TECHNICAL AND ECONOMICAL ASPECTS OF SO_2 AND NO_X REMOVAL FROM FLUE GAS BY ELECTRON BEAM IRRADIATION

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ABSTRACT

The emission of sulfur dioxide (SO_2, also SO_3) and nitrogen oxides (NO, NO_2, called NO_x) from fossil fuel burning power and industrial plants is one of the major sources of environmental pollution. These pollutants are named as "acid gases" causing acid rain and also "indirect greenhouse gases" contributing greenhouse effect. Acid rain damages forest, agriculture fields and flora, and cause public health concerns in regions having a number of industrial plants.

Today, many countries have started to impose industrial emission limits and this movement has generated renewed interest in finding viable and cost effective solutions to SO_2 and NO_x pollution control. The conventional technologies, wet scrubbing de-SO_2 and de-NO_x, now reached their full potential therefore these methods are not expected to provide further improvements in terms of efficiency or reduction in construction costs. However, new technologies are being investigated for industrial scale commercial viability. One of them is electron beam process, which is dry scrubbing process and simultaneously removes SO_2 and NO_x, and useful by-product for agriculture fertilizer.

In this study, the economical and technical aspects of electron beam flue gas treatment process are discussed. Because an electron accelerator facility with electron beam energy of 500 KeV and electron beam current of 20 mA will be installed at ANRTC in TURKEY.

1. INTRODUCTION

Environmental problems, caused by the increased world energy demands have become a serious problem in many countries. Air pollutants such as SO_2 and NO_x generated mainly by combustion fossil fuels turn ultimately into sulfuric acid and nitric acid in the atmosphere and rain containing these substances is called acid rain. Acid rain affects lakes, marshes, rivers, soil and forests. In addition it kills trees or corrodes cultural properties by adhering to them.

Energy, supply and the presence of emission-control legislation determine the emissions of pollutants. Especially the kind of the fossil fuel has a great influence on the emissions. For example, the uncontrolled SO_2 emissions can vary between 550 mg/m^3 and 14000 mg/m^3 from coal burning, between 125 mg/m^3 and 1300 mg/m^3 for combustion of light and heavy oil and between 0 mg/m^3-25 mg/m^3 for gas combustion. NO_x emissions can vary between 300 mg/m^3 for natural gas and 1800 mg/m^3 for hard coal.

National standards or emission limits for SO_2 and NO_x emitted from cola-fired combustion were introduced in the early 1970s in the U.S. and Japan. In the 1980s, such environmental regulations became progressively more stringent and more widespread. Emission limits have been introduced in many countries as indicated Table 1(1). Such limits may depend on the kind of plant, (new/old), the size of plant and the fuel used. Emission limits vary from country to country for the same plant. In Turkey the 1986 Regulation on Air Quality Control sets emission limits with penalties for combustion plants as well as global emission limits in industrial and non-industrial regions (see Table 2)(2).

Main tools for reduction of pollutants or to reach introduced emission limits are emission-control technologies. Today, the conventional technologies wet scrubbing for SO_2 reduction covers about 90% of the European installed Flue Gas Desulfurization (FGD) and for NO_x reduction, combustion modification are widespread technology. The secondary measure used for the removal NO_x from flue gas is the Selective Catalytic Reduction (SCR).

On the other hand, the researchers and engineers have searched for new, cost-effective technologies for simultaneous removal SO_2 and NO_x. One of them the Electron Beam Flue Gas Treatment (e-beam FGT) system is proposed to be employed in industrial scale. The purpose of this paper is to present a new scrubbing simultaneous desulfurization and denitrification e-beam FGT process.

2. ENERGY SOURCES AND ENVIRONMENTAL IMPACTS IN TURKEY

Turkey's energy consumption and imports are experiencing rapid growth, as is the Turkish economy. The International Energy Agency (IEA) has estimated Turkey's electric power consumption growth to be 9 percent per year between 1975 and 1995. As of December, The Turkish Ministry of Energy and Natural Resources (MENR) reported that electric generation capacity was 26226 MWe and electric power consumption is expected to continue to grow rapidly at approximately 8 percent per year (3). This could lead to building a total installed generating capacity of 65 GWe by 2010. MENR is planning for a very large increase in electric generating capacity over the next twenty years as indicated Table 3(4). Turkey estimates that there are potential indigenous sources for 246 billion kWh per year of electric power generation, as 105 billion kWh from lignite, 16 billion kWh from hard coal, and 125 billion kWh from hydroelectric resources (5).

Coal (hard and lignite) is the largest energy sources produced in Turkey. Figure 1 shows production of lignite and hard coal. Hard coal is imported over 6 million short tons each year and is used mainly for electric power steel making and cement production. There is also considerable production of lignite within Turkey and about 75% of it are used as fuel source for electric power. Lignite has a very low calorific value and high sulfur, dust and ash content.

The growth in the use of fossil fuels in Turkey has led to a growth in emissions of pollutants. According to the Turkish State Institute of Statistics, SO_2 and NO_x emissions are increasing (see Table 4)(6). This situation has created environmental problems. Turkish environmental policy considers that energy policy should take into account environmental problems and that a balance should be found between increase in energy demand that are required for economic development and environmental concerns. The Government, as well as municipalities, has taken several measures to reduce pollution from energy sources. Municipalities have attempted to replace lignite consumption in the residential sector of major towns by importing low sulfur coal and by promoting natural gas consumption. 1986 law on air quality requires the building of FGT facilities for new lignite power plants. For existing plants, the Government decides investments on FGD units on a case-by-case basis. Two units were commissioned in the 300 MW Cayirhan electricity plant and 420 MW Orhaneli electricity plant. For Yatagan, Gokova and Kemerkoy electricity plants contracts of the construction of FGD were signed (7). Preferred all FGD is wet scrubbing FGD process for SO_2 and for NO_x combustion modification has been used in Turkey.

3. ELECTRON BEAM FLUE GAS TREATMENT PROCESS

E- beam FGT process is very versatile and an effective process to remove simultaneously sulfur dioxide (SO_2) and nitrogen oxides (NO_x) from of the flue gas produced in the combustion of fossil fuel. This process is a dry process using electron beam irradiation in the presence of ammonia to initiate chemical conversion of sulfur and nitrogen oxides into an aerosol which can be easily collected by conventional methods using an electron precipitators or bag house filter.

The flue gas flows into the process vessel then gas mixture is subjected to an intense field of energized electrons, which collide with the flue gas molecules resulting in molecular ionization. These ions interact with flue gas constituents resulting in the creation of free atoms and radical species such as O, OH, N and HO_2. These are capable of rapid reaction with SO_2 and NO_x and water in the flue gas to ultimately yield a mixture of fine mist and vapor of sulfuric acid (H_2SO_4) and nitric acids (HNO_3). In the presence of ammonia (NH_3), these acids are converted to ammonium sulfate $(NH_4)_2SO_4$ and ammonium nitrate (NH_4NO_3)(Fig. 2).

While the NO_x removal process is purely radiation induced, the SO_2 is not only removed by irradiation but also by a thermal reaction. The removal of NO_x is not only an oxidation process, but also up to 20% NO is reduced to N_2 by reaction with N and NH_2, and N_2 and 10% of the NO_2 react with NH_2, yielding N_2O (Table 5).

When the Electron Beam Process is used the clean the flue gas from thermal power plant as shown in Fig. 3, the flue gas is first cleaned of fly ash by a particle collector. Then it cooled to an appropriate temperature by the spray cooler and it is passed, together with the ammonia that has been near-stoichiometric amount into the process vessel, where high energetic electron beams irradiate it. Active radicals produced by the electron beam irradiation react with SO_2 and NO_x in the flue gas to form H_2SO_4 and HNO_3, respectively. These acids react with the added ammonia to form ammonium sulfate and ammonium nitrate. These salts are recovered as a dry powder using a conventional particle collector. The collected powder is potentially salable as an agricultural fertilizer. Other organic compounds such as Volatile Organic Compound (VOC's) can also be treated using the same principle (13).

4. PILOT PLANTS AND INDUSTRIAL INSTALLATIONS OF ELECTRON BEAM FLUE GAS TREATMENT

The potential of using radiation to initiate the process aimed at removal of the toxic gases SO_2 and NO_x from combustion flue gas, in order to prevent environmental pollution, was recognized in the early 1970s by Ebara Corporation in Japan. The first batch test studies defined the radiation chemical reactions of SO_2 and NO_x resulting from the irradiation of flue gas. The success of these initial batch tests indicated a future potential use for the electron beam process (14-15). Then various tests and small pilot plants have been conducted around the world. The technical and economical feasibility has been confirmed by larger scale demonstration facilities because for scaling up of the flue gases from coal combustion cleaning process is only possible after collecting experimental data in, pilot plant with volumetric flow rate exceeding 10000 Nm^3/h. As far as cleaning of flue gas from coal combustion is concerned, such as electron beam treatment installations have been built in Indianapolis-USA; Badenwerk-Germany; Kaweczyn-Poland and Chubu-Japan. The tests performed in these installations proved that high efficiency of removal of SO_2 and NO_x could be achieved (see Table 6).

As a result, the features of e- beam FGT system can be summarized as follows (16-20):

1) Electron beam irradiation is capable without catalyst of converting SO_2 and NO_x in

combustion gases into aerosol that is removable with an electrostatic precipitator, **2)** SO_2 and NO_x can be remove simultaneously and high efficiency, **3)** the removal efficiency is depends on relative humidity, temperature, irradiation dose and amount of ammonia. **4)** electron beam process is dry process without any waste water treatment, **5)** irradiation dose of the flue gas can be changed between 10 kGy and 20 kGy, **6)** no need to use expensive catalyst for NO_x removal, **7)** the useful by product of the e-beam FGT process as an agricultural fertilizer is composed of two ammonium salts; ammonium sulfate and ammonium nitrate. Depending on the coal sulfur content and the level of nitrogen oxides contained in the flue gas, the nitrogen content of the by product mixture will vary between 21% and 35%, **8)** The process is carried out with high power, low energy electrons typically 300-700 KeV, several hundred kW, **9)** simple system with easy operation in reliable and commercial viability for industrial scale and smaller space requirement and is competitive with all conventional flue gas treatment systems, **10)** e-beam FGT process can be used for treatment of flue gas from oil or coal fired power plants, incineration plants, industrial boiler, furnaces and for automobile tunnel.

The positive results of the tests performed on laboratory and pilot installations have led to decision concerning design and construction of the industrial demonstration plant for e-beam FGT. Ebara Corporation, with the co-operation of the Chinese government, has in 1997 completed the first commercial e-beam FGT process installation, which is sited at the coal-fired Chengdu Power Station in China. Design conditions of this retrofit facility are: Volumetric flow of flue gas approximation 300000 Nm^3/h, SO_2 contents in flue gas 1800 ppm, efficiency removal of SO_2 80% and by product output rate 2470 kg/h (21). Then e-beam FGT is proposed to be employed Pomorzany in Poland, with the co-operation of the Japanese government and IAEA, for the simultaneous removal of SO_2 and NO_x from flue gases emitted by two Benson type boilers of power 56 MWe each supplying additional steam for heating purposes up to 40 MWth each. E-beam FGT has been completed one Benson boiler of 56 MWe. The parameters of e-beam FGT are chosen so as to guarantee efficiency of removal of NO_x up to 80% and 90% reduction of SO_2 are expected (22).

In addition to the systems operation in China and Poland, a large, full-scale installation of the e-beam FGT is now under construction at a major thermal power plant in Japan with start up in 1999.

5. ECONOMICAL ASPECTS OF ELECTRON BEAM FLUE GAS TREATMENT

Up to now, researchers, companies and consultants have been made many costs of analyses. It is very different to make comparisons of these analyses because the different people doing the estimates make many different assumptions. One of the assumptions is always the cost of the accelerators. Because the cost of basic apparatus which includes the price of accelerator is 60% of total investment cost. The prices of electron accelerators depend on electron energy, beam power, electrical efficiency, physical size and etc.

In general, due to high electrical efficiency and beam power level the most promising construction for industrial scale flue gas treatment capable of fulfilling this requirement are direct current (dc) accelerators such as transformers and linear induction accelerators (23). Table 7 shows the prices of dc accelerator (24).

Figure 4 shows the electron beam power required for various power plants capacities. As can be seen from Figure, the beam power requirement is estimated to be about 1% of the output power of the generating plant (per 10 kGy of dose). For example 100 MWe plant would need 1.1 MW of absorbed electron beam power, which exceed the capacities of any industrial electrons that are available today. These high power requirements could be provided with six to eight 200 kW units. Using a smaller number of more powerful future machines could eventually reduce the cost of a project on this scale.

In Figure 5, the comparison of the investment costs for 28 different systems of removal of SO_2 and NO_x from flue gases is illustrated (25). It can be seen Figure the investment cost of projected e-beam FGT process is on the level 190-210 $/kWe of the installed electrical power and it is competitive to the other FGD. The NO_x would be removed at the same cost, whereas an additional Selective Catalyst Reduction (SCR) unit would be required with any of the system shown for a capital cost of 80-100 $/kW to remove NO_x.

Figure 6 shows the 30-year leveled cost for 28 different FGD systems in relation to one ton of removed SO_2 (25). Significant competitiveness of the electron-beam system to the system is evident.

6. CONCLUSION

Turkey is a party to many international environmental agreements such as Air Pollution, Hazardous wastes, Ozone Layer Protection and etc. Turkey is seeking admission on the European Union (EU) and trying to meet EU standards. Therefore Turkey is requiring FGD units all newly commissioned coal power plants and is retrofitting FGD onto older units.

In the Electric Power Research Institute (EPRI-USA) study, it was pointed out that e- beam FGT is one of the four most promising second-generation system recommended for simultaneous removal of SO_2 and NO_x from among 70 checked technologies for simultaneous SO_2 and NO_x removal from the flue gas (25). E- beam FGT system for existing plants retrofits in Turkey rated equivalent or preferable to FGD+SCR. The system can be easily configured to meet any future expected emission control requirements since it is simple system with easy operation and the area needed is far less than conventional wet scrubbing FGD and is competitive with all conventional FGD. In addition this system may provide answers for difficult pollution control problems in the future. Therefore, we will set up the first batch test studies in our laboratory using ICT type electron accelerator with electron beam energy of 0.5 MeV, electron beam current of 20 mA and beam power of 10 kW to collect the data necessary for designing equipment of small pilot plant.

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Table 1. Range of national emission standards for SO_2 (mg SO_2 /Nm^3, %6 O_2) and for NO_x (mg NO_2 /Nm^3, %6 O_2).

Country	**New plants**		**Existing plants**	
	SO_2	**NO_x**	**SO_2**	**NO_x**
Austria	200-1620	200-400	200-2000	200-400
Canada	715	740	---	---
Denmark	400-2000	650 (200)	810	---
Finland	380-2540	200-400	620-1540	200-620
France	400-2000	650-1300	400-2000	---
Germany	400-2000	200-500	400-2500	200-1300
Greece	400-2000	650-1300	400-2000	---
Ireland	400-2000	650-1300	---	---
Italy	400-2000	200-650	400-2000	200-650
Japan	---	410-510	---	620-720
Poland	540-1755	460	675-4160	---
Portugal	400-2000	650-1300	---	---
Spain	400-2000	650-1300	2400-9000	---
Sweden	160-540	140	160-920	(140-560)
Switzerland	430-2145	200-500	430-2145	200-500
U.K.	400-3000	650-300	2000-3000	---
U.S.A.	750-1480	615-980(550)	1480	---

Table 2. National SO_2 and NO_x emission limits values for Turkey.

<table>
<tr><th rowspan="3">Fuel Type</th><th colspan="5">SO_2 Emissions (mg/Nm^3)</th><th colspan="2" rowspan="2">NO_x Emissions (mg/Nm^3)</th></tr>
<tr><th colspan="2"><300 MWt</th><th colspan="3">>300 MWt</th></tr>
<tr><th>Existing plant</th><th>New Plant</th><th colspan="2">Existing plant</th><th>New plant</th><th>Existing plant</th><th>New plant</th></tr>
<tr><td>Coal</td><td>3200</td><td>2000</td><td>---</td><td>3200</td><td>1000</td><td>1000</td><td>800</td></tr>
<tr><td>Liquid fuel</td><td>3200</td><td>1700</td><td>---</td><td>1700</td><td>800</td><td>1000</td><td>800</td></tr>
<tr><td>Gaseous fuel</td><td>60</td><td>60</td><td>60</td><td>60</td><td>60</td><td>500</td><td>500</td></tr>
</table>

Table 3. Electric Power Capacity Development in Turkey.

Fuel Type	**1997**		**2010**		**2020**	
	Installed Capacity (MWe)	Generation (GWh)	Installed Capacity (MWe)	Generation (GWh)	Installed Capacity (MWe)	Generation (GWh)
Coal	6.389	33.906	16.106	104.035	26.906	174.235
Natural Gas	3.501	21.987	18.856	125.548	34.256	225.648
Fuel Oil & Diesel	1.889	7.463	3.125	17.993	8.025	49.842
Nuclear	0	0	2000	14.000	10.000	70.000
Hydro & Renewables	10.122	39.833	24.982	85.719	30.031	104.043
Total	**21.901**	**103.188**	**65.069**	**347.294**	**109.218**	**623.768**

Table 4. SO_2 and NO_x emissions from power plant and industrial process in Turkey (in thousands of tonnes).

Sources		**Years**							
		1990	1991	1992	1993	1994	1995	1996	1997
Power Plant	SO_2	744.5	775.7	807.1	750.0	812.6	815.1	871.3	942.7
	NO_x	52	55.4	60.8	62.1	72.7	99.7	-	-
Industrial Process	SO_2	68.25	68.26	74.15	76.44	77.87	78.92	92.21	95.50
	NO_x	11.25	12.87	13.67	13.5	9.62	18.5	18.77	19.21
Total	SO_2	812.75	843.96	881.25	826.44	890.47	894.02	963.51	1038.2
	NO_x	63.25	68.27	74.47	75.6	82.32	118.2	18.77	19.21

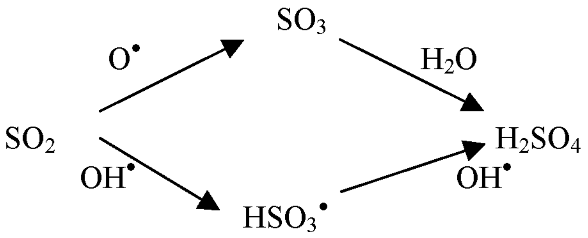
* DIE does not compile emissions for 1998-1999.

Table 5. Main reactions pathways for SO_2 and NO_x removal (9-11).

I- Formation of free radicals

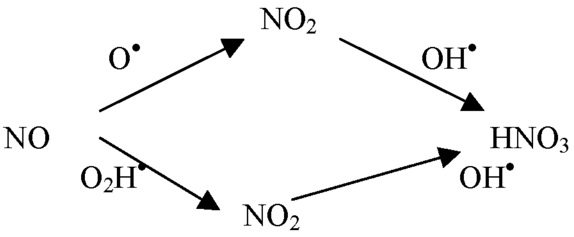
$N_2, O_2, H_2O + e^- \longrightarrow OH^\bullet\ O^\bullet, HO_2^\bullet, N^\bullet$

II- Oxidation of SO_2 and formation H_2SO_4



$SO_2 + O^\bullet \longrightarrow SO_3$
$SO_3 + H_2O \longrightarrow H_2SO_4$ or
$SO_2 + OH^\bullet \longrightarrow HSO_3$
$HSO_3 + OH^\bullet \longrightarrow H_2SO_4$

III- Oxidation of NO_x and formation HNO_3



$NO + O^\bullet \longrightarrow NO_2$
$NO_2 + OH^\bullet \longrightarrow HNO_3$ or
$NO + O_2H^\bullet \longrightarrow NO_2$
$NO_2 + OH^\bullet \longrightarrow HNO_3$

$NO \xrightarrow{N\bullet,\ NH_2} N_2$ (NO%20)

$NO_2 \xrightarrow{NH_2} N_2O$ (NO%10)

IV- Reaction of the acids with NH_3 in solid by-product

$H_2SO_4 + 2\,NH_3 \longrightarrow (NH_4)_2SO_4$

$HNO_3 + NH_3 \longrightarrow NH_4NO_3$

Thermally removal of SO_2

$SO_2 + 2\,NH_3 \longrightarrow (NH_3)_2SO_4$

$(NH_3)SO_2 + 2H_2O \longrightarrow (NH_4)_2SO_4$

Table 6. Industrial pilot plants(15).

Institution Year	Volumetric Flowrate	Accelerators	SO_2/NO_x concentration (ppm)	NH_3 (ppm)	Temperature (°C)	SO_2/NO_x remove efficiency (%)
Ebara Indianapolis 1984-88	8000-24000 Nm^3/h Coal	2x800 kV 160 kW 200 mA	1000/400	Stoci.	65-149	96/83
Badenwerk Karlsruhe 1985	10000-20000 Nm^3/h Coal	260-300 kV 180 kW	50-500/ 300-1000	Stoci.	70-100	94/80
ICHTJ-Kaweczyn Plant 1992	20000 Nm^3/h Coal	500-700 kV 2-50 kW	200-600 250	Stoci.	60-120	92/82
Ebara-JAERI Chubu 1992	12000 Nm^3/h Coal	800 kV 36 kWx3 (=108 kW)	800-1000 150-300	Stoci.	65	98/85

Table 7. Accelerator Rating and Estimated Prices Direct Current Systems.

Manufacturer / Type of dc accelerators	Energy MeV	Current mA	Power kW	Price $USA
Energy Sciences / Iron Core	0.125	150	18.75	340000
	0.200	500	100	550000
	0.300	500	150	950000
Radiation Dynamics / Dynamitron	0.5	160	80	900000
	1.0	100	100	1300000
	1.5	67	100	1600000
	3.0	33	100	2100000
	5.0	30	150	3600000
VIVIRAD /ICT	0.8	100	80	1300000
	1.0	100	100	1400000
	1.5	67	100	1600000
	2.0	50	100	1800000
	2.5	40	100	2000000

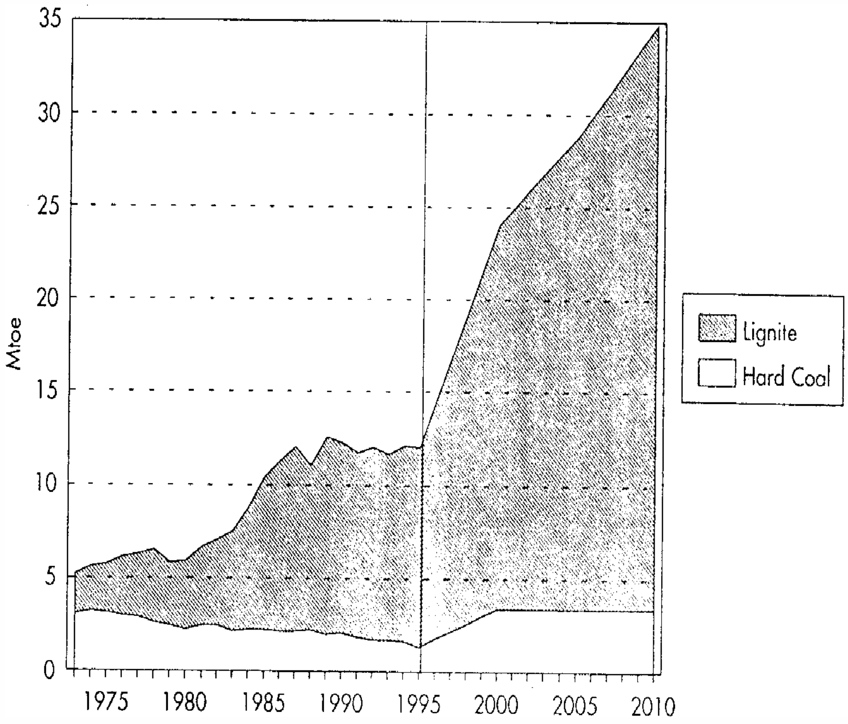


Figure 1. Coal Production of Turkey, 1973-2010(3).

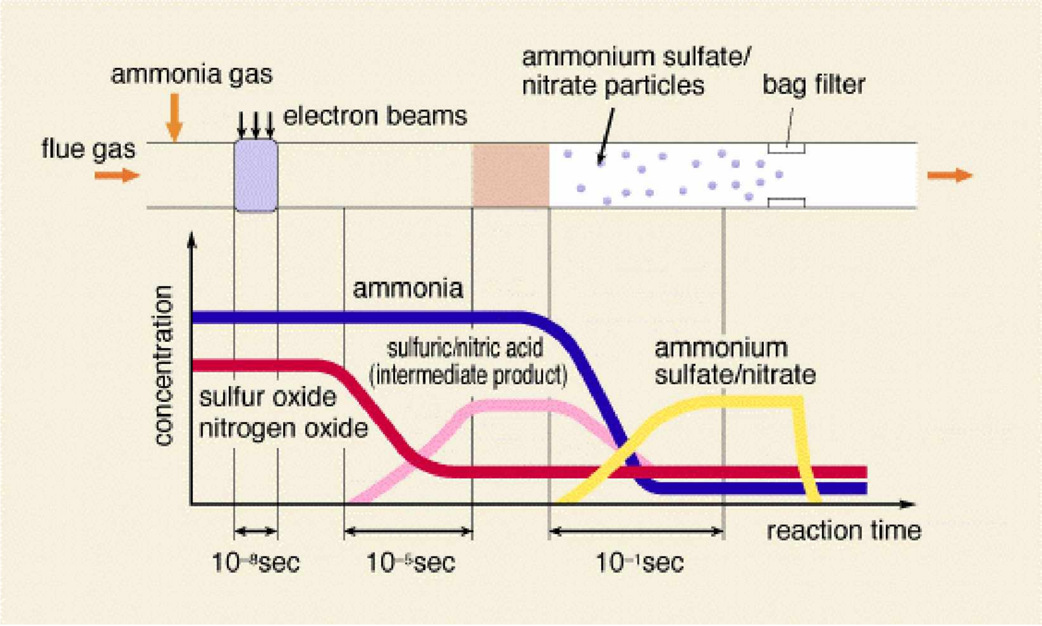


Figure 2. Reaction of sulfur and nitrogen oxides with ammonia under the irradiation of electron beams (8).

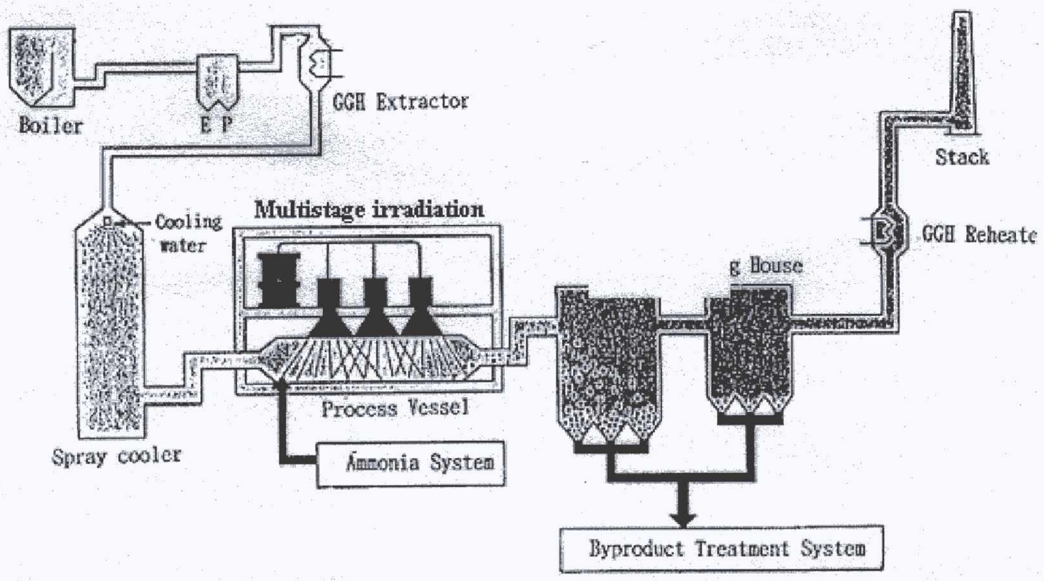


Figure 3. The flow diagram of electron beam flue gas treatment from power plant (12).

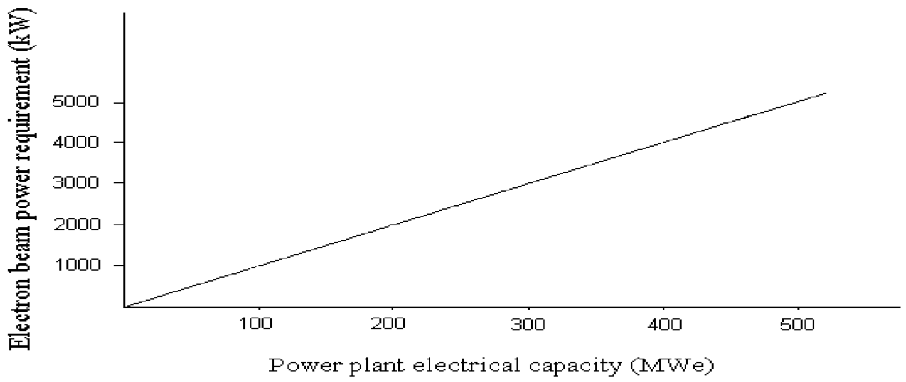


Figure 4. Electron beam power requirement versus power plant electrical capacity.

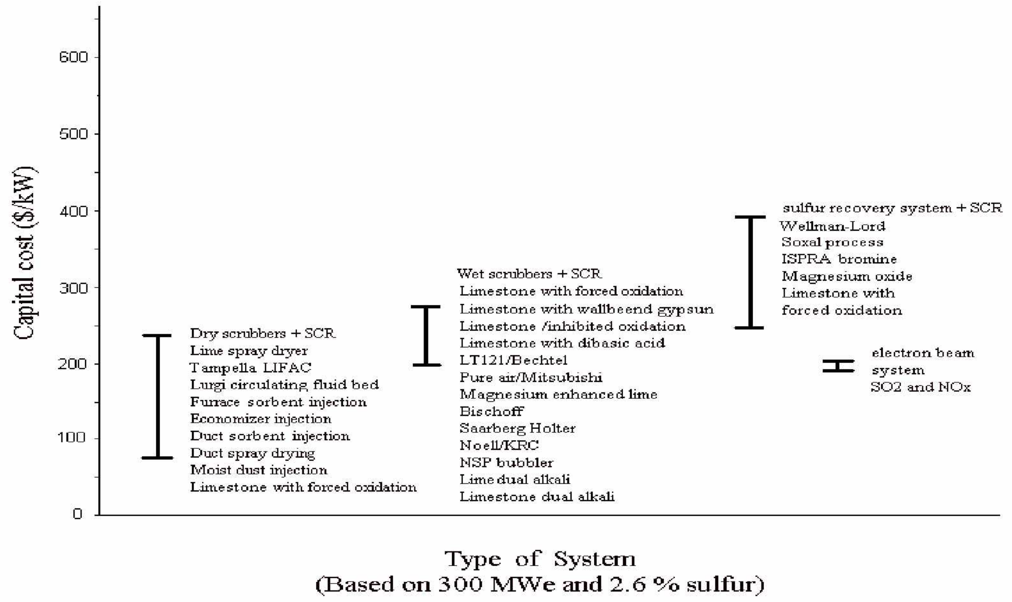


Figure 5. Capital cost for removing SO_2 and NO_x from flue gas (in $/kW).

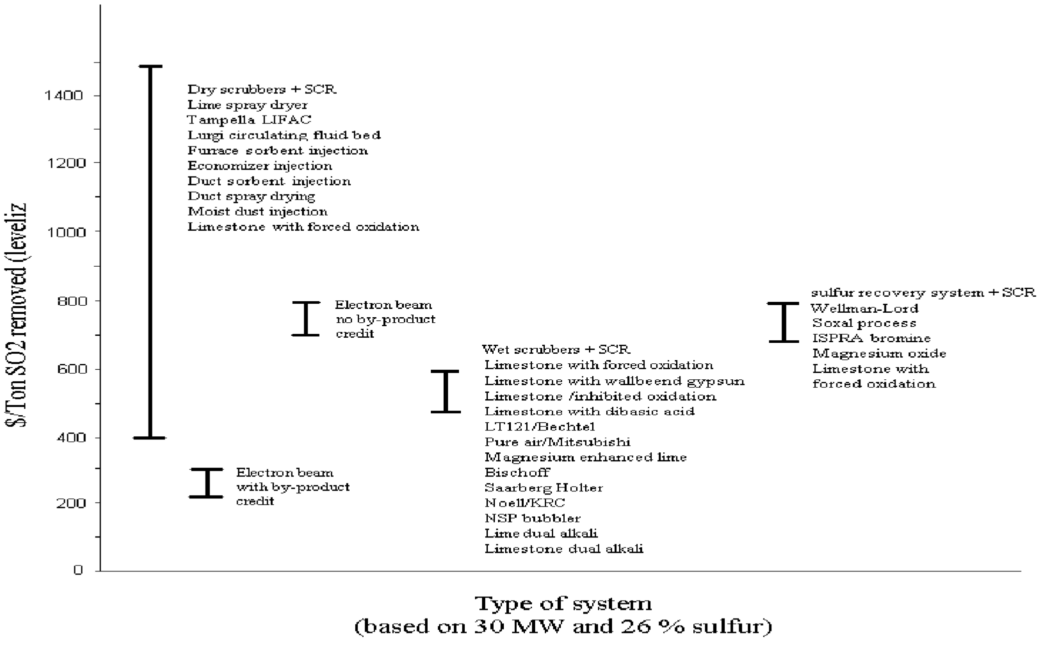


Figure 6. Cost for removing SO_2 from flue gas (the 30 years leveled, $/ton).