

# MECHANISMS OF HF BONDING IN DRY SCRUBBER IN ALUMINIUM ELECTROLYSIS

## MEHANIZMI VEZAVE HF V ČISTILNEM SISTEMU PRI ELEKTROLIZI ALUMINIJA

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Modern dry scrubbers in electrolytic winning of aluminium operate with very high efficiency, typically above 99 %, and all but the fugitive fluoride losses are returned into electrolytic cell. The principle of purification of exhaust gases from electrolytic cells is adsorption of HF onto primary alumina in dry scrubber reactors, where gases from cells and flow of active (primary) alumina run into each other and react. It is very important how the reaction between gases and primary alumina takes place and which chemical mechanisms are taking part. Nevertheless, also industrial conditions are playing an important role in efficiency of the scrubbing reaction.

In references on dealing with related systems there can be found that most research was made to improve dry scrubbing systems and their efficiency, but not much was done to explain chemical mechanisms of fluoride bonding on active alumina that is essential for the cleaning process of exhaust gases. Chemical and micro-chemical analyses enabled to determine the fraction of bonded fluoride on the surface and in the interior of the fluorinated alumina grains. Also the correlation between the most efficient fluoride bonding on active alumina and real industrial conditions was determined.

**Key words:** chemical adsorption, HF-alumina interaction, fluoride bonding mechanism, EDS, dry scrubber

Večina čistilnih naprav pri proizvodnji primarnega aluminija ima učinkovitost večjo od 99 % in ves ujeti fluor se vrača v proces elektrolize. Čiščenje plinov HF iz elektroliznih celic deluje po principu vezave fluora na primarno glinico, ki se dozira v reaktor čistilne naprave, skozi katero tečejo plini. Zato je zelo pomembno, kako poteka vezava fluora na aktivno glinico in kakšni so najugodnejši pogoji za to.

V prejšnjih raziskavah je bilo veliko narejeno na področju učinkovitosti čistilnih sistemov, mehanizmi vezave fluora na aktivno glinico pa še niso bili podrobno raziskani. S kemijsko in EDS-analizo elementov smo ugotovili delež vezanega fluora na površini in v notranjosti zrn glinice. Poiskali smo povezavo med učinkovitostjo mehanizma kemijske vezave fluora na aktivno glinico in industrijskimi pogoji, pri katerih poteka čiščenje plinov, ki nastajajo med procesom elektrolize.

**Ključne besede:** kemijska adsorpcija, interakcija glinica-HF, mehanizmi vezave fluora, EDS, čistilni sistem

## 1 INTRODUCTION

Aluminium is one of the most important and widely used metals in industry and in everyday life in modern world, also. Pure aluminium is extracted by electrolysis of alumina ( $\text{Al}_2\text{O}_3$ ) prepared from bauxite. Primary aluminium is extracted from alumina with electrolytic process according to the  $2 \text{Al}_2\text{O}_3 + 3 \text{C}_{(\text{graphite})} \rightarrow 4 \text{Al} + 3 \text{CO}_2(\text{g})$  reaction. The process, with additives of cryolite,  $\text{AlF}_3$ ,  $\text{CaF}_2$  etc. into electrolyte, proceeds at temperatures below 1000 °C and at constant DC, most frequently 180 kA to 190 kA. Electrolytic cells are connected in series in order to keep constant electrical current in all the cells according to the Ohm's law.

Like in all the other industries, the major driving force in the primary aluminium industry over the last 20 years has been to produce more metal of better quality at lower costs. But production of greater quantities of metal results in significant increase of emissions. Hence, aluminium industry has developed unique industrial emission control and recovery systems. Fluoride emissions of the highest concern during the electrolytic process are those related to cryolite, ( $\text{Na}_3\text{AlF}_6$ ), chiolite,

( $\text{Na}_5\text{Al}_3\text{F}_{14}$ ), and atmolite, ( $\text{NaAlF}_4$ ) particulates, and to HF,  $\text{CF}_4$ , and  $\text{C}_2\text{F}_6$  gases<sup>1</sup>. The focus in this paper was directed to fluorides that were caught and bonded onto the alumina surface during the cleaning process.

Minimizing the fluoride emission in aluminium electrolytic cells has many positive effects; reduction of local and global environmental impacts of the process, improved working environment as well as economic effects and advantages in cell operation.

Efficiency of removal of fluorides from flue gases in modern dry scrubbing systems is now higher than 99 %, and fluoride emissions from smelters are typically close to 0.5 kg F/ton Al<sup>2,3</sup>. Nevertheless, further reduction of fluoride losses through emissions can lead to chemically more stable electrolyte and the level of fugitive fluoride emissions (emissions through the pot-room roof) is thus reduced, too. Fugitive emissions are estimated to be 4–5 times higher than the stack ones<sup>3</sup> of which up to 80 % may be represented by standard background emissions<sup>4-6</sup>.

In the past there have been some significant but limited studies on exact contributions of various sources

to the total fluoride emissions from cells.<sup>7,8</sup> In 1963 Henry<sup>7</sup> measured the influence of a number of variables in 10 kA experimental aluminium reduction cells on particulate and gaseous emissions. In 1972 Grjotheim et al.<sup>8</sup> prepared a review of available data for careful assessment of contributions of important parameters. Mathematical models to predict total fluoride losses were based on these data.<sup>9,10</sup> Over 30 years of research brought to improved efficiency of existent cleaning systems and to an examination of fluoride bonding mechanism on active alumina in dry scrubbing reactors.

Principle of the dry scrubbing system is simple. Scrubbers operate by direct extraction of flue gases from electrolytic cells into reactors where gases react with active alumina. At first, poisonous fluoride and HF are adsorbed from the gas mixture onto active alumina surface. Then gases with active alumina are transported through bag filters where solid sandy alumina with adsorbed gases is removed. The fluoride-enriched alumina is after filtration returned back into electrolytic process. Effectiveness of the cleaning process depends on details of the system and the process. Continuous sustaining "equal parts of alumina" in the process gas stream represents the opportunity of modern dry scrubbers to reduce fluoride emissions<sup>11</sup>.

Most of dry methods essentially consist of adsorption and chemisorption of HF from flue gases coming from aluminium cells by active alumina. Research projects mainly deal with various technologies and their improvements, rarely with exact mechanisms how HF is actually bonded onto raw alumina. Dando<sup>13</sup> made review of experiments that were performed from 1970 till now. However, it is well known that more than one mechanism of HF bonding onto primary alumina was proposed but none of existent hypotheses was undoubtedly confirmed with analyzing techniques, such as XRD, XPS, TGA, NMR etc., were used in various experiments and analyses.

Primary focus in previous examinations of alumina – HF systems was directed to various types of alumina and their capacity for HF adsorption. The results of these studies have been used to propose mechanisms of HF adsorption on alumina. Two basic models emerged:

- 1) physical adsorption of HF on the alumina surface (hydroxyl groups bonded to surface and/or physisorbed by water) to form alternating layers of HF and H<sub>2</sub>O<sup>14</sup>, or
- 2) direct chemisorption of HF at reactive sites on the alumina surface with formation of Na-F and/or Al-F species and with additional monolayer being physically adsorbed on top of chemisorbed layer<sup>15</sup>.

However, Wagener et. al. observed that alumina readily adsorbs HF under either hydrous or anhydrous conditions<sup>16</sup>. Some authors<sup>17,18</sup> believe that certain number of H<sub>2</sub>O molecules is needed to bind HF molecules to the surface of alumina. Others<sup>19</sup> believe that an Al<sub>2</sub>O<sub>3</sub>·*n*HF type of compound is formed which is trans-

formed into AlF<sub>3</sub> when heated above 300 °C. Several research works have shown that both mechanisms took place depending on process conditions. However, Wagener et. al.<sup>16</sup> concluded that H<sub>2</sub>O did not play an essential role in the alumina-HF interaction. HF was not only adsorbed physically, but it reacted with the exposed alumina surface to form an AlOF or Al(F,OH)<sub>3</sub> type of compound. If a large excess of HF has passed over alumina also AlF<sub>3</sub> was formed (and alumina particles became soft and friable).

Our research represented a more theoretical analysis of chemical bonding reactions. There exist two possibilities for HF bonding on primary alumina. The first one is the Lewis acid-base complex and the other one is the theory of hydrogen bonding. Lewis theory claims that acid can take electron pair and base can donate it. Al<sup>3+</sup> is by definition Lewis hard base and F is Lewis hard acid. Due to their chemical properties they form together most stable complex.

The other theory is the theory of hydrogen bonding. This theory was already well described in some papers<sup>14,20,21</sup>. Basically, it is a surface process where humidity is present. The reaction mechanism involves few steps: H<sub>2</sub>O adsorption forming an aqueous layer on the alumina surface; HF adsorption to acidify the surface water layer; dissolution of the alumina surface to form AlO<sub>2</sub><sup>-</sup> and AlOH<sup>2-</sup>, and precipitation of AlF<sub>x</sub>(OH)<sub>3-x</sub> · *n*H<sub>2</sub>O. The overall adsorption rate is controlled by the rate of the surface chemical reactions rather than by transport of fluid phase, mass transfer, and intraparticle diffusion.

## 2 EXPERIMENTAL WORK

Smelting grade alumina samples, both primary and reacted, were analyzed as-received from TALUM company, Kidričevo. The reacted alumina was prepared in industrial conditions. Primary alumina passed through the dry scrubber system where HF from electrolytic cells was bonded in controlled reactor conditions to vapour-phase HF. The temperature in the dry scrubber system was about 90 °C (363 K). The flow rate of air sucked from electrolytic cells into dry scrubber system was of 500 000 m<sup>3</sup>/h and all the air passed through six reactors into which new (primary) alumina was dosed.

Electron microscope was used to analyze bonding of fluoride onto primary alumina. Sandy alumina before and after the dry scrubbing was examined in scanning electron microscope (SEM – JEOL-JSM 6500F). There were made also micro-chemical analyses with energy dispersive X-ray spectroscopy (EDS Oxford Instruments INCA x-sight ENERGY 400). This technique is an analytical technique used for the analysis of a sample, limited to detection of about 0.1 % of chemical elements and to 1–3 μm of analyzed volume, depending on analyzed materials.

Cross-section micro-chemical EDS analyses of fluorinated alumina grains were made with larger grains to find differences in fluoride concentrations on the surface and in the interior of grains. Alumina sample was prepared as metallographic sample with grinding and polishing.

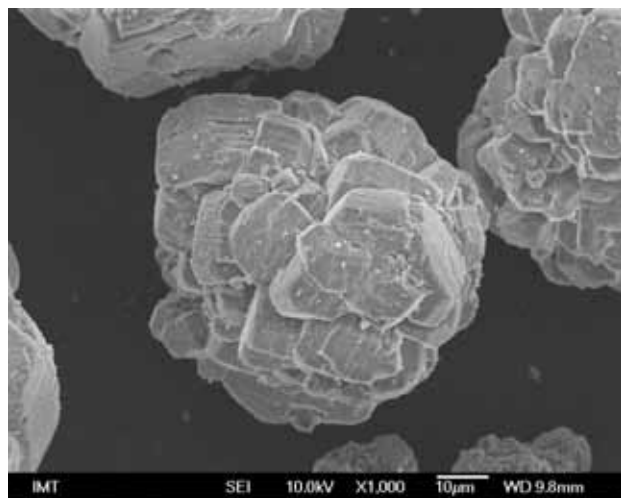
Chemical analyses of fluoride in the fluorinated alumina were made by standard Pechiney method with ion-selected electrode (Thermo ORION EA940, electrode: Thermo 9409 BM).

### 3 RESULTS AND DISCUSSION

Alumina grains had large surface area because of their morphology (**Figure 1**). Larger was the surface more of vapour-phase HF could be bonded onto alumina in reactors, and less HF escaped into environment through the chimney after dry scrubbers.

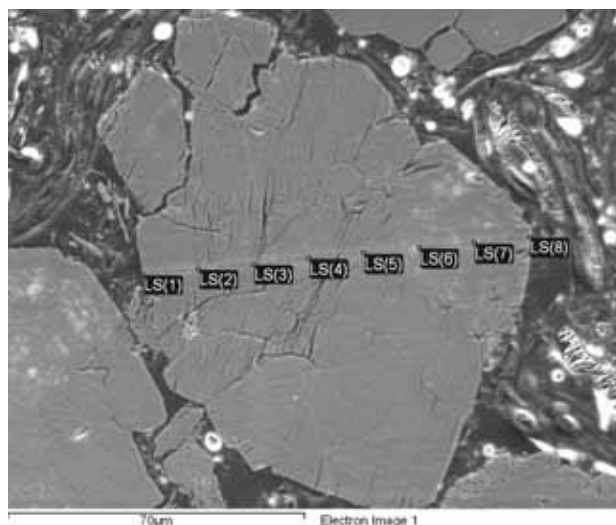
Some authors<sup>22</sup> used TGA, XRD and NMR and proposed that fluorides were adsorbed onto alumina in at least 2 ways, i.e. as mobile and as rigid species. Though no real structures were identified, it was hypothetically proposed that adsorbed fluoride existed as surface-bonded species or as fluoride incorporated into the alumina structure network (Al-F-Al bonds), respectively. We have used EDS technique to analyze fluorinated alumina grain to find differences in fluoride concentrations on the surface of alumina grain and in its interior. **Figure 2** shows fluorinated alumina grain with a line of discrete spots analyzed with the EDS.

Results of EDS analyses are presented in **Figure 3**. More fluoride was detected on the grain surface than in the interior. This indicated that adsorption as well as diffusion progressed from surface into interior. However, there was difference in intensity of fluoride bonding; greater amount of fluoride was found on the surface. Reduced oxygen content and increased fluoride content



**Figure 1:** SE image of grain of alumina

**Slika 1:** Slika sekundarnih elektronov z vrstičnim elektronskim mikroskopom zrna glinice



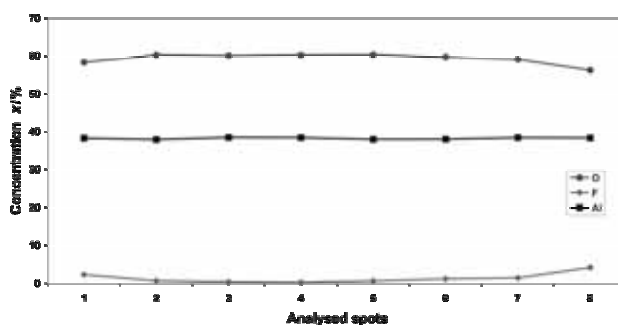
**Figure 2:** SE image of EDS discrete-point line analysis of fluorinated alumina

**Slika 2:** Slika sekundarnih elektronov z vrstičnim elektronskim mikroskopom zrna glinice z označenimi mesti linijske analize EDS fluoriranega zrna glinice

were determined on the grain surface. The ratio of elements detected with the EDS enabled to propose that  $\text{AlF}_3$  and  $\text{Al}_2\text{O}_3$  were the most probable compounds on the grain surface. Alumina represented substratum on top of which aluminium fluoride was bonded.

Results confirmed the theory of Lewis acid-base complex since by definition Lewis hard acid  $\text{Al}^{3+}$  and Lewis hard base  $\text{F}^-$  most likely formed strong complex. Reaction:  $\text{Al}_2\text{O}_3 + 6 \text{HF} \rightarrow 2 \text{AlF}_3 + 3 \text{H}_2\text{O}$  took place on the surface of alumina grains. Less oxygen and more fluoride was present there (**Figure 3**). On the other hand, alumina content was constant through the whole grain cross section.

However, the hydrogen bonding reaction was still taking place in the process. It depended on temperature in reactors that varied with the surrounding temperature and with the humidity level in reactors. Results of chemical analyses of fluoride in fluorinated alumina from dry scrubbers enabled to determine fluoride contents in different periods of year. In summer when the average day temperature of surrounding was between



**Figure 3:** EDS discrete-point line analysis of fluorinated alumina

**Slika 3:** Linijska analiza fluoriranega zrna glinice z EDS-tehniko

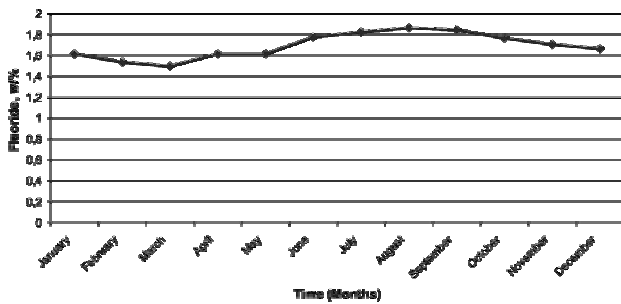


Figure 4: Chemical analyses of fluoride in fluorinated alumina  
Slika 4: Kemijska analiza fluora v fluorirani glinici

20 °C and 25 °C (month average; every-day temperature was measured at 2 p. m.) also temperature in reactors was higher, above 105 °C. In winter, temperature in reactors was only about 80 °C since the surrounding temperature was about 0 °C. When temperature in reactors was above the temperature of water evaporation more fluoride was bonded onto alumina. Thus in warmer months, from June to September, more fluoride was detected in the fluorinated alumina (Figure 4). In conditions when humidity was low more fluoride was bonded as  $\text{AlF}_3$  compound by the principle of Lewis acid-base complex. In colder months when the temperature in reactors did not exceed 85 °C, more  $\text{H}_2\text{O}$  was present and more fluoride was bonded by hydrogen bonding mechanism. However, relation between the humidity level and the fluoride bonding was obvious; higher temperature, less humidity, and more fluoride was loaded onto alumina. Molecules of water occupied the surface of alumina and thus less fluoride could be adsorbed. Mechanisms of possible bonding<sup>13</sup> of vapour-phase HF on new (primary) alumina are shown in Figure 5. One possibility was that fluoride was bonded directly on alumina (aluminium atoms) instead of on terminal hydroxyls (OH groups) (Figure 5 A). On the other hand, fluoride bridging to alumina by hydrogen bonding could exist too. The most efficient bonding of fluoride was achieved when fluoride was bonded as

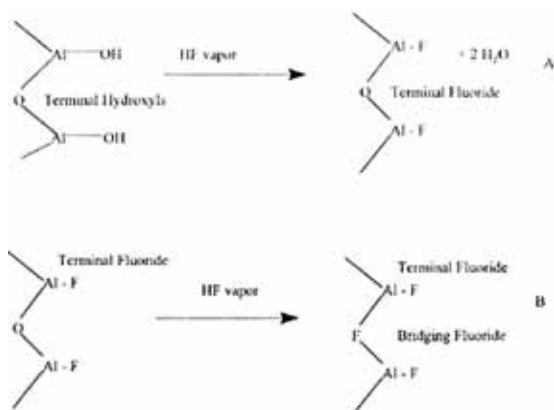


Figure 5: Scheme of mechanisms of vapour-phase HF bonding onto primary alumina<sup>13</sup>

Slika 5: Shema vezave HF na primarno glinico<sup>13</sup>

bridging fluoride and also as terminal fluoride (Figure 5 B).

Small amounts of fluoride were detected with the EDS analytical technique also in the interior of grains. Continuous adsorption of fluoride, in excess of surface monolayers, took place with diffusion of surface bonded fluor into the alumina lattice to displace oxygen in bridging sites. This could also occur by direct continuous reaction of alumina with vapour-phase fluoride to displace the bridging oxygen, followed by continuous diffusion of fluoride into alumina surface. Growth of aluminium fluoride on surface impeded but did not stop the continuous diffusion of fluor into the alumina lattice that could cause alumina decay in reactors due to limited contact time inside the reactor.

#### 4 CONCLUSIONS

Comparison of data obtained in this study with observations collected from previously published examinations of related systems strongly supports findings on the dry scrubber reactor chemistry and retention of fluoride. Significant conclusions can be made from chemical microanalyses of alumina grains and relations between the fluoride bonding and industrial conditions depending on external conditions.

Micro-chemical analyses confirmed the theory of fluoride bonding on the surface of alumina. A very small amount of fluoride was also found in the interior of grains, but diffusion gradient was not large since the layers of bonded fluoride on the surface have hindered penetration of fluor into the interior of grains.

Important finding of this paper was the correlation between chemical reaction of vapour-phase HF and primary alumina in dry scrubber reactors and the industrial temperature conditions. In the warmer season when average daily temperature was 20 °C to 25 °C, temperature in reactors increased to over 100 °C and chemical analyses confirmed higher contents of fluoride on reacted alumina. Less fluoride was detected in periods when the average daily temperature was below 5 °C and temperatures in reactors were around 80 °C. This temperature difference influenced the fluoride adsorption, because it was related to chemical reaction that took place on the surface of alumina grains. Less fluoride was bonded with hydrogen bridges and more of it was chemisorbed directly onto the surface as  $\text{AlF}_3$ .

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