Desulphurization of combustion flue-gases by Wet Oxidation Scrubbing (WOS)

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Abstract
In this work, we report the experimental findings of an innovative flue-gas desulphurization process based on the wet oxidation scrubbing (WOS), using sodium chlorite (NaClO₂) which offers strong oxidizing power even in acid conditions, generally unfavorable for the absorption of acid gases. For this reason, it was tested in order to obtain the solubility data of SO₂ and compare them with those in a pure seawater. Experimental results showed that the solubility of SO₂ in sodium chlorite seawater-based solution (0.2% w/w) increased about 20-30% compared to pure seawater.

Introduction
Flue-gas desulphurization (FGD) units are commonly used for the capture of SO₂ deriving from both land combustion stations and marine diesel engine exhausts. Current regulations on SO₂ emissions for land stations and marine transport (IMO Marpol) are increasingly stringent and force for a prompt development of efficient processes to increase the desulphurization performances and, at the same time, allowing a size plant reduction, especially for naval field where the space is very limited [1,2]. Wet-FGD scrubbers have been generally preferred to dry or semi-dry processes due to the better removal performance and for minor scale and clogging problems of the equipment [2,3]. Conventional wet processes can be enhanced with the use of basic additives in aqueous solution such as ammonia (NH₃), caustic soda (NaOH), or other alkaline compounds, such as a seawater [2,4]. Another interesting alternative could be the use of oxidizing chemicals in aqueous solution that allow more effective SO₂ absorption thanks to oxidative mechanisms that lead to the formation of sulphates. This technology is able to offer a considerable saving in terms of capital and operating costs, also associated to a plant size reduction because requires less water consumption. However, a high consumption of the oxidizing reagent could be required; hence, an optimization of its dosage is mandatory.

The current literature on wet oxidation scrubbing identifies the following substances as chemicals with oxidizing properties: NaClO₂ [5], H₂O₂ [6], Na₂S₂O₈ [7] and Fe²⁺-EDTA [8]. Sodium chlorite (NaClO₂) is one of the most promising additives thanks to its oxidizing nature both in alkaline and acidic conditions. Under acid conditions, NaClO₂ has a greater oxidative potential due to the
formation of further oxidants, such as ClO$_2$(aq) and Cl$_2$(aq). The correct assessment of the thermodynamic behavior of oxidative solution towards SO$_2$ is a mandatory step for the optimization of a wet oxidation scrubber for FGD process. This work aims to test the oxidative performance of sodium chlorite in seawater-based solutions by measuring the solubility of SO$_2$ and finally compare it with the solubility data in a pure seawater [4]. The experiments were performed in a feedbatch bubble column fed with a simulated flue-gas containing SO$_2$ from 100 to 2000 ppmv, using a pure seawater and sodium chlorite (0.1% and 0.2% by weight) seawater-based as absorbing solutions.

**Theory on oxidative absorption of SO$_2$ in chlorite aqueous solutions**

SO$_2$ gas can be absorbed by aqueous NaClO$_2$ solutions and oxidized to generate different ions such as SO$_3$$^{2-}$, HSO$_3^-$, SO$_4^{2-}$. On contrary, ClO$_2^-$ is mainly reduced to ClO$^-$ and Cl. A drawback of sodium chlorite is that it has good oxidizing ability at low pH, even if acidic conditions are generally unfavorable for acid gases absorption, such as SO$_2$ [5,9]. Nevertheless, the chlorite solutions allow its capture by oxidation acidic mechanisms [5,9]. In fact, the low pH values have a strong impact on the formation of the other strong oxidizers, i.e. ClO$_3$(g) and Cl$_2$(g).

Park et al. [9] suggest that the reaction pathways can be divided into two different reactive schemes, depending on whether the reaction occurs under acidic conditions or not. The alkaline oxidation mechanism of SO$_2$(g) in NaClO$_2$ aqueous solution include the liquid-gas phase equilibrium [4], SO$_2$ hydrolysis reactions in water [4] and oxidation reactions with chlorite [9]:

$$SO_2(g) \rightleftharpoons SO_2(aq)$$  \hspace{1cm} (1)

$$SO_2(aq) + 2H_2O \rightleftharpoons HSO_3^- + H_3O^+$$  \hspace{1cm} (2)

$$HSO_3^- + H_2O \rightleftharpoons SO_3^{2-} + H_3O^+$$  \hspace{1cm} (3)

$$2HSO_3^- + ClO_2^- + 2H_2O \rightarrow 2SO_4^{2-} + Cl^- + 2H_3O^+$$  \hspace{1cm} (4)

$$2SO_3^{2-} + ClO_2^- \rightarrow 2SO_4^{2-} + Cl^-$$  \hspace{1cm} (5)

The overall reaction with NaClO$_2$ aqueous solutions could be obtained from the previous equations (Eqs. (1-5)) as also proposed by Krzyzynska and Hutson [10].

$$SO_2(aq) + ClO_2^- + 2H_2O \rightarrow 2H_2SO_4(aq) + Cl^-$$  \hspace{1cm} (6)

Chien et al. [11] showed with experimental measurements that all the sulphur present as SO$_2$ into the flue-gas is completely converted to its maximum oxidation state (i.e. as sulfates), in fact: the standard Gibbs free energy is negative at room temperature and atmospheric pressure ($\Delta G^\circ = -853$ kJ/mol) for Eq. (6), as calculated according to Hess’s law using data provided by Perry and Green [12].

The absorption of SO$_2$ with NaClO$_2$ rapidly lowers the solution pH, activating an acidic oxidation mechanism thanks to ClO$_2$ ($\Delta G^\circ = -211$ kJ/mol) and Cl$_2$ ($\Delta G^\circ = -98$ kJ/mol) formation [9,13].
The color of solution changes from yellowish (moderately acid pH) rapidly becoming greenish (strongly acid pH) associated a pungent odor due to chlorine-based gas [9,11]. The overall reactions for SO₂ oxidation under acidic conditions are shown below [5,9]:

\[
5\text{SO}_2(aq) + 2\text{ClO}_2(aq) + 6\text{H}_2\text{O} \rightarrow 5\text{H}_2\text{SO}_4(aq) + 2\text{HCl}
\]

(9)

\[
\text{SO}_2(aq) + \text{Cl}_2(aq) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4(aq) + 2\text{HCl}
\]

(10)

The standard Gibbs free energies of the reactions with chlorine dioxide and chlorine are -1255 kJ/mol and -223 kJ/mol, respectively.

Kaczur [13] retrieved the standard redox potentials of ClO₂⁻/Cl⁻ (1.59 V), ClO₂/Cl⁻ (1.51 V), Cl₂/Cl⁻ (1.35 V), confirming that ClO₂ and ClO₂⁻ have similar values, greater than Cl₂. Park et al. [9] observed that oxidation reaction by chlorine was not predominant since its formation from chlorite decomposition can be considered as negligible with respect to chlorine dioxide generation. Hence, it is possible to consider both the oxidation pathways showed in Eq. (6) and Eqs. (9,10) as active reaction mechanisms under acidic conditions.

Moreover, chlorine-based compounds can be present also in gaseous stream, determining an additive oxidative mechanism due to ClO₂ and Cl₂ desorption [10]. Therefore, the reactive mechanism in Eqs. (9,10) taken into account in aqueous solution must be considered also for the gas phase.

Materials and Methods

The simulated flue-gas was prepared by mixing SO₂ (5000 ppm. in N₂) with N₂ (99.99%) both available in pressurized cylinders supplied by Rivoira Gas (Italy). The absorbing solutions were a seawater (pH 8.2) and two solutions based on seawater with sodium chlorite (NaClO₂) at 0.1% w/w (pH 8.33) and 0.2% w/w (pH 8.55). Sodium chlorite was purchased from VWR International Chemicals with technical grade (80% w/w).

The seawater was characterized by ionic chromatography (Metrohm AG, 883 Basic IC PLUS) and its chemical properties are reported in Flagliello et al. [4]. The pH of the aqueous solutions was measured with a digital pH-meter (PCE-228 model).

Absorption experiments aimed to assess SO₂ solubility data and were performed at 25°C and 1 atm in a feed-batch bubble column consisting in a Pyrex glass vessel (inner diameter: 30 mm; total length: 300 mm) provided with an external jacket (42mm i.d.) with recirculating water for a fine-tuning of the system temperature. The bubble column was equipped with a gas distributor using a porous septum P-2 (40 - 100 micron) for small bubbles formation in order to increase the gas-liquid contact surface.

Gas flow rate was measured and controlled with two flowmeters (ASA, E5-2600/A/H model) and gas temperature was kept constant by an Omron PID
controller. Temperature in the bubble column and at the inlet and the outlet gas lines were measured by a digital thermometer with three reading channels (PCE Instruments, T-390 model). Pressure was controlled by two manometers installed on the inlet and outlet gas lines of the bubble column (WIKA, 232.50 model).

The flowsheet of the experimental device is similar to set-up used in Flagiello et al. [4], and is showed in Figure 1:

Figure 1. Experimental set-up for SO₂ absorption tests.

For each test, 17 g of absorbing solution (M₅) was charged into the bubble column and a constant volumetric flow (Gₘₐₜ = 60 L/h) of simulated flue-gas (C°₅ = 100-2000 ppm, corresponding to a mole fraction of SO₂ y°₅ = 0.0001-0.002 mol/mol, balance N₂) was fed, until saturation (t*, [s]). Time course of SO₂ concentration in the gas flowing out from the column, C₅ (or y₅), was followed with an IR gas analyzer (ABB O2020®) obtaining the so-called breakthrough curves.

The mass balance on SO₂ over the feed-batch column allows calculating the mole fraction of total SO₂ dissolved (x₅*) in the absorbing solution at equilibrium with the initial gas concentration of SO₂ (C°₅), as detailed in Flagiello et al. [4]:

\[ x₅^* = \frac{Gₘₐₜ M₅}{M₅} \int_{t=0}^{t=t^*} (y°₅ - y₅) dt \]  

where Gₘₐₜ [mol/s] is the molar flow rate of flue-gas and MWs [g/mol] is the molecular weight of the absorbing solution.

Results and Discussion

Figure 2 reported the solubility data (A) and pH values of saturated absorbing solutions (B) obtained during the SO₂ absorption in the bubble column, using a pure seawater and sodium chlorite seawater-based solutions at 0.1% and 0.2% w/w.
Experimental results in Figure 2 (A) showed an almost linear trend with increasing SO\textsubscript{2} concentration similar to Henry’s law for a purely physical absorption, except for low concentrations where the behavior of the solubility curves is typical of chemical absorption patterns. When the sodium chlorite content in the solution is increased, a considerable enhance in SO\textsubscript{2} solubility was observed especially for the seawater-based solution was doped with 0.2% w/w of NaClO\textsubscript{2}. The solubility values for pure seawater and for the solution doped with 0.1% of NaClO\textsubscript{2} were very similar, probably because the low chlorite content did not allow a strong activation of the acidic oxidative mechanisms which leads to additional oxidizers formation such as chlorine (Cl\textsubscript{2}) and chlorine dioxide (ClO\textsubscript{2}). The establishment of acidic conditions were experimentally observed during the tests; in fact, the two chlorite solutions rapidly became greenish and then returned yellow light until transparent when the system reached saturation. The staining sequence was slower in 0.2% w/w doped solutions and this confirmed that a prolonged activation of the oxidative mechanisms in acidic conditions improved absorption performance. The pH of the saturated solutions (Figure 2 (B)) deriving from chlorite addition (1.5-2.5) were below those retrieved for the pure seawater (3.5-4.0) and this confirmed a greater quantity of SO\textsubscript{2} absorbed and converted into sulfuric acid. In addition, the results showed that as the chlorite content in solution increased, increasingly acid pH was reached.

Conclusions
In this work, an innovative study was proposed on wet oxidation scrubbing (WOS) for the flue-gas desulphurization from coastal combustion stations and marine diesel engine applications using sodium chlorite as oxidative chemical. Experimental results showed that the solubility of SO\textsubscript{2} increased about 20-30% compared to pure seawater when chlorite was added to 0.2% by weight, while only 2-9% increase was achieved with 0.1%. The oxidation process, unlike conventional chemicals such as NaOH, NH\textsubscript{3} or other alkaline species, was strongly favored by...
the acidic conditions that prevailed during SO₂ capture until the total consumption of NaClO₂. In addition, it was observed that chlorite solutions reach a lower final pH than pure seawater, confirming a greater amount of SO₂ captured. The equilibrium data retrieved are a mandatory step for a thorough scrubber design and optimization for WOS unit in order to improve desulphurization performance compared to current technologies in use.

References