

# Interaction of chloride solutions with plasma-supplied reactive oxygen species-transferring reactivity from gas to liquid

V. Jirásek and P. Lukeš

*Institute of Plasma Physics, Czech Academy of Sciences, Prague, Czech Republic*

**Abstract:** Chemical changes after interaction of NaCl and PBS solutions with ROS supplied by He/O<sub>2</sub> APPJ plasma jet were studied. It was found that the treatment of NaCl led to a large increase of pH over 10 and formation of sodium hypochlorite, chlorite, and chlorate. PBS solutions were also treated with or without taurine as a HOCl scavenger. The transfer of reactivity from gas to liquid led to plasma activated solution with post-discharge chemistry of oxychlorine species, active for couple of hours.

**Keywords:** reactive chlorine species, hypochlorite, plasma activated solution

## 1. Introduction

In plasma medicine and plasma agriculture, biological materials often natively contains solutions of Cl<sup>-</sup> anions. Plasma sources working in the ambient air or fed by gases containing traces of oxygen or water vapour provide reactive oxygen species (ROS). As it was found in photolysis or radiolysis experiments, these ROS are able to oxidize Cl<sup>-</sup> resulting in the oxychlorine species (acids, their anions or dissolved oxides) with Cl present in various oxidations states. Due to the pronounced reactivity of these liquid-phase chlorine compounds, interactions with other compounds in the used cultivating media, cells or free biomolecules can be awaited. On the other hand, sometimes the awaited ROS effect could be masked by their consumption with Cl<sup>-</sup> and other chlorine compounds. This is also the case of more stable liquid-phase compounds, e.g. the hypochlorous acid (HOCl) or its conjugate base, the hypochlorite ion (OCl<sup>-</sup>) are known to rapidly react with hydrogen peroxide and nitrite, two of commonly produced species when plasma is in contact with water on the open air.

In this contribution, we highlight two essential features: i. the importance of O atoms and their behaviour in Cl<sup>-</sup> solutions and ii. the post-treatment activity of the chlorine compounds in the solution.

## 2. Experimental

The experiments were conducted using the standard type of  $\mu$ -APPJ (COST Reference Jet [1]) supplied by RF voltage (215-230 V RMS, 13.56 MHz) and operating with the gas mixture consisting of 1.4 slm He and 8.4 sccm O<sub>2</sub>. The distance of visible plasma channel to the liquid surface was 4 mm. 3 ml solution of NaCl or PBS were treated for 2-20 min. The concentrations of HOCl and OCl<sup>-</sup> were measured by UV spectrometry, ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup> by ion chromatography and TauCl by the colorimetric method. Further details can be found in [2].

## 3. Results and discussion

Hypochlorite ion is the major product in the treated unbuffered NaCl solution. It captures H<sup>+</sup> ions and causes pH increase over 10 (see Fig. 1).

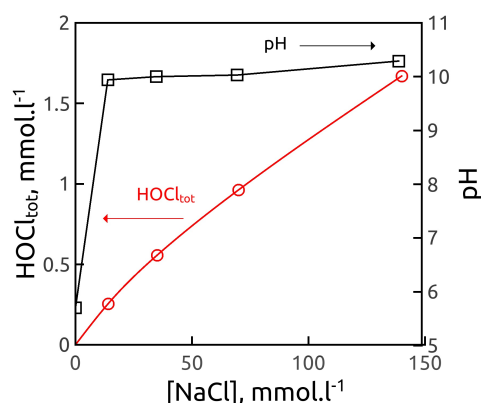


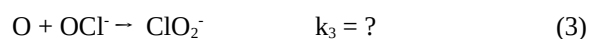
Fig. 1. Concentration of  $\text{HOCl}_{\text{tot}} = \text{HOCl} + \text{OCl}^-$  and final pH of the unbuffered plasma-treated NaCl solution in dependence on its initial concentration.  $U_{\text{RMS}} = 215 \text{ V}$ .

We suggest that oxygen atoms, which are produced in the jet in rather high concentration [3], dissolve in water and undergo immediately the following competitive reactions:



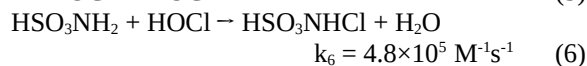
In support for this suggested competition, OCl<sup>-</sup> formation is strongly dependent on the NaCl concentration at the values corresponding to a large excess over possible O(aq) concentrations (see Fig. 1).

Alongside with the hypochlorite, the chlorite and chlorate ions were also measured in the treated solution. The appearance of higher chlorine oxidation states can be explained by the following reactions in the liquid phase:





In order to support this mechanism, we used taurine as a hypochlorite scavenger *in situ* during the plasma treatment, i.e. the taurine-PBS solution was treated [2]:



In simultaneous experiments, taurine was added after the PBS treatment to convert produced hypochlorite into  $\text{HSO}_3\text{NHCl}$ . As can be seen in Fig. 2, when scavenging *in situ*, the concentration of  $\text{HSO}_3\text{NHCl}$  was directly proportional to the treatment time, while when added only after the treatment, a levelling off was observed with much lower  $\text{TauCl}$  concentrations.

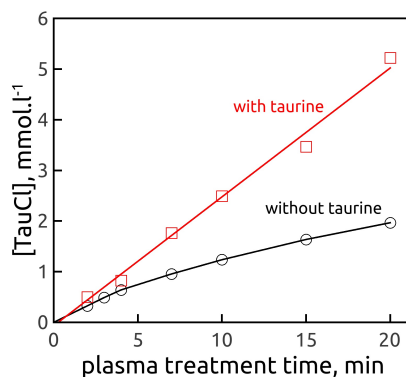


Fig. 2. Concentration of  $\text{TauCl}$  as a result of  $\text{HOCl}$  reaction with taurine added either before (red line) or after (black line) the plasma treatment in dependence on the treatment time. The PBS solution (5 mM of  $\text{H}_2\text{PO}_4^-$ , 140 mM of  $\text{NaCl}$ , pH = 7.5) was treated.  $U_{\text{RMS}} = 230 \text{ V}$ .

The difference increased from 30% to 170% with the treatment time from 2 to 20 min. Scavenging by taurine eliminates reactions (3) and (4), which is more effective at higher times where higher hypochlorite concentrations accelerate the reactions.

It was found that the unbuffered treated 140 mM  $\text{NaCl}$  solution exhibited post-treatment reactions. Fig. 3 shows time course of chlorine compounds concentrations after the 20-min discharge treatment. The process can be divided into two phases. During the initiation phase, the decreasing pH slowly converts  $\text{OCl}^-$  to  $\text{HOCl}$ . As the pH drops below 9, the oxidation of  $\text{ClO}_2^-$  by  $\text{HOCl}/\text{OCl}^-$  leads to  $\text{ClO}_3^-$ , which is complete in 350 min. The observed behaviour is well described by the mechanism known from the water chlorination chemistry [4]. It is centered around the reaction (4) and can be considered as oxidation of  $\text{ClO}_2^-$  by  $\text{HOCl}$  catalyzed by acids and chloride ions. The described activity of the treated solution represents a perfect example of a transfer of reactivity from plasma-produced gas to liquid.

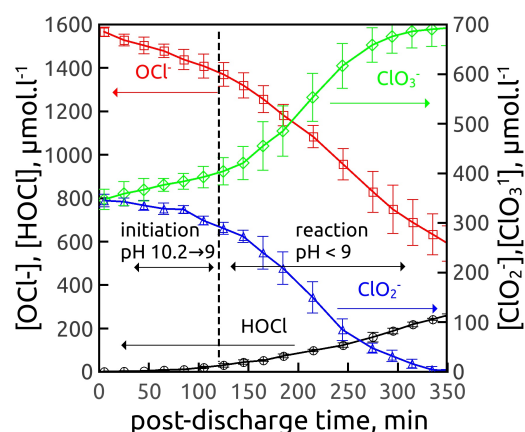


Fig. 3. Concentration of oxychlorine species in the plasma-treated solution in dependence on the post-treatment time. The non-buffered solution (140 mM  $\text{NaCl}$ ) was treated.  $U_{\text{RMS}} = 215 \text{ V}$ .

All the above described results could be well obtained thanks to working under closed atmosphere of working  $\text{O}_2/\text{He}$  gas excluding humid air, which would otherwise lead to  $\text{H}_2\text{O}_2$  and  $\text{NO}_2^-$  in the solution, which react rapidly with  $\text{OCl}^-/\text{HOCl}$  and convert it back to chloride ions. In the present reaction system, O atoms are responsible for enabling the oxychlorine liquid chemistry. This does not exclude participation of other ROS like  $\text{OH}$ ,  $\text{O}_2^{\cdot-}(\Delta)$  or  $\text{O}_3$  in hypochlorite formation in other plasma-liquid systems, although it seems much less effective for a number of reasons.

### 3. Conclusions

Oxygen atoms produced by APPJ plasma jet can be converted to hypochlorites rather than to ozone in concentrated  $\text{Cl}^-$  solutions. The hypochlorites are further partially transformed to chlorites and chlorates. The solutions remain reactive after the treatment for several hours, keeping high oxidation potential. The system thus presents a perfect example of transferring the plasma afterglow reactivity into the liquid. The possible formation of hypochlorite and its reactions with other liquid-phase components should always be considered when biological samples are treated by plasma producing ROS.

### Acknowledgement

This work was supported by the Czech Science Foundation (project No. 19-25026S).

### 4. References

- [1] J. Golda *et al*, J. Phys. Appl. Phys. **49**, 84003 (2016) .
- [2] V. Jirásek and P. Lukeš, Plasma Sour. Sci. Technol., in print (2019)
- [3] D. Ellerweg *et al*, New J. Phys. **12**, 013021 (2010).
- [4] B. Kormányos *et al*, Inorg. Chem. **47**, 7914 (2008).