Recovery of sulfur dioxide from flue gas for sulphuric acid production

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Abstract: *The paper presents a review of the literature relative to the flue gas desulfurization methods for sulphuric acid (H_2SO_4) manufacturing. The covered topics include wet and dry methods. Particular attention has been paid to the desulfurization of the flue gas from the copper smelting industry that can lead to a generation of SO_x rich streams resulting in high profitability of H_2SO_4 production.*
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1. Introduction

Economic activity, especially production, affects the environment by introducing substances into the air, water, soil or ground. These emissions cannot always be avoided, but a special care has to be taken to minimize them in accordance with the law. This means that an appropriate permit must be obtained for the introduction of substances or energy into the environment, and sometimes appropriate methods of preventing or reducing emissions must be applied.

Desulfurization is mostly associated with the treatment of boiler flue gases and waste gases from crude oil processing, sulfuric acid production and smelting/ metal processing. It is aimed at converting SO_2 into a substance easy to remove both from the gas and from the treatment system. These operations result in the recovery of sulfur in the form of commercial products or the generation of sulfur waste. In the literature may be found different techniques of desulfurization, however, due to techno-economic problems and difficulties in scaling-up from laboratory to industry level, only a few of them have found wide appliances.

The aim of this paper is to review the methods of gas desulphurization, with particular emphasis on technologically mature methods enabling sulphuric acid production from boiler flue gases and waste gases from crude oil processing, smelting and metal processing or sulphuric acid production.

2. Overview of available wet methods

These methods are implemented using a scrubber located in the flue gas duct (upstream of the chimney). As a result of contact with water or a solution, the purified gases are cooled to a temperature of about 365 K, since the stack temperature is about 420 K. The most important issue in these methods is the concentration of SO_2, since sulphur recovery in the form of H_2SO_4 can be carried out when SO_2 + SO_3 > 0.3% v/v. Several important facts should be taken into consideration, namely:

- purified gases must be heated before being directed to the chimney,
- few methods are able to provide the required degree of desulphurization in a given range of concentrations,
- removing water from a product is expensive.

The choice of method is determined by the degree of desulfurization.

The lime method

The method is based on absorption and chemical reaction of SO_2 in a suspension of lime or limestone. The CaSO_3 and CaSO_4 in the form of sludge or wet solid in most cases is waste. According to [2] it is believed that once the lime methods have been properly adapted to the conditions in metallurgy and optimized, they may prove to be crucial for this industry. The conditions in the stack are favorable for the formation of SO_3 and sulfuric acid from flue gases. When the concentration of SO_3 drops below the dew point temperature, a reaction occurs with the vapor H_2O and forms H_2SO_4 in the form of droplets. These droplets are diluted to an equilibrium concentration. An important aspect in any project is the costs incurred, thus in this case the best solution is to mix the purified gases with a corresponding volume of hot, untreated flue gas stream taken from the boiler or precipitator. Also important is the amount of heat that must be applied to heat the purified gases to prevent condensation prior to emission from the stack and to ensure adequate lift and dispersion in the atmosphere. This property is due to the physicochemical characteristics of the flue gases and the design of the chimney and the conditions of dissipation.

Magnesium regeneration method

This is one of the desulfurization methods, in which hydrated (IV) and (VI) magnesium sulfates and unreacted MgO are obtained. The separated solid products are dried and then calcined at temperature 1080-1300 K. As a result of this operation, MgO is regenerated and SO_2 is recovered. The dry waste gas from calcination contains about 5-15% v/v of SO_2 which is used to produce H_2SO_4. Despite the many different details of this method, such as the use of activators, blocking the interior of the apparatus with a deposit of solid or regeneration of the absorbent, it has found many applications in metallurgical processes. Like many technological processes, it has certain limitations, e.g. high corrosion and erosion risks or the necessity of proper dedusting. Nowadays, this method is most popular in the Czech Republic and the USA [4].

The Cat-OX method

In metallurgy, there are many methods to desulfurize flue gases that have been developed by industry companies. The Cat-OX method, developed by Monsanto, involves oxidising SO_2 to SO_3 using a catalyst V_2O_5 catalyst at a temperature of 700-750 K, followed by cooling of the gases and absorption of H_2SO_4. The resulting H_2SO_4 is already an 80% product. Unfortunately, the Cat-OX method, has proved to be another method that poses great corrosion problems. At the very beginning of the operation it requires a thorough preliminary purification of the gas, generating huge economic costs.

Lurgi-Sulfacid method

The next company to implement a desulfurization method is Lurgi-Sulfacid, which uses a layer of activated carbon sprinkled with water. The end product is only 10-20% H_2SO_4. The method is used in the removal of SO_2 of waste gases from chemical and metallurgical processes when the concentration of SO_2 is ≥ 2% v/v [2].

Degussa absorption method

According to the method developed by Degussa, SO_2 is sprinkled with an oxidized water in a separate column. The process makes possible to reduce the concentration of SO_2 in the flue gas to about 20 mg/Nm^3. In this method it is obtained 70% H_2SO_4.

Solinox method

Solinox regenerative desulfurization is based on absorption of SO_2 in liquid ethylene glycol esters, followed by desorption of SO_2 by means of elevated temperature, pressure reduction or gas stream desorption. The aim of the method is to reduce sulphur dioxide emissions by means of a waste-free and highly efficient installation. The sulfur dioxide-treated inlet gases leave the absorption zone through a stack bottom isolating the liquid circuits and enter the sorbent residue backwash zone. Although the sorbent vapours have a very low vapour pressure at this point, due to the large amount of gases and the entrainment of the liquid droplets by the gases, sorbent losses cannot be neglected. The low temperature of the water for leaching the sorbent residue caused by the low gas inlet temperature and the water evaporation is compensated in the heat exchanger. The treated inlet gases are discharged to the atmosphere via a chimney [1]. Solinox installation works i.a. KGHM Legnica Copper Smelter.

Microbiological reduction of SO_2

One of the most interesting methods is microbiological reduction of SO_2 developed by the Paques-Hoogovens company from the Netherlands. The whole process is carried out in three cycles, consisting of absorption of SO_2, bioreaction with SO_2 and separation of elementary sulphur. Absorption SO_2 is characterized by the production of H_2S, which is oxidized to sulphur in a biologically controlled environment. The whole operation takes place in a settling tank where the sulfur suspension is concentrated. This suspension is subjected to dehydration in a vacuum filter. In order to obtain high quality sulphur, it is subjected to thermal refining. The desulphurization degree of this method is up to 98% [3].

BIPOLAR electrolytic process

Stuffer Technology has implemented the BIPOLAR electrolytic process, which proceeds in two stages. In the first stage, a column filled with rings or saddles made of a material with good electrical conductivity, e.g. phosphosilicon alloy with 12% Si content, is used for absorption of SO_2 in an aqueous solution of sulphuric acid. In the second stage, by electrolysis of sulphuric acid (IV) at a potential of about 0.6 V, it is oxidized to acid (VI) with release of hydrogen. As a result, 40-48% sulfuric acid is obtained, depending on the conditions of the process.

3. Overview of available dry methods

As the name suggests, dry desulphurization methods proceed in dry state i.e. in gas-solid system/ waste products/ utility desulphurization products. They are characterized by adsorption on solid sorbents - metal oxides or activated carbon and absorption with chemical reaction with simultaneous drying of desulfurization products. Dry methods in comparison to wet methods allow to avoid problems connected with pH control, settling of solids in the apparatus, accumulation of liquid waste or heating of purified gases.

Sorption of SO_2 on solid sorbents

In the FW-BF (Foster Wheeler Bergbau, Forschung) method, SO_2 is adsorbed in a mobile layer of active coke, at 400 K, from a dusted flue gas. In this case, if the plant contains a so-called RESOX node, in which the reducer SO_2 anthracite or coke oven gas is the reducer, the desulphurisation product is a concentrated stream of SO_2 or elementary sulphur. As a result, the formed sulphuric acid diffuses from the pores to the liquid layer on the particle surface, from where it is washed out with demineralised water to obtain sulphuric acid (VI) of 10-20% concentration. This method has found recognition in metallurgical processes, because it enables the removal of SO_2 from waste gases. Sorbents in this method are oxides of Mn, Fe, Cu, Co, Zn and others. Due to the significant rate of the reaction with SO_2, the method provides satisfactory economic results. It should be remembered, however, that this method requires the use of adsorption units of large dimensions [2]. Recently there were developed methods that allow the use of activated carbons produced from unburned carbon for the purpose of FW-BF [4-5].

Another oxide that deserves attention is CuO, because due to the its catalytic action, SO_2 oxidises to SO_3. An important element during adsorption is the decrease in efficiency with time and the decrease in mechanical strength of the granules. At higher temperatures Cu i SO_2 is regenerated by means of H_2, CO or light hydrocarbons. This operation takes place at temperatures not exceeding 680 K due to minimization of hydrogen consumption and better copper activity. Desulphurisation efficiency based on sorption SO_2 on CuO is over 95%. Despite the high investment cost, this process has great potential for practical applications.

Desulphurisation by spray drying

Absorption with chemical reaction SO_2 in droplets of alkaline solution occurs simultaneously with spray drying. Unreacted reactants, or desulfurization products, are released as powder. The reactants in this process are solutions of soda or $Ca(OH)_2$. $Ca(OH)_2$ is the most applicable due to insolubility of desulphurization products in water. SO_2 contained in the gas, is absorbed on the surface of droplets, penetrates into the interior, undergoes oxidation and reacts with $Ca(OH)_2$ to form calcium sulfite and sulfate. As a result of water evaporation, the flue gas temperature drops to 10-20 K above the dew point temperature of 333-344 K. Physical changes in the droplets of the suspension have a great influence on the desulfurization rate, through oxidation SO_2 in the liquid phase of the droplets [6].

A similar phenomenon can be observed in smog formation and "acid rain" processes. Therefore, in order to achieve a high desulphurization rate with low sorbent consumption, the process should be carried out at a temperature close to the adiabatic saturation temperature of the waste gases. Better efficiency is also ensured by recirculation of part of the separated solids due to increased contact surface area of the reactant phases in the dryer and faster formation of solid phase nuclei, increasing the utilization rate of $Ca(OH)_2$. This is a very expensive process and any by-product is not economically viable.

4. Summary

A comparative analysis between the methods requires taking into account many aspects, such as the demand for reagents and energy, operation and maintenance, waste collection and neutralization, as well as the costs incurred, which to a large extent determine the realization of the process. Process efficiency is an indicator thanks to which it is possible to visualize the effectiveness of the actions taken. When this value is compared in dry methods, in which a higher stoichiometric sorbent ratio is required to achieve the same levels SO_2 and at the same time are considerably more expensive, it can be concluded that the process is not very cost-effective [7].

However, due to the many times higher cost of the reagent $Ca(OH)_2$ than $CaCO_3$, dry methods are preferred for desulfurization of flue gases from combustion of low-sulfur coals. In addition, due to the elimination of large volumes of slurry streams and the heating of treated gases, the energy requirement is significantly lower. From the practical point of view, in the industry, the key is the facilitated operation with reduced maintenance, due to the elimination of many nodes and apparatuses or blocking of the interior of the apparatus with deposits or reduced corrosion, this method is mainly preferred in the processes of gas purification from smaller emission sources. However, the role of environmental protection development is crucial in today's investments, metallurgical and chemical processes and, above all, in industry. Constantly changing environmental laws and EU standards regulate the level of emissions without regard to both investment and economic costs. Therefore, each branch of the economy uses the tools that are the most necessary for it and at the same time duly effective.

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