two conveyors. One is longitudinal of the bottom of ESP and grabs by-product from the walls and electrical discharge system. The second is the cross conveyer and by-product is conveyed through discharge airlock system and it was transferred to the product handling system to package.

In the operation period a lot of deposits of ammonium sulfate and nitrate inside electrostatic precipitator were formed. Any three months we had to stop the whole system and clean Electrostatic precipitator from this deposit. This was one of the major problems of the EB Pilot Plant.
3.5. By-product handling system

By-product is grabbed from ESP by longitudinal and cross conveyers and after that is moved to by-product handling system. Here rolling airlock discharge system for by-product handling is mounted. After that crashing system to prevent staking of the by-product is installed. By-product is collected in 500 kg bags through double sleeve. When one bag is filled, another sleeve is opened.

In the operation period some of the sleeve was plugged. To prevent the plugging of the sleeves, it was mounted the hammer.

3.6. Ammonia facility

Liquid ammonia, necessary for the process, is supplied by tank trucks and is unloaded to a constant storage tank with volume of 50 m$^3$. Before injection into the flue gas, ammonia is evaporated in small evaporator. After that evaporated ammonia gas is mixed with hot air and goes to the two ways, gas - water nozzles and injected at inlet of reactor. Water dissolves ammonia salts and prevents formation of deposit. This system is very good for low temperature process, in which mainly SO$_2$ is removed as in EB Pilot Plant.

In the operation period there wasn’t observed any problems.

The main flue gas fan overcomes the aerodynamic resistance in the installation. The purified flue gases are taken to the stack.

4. RESULTS OF CONTINUOUSLY OPERATION OF THE EB PILOT PLANT

The main task of the constructed EB Pilot installation at the Maritsa East 2 Thermal Power Plant for simultaneous reducing SO$_2$ and NO$_x$ from the flue gases was to prove the applicability of the electron beam technology at power plants fired by Bulgarian lignite coal. This lignite coal have high ash content at air-dried base $A^d$ - from 30% to 45% and high moisture $W^t$ as well - from 57.2% to 52.5%. Low calorific value $Q_{i}$ of 1196 kcal/kg to 1603 kcal/kg and high concentration of sulfur make the Bulgarian lignite coal unique in their usage as fuel for the thermal power plants at the Maritsa East region. Flue gases from the process of coal burning are typical with the prevailing content of SO$_2$ compared to NO$_x$ and with the small change in these two parameters and the relative stability of their average value.

Very important parameter is high concentration of sulfur dioxide SO$_2$ in the incoming flue gases from 16 095 up to 16 151 mg/Nm$^3$. The nitrogen oxides (NO$_x$) content is from 112 up to 390 ppm. Main process parameters are specified in Table II.
TABLE II. PROCESS PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas flow</td>
<td>10 000 Nm$^3$/h</td>
</tr>
<tr>
<td>SO$_2$ concentration (inlet)</td>
<td>17 000 – 21 000 mg/Nm$^3$</td>
</tr>
<tr>
<td>NO$_x$ concentration (inlet)</td>
<td>200 - 250 mg/Nm$^3$</td>
</tr>
<tr>
<td>Temperature at the process vessel inlet</td>
<td>62 - 67 °C</td>
</tr>
<tr>
<td>Absorbed dose</td>
<td>0 - 10 kGy</td>
</tr>
<tr>
<td>Ammonia consumption</td>
<td>35 - 50 kg/h</td>
</tr>
<tr>
<td>Secondary cooling water consumption</td>
<td>300 l/h</td>
</tr>
<tr>
<td>Process air consumption</td>
<td>135 m$^3$/h</td>
</tr>
<tr>
<td>Electricity consumption</td>
<td>150 kWh</td>
</tr>
<tr>
<td>Amount of by-product obtained</td>
<td>150 - 200 kg/h</td>
</tr>
</tbody>
</table>

The result of continuous operation at the Pilot Electron Beam Installation was carried out together with control tests for the trustworthiness of the physical and chemical measurements and their calibration, as well as their impact on the computer information system for operational management of the processes in the installation. The chart flow diagram of Pilot Plant and computer scheme of EBFGT Pilot Plant are presented in Fig. 4 and 5.

FIG. 4 Chart Flow Diagram of Pilot Plant
The removal efficiency of SO$_2$ was 99.4% and NO$_x$ was 82.9% when the stoichiometric ammonia quantity $\alpha$ was 0.70, stoichiometric water quantity $\beta$ was 0.8, stoichiometric air quantity $\gamma$ was 1.0 and dose rate was 3.93 kGy.

The operation experience gives reasons to make the following conclusions:

- The lignite coal have low calorific value from 1196 kcal/kg to 1603 kcal/kg and high sulfur content resulting in high concentration of sulfur dioxide SO$_2$ in the flue gases from 16 095 up to 16 151 mg/Nm$^3$.
- The temperature after the spray cooler is kept in the range of 62-65°C, so there is no corrosion of the surfaces of cooler and reactor;
- The measured dew point of the flue gases is 58 °C.
- The measured humidity of the incoming flue gases is 16-18 % depending on the fuel and the content of additional air ($O_2$) in the flue gases. This indicator is necessary for the stoichiometry calculations.

Detailed studies were done with respect to the effect of the following parameters: temperature at the spray cooler and reactor inlet, dose rate, effect of the nozzles water sprinkling, effect of the ammonia supply for the flow rate from 5,000 up to 10,000 nm$^3$/h.
After long operation experience the best operating parameters were set as follows:

- Temperature after spray cooler $t_k$ 62-65°C;
- stoichiometric ammonia quantity $\alpha$ 0.85-0.95;
- stoichiometric water quantity $\beta$ 0.6-0.9;
- stoichiometric air quantity $\gamma$ 1.0;
- dose rate about 4 kGy.

The results of the studies are shown in the Table III.

### TABLE III. INVESTIGATION RESULT OF PROCESS PARAMETERS.

<table>
<thead>
<tr>
<th>№</th>
<th>Parameter</th>
<th>Dimension</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Flue gases flow rate</td>
<td>Nm³/h</td>
<td>5 000 6 000 7 000 8 000 9 000 10 000</td>
</tr>
<tr>
<td>2</td>
<td>Temperature before the reactor</td>
<td>°C</td>
<td>68.3 65.9 65.9 61.0 63.9 65.7</td>
</tr>
<tr>
<td>3</td>
<td>Stoichiometric ammonia consumption - $\alpha$</td>
<td>-</td>
<td>0.90 0.90 0.75 0.85 0.90 0.85</td>
</tr>
<tr>
<td>4</td>
<td>Stoichiometric water consumption - $\beta$</td>
<td>-</td>
<td>0.20 0.90 0.90 0.60 0.90 0.85</td>
</tr>
<tr>
<td>5</td>
<td>Stoichiometric air consumption - $\gamma$</td>
<td>=</td>
<td>1.00 1.00 1.00 1.00 1.00 1.00</td>
</tr>
<tr>
<td>6</td>
<td>Ammonia consumption</td>
<td>kg/h</td>
<td>16.3 21.41 24.6 26.82 33.4 31.79</td>
</tr>
<tr>
<td>7</td>
<td>Dose rate</td>
<td>kGy</td>
<td>9.29 6.93 4.98 3.96 3.95 3.94</td>
</tr>
<tr>
<td>8</td>
<td>Efficiency of SO₂ removal</td>
<td>%</td>
<td>99.1 99.6 92.9 93.4 98.2 97.8</td>
</tr>
<tr>
<td>9</td>
<td>Efficiency of NOₓ removal</td>
<td>%</td>
<td>90.7 85.8 80.4 89.1 84.4 86.3</td>
</tr>
</tbody>
</table>

**FIG. 6. Influence of ammonia stoichiometry on SO₂ and NOₓ removal efficiency**
Ammonia stoichiometry has direct influence on SO₂ removal (Fig. 6). The change of ammonia stoichiometry by step of 0.1 obviously results in change of SO₂ removal efficiency.

**FIG. 7.** Influence of dose rate change on SO₂ and NOₓ removal efficiency.

The change of dose rate has direct influence on NOₓ removal and has not influence on SO₂ removal efficiency (Fig. 7). The efficiency of NOₓ removal was following the dose rate change.

**FIG. 8.** Influence of dose rate change on SO₂ and NOₓ removal efficiency.

Fig. 8 shows that the removal efficiency of NOₓ is following the staircase change of dose rate. After 6 kGy dose rate change has smaller influence of NOₓ removal. There is no influence of dose rate change on efficiency of SO₂ removal.

64
The stoichiometry of water $\beta$ has influence on efficiency of SO$_2$ removal up to 0.70. After that up to 0.85 the impact of $\beta$ change is smaller (Fig. 9). The dose rate is “0”, flow rate is 6000 Nm$^3$/h and $\alpha$ is 0.84.

FIG. 9. Influence of stoichiometry of water quantity $\beta$ change from “0” up to 0.85 on efficiency of SO$\textsubscript{2}$ removal. Dose rate is “0”, flow rate is 6000 Nm$^3$/h, and ammonia stoichiometry $\alpha$ is 0.84.

FIG. 10. Dependence of temperature in the inlet of reactor on efficiency of SO$\textsubscript{2}$ removal.
Working Material

When temperature in the outlet of spray cooler and inlet of the reactor is 70°C the efficiency of SO₂ removal is small. When temperature in the outlet of spray cooler and the inlet of the reactor decreases to 65°C the efficiency of SO₂ removal increases (Fig. 10).

The flue gas flow rate have more bigger influence on removal efficiency of SO₂ and NOₓ between 5000 up to 7500 Nm³/h and less from 8000 to 10 000 Nm³/h. (Fig. 11) The flow rate of flue gas is changed with stabilized process parameters contributed of the revealing of this influence.

Operation experience of the EB Pilot plant allows formulating following observations:

1. The efficiency of SO₂ and NOₓ removal depends mainly on the flue gas temperature, the absorbed dose, the stoichiometric ammonia rate, the humidity etc., where for SOₓ efficiency reaches more than 95 % and for NOₓ – 70-85 %.

2. The technology tests show that the higher SO₂ concentration and the moisture of flue gas, the higher efficiency of purification. This means good results of the tests and a strongly competitiveness to the FGD technology.

3. The by-product from pilot plant is valuable both separately, after granulation and as an appropriate component in the production of blended fertilizers.

4. The main goal of the pilot installation was to gather research and operational experience in the process of flue gas treatment and generation of a useful by-product with a clear market value. This goal was extended for searching the possibilities of the technology improvement and for using it at units fired by other fuel in Bulgaria and in South East Europe.

5. The research should be continued after the completion of the present tasks, for which the installation was constructed.

6. According to our understanding of the obtained results and foreseen decision for construction of an Industrial Electron Beam Installation, all the research, tests and studies have to be directed to accumulate specific experience in this field.
5. CONCLUSIONS

1. The EB technology is dry process without generating any waste product.

2. The EB Pilot Plant successfully removes sulfur and nitrogen oxides.

3. Very high efficiency was achieved with respect to desulphurization (DeSO₂) - up to 99% and with respect to de-nitrification (DeNOx) - up to 90%.

4. The technology allows decomposition of VOC (volatile organic compound) such as Polycyclic Aromatic Compound (PAC) and persistent organic pollutants (POP).

5. Useful by-product is collected from EB installation as ammonium sulfate and ammonium nitrate and may be used like fertilizers in Bulgaria or abroad.

6. It is an intention to offer EBFGT Pilot Plant at TPS Maritsa East 2 for IAEA training center for specialists from different countries. Since September 2005 the installation was closed because of the construction of new FGD Plant for units 1 to 4 nearby.

REFERENCES

Abstract

The electron beam flue gas treatment process is one of the most promising technologies in the modern environmental protection. The technology allows the simultaneous removal of acidic pollutants such as SO\textsubscript{2} and NO\textsubscript{x} with high efficiency and decomposition of VOC (volatile organic compounds) without generating any wastes. These pollutants are named “acid gases” that cause acid rain and damage forests, agriculture fields and flora as well as public health. After successful operation of Electron Beam Flue Gas Treatment Pilot Plant at Maritsa East 2 TPS, the Bulgarian Ministry of Economy and Energy has taken decision for implementation EB technology in the industrial scale at “Sviloza” TPS in Svishtov, Bulgaria. The Industrial Electron Beam Flue Gas Treatment Plant (IEBFGTP) covers 100% of the flue gases generated from all units of TPS “Sviloza” JSC, Svishtov. This Thermal Power Station generates flue gases from all boilers – 600 000 Nm\textsuperscript{3}/h, with emission of SO\textsubscript{2} → 2800 – 4800 mg/Nm\textsuperscript{3}, NO\textsubscript{x} → 1200 – 1600 mg/Nm\textsuperscript{3} and dust → 200 – 1400 mg/Nm\textsuperscript{3}. The major objective of the electron beam project is to reduce harmful emissions of SO\textsubscript{x}, NO\textsubscript{x} and VOC by 85%. The by-product generated by the electron beam plant is ammonium sulfate and ammonium nitrate and it can be used as fertilizer in the Bulgarian agriculture sector and abroad.

1. INTRODUCTION

The conference entitled Environment for Europe (Sofia, October 1995) defined, as one of the most important initiatives, to decrease the air pollution with sulfur and nitrogen oxides. These emissions are the main pollutants of the air in Bulgaria, where the real load of 150-160 kg of sulfur oxides per person annually defines the country as one of the “hot spots” on the continent.

The power plants burning Bulgarian local coal, which due to the high content of combustible sulfur cause the main pollution with sulfur oxides in Bulgaria – 14 000-20 000 mg/Nm\textsuperscript{3}.

The power plants firing imported hard coal, which due to the specificity of the combustion method used – high calorific fuel and combustion with high temperatures of 1600-1700 °C in the furnace zone (wet slag formation), generate the main quantities of nitrogen oxides ~ 2000 mg/Nm\textsuperscript{3}.

The small electric power and heat generating plants on liquid fuels with 3.5% sulfur content emit the two types of pollutants. In Bulgaria these plants include all the district heating plants that burn heavy oil, small factory plants and industrial boilers mainly types KM-12 and PKM-12, which, though being small by unit capacity, do have a significant effect on the environment. The emissions from boilers which burn heavy oil are about 6 500 mg/Nm\textsuperscript{3} of sulfur oxides and about 400 – 600 mg/Nm\textsuperscript{3} of nitrogen oxides.

2. DESCRIPTION OF THE PROJECT

On the base of the feasibility study made, comparing different options it is concluded that Electron Beam Technology is the most appropriate for cleaning waste gases generated from the thermal power station (TPS) Sviloza Ltd. The present paper will give evidences about selection of the technology and the benefits expected after process implementation. The results from the experimental work on the by-product manufacturing on the way to obtain more valuable fertilizers are also provided. Principle scheme for production of extruded complex fertilizers on the base of the product will be shown additionally. Conclusions made are supported by the data from the agrochemical efficiency of the new fertilizers produced.

TPS “Sviloza” JSC, Svishtov is located on the Danube river coast, i.e. on Bulgarian-Romanian border. The figure 1 shows the place where Industrial EB Installation will be located.
FIG. 1. Place for Industrial EBFGT Installation at “Sviloza” TPS.

Figure 2 shows the possible implementation of EBFGT technology which can be applied at “Sviloza” TPS.

FIG 2. Possible implementation of EBFGT technology which can be applied at “Sviloza” TPS.
“Sviloza” TPS JSC, Svishtov is a joint-stock company generating both electricity and heat. The Thermal Power Station was built within 1965 - 1971 and provides electricity and heat to “Sviloza”-JSC. The surplus of electricity is sold to the National Energy Grid.

**Capacity**
- Electricity (gross) 120 MW
- Heat (steam and boiled water) 280 MW
- Desalted water 200 m³/h

TPS “Sviloza” JSC, Svishtov consists of the following equipments:

1. Boilers – 4 units, 220 t/h each one, steam pressure 10 Mpa, temperature 540ºC;
2. Turbo aggregates – 2 units general capacity 120 MW;
3. Water deionization installation with capacity 200 m³/h.

TPS “Sviloza” JSC, Svishtov is to produce electricity and heat over the next 20 years.

### 3. SCOPE OF THE PROJECT

The scope of the project includes:

- procurement of the main equipment (reactors, accelerators, DC transformer, electrical system, ESP etc.);
- building reinforced concrete foundations and installing reactors with accelerators, DC transformers and an electrostatic precipitator (ESP) as well as auxiliary equipment.

The scope of local contribution includes:

- preparing of the ground plate for Industrial Electron Beam Flue Gas Treatment Plant;
- delivery of the AC system;
- assembling the mechanical, electrical components and the AC system;
- delivery of the ammonia supply system;
- assembling of the ammonia supply system;
- installation, testing and commissioning of the EB facility.

The commissioning of the Industrial Electron Beam Flue Gas Treatment Plant and its subsequent operation is expected to have a major economic benefit as a result of the by-product ammonium sulphate and ammonium nitrate sale to the agricultural market – the amount being of 2 000 000 Euro annually. That amount will help decrease operation expenditure for EB installation with about 50%.

The main positive effects are as follows:

- Reduction of harmful SO₂, NOₓ and VOC emissions by 85% from the flue gases generated by TPS “Sviloza” JSC.
- Generation of useful by-product of EB installation as ammonium sulfate and ammonium nitrate based fertilizers.

The Industrial Electron Beam Flue Gas Treatment Plant (IEBFGTP) covers 100% of the flue gases generated from all units of TPS “Sviloza” JSC, Svishtov. This Thermal Power Station generates flue gases from all boilers – 600 000 Nm³, with emission of SO₂ → 2800 – 4800 mg/Nm³, NOₓ → 1200 – 1600 mg/Nm³ and dust → 200 – 1400 mg/Nm³.

According to the Kyoto Protocol after 2008 it is necessary to reduce above mention pollutants within 50%. Industrial Electron Beam Flue Gas Treatment Plant at TPS “Sviloza” JSC, Svishtov will
reduce those pollutants at least of 85% and especially emission of $\text{SO}_2 \rightarrow 90 - 92\%$. Maximum operation term of EB Plant is 25 years.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_2$</td>
<td>2958 (885-5061)</td>
<td>1080</td>
</tr>
<tr>
<td>$\text{NO}_x$</td>
<td>1269 (868 -1670)</td>
<td>1200 at 31.12.2015 600 from 01.01.2016</td>
</tr>
<tr>
<td>Dust</td>
<td>821 (164 -1479)</td>
<td>100 at 31.12.2007 250</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

The project for realization of “Industrial Electron Beam Flue Gas Purification plant” at TPS “Sviloza” JSC is supported from Government of Bulgaria like Ministry of Economy and Energy, Ministry of Environment and Water, municipality of Svishtov and municipality of Zimnic, Romania.

Financing will be realized by Bulgarian and Foreigners Banks.

Existing technical and economical assessment of the effect from the realization of that project will take part the Bulgarian Academy of Science, Chemical Institute, Energoproject and others.

TPS “Sviloza” JSC is ready to prepare public – government properties for managing industrial electron-beam installation in Svishtov. In this organization will take part Municipality of Svishtov, TPS “Sviloza”, Bulgarian Academy of scientist, Chemical Institute, Energoproject and others, under management of Ministry of Economy and Energy.

### Project Implementation Schedule (Indicative)

<table>
<thead>
<tr>
<th>Project Activity</th>
<th>Start</th>
<th>Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feasibility study</td>
<td>01/10/2005</td>
<td>31/04/2006</td>
</tr>
<tr>
<td>Cost / benefit analysis</td>
<td>01/04/2006</td>
<td>30/08/2006</td>
</tr>
<tr>
<td>Environment impact assessment</td>
<td>01/12/2006</td>
<td>31/04/2007</td>
</tr>
<tr>
<td>Design studies</td>
<td>01/04/2007</td>
<td>30/12/2007</td>
</tr>
<tr>
<td>Tender documents for equipment delivery, construction and technical supervision. Tendering</td>
<td>01/10/2007</td>
<td>31/12/2007</td>
</tr>
<tr>
<td>Construction</td>
<td>01/12/2007</td>
<td>31/05/2009</td>
</tr>
<tr>
<td>Test of system</td>
<td>01/06/2009</td>
<td>31/10/2009</td>
</tr>
<tr>
<td>Operating phase</td>
<td>01/11/2009</td>
<td>31/12/2009</td>
</tr>
</tbody>
</table>

**Poland** 14-18 May 2007

*FIG 3. Project Implementation Schedule*
Expected results from the project

Environment results
- Dry process without any waste product;
- Simultaneous removal of NO\textsubscript{x} and VOC by 80%;
- Simultaneous removal of SO\textsubscript{x} by 92%;
- Reduction of annual emission of NO\textsubscript{x} from 3040 t/a to 610 t/a;
- Reduction of annual emission of SO\textsubscript{x} from 12 200 t/a to 650 t/a;
- Annual by-product production from SO\textsubscript{x} - ammonium sulfate 23 800 t/a and from NO\textsubscript{x} - ammonium nitrate 4200 t/a;
- High efficiency in removal of all harmful components;
- Reduction trans-border pollutants up to 85% from SO\textsubscript{x}, NO\textsubscript{x} and VOC.

Economic results
- Low capital and operation cost and small space;
- The economical benefit is expected after commissioning of Industrial Electron Beam Flue Gas Treatment Plant, and sales the by products to agriculture market - ammonium sulfate and ammonium nitrate, which are fertilizers – 28 000 t/a, at total amount of 2 000 000 Euro annually. With this sum operation expenditure for EB Installation will decrease by about 50%.

Social results
The Industrial Electron Beam Flue Gas Treatment Plant will be give additional job of 50 - 60 persons - operational staff. The population of Svishtov is around 45 000 – 50 000 and a considerable part of those people are unemployed. The unemployment rate in the region is around 10 – 15 %. The operational lifetime of the project is 25 years and expected Payback period is 11 years, IRR 7%.

4. PRODUCTION OF FERTILIZERS

On the basis of the results obtained from the studies made about the properties and the composition of the by-product received from the operation of the EB installation in Maritsa East 2 TPP, which contains about 95% ammonia sulfate, 2% ammonia nitrate and 3% moisture, as well as the study made in respect to the mineral fertilizers that are produced and used, enough proofs have been obtained in favor of the new product, showing that this new by-product can be separately used as a mineral fertilizer and also can be used as an appropriate component in the production of a large range of mixed fertilizers, which meet the requirements of the best agrochemical practice. Simulation of the processes of granulation by pressing and extruding shows that fertilizer mixes with different composition, appropriate for different soils and different crops can be produced in different geometrical sizes, providing possibilities for individual fertilizing of perennial plants too. Testing has started with some of the produced samples, in order to find out the chemical efficiency of the obtained fertilizers.

All stated here shows that there are favorable conditions in Bulgaria for the application and wide use of the new product, separately or in the form of sulfur nitrate or complex balanced mineral or organic mineral fertilizers.

The total needs of ammonia sulfate in Bulgaria are estimated up to 250 000 tons/ year at an average sale price in the European Union - 65 $/t, and in the United States the price has reached 187 $/t. There are good opportunities for export of large quantities of different fertilizers in the region.
5. CONCLUSIONS

1. The construction of a new “Industrial Electron Beam Flue Gas Purification Plant”, for simultaneous removal of sulphur and nitrogen oxides and VOC from the flue gases generated by the units of “Sviloza” TPS JSC, is very important solution for Bulgaria.

2. The projects for realization of “Industrial Electron Beam Flue Gas Purification Plant” at TPS Sviloza” is supported from Government of Bulgaria like Ministry of Economy and Energy, Ministry of Environment and Water, municipality of Svishtov and municipality of Zimnic, Romania. Existing technical and economical assessment of the effect from the realization of that project will take part the Bulgarian Academy of Science, Chemical Institute, Energoproject and others.

3. The total needs of ammonia sulfate in Bulgaria are estimated up to 250 000 tons/ year at an average sale price in the European Union - 65 $/t, and in the United States the price has reached 187 $/t. There are good opportunities for export of large quantities of different fertilizers in the region.

4. The commissioning of the Industrial Electron Beam Flue Gas Treatment Plant and its subsequent operation is expected to have a major economic benefit as a result of the by-product ammonium sulfate ammonium nitrate sale to the agricultural market the amount being of 2 000 000 Euro annually. That amount will decrease operation expenditure for EB installation by about 50%.

REFERENCES

[1] Technical parameters from TPS “Svilosa” were taken from license for production electricity and head for next 20 years.


OVERVIEW OF FLUE GAS TREATMENT IN BRAZIL

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Institute for Nuclear and Energy Research (IPEN)
* Radiation Technology Center (CTR)
** Cyclotron Accelerator Center (CAC)
Sao Paulo, Brazil

Abstract

The coal mines in Brazil are primarily located in southern part areas. The total coal reserves are approximately 32.8 billions tons, 89% of which are located in Rio Grande do Sul state. The Brazilian agriculture potentiality is very high, mainly due to the availability of flat land and the existence of industrial capacity to supply the main fertilizers needs. Electron beam flue gas treatment process ensures simultaneous removal of SO₂ and NOₓ from flue gases by single process, requiring no additional wastewater treatment system and can produce useful nitrogen fertilizer consisting of ammonium sulfate (NH₄)₂SO₄ and ammonium nitrate NH₄NO₃ as by-products. During the TC Project BRA/8/021 - Pilot Plant for Electron Beam Purification of Flue Gas supported by IAEA (1995-1996), a laboratory facility for electron beam flue gas treatment was set at IPEN. In 1997, an official request from Brazilian Government, Ministry of Science & Technology (MCT) and IPEN was made for the Japan Consulting Institute (JCI) to prepare feasibility studies of air pollution control by electron beam flue gas treatment in three power generation companies. These companies are responsible for the power generation, the transmission and the supply of electricity to Brazil: Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A., Presidente Medici – Companhia Estadual de Energia Eletrica (CEE) and Piratininga – AES Eletropaulo Thermal Power Plants.

1. INTRODUCTION

1.1. Brazilian energy sources

The population of Brazil is 187 millions as of 2006, 81.3% of which is located in urban areas. The portion of total residences receiving supply of electricity and Liquefied Petroleum Gas (LPG) or Natural Gas is 82%, while the portion of residences using firewood as fuel is 18% in the country.

The Gross National Product (GNP) of Brazil is US$ 1100 billion with 3.7% annual growth in 2006. The proven petroleum reserve and natural gas reserve is 11.8 billions of barrels and 306.4 billion of cubic meters, respectively. The daily petroleum production averaged 1 718 000 barrels in 2006. The measured coal reserve is 32.8 billion of tons. The hydraulic electrical potential already inventoried is 260.1 GW in 2005 [1].

The electric energy produced in Brazil by hydroelectric power plants represented 73%, while coal and oil-fired power generations contributed with 2% and 1%, respectively, in 2006. The Ministry of Mine and Energy estimated the same participation of these generation sources in 2016 [2].

1.2. Environmental protection projects

The Institute for Nuclear and Energy Research (IPEN) is a Government of State of Sao Paulo owned institution, associated to the University of Sao Paulo (USP) and supported and operated technical and administratively by the National Nuclear Energy Commission (CNEN), a federal agency of the Ministry of Science and Technology (MCT). In Brazil, the Federal Government has the monopoly of the mining of radioactive resources, the production and the commerce of nuclear products. This monopoly is carried out by the National Nuclear Energy Commission (CNEN).

The IPEN is recognized as a national leader institution in areas like, radiopharmaceuticals, industrial applications of radiation, research nuclear reactor operation and utilization, material science and technology, laser technology and applications and also in nuclear technology education with its post-graduation program in Nuclear Technology. The IPEN’s main radioactive and nuclear facilities are two research nuclear reactors (100 W and 5 MW), two cyclotron accelerators (18 MeV and 30 MeV), radiopharmaceuticals and nuclear fuel productions, two industrial electron beam
accelerators, both with energy of 1.5 MeV (37.5 kW and 97.5 kW) and one multipurpose gamma irradiator (37 PBq) for research, development and contract services.

The mission of Radiation Technology Center (CTR) at IPEN is “to apply the radiation and radioisotope technologies in the Industry, Health, Agriculture and Environment, producing scientific knowledge, forming human resources, transferring technology and generating products and services for customers”. In the environmental protection field applying radiation processing at CTR, the most important achievements were the coordination of the IAEA TC Project BRA/8/025 - Electron Beam Treatment of Wastewater (1993-1997), elected a Model Project by Agency in 1995 and the IAEA TC Project BRA/8/021 – Pilot Plant for Electron Beam Purification of Flue Gas (1995-1996).

1.3. Coal power generation and coal industry

The coal mines in Brazil are primarily located in southern part areas including the States of Rio Grande do Sul, Santa Catarina, Parana and Sao Paulo. The total coal reserves in Brazil are approximately 32.8 billion tons, 89% of which are located in Rio Grande do Sul (RS) State. The total amount of the production in Rio Grande do Sul State occupies 58% of the national production, while the Company Rio Grande do Sul of Mining (CRM), the biggest coal production in Brazil based in RS State, produces 35% of the national’s coal production.

At present, coal-fired thermal power generation does not have a share in total power generation, when compared on hydraulic power generation in Brazil. In the future, however, it is most likely that coal will be a major energy supply source in the coal-production regions in the south.

1.4. Demand and supply of fertilizer in Brazil

The Brazilian agriculture potential is very high, mainly due to the availability of flat land and the existence of industrial capacity to supply the main fertilizers needs. Also Brazilian agriculture can improve the productivity mainly by using more advantage technologies, by the application of more fertilizer and by the mechanization of the culture.

At present, forty three percent on the total export comes from the agro-business in Brazil. As the historical growth rate of the agro-vegetable production has been 4.1% per year, since 1970. The annual agro-vegetable production can be evaluated around 200 millions tons. Considering a consumption of 8.1% in weight of fertilizer per agro-vegetable production and the historical growth rate of 1.6% per year for NPK per cultivated hectare, the annual fertilizer consumption can be estimated in 20 million tons.

The Brazilian soil is poor in sulfur and the farmers use ammonium sulfate as nitrogen and sulfur source. The nitrogen participation in total fertilizer consumption is in average 10% and 20% of the consumed nitrogen is from ammonium sulfate. The ammonium sulfate consumption could be partially converter by the fertilizer produced from flue gas treatment by electron beam accelerator process, reducing the importation of ammonium sulfate and sulfur. There are also in Brazil two ammonia suppliers, which export the most products on the grounds.

2. ENVIRONMENTAL REGULATION ON AIR POLLUTION IN BRAZIL

The federal constitution in Brazil estipulate that the measures for environmental protection including air pollution control is concurrently conduced both by the federal government and by the governments in the level of state, city and town [3].

2.1. Environmental conservation policy

The basic pollution control and environmental conservation polices are set forth and being executed according the laws, licenses and regulations.
2.1.1. Law 6938/81

- Established the objectives and tools for the Environmental Policy Incorporated, for the first time, the concept of reconciling economic development with the preservation of the environment;

- Creation of the National Environmental System (SISNAMA), made up by the National Environmental Council (CONAMA) and by federal and state-level executive agencies. The SISNAMA includes not only the ministries and sectorial organizations of the federal administration directly responsible for the environment, but also state and municipal-level agencies, professional associations and non-governmental organizations; and

- The CONAMA is designed to advise, study and propose government policy guidelines for the environment and natural resources, as well as to consider rules and standards by the national Resolutions, compatible with environmental protection. It was commissioned to define the criteria to be adopted by Environmental Impact Assessments (EIA) for issuing those licenses, thereby ensuring public access to information on damage caused to the environment and environmental protection actions.

2.1.2. Licensing process

- Preliminary Licensing (LP) – requires the submission and approval of the plant mains characteristics and pollution control systems concept, the EIA, usually for major projects. The LP viabilities for one determined area;

- License to install the facilities (LI) – requires the projects documents of the pollution control systems, that must be consistent with the EIA and are used as basic reference for inspection during construction; and

- License to Operate (LO) – is obtained after inspections of the installed pollution control systems, operation condition and compliance with environmental regulations and effluent standards. The LO is periodically renewed, after annual inspection and compliance verification.

2.1.3. Environmental regulation on air pollution

- The CONAMA Resolutions 018/88, 004/88, 003/89 and 010/89 – establishes maximum limits for polluting emissions from engines and new motor-propelled vehicles; The CONAMA Resolution 005/89 – describes the National Air Pollution Control Program and it classifies the territory into three area classes. Actually, the primary quality standard is in vigor for the area Classes II and III:

  - Class I – areas to be preserved, such as, National Parks and Reserves, where the air quality is to be kept as natural as possible;

  - Class II – areas where the level of deterioration is limited by the secondary air quality standard (minimum impact on welfare of the population and on the environment); and

  - Class III – development areas, where the level of deterioration is limited by the primary air quality standard and can to affect the health of the population.

- The CONAMA Resolution 003/90 of 28/06/1990 – establishes the primary and secondary standards to be accomplished according to the area classification, for the pollutants, smoke, total suspended particulates (TSP), inhaler suspense particulates (ISP), sulfur dioxide (SO₂), carbon monoxide (CO), ozone (O₃) and nitrogen dioxide (NO₂) and criteria for acute air pollution episodes. The Environmental and Emission Standards and the Criteria for Acute Air Pollution Episodes at CONAMA Resolution 003/90 are illustrated in Tables I and II; and

- The CONAMA Resolution 008/90 of 06/12/1990 – establishes the emission standards to external combustion industrial equipment for opacity, TSP and SO₂. The Emission Standards at CONAMA Resolution 008/90 are illustrated in Table III. There is not NOₓ and volatile organic compounds (VOC) emission limits from Stationary Sources in Brazil.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary Standards (µg/m$^3$)</th>
<th>Secondary Standards (µg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Averaging Time</td>
<td>24 hours</td>
<td>1 year</td>
</tr>
<tr>
<td>24 hours</td>
<td>24 hours</td>
<td>1 year</td>
</tr>
<tr>
<td>Smoke</td>
<td>150</td>
<td>60</td>
</tr>
<tr>
<td>Total Suspended Particulates (TSP)</td>
<td>240</td>
<td>80</td>
</tr>
<tr>
<td>Inhaler Suspense Particulates (ISP)</td>
<td>150</td>
<td>50</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>365</td>
<td>80</td>
</tr>
<tr>
<td>CO</td>
<td>40 000$^*$</td>
<td>10 000$^*$</td>
</tr>
<tr>
<td>Ozone</td>
<td>160$^*$</td>
<td>-</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>320$^*$</td>
<td>100</td>
</tr>
</tbody>
</table>

Notes: $^*$ 1 hour; and $^{**}$ 8 hours average.

TABLE II. THE CRITERIA FOR ACUTE AIR POLLUTION EPISODES - CONAMA RESOLUTION 003 OF 06/28/1990.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Levels</th>
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<tbody>
<tr>
<td></td>
<td>Caution</td>
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<tr>
<td>Sulfur Dioxide (µg/m$^3$)</td>
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<tr>
<td>Total Suspended Particle (TSP)</td>
<td>375</td>
</tr>
<tr>
<td>(µg/m$^3$) - 24h</td>
<td>65 000</td>
</tr>
<tr>
<td>SO$_2$ x TPS</td>
<td>15</td>
</tr>
<tr>
<td>Carbon Monoxide (ppm) - 8 h</td>
<td>400</td>
</tr>
<tr>
<td>Ozone (µg/m$^3$) - 1 h</td>
<td>250</td>
</tr>
<tr>
<td>Nitrogen Dioxide (µg/m$^3$) - 1 h</td>
<td>1130</td>
</tr>
</tbody>
</table>
### TABLE III. EMISSION STANDARDS ON CONAMA RESOLUTION 008/90 OF 06/12/1990.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Output / Area Classification</th>
<th>Emission Limit (g/10^8 kcal)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>COAL</td>
</tr>
<tr>
<td></td>
<td>&lt; 70MW – Class I</td>
<td>Special Allowance</td>
</tr>
<tr>
<td></td>
<td>&gt; 70 MW – Class I</td>
<td>Not Allowance</td>
</tr>
<tr>
<td></td>
<td>&lt; 70 MW</td>
<td>TSP</td>
</tr>
<tr>
<td></td>
<td>Classes I &amp; II</td>
<td>SO₂</td>
</tr>
<tr>
<td></td>
<td>&gt; 70 MW</td>
<td>TSP</td>
</tr>
<tr>
<td></td>
<td>Classes I &amp; II</td>
<td>SO₂</td>
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<td>&gt; 70 MW – Class I</td>
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<td></td>
<td>&lt; 70 MW</td>
<td>TSP</td>
</tr>
<tr>
<td></td>
<td>Class I**</td>
<td>SO₂</td>
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<tr>
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<td>&lt; 70 MW</td>
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<tr>
<td></td>
<td>Classes II &amp; III</td>
<td>SO₂</td>
</tr>
<tr>
<td></td>
<td>&gt; 70 MW</td>
<td>TSP</td>
</tr>
<tr>
<td></td>
<td>Classes II &amp; III</td>
<td>SO₂</td>
</tr>
</tbody>
</table>

**Notes:**  
* TSP - Total Suspended Particulates and  
** Biggest annual consumption = 3000 ton. The emission limit for opacity is 20%, equivalent to Ringelmann #1.

3. LABORATORY FACILITY FOR ELECTRON BEAM FLUE GAS TREATMENT

During the TC Project BRA/8/021 – Pilot Plant for Electron Beam Purification of Flue Gas supported by IAEA (1995-1996), a laboratory facility for electron beam flue gas treatment was set in the Radiation Technology Center at IPEN [4]. This facility was assembling together the Electron Beam Accelerator (EBA), model JOB-188, energy of 1.5 MeV, 37.5 kW, made by Radiation Dynamics, Inc. (RDI), which is presented in Figure 1.

![Electron Beam Accelerator, RDI model JOB-188, 1.5 MeV and 37.5 kW at IPEN.](image_url)
The maximum flow rate treated at IPEN’s laboratory plant, applying the EBA was 1 Nm³/h. Connected to the main line of this facility there were installed tubes to conduct steam and pure gases from the bottles (SO₂, NH₃, NO₂ and CO₂), thermocouples, flow meters, irradiation chamber with titanium foil window (40 µm), electrostatic precipitator, monitoring points and gas analyzer equipment for SO₂, NO and NH₃ measurements. All the line, tubes and irradiator chamber were assembled on stainless steel, with thermal isolation. The dosimetric studies of the flue gas treatment process were made by CTA film and N₂O. Figure 2 presents the Gas Analyzer equipment, model Radas 2 associated with a Gas Sampling Unit, model CFP-306 made by Hartman Braun and Shimadzu, respectively. The measured component are NO (0-100/1000 ppm) and SO₂ (0-300/3000 ppm).

The IPEN’s laboratory facility of electron beam flue gas treatment demonstrated and also suggested that this technology was economic and a competitive alternative to combined wet flue gas desulphurization and selective catalytic reduction for coal fired power stations [5, 6].

FIG. 2. Gas Analyzer equipment, model Radas 2 associated with a Gas Sampling Unit, model CFP-306 made by Hartman Braun and Shimadzu, respectively, installed in the laboratory facility for electron beam flue gas treatment at IPEN.

4. FEASIBILITY STUDIES OF AIR POLLUTION CONTROL BY ELECTRON BEAM FLUE GAS TREATMENT PROCESS IN BRAZIL

4.1. Japan Consulting Institute support

Environmental problems have recently become a major issue for governments worldwide. Air pollution control, in particular, is one of the important areas that a great deal of their attentions has to be paid on governmental basis. With regard to power generation an expansion plan compatible with sound environment has to be developing, since a thermal power plant could be fixed source of a considerable amount of air pollutants.

Under this situation an official request from Brazilian Government, Ministry of Science & Technology (MCT) and Institute for Nuclear and Energy Research (IPEN) was made for the Japan Consulting Institute (JCI) to prepare feasibility studies of air pollution control by electron beam flue gas treatment in three power generation companies in 1997. These companies are responsible for the power generation, the transmission and the supply of electricity to Brazil: Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A., Presidente Medici – Companhia Estadual de Energia Eletrica (CEEE) and Piratininga – AES Eletropaulo Thermal Power Plants (TPPs) in Brazil. These studies carried out by JCI, MCT and IPEN were to assess the feasibility of installing the Electron Beam
Accelerator (EBA) system to control sulfur oxides, nitrogen oxide and suspended particulates matters emission in those TPPs.

The EBA process is considered to be the process which is most suitable for the installation in the TPP under the present studies based on the following:

- Simultaneous removal of both SO$_2$ and NO$_X$ by single process;
- Dry process requiring no additional wastewater treatment system;
- Simple system with less space required and easy operation; and
- Both SO$_2$ and NO$_X$ pollutants are recovered as valuable nitrogen fertilizer which contains a certain portion of sulfur, which are imported in Brazil as intermediate raw material for production of ammonium sulfate, since no domestic sulfur resources are available.

The EBA system can transform SO$_X$ (SO$_2$ and SO$_3$) and NO$_X$ (NO$_2$ + NO) into a useful nitrogen fertilizer consisting of ammonium sulfate (NH$_4$)$_2$SO$_4$ and ammonium nitrate NH$_4$NO$_3$. The collected fertilizer can be used to cultivate such crops as vegetables, corn and wheat. Especially, the southern region of Brazil harboring the thermal power station in its center is one of the nation’s major grain crop growing belts requiring large amounts of fertilizers.

4.2. Economical evaluation of the EBA system

The economic evaluations of the EBA systems proposed for the Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A., Presidente Medici – Companhia Estadual de Energia Eletrica (CEEE) and Piratininga – AES Eletropaulo Thermal Power Plants (TPPs) in Brazil were carried out under the considerations:

- **Variable cost** - by-product income and utility cost (electrical power, process water, steam and ammonia);
- **Fixed cost** - depreciation, interest, maintenance and employee;
- **Annual operation cost**; and
- **Annual electricity**.

4.3. Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A.

The Jorge Lacerda Thermal Power Plant is located near Tubarao City, in Santa Catarina (SC) State of the south area of Brazil. This power plant presented in Figure 3 is a coal fired thermal power plant, and is managed by Eletrosul Centrais Eletricas do Sul do Brasil S.A. The ELETROSUL Company income was US$ 104.8 million in 2006. Jorge Lacerda is the biggest coal fired thermal power plant in South America.

This thermal power plant consists of seven units and the total capacity and amount of fuel used are 832 MW and 463.3 tons/h (2 395 377 tons/year), respectively. The UPLA A I (2x50 MW) and UPLA A II (2x66 MW) units were built in 1965 and 1973. The UPLB B III (2x125 MW) and UPLC C IV (350 MW) units were built in 1980 and 1997, respectively.

Coal used as fuel in this power plant is available in Santa Catarina State and transported to the storage yard by train. The sulfur content of this coal is 1.8 - 2.3 wt% and ash content is 39 - 44 wt%. The boiler flue gas is discharged through dry type electrostatic precipitator (ESP), in which about 98% of fly ash is collected. The collected fly ash in the ESP is transported to the storage silo by pneumatic conveyors and sold to the cement factories near the power plant. The bottom ash of boilers is transported by hydraulic conveyor to the ash pond, and the water used for this conveyor system is recycled.

In Brazil, hydroelectric power plants are in base load operation and thermal power plants are supplementary used. Thus the annual operation load of thermal plant is relatively low (50% – 60%). However, hydroelectric power plants reach to the limitation of construction and the demand for thermal power plants is increasing.
4.3.1. Technical description of the proposed flue gas treatment system

Table IV shows the expected reduction of air pollutants at Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A. in 1997 [7]. The technical descriptions of the proposed flue gas treatment system were:

- **Installation**: one boiler of 125 MW (UPLB B III n° 6);
- **Gas flow rate**: 480,000 Nm$^3$/h;
- **Temperature inlet and outlet**: 180°C and 90°C, respectively;
- **Source of flue gas**: coal firing boiler flue gas (sulfur content, dry base: 1.99%);
- **Coal consumption**: 74.7 ton/h;
- **Calorific value**: 4500 kcal/kg;
- **Electron Beam Accelerators**: 4 equipments, scanning type, 800 kV and 500mA;
- **Power supplies**: 2 equipments, D.C. high voltage (800 kV x 1,000 mA);
- **By-product collecting equipment**: dry type electrostatic precipitator;
- **Efficiency removals of SO$_X$ and NO$_X$**: 80% and 25%, respectively;
- **Operating and maintenance requirement**: 13 persons;
- **Total cost**: US$ 37,000,000
- **Finance**: Long term soft bank loan of US$ 22,200,000;
- **Coverage**: 60% of the total project cost;
- **Repayment period**: 25 years, 1.8% per year; and
- **Increase of electricity cost**: 0.00109/kWh (3.6%).

The current electric charge by Jorge Lacerda – Eletrosul Centrais Eletricas do Sul do Brasil S.A. Thermal Power Plant of US$ 0.03/kWh will be increased to US$ 0.03109/kWh, by installation of the EBA System for 125 MW and its ratio is equivalent to 3.6% rise.
TABLE IV. EXPECTED REDUCTION OF AIR POLLUTANTS AT JORGE LACERDA - ELETROSUL CENTRAIS ELETRICAS DO SUL DO BRASIL S.A. LOCATES AT TUBARAO CITY, SANTA CATARINA STATE.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Air Pollutants</th>
<th>EBA System Base (80% De-SO₂, 25% De-NOₓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas Flow Rate*</td>
<td>480 000 Nm³/h (125 MW)</td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>1.739 ppmv</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>446 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>1100 mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>7.3%v</td>
</tr>
<tr>
<td>Outlet</td>
<td>SO₂</td>
<td>347 ppmv</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>334 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>50 mg/Nm³</td>
</tr>
<tr>
<td>Reduction</td>
<td>SO₂</td>
<td>1,769 kg/h</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>103 kg/h</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>467 kg/h</td>
</tr>
</tbody>
</table>

Note: * Wet base.

4.4. Presidente Medici – Companhia Estadual de Energia Eletrica (CEEE)

The Presidente Medici Thermal Power Plant is located in Candiota City, in Rio Grande do Sul (RS) State of the south area of Brazil. This power plant presented in Figure 4 is a coal fired thermal power plant, and is manager by Companhia Estadual de Energia Eletrica. The CEEE Company income was US$ 96.3 million in 2006.

This thermal power plant consists of two units - Phase A (2x63 MW) and Phase B (2x160 MW) and the total capacity and amount of fuel used are 446 MW and 185.6 tons/h (1,307,789 tons/year), respectively. The Phase C (1x350 MW) will be concluded in 2009, when the new total capacity will be 796 MW.

Coal used as fuel in this power plant is available on the Candiota deposit, near the installation in Rio Grande do Sul State. The sulfur content of this coal is 1.61 wt% and ash content is 55 wt%, with causes ash handling trouble. The boiler flue gas is discharged through dry type electrostatic precipitator (ESP), in which about 98% of fly ash is collected. The collected fly ash in the ESP is transported to the storage silo by pneumatic conveyors and sold to the cement factories near the power plant. The bottom ash of boilers is transported by hydraulic conveyor to the ash pond, and the water used for this conveyor system is recycled.

In Brazil, hydroelectric power plants are in base load operation and thermal power plants are supplementary used. Thus the annual average operation load of thermal plant is relatively low (40%). However, hydroelectric power plants reach to the limitation of construction and the demand for thermal power plants is increasing. The load factor of the Presidente Medici Thermal Power Plant is 35%-40% and 60%-70%, Phases A and B, respectively.
4.4.1. Technical description of the proposed flue gas treatment system

Table V shows the expected reduction of air pollutants at Presidente Medici – Companhia Estadual de Energia Eletrica (CEEE) Thermal Power Plant in 1997 [8]. The technical descriptions of the proposed flue gas treatment system were:

- Installation: one boiler of 160 MW (Phase B);
- Gas flow rate: 884 380 Nm$^3$/h;
- Temperature inlet and outlet: 180°C and 90°C, respectively;
- Source of flue gas: coal firing boiler flue gas (sulfur content, dry base: 1.61%);
- Coal consumption: 185.6 ton/h;
- Calorific value: 3078 kcal/kg;
- Electron Beam Accelerators: 7 equipments, scanning type, 800 kV and 500mA;
- Power supplies: 4 equipments, D.C. high voltage (3 units 800 kV x 1,000 mA, 1 unit 800 kV x 500 mA);
- By-product collecting equipment: dry type electrostatic precipitator;
- Efficiency removals of SOX and NOX: 80% and 50%, respectively;
- Operating and maintenance requirement: 13 persons;
- Total cost: US$ 47 700 000
- Finance: Long term soft bank loan of US$ 28 620 000;
- Coverage: 60% of the total project cost;
- Repayment period: 25 years, 1.8% per year; and
- Increase of electricity cost: 0.00055 kWh (1.7%).
The current electric charge by Presidente Medici – Companhia Estadual de Energia Eletrica (CEEE) Thermal Power Plant of US$ 0.032/kWh will be increased to US$ 0.03255/kWh, by installation of the EBA System for 160 MW and its ratio is equivalent to 1.7% rise.

### TABLE V. EXPECTED REDUCTION OF AIR POLLUTANTS AT PRESIDENTE MEDICI – COMPAHIA ESTADUAL DE ENERGIA ELETRICA (CEEE) THERMAL POWER PLANT LOCATES AT CANDIOTA CITY, RIO GRANDE DO SUL STATE.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Air Pollutants</th>
<th>EBA System Base (80% De-SO(_2), 50% De-NO(_X))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>Gas Flow Rate(^*)</td>
<td>884 380 Nm(^3)/h (160 MW)</td>
</tr>
<tr>
<td></td>
<td>SO(_2)</td>
<td>1680 ppmv</td>
</tr>
<tr>
<td></td>
<td>NO(_X)</td>
<td>260 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>3000 mg/Nm(^3)</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>9.4%v</td>
</tr>
<tr>
<td>Outlet</td>
<td>SO(_2)</td>
<td>336 ppmv</td>
</tr>
<tr>
<td></td>
<td>NO(_X)</td>
<td>130 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>50 mg/Nm(^3)</td>
</tr>
<tr>
<td>Reduction</td>
<td>SO(_2)</td>
<td>3 076 kg/h</td>
</tr>
<tr>
<td></td>
<td>NO(_X)</td>
<td>214 kg/h</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>2 364 kg/h</td>
</tr>
</tbody>
</table>

Note: \(^*\) Wet base.

### 4.5. Piratininga – AES Eletropaulo

This feasibility study concerned the development and application of a SO\(_2\) and NO\(_X\) simultaneous gas treatment was carried out through a 135 MW electron beam flue gas treatment demonstration plant at Piratininga-AES Eletropaulo Thermal Power Plant locate at Sao Paulo, the biggest city in Brazil, around 16 million inhabitants in 1997. This power plant belongs to a service electric utility necessary for the supply of energy to more than 5800.00 customers, covering an area of 21.168 km\(^2\) where approximately 20.2 million people live. This plant was a 470 MW, 2x100 MW built in 1954 and 2x135 MW erected in 1960, oil fueled (at full load, 2800 tons/day). The oil was low sulfur content, less than 1%, but the feasibility study had considered the mode of operation and another cheaper fuel supply, with sulfur content till 3.0%. It was estimated to use a flue gas rate of 370 000 Nm\(^3\)/h for 135 MW generated by the plant.

The Electron Beam Accelerator (EBA) process had aimed to reduce SO\(_2\) and NO\(_X\) gas pollutant emissions attending the Brazilian environmental laws including the expected law for NO\(_X\) levels. The process consisted in electron beam irradiation (above 0.8 MeV) of burning gas from the plant at ammonia presence forming as reaction product ammonium sulfate and nitrate that were collected as dry dust at an electrostatic precipitator. This was economically useful to the plant and to Brazil, a mainly agricultural country. Figure 5 presents Piratininga-AES Eletropaulo Thermal Power Plant locates at Sao Paulo City. The AES Eletropaulo Company income was US$ 186.7 millions in 2006.
4.5.1. Technical description of the proposed flue gas treatment system

Table VI shows the expected reduction of air pollutants at Piratininga-AES Eletropaulo Thermal Power Plant in 1997 [9, 10]. The technical descriptions of the proposed flue gas treatment system were:

- Installation: one boiler of 135 MW (n° 3 or 4);
- Gas flow rate: 370 000 Nm$^3$/h;
- Temperature inlet and outlet: 150°C and 90°C, respectively;
- Source of flue gas: heavy oil firing boiler flue gas (sulfur content: 3%);
- Oil consumption: 0.25 ton/h;
- Calorific value: 10 000 kcal/kg;
- Electron Beam Accelerators: 3 equipments, scanning type, 800 kV and 500mA;
- Power supplies: 2 equipments, D.C. high voltage (800 kV x 1000 mA, 800 kV x 500 mA);
- By-product collecting equipment: dry type electrostatic precipitator;
- Efficiency removals of SO$_X$ and NO$_X$: 80% and 65%, respectively;
- Operating and maintenance requirement: 13 persons;
- Total cost: US$ 30 800 000;
- Finance: Long term soft bank loan of US$ 18 480 000;
- Coverage: 60% of the total project cost;
- Repayment period: 25 years, 1.8% per year; and
- Increase of electricity cost: 0.00102/kWh (2.4%).

The current electric charge by Piratininga-AES Eletropaulo Thermal Power Plant of US$ 0.042/kWh will be increased to US$ 0.04302/kWh, by installation of the EBA System for 135 MW and its ratio is equivalent to 2.4% rise.
TABLE VI. EXPECTED REDUCTION OF AIR POLLUTANTS AT PIRATININGA-AES ELETROPAULO THERMAL POWER PLANT LOCATES AT SAO PAULO CITY.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Air Pollutants</th>
<th>EBA System Base (80% De-SO₂, 65% De-NOₓ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>Gas Flow Rate*</td>
<td>370 000 Nm³/h (135 MW)</td>
</tr>
<tr>
<td></td>
<td>SO₂</td>
<td>2040 ppmv</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>160 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>400 mg/Nm³</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>10%v</td>
</tr>
<tr>
<td>Outlet</td>
<td>SO₂</td>
<td>408 ppmv</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>56 ppmv</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>50 mg/Nm³</td>
</tr>
<tr>
<td>Reduction</td>
<td>SO₂</td>
<td>1553 kg/h</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>71 kg/h</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>117 kg/h</td>
</tr>
</tbody>
</table>

Note: * Wet base.

Air pollutants conversion study of combustion gas generating by oil fueled thermoelectric power plant to fertilizer by-product was presented to obtain a Master of Science, as well as, the socioeconomic and environmental consequences of the substitution of fuel oil for natural gas at the Piratininga-AES Eletropaulo Thermal Power Plant were also carried out on a Doctorate in Nuclear Technology – Applications at IPEN, in 2001 and 2005 respectively [11, 12].

5. CONCLUSIONS

Electron beam flue gas treatment process ensures simultaneous removal of SO₂ and NOₓ from flue gases by single process. It is a dry process requiring no additional wastewater treatment system, most suitable for the installation in the thermal power plants under the present studies. The EBA process can transform SOₓ (SO₂ and SO₃) and NOₓ (NO₂ + NO) into a useful nitrogen fertilizer consisting of ammonium sulfate (NH₄)₂SO₄ and ammonium nitrate NH₄NO₃. The valuable collected fertilizer can be used to cultivate such crops as vegetables, corn and wheat in Brazil.

The future of the electron beam application for flue gas treatment depends on technical developments to make the radiation technology very competitive for environmental applications. Due to this fact it is necessary:

- To establish new applications for EBA process in petrochemical complexes, incinerators and mines;
- To carry out R&D works in EBA systems and power supplies (capacity) supported by IAEA, including interregional projects;
- To promote fertilizer marketing for the valuable collected fertilizer (by-products); and
- To reach reliability, decreasing the power consumption and capital cost, optimizing the engineering technology and equipment to improve installation’s stability.

The overview of flue gas treatment in Brazil demonstrates the importance of reestablishing the partnership and works with the Thermal Power Plants in the South of Brazil, after the privatization process: Presidente Medici - CEEE (446 MW) and Jorge Lacerda - ELETROSUL (823MW). The profitable experience from Japan and Poland in EBA process and IAEA collaborations will be very important.
6. ACKNOWLEDGMENTS

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- International Atomic Energy Agency (IAEA);
- Japan Consulting Institute (JCI), Japan Government;
- Ministry of Science and Technology (MCT) and National Nuclear Energy Commission (CNEN), Brazilian Government;
- Eletrosul Centrais Eletricas do Sul do Brasil S.A. (ELETROSUL), Jorge Lacerda Thermal Power Plant;
- Companhia Estadual de Energia Eletrica (CEEE), Presidente Medici Thermal Power Plant; and
- AES Eletropaulo, Piratininga Thermal Power Plant.

REFERENCES


OVERVIEW OF THE EBFGT INSTALLATION SOLUTIONS APPLICABLE FOR FLUE GASES FROM VARIOUS FUELS COMBUSTION

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aInstitute of Nuclear Chemistry and Technology, Warsaw, Poland
bInstitute of Atomic Energy, Otwock-Świerk, Poland

Abstract

The overview of the solutions used in EBFGT process and adaptation of process parameters for flue gas from combustion of various fuels was presented. The inlets parameters of flue gas from four fuels with high emission of pollutants, process parameters and process constrain were analysed. Also the main problems of this technology and their solutions were presented.

1. INTRODUCTION

Up to now Electron Beam Flue Gas Treatment (EBFGT) technology found industrial application for cleaning of flue gases from combustion of hard coal. In laboratory and pilot plant EBFGT technology was considered for purification of flue gases from combustion other fuels and gases from other processes like sintering, painting or chemical processes. Typical values of pollutants’ concentrations from combustion of four the most popular fuels are presented in Table I.

TABLE I. COMPOSITION OF FLUE GAS FROM VARIOUS SOURCES

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>SO₂ ppm</th>
<th>NOₓ ppm</th>
<th>HCl ppm</th>
<th>HF ppm</th>
<th>VOC mg/Nm³</th>
<th>Ash content dry base %</th>
<th>Water content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission limit</td>
<td>400-850 mg/Nm³</td>
<td>400-460 mg/Nm³</td>
<td>5-250 mg/Nm³</td>
<td>2-4 mg/Nm³</td>
<td>–</td>
<td>50-350 mg/Nm³</td>
<td>–</td>
</tr>
<tr>
<td>Hard coal</td>
<td>350-2000 150-1000</td>
<td>30-125</td>
<td>5-60</td>
<td>–</td>
<td>2-30</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>Lignite</td>
<td>100-5600 100-500</td>
<td>10-60</td>
<td>0.3-30</td>
<td>–</td>
<td>15-40</td>
<td>20-50</td>
<td></td>
</tr>
<tr>
<td>Municipal Waste</td>
<td>190-300 50-210</td>
<td>750</td>
<td>11</td>
<td>20</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Heavy oil</td>
<td>500-1600 50-250</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.2-0.8</td>
<td>&lt; 1</td>
<td></td>
</tr>
</tbody>
</table>

The EB process design should take into consideration three groups of parameters:

- inlet gas parameters,
- process parameters, which should be designed to fulfill the constrains in next point,
- emission limits, by-product quality, safety, economical and technical constrains.

2. INLET GAS PARAMETERS

The most important inlet gas parameters are:

- gas flow rate,
- SO₂ concentration,
• NO\textsubscript{x}, concentration,
• HCl and HF concentration,
• fly ash concentration,
• temperature,
• humidity.

Gas flow rate determinates the size of apparatus. Higher flow rates usually reduce cleaning cost of gas related to unit of volume of treated gas.

SO\textsubscript{2} concentration in flue gas depends on sulphur content in fuel. In fossil solid fuels part of sulphur is in mineral phase and reminds in ash. The coal and heavy oil with high sulphur content are cheaper than low sulphur one. It can be important factor in economical balances. EB-method easy reduces SO\textsubscript{2} with high efficiency, low energy consumption and gives valuable by-product as a fertilizer.

NO\textsubscript{x} concentration in flue gas depends on nitrogen content in fuel as well as burning conditions. New burners’ constructions, recirculation of combustion gases and better controlled air introduction into burning chamber can significant reduce NO\textsubscript{x} concentration in flue gas. But usually it is not sufficient for more severe limits of emission expected in near future. Combining of low emission burners with EB – process allows for NO\textsubscript{x} reduction bellow emission limits with low energy consumption.

HCl and HF concentration in flue gas depend on chlorine and fluorine content in fuel. These pollutants easy react with NH\textsubscript{3}, which is used in EB process. NH\textsubscript{4}Cl and NH\textsubscript{4}F in low concentrations don’t reduce value of by-product.

Fly ash concentration in flue gas from coal combustion is high. Dedusting units are installed at such boilers, usually electrostatic precipitators, to reduce fly ash content to 40 – 100 mg/Nm\textsuperscript{3}. Otherwise fly ash is collected together with by-product. Concentration of fly ash in by-product should be less than 1%.

Temperature of inlet flue gas usually is in range 100 to 200°C. It is reduced usually by evaporation of pulverized water.

Humidity of inlet flue gas depends on combusted fuel, its moisture and humidity of air used in burning process. Combustion of dry hard coal gives humidity of flue gas ca 5%. Correspondingly wet lignite gives humidity 14 to 18% and heavy oil - ca 9%.

3. PROCESS PARAMETERS

The main process parameters in EBFGT process are:

• dose,
• temperature,
• humidity of flue gas,
• ammonia stoichiometry,
• flue gas residence time.

3.1. Dose

The dose is defined as electrons energy absorbed in mass unit of flue gas. The most energy consumed in the process, up to 50% of total consumption, is used for acceleration of electrons. Reduction of SO\textsubscript{2} and NO\textsubscript{x} increases with the increase of dose, but in different ways. The dose less than 4 kGy is enough for high reduction of SO\textsubscript{2}, up to 90%. Much higher dose is necessary for
reduction of NO\textsubscript{x} [1]. The typical relations between reductions of SO\textsubscript{2} and NO\textsubscript{x} and dose are presented in Fig. 1. For improvement of economy of EB process, there were made a number of works leading to better utilization of electrons energy in reduction of NO\textsubscript{x}. The common idea of this work was to improve the uniformity of irradiation of flue gas stream in the reactor.

3.1.1. Correction of flow patterns

The dose distribution curves inside reactor shows very high dose near the window and several times lower near the opposite side of reactor (Fig. 2). Another idea to improve uniform irradiation is the proper formation of the velocity of stream. The streams with higher velocity flows near the window and the time of irradiation is shorter. The streams, which flow farther from window flows slowly and time of irradiation is longer. The model calculations for various arrangements at inlet to reactor are presented in Fig. 3 [5].
FIG. 2. Dose distribution in reactor for one accelerator at Kawęczyn pilot plant.

3.1.2. Multistage irradiation

It was found during pilot plant experiments in Kawęczyn and Nagoya [2, 3, 4] that two stage (Kawęczyn) and three stage irradiation (Nagoya) can improve reduction of NO\textsubscript{x} over 20% with the same total dose (Fig. 4). It was also found [4] that better effect is when total dose is distributed in 60% at the first accelerator and 40% in the second accelerator.
3.1.3. Double side irradiation

In Nagoya experiments [2] with three accelerators, better results were achieved when the middle accelerator was located in the opposite side of reactor (Fig. 5). That observation was confirmed by model calculations for different relative locations of both accelerators for Kawęczyn plant conditions [10]. In big industrial plants, with capacity over 500 thousand m$^3$/h, a few numbers of accelerators should be installed. In such case they should be located on both sides of reactor.

FIG. 4. Effect of double irradiation on NO$_x$ removal efficiency.

FIG. 5. NO$_x$ removal efficiency for both side gas irradiation.
3.1.4. Reactor crossection shape and dimensions

The industrial reactors have circular (Pomorzan) or rectangular shape (Ebara) [6]. The distance between window and opposite side of reactor should be long enough to absorb about 95% of energy of electrons. It means that the dimensions of reactor depend on electrons energy. Usually electrons have energy 0.7 to 1 MeV. For example Pomorzany EBFGT plant reactor was designed for electrons energy 0.8 MeV. After some time of operation, producer of accelerators reduced energy to 0.7 MeV. It reduced efficiency of NO\textsubscript{x} removal for the same dose. Reduction of the distance from window to the bottom of reactor from 2500 to 1850 mm improved significantly efficiency removal of NO\textsubscript{x}.

An ideal shape the crossection of reactor should be similar to dose distribution curves. It allows reducing space with lower irradiation of gas. But there are some problems with production such reactor. It seems that circular crossection with window parallel to axis of reactor is more close to ideal solution. In case of rectangular crossection of reactor the windows were installed perpendicular to reactor axis.

3.2. Temperature and humidity

Temperature of process is an important parameter in SO\textsubscript{2} reduction process. SO\textsubscript{2} removal efficiency increase with decrease of process temperature. Influence of temperature on removal of NO\textsubscript{x} is smaller and is opposite than in the case of SO\textsubscript{2} (Fig. 6). The optimal temperature usually is between 60 to 75°C. Usually flue gases from boilers have too high temperature for EB-process and too low humidity. The reduction of temperature is achieved by evaporation of water in stream of gas and is combined with growth of humidity.

An optimal humidity of gas in EB-process is in the range of 12 to 16% vol. H\textsubscript{2}O (Fig.7). To low humidity results in lowering of SO\textsubscript{2} removal. To high can lead to condensation of water at colder surfaces and corrosion problems as well as increase of the water content in by-product. Also ESP producers need the temperature ca 15°C higher then dew point for proper operation of this apparatus. Dew point for 12% vol. of H\textsubscript{2}O in flue gas is 50°C and for 16% is 56°C. Water heat of evaporation is high and reduction the temperature of gas by 10°C causes growth of its humidity by 0.73%.

**FIG. 6. Effect of gas temperature on NO\textsubscript{x} and SO\textsubscript{2} removal efficiencies.**
Reduction of the temperature to the optimal one, in the process of full evaporation of water (Fig. 8), doesn’t usually give demand humidity. It depends on temperature of gas at inlet to spray cooler and its humidity. Humidity of inlet gas depends mainly on kind of fuel and humidity of air used in combustion. In the case of combustion of dry hard coal with dry air, flue gas humidity is ca 5%. To reach humidity 12% inlet gas temperature should be ca 160°C. If that temperature is lower, then the proper humidity needs addition of some amounts of steam.
Another solution, tested first time in Kawęczyn pilot plant, is a system with partial evaporation of water and its circulation (Fig. 9). In circulation system water can be heated or cooled if humidity of gas is too high. High humidity of flue gas is when wet coal is burned, usually lignite from mines near electric power stations. In liquid fuels like heavy oil there is more hydrogen in molecules of hydrocarbons and humidity of flue gas from combustion with relative dry air is ca 9%. Then inlet temperature of flue gas in range 120 – 130°C is enough to reach humidity 12% vol. in full evaporation system. Full evaporation system (Fig. 8) is simpler than with circulation of water one but need very fine dispersion of water in water – air nozzles. Compressed air needs relative high investment and operation costs. In system with circulation of water (Fig. 9) some amounts of SO₂, SO₃, HCl, HF dissolves in water. Moreover the circulated water collects particulates of fly ash. Acidic gases dissolved in water should be neutralized by NH₃ and sludge of dust removed on filter. In this system relative humidity of gas leaving scrubber is near 100% and in some cases should be reduced. It can be done by leading some amount of flue gas directly to outlet of scrubber and mixing with treated gas. In the case of high dose or high concentration of SO₂, flue gas temperature increases in reactor due to energy absorption and heat of chemical reactions. 1 kGy dose absorbed in gas increases its temperature about 1°C. Reduction of 100 ppm of SO₂ with formation of (NH₄)₂SO₄ increases the flue gas temperature about 4°C. This growth of flue gas temperature sometimes is enough for proper operation of ESP. In some cases it can be too high and need additional cooling by spraying of water in reactor (Ebara solution).

FIG. 9. Partial evaporation cooling system.
Working Material

The temperature for good operation of ESP is an order of 75 to 80°C. It can be too low to avoid the condensation of water in stack. The temperature at inlet to stack depends on its construction. Usually old stacks need temperature of flue gas higher than 110°C. Then flue gases after ESP should be heated in gas – gas heater or by mixing with untreated gas with high temperature (Pomorzany). Another solution is construction of wet stack. But this solution elevates investment costs.

3.3. Ammonia stoichiometry

In EBFGT method ammonia is added for neutralization of acidic pollutants. Reactions of neutralization proceeds in gas phase and ammonia should be introduced in gaseous form. Usually ammonia is supplied in liquid state under pressure in railway or car cisterns. Liquid ammonia is stored in pressurized tanks and after evaporation mixed in proper amount in flue gas stream. From safety reasons it is recommended to use of double walls tanks with controlled ammonia concentration between walls. The same reasons recommend underground location particularly in hot climates.

Distributors of ammonia in flue gas ducts need proper design to avoid deposits of solid product of reaction of ammonia with SO\textsubscript{2} or NO and fly ash, which can plug outlet of ammonia orifices. Amount of ammonia added should be automatically controlled. Too much of ammonia cause to high emission of this gas (ammonia slip), which is assumed to be lower than 100 ppm. To low amount of added ammonia can reduce removal of pollutants, particularly of SO\textsubscript{2}, and increases acidity of by-product. Pilot plant and industrial data shows that optimal ammonia stoichiometry is about 0.9 [7].

Pomorzany Electric Power Station is located close to living area. In a short distance there are big apartment houses. For safety reasons the ammonia is supplied in the form of 25% ammonia water. Part of ammonia in form of ammonia water is sprayed in spray cooler and the rest is separated from water in distillation column and is introduced in gaseous form into flue gas duct.

3.4. Flue gas residence time

A high energy electron induces a great number of fast radical reactions in irradiated gas. The reactions are followed by much slower chemical reaction and formation of salt aerosols. These processes need much more time to reach conversion close to equilibrium. Results of experiments on SO\textsubscript{2} and NO\textsubscript{x} reduction in Kawęczyn Pilot Plant were elaborated in the following formula:

\[
\eta_{SO_2} = 0.96(144.9787 - 1.12341T + 0.00267T^2)(0.85732 + 0.01423H)(0.98528 + 0.00226D)(1.1777 - \frac{0.79092}{\tau})
\]

\[
\eta_{NO_x} = 81.0763(1 - \exp(-0.25876D)(1.03495 - 0.00007(NO_x)_0)(0.95797 + 0.002\tau(H \cdot T)^{0.125})
\]

In both equations there is residence time \( \tau \) as a parameter.

Results of the calculations for \( T = 60^\circ \text{C}, H = 10\%, (NO_x)_0 = 200 \text{ ppm}, D = 5 \text{ kGy} \) and \( \tau = 4 \) to 12 s are presented in Fig. 10. From this picture follows that the removal efficiency of SO\textsubscript{2} and NO\textsubscript{x} increases with increase of the residence time, but the effect on removal of SO\textsubscript{2} is much bigger. Increase of residence time needs bigger volume of reactor, which elevates investment cost. In such case residence time should be optimized. That effect was also observed in German experiments [8].
4. LIMITS AND CONSTRAINTS

Limits and constraints in EBFGT process are as follows:

- emission limits of pollutants, ammonia and by-product,
- by-product quality,
- technical problems,
- safety problems,
- economical constraints,
- reliability of the process.

4.1. Emission limits

Emission limits for main pollutants are presented in Table 1. That data fulfills EU standards and may be different in other countries. Generally EBFGT technology can reduce concentrations of SO$_2$ and NO$_x$ below the emission limits. By the way it can reduce emission of HCl, HF and organic compounds which emission up to now is not limited for flue gas from combustion process but is important for clean air. Some of unreacted ammonia is emitted in cleaned flue gas. It emission is assumed to be less than 100 ppm.

By-product is collected in electrostatic precipitator (ESP). Efficiency of collecting for these aerosols is high and it is easy to reach emission of aerosols less than 50 mg/Nm$^3$ of flue gas. Some by-product can be form in reactions of residual SO$_2$ and NH$_3$ after ESP but it is not significant amount. Such emission doesn’t make the visible effects in surrounding.

4.2. By-product quality

Big advantage of EBFGT technology is valuable by-product, which can be used as fertilizer. It has to fulfill requirements of standards for nitrogen fertilizer. The main requirements are:
Working Material

- nitrogen content more than 21%,
- unsoluble part less than 1%,
- water content less than 1.5%,
- acidity less than 0.3% $\text{H}_2\text{SO}_4$.

All analysis of by-product shown that heavy metals contents like Pb, Hg, Cd, As and Cr are much bellow of limits [8, 9], at the level of traces.

By-products received in pilot and industrial plants fulfill these limits. The field experiments in a few countries confirm that by-product is a good quality nitrogen and sulphur fertilizer.

By-product is collected in ESP in the form of fine powder. For transportation purposes, it is better to make it denser for example by granulation. Granulation reduces significantly dusting of by-product and its secondary emission. Such emission causes serious corrosion problems in buildings and equipment.

4.3. Technical problems

Each apparatus should be designed for long operation and process conditions. Our experience shows that all apparatus, with exception of accelerators, fulfils that demands. But there are two problems, which should be taken its consideration in next constructions. They are:

- deposition of by-product on inside walls of equipment,
- corrosion problems.

By-product deposits in bigger amounts inside reactor duct between reactor and ESP at distribution grid at inlet to ESP and ESP walls. Removal of deposits from distribution grid and inside ESP seems to be solved by stronger hammering and proper their design. Removal of deposits from inside walls is made manually and should be improved in next constructions.

Corrosion problems are significant in case of carbon steel and low temperatures. At low temperatures by-product particularly with high content of $\text{NH}_4\text{NO}_3$ absorb moisture from air and creates concentrated solutions of by-product that are very corrosive. To prevent the corrosion the equipment should be made of stainless steel or should be very good protected if they are made from carbon steel. ESP have a heated walls, bottoms and electric insulators heated by blowing of hot air. That significant reduces corrosion problems. The electrodes and bottom in ESP should be made of stainless steel because it is difficult to make the proper protection. Corrosive problems in spray cooler can be reduced by addition of ammonia to water and neutralization of acids.

4.4. Safety problems

In EB-process there are two factors dangerous for people:

- radiation,
- ammonia.

The sources of radiation are accelerators while they operate. Part of electrons in collision with metal causes emission of X-rays. That needs proper shielding of reactor and alarm systems. Up to now there was no accidents caused by irradiation and shielding with other prevention systems working well.

Ammonia is hazardous gas for people and environment. Fortunately it is well detected by smelling in small concentrations, lower than limits. Liquid ammonia is used in many other installations and conditions of safety operation of that installations are good known. During operation of pilot and industrial EBFGT plants there were no accidents with ammonia.
4.5. Economical constrains

EBFGT process will be perspective if will be competitive in costs with other FGT processes. Its advantages are:

- simple and easy for control installation,
- valuable by-product heaving a growing market,
- comparable with other FGT processes investment and operation costs,
- reduction of SO₂, NOₓ, HCl and VOC in one process,
- dry process without wastes,
- perspectives for reduction of costs during its developing,
- in connection with other technical solutions like low NOₓ emission burners EBFGT can reduce SO₂ and NOₓ with low energy consumption,
- process is flexible and can be easy adjusted to changes of boiler load, which allows to save electric energy,
- the growing market for accelerators should reduce their cost and increase their reliability,
- construction of new EBFGT bigger plants should reduce costs of flue gas cleaning related to unit of treated gas,
- low cost of removal of SO₂ allows to use cheaper fuels with high content of sulphur.

4.6. Reliability of EBFGT process

Up to now the reliability of EBFGT process is limited by reliability of accelerators. It seems that the effort of producers of accelerators and competition between them should lead to significant increase of their reliability. It is expected reduction of the producers costs of maintenance of accelerators during guarantee period. It should be noticed that the negative opinions on accelerators are based on experience with one type of the machines manufactured by the same producer. There exist 4 to 5 producers of accelerators of such power in the world and up to now there is no data about their reliability.
CONCLUSIONS

1. The EBFGT process is still in developing state.
2. Mathematical methods of modeling of processes in EB reactor seems to be very useful for improvement of new facilities construction.
3. The problems occurring in EBFGT industrial installations and proposals of solutions should be discussed under IAEA auspices.
4. The studies on application of EBFGT process for flue gases from combustion of fuels other than hard coal should be continued.

REFERENCES


ECONOMIC FEASIBILITY OF EBFGT TECHNOLOGY FOR REMOVAL OF POLLUTANTS FROM COMBUSTION OF LIQUID FUELS

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\textsuperscript{d}Institute of Atomic Energy, Otwock-Świerk, Poland

Abstract

A project on feasibility of electron beam flue gas treatment (EBFGT) technology at oil fired boiler was conducted for Saudi Arabian Oil Company (Saudi Aramco). As part of this project, economic feasibility of EBFGT technology was performed for heavy oil fired boilers in Saudi Arabia. Economic evaluation was performed for two options of EBFGT installation; the first for 65 000 Nm\textsuperscript{3}/h and the second for 130 000 Nm\textsuperscript{3}/h. The main factors affecting investment and operation costs were discussed and costs were compared to conventional methods. The results of the evaluation showed that EBFGT method is economically attractive.

1. INTRODUCTION

Emission of harmful compounds to the atmosphere caused by fossil fuels combustion is a global problem with great importance. Sulfur and nitrogen oxides are among the most important pollutants due to their great global emission and long range transport in the atmosphere. Apart of conventional technologies designed for removal of one pollutant in one process, simultaneous technologies being able to remove two or more pollutants in the same process are developed. Among such emerging technologies, electron beam flue gas treatment (EBFGT) technology is the most promising and was already implemented in few industrial plants in different parts of the world.

In order to evaluate the potential of using EBFGT technology for flue gas from combustion of fuel oil, Saudi Aramco initiated a project entitled "Feasibility Study for Electron Beam Flue Gas Treatment (EBFGT) at Oil Fired Boiler" which was conducted by King Abdulaziz City for Science and Technology (KACST) in Saudi Arabia and Institute of Nuclear Chemistry and Technology (INCT) in Poland. Laboratory experiments demonstrated that the technology may be used for treatment of flue gases from combustion of heavy oil and identified factors which influence the process. Flue gas generated during heavy oil combustion is characterized by high humidity, high sulfur dioxide content and relatively low nitrogen oxides concentration. In spite of this, the process undergoes similar trends as in the flue gas from coal fired boilers. Therefore, most of the solutions applied in existing EBFGT installations may be applied in this case with some modifications to take into consideration different flue gas conditions.

Technical solutions for two options of electron beam facility for treatment of flue gas from heavy oil burning boilers were elaborated. The first option was assumed for flow rate of 65 000 Nm\textsuperscript{3}/h, while the second one for 130 000 Nm\textsuperscript{3}/h. On this basis, economic evaluation of investment and operation cost of the installation were estimated. Factors affecting costs of the installation are presented in this paper.

2. EBFGT PLANT DESCRIPTION

There are two main fuels being used in Saudi Arabia; fuel oil and fuel gas. Fuel gas combustion generates almost no SO\textsubscript{2} and NO\textsubscript{x} emission, but the cost of the gas is much higher than heavy fuel oil. In addition, the combusted gas is a valuable substrate used in chemical industry. Therefore, it is attractive to use heavy residuals from oil refining as a fuel with application of emission control technologies. Analysis of technical and economic feasibility for application of electron beam flue gas
treatment technology for treatment of flue gas from heavy oil combustion in one of the oil refineries in Saudi Arabia was the aim of this project.

Laboratory scale experiments were performed with three types of Arabian Oil on the first stage of the project. High removal efficiency of SO\(_2\) and NO\(_x\) up to 99% for SO\(_2\) and 90% for NO\(_x\) (98% and 85%, respectively for optimum conditions) can be achieved for Arabian Heavy Oil fired boiler with use of EBFGT technology.

Results of optimization study indicate that with the exception of dose, removal of sulfur dioxide and nitrogen oxides depends on different process conditions. By controlling these conditions it is possible to obtain maximum removal efficiencies. NO\(_x\) removal is mostly energy consuming, while SO\(_2\) removal is sensitive to temperature, humidity and ammonia stoichiometry. The proper selection of process conditions (gas humidity 10-15 vol. %, NH\(_3\) stoichiometry 0.90-0.95 and gas temperature 60-70\(^\circ\)C) guarantees high SO\(_2\) removal efficiency at low energy consumption. A dose of 6-9 kGy is sufficient to achieve simultaneous removal of over 90% SO\(_2\) and 70% NO\(_x\) from flue gas under optimum operating conditions. Higher NO\(_x\) removal efficiencies require higher energy consumption. The optimum parameters were very similar for all three types of oil. This means that EBFGT technology may be applied for any kind of oil.

According to analysis of local requirements, two options of EBFGT installation were selected for the project. The first is foreseen for treatment of 65 000 Nm\(^3\)/h (flue gas from one boiler) of flue gas, while the second one for 130 000 Nm\(^3\)/h (a set of two boilers). Since the boilers are identical, the rest of parameters are common for both options. The main design parameters of the installation are presented in Table I.

Due to differences of flue gas parameters in relation to flue gas from coal combustion, some different solutions were elaborated. The electron beam flue gas treatment plant is proposed to be composed of such units as:

- Gas-gas heat exchanger
- Flue gas conditioning unit integrated with dust removal system
- Ammonia storage and dosing system
- Reaction unit including reaction vessel, accelerators with supporting structure and biological shielding of radiation
- By-product handling and storage unit with electrostatic precipitator
- Flue gas ducts and auxiliary fan
- Control and monitoring system.

The conceptual scheme of discussed EBFGT installation is presented in Figure 1.
### TABLE I. DESIGN PARAMETERS OF ELECTRON BEAM INSTALLATION FOR TREATMENT OF FLUE GAS FROM HEAVY OIL COMBUSTION

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Option 1 (One Boiler)</th>
<th>Option 2 (Two Boilers)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>General data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of boilers</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Fuel consumption</td>
<td>4096 kg/h</td>
<td>8192 kg/h</td>
</tr>
<tr>
<td>Air excess</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Boiler efficiency</td>
<td>92%</td>
<td>92%</td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel type</td>
<td>Heavy Fuel Oil</td>
<td>Heavy Fuel Oil</td>
</tr>
<tr>
<td>Low heating value</td>
<td>9795 kcal/kg</td>
<td>9795 kcal/kg</td>
</tr>
<tr>
<td>Fuel ultimate analysis</td>
<td>C - 85.28 wt %</td>
<td>C - 85.28 wt %</td>
</tr>
<tr>
<td></td>
<td>H - 11.07 wt %</td>
<td>H - 11.07 wt %</td>
</tr>
<tr>
<td></td>
<td>S - 3.05 wt %</td>
<td>S - 3.05 wt %</td>
</tr>
<tr>
<td></td>
<td>ash - 0.3 wt %</td>
<td>ash - 0.3 wt %</td>
</tr>
<tr>
<td><strong>Flue gas parameters</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volumetric flow rate (wet basis)</td>
<td>65 000 Nm$^3$/h</td>
<td>130 000 Nm$^3$/h</td>
</tr>
<tr>
<td>Temperature after economizer</td>
<td>224°C (min. 188°C)</td>
<td>224°C (min. 188°C)</td>
</tr>
<tr>
<td>Composition (wet basis):</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N$_2$ - 71.62% vol.</td>
<td>N$_2$ - 71.62% vol.</td>
</tr>
<tr>
<td></td>
<td>CO$_2$ - 11.24% vol.</td>
<td>CO$_2$ - 11.24% vol.</td>
</tr>
<tr>
<td></td>
<td>SO$_2$ - 1503 ppmv</td>
<td>SO$_2$ - 1503 ppmv</td>
</tr>
<tr>
<td></td>
<td>(5169 mg/Nm$^3$ d.b., 3% O$_2$)</td>
<td>(5169 mg/Nm$^3$ d.b., 3% O$_2$)</td>
</tr>
<tr>
<td></td>
<td>NO$_x$ - 233 ppmv</td>
<td>NO$_x$ - 233 ppmv</td>
</tr>
<tr>
<td></td>
<td>(576 mg/Nm$^3$ d.b., 3% O$_2$)</td>
<td>(576 mg/Nm$^3$ d.b., 3% O$_2$)</td>
</tr>
<tr>
<td></td>
<td>Dust - 171 mg/Nm$^3$</td>
<td>Dust - 171 mg/Nm$^3$</td>
</tr>
<tr>
<td><strong>Removal and operational requirements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emission limits:</td>
<td>SO$_2$ - 340 ng/J</td>
<td>SO$_2$ - 340 ng/J</td>
</tr>
<tr>
<td></td>
<td>(1198 mg/Nm$^3$ d.b., 3% O$_2$)</td>
<td>(1198 mg/Nm$^3$ d.b., 3% O$_2$)</td>
</tr>
<tr>
<td></td>
<td>NO$_2$ - 130 ng/J</td>
<td>NO$_2$ - 130 ng/J</td>
</tr>
<tr>
<td></td>
<td>(458 mg/Nm$^3$ d.b., 3% O$_2$)</td>
<td>(458 mg/Nm$^3$ d.b., 3% O$_2$)</td>
</tr>
<tr>
<td></td>
<td>NH$_3$ - 150 mg/Nm$^3$</td>
<td>NH$_3$ - 150 mg/Nm$^3$</td>
</tr>
<tr>
<td></td>
<td>dust - 43 ng/J</td>
<td>dust - 43 ng/J</td>
</tr>
<tr>
<td></td>
<td>(126 mg/Nm$^3$)</td>
<td>(126 mg/Nm$^3$)</td>
</tr>
<tr>
<td>Required removal rates:</td>
<td>SO$_2$ - 77%</td>
<td>SO$_2$ - 77%</td>
</tr>
<tr>
<td></td>
<td>NO$_x$ - 21%</td>
<td>NO$_x$ - 21%</td>
</tr>
<tr>
<td>Outlet flue gas temperature</td>
<td>min. 110°C</td>
<td>min. 110°C</td>
</tr>
<tr>
<td>Availability</td>
<td>min. 8000 hour/year</td>
<td>min. 8000 hour/year</td>
</tr>
</tbody>
</table>
FIG 1. General layout of EBFGT installation
Inlet flue gas has high temperature and humidity, so commonly used water evaporation will not be sufficient in this case. The aim of heat exchanger is to decrease inlet flue gas temperature to the level appropriate for spray cooling and the obtained heat is utilized for increase of the temperature of treated flue gas at outlet of installation over dew point.

Flue gas conditioning unit is designed to adjust the flue gas parameters to optimal humidity and temperature for radiation induced flue gas treatment process. As this process will be realized by duct water spraying with water recirculation, flue gas cooling and humidification will be integrated with dust removal process.

Pure ammonia is foreseen for use as the main reagent of the process. It will be delivered and stored in the liquefied form. After evaporation, gaseous ammonia will be injected into the duct upstream the reaction vessel. Part of ammonia will be used for neutralization of SO$_2$ and other acid compounds absorbed in re-circulated water.

Reaction unit covers reaction vessel with accelerators, radiation protection system and supporting equipment as accelerator cooling, ventilation etc. Proper selection of accelerators and reaction vessel construction is essential for removal efficiency and availability of the whole installation. Reaction vessel is foreseen as circular in cross-section and diameter of 2.5 m. Double irradiation by two electron accelerators installed in series is designed. For option 1 (65 000 Nm$^3$/h) two accelerators of 800 keV, 100 kW each were selected, while for option 2 (130 000 Nm$^3$/h) two accelerators of 800 keV, 200 kW each were recommended.

The by-product of the process will be collected by electrostatic precipitator and granulated in order to decrease its bulk density. The by-product shall be utilized as a substrate for fertilizer production. Short time storage of by-product in storage house is also anticipated.

As the flue gas pass through the installation, it will cause pressure drop. Therefore, inducted draft fan of total power 80 kW for option 1 (160 kW for option 2) is foreseen.

Computer control and monitoring system integrated with refinery management system is anticipated. Such a system will allow for supervision and control of process parameters under normal, transient, alarm and break down conditions as well as data acquisition by a small number of operators.

Auxiliary services such as by-product analysis laboratory will be correlated with existing refinery activities.

Materials demand and energy consumption anticipated for described electron beam flue gas treatment installation is presented in Table II.

<table>
<thead>
<tr>
<th>TABLE II. RAW MATERIALS DEMAND AND ENERGY CONSUMPTION.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Demand</td>
</tr>
<tr>
<td>Energy [kW]</td>
</tr>
<tr>
<td>Main raw materials</td>
</tr>
<tr>
<td>Ammonia [kg/h]</td>
</tr>
<tr>
<td>Process water [kg/h]</td>
</tr>
<tr>
<td>Auxiliary raw materials</td>
</tr>
<tr>
<td>Demineralized water</td>
</tr>
</tbody>
</table>
The following staff is anticipated for EBFGT installation operation:

- Plant manager: 1 post
- Operators: 3 posts
- Technicians: 1 post
- Laboratory staff: ½ post

For staff requirements a three shift working schedule is assumed.

3. COST EVALUATION OF EBFGT INSTALLATION:

Total investment cost of electron beam flue gas treatment installation planned at selected oil refinery was evaluated for 13 800 000 USD in the case of option 1 (flue gas flow rate 65 000 Nm$^3$/h) and 19 200 000 USD in the case of option 2 (flue gas flow rate 130 000 Nm$^3$/h). The elements of investment cost are presented in Table III.

### TABLE III. INVESTMENT COST OF EBFGT INSTALLATION AT OIL REFINERY.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
<th>Cost [1000 USD]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Option 1</strong></td>
<td><strong>Option 2</strong></td>
</tr>
<tr>
<td></td>
<td>(65 000 Nm$^3$/h)</td>
<td>(130 000 Nm$^3$/h)</td>
</tr>
<tr>
<td>1</td>
<td>Site engineering and design</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>Heat exchanger</td>
<td>530</td>
</tr>
<tr>
<td>3</td>
<td>Gas conditioning unit</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>Ammonia storage and dosing</td>
<td>510</td>
</tr>
<tr>
<td>5</td>
<td>Accelerators</td>
<td>1600</td>
</tr>
<tr>
<td>6</td>
<td>Reactor with radiation shielding</td>
<td>800</td>
</tr>
<tr>
<td>7</td>
<td>By-product ESP</td>
<td>2600</td>
</tr>
<tr>
<td>8</td>
<td>By-product handling and storage</td>
<td>610</td>
</tr>
<tr>
<td>9</td>
<td>Auxiliary fan</td>
<td>300</td>
</tr>
<tr>
<td>10</td>
<td>Ducts and piping</td>
<td>480</td>
</tr>
<tr>
<td>11</td>
<td>Electric power supply system</td>
<td>400</td>
</tr>
<tr>
<td>12</td>
<td>Control and monitoring system</td>
<td>1100</td>
</tr>
<tr>
<td>13</td>
<td>Structural elements</td>
<td>450</td>
</tr>
<tr>
<td>14</td>
<td>Land development</td>
<td>590</td>
</tr>
<tr>
<td>15</td>
<td>Supervision, training, start-up</td>
<td>1500</td>
</tr>
<tr>
<td>16</td>
<td>Reserve (10%), spare parts</td>
<td>1250</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td><strong>13 800</strong></td>
</tr>
</tbody>
</table>

The investment cost evaluated in this paper was elaborated according to best available data including offers from equipment manufacturers (ESP, accelerators) and it meets the cost level of such investment. Nevertheless the costs of elements as well as the overall cost may vary depending on the chosen suppliers and general contractor.

The design criteria determined minimum availability of electron beam flue gas treatment installation in selected oil refinery for 8000 hours/year. Calculations of annual operation cost of the installation were performed assuming 95% availability which gives 8320 hours/year of continuous operation of oil refinery.

The expenses connected with operation of the EBFGT installation were divided into fixed and variable costs. Fixed costs cover labor and maintenance costs.
Labor cost was calculated for 4.5 posts (as indicated earlier). Assuming mean cost of one post for 50 000 USD/year, labor cost gives 225 000 USD/year. Fixed maintenance cost was assumed at the level of 5% of the equipment value. Therefore, it gives 330 000 USD per year for option 1 and 450 000 USD for option 2. Such expenses should cover all the maintenance requirements.

Variable costs cover process water, ammonia and electric energy.

Demand for process water is 2.085 ton/hour for option 1 and 4.169 ton/hour for option 2. Accordingly, cost of process water for annual operation of 8320 hours and water price 3.2 USD/ton will be 55 500 USD/year for option 1 and 111 000 USD/year for option 2.

Price of ammonia was assumed at 310 USD/ton. Therefore, for ammonia demand of 111 kg/hour for option 1 and 222 kg/hour for option 2, ammonia cost will be 286 000 USD/year (option 1) and 576 000 USD/year (option 2).

Electric energy cost was calculated for the demand of 800 kW for option 1 and 160 kW for option 2. As was previously mentioned, price of electricity is 26.7 USD/MWh. Therefore, cost of energy is calculated for 177 000 USD/year for option 1 and 355 USD/year for option 2.

The expenses will be partly compensated by sale of obtained by-product for agricultural purposes. Usually income from sale of by-product shall cover expenses of raw materials. By-product yield was calculated to be 460 kg/hour and 920 kg/hour depending on the option of installation. The income depends on the price negotiated with the by-product buyer. Assuming mean market price of ammonium sulfate 135 USD/ton, the income will reach 516 000 USD/year for option 1 and 1033 USD/year for option 2.

The annual expenses for operation of the planned EBFGT installation are presented in Table IV.

<table>
<thead>
<tr>
<th>Cost element</th>
<th>Value [1000 USD]</th>
<th>Option 1 (65 000 Nm³/h)</th>
<th>Option 2 (130 000 Nm³/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed costs:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Labor</td>
<td>225</td>
<td>225</td>
<td></td>
</tr>
<tr>
<td>Maintenance</td>
<td>330</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>Total fixed costs</td>
<td>555</td>
<td>675</td>
<td></td>
</tr>
<tr>
<td>Variable costs:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process water</td>
<td>56</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>286</td>
<td>573</td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>177</td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>Total variable costs</td>
<td>519</td>
<td>1039</td>
<td></td>
</tr>
<tr>
<td><strong>Total expenses</strong></td>
<td><strong>1074</strong></td>
<td><strong>1714</strong></td>
<td></td>
</tr>
<tr>
<td>Incomes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sale of By-product</td>
<td>516</td>
<td>1033</td>
<td></td>
</tr>
<tr>
<td><strong>Total annual costs</strong></td>
<td><strong>558</strong></td>
<td><strong>681</strong></td>
<td></td>
</tr>
</tbody>
</table>

Total annual operation cost of proposed EBFGT installation will reach 558 000 USD/year for option 1 and 681 000 USD/year for option 2. The costs shown above are direct annual expenditures connected with operation of EBFGT installation and don't cover any non-cash expenditures as amortization or bank credit costs.
4. DISCUSSION

The removal of SO\textsubscript{2} and NO\textsubscript{x} from flue gas is normally realized by combination of de-SO\textsubscript{2} and de-NO\textsubscript{x} methods. The removal efficiency of both systems (i.e. electron beam and combined wet FGD and SCR) is comparable. The desulfurization efficiency is at least 95% (achieving 98%) in the case of EB technology, while it is reported at the level of 95 – 99% in the case of wet FGD technique. Similarly, NO\textsubscript{x} removal efficiency based on EB technology is at the level of 70% (in pilot plant it was reported up to 80%) while SCR efficiency is usually 70 – 80%. The efficiency of SNCR process is much lower.

Wet scrubber technologies are the most often used methods for SO\textsubscript{2} emission reduction in the energy sector. The market share is about 84% of the total capacity of all desulfurization methods. The most applied method among all wet scrubber technologies is wet lime/limestone scrubbers (70% market share). The estimations of SO\textsubscript{2} emission reduction cost differ substantially. Even analyzing the same technology gives different results. It could be explained as an effect of a specific situation: technical or economic conditions, power plant localization, age of power plant and interest rate assumed for investment calculation purposes. Therefore, the information about capital and operation costs presented in publications usually cannot be directly applied to local conditions.

The evaluation of economical factors of main flue gas desulfurization methods was given by Kaminski et al. [1]. Estimations of investment costs were made for a 300 MW\textsubscript{e} power plant, which combuts coal of 2.6% sulfur content. The investment costs of wet scrubbing methods were given at the level of 190 – 240 USD/kW, while levelized cost was reported 420 – 476 [USD/ton of SO\textsubscript{2} removed]. The data are given in 1990 US dollars.

According to the World Bank Group [2], the retrofit wet FGD installation costs 100 – 150 USD/kW, while new one costs 70 – 150 USD/kW. Unfortunately the data are general and no specific SO\textsubscript{2} removal method is indicated. It is worth to notice that this kind of pollution control facility is installed mostly in large power plants of size above 500 MW\textsubscript{e}. So in the case of smaller installations (about 120 – 250 MW\textsubscript{e}) the investment cost should be higher. The data given by Kaminski comply with 300 MW unit and certain methods, therefore they are more reliable.

On the other hand, wastewater treatment plants are to be built with FGD units due to considerable amount of wastewater generation during the installation operation. The cost of construction and operation of wastewater treatment plant is usually not reported as a cost of FGD plant.

Kaminski reports operation cost of wet scrubbing methods for 1.4 USD/MWh\textsubscript{e} [1]. According to World Bank Group data [2] the total O&M costs are from 6.6 to 13 USD/MWh, while variable costs vary from 1.5 to 3.3 USD/MWh for retrofit installations and 1.3 to 3.2 USD/MWh for new ones. This gives annual variable costs at the level 12 750 to 28 050 USD/MW and total operation costs at the level 56 100 to 102 000 USD/MW for 8500 hours of annual operation.

The retrofit SCR installations’ investment costs are usually 59 – 112 USD/kW, depending on the plant size and difficulty and scope of retrofit [3]. For new facilities such costs are 45 – 60 USD/kW\textsubscript{e}. SNCR installations are much cheaper and cost about 15 – 30 USD/kW\textsubscript{e} for new plants. The costs are given in USD for 1996.

In the case of SCR methods, the operation costs are reported to be in the range of 3800 – 4600 USD/MW\textsubscript{e} (from 2.667 000 USD for 700 MW\textsubscript{e} unit to 580 000 USD for 125 MW\textsubscript{e} unit) [3]. Similar to capital cost, SNCR operation costs are about 1/3 lower than SCR costs.

In the case of flue gas treatment from oil fired boiler without modification of boiler itself, the most useful and popular solution is combination of wet SO\textsubscript{2} scrubbing and removal of nitrogen oxides by SCR or SNCR method. The investment and operation costs of such combination are presented in Table V.
TABLE V. INVESTMENT AND OPERATION COSTS OF COMBINATION OF CONVENTIONAL DE-SO\textsubscript{2} AND DE-NO\textsubscript{x} METHODS.

<table>
<thead>
<tr>
<th>Flue gas treatment method</th>
<th>Investment cost [USD/kW]</th>
<th>Annual operational cost (variable) [USD/MW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet SO\textsubscript{2} scrubbing</td>
<td>190 – 240</td>
<td>12 750 to 28 050</td>
</tr>
<tr>
<td>Selective Catalytic Reduction</td>
<td>60 – 110</td>
<td>3800 – 4600</td>
</tr>
<tr>
<td>Selective Non Catalytic Reduction</td>
<td>15 – 30</td>
<td>2500 – 3000</td>
</tr>
</tbody>
</table>

Combination of methods:
- Wet de-SO\textsubscript{2} + SCR: 250 – 350 USD/kW, 16 550 – 32 650 USD/MW
- Wet de-SO\textsubscript{2} + SNCR: 205 – 270 USD/kW, 15 250 – 31 050 USD/MW

The investment costs of conventional installations for SO\textsubscript{2} removal are equal to 190 – 240 USD/kW while NO\textsubscript{x} control installations cost 60 – 110 USD/kW (SCR) or 15 – 30 USD/kW (SNCR), which result in total costs as high as 250 – 350 USD/kW for emission control of both pollutants. The data are given for 300 MW and larger units. One should remember that for smaller units, the unit cost should be multiplied two – three times. According to other paper [4], the cost of combined wet FGD and SCR system is estimated for 270 – 474 USD/kW\textsubscript{e} for units of 300 – 50 MW\textsubscript{e}. Annual operation cost varies from 15 000 to over 30 000 USD/MW.

Proposed electron beam flue gas treatment installation is designed either for 65 000 or 130 000 Nm\textsuperscript{3}/h. Investment and operation costs of option 1 and option 2 were estimated as 14 - 19 millions USD and 500 – 700 thousands USD/year, respectively. Flow rate of 130 000 Nm\textsuperscript{3}/h corresponds with 30 – 35 MW\textsubscript{e} unit. In this case, the investment costs of combination of FGD and SCR method will be 10 -15 millions USD based on data given for larger units. As the facility is very small, the unit cost shall rise and total investment cost could be as high as 20 million USD. In such case, cost does not contain wastewater treatment plant and gypsum landfill site preparation. That cost is comparable with estimated cost of EBFGT facility. On the other hand, SO\textsubscript{2} removal cost by conventional methods was based on 1990's US dollars and NO\textsubscript{x} removal costs on 1996's US dollars. Therefore, the EBFGT installation can be even more competitive nowadays.

The low value of annual variable operation cost may be estimated as 16 000 USD/MW, which gives 560 000 USD/year for 35 MW unit. As amortization, financial and administration costs cover most of fixed operation costs this part was omitted from first approximation. This number is close to total operation costs of EBFGT installation which include labor and maintenance costs as fixed ones. In the case of high operation cost (30 000 USD/MW), electron beam flue gas treatment facility is much cheaper solution.

In general, the investment cost of EBFGT installation depends on flow rate of treated flue gas, inlet parameters (temperature, humidity, pollutants concentrations) and removal requirements. With increase of the installation size the overall investment cost increases, but the unit cost decreases, especially in the case of small and medium facilities. The variation of unit investment cost according to installation size may reach even two times. This dependence for coal fired boilers was estimated by Jackowski et al. [5] as presented in Figure 2.
Sulfur dioxide is removed in both thermal and radiochemical processes, therefore higher SO\(_2\) removal may be obtained by optimization of the flue gas parameters at the inlet to reaction vessel. NO\(_x\) removal process efficiency depends mostly on absorbed dose, so higher removal requirements result in larger accelerators and higher energy consumption. In addition, it was noticed that for constant dose, total removal of NO\(_x\) (mg/Nm\(^3\)) increases with increase of inlet concentration of pollutant, while relative NO\(_x\) removal (%) decreases. In this case, higher dose must be applied to assure the required removal level. In this way, higher inlet concentrations of nitrogen oxides promote higher investment and operation costs of installation.

Generally, from the view point of removal requirements, there can be two distinguished types of EBFGT installation. First one designed for high SO\(_2\) and low NO\(_x\) removal efficiency requires lower doses (2 – 6 kGy) which results in smaller accelerators and lower consumption of energy. In this case flue gas conditioning is crucial from operational point of view. The second case of high removal efficiency of both SO\(_2\) and NO\(_x\) requires much higher doses (10 – 12 kGy), higher power of accelerators and higher energy consumption. Although accelerator cost may be even twice higher in this case, the overall investment cost of installation rise not more than 20% due to cost of other components which are similar.

As far as structural elements, one of the most important factors which have impact on the reliability of the electron beam flue gas treatment installation is proper material selection due to high corrosive conditions inside the installation. The use of stainless steel and other techniques of corrosion protection are expensive, but allow for long life of the elements and reduce further maintenance cost. The second important cost rising element is heavy concrete bunker for radiation shielding of reaction chamber, which is essential due to safety measures.

Accelerators with supporting equipment are considered as the most expensive devices in the total cost of the installation. In fact the prices of accelerators cover about 10 – 15% of total investment cost. Other expensive devices in the system are: electrostatic precipitator with by-product handling system and control and monitoring unit. Not less important is the cost of piping and structural
elements which are made on site. However, if the plant can be built as a compact system, the cost of ducts and piping will be reduced.

Two main factors affecting operation cost of EBFGT installation may be distinguished: energy consumption and ratio of price of by-product (fertilizer) to price of ammonia. As energy and ammonia costs are the main factors responsible for the operational expenses of the installation, the income from sale of by-product allows reducing the total operation cost of flue gas treatment. Normally the income from by-product shall at least cover the expenses for raw materials needed for the process. If the price of by-product is closer to the market price of fertilizer, it can cover most of the variable operation costs of the installation.

Apart of technological aspects of electron beam flue gas treatment technology, the economic feasibility of the method is essential for the acceptance of technology in the industry. Emission control investments are of non-profit type, but reduction of the cost of such installation is expected by investors. Full understanding of the factors affecting the costs of EBFGT technology will allow the improvement of the process not only from technological point of view, but also optimization of the process costs.

5. CONCLUSIONS

1. Previous results of laboratory scale experiments on different types of fuel oil demonstrated technical feasibility of EBFGT for flue gas treatment from oil fired boiler. High efficiency of SO$_2$ and NO$_x$ removal was also achieved.

2. Electron beam flue gas treatment technology is the only one in which removal of SO$_2$ and NO$_x$ is achieved in single stage, the process is dry, no wastewater is generated and income from sale of by-product is reasonable.

3. The study shows that the technology is highly competitive compared to conventional ones from economic point of view.

4. The development of the technology shall cover not only engineering aspects, but also improvement of economic feasibility which will allow for increasing the competitiveness of EBFGT technology compared to conventional methods.

REFERENCES


[2] "Wet flue gas desulfurization (FGD)"


Summary

Generated by-products from E-beam cleaning systems of industrial waste gases have been studied using different techniques like TG-DTA systems, Electron Microscopy, X-Ray diffraction and IR spectroscopy methods. On the base of the investigations it was found that the composition of the by-product varies depending on the content of pollutants in the waste gases and technological parameters during cleaning process. Size of particles and thermal stability of the by product were determined. Content of ammonium sulphate as a main component, ammonium nitrate and heavy metals content is also determined and discussed. During thermal treatment of the by-product at temperature range 543-663K half of the ammonia is released in the gas phase. Kinetic parameters of the thermal decomposition are determined and it is confirmed that for waste gases containing mainly SO$_x$ as a pollutants they are very close to the pure ammonium sulphate.

By-product from demonstration E-beam installation at Maritsa-East -2 TPP is used to produce mixed fertilisers using milled Tunisia phosphorites or tribo-activated mixtures of the by-product, Tunisia phosphorite, potassium sulphate and ashes from electrostatic precipitators of TPP. It was found that during thermo-tribo-chemical treatment of selected mixtures different type of fertilisers could be produced, where the soluble forms of Phosphorous may vary, depending on the conditions. During thermal treatment about half of ammonia is released in the gas phase opening a way for partial recycling of ammonia to the cleaning process. Agrochemical tests of the fertilisers on the base of by-product confirm their efficiency.

Key words: E-beam cleaning, by-products, utilisation

1. INTRODUCTION

The thermal power plants contribute 38% of the national production of electrical energy in Bulgaria. Most of the power capacities have been commissioned in mid 80'ties, thus their facilities need modernization in order to comply with environmental law. Three trends are obvious in the energy sector: industrial energy consumption increase, decommissioning of big nuclear power facilities and need of development of local thermal power capacities [1]. However this must be in compliance with the new stricter environmental standards. As a positive step we may consider the introduced desulphurization units in TPS Maritsa–East 2 FGD cleaning installations. Two FGD installations are using the traditional limestone process

In November 2003 the Electron Beam Demonstration plant (EBDP) started operation tests at the TPS Maritsa–East 2. The EBDP treats 10 000 Nm$^3$/h flue gas and produces up to 200 kg/h ammonium sulfate as a by-products. The present paper investigates the physical, chemical and thermal properties of the by-product from this installation, but its mixtures with other components are also studied in view of visible recycling partially of ammonia. Legal requirements of EU are also taken into account [4-8].

2. EXPERIMENTAL

Eight samples of ammonium sulphate (AS-2 to AS-9) have been taken from EBDP during the period 01.02.2004 – 30.03.2004. Most of them are when the NH$_3$ norm is 0.95 from the stoichiometric one, but also by-products, produced at relatively very low norm have been taken also for comparison (Table I).
Different techniques and methods have been applied in the process of the study. The main components have been determined, using standard chemical analysis, when for micro components ICP method has been applied. pH and electrical conductivity (EC) of 0.8-4% water solutions were measured, using “LP-17” pH-meter and CDRV-62 conductivity meter, calibrated with 1M KCl. Thermal analysis were performed at Stanton Redcroft thermal analyzer in temperature range 289-1273 K. Heating rate for all samples is 10°K·min⁻¹ and samples’ mass is 0.100 g. As a control sample (AS-0) ammonium soleplate, p.a. grade was chosen. DRON X-Ray diffraction apparatus was used to determine the main solid phases. Optical and electron microscopy have been applied for determining crystal shape and size. NETSCH plasticimeter and extrusion press were used for compaction properties. Solid waste sludge from production of calcium mono-phosphate, Tunisia phosphorite, potassium sulfate and ashes from TPS Maritsa-East-1 are used for producing mixed fertilizers.

1. RESULTS AND DISCUSSION

The results for the content of main components and micro components are given in table II and III. Crystal’s size and shape are given on Fig.1, compared with pure Merck product.
particles are uniform. As a result the volume density is 768-845 kg/m$^3$, but the real density is very close to the pure ammonium sulphate - 1767 kg/m$^3$.

\[(\text{NH}_4)_2\text{SO}_4, \text{ Merck} \]
magnification 100, marker 100 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, \text{ Merck} \]
magnification 400, marker 100 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.4 \]
magnification 1400, marker 10 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.4 \]
magnification 1000, marker 10 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.7 \]
magnification 2600, marker 10 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.7 \]
magnification 1400, marker 10 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.9 \]
magnification 1300, marker 10 $\mu$m

\[(\text{NH}_4)_2\text{SO}_4, N=0.9 \]
magnification 600, marker 100 $\mu$m

**FIG. 1.** Electron microscopy photos of by-products from EBDP, compared with pure ammonium sulfate from Merck Company
Measurements of pH and electrical conductivity show that when the mass concentration of the by-product in the water solution is increases from 0.8 to 4%wt, then the pH value (Table IV) is quite stable and there is rise of conductivity (Table V). The pH is more acidic when the norm of ammonia is lower and it is logical. The acidity of the different samples (pH from 5.09 to 4.13) is stronger that the control sample (pH=5.70). This is explained by the availability of stronger nitrate ion from the ammonium nitrate.

**TABLE IV. MEASUREMENTS OF PH OF WATER SOLUTIONS OF THE BY-PRODUCT FROM EBDP**

<table>
<thead>
<tr>
<th>Content of by-product, %wt</th>
<th>AS-0</th>
<th>AS-2</th>
<th>AS-3</th>
<th>AS-4</th>
<th>AS-5</th>
<th>AS-6</th>
<th>AS-7</th>
<th>AS-8</th>
<th>AS-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>5.70</td>
<td>5.09</td>
<td>4.19</td>
<td>4.46</td>
<td>4.71</td>
<td>5.60</td>
<td>5.20</td>
<td>4.60</td>
<td>4.13</td>
</tr>
<tr>
<td><strong>1.6</strong></td>
<td>5.39</td>
<td>4.66</td>
<td>3.88</td>
<td>4.28</td>
<td>4.66</td>
<td>4.71</td>
<td>4.72</td>
<td>4.36</td>
<td>3.98</td>
</tr>
<tr>
<td><strong>2.4</strong></td>
<td>5.30</td>
<td>4.56</td>
<td>3.82</td>
<td>4.08</td>
<td>4.36</td>
<td>4.62</td>
<td>4.60</td>
<td>4.21</td>
<td>3.86</td>
</tr>
<tr>
<td><strong>3.2</strong></td>
<td>5.20</td>
<td>5.51</td>
<td>3.80</td>
<td>4.04</td>
<td>4.33</td>
<td>4.45</td>
<td>4.54</td>
<td>4.15</td>
<td>3.82</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>5.11</td>
<td>4.40</td>
<td>3.74</td>
<td>4.03</td>
<td>4.29</td>
<td>4.43</td>
<td>4.43</td>
<td>4.09</td>
<td>3.76</td>
</tr>
</tbody>
</table>

**TABLE V. MEASUREMENTS OF ELECTRICAL CONDUCTIVITY OF THE BY-PRODUCT, 10^{-3}S·CM^{-1}**

<table>
<thead>
<tr>
<th>Content of by-product, %wt</th>
<th>AS-0</th>
<th>AS-2</th>
<th>AS-3</th>
<th>AS-4</th>
<th>AS-5</th>
<th>AS-6</th>
<th>AS-7</th>
<th>AS-8</th>
<th>AS-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>11.63</td>
<td>11.6</td>
<td>11.59</td>
<td>11.35</td>
<td>11.43</td>
<td>11.64</td>
<td>11.41</td>
<td>78.2</td>
<td>77.7</td>
</tr>
<tr>
<td><strong>1.6</strong></td>
<td>21.2</td>
<td>20.5</td>
<td>20.7</td>
<td>20.7</td>
<td>20.5</td>
<td>20.4</td>
<td>20.3</td>
<td>44.4</td>
<td>43.5</td>
</tr>
<tr>
<td><strong>2.4</strong></td>
<td>29.9</td>
<td>29.0</td>
<td>29.2</td>
<td>28.8</td>
<td>29.1</td>
<td>28.6</td>
<td>28.2</td>
<td>31.4</td>
<td>31.6</td>
</tr>
<tr>
<td><strong>3.2</strong></td>
<td>37.7</td>
<td>35.9</td>
<td>36.5</td>
<td>36.9</td>
<td>36.8</td>
<td>37.0</td>
<td>36.9</td>
<td>25.6</td>
<td>25.1</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>45.0</td>
<td>44.2</td>
<td>47.8</td>
<td>47.5</td>
<td>46.7</td>
<td>47.7</td>
<td>44.1</td>
<td>20.9</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Granulation of the powder by-product is easily achievable using different methods, like pan-, press- or extrusion compaction techniques. It is well mixed with other fertiliser component. Most suitable are the other nitrogen fertilisers (urea and ammonium nitrate), super phosphate or natural phosphates. So the by-product could be used for production of number mixed fertilisers, depending on the agrochemical needs of soils and plants. The optimal conditions, related to the pressure and water content, are directly related to the ratio between the main components. So the water content may vary from 0.6 to 11% in the mixtures and the pressure – from 0.1 to 21 MPa. The granule static straight for different mixed fertilisers with the by-product in it vary from 14 to 46 kg/cm² and it is above the standard requirements. Derivatograms Fig. 2 - 5 of pure ammonium sulphate and by-products generated at different ammonia norm are shown and they characterize thermal stability and mechanism of thermal decomposition of the by-product.
FIG. 2. Derivatogram of Merck pure ammonium sulfate

FIG. 3. Derivatogram of the by-product - norm of ammonia 0.4
As it can be seen from tables VI and VII the temperature ranges and kinetic parameters of thermal decomposition of the by-product from EBDP are quite close to the pure Ammonium sulfate and the main differences are related to the content of Ammonium nitrate. Its thermal decomposition is at lower temperatures.
## TABLE VI. TEMPERATURE RANGES AND WEIGHT LOSSES OF MERCK (NH₄)₂SO₄ AND BY-PRODUCT FROM EBDP

<table>
<thead>
<tr>
<th>No</th>
<th>Temperature, K</th>
<th>Weight Losses, %</th>
<th>Stage weight losses, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflection point</td>
<td>Start</td>
<td>End</td>
</tr>
<tr>
<td>Merck</td>
<td>581.5</td>
<td>510.5</td>
<td>628.6</td>
</tr>
<tr>
<td>Merck</td>
<td>708.6</td>
<td>628.6</td>
<td>749.8</td>
</tr>
<tr>
<td>Merck</td>
<td>Total weight losses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃=0.9</td>
<td>370.7</td>
<td>339.2</td>
<td>394.3</td>
</tr>
<tr>
<td>NH₃=0.9</td>
<td>594.5</td>
<td>512.4</td>
<td>624.3</td>
</tr>
<tr>
<td>NH₃=0.9</td>
<td>705.2</td>
<td>624.3</td>
<td>744.2</td>
</tr>
<tr>
<td>NH₃=0.9</td>
<td>Total weight losses</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## TABLE VII. KINETIC DATA FOR PURE AMMONIUM SULFATE AND BY-PRODUCTS

<table>
<thead>
<tr>
<th>Norm of NH₃</th>
<th>Stage</th>
<th>Rate constant</th>
<th>Pre-exp. factor min⁻¹</th>
<th>Activation energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>I</td>
<td>1</td>
<td>27.11</td>
<td>136.71</td>
</tr>
<tr>
<td>0.4</td>
<td>II</td>
<td>1</td>
<td>31.30</td>
<td>186.83</td>
</tr>
<tr>
<td>0.7</td>
<td>I</td>
<td>1</td>
<td>31.28</td>
<td>156.13</td>
</tr>
<tr>
<td>0.7</td>
<td>II</td>
<td>1</td>
<td>30.50</td>
<td>179.50</td>
</tr>
<tr>
<td>0.9</td>
<td>I</td>
<td>1</td>
<td>29.98</td>
<td>149.52</td>
</tr>
<tr>
<td>0.9</td>
<td>II</td>
<td>1</td>
<td>29.64</td>
<td>176.02</td>
</tr>
<tr>
<td>0.9</td>
<td>II</td>
<td>1</td>
<td>27.97</td>
<td>140.73</td>
</tr>
<tr>
<td>0.9</td>
<td>II</td>
<td>1</td>
<td>32.23</td>
<td>191.81</td>
</tr>
</tbody>
</table>

On the base of results obtained thermal decomposition of the by-product can be described by the well-known transformations of the ammonium sulfate, as follows:

**I Stage – 543 – 663K, 16.1-17.8% weight losses**

\[(\text{NH}_4)_2\text{SO}_4 = \text{NH}_4\text{HSO}_4 + \text{NH}_3\]  
\[2(\text{NH}_4)_2\text{SO}_4 = (\text{NH}_4)_3\text{H(SO}_4)_2 + 2\text{NH}_3\]  

**II Stage – 653 – 813K, 76.7-78.3% weight losses**

\[(\text{NH}_4)_3\text{H(SO}_4)_2 = 2\text{NH}_4\text{HSO}_4 + \text{NH}_3\]  
\[(\text{NH}_4)_3\text{H(SO}_4)_2 = (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NH}_3 + \text{H}_2\text{O}\]  
\[\text{NH}_4\text{HSO}_4 = \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O}\]  

The residue of (NH₄)₂S₂O₈ can be decomposed, according to reaction (6)

\[(\text{NH}_4)_2\text{S}_2\text{O}_8 = 2\text{NH}_3 + 2\text{SO}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2\]  

The chemical composition of the by-product from industrial installation in Chengdu – China consists of 92% ammonium sulphate, 1% ammonium nitrate, and 7% fly ash [9]. The by-product from industrial installation in Poland has also different composition and thermal behaviour due to higher content of ammonium chloride.
It is interesting to point out that the content of the heavy metals is higher when the ammonia norm is higher there is a tendency of increasing the content of some heavy metals (Table VIII).

3.1. Mixed balance fertilisers

Solid waste sludge from production of calcium mono-phosphate, ammonium sulphate and potassium sulphate are used as a raw material for production of mixed fertilisers and ashes from dust cleaning systems of coal production and thermal power stations (TPS) is used as a sorption capacity improving component. The dry sludge composition is 24.82% wt $P_2O_5$/total, 14.23% wt $P_2O_5$/citric acid soluble, 0.52% wt $P_2O_5$/water soluble, 38.71% wt CaO, 4.05% wt F, 6.29% wt S (mainly as a gypsum), 1.88% wt SiO$_2$, 1.07% wt $R_2O_3$, 0.07% wt $K_2O$, 0.056% wt Cl. Ammonium sulfate is p.a. grade from Alerus Ltd containing 99.5% wt (NH$_4$)$_2$SO$_4$. As impurities 0.001% NO$_3^-$, 0.0003% Cl$^-$, 0.0005% PO$_4^{3-}$, 0.0002% Fe, 0.00002% As and 0.0002% sum of other heavy metals are specified by the supplier. Potassium sulphate is also p.a. grade and the content of main compound is 99.29% wt. The main impurity in it is 0.48% water. The main components of mixed ashes from Maritsa East-1 thermal power station and briquette plant /ME-1B/ (without volatile components) in % wt are as follows: 41.30 SiO$_2$, 16.91 Fe$_2O_3$, 18.5 Al$_2O_3$, 8.3 CaO, 4.11 MgO, 1.72 K$_2O$, and 3.91 SO$_3$. The 19 different mixtures were treated and from each of these activated powders 30 tablets with diameter 10 mm have been produced. Content of the raw materials used in the mixtures are given in Table IX. The selection of the components ratio is on the base of the agrochemical requirements to obtain suitable content of the nutrients and ratio between in the final products.

TABLE IX. CONTENT OF THE RAW MATERIALS AND PROPERTIES OF THE TREATED MIXTURES, %WT

<table>
<thead>
<tr>
<th>№</th>
<th>(NH$_4$)$_2$SO$_4$</th>
<th>P$_2$O$_5$/sw</th>
<th>K$_2$SO$_4$</th>
<th>Ash</th>
<th>SS*</th>
<th>SC**</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>%wt</td>
<td>%wt</td>
<td>%wt</td>
<td>%wt</td>
<td>10$^{-1}$ MPa</td>
<td>%wt</td>
</tr>
<tr>
<td>1-4</td>
<td>35.42</td>
<td>37.70</td>
<td>10.21</td>
<td>16.67</td>
<td>100</td>
<td>15.34</td>
</tr>
<tr>
<td>1-6</td>
<td>38.93</td>
<td>27.62</td>
<td>16.79</td>
<td>16.66</td>
<td>65.9</td>
<td>27.64</td>
</tr>
<tr>
<td>1-7</td>
<td>25.69</td>
<td>40.94</td>
<td>16.71</td>
<td>16.66</td>
<td>100</td>
<td>19.83</td>
</tr>
<tr>
<td>1-8</td>
<td>26.71</td>
<td>28.42</td>
<td>11.56</td>
<td>33.31</td>
<td>53.44</td>
<td>18.85</td>
</tr>
<tr>
<td>1-9</td>
<td>25.80</td>
<td>34.36</td>
<td>13.95</td>
<td>25.89</td>
<td>78.38</td>
<td>20.98</td>
</tr>
<tr>
<td>1-10</td>
<td>32.96</td>
<td>29.23</td>
<td>11.89</td>
<td>25.92</td>
<td>78.38</td>
<td>23.40</td>
</tr>
<tr>
<td>1-14</td>
<td>28.70</td>
<td>30.52</td>
<td>14.88</td>
<td>25.92</td>
<td>77.78</td>
<td>20.78</td>
</tr>
</tbody>
</table>

*Static straight; **Sorption capacity

Thermal stability and phase content of the products are given in table X and Fig. 6-10.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I Stage</td>
<td>298.4 – 363.1</td>
<td>1.1</td>
</tr>
<tr>
<td>II Stage</td>
<td>436.1 – 467.5</td>
<td>2.4</td>
</tr>
<tr>
<td>III Stage</td>
<td>542.6 – 746.7</td>
<td>8.3</td>
</tr>
<tr>
<td>IV Stage</td>
<td>695.1 – 882.7</td>
<td>5.5</td>
</tr>
<tr>
<td>V Stage</td>
<td>746.7 – 982.7</td>
<td>9.4</td>
</tr>
<tr>
<td>VI Stage</td>
<td>982.7 – 981.1</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>48.8</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>inflexion point</td>
<td></td>
</tr>
<tr>
<td>1-6</td>
<td>293.4 – 375.4</td>
<td>1.3</td>
</tr>
<tr>
<td>III Stage</td>
<td>436.9 – 501.6</td>
<td>3.9</td>
</tr>
<tr>
<td>IV Stage</td>
<td>501.6 – 701.6</td>
<td>17.2</td>
</tr>
<tr>
<td>V Stage</td>
<td>701.6 – 766.4</td>
<td>9.6</td>
</tr>
<tr>
<td>VI Stage</td>
<td>766.4 – 863.9</td>
<td>6.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>51.4</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-7</td>
<td>292.6 – 343.4</td>
<td>1.8</td>
</tr>
<tr>
<td>III Stage</td>
<td>450.8 – 477.1</td>
<td>1.5</td>
</tr>
<tr>
<td>IV Stage</td>
<td>508.2 – 593.4</td>
<td>5.4</td>
</tr>
<tr>
<td>V Stage</td>
<td>669.7 – 742.6</td>
<td>6.6</td>
</tr>
<tr>
<td>VI Stage</td>
<td>742.6 – 863.9</td>
<td>8.7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>39.9</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-8</td>
<td>309.8 – 372.1</td>
<td>1.8</td>
</tr>
<tr>
<td>III Stage</td>
<td>436.9 – 500.0</td>
<td>1.8</td>
</tr>
<tr>
<td>IV Stage</td>
<td>529.5 – 589.3</td>
<td>5.7</td>
</tr>
<tr>
<td>V Stage</td>
<td>655.7 – 714.8</td>
<td>7.4</td>
</tr>
<tr>
<td>VI Stage</td>
<td>714.8 – 863.1</td>
<td>16.7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>52.4</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-9</td>
<td>292.6 – 373.0</td>
<td>2.8</td>
</tr>
<tr>
<td>III Stage</td>
<td>445.1 – 475.4</td>
<td>1.5</td>
</tr>
<tr>
<td>IV Stage</td>
<td>504.9 – 589.3</td>
<td>5.9</td>
</tr>
<tr>
<td>V Stage</td>
<td>660.7 – 721.3</td>
<td>7.3</td>
</tr>
<tr>
<td>VI Stage</td>
<td>721.3 – 866.4</td>
<td>13.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>46.7</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-10</td>
<td>291.8 – 376.2</td>
<td>3.0</td>
</tr>
<tr>
<td>III Stage</td>
<td>450.8 – 477.0</td>
<td>1.0</td>
</tr>
<tr>
<td>IV Stage</td>
<td>502.5 – 600.0</td>
<td>8.2</td>
</tr>
<tr>
<td>V Stage</td>
<td>683.6 – 736.1</td>
<td>6.2</td>
</tr>
<tr>
<td>VI Stage</td>
<td>736.1 – 868.9</td>
<td>13.3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>54.4</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-14</td>
<td>304.9 – 370.5</td>
<td>2.2</td>
</tr>
<tr>
<td>III Stage</td>
<td>440.2 – 477.0</td>
<td>1.3</td>
</tr>
<tr>
<td>IV Stage</td>
<td>500.0 – 606.6</td>
<td>9.6</td>
</tr>
<tr>
<td>V Stage</td>
<td>667.2 – 726.2</td>
<td>7.1</td>
</tr>
<tr>
<td>VI Stage</td>
<td>726.2 – 877.0</td>
<td>15.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>52.1</strong></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Temperature Range</th>
<th>Mas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>302.5 – 418.9</td>
<td>8.4</td>
</tr>
<tr>
<td>III Stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV Stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V Stage</td>
<td>520.5 – 750.0</td>
<td>37.3</td>
</tr>
<tr>
<td>VI Stage</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>79.5</strong></td>
<td></td>
</tr>
</tbody>
</table>

* inflexion point
6. X-Ray diffraction intensities

FIG.
FIG. 7. X-Ray diffraction intensities
FIG. 8. TG-DTA-DTG curves
Soluble forms come out and the content of them increases from 56.7% to 85.2-91.7% from the total phosphorous content in the samples. It is obvious that during samples’ treatment new solid phases are formed and some phosphorous substances are transformed mainly to water-soluble structures. Static straight of the tablets varies from 0.39 to 10 MPa and the water sorption capacity is in the range 15.34-27.64%. Water sorption capacity has the maximum value for sample 1-6.

On the way to understand the new solid structures selected samples were studied by using TG-DTA and X-ray diffraction methods. Obtained data shown on table VI and figures 6 - 7 of the tablets and ashes confirm the formation of potassium silicate and calcium and ammonium-potassium pyrophosphates as new solid phases. This re-arrangement in the solid phase takes place during mechanic-chemical activation and follow up compaction. It is also associated with re-arrangement of water in the samples, because the changes in both the plasticity of the samples and in water releasing during TG-DTA studies were observed. Formation of sulfate adducts is also possible, but it is very difficult to confirm by the methods used.

The TG-DTA curves of ashes (Fig. 8) show that by increasing temperature, weight losses are observed in two temperature intervals. The first one (302.5-418.9K) is obviously associated with free water releasing and the endothermic effect confirmed also that. Evaporation of some volatile impurities is also possible. The main losses and the large exothermic effect in temperature range 520-912K is a result of two-step oxidation of organic compounds and carbon from ashes. It should be point out that the content of stable inorganic components (mainly SiO$_2$ and Fe$_2$O$_3$), as it is confirmed from X-Ray intensities, are only 20.5%. This explains the high sorption capacity observed for studied samples.

The thermal behaviour of the new products characterizes the individual properties of the main raw components, but it is more complicate and indicates new interactions related to the new solid phases and dehydrations. It is obvious that the process is a multistage and it includes various reactions taking place when the temperature increases. The first stage thermo gravimetric changes represent the free water releasing (from 1.1 to 3%) and it is followed up by the dehydration of gypsum component (two steps as it is well known). The stages are related to the decomposition of the ammonium sulphate. Weight losses and endothermic effects determined correspond well with the changes of the ratio between raw materials used. Higher temperature range changes (660-981K) are new thermal effects typical for dehydration and condensation of phosphorous salts formed. The total weight losses vary from 39.9 to54.4% and it is in a good correlation with the content of volatile part of ashes and water and ammonia content in the other raw materials used.

Total weight losses are control mostly by the content of ammonium sulphate and ash in the initial mixture and the minimum value is 39.9% (sample 1-7). Maximum total weight losses are 54.4% and then the content of ammonium sulphate and ash has their maximum (sample 1-10). In the low temperature range (293-375K) the most stable are mixtures 1-6 and 1-4, where the content of nitrogen and phosphorous components have their maximum and ash and potassium components are at their minimum content. Taking into account that the NPK ratio and the other properties of the tablets, those samples could be classified as an optimal for fertilization use.

By using extrusion pres different mixtures with total water content 13.4%, have been compacted. The resistance is in the range 500—680 N/cm$^2$ and it confirms that this technology could be applied in the practice. 500 kg mixed fertilizers have been produced and the sorption capacity of them is in the range 26-39%. Pot experiments have confirmed their high agrochemical efficiency.

### 3.2. Thermal treatment of by-product with Tunisia phosphorite

Tunisia phosphorite /TF/ contain (mass %): 29.58P$_2$O$_5$, 48.40CaO, 6.48CO$_2$, 3.58SO$_3$, 1.88SiO$_2$, 2.74F, 1.38Na$_2$O, 0.07K$_2$O, 0.056Cl. Ammonium sulfate (AS) is a by-product from EBDP that contains 99.2% AS. “Stanton Redcroft” and “Setaram” are the thermoanalysers. The studies, conducted under a dynamic heating regime involved samples weighing 15.20 ± 0.4 mg, within a temperature range of 298-1273K, heating rate 10K.min$^{-1}$ and air flow-rate 50 ml/min.

A thermal analysis coupled with evolved gas phase analysis was carried out at 10 K.min$^{-1}$ heating rate and 50 ml/min air flow in open corundum crucible; sample mass ~20 mg and the Setaram
LabSys 2000 instrument is used. On-line gas composition was monitored using FTIR gas analyser (Interspectrum). The Ranger-AIP Gas cell S/N 23790 (Reflex Analytical Co) with 8.8 meters path length was maintained at 423 K. Spectra were recorded in the 600-4000 cm\(^{-1}\) region with a resolution of 4 cm\(^{-1}\) and 4 scans per slice. The released gases were identified using characteristic infrared absorption wavelengths: for NH\(_3\) at 930 and 963 cm\(^{-1}\), SO\(_2\) at 1345 and 1378 cm\(^{-1}\), H\(_2\)O at 1520, 1700, and 3855 cm\(^{-1}\), N\(_2\)O at 2358 and 2242 cm\(^{-1}\), CO\(_2\) at 2348, 2360 and 670 cm\(^{-1}\). The profiles of the gas emissions were obtained as temperature derivatives of the peak area integrated above baseline from 900 to 983 cm\(^{-1}\) for NH\(_3\), from 1309 to 1400 cm\(^{-1}\) for SO\(_2\), from 2260 to 2405 cm\(^{-1}\) for CO\(_2\) and from 2138 to 2274 cm\(^{-1}\) for N\(_2\)O. H\(_2\)O spectrum is masked by NH\(_3\) spectra. Gaseous HF was not identified because of the lack of IR spectral information. Condensation of NH\(_4\)F in a cooler part of the furnace (~423K) of the thermal analyzer could also take place. The studies conducted in isothermal heating conditions involved ceramic crucibles with sample weight of 200 mg. X-ray powder diffraction analyses were conducted using a DRON diffractometre, with CuK\(_\alpha\) radiation. The analysis was conducted by comparing experimental spectrums with the JCPDS database (JCPDS, Powder Diffraction File (PDF), Set 1(89, Joint Committee on Diffraction Standards, Philadelphia PA, 2001)). The infrared spectrums of the samples were established on a Spekord M-80 made by Carl Zeis Jena in an interval of 650-4600 cm\(^{-1}\). The weight ratio between two components is 1:1. TG, DTG and DTA-data are presented in Table XI and Fig. 9.

### Table X. Mass losses during thermal treatment under dynamic heating up to 1273 K (“STANION REDCROFT”) of TF + AS (weight ratio 1:1)

<table>
<thead>
<tr>
<th>No</th>
<th>Temperature, K</th>
<th>Mass losses, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflexion point</td>
<td>Start</td>
</tr>
<tr>
<td>1.</td>
<td>443.0</td>
<td>417.8</td>
</tr>
<tr>
<td>2.</td>
<td>580.4</td>
<td>514.9</td>
</tr>
<tr>
<td>3.</td>
<td>624.1</td>
<td>607.2</td>
</tr>
<tr>
<td>4.</td>
<td>684.1</td>
<td>635.4</td>
</tr>
<tr>
<td>5.</td>
<td>924.7</td>
<td>871.1</td>
</tr>
<tr>
<td>6.</td>
<td>1055.3</td>
<td>982.3</td>
</tr>
<tr>
<td>7.</td>
<td>1131.8</td>
<td>1085.7</td>
</tr>
<tr>
<td>Total:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis of TG-DTG-DTA-dependencies related to the decomposition of TF and AS mixture shows that the reactions are based on the behaviour of (NH\(_4\))\(_2\)SO\(_4\) [11-14]. A total of 56.6% mass losses were registered in the temperature range of 293-1273K. The reactions occurring at temperatures up to 1273 K are determined by the registered mass losses and endo-effects at 580, 624, 684, 924, 1055, 1131 K that have formed three main transformation temperature ranges – 500-700K, 900-1000K and 1000-1150K. The mass losses (39.3%) in the first temperature range (up to 700K) show that the most intensive interactions occur at temperatures up to 700K. The gas components emitted during decomposition of (NH\(_4\))\(_2\)SO\(_4\), such as NH\(_3\), SO\(_3\), H\(_2\)O form a suitable gas media for formation of ammonia-calcium ortho-, poly-, meta and pyrophosphates, which is mentioned by other researchers as well [12-16]. The endo-effect occurring at 624K and the stepwise character of the TG curves is an indication for reactions rate, resulting ammonia-calcium phosphates and follow up dehydration. Our initial assumptions are confirmed by the results of the studies, using a Setaram thermal analyzer, coupled with a simultaneous evolved gas analyzer. The results are presented in Fig. 10 and Table XII.
TABLE XI. MASS LOSSES DURING THERMAL DECOMPOSITION UP TO 773 K (“SETARAM”) OF TF + AS (WEIGHT RATIO 1:1)

<table>
<thead>
<tr>
<th>No</th>
<th>Temperature, K</th>
<th>Mass losses, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inflexion point</td>
<td>Start</td>
</tr>
<tr>
<td>1.</td>
<td>591.4</td>
<td>523.0</td>
</tr>
<tr>
<td>2.</td>
<td>635.2</td>
<td>616.2</td>
</tr>
<tr>
<td>3.</td>
<td>670.1</td>
<td>652.5</td>
</tr>
<tr>
<td>4.</td>
<td>699.3</td>
<td>683.5</td>
</tr>
<tr>
<td>5.</td>
<td>754.6</td>
<td>734.1</td>
</tr>
<tr>
<td>TOTAL:</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The gas analysis data provide additional evidences about reactions occurring between the components of the mixture in the 273-773K temperature range. The concentrations of released gasses coincide with the thermal effects registered on DTG-DTA curves in Fig. 10. Nitrogen from the system is emitted as ammonia at 648K and 780K and as nitrous oxides at 603 and 755K. Sulphuric oxides (such as $SO_x$) in waste gasses are registered at 722K. These results confirm that during low-temperature range (500-650K) AS starts to decompose and as a result mainly $NH_4HSO_4$ and ammonia are generated.

The emissions of sulphur oxides registered at 722K prove that the $NH_4HSO_4$ is thermally unstable and starts to decompose, releasing ammonia and sulphur oxides. The registered amount of emitted ammonia and sulphur, carbon and nitrogen oxides is only a part in comparison with the decomposition of chemically pure ammonium sulphate. Obviously, some of these gas components participate in secondary reactions.

X-ray powder diffraction analysis of initial, intermediates and final products from decomposition of a TF and AS mixture (1:1). The results show that at temperatures up to 723K calcium hydrogen-orthophosphates and hydrogen-pyrophosphates, as well as $NH_4CaP_3O_9$ are presented in the solid phase. The X-ray shows weak low-intensity diffraction lines of polyphosphate. When the treatment temperature is raised up to 973K, $\alpha$-Ca$_3$P$_2$O$_5$, Ca$_3$(PO$_4$)$_2$ and CaSO$_4$ are registered. The main phases in the end products at temperatures as high as 1273 K are Ca$_5$F(PO$_4$)$_3$, Ca$_3$(PO$_4$)$_2$, $\alpha$-Ca$_3$P$_2$O$_5$ and CaSO$_4$.

An infrared spectrum of initial mixture, intermediates and final products from decomposition of TF and AS mixture (1:1) is represented in Fig. 9. The compounds formed during the thermal treatment were identified on the basis of identified functional groups. They are presented in Table XIII.
Working Material

FIG. 9. TG, DTG, DTA curves of TF+ AS mixture, 1:1, heated up to 1273 in air-medium

TABLE XII. INFRARED SPECTROSCOPY DATA ABOUT INTERMEDIATES AND FINAL PRODUCTS FROM THERMAL TREATMENT OF A TF AND AS MIXTURE (1:1) AT DIFFERENT TEMPERATURES

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Identified phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dynamic heating regime</td>
</tr>
<tr>
<td>673 K</td>
<td>Ca₅F(PO₄)₃, CaCO₃, CaHPO₄, CaH₂P₂O₇, NH₄CaP₃O₉, CaSO₄</td>
</tr>
<tr>
<td>973 K</td>
<td>Ca₅F(PO₄)₃, CaCO₃, CaH₂P₂O₇, β-Ca₂P₂O₇, β-Ca₃(PO₄)₂, CaSO₄</td>
</tr>
<tr>
<td>1273 K</td>
<td>Ca₅F(PO₄)₃, CaCO₃, β-Ca₃(PO₄)₂, β-Ca₂P₂O₇, CaSO₄</td>
</tr>
<tr>
<td></td>
<td>Isothermal treatment</td>
</tr>
<tr>
<td>723 K</td>
<td>Ca₅F(PO₄)₃, CaCO₃, CaHPO₄, CaH₂P₂O₇, β-Ca₂P₂O₇, β-Ca₃(PO₄)₂, NH₄CaP₃O₉, CaSO₄</td>
</tr>
<tr>
<td>973 K</td>
<td>Ca₅F(PO₄)₃, β-Ca₃(PO₄)₂, β-Ca₂P₂O₇, CaSO₄</td>
</tr>
<tr>
<td>1273 K</td>
<td>Ca₅F(PO₄)₃, β-Ca₃(PO₄)₂, β-Ca₂P₂O₇, CaSO₄</td>
</tr>
</tbody>
</table>

The infrared spectroscopy results are consistent with the X-ray powder diffraction analysis data. Unlike the X-ray powder diffraction analysis, the infrared spectroscopy data confirm deformation and stretching vibrations of CO₃²⁻ and it proves the presence of free CaCO₃ in the treated samples at temperatures up to 973 K - δ CO₃ (865 cm⁻¹), νₕ CO₃ (1435, 1460 cm⁻¹) (it is as an impurity in a phosphorite). The occurrence of the νₕ CO₃ line at 1540-1560 cm⁻¹ could be explained with the introduction of a carbonate ion in the structure of apatite and production of carbonate apatite [15-19]. The line of asymmetric stretching vibration present in νₕ SO₄ (670-680 cm⁻¹, 1100-1120 cm⁻¹) is evidence of sulfate in the samples only CaSO₄ at temperatures above 973K. When temperatures are higher then 673K NH₄HSO₄ becomes thermally unstable.
FIG. 10. Simultaneous TG-DTG-DTA curves with evolved gas analysis for TF+AS mixture, 1:1
Working Material

The infrared spectroscopy data confirm the generation of CaH$_2$PO$_4$ by the presence of asymmetric stretching vibration lines - $\nu_\alpha$ OH (2420, 2780, 2800 cm$^{-1}$) and deformation fluctuation - $\delta$ OH (1220, 1635, 1660, 1670 cm$^{-1}$) of OH groups where hydrogen participates in POH type acid ions with strong hydrogen links. The lines $\nu_\alpha$ OH (1200-1220, 2300-2370 cm$^{-1}$) prove the structurally bonded water in the phosphate ion presented as CaHPO$_4$. The main phases in the final products of treatment at highest temperatures are $\beta$-Ca$_3$(PO$_4$)$_2$ and CaSO$_4$.

3.3. Discussion

The results from the thermal analyses under various heating regimes and the X-ray powder diffraction and spectroscopic analyses prove formation of the following compounds: at temperature 653K - NH$_4$HSO$_4$, (NH$_4$)$_2$SO$_4$, 2CaSO$_4$, CaHPO$_4$; at 683K – NH$_4$Ca$_3$P$_2$O$_7$; at 733K – Ca$_2$P$_2$O$_7$ and Ca(PO$_4$)$_2$; at 1273K – the final phosphorous containing solid phase products are Ca$_3$(PO$_4$)$_2$ and Ca$_5$P$_2$O$_7$. The interactions occurring in the gaseous phase generate NH$_3$, CO$_2$, SO$_x$ and N$_2$O$_y$.

The studies suggest the following chemical mechanism:

523 – 607K

\[ (\text{NH}_4)_2\text{SO}_4 = \text{NH}_4\text{HSO}_4 + \text{NH}_3 \]  
\[ 2(\text{NH}_4)_2\text{SO}_4 = (\text{NH}_4)_2\text{HSO}_4 + \text{NH}_3 \]  
\[ 2\text{CaCO}_3 + 3(\text{NH}_4)_2\text{SO}_4 = (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 + 4\text{NH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O} \] (3)

607-653K

\[ \text{Ca}_3(\text{PO}_4)_2 + 3\text{NH}_4\text{HSO}_4 = (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 + 3\text{CaHPO}_4 + \text{HF} + \text{NH}_3 \] (4)
\[ 4\text{Ca}_3(\text{PO}_4)_2 + 3\text{NH}_4\text{HSO}_4 = (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 + 6\text{Ca}_3(\text{PO}_4)_2 + 4\text{HF} + \text{NH}_3 \] (5)
\[ 2\text{CaCO}_3 + \text{Ca}_3(\text{PO}_4)_2 + 6\text{NH}_4\text{HSO}_4 = 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 + 3\text{CaHPO}_4 + 2\text{CO}_2 + \text{HF} + 2\text{NH}_3 + 2\text{H}_2\text{O} \] (6)
\[ \text{CaCO}_3 + 2\text{Ca}_3(\text{PO}_4)_2 + 3\text{NH}_4\text{HSO}_4 = (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 + 3\text{Ca}_3(\text{PO}_4)_2 + \text{CO}_2 + 2\text{HF} + \text{NH}_3 + \text{H}_2\text{O} \] (7)

653-683K

\[ (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{CaSO}_4 = 2\text{CaSO}_4 + \text{NH}_4\text{HSO}_4 + \text{NH}_3 \] (8)
\[ \text{Ca}_3(\text{PO}_4)_2 + \text{NH}_4\text{HSO}_4 = \text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + 4\text{CaSO}_4 + \text{HF} + 3\text{NH}_3 + \text{H}_2\text{O} \] (9)
\[ 3\text{CaHPO}_4 + 2\text{NH}_4\text{HSO}_4 = \text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + 2\text{CaSO}_4 + \text{NH}_3 + 3\text{H}_2\text{O} \] (10)
\[ \text{CaCO}_3 + 3\text{CaHPO}_4 + 3\text{NH}_4\text{HSO}_4 = \text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + 3\text{CaSO}_4 + \text{CO}_2 + 2\text{NH}_3 + 4\text{H}_2\text{O} \] (11)
\[ 3\text{Ca}_3(\text{PO}_4)_2 + 7\text{NH}_4\text{HSO}_4 = 2\text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + 7\text{CaSO}_4 + 5\text{NH}_3 + 6\text{H}_2\text{O} \] (12)
\[ \text{CaCO}_3 + 2\text{CaHPO}_4 + \text{NH}_4\text{HSO}_4 = \text{Ca}_3\text{P}_2\text{O}_7 + \text{CaSO}_4 + \text{CO}_2 + \text{NH}_3 + 2\text{H}_2\text{O} \] (13)

683-733K

\[ (\text{NH}_4)_3\text{H}((\text{SO}_4))_2 = (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NH}_3 + \text{H}_2\text{O} \] (14)
\[ (\text{NH}_4)_3\text{H}((\text{SO}_4))_2 + \frac{1}{2}\text{O}_2 = 2\text{NH}_4\text{HSO}_4 + \text{NH}_3 \] (15)
\[ \text{NH}_4\text{HSO}_4 = \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \] (16)
\[ 2\text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + \text{CaSO}_4 = 3\text{Ca}_3(\text{PO}_4)_2 + \text{SO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \] (17)
\[ 2\text{NH}_4\text{Ca}_3\text{P}_2\text{O}_7 + 4\text{CaSO}_4 = 3\text{Ca}_3\text{P}_2\text{O}_7 + 4\text{SO}_3 + 2\text{NH}_3 + \text{H}_2\text{O} \] (18)

733-770K

\[ 2\text{CaHPO}_4 = \text{Ca}_3\text{P}_2\text{O}_7 + \text{H}_2\text{O} \] (19)

883-1033K
Working Material

\[
\text{Ca}(\text{PO}_3)_2 + \text{CaSO}_4 = \text{Ca}_2\text{P}_2\text{O}_7 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad (20)
\]

\[
(\text{NH}_4)_2\text{S}_2\text{O}_8 = 2\text{NH}_3 + 2\text{SO}_3 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (21)
\]

\[
\text{Ca}_2\text{P}_2\text{O}_7 + \text{CaCO}_3 = \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_2 \quad (22)
\]

\[
\text{CaCO}_3 \text{ (free bonded) } = \text{CaO} + \text{CO}_2 \quad (23)
\]

1033-1273K

\[
\text{Ca}_2\text{P}_2\text{O}_7 + \text{CaSO}_4 = \text{Ca}_3(\text{PO}_4)_2 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad (24)
\]

\[
\text{Ca}_2\text{P}_2\text{O}_7 + \text{CaCO}_3 = \text{Ca}_3(\text{PO}_4)_2 + \text{CO}_2 \quad (25)
\]

\[
\text{CaCO}_3 \text{ (structurally bonded) } = \text{CaO} + \text{CO}_2 \quad (26)
\]

The reactions that produce the highest mass losses in individual temperature ranges are 1, 8, 9, 13, 16, 20 and 26. The process of thermal decomposition of the mixture starts at 520K with the breaking of one covalent bonds in the AS molecule and with reactions 1 and 2 occurring with an accompanying endo-effect at 580K and mass losses of 12.4%. The registered release of ammonia in that temperature range confirms the possibility to recycle ammonia in the cleaning process. The phase studies of the solid and gas products and intermediates prove that reactions generating major part of soluble phosphorous compounds occur in a temperature range 500-700K. The phase composition of solid products and, respectively, the content of soluble phosphates could be controlled by the temperature and partial pressure of the main gas components. By selection of treatment conditions the mineral fertilizer characteristics could be controlled on the way to achieve the best agrochemical efficiency.

4. CONCLUSIONS

Data about thermal decomposition of phosphorite and (NH_4)_2SO_4 mixture in weight ratio 1:1 under dynamic and isothermal heating regime in air gas environment have shown that about half of the ammonia could be recovered and recycled in the cleaning process at temperatures 500-700K. The obtained solid-phase products CaHPO_4, NH_4CaP_3O_9, Ca_2P_2O_7, Ca(PO_3)_2 and Ca_3(PO_4)_2 are valuable slow releasing nutrients fertilisers.

Control of the initial raw materials ratio permits obtaining final products with properties complying with EU standards for fertilizers. The optimal content of the initial mixture is in the range 35-39% ammonium sulfate, 27-35% phosphorous solid waste or low grade natural phosphates, 11-16% potassium sulfate and 16-20% ash. Application of the by-product from EB technology could be realized as fertilizer in different direction like:

− single nitrogen fertilizer;
− Sulfo-nitrate fertilizer on the base of ammonium sulphate and ammonium nitrate mixtures;
− NPS fertilizers on the base of soft natural phosphorites and ammonium sulphate
− Mixed NPKS fertilizers on the base of ammonium sulphate, superphosphates and potassium sulphate or potassium chloride;
− Complex NPKS fertilizers, including sorbents
− Mixed organomineral fertilizers.

Additional studies are needed to assess the efficiency of the process of ammonia recycling and agrochemical efficiency of the new fertiliser products.
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COLD PLASMA AND ITS APPLICATION FOR EMISSION CONTROL IN POWER PLANTS

R.R. SONDE
National Thermal Power Corporation, India

1. INTRODUCTION

Coal is the mainstay of the fuel for power plant boilers. Today, the installed power generation capacity of the country is 104,917 MW which is slated to grow further to 149,525 MW by the end of year 2007. 71% of the power comes from the thermal route out of which 78% is derived from coal. India has a coal reserve of 211 billion tons out of which 82 billion tons are the proven reserves. The present coal mining rate is 300 million tons per annum. Hence, in all likelihood, Indian coal will continue to play a dominant role in the power growth of India.

However, Indian coal has typical characteristic of very high ash content [up to 50%] along with moderate sulfur content. However, with the promulgation of new environmental norms, aging power generating units and use of coal of varied quality, it is becoming increasingly difficult to meet stringent SPM levels. Also, the promulgation of new environmental norms is in offing for SO$_x$ and NO$_x$ emission level we shall further restrict the elbow room of power plants.

All modern power stations are conventionally provided with ESPs for abatement of SPM emissions. These ESPs typically have an efficiency of 99.5% plus. However, achieving a good particle emission value with very high resistivity Fly Ash [$>10^{14}$ ohm-cm] is, even today, a challenge. Consequently, power stations are hard pressed to comply with the SPM emission regulations of 100 ppm and 50 ppm. For removal of NO$_x$ and SO$_x$ from the exiting flue gas, typically Selective Catalytic Reduction (SCR) or Selective Non-Catalytic Reduction (SNCR) process and Wet or Dry scrubbing process is used which converts the NO$_x$ and SO$_x$ to free nitrogen and gypsum using anhydrous ammonia and lime stone respectively. However, all of these methods put a big penalty on the performance level of the auxiliary equipment, space requirement and reliability of the plant and the cost of power.
2. CONVENTIONAL GAS CLEANING SYSTEM: A BRIEF

As indicated in the fig. 1, flue gas cleaning essentially involves removal of SO\textsubscript{x} and NO\textsubscript{x} apart from the suspended particulate matter.

### 2.1. De-Sulfurization System: Wet Process

1) Wet Limestone Scrubbing

This process for the removal of SO\textsubscript{x} from the flue gas uses limestone slurry in water which comes into contact with the flue gas after it has been passed through the particulate filtering unit operation of choice. The base reaction is as follows:

$$\text{SO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_3 + \text{H}_2\text{O} + \text{CO}_2.$$  

- The gas dissolves in the slurry and forms gaseous carbon dioxide and solid calcium sulfite
- This calcium sulfite is then oxidized to form calcium sulfate.
- Calcium sulfate i.e. gypsum, is sold on the open market for use in wallboard, plaster etc.
- Once the process is complete, the slurry is circulated from the holding tank.
- Fresh limestone is added to an effluent hold tank from which it will be added to the system
- The final destination for the limestone slurry is a landfill.

2) The Wellman- Lord Process

- The active reagent (aqueous sodium solution) used for removal of SO\textsubscript{2} is regenerated.
In the main absorber the flue gas is scrubbed with aqueous sodium sulphite solution, forming sodium bisulphite which is decomposed by steam heating in an evaporative crystalliser to produce sodium sulphite and SO$_2$.

SO$_2$ gas stream can be treated to make suitable by-product (H$_2$SO$_4$ or elemental sulphur).

This process is expensive to install but relatively cheap to operate.

3) Ammonia Scrubbing

Ammonia is used as scrubbing agent and final product is ammonium sulphate which is a high value product that can be used in fertilizers. There could be a commercial risk associated because price of ammonium sulphate and ammonia are both very volatile. The plant is expensive to build and requires a large area. The process has the advantage that there is no waste water discharge and less problems of scaling and blockage.

4) Sea water washing

This method uses untreated sea water to scrub flue gas, natural alkalinity of sea water neutralises SO$_2$. After scrubbing, the water used is treated with air to reduce its chemical oxygen demand and its acidity and then discharged back to sea. This process does not require solid sorbent as a reagent, it is limited to use at coastal sites.

2.2. De-Sulfurization System: Semi Dry Process

1) Dry Alkaline System

This unit operation must be placed before the filtering system for particulates, as opposed to the previous system.

This process for the removal of SO$_x$ from the flue gas uses alkaline particles that are added to the flue gas, where they react with the SO$_x$ present in the system and the end result particles are then large enough to be collected in the filtering system.

There are several different sorbents available to accomplish this task, including the use of lime (CaO) to produce the calcium sulfite without the creation of carbon dioxide.

This system has fewer problems with corrosion and deposition.

However, this process loses the production of gypsum (except for a system that uses calcium oxide) that can be removed and sold to an outside buyer.

2) Circulating Fluidised Bed (CFB)

Flue gas is passed through a dense mixture (fluidised bed) of lime (Ca(OH)$_2$), reaction products and fly ash which removes SO$_2$, SO$_3$ and HCl. Final product is a dry powdered mixture of calcium products which has to be disposed off.

This process is cheap to install, requires small space, has a high SO$_2$ removal efficiency, accommodates very rapid changes in inlet SO$_2$ concentration, has small scaling, plugging or corrosion problems. However it is expensive to operate and generates waste products that have to be disposed off.

3) Spray-dry process

Flue gas is carried into spray dryer vessel where it comes in contact with finely atomized spray of lime and by-product slurry. This removes SO$_2$, SO$_3$ and HCl from flue gas.

4) Duct spray-dry process

The lime slurry is sprayed directly into the duct. The lime reacts with acid gases to produce dry powdered mixture of calcium compounds. This process is used where moderate degree of desulphurisation (50-70%) is required.
2.3. De-Sulfurization System: Dry Process

1) Sodium Bicarbonate

This process involves the direct injection of dry sodium bicarbonate into the flue gas duct downstream of the air heater, to react with and remove acidic compounds such as SO$_2$, SO$_3$ and HCl. The final product is a dry product of sodium compounds and fly ash. It is suitable primarily for those applications where a moderate degree of desulphurisation (70%) is required at low capital cost, although the reagent, sodium bicarbonate is relatively expensive.

Addition of sodium bicarbonate into the flue gas causes it to react in the following manner:

$$2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$$

This allows for the sodium carbonate to react with the oxygen and sulfur dioxide in the flue gas to form sodium sulfate and carbon dioxide as follows:

$$\text{Na}_2\text{CO}_3 + \text{SO}_2 + 0.5\text{CO}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2$$

With the creation of solid sodium sulfate, the desulfurization of the gas is complete. However, with the addition of a few more chemicals and reactions, beneficial end results can be obtained, as well as the recycling of the sodium bicarbonate. If ammonia is added to water slurry with carbon dioxide, ammonium bicarbonate can be formed through the following reaction:

$$\text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HCO}_3$$

If this ammonium bicarbonate slurry is added to the sodium sulfate slurry as created above, the following reaction takes place, which recycles the sodium bicarbonate initially added.

$$2\text{NH}_4\text{HCO}_3 + \text{Na}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2\text{NaHCO}_3$$

This recycling of the sodium bicarbonate is of course not complete, but does provide significant impact when making a selection for SO$_x$ removal. As a further bonus, the ammonium sulfate can be reacted further to create potassium sulfate, which is a common fertilizer component and can be sold to offset costs.

$$2\text{NaHCO}_3 + \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 + \text{2NaHCO}_3$$

2) Furnace sorbent injection

In this dry hydrated lime is blown pneumatically into the furnace typically above the burners. This removes up to 70% of the SO$_2$ from the flue gas. Spent sorbent is extracted with the fly ash in an ESP.

It is one of the cheapest FGD process to install but can be expensive to operate because it is inefficient in its use of sorbent. It is well suited for retrofit situation, for only a low SO$_2$ removal efficiency is required and little space available in the unit plant area. Fly ash cannot be separately collected therefore it has to be dumped along with solid by-product.

2.4. De-Nitrification System

1) Selective Catalyst Reduction

Through the use of ammonia or a similar agent, the NO$_x$ emissions can be controlled post-combustion through the use of selective catalyst reduction. When the ammonia is injected into the flue gas immediately before it passes over a catalyst (usually vanadium or titanium), the following reactions take place.

$$4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O}$$

$$8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$$

As can be seen from this pair of chemical equations, both NO and NO$_2$ are reduced and removed as nitrogen and the only other by-product is water.
Working Material

- These two compounds are the two principal components of NO\textsubscript{x} pollution. Others show up in extraordinarily small terms, and are ignored.
- With a molar ratio of approximately 0.95-1.00, there is a 90% reduction in NO\textsubscript{x}.

2) Selective Non-Catalyst Reduction

This process is very similar to the selective catalyst reduction except that there is no catalyst involved in the process, and it’s done much closer to the combustor as a higher temperature is needed in place of the catalyst effect. The reactions are the same as above and are again listed below.

\[ 4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \]

\[ 8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \]

In this process, there is just a simple injection of ammonia into the flue gas stream coming directly out of the combustor so that local molar ratios are approximately 2:1 ammonia to NO\textsubscript{x}, so as to assure an almost full conversion of the pollutant NO\textsubscript{x} to N\textsubscript{2}, an obviously benign gas.

3. PLASMA BASED GAS CLEANING SYSTEM

Non-Thermal Plasma (NTP) destruction is one type of Advanced Oxidation Process (AOP) that results in the destruction of a wide variety of emissions, including. In essence, NTP technologies produce free radicals, and promote oxidation and molecular dissociation to enable enhanced chemical reactions that destroy hazardous emissions.

NTP technologies differ from thermal plasma technologies in that the temperature of the bulk gas remains low for the NTP case, but is elevated for the thermal case. This is because energetic electrons are produced in NTPs without heating the entire gas stream to high temperatures. The plasmas produced by NTP processes are sometimes referred to as cold plasmas, because of this unique low-temperature property. Therefore, one advantage that NTP technologies have over thermal plasma discharge is that less energy is required for NTP processes to achieve the same degree of chemical reaction. There are several main types of NTP reactor technologies, including electron beam, dielectric barrier discharge, pulsed corona discharge, and flow stabilized discharge. The technologies are similar in that they all generate energized electrons that collide with atoms and molecules in the contaminated gas and create highly reactive chemical species. The reactive species, in turn, react with pollutants in the gas and transform the pollutants into more controllable compounds.

The general process for NTP destruction is depicted schematically in Figure 2 shown below.

---

**FIG. 2. General scheme of the non-thermal plasma gas treatment**
The differences between the technologies lie in the manner in which the energized electrons are generated and introduced to the gas stream. For the electron beam method, electrons are generated externally from the gas. For all of the discharge technologies, electrons are generated by discharge electrodes within the gas stream. The various discharge technologies vary in the way they avoid arcs from forming across the electrodes. If the current is increased to high levels, the energy consumption increases, and the efficiency is reduced. Moreover, the plasma begins to change from non-thermal to thermal, whereby the background gas is energized along with the electrons.

Advantages of Plasma based Gas Cleaning System:

1. In a single process step, SO\textsubscript{2} and NO\textsubscript{x} are removed simultaneously.
2. It gives usable and valuable by-products (fertilizers). Deposition of waste material containing water soluble salts is avoided.
3. Operation and investment costs of the process are very competitive. Profit gained from product sale may lower flue gas cleaning cost significantly.
4. The process consumes low energy for off gases with high SO\textsubscript{2} concentration.
5. The process operates depending on required SO\textsubscript{2} removal efficiency in a broad temperature range (55-90°C) which is not possible in case of wet gypsum process. In certain configurations, energy consumption for reheating of the flue gas is avoided or minimized.
6. Process may be used for small as well as large plants.

Limitations of Plasma based Gas Cleaning System:

1. Energy consumption is relatively high, especially for flue gases with high NO\textsubscript{x} and low SO\textsubscript{2} concentrations. Further reduction of energy consumption by process improvement is required.
2. Special attention is required for aerosol formation which results in potential clogging of filters and deposition in the flue gas ducts.
3. Initial investment costs are rather high and accelerator is the major contributor. As its use will be increased, accelerator cost is expected to reduce in coming years.

The Non thermal plasma for conditioning of flue gas coming out of fossil fired power plant can be of two types:

a) In-situ plasma generation: Electron beam and accelerator mechanism
b) External plasma generation: Pulsed Corona and Corona shower system

3.1. In-situ Plasma Generation: Electron Beam and Accelerator Mechanism

Electrons and ions are produced in the gas phase when electrons or photons with sufficient energy collide with the neutral atoms and molecules (i.e. electron impact ionization or photo-ionization). There are various ways by which energy can be supplied to create these charged particles (i.e. electrons or ions). Thermal energy (as in flames) is commonly supplied form of energy where exothermic chemical reactions of the molecules are used as prime energy source. Adiabatic compression of the gas is also capable of heating gas up to the point of charged particle generation (also called as plasma). Another way to supply energy to a gas reservoir is via energetic beams (of electrons) that moderate in a gas volume. These beams normally remain unperturbed by electric and magnetic fields, property which is used in their acceleration and transportation (Fig. 3).
Any volume of a neutral gas always contains few electrons and ions due to the result of interaction of cosmic rays or radioactive radiation. These charged particles can be accelerated by means of electric fields. These charge carriers are then utilized in creating new charged particles by colliding them with atoms and molecules in the gas or with the surfaces of the electrodes. This cloud of charged particles can then be scanned and transported by means of magnetic fields (as a cloud itself or as a beam) and allowed to interact with the target product to be irradiated. High energy electron beam is generated by an accelerator system. This beam is uniformly swept across the product (in this case flue gas) using a magnetic beam scanning system. A thin exit window (usually made up of Ti) is used for electron beam irradiation. Product is passed through scanned beam in a highly controlled manner. As can be seen, accelerator is the heart of the whole system. There are various types of accelerators and their classifications are explained below.

### 3.1.1 Particle Accelerators

High energy physics research is the main driving force in continuous development of particle accelerators. The traces can be found from 1895 when Lenard (who ultimately won Noble Prize) used 100 keV electrons to study electron scattering on gases. Rutherford (1919) believed that he needed a source of many MeV to study nucleus (though not possible at that time). From that period, extensive research in this field has resulted in development of various accelerators of increasing energies. The Livingston chart (Fig. 4) represents in a striking manner how the succession of new ideas and new technologies has relentlessly pushed up accelerator beam energies over five decades at a rate of over one and a half orders of magnitude per decade. One repeatedly sees a new idea, which rapidly increases the available beam energy, only to be surpassed by another new idea. In the meantime, first idea continues to grow into a saturation state.

Based on the energy, accelerators are classified as low, medium and high energy accelerators.
Low energy accelerator

Accelerators in the range of 400 keV to 700 keV come in this category. The beam currents are available from 25 mA to 250 mA approximately. They are generally of self shielded type. Applications are found in surface curing of thin films, laminations, production of antistatic, antifogging films, wood surface coatings etc. They have small penetrating ranges.

Medium energy accelerators

Systems with energy range 1 MeV to 5 MeV fall in this category. These systems are characterized by beam powers and usually have a range of 25 kW to 150 kW. The typical applications include cross linking of thicker cross sections of materials, polymer rheology modification, color
enhancement of gem stones, medical product sterilization and food irradiation. They have high penetration ranges.

High energy accelerators

Accelerators with energy range 5 MeV to 10 MeV fall in this category. Scanned beams of power 25 kW to 350 kW are available. They have the highest penetration depths. Typical applications include bulk product irradiation, food disinfection, waste water treatment, and medical product sterilization.

3.2. External Plasma Generation: Pulsed Corona and Corona Shower System

Pulsed corona discharge is another category of NTP technology that has received considerable attention recently. In pulsed corona systems, a pulsed voltage is used to prevent the current from increasing to the point where spark discharges occur. The resulting environment is one that is analogous to the environment generated with dielectric barrier systems, in which micro- or streamer discharges are present.

Two common types of pulsed corona discharge technologies include the wire-coaxial reactor and the wire-plate reactor. In a pulsed corona reactor, the applied voltage is applied such that it is below the ion frequency. This enables the excitation of electrons without the excitation of heavier ions, and minimizes the energy input by avoiding the motion of heavy ions. For pulsed power systems, a traveling wave electric field can be induced to enhance electron excitation by use of a power supply that is able to generate a very large rate of current change in discharge. One limiting factor of pulsed technologies is scalability. This is because the impedance of electrode system and the size of the reactor are proportional. This challenge can be dealt with by improving impedance matching, and with optimization of electrode design.

As with other NTP technologies, the plasma that is formed in pulsed corona system leads to enhanced chemical reactions, and to the ultimate destruction of the pollutant. In flow stabilized discharge systems, the electrodes are continuously cooled by the rapid flow of gas that flows directly through the inside of the electrodes. This high flow-rate gas prevents the streamer discharges from becoming unstable. There are several systems with different types of geometries which can be investigated, including the corona torch, capillary tube, corona radical injection, and corona radical shower configurations. Typically, flow stabilized discharge is for degrading fairly stable gases. The figure 5 shows the cost comparison of various plasma technologies.
3.3. Flue gas conditioning process with reaction mechanism

It is commonly known that free radicals such as OH*, O* etc have very high oxidizing strength. This property is used in flue gas cleaning process. In this system, the combustion exhaust gas containing molecules such as oxygen (O₂) and water vapor (H₂O) are irradiated with electron beam to form radicals such as OH*, O* and HO₂*. The general reaction mechanisms of the process are presented in the figure 6.
As can be seen from figures 6 and 7, high energy electrons are a good tool for processing of gases. The energy of the electrons is absorbed by the components of the gaseous mixtures in proportion of their mass fractions. In case of electron beam irradiation, only 6% or less of the absorbed energy is dissipated in vibrational excitation of the molecules. Most of it is consumed in dissociation and ionization of molecules and finally in the formation of the free radicals OH*, N*, O*, H*, HO2*. Pollutants are good scavengers for these radicals which ultimately results in pollutant oxidation. Flue gas contains water vapors which react with oxidized products to form acids (H2SO4 and HNO3). These acids subsequently react with pre-injected ammonia to form ammonium sulfate and nitrate. These salts are recovered as a dry powder and can be sold in domestic markets as fertilizers.
By looking at the figures, it can be inferred that NO\textsubscript{x} removal is a radiation induced process whereas SO\textsubscript{2} removal is dominated by both pathways i.e. thermo-chemical oxidation and a radiation induced process.

After studying various reaction pathways, a brief account of the existing important results is presented in the next section. These results are reproduced from the available literature. The experiments for these results were carried out either at pilot scale or commercial scale.

4. PROBABLE CONFIGURATION OF THE ELECTRON BEAM PROCESS FOR INTEGRATED EMISSION CONTROL FOR INDIAN POWER PLANTS:

The schematic figures 8 and 9 show the probable arrangement of integrating the EB process for emission control in low sulphur high ash coal. A small stream of de-ashed flue gas is processed through EB for conversion of SO\textsubscript{2} to SO\textsubscript{3} which is mixed with the incoming flue gas for adjusting its resistivity for enhanced performance of the ESP.
FIG. 8. Electron beam: Integrated emission control

FIG. 9. External Plasma: Integrated emission control
PROCESSING OF VOLATILE ORGANIC COMPOUNDS BY MICROWAVE PLASMAS

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Abstract

In this paper atmospheric pressure microwave discharge methods and devices used for producing the non-thermal plasmas for processing of gases are presented. The main part of the paper concerns the microwave plasma sources (MPSs) for environmental protection applications. A few types of the MPSs, i.e. waveguide-based surface wave sustained MPS, coaxial-line-based and waveguide-based nozzle-type MPSs, waveguide-based nozzleless cylinder-type MPS and MPS for microdischarges are presented. Also, results of the laboratory experiments on the plasma processing of several highly-concentrated (up to several tens percent) volatile organic compounds (VOCs), including Freon-type refrigerants, in the moderate (200-400 W) waveguide-based nozzle-type MPS (2.45 GHz) are presented. The results showed that the microwave discharge plasma fully decomposed the VOCs at relatively low energy cost. The energy efficiency of VOCs decomposition reached 1000 g/kWh. This suggests that the microwave discharge plasma can be a useful tool for environmental protection applications. In this paper also results of the use of the waveguide-based nozzleless cylinder-type MPS to methane reforming into hydrogen are presented.

1. INTRODUCTION

The emission of SO2, NOx (NO, NO2), CO, CO2, volatile organic compounds (VOCs) and other gaseous pollutants to the atmosphere influence heavily our environment. They cause acid rains, depletion of the ozone layer, greenhouse effect, etc. Human beings, animals and plants suffer due to direct and indirect influence of the gaseous pollutants.

Therefore, efficient methods for the control and reduction of gaseous pollutant emission are strongly required. Nowadays, conventional methods, e.g. adsorption, absorption, catalytic combustion seem not to be efficient enough. Recently, potential of the atmospheric pressure thermal (e.g. DC torches from plasmatrons, RF torches) and non-thermal (e.g. electron beam, DC and pulsed corona discharges, corona discharges in packed-bed reactors, dielectric barrier discharges, surface discharges, microwave discharges) plasma methods for the processing of gaseous pollutants have been tested [1-5]. As shown in [1-5], some of the non-thermal plasma methods have been proved to be efficient for the destruction of gaseous pollutants (SOx, NOx, VOCs) of relatively low concentration [up to 1000 ppm (i.e. 0.1%)] in the working gas. On the other hand, it has been found that the microwave non-thermal plasmas have the potential for efficient processing of of gaseous pollutants (mainly VOCs) of relatively high concentration (up to tens %) in the working gas [6-10]. Recently the non-thermal microwave plasma has efficiently been used for production of hydrogen by means of the plasma reforming of methane [11].

In this paper we deal with the microwave plasmas classified as the atmospheric pressure non-thermal plasmas at elevated working gas temperature (up to 4000 K), which can be used for gas processing. This temperature is too low to form the local thermal equilibrium (LTE) of the plasma; however it can be helpful in the processing of stable VOC molecules.

A few types of the MPSs, i.e. the waveguide-based surface wave sustained MPS, coaxial-line-based and waveguide-based nozzle-type MPSs, waveguide-based nozzleless cylinder-type MPS, and microwave microplasmas, which have the potential for gas processing [6-11] will be presented. We also show results of the study of decomposition of several highly-concentrated VOCs using the nozzle-type MPSs and results of the reforming of methane CH4 to produce hydrogen H2 with the use of the waveguide-based nozzleless cylinder-type MPS.
2. ATMOSPHERIC PRESSURE MICROWAVE DISCHARGES

The microwave plasmas operating at atmospheric pressure can be induced by a few types of microwave field applicators: (a) microwave resonant cavities, (b) inductive-coupled MPSs, (c) coaxial-line-based surface wave sustained MPSs (surfatrons), (d) waveguide-based surface wave sustained MPSs (surfaguides), (e) coaxial-line-based nozzle-type MPSs, (f) waveguide-based nozzle-type MPSs, (g) waveguide-based nozzleless cylinder-type MPSs, and (h) MPSs for generating microdischarges.

The atmospheric pressure microwave plasmas generated in the microwave resonant cavities, inductive-coupled MPSs, surfatrons, surfaguides and waveguide-based nozzle-type and nozzleless cylinder-type MPSs are sustained within a dielectric (e.g., fused silica) tube inserted into the microwave field applicator. This can cause some problems when large power densities are deposited into the plasma, resulting in deterioration of the tube due to plasma-tube interactions. A solution to these problems is a high flow of the operating gas through the dielectric tube, which can convey the produced heat. Another solution is using an additional gas flow, called a gas swirl, together with the main gas stream to protect the walls from heat deterioration. Using either the high working gas flow or additional gas swirl weakens the microwave power limitations imposed on the MPSs used for gas treatment.

Below, five types of the MPSs are described: waveguide-based surface wave sustained MPS, coaxial-line-based nozzle-type MPS, waveguide-based nozzle-type MPSs, waveguide-based nozzleless cylinder-type MPS, and MPS for generating microdischarges. The main parts of the MPS are a microwave generator (magnetron), microwave supplying and measuring system, and gas supplying system. Depending on the MPS, the microwave power is supplied from a magnetron to the discharge generator by a coaxial cable or rectangular waveguide.

In all the microwave plasma discharge experiments, carried with the MPSs mentioned, the gas flow rate was automatically controlled by a mass flow controller. Composition of the gas mixtures before and after the plasma processing was determined using an FTIR spectrophotometer (Perkin Elmer 16 PC) and gas chromatograph (SRI 8610C).

2.1. Waveguide-Based Surface Wave Sustained MPS

The waveguide-based surface wave sustained MPS is shown in Fig. 1. A microwave (2.45 GHz) power of about a few hundred watts is supplied from a magnetron via a standard WR-430 rectangular waveguide with a reduced-height section. The discharge in the form of a plasma column is generated inside a quartz tube cooled with a lossless liquid. The impedance-matching function is achieved by the use of one intrinsic tuning element in the form of movable plunger placed at the end of the waveguide. The movable plunger enables minimizing the reflected microwave power.

The waveguide-based surface wave sustained MPSs find practical applications in elemental analysis, gas purification, environmental protection, diamond deposition, surface treatment, sterilization [12]. Purification of noble gases using waveguide-based surface wave sustained MPSs has been implemented in industry. Removing impurities (such as CF$_4$ and CH$_4$) from xenon and krypton the concentration below 1 ppmv is possible [13]. The MPSs are also used in semiconductor industry for abatement of etch process effluent gases containing perfluorinated compounds (PFCs) and SF$_6$ [14].

2.2. Coaxial-Line-Based Nozzle-Type MPS

The nozzle-type MPSs first appeared as structures based on microwave coaxial line components (e.g. [15]). In these coaxial-line-based MPSs the microwave plasmas are induced in the form of a plasma “flame” at the open end of a rigid coaxial line, at the tip of its inner conductor (Fig. 1). The power-handling capability of coaxial-line-based microwave discharges is generally limited to much less than 1 kW due to the low thermal strength of the coaxial line components.
FIG. 1. The photographs of the waveguide-based surface wave sustained MPS: a) front view, b) top view.

The experimental setup with the coaxial-line-based nozzle-type MPS is shown in Fig. 2. A microwave (2.45 GHz) power of about 70-100 W is supplied to the MPS through a standard 50 Ω coaxial cable with the use of a coupler (microwave antenna). The discharge in the form of a plasma flame is generated inside a quartz tube directly above the metal conical nozzle. The impedance-matching function is achieved by a movable plunger located between the inner and outer conductor. This MPS was used by us for destruction of fluorinated hydrocarbons (e.g. [8, 9]).

FIG. 2. The coaxial-line-based nozzle-type MPS.
2.3. Waveguide-Based Nozzle-Type MPSs

Parallel with the coaxial-line-based nozzle-type MPSs the so-called waveguide-based nozzle-type MPSs have been developed (e.g. [16-18]). In these applicators the microwave plasma is also induced in the form of a plasma flame at the tip of a field-shaping structure that is similar to that of the coaxial-line-based nozzle-type MPSs. However, the microwave power is fed into this structure through a waveguide (usually rectangular at 2.45 GHz). In the modern waveguide-based nozzle-type MPSs, the microwave power is delivered to the field-shaping structure having the form of a conductor with a conical nozzle through a waveguide with a reduced-height section [18].

Since both nozzle-type MPSs, the coaxial-line-based and waveguide-based, are gas flowing systems, they are particularly suitable for processing various gases or materials carried by these gases.

Two type of the waveguide-based nozzle-type MPSs equipped with a nozzle have been tested, i.e. the waveguide-based nozzle-type MPS operated at relatively low gas flow rate (a few l/min) [8-10] and the waveguide-based nozzle-type MPS operated at relatively high gas flow rate (a few hundreds l/min).

2.3.1. Waveguide-Based Nozzle-Type MPS Operated at Low Gas Flow Rate

The experimental setup with the waveguide-based nozzle-type MPS operated at low gas flow rate (a few l/min.) is shown in Fig. 3. A microwave (2.45 GHz) power of about a few hundred watts is supplied from a magnetron via a standard WR-430 rectangular waveguide to the field-shaping structure having the form of a conductor with a conical nozzle (Fig. 3b). The discharge in the form of a plasma flame is generated inside a quartz tube directly above the metal conical nozzle. The discharge is stabilized inside the quartz tube and protected from the discharge heat [6].

A disadvantage of the both presented waveguide-based nozzle-type MPSs is the use of the nozzle, which is vulnerable to erosion. Such a disadvantage has been avoided in the waveguide-based nozzleless cylinder-type MPS presented below.

2.3.2. Waveguide-Based Nozzle-Type MPS Operated at High Gas Flow Rate

The photo and sketch of the waveguide-based nozzle-type MPS operated at high gas flow rate (a several hundred l/min.) are shown in Figs. 4a and 4b, respectively. Two flows are formed in a glass cylinder placed coaxially with the nozzle: central flow (the processed gas) and an additional swirl flow (nitrogen). The processed gas flow is introduced centrally to the discharge zone through a conical nozzle. The nitrogen flow is supplied tangentially through the four inlets, as shown in Fig. 4b, creating a spiral vortex flow in the glass cylinder. This stabilizes the discharge in the centre of the cylinder and protects the wall from the discharge heat [6].

A disadvantage of the both presented waveguide-based nozzle-type MPSs is the use of the nozzle, which is vulnerable to erosion. Such a disadvantage has been avoided in the waveguide-based nozzleless cylinder-type MPS presented below.
2.4. Waveguide-Based Nozzleless Cylinder-Type MPS

The experimental setup with the waveguide-based nozzleless cylinder-type MPS is shown in Fig. 5. In this case a microwave (2.45 GHz) power of about a few thousands watts is supplied to the MPS from a magnetron via a standard WR-284 rectangular waveguide with a reduced-height section. The plasma generated inside the glass discharge cylinder is stabilized by injecting a swirl gas, creating a vortex flow in the cylinder. The gas swirl also protects the cylinder wall from the discharge heat [6, 11, 19].

The waveguide-based nozzleless cylinder-type MPS exhibits stable operation at power levels from about 600 W up to 6000 W, provided that the total gas flow is sufficiently large (from 30 up to several hundreds l/min).

The waveguide-based nozzleless cylinder-type MPS was used by us for producing hydrogen $H_2$ in the process of plasma reforming of methane $CH_4$ [11].

2.5. MPS for Microdischarges

Nowadays, there is a growing interest in microdischarge sources at atmospheric pressure [20]. The microdischarges at atmospheric pressure find practical applications in various fields such as gas
operated cleaning systems, microwelding, surface modification, light sources. They can find also the use in the biomedical applications such as sterilization of medical instruments, high-precision surgery, cells treatment and deactivation of bacteria and viruses.

The experimental setup with an MPS for microdischarges is shown in Fig. 6. The MPS for microdischarges exhibits stable operation in Ne, Ar, N₂ and air at atmospheric pressure in the form of a small plasma jet at absorbed microwave powers of 6-80 W and gas flow rates of 0.5-25 l/min.

The microdischarge MPS shown in Fig. 6 is simple and cheap. The parameters (dimensions, temperature, electron density) of the microplasma jets can be changed in a wide range. This suggests that the presented MPS can find practical applications in various fields. Our research on using this MPS to gas microprocessing is under progress.

3. GAS PROCESSING BY MICROWAVE PLASMAS – SELECTED RESULTS

3.1. Results of Decomposition of VOCs

The decomposition of several VOCs: aliphatic hydrocarbon (H-C) - methane CH₄, aromatic H-C - toluene C₆H₅CH₃, halogenated aliphatic H-Cs - carbon tetrachloride CCl₄ and chloroform CHCl₃, aromatic chlorofluorocarbons: CCl₃F (CFC-11) and CCl₂F₂ (CFC-12), hydrochlorofluorocarbon CHClF₂ (HCFC-22), hydrofluorocarbon C₂H₄F₄ (HFC-134a) and fluorocarbon C₂F₆ (CFC-116) in their mixtures with synthetic air or nitrogen in the atmospheric-pressure plasmas generated by the waveguide-based nozzle-type MPS operated at low gas flow rate (Fig. 3) was tested. Air or N₂ were used as a carrier gas to dilute and transport the VOCs to the microwave plasma. The use of N₂ is recommended due to fewer problems with harmful by-products [8-10].

In our investigations the concentrations of the processed VOCs were relatively high, i.e. usually a few percent. The use of moderate microwave powers of 200-400 W allowed to increase the initial concentration of the VOCs to several tens percent. For example, the initial concentrations of CCl₃F (CFC-11) in air or nitrogen ranged 10-50 % vol.

The performance of the waveguide-based nozzle-type MPS (low gas flow rate) when used for CFC-11 decomposition in N₂ at moderate microwave powers is illustrated in Table I. As it is seen the CFC-11 decomposition efficiency is high and approaches 100 % when CFC-11 initial concentration is 10 %, almost regardless of the gas flow rate. However, when CFC-11 initial concentration is 50 %, the CFC-11 decomposition efficiency reaches 100 % only if the gas flow rate is 1 l/min., decreasing to about 60 % with increasing gas flow rate to 3 l/min. Generally, with increasing the gas flow rate, the
resident time of the processed gases in the plasma decreases, resulting in lower value of the decomposition efficiency.

TABLE I. THE WAVEGUIDE-BASED NOZZLE-TYPE MPS (LOW GAS FLOW RATE). SELECTED DATA ON THE SPECIFIC ENERGY DENSITY (SED), DECOMPOSITION EFFICIENCY (DE), REMOVAL RATE (RR) AND ENERGY EFFICIENCY (EE) OF THE DECOMPOSITION OF CCl₂F₂ (CFC-11) IN ITS MIXTURE WITH NITROGEN.

<table>
<thead>
<tr>
<th>Initial concentration</th>
<th>Microwave power</th>
<th>Flow rate</th>
<th>SED</th>
<th>DE</th>
<th>RR</th>
<th>EE</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>W</td>
<td>l/min</td>
<td>kWh/m³</td>
<td>%</td>
<td>g/h</td>
<td>g/kWh</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>1</td>
<td>5.0</td>
<td>100</td>
<td>170</td>
<td>570</td>
</tr>
<tr>
<td>50</td>
<td>400</td>
<td>3</td>
<td>2.2</td>
<td>60</td>
<td>310</td>
<td>775</td>
</tr>
<tr>
<td>50</td>
<td>200</td>
<td>2</td>
<td>1.7</td>
<td>60</td>
<td>210</td>
<td>1000</td>
</tr>
</tbody>
</table>

The best values of the specific energy density, the removal rate and energy efficiency of CFC-11 decomposition were 1.7 kWh/Nm³, 310 g(CFC-11)/h and 1000 g(CFC-11)/kWh respectively, depending on the gas flow rate and microwave power delivered to the discharge (Table I). The best conditions for CFC-11 destruction (highest decomposition efficiency at relatively attractive values of the removal rate and energy efficiency) occurred for the CFC-11 initial concentration, gas flow rate and microwave power of 50%, 1 l/min. and 300 W, respectively.

The results of destruction of CFC-11 and other harmful gases were in detail presented in [8-10].

3.2. Results of Production of Hydrogen via Methane Reforming

The reforming of methane CH₄ to produce hydrogen H₂ in the atmospheric-pressure plasma generated by the waveguide-based nozzleless cylinder-type MPS (Fig. 5) was tested [11].

In this MPS, the plasma was stabilized by an additional swirled nitrogen flow (50 or 100 l/min). The methane flow rate was up to 175 l/min. The absorbed microwave power could be changed from 3000 W to 5000 W. The hydrogen production rate and the corresponding energy efficiency were up to 255 g [H₂] / h and 84 g [H₂] / kWh, respectively.

Comparison of the energy efficiencies of hydrogen production for different conventional and plasma methods is given in Table II. In general, the conventional methods (steam reforming [21], water electrolysis [22]) exhibit lower energy efficiency of hydrogen production than plasma methods, except for the dielectric barrier discharge [23]. As seen from Table II, the energy efficiency of hydrogen production by the conventional methods is 3-4 times lower than that in the MPS. It is worth mentioning that the microwave plasma method presented by us is more efficient than other plasma methods operated without a catalyst (dielectric barrier discharge [23] and gliding arc [24]).

When air is used as an additive to methane, as for example in the methane steam reforming [21], the emission of oxide compounds, e.g. carbon oxides and nitrogen oxides, is present. Our experiment was carried out without any admixture of air, thus we avoided emission of any oxygen compounds, some of which are harmful.
TABLE II. COMPARISON OF THE ENERGY EFFICIENCY OF HYDROGEN PRODUCTION VIA METHANE REFORMING FOR DIFFERENT METHODS (INCLUDING OUR RESULTS).

<table>
<thead>
<tr>
<th>Hydrogen production method</th>
<th>Initial gas composition</th>
<th>Energy efficiency [g [H₂] / kWh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONVENTIONAL METHODS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming of methane [21]</td>
<td>CH₄ + H₂O + air</td>
<td>20</td>
</tr>
<tr>
<td>Water electrolysis [22]</td>
<td>-</td>
<td>21</td>
</tr>
<tr>
<td>PLASMA METHODS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waveguide-based cylinder-type MPS (our results without catalyst)</td>
<td>CH₄ + N₂</td>
<td>74</td>
</tr>
<tr>
<td>Waveguide-based cylinder-type MPS (our results with catalyst)</td>
<td>CH₄ + N₂</td>
<td>84</td>
</tr>
<tr>
<td>Dielectric barrier discharge [23]</td>
<td>CH₄ + air</td>
<td>6.7</td>
</tr>
<tr>
<td>Gliding arc [24]</td>
<td>CH₄ + H₂O + air</td>
<td>40</td>
</tr>
</tbody>
</table>

4. SUMMARY

Several MPSs suitable for gas processing (e.g. decomposition of VOCs and hydrogen production via methane reforming) were presented in this paper.

It was found that the energy efficiency and rate of removal of harmful gases (e.g. Freons) obtained using the waveguide-based nozzle-type MPS are superior to those when other plasma methods (e.g. corona, gliding and arc discharges) were employed for this purpose.

The production rate of hydrogen and the energy efficiency of hydrogen production by the waveguide-based nozzleless-type MPS are attractive. The absence of oxygen compounds as by-products in the off-gas is highly beneficial. The proposed microwave plasma system for hydrogen production via methane reforming is expected to be of low cost and effective, and thus promising for industrial implementation.

5. ACKNOWLEDGMENTS

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THE REMOVAL OF VOC FROM AIR USING EB, MW AND CATALYST - LABORATORY PLANT RESULTS

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Abstract

A new hybrid technique for the VOCs removal from gases, based on the combined use of EB induced NTP (non-thermal plasma), MW induced NTP and catalytic oxidation, named “EB+MW-plasma catalysis”, is presented. The main goal of our research was to combine the features of each known technique used in gas pollution control, i.e. the very high efficiency of EB in converting VOCs to intermediate products, the ability of MW to produce and sustain NTP in large electrodeless reactors, and the important role of catalysts in the complete conversion to CO$_2$ and H$_2$O. Our experiences shown that the two means of treating the gases are complementary: the catalytic oxidation in the presence of MW is efficient for high VOC initial concentrations and low flow rates while the exclusive use of the EB irradiation determines high decomposition efficiencies only in the case of very low concentrations of VOC but for large flow rates. Real synergistic effects between NTP and catalysis were obtained by introducing the catalyst into the irradiation zone. The main conclusion of this work is that the combined treatment EB+MW+catalyst improves both decomposition efficiency and oxidation efficiency. The EB+MW+Catalysis method demonstrated good results on a wide range of concentrations and flow rates.

1. OBJECTIVE OF THE RESEARCH

A new hybrid technique for the VOCs removal from gases, based on the combined use of EB induced NTP (non-thermal plasma), MW induced NTP and catalytic oxidation, named “EB+MW-plasma catalysis”, is presented. The main goal of our research was to combine the features of each known technique used in gas pollution control, i.e. the very high efficiency of EB in converting VOCs to intermediate products, the ability of MW to produce and sustain NTP in large electrodeless reactors, and the important role of catalysts in the complete conversion to CO$_2$ and H$_2$O.

2. INTRODUCTION

The main sources of volatile organic compounds (VOCs) emissions in Romania, from industry are the following: the use of solvents in various activities (protection coatings, cleaning and trimming of surfaces, wood impregnation); various production processes (manufacturing of lacquers and adhesives, extraction and refining of vegetable oils) and combustion units. VOCs must be removed from industrial waste streams to meet the more and more stringent regulations of discharge limits. There are many competing technologies for removal of VOCs and the oxidation in non-thermal plasma (NTP) is one of the most promising.

3. MATERIALS AND METHODS

3.1. Experimental installations

Several types of reactors for treating the gases that contain VOCs were built:

- A reactor that allows the irradiation of gases with MW. This reactor was used as such (empty), or with a catalyst – MWR;
- A small reactor, that allows the irradiation of gases with EB – EBR1;
- A larger reactor (93L), for the treatment of gases with EB, and a layer of catalyst was also introduced in this reactor: EBR-2;

These reactors possess systems for the adjustment and continuous measurement of the irradiation flux (with MW and EB). A magnetron with adjustable power (maximum 850 W) and with a frequency of 2.45 GHz was used as a MW generator.
Two types of electron beam accelerators are available for these studies: electron linear accelerators ALIN-10, built in the Electron Accelerator Laboratory, NILPR, Bucharest, Romania, and ILU-6M which was built at the Institute of Nuclear Physics, Novosibirsk, Russia. ALIN-10 is of traveling-wave type, operating at a wavelength of 10 cm. The optimum values of the EB peak current $I_{EB}$ and EB energy $E_{EB}$ to produce maximum output power $P_{EB}$ for a fixed pulse duration $\tau_{EB}$ and repetition frequency $f_{EB}$ are as follows:

ALIN-10: $E_{EB} = 6.23$ MeV; $I_{EB} = 75$ mA; $P_{EB} = 164$ W ($f_{EB} = 100$ Hz, $\tau_{EB} = 3.5$ $\mu$s)

Direct collection of a part of the electron beam is used as an absorbed dose rate monitoring method by sampling during the irradiation process. This monitor who intercepts only a fraction of the scattered electron beam gives, together with its associated electronics instrumentation, a relative value of the absorbed dose rate. It has been first calibrated by several chemical systems (such as the Ceric Dosimeter) placed at the position where the irradiation is performed.

The ILU-6M accelerator is semi-industrial equipment which is installed in a vertical position inside the irradiation room. The ILU-6M electron beam source is a resonator-type accelerator, operating at $115\pm5$ MHz. This accelerator generates electron beam pulses of 1.8 MeV, 0.375 ms duration and 0.32 current peak intensity. The maximum output EB average current and EB output power is of 6 mA and 10.8 kW, respectively. The cross-sectional size of the scanned EB at the vacuum window exit is 1100 mm x 65 mm.

The microwave reactor MWR (Fig. 1), used in these experiments is an elongated cylindrical cavity (ECC) of 90 mm inner diameter and 940 mm long, adapted to operate in the $TM_{01n}$ mode (n is an integer in the range of 0 to 5), containing a concentric quartz tube of 20 mm outer diameter and 16 mm inner diameter. ECC is excited with a rectangular waveguide propagating the microwave electric field parallel to its axis.

In order to study the oxidation of VOCs, a layer of silicon carbide pieces was used as an efficient MW absorbent (for preheating gases) and a $V_2O_5$ catalyst bed was placed inside the quartz tube. The position of the silicon carbide layer into the quartz tube is essential for the ECC impedance matching, i.e. for the minimization of the ratio $Power_{reflected}/Power_{forward}$ as is shown in Fig. 1.

The MW injection system of the ECC consists of a controlled microwave generator with a 2.45 GHz magnetron of 850 W maximum output power, a waveguide launcher, a ferrite circulator, a dual directional coupler for forward and reflected power monitoring and a three-stub tuner for impedance matching (Fig. 1).

The EBR reactors (Fig. 2) are designed like a Faraday cage (the EBR consists of two concentric metallic cylindrical vessels) in order to permit the EB average current monitoring during the gaseous mixture irradiation.

Initially, the EBR-1 reactor was built, having a volume of 4.2 L, and afterwards, the EBR-2 reactor was built, and having a volume of 93 L. EBR-1 is equipped with different devices, such as valves, gas circulating pump, manometer, etc, in order to be used for both single gas passage and multiple gas passage through the inner cylindrical vessel. The EB is introduced perpendicular to the upper end plate of each cylindrical vessel through a 100 $\mu$m-thick aluminum foil. The EB current is collected on the electrical isolated inner vessel, integrated and displayed on the control desk. The gases were irradiated at 6 $\mu$A EB average current.
Subsequently, the EBR-2 reactor was built, having a volume of 93 L and a length of 3 m. The larger volume of the reactor permitted us to obtain a longer residence time for the gas and a better conversion of the gas, and, moreover, the extended length favors the better absorption of the electrons’ energy (6.23 MeV). The accelerated electron beam was not scanned at the ALIN-10 horizontal exit port in order to benefit from the free scattering of the high energy of the EB along the EBR axis which is about 3 m long. An average current of EB irradiation of about 13-17 µA was obtained.

With the help of these reactors, several installations used for the study of the VOCs decomposition processes were built. The installation that contains the EBR-2 and MWR reactors is presented in Fig. 3. All these installations contain the following components:

- A system used for generating a synthetic gaseous mixture made up of air, one or several VOCs, water vapors and, sometimes, argon. This system allows for the continuous provision of a gas flow rate with stable concentrations of VOC and of water;
- An irradiation reactor (MW or EB), or a series of two reactors (MW+EB or EB+MW);
- A system for taking samples of the gas, made up of a solenoid valve and of a Tedlar bag;
- A system for the analysis of gaseous samples, which is used for determining the concentrations of carbon oxides and of organic compounds in vapor state. This system contains three gas
3.2. Results and discussions

These installations were used to study the VOCs decomposition process, taking place in several stages (see Table I).

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reactor type</th>
<th>Irradiation source</th>
<th>Flow type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MWR – without catalyst</td>
<td>Magnetron (400W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>MWR – with catalyst</td>
<td>Magnetron (400W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td>2</td>
<td>EBR-1 without catalyst</td>
<td>ALIN-10 (6.23 MEV, 37W) ILU - 6M (1.8 MeV, 630W)</td>
<td>Static</td>
</tr>
<tr>
<td></td>
<td>EBR-2 without catalyst</td>
<td>ALIN-10 (6.8 MEV, 68W)</td>
<td>Static</td>
</tr>
<tr>
<td></td>
<td>EBR-2 without catalyst</td>
<td>ALIN-10 (6.8 MEV, 68W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td>3</td>
<td>EBR-2 without catalyst</td>
<td>ALIN-10 (6.8 MEV, 68W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>MWR – with catalyst</td>
<td>Magnetron (400W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>EBR-2 with catalyst</td>
<td>ALIN-10 (6.8 MEV, 68W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>MWR-with catalyst</td>
<td>Magnetron (400W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>EBR-2 without catalyst</td>
<td>ALIN-10 (6.8 MEV, 68W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td>4</td>
<td>EBR-2 with catalyst</td>
<td>ALIN-10 (6.23 MEV, 106W)</td>
<td>Dynamic</td>
</tr>
<tr>
<td></td>
<td>MWR- with catalyst</td>
<td>ALIN-10 (6.23 MEV, 106W)</td>
<td>Dynamic</td>
</tr>
</tbody>
</table>

In all experiments, the VOCs decomposition process was observed, by determining the concentrations of carbon oxides and of volatile organic compounds (the initial ones, but also the newly appeared ones). In order to achieve a better assessment of the oxidation process two efficiencies have been determined.
- Eff\(_1\) is the removal efficiency:
\[
Eff_1 = \frac{[VOC]_0 - [VOC]_t}{[VOC]_0} \times 100
\]

Where:
- \([VOC]_0\) is the initial concentration of VOC, ppmv;
- \([VOC]_t\) is the concentration of VOC after treatment, ppmv;

- Eff\(_2\) is the efficiency for the conversion of VOC into carbon oxides:
\[
Eff_2 = \frac{No.\, Catoms}{[VOC]_0 - [VOC]_t} \times 100
\]

Where:
- \([VOC]_0\) is the initial concentration of VOC, ppmv;
- \([VOC]_t\) is the concentration of VOC after treatment, ppmv;
- \([CO_2]_t\) is the concentration of CO\(_2\) after treatment, ppmv;
- \([CO_2]_0\) is the initial concentration of CO\(_2\) from air, ppmv;
- \([CO]_t\) is the concentration of CO after treatment, ppmv;

3.1.1. The irradiation of gases only with microwave (with or without a catalyst, dynamic conditions)

The first set of experiments was made with the microwave reactor MWR-1 (Fig. 1). Toluene and hexane at high concentrations (~2% vol.) and small air flow rates (~100 l/h) were used. In the absence of the catalyst, the process still takes place but with a low efficiency (< 40%). In order to increase the amount of energy absorbed, the gases have to contain a large concentration of water (15-30% vol.). The presence of argon (10-20% vol.) determines an increased efficiency in the VOCs removal. The experiments carried out in the presence of a common oxidation catalyst (V\(_2\)O\(_5\)) allowed an improvement of removal efficiency of VOC. In this case, dry gases were used and an absorbent microwave ceramic was present for their preheating and it was placed within the reactor in front of the catalyst.

It is acknowledged that the catalytic oxidation takes place with a better efficiency at temperatures of approximately 500°C. In the MWR reactor we were especially interested in the heating of the catalyst (at a temperature of 300-400°C), the temperature of gases at their exit from the reactor being of only 70-80°C. This constitutes an important advantage of the method, as the energy consumption is minimum and the installation does not need complicated heat exchangers.

An important disadvantage of catalytic oxidation in the presence of MW irradiation results from the severe reduction in the efficiency of VOCs removal at low concentrations of VOC or at higher air flow rates (Fig. 4 and 5).
FIG. 4. The influence of the initial concentration of toluene on the concentration of the treated gases and on the efficiency of toluene removal; MW power= 400 W; Oxidation on SiC+catalyst, dry gases, air flow rate 100 l/h.

FIG. 5. The influence of air flow rate upon the efficiencies of toluene removal oxidation on SiC+catalyst, MW power= 400 W; [toluene]₀=600 ppmv

The efficiency in the removal of VOC was increased with the microwave power (fig. 6). However, this is limited by the potential damaging of the catalyst (melting and sintering) at excessively high temperatures.

FIG. 6. The influence of MW power upon the efficiencies of toluene removal, oxidation on SiC inside MWR, air flow rate=400l/h, [toluene]₀ =608 ppmv.
3.2.2. The irradiation of gases using only EB – static conditions.

A set of experiments with the EB irradiation of the gaseous mixture was carried out in static conditions on the EBR-1 reactor (Fig. 2a). An average EB (6.23 MeV) current of 6 µA was used.

The favorable effect of water (at saturation pressure in gases) in the irradiation process has been shown. It is known that, by irradiation, water produces OH radicals, which are very efficient oxidizing agents. The conversion of VOC into CO and CO$_2$ is always lower than the overall conversion of VOC into any products which means that some of the VOCs are transformed into solid particles. This is a characteristic of the irradiation process that produces a great number of active radicals. At low temperatures, these radicals do not all oxidize, but they recombine themselves. The experiment shows that the degradation process of VOCs is more efficient at lower concentrations and the efficiencies rise as the irradiation dose rises (Fig. 7B).

![Graph A](image1)

**FIG. 7:** Results obtained for hexane removal from gases by electron beam treatment static conditions; EBR-1; 6.23 MeV; 6mA; 37W.

A - the influence of the presence of water on the concentrations of the products; B - the influence of initial hexane concentration on the efficiency of hexane removal

The results from Fig. 8 are obtained for different VOCs: hydrocarbons (hexane and toluene), alcohol (isopropanol), ester (ethyl acetate) and ether (ethyl ether). For all these compounds, the general characteristics of decomposition caused by EB irradiation are present: higher decomposition rates at smaller concentrations, higher decomposition rates as compared to conversion into total oxidation products, etc.

![Graph B](image2)

**FIG. 8.** Results obtained for different VOC organic compounds treatment by electron beam, static conditions; EBR-1; 6.23 MeV; 6mA; 37W.
The next experiments were carried out on the EB-R1 reactor irradiated by the ILU-6M accelerator. In Table II the results obtained with the accelerators ALIN-10 and ILU-6M are presented comparatively. Both the features of the irradiation and the efficiencies obtained can be noticed. Even if the experiments were carried out so as to obtain similar VOCs removal efficiencies, the decomposition rates are different. With the ILU-6M accelerator higher decomposition rates (expressed in ppmv / min) are obtained, as well as a higher energy efficiency (expressed in ppmv/(min*W)). A possible explanation might be the reduced length of the EBR-1 reactor (275 mm), which does not permit an efficient absorption of ALIN-10 high energy electrons.

TABEL II. THE RESULTS OBTAINED FOR THE DECOMPOSITION OF HEXANE FROM AIR BY EB TREATMENT IN EBR-1, USING TWO DIFFERENT ACCELERATORS

<table>
<thead>
<tr>
<th>Irradiation conditions</th>
<th>Results obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Efficiencies</td>
</tr>
<tr>
<td></td>
<td>$\text{Eff}_1$</td>
</tr>
<tr>
<td>Accelerator type</td>
<td></td>
</tr>
<tr>
<td>ALIN-10</td>
<td>ILU-6M</td>
</tr>
<tr>
<td>Current 6µA</td>
<td>20</td>
</tr>
<tr>
<td>Energy 6.23MeV</td>
<td>35</td>
</tr>
<tr>
<td>Power 37 W</td>
<td>63</td>
</tr>
<tr>
<td>Current 350 µA</td>
<td>38</td>
</tr>
<tr>
<td>Energy 1.8MeV</td>
<td>58</td>
</tr>
<tr>
<td>Power 630 W</td>
<td></td>
</tr>
</tbody>
</table>

The EBR-2 reaction chamber was tested by studying the decomposition of toluene from gases through irradiation in a static regime (Fig. 9).

FIG. 9. Results obtained for toluene removal from gases by EB treatment, static conditions, using EBR-2 reactor (6.8 MEV, 68W), and [toluene]$_0$ = 740 ppmv.
The main features of VOCs removal process using the EB irradiation of gaseous mixture are established:

- The conversion of VOCs into CO and CO$_2$ is always smaller than the overall conversion of VOCs into any products which means that some of the VOCs are transformed into solid particles;
- The organic compounds resulting from partial oxidation reactions are formed in small amounts and the main by-products are solid particles – aerosols;
- The VOCs decomposition efficiency is increased by: small VOC concentration; high irradiation time, as well as the presence of water vapors at the saturation concentration;
- The process of VOCs decomposition through EB irradiation is efficient for a wide range of compounds that have been tested: hydrocarbons (hexane and toluene), alcohol (isopropanol), ester (ethyl acetate) and ether (ethyl ether).
- The VOCs decomposition rate (ppmv/(min*W)) is twice or three times higher at the irradiation with EB having an energy of 1.8 MeV, than the decomposition rate obtained at the irradiation with EB having an energy of 6.23 MeV; This effect is due to the higher power level and beam utilization efficiency of the ILU-6M accelerator in these experiments.

3.2.3. Combined irradiation of gases: EB irradiation and catalytic oxidation under MW irradiation

A laboratory hybrid installation (LHI) was designed for VOCs treatment by successive EB irradiation and catalytic oxidation under MW irradiation. Several experiments have been carried out using the EBR-2 reactor chamber, connected to the MWR-1 oxidation reactor.

Subsequently, several experiments with continuous flow rate have been carried out, keeping a residence time in the EBR-2 reaction chamber in the range of 5-15 min. The air flow rates that were used range between 600-1200 l/h. At these flow rates, the efficiency of oxidation under MW irradiation is quite small (see Fig.5). In the successively combined treatment system, the VOCs removal efficiencies are increased substantially (Fig. 10).
successive treatment of the type EB+MW leads to better results. This fact may be caused by the formation of active radical species (during the EB treatment) which can be easily transformed into total oxidation products after being exposed to the MW reactor.

![Graph](image1)

**FIG. 11.** Results obtained for toluene removal from gases by MW, EB, EB+MW or MW+EB treatment, continuous air flow (400 l/h); [toluene]₀=608 ppmv.

Figure 12 presents the results obtained at the treatment of an air and hexane mixture. In this case, also, the same feature that was noticed at toluene treatment applies: the successive use of the EBR-2 and MWR reactors with a catalyst allows us to obtain the highest removal efficiency possible and a quite high oxidation efficiency.

![Graph](image2)

**FIG. 12.** Results obtained for hexane removal from gases by MW, EB or EB+MW treatment, continuous air flow (400 l/h); [hexane]₀=608 ppmv.

The examination of the reported results as well as of our experiments performed with the LHI installation in a two-stage process, first in the EB reactor and then in the MW reactor, suggested that the enhancement of the synergistic effects between NTP and catalysis can be expected by using the catalyst inside a reactor simultaneously irradiated with EB and MW.

3.2.4. The irradiation of gases with EB in the presence of a catalyst and the combined irradiation with EB (with a catalyst) and with MW (with a catalyst).

The EBR-2 reactor was used, and inside it a 4 cm thick catalyst layer was placed. In front of this catalyst layer there is an electric system of gas heating. Only a hot catalyst was used for the experiments into this reactor. If the catalyst is cold, the VOCs might be adsorbed by its surface, which would cause errors in the determination of the removal efficiency. For this reason, throughout the whole experiment, the hot catalyst was maintained, having a temperature of 200-220°C (the temperature in the catalyst layer was continuously measured using a thermocouple introduced inside the catalyst layer).
The irradiations were carried out using the ALIN-10 accelerator, which functioned with electron energy of 6.23 MeV and with a current of 17 µA, that is with a power of 104 W; the electron beam was not scanned. The MW irradiation was realized using a 2.45 GHz magnetron, which was adjusted at a power of 400 W.

The experiments aimed at determining the VOCs removal efficiencies in the presence of the catalyst, and in the presence of the catalyst subject to EB irradiation. Finally, several experiments were carried out using the two successive reactors: EBR-2 followed by MWR, both of them containing a catalyst layer.

In the first set of experiments, a mixture of toluene, hexane and air was used, in similar concentrations (285 ppmv), and the influence of the gas flow rate upon the VOCs removal efficiencies was observed.

Figure 13 presents, comparatively, the results obtained at the treatment of the gas in the following conditions:

- In the presence of the catalyst (electrically heated) inside the EBR-2 reactor, without irradiation – A. One can notice how the V₂O₅ catalyst becomes active in the VOCs removal from air at relatively low temperatures, of approx. 200°C. In these conditions, the efficiencies in the removal of hexane and of toluene are quite high (93.2 at 60% for hexane and 85.3 at 81.8% for toluene), but they decline with the increase of the air flow rate (at the same VOCs concentration). However, in these conditions, the oxidation efficiency for carbon oxides is quite low (37 at 21%), and it declines with the increase of the gas flow rate.

- In the presence of the catalyst (electrically heated) inside the EBR-2 reactor, irradiated with EB – B. One can notice that, when the catalytic oxidation takes place in the presence of the EB irradiation, the hexane and toluene removal and oxidation efficiencies increase significantly. However, the efficiencies present the same declining tendency when the gas flow rate increases.

- The results obtained at the successive treatment of the gases in two serial reactors, in which there is a catalyst, which is subject to EB irradiation, in the first reactor, and to MW irradiation in the second reactor - C. It can be noticed that when the two catalytic EBR-2 and MWR reactors are used successively, the efficiency of the process is significantly improved. At low flow rates, it is especially the total oxidation (Eff2) that increases, while at high flow rates, both efficiencies increase.

Further on, toluene was used for the experiments, in various concentrations (100-580 ppmv). Subsequently, several experiments were carried out, and they included the treatment of the gaseous mixture inside the EBR-2 reactor, and then inside the series of EBR-2 and MWR reactors. The results obtained are presented in figure 14. The favorable effect of the EB irradiation on the catalytic oxidation of toluene can be noticed, as well as the increased efficiency obtained when using a series of two catalytic reactors, in which the catalyst is activated through EB irradiation (in the first one), and through MW irradiation (in the second one). This effect can be noticed for the whole range of concentrations used.
FIG. 13. The influence of the gas flow rate and of the irradiation type upon the hexane and toluene removal and oxidation efficiencies obtained at: catalytic oxidation (the catalyst in the EBR-2 reactor) – A, catalytic oxidation in the presence of EB – B and catalytic oxidation in a series of two successive EBR-2 and MWR reactors - C.

FIG. 14. The removal and oxidation efficiencies obtained at the catalytic oxidation of gases containing toluene (the catalyst in the EBR-2 reactor) – A, catalytic oxidation in the presence of EB – B and catalytic oxidation in a series of two successive EBR-2 and MWR reactors - C.
4. CONCLUSIONS

The main idea of this research was to combine the complementary characteristics of several techniques of gas treatment:

- the very high efficiency of EB in converting VOCs to intermediate products by OH radical reactions;
- The ability of MW to produce and sustain NTP in large electrodeless reaction vessels. It is also important to mention the MW capacity of selectively heating the oxidation catalyst and of allowing for the realization of the catalytic process at gas temperatures which are far lower than in the conventional procedures;
- The important role of catalysts in the complete oxidation of the intermediate products.

The experimental results demonstrate that:

- The catalytic oxidation in the presence of MW is an efficient process, but only at high VOCs concentrations and at low gas flow rates (residence time long enough to permit the preheating of the gas directly on the hot surface of the catalyst);
- The treatment of gases with EB is more efficient when the initial VOCs concentration is lower. The treatment can be performed at high gas flow rates, because there is no need for the preheating of gases. However, gases containing a great amount of water vapors are used, in order to increase the concentration of the OH reactive species;
- It is possible to perform the treatment of gases on a catalyst irradiated with EB at low temperatures (approx. 200°C), and the efficiencies obtained are significantly higher than the ones obtained at the EB irradiation alone.
- The treatment of gases in a series of two reactors, in which there is a catalyst which is subject to EB irradiation (in the first one), and to MW irradiation (in the second one), led to the obtaining of the best results in VOCs removal efficiency and complete oxidation. Moreover, this technique can be applied on large concentration ranges and flow rates, as well as on a wide range of VOCs.
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COMPARISON OF DECOMPOSITION CHARACTERISTICS BETWEEN AROMATIC AND ALIPHATIC VOCS USING ELECTRON BEAM

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Abstract

The removal efficiency of n-decane (C\textsubscript{10}H\textsubscript{22}) by electron beam was the highest among aliphatic VOCs of concern, and that of n-hexane (C\textsubscript{6}H\textsubscript{14}), n-butane (C\textsubscript{4}H\textsubscript{10}), and methane (CH\textsubscript{4}) followed. On the other hand, in terms of aromatic VOC decomposition efficiencies, benzene (C\textsubscript{6}H\textsubscript{6}) decomposition was the lowest and that of toluene (C\textsubscript{7}H\textsubscript{8}), ethylbenzene (C\textsubscript{8}H\textsubscript{10}), and p-xylene (C\textsubscript{8}H\textsubscript{10}) were similar. It was also found that there was increase in by-product (untreated VOC, CO, CO\textsubscript{2}, O\textsubscript{3}, and other compounds) formation as well as all VOC removal efficiencies. It was demonstrated that the removal efficiency of VOC increased as its concentration decreased and the irradiation dose increased. In addition, low removal efficiency was observed because helium was relatively stable compared to the other gases, and nothing but electrons produced by electron accelerator reacted with VOC. It was also found that relative humidity had some effects on the decomposition rates of VOC. The removal efficiency at the 100 % RH condition was slightly higher than that at 7.4 % RH (dry condition) due to OH radical formation.

1. INTRODUCTION

Volatile organic compounds (VOCs) have been well-documented as one of the most important ozone (O\textsubscript{3}) precursors. Many countries have concerns about reducing VOCs because they have adverse effects on human health as carcinogenic and toxic substances [1, 2]. There are many different conventional techniques to control VOCs emissions from a variety of industrial processes. They are carbon adsorption, absorption, catalytic oxidation, thermal incineration, and biotreatment [3, 4]. The method of VOC removal by electron beam (EB) irradiation has been taken into account as one of the most recent novel technologies [1, 5, 6]. EB process can be operated economically for the low VOC concentrations diluted in high volume flows at room temperature [7, 8]. The EB operation time is quite short because the electrons are generated during 10\textsuperscript{-18}~10\textsuperscript{-12} seconds and interact with the gas molecules. Besides, this reaction produces free radicals and ions during 10\textsuperscript{-8}~10\textsuperscript{-1} seconds. In this study, the degradation characteristics of n-hexane were mainly investigated for different concentrations, background gases (oxygen, nitrogen, air, and helium), absorbed doses (kGy, kJ/kg), and relative humidities (RH) using electron beam irradiation. In addition, the decomposition rates of saturated aliphatic VOCs (methane, n-butane, n-hexane, and n-decane) were compared, and those of aromatic and aliphatic VOC were also compared.

2. EXPERIMENT

An electron beam accelerator (1 MeV, maximum power 40 kW, ELV4 type) was used for electron beam irradiation. One liter of oval tedlar reactors (SKC, USA) were used in order to control hexane under various background gases, different concentrations, and absorbed doses during the batch treatment. The hexane decomposition system using EB irradiation is depicted in FIG. 1 and FIG. 2. The absorbed dosage was operated in the range of 2.5 to 10 kGy. Different concentrations (140, 300, and 600 ppmC) of reactors with various background gases were put onto a conveyor system and passed under the scanning window of the electron accelerator at a speed of 10 m/min.

A GC/FID (HP5890 Series II, Hewlett Packard, USA) was used to make quantitative analysis of the samples. The GC column was HP-1 (25m × 0.32mm × 0.52(m)). Sampling was conducted using adsorbent trap (Carbopack B / CarboxenTM 1000) for the qualitative analysis. GC/MSD (Clarus 500, Perkin Elmer, USA) coupled with thermal desorber (Aerotrap 6000, Tekmar, USA) was also employed. The sample trap was then desorbed using helium (25 mL/min) at 250°C for 5 min with the desorbed material collected in a cryotrap at -150°C. The hexane samples were transferred to a cryofocus trap at -150°C through a transfer line held at 190 °C. Finally, the chemicals concerned were
injected into a GC capillary column DB-1 (50m × 0.32mm × 5.0µm). A CO/CO₂ analyzer (Gas Data PAQ, UK) was adopted to measure the amount of CO and CO₂. The relative standard deviation (RSD) obtained from the quantitative analysis turned out to be less than 7.6%.

**FIG. 1. VOC decomposition using electron beam technique (Batch system).**

**FIG. 2. VOC decomposition using electron beam technique (Continuous flow system).**
3. RESULTS AND DISCUSSION

3.1. Effects of the background gas

Approximately 140 ppmC of hexane mixed with ultra-high purity He, N\textsubscript{2}, O\textsubscript{2}, and Air atmosphere was controlled by EB irradiation in order to determine the mechanism of hexane decomposition. Fast moving primary electrons interact with the background gas molecules, and this reaction produces ions, electron-ion pairs, and free radicals through ionization and excitation processes. Major free radicals are OH\textsuperscript{-}, HO\textsuperscript{2+}, O\textsuperscript{-}, N\textsuperscript{-} and H\textsuperscript{-}. These primary and secondary activated species rapidly react with VOCs. FIG 3 suggests that the hexane removal efficiency (49 % at 10 kGy) under helium atmosphere should be considerably lower than that under the other gases (95~98 % at 10 kGy). The low removal efficiency is expected because helium is relatively stable compared to the other gases, and nothing but electrons produced by electron beam react with hexane. The removal efficiency when mixed with oxygen, nitrogen, and air atmospheres was much higher than that of helium. In general, the decomposition efficiency of hexane (140 ppmC) under the He, N\textsubscript{2}, O\textsubscript{2}, and Air atmosphere increased as the absorbed dose increased.

![FIG. 3. Removal efficiency of Hexane (140 ppmC) by background gases.](image)

3.2. Effects of the initial concentration and humidity

The decomposition characteristics of hexane at various concentrations in an air atmosphere are seen in FIG. 4. It was found that the removal efficiency of hexane increased with a decrease in initial concentration. In the range of 2.5 to 10 kGy, the removal efficiencies at 140, 300, and 600 ppmC were 63~96%, 46~88%, and 23%~50%, respectively. This trend of hexane degradation agrees with those of previous studies [7, 8].
The removal efficiency of hexane with respect to relative humidity (RH) inside the reactor is presented in FIG. 5. If H₂O (water vapor) is added to the air environment while using EB irradiation, the chemical reaction rate becomes faster because of OH radical formation. Therefore, it was found that there was a 2 to 6 % removal difference between 50 and 100 % RH conditions. More extensive studies on humidity effects need to be carried out in the future to get a more clear understanding of this OH radical effect.

3.3. Formation of carbon monoxide (CO) and carbon dioxide (CO₂)

Concentrations of carbon monoxide (CO) and carbon dioxide (CO₂) generated by EB irradiation are shown in FIG. 6 and 7. Although both CO and CO₂ concentrations increased in proportion to the dosage increment, slight differences between two initial hexane concentrations were observed. This can be explained through carbon mass balance because the initial hexane concentrations were low.
3.4. Comparison of hexane and aliphatic VOCs decomposition

The removal efficiencies were compared with respect to absorbed doses in order to study the decomposition characteristics hexane and aliphatic VOCs. The decomposition rate of methane was very low as 8 % and of n-decane was almost 100 % at 10kGy. The rate of aliphatic VOCs appears to be increasing depending upon number of carbon. As an aliphatic VOC removal result, the removal efficiency of n-decane(C\textsubscript{10}H\textsubscript{22}) by electron beam was the highest and that of n-hexane(C\textsubscript{6}H\textsubscript{14}), n-butane(C\textsubscript{4}H\textsubscript{10}), and methane(CH\textsubscript{4}) followed.
3.5. Comparison of hexane and aromatic VOCs decomposition

In terms of aromatic VOC decomposition efficiencies, benzene decomposition was the lowest and that of toluene, ethylbenzene, and p-xylene was similar. The decomposition rate of hexane as aliphatic VOC was as higher as 15% compared to that of toluene at 10 kGy. Comparing reaction rate constants with OH radical for hexane($5.36 \times 10^{-12}$) and toluene($5.96 \times 10^{-12}$), these values were similar, however decomposition rate of hexane was higher than that of toluene. This suggested that aromatic VOC with benzene ring should be more difficult to decompose than aliphatic VOC with a series of carbon chain although they have similar reaction rate constants with OH radical.
4. CONCLUSION

The application of a novel control technique using electron beam irradiation has been studied to control hexane contained in various background gases (helium, nitrogen, oxygen, and air). This study demonstrated that the removal efficiency of hexane increased as its concentration decreased and the irradiation dose increased. The maximum hexane removal efficiencies at 10 kGy were 98.4, 96.4, 95.2, and 49.1 %, respectively with nitrogen, air, oxygen, and helium atmospheres. Additionally, the maximum hexane decompositions at the initial concentrations of 140, 300, and 600 ppmC were determined to be 96.4, 88.3, and 49.9 %, respectively. It was also found that relative humidity (RH) had some effects on the decomposition characteristics of hexane. The removal efficiency at the 100 % RH condition was slightly higher than that at 50 %. As an aliphatic VOC removal result, the removal efficiency of n-decane(C\textsubscript{10}H\textsubscript{22}) by electron beam was the highest and those of n-hexane(C\textsubscript{6}H\textsubscript{14}), n-butane(C\textsubscript{4}H\textsubscript{10}), and methane(CH\textsubscript{4}) followed. On the other hand, in an aromatic VOC decomposition efficiency, benzene(C\textsubscript{6}H\textsubscript{6}) decomposition was the lowest and those of toluene(C\textsubscript{7}H\textsubscript{8}), ethylbenzene(C\textsubscript{8}H\textsubscript{10}), and p-xylene(C\textsubscript{8}H\textsubscript{10}) were similar. Further comparison studies on the degradation characteristics of other aliphatic and aromatic VOC under continuous flow system should be performed to determine more characteristic control parameters.

REFERENCES

REMOVAL OF CHLORINATED ORGANIC COMPOUNDS FROM GAS PHASE USING ELECTRON BEAM TECHNOLOGY

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Abstract

Selected chlorinated organic compounds (Cl-HC), which are emitted from coal fired power plants, waste incinerators, chemical industry etc., are very harmful to the environment and human’s health. Some of them are listed as carcinogenic compounds by USA EPA. Recent studies show that some chlorinated organic compounds are suspected to be precursors for dioxins formation. Chlorinated organic compounds decomposition in air in an electron beam (EB) generated plasma reactor technology was studied. We selected cis-dichloroethylene (cis-DCE), 1,4-dichlorobenzene (1,4-DCB), 1-chloronaphthalene as studied objects. It is found that chlorinated organic compounds can be decomposed in an electron beam generated plasma reactor. The order of decomposition efficiency of these compounds are: cis-DCE > 1,4-DCB > 1-chloronaphthalene.

1. INTRODUCTION

With industrial progress and human activity, a large amount of man-made organic pollutants have been emitted into atmosphere. These pollutants emission causes serious environmental problem. Different technologies have been studied in order to diminish these pollutants emission from source station.

Non-thermal plasma is a promising technology to treat toxic organic compounds. PCDD/F can be removed from off-gases of municipal solid waste incinerators using this technology. Over 90% PCDD/F was decomposed at 14 kGy absorbed dose when initial concentration of PCDD/F was in the range of 0.35-12.4 ng-TEQ/m$^3$N [1]. Chlorinated compounds, such as chlorobenzene and chlorophenol, were suspected as precursor for dioxins formation. It is possible to destruct these precursors of chlorinated compounds to diminish dioxins formation in the combustion process. In this work, we chose cis-DCE, 1,4-DCB and 1-chloronaphthalene as representative compounds. Their decomposition under electron beam irradiation was examined.

2. EXPERIMENTAL

Model gas preparation, irradiation condition and analytical condition of cis-DCE were described in details previously [2]. Setup for preparation of 1,4-DCB can be referred to Sun et al. [3]. We made a minor revision of this set-up and connected glass vessel reactors with parallel connection instead of series connection. Irradiation condition and analytical method for 1,4-DCB were the same as that which were described in [3]. Experimental method of 1-chloronaphthalene can be referred to that of 1,4-DCB. Concentrations of water vapor in these gas mixtures are 300 ppm for cis-DCE and 170 ppm for 1,4-DCB and 1-chloronaphthalene, respectively.

3. RESULTS AND DISCUSSION

Dependence of cis-DCE degradation in function of dose and compound concentration was investigated. The results are presented in Fig.1. Cis-DCE concentration linearly decreases with the absorbed dose increasing. G-value of cis-DCE was calculated from the data presented in Fig.1. G-value is increased with the initial concentration of cis-DCE increasing, from 3.45 (molecules/100eV) at 271 ppm to 9.53 (molecules/100eV) at 1529 ppm.
Figure 2 presents the results of degradation of cis-DCE and its products formation under EB-irradiation for the initial concentration of cis-DCE being 661.0 ppm. The concentrations of cis-DCE and its products were given in relative carbon concentration as Y-axis in Fig.2. TC, TOP, IC and trans-DCE are the abbreviations of Total Carbon, Total Organic Products, Inorganic Carbon and Trans-Dichloroethylene, respectively. TC is nearly 100% which means aerosol carbon compounds are barely formed in this irradiation process. About 90% organic compounds are formed at 37.95 kGy absorbed dose but most of them are not identified except trans-DCE in this work. CH$_2$=CHCl, CH$_2$=CCl$_2$, CHCl=CCl$_2$ and CH$_2$CICOCICl are not detected as irradiation organic products. Formation of Inorganic Carbon (CO + CO$_2$) is below 10%.

Degradation of 1,4-DCB and 1-chloronaphthalene in an air mixture was investigated and the results are presented in Figs. 3 and 4, respectively. Concentrations of 1,4-DCB or 1-chloronaphthalene in an air mixture decrease with the absorbed dose increasing. This phenomenon is similar to that of cis-DCE degradation. It needs higher energy of decomposing 1,4-DCB or 1-chloronaphthalene compared with that of cis-DCE. It can be explained by the mechanism of these pollutants decomposition and their irradiation products formation.
Mechanism of trans-DCE decomposition has been described in details [2]. Cis-DCE degradation and its products formation can be referred to that of trans-DCE. It is well known that when fast electrons from beams are absorbed in the carrier gas, they cause ionization and excitation processes of the nitrogen, H₂O and oxygen molecules in the carrier gas. Primary species and secondary electrons are formed. These primary species and thermalized secondary electrons cause organic pollutants decomposition. For cis-DCE, the main reaction pathway causing cis-DCE degradation and its products formation is Cl⁻ dissociative secondary electron attachment followed by peroxy radical decomposition. The reactions are given below:

\[
\begin{align*}
\text{e} + \text{cis-CHClCHCl} & = \text{Cl}^- + \text{CHClCH} \\
\text{Cl} + \text{cis-CHClCHCl} & = [\text{CHCl}_2\text{CHCl}]^* \\
\text{Cl} + \text{trans-CHClCHCl} & = [\text{CHCl}_2\text{CHCl}]^* \\
[\text{CHCl}_2\text{CHCl}]^* & = \text{Cl} + \text{trans-CHClCHCl} \\
[\text{CHCl}_2\text{CHCl}]^* & = \text{Cl} + \text{cis-CHClCHCl} \\
[\text{CHCl}_2\text{CHCl}]^* + \text{M} & = \text{CHCl}_2\text{CHCl}
\end{align*}
\]

(M: any species in the reaction system)
According to Atkinson, R. [5], the branching ratio of R3a : R3b : R3c are 0.08 : 0.20 : 0.72, respectively.

Trans-DCE is formed through reaction R1, R2 and R3a. Similar to cis-DCE, trans-DCE is degraded too.

CHCl₂CHCl radical produced from reaction R3c go through mechanism of peroxyl radicals:

\[ \text{O}_2 + \text{CHCl}_2\text{CHCl} = \text{CHCl}_2\text{CHCl(O}_2) \] (R4)

\[ 2\text{CHCl}_2\text{CHCl(O}_2) = 2\text{CHCl}_2\text{CHCl(O)} + \text{O}_2 \] (R5)

\[ \text{CHCl}_2\text{CHCl(O)} = \text{HCl} + \text{CHCl}_2\text{CO} \] (R6a)

\[ \text{CHCl}_2\text{CHCl(O)} = \text{HOCOCI} + \text{CHCl}_2 \] (R6b)

\[ \text{CHCl}_2\text{CHCl(O)} + \text{O}_2 = \text{CHCl}_2\text{COCl} + \text{HO}_2 \] (R6c)

According to Hasson and Smith’s work [4], the branching ratio of reactions (R6a : R6b : R6c) is (0.15 ± 0.08) : (0.77 ± 0.08) : (0.08 ± 0.02). Reaction R6b is the main channel. HOCOCI formed in reaction R6b, which can not be analyzed by using a GC-FID, is possible one of the main organic products. OH radicals contributing to cis-DCE decomposition are less than 10%.

Mechanism of chlorinated aromatic hydrocarbons, such as 1,4-DCB or 1-chloronaphthalene, is a little different from that of cis-DCE. At the beginning stage of irradiation, secondary electron attachment and positive charge transfer reactions play main roles for 1,4-DCB or 1-chloronaphthalene decomposition; At the late stage of irradiation, radical reactions play very important role for chlorinated aromatic hydrocarbons decomposition. Because the rate constants of Cl radicals with chlorinated aromatic hydrocarbons (usually \(1.0 \times 10^{-15} - 1.0 \times 10^{-16}\)) are much smaller than OH radicals (\(1.0 \times 10^{-12} - 1.0 \times 10^{-13}\)), Cl radical addition reaction followed by peroxyl radical reactions pathway is not so important for chlorinated aromatic hydrocarbons decomposition in air mixture; OH radicals reaction is more important for chlorinated aromatic hydrocarbons decomposition in low or high humidity gas mixture.

Some positive charge transfer reactions, such as \(\text{N}_2^+\), cause benzene ring cleavage of chlorinated aromatic hydrocarbons. Aliphatic by-products are formed. Hirota et al. [6] and Han et al. [7] observed some aliphatic organic compounds formed from chlorobenzene decomposition in an air mixture under EB-irradiation.

The generalized chemical reactions can be written as:

\[ \text{Cl}-\text{PAH} + \text{M}^+ = \text{M} + (\text{Cl}-\text{PAH})^+ \quad \text{(R7)} \]

\[ (\text{Cl}-\text{PAH})^+ = \text{products} \quad \text{(R8)} \]

\[ (\text{Cl}-\text{PAH})^+ + \text{radicals/neutral} = \text{products} \quad \text{(R9)} \]

\[ \text{e} + (\text{Cl}-\text{PAH}) = \text{Cl}^- + (\text{PAH}) \quad \text{(R10)} \]

\[ \text{OH} + (\text{Cl}-\text{PAH}) = \text{products} \quad \text{(R11)} \]

\[ \text{Cl} + (\text{Cl}-\text{PAH}) = \text{products} \quad \text{(R12)} \]

\[ (\text{PAH}) + \text{Radicals/neutral/M}^+ = \text{products} \quad \text{(R13)} \]

(\text{PAH}) is a radical species in reactions R10 and R13.
4. CONCLUSIONS

Selected chlorinated organic compounds can be decomposed using electron beam technology. The decomposition efficiency of chlorinated organic compounds is in the order (from higher to lower): cis-DCE > 1,4-DCB > 1-chloronaphthalene. The decomposition products of these pollutants need to be further investigated.

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RADIATION-INDUCED DESTRUCTION OF ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS BY DUAL OXIDATION/REDUCTION MECHANISM

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Abstract

This research presents the feasibility and mechanisms of using high energy electrons for the dechlorination of polychlorinated biphenyls (PCBs) in marine sediment, and hazardous organic compounds in waste water. The remediation of the organic contaminants by ionizing radiation is achieved by means of both reduction and oxidation processes. PCBs in marine sediment can be effectively dechlorinated by reduction, while toxic organic compounds in water are removed mainly by oxidation. Radiolytic degradation of aqueous suspensions of PCBs in marine sediments in the presence of isopropanol was also studied. Addition of isopropanol was necessary to enhance the radiolytic yield and the dechlorination of PCBs.

Also presented are results from an examination of the oxidative and reductive effects of electron-beam irradiation on the concentrations of six organic solvents in water. The organic solvents in water were prepared to mimic a pharmaceutical waste stream. Radiation-induced destruction of benzene was also investigated using pulse radiolysis technique. Pulse radiolysis with spectrophotometric and conductometric detection was utilized to study the formation and reactions of radicals from benzene and dienes in aqueous solutions. The benzene OH adduct, \( \cdot C_6H_6OH \), reacts with \( O_2 \) (\( k = 3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} \)) in a reversible reaction. The peroxyl radical, \( HOC_6H_6O_2^\cdot \), undergoes \( O_2^\cdot \) elimination, bimolecular decay, and reaction with benzene to initiate a chain reaction, depending on the dose rate, benzene concentration, and pH. The occurrence of the chain reaction is demonstrated in low-dose-rate gamma radiolysis experiments where the consumption of \( O_2 \) was monitored.

1. INTRODUCTION

Destruction of volatile and semivolatile organic contaminants in various matrices such as transformer oil, soils and water has been an important environmental issue for many years. These pollutants, which are a result of human activities, have adverse impacts on the environment and on human health. These problems have given rise to numerous research programs focused on the development of treatment (remediation) methods. The radiation-induced degradation method is shown to be an effective treatment method.

PCBs are chemically stable and they tend to bioaccumulate in living organisms [1]. Due to the bioaccumulation and toxicity of PCBs, the remediation of PCBs associated with sediment has been considered an important issue for many years. Contamination of marine sediments with hydrophobic compounds such as PCBs is present at numerous harbors, estuaries, lakes and rivers throughout the world. Approximately 10% of the sediment underlying surface of water in the United States poses health risks to fish and eventually to wildlife and humans [2].

High-energy electron treatment of matrices contaminated with organic compounds can effectively destroy contaminating compounds especially in aqueous solutions. Research performed in this laboratory and in others has demonstrated that ionizing radiation produced by gamma (\( \gamma \)) rays and high-energy electrons is remarkably effective in transforming PCBs into less problematic species. The PCBs may be reduced to inorganic chloride and biphenyl (both of which are environmentally acceptable), while the organic solvent or oil may remain practically unchanged and can be recycled. Studies have pointed to these beneficial outcomes [3, 4]. Radiolysis has been shown to effectively dechlorinate PCBs in water [5], aqueous micellar systems [6], alcohols [7], and transformer oil [3, 4]. Ultra-violet (UV) irradiation of PCB-laden transformer oils has also been shown to effectively dechlorinate PCB congeners [8].

There are few studies related to the radiolytic degradation of PCBs associated with sediment. However, due to their hydrophobicity, PCBs in organic matrices such as organic-rich sediments can only be effectively solubilized in water with the use of an organic co-solvent [9]. In the present study, the electron beam treatment of PCBs in marine sediment suspensions using isopropanol as co-solvent was studied by irradiating aqueous suspensions of marine sediments (Standard Reference Material...
Working Material

(SRM) 1944 New York/New Jersey Waterway Sediment) [10]. Basically, all of the oxidizing radicals generated by ionizing radiation are scavenged by the non-target organic compounds (i.e. co-solvent), which are present at much higher concentrations than the PCBs. However, reducing radicals, such as the solvated electron which are produced by radiolysis, selectively dissociate carbon-chloride bonds in preference to other possible competitive reactions.

Organic solvents are also frequent contaminants in aqueous streams such as ground water, drinking water, and industrial wastes and must be removed. The removal of volatile organic compounds (VOCs) from waste- and drinking-water is of long-standing interest. The Toxic Release Inventory (TRI) by EPA reports billions of pounds of toxic materials are released to the environment each year [11]. In the 2004 TRI report, 4.2 billion pounds of on-site and off-site disposal or other releases of 650 toxic compounds were reported from 23 675 facilities on EPA’s TRI program. Chlorinated olefins such as trichloroethylene, chloroform, tetrachloroethylene, methylene chloride; aromatic compounds, such as benzene, toluene, styrene, m-xylene, o-xylene and chlorobenzene; organic solvents, such as methanol, methylene ketone, hexane and formic acid, and nitro esters such as nitroglycerin, are among these pollutants. Electron beam radiation processing, with its high potential to destroy and remove organic solvents from wastewater, has overcome many of the problems that the other techniques encounter [12, 13]. Many VOCs, such as benzene, often exceed state and federal drinking water standards [14, 15]. Ozonation can be a thorough clean-up strategy though the degradation of organic compounds is fairly selective due to the low reactivity of ozone toward many target species [16]. A more general oxidant, the hydroxyl (\( \cdot \)OH) radical, is often required to react with recalcitrant organic compounds in waste- and drinking-water treatment streams [17]. This radical may be produced in the decomposition of ozone and is easily generated by the radiolysis of water.

Volatile organic compounds in aqueous solutions can be effectively destroyed by ionizing radiation without any net undesirable effects. High energy electron irradiation of water produces three primary transient species: hydrated electrons, hydroxyl radicals and hydrogen atoms. Organic compounds are ultimately converted to carbon dioxide and water. Halogenated compounds in waste streams are converted to inorganic acid, which can be removed by simple water scrubbing or neutralized prior to disposal. There is minimal residual contamination. Therefore the destruction cost is much less than competitive methods such as incineration, which has poor public approval.

Briefly, radiolysis of aqueous solutions leads to the production of hydrated electrons (e\(_{\text{aq}}^–\)), hydroxyl radicals (\( \cdot \)OH), and hydrogen atoms:

$$\text{H}_2\text{O} \rightarrow e_{\text{aq}}^–, \cdot \text{OH}, \text{H}^+, \text{H}_2\text{O}_2, \text{H}_2$$  \hspace{1cm} (1)

with the following yields in units of \( \mu \text{mol J}^{-1} \): \( G(e_{\text{aq}}^–) = G(\text{H}_2\text{O}^+) = G(\cdot \text{OH}) = 0.29; \ G(\text{H}^+) = 0.062; \ G(\text{H}_2) = 0.042; \ G(\text{H}_2\text{O}_2) = 0.082. \)

1.1. Dechlorination of PCBs in Sediment.

The radiation chemistry of dechlorination of PCBs in a non-homogeneous system such sediment slurries can not be predicted, however, a portion of the sediment-associated PCBs are extracted into the aqueous isopropanol phase and we can outline the degradation mechanisms that occur within this phase. Hydroxyl radicals react with PCBs via addition to the phenyl rings to produce various isomeric PCB adduct radicals (\( \cdot \text{ArCl(OH)} \)). The \( \text{ipso} \) isomers (resulting from the addition of \( \cdot \text{OH} \) on the same carbon that bears a Cl atom) undergo very rapid elimination of HCl to form phenoxy type radicals:

$$\text{ArCl} + \cdot \text{OH} \rightarrow \cdot \text{ArCl(OH)} \rightarrow \text{ArO}^– + \text{HCl}$$  \hspace{1cm} (2)

Addition at the \( \text{ipso} \) positions is significant with highly chlorinated PCBs but becomes less likely as the degree of chlorination is diminished. However, because hydroxyl radicals are highly reactive with most other organic compounds, degrading trace contaminants in a medium with a high background of organics is not efficient by hydroxyl radicals. On the other hand, the hydrated electron is a strong reducing agent whose reactivity depends on the availability of a suitable vacant orbital and does not react with saturated organic compounds such as hydrocarbons and alcohols. Rather, it is
preferentially captured by PCB molecules. The carbon-chlorine bond breaks very rapidly through a
dissociative electron capture process:

\[ \text{e}^{-}_{\text{aq}} + \text{ArCl} \rightarrow \text{Ar}^{+} + \text{Cl}^{-} \]  \hfill (3)

Hydrated electrons also react very rapidly \((25)\) with oxygen \(\text{e}^{-}_{\text{aq}} + \text{O}_2 \rightarrow \text{O}_2^{2-}\) and with the
\(\text{H}_3\text{O}^{+}\) formed in the radiolysis \(\text{e}^{-}_{\text{aq}} + \text{H}_3\text{O}^{+} \rightarrow \text{H}^{+} + \text{OH}^{-}\). These reactions will compete with the
dechlorination process but are easily prevented by purging the system with nitrogen and by adding
alkaline buffers. Chloride ions, typically abundant in marine sediment, may be oxidized by \(^{\cdot}\text{OH}\) radicals in acidic solutions to form \(\text{Cl}_2^{2-}\) radicals and then \(\text{Cl}_2\). Both of these species may react with
aromatic compounds to form chlorinated products, a reaction that would reverse the desired
dechlorination process. However, this is easily prevented by the addition of an \(^{\cdot}\text{OH}\) radical scavenger
like isopropanol.

PCBs that remain in association with or within the sediment phase may undergo dechlorination
by thermalized electrons that may be formed at particle sites. However, the yield of such electrons is
expected to be relatively low and, because of their limited mobility, they are effective only when
produced in the immediate vicinity of the PCB molecule. Direct effect of radiation on the PCBs, i.e.
the deposition of ionizing energy directly onto a PCB molecule, whether in the liquid or the solid
portion of the slurry, can also lead to dechlorination. The contribution of such a process, however, is
very low \([18]\) since the ionizing energy is indiscriminately absorbed in all the medium molecules.

1.2. Destruction of Organic Compounds.

The hydroxyl radical initiates the decomposition of organic compounds generally through the
creation of carbon-centered radicals through addition or abstraction reactions, and the subsequent
formation of peroxyl radicals by reaction with molecular oxygen. The degradation of benzene by \(^{\cdot}\text{OH}\) radicals in aqueous solutions, however, is more complex due, it is thought, to the reversibility of this
reaction \([19]\), and has been an on-going research focus for several decades. In addition, the peroxyl
radicals may eliminate \(\text{O}_2^{2-}\), decay by bimolecular self-reaction, undergo internal rearrangements, or
react with other solutes. In the present study, we have investigated the reaction of \(^{\cdot}\text{OH}\) with benzene in
the presence of oxygen through the use of pulse radiolysis with both conductivity and
spectrophotometry as detection techniques, and by the use of gamma radiolysis, monitoring the
consumption of oxygen in the course of the reaction. The reactions were examined as a function of
dose rate, pH, and solute concentrations.

2. EXPERIMENTAL

2.1. PCB Contaminated Sediment Slurries.

Experiments were carried out with a dry marine sediment reference material, collected from
New York/ New Jersey waterways, namely SRM 1944 \([10]\). The sediment is well-characterized for a
range of PCB congeners (naturally present in the material) (Table I). The total organic carbon in this
material is \((4.4 \pm 0.3)\) % (mass fraction).

Samples of SRM 1944 (~3 g) were mixed with 30 ml of 1:1 (v:v) buffered water/2-propanol
mixture before irradiation treatment. The aqueous medium in all these experiments contained 10 mmol
\(\text{L}^{-1}\) sodium carbonate/bicarbonate buffer (5 mmol \(\text{L}^{-1}\) of each) at pH 10.3 to neutralize the acid
produced upon dechlorination (\(\text{H}_2\text{O}^{+}\)).

Marine sediment slurries were irradiated using the University of Maryland Varian linear
accelerator capable of producing an electron beam energy range between 1 to 8 MeV. Samples were
purged for 15 min with \(\text{N}_2\) to remove oxygen and then irradiated under continuous mixing at a dose
rate of 10 Gy/pulse. The following doses were applied to triplicate samples: 0, 10, 50, 100, 200, and
500 kGy. Radiation dosimetry was performed using Far-west film techniques.
TABLE I. CERTIFIED CONCENTRATIONS FOR SELECTED PCB CONGENERS IN SRM 1944 [10].

<table>
<thead>
<tr>
<th>PCB Congeners</th>
<th>Sub. Pattern</th>
<th>Mass Fractions in ng/g (dry-mass basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 8</td>
<td>(2,4'-Dichlorobiphenyl)</td>
<td>22.3 ± 2.3</td>
</tr>
<tr>
<td>PCB 18</td>
<td>(2,2',5-Trichlorobiphenyl)</td>
<td>51.0 ± 2.6</td>
</tr>
<tr>
<td>PCB 28</td>
<td>(2,4,4'-Trichlorobiphenyl)</td>
<td>80.8 ± 2.7</td>
</tr>
<tr>
<td>PCB 31</td>
<td>(2,4,5-Trichlorobiphenyl)</td>
<td>78.7 ± 1.6</td>
</tr>
<tr>
<td>PCB 44</td>
<td>(2,2',3,5'-Tetrachlorobiphenyl)</td>
<td>60.2 ± 2.0</td>
</tr>
<tr>
<td>PCB 49</td>
<td>(2,2',4,5'-Tetrachlorobiphenyl)</td>
<td>53.0 ± 1.7</td>
</tr>
<tr>
<td>PCB 52</td>
<td>(2,2',5,5'-Tetrachlorobiphenyl)</td>
<td>79.4 ± 2.0</td>
</tr>
<tr>
<td>PCB 66</td>
<td>(2,2',4,4'-Tetrachlorobiphenyl)</td>
<td>71.9 ± 4.3</td>
</tr>
<tr>
<td>PCB 87</td>
<td>(2,2',3,4,5'-Pentachlorobiphenyl)</td>
<td>29.9 ± 4.3</td>
</tr>
<tr>
<td>PCB 95</td>
<td>(2,2',3,5',6-Pentachlorobiphenyl)</td>
<td>65.0 ± 8.9</td>
</tr>
<tr>
<td>PCB 99</td>
<td>(2,2',4,4,5'-Pentachlorobiphenyl)</td>
<td>37.5 ± 2.4</td>
</tr>
<tr>
<td>PCB 101</td>
<td>(2,2',4,5,5'-Pentachlorobiphenyl)</td>
<td>73.4 ± 2.5</td>
</tr>
<tr>
<td>PCB 105</td>
<td>(2,2',3,4,5'-Pentachlorobiphenyl)</td>
<td>24.5 ± 1.1</td>
</tr>
<tr>
<td>PCB 110</td>
<td>(2,3,3',4,6-Pentachlorobiphenyl)</td>
<td>63.5 ± 4.7</td>
</tr>
<tr>
<td>PCB 118</td>
<td>(2,2',3',4,5'-Hexachlorobiphenyl)</td>
<td>58.0 ± 4.3</td>
</tr>
<tr>
<td>PCB 128</td>
<td>(2,2',3,3',4,4'-Hexachlorobiphenyl)</td>
<td>8.47 ± 0.28</td>
</tr>
<tr>
<td>PCB 138</td>
<td>(2,2',3,4,4',5'-Hexachlorobiphenyl)</td>
<td>62.1 ± 3.0</td>
</tr>
<tr>
<td>PCB 149</td>
<td>(2,3,3',4,5,6-Hexachlorobiphenyl)</td>
<td>49.7 ± 1.2</td>
</tr>
<tr>
<td>PCB 151</td>
<td>(2,2',3,5,5',6-Hexachlorobiphenyl)</td>
<td>16.93 ± 0.36</td>
</tr>
<tr>
<td>PCB 153</td>
<td>(2,2',4,4,5,5'-Hexachlorobiphenyl)</td>
<td>74.0 ± 2.9</td>
</tr>
<tr>
<td>PCB 156</td>
<td>(2,3,3',4,4',5'-Hexachlorobiphenyl)</td>
<td>6.52 ± 0.66</td>
</tr>
<tr>
<td>PCB 170</td>
<td>(2,2',3,3',4,4',5'-Heptachlorobiphenyl)</td>
<td>22.6 ± 1.4</td>
</tr>
<tr>
<td>PCB 180</td>
<td>(2,3,3',4,4',5,5'-Heptachlorobiphenyl)</td>
<td>44.3 ± 1.2</td>
</tr>
<tr>
<td>PCB 183</td>
<td>(2,2',3,4,4',5,6-Heptachlorobiphenyl)</td>
<td>12.19 ± 0.57</td>
</tr>
<tr>
<td>PCB 187</td>
<td>(2,2',3,4,5,5',6-Heptachlorobiphenyl)</td>
<td>25.1 ± 1.0</td>
</tr>
<tr>
<td>PCB 194</td>
<td>(2,3,3',4,4',5,5'-Octachlorobiphenyl)</td>
<td>11.2 ± 1.4</td>
</tr>
<tr>
<td>PCB 195</td>
<td>(2,2',3,3',4,4',5,6-Octachlorobiphenyl)</td>
<td>3.75 ± 0.39</td>
</tr>
<tr>
<td>PCB 206</td>
<td>(2,2',3,3',4,4',5,5,6-Nonachlorobiphenyl)</td>
<td>9.21 ± 0.51</td>
</tr>
<tr>
<td>PCB 209</td>
<td>Decachlorobiphenyl</td>
<td>6.81 ± 0.33</td>
</tr>
</tbody>
</table>

For analysis, the aqueous layer of each electron beam irradiated sediment sample was decanted, and the sediment portions were extracted with the pressurized fluid extraction with hexane and acetone (50:50 v/v). The concentrated extracts were passed through silica solid-phase extraction (SPE) cartridges with 15 mL of 10% methylene chloride in hexane (v/v) and concentrated to approximately 0.5 mL as above. Calibration solutions consisting of SRMs 2262 and 2274 and three control samples, SRM 1944 as received, were also extracted using the same conditions described above [9]. The aqueous portions of the ionizing radiation samples were extracted three times by liquid-liquid partitioning with 20-mL aliquots of hexane. The aliquots were concentrated to approximately 0.5 mL, passed through silica SPE cartridges with 15 mL of 10% methylene chloride in hexane (v/v), and concentrated to a final volume of approximately 0.5 mL. These concentrated aliquots were combined with the sediment extracts and fractionated on a semipreparative aminopropylsilane liquid chromatographic (LC) column (to isolate the PCB congeners and several lower polarity pesticides).
The extracts were analyzed for the determination of the concentrations of PCB congeners using gas chromatography with mass spectrometry (GC/MS) with a relatively nonpolar column. The concentrations of PCBs determined in the control material SRM 1944 were similar to the concentrations reported on the SRM 1944 Certificate of Analysis.

### 2.2. Aqueous Solutions of Volatile Organic Compounds.

The composition of the water matrix was designed to simulate the composition of organic solvent waste streams from the pharmaceutical industry. The concentration of these compounds in water ranged from < 1 mg/g (toluene) to about 27 mg/g (dimethylformamide) (Table II). Aqueous solutions of these organic compounds were irradiated in the absence and presence of sodium carbonate. Sodium carbonate was added to increase the pH to about 10. Electron beam irradiation of organic solvents in water was performed using a chamber (~ 2 L) designed at University of Maryland to fit within the Varian linear accelerator. The chamber is made of type 304 stainless steel in order to withstand the radiation, chemical and temperature resistance required in this application. Radiation dosimetry was performed using the Fricke solution and Far-west film techniques. The samples were irradiated with dose rate of ~0.40 Gy/pulse.

The concentrations of organic compounds in water were determined by GC/MS. The organic compounds were extracted from aqueous solutions using a microextraction technique [20]. Three sub-samples, about 25 mL each (gravimetrically measured), of the water drawn from the radiation chamber at each dose were extracted with n-butanol. Specifically, each sub-sample was gravimetrically transferred to a glass amber vial and micro-extracted with 2 mL of n-butanol and about 4.5 g of sodium chloride. This extraction method is similar to EPA methods 504 and 505 [20]. Each sample was manually shaken for about 1 min. The butanol was removed from the water surface using glass pipet and transferred to an autosampler vial. A weighed aliquot of a gravimetrically prepared internal standard solution of perdeuterated or carbon-13 labeled solvents in water was added to each sample prior to extraction. Aliquots of gravimetrically prepared calibration solutions of solvents in water were extracted alongside the samples for quantification purposes. The extracts were analyzed for the determination of the concentrations of solvents in water using GC/MS (HP 6890 series) and two different columns designed for the GC analysis of volatile compounds (DB-VRX, and DB-624).

### TABLE II. ORGANIC COMPOUNDS\(^a\) IN AQUEOUS SOLUTIONS

<table>
<thead>
<tr>
<th>Organic Solvents(^b)</th>
<th>Formula Wt.</th>
<th>Quantitative GC/MS ion(^c)</th>
<th>Concentration (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>non-buffered</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH(_3)OH</td>
<td>31.35</td>
<td>10.884</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>C(_2)H(_3)N</td>
<td>41.44</td>
<td>22.413</td>
</tr>
<tr>
<td>Acetone</td>
<td>C(_3)H(_6)O</td>
<td>43.46</td>
<td>5.461</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>C(_2)H(_4)O(_2)</td>
<td>61.63</td>
<td>0.433</td>
</tr>
<tr>
<td>Toluene</td>
<td>C(_7)H(_8)</td>
<td>91.98</td>
<td>0.093</td>
</tr>
<tr>
<td>Dimethyl-formamide</td>
<td>C(_3)H(_6)NO</td>
<td>73.80</td>
<td>26.796</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>Na</td>
<td>10.69</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>CaCl(_2)</td>
<td>Na</td>
<td>10.69</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na(_2)CO(_3)</td>
<td>Na</td>
<td>Not added</td>
</tr>
</tbody>
</table>

\(^a\)solutions gravimetrically prepared with chromatographic grade water.

\(^b\)organic solvents listed in order of increasing gas chromatography retention time

\(^c\)second ion in italics is for perdeuterated or carbon-13 labeled compound (ethyl acetate)
2.3. Destruction of Benzene.

The kinetics of formation and decay of transient species were determined by spectrophotometric pulse radiolysis at the National Institute of Standards and Technology (NIST) [21]. Pulse conductometric measurements were carried out at the Gray Laboratory [22]. As stated above, radiolysis of aqueous solutions by high-energy electrons generates \( \cdot \)OH radicals, hydrated electrons (e_{aq}), and H* atoms. The yield of \( \cdot \)OH in aqueous solutions saturated with \( N_2O \) is enhanced by the conversion of e_{aq} to \( \cdot \)OH [\( N_2O + e_{aq} \rightarrow \cdot \)OH + N\(_2\) + OH\(^{-} \)]. Hence the predominant radical species in such solutions is \( \cdot \)OH (5.8 x 10\(^{-10}\) mol J\(^{-1}\)) accompanied by a much lower yield of H*. Thus the main reactions observed in \( N_2O \)-saturated aqueous solutions of benzene are those of \( \cdot \)OH radicals. The transient species formed by these reactions undergo subsequent reactions, which were studied in the presence and absence of oxygen.

The peroxyl radicals were produced in irradiated aqueous solutions saturated with a 1:1 mixture of \( N_2O \) and \( O_2 \), which results in 17 mmol L\(^{-1}\) \( N_2O \) and 0.6 mmol L\(^{-1}\) \( O_2 \). These concentrations ensure that almost all e_{aq} are converted to \( \cdot \)OH and do not react with \( O_2 \). The transient absorption spectra of the peroxyl radicals were corrected for the small contribution of \( O_2^{2•−} \) (G(\( O_2^{2•−} \)) = 0.06 \( \mu \)mol J\(^{-1}\)) that is produced by the reaction \( H^* + O_2 \rightarrow HO^•_2/O_2^{•−} \) (\( k = 2 \times 10^{10}\) L mol\(^{-1}\) s\(^{-1}\)) [23]. Since benzene used in this study is volatile and escape from the aqueous solution upon bubbling with the gas mixture, all solutions were first saturated with the gases and then the appropriate amount of the organic compound was added and the solution was kept under an atmosphere of the gas mixture without bubbling (or, for \( O_2 \) consumption measurements, the vessel was sealed).

A standard Clark oxygen electrode (Orion), fitted in an airtight irradiation vessel, was used to measured oxygen concentration changes before, during, and after irradiation. The concentration of oxygen was adjusted by varying the partial pressure of oxygen in \( N_2O/O_2 \) and \( N_2/O_2 \) mixtures.

The yield of \( O_2^{2•−} \) formed from peroxyl radicals was determined by conductometric and spectrophotometric methods. Two spectrophotometric methods were used in this study: (1) direct monitoring of the absorption of \( O_2^{2•−} \) at pH (9-10.3) at 245 nm (molar absorption coefficient \( \varepsilon^{245} = 2350\) L mol\(^{-1}\) cm\(^{-1}\)) [24], and (2) an indirect method, by using tetranitromethane, which reacts with \( O_2^{2•−} \) (\( k = 1.9 \times 10^{8}\) L mol\(^{-1}\) s\(^{-1}\)) to produce nitroform anion, C(NO\(_4\))\(^{−} \), and then monitoring the absorption at 350 nm (molar absorption coefficient \( \varepsilon^{350} = 15 000\) L mol\(^{-1}\) cm\(^{-1}\)) [25].

\[
C(NO_2)_4 + O_2^{•−} \rightarrow C(NO_2)_3^{−} + NO_2 + O_2
\]

In these experiments, precautions were taken to avoid direct reaction between e_{aq} and C(NO\(_2\))\(_4\) by maintaining [C(NO\(_2\))\(_4\)] much smaller than [\( N_2O \)] and [\( O_2 \)].

For measuring the dose per pulse, the SCN\(^{-} \) method was used, taking \( \varepsilon^{480} = 7600\) L mol\(^{-1}\) cm\(^{-1}\) and \( G(\text{SCN})^{2•−} = 0.68\) \( \mu \)mol J\(^{-1}\).

3. RESULTS AND DISCUSSION

3.1. PCB Contaminated Sediment.

Samples of SRM 1944 were mixed with an aqueous alcohol solution and irradiated with an electron beam under continuous stirring in an airtight flask [9]. During this process, some PCB congeners are extracted into the liquid phase and undergo dechlorination within that phase; the rest remain within the sediment and undergo dechlorination either within the solid phase or at the interface. After the irradiation, solvent extracts of PCBs from both media were combined and analyzed using GC/MS. The results for individual PCB congeners indicate that the concentrations of PCBs in electron-irradiated sediment samples decrease as a function of dose. Figure 1 shows the decrease in concentration of hexachlorobiphenyls as a function of dose. The total dechlorination of PCBs upon 500 kGy is shown in Figure 2. The results indicate 83% decrease in total PCBs concentrations. The relatively low radiation yield is likely due to the fact that some of the PCBs remain within the solid phase and do not react with e_{aq} formed in the liquid phase.
Scavenging of $e_{aq}^-$ by the protons formed upon radiolysis is prevented by the use of the carbonate buffer, which keeps the solution at pH > 7. Other compounds present in the sediment, which may react with $e_{aq}^-$, are metal ions present in the sediment. Since all of these ions react with hydrated electron very rapidly and these assumed concentration are higher than the concentration of PCBs, it is likely that large fraction of hydrated electrons are scavenged by the metal ions.


Some of pharmaceutical waste streams generally contain organic components including, solvents such as acetonitrile, acetone, toluene, ethyl acetate, dimethylformamide, and methanol at various concentrations (Table II). These solvents react with $^\cdot$OH, $e_{aq}^-$ and H at various reaction rate constants. Radiation-induced destruction of these organic compounds in aqueous solutions was investigated. Experiments were carried out in the presence and absence of carbonate.

FIG. 1. Concentrations (ng g$^{-1}$) of Hexachlorobiphenyls (PCB 151, PCB 149, PCB 153, PCB 138, PCB 128 and PCB 156) in Electron Beam Irradiated slurries of SRM 1944 (New York/New Jersey Waterway) Sediments as a Function of Dose (kGy).

The concentrations of all six organic compounds decreased upon 500 kGy dose. Percent change of organic compounds range from about 8 % for acetonitrile to 82 % for acetone in the non-buffered solution, and 7 % for acetonitrile to 91 % for acetone in buffered solution.

3.4. Radiolytic Oxidation of Benzene in the Presence of Oxygen.

Benzene reacts with $^\bullet$OH radicals ($k = 7.8 \times 10^9$ L mol$^{-1}$ s$^{-1}$) [26] to form the hydroxycyclohexadienyl radical, HOC$_6$H$_6$$^\bullet$, which absorbs at 315 nm. The OH-adduct radical decays by second-order self-reactions but the decay is accelerated and becomes first-order in the presence of O$_2$.

The rate of first-order decay at 315 nm increases linearly with [O$_2$] and from the slope of the line we derive a rate constant of $(3.3 \pm 0.4) \times 10^8$ L mol$^{-1}$ s$^{-1}$, in agreement with the previous result [27].

The reaction of the OH-adduct with O$_2$ can be monitored also at 265 nm, where the peroxyl radical produced, HOC$_6$H$_6$O$_2$$^\bullet$, has a higher absorption coefficient than HOC$_6$H$_6$$^\bullet$. The absorbance at 265 nm which therefore represents the concentration of HOC$_6$H$_6$O$_2$$^\bullet$ exhibits a fast buildup over 30 μs; it is followed by a much slower buildup, which reaches a plateau at ~300 μs after the pulse [27]. The slow buildup follows first-order kinetics with a rate constant of $(9.6 \pm 1.3) \times 10^3$ s$^{-1}$ at a dose of 14 Gy per pulse. The spectrum at the end of the slow buildup exhibits a peak at 265 nm. The differential UV spectrum of the stable products in the pulse-irradiated solution (not shown) also exhibits a similar peak, suggesting that the products formed at ~300 μs after the pulse are stable products. The spectrum of the final products as determined by spectrophotometry is identical to that of phenol, and indeed, phenol has been reported as one of the major radiolytic products in this system. Phenol is formed from the peroxyl radical by elimination of O$_2$$^\bullet$. 

![Graph showing the total dechlorination of PCBs in aqueous/isopropanol slurries of marine sediment and formation of biphenyl as a function of dose.](image-url)
At a much lower dose rates, the kinetics of the formation of $O_2^-\cdot$ (reaction 5) was simultaneously followed at 245 nm and by conductometry at basic and natural pH in 1:1 N$_2$O/O$_2$-saturated solutions (Figure 3a). At 245 nm $O_2^-\cdot$ exhibits an absorption peak with a molar absorption coefficient of 2350 L mol$^{-1}$ cm$^{-1}$, which is twice as intense as the absorbance of HOC$_6$H$_5$O$_2^-\cdot$ ($\varepsilon_{245} = (1100 \pm 110)$ L mol$^{-1}$ cm$^{-1}$). The buildup observed at 245 nm follows first-order kinetics with a rate constant of $(3.5 \pm 0.5) \times 10^3$ s$^{-1}$ at 2.5 Gy per pulse. These results demonstrate that the observed $O_2^-\cdot$-elimination reaction at higher dose rate (9.6x10$^3$ s$^{-1}$ at 14 Gy per pulse) includes a significant contribution from bimolecular decay.

Figure 3a also shows a concurrent change in conductivity. The fast decrease in conductivity is attributed to partial formation of HO$_2^-\cdot$ by the reaction $H^+ + O_2 \rightarrow$ HO$_2^-\cdot$, and the subsequent reaction of HO$_2^-\cdot$ ($pK_a = 4.7$) with OH$^-$ at pH 9.7. Since OH$^-$ is replaced by $O_2^-\cdot$, which has a much lower conductance ($65 \ \Omega^{-1} cm^2$ equiv$^{-1}$ vs. $182 \ \Omega^{-1} cm^2$ equiv$^{-1}$ at 21°C), the overall conductivity of the solution decreases. It should be mentioned that $O_2^-\cdot$ is very long-lived in alkaline solutions $[2k \sim 10^3 L \ \Omega^{-1} cm^{-1} s^{-1} \ \text{at} \ \text{pH} \sim 10]$ so that its disappearance does not play a role in our experiments. The slower decrease in conductivity takes place with a rate constant of $(3.0 \pm 0.5) \times 10^3$ s$^{-1}$, which is in agreement with the slow buildup observed at 245 nm, $(3.5 \pm 0.5) \times 10^3$ s$^{-1}$. Elimination of $O_2^-\cdot$ is known to be base-catalyzed, involving deprotonation (HOC$_6$H$_5$O$_2^-\cdot$ + OH$^-$ $\rightarrow$ OC$_6$H$_5$O$_2^-\cdot$) followed by release of $O_2^-\cdot$. This leads to the observed decrease in the conductivity. The $O_2^-\cdot$-elimination process becomes unimportant at high dose per pulse and at natural pH. In fact, at very high dose per pulse the decay at 245 nm followed second-order rate law, representing the self-reaction of HOC$_6$H$_5$O$_2^-\cdot$ (Figure 3b).

$G(O_2^-\cdot)$ was measured using the conductivity and the tetrabromomethane methods. As shown in Figure 4, $G(O_2^-\cdot)$ decreases as the dose per pulse increases in pulse irradiated aqueous solution of benzene saturated with N$_2$O/O$_2$ at pH 9.3 - 10. Figure 4 also shows that the two methods give very similar results. The decrease in $G(O_2^-\cdot)$ with increasing dose per pulse is due to enhanced probability of second-order decay of the HOC$_6$H$_5$O$_2^-\cdot$ radical.

Radiolytic consumption of oxygen, $G(-O_2)$, is an important tool for elucidating peroxy radical reaction mechanisms. Experiments were carried out under a steady-state radiolysis condition using a $^{60}$Co-source at comparatively low dose rate, 2.7 Gy min$^{-1}$. The solutions were at natural pH (~ 6.5 - 7) and contained various concentrations of benzene and $1 \times 10^{-5}$ mol L$^{-1}$ EDTA and were saturated with N$_2$O/O$_2$ mixtures; the purpose of the EDTA was to complex possible Fe$^{3+}$ contamination that might raise extraneous OH. The total dose used consumed less than half of the O$_2$ initially present in the solution and the decrease in [O$_2$] was linear with dose. Under these conditions, the steady-state radical concentration is very low and secondary radical-radical reactions are less likely. Thus, we would expect the system to be dominated by the equilibrium 2, -2, followed by reaction 3, the elimination of O$_2^-\cdot$ and production of phenol. The O$_2^-\cdot$ could disproportionate, react with the OH-adduct, or react with the peroxy radical, HOC$_6$H$_5$O$_2^-\cdot$. These latter two reactions likely lead to the formation of
hydroperoxides. Since the disproportionation of $\text{O}_2^{•−}$ produces $\text{O}_2$ and $\text{H}_2\text{O}$, this suggests that the maximum value of $G(-\text{O}_2)$ would be $G(\text{OH}) − G(\text{O}_2^{•−})/2$, i.e. 0.58 $\mu$mol J$^{-1}$ minus half the contribution of the elimination reaction 5. Our results show (Figure 4b), however, that at all benzene concentrations used in this study, $G(-\text{O}_2)$ is at least 0.58 $\mu$mol J$^{-1}$ and that it increases substantially with the concentration of benzene. At concentrations of less than 5 mmol L$^{-1}$, $G(-\text{O}_2)$ is about 0.6 $\mu$mol J$^{-1}$; above this concentration the G-value increases rapidly to about 2 $\mu$mol J$^{-1}$. These results strongly suggest that in addition to $\text{O}_2^{•−}$-elimination, peroxyl radicals react with benzene to lead to further consumption of oxygen. The only likely reaction with benzene is addition.

\begin{equation}
\text{H}_\text{O} \text{OH} \rightarrow \text{H}_\text{O} \text{O} \cdot \text{H}
\end{equation}

The carbon-centered radical thus formed can itself react with oxygen, forming a new peroxyl radical, which can further react with benzene, propagating the chain.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure}
\caption{Absorbance and Conductivity of the reaction products.}
\end{figure}

\textit{a)
b) FIG. 3. Pulse radiolysis of N$_2$O/O$_2$-saturated aqueous solutions of 20 mmol L$^{-1}$ benzene.
(a) Time dependence of the absorption at 245 nm and conductivity change following 30 ns pulse at pH 10, 2.4 Gy per pulse.
(b) Bimolecular decay of *O$_2$C$_6$H$_5$OH peroxyl radicals at 245 nm, following 20 ns pulse, 40 Gy per pulse.

a)
b. FIG. 4. Radiolysis of N$_2$O/O$_2$-saturated aqueous solutions of benzene.
(a) $G(O_2^*)$ as a function of dose per pulse in pulse irradiated 20 mmol L$^{-1}$ benzene, at pH 9.3 – 10.
(b) $G(-O_2)$ as a function of [benzene] under gamma-radiolysis at pH 6.6-7, dose rate 2.7 Gy min$^{-1}$. 
REFERENCES


CONTROL AND MONITORING SYSTEMS FOR ELECTRON BEAM FLUE GAS TREATMENT TECHNOLOGY

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Abstract

The reliable and accurate measurements of gas parameters in essential points of industrial plant are necessary for its proper operation and control. Natural flue gases there are only at the inlet. At other points of plant gas parameters are strongly modified by process control system. The principal role of process monitoring system is to provide the Computer System for Monitoring and Control with continuous recording of process parameters. The main goal of control system is to obtain the optimal \( \text{SO}_2 \) and \( \text{NO}_x \) removal efficiencies by control of amount of spray water at the spray cooler, amount of \( \text{NH}_3 \) injection to flue gas and adjustment of electron beam current. The structure of the process control system is based on algorithms describing functional dependence of \( \text{SO}_2 \) and \( \text{NO}_x \) removal efficiencies. The best available techniques should be applied for measurements of flue gases parameters at essential points of installation and for digital control system to assist plant operators in the analysis and optimization of plant operation, including integrated emission control.

1. INTRODUCTION

The electron beam flue gas treatment technology was developed in 1972 in Japan [1]. Research on the process has been carried out in laboratory and pilot plants in Japan [2], USA [3], Germany [4] and Poland [5]. It should be noted that IAEA has also played an important role in the development of this technology. The experiences gained during these studies have allowed the preparation of full-scale industrial plant designs. This technology has already been implemented in three industrial plants: two in China at Thermal Power Plants (TPP) Chengdu and Hangzhou and one in Poland at Electric Power Station (EPS) Pomorzany. Table I presents the main parameters of these plants.

<table>
<thead>
<tr>
<th>Table I. Main Parameters of Industrial E-Beam Installations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>Flue gas flow rate</td>
</tr>
<tr>
<td>Inlet flue gas temperature</td>
</tr>
<tr>
<td>Inlet ( \text{SO}_2 ) concentration</td>
</tr>
<tr>
<td>Inlet ( \text{NO}_x ) concentration</td>
</tr>
<tr>
<td>( \text{SO}_2 ) removal efficiency</td>
</tr>
<tr>
<td>( \text{NO}_x ) removal efficiency</td>
</tr>
<tr>
<td>Electron beam parameters</td>
</tr>
</tbody>
</table>

Monitoring and control system for industrial plant as well as applicable analytical methods are the goal of the paper. This paper is based on the designs of these systems prepared for Polish industrial plant. The designs were presented during the special Meeting IAEA in Vienna and then implemented in the constructed plant. During the five-year operation of the plant these systems were verified. The paper presents final version of the requirements for these systems.
2. MONITORING SYSTEM

Increasingly stringent environmental regulation combined with power industry deregulation has forced utilities to improve operating efficiencies of their units in an effort to reduce overall operating costs and minimize pollutant emissions. The emissions from an individual stationary source should not exceed the legislated limit. When fossil fuel with high sulfur content is burnt in the boiler then high \( \text{SO}_2 \) and \( \text{NO}_x \) concentrations are present in the flue gas. The postcombustion technologies should be used for reduction of both pollutants. The electron beam flue gas treatment (EBFGT) technology ensures simultaneous removal of \( \text{SO}_2 \) and \( \text{NO}_x \) with high removal efficiencies under optimal conditions for this process realization. The monitoring and control system is extremely important for achieving a successful operation of the plant. The principal role of process monitoring system is to provide the Computer System for Monitoring and Control with continuous recording of the process parameters and evaluation of the emission. The industrial plant is designed for continuous operation with small number of staff. The general tasks of the monitoring system are:

- continuous, reliable and precise measurements parameters of flue gases, electron beams and reagents adding to the flue gas having direct influence on the efficiency of \( \text{SO}_2 \) and \( \text{NO}_x \) removal as well as on the operation of the whole industrial plant,
- acquisition and visualization of process parameters. Visualization of flow charts on high-resolution monitor including visualization of regular updated measurement data,
- storage and evaluation of process parameters, media consumption and pollutants emission from plant. Data acquisition and processing should be performed automatically and the report from plant emission should be sent directly to the regulatory authority for checking. Preparation of reports (obligatory or on request).

The presentation of all data should take place in the control room of the plant on high-resolution monitors and on videoscreen. Furthermore presentation takes place in the operator station for boilers and in the ecological department of EPS. Fig. 1 presents the scheme of the process monitoring and control system of the industrial plant.

The electron beam flue gas treatment process is realized in the following technological steps:

- inlet where initial parameters of flue gases should be determined,
- spray cooler where humidification and cooling the gases is performed,
- ammonia dosage to flue gases,
- irradiation of flue gases in the process vessel by high-energy electron beams from two accelerators,
- precipitation of by-product using electrostatic precipitator,
- outlet where final parameters of purified flue gases should be determined.

In each of the above steps the monitoring and control system realizes specific tasks. The actual values of process parameters, determined by monitoring system, are employed for the technological modification realized by control system. The information from monitoring system can be used to enhance process data and to allow feedback and feedforward control in the plant as well are useful for boiler operators.
2.1. Organization of monitoring system

In the plant inlet the following gas parameters should be measured: flow rate, temperature, pressure, humidity, particulate and concentration of SO₂, NO/NOₓ and O₂. Gas composition strongly depends on the combustion conditions in the boiler and quality of used fuels. It is recommended that the fly ash content in the flue gases at plant inlet should be lower than 50 mg/Nm³. High particulate concentration will complicate plant operation as well as decrease the quality of obtained by-product. Normally the SO₂ and NOₓ concentrations are high and exceed the allowed emission levels. Electron beam flue gas treatment process is applied for simultaneous removal of SO₂ and NOₓ from flue gases. The gas humidity and temperature should be modified in spray cooler to achieve optimal conditions for their irradiation in the process vessel. In the spray cooler atomized water is injected into flue gases by means of dual fluid air-water nozzles. The parameters of water and compressed air supplied nozzles and obtained gas temperature and humidity at outlet of spray cooler should be recorded. If the obtained gas humidity is lower than the required optimal value then water steam should be additionally injected to spray cooler and its parameters should be recorded. Near stoichiometric amount ammonia is injected to the humidified flue gases before their inlet to process vessel. Such gas mixture is irradiated in the process vessel. Two-stage irradiation enhances NOₓ removal from flue gases.

The flow rate of flue gases at the inlet to process vessel and applied electron beams current are necessary for calculation of irradiation dose. The flue gas leaving the process vessel contains a mixture of ammonium sulfate and ammonium nitrate. The particles are generally small and hygroscopic. It was found in the Indianapolis and Nagoya Pilot Plants that an electrostatic precipitator (ESP) is the most effective collector of this by-product. After the by-product is collected it will go to a granulator for processing and ultimately to storage and shipment to users. The final parameters of purified flue gases are determined at the plant outlet. The outlet concentrations of SO₂, NO/NOₓ, O₂, NH₃ and fly ash content are important process parameters. These values are used for determination of the obtained SO₂ and NOₓ removal efficiencies and for control plant operation. Additionally these values are used for preparation of the obligatory ecological report delivered by modem to provincial environmental agency. Many countries such as Germany, the UK and the USA have set reporting formats. In addition to this individual utilities may have to produce internal reports. Conversion to standard temperature and pressure, the reference value of O₂ and on dry basis may be required within Europe, whereas in the USA the emissions are reported in terms of mass flow or mass emitted per kJ of thermal input.
3. CONTROL SYSTEM

The general tasks of the control system are:

- on-line adjustment of control parameters,
- supervision and control of process parameters under normal, transient, alarm and breakdown condition,
- signaling and registering of the alarm states.

Digital control system is used to store measured data and to assist plant operator in their analysis and optimization of plant operation. Effective control of the plant can improve the removal efficiencies of SO$_2$ and NO$_x$ from flue gas. Many component of the industrial plant are equipped with its own control system and energy saving operation system, for example electron accelerators and ESP. All individual sub-systems of the plant are tied together and are controlled as a unit to ensure successful operation of the plant and to meet environmental standards and regulations. The structure of the process control system is based on algorithms describing functional dependence of SO$_2$ and NO$_x$ removal efficiencies.

3.1. Control of spray cooler operation.

The flue gases leaving the coal-fired boiler and its ESP have high temperature (usually above 120°C) and low humidity (4-6% vol.) Fig. 2 presents the dependence of SO$_2$ and NO$_x$ removal efficiencies on gas humidity.

![Graph](image)

*FIG. 2. Effect of moisture on NO$_x$ and SO$_2$ removal efficiencies [6].*

The optimal removal efficiencies of both pollutants are obtained for gas humidity greater than 11% vol. More complicated are dependencies of SO$_2$ and NO$_x$ removal on gas temperature (Fig.3 [6]). SO$_2$ removal efficiency strongly increases with lowering gas temperature. This contrasts with NO$_x$ removal which increases with the increase of gas temperature. Then the gas temperature at the outlet of spray cooler should be chosen depending on requested SO$_2$ and NO$_x$ removal efficiency from flue gases.
Humidification and cooling of the flue gases is performed in a spray cooler. Atomized water is injected into flue gases by means of dual fluid air-water nozzles. The spray cooler is operated with a dry bottom, i.e. all of the water droplets injected into the flue gases are evaporated. The amount of sprayed water (FRQ-2.4) is controlled by the gas temperature at the outlet of spray cooler (TRC-3.1). The pressure of compressed air (PRC-2.2) should be greater than the pressure of hot water (PR-2.3) delivered to nozzles. The nozzle producer determines the relationship between these pressures. This relationship should take into account the controller $X_3$ that controls the pressure of air. The amount of sprayed water is sufficient for the reduction of flue gases temperature to requested value but may not be enough to increase the humidity to 11% vol. Therefore in the bottom part of the spray cooler, the water steam is added. The amount of added steam is controlled by humidity control system (MRC-3.2). The measurement of the pressure drop between the inlet and the outlet of spray cooler is used for control operation of the whole spray cooler. At the bottom of the cooler may collect some water (in case of non proper dispersion of water by nozzles) and fly ash carried by flue gases. These deposits may increase the measured pressure drop. If this value is higher than permissible one, then alarm signal arrives in Computer Control System.

3.2. Control of ammonia dosage to flue gases.

Fig. 4 presents dependence of $\text{SO}_2$ and $\text{NO}_x$ removal efficiencies on ammonia stoichiometry.
FIG. 4. Effect of ammonia on removal of NO\textsubscript{x} and SO\textsubscript{2} [6].

The optimal removal efficiency of both pollutants are obtained for ammonia stoichiometry greater than 0.9. In general two types of process control are employed for control of ammonia dosage system: feedforward and feedback. In feedforward control the required amount of ammonia is calculated from the inlet SO\textsubscript{2} and NO\textsubscript{x} concentration, the flue gases flow rate and the required NH\textsubscript{3} stoichiometry. Due to the fact that the SO\textsubscript{2} and NO\textsubscript{x} removal efficiency is never 100% (due to imperfect mixing of the NH\textsubscript{3} with the NO\textsubscript{x} and SO\textsubscript{2} for example), a fraction of the NH\textsubscript{3} remains unreacted and exits in the plant outlet (the so-called ammonia slip). In practice it is desirable to keep the ammonia slip as low as possible due to the environmentally harmful effect of ammonia. In feedback control the ammonia dosage is controlled on the basis of outlet SO\textsubscript{2}, NO\textsubscript{x} and NH\textsubscript{3} concentrations. The ammonia dosage to the flue gases is controlled by controller X\textsubscript{1} employed combined system: a feedforward control ensures a fast system response, while the NH\textsubscript{3}/(NO\textsubscript{x}+SO\textsubscript{2}) ratio is automatically fine-tuned by means of the measured outlet NH\textsubscript{3}, NO\textsubscript{x} and SO\textsubscript{2} concentrations. In the Polish industrial plant part of ammonia is dosing to the spray cooler and the rest is adding to the flue gases before their inlet to process vessel. The optimal SO\textsubscript{2} removal efficiency was obtained when the half of NH\textsubscript{3} is adding to spray cooler [7].

3.3. Control of electron beam flue gases irradiation in the process vessel.

Flue gases are irradiated in process vessel by high-energy electron beam from two accelerators. Fig. 5 presents the dependence of SO\textsubscript{2} and NO\textsubscript{x} removal efficiencies on dose.

FIG. 5. Dose dependence of SO\textsubscript{2} and NO\textsubscript{x} removal efficiencies.

It is necessary to apply a high dose to obtain a high NO\textsubscript{x} removal. NO\textsubscript{x} removal is a radiation-induced process. The SO\textsubscript{2} removal is based on two different pathways: thermochemical oxidation and a radiation-induced process. At zero doses, the SO\textsubscript{2} removal efficiency is caused by a thermal reaction of SO\textsubscript{2} and NH\textsubscript{3} in the presence of moisture. These reactions take place in the gas phase as well as in...
the surface such as those on the filter cake of the baghouse and the collector plates of the ESP. Fig. 5 shows that the optimal SO₂ removal efficiencies are obtained for doses smaller than 8 kGy.

The improvement in NOₓ removal is achieved by multi-stage irradiation and by adequate dose distribution between irradiation stages [8]. In this paper two-stage irradiation was assumed in which optimal dose distribution is following: first-stage - 56% and second-stage – 44% of total dose. Control of the electron beam irradiation process is based on dose dependency of NOₓ removal efficiency. NOₓ removal efficiency is strongly affected by inlet NOₓ concentration. Higher NOₓ removal is achieved with higher absorbed dose and with lower inlet NOₓ concentration. Controller X₂ is applied for control of irradiation process. The total accelerator electric beam current is determined by the: inlet NOₓ concentration, the required NOₓ removal efficiency and the flow rate of flue gases at inlet to process vessel. This is feedforward control. In feedback control, the actual outlet NOₓ concentration is compared with requested NOₓ concentration and adjusted.

The electron beams with the moderate electron energy and high beam power should be applied for irradiation of flue gases. In the Chengdu Industrial Plant, two accelerators of 800 keV x 400mA with one power supply from Nisshin High Voltage Co. (Japan) are installed. Such system is delivered with own computerized control system.

4. ANALYTICAL METHODS.

For monitoring and controlling of the EBFGT process, the reliable and accurate measurements of flue gases composition at the essential points of e-b installation are indispensable. In the selection of measuring equipment it is necessary to consider the specifics of treatment process. The parameters of flue gases emitted from coal-fired boiler and dusted by ESP are monitored at the plant inlet. In the spray cooler the humidity of flue gases increases to level 10-12 % vol. and gas temperature is lowered. The elevated humidity complicates the gas analysis both at the outlet of humidifier and the subsequent ones. Ammonia is injected to flue gases before their inlet to process vessel. At the process vessel an essential changes of flue gases composition occurs as a result of thermochemical and radiation-induced processes. The gases leaving the irradiation vessel are a multicomponent three–phase system. The gas phase is characterized by significantly reduced SO₂ and NO concentrations, a slightly increased NO₂, the presence of unreacted NH₃, a small concentration of nitrous oxide N₂O (a gas treatment by–product) and nearly unchanged CO₂, CO, O₂, N₂ and water vapour content. The liquid phase consists of sulfuric acid and nitric acid aerosols. The solid phase is formed of by-product particulates of ammonium sulphate and nitrate. At the ESP about 99 % of by-product and significant amount of liquid phase are removed. The parameters of purified flue gases are monitored at the plant outlet.

Measurements of gas composition at this point are extremely difficult for the following reasons: low gas temperature and its high humidity, the presence of unreacted NH₃ and content of fine particulates of by-product which are hygroscopic and are of submicron size [9]. For minimalization of these negative influences, the extractive gas analysis system should be equipped with the following special components:

− sample probe should be equipped with heated gas filter with proper pore size. Gas filter should be kept at the temperature above acid dew point of flue gases and it should be regularly cleaned (blowback of dry and hot inert gas).
− hot ammonia scrubber for removing gaseous ammonia from purified flue gases. It should be installed at the outlet of gas filter.
− sample transporting line should be kept at temperature above acid dew point of flue gases.
− in the sample conditioning unit, water vapour should be carefully removed from sample gas and the condensate should be automatically discharged by pumping it off. In the conditioning unit the acid filter should be used.

All the measuring devices, installed at industrial plant, should satisfy the following requirements:
Working Material

- each component of monitoring system should be selected in order to ensure high precision, selectivity and long-term stability,
- each set-up should adapted for uninterrupted and unattended operation,
- the availability of each measuring set-up higher than 90 %,
- analog output – current signal 4-20 mA,
- simple method of calibration,
- manufacturers of installed gas analyzers systems should have at least one of certificates such as ISO, EPA, TUV, MCERTS for offered instrumentations.
- the monitoring system should comply with national environmental standards, especially the measurements of gas composition at the plant outlet which are used by environmental agencies for analysis of ecological noxiousness of leaving flue gases.

The best available techniques should be used for measurement of flue gas parameters in the industrial plant. From the experiences gained during Kawęczyn pilot plant and Pomorzany industrial plant operation the following measuring devices are recommended for application (Table II).

**TABLE II. ANALYTICAL METHOD RECOMMENDED FOR APPLICATION IN THE INDUSTRIAL PLANT.**

<table>
<thead>
<tr>
<th>Flue gases parameter</th>
<th>Measuring method</th>
<th>Measuring device</th>
<th>Special requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>in-situ</td>
<td>Annubar (multiple-point Pitot tube) or ultrasonic flow meter</td>
<td>correction for flue gases temperature, pressure and humidity, regular blowback of the probe</td>
</tr>
<tr>
<td>Dust concentration</td>
<td>in-situ</td>
<td>Double-pass transmissometer for high dust concentration and back scatter device for low-level concentration</td>
<td></td>
</tr>
<tr>
<td>SO₂ concentration</td>
<td>extractive</td>
<td>Pulsed U.V. fluorescence analyzer or NDUV analyzer or NDIR analyzer</td>
<td></td>
</tr>
<tr>
<td>NO/NOₓ concentration</td>
<td>extractive</td>
<td>Chemiluminescence NO-NO₂-NOₓ analyzer or NDIR analyzer with NO₂-NO converter</td>
<td></td>
</tr>
<tr>
<td>H₂O concentration</td>
<td>in-situ</td>
<td>Diode laser spectrometer in the IR spectrum</td>
<td>application of heated device to avoid water condensation on lenses</td>
</tr>
<tr>
<td>NH₃ concentration</td>
<td>in-situ</td>
<td>Diode laser spectrometer in the IR spectrum</td>
<td>application of heated device to avoid water condensation on lenses</td>
</tr>
</tbody>
</table>
Periodic verification of continuous measurement of the main pollutants should be performed using Standard Reference Methods (SRMs) specific for each pollutant [10]. The SRMs are also used for calibration of the in-situ gas analyzers. Figures 6 and 7 present the control room and the scheme of Polish industrial plant at EPS Pomorzany.

FIG. 6. Control room at EPS Pomorzany.
5. CONCLUSION

Electron beam flue gas treatment process ensures simultaneous removal of SO$_2$ and NO$_x$ from flue gases. High removal efficiencies of both pollutants are obtained at optimal conditions for process realization. The monitoring and control systems are extremely important for achieving successful operation of the plant. The monitoring system should provide reliable and accurate measurements of gas parameters in essential points of industrial plant. The best available analytical techniques should be applied. Actual values of process parameters are employed by control system for their technological modification to ensure optimal conditions for electron beam irradiation of flue gases in the process vessel. The above requirements for monitoring and control systems are based on the experiences gained during operation of Kawęczyn pilot plant and Pomorzany industrial plant.
REFERENCES

TECHNICAL ASPECTS OF FLUE GAS IRRADIATION

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Abstract

Removal of SO\textsubscript{2} and NO\textsubscript{x} from flue gases in fossil-fueled power plants by irradiation with accelerated electrons was first investigated in Japan more than 30 years ago. This process has since been extensively evaluated in several pilot facilities in Japan, the USA, Germany, Poland, Bulgaria and China. Recently, it has advanced to the demonstration plant stage in Poland, Japan and China. Except for the initial research facility in Japan, which had a 5.5 MeV microwave linear accelerator, these facilities have used relatively low-energy dc accelerators rated from 0.3 MeV to 0.8 MeV. An attractive feature of such accelerators is their high electrical efficiency, which can exceed 90%. However, the electron beam power dissipated in the two titanium beam windows, the first on the accelerator and the second on the flue gas duct, and in the air space between the windows must also be taken into account. These beam power losses have been calculated as 54% at 0.50 MeV and 28% at 0.75 MeV, but they decrease further to 17% at 1.0 MeV, 9.3% at 1.5 MeV, 6.7% at 2.0 MeV, 5.2% at 2.5 MeV and 4.6% at 3.0 MeV. The use of accelerators providing electron energies higher than 0.75 MeV could facilitate the generation and delivery of the high beam current and beam power requirements for large electric power plants, which are about 1% to 2% of the electrical power output of the plant. Most of the pilot and demonstration facilities have used ammonia gas to neutralize the acid vapors produced during the irradiation process. The resulting by-products are ammonium sulfate and ammonium nitrate, which have value as agricultural fertilizers. On the other hand, two pilot facilities, one in the USA and the other in Japan, have shown that slaked lime (calcium hydroxide) is a possible alternative to ammonia. The resulting by-products in this case are calcium sulfate and calcium nitrate, which can be used as soil amendments or to make gypsum board (drywall) for interior construction in homes and industrial buildings. In contrast to ammonia, slaked lime gives somewhat different results from the irradiation process. It is more effective in removing nitrogen oxides, whereas ammonia is more effective in removing sulfur dioxide. For power plants which are already equipped with wet limestone scrubbers for sulfur dioxide, the addition of an electron beam facility with lime neutralization could be a more attractive way to remove the residual nitrogen oxides than selective catalytic reduction. The calcium nitrate so produced would be a safer by-product than ammonium nitrate with a low concentration of ammonium sulfate, which could be mixed with fuel oil to make an explosive material.

1. INTRODUCTION

The electron beam flue gas irradiation process was originally demonstrated in Japan during the 1970s [1, 2]. The Ebara Corporation cooperated with the Japan Atomic Energy Research Institute to develop and implement this process, which can remove both sulfur dioxide and nitrogen oxides. Since then, it has been extensively evaluated in several pilot facilities in Japan, the USA, Germany, Poland, Bulgaria and China. The design and performance data of the Ebara pilot facility at the Indianapolis Power and Light Co. in Indianapolis, Indiana USA, have been presented in detailed reports [3-6]. The favorable results from all of these studies have justified the construction of larger demonstration facilities in Poland, China and Japan to irradiate flue gases from coal-fired power plants [7-12].

Except for the initial research facility in Japan, which had a low-power 5.5 MeV microwave linear accelerator, and the pilot facility in Karlsruhe, Germany, which used an extended-beam, 0.3 MeV direct current (dc) accelerator, all of the other pilot facilities have used dc accelerators with scanning beams and electron energies of about 0.7 MeV to 0.8 MeV. Flexible high-voltage cables can be used in this energy range to connect the high-voltage generators to the electron accelerators, thereby reducing the space needed for the shielded irradiation equipment. Electron beam power ratings for these pilot facilities have been in the range of 40 kW to 80 kW per accelerator.

Generators and accelerators with much higher beam power ratings have been developed for the demonstration facilities. The Chengdu EBA installation at the Huaneng Chengdu Thermal Power Plant and the Hangzhou EBA installation at the Hangzhou Xietlan Thermal Power Plant are each equipped with two accelerators rated for 320 kW of beam power at 0.8 MeV. The Jingfeng Thermal Power Plant near Beijing is equipped with two accelerators, each rated for 500 kW at 1.0 MeV, and one rated for 300 kW at 1.0 MeV. The EPS Pomorzany power plant in Szczecin, Poland, is equipped with four
electron accelerators, each designed for 300 kW at 0.75 MeV. These have been operated continuously with 260 kW at 0.7 MeV to provide a total electron beam power of slightly more than 1000 kW.

The average absorbed dose in the flue gas is in the range from 5 kGy to 10 kGy, depending on the composition of the gas and the desired SO$_2$ and NO$_x$ removal efficiencies. This dose requires an absorbed electron beam power in the range from 1% to 2% of the electrical power output of the plant. In the USA, the average capacity of new coal-fired power plants under construction or recently proposed is in the range from 500 MW to 600 MW [13]. A 500 MW coal-fired plant would need from 5 MW to 10 MW of absorbed electron beam power. Assuming 500 kW per accelerator, a plant of this size would require at least 10 to 20 accelerators, and somewhat more to compensate for the losses in transmitting the electron beam into the flue gas. These very high power requirements for treating flue gases present an opportunity to utilize even more powerful accelerators, which could reduce the total capital cost of the irradiation facility by reducing the number of accelerators and their ancillary equipment.

2. ADVANTAGES OF HIGHER ELECTRON ENERGIES

An advantage of using electron energies higher than 0.75 MeV is the improvement in efficiency for transmitting the electron beam from the accelerator into the flue gas [14]. Another advantage is the reduction in beam current for the same beam power, which would facilitate the generation and delivery of the high beam current and beam power requirements for large electric power plants.

The beam window losses have been calculated by using the ITS3 TIGER Monte Carlo code [15]. The one-dimensional, depth-dose distribution in the beam windows, the air space between the windows and the flue gas (simulated with the composition and density of air), when irradiated with an incident electron energy of 0.75 MeV, is shown in Figure 1. The beam windows on the electron accelerator and the flue gas vessel are both 50 µm (micrometers) of titanium. Thinner 25 µm windows have been found to be unreliable for this irradiation process [4]. The air space between the windows is 15 cm. The horizontal scale is the depth in cm multiplied by the volume density in g/cm$^3$. This can also be called the area or areal density in g/cm$^2$. The vertical scale is the energy deposition per electron in MeV/(g/cm$^2$). The areas under the curve represent the energy depositions in MeV per electron in each material.

![Depth-Dose Distribution - 0.75 MeV](image)

*FIG. 1. Calculated one-dimensional depth-dose distribution showing the electron energy depositions in the two titanium beam windows, the air space between the windows and the irradiated flue gas (air) at 0.75 MeV. The labeled areas under the curve give the energy depositions in MeV per electron.*
Similar calculations have been done with incident electron energies ranging from 0.50 MeV to 3.0 MeV. The electron energy losses in the beam windows and in the air space between the windows and also from electron backscattering are shown in Figure 2. The sum of these losses is 54% of the incident energy at 0.50 MeV, 28% at 0.75 MeV, 17% at 1.0 MeV, 9.3% at 1.5 MeV, 6.7% at 2.0 MeV, 5.2% at 2.5 MeV and 4.6% at 3.0 MeV. The percent of incident energy transmitted through the windows is shown in Figure 3. It is 46% at 0.50 MeV, 72% at 0.75 MeV, 83% at 1.0 MeV, 90.7% at 1.5 MeV, 93.3% at 2.0 MeV, 94.8% at 2.5 MeV and 95.4% at 3.0 MeV. It appears that most of the gain in transmission efficiency would be obtained by increasing the incident energy to 1.5 MeV or 2.0 MeV. The electron beam current needed to transmit 500 kW through the windows while compensating for the losses mentioned above (but not for losses to the vessel walls) is shown in Figure 4. It is 2,150 mA at 0.5 MeV, 923 mA at 0.75 MeV, 604 mA at 1.0 MeV, 367 mA at 1.5 MeV, 268 mA at 2.0 MeV, 211 mA at 2.5 MeV and 175 mA at 3.0 MeV. Increasing the electron energy by a factor of 2.0 from 0.75 MeV to 1.5 MeV would reduce the electron beam current requirement by a factor of 367/923 = 0.40 or 1/2.5 (the additional reduction in beam current comes from the reduced window losses).

**FIG. 2.** Percentage of electron energy losses in the two 50 micron titanium beam windows, the 15 cm air space between the windows and backscattering from the windows as a function of the incident electron energy from 0.50 MeV to 3.0 MeV.
FIG. 3. Percentage of incident electron energy transmitted through the two 50 micron titanium beam windows and the 15 cm air space between the windows as a function of the incident electron energy from 0.50 MeV to 3.0 MeV.

FIG. 4. Incident electron beam current in mA needed to transmit 500 kW through the two 50 micron titanium beam windows and the 15 cm air space between the windows as a function of the incident electron energy from 0.50 MeV to 3.0 MeV. Power losses to the vessel walls are not included.
Three-dimensional calculations of the depth-dose distributions in air inside a cylindrical steel vessel have been done for incident electron energies of 1.5 MeV and 2.5 MeV with the MCNPX 2.5.0 Monte Carlo code [16]. A graph of the results for 1.5 MeV, a vessel radius of 5.0 m and a length of 7.0 m is shown in Figure 5. Data for net energy absorption in the gas with vessel radii from 1 m to 6 m at both 1.5 MeV and 2.5 MeV are shown in Figure 6. It is evident that a radius of 5 m would be sufficient to absorb most of the electron energy at 1.5 MeV. In this case, the percent of incident energy absorbed in the gas inside the vessel is 89.8%. Since the percent of incident energy transmitted through the beam windows is 90.7%, then the percent electron energy lost in the walls of the vessel is only 90.7 – 89.8 = 0.9%. With a 4 m radius, the energy absorbed in the gas is 86.3%, so the energy lost in the vessel walls is 90.7 – 86.3 = 4.4%. With a 3 m radius, the energy absorbed in the gas is 75.9%, so the energy lost in the vessel walls is 90.7 – 75.9 = 14.8%. With a 2 m radius, the energy absorbed in the gas is 59.5%, so the energy lost in the vessel walls is 90.7 – 59.5 = 31.2%. These figures indicate that the vessel radius should be at least 4 m and preferably 5 m to minimize the energy lost in the walls with an incident electron energy of 1.5 MeV. These large sizes may be acceptable for a 500 MW power plant, where the flue gas ducts and stack dimensions are also large.

FIG. 5. Calculated three-dimensional depth-dose distribution in a cylindrical vessel filled with flue gas (air) at the normal atmospheric density of 1.2 kg/m³, taking account of the energy losses in the beam windows and the air space between the windows. Vessel radius is 5 m. Vessel length is 7 m.
3. HIGH-ENERGY, HIGH-POWER ACCELERATORS

3.1. Constant Potential Accelerators

For electron energies above 0.8 MeV, a flexible high-voltage cable cannot be used to connect the high-voltage generator to the accelerator. However, this connection can be made with a rigid, gas-insulated, high-voltage transmission line, as shown in Figure 7. A photograph of a 1.5 MeV, 150 kW Dynamitron® accelerator is shown in Figure 8. This design was developed many years ago by RDI, which is now a part of IBA Industrial, Inc. [17]. With one cascaded-rectifier circuit, as shown by the diagram in Figure 9, this type of generator can supply an electron beam load of 100 mA. With two rectifier circuits in parallel, the beam load can be 200 mA. With four parallel rectifier circuits, as shown by the diagram in Figure 10, the beam load can be 400 mA [18]. Therefore, the beam power can be 600 kW at 1.5 MeV. This transmission-line configuration, with one or two rectifier circuits, has been used in many facilities for irradiating commercial products, such as insulated wire, plastic tubing and rubber parts for automobile tires. For very high-current, high-power applications, such as irradiating flue gases, this configuration can be extended to connect a single high-voltage generator to multiple accelerators, as shown by the diagram in Figure 11 [19]. This concept has also been adopted by the Budker Institute of Nuclear Physics and the Efremov Research Institute [20-23]. Delivering the total beam power with multiple accelerators is consistent with data showing that multiple electron beams, displaced along the flue gas duct, are more effective than a single beam for removing nitrogen oxides from flue gases [7]. This might be evidence for a dose-rate effect, wherein very high concentrations of ions and free radicals can be less effective because of reactions between these active components of the irradiated gas.
FIG. 7. Diagram of a Dynamitron® system with a gas-insulated, rigid transmission line connecting the high-voltage generator to the electron accelerator. This configuration has been used in the energy range from 0.50 MeV to 1.5 MeV.

Fig. 8. Photograph of a Dynamitron® system with a gas-insulated, rigid transmission line connecting the high-voltage generator to the electron accelerator. This model is capable of producing 150 kW of electron beam power at 1.5 MeV.
FIG. 9. Diagram of a Dynamitron® high-voltage generator with one cascaded-rectifier circuit.

FIG. 10. Diagram of a Dynamitron® high-voltage generator with four parallel rectifier circuits.
3.2. Radio Frequency Accelerators

Radio frequency (rf) accelerators can produce high-energy, high-power electron beams without needing high-voltage generators. The Rhodotron® accelerators, made by IBA Industrial, Inc., achieve high electron energies by passing the beam repeatedly through a large, coaxial, resonant cavity [24]. A diagram of the beam paths is shown in Figure 12. A three-dimensional drawing of the coaxial resonant cavity is shown in Figure 13. In a typical Rhodotron, the electrons gain 1 MeV of energy per pass through the cavity. Higher energies are obtained via multiple passes through the same cavity. With ten passes, 10 MeV, 20 mA, 200 kW beams have been produced. The rf power is generated with a self-tuning tetrode amplifier at a frequency of 107.5 MHz [25-27]. Continuous wave (cw) excitation of the cavity produces a continuous electron beam, which is bunched at the resonant frequency. The absence of macro-bunching reduces the peak beam current, in comparison to a microwave linear accelerator (linac) with the same average beam power. The very short time interval (about 9 ns) between beam bunches allows the beam to be scanned as rapidly as a dc beam without producing gaps on a moving product conveyor or a stream of liquid or gaseous material.
FIG. 12. Diagram of the electron beam paths in a six-pass Rhodotron® accelerator.

FIG. 13. Three-dimensional drawing of a ten-pass Rhodotron® cavity showing the rf amplifier at the top of the cavity and the electron beam deflecting magnets located around the middle of the cavity.
A more powerful Rhodotron, Model TT1000, has recently been developed, which can produce a 7.0 MeV, 100 mA, 700 kW electron beam [28]. A photograph of this accelerator is shown in Figure 14. The beam passes through the cavity six times, gaining 1.17 MeV per pass. The cavity size is the same as the 10 pass, 10 MeV model and resonates at the same frequency. The main difference in the six-pass version is the larger tetrode amplifier tube, which can provide more than one megawatt of rf power. In order to provide more beam current and beam power with lower electron energies, multiple beams can be injected into the same cavity with separate electron guns. The concept of accelerating two beams with two passes per beam is shown in Figure 15. In this case, each beam could provide 125 mA or 313 kW at 2.5 MeV. The total beam power would be 625 kW. Beam focusing requirements would limit the current in each beam. Another concept of accelerating six beams with one pass per beam is shown in Figure 16. In this case, each beam could provide 100 mA or 150 kW at 1.5 MeV. The total beam power would then be 900 kW. All six beams could be injected into the same flue gas duct with a suitable beam focusing and deflecting system. An alternative concept would be to inject three beams into one duct and three into a parallel duct. Even with this much electron beam power, a 500 MW power plant would need at least 5 to 10 of these accelerators.

FIG. 14. A photograph of the six-pass Model TT1000 Rhodotron® which can produce an electron beam of 100 mA or 700 kW at energy of 7.0 MeV.
FIG. 15. Diagram of a two-beam, two-pass Rhodotron® system. The electron beam current from each source can be 125 mA and the final energy can be 2.5 MeV. The total beam power can be 625 kW.

FIG. 16. Diagram of a six-beam, one-pass Rhodotron® system. The electron beam current from each source can be 100 mA and the electron energy can be 1.5 MeV. The total beam power can be 900 kW.
4. ACID NEUTRALIZATION WITH SLAKED LIME

The use of slaked lime to neutralize the sulfuric and nitric acid vapors, which are produced by the irradiation process, could be an alternative to ammonia for power plants that are equipped with wet limestone scrubbers for removal of sulfur dioxide. Many power plants in the USA already have such scrubbers, which are very effective for removing sulfur dioxide, but are inefficient for nitrogen oxides. In contrast, the electron beam process is effective in removing both the sulfur dioxide and the nitrogen oxides. When it is used to treat flue gas that has not gone through a wet limestone scrubber, the concentration of ammonium sulfate is usually much greater than that of ammonium nitrate. Whereas ammonium sulfate with a small concentration of ammonium nitrate is a safe material, ammonium nitrate with a small concentration of ammonium sulfate could be mixed with fuel oil to make an explosive material. With these conditions, the addition of an electron beam facility with slaked lime neutralization to a power plant that already has a wet limestone scrubber could be a more attractive way to remove the residual nitrogen oxides than selective catalytic reduction.

Cottrell Environmental Sciences and the High Voltage Engineering Corporation installed and evaluated a pilot electron beam irradiation facility with slaked lime neutralization at the TVA Shawnee Steam Plant in Paducah, Kentucky, USA [29, 30]. This project was supported by the U.S. Department of Energy (DOE). The NKK Corporation installed and evaluated a smaller pilot facility of this type at the Matsudo Waste Disposal Center in Matsudo, Japan [31]. This project was supported by the Japanese Atomic Energy Research Institute (JAERI).

A diagram of the Cottrell/High Voltage Engineering treatment process is shown in Figure 17. A mixture of water and slaked lime is pumped into the flue gas with a spray reactor. In addition to adding lime, this adds water, which is needed in the irradiation process to produce the acid vapors, and it also lowers the temperature of the flue gas, which increases the efficiency of the removal process. Slaked lime (calcium hydroxide) can be produced by heating limestone, CaCO₃, to form calcium oxide, CaO, which is then reacted with water to form calcium hydroxide, Ca(OH)₂. The composition of the flue gas entering the spray reactor is shown in Table I and the composition of the gas mixture leaving the spray reactor is shown in Table II. These data show that the concentration of sulfur dioxide was reduced from 1000 parts per million (ppm) to 300 ppm by reaction with the calcium hydroxide before the gas was irradiated. However, the concentration of nitrogen oxides, 350 ppm, was the same entering and leaving the spray reactor.

![FIG. 17. Diagram of the Cottrell/High Voltage Engineering flue gas treatment process. A mixture of water and slaked lime is injected into the flue gas stream with a spray reactor. The gas mixture is then irradiated and passed through a fabric filter to remove the particles of calcium sulfate and nitrate.](image-url)
TABLE I. TYPICAL FLUE GAS COMPOSITION INTO SPRAY DRYER. TEMPERATURE 150°C. DATA FROM REFERENCE [30].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>72%</td>
</tr>
<tr>
<td>O₂</td>
<td>5%</td>
</tr>
<tr>
<td>CO₂</td>
<td>13%</td>
</tr>
<tr>
<td>H₂O</td>
<td>10%</td>
</tr>
<tr>
<td>SO₂</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>NOₓ</td>
<td>350 ppm</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>a. gm/ACM</td>
</tr>
</tbody>
</table>

TABLE II. TYPICAL FLUE GAS COMPOSITION OUT OF SPRAY DRYER. TEMPERATURE 66°C. DATA FROM REFERENCE [30].

<table>
<thead>
<tr>
<th>Gas</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>70%</td>
</tr>
<tr>
<td>O₂</td>
<td>4%</td>
</tr>
<tr>
<td>CO₂</td>
<td>12%</td>
</tr>
<tr>
<td>H₂O</td>
<td>14%</td>
</tr>
<tr>
<td>SO₂</td>
<td>300 ppm</td>
</tr>
<tr>
<td>NOₓ</td>
<td>350 ppm</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>3.7 gm/ACM</td>
</tr>
<tr>
<td>CaSO₃</td>
<td>1.4 gm/ACM</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.7 gm/ACM</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.7 gm/ACM</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>0.7 gm/ACM</td>
</tr>
</tbody>
</table>

A diagram of the electron beam pilot facility at the TVA Shawnee Steam Plant is shown in Figure 18. Two accelerators were connected to one high voltage generator with flexible cables. The generator was an Insulating Core Transformer (ICT) made by High Voltage Engineering [32]. The operating voltage was 0.75 MeV and the beam current in each accelerator was 50 mA. The total beam power was 75 kW. The irradiation chamber was located underground for radiation shielding. Both beams were directed downward and the flue gas was mixed with a vortex damper to compensate for the non-uniform dose distribution in the gas. The gas rotated twice while passing each accelerator. The gas duct had a diameter of 1.8 m and a length of 6 m. The measured dose distribution in air indicated that the gas absorbed about 70% of the electron beam power output.
FIG. 18. A diagram of the electron beam pilot facility at the TVA Shawnee Steam Plant. Two accelerators, each with 50 mA of beam current were connected to one 0.75 MeV ICT high voltage generator with flexible cables. The total beam power was 75 kW. The irradiation chamber was located underground for radiation shielding.

The flue gas mixture was irradiated with the two electron beams to produce sulfuric and nitric acid vapors, which then reacted with the slaked lime to produce fine particles of calcium sulfate and calcium nitrate. These particles were subsequently removed by passing the gas through a fabric filter. The efficiencies for removing the sulfur and nitrogen oxides are shown in Figure 19 as a function of the absorbed dose. These data show that the efficiencies for removing nitrogen oxides were higher than the efficiencies for removing sulfur dioxide. The labels on the curves show that increasing the moisture content from 6% to 14% by volume at 100°C increased the removal efficiencies for both the sulfur and nitrogen oxides. Similar curves in Figure 20 show that reducing the temperature from 135°C to 65°C at 14% moisture increased the removal efficiencies for both sulfur and nitrogen oxides. With these conditions of high moisture and low temperature, about 95% of the nitrogen oxides could be removed with an absorbed dose of 5 kGy.
FIG. 19. Curves showing the percent removal of sulfur and nitrogen oxides as a function of the absorbed dose at 100 °C. Increasing the moisture content from 6% to 14% increased the removal efficiencies for both gases.

FIG. 20. Curves showing the percent removal of sulfur and nitrogen oxides as a function of the absorbed dose at 14% moisture. Reducing the temperature from 135 °C to 60 °C increased the removal efficiencies for both gases.
5. CONCLUSION

Electron energy losses in the dual beam windows and the intervening air space could be significantly reduced by increasing the electron energies to at least 1.5 MeV. The lower electrical efficiencies of accelerators with higher energies would be partially compensated by the lower electron energy losses in the two beam windows and the air space between the windows. Gas-insulated, rigid transmission lines can connect high-voltage generators to multiple accelerators without the voltage limitation of 0.8 MV, which is imposed by flexible high-voltage cables.

In comparison to accelerators with electron energies in the range of 0.7 to 0.8 MeV, accelerators with higher electron energies can provide higher beam powers with lower beam currents. This could be an advantage for supplying the high beam current and beam power needed for very large electric power plants. Modern high-energy, high-power electron accelerators are capable of meeting these substantial current and power requirements with multiple systems.

The use of slaked lime vs ammonia for neutralizing the acid vapors produced by the irradiation process could be attractive for electric power plants that are already equipped with wet lime scrubbers to remove sulfur dioxide. This could eliminate the need to sell fertilizer to recover the significant cost of ammonia, and it could reduce the risk of producing, storing and disposing of large quantities of ammonium nitrate with low concentrations of ammonium sulfate, which would be considered a hazardous material in the USA.

REFERENCES


MCNPX 2.5.0 Monte Carlo Code, LANL, CCC-730 (2006). This code is available from the Radiation Safety Information Computational Center (RSICC), Oak Ridge, TN 37831, USA.


HIGH POWER ACCELERATOR FOR ENVIRONMENTAL APPLICATION

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Abstract

The problems of environmental damage and degradation of natural resources are receiving increasing
attention throughout the world. The increased population, higher living standards, increased urbanization and
enhanced industrial activities of humankind are all leading to degradation of the environment. Increasing
urbanization has been accompanied by significant environmental pollution, given the seriousness of the situation
and future risk of crises, there is an urgent need to develop the efficient technologies including economical
treatment methods. Therefore, cost-effective treatment of the stack gases, wastewater and sludge containing
refractory pollutant with electron beam is actively studied in EB TECH Co. Electron beam treatment of such
hazardous wastes is caused by the decomposition of pollutants as a result of their reactions with highly reactive
species formed from radiolysis. However, to have advantages over existing processes, the electron beam process
should have cost-effective and reliable in operation. Therefore high power accelerators (400kW~1MW) are
developed for environmental application and they show the decrease in the cost of construction and operation of
electron beam plant. [1] In other way to reduce the cost for treatment, radical reactions accompanied by the other
processes are introduced, and the synergistic effect upon the use of combined methods such as electron beam
treatment with catalytic system, biological treatment and physico-chemical adsorption and others also show the
improvement of the effect of electron beam treatment.

1. INTRODUCTION

Electron beam processing is non-chemical, and uses fast formation of short-lived reactive
radicals that can interact with a wide range of pollutants in gas, water and sludge. Such reactive
radicals are strong oxidizing or reducing agents that can transform the pollutants in the wastes. The
first studies on the radiation treatment of wastes were carried out in the 1950s principally for
disinfection. In the 1960s, these studies were extended to the purification of water and wastewater.
After some laboratory research on industrial wastewaters and polluted groundwater in 1970s and
1980s, several pilot plants were built for extended research in the 1990s. The first full-scale
application was reported for the purification of wastewater at the Voronezh synthetic rubber plant in
Russia. Two accelerators (50 kW each) were used to convert the non-biodegradable emulsifier,
‘nekal’, present in the wastewater to a biodegradable form [2]. The installation treats up to 2,000 m³ of
effluent per day. A pilot plant of 1.000 m³/d for treating textile-dyeing wastewater has been
constructed in Daegu, Korea with 1MeV, 40kW electron accelerator [3]. The removal of SO₂ using an
electron was demonstrated in 1970 - 1971.

Irradiation of flue gas resulted in the conversion of SO₂ to an aerosol of sulfuric acid droplets
that were easily collected [4]. Ebara Co. used an electron accelerator (0.75 MeV, 45 kW) to convert
SO₂ and NOₓ into a dry product containing (NH₄)₂SO₄ and NH₄NO₃ that was usable as a fertilizer.
Two larger scale plants were constructed in Indianapolis, USA [5] and Karlsruhe, Germany [6]. The
Indianapolis plant was equipped with two electron accelerators (0.8 MeV, total power160 kW) and
had a gas flow capacity of 1.6 - 3.2 ×10⁷ m³/h with gas containing 1000 ppm SO₂ and 400 ppm NOₓ.
In Karlsruhe, two electron accelerators (0.3 MeV, total power 180 kW) were used to treat 1 - 2 ×10⁷
m³/h flue gas containing 50 - 500 ppm SO₂ and 300 - 500 ppm NOₓ. The engineering design
technology for electric utility applications was established at the pilot plant in Kaweczyn, Poland (2
×10⁷ Nm³/h) using two accelerators (50 kW, 700 keV each) [7].

It has been shown [8] that a dose of 2-3 kGy destroys more than 99.9% of the bacteria present in
sewage sludge and causes almost complete dehelminthiasis and deactivation of the agents that cause
disease in animals. Doses of this magnitude are employed for the radiation treatment of sewage
sludges at a commercial plant in Geiselbullach (Germany) [9] with a slightly higher dose (4 kGy) at a
pilot plant near Boston (USA) [10]. Higher doses (up to 10 kGy) are required to inactivate more
radiation-resistant organisms. Doses of 10 kGy were used at a sewage treatment plant in Albuquerque,
New Mexico (USA) [11, 12] and at an installation in the Ukraine [13].
Radiation technologists have been investigating the use of high-energy radiation for environmental treatment. The major advantage of radiation technology is that the reactive species are generated in-situ during the radiolysis process without addition of any chemicals. The results of practical applications have confirmed that radiation technology can be easily and effectively utilized for treating large quantities of wastes [14 - 16].

2. ACCELERATORS REQUIRED FOR ENVIRONMENTAL APPLICATION

The most important factor in controlling the economics is the cost of the electron accelerator in use. Accelerator manufacturers produce many different kinds of electron accelerators with an energy range from 0.5 to 10 MeV and beam power range from 50 to 600 kW. For flue gas treatment, electron energies of approximately 0.7 ~ 1.0MeV are adequate, but electron beams of energy more than 1.0 MeV are useful for wastewater treatment and sewage sludge treatment. Such energy levels provide enough penetration of accelerated electrons into wastes when applied to admissible regimes. Accelerators with beam energy greater than 5 MeV are being manufactured at low beam power (less than 50 kW). Low beam power is adequate for experimental and pilot plants but not for large-scale treatment in commercial applications. Therefore, medium energy accelerators achieve maximum practical use for flue gas and wastewater treatment. However higher energies are useful for sludge treatment. The beam power of such accelerators reaches 600 kW, and there are several applications calling for manufacture of accelerators of beam power up to 1 MW. The basic criteria for accelerators for environmental application are:

- High beam power to increase productivity and reduce unit operational cost
- High electrical efficiency to reduce demand and unit operating cost
- High beam utilization to increase productivity and reduce unit operation cost.

As is shown in Fig. 1, the cost of accelerators is governed by their beam power and the accelerator with the highest power has the lowest unit cost for power generation and is the most economical in environmental application.

**FIG. 1. Cost for unit power versus power of industrial accelerators**
3. APPLICATION OF HIGH POWER ACCELERATORS FOR WASTEWATER TREATMENT

The key to the successful implementation of electron beam in environmental protection depends on how to manage the economies in its application. To compete with other processes in economic evaluation, the electron beam system should be operated with cost-effective accelerator with enough low doses. Therefore high power accelerators are introduced to environmental application. The most powerful and reliable accelerator for wastewater treatment is 1 MeV, 400 kW accelerator which has produced together with EB-TECH Co. and BINP, Russia [1].

This accelerator can deliver the maximum 400 kW of electron beam power through 3 irradiators which has the double extraction windows. Titanium foils are used for window materials and are cooled by air jet blow and water. High voltages are generated through the inductions of coils in main body and SF$_6$ gases are used for protecting electrical discharges. The first accelerator of this figure has installed in Daegu Dyeing Industrial Complex (DDIC), Korea for treating industrial wastewater from textile dyeing industries (see Fig. 2).

Cost for such high power accelerator is around 2.0 M$ for installation and building, piping, other equipment and construction works could be estimated 1.5 M$. Even by considering the additional cost for tax, insurance and documentation as 0.5 M$, the overall capital cost for plant construction and operating are approximately 4.0 M$ and 1.0 M$ as stipulated in table I and table II.

<table>
<thead>
<tr>
<th>Cost</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>Cost for Land, R&amp;D, Approval from Authorities are not included</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>4 M$</td>
</tr>
</tbody>
</table>

TABLE I. CONSTRUCTION COST FOR INDUSTRIAL PLANT (UNIT: M$)
TABLE II. OPERATING COST FOR INDUSTRIAL PLANT (UNIT: K$)

<table>
<thead>
<tr>
<th>Items</th>
<th>Addition of E-beam</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Invest (k$)</td>
<td>(4000)</td>
<td></td>
</tr>
<tr>
<td>Interest</td>
<td>240</td>
<td>6%</td>
</tr>
<tr>
<td>Depreciation</td>
<td>200</td>
<td>20 yrs</td>
</tr>
<tr>
<td>Electricity</td>
<td>320</td>
<td>800 kW</td>
</tr>
<tr>
<td>Labor</td>
<td>100</td>
<td>3 shift</td>
</tr>
<tr>
<td>Maintenance, etc.</td>
<td>80</td>
<td>2%</td>
</tr>
<tr>
<td>Total cost</td>
<td>940</td>
<td>~ 1 M$/yr</td>
</tr>
</tbody>
</table>

Above estimation doesn’t include the cost for land, R & D and the cost for the approval form authorities. Construction period includes 17 months in civil and installation works and 3 months for trial operation. To estimate the operation cost, the electricity consumption of accelerator and other equipment is calculated as 500 kW (80% efficiency) and 300 kW to the total of 800 kW. Based on the year round operation (8000 hr/yr), it costs 320 000 $/yr when the cost of electricity (kWh) was assumed to be 0.05 $. The labor cost of operator is calculated on 3-shift work and is approximately 100 000 $/yr. Therefore, the actual operation cost for 10 000 m$^3$/day plant comes up to around 1.0 M$/yr including the interest and depreciation of investment and is 0.3 $ for each m$^3$/day of wastewater.

4. CONCLUSIONS

4.1. Requirements of Electron Accelerator for Environmental Application

Accelerators for environmental application should be satisfied in followings:
- Accelerator itself has strong and firm configuration for year round operation,
- Economical in power consumption,
- Easy and safe operation.

Introduction of more powerful accelerator combined with useful additive system (such as MW, Catalytic system, Bio-system etc.) could make economical and technical advantages in competition with other conventional methods.

4.2. High power Accelerators for Environmental Application.

High power accelerator of several hundreds kilowatts has been already introduced in environmental applications, and they proved the economical advantages. 600 kW accelerator for flue gas treatment in Chengdu and Pomorzany plant and 400 kW accelerator for wastewater treatment in Daegu (DDIC) showed the good examples of high power accelerators in environmental application. For further application, careful studies of reliabilities of such high power accelerators are required.
REFERENCES


Abstract

Commercializing reliable affordable electron beam flue gas treatment technology requires both, the optimization of accelerator technology and chemical reaction chambers. Moreover, this engineering process involves the integration of beam specific characteristics, such as dosage distribution and penetration of electrons into the flue gas stream. In consideration of the treatment economy, it might be required to calculate the overall process performance without merely limiting the evaluation to accelerator efficiency. For example, a higher energy beam, 1MeV to 2 MeV, reduces the losses in the beam window and penetrates further into the gas stream and, therefore, increases the overall process economy. The energy distribution should be optimized with respect to the configuration of the chemical reaction chamber in order to treat the flue gas uniformly. All these measures are required to achieve high removal rates in large flue gas streams. Today removal rates of more than 99% SO$_x$ and more than 80% SO$_x$ are required to be compliant with future emission legislations. It is planned to establish a 100,000m³ electron beam flue gas treatment facility that can achieve constant removal rates of higher than 99.4% SO$_x$ and more than 80% NO$_x$. The high removal rates would allow us to place CO$_2$ capture technologies down stream of the EBFGT facility.

1. INTRODUCTION

Since the 1970s, laboratories and pilot demonstrations by the Japan Atomic Energy Research Institute (JAERI), the University of Tokyo, have known the treatment of industrial flue gases by exposure to electron beams (EBFGT). Since then, a number of installations have been built worldwide, leading in 2000 to the most recent facility - treating up to 270 000 Nm$^3$/h of flue gas - at the Pomorzany power station in Poland. This installation has provided technical information that allows formulating requirements on the next generation of EBFGT facilities.

Analyzing the operational data of existing EBFGT facilities, a number of technical modifications can be applied in order to increase the reliability of the EBFGT. Such changes are focusing on the electron beam accelerator and the support systems. Chemical reactor and electron beam system are required to interface directly, in a way to match the footprint of existing plants and to optimize the dosage. Electron beam steering and electron beam windows are directly related to the dosage delivered to the flue gas stream and, therefore, determine the overall process efficiency.

In order to achieve wider acceptance in industrial facilities, reliability is of highest priority. Assuming that preventive maintenance is required to operate a facility, redundancy is one solution to achieve a high availability of the system. Moreover, industry is looking for turnkey solutions in order to apply the EBFGT process in the same way as competitive technologies. EBFGT systems need to be maintained and operated for a minimum of 10 years, realistically looking at a lifetime of 15 to 20 years.

Dynamically changing legislation, such as greenhouse gas legislations, will require the implementation of CO$_2$ capture options down stream of EBFGT installations. Research should consider “electron beam multi pollution control processes” as being capable to treat flue gases in preparation for any down stream CO$_2$ treatment. Thus, it might be required to focus on specific pollutants, such as SO$_x$, in order to allow alternative down stream procedures to take place. It is known that CO$_2$ sequestration or catalytic reactions will require the removal of SO$_x$ at very low concentrations. In addition, sequestration technologies (such as CO$_2$ compression) will require a very low temperature upstream of the flue gas compressor.

2. MAIN DISCUSSION

Existing EBFGT facilities show that electron beam accelerators have a large potential to increase the process reliability and the treatment economics. The second-generation design of accelerators will fundamentally differ from past systems. In order to achieve this improvement, the accelerator and the chemical reactor will be matched in order to
- Optimize dosage distribution in the reactor
- Increase net energy delivered into flue gas stream
- Reduce footprint of EBFGT facilities.

The following chart is a risk management analysis of possible failure points in an EBFGT facility, utilizing DC accelerator technology. Dr. Zimek [7] from the Institute of Nuclear Chemistry and Technology in Warsaw presented possible EBFGT failure points in May 2007, representing operational data collected by the institute. The chart does not differentiate between failures related to the accelerator hardware or failures related to the design of the facility.

![EBFGT Failure Analysis](image)

The chart characterizes each failure point with a risk and an impact number; whereas 1 is low and 10 is high. Thereafter, the Risk-Impact leverage is calculated in order to allow a better identification of failures. In order to utilize the existing results and experience from current EBFGT operations, the design of accelerator and chemical reactor must be reviewed. Design iterations will allow improving the pollution removal rates and prolong mean time between failures. A possible first step is to decide upon an accelerator technology that integrates all requirements and allows future upgrades.

The accelerator will operate at 1.0 to 1.5 MeV, allowing the beam to transit efficiently through a segmented beam window. High beam current acceleration methods such as microwave cavities or induction cells should

- have mechanical stability at high energy levels; analytical results of surface stresses in the cavity or induction cell require technical solutions
- allow heat management to ensure optimal operation at various modes
- be flexible in order to allow retrofit into existing facilities; all power transmission must be cables
- allow future growth to increase the beam power to 1 MW

The design of the accelerator must be reliable and accessible for preventive maintenance; a mean time between failures of 2000 to 6000 hours is required. Preventive maintenance will allow exchanging parts before failure, limiting the mean down time to 16 hours or less. Preventive maintenance considerations require that the beam accelerator can be de-energized in order to service. A full scale EBFGT facility will allow each accelerator to be designed with its own power supply and chemical reaction chamber. Subsequently, the flue gas stream will be divided into sub streams of 100 000 m$^3$ each.
The major advantage of splitting the main gas stream is the ability to shut down one system for maintenance, without disrupting the treatment process. Each reactor has an in-flow guiding the gas stream and exposing the gas to the electron beam for a prolonged period. The electron beam will scan across the gas stream and is pulsed in order to:

- allow optimized energy control
- synchronize the scan with the segmented beam window.

The reaction chamber will have either a square flue gas inflow opening or a round pipe. The size of the inflow will be designed to reduce the flue gas velocity to approximately 7.5 m/s. The accelerator will be interfaced with an angular incident to the gas direction in order to allow full penetration across and along the gas stream. The accelerator interface has segmented beam windows as shown in Figure 2 (above), which allows the electron beam to transit from the beam generation section into the flue gas chamber. The window-segment is a key component in increasing system reliability by less mechanical stress and better temperature control of the window. To ensure optimal facility up-time, the beam window will be replaced on a preventive maintenance schedule.

Figure 3 shows a round reactor design; it has an in-flow (d) that will guide the gas stream in a cyclonic motion, and expose it to the electron beam for a prolonged period. This circular gas flow allows the steering of the electron beam in a very efficient way and, therefore, optimizes the exposure of the gas stream. The electron beam is steered digitally and can be modified online. Thus, the deflection pattern and the beam intensity can be regulated in real time by monitoring the SO\textsubscript{X} and NO\textsubscript{X}. 
sensors. The implementation of this control loop will result in the optimization of the electric energy consumption of the electron beam accelerator.

After exposure to the electron beam, the flue gas will flow in a propagation chamber, which allows the chemical reaction to form the \( \text{NH}_4\text{NO}_3 \) and \((\text{NH}_4)_2\text{SO}_4\) particulate. The dead-time chamber is designed in such a way that all acids form inside a vessel which is corrosion-protected. As a result, an increase in corrosion down stream from the reactor outlet (e) is not expected. Hence, the accelerator-reactor system can be retrofitted into existing facilities with carbon steel piping.

![FIG. 4. Rectangular reaction chamber](image)

Figure 4 shows the rectangular reaction chamber and the angled accelerator interface. The inflow of the flue gas is at almost vertical direction on the upper side of the chamber. The cut away view shows the accelerator interface in angular configuration with the segmented beam windows. Each reaction chamber and accelerator will treat 100 000 m\(^3\)/h and, therefore, larger EBFGT facilities will have between 2 to 6 reaction blocks. This configuration will allow redundant operation; thus, maintenance can be scheduled without interruption of the flue gas treatment. Flue gas flow rates, plant layouts and space availability on site will determine reactor configuration and size.

In light of the worldwide focus on CO\(_2\) as man made cause of global warming, EBFGT is an important technological solution. Most CO\(_2\) capture procedures require the removal of SO\(_x\) (sulfur) in order not to impact down stream CO\(_2\) reactions or sequestration technologies.
Figure 5 outlines (in simplified version) the steps for an integrated flue gas treatment solution, targeting multi pollution removal. Our current scope of work for implementing EBFGT technology is staged in 2 phases. In phase 1 we are targeting the removal of SO\(_x\) and NO\(_x\) emissions in order to comply with future emission legislations. The EBFGT facility will be optimized to have a maximum emission of 150 mg/Nm\(^3\) SO\(_x\) and NO\(_x\). After establishing the base operational data, we will start phase 2: optimization of removal rates for SO\(_x\). The high removal rate of SO\(_x\) will allow accommodating down stream of the EBFGT CO\(_2\) capture technology such as sequestration or catalytic reactions. Integrating CO\(_2\) capture technologies down stream will allow us to test the economic viability of CO\(_2\) procedures.

Concurrently with the development of technical solutions for the EBFGT technology, we will focus on the value proposition to the end user (such as power plants), thus meet their business objectives. Electron beam technology can establish significant financial and economic benefits in many ways. Some of the key benefits are the more efficient utilization of plant infrastructures, possible lower overall fuel costs, and the selling of a by-product (fertilizer). Moreover, the management has to evaluate the importance of delivering an improved product, such as clean energy, at a higher price.

Stabilizing spot market prices of fuels will improve the sustainability of the operation. In the past, fuel prices experienced considerable fluctuations due to seasonal cycles, and escalated on account of unforeseen events such as hurricanes and other natural disasters. EBFGT might allow to combust locally available dirty fuels, such as high sulfur fuels, without exceeding emission limits. Emission regulations are expected to become more restrictive and will be enforced by Governments. Emission caps will result in the restriction of facility outputs, in particular of facilities lacking emission control technology. The incurring costs of such shut downs can be expressed as “costs of lost opportunity to deliver the product”.

The successful integration of Electron Beam Flue Gas Treatment will require an analysis of the financial impact of said technology on industry. Based on the financial results, including short- and mid-term cash flow, a number of financing strategies can be developed. In light of the worldwide focus on CO\(_2\) and other pollutants (such as SO\(_x\) and NO\(_x\)) as man-made cause of global warming, emission control equipment will attract venture capital, other environmental oriented funds and the public markets.
3. CONCLUSIONS

EBFGT technology is a building block towards a multi pollution control procedure that provides economic viability. Current design efforts target the reliability of the equipment and the affordability of environmental technology. The treatment of flue gas and the removal of sulfur oxide and nitrogen oxides are key steps towards pollution reduction, and are achievable technological goals with minimized financial impact to current operations. In addition, this technology is perfect for already existing plants as retrofit application as well as for new facilities.

The biggest question regarding environmental pollution control is not the technology, but more the willingness to integrate such procedures in industrial operations. Without enforced emission laws, it will be very difficult to motivate key polluters to clean up their operation and, therefore, governments are asked to react accordingly.

REFERENCES

PRESENT STATE OF WORKS ON DEVELOPMENT OF ELECTRON ACCELERATORS FOR ENERGY CONSUMING PROCESSES AT EFREMOV RESEARCH INSTITUTE

A.S. IVANOV, V.P. MAZNEV, V.P. OVCHINNIKOV, M.P. SVININ, N.G. TOLSTUN
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1. INTRODUCTION

High voltage (HV) electron accelerators for industrial usage are being developed at Efremov Research Institute for more than 40 years. During this period more than 50 accelerators with energies from 0.3 to 2.5 MeV and beam power up to 100 kW were delivered to our Customers [1].

Long experience of the accelerators’ operation in various production lines has shown that they respond to requirements on industrial equipment. Accelerating voltage of the accelerators is produced by cascade generators on a base of one- or three-phase transformer-rectifiers (TR). Compressed gas is usually used as main insulation matter but we have a rather long experience of usage of oil-barrier polymer film insulation as well. List of the accelerators and their main parameters and features are given in table I.

TABLE I. HV ELECTRON ACCELERATORS DEVELOPED BY EFREMOV RESEARCH INSTITUTE

<table>
<thead>
<tr>
<th>№</th>
<th>Model</th>
<th>E, MeV</th>
<th>P, kW</th>
<th>Year of development</th>
<th>Q-ty</th>
<th>Main features</th>
<th>Type of HV insulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RTE(D)-1</td>
<td>1.0</td>
<td>3</td>
<td>1967</td>
<td>6</td>
<td>400 Hz resonant transformer</td>
<td>Compressed gas</td>
</tr>
<tr>
<td>2</td>
<td>Electron-1-4</td>
<td>0.7</td>
<td>10</td>
<td>1963-78</td>
<td>24</td>
<td>400 Hz single-phase TR with grounded magnetic core</td>
<td>Oil-barrier polymer film</td>
</tr>
<tr>
<td>3</td>
<td>Aurora-1,2</td>
<td>0.5</td>
<td>25</td>
<td>1975-76</td>
<td>5</td>
<td>50 Hz three-phase TR with grounded magnetic core and cable feeder</td>
<td>Oil-barrier polymer film, cable with polyethylene insulation</td>
</tr>
<tr>
<td>4</td>
<td>Aurora -3-9</td>
<td>0.3-0.75</td>
<td>20-75</td>
<td>1980-90</td>
<td>11</td>
<td>50 Hz three-phase TR with grounded magnetic core and cable feeder</td>
<td>Compressed gas, cable with polyethylene insulation</td>
</tr>
<tr>
<td>5</td>
<td>Model of powerful accelerator</td>
<td>1.0</td>
<td>100</td>
<td>1980</td>
<td>1</td>
<td>50 Hz double three-phase TR with grounded magnetic core</td>
<td>Compressed gas</td>
</tr>
<tr>
<td>6</td>
<td>Electron-6</td>
<td>1.5-2.5</td>
<td>60</td>
<td>1987</td>
<td>1</td>
<td>500-750 Hz single-phase TR without iron core</td>
<td>Compressed gas</td>
</tr>
<tr>
<td>7</td>
<td>Electron -7</td>
<td>1.0</td>
<td>100</td>
<td>1988</td>
<td>2</td>
<td>500-750 Hz single-phase TR without iron core</td>
<td>Compressed gas</td>
</tr>
<tr>
<td>8</td>
<td>Electron -10</td>
<td>0.75</td>
<td>50</td>
<td>1994</td>
<td>4</td>
<td>600-850 Hz single-phase TR without iron core</td>
<td>Compressed gas</td>
</tr>
</tbody>
</table>

Listed accelerators have been delivered for various radiation technologies: curing of coatings, polymers’ modification, monomers’ incrementation to fabrics, rubber radiation vulcanization, all in commercial scale, and for pilot installations for environmental protecting technologies – irradiation of matters in gaseous phase.
Basing on experience of pilot and several full-scale installations already built for electron beam treatment of gases one can conclude that optimal electron energy lays in a region 0.8 – 1.0 MeV, which allows to create installations with high efficiency and high beam power utilization, and beam power – up to 1 MW. Accelerators within the same energy and power ranges may be applied also for liquid matters treatment.

From these considerations, accelerating voltage of 1 MV and beam power 500 kW have been chosen as initial ones when selecting basic schematic, design and technological solutions of the environmentally oriented accelerator under development.

2. VALIDATION OF BASIC SCHEMATIC AND DESIGN SOLUTIONS

The most important requirements for a high power accelerator are:

1. High wall plug – electron beam efficiency coefficient;
2. High operating reliability.

Experience of the accelerator technique verifies that main elements of the already built accelerators – HV generators, electron sources, accelerating tubes, outlet windows, have quite sufficient reliability in the power range up to 100 kW thus providing the accelerators’ users with annual running hours of 6 – 7 thousand hours. For the environmentally oriented powerful machines this parameter should be raised up to 8 thousand hours.

2.1. HV generator

The highest coefficient of efficiency (92-95%) can be reached by using three-phase TRs with closed magnetic core fed by industrial net voltage frequency 50-60 Hz. The TRs of this type have no fundamental restrictions on power grow, for example, several years ago we completed preliminary design project of a DC source with output voltage 2 MV and power 100 MW [2]. Dimensions of this type of TR for a fixed voltage do not noticeably grow if its power increases, rectified voltages ripple is quite low (±5.6% for a three-phase bridge rectifying circuit) at regulation limits from zero to a full power, that is adequate to provide irradiation field sizes stability with the beam scanning along outlet window (windows).

HV generators built on this basis were thoroughly studied during development and operation of “Aurora” series accelerators with energies from 0.3 to 0.75 MeV and beam power up to 75 kW (see Fig. 1) that were being built by our institute for the years (see table I, pp.2, 3), and also in a model of the powerful accelerator (ibid, p.4).

FIG 1. Three-phase TR of “Aurora-9” accelerator, 0.75 MV, 150 mA
2.2. High voltage insulation

Oil-barrier insulation of HV structure has higher electric strength than gas one, it does not require any gas pumping and gas drying stations, because of above reasons it is wildly used in electrical engineering, in particular in power transformers. Due to that features we used this type of insulation (with addition of polymer film layers to cardboard barriers) in several models (“Electron-3.4”, “Aurora-1.2”), some of these accelerators are being run for today. Experience of exploitation of the accelerators has shown that this kind of insulation is quite sensitive for fast transients. Unlike powerful transformers, loaded on a stable or slow changing load, during operation of the accelerators fast transients are possible. They can be caused by electric partial or full breakdowns in an accelerating structure, or emergency switches off of the accelerators by technological or other reasons. Such abrupt transients lead to non-linear redistribution of voltage in TR’s elements due to parasitic capacities discharges, following by local over-voltages, and in result – appearance of partial discharges in the barriers material causing with time an electric breakdown of insulation structure and the accelerator damage. The same happens to solid cable insulation conducting high voltage from HV generator to the accelerating structure.

Gas insulation is free from above disadvantages. Due to this reason it (namely SF₆) was chosen for the powerful accelerator under development.

2.3. Electron source and accelerating tube

Emitters made from lanthanum hexaboride (LaB₆) provide stable and continuous operation with emission current density up to 1 A/cm² under pressure about 10⁻⁶ torr, do not require fore training and due to that features are wildly used in HV accelerators.

Electron sources with 6 mm diameter emitting pellet are used in the accelerators manufactured in our institute for a beam current of 100 mA. Theirs heating power is about 50 W, typical life time – several thousand hours.

The same current density level was taken for an electron source for several hundred mAs accelerator, so emitter diameter has been increased to 13 mm and heater’s power has risen up to about 100 W (see Fig. 2) that, as we hope, insures the same level of a life-time.

As it is known, electron beam acceleration is taking place in an accelerating tube. The tube is combined from cylindrical ceramic insulators and metal electrodes formed as plane diaphragms glued or welded to each other.

Electron precipitation on the tube electrodes depends on the beam diameter and current. Field experience shown, that for beam currents of 100 mA minimally sufficient diameter of the electrodes’ aperture is in an order of 35 mm. Such a diameter allows get ample vacuum in the electron source.
region and stray beam current on the tube electrodes does not exceed $10^{-6}$ A. As it shown in [3], when current density distribution across axial symmetrical beam agrees with Gauss law: $J=J_0 \exp(-r^2/r_b^2)$, where $J_0$ – current density on the axis of symmetry, $r_b$ – beam effective radius determined as a radius where current density is lesser than $J_0$ in $\epsilon$ times, than ratio of beam current ($I_b$) to a current absorbed by electrodes ($I_e$) is equal to $I_b/I_e = \exp(r_e^2/r_b^2)$, and electrode aperture ($d=2r_e$) for the same current density and the beam current level on electrodes of $10^{-6}$ should be risen up to 80 mm. In the same time increasing of an aperture provides better conditions for the accelerating tube pumping.

From these reasons the electrodes aperture of tube has been taken equal to 80 mm and overall diameters of insulators 205 mm, longitudinal electric field strength was chosen slightly lower than 1 MV/m.

2.4. Accelerator assembly layout

Basic units of HV accelerator are HV generator, creating DC high voltage, an accelerating structure consisting from an accelerating tube and electron source and electron beam field forming system comprised from a vacuum chamber, an outlet window and beam scanning device. Mutual arrangement of HV generator and accelerating structure in many respects determines the accelerator size and cost as well as the accelerator’s premises dimensions.

The most compact machines are those where TR and accelerating structure are put in the same pressure tank, but characteristic feature of any transformer is a presence of alternative magnetic field which makes difficult to combine before-mentioned two units in one volume. This problem has been successfully solved for single-phase TRs without iron core (accelerators of ELV series made by BINP and Electron-6-10 by our institute, table I, pp. 6-8) by placing the accelerating tube on the TR axis of symmetry (cross component of the magnetic field here is minimal) and by electromagnetic screening of the tube [4,5].

There are no places in three-phase TR’s with closed magnetic core where magnetic induction vector is equal or to zero value and to exclude completely influence of stray magnetic fields on accelerated electrons is possible if arrange these two main units in separate high pressure tanks conducting HV by a feeder filled also with gas to avoid before mentioned faults of solid and oil-barrier insulation. Exactly this version of the accelerators’ design was purposed by us in 1994 for the tender for electric station in Pomorzany, Poland.

Continue with three-phase TR’s theme, in a case when a number of the core rods is doubled and the same phases are put on the rods set oppositely, as it is shown in Fig. 3, than stray magnetic field of the opposite phases are being compensated and the accelerating tube can be put on the TR axis. This idea was studied and purposed for a powerful accelerator (2 MeV, 1 MW) and lately realized in its model (1 MeV, 100 kW, see table I, p. 4, Fig. 3 and Fig. 4). The solution has confirmed its validity but volume of pressure tank grows in this case almost twice and for these reasons we did not proceed further with this idea [6].
FIG 3. Schematic view and rectifying circuit of three-phase double TR for the HV electron accelerator.
1 – high pressure tank; 2 – magnetic rod; 3 – yoke; 4 – primary winding; 5 – secondary winding coil; 6 – grounded electrode; 7 – HV electrode; 8 – electron source; 9 – accelerating tube; 10 – diodes.
FIG 4. Assembly process of double three-phase TR on 1 MV.

Trying to find solution for arrangement of the TR and accelerating structure in the same tank we carried out some investigations in recent years and found that in a case when current-carrying elements of TR are dived in space with the accelerating structure and the latter is electromagnetically screened, than magnetic field influence can be suppressed down to acceptable level.

Exactly this arrangement of the main units has been taken for the environmental powerful accelerator under development.

2.5. Electron beam irradiation field forming system

Electron beam irradiation field forming system creates irradiation field of required size on an object under treatment, in our case by scanning the beam along foil outlet windows. Average beam current density on the foil providing life time of the foil for several thousand hours should not be higher than 0.1 mA/cm² in condition of effective cooling. Beam power losses in the foil can be removed by different methods; two of them are the most common: 1. by air blowing on the foil; 2. contact one – by heat removal by its conducting via foil to a water cooled supporting grid.

First method is prevalent. Its merits are a comparatively simple window design, possibility to use a rather wide in cross direction windows and not severe requirements on the beam quality (the beam can be as large as several cm on the foil). From the other hand, it requires rather high electric power for the blowing devices and has a possibility of the foil rupture, which can not be completely excluded, and which may cause a serious damage of the accelerator requiring a rather time-taking repair.

During the last years we use supporting grids with water-cooled frame in the outlet devices of our accelerators. The grids have ribs of special form making transparency of the grid for electrons higher than its optical transparency. This effect has been verified experimentally, for example for the grid with optical transparency of 85%, the electron one is 92%, i.e. beam current losses in the grid are lower in two times. As a distance between the ribs is small, during the foil aging caused by gradual changing of its structure, no foil rupture and following sucking it into a vacuum chamber is taking
place but some gradually and slow growing leak appears thus informing about necessity to replace the foil.

Heat conduction through the ribs to a water-cooled grid’s frame the more effective the shorter the ribs are, because of this more narrow windows are preferable, that, accordingly puts more severe requirements on the beam quality, in particular, its diameter should be 0.5-1.0 cm, that in one’s turn, calls for higher scanning frequency to avoid the foil instantaneous overheating.

There is no need for any air blowing of the window with supporting grid and it is possible to exclude, in principle, additional foil of a reactor (that would increase the whole process efficiency) but this idea of course should be preliminary studied and experimentally confirmed.

3. BRIEF DESCRIPTION OF THE ACCELERATOR

Taking into account before mentioned considerations we developed and manufactured accelerator for environmental purposes, its main technical characteristics are given in table II.

<table>
<thead>
<tr>
<th>№</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Accelerating voltage, MV</td>
<td>0.8-1.0</td>
</tr>
<tr>
<td>2.</td>
<td>Instability of the accelerating voltage (not counting ripple with frequency higher than 50 Hz), %, not higher</td>
<td>±5</td>
</tr>
<tr>
<td>3.</td>
<td>Electron beam current, mA</td>
<td>0-500</td>
</tr>
<tr>
<td>4.</td>
<td>Beam current instability, %, not higher</td>
<td>±2</td>
</tr>
<tr>
<td>5.</td>
<td>Rated power of the accelerator, kW</td>
<td>500</td>
</tr>
<tr>
<td>6.</td>
<td>Scanning length of electron beam, cm</td>
<td>200-240</td>
</tr>
<tr>
<td>7.</td>
<td>Non-uniformity of linear current density measured on 10 cm distance from the outlet window foil, %, not higher</td>
<td>±10</td>
</tr>
<tr>
<td>8.</td>
<td>Beam scanning frequency, Hz</td>
<td>≥400</td>
</tr>
<tr>
<td>9.</td>
<td>Wall plug – electron beam conversion efficiency at the rated power (500 kW), %</td>
<td>≥90</td>
</tr>
<tr>
<td>10.</td>
<td>Annual error-free running time, %</td>
<td>≥90</td>
</tr>
</tbody>
</table>

The accelerator HV generator, the electron source and accelerating tube are placed in a tank filled with compressed insulating gas. High voltage is generated by three-phase TR with closed grounded magnetic core and parallel cascades feeding supplied from industrial net 3×380 V, 50 Hz.

Magnetic core of the TR is a spatial-symmetrical structure combined from three vertical rods and two circular yokes closing magnetic flux. Three primary windings are wound on the magnetic rods and connected to thyristor voltage regulator. Three secondary windings are composed from coaxial to the primary windings separate coils. Every three secondary winding coils located on the same level but on different rods are connected into star circuit and together with 6 diodes, switched into three-phase rectifying bridge circuit, create separate rectifying cascade. The cascades connected by DC voltage in series.

Diode type electron source with LaB$_6$ emitting pellet is heated from special winding, current regulation made through a fiber-optic channel.

The accelerating tube consists from ceramic insulators and metal electrodes hermetically glued. Resistive voltage divider connected to the outer parts of the electrodes. The tube is incorporated into HV structure common with TR and placed lower than the windings. The whole HV structure is surrounded by gradient rings.

Electromagnetic lens, beam scanning and extraction device allows to extract accelerated electron into atmosphere and create irradiation field of required sizes. Extraction device consist of four
outlet windows directed in parallel, each window have supporting water cooled grid. Four ion pumps are installed directly on a vacuum chamber of the beam irradiation field extraction system.

The accelerator is equipped with automated control system on a base of industrial computer providing parameters regulation in preset limits and automatic switch off of the accelerator in emergency situations. The controls and monitoring units combined in the control rack.

The accelerator is assembled at our testing facility and being under adjustment. We are working to get full set of the parameters.

The accelerator outlet window is shown in Fig. 5, in Fig. 6 and Fig. 7 can be seen the accelerator’s HV structure with a lid removed from the pressure tank.

**FIG 5. Outlet window with supporting grid of powerful electron accelerator.**

**FIG 6. Assembled HV accelerator with three-phase TR 1 MV, 500 kW, view from above.**
4. CONCLUSION

Necessity to decrease anthropogenic environmental pollution puts a task of development of HV accelerators for introduction of nature conservation technologies in commercial scale. High efficiency and operation reliability in a power range noticeably higher than already mastered level are required.

In design of the accelerators basic units, namely, HV generators, accelerating structures, electron beam irradiation field forming systems and extraction devices solutions that demonstrated already theirs operational capacity in the machines of a lesser power may be used. From the other hand, experience gained by already full-scale built powerful installations shows that a number of problems remain unsolved that put obstacles on a way of wide implementation of exhaust gases irradiation processing.

Attempts to built the accelerator meeting all requirements in a frame of specific contracts, although already shown noticeable progress in a sense of the power grow, acquiring of very valuable experience, carry some risk caused by insufficient study of the problems connected with power increasing, lack of time and means for the thorough research works.

It looks reasonable to suggest creation of full-scale pilot installation with HV accelerator of required power (1 MW, for example) not bound to a specific commercial contract, where researches and studies of the accelerator main systems, theirs optimization and longevity tests can be carried out thus providing development of the accelerator into really reliable and effective tool for applying to environmental tasks.
REFERENCES


DOSIMETRY FOR COMBUSTION FLUE GAS TREATMENT WITH ELECTRON BEAM

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Abstract

The electron beam treatment of flue gas is one of the new technologies. There are several reasons for carrying out dosimetry at various phases of the project as understanding the process and optimizing the equipment, for process control and for troubleshooting in case of malfunction etc. The main challenge in measuring dose for flue gas applications is that the medium being irradiated is gaseous. Two general approaches for dose measurements are: adding/placing some dosimeters in the reaction vessel (gas) and using the components of the gas itself as a dosimeter. Various techniques and methods have been tried which are discussed in this paper.

1. INTRODUCTION

Combustion of oil and coal generates flue gas which contains harmful components such as SO₂ and NOₓ. Chmielewski [1] has tabulated concentrations of these two and other pollutants in flue gases from burning hard coal, lignite, municipal waste and copper smelters. Their emission into the atmosphere needs to be strictly controlled, since such pollutants affect people’s health, increase corrosion, and destroy cultivated soil and forests. It is generally assumed that the SO₂ and NOₓ emission standards for power plants and industrial burners can only be met by secondary, i.e. post-combustion flue gas cleaning techniques [2]. Thus, the only option in the case of existing boilers, when large changes to the combustion process cannot be introduced, is to control the emissions. Several technologies exist for flue gas cleaning. Conventional air pollution control technology (wet scrubbing and selective catalytic reduction – SCR) has been developed in Japan, Germany and the USA to a state which will not allow significant cost reduction in the near future, especially for medium-sized boilers (50-300 MWe). Desulphurization of flue gas is usually accomplished using a wet method, in which a large quantity of wastewater has to be treated. On the other hand, NO is difficult to remove because of its low reactivity. The modification of combustion furnaces and process for further reducing the emission of NO has not been achieved yet.

The new methods must have advantages (dry system without any wastewater treatment, simultaneous SO₂ and NOₓ removal, simple system with easy operation, no expensive catalysts for NOₓ removal, useful by-product) over the conventional ones with higher removal efficiency and lower cost to be accepted in the market in near future. The electron beam treatment of flue gas is one of these new technologies. Its success in significantly reducing SO₂ and NOₓ has already been demonstrated in many pilot plants and a few full commercial plants.

There are several advantages in employing ionizing radiation (electrons) for this purpose, including [3]:

- several polluting gases are removed simultaneously with high efficiency,
- dry system without any wastewater treatment,
- simple system with easy operation,
- compact plant, thus easy for retrofitting in an existing power station,
- high energy efficiency, and
- by-product can be used as fertilizer.

The process proposed, requires beam power of 300 kW or more, and electron energy in the range of 0.8 to 1 MeV. Accelerators suitable to fulfill such requirements are based on high-power, high-voltage transformers according to the present state-of-the-art accelerator technology. The electron beam technology is relatively flexible and adaptable to local conditions. The process can be easily adapted for different removal efficiency levels and adjusted for use with different fuels. Also,
retrofitting of existing facilities to reduce NO\textsubscript{x} and SO\textsubscript{2} concentrations to meet low-space requirements is an attractive option.

The small-scale experiments and results obtained in pilot plant facilities showed that SO\textsubscript{2} and NO\textsubscript{x} can be simultaneously removed from irradiated flue gas from coal-fired, crude-oil and gas-fired power plants. The direct technological goal of flue gas irradiation is the formation of highly reactive species like ions, low energy electrons, molecular ions, free radicals and also excited atoms and molecules, which are capable to oxidize SO\textsubscript{2} and NO\textsubscript{x} into SO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} and to convert them into acids with the presence of water. This is a dry-scrubbing process of simultaneous SO\textsubscript{2} and NO\textsubscript{x} removal. Researchers have shown that irradiation of flue gases with an electron beam can bring about chemical changes that make removal of these substances easier.

There are several energy related process parameters that impact the efficacy of the process and thus the success of the technology, and therefore it is essential that their values during the process are well determined. The primary ones are:
- **process dose**, that is the minimum dose required to achieve the desired levels of the pollutants; this value drives the entire process. Of course, its value generally would depend on many other process parameters, such as initial pollution concentration, temperature and humidity. Thus, its value must be determined for the case under consideration.
- **dose distribution in the reaction vessel**; as discussed earlier non-uniformity of dose reduces removal efficiency, especially of NO\textsubscript{x}. Thus, various ways may be employed to make dose more uniform in the reaction vessel. Thus, the distribution needs to be measured to see the effect of this and to select the optimum case. Information about dose distribution also would help to determine the optimum size of the reaction vessel.
- **energy utilization efficiency**; that is the energy absorbed by gas and used for chemical reactions in the reaction vessel as compared to what was emitted by the radiation source, generally electron accelerator. The economics of the process strongly depends on the cost of the electron beam power delivered to the flue gas. Thus, efficiency of the electron accelerators becomes one of the most important issues to be resolved before this technology can be widely used in a full power plant installation.

In general, there are several reasons for carrying out dosimetry at various phases of the project. For example, in research phase, it is necessary for understanding the process and optimizing the equipment; in pilot scale facilities, this information needs to be reconfirmed that scaling has not affected the results, and in industrial facilities dosimetry may be needed for process control and for troubleshooting in case of malfunction.

The main challenge in measuring dose for flue gas applications is that the medium being irradiated is gaseous. And it is not placed in containers like medical devices or foodstuff for irradiation. For flue gases, some part can move relative to other parts. This complicates interpretation of dosimetry results. Two general approaches for dose measurements are: i) adding/placing some dosimeters in the reaction vessel (gas), and ii) using the components of the gas itself as a dosimeter. Various techniques and methods have been tried which are discussed below.

2. DOSE AND DOSE DISTRIBUTION MEASUREMENT.

The basic data for estimation of the radiation dose being absorbed in gas may be obtained from measurement of the gas temperature increase in irradiation zone; the ratio of the gas thermal energy raise to its mass flow gives the average dose rate. This method (Fig. 1 below) is the simplest and gives on-line data, but needs some verification to make possible evaluation of errors due to RV walls heating or gas volume increase in RV.

262
Additional measurements can be performed using well known solid-state dosimeters like PVC or CTA, but in this case the hardware arrangement and the measurement procedure become more complicated. Fig. 2 shows possible location of CTA dosimeter stripes in perpendicular crosssection of RV and typical readout of CTA optical density changes due to radiation absorbed.

Data recorded from irradiated CTA matrix contain much more information than this provided by average dose measurement, after digital processing and image transformation it is possible to obtain dose map of examined RV crosssection (Fig. 3).
Another suitable from point of view of irradiated medium type dosimetry technique is applying a gas dosimeter. There are several compounds that can be used as gas-based dosimeters, the one known from literature is N$_2$O, which radiation decomposition reactions and reaction rates are described in [2.]

TABLE I. N$_2$O RADIATION DECOMPOSITION REACTION RATES. (CITATION FROM RADIAT. PHYS. CHEM., 1976, VOL. (6), P. 88.)

<table>
<thead>
<tr>
<th>Dose rate [eV·g$^{-1}$·s$^{-1}$]</th>
<th>G (N$_2$)</th>
<th>G (NO)</th>
<th>G (O$_2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25·10$^{17}$ to 1·10$^{18}$</td>
<td>10.0 ± 0.2</td>
<td>3.4 ± 0.3</td>
<td>4.0 ± 0.4</td>
<td>89</td>
</tr>
<tr>
<td>8.3·10$^{15}$</td>
<td>10.1</td>
<td>5.1</td>
<td>3.8</td>
<td>90</td>
</tr>
<tr>
<td>1·10$^{27}$</td>
<td>12.4 ± 0.3</td>
<td>5.6</td>
<td>4.8</td>
<td>42, 92, 93</td>
</tr>
<tr>
<td>2·10$^{28}$</td>
<td>12.3 ± 0.3</td>
<td></td>
<td></td>
<td>14</td>
</tr>
</tbody>
</table>

As the products of N$_2$O radiation decomposition are pure oxygen and nitrogen gases of ppm magnitude of concentration, this method cannot be used for in situ measurements in Reactor Vessel; it can be used for calibration of another type of dosimeter, like CTA to be used with gas phase for quantitative measurements.

The analysis of O$_2$ and N$_2$ yield must be carried out by Gas Chromatograph instrument and extreme care must be taken for the purity of original N$_2$O gas and all of steps of gas samples handling procedure. Any leakage of air into experimental equipment would make the final dose reading completely erroneous.
FIG. 4. The experiment with irradiation N$_2$O in small glass bottle in different conditions. (Together with the bottle there are stripes of CTA put along for comparison.) The graph given below (Fig. 5) shows the experiment results as dependence of dose in N$_2$O vs. dose reading from CTA.

As it can be easily seen, the relationship is very close to linear, but the coefficient, which is almost 3, needs some explanation. The solid-state CTA dosimeter sensitivity for electrons of energy below 100keV is not guaranteed by the manufacturer, as the electrons penetration depth is too low to induce chemical changes in material. But from the point of view of the electrons contribution into reactions yield in the gas, these of energy below 100keV give most part, because of growing incidence crosssection of electrons with gas molecules.

FIG. 5. Dependence of dose measured in N$_2$O vs. dose reading from CTA
3. CONCLUSION

There is no versatile method for measurement of dose in the gas as well as dose distribution. Some methods, like calorimetric can be easily applied in industrial conditions, but don’t provide the information about dose distribution over the Radiation Field. Another, based on solid-state dosimeters, can give us good mapping of dose in Reactor Vessel, but in limited dose and electrons energy range. The selection of a particular method in this case, should be preceded with consideration of what kind of data is to be collected and what are the technical specifications of a gas irradiation system.

REFERENCES


RELIABILITY OF HIGH POWER ELECTRON ACCELERATORS FOR RADIATION PROCESSING

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Abstract

Accelerators applied for radiation processing are installed in industrial facilities where accelerator availability coefficient should be at the level of 95% to fulfill requirements according to industry standards. Usually the exploitation of electron accelerator reviles the number of short and few long lasting failures. Some technical shortages can be overcome by practical implementation the experience gained in accelerator technology development by different accelerator manufactures. The reliability/availability of high power accelerators for application in flue gas treatment process must be dramatically improved to meet industrial standards. Support of accelerator technology dedicated for environment protection should be provided by governmental and international institutions to overcome accelerator reliability/availability problem and high risk and low direct profit in this particular application.

1. INTRODUCTION

The present status of development and manufacturing of electron accelerators is suitable for high capacity radiation processing. Automatic control, reliability and reduced maintenance, adequate adoption to process conditions, suitable electron energy and beam power are the basic features of modern accelerator construction. Electron beam plants can transfer much higher amounts of energy into the irradiated objects than other types of facilities including gamma plants. That provide opportunity to construct technological lines with high capacity and they are more technically and economically suitable with high throughputs, short evidence time and grate versatility.

The progress in accelerator technology is tightly attached to the continuously advanced development in many branches of technical activity. The computers and automatic control systems, electronic components including power switches, modulator macropulses technology, new generations of microwave sources are the best examples availability of the power determine components in modern accelerator technology. The new accelerators ideas and constructions are being developed continuously. The most significant advantages of application electron beam sources in radiation processing facilities are related to:

- Availability of high power electron beam suitable for high capacity process with very short exposure time,
- Strictly controlled irradiation zone defined by parameters of electron beam scanning system,
- High fraction energy of electron beam deposited in irradiated object,
- Simple product handling systems for continuous and unit operation irradiation process,
- Safety (electron beam shut off capabilities to stop irradiation),
- Well established accelerator technology and accelerator producers,
- Economic advantages of electron beam processing,
- Easy control of irradiation process,
- Facility compactness,
- Economy of the process.

Accelerators which have been developed and are being used for radiation processing can be divided on following three main groups depend on their construction and electrical field implementation in electrons accelerating process:

- Direct DC transformer accelerators (low and medium energy level),
- RF resonance cavity accelerators (medium and high energy level),
Microwaves linear accelerators (*medium and high energy level*).

The most suitable type of accelerator for certain application depends at first on required electron energy which is directly related to density and structure of irradiated objects and beam power which defines total capacity of the installation. The accelerator selection criteria are as follow:

- Average beam power (*productivity*),
- Electron energy (*penetration*),
- Price (*investment cost*),
- Electrical efficiency (*cost of accelerator exploitation*),
- Size (*building geometry and size*),
- Reliability (*availability >95%*).

It should be noticed that accelerators are not primarily optimized with respect to reliability.

2. RELIABILITY/AVAILABILITY OF ACCELERATORS APPLIED IN ACCELERATOR PROCESSING

High accelerator reliability is especially important during intense accelerator exploitation in the field of radiation processing. Share of maintenance and spare parts cost in exploitation cost grows significantly when accelerator reliability is poor. Electron accelerators spare parts and major maintenance services are available and usually provided by accelerator manufacturers. Presently highly trained personnel are not required to run accelerators because of simplicity of its operation under computer support. High frequency accelerators are more costly to operate due to their more complex construction and much more expensive spare parts like klystrons and magnetrons to compare with direct ones.

Reliability of the accelerators has not been recognized for a long time as real problem of radiation facility exploitation [1]. Only relatively recently high priority of reliability issue is given in accelerator design for very few specific applications like medical accelerators and future huge facilities for high-energy physics exploration [2, 3]. The following definitions are used to describe accelerator reliability/availability problem:

**RELIABILITY**: PROBABILITY that a system can perform its intended function for a specified time interval under stated conditions. High reliability is required when repair of sensitive sub-components are long (or difficult). On the other hand if each failure can be repaired in a very short time so that the system has a high availability, and the maintenance costs are reasonable, the poor reliability may be acceptable.

**AVAILABILITY**: fraction of TIME during which a system meets its specification. High availability is required if continuous service is priority.

**MEAN TIME BETWEEN FAILURE (MTBF)** is the mean number of time units during which all parts of a system perform within their specified limits, during a given time interval. Long period between failures (MTBF) indicates high accelerator reliability.

**MEAN DOWN TIME (MDT)**, the average time a system is unavailable due to a failure. This time includes the actual repair time plus all delays associated with the repair (finding the spare part, etc). Short accelerator down time (MDT) is characteristic for accelerators with high availability level.

**MEAN TIME TO REPAIR (MTTR)** is the sum of corrective maintenance time divided by the total number of failures during a given time interval. Short accelerator repair time (MTTR) is characteristic for well trained personnel and easy access for spare parts.

**REDUNDANCY** is the existence of more than one means for accomplishing a given function. Equipment should not work at full capacity, and some margin must be allowed. Redundancy well describes quality of accelerator design.
Low accelerator reliability/availability (means high risk investment decision) can be recognized as result of following reasons:

- Prototype accelerator construction (*limited exploitation experience*),
- Parameters on the edge of present limits (*unproven working conditions*),
- Components with limited life time (*magnetron*),
- Difficulties in spare parts availability (*limited access*),
- Poor accelerator reliability (*improper design and poor quality components*).

When weak point of certain accelerator construction is established a suitable availability level can be achieved by redesign and reconstruction of critical components or subsystems but it is a matter of finance, manpower and time.

![FIG. 1. Typical statistic of failures during accelerator exploitation](image1)

![FIG. 2. Typical relation between number of failures and sum of the time when a system can not perform its intended function](image2)

Fig. 1 shows typical statistic of failures during the first period of accelerator exploitation. Typically starting up and accelerator commissioning periods are the most difficult in respect to
accelerator reliability. Ageing of components and subsystems becomes a problem for longer exploitation time. Typical relation between number of failures and sum of the time when a system can not perform its intended function is displayed on Fig. 2. The most common are short breakdowns. Only few events are responsible for large downtime. Critical parts of accelerator construction in relation to accelerator reliability are as follow:

- Subsystems;
  - Beam scanning system,
  - Vacuum system,
  - Control system (overload conditions of voltage, current, temperature and other),
  - Cooling system (also emergency switch off).
- Components short life time;
  - Power component (klystrons, magnetrons, thyratrons, vacuum triodes),
  - Electron gun.
- Output window construction;
  - Thickness, dimensions and shape,
  - Window material,
  - Window cooling system.
- Voltage isolation;
  - Electrical breakdowns,
  - Oil/Gas isolation,
  - Withstand voltage level.
- Other;
  - Unsuitable construction.

2.1. Major failure examples

Accelerator failures are not predictable events in general. The most common problems are different for different accelerator construction. The most characteristic failures are connected to electron gun (cathodes) replacement, electrical breakdowns consequences, vacuum and cooling systems inefficient work. The chain of events can be observed in some separate cases. Such situation can be illustrated on example of RF window breakdown (Fig. 3.a) happened in linear accelerator Elektronika 10/10. The primary event was related to electrical spark (breakdown) which damaged ceramic window. RF window separates waveguide where nitrogen under 5 atm pressure is applied and accelerating section with vacuum level $10^{-6}$ Torr. In consequence nitrogen stream enter accelerating section and destroy output window (Fig. 3.b). The same time electron gun cathode was damaged.
Some accelerator constructions suffer from frequent problems with electron gun. It is related mainly to quality of the cathodes used in certain gun construction. The failures are mainly connected to heater damage and breakdowns between heater and cathode material. Construction of gun cathode installed in linear microwave accelerator LAE/13/9 is shown on Fig. 4. The quite good statistic was collected over the period 30 years of accelerator exploitation (Fig. 5).
As it can be easily notice 24 cathodes lifetime is bellow 400 h. Life time of other 24 cathodes is uniformly distributed in time interval 400-5000 h. It is obvious that cathode has some technical capabilities. Unfortunately non proper technology was applied by manufacturer to provide Al2O3 isolation between cathode material and heater. On the other hand cheap cathode units do not created economical problem and quick cathode replacement procedure do not affect significantly accelerator availability.

Much better results regarding cathode lifetime are observed during exploitation linear microwave accelerator Elektronika 10/10 used for radiation sterilization and provided by different manufacturer with different cathode construction with similar technical capabilities. The statistic covers period of 15 years accelerator exploitation is shown in Table I. The cathode life time is over 8000 h and cathode replacement is due to weak emission not due to cathode failure.

The typical reasons of accelerator failure are connected to life time of power components applied in certain accelerator. In case of accelerator Elektronika 10/10 magnetrons are applied as a source of microwave energy. The statistic connected to those devices is provided by Table II. Average lifetime of the magnetrons is to be 1155 h only. It can be easily noticed that quality of such components is not perfect. Only one from 12 units is characterized by weak emission which usually indicates ageing effect. Quite different situation is related to accelerator LAE 13/9 where klystrons are applied as microwave sources (Table III).
TABLE I. EXPLOITATION OF ELECTRON GUN CATHODES INSTALLED IN LINEAR ACCELERATOR
ELEKTORNIKA 10/10

<table>
<thead>
<tr>
<th>No</th>
<th>Year of installation</th>
<th>Life time [h]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1992</td>
<td>9000</td>
<td>Weak emission</td>
</tr>
<tr>
<td>2</td>
<td>1998</td>
<td>4500</td>
<td>Replaced in a good condition together with accelerating section</td>
</tr>
<tr>
<td>3</td>
<td>2001</td>
<td>600</td>
<td>Damaged as a result of broken RF window and output foil</td>
</tr>
<tr>
<td>4</td>
<td>2001</td>
<td>8200</td>
<td>In operation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average lifetime 8600</td>
</tr>
</tbody>
</table>

TABLE II. EXPLOITATION OF HIGH POWER MAGNETRONS IN LINEAR ACCELERATOR
ELEKTORNIKA 10/10

<table>
<thead>
<tr>
<th>No</th>
<th>Life time [h]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200</td>
<td>Heater breakdown</td>
</tr>
<tr>
<td>2</td>
<td>948</td>
<td>Bad vacuum</td>
</tr>
<tr>
<td>3</td>
<td>792</td>
<td>HV breakdowns</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>HV breakdowns</td>
</tr>
<tr>
<td>5</td>
<td>829</td>
<td>Bad vacuum</td>
</tr>
<tr>
<td>6</td>
<td>613</td>
<td>HV breakdowns</td>
</tr>
<tr>
<td>7</td>
<td>184</td>
<td>HV breakdowns</td>
</tr>
<tr>
<td>8</td>
<td>2338</td>
<td>HV breakdowns</td>
</tr>
<tr>
<td>9</td>
<td>2130</td>
<td>Weak emission</td>
</tr>
<tr>
<td>10</td>
<td>1468</td>
<td>In operation</td>
</tr>
<tr>
<td>11</td>
<td>2042</td>
<td>Heater breakdown</td>
</tr>
<tr>
<td>12</td>
<td>1300</td>
<td>In operation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average lifetime 1155 [h]</td>
</tr>
</tbody>
</table>

The average lifetime of applied klystrons was found to be 6648 h. This is much higher than in the case of magnetrons used as source of microwave energy. It should be noticed that both devices operate based on different concepts. Klystron acts as amplifier with stable operating conditions, whereas magnetron is self excited generator which stability and life time is the main technical issue.

TABLE III. EXPLOITATION OF HIGH POWER KLYSTRON IN LINEAR ACCELERATOR LAE 13/9

<table>
<thead>
<tr>
<th>No</th>
<th>Life time [h]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4820</td>
<td>Heater breakdown</td>
</tr>
<tr>
<td>2</td>
<td>8937</td>
<td>Bad vacuum</td>
</tr>
<tr>
<td>3</td>
<td>6222</td>
<td>Weak emission</td>
</tr>
<tr>
<td>4</td>
<td>3167</td>
<td>Weak emission</td>
</tr>
<tr>
<td>5</td>
<td>2814</td>
<td>Weak emission</td>
</tr>
<tr>
<td>6</td>
<td>7481</td>
<td>Weak emission</td>
</tr>
<tr>
<td>7</td>
<td>8723</td>
<td>Weak emission</td>
</tr>
<tr>
<td>8</td>
<td>4689</td>
<td>Bad vacuum</td>
</tr>
<tr>
<td>9</td>
<td>12981</td>
<td>Weak emission</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average lifetime 6648 [h]</td>
</tr>
</tbody>
</table>
Accelerating sections applied in direct accelerators are usually composed from metal electrodes and isolation rings made of ceramic or polymeric materials. Vacuum welding technology are used to connect together metal electrodes and ceramic rings. That difficult and expensive method is replaced by polymer glue which is applied when metal electrodes and polymer isolations rings are used. Unfortunately in certain construction deformation of accelerating structure is being observed (Fig. 6) which directly interferes with electron beam optics and leads in result to beam current reduction and consequently eliminate that device.

![FIG. 6. Deformation of accelerating section at place of installation electron gun](image)

Such deformation process of accelerating structure can be initiated under specific condition of accelerator exploitation and its construction. The most significant reasons which may lead to accelerating section deformation are listed bellow:

- High power of cathode heater what leads to high temperature (>80°C) of accelerating section elements located in close distance to electron gun,
- Lack of sufficient cooling system,
- Application of polymer glue with not suitable properties,
- Heavy mechanical load located on the top of accelerating section which creates forces leading in long period of time to mechanical deformation.

The output electron beam system construction is very important from point of view technological performance of accelerator facility. The most sensitive part of the output system is thin output window foil usually made of titanium. It can be recognized several reason when inadequate quality of output system with titanium foil creates long and expensive breakdown in accelerator exploitation as a result of window foil implosion (Fig. 7):

- Bad quality of titanium foil,
- Distortion of beam scanning pattern,
- Insufficient interlock system which is not able recognize on time distortion of beam scanning pattern,
- Insufficient air cooling system,
− Hard particles in cooling air which could damage output foil,
− Improper design the shape of foil and its supporting system.

A) B)

FIG. 7. Scanner after implosion (A) and broken accelerator titanium foil (B)

The characteristic features of accelerator design which may leads to frequent failures events and consequently reduce accelerator availability are as follow:
− Prototype accelerator construction with limited exploitation experience,
− Parameters on the edge of present limits,
− Improper design of selected systems,
− Difficulties in spare parts availability,
− Difficult interchangeability of the components,
− No share reliability experience policy,
− No active efforts to redesign faulty systems according to exploitation experience.

3. QUALITY OF ACCELERATOR CONSTRUCTION AND EXPLOITATION

High-power electron accelerators for radiation processing are composed from the following main systems and components:
− Injector (gun and gun supply system),
− Main power support system (DC power supply and/or pulse modulator; RF or microwave sources),
− Output device (beam delivery system),
− Control and safety interlock systems,
− Auxiliary systems (air and water cooling, vacuum system, power line supply).

Quality requirements regarding accelerator construction and exploitation can be divided on following three main directions:
− Quality of components and subsystems,
− Design quality,
− Quality of exploitation and servicing.
Parallel efforts are necessary regarding: components, design, exploitation and servicing quality to achieve suitable accelerator availability/reliability. Share reliability experience is also needed to reduce accelerator down time and apply technical solutions already tested.

3.1. Quality of components and subsystems

Quality of the components and subsystems are characteristic for certain manufacturing technology applied by producers of different devices. Components can be divided on those which are characterized by limited (like RF tubes) or unlimited (like semiconductors components) lifetime. Accelerator reliability/availability can be improved in respect to component quality by proper design and exploitation. The following steps can be taken:

− Implementation of component redundancy (design),
− Components with limited lifetime (like RF tubes) can be replaced after a pre-determined operation time,
− Unlimited lifetime components should be periodically inspected and tested,
− Components and system upgrades based on lost time,
− Replacement of 25-30 years old components.

Reliability of electronic components is characterized by random failures and is differ to mechanical components reliability which is mostly described by aging and overstresses. As a starting point of any reliability oriented design should be identification in advance the causes of all possible failures that may occur in the system. The following components can be recognized as critical from point of view accelerator reliability/availability:

− Gun (type of gun, cathode life time),
− RF source (klystron, magnetron, life time),
− Output foil,
− Pulse power components.

3.2. Design quality

The principal criteria of accelerator design optimized with respect to reliability are listed bellow:

− Design for fast interchangeability of components,
− Fault diagnostics included to accelerator control system,
− Separation of vacuum sub-systems with shut-off valves,
− Automation to avoid human mistake („Plug and play” design concept),
− Design optimization with suitable margins (redundancy),
− Electrical mains drops consequences should be foreseen and avoided,
− Modular design at all levels,
− Automated ramping procedure to recover HV or RF power and electron beam,
− Ability for long exploitation (18 h/day, round o’clock)

3.3. Quality of exploitation and servicing

The terms of accelerator exploitation and servicing have a great influence on accelerator reliability/availability. The following actions can significantly improve quality of exploitation servicing:

− Existence accelerator repair and component replacement procedures,
− Suitable operator’s training,
− Experts on standby ready to intervene,
− Quick troubleshooting procedures,
− Recording and analyzing failures, implementation strategies to make them disappear,
− Rigorous spare parts policy (ready-to-operate units available and spare parts),
− Preventive maintenance (devices are replaced after predetermined operation time),
− Built in preventive maintenance scheduling and monitoring,
− Missing cooling abilities,
− Starting up and closing down procedures (switching of power line abruptly causes faster ageing).

Preventive maintenance procedures should be established for certain accelerator because of differences in construction and requirements connected to applied concept of accelerator design (direct, RF, microwave accelerators). Accelerator manufacturers should provide sufficient information related to preventive maintenance activity (every day, week, quarter, year). The maintenance should also include such activity as:

− Regular replacement of water and air filters,
− Regular replacement of belts, hoses, and lubricants,
− IR detection of electrical connections (3 years cycle),
− Cleaning of HV cables and components (6 months cycle),
− Vibration/frequency analysis of rotating equipment (3 months cycle).

Repair time may have considerable influence on the availability of the accelerator. Repair procedures provided by accelerator manufactures should describe in details:

− Fault detection and diagnosis process,
− Preparation time needed to start the repair,
− Fault correction,
− Post-repair parameters verification,
− Restart of the system.

Electron accelerators for radiation processing are being applied since 1956 were first commercial facility has been used. Quick progress in accelerator technology eliminated early accelerators design. The present level of accelerator development can fulfill requirements (electron energy, beam power) coming from industry applying radiation technology. Long exploitation of accelerators becomes current issue. Extended time of accelerator exploitation (over 20-30 years) creates problem with spare parts availability. The other common problem is related to available technical parameters which are usually different to compare with nominal parameters specification. The typical equipment aging problems are related to:

− Electrical connections oxidizing,
− HV breakdown of dirty cables,
− Availability of spare parts,
− Communication faults,
− Calibration and stability problems.
Maintaining accelerator availability over the long term will require significant resource commitment or a reduction of the machine performance requirements.

4. CONCLUSIONS

Accelerator reliability should be recognized as very important for any industrial facility including environmental applications. Particularly the reliability of high power accelerators for environmental protection must be drastically improved with respect to the present situation. High accelerator reliability/availability according to industrial standards can be achieved by parallel efforts related to components, design, exploitation, and servicing quality. Reliability (availability) should be now a priority for electron accelerators designers. Reducing the downtime due to long failures is mostly financial issue. It should be noticed that reliability oriented accelerator design may increase cost of the accelerator by 30-50% to compare with a nominal design. Life time of certain accelerator components should be extended. The terms of accelerator exploitation and servicing have a great influence on accelerator reliability/availability.

REFERENCES

HIGH POWER ELECTRON ACCELERATORS FOR FLUE GAS TREATMENT

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Abstract

Flue gas treatment process based on electron beam application for SO$_2$ and NO$_x$ removal was successfully demonstrated in number of laboratories, pilot plants and industrial demonstration facilities. The industrial scale application of an electron beam process for flue gas treatment requires accelerators modules with a beam power 100-500 kW and electron energy range 0.8-1.5 MeV. The most important accelerator parameters for successful flue gas radiation technology implementation are related to accelerator reliability/availability, electrical efficiency and accelerator price. Experience gained in high power accelerators exploitation in flue gas treatment industrial demonstration facility was described and high power accelerator constructions have been reviewed.

1. INTRODUCTION

Above 1200 accelerators have been build for radiation processing (the total number of accelerators applied in science, medicine and industry amounts above 15 000). The recent progress in accelerator technology development based on new accelerator constructions and modern components application is focused on:

- Accelerator technology perfection (electrical efficiency, cost);
- Reliability according to industrial standards;
- Accelerators for MW power beam level;
- Compact accelerator constructions;
- Very low energy, powerful accelerators.

Although there are many different types of accelerators offering a wide range of performance ratings, only few would be suitable for particular application. The basic specifications for the electron energy, beam current and beam power should be derived from the process requirements (absorbed dose distribution, the product size, the shape and density, and the throughput rate) to ensure satisfactory results with minimum capital and operating costs [1]. The full scale industrial implementation of an electron beam process for flue gas treatment requires accelerators modules with a beam power 100-500 kW and electron energy range 0.8-1.5 MeV. Power plant offering 500 MW of electrical power may require above 5 MW of electron beam power deposited the flue gas emitted during combustion process [2].

2. ACCELERATOR TECHNOLOGY FOR ENVIRONMENTAL APPLICATION

Accelerator technology was found to be useful in many radiation processes applied for environment protection. Table I illustrates capability to electron beam treatment in gas, liquid and solid phase of matter.
TABLE I. RADIATION TECHNOLOGY APPLIED IN ENVIRONMENT PROTECTION

<table>
<thead>
<tr>
<th>Phase</th>
<th>Object</th>
<th>Additives</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>Flue gas</td>
<td>(\text{SO}_2; \text{NO}_x)</td>
<td>Removal</td>
</tr>
<tr>
<td></td>
<td>VOC</td>
<td>Organic compounds</td>
<td>Degradation, removal</td>
</tr>
<tr>
<td>Liquid</td>
<td>Drinking water</td>
<td>Chemical pollutants</td>
<td>Degradation, removal</td>
</tr>
<tr>
<td></td>
<td>Wastewater</td>
<td>Bacteria; viruses; parasites</td>
<td>Hygienization</td>
</tr>
<tr>
<td></td>
<td>Industrial wastes</td>
<td>Organic and nonorganic compounds</td>
<td>Degradation, removal</td>
</tr>
<tr>
<td>Solid</td>
<td>Sewage sludge</td>
<td>Bacteria; viruses; parasites</td>
<td>Hygienization</td>
</tr>
<tr>
<td></td>
<td>Solid materials</td>
<td>Agriculture wastes</td>
<td>Transformation</td>
</tr>
</tbody>
</table>

The selection of accelerator parameters depends on technological process requirements which are directly connected to density of irradiated material. Flue gas treatment process has been investigated since 1970, when first experiment in that field was performed in Japan [3]. The research study was carried on in many laboratories in different countries as it can be seen in Table II. According to presented data accelerator performances in laboratory facilities for flue gas treatment are not critical. Energy range covers 0.22-12 MeV and beam power 3.6-22 kW. Efficient utilization of electron beam and related to that economical parameters of laboratory facilities with flue gas flow rate bellow 1000 Nm\(^3\)/h are not important from point of view technology development.

TABLE II. BASIC PARAMETERS OF ACCELERATORS APPLIED IN FACILITIES FOR FLUE GAS TREATMENT

<table>
<thead>
<tr>
<th>Type of installation</th>
<th>Energy ([\text{MeV}])</th>
<th>Power ([\text{kW}])</th>
<th>Type of accelerator</th>
<th>Company, country</th>
</tr>
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<tbody>
<tr>
<td>Laboratory installation</td>
<td>12</td>
<td>1.2</td>
<td>Linac</td>
<td>Ebara, Japan</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>15</td>
<td>Cockroft-Walton</td>
<td>JAERI, Japan</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.2</td>
<td>Dynamitron</td>
<td>University, Tokyo, Japan</td>
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<tr>
<td>Flue gas flow rate: &lt;1000 Nm(^3)/h</td>
<td>0.22</td>
<td>22</td>
<td>Transformer</td>
<td>Uni. Karlsruhe, Germany</td>
</tr>
<tr>
<td>Pilot installation</td>
<td>0.3</td>
<td>3.6</td>
<td>&quot;</td>
<td>KfK, Germany</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>5</td>
<td>&quot;</td>
<td>INCT, Poland</td>
</tr>
<tr>
<td>Flue gas flow rate: 1000-20000 Nm(^3)/h</td>
<td>0.8</td>
<td>2 x 45</td>
<td>-</td>
<td>Ebara, Japan</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>2 x 40</td>
<td>-</td>
<td>Research Cottrel, USA</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>2 x 90</td>
<td>Curtain</td>
<td>Badenwerk, Germany</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>15</td>
<td>Cockroft-Walton</td>
<td>KfK, Germany</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>15</td>
<td>&quot;</td>
<td>Ebara, Japan</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>2 x 50</td>
<td>Transformer</td>
<td>INCT, Poland</td>
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<tr>
<td></td>
<td>0.8</td>
<td>3 x 36</td>
<td>&quot;</td>
<td>Ebara, Japan</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>2 x 12.5</td>
<td>Cockroft-Walton</td>
<td>Ebara, Japan</td>
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</table>

The accelerator parameters for pilot plant facilities with flow rate 1000-20000 Nm\(^3\)/h are more specific. Electron energy is within the range 0.3-0.8 MeV and beam power which depends on flue gas flow rate is 25-180 kW (Table II). The principal accelerator parameters of accelerator module according to present experience for pilot and industrial facility for flue gas treatment according to described above accelerator selection definition should be as follow:
Electron energy 0.8 – 1.5 MeV
Beam power 100 – 500 kW

Experience gained in practical application of accelerator technology for environmental application shows clearly that the accelerator selection criteria should be extended and seriously considered regarding the following accelerator performances:

- Accelerator reliability/availability,
- Accelerator electrical efficiency,
- Accelerator price.

2.1. Accelerator reliability/availability

Accelerators applied for flue gas treatment facilities were in primary approach installed in power stations where electricity production is based on fossil fuel combustion process. The power station availability coefficient is very high and typical operation period is within the range 6000 - 8000 h/year. The same time accelerator availability coefficient should be above 95% level to fulfill requirements according to power industry standards.

The exploitation of electron accelerators installed in Pomorzany Power Station, Szczecin, Poland reviled the number of long lasting failures which were related to: broken isolation of HV transformers, output windows implosions, accelerating sections deformation, HV cable connector breakdown, and output window water cooling system improper design. The characteristic features of exploitation of prototype transformer accelerators installed in Pomorzany Power Station provided by NHV from Japan were connected to limited exploitation experience, parameters on the edge of present limits, improper design of selected systems, difficulties in spare parts availability, difficult interchangeability of the components, no share reliability experience policy, and no active efforts to redesign faulty systems according to exploitation experience.

Some of listed above technical shortages can be overcome by practical implementation the experience gained in accelerator technology development by different accelerator manufactures. High power accelerator reliability/availability must be dramatically improved to meet industrial standards. Support of accelerator technology dedicated for environment protection should be provided by governmental and international institutions to overcome accelerator reliability/availability problem and high risk and low direct profit in this particular application.

2.2. Accelerator electrical efficiency

Accelerator electrical efficiency depends on principle of accelerator operation and auxiliary equipment provided by certain accelerator manufacturer. Electrical energy consumption which is defined by beam power and electrical efficiency has significant influence on cost of accelerator exploitation. Table III illustrates the share of electrical energy cost in exploitation costs of radiation sterilization facility and facility for flue gas treatment where accelerators with different electrical efficiency were applied. As it can be noticed easily the share of electrical energy cost in exploitation costs depend primary on the investment cost related to beam power level. High investment cost of radiation sterilization facility means low share of electrical energy cost in spite of very low electrical efficiency of linear accelerators which are commonly used in such facilities. If such investment cost is low, like for flue gas treatment facility, the share of bank credit repayment in exploitation cost is also low. That is why the share of electricity cost in flue gas treatment facility is high in spite of relatively high electrical efficiency of applied accelerator.
TABLE III. THE COMPARISON OF SELECTED EXPLOITATION COEFFICIENT OF FACILITIES FOR RADIATION STERILIZATION AND FLUE GAS TREATMENT

<table>
<thead>
<tr>
<th>Type of cost [k$]</th>
<th>Radiation sterilization; Accelerator parameters 10 MeV, 20 kW;</th>
<th>Flue gas treatment; Accelerator parameters 0.8 MeV, 1200 kW;</th>
</tr>
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<tr>
<td>Facility investment cost</td>
<td>7500</td>
<td>18000</td>
</tr>
<tr>
<td>Facility investment cost per 1 kW beam power [$]</td>
<td>375</td>
<td>15</td>
</tr>
<tr>
<td>Type of accelerator</td>
<td>Microwave linac</td>
<td>Transformer</td>
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<tr>
<td>Electrical efficiency</td>
<td>10%</td>
<td>80%</td>
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<tr>
<td>Exploitation cost:</td>
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<td></td>
</tr>
<tr>
<td>- total</td>
<td>1550</td>
<td>2960</td>
</tr>
<tr>
<td>- electrical energy</td>
<td>40</td>
<td>480</td>
</tr>
<tr>
<td>Share of electrical energy cost in exploitation costs</td>
<td>2.6%</td>
<td>16.3%</td>
</tr>
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</table>

TABLE IV. ELECTRICAL SUPPLY OF ELECTRON ACCELERATOR EPS 800-375, NISSIN HV

<table>
<thead>
<tr>
<th>Beam power</th>
<th>600 kW</th>
</tr>
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<tbody>
<tr>
<td>Power consumption</td>
<td></td>
</tr>
<tr>
<td>Power supply</td>
<td>6 kV, x 3</td>
</tr>
<tr>
<td>Control power</td>
<td>380 V, x 3</td>
</tr>
<tr>
<td>Vacuum power</td>
<td>380 V, x 3</td>
</tr>
<tr>
<td>Power consumption</td>
<td>682 kW</td>
</tr>
<tr>
<td>Power efficiency</td>
<td>88 %</td>
</tr>
<tr>
<td>Ventilation and air cooling</td>
<td></td>
</tr>
<tr>
<td>Window cooling blower</td>
<td>150 kW</td>
</tr>
<tr>
<td>Ozone exhaust blower</td>
<td>11 kW</td>
</tr>
<tr>
<td>Total power consumption</td>
<td>843 kW</td>
</tr>
<tr>
<td>Total power efficiency</td>
<td>71 %</td>
</tr>
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The role of electrical energy consumed by auxiliary equipment is well described by data provided in Table IV. The optimization of all accelerator systems to minimize electrical energy consumption should be performed by accelerator manufactures to improve electrical efficiency coefficient. The block diagram presented on Fig. 1 shows the main components of high power accelerator which may consume electrical energy.
2.3. Accelerator price

Influence of accelerators price (beam power cost) on radiation processing technology implementation is well characterized by data presented in Table V. It should be noticed that flue gas treatment technology which has no commercial value requires extremely low beam power investment cost.

TABEL V. RADIATION PROCESS EFFECTIVENESS

<table>
<thead>
<tr>
<th>Acceptable price of 1 W electron beam power</th>
<th>Type of radiation process</th>
<th>Product characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-250 $/W</td>
<td>Semiconductors modification</td>
<td>Low dose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Small scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High unit price</td>
</tr>
<tr>
<td>100-50 $/W</td>
<td>Radiation sterilization</td>
<td>Medium dose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Large scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Medium unit price</td>
</tr>
<tr>
<td>&lt;2.5 $/W</td>
<td>Flue gas treatment</td>
<td>Low dose</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Very large scale</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No commercial value</td>
</tr>
</tbody>
</table>
3. DIFFERENT CONCEPTS OF HIGH POWER ELECTRON ACCELERATORS

The basic principle of any accelerator is that the electric field acts on electrons as charged particles and gives the energy equal to the voltage difference across the acceleration gap. The electric field comes directly from high voltage electrodes or indirectly from the electromagnetic field. The major difference between different accelerators applied in radiation processing is the method by which electric field is generated. Due to energy range and beam power level the most common constructions for radiation processing are direct accelerators, single cavity resonant accelerators and microwave linacs. The most suitable high power accelerator constructions for industrial scale flue gas treatment process are at present direct power line transformer accelerators. Different constructions of high power accelerators have been described in literature. Some of them could be selected for flue gas treatment process if their manufactures would be able to fulfill all requirements regarding electron energy, beam power, electrical efficiency, reliability/availability according to industrial practice and low price related to beam power.

3.1. CW Linear accelerator

The family of compact modular continuous wave (cw) linear electron accelerator has been designed and tested. The accelerator modules are now capable to accelerate 50 mA average beam current with electron energy increments 600 keV what corresponds to 30 kW beam power [4]. Klystron operated at frequency 2.45 GHz was used. Electrical efficiency of the accelerator based on designed modules amounts 40%. Although high power microwave sources are now available, presented construction does not fit requirements of flue gas treatment process due to relatively low average current and low electrical efficiency.

3.2. Single cavity resonance accelerator

TT 1000 Rhodotron capable to deliver 5 and 7 MeV electron beams with average current intensity of 100 mA has been designed and tested [5]. The electron accelerating concept is based on single cavity which is crossed several times by recirculation electron beam. Beam power up to 700 kW has been obtained with maximum electrical efficiency 55 %. Several beams passing the same cavity concept is under consideration to increase average beam current and maintain high beam power with lower electron energy level. This conceptual design has not been tested yet.

3.3. High power compact transformer electron accelerator

High power compact transformer electron accelerator has been designed and tested at Institute of Nuclear Physic in Novosibirsk, Russia in connection to development of accelerating unit for experiments in the field of high energy physics [6]. Compact power supply operated at 1 MV voltage with power 300 kW and outside diameter 1.2 m was used. The size of power unit was reduced due to applied 1 kHz power line frequency and SF₆ gas isolation. Power supply electrical efficiency of 95 % has been achieved. The power supply was connected to accelerating section by HV feeder with gas isolation. Unfortunately this very promising construction has not been commercialized and there is no evidence about its exploitation performances.

3.4. High repetition pulsed accelerator

Design of the multi-beam accelerator was reported by Dolbilov et al. from JINR, Dubna, Russia [7]. The parameters of the accelerator are as follow:

- Energy 600-700 kV
- Beam power up 300-350 kW
- Pulse current 5 A
- Pulse duration 10-20 µs
- Frequency 10-20 kHz
- High efficiency 95%
Low energy losses in extraction window.

A coaxial spiral-line resonator serves as a high voltage power supply. Electron beams are generated by a mosaic cold cathode with threshold emission. Cold pyrolitic cathodes are located in such way that electrons emitted from a given cathode go to corresponding window. Threshold level is close to max. voltage and the electron energy dispersion are smaller than 15%. High beam current, high beam power, low cost, high reliability are expected. Unfortunately there is no evidence about industrial application of this interesting construction.

3.5. **Induction accelerator**

Induction accelerators are capable to deliver high power electron beams at energies of 1-10 MeV. Induction accelerator based on all-solid-state technology (modulator efficiency 85 %) is in operation at Science Research Laboratory, Somerville, U.S.A. [8, 9]. Following parameters have been obtained:

- Electron energy 1.5 MeV
- Pulse duration 50 ns
- Pulse beam current 500 A
- Repetition rate 5 kHz
- Beam power up to 500 kW
- Efficiency: >50 %

Series of experiments were performed at SRL to demonstrate the capabilities of induction linacs for industrial applications. In spite of shown promise there is no commercial proposals regarding to high power industrial induction accelerator with confirmed performances including reliability.

3.6. **Coupled-Multiplier Accelerator**

A new approach to efficient high voltage generation at MV level has been recently demonstrated [10]. High voltage is produced by a series of modules, each of which consists of a high-power alternator, step-up transformer, and 3-phase multiplier circuit. The alternators are connected mechanically along a rotating shaft driven by electrical motor. Relatively low cost and efficiency 67 % have been reported. The first 1 MV and 100 kW of the coupled multiplier accelerator will be installed at a petrochemical plant and used to treat industrial wastewater. 2 MeV and 200 kW accelerating unit has been designed.

4. **ACCELERATORS FOR FLUE GAS TREATMENT**

The principal parameters to be achieved for accelerators applied for flue gas treatment in pilot and industrial facility are as follow:

- Electron energy 0.8 – 1.5 MeV
- Beam power 100 – 500 kW
- High reliability for long time operation (6000 h/y),
- Availability >95 %,
- Electron beam cost ~2.5 $/W,
- Electrical efficiency >80 %,
- High current density, low level losses windows,
- Fault protection systems.

Manufacturers of high power transformer accelerators who are interested and capable to participate in practical implementation flue gas treatment technology are listed bellow:

- RDI - Radiation Dynamics, USA (power line frequency transformer),
Wasik Associates, USA (power line frequency transformer).
- NIIIEFA - Sci. Inst. of Electrophysical Apparatus, Russia (power line frequency transformer),
- BINP - Institute of Nuclear Physics, Russia (coreless transformer),
- Vivirad, France (ICT transformer).

5. FINAL REMARKS

Appropriate accelerator selection should be performed to meet all technical and economical conditions for successful process implementation. Power line frequency, high voltage transformers for high power accelerates are at the moment the best solution for flue gas treatment process because of: level of beam power, size, electrical efficiency and cost. It should be noticed that any practical accelerator construction must be compromise between size, efficiency and cost. Best accelerator selection for proper radiation facility design should be performed with possibly:

- Low electron energy,
- High beam power,
- High accelerator electrical efficiency,
- High beam utilization,
- High availability.

Special attention should be devoted to optimization electrical energy consumption for accelerator and auxiliary equipment installed in radiation facility. The electrical efficiency has significant influence on cost of facility exploitation. Reliability/availability of high power accelerator plays critical role for any industrial facility including environmental applications.
REFERENCES


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