



# Chemi-Electro-Hydrodynamic of Sulphur Dioxide Absorption By Electrified Water Sprays

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This paper explores the effects of electrification of water sprays on the absorption of sulphur dioxide from exhaust gases. Electrification is associated with an appreciable improvement of sulphur dioxide absorption rate with low supplementary costs and candidates to be a valuable innovation for spray tower absorbers. Similar phenomena occur during thunderstorms, when scavenging of gases and aerosol are enhanced by the electric charge of raindrops.

This paper aims to describe the effects of electrification on SO<sub>2</sub> absorption on the bases of experimental and theoretical analyses. The experiments involve absorption tests in lab-and pilot scale facilities, while theoretical modelling to assess the chemical and physical properties of charged droplets, their hydrodynamics and their mass transfer rates are presented. Water electrification is accompanied by a number of chemical-physics and morphological modifications of the sprayed droplets that modify the conventional absorption rate of soluble gases. The experimental and theoretical evidences indicate the need to analyse the electrified absorption within a new and integrated theoretical framework that we define chemi-electro-hydrodynamics (CEHD).

## 1. Introduction

The presence of acid gases in the exhausts of power plants, industrial processes and internal combustion engines is one of the most widespread environmental problems and their removal is among the oldest priorities of environmental regulations. Several control technologies are available to achieve substantial removal of SO<sub>x</sub>, HCl, NO<sub>x</sub>. Wet scrubbing processes are among the most effective ones for SO<sub>2</sub> and HCl capture while their application to NO<sub>x</sub> removal is reduced due to the success of SCR and NSCR techniques. Wet scrubbing is based on the chemical absorption of acid gases into water based solutions containing carbonates, hydroxides or oxidants. The design of absorption processes is an optimal compromise between effective and minimal use of the chemical solutions and compactness of the scrubber. To achieve this task, for a given sorbent, the maximization of the mass transfer rates and the minimization of pressure drops is required. Most of the efforts of chemical engineers working in the field are concentrated on the development of packing, trays, column internals and spray patterns to accomplish these objectives.

Spray electrification is used in many industrial applications as a way to improve spray generation and liquid dispersion. Water electrified scrubbers were also proposed as a way to improve the capture of submicron particles, as reported, for example, in the work Di Natale et al. (2015) and Jaworek et al. (2006). The electrostatic scrubbing consists in contacting the polluted gas with an electrified spray in a suitably designed scrubber; optionally, the gas can be exposed to a corona source before entering the device (e.g. Carotenuto et al., 2010).

The nature of droplets-gas interactions in an electrostatic scrubber suggests that attractive electrodynamic forces may arise between the charged droplets and oppositely charged ions as well as with dipolar molecules, as SO<sub>2</sub>. This paper aims to provide experimental evidences on the wet electrostatic absorption of SO<sub>2</sub>

together with a preliminary analysis of the effects of electrification on the underpinning physical-chemical phenomena.

## 2. Experimental evidences

Although, at the best of our knowledge, the first studies on electrostatic absorption date back to the middle seventies, there are a handful of experiments on this argument, most of which focused on desulphurization. These can be divided in two main categories: experiments in lab or pilot scale scrubbers with induction or contact electrified sprays of large flow rates (some L/min) and experiments in lab-scale electrospray units, for which liquid flow rates are some mL/min and the spray consisted in a train of isolated droplets. Although the first category of experiment are closer to full scale applications, the authors believe that electrospray units are the simplest and the most robust laboratory scale facilities due to the possibility of coupling detailed optical analysis to charge measurements and absorption rate determination, providing a wider set of experimental data.

Figure 1 resumes most of the experiments available in the pertinent literature regarding the electrified absorption of SO<sub>2</sub> in water. Figures 1a-c refers to induction or contact electrified sprays, Figures 1d-f to electrospray units.

Figure 1a reports some of the results reported by Dou et al. (2008). These experiments were performed with a lab-scale spray dryer using lime suspension to capture SO<sub>2</sub> and using both contact and induction charging with an electric potential of up to ±10kV. The experiments showed an improvement of SO<sub>2</sub> removal efficiency, with better performances for the conduction charging. As a consequence of the charge-dipole interactions between droplets and SO<sub>2</sub>, the sign of applied potential did not cause appreciable differences in the removal efficiency.

Figure 1b shows the results of Wang (2013) who operated a co-flow spray scrubber using 3% Ca(OH)<sub>2</sub> in water. The experiments were carried out at different SO<sub>2</sub> concentration and liquid loadings. Water electrification enhanced the absorption efficiency by 5-10% applying a charging potential up to +15kV. The potential required to maximize the efficiency decreased for higher Ca/S ratios and lower SO<sub>2</sub> concentration.

Figure 1c resumes the results achieved by Di Natale et al. (2016) in a pilot scale seawater scrubber operated at different inlet gas temperature (seawater temperature kept at 20°C). The experiments proved that charging both the gas and the water spray the scrubber reduces the SO<sub>2</sub> emission by more than 50% compared with uncharged sprays, for all the operating temperatures.

Figure 1d shows some of the results achieved by Matteson and Giardina (1974), which provided an indirect determination of the mass transfer coefficients as a function of the surface charge density applied on the droplets. The authors noticed a significant improvement of the mass transfer coefficient that can even doubling by increasing the square value of the droplet surface charge density as high as  $1.6 \cdot 10^6 \text{ C/m}^2$ .

Figure 1e describes the dimensionless SO<sub>2</sub> absorption capacity of electrified liquid droplets used to scrub a 210 mL/min of pure SO<sub>2</sub> at different water flow rates and applied electric field levels. The term of normalization is the equilibrium absorption capacity, set at 94 mg/cm<sup>3</sup>. The authors indicate that for the geometry of the lab scale apparatus, the increase of mass transfer coefficient due to spray improvements were overwhelmed by the reduction of droplet residence times, leading to a reduced absorption capacity.

Finally, Figure 1f reports the experimental results of Di Natale et al. (2016) obtained with a batch reactor in which a volume of gas ( $V=2 \text{ L}$   $c_0=1000\text{ppm SO}_2$  balance N<sub>2</sub>) is scrubbed by a train of water droplets ( $L= 1 \text{ mL/min}$ ) either uncharged and charged by electrospraying, at a potential of -2.4 kV by. These experiments were enriched with the same experimental data at +2.4 kV. The absorption rate increases with charging and that the sign of the applied potential has a slight influence on the actual absorption rate. Model calculations indicated that the mass transfer rates for charged sprays are 57% higher than for uncharged spray (Di Natale et al., 2016).

## 3. Modelling analyses

The absorption of a soluble gas in a liquid droplet is determined by a series of relevant properties and phenomena, which can be summarized as:

- The shape, the size and the surface area of the absorbing droplet;
- The physical properties of the liquid-gas interface;
- The chemical-physical equilibria determining the partition of the absorbed specimen in the gas;
- The fluid dynamic field of the gas phase close to the droplet and the internal motions within the droplet;
- The temperature, pressure and humidity of the gas stream.

Besides, in a spray scrubber, the absorption rate is determined by the liquid-to-gas mass ratio, the spatial distribution of droplets swarm and the residence time of the gas within the unit. This section discusses how water electrification affects most of the aforementioned phenomena. These effects are all candidate to contribute to the observed improvement of the absorption rate for charged sprays.

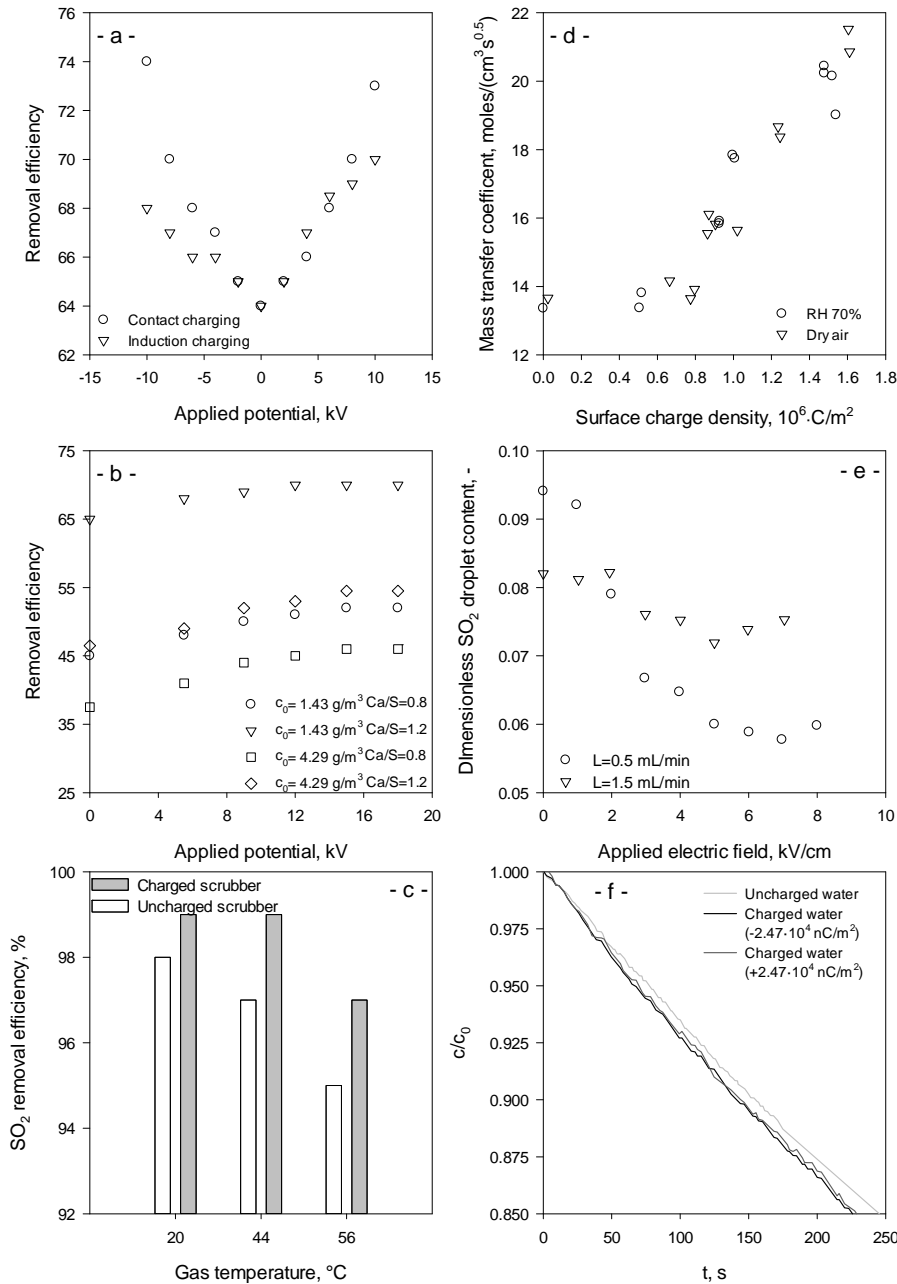


Figure 1. Experimental evidences on wet electrostatic absorption. a. Dou et al. (2008) – SO<sub>2</sub> removal efficiency in an electrified spray dryer as a function of applied potential; b. Wang et al. (2013) – removal efficiency in an electrified scrubber as a function of applied potential parametric with Ca/S ratio and initial SO<sub>2</sub> concentration; c. Di Natale et al. (2016) – Effect of temperature and electrification in seawater scrubbers operated either uncharged or with 15 kV droplet charging potential and 15 kV gas corona charging potential. d. Matteson and Giardina (1974) – SO<sub>2</sub> mass transfer coefficient of charged water droplets as a function of the droplet surface charge; e. Carleson and Berg (1983) – Dimensionless SO<sub>2</sub> concentration in the liquid phase as a function of the electric field applied to the spray in 200 mL/min of pure SO<sub>2</sub> gas. f. Di Natale et al. (2016) – Time course of dimensionless SO<sub>2</sub> concentration in a closed vessel (V = 2 L) scrubbed by uncharged and charged droplets at flow rate of L = 1 mL/min.

### 3.1 Effects of electrification on the morphology of sprayed droplets

Several scientific studies in the last decades are aimed to explain the physics of electro spraying and induction spraying of water and an review of these studies is outside the scopes of this paper. The charging process by electro spray is usually used for low liquid flow rates (as those described in the experiments of Matteson and Giardina, 1974 and Di Natale et al. 2016). Electro spraying gives rise to high charge levels and to a number of spraying regimes mostly depending on the applied electric field and the liquid flow rate. The applied electric potential raises a higher deformation of the liquid meniscus that produces an increasing number of smaller droplets (e.g. Mucherino, 2017).

For induction sprays, it is not clear whether the electrification may have an effect on the droplets size and shape, but the alteration of primary atomization patterns (Manna et al., 2016) suggests that a certain reduction of the droplet size may occur. This is however expected to be smaller than that observed for electro sprays.

Needless to say, the generation of finer droplets for a spray operated at the same flow rate improves the liquid-gas interfacial area, which is beneficial for any absorption process. This effect was already observed in most of the experimental studies described in Figure 1.

Another relevant consequence of the spray electrification is the onset of droplet deformations. Indeed, most of the optical analyses in the electro spray studies indicated that droplets are not spherical as soon as they are sprayed and that, as they move in region of lower electric fields, their shape approach a spherical one (e.g. Mucherino, 2017). Indeed, we observed that the droplets are mostly ellipsoidal and, both during their formation and fall, they pulsate with a characteristic frequency that changes with applied potential and liquid flow rate. This is consistent with Lopez-Herrera et al. (2011), which showed that electric charges give rise to droplet oscillation associated to additional vortices and to an increase in the interfacial area.

This deformation has a very important role in raising the mass transfer coefficient and was often used in practical application to improve the performances of spray towers when large flow rates and large droplets are required (Clift et al., 1978). In this sense, electrification promotes oscillation also for water droplets that are expected to be rigid in absence of charge for their size and for their falling velocities (e.g. Clift et al., 1978).

### 3.2 Effects of electrification on the physical properties of the water-gas interface

In the last years, some experimental evidences triggered an intense debate regarding the charge displacement over the surface of neutral water and the capacity of distilled water to store electric charges. This discussion is far for providing a definite solution, but most of the researchers now agree that the air-water interface usually carry a negative charge with a preferential orientation of hydrogen bonds giving rise to a well-structured surface, and that water clusters may appear in its proximities (e.g. Chaplin, 2009; Ovchinnikova and Pollack, 2009).

The most common observation related to water electrification is a modification of the interfacial tension, which is considered as the key physical property responsible for the observed hydrodynamic regimes of electro sprays. On the other hand, Santos et al. (2011) reported that electrification does not seem to alter density and viscosity of charged droplets. Several papers correlated the air-water surface tension to the charges deposited on a droplet. Matteson and Giardina (1974) proposed a quadratic dependence of surface tension on droplet charge. The authors considered such variation as the main responsible for the improvement of absorption rate observed in their experiments. Indeed, they started from the assumption that, in order for the droplet to exist with a lower surface tension, the spreading pressure of the air-water interface has to be higher. Since this pressure is related to the concentration of water molecules, the authors associated the droplet charge to the number of available adsorption sites. Accordingly, they suggested the following expression for the mass transfer coefficient of charged droplets:

$$k = k_0 \left( 1 + \frac{q_s^2}{c \pi_0} \right) \quad (3)$$

where:  $k$  is the actual global mass transfer coefficient,  $k_0$  the global mass transfer coefficient without droplets charge,  $\pi_0$  is  $1.7 \cdot 10^{-6}$  N/m,  $c$  is equal to  $2.56 \cdot 10^{-4}$  F/m<sup>2</sup> and  $q_s$  is the superficial droplet charge in C/m<sup>2</sup>.

The authors envisage that the uncertain determination of correct interfacial properties of charged droplets is one of the most critical lack of knowledge of wet electrostatic scrubbing. This complexity depends on many factors, as i) the physical and chemical phenomena involved in the determination of the actual properties of uncharged water (e.g. Chaplin, 2009); ii) the effects of size and curvature of the liquid drops (e.g. dell'Erba et al., 1999) and iii) the difficulties associated with measuring the properties of an isolated droplet without inducing undesired perturbations.

Also theoretical thermodynamic determinations are complex since the chemical potential of any  $i$ -th specimen has to be applied with its general expression:

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F V \quad (4)$$

where,  $\mu_i$  is the chemical potential, the apex  $^0$  indicate the standard condition,  $R$  is the gas constant,  $T$  is the temperature,  $a_i$  is the ion activity,  $z_i$  is the ion valency,  $F$  is the Faraday constant and  $V$  is the applied potential. Therefore, the chemical potentials of the ionic species in liquid phase are influenced by the electric field generated by the high voltage electrode, the ground and the spatial distribution of the droplets swarm, and the effective applied potential is hard to be determined.

### 3.3 Effect of electrification on the solubility of sulphur dioxide

A charged droplet falling into a gas cannot simply verify electroneutrality condition. This observation has a relevant effect on the chemical-physical equilibria of dissolved ions. Burgo and Galembeck (2015) correlated the water charge to the excess or lack of  $\text{OH}^-$ : In an ionic liquid as water, it is indeed unlikely that electrons may exist freely in a drop and the number of free ions in the liquid provide a reservoir of charge far larger than the number of actual charge normally deposited on a drop. The excess of charge in water is likely to be related to an alteration of chemical equilibria and may give rise to pH alteration. The typical values of droplet charge-to-mass ratio in an electrified spray is 0.1-10 mC/kg (Carotenuto et al., 2010) corresponding to  $10^{-9}$  -  $10^{-7}$  N (number of equivalents of electron per litre). Therefore, it is very hard to measure the pH variations associated to free charges. A similar conclusion was derived by Burgo and Galembeck (2015). Nevertheless, there may be an effect on the actual activity coefficients used for water solution, whose formulation mostly suppose electroneutrality. These considerations, together with the aforementioned dependence of chemical potentials on electric potentials pose a hindrance on the determination of chemical equilibria and gas solubility in charged droplets.

### 3.4 Effect of electrification on the fluid dynamic fields in the gas and the liquid phase

In a wet electrostatic scrubbing process many simultaneous phenomena affect the fluid dynamics of both the gas and the liquid phases and give rise to different spray regimes at different applied potential, system geometry, liquid and water flow rates.

As discussed before, electrification lowers droplets surface tension while preserving their density and viscosity. The presence of intense electric fields and the proximity of other droplets carrying charges of the same polarities widen the spray angle for both electrosprays (Jaworek et al., 2006) and induction charged sprays (e.g. Manna et al., 2017). The lower surface tension and the same pulsating dynamics of primary jet break up lead to the formation of droplets that oscillate. At date, there are clear evidences of droplets oscillation close to the nozzle, but is not clear if and at what distance the droplets oscillation stops. The different spray patterns and the droplet deformation obviously modify the overall fluid dynamic field of the gas and induce internal motion in the liquid phases (e.g. Clift et al., 1978). Both these effects can produce significant effects on the mass and heat transfer coefficients of sprayed droplets, both in the gas and in the liquid phases. While fluid dynamic field can be well studied for electrospray systems, a reliable analysis for induction sprays at high flow rate is far from being available and represent one of the main lack of knowledge of electrostatic absorption.

### 3.5 Effect of electrification on temperature, pressure and humidity of the gas stream.

Water electrification can modify the temperature and humidity of the scrubbed gas because of the faster droplet evaporation/condensation lead to the higher heat and mass transfer rates and of the production of finer droplets. These effects are hardly to quantify. Electrification is not expected to generate any effects on the gas pressure.

## 4. Conclusion - Toward a model for chemi-electrohydrodynamics of gas absorption of charged droplets.

Experimental evidences, although scarce, clearly indicates that electrification of water spray improve the  $\text{SO}_2$  absorption rate of spray towers and spray-driers. Similar processes are present also in nature, as for example in the in-cloud and below-cloud absorption of acid gases, not only during thunderstorms. In practice, it is very difficult to describe and predict the performances of a large scale wet electrostatic absorber and the improvements related to electrification can be more or less evident. However, wet electrostatic scrubbers for submicron particle captures are now at pilot and industrial scales and it is worth to understand how to modify their process design and operating conditions to maximize the simultaneous absorption of acid gases.

The description of wet electrostatic scrubbing for gas absorption is a complex problem involving many simultaneous phenomena which are linked in a non-linear way. The creation of a swarm of charged droplet and the presence of high voltage electrodes and grounded surfaces give rise to modifications of the

conventional spray patterns, as well as to the droplet-gas heat and mass transfer rates. Following a microscopic approach, conventional momentum, heat and mass balance equations should be modified to include electric field effects on stress tensors and heat and mass fluxes. Indeed, the presence of imposed charges generates modifications to the chemical and physical properties of the droplets and the same thermodynamic parameters (including the chemical equilibria of dissolved ions) become a function of the droplet charge itself and of the applied potential. This last varied along the scrubber, being a function of the electrodes and the scrubber walls geometries as well as of the spatial distribution and charge levels of the swarm of sprayed droplets. The presence of ionized gases further enhance the problem complexity. At the moment, only momentum balance equations in non-ionized gases are available within the framework of electrohydrodynamics, while further insights are needed to achieve reliable heat and mass transfer equations. The multiplicity of the underpinning physical-chemical phenomena and the constraints posed by the experimental setup make difficult the assessment of a framework of knowledge within which compare and analyse the experimental results. In our opinion, there is a clear need to analyse the electrified absorption within a new theoretical framework, in which electrodynamic, chemistry and engineering aspects are properly integrated and for which we propose the definition of chemi-electrohydrodynamics (CEHD). Many efforts are needed to properly apply CEHD studies to natural processes or full scale plants, but the potential improvement on absorption related to wet electrostatic scrubbing warrant further pursuits to this research.

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