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## New process for simultaneous removal of CO<sub>2</sub>, SO<sub>X</sub> and NO<sub>X</sub>

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### Abstract

A method for simultaneous removal of CO<sub>2</sub>, SO<sub>X</sub> and NO<sub>X</sub> from industrial flue gases through the injection of ozone diluted in nitrogen, oxygen or nitrogen/oxygen mixtures, as an oxidizing agent and with the addition of specific sequestrants, that induce the precipitation of nitrates and sulphates, is presented. This new process is related with the conventional CO<sub>2</sub> removal method using chemical absorption, but presents as main innovation the possibility to remove also simultaneously SO<sub>X</sub> and NO<sub>X</sub>.

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*Keywords:* simultaneous removal; CO<sub>2</sub>; chemical absorption; specific sequestrants; ozone.

### 1. Introduction

Air pollution is a major problem in urban areas, due to the high concentration of polluting sources. The term "air pollutant" is used to describe all substances that may be harmful to humans, animals, vegetation and materials. There are many routes for air pollutants to enter the human body. This contact can occur not only by inhalation and dermal contact, but also by the ingestion of contaminated food due to their contact with polluted water and soil. The interaction of humans with air pollutants gives rise to critical and chronic health problems [1].

Environmental problems, resulting from emissions of pollutants from the combustion of solid, liquid and gas in various stationary and mobile energy systems, as well as, emissions from industrial plants, have become a global problem. This involves not only pollutants such as SO<sub>X</sub> (mainly SO<sub>2</sub>), NO<sub>X</sub> (almost NO, but also NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>)

and particulate matter, but also greenhouse gases (GHG) such as carbon dioxide (CO<sub>2</sub>) [1-2]. It has long been known that, in addition to being dangerous to human health, sulfur dioxide (SO<sub>2</sub>) emissions contribute to the acidification of soil and waterways, and to the formation of acid rain [3]. Nitrogen oxides (NO<sub>X</sub>) are regarded as major pollutants of the atmosphere, as they are responsible for environmental problems such as photochemical smog, visibility degradation, acid rain, particle formation in the atmosphere, and also the global warming caused by N<sub>2</sub>O. They are also responsible, particularly NO<sub>2</sub>, for respiratory infections in adults and, in the case of children, the long exposure to this pollutant may cause chronic lung injury [2]. The Kyoto Protocol, signed by 175 countries, resulted in one of the most important forums held in 1997, in which the participants agreed to reduce greenhouse gas emissions to levels 5.2% lower than in 1990 during the period 2008-2012 [4].

In August 2010, the Environmental Protection Agency of the United States (EPA) has proposed a new standard for transport, CATR (Clean Air Transport Rule), which stated that SO<sub>2</sub> emissions should be

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reduced by 71% beyond the levels recorded in 2005 by 2014, and  $\text{NO}_x$  emissions should be reduced by 52% during the same time period [5]. Similar action was taken in the European Union for  $\text{NO}_x$  and  $\text{SO}_2$  emissions from coal-fired power plants, but in this case, the emissions were subject to more stringent emission limits [5].

In order to reduce emissions of major air pollutants ( $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$ ) from industrial plants, the ideal solution is to perform a simultaneous absorption of these gases, as there are several processes for the absorption of each of the mentioned pollutant gases, but considered separately.

The main difference, between this process and other previously developed, is the possibility of simultaneous removal of  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{SO}_x$ , whereas the aqueous amine solution can be regenerated and sequestering agents, upon contact with the gaseous pollutants, can be processed into products having commercial value.

At first sight, this simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$  using specific sequestering agents does not seem possible due to fact that the majority of the sequestering agents would lose their activity upon the precipitation of the respective carbonate. Surprisingly, the formation of the carbonate is delayed by the formation of a soluble intermediary and the kinetic control allows the precipitation of the nitrate and the sulfate before the carbonate formation.

The  $\text{CO}_2$  is mainly involved in the formation of a complex with the amine, and this complex is very stable at normal absorption temperature, ranging between 30 °C and 50 °C. Under these conditions, the effective concentration of free  $\text{CO}_2$  inside the absorber is very low.

## 2. Process overview

The present work describes a process for simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$  from industrial flue gases [6]. The process is related with the conventional  $\text{CO}_2$  removal process, using chemical absorption, making also possible the simultaneous removal of  $\text{SO}_x$  and  $\text{NO}_x$  through the injection of ozone as oxidizing agent and introducing specific sequestrants. The conventional  $\text{CO}_2$  removal process comprises the following steps:

- a) Contact of the flue gas and the oxidizing agent (ozone), with the solvent used in the absorption of carbon dioxide, and with the sequestrants used in the removal of the sulfur

and nitrogen oxides, counter currently, inside an absorber;

- b) Regeneration of the solution, which retained the carbon dioxide, by heating inside a regeneration column. A regenerated solution and a stream containing mostly carbon dioxide is obtained.

According to the developed work, the regenerated solution obtained in step b) is reused in step a) as a solution for the absorption of carbon dioxide.

Figure 1 presents the scheme of the conventional  $\text{CO}_2$  removal process (black line) in comparison with the developed process (red and black process).

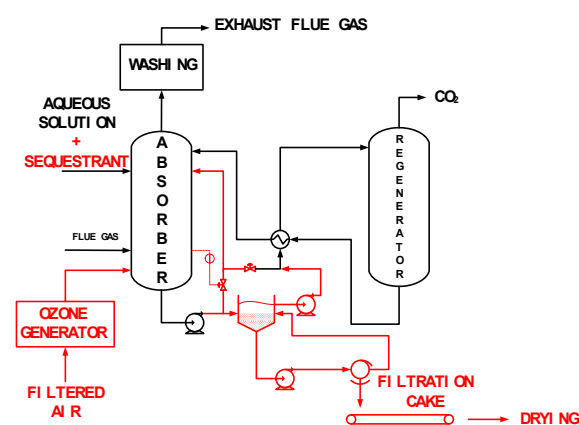


Fig. 1. Scheme proposed for the new process [6].

Compared to the conventional process for chemical absorption of  $\text{CO}_2$ , this process also introduces some new steps, as follows:

- a<sub>1</sub>) Injection of ozone as oxidizing agent and the introduction of specific sequestrants, used in the removal of sulfur and nitrogen oxides, in countercurrent, inside the absorption column;
- a<sub>2</sub>) Filtration of the precipitated salts resulting from the contact between the sequestrants and the sulfur and nitrogen oxides, after thickening in a clarifier. This step must take place after step a) of the conventional  $\text{CO}_2$  chemical absorption process;
- a<sub>3</sub>) Drying of the filtration cake obtained in a<sub>2</sub>), which should take place before stage b) of the conventional  $\text{CO}_2$  chemical absorption process.

According to this new process, the clear phase of step a<sub>2</sub>) can be conducted to step b). It is important to note that, the agitation caused by gas bubbles, instead of causing dispersion of the slurry, causes a good separation and thickening of the slurry, so it will facilitate the respective separation by filtration.

The solvent used may include, for example, amines, alkanolamines or urea. The sequestering agents may be formed by alkaline compounds, selected from alkali metal salts, alkaline earth metal salts, urea or ammonia.

Apparently, this simultaneous removal seemed not to be possible, as the presence of CO<sub>2</sub> could lead to high consumption of metal hydroxide, at a significant loss, as it is likely to form the respective carbonate, which precipitates and is subsequently removed in the filter. However, carbonate formation is retarded (having a slower kinetics) by formation of a soluble intermediate and, thus, the kinetic control allows the preferential formation and precipitation of the nitrate, and sulfite occurs before the formation and precipitation of the carbonate. (Santos et al., 2015)

Thus, much of the metal hydroxide is effective in removing NO<sub>x</sub> and SO<sub>x</sub>, not being destroyed by CO<sub>2</sub>, as would be expected. In fact, much of the CO<sub>2</sub> is immediately involved in the complex with the amine due to nucleophilic attack of the amino group to the carbonyl group, and so the free CO<sub>2</sub> effective concentration is usually very low, inside the absorber, which, moreover, is important for ensuring effective step absorption.

### 3. Process description

Other characteristics and advantages of the new process will be clarified in the following description. Figure 2 shows, schematically, the method proposed in this paper. Figure 3 presents, schematically, and alternative to the new process, where the nitrogen and sulfur oxides removal stage is performed downstream of the conventional CO<sub>2</sub> capture process. Figure 4 presents, schematically, another alternative to the new process, where nitrogen and sulfur oxides removal stage is performed upstream of the conventional CO<sub>2</sub> capture process. Comparing the new developed process with the presented alternatives it is possible to conclude that the presented process is more viable economically, as it has the advantage of managing the integration of the NO<sub>x</sub> and SO<sub>x</sub> removal, apart from the conventional CO<sub>2</sub> capture process, without the need of adding any other removal unit. This results in a reduction of the investment and operating costs.

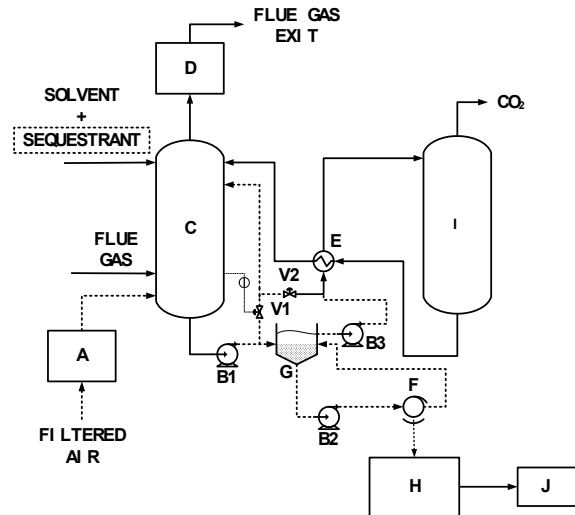


Fig. 2. Global proposal scheme for the new process [6].

The absorber (C) can be a conventional absorption column, as a plate column or a packed bed column.

Inside the absorber (C), the solvent retains and absorbs the carbon dioxide present in the flue gas. NO and SO<sub>2</sub>, present in the flue gas are oxidized to NO<sub>2</sub> and SO<sub>3</sub>, respectively, through the injection of the oxidizing agent. This oxidation allows better contact with the sequestering agents and results in an easier precipitation of nitrates and sulfates. The cleaned flue gas exits at the top of the absorber, passing through a gas washer (D) and then released to the atmosphere.

The solvent that retains the carbon dioxide, as well as the nitrates and sulfates from the reaction of NO<sub>x</sub> and SO<sub>x</sub> with the sequestering agent, exits at the bottom of the absorber (C), feeding the pump (B1).

Afterwards, the mixture can be fed to the decanter (G), allowing the thickening of the solid phase, or, in case of a small or negligible amount of solids, this mixture can be recycled back to the absorber (C), or, be fed to the heat exchanger (E).

Inside the decanter (G), the separation of the two phases, through settling and thickening of the solid phase takes place. Then, the mixture goes to pump (B2), which conducts the mixture to a rotary vacuum drum filter (F), where the filtration of the solid phase takes place. In the rotary vacuum drum filter (F), the separation of the two phases, allows to obtain a filtration cake, which was sent by a conveyor (H) to a dryer (J), in order to proceed to its drying process. The liquid phase returns to the decanter (G). The supernatant phase is taken out by the pump (B3).

As mentioned before, if the amount of solids is too low, through the opening of the valve (V1), it is possible to recycle the mixture back to the absorber

(C), or, in case of an inexistent solid phase, to flow through the heat exchanger (E), by opening the valve (V2). This line goes together with the current coming from decanter (G), entering the heat exchanger (E).

The heat exchanger (E) allows the heat transfer between the current entering the regenerator (I), and the current that exits the bottom of the regenerator (I) with a higher temperature. This equipment allows the energy integration of the process, because it warms the current that enters the regenerator (I), entering with a higher temperature, decreasing the needed amount of heat to be supplied in order to proceed with the regeneration of the solution, and cools down the exit current, allowing the regenerated solvent to enter the absorber (C) at a temperature closer to the desired temperature for the carbon dioxide absorption, resulting in a more efficient process.

Inside the regenerator (I) the regeneration of the solvent, containing carbon dioxide, takes place. This regeneration is achieved by heating the solvent, and a reaction that is the opposite of the absorption reaction occurs, releasing the absorbed carbon dioxide, and thus regenerating the solvent. The solvent is heated in the bottom of the regenerator (I), where the reboiler is placed. The regeneration temperature will depend on the organic compound in the solvent.

The regenerator (I) can be a column such as, for example, a plate column, thus allowing a better contact between the liquid phase and gaseous phase, resulting in the increase of the solvent regeneration efficiency.

Then, the regenerated solvent flows through the heat exchanger (E), in order to cool down by changing heat with the current that is entering the regenerator (I), and it is recycled to the absorber. From the top of the regenerator (I), a gaseous current that contains predominantly carbon dioxide, exits and goes for ulterior treatment.

Figure 3 shows, schematically, an alternative to the main process for simultaneous removal, where the removal of the nitrogen and sulfur oxides is performed downstream of the conventional process for carbon dioxide capture. Flue gas enters the absorber (C), and the flue gas can be produced, for example, from the combustion of hydrocarbons in a boiler or by combustion in a gas turbine. This flue gas contains around 50 to 80% of nitrogen, 5 to 20% of carbon dioxide, 2 to 10% of oxygen and the remaining percentage corresponds to  $\text{SO}_x$ ,  $\text{NO}_x$  and particles. The flue gas will circulate with a pressure between 0.1 MPa abs. and 10 MPa abs. and with a temperature of around 40 °C to 400 °C.

Inside the absorber (C), the flue gas contacts with the solvent, flowing in counter-current. Selection of solvent depends on its carbon dioxide loading capacity, comprising an aqueous solution containing one or more organic compounds capable of absorbing carbon dioxide. The carbon dioxide removal in Figure 3 is performed in the conventional  $\text{CO}_2$  capture and separation process.

The absorber (C) can be a conventional absorption column, as a plate column or a packed bed column.

$\text{CO}_2$  free flue gas exits the absorber (C) at the top, entering the scrubber (S), where, by contacting with the sequestering agents flowing in counter-current along with the oxidizing agent, the removal of nitrogen and sulfur oxides takes place.  $\text{NO}$  and  $\text{SO}_2$ , present in the flue gas are oxidized to  $\text{NO}_2$  and  $\text{SO}_3$ , respectively, through the injection of the oxidizing agent. This oxidation allows easier contact with the sequestering agents and results in an easier precipitation of nitrates and sulfates.

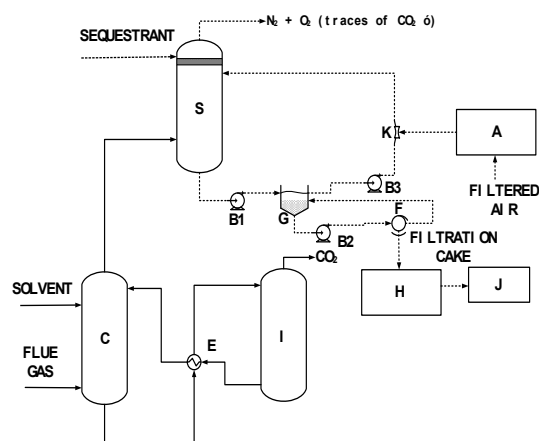


Fig. 3. Alternative scheme for the new process considering  $\text{NO}_x + \text{SO}_x$  removal stage downstream the conventional  $\text{CO}_2$  removal process [6]. Dashed line indicates the process modifications that allow simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$ .

The organic compounds referred above can be, for example, amines (primary, secondary, tertiary, cyclic or linear, aromatic or aliphatic), alkanolamines (primary, secondary, tertiary) or urea. The sequestrants are, generally, saturated aqueous solutions with alkaline compounds. These compounds can be, for example, alkali metals salts, alkaline earth metals salts, urea or ammonia. Figure 3 shows the overall process: the full line indicating conventional process and the dashed line, indicating the process that allows the simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$ .

Nitrates and sulfates, from the reaction of  $\text{NO}_x$  and  $\text{SO}_x$  with the sequestering agent, exits at the bottom of the absorber (S), feeding the pump (B1). Afterwards, the mixture can be fed to the decanter (G), allowing the thickening of the solid phase.

Inside the decanter (G), the separation of the two phases, through settling and thickening of the solid phase, takes place. Then, the mixture goes to pump (B2), which conducts the mixture to a rotary vacuum drum filter (F), where the filtration of the solid phase takes place. In the rotary vacuum drum filter (F), the separation of the two phases, allowed to obtain a filtration cake, that was sent, by a conveyor (H), to a dryer (J), in order to proceed to its drying process. The liquid phase returns to the decanter (G). The supernatant phase is taken out by the pump (B3) and recycled back to the scrubber (S).

The oxidizing agent injected in the scrubber (S) is produced from filtered air that goes through the ozone generator (A). The produced ozone flows inside the scrubber (S), through a Venturi tube (K).

Figure 4 shows, schematically, an alternative to the main process for simultaneous removal, where the removal of the nitrogen and sulfur oxides is performed upstream of the conventional process for carbon dioxide capture. Flue gas enters the scrubber (S) and can be result, for example, from the combustion of hydrocarbons in a boiler or by combustion in a gas turbine. This flue gas contains around 50 to 80% of nitrogen, 5 to 20% of carbon dioxide, 2 to 10% of oxygen and the remaining percentage corresponds to  $\text{SO}_x$ ,  $\text{NO}_x$  and particles. The flue gas will circulate with a pressure between 0.1 MPa abs. and 10 MPa abs. and with a temperature of around 40 °C to 400 °C.

Flue gas enters the scrubber (S), where, by contacting with the sequestering agents that flow in counter-current, along with the oxidizing agent, the nitrogen and sulfur oxides removal takes place.  $\text{NO}$  and  $\text{SO}_2$ , present in the flue gas, are oxidized to  $\text{NO}_2$  and  $\text{SO}_3$ , respectively, through the injection of the oxidizing agent.

This oxidation allows the contact with the sequestering agents, and results in an easier precipitation of nitrates and sulfates. Figure 4 shows the whole process: the full line, conventional process and the dashed line, the process that allows the simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$ .

The sequestrants are, generally, saturated aqueous solutions of alkaline compounds. These compounds can be, for example, alkali metals salts, alkaline earth metals salts, urea or ammonia.

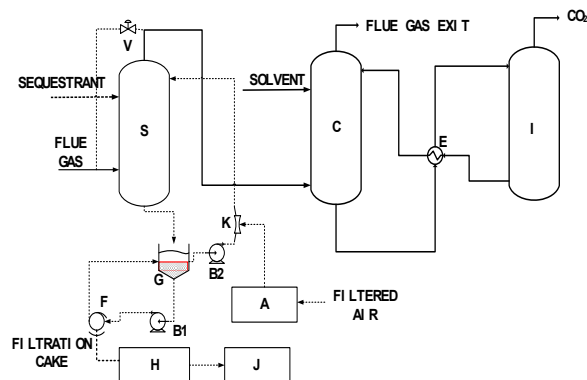


Fig. 4. Alternative scheme for the new process [6] considering  $\text{NO}_x+\text{SO}_x$  removal stage upstream the conventional  $\text{CO}_2$  removal process [6]. Dashed line indicates the process modifications that allow simultaneous removal of  $\text{CO}_2$ ,  $\text{SO}_x$  and  $\text{NO}_x$ .

The nitrates and sulfates from the reaction of  $\text{NO}_x$  and  $\text{SO}_x$  with the sequestering agent, exits at the bottom of the absorber (S), feeding the decanter (G), thus allowing the thickening of the solid phase.

Inside the decanter (G), the separation of the two phases, through settling and thickening of the solid phase takes place. Then, the mixture goes to pump (B1), which conducts the mixture to a rotary vacuum drum filter (F), where the filtration of the solid phase takes place. In the rotary vacuum drum filter (F), the separation of the two phases, allowed to obtain a filtration cake, that was sent, by a conveyor (H), to a dryer (J), in order to proceed to its drying process. The liquid phase returns to the decanter (G). The supernatant phase is taken out by the pump (B2) and recycled back to the scrubber (S).

The oxidizing agent injected in the scrubber (S) is produced from filtered air that goes through the ozone generator (A). The produced ozone flows inside the scrubber (S), through a Venturi tube (K).

Cleaned flue gas exits the scrubber (D) at the top, entering the absorber (C), where the flue gas contacts with the solvent that flow in counter-current. Selection of solvent depends on its carbon dioxide loading capacity, comprising an aqueous solution containing one or more organic compounds capable of absorbing carbon dioxide. The carbon dioxide removal shown in Figure 4 takes place as in the conventional  $\text{CO}_2$  capture and separation process.

The organic compounds referred above can be, for example, amines (primary, secondary, tertiary, cyclic or linear, aromatic or aliphatic), alkanolamines (primary, secondary, tertiary) or urea.



#### 4. Tests for proof of concept

The following test was performed in order to prove this concept on a pilot-unit. The prepared solvent consists on an aqueous solution containing 30 percent, in weight, of MEA (monoethanolamine). The used sequestrant was an aqueous “slurry” containing 10 percent, in weight, of sodium hydroxide. The flue gas to be treated circulated at a flow of 1.2 Nm<sup>3</sup>/h and having the following composition: 14.75% CO<sub>2</sub>, 76.23% N<sub>2</sub>, 5.81% O<sub>2</sub>, 480 ppm SO<sub>x</sub>, 50 ppm CO and 420 ppm NO<sub>x</sub> (as NO<sub>2</sub>). In order to remove CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub>, ozone (as oxidizing agent) was diluted in oxygen and introduced, at a mass percentage of 5%, along with the solvent, inside the absorber (C), at a flow of 0.04 m<sup>3</sup>/h. The filtration of the solids formed inside the absorber (C), originated from the reaction of the sequestrant with NO<sub>x</sub> and SO<sub>x</sub>, takes place on a rotary vacuum drum filter (F), with a vacuum pressure of 0.04 MPa. Regeneration of the solvent, coming from the bottom of the absorber (C), takes place in the regenerator (I) by distillation. The temperatures inside the regenerator (I), at the top and at the bottom, are 120 °C and 40 °C, respectively. The amount of obtained solids ranges from 0.4 kg to 0.6 kg.

#### 5. Conclusions

Companies using CO<sub>2</sub> and/or acid gases absorption equipment actively look for NO<sub>x</sub> and SO<sub>x</sub> removal systems. Unlike current DeNO<sub>x</sub> systems that are very expensive in terms of investment and operative costs, this new process presents a more moderate investment cost, as well as lower operating costs, thus resulting in very significant savings.

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