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Technical and Economical Assessment of SO_3/SO_2 Removal from Sulphuric Acid Plants in a Petrochemical Industry and Conversion to Ammonium Sulfate

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In the present study, various methods to control sulfur oxides emission from stacks of sulfuric acid production plants have been investigated. Considering their advantages and disadvantages, functional conditions and the amount of sulfur oxides removal, the researchers investigated various catalytic methods of sulfur oxides removal by flue gas desulphurization methods. Flue gas desulphurization (FGD) processes received more attention due to using dry washing and producing recyclable products which can be utilized to produce useful products to compensate for some part of the capital cost. Among these methods, two of which were chosen for this study. The first method was desulphurization by ammonia (Plant A) and the second one was a combination of the first method and dry scrubbing process with calcium hydroxide as the sorbent material (Plant B). Simulation of the systems was carried out through HYSYS v3.1 software. As the technical functions of both of the methods in removal of sulfur oxides were nearly the same, they were compared to each other from the economic point of view. As removal of sulfur oxides was nearly the same (110 tones daily) in both methods, the external costs of production reduction of SO_X as a pollutant substance is the same. Therefore, economic index of these two methods were calculated through COMFAR III software. Consequently, the more economical method for desulphurization of sulfuric acid production plants has been chosen.

Key Words: Sulfur oxides emission, Flue gas desulphurization, Simulation, External cost.

INTRODUCTION

Sulfur oxides are among the main air pollutants with vast environmental and hygienic damages. Moreover, there are new standards set by governments and international organizations to confine the amount of SO_2 emission from the factories' stacks. There are various methods for sulfur oxides removal from stacks. Some of which are as follows: Scala *et al.*[1] used dry desulphurization in Italy. Xiaoxun[2] used flue gas desulphurization (FGD) process with a powder-particle spouted bed of limestone in Japan. Meikap *et al.*[3] used multistage scrubber for removal of sulfur oxides with water sorbent in India. Bandyopadhyay and Biswas[4] used flue gas desulphurization with calcium hydroxide as dual sorbent in India. Zheng *et al.*[5] used dry scrubber productions in wet flue gas desulphurization plants in Denmark. Lin *et al.*[6] used FGD with silica $Ca(OH)_2$ as the sorbent in Taiwan. Buchardt *et al.*[7] used wet flue gas desulphurization plants with adipic acid as the organic sorbent in Denmark. Sarkar *et al.*[8] used horizontal co-current gas-liquid scrubber by using water sorbent in India. Giakoumelou *et al.*[9] used catalytic process of sulfur oxides removal by using V_2O_5/SiO_2 and V_2O_5-$CsSO_4/SiO_2$ in Romania. Palomares *et al.*[10] used catalytic process of sulfur oxides removal by using Co/Mg/Al. Taarit and Lunsford[11] used catalytic process of sulfur oxides removal by using magnesium oxides. Vadjic and Gentilizza[12] catalytic process of sulfur oxides removal by using manganese oxides in Yugoslavia and Xue *et al.*[13] used catalytic process of sulfur oxides removal by using platinum complexes. However, in all of the above mentioned methods sulfur oxides pollutants were produced during the combustion of fossil fuels which contained sulfur. While, in sulfuric acid plants of petrochemical industries sulfur is used instead of fossil fuels to produce SO_2. The leakage of produced gases is the source of emission of these pollutants to the atmosphere. Sulfur oxides removal from sulfuric acid plants stacks of petrochemical industries decreases the amount of environmental pollutants and their damages as well as their external costs. Moreover, it makes it possible to recycle useful products from sulfur oxides[14]. The main purpose of the present study is identifying an optimal economical and technical process for removal of sulfur oxides from sulfuric acid plants stacks of a petrochemical unit and to change sulfur oxides into useful products such as ammonium sulfate, ammonium sulfite, and calcium sulfite which can be used in the same plant or other units or they can be sold separately.

Sulfur oxides removal processes: The process of sulfur oxides output control from sulfuric acid plants of petrochemical industries includes two processes: catalytic removal processes and FGD processes.

Catalytic removal of sulfur oxides occurs by using some precious metals such as platinum, palladium, rhodium and so forth on dehydrated beds with fine internal holes. This method enjoys a high efficiency and low energy consumption. Moreover, in comparison to wet processes it does not have similar problems such as sewage and sludge disposal, probable sedimentation and corrosion. However, their main problems such as higher capital costs, higher required experience and expertise, lack of information and enough research and so forth made us use FGD processes for desulphurization in sulfuric acid plants stacks in present study[15].

Flue gas desulphurization processes are classified into dry or wet methods or disposal or recycle methods[2]. Dry methods which have industrial usages mostly have low efficiency which hardly reaches to 75 %. While, wet processes can reach to the efficiency higher than 90 % even up to 99 %. In addition, the consumption of sorbent is 1.4 to 3 times of stoichiometry measure. As a result, the operational costs of consumed sorbent increase. If the recycling of sorbent is being used, it will need vast establishments for which the constant costs increase. While, by using wet processes one can achieve the above-mentioned separation percentages effectively without any cost increase. Moreover, the ratio amount of sorbent consumption in stoichiometry measure is much lower than that of dry processes. However, they have some problems such as rolling of circulation slurry in the scrubber, probable sedimentation of solids, corrosion and problems caused by transportation and disposal of sludge made by poor separation of liquid from solid which will lead to environmental damages[16]. Dry FGD processes are utilized with low output sulfur oxides and wet processes are mostly used in plants with high output sulfur dioxide. Unlike power plants in sulfuric acid plants, sulfur itself is burned to produce SO_2, thus the amount of output sulfur oxides from stacks is high. Therefore, it is not possible to use only dry desulphurization. Accordingly, at the present study recovery processes (production of useful products) and dry FGD processes have been investigated on the stacks of sulfuric acid plants of a petrochemical unit to escape from the problems of limestone and limestone rocks wet scrubbers also to produce useful products.

EXPERIMENTAL

Sulfuric acid plants of the investigated petrochemical unit use touching method and emit 110.67 tones of SO_2 and SO_3 into the atmosphere daily. This amount of pollution is much higher than the environmental standard of sulfur oxides. It, moreover, leads to environmental damages and emission of 110.67 tones of waste sulfur oxides from stacks.

In the present study, to control the output sulfur oxides from stacks of sulfuric acid plants two processes have been chosen from dry FGD and recovery FGD processes. The first method was desulphurization by ammonia as the sorbent (plant A) and combination of the first method with dry desulphurization by calcium hydroxide sorbent was chosen as the second method (plant B). Recovery processes (production of useful products) are strongly based on the system location *i.e.* production sale revenues and waste disposal costs. These are the two main economical factors to choose of the first method. The first method was taken because there was a fertilizer production unit in the investigated petrochemical unit which was producing NH_3 in the form of sewage. Also, useful products such as ammonium sulfite and sulfate resulting from the chemical reactions could be used to produce fertilizers. The second method was chosen, for dry FGD is a simple process and it does not need any instruments to extract solid waste from liquid materials, pumps, pipes for return of slush and reheating instruments for the stacks' gas and water. It, furthermore, does not produce any waste material, it utilizes calcium hydroxide which is comparatively a cheap sorbent. It also produces calcium sulfite as a useful solid material.

Considering high sulfur oxide output from stacks of the investigated sulfuric acid plants (110 tones per day) and to increase the efficiency and the amount of useful products, and to decrease the costs, researchers examined the second method in two serial stages. At the first stage, a high amount of output sulfur oxides was removed from the stacks through using dry scrubber with calcium hydroxide as the sorbent with fewer costs and relatively less Ca/S ratio. In the second stage, the left sulfur oxides were removed with less ammonia and thus with fewer costs in comparison to the first method[13,17].

The identification of the function of the two suggested methods and to compare their efficiency, the condition of the investigated unit was simulated through using HYSYS v3.1 software. Then, the first method (plant A) and the second method (plant B) were simulated through running HYSYS v3.1 software, too.

To compare the economical status of plants A and B only the costs and revenues of these two units were taken into consideration for analysis as the costs and revenues of the other units of sulfuric acid plant were similar. To calculate the Tables and economical indexes of each plant Microsoft Excel and COMFAR III software which is designed by United Nations Industrial Development Organization (UNIDO) were utilized. To use COMFAR III the basics and assumptions of each plant including the capital costs, supply of resources, production costs, annual revenues, *etc.* were computed by Microsoft Excel. Based on the standards of accounting all the economical Tables of plants A and B were calculated by Microsoft Excel. Hence, the required indexes for analysis of profits and costs of plants were provided and investigated. The expected year for the implementation of plants is 2008 during which all the activities related to negotiation with foreign manufacturers, registration of orders, opening of letter of credit, transportation, installment and so on will be completed. The impact of implementation of each plant on costs increase and sale revenues of petrochemical materials will be predicted and introduced from the beginning of 2009. The life span or implementation period for the project is predicted to be 15 years and cash flow is considered form 2009 to 2023 periods.

RESULTS AND DISCUSSION

The results of the simulations of the stacks' conditions, such as temperature, humidity, sulfur combinations and their tonnage, *etc*. were verified through comparison to the real situation of the sulfuric acid plant of the investigated petrochemical unit and following results were attained. Fig. 1 demonstrates the simulation results of the sulfuric acid plant attained through running HYSYS v3.1 software.

Results of desulphurization process simulation with ammonium through running HYSYS v3.1 software: In the first method scrubber with ammonia was used to remove output sulfur oxides from stacks. During this process 1650 tones of water, 26.22 tones of ammonia and 110.67 tones of sulfur oxides from the sulfuric acid plant, enter the scrubber. According to number 1 reaction to number 4, SO_2 and SO_3 were removed entirely and reached to the least amount of standards. Moreover, 89.66 tones of ammonium sulfate and sulfite and 1083.12 cubic meter of acidic sewage with 9.376 ºC were produced.

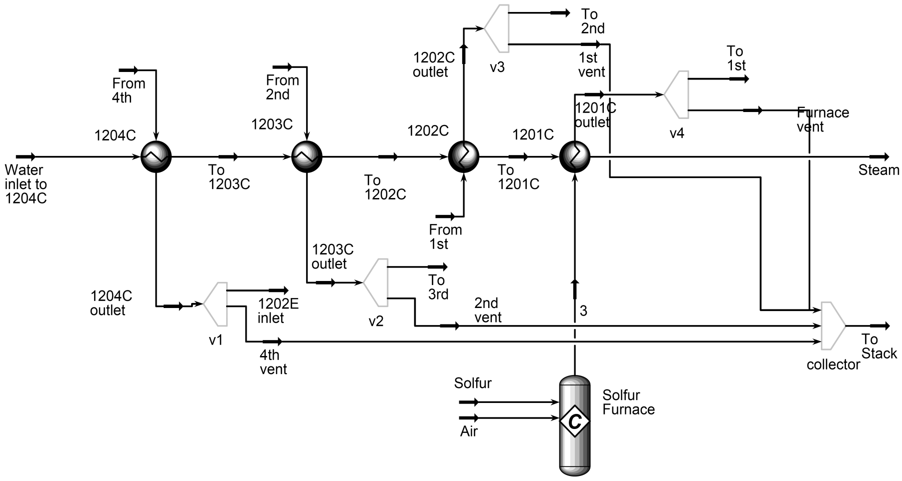

Fig. 1. Simulation results of the sulfuric acid plant attained through running HYSYS v3.1 software

$$2NH_4OH + SO_2 \rightarrow (NH_4)_2SO_3 + H_2O \quad (1)$$

$$(NH_4)_2SO_3 + SO_2 + H_2O \rightarrow 2NH_4HSO_3 \quad (2)$$

$$2NH_4HSO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_3 + 2SO_2 + 2H_2O \quad (3)$$

$$(NH_4)_2SO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + SO_2 + H_2O \quad (4)$$

Fig. 2 demonstrates simulation results of desulphurization process with ammonia scrubber through running HYSYS v3.1 software (Plant A). Results of desulphurization process with ammonia (plant A) are demonstrated in Table-1 in summary.

TABLE-1
SIMULATION RESULTS OF DESULPHURIZATION PROCESS WITH AMMONIUM THROUGH RUNNING HYSYS V3.1 SOFTWARE

Parameters	Input to FGD	After entering ammonia scrubber
Total (SO_2 + SO_3) input in to the stacks (ton/day)	110.67	≈ 0.000
Total (SO_2 + SO_3) input in to the stacks (ppm)	70000	≤ 100
Ammonium sulfite (ton/day)	0.000	87.535
Ammonium sulfate (ton/day)	0.000	2.124
Total ammonium sulfate and sulfite (ton/day)	0.000	89.6
Acidic wastes (m^3/day)	0.000	1083.12

Simulation results of combination of dry desulphurization process with calcium hydroxide and ammonia scrubber: This process includes two stages. In first stage, 95.05 tones of calcium hydroxide and 110.67 tones of sulfur oxides come into calcium hydroxide scrubber daily. According to reactions number 5 to number 9, 95.64 tones of calcium sulfite were produced.

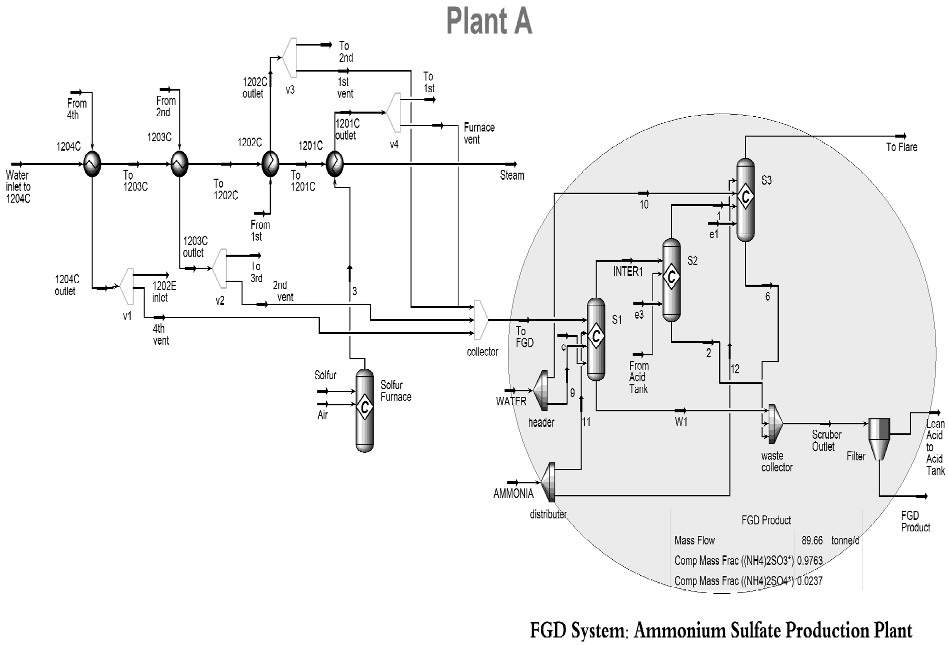

Fig. 2. Simulation results of desulphurization process with ammonia scrubber through running HYSYS v3.1 software (Plant A)

$$SO_2(g) \rightarrow SO_2(aq) \tag{5}$$

$$SO_2(aq) + H_2O(l) \rightarrow H_2SO_3(l) \tag{6}$$

$$H_2SO_4 \rightarrow HSO_3^{\ +} + H^+ \rightarrow SO_3^{\ 2-} + 2H^+ \tag{7}$$

$$Ca(OH)_2(s) \rightarrow Ca(OH)_2(aq) \rightarrow Ca^{2-} + 2OH^- \tag{8}$$

$$SO_3^{\ 2-} + Ca^{2+} + 0.5H_2O(l) \rightarrow CaSO_3{\cdot}0.5H_2O(s) \tag{9}$$

One of the advantages of this solid useful product is that its separation from liquid is easy. Moreover, there is a good market for calcium sulfite and its sale would compensate for the capital costs to some extent. From 110.67 tones of input sulfur oxides in the first stage, 59.6 tones of three sulfur oxide would remove entirely and 51.07 tones which remained would enter the second stage and removed entirely through ammonia scrubber. In addition to refinement of SO_2 and SO_3 from output gases, 7.755 tones of ammonium sulfate and ammonium sulfite as useful products and 670.56 cubic meter of acidic sewage would be produced daily. Fig. 3 demonstrates simulation results of combination of dry desulphurization process with calcium hydroxide and ammonia scrubber through running HYSYS v3.1 software.

The simulation results of desulphurization with ammonia are demonstrated in Table-2.

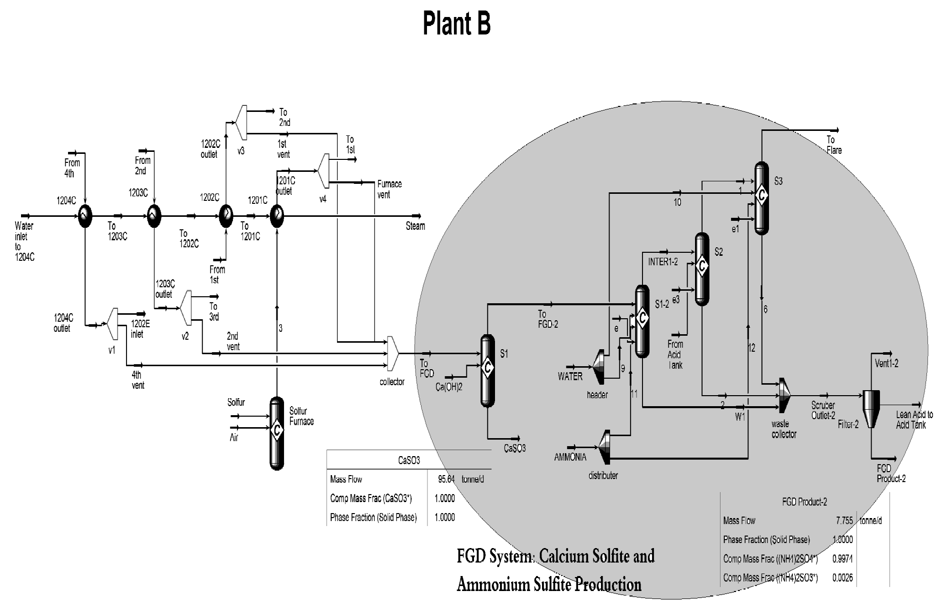

Fig. 3. Simulation results of combination of dry desulphurization process with calcium hydroxide and ammonia scrubber through running HYSYS v3.1 software

TABLE-2
RESULTS OF SIMULATION OF DRY SCRUBBER WITH CALCIUM HYDROXIDE SORBENT AND SCRUBBER WITH AMMONIA SORBENT IN PLANT B

Parameters	Input into FGD processes	Output from the first stage	Output from the second stage	FGD out put
Combination of input SO_2+SO_3 to the stacks (ton/day)	110.67	59.6	≈0.000	≈0.000
Combination of input SO_2+SO_3 to the stacks (ppm)	70000	3620	≤100	≤100
Ammonium sulfite	0.000	0.000	7.7348	7.7348
Ammonium sulfate	0.000	0.000	0.02016	0.02016
Combination of ammonium sulfite and sulfate	0.000	0.000	7.755	7.775
Calcium sulfite	0.000	95.64	0.000	95.64
Ammonia	2.000	0.000	0.000	0.000
Calcium hydroxide	59.05	0.000	0.000	

Econometrics results of two desulphurization processes (Plants A and B) through running COMFAR III economical software: Having two different assumptions, the economical indexes for each choice were estimated. In both plants SO_X pollutant is reduced equally (110 tones per day), the revenue gained by decrease in external costs is the same. Thus, one can ignore the revenue in both plants. Consequently, in the first assumption the external costs were ignored in order to calculate the actual profit or the pay back rate to the investor. In second assumption in order to estimate the entire revenues gained by these environmental projects, the decrease of external costs made by removal of SO_X was considered as one of the revenues of the project. After estimation of capital costs, production costs and revenues gained through implementation of each plant, the entire economical data was entered to COMFAR III software. Then, the economical results of each plant were compared to other plants to decide about proper desulphurization plant.

Constant costs of investment: The constant cost of investment is the main part of economical analysis in which the primary costs for establishment of the plants have been computed both in Rials and in Euro. The constant capital costs in plant A and plant B are 1,476,985 Euro equivalent to 10,740,225,128 Rials, 1,897,299 Euro equivalent to 13,805,586,745 Rials, respectively.

Production costs: Production costs are the costs which should be paid during the production period in desulphurization plants. The production costs in plant A and B generally include the supply of raw materials, repair and maintenance costs, staff costs, tax and fee. Raw material costs include annual costs for providing 8783.7 tones of ammonia and 553875 cubic meter water in plant A and providing 670 tones of ammonia, 264194 cubic meter of water and 19781 tones of calcium hydroxide annually in plant B. Supplying energy in each of the plants includes providing electricity and cooling water. In plant A 1,051,263 cubic meter cooling water and 1,351,624 kilowatt/h electricity and in plant B 1,892,274 cubic meter cooling water and 2,432,924 kilowatt/h electricity is required. As repair costs at initial years are less than the final years, the prediction of repair and maintenance costs in the first five years relative to equipment costs would be 10 % which will be increased 5 % every five years. Sewage disposal costs include disposal costs of 362,845 cubic meters of acidic wastes in plant A and 224,637 cubic meters of acidic wastes in plant B. Staff costs in desulphurization plants were computed by using the Tables provided by Management and Planning Organization for the basic salaries and staff number required for each plant. As the required number of staff for each method is similar, staff costs in both plants A and B are predicted equal to 20,685 Euros. To calculate the depreciation, direct method or direct line as the simplest and most common method, was utilized. In this method the assumption is based on the fact that constant possession during its whole useful life depreciates in a consistent way. Considering the useful life of equipment and instruments which is about 15 years, the depreciation of these equipment is calculated by direct method for 15 years[18]. In addition, paying costs' taxes according to tax laws of the country is considered as a part of production costs and would be distracted from the annual revenues. The sale, production and operation costs of plant A and plant B for first year 2009 and for last year 2023 are 664,780.82 Euro and 596,045.12 Euro, respectively.

Sensitivity analysis examination of plants A and B through running COMFAR III software: At the present study other costs are computed without considering inflation rate and through constant way for different years. Therefore, through running COMFAR III economical software in both desulphurization plants, the sensitivity analysis examination was examined to take the inflation rate in to consideration. To do so, in sensitivity analysis examination, COMFAR III changed the sale revenues, increase of constant costs of investment and operational costs from +20 to -20 %. Then, the internal efficiency rate was computed by using the results of these changes. Figs. 4 and 5 demonstrate the sensitivity analysis examination of plants A and B. In compare to plant B, plant A enjoys more desirable sensitivity analysis examination. Because of the changes implemented in the above mentioned parameters the internal rate of return of plant A is about 27 % while plant B has a negative internal rate of return, because of the changes in operational costs and sale revenues.

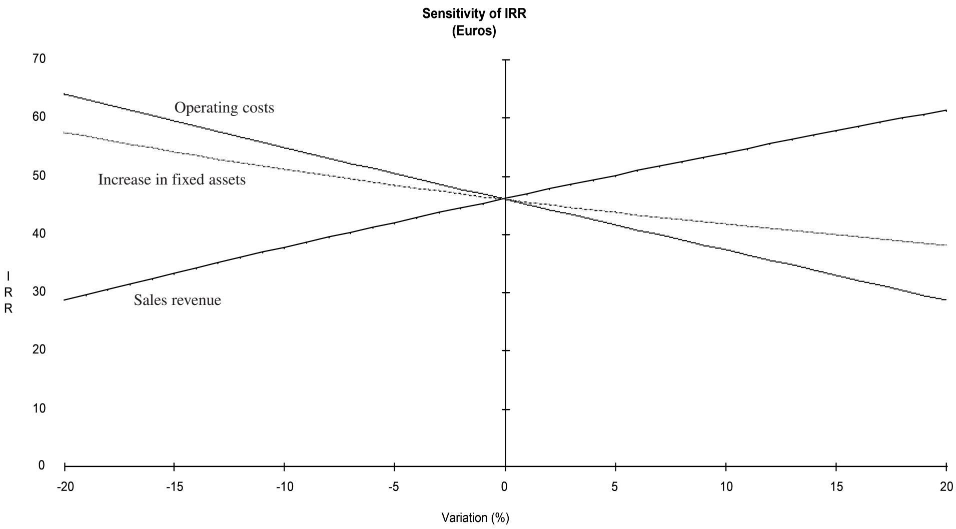

Fig. 4. Sensitivity analysis examination of plant (A) through running COMFAR III software

In the second assumption both plants A and B have gained 39,509,927 Euros revenue as the result of external costs decrease achieved by removal of SO_X gases. The decrease of external costs of each tone of SO_X is about 1066 Euros and in both plants 110 tones of SO_X pollutant was removed daily. In Table-3 the revenue gained by decrease of external costs is demonstrated.

TABLE-3
COMPUTATION OF REVENUES GAINED THROUGH DECREASE OF EXTERNAL COSTS OF SO_x EMISSION FROM INVESTIGATED SULFURIC ACID PLANT

Pollutant	Pollutant removal per day (ton/day)	Annual pollutant removal (ton/year)	Unit price (Euro)	Annual revenue (Euro)
Decrease of social costs of SO_x emission	110.67	36850	1066	39,207,803

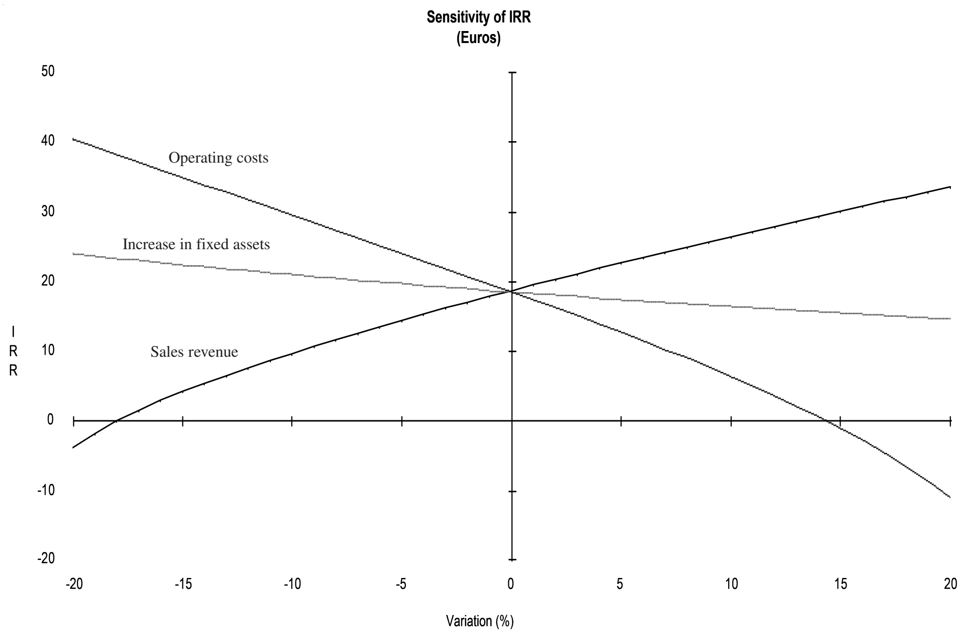

Fig. 5. Sensitivity analysis examination of plant (B) through running COMFAR III software

Conclusion

Considering the results of simulation by HYSYS v3.1 in plant A, there is about 110 tones of sulfur oxides removal per day and 89.66 tones production of useful products *i.e.* ammonium sulfate and ammonium sulfite per day. In plant B which has two stages, in addition to removal of 110 tones of sulfur oxides per day, at the first stage 95.64 tones of useful product *i.e.* calcium sulfite is produced daily and in the second stage 7.755 tones of useful products *i.e.* ammonium sulfate and ammonium sulfite are produced daily. These products can be consumed in the petrochemical units or be sold to compensate for the capital costs. Considering the results of the economical analysis, at the first assumption (without considering the external costs) the constant capital costs in plant A is 1,475,985 Euros less than plant B (1,897,299 Euros). Moreover, the required cash flow in plant A is 246,350 Euros which is less than plant B (417,737 Euros). Also, the internal rate of return in plant A is about 46 % more than plant B (about 18%). The normal payback period in plant A is 3 years less than plant B (5 years) and dynamic payback period in plant A is 4 years less than plant B (14 years). The net present value (NPV) which is one of the main criterion in economical comparisons is higher in plant A (2,142,919 Euros) than in plant B (67,614 Euros) which is the sign of a better cash flow in plant A. considering the results of the second assumption, in case of implementation of the plans in both plants there would be about 39,270,803 Euros revenues as the result of decrease in external costs. Consequently, in comparison to plant B plant A is more economical.

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