DESULPHURISATION OF WASTE GASES FROM THE INDUSTRIAL PROCESSES

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Abstract: It is discussed the most usual chemical methods and alternative technologies of desulphurisation of waste gases from the industrial processes.
The advantage of using chemical methods vs. electrochemical methods is given by low price costs of first ones. These methods are useful at laboratory scale, and do not necessitate complex laboratory apparatus.
The advantages of the electrochemical methods are completed by the small consumption of energy that is necessary and the pollution, which is extremely small for them.

Keywords: desulphurisation, SO_2, waste gases, absorption.

1. INTRODUCTION

The sulphur compounds that exist in the atmosphere are made mostly of H_2S, SO_2, SO_3 and sulphates [1]. They enter the atmosphere on a large scale, through human activities. It is estimated that almost 65 million tones of sulphur per year enter the atmosphere by anthropological activities, mostly by fuels combustion [2].

Acidic emissions of sulphur dioxide (SO_2) and nitrogen oxides (NOx) arise from many industrial sources as a result of combustion processes. In the UK in 1999, power stations contributed with 65% of all SO_2 emitted in the UK. Other industries were responsible for 21%.

H_2S that enters the atmosphere is rapidly converted to SO_2 by the following process [3]:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \tag{1}$$

The reaction (1) takes places according to the following mechanism:

$$H_2S + HO\bullet \rightarrow HS\bullet + H_2O \tag{1a}$$
$$HS\bullet + O_2 \rightarrow HO\bullet + SO \tag{1b}$$
$$SO + O_2 \rightarrow SO_2 + O \tag{1c}$$

The primary source of SO_2 is coal, which contains a big quantity of sulphur that needs to be removed with great expenses in order to maintain the quantity of SO_2 to an acceptable level. Approximately half of the quantity of sulphur in coal is pyrites and the other half is made of organic compounds that contain sulphur. The making of SO_2 by pyrites combustion is given by the reaction:

$$4 \text{ FeS}_2 + 11 \text{ O}_2 \rightarrow 2 \text{ Fe}_2\text{O}_3 + 8 \text{ SO}_2 \tag{2}$$

2. CHEMICAL METHODS OF DESULPHURISATION

A great number of methods are used in order to remove sulphur and sulphur oxides from fuels before combustion and from the resulted gas after combustion. Most of those efforts focus on coal.

A first chemical method of furnace gases desulphurisation is by the coal's combustion in fluid-bed; the process consists of burning the coal in a bed of divided limestone or dolomite. The calcination of the limestone takes place according to the reaction (3):

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_{2(g)} \tag{3}$$

and the produced lime absorbs the SO_2:

$$\text{CaO} + \text{SO}_2 + \tfrac{1}{2} \text{ O}_{2(g)} \rightarrow \text{CaSO}_4 \tag{4}$$

Krüger has developed a patent pending fluid-bed process for removal of dissolved heavy metals by adsorption/co precipitation. The waste product is a very compact granulates with a very low water content of 10-20%. Sludge is not produced. The fluid-bed technique was tested at a coal-fired power station with wastewater from the flue gas desulphurisation (FGD) unit for removal of heavy metals from the wastewater. By dosing only potassium permanganate to the wastewater, the content of dissolved nickel, cadmium and zinc was reduced by respectively 99%, 92% and 97% at optimum treatment in one fluid-bed reactor. The weight of waste product produced will constitute less than 25% of the waste product produced by the present traditional chemical precipitation [4].

Table 1 presents the most important systems of gases absorption that is classified in wet and dry systems. A dry system involves the introduction of the limestone or dolomite in a reactor, followed by the removal of the lime that didn't react and the sulphates. The total reaction for dolomite is:

$$\text{CaCO}_3 \cdot \text{MgCO}_{3(s)} + \text{SO}_{2(g)} + \tfrac{1}{2} \text{ O}_{2(g)} \rightarrow \text{CaSO}_{4(s)} + \text{MgO}_{(s)} + 2 \text{ CO}_{2(g)} \tag{5}$$

Table 1. The main gases absorption systems

Process	Chemical reactions	Advantages or disadvantages
Lime absorption	$\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$	things needed ~ 200kg lime per tone C, great quantities of waste product appear
Limestone absorption	$\text{CaCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_{2(g)}$	pH smaller then that of the limestone and not enough
MgO absorption	$\text{Mg(OH)}_2 + \text{SO}_2 \rightarrow \text{MgSO}_3 + 2\text{H}_2\text{O}$	The sorbent can be regenerated
Absorption based on Na	$\text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow 2\text{NaHSO}_3$ $2\text{NaHSO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} + \text{SO}_2$	There are no great technological limitations; annual costs are relatively big
Absorption with alkaline solutions	$2\text{NaOH} + \text{SO}_2 \rightarrow \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$ $\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_{3(s)} +$ $+ 2\text{NaOH (NaOH regeneration)}$	It allows the regeneration of alkaline solutions based on Na (expensive), lime (cheap)

Another method is waste gases desulphurisation which includes the absorption of $SO_{2(g)}$ into a aqueous solution of sulphide in order to form ions of sulphites and sulphates, the supplementary absorption of SO_2 and the formation of bisulphite. Bisulphite can be reduced to sulphide and used in the first phase of the absorption [5].

The simultaneous removal of NO and SO_2 takes place through a process of absorption in which the apparatus used contains an absorption column filled with aqueous solution of chelates and sulphides. The oxidized metallic chelates at an inactive state are electrochemically reduced [6-8].

The oxidative removal of SO_2 on active coal can also be done by transforming it in $H_2SO_{4(aq)}$ at 30-100^{0}C by a succession of the processes of absorption, oxidation, hydration, on fibres of polyacrilonitril. SO_2 in concentration of 1000 ppm in the furnace gas has been completely removed for a period of 60 h [9-11].

It is important to mention Nuig and Li [12] and their work on catalytic oxidation of SO_2 and NO due to corona discharge and the effect of humidity on the oxidation of furnace gas containing SO_2, NO and air.

H_2S is removed from the gas stream by selective oxidation to elemental sulphur over a regenerate catalyst at ambient temperature. In a separate step, the sulphur-charged catalyst is regenerated by evaporation of the elemental sulphur, thus restoring catalyst activity. The durable Selox catalyst ensures stability over many absorption-regeneration cycles, hence limited waste production and interesting economics [13]. The standard Selox process can be economically applied in the purification of gases with H 2 S concentrations between 0 and 5,000 ppmv and daily sulphur production rates up to 10 tons.

The Selox process has several key advantages compared to alternative processes available on the market.

These are: dry bed absorption, no liquids involved, low energy consumption, no consumption of chemicals, catalyst regenerate on site, high quality sulphur as product, durable catalyst, high absorption capacity (up to 50wt% sulphur), selective towards H_2S, no interfering absorption of e.g. CO_2, simple process scheme and process control, flexible towards feed gas fluctuations, odour-free cleaned gas (H_2S < 1 ppmv), basically no chemical waste.
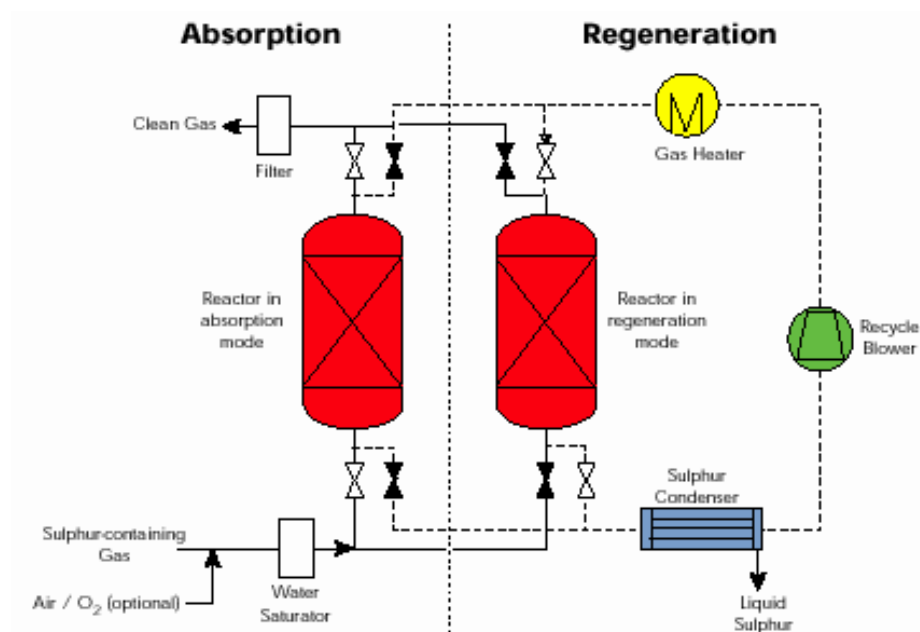

Fig. 1. The Selox process

3. ELECTROCHEMICAL METHODS OF DESULPHURISATION

Electrochemical gas purification methods can be applied basically in two steps. In the first step, gases to be removed are absorbed in an aqueous electrolyte. Then, in the second step, they can be converted into harmless components via electrochemical oxidation or electrochemical reduction. This study investigated the feasibility of electrochemical removal of sulphite ions arising from the absorption of sulphur dioxide in an aqueous electrolyte. The removal efficiency, current efficiency, and energy consumption were determined at different initial sulphite ion and electrolyte concentrations and applied currents. Furthermore, linear sweep voltammetry studies were performed using a graphite electrode in sulphuric acid. It has been concluded from all these experiments that sulphur dioxide can successfully be removed using an electrochemical method [14].

The electrochemical process with membrane has as a key element the electrochemical cell that uses a selective membrane for SO_x; the removal of SO_x takes place in a proportion of 90%, with a good efficiency. The capillarity forces of the membrane and the porous electrodes create equilibrium; in order to maintain the enlarged surface of the electrode it is necessary to keep the electrolyte in the membrane, allowing the drying of the electrodes pores [15].

The selective removal of SO_2/NO from the furnace gas, at high temperature, is being done by using the electrolyte: $K_2S_2O_7/V_2O_5$ at 400^0C, porous Ni oxide electrodes and an electrolytic ceramic matrix, Si_3N_4. The furnace gas introduced (SO_2: 0,3%; O_2: 3%; N_2) is oxidized by the transformation of SO_2 to SO_3, reduced to sulphite and transported to anode. The removal of SO_2 has been achieved with an efficiency of almost 100% [16].

Removing SO_2 from the atmosphere has been studied by electrolyse of metallic sulphurs:

$$MS + 4\ OCl^- \Leftrightarrow MSO_4 + 4\ Cl^- \tag{6}$$

The metal M is transformed in a sulphate that does not harm the environment [17].

The desulphurisation of polluting gases with sulphur by electrochemical conversion is one of the basic concerns as far as the minimum reduction of pollution is concerned. Gases as SO_x are generally transferred by absorption or by the reaction of aqueous solutions, before oxidation or electrochemical reduction. This conversion can be achieved in two ways:

a) the gas is absorbed directly into an electrochemical cell (a process in an inner cell);

b) the gas is absorbed in a separate reservoir and then transferred in an electrochemical cell (a process of outer cell) [18].
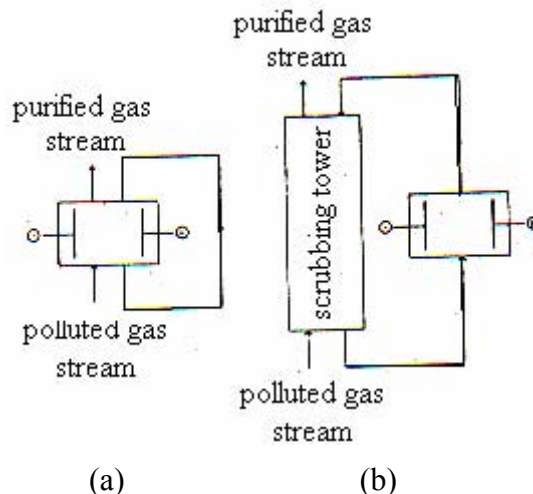

(a)   (b)

Fig. 2. Electrochemical conversion by cell process: (a) inner; (b) outer

The removal by processes in inner cell involves the oxidation of SO_2 to H_2SO_4, according to the following redox system:

$$SO_2 + 2\,H_2O \rightarrow SO_4^{2-} + 2\,e^- + 2\,H^+ \tag{7}$$

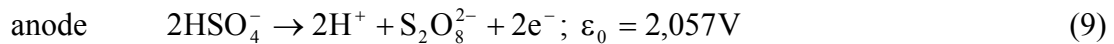At laboratory scale, the reaction takes place in a reactor with anode in fixed-bed [18].

At industrial scale, the pollutant needs to be transferred from the gas phase to a phase where it can react at the electrode's surface, in order to be converted to a harmless product. This transfer needs the absorption in liquid phase, the transfer rate being dependent on the pollutant concentration in the gas phase and the pollutant's solubility in liquid phase. The concentration of the compounds having sulphur in the waste gases and their solubility in aqueous environment are small. In the absorption processes for removing the gas pollutants, this solubility is increased by the presence of a reactive (NaOH, limestone).

The outer cell processes avoid the difficulties at industrial scale. The separation of the absorption and electrolyses equipment allows the use of the standard equipment for both operations. The following processes are successfully used: Ispra Mark 13A, desulphurisation "peracid", Saraberg – Holter – Lurgi (SHL). The process of furnace gases desulphurisation Ispra Mark 13A has been tested on a pilot installation [19, 20].

An installation of industrial scale has been built in Sardinia, having a capacity of 32000 $m^3 \cdot h^{-1}$ furnace gases. The Ispra Mark 13A process produces two important compounds: H_2SO_4 and hydrogen, being based on the chemical equation (3):

$$SO_2 + Br_2 + H_2O \rightarrow H_2SO_4 + 2HBr, \ 2HBr \rightarrow H_2 + Br_2 \tag{8}$$

In the "peracide" desulphurisation procedure, SO_2 is oxidized to H_2SO_4 in a scrubber and we obtain the peroxodisulphuric acid. The electrochemical process is based on the following reactions:

anode $\qquad 2HSO_4^- \rightarrow 2H^+ + S_2O_8^{2-} + 2e^-; \ \varepsilon_0 = 2,057V$ $\qquad\qquad$ (9)

cathode $\qquad 2H^+ + 2e^- \rightarrow H_2$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (10)

In the scrubber we have the following oxidation reaction:

$$2H_2O + SO_2 + S_2O_8^{2-} \rightarrow 3HSO_4^- + H^+ \tag{11}$$

The liquid from the scrubber is composed of a diluted solution of $H_2SO_{4(aq)}$ (200 g/L) and the absorption phase can be realized in a column packed. There are obtained concentrations under 500 ppm SO_2. The process has been applied on industrial scale for the purification of waste gases that came from a factory producing H_2SO_4 [18, 21].

An experimental parameter study was conducted in a pilot-scale jet bubbling reactor for wet flue gas desulphurisation (FGD). The pilot plant is downscaled from a limestone-based, gypsum producing full-scale wet FGD plant. Important process parameters, such as slurry pH, inlet flue gas concentration of SO_2, reactor temperature, and slurry concentration of Cl^- have been varied. The degree of desulphurisation, residual limestone content of the gypsum, liquid phase concentrations, and solids content of the slurry were measured during the experimental series.

The SO_2 removal efficiency increased from 66.1% to 71.5% when the reactor slurry pH was changed from 3.5 to 5.5. Addition of Cl^- (in the form of $CaCl_2 \cdot 2H_2O$) to the slurry (25 gCl^-/L) increased the degree of desulphurisation to above 99%, due to the onset of extensive foaming,

which substantially increased the gas–liquid contact area. An increase in the inlet flue gas SO_2 concentration from 502 to 991 ppm led to a decrease in the SO_2 removal efficiency from 80.1% to 69.4%. A temperature increase from 296 to 323 K caused a reduction in the degree of desulphurisation from 69.4% to 68.1%, but this result is almost within the experimental uncertainty. The residual limestone level in the gypsum formed increased with increasing values of reactor slurry pH, inlet flue gas SO_2 concentration, and slurry concentration of Cl^- [22, 23].

4. CONCLUSIONS

Gaseous pollutants that affect human health destroy vegetation and damage materials and art treasures can be converted into harmless components by electrochemical reactions. The sulphur compound that exists in the atmosphere in big quantities can be removed by chemical and electrochemical methods. The chemical methods involve obtaining big quantities of waste products and are very expensive. [24] The electrochemical methods are used more often than the chemical methods because of the fact that are not polluting [25]. The rate of the processes can be rigorously controlled and they are not big energy consumers [19, 20].

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