Enhanced SO₂Removal by Using Charged Water Droplets

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This paper reports preliminary results on the absorption of SO₂ from water charged droplets, produced by an electrospray operated in dripping mode. Our results show that the water charging allows a ≈50% increase of the SO₂ absorption rate. Since the SO₂ mass transfer coefficient depends mainly on the liquid-side mass transfer coefficient, we envisage that the increase of SO₂ absorption rate is ascribable to the occurrence of droplet deformation and oscillation, driven by the reduction of surface tension caused by the presence of excess charge on the droplet surface. Experiments were successfully interpreted in light of an absorption model that specifically address the droplet formation and fall and considered the model of Matteson and Giardina (1974) to account the droplet charge effect.

1. Introduction

This paper is part of an ongoing study aimed to investigate how electrically charged droplets interact with SO₂, a dipolar molecule representing the main pollutant of industrial flue gases and Diesel engines exhausts. This phenomenon is present, for example, in wet electrostatic scrubbers (WES). These are new devices for gas cleaning specifically designed to capture ultrafine and nanometric particles from industrial (Di Natale et al., 2015a) and engines exhausts; Di Natale and Carotenuto, 2015b) that can simultaneously remove gaseous compounds, like SO₂ (e.g. Di Natale et al. 2013). The work of Jaworek et al (2006) is an early reference review on wet electrostatic scrubbing for micrometric particle capture.

There are few studies on absorption of SO₂ by charged droplets and the largest majority of them considered the interactions between a charged water spray and a gas stream containing SO₂. Dou et al. (2008) demonstrated that a spray of charged water exploited a higher absorption rate (up to one order of magnitude) than the same uncharged spray and Byun et al. (1998) showed that electrification is advantageous also for spray drying technologies. In spite of this valuable result, it is complex to understand the underpinning physics of the process due principally to the complexities of charged sprays fluid dynamics. In fact, Duo et al (2008) suggested that a main reason for SO₂ absorption rate increment is the reduction of droplet size and the better gas mixing that derive from the presence of electric charge on the sprayed liquid. Recently, Gogulancea and Lavric (2014) proposed the use of electron beam assisted absorption to capture SO₂, confirming that gas oxidation affects absorption rate.

The electric charge on the spray droplets influences the absorption process in several ways. In particular, two main aspects should be considered: i) the effect of electric charges on chemical equilibrium of SO₂ dissolution in water and ii) the effect of electric charge on the rate of SO₂ mass transfer.

The presence of electric charges in the droplets may influence the chemical speciation of dissolved SO₂. Several issues have arisen considering the effects of droplet charges on chemical speciation of dissolved ions. Anyway, if we consider the typical values of droplet charge-to-mass ratio in an electrified spray, as a value between 0.1 - 10 mC/kg (Carotenuto et al., 2010), corresponding to 10^{-9} - 10^{-7} N (number of equivalents of electron per litre). This concentration is likely to produce negligible effects on the water chemical speciation. As regard the effects of electric charge on mass transfer rate, the pertinent literature provided three main indications related to: i) the reduction of droplets surface tension; ii) the occurrence of turbulence phenomena

on the droplets surface and iii) the occurrence of electrostatic interactions between charged droplets and dipoles of gas molecules, as SO_2. The first option was considered by, e.g. Matteson and Giardina (1974) that related the reduction of surface tension to an increase in the degree of polarization of interfacial water molecules. This was connected to an increase of the concentration of OH^- at the droplet interface and a parallel increase of SO_2 absorption rate. Lopez-Herrera et al. (2011) showed that electric charges cause droplet oscillation that may give rise to additional vortices and increase the interfacial area and the mass transfer rate (Clift et al., 1978) .Finally, Wang and Luo (2011) presented a model for the capture of SO_2 on charged droplets based on the assumption that the additional mass transfer is related to the electrostatic interactions between the droplet charges and the SO_2 dipole However, its derivation is valid in the pure void, when the thermic motion of the gas are absent.

In this work, we developed a new experimental procedure based on the use of an electrospray exerted in dripping mode to produce a stable train of droplets with identical size and charge level. In this way, the fluid dynamics of the water spray was extremely simplified and easily tuneable. The experiments included optical analysis of the droplets to infer their size (and shape), evaluation of the droplets charge and measurements of SO_2 absorption. To interpret experimental data, we developed a physical mathematical model for SO_2 absorption that includes both the formation and the falling of the droplets and considers the theoretical models of Matheson and Giardina (1974) to take into account the interfacial interactions of SO_2 with the charged droplet.

2. Materials and methods

The experimental approach was based on the use of a lab-scale WES chamber equipped with one electrospray nozzle, operating in dripping mode. Regular train of droplets was produced, which were able to scrub a particles-laden gas contained in the chamber. The system was operated batchwise and the SO_2 concentration was measured over time. The experimental plant layout is shown in Figure 1.
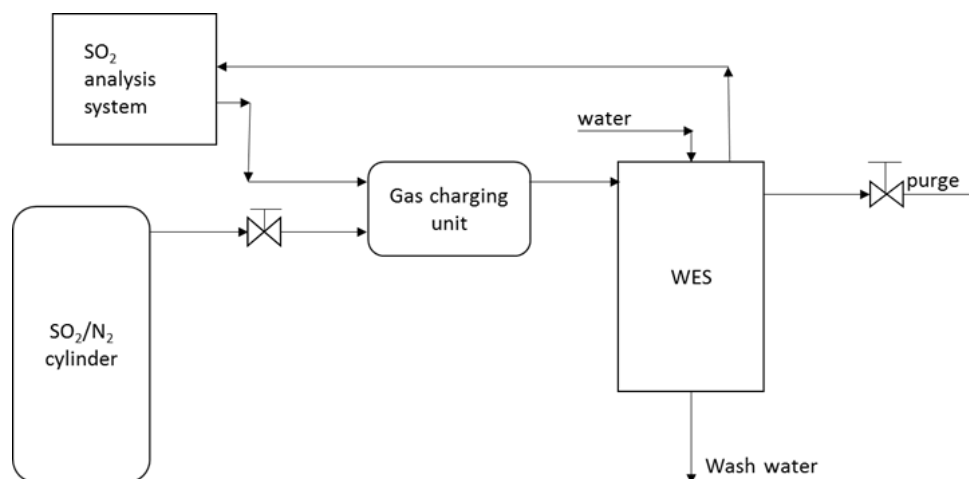

Figure 1: Plant layout

The main components of the plant are: the water electrostatic scrubber (WES), which included the charged droplet generation system, the gas charging unit (GCU), described in D'Addio et al. (2013) and experimented in D'Addio et al. (2014), and the gas analysis instrumentation, which was a ACD MAG3000C equipped with a chiller and a dryer to avoid interferences in the SO_2 measurement.

The cylindrical WES chamber (height: 200 mm, ID: 100 mm) was made of Plexiglas®. The dimensions of the chamber were selected to facilitate operation and maintenance procedures and to allow easy placement of measurement probes. The lateral surface of the WES was covered with a wire mesh and connected to ground potential to shield the chamber from external electric noises. The WES chamber had a removable lid on the top that contains the electrospray nozzle assembly, which was capable of producing a train of droplets with known size and charge values. The gas was sampled through a hole on the lateral surface. Once sampled, the gas was recirculated in the chamber. This recirculation avoided the pressure decrease in the WES chamber, which might cause the unwanted entrance of ambient air, and it assured well mixing conditions.

The charged droplets generation system consisted in a stainless steel capillary needle (OD = 0.8 mm, ID = 0.25 mm) coaxial to a grounded steel ring encased in a PTFE box and connected to a high voltage power supply (Bertan, mod. 230-20R). The needle tip was located 1 mm below the ring lower surface (D'addio et al.

2014). The liquid was fed into the needle using a syringe pump. The liquid flow rate was controlled with a rotameter (Rota Yokogawa, mod. RAGK41) operating between 0.15 - 2.2 mL/min. Water electric conductivity was measured with the Elmertron conductivity meter (mod. CPC-401). The humidity and the temperature of the unit were monitored according to the experimental procedure of Di Natale et al. (2016).

The gas was a calibrated mixture with $1,000 \pm 50$ ppm$_v$ of SO_2 in N_2. The sprayed liquid was distilled water with HCl having a pH of 2.5 ± 0.05. This acid pH value was chosen to operate with a pure physical absorption system with the solubility depending only on SO_2 liquid-vapour equilibrium.

In order to provide a correct interpretation of experimental results, a detailed analysis of sprayed droplet size, frequency and charge is required. This was carried out according to D'Addio et al. (2014).

The experimental protocol for SO_2 absorption consisted in: 1) filling the WES chamber with the SO_2-laden gas, 2) switching on the water electrospray and then 3) measuring SO_2 concentration over time. The tests were carried out batchwise for 10 min. To compare experiments performed in different days and with different gas cylinders, the ratio c/c_0 between the instantaneous and the initial value of SO_2 concentration were plotted against the test time, t. In the experimental timeframe, the concentration of SO_2 in the WES chamber follows an almost linear time-course, and each test was resumed with a characteristic slope named β. Each test was repeated in triplicate and the values of β were averaged. The maximum standard deviation of β data was 3 %, testifying the accuracy of the experimental tests. The tests were carried out as the cycle run: 1. blank test (without sprayed water); 2. Test with uncharged water; 3-4. 2 run tests with water charged at 2.4 kV; 5. Test with uncharged water; 6. Blank test. While specific values of the slopes β may have small variations, the tests 3-4 and 2-5 were always consistent (their differences are negligible) and the relative differences among the two couple of runs were preserved. In this set of experiments, the GCU unit was switched off.

The time course of gas SO_2 concentration in the WES chamber was modelled as the sum of two contributions:

$$\frac{dC}{dt} = -r_{droplets} - r_{reactor} \tag{1}$$

where $r_{droplets}$, and $r_{reactor}$, are the rate of abatement of droplets and reactor.

The reactor contribution is the depletion of SO_2 due to reactor, pipes and analyzer. This phenomenon was investigated through specific blank tests, carried out without spraying droplets and was shown to follow a linear trend over time. The reactor contribution was thus modelled as:

$$r_{reactor} = \Lambda_b \tag{2}$$

Λ_b was 0.0381 µmol/min with $R^2 = 0.996$.

The $r_{droplets}$ is, as follows:

$$r_{droplets} = f\left(n_{form} + n_{fall}\right) \tag{3}$$

where f is the droplets frequency and n_{form} and n_{fall} are the quantity of SO_2 absorbed by each droplet captured during droplet formation and fall. Droplet formation and droplet fall were separately considered because of the different hydrodynamic conditions governing these phenomena. Eqs(4) and (5) were used, respectively, for droplet formation and fall.

$$\frac{dn}{dt} = K_G(t)S(t)\left(y(t) - m\frac{n}{V(t)}\right) \tag{4}$$

$$\frac{dn}{dt} = K_G(t)S\left(y(t) - m\frac{n}{V}\right) \tag{5}$$

where n are the moles of SO_2 absorbed in the liquid, y is the gas molar fraction of SO_2, K_G is the overall mass transfer coefficient, S is the droplet surface area, V is the droplet volume and m is the slope of the equilibrium line. This was estimated by as 0.028 according to Wilhelm et al. (1977).

In Eq(5), the mass transfer coefficient in the gas phase were considered as a time variable since droplets accelerate during their fall. During formation, the droplet size varied with the integration time, changing K_G, S and V. The overall mass transfer coefficient was estimated as:

$$K_G = \left(\frac{1}{k_y} + \frac{m}{k_x}\right)^{-1} \tag{6}$$

For droplet formation, the mass transfer coefficient was calculated considering the correlations for k_x and k_y given by the penetration theory, according to Angelo et al. (1966).

$$k_y(t) = \frac{Sh_g(t)D^g_{SO_2}}{D(t)} = \frac{[2+0.6\,Re(t)^{0.5}Sc^{0.5}]D^g_{SO_2}}{D(t)} \tag{7}$$

$$k_x(t) = \sqrt{\frac{4D^l_{SO_2}}{\pi t}} \tag{8}$$

where D^g_{SO2} and D^l_{SO2} are the SO_2 diffusivity in the gas and the water. The droplet diameter $D(t)$ is:

$$D(t) = \sqrt[3]{\frac{6Qt}{\pi}}$$

(9)

Where Q is the water flow rate. The variation of droplet size influences the Reynolds number (the relative velocity between drop and gas were kept constant) and the Sherwood number, Sh_g, depends on the time instant.

For the droplet fall similar considerations were done, but it was taken into account that liquid side mass transfer coefficient is different due to the vortexes induced by the drag forces exerted by the gas. The model of Amokrane and Caussade (1999) was then used. They considered that the vortexes on the droplet surface could transport the pollutant inside the droplet. Thanks to this behavior, the droplet showed always a regenerated surface so the liquid side mass transfer coefficient is one order of magnitude higher than that predicted by penetration theory. Finally, following the model of Matteson and Giardina (1974), an enhancement factor was considered for the liquid mass transfer coefficient:

$$k_x = k_{x0}\left(1 + \frac{q_s{}^2}{c\,\pi_0}\right)$$

(10)

where: k_x is the actual global mass transfer coefficient, k_{x0} global mass transfer coefficient without droplets charge, π_0 is 1.7×10^{-6} N/m, c is equal to 2.56×10^{-4} F/m^2 and q_S is the superficial droplet charge in C/m^2.

It is worth noticing that the expressions for the mass transfer coefficients are known to be inaccurate for large droplets with internal circulation and shape oscillation (Clift et al., 1978). Therefore, in order to achieve a proper data fitting, the overall mass transfer coefficient in Eq(6), was corrected by a factor ψ.

The initial value for the iterations in Eq(4) was 0 whereas that for Eq(5) was the final concentration obtained from Eq(1). It was assumed that pseudo-steady state conditions hold for the gas concentration under which each droplet falls.

3. Results and discussion

Figures 2 and 3 show pictures of droplet formation sequences at 0 and 2.4 kV. The formation of uncharged droplets required almost 370 ms, while the formation of charged ones required almost 170 ms. Accordingly dripping frequency varied from 2.7 Hz (at 0 kV) to 5.88 Hz (at 2.4 Kv). Consequently, charged droplets are smaller than uncharged one. This was related to the reduction of surface tension with charge level, which is responsible for the detachment of smaller droplets from the needle.

Figure 4 shows pictures of droplets at a distance of 0.1 m from the needle and at potentials of 0 and 2.4 kV. The droplets were spherical at 0 kV, where they had an average diameter of 2.6 mm. Differently, at 2.4 kV, the droplets oscillated between the two shapes (A) and (B). The two pictures in Figure 4 are two subsequent frames at time lapse of 10 ms, thus the oscillation droplet frequency is of the order of 100 Hz. The charged droplets had a lower size respect to uncharged ones, the average size is 1.9 mm and the height-to-width ratio varied from 1.95 to 1.20. This deformation is quite unexpected and mirrors the reduction of droplet surface tension with the imposed electric charge (Matteson and Giardina, 1974).

The measurement of droplet charge at 2.4 kV was 0.28 nC, which corresponds to a surface charge q_S of 2.47 $\times 10^4$ nC/m^2.
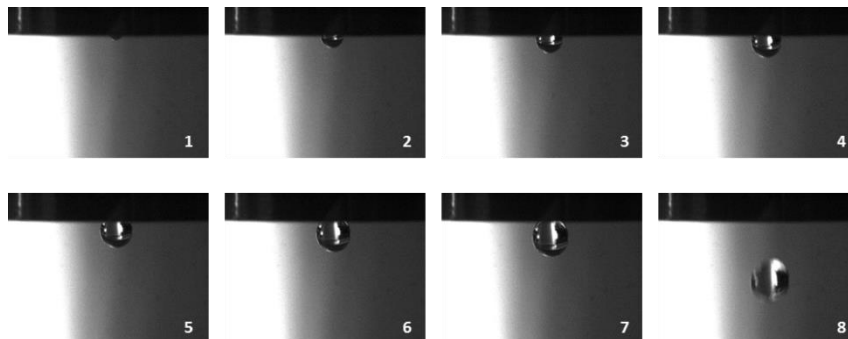

Figure 2: Pictures of droplet formation sequence at 0 kV. The elapsed time for pictures 1-7 was 110 ms, while picture 8 was taken 10 ms after picture 7

Figure 3: Pictures of droplet formation sequence at 2.4 kV. The elapsed time for pictures 1-4 was 110 ms while picture 5 was taken 10 ms after picture 4
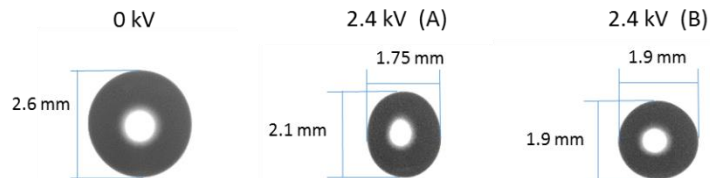

Figure 4: Pictures of droplet fall at 0.1 m below the needle at 0 and 2.4 kV

Experimental plot on the absorption of SO_2 by charged and uncharged droplets, as well as for the blank tests, are shown in Figure 5. Experiments revealed that the setup itself was responsible for about 30 % of the removed SO_2 (capturing about 50 ppm of SO_2 after 200 s). The net contribution of sprayed droplets is well distinguishable from the blank test and the SO_2 absorbed by the water after 200 s is the 13 % higher for charged than for uncharged droplets. The slopes β for 0 and 2.4 kV were 2.07 $\times \cdot 10^{-5}$ mol/m^{3}s and 2.67 $\times \cdot 10^{-5}$ mol/m^{3}s, respectively. For the blank tests β was 7.56 $\times \cdot 10^{-6}$ mol/m^{3}s regardless the needle charging potential. Best fitting among model and experiments was achieved with a factor ψ= 2. It is worth noting that the model is highly sensitive to the value of ψ. When the model is applied to the test with charged droplets in absence of the term of Matteson and Giardina (1974), the predicted β was 2.33$\cdot \times$ 10^{-5} mol/m^{3}s against the experimental slope of 2.67 $\times \cdot 10^{-5}$ mol/m^{3}s. When the electrostatic term is added, the model predicted a slope of 2.70 $\times \cdot 10^{-5}$ mol/m^{3}s.

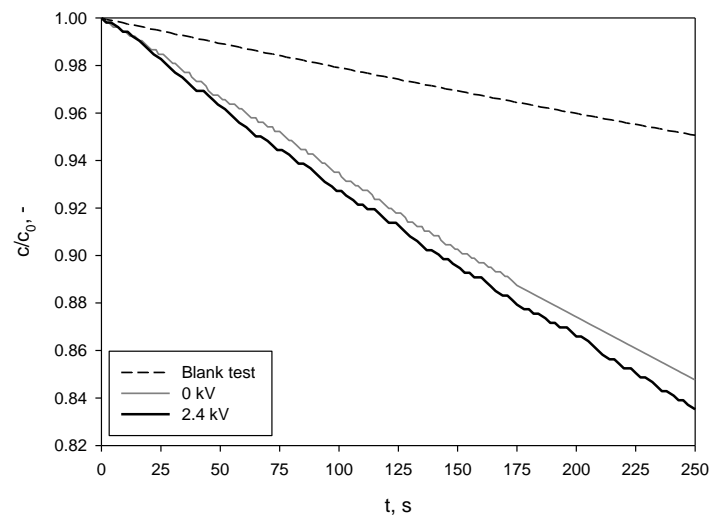*Figure 5: Dimensionless SO_2 concentration time course in the WES chamber during blank test (no water) and with uncharged and charged water*

4. Conclusions

In this work, we reported preliminary results on the capture of SO_2 taking place in a closed vessel by means of a train of charged droplets. Experiments included optical analysis of the droplets during both their formation and fall as well as the analysis of the time course of SO_2 concentration in the vessel. We developed an absorption model including the contribution of droplet formation and fall as well as of the reactor contribution. Two sets of experiments were performed to compare the behaviour of charged and uncharged droplets. The experiments highlighted that, due to the effect of electric charge on the surface tension, the droplets broke up

earlier and oscillated during fall. After subtracting the reactor contribution, the mass transfer rate for charged droplets was 1.57 time higher than that of uncharged droplets.

We envisage that droplet oscillation and charge give rise to an increase of mass transfer coefficient that was considered according to the approach of Matteson and Giardina (1974). The model was calibrated for uncharged water and provided a good agreement with experimental data performed with charged droplets.

The current experimental and modelling analysis, however, is not able to exploit whether the increase of SO_2 absorption rate is related to droplet deformation or to the occurrence of specific charge-dipole interactions between droplets and SO_2 molecules. Further studies are thus required to address this point.

Acknowledgements

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