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Numerical modeling of sulfur removal from waste gas from oil refining process

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ABSTRACT
Sulfur compounds present in atmosphere mainly comprise H_2S, SO_2 and SO_3 and sulfates. Sulfur enter in the atmosphere to a large extent, through human activities. It is estimated that about 65 million tons of sulfur per year enter in the atmosphere through anthropological activities, mainly by burning fuels. This paper presents effects of sulfur compounds on atmosphere and human activity. Also presents a numerical model of the effects of sulfur dioxide absorption on chemical solution. is received.
Keywords – sulfur, compounds, modeling, process, chemical.

I. INTRODUCTION

Refining plants are fully integrated industrial complexes that manage huge quantities of raw materials and materials while being large consumers of energy and water resources [1].

Both in the processes of oil refining and processing of gases and petroleum products and in the stage of storage and delivery of finished products, petrochemical installations generate emissions into the atmosphere, water and soil.

That is why the management of the environment and pollutants has become a major activity in the development of refineries.

The type and quantities of emissions to the environment from refineries are usually well-known and therefore well-known [2].

The main air pollutants generated by the petrochemical industry are oxides of carbon, nitrogen and sulfur, particles (generated mainly in combustion processes) and volatile organic compounds.

In refineries [3] water is used in production processes as well as for cooling.

The use of water can also lead to its contamination with petroleum compounds. The main pollutants in water are hydrocarbons, sulfides, ammonia and some metals.

Compared to the huge volumes of raw materials they process, refineries do not generate substantial amounts of waste. Currently, waste generated by refineries is predominantly in the form of tars, non-specific refinery waste (household,

demolition, etc.) and spent chemicals (eg acids, amines, catalysts) [4].

Atmospheric emissions are the main pollutants generated by oil refineries and, to a much lesser extent, by gas installations (respectively the number of emission points, tons of emissions, number of BAT produced) [6].

Thus for every million tons of crude oil processed (European refineries range from 0.5 to over 20 million tons), refineries emit between 20,000 and 820,000 tons of carbon dioxide, 60-700 tons of nitrogen oxides, 103,000 tons of particles, 30-6,000 t of sulfur oxides and 50-6,000 t of volatile organic compounds.

They generate between 0.1 and 5 million tons of wastewater and between 10 and 2000 tons of solid waste for every million tons of refined crude oil.

These very large differences between emissions from different European refineries can be partly explained by differences in integration and the type of refineries (eg simple or complex).

But the main differences are with different environmental regulations in Europe.

The main emissions to air from gas installations are CO_2, NO_x SO_2 and VOC.

Water and waste are usually less important than in the case of oil refineries.

Given the progress made by refineries in reducing atmospheric sulfur emissions, the focus has begun to shift to VOCs (including odors), particulates (size and composition) and NOx, as it is generally in environmental discussions.

When the debate on carbon dioxide grows, it will also severely affect refineries.

Refinery wastewater treatment techniques are mature techniques, with the focus now on prevention and reduction. Reducing water consumption and / or water pollutant concentrations can have an effect on reducing final pollutant emissions [1].

The present paper aims to present the technologies for the recovery of sulfur from flue gases as well as the numerical modeling of the effect of sulfur dioxide absorption on pH. The experiments tried to highlight which method is more useful in the recovery of sulfur dioxide as well as the evolution of pH depending on the amount of sulfur in the water.

II. HEALTH EFECTS OF SO_2 ON HUMAN AND PLANT

SO_2 from the atmosphere has an effect mainly on the respiratory tract, causing its irritation.

In December 1930, in the Meuse River Valley in Belgium, hot springs contained waste products from a large number of industrial sources, with SO_2 levels reaching 38 ppm and killing 60 people.

In October 1948, a similar accident caused the disease of more than 40% of the population of the city of Donora, Pennsylvania and 20 people died, with concentrations of 2 ppm $SO2$ in the air [5].

III. SO_2 REACTIONS IN THE ATMOSPHERE

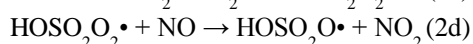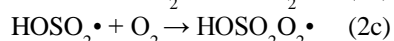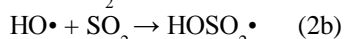SO_2 reactions in the atmosphere are influenced by temperature, humidity, light intensity and air transport.

Possible ways in which SO_2 can react in the atmosphere are [7]:

a) Photochemical reactions; in the presence of light the reaction takes place:
$$SO_2 + h\nu \rightarrow SO + O \quad (1)$$
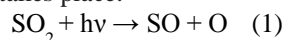
b) Photochemical and chemical reactions in the presence of nitrogen oxides and/or hydrocarbons (olefins).

The presence of hydrocarbons and nitrogen oxides contributes to the oxidation of $SO2$ in the atmosphere:
$$\text{R-H} + O_2 \rightarrow RO\bullet + HO\bullet \quad (2a)$$
$$HO\bullet + SO_2 \rightarrow HOSO_2\bullet \quad (2b)$$
$$HOSO_2\bullet + O_2 \rightarrow HOSO_2O_2\bullet \quad (2c)$$
$$HOSO_2O_2\bullet + NO \rightarrow HOSO_2O\bullet + NO_2 \quad (2d)$$

c) Chemical reactions in water droplets, in particular those containing metal salts and NH_3.

In the relatively dry atmosphere it is possible for SO_2 to be oxidized by reactions that take place in water droplets.

This process is much faster in the presence of NH_3, which reacts with SO_2 to produce bisulfite and sulfite ions in solution:
$$NH_3 + SO_2 + H_2O \rightarrow NH_4^+ + HSO_3^- \quad (3a)$$
$$NH_3 + HSO_3^- \rightarrow NH_4^+ + SO_3^{2-} \quad (3b)$$
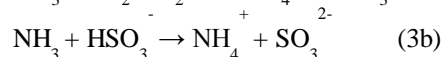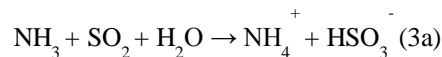
The process of total oxidation of $SO2$ in the aqueous phase is complicated and involves the transport, diffusion of the species in drops, hydrolysis and ionization, oxidation of SO_2 through the following global process:
$$[O] + S(IV) \rightarrow 2H^+ + SO_4^{2-} \quad 4)$$
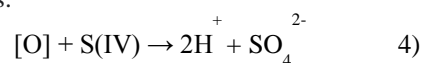
Where [O] is the oxidizing agent and S(IV) is aqueous SO_2 or SO_3^{2-}.

IV. CHEMICAL METHODS OF DESULPHURISATION

SO_2 is harmful to plants. Exposure to high concentrations of SO_2 destroys leaf tissue.

Leaf bleaching or yellowing occurs.

It has been shown that by exposing to a concentration of 0.15 ppm SO_2 for 72 hours, wheat and barley production is reduced to 42-44%.
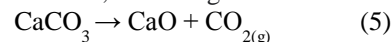
Long-term exposure to low SO_2 concentrations may be more harmful to the crop than short-term exposure to high SO_2 concentrations

A large number of processes are used to remove sulfur and sulfur oxides from fuels before combustion and from gas after combustion.
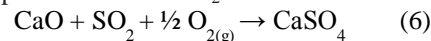
Most of these efforts focus on coal.

A first chemical method of desulfurization of blast furnace gases is by fluidized bed combustion of coal; the process consists of burning coal in a bed of finely divided limestone or dolomite [8].

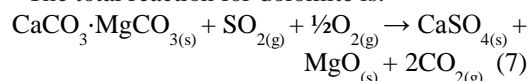The lime stone is calcined, according to the reaction:
$$CaCO_3 \rightarrow CaO + CO_{2(g)} \quad (5)$$
and the lime product absorbs SO_2:
$$CaO + SO_2 + \tfrac{1}{2} O_{2(g)} \rightarrow CaSO_4 \quad (6)$$

A dry system involves the introduction of lime or dolomite into a reactor, followed by the removal of unreacted lime and sulfates.

The total reaction for dolomite is:
$$CaCO_3 \cdot MgCO_{3(s)} + SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CaSO_{4(s)} + MgO_{(s)} + 2CO_{2(g)} \quad (7)$$

Another method is to desulfurize the waste gas which includes the absorption of SO_2 (g) in an aqueous solution of sulfide to form sulfite and sulfate ions, the additional absorption of SO_2 and the formation of bisulfite. Bisulfite can be reduced to sulfide and used in the first absorption phase.

Simultaneous removal of NO and SO_2 from the furnace gas takes place through an absorption process in which the apparatus used comprises an absorption column filled with an aqueous solution of chelates and sulfide salts.

Oxidized metal chelates in an inactive state are electrochemically reduced.

It is also possible to carry out the oxidative removal of SO_2 on activated carbon by transforming it into H_2SO_4 (aq) at 30 - 1000C by the succession of absorption, oxidation, hydration processes on polyacrylonitrile fibers.

SO_2 at 1000 ppm in the furnace gas was completely removed over a period of 60 h.

V. DETERMINING THE EVOLUTION OF WATER pH AS A FUNCTION OF DESORBER SO_2

pH is the logarithm with the changed sign of the ion concentration in the solution.

The notion of pH expresses quantitatively the acidity (or basicity) of a substance, based on the concentration of ions called hydronium H_3O^+.

For highly dilute solutions it is considered that the pH is no longer equal to the hydronium concentration, but to the molar concentration of the solution.

To define the pH, the logarithmic scale is used to represent the activity of the hydrogen ion in the solution.

The pH is equal to the negative logarithm of the H^+ ion concentration ($H^{+3}O$):

$$pH = -lg\ (a_{H+}) \qquad (8)$$

a_H^+ represents the activity of H^+ ions and is not similar to the ion concentration.

The activity represents the effective concentration of hydrogen ions, and is in fact the ability of other ions to block the participation of the H_+ ion in various chemical reactions.

In dilute solutions the activity is approximately equal to the value of the H^+ ion concentration (H_3O).

Taking these into account, the pH is expressed dimensionally [8]:

$$pH = -lg\ (H^+/1\ mol/L) = -lg\ H^+) \qquad (9)$$

$0 \leq pH \leq 7 \Rightarrow$ pH acid | acid solution
$pH = 7 \Rightarrow$ pH neutral | neutral solution
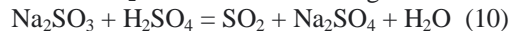$7 \leq pH \leq 14 \Rightarrow$ basic pH | basic solution

We experiment consisted in performing chemical analyzes to highlight:
a. How does the pH of an aqueous solution evolve on contact with SO_2,
b. How does the pH of a solution treated with SO_2 evolve in its distillation process,
c. How the pH of a $CuSO_4$ solution evolves in the NaOH treatment process.

The first experiment aimed to monitor the pH variation depending on the water absorption of the amount of SO_2.

To have SO_2 we used the following reaction:
$$Na_2SO_3 + H_2SO_4 = SO_2 + Na_2SO_4 + H_2O \quad (10)$$
SO_2 was distilled in an acid medium by air entrainment (Figure 1).

I collected it in a solution of hydrogen peroxide, being then transformed into sulfuric acid, which he measured by acidimetry.
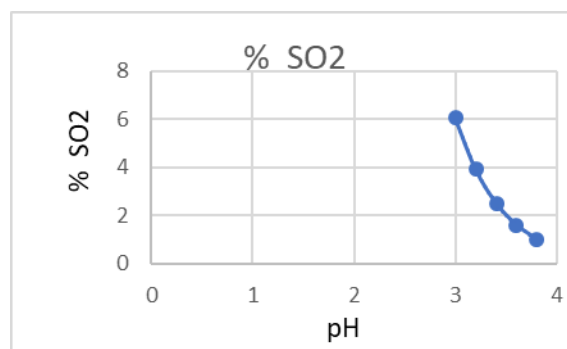

Fig.1. Evolution of % SO_2 function by pH

In this case equation to description evolution of % SO_2 (y) function by pH (x) is:
$y = -4.4792x^3 + 52.134x^2 - 204.77x + 272.1$ (11)
and $R^2 = 1$.

Distillation of solution Sulfur whit Water

Sulfur water was distilled by the method of distilling petroleum products, following the pH of the solution obtained.
The purpose of this experiment is to concentrate the final sulfur solution (Figure 2).
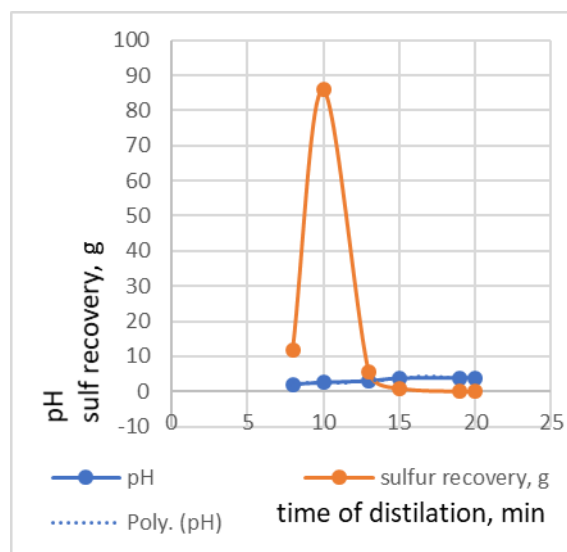

Fig.2. pH and sulfur recovery in distillation of solution, water-sulfur

Equation to description process of distillation of pH evolution function by time to distillation is:

$$Y = 0.0003x^5 - 0.0234x^4 + 0.643x^3 - 8.578x^2 + 55.657x - 138.58 \quad (12)$$

Absorption on activated carbon of sulfur

I distilled the sulfur water by the method of distilling the petroleum products, after which I passed it through an activated carbon filter, following the pH of the obtained solution.
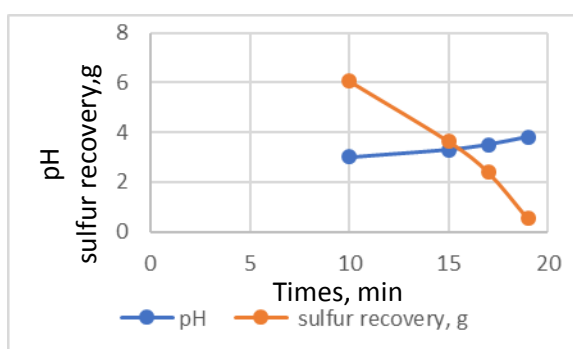The purpose of this experiment is to concentrate the final sulfur solution (Figure 3).

Fig.3. pH and sulfur recovery in distillation of solution, water-sulfur by carbon activated bed

Determination of the pH evolution for the sulfur recovery process with NaOH

Process equation is:
-pH variation function to time measurement is:

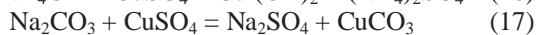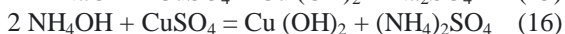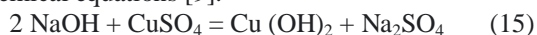$$y = -0.0065x^3 + 0.2517x^2 - 3.7102x + 24.448 \quad (13)$$

-sulfur recovery function to time measurement is:

$$y = -0.0065x^3 + 0.2517x^2 - 3.7102x + 24.448 \quad (14)$$

Proceed wet

To observe the evolution of pH in the case of a sulfur treatment process with NaOH we treated $CuSO_4$ (which can be obtained in the sulfur recovery process) and then we treated it with NaOH (Figure 4).
Chemical equations [9]:

$$2\ NaOH + CuSO_4 = Cu\ (OH)_2 + Na_2SO_4 \quad (15)$$
$$2\ NH_4OH + CuSO_4 = Cu\ (OH)_2 + (NH_4)_2SO_4 \quad (16)$$
$$Na_2CO_3 + CuSO_4 = Na_2SO_4 + CuCO_3 \quad (17)$$

The equation of pH depends on the amount of NaOH added is:

$$y = -0.0003x^4 + 0.0068x^3 - 0.0547x^2 + 0.2342x + 3.8 \quad (18)$$

In every cases to simulation and mathematical modeling, equation to description process is normally correctly because R^2 (R squared is coefficient of determination) is equal to 1.

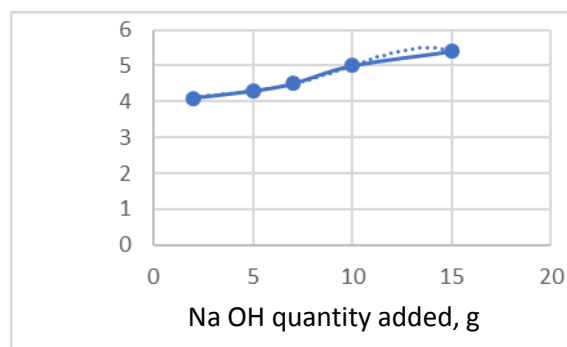This equation (11,12,13,14) describe sulfur recovery by chemical process.

Fig.4. pH in distillation of solution, water-sulfur by NaOH solution

VI. CONCLUSION

The present paper is intended to be a complex study of research in the field of sulfur recovery from flue gases.

Starting from the need to limit the air emissions of certain pollutants, including sulfur dioxide (SO2), from the petrochemical industry, we managed to identify the amount of pollutant (sulfur dioxide) emitted in industrial processes in refineries.

We also studied the methods of reducing flue gas emissions.

At the same time we presented the results of the experiments performed in the laboratory of Ovidius University, as well as a numerical model resulting from performing these experiments, namely comprising the effect of sulfur dioxide absorption on pH.

The experiments tried to highlight which method is more useful in the recovery of sulfur dioxide as well as the evolution of pH depending on the amount of sulfur in the water.

The paper is very well documented, containing a significant number of studies and books read and included in the bibliography.

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