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## EXPERIENCE WITH A COMMERCIAL WET-SCRUBBER (ALUSUISSE) USED IN UNCONVENTIONAL SEAWATER ENVIRONMENT

An experience gained in the closed aluminum smelter in Šibenik (Croatia) is described in order to highlight possible similar problems anywhere in the world, when commercial wet-scrubber, designed for fresh water, is used in an unconventional seawater environment. Lime treatment process was used to remove fluoride as an insoluble calcium fluoride. Wet-scrubbing in real system is compared with that in model system, using the SOLGASWATER program (ERICSSON, 1979) for heterogeneous equilibria. It is shown that chemical modelling can help to control the wet-scrubbing process and thus to avoid the undesirable breaking of pipelines. The removal of fluoride at pH 5.4 in the form of insoluble cryolite, using lime slurry process and seawater in recirculation, is suggested to be an alternative to precipitation of calcium fluoride.

Environmental consequences of partial discharging aluminum and fluoride into the marine environment are discussed in comparison with ecosystem response to volcanic aerosol.

### 1. INTRODUCTION

A large aluminum smelter in Šibenik, situated at the Adriatic coast (Croatia), used a commercial wet-scrubbing system of the Alusuisse type (designed for fresh water in recirculation) since 1973 for number of years. As described by KRSTULOVIĆ et al. (1974), waste water was treated by lime slurry, contained dissolved aluminum cell gases ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SiF}_4$ ,  $\text{CF}_4$  and  $\text{HF}$ ) and solid particles ( $\text{Al}_2\text{O}_3$  and soot). In a large precipitation tank simultaneously three processes occur:

- dissolution of aluminum oxide in the presence of complex forming fluoride;
- nucleation and crystal growth of calcium fluoride or some other fluoride salt;
- sedimentation of solid particles.

Due to the shortage of fresh water, seawater was used in recirculation, leading to the deviation from normal process. Quality of regenerated water ( $\text{pH} = 6.5$ ,  $F = 20 \text{ mgdm}^{-3}$  and solid particles  $10 \text{ mgdm}^{-3}$ ) was never attained. Difficulties in the functioning of wet-

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scrubbing of aluminum cell gases have been described (BILINSKI and RADULOVIĆ, 1985). It was suggested, based on model experiments by BILINSKI et al. (1984) the possibility of using calcined natural dolomite ( $\text{CaO} \times \text{MgO}$ ) in neutralization process, as an alternative to lime slurry process. Enormous damage occurred in the aluminum smelter, operating with seawater in recirculation. It has been neglected that physico-chemical processes changed in seawater compared to freshwater environment. Fluorine was released to the environment and finally the pipelines were broken, because precipitation of calcium fluoride shifted outside of precipitation tank.

Aluminum smelter was closed in the meantime and the fluorine problem was forgotten in Croatia. Inspired by more recent literature (BAALINA et al. 1996; 1997; GAGO et al. 2002; FROGNER KOCKUM et al. 2006) the old problem, briefly mentioned by BILINSKI et al. (1983) is now revisited. The objectives of the present work are to present experience with fluoride removal when seawater is used in recirculation in a shortage of freshwater. It is aimed that similar problems are avoided somewhere else in the world. An equilibrium model, describing chemical processes in the wet-scrubbing system of aluminum cell gases will be presented, using the computer program SOLGASWATER (ERIKSSON, 1979). Environmental problems, which can occur in soil and marine environment, will be discussed.

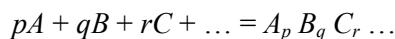
## 2. RESULTS AND DISCUSSION

Theoretical description of the chemical behavior of fluoride and aluminum in precipitation tank with seawater in recirculation could be obtained using an equilibrium model, based on the principle of chemical thermodynamics. The SOLGASWATER program of ERIKSSON (1979) was used here. Besides that, the most influential paper was that of SILLÉN (1961), who presented a model for the ocean system. The SOLGASWATER program, because of its flexibility and generality, provides a valuable tool for the study of the chemistry of multicomponent, multiphase, aqueous systems, as was demonstrated by INGRI (1978).

In order to simulate the real and scrubbing system, the minimum number of eight components (chemical species) to describe it, was used. These eight components are:



The set of 33 aqueous species and of 9 solid phases, which are relevant to the model system, was chosen. Thermodynamic data were selected, valid for 25 °C and ionic strength  $I = 0.5$  (Critical Stability Constants, 1976). Table 1 presents a composition matrix, containing chosen aqueous species and solid phases. The formation constants presented as  $\log \beta_{\text{pqr}...}$  are defined according to general equilibrium:



where  $A = \text{H}^+$ ,  $B = \text{Na}^+$ ,  $C = \text{Mg}^{2+}$ , ...

Table 1

Composition matrix containing 33 aqueous species and 9 solid phases

Species/Solids	Log $\beta_{\text{pq}r\dots}$	H <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>2</sub> <sup>(aq)</sup>
		<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	<i>t</i>	<i>u</i>	<i>v</i>	<i>x</i>
H <sup>+</sup>	0.000	1	0	0	0	0	0	0	0
OH <sup>-</sup>	-13.760	-1	0	0	0	0	0	0	0
Na <sup>+</sup>	0.000	0	1	0	0	0	0	0	0
NaF <sup>0</sup>	0.960	0	1	0	0	0	1	0	0
Mg <sup>2+</sup>	0.000	0	0	1	0	0	0	0	0
MgF <sup>+</sup>	1.310	0	0	1	0	0	1	0	0
MgSO <sub>4</sub> <sup>0</sup>	1.010	0	0	1	0	0	0	1	0
MgCO <sub>3</sub> <sup>0</sup>	-13.530	-2	0	1	0	0	0	0	1
MgHCO <sub>3</sub> <sup>+</sup>	-5.700	-1	0	1	0	0	0	0	1
Ca <sup>2+</sup>	0.000	0	0	0	1	0	0	0	0
CaF <sup>+</sup>	0.600	0	0	0	1	0	1	0	0
CaCO <sub>3</sub> <sup>0</sup>	-13.370	-2	0	0	1	0	0	0	1
CaHCO <sub>3</sub> <sup>+</sup>	-5.620	-1	0	0	1	0	0	0	1
Al <sup>3+</sup>	0.000	0	0	0	0	1	0	0	0
AlF <sup>2+</sup>	6.100	0	0	0	0	1	1	0	0
AlF <sub>2</sub> <sup>+</sup>	11.120	0	0	0	0	1	2	0	0
AlF <sub>3</sub> <sup>0</sup>	15.000	0	0	0	0	1	3	0	0
AlF <sub>4</sub> <sup>-</sup>	18.000	0	0	0	0	1	4	0	0
AlF <sub>5</sub> <sup>2-</sup>	19.400	0	0	0	0	1	5	0	0
AlF <sub>6</sub> <sup>3-</sup>	19.800	0	0	0	0	1	6	0	0
AlOH <sup>2+</sup>	-5.260	-1	0	0	0	1	0	0	0
Al(OH) <sub>2</sub> <sup>+</sup>	-9.880	-2	0	0	0	1	0	0	0
Al(OH) <sub>3</sub> <sup>0</sup>	-15.520	-3	0	0	0	1	0	0	0
Al(OH) <sub>4</sub> <sup>-</sup>	-21.960	-4	0	0	0	1	0	0	0
Al <sub>2</sub> (OH) <sub>2</sub> <sup>6+</sup>	-7.480	-2	0	0	0	2	0	0	0
Al <sub>3</sub> (OH) <sub>4</sub> <sup>6+</sup>	-12.460	-4	0	0	0	3	0	0	0
F <sup>-</sup>	0.000	0	0	0	0	0	1	0	0
HF	2.930	1	0	0	0	0	1	0	0
HF <sub>2</sub> <sup>-</sup>	3.520	1	0	0	0	0	2	0	0
SO <sub>4</sub> <sup>2-</sup>	0.000	0	0	0	0	0	0	1	0
CO <sub>2</sub> <sup>(aq)</sup>	0.000	0	0	0	0	0	0	0	1
HCO <sub>3</sub> <sup>-</sup>	-6.040	-1	0	0	0	0	0	0	1
CO <sub>3</sub> <sup>2-</sup>	-15.580	-2	0	0	0	0	0	0	1
Cryolite	33.840	0	3	0	0	1	6	0	0
Fluorite	9.280	0	0	0	1	0	2	0	0
Selaite	7.300	0	0	1	0	0	2	0	0
Brucite	-16.670	-2	0	1	0	0	0	0	0
Nesquehonite	-11.370	-2	0	1	0	0	0	0	1
Hydromagnesite	-48.300	-8	0	4	0	0	0	0	3
Gibbsite	-8.400	-3	0	0	0	1	0	0	0
Gypsum	3.330	0	0	0	1	0	0	1	0
Calcite	-9.220	-2	0	0	1	0	0	0	1

In model calculations, concentrations ( $\text{mol dm}^{-3}$ ) of total calcium and fluoride were taken as those present in most samples from the wet scrubber, analyzed in the analytical laboratory of the factory. A guess of total aluminum concentration was arbitrarily chosen above solubility limit of gibbsite, because aluminum was not analyzed during waste treatment. Concentrations of total sodium, magnesium, sulfate and  $\log \text{CO}_2(\text{aq})$  were taken as those in natural seawater. Two imaginary experiments were designed with seven constant and one variable component. Results of the experiment, in which pH was a variable, are presented in Figure 1. Concentrations  $C_i$  in  $\text{mol dm}^{-3}$  of each species containing fluoride are presented in a logarithmic form and plotted versus pH. Solid phases, which precipitate at different pH values are presented with broken lines.

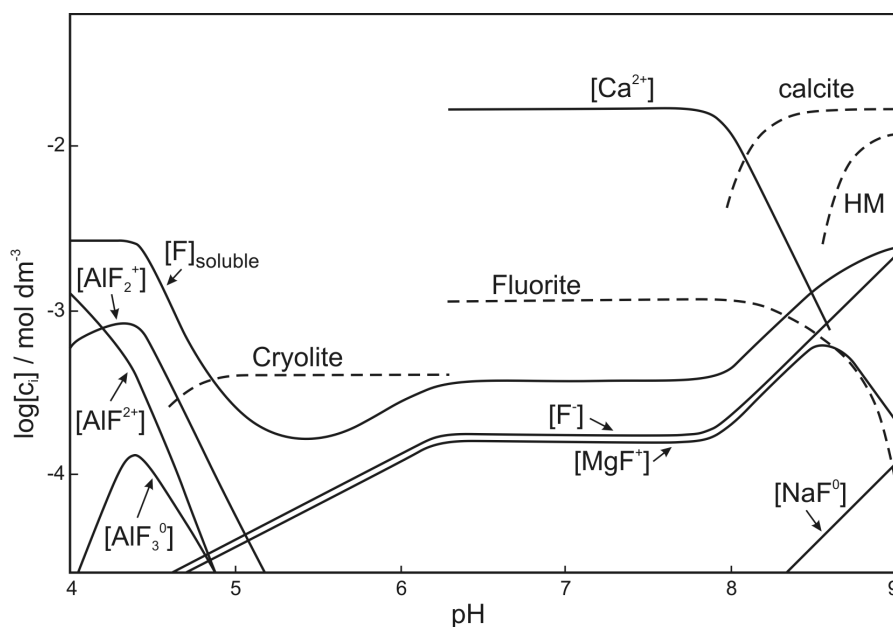


Fig. 1. Model calculation of heterogeneous equilibria in wet-scrubber.

Concentration of soluble fluoride is presented in equilibrium with various soluble complexes and solid phases from table 1, at variable pH. Total concentrations ( $\text{mol dm}^{-3}$ ) are:  $[\text{Na}] = 0.5000$ ,  $[\text{Mg}] = 0.0536$ ,  $[\text{Ca}] = 0.0175$ ,  $[\text{Al}] = 0.0200$ ,  $[\text{F}] = 0.0026$ ,  $[\text{SO}_4] = 0.0282$  and  $\log \text{CO}_2(\text{aq}) = -4.87$

From the model calculation one can expect in the technological process the formation of cryolite at  $\text{pH} < 6.3$ , of fluorite at  $\text{pH} 6.3\text{--}8$ , of calcite at  $\text{pH} > 8$  and of hydromagnesite at  $\text{pH} > 8.6$ . From the model calculation in Figure 1 one can conclude that the best removal of fluoride is at  $\text{pH} 5.4$ , when cryolite precipitates. According to Aluisse patent No. 22964, applicable for fresh water, the precipitation of cryolite with seawater in recirculation was not considered as possible removal mechanism for

fluoride. The model further shows in Figure 2 that concentrations of soluble aluminum is determined by solubility of gibbsite, which is partly dissolved in fluoride in acid solutions. Most labile Al at pH = 5.4 is bound to fluoride and the activity of toxic  $\text{Al}^{3+}$  is extremely low.

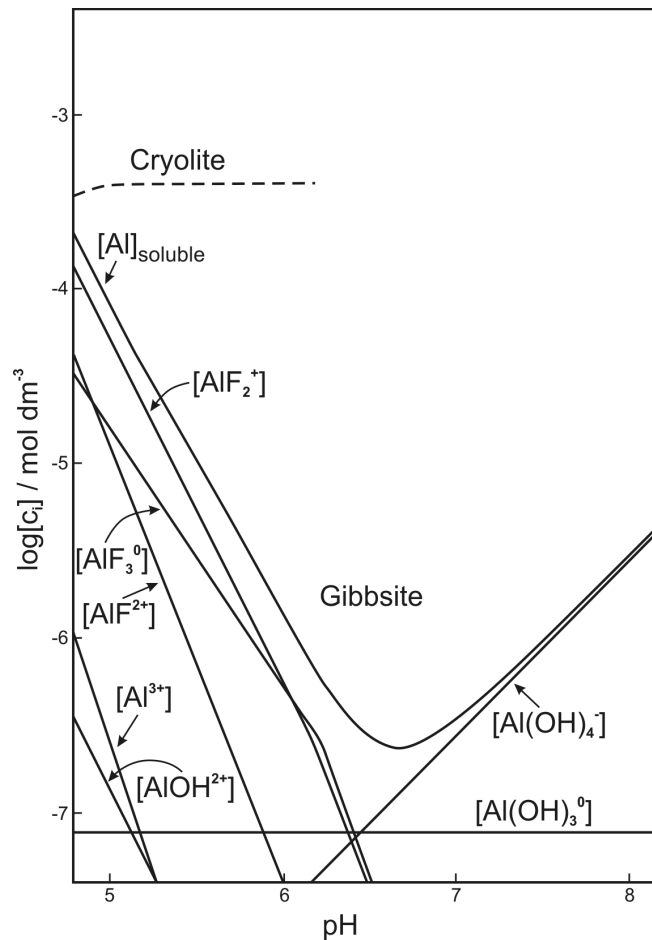


Fig. 2. Model calculation of total soluble aluminum, determined by solubility of gibbsite, in equilibrium with various soluble Al-complexes, at variable pH. Total concentrations ( $\text{mol dm}^{-3}$ ) are:  $[\text{Na}] = 0.5000$ ,  $[\text{Mg}] = 0.0536$ ,  $[\text{Ca}] = 0.0175$ ,  $[\text{Al}] = 0.0200$ ,  $[\text{F}] = 0.0026$ ,  $[\text{SO}_4] = 0.0282$  and  $\log \text{CO}_2(\text{aq}) = -4.87$

Similar aluminum speciation was described in aqueous extracts of forest soils in vicinity of aluminum smelter in NW Spain (GAGO et al. 2002). In the real technological process about 5–8% of regenerated water is discharged in the factory sewage system and then into the sea (pH = 8).

In the second imaginary experiment, total fluoride was a variable.

Model calculation presented in Figure 3 shows that in the regenerated/seawater mixture Al hydroxo species dominate. Thus, toxic effects of aluminum will be decreased. Similar conclusion was obtained when volcanic aerosol was mixed with seawater (FROGNER KOCKUM, 2006).

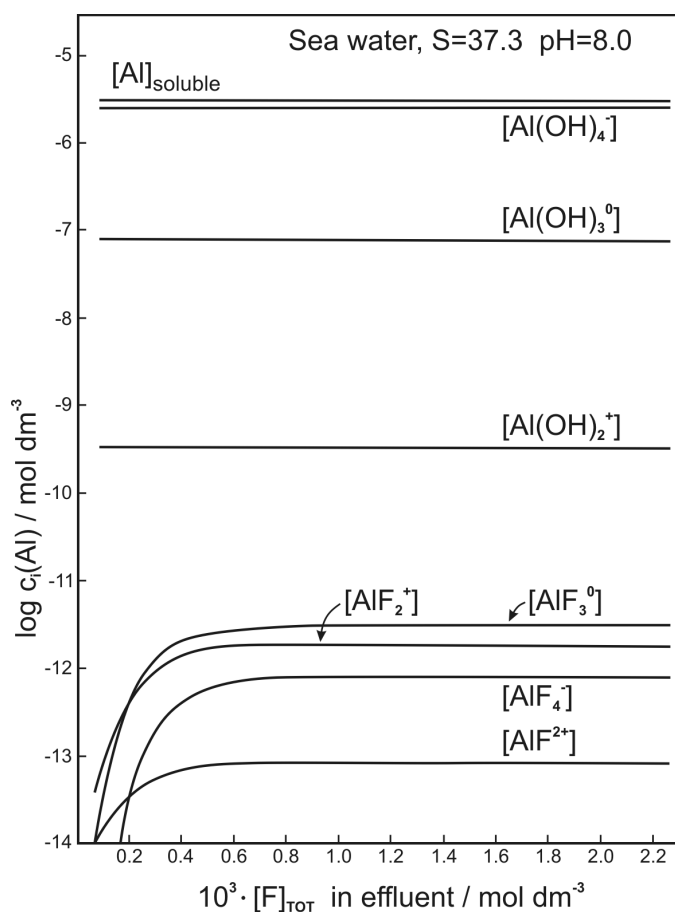


Fig. 3. Model calculation in which total fluoride in effluent is variable, shows aluminum complexes formed when waste water is discharged to seawater. Total concentrations ( $\text{mol dm}^{-3}$ ) are:  $[\text{Na}] = 0.5000$ ,  $[\text{Mg}] = 0.0536$ ,  $[\text{Ca}] = 0.0175$ ,  $[\text{Al}] = 0.0200$ ,  $[\text{SO}_4] = 0.0282$ ,  $\log \text{CO}_2(\text{aq}) = -4.87$  and  $\text{pH} = 8.0$

In Figure 4 are presented concentrations of predominant fluoride species at seawater conditions. Typical marine concentrations range from 0.063 to 0.079 mM (WHO, 2002). Model calculation shows that upon increasing of total fluoride in effluent, concentration of soluble fluoride in seawater can be almost ten folds compared to natural concentration. It could inhibit the growth of marine dinoflagelates, like *Amphidinium carteri* (ANTIA and KLUT, 1981).

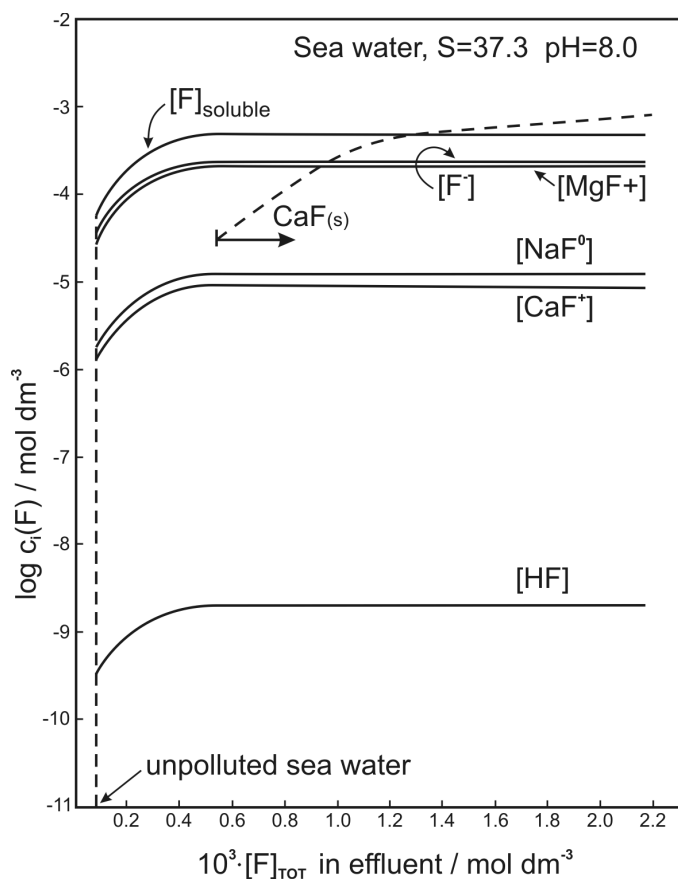


Fig. 4. Model calculation in which total fluoride in effluent is variable, shows fluoride species formed when waste water is discharged to seawater. Total concentrations ( $\text{mol dm}^{-3}$ ) are:  $[\text{Na}] = 0.5000$ ,  $[\text{Mg}] = 0.0536$ ,  $[\text{Ca}] = 0.0175$ ,  $[\text{Al}] = 0.0200$ ,  $[\text{SO}_4] = 0.0282$ ,  $\log \text{CO}_2(\text{aq}) = -4.87$  and  $\text{pH} = 8.0$

Model calculations were compared with the data for the real system. They were supported by X-ray diffraction pattern of a typical sludge formed at the main filter, on which  $\text{Al}_2\text{O}_3$ , cryolite, graphite and calcite were found. Nucleation and crystal growth of fluorite were not performed within available 90 minutes, what was an operational condition in the process and have continued outside of the main filter, instead in the precipitation tank. Solid phases ( $\text{Al}_2\text{O}_3$ , cryolite, calcite and fluorite) precipitated outside the main filter, at the filterbed of the wet scrubbing equipment. Pure fluorite was formed in the pipelines of the wet scrubbing equipment.

For comparison, X-ray diffraction pattern of sludge from commercial wet-scrubbing with freshwater in recirculation in Mostar (BiH), working properly, shows only  $\text{Al}_2\text{O}_3$  and fluorite. It was suggested that cryolite in the system with seawater in recirculation formed from aluminum fluoro complexes and sodium present in seawater.

### 3. CONCLUSIONS

Commercial wet-scrubbing equipment of Alusuisse type, originally designed for fresh water, does not work well with saline water in recirculation if precipitation of fluorite is the main removal mechanism of fluoride, due to its high solubility (influence of ionic strength and of magnesium).

Precipitation of less soluble cryolite at pH = 5.4 as an alternative can be recommended. Concentration of fluoride in regenerated water can be expected to be around  $10 \text{ mgdm}^{-3}$ .

Concentration of soluble aluminum, when waste water is discharged to the sea, does not present environmental danger, as all aluminum will be in the form of  $\text{Al}(\text{OH})_4^-$ .

Soluble fluoride will be in the form of  $\text{F}^-$  and  $\text{MgF}^+$ . Based on recent literature, discharged fluoride could inhibit growth of marine dinoflagellates and thus could have environmental consequences.

Chemical modeling gives very good picture about the fluoride and aluminum speciation in various stages of the system (pH varied from acid waste water to neutralized regenerated water) and can help to control the process in the real system.

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