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POSSIBLE USE OF ELECTRON BEAM TREATMENT FOR REMOVAL OF SO2 IN OFF-GASES FROM COPPER SMELTERS. Preliminary Tests Results

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ABSTRACT

The Chilean Nuclear Energy Commission is currently performing a pre-feasibility study concerning possible utilization of electron-beam process for removal of SO_2 from different types of sulfurous streams from copper smelters. First part of the project was related to verify, in a experimental line at Institute of Nuclear Chemistry and Technology, INCT, Poland, the behaviour of the process for simulated off-gases ~~gases~~ with very high SO_2 content, between 5% to 15 % by volume.

Tests were performed at laboratory stage and with a flowrate of 5 Nm^3/hr, using an ILU-6 electron accelerator, with the following results:

a) High removal efficiencies of SO_2, up to 90 %, were achieved for simulated off-gases ~~gases~~ containing up to 15 % of SO_2;
b) Required dose was in the range 5 to 8 kGy;
c) Big influence of NH_3 stoichiometry and gas humidity on SO_2 removal efficiency;
d) Rapid generation of sub-micron solid by-product, in great amount, that causes deposits on ducts and filtration units.

This work presents the experimental results and discuss its technical projections in the field of interest.

INTRODUCTION

Treatment of flue gases by electron-beam technology, EBDS process, has emerged as a very interesting technological option, that allows control of both, sulfur oxides and nitrogen oxides from combustion flue-gases, through a dry-scrubber process with the production of a valuable by-product for use as fertilizer, (Frank and Hirano, 1990;Ellison, 1994).

Electron beam process has been developed to be applied for flue gases treatment in power utilities. For that reason, there are not documented experience concerning utilization of electron beam process for off-gases with content of SO_2 higher than 3000 ppm. Nevertheless, some references have mentioned use of electron beam process in metal smelters in Rusia, for treating off-gases with SO_2 contents up to 7000 ppm, without addition of ammonia, (Woods and Pikaev, 1994).

The EBDS process was developed originally by Japanese companies, and its further development has been sponsored by international organisations such as International Atomic Energy Agency, Forschung Zentrum of Karlsruhe, Japanese Atomic Energy Research Institute, and the Polish Institute for Nuclear Chemistry and Technology, among others. Its optimal parameters for that use have been obtained through basic experiments and operation of pilot plant facilities, located mainly at the above mentioned institutions. Actually, there are projects for construction of two industrial facilities, at full-size scale, in Poland, (Chmielewski *et al.*, 1992), and China (Derong, 1996).

The Chilean Nuclear Energy Commission, under the sponsorship of International Atomic Energy Agency, IAEA, with the advisory of experts from IAEA and from Institute of Nuclear Chemistry and Technology of Warsaw, Poland, is developing a project oriented to analyse, verify and evaluate possible aplication of electron-beam process for SO_2 removal from off-gases from chilean copper smelters, (Villanueva and Ahumada, 1994).

Electron-beam process shows some favourable features that can be used advantageously for eventual service in the treatment of copper smelter off-gases. Among these are:

- high level of removal efficiency for SO_2, between 85 to 95 %, achievable with low irradiation dose;
- removal efficiency of SO_2 relatively independent of inlet SO_2 content;
- removal efficiency of SO_2 tends to increase at higher levels of SO_2 concentration, in the range of present development, i.e, namely up to 3000 ppm SO_2;
- good efficiency also for control of SO_3/ H_2SO_4, always present in the exit gases from SO_2 removal.

In addition to that, electron-beam process is compact, with low space requirements which makes a significant advantage in already-built facilities, with good reliability demonstrated through long-time operation of pilot plants, no waste water is produced in the process, relatively low capital investment and operating costs, competitive with other similar processs specially due to economic return due to by-product generation, ammonium sulfate, valuable fertilizer, (Ellison and Díaz, 1989; Ellison and Makanski, 1989).

FUNDAMENTALS OF ELECTRON BEAM PROCESS, EBDS.

Chemistry of electron beam process for SO_2 concentration up to 3000 ppm is well established, (Matzing, 1986). When high-energy electrons are applied for flue gas irradiation, quantities of free radicals and atoms are generated. In the first stage of the process, the interaction of these electrons and off-gas results in ionization and dissociation. The fraction absorbed by each component is proportional to its partial pressure.

In second stage the radicals and atoms react with SO_2 and NO_x to form, in presence of water, sulfuric and nitric acids. More than 760 reactions were listed in Agate Code to describe undergo processes.

Main reactions where SO_2 is involved are listed below:

$$SO_2 + HO_2 \rightarrow SO_3 + OH \tag{1}$$

$$SO_2 + OH + M \rightarrow H\,SO_3 + M \tag{2}$$

$$SO_2 + O + M \rightarrow SO_3 + M \tag{3}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{4}$$

$$H_2SO_4 + 2\,NH_3 \rightarrow (NH_4)_2\,SO_4 \tag{5}$$

Last stage is the solid by-product ~~product~~ formation. Acids are converted into ammonium sulfate and nitrate to be collected by filtering system. Efficiency of electron-beam process was analyzed in many experimental facilities and process conditions, (Namba *et al.*, 1993; Tokunaga *et al.*, 1993).

Last data shows that 95 % of SO_2 removal efficiency can be obtained at dose rate of 5kGy, when water content and thermal reaction conditions are properly adjusted.

EXPERIMENTAL

Tests were conducted at laboratory installation of Institute of Nuclear Chemistry and Tecnology in Warsaw. The goal was to determine the SO_2 removal efficiency from simulated flue-gases with high SO_2 concentration, in the range 5 % up to 15 % ppm SO_2 by volume. Source of flue-gases was a small boiler for heating purposes, fueled by natural gas. Required composition for simulated gases were adjusted by addition of specific gas components like SO_2 and NH_3 to the flue-gas stream, and also through the use of a laboratory steam vaporizer for the adjustement of water content.

Irradiation stage was carried out by an electron accelerator ILU-6, with following characteristics:

- beam energy : 770 keV

- pulse duration : 400 us
- pulse current : 0.35 A (350 mA)
- repetition rate : 2-80 Hz

Laboratory unit has been described in the literature (Chmielewski *et al*, 1992) and layout is shown in Figure 1a.

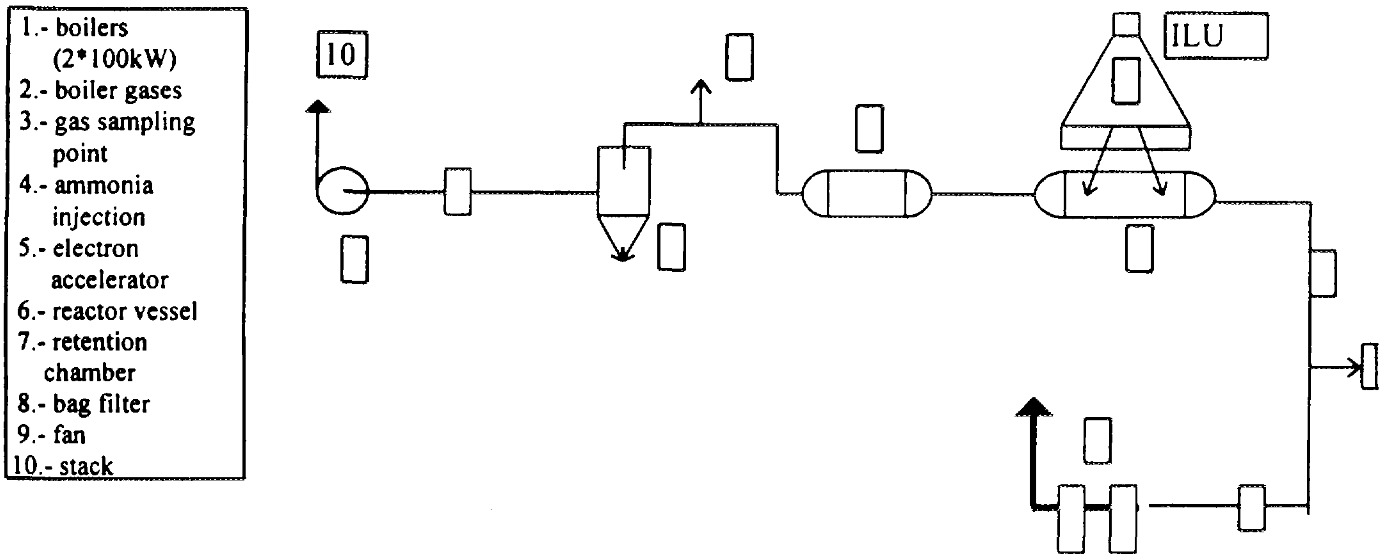

Figure 1a. Flow-diagram of INCT Laboratory Installation

Calibration and Monitoring of Experimental System.

Gas flowrate for tests was calibrated and adjusted at the level of 5 [Nm^3/hr].

Measurement of gas composition before and after irradiation was performed to determine the SO_2 removal efficiency achieved under different experimental conditions. At inlet to the installation high concentrations of SO_2 (up to 15 % vol.) were measured. Exit gas leaving irradiation chamber contains, in addition to lower concentration of SO_2, unreacted NH_3, aerosol of sulfuric acid and solid particles of ammonium sulfate of submicron size. They were highly higroscopic and tended to clog the gas sample line. In order to separate them, a set of gas filters was inserted at beginning of gas sample line.

Dilution technique was used for the measurement of high SO_2 concentration, in order to prevent saturation of monitors with highly corrosive gases.

Gas analysers were calibrated each day, using standard gases, before the series of experiments.

Sampling and filtering devices were tested during long periods, maintaining sample line temperature over 150°C.

In order to obtain high accuracy of measurement, gas leakage was reduced to the minimum, using proper gaskets and sealants, and performing every day, an oxygen test, i.e, determination of O_2 content at the inlet and outlet. Similar conditions equivalent to 5 % gas leakage were maintained during all sets of experiences. Experimental data were corrected because of leakage presence.

Temperature sensors were installed in selected points on ducts and reaction vessel. Gas temperature in reaction vessel was adjusted in the range 70-100°C. Nessler method was used to determine ammonia content at the outlet of installation and EPA Method 4, was used to measure water content in off-gases.

Irradiation dose of flue-gas was changed by using different repetition rate of electron pulses. Losses of energy due to the electron beam passing through of accelerator window, layer of air, reactor chamber window, etc. PVC irradiated foil was used to determine the fraction of electron beam that enters into the reaction vessel.

RESULTS AND DISCUSSION

Record of temperature measured at inlet and outlet of process vessel and after retention chamber clearly indicate a jump of gas temperature after irradiation with different dose. NH_3 injection also make a temperature effect. The gas temperature at the process vessel inlet had to be relatively high (over 100°C) because of applied humidity of gas and intense product deposition process at the inlet gas transport system. By-product had to be removed each day from process vessel and bag filter to avoid gas flow reduction.

Experimental results considering SO_2 removal efficiency versus different relevant independent parameters were obtained as follows:

1.- Strong dependence of NH_3 stoichiometry on SO_2 removal efficiency was observed, as shown in Fig. 1. Experiments were performed in the range of SO_2 content from 5 % up to 15 %.

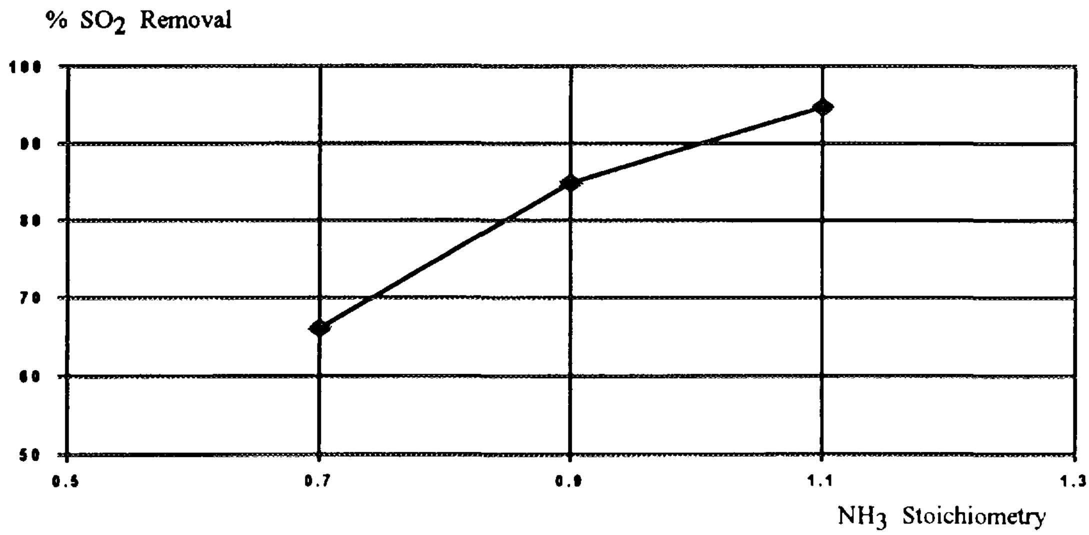

Figure 1. SO_2 Removal Efficiency Vs NH_3 Stoichiometry.

2.- Without e-beam irradiation, only 57 % of SO_2 can be removed from reaction between ammonia and water vapor, in gas-phase, while moderated irradiation dose in the range 6 - 7 kGy, increase SO_2 removal efficiency up to 88 %. General results are shown in Fig. 2.

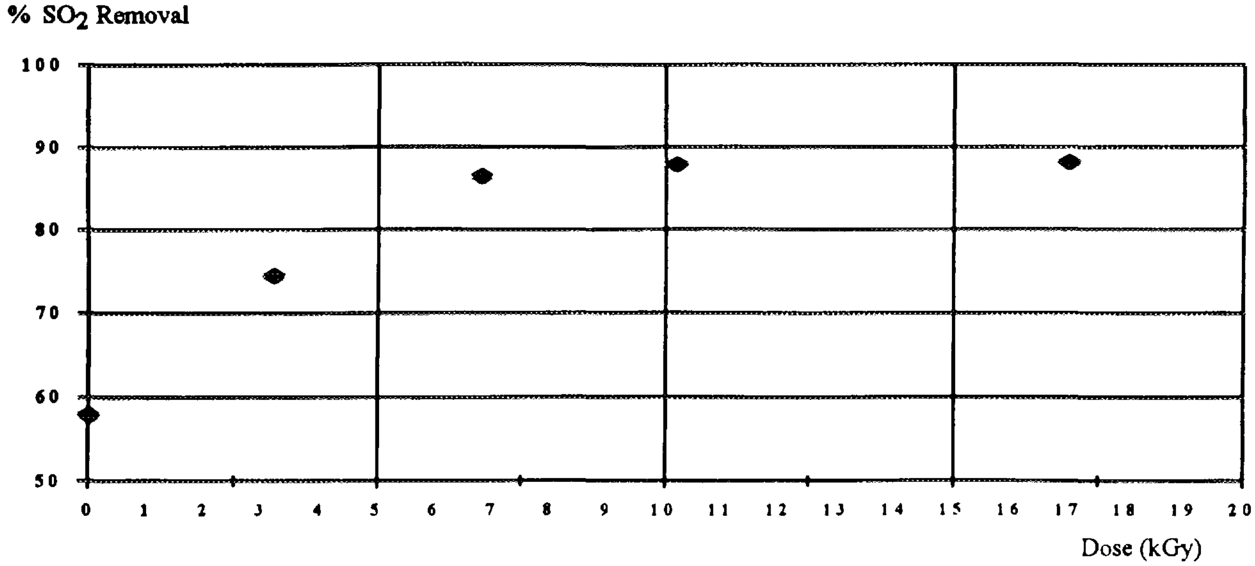

Figure 2. % SO_2 Removal Efficiency vs Dose

3.- A sharp influence of gas humidity on SO_2 removal was found, as shown in Fig. 3. This effect could also be atributed to the high SO_2 content in experimental gases.

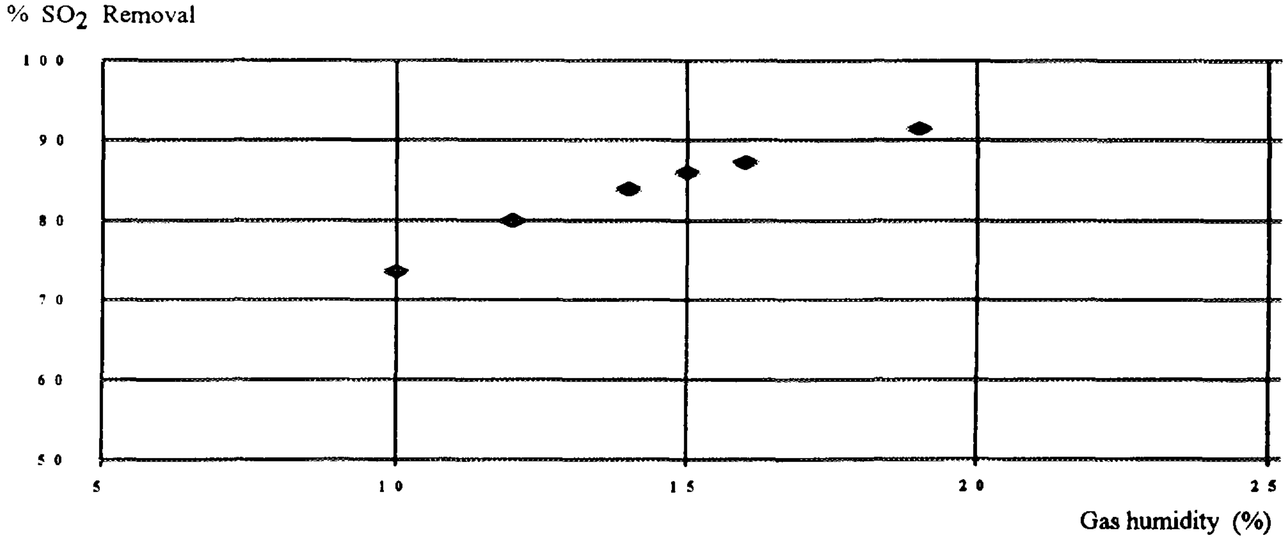

Figure 3. % SO_2 Removal Efficiency vs Gas Humidity.

4.- In the other hand, no significative temperature effect was found at the gas temperature range 105-118°C measured at the inlet process vessel, as shown in Fig. 4.

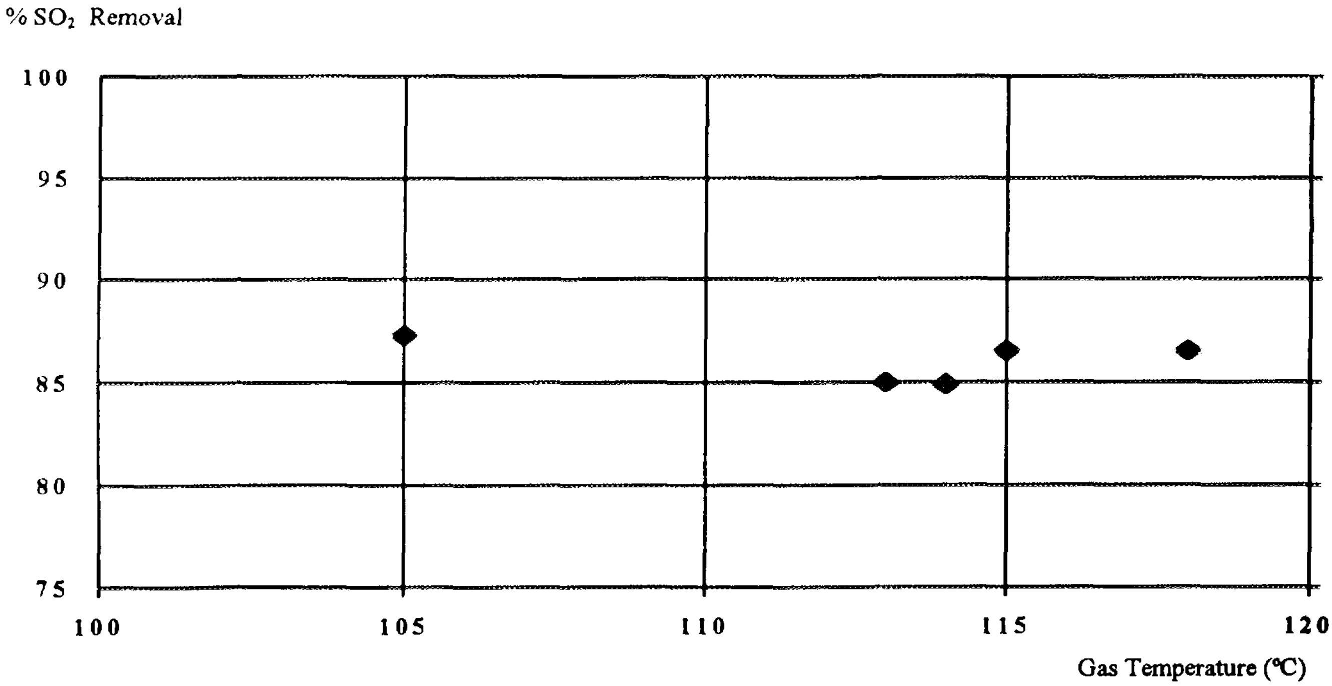

Figure 4. % SO_2 Removal Efficiency versus Inlet Temperature

5.- Concentration of unreacted NH_3 at outlet of laboratory installation was measured, resulting in an average level of 213 ppm, quite small considering inlet NH_3 concentration. This low level of NH_3 slip could not be obtained without irradiation.

6.- High amount of submicron and higroscopic product is produced under NH_3 and electron beam influence on simulated off-gas with high SO_2 content. Product was deposited on different parts of the installation specially on sharp edges and narrowings, tending to fully block gas flow. The by-product could be easily removed using water stream due to its high solubility.

Economic Considerations

For this first stage of current project, experimental data were used to develop some technical and economic evaluations for e-beam use in gas with SO_2 content about 10 % by volume. For this high range of SO_2 content, preliminary economic evaluation of the process does not not result favorable due to high investment and operational costs involved, derived mainly of present unavailability of ammonia supply in the country, which resulted a key factor because of great quantity of raw material consumed. Other factor that was taken into account was the need to have a preliminary cleaning stage for process gases, in order to obtain a clean by-product, usable as a fertilizer, that for this case results rather expensive. Also, at present time, the existence of a very big market for sulfuric acid in the country, makes any other by-product option not attractive.

Later, in the second stage of the project, it is under analysis possible use of e-beam process for different types of sulfurous gases, in the intermediate and diluted range of SO_2 content. These new scenarios have arised from an analysis of present and projected level of control of SO_2 in chilean copper smelters that indicates for some smelters the need to count with some technological options for the removal of SO_2 from diluted gases, that could be economically atractive and cost-effective.

For this intermediate and diluted range of gases, it has been established options in by-product obtention, through electron beam irradiation process, such as diluted sulfuric acid, which could be used as a feedstock to increase acid production in established plants, or ammonium sulphate, granular type for use as a blend of fertilizers. Present analysis, tests and evaluations for these scenarios are under development.

CONCLUSIONS

Electron-beam irradiation process could be applied, for the removal of SO_2 from high-sulfur content off-gases, as demonstrated by experimental tests, described in this work.

Relevant parameters for the application of the process to high-sulfur content gases are ammonia stoichiometry, gas humidity and irradiation dose, whose experimental values found are not rather different than those used for low SO_2 content application of e-beam process.

Experimental results can be summarized as follows:

a) High removal efficiencies of SO_2, up to 90% were achieved under specific experimental conditions, for simulated off-gases with SO_2 contents up to 15%, under electron beam and ammonia injection application;

b) Required dose was in the range 5 to 8 kGy;
c) Big influence of NH_3 stoichiometry on SO_2 removal efficiency; recommended range between 0.9 and 1.0;
d) Sharp influence of gas humidity on SO_2 removal efficiency, range needed higher than 15%.

Data obtained during laboratory experiments could be used for technical and economic evaluation of the process for possible full-scale applications. Nevertheless, the high consumption of ammonia as a raw material, for this range of off-gases, together with its present domestic unavailabilty, suggest that use of EBDS process for highly concentrated off-gases is not cost-attractive.

Nevertheless, further analysis of actual control of SO_2 in chilean copper smelters have determined the need for some smelters to have cost-effective technological options for eventual treatment of diluted gases from residual sulfur emissions. For that reason, present efforts of the project are devoted to evaluate possible use of e-beam for these type of gases, with alternative by-products such as diluted sulfuric acid or ammonium sulphate. This work is presently under development.

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