

## FLUE GAS DESULFURIZATION METHODS TO CONSERVE THE ENVIRONMENT

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### ABSTRACT

After the observation of serious environmental damages resulting from industrial activities, air pollution reduction has become globally very important.

Fuels and flue gas desulfurization methods in power plants are applicable for petroleum derived fuels consuming units. But in coal fuel power plants, only Flue Gas Desulfurization (FGD) can be used.

Therefore, the substitution of (natural) gas for power plants fuels has become a common way, due to its low sulfur content and lower excess air requirement. But, for existing power plants and before changing their fuels to natural gas, a suitable FGD method should be selected.

In this article appropriate power plant FGD methods are studied. Our calculation addresses the dry adsorption method plus (elemental) sulfur production as the most economical one.

**Keywords:** Flue Gas Desulfurization; SO<sub>2</sub> Adsorption; Power Plants Environmental Problems; Claus Sulfur (Recovery) Plant.

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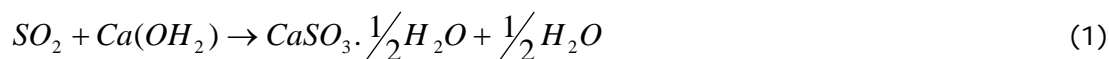
### 1. Introduction

SO<sub>2</sub>, NO<sub>x</sub>, CO<sub>2</sub> and CO are air pollutants, among which SO<sub>2</sub> has the greatest share and can be emitted via the combustion systems of various industrial factories, e.g. power plants, industrial boilers and incinerators [7, 4].

There are many industrial processes for sulfur elimination from gaseous streams. Although the most common desulfurization methods are the "Wet" types, the total and the annual costs of the "Dry" ones are considerably less, due to simplicity, less water consumption and easier residues handling. The "Dry" methods are easily installed and require less space. Hence, they are good choices for the existing units modernization [1, 3, 5, 6, 7].

Since the SO<sub>2</sub> recovery efficiency in "Dry" methods (50-60%) is considerably less than the "Wet" Ones (93-98%), the dry methods are recommended in cases where SO<sub>2</sub> emission is low [1, 2, 6, 7].

In "Semi-Dry" method-which is applicable for the small to medium sized industrial boilers- the adsorber is directly and pneumatically injected as a powder. The main chemical reaction is [2, 5, 6]:



A small portion of calcium sulfite is oxidized to salable gypsum, according to the following chemical reaction [2, 5, 6]:



Scrubbers are categorized – on the basis of their produced solids usage method – into two groups: once-through (without recycle stream) and regenerable (with recycle). In the once-through method, the spent adsorbent is used as a disposable residue or a side-product.

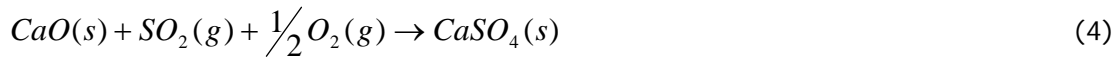
Scrubber system with regenerable adsorber will return it to the system and have a higher cost. But they are used when higher desulfurization efficiency is required [6].

If limestone is used as the adsorbent, the SO<sub>2</sub> adsorption proceeds via two paths (according to the CO<sub>2</sub> partial pressure):

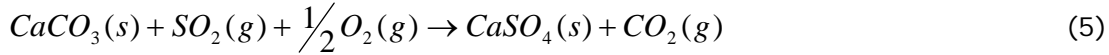
I. Under the low pressure and high temperature, calcium carbonate is rapidly calcined:



This reaction is followed by CaO sulphation:



II. Under the high pressure and low temperature, the first reaction is not thermodynamically viable and SO<sub>2</sub> adsorption progresses via the direct calcium carbonate sulfation:



The CaSO<sub>4</sub> layer which is formed during the direct sulfation of CaCO<sub>3</sub> is more porous than the sulfate layer formed by the calcined limestone sulfation.

The porosity difference is due to the CO<sub>2</sub> formation at the reaction interface, during the direct sulfation.

The main problem of the natural limestone (dolomite) usage is the environmental problem, associated with huge amounts of limestone and disposed solid residue [4].

The successful performance of many SO<sub>2</sub> recovery systems in Europe, US and Japan shows that the required technology for major SO<sub>2</sub> emissions scrubbing exists. Of course, a certain chemical process cannot be used for all of SO<sub>2</sub> elimination cases but, for any SO<sub>2</sub> problem or combination of problems, some solutions can be proposed.

The environmental conservation laws necessitate that not only the SO<sub>2</sub> gas itself should be separated, but also the formed residue during the SO<sub>2</sub> scrubbing should be disposed in an appropriate way (e.g. for sulfuric acid production). [8]

The flue gas desulfurization equipment can be divided into four groups:

1. The large and extensive units, which consume a water-chemicals mixture and produce a solid residue.
2. The medium and extensive units, which consume a water-chemicals mixture and produce a liquid residue.
3. The extensive units which consume only water and produce a liquid residue, from which SO<sub>2</sub> should be separated.
4. FGD equipment which are connected with another industrial process residue stream, and recovers its water or alkaline constituents.

In industries, in which the consumed fuel contains a lot of sulfur, the solid residue producing FGD methods are more favorable because they are consumed more easily.

## 2. Various desulfurization methods

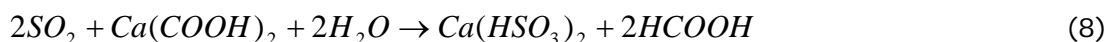
### 2.1 Wet absorption methods

#### 2.1.1 Absorption by sodium sulfite solution [12]



In this method the flue gas pollutant content is reduced from 4500-6000ppm to about 580 ppm. This is done, using an evaporator or crystallizer, which reduces the SO<sub>2</sub> temperature and pressure to the required values for the process. Due to the very high reaction rate of sulphite oxidation to sulphate, the caustic solution consumption will be 50% more than the design value. This can be reduced by using antioxidants like hydroquinone to 25%. This process can be used for the cases of having a lot of solid particles in the flue gas, by installing a prescrubber.

#### 2.1.2 Absorption by calcium hydroxide solution



In this method, HCl and HF elimination is about 98% and that of SO<sub>2</sub> is 90%. The SO<sub>2</sub> concentration in the exhaust gas shows many fluctuations during an interval of 2-5 minutes.

In this method, the SO<sub>2</sub> content is decreased from 6500ppm to an acceptable value. In the first section, the solution is contacted by gas via a venturi scrubber or absorption ducts. Then, the separation of the refined gas from the liquid is done in a centrifugal separator. The soluble calcium bi-sulfite which goes to the oxidation section by the liquid is converted to calcium sulfate crystals by air blowing.

### 2.1.3 Absorption by limestone and magnesium oxide <sup>[9]</sup>

Due to the increasing cost of energy, the lime price will also increase. Thus, it is better to use limestone with a little of magnesium compounds. This will absorb SO<sub>2</sub> by a concentration of about 5500ppm. In all equipment, operating on the basis of using limestone slurry (scrubber, spray tower and turbulent contact absorber), a considerable concentration of magnesium ion has a great effect on the SO<sub>2</sub> absorption.

The water solubility of CaCO<sub>3</sub> is about 100 times less than that of lime (CaO). But by magnesium addition, the sulfite concentration in the solution is increased and the SO<sub>2</sub> absorption will be improved. This is sufficiently economic, thus there is no objection to the magnesium addition.

### 2.1.4. Absorption by Citrex Process <sup>[14]</sup>

In this method, a buffered citrate solution satisfactorily eliminates SO<sub>2</sub> at 43-60°C. This happens in a countercurrent absorption column. The citric acid consumption depends on the following equilibrium relations:



The SO<sub>2</sub> absorbent solution coming from the plant is contacted with H<sub>2</sub>S in an atmospheric reactor at 65 °C and SO<sub>2</sub> is converted to sulfur and water. The reaction chemistry is complex and finally results the following reactions:



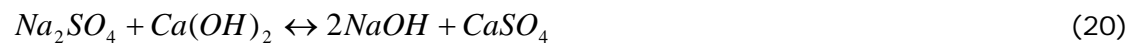
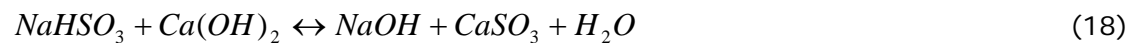
The produced sulfur is separated in the form of sulfur foam, via the floatation method. The advantage of this method is that its by-product is the salable sulfur.

### 2.1.5. Absorption by Two-alkali <sup>[15]</sup>

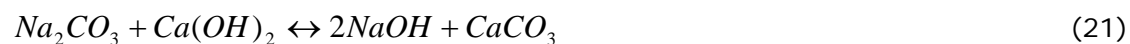
This process is based on the SO<sub>2</sub> elimination by a dilute (0.01 normal) sodium hydroxide solution. The reactions are:



The produced sodium salts are completely soluble, and there is no precipitation problem in the scrubber. The next problem is the spent sodium hydroxide recovery, which is done as following:



After CaSO<sub>3</sub> and CaSO<sub>4</sub> precipitation, Ca<sup>++</sup> remains in the solution (usually about 8000ppm), and should be reduced to about 200ppm. Accordingly Na<sub>2</sub>CO<sub>3</sub> is used.



CO<sub>2</sub> addition is also necessary for the reaction completeness:



This process has fewer problems in chemistry, equipment and construction material. Costs are more than estimates, but the effects and results are mostly compensating.

### 2.1.6 Absorption by ammonium sulfite solution

In this method the flue gas is washed by ammonia solution and then is heated to be distributed well. The absorbent solution is sent to the evaporator for the decomposition of sulfides to  $\text{SO}_2$ ,  $\text{NH}_3$  and water. In the next stage  $\text{SO}_2$  reacts with the existing  $\text{H}_2\text{S}$  in the reactor to produce sulfur. It is noteworthy to say that to provide this  $\text{H}_2\text{S}$ , the  $\text{SO}_2$  itself or the  $\text{H}_2\text{S}$  produced in the adjacent industrial units can be used. This is done via the conversion of two thirds of  $\text{SO}_2$  to  $\text{H}_2\text{S}$  by a special catalyst and the reducing gas. The reducing gas can either be methane to LPG hydrocarbons or produced from coal. Benefits of this method are having no environmental problems, effective  $\text{SO}_2$  recovery, low investment, low operating cost and reliability.

### 2.1.7. Absorption by sulfuric acid and catalyst

In this method,  $\text{SO}_2$  concentration is reduced from 3000ppm to less than 50ppm. This is done via the preliminary dust elimination by water and then passage of the cooled gas through the absorption column. In this column,  $\text{SO}_2$  and  $\text{SO}_3$  are scrubbed by dilute sulfuric acid and a catalyst at 50-70°C. This considerably reduces the required water volume for the complete  $\text{SO}_2$  absorption. The scrubbed gas exits from the column top. Sulfurous acid, dilute sulfuric acid and the catalyst are drained from the column bottom and are aerated. In this way the  $\text{SO}_2$  conversion reaction to the sulfuric acid is done. The catalyst is also recovered.

### 2.1.8. Two- stage absorption by lime solution

Primarily, the  $\text{SO}_2$  rich gas is cleaned and cooled by water. Then the solid particles and lime solution impurities are eliminated and lime slurry is prepared. The absorption reaction dominantly depends on the lime solubility. Experiments show that higher pH produces a higher ratio of liquid to gas and higher absorption efficiency. Lower pH, increases the conversion ratio of lime to calcium sulfite or sulfate. The gypsum crystals are primarily added to the solution, to facilitate its crystallization.

### 2.1.9. Absorption by sodium sulfite <sup>[12]</sup>

In this method the  $\text{SO}_2$  rich gas is blown through the absorption column and is contacted by the 20% sodium sulfite solution.  $\text{SO}_2$  and dust are previously eliminated by an up-flowing stream, in a vertical venturi scrubber. In this manner more than 95% of  $\text{SO}_2$  is scrubbed. There exists a gas-liquid separator at the top of the absorber column.  $\text{SO}_2$ -free flue gas exits this column top and an  $\text{SO}_2$ -rich sodium Bi-sulfite solution leaves the column bottom. The sodium Bi-sulfite solution is sent to an evaporator and a crystallizer, to be recovered. The evolved  $\text{SO}_2$  can be converted to free elemental sulfur or sulphuric acid. The precious gypsum by-product can also be obtained by adding  $\text{Ca}(\text{OH})_2$  to the sodium Bi-sulfite solution.

## 2.2 Dry adsorption methods

### 2.2.1. Adsorption by copper oxide <sup>[10,11]</sup>

Although this method can be used for cleaning the Claus unit tail gas, but mostly is applied in flue gas  $\text{SO}_2$  recovery, for large power plants steam boilers.

This process uses a fixed bed of copper oxide on the alumina support, to adsorb  $\text{SO}_2$  from the hot flue gas at 400°C (optimum). The catalyst recovery is done by a hot reducing gas (e.g.  $\text{H}_2$  or  $\text{H}_2/\text{CO}$ ). Required hydrogen is supplied by steam reforming or partial oxidation processes.

There is no need to have a high purity, for the  $\text{SO}_2$  separated. This  $\text{SO}_2$  can be used to produce (elemental) sulfur, sulfuric acid or other by- products. The  $\text{SO}_2$  recovery is about 90%.

For the Claus unit tail gas desulfurization, the tail gas is primarily burnt to oxidize all the sulfur compounds to  $\text{SO}_2$ . Then; the flue gas is cooled down to 400°C and is passed through the  $\text{CuO}$  bed. The recovered  $\text{SO}_2$  is returned to the Claus unit.

The gas leaving the catalyst bed contains 1500-3000ppmv  $\text{SO}_2$ . A  $\text{SO}_2$  scrubbing system for a 100 LTPD Claus unit has a cost of 2.5 times of the Claus unit itself.

### 2.2.2. Dry adsorption FW-BF <sup>[13]</sup>

This method uses activated carbon for  $\text{SO}_2$  adsorption.

If the unit feed is received from the Claus unit, primarily is burnt at 538 °C and mixed with air to reduce the air oxygen content to about 3.5vol%. Then the gas is cooled and sent to an adsorption column. SO<sub>2</sub>, steam and oxygen are adsorbed over the catalyst surface at 120-150 °C (in the form of sulfuric acid). The exiting gas contains less than 200ppmv SO<sub>2</sub>. The catalyst regeneration is done at 650-980°C and releases SO<sub>2</sub> with about 20% concentration. At the next step the released gas is decomposed to sulfur and oxygen. This method eliminates more than 90% of SO<sub>2</sub> and 60-70% of NO<sub>x</sub>. The shape and size of the activated carbon particles and beds should be such that no appreciable pressure drop in gas phase is produced.

### 2.2.3. Catalytic oxidation method

In this process, the flue gas (after dust scrubbing by mechanical and electrostatic precipitators) is passed through a catalytic reactor of SO<sub>2</sub> to SO<sub>3</sub> conversion, containing V<sub>2</sub>O<sub>5</sub> catalyst. This cools the flue gas to 300°C. Then, the SO<sub>3</sub> is converted to 80wt% sulfuric acid, in an absorption column. This acid is concentrated to 94wt%, in the concentrator. This product is cooled and stored. Gypsum is another salable product of this method. The scrubbed flue gas leaving the absorption column is heated again, or directly sent to a stack. The SO<sub>2</sub> recovery is reported to be 90%.

### 2.2.4. Manganese oxide application method (Mitsubishi)

Flue gas enters an adsorption column, uniformly containing the manganese oxide powder. The gas temperature is 100-180°C and the adsorbent consumption is 150-250 grams for each cubic meter of gas. SO<sub>2</sub> and SO<sub>3</sub> produce manganese sulfate with the manganese oxide. Then, 90% of the unreacted oxide and manganese sulfate mixture is collected by passing through a cyclone. An electrostatic precipitator separates the remaining 10%, and is converted to a 70% water content paste.

Then, by air and ammonia injection through this paste in the reducing column, the ambient temperature oxidation is done. The result will be a solution, containing manganese oxide and ammonium sulfate. Its oxide is returned to the adsorption column, after being separated by a filter. The remaining solution is sent to the crystallizer to recover ammonium sulfate crystals.

By heating this solution, ammonia is separated and sent to the reducing column. The only practical problem of this process is the construction and size of the atomizer plate holes of the reducing column. This is due to the choking probability of these holes by the paste, and can be solved by the proper determination of holes diameter and air velocity.

It is expected that the FGD systems costs will be reduced in the future, at least due to four reasons:

1. The total cost of industrial units will decrease due to the obtaining experience and reliability, by their operating personnel.
2. Using the waste water streams of the unit or adjacent units reduces the chemicals costs.
3. Usually, industries like metals smelting, textiles and paper manufacturing, produce alkaline waste waters. By using these steams, not only the operating costs are reduced, but also FGD systems total costs are also decreased. This is because, the necessary equipment for storage and blending of purchased chemicals are eliminated.
4. Most of FGD equipment are considered at the primary design stage of the industrial unit. Therefore, the total unit cost is reduced.

## 3. Conclusions

These methods can be compared from some points of view.

Absorption methods, in which solid metal salts are produced, have considerable costs of solid handlings. Moreover, in some processes the produced solids (sulfite and bi-sulfite) require environmental friendly disposal methods. Because, besides making precipitation, they are categorized as dangerous materials from the environmental point of view (due to the intense oxygen elimination in water, their disposal in the naturally found waters, is forbidden).

As an example, about thirty years ago, the capital and operating cost of slurry stabilization and disposal, was estimated to be about 3.2 US\$ for each ton of coal consumed.

Today, considering the global inflation and location factors, this is estimated to be about 11 US\$/ton

In industries with high sulfur fuel consumption, the liquid waste water producing systems are even less applicable, due to more problems of waste disposal, in comparison with solid wastes. Considering the techno-economical data of manufacturers, it seems that catalytic sulfur producing methods are superior ones, even from the economic point of view. In fact, for smaller industries, the absorption methods producing solid salts are over ally more economical. But, as the industry capacity increases, catalytic methods prove to be more feasible.

FGD systems costs for solid wastes handling (including operating and total unexpected costs) are estimated to be 9.5-18 US\$/ton of burnt coal. Chemical cost is about 25-35 % of the operating cost. The total investment for a 35 MW or more power plant can be about 82 US\$/KW and 215 US\$/KW for a 5 MW power plant.

The investigation results for the two wet and dry methods (applicable to a real case study) are:

#### **A) Wet Method,**

##### **Assumptions:**

1. Prices basis of 1978 in the US for the capital and annual revenue requirements.
2. Annual global inflation rate of 3.3%
3. 7000 hours annual working time and 80% sulfur removal efficiency
4. 30 years life time for equipment
5. Calcium sulfite to sulfate conversion cost, to be invested as out sourcing, excluding the by-products sales (e.g. gypsum).
6. Location factor of 1.3 for Iran

For a 600 MW power plant and two options of  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$  for the wet method, the result(in 2009)is :

Costs ( $10^6$ US\$)	$\text{CaCO}_3$	$\text{Ca}(\text{OH})_2$
Capital	127.8	114.2
Annual operating	52.4	54.4

#### **B) Dry Method (Catalytic Method)**

##### **Assumptions:**

1. Prices basis of 1973 of the US Gulf Coast.
2. Annual global inflation rate of 3.3%
3. 7000 hours annual working time by about one million tons of heavy fuel oil (3 wt% sulfur) consumption and 80% operating load
4. Capital cost includes overhead, tax, assurance and gross capital investment of 20% per year.
5. FGD system cost includes the stand-alone hydrogen production (For catalyst regeneration) and  $\text{H}_2\text{S}$  production (for Claus process sulfur production).
6. Salable sulfur price of 8US\$/ton (now more than 70 US\$/ton).
7. Electricity price of 1.3 cent for each KW.hr., fuel gas price (for hydrogen production) of 6 cents for each million Btu heating value.

Costs ( $10^6$ US\$) in 2009	Catalytic Method
Capital	112.2
Annual operating	36.0

As can be observed, even for 600-650 MW power plants, the catalytic FGD method is more economical. Besides, there are no environmental waste disposal (or waste dumping) problems. Moreover, in the vicinity of large petroleum refineries, their excess hydrogen production (for catalyst recovery) or excess sulfur recovery plant capacity (for sulfur production), can also be used.

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