Laboratory Study of a Technology for the Treatment of Aluminum Smelter Liquid Wastes with Alumina

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Abstract

The article presents the results of the first laboratory tests of the adsorption technology of sodium fluoride from waste waters and scrubbing solutions for aluminum production by metallurgical sand-type alumina. The technology allows to produce alumina saturated with fluoride salts. After drying of excess moisture, this may be used in the electrolytic production of aluminum, reducing the consumption of fresh cryolite and aluminum fluoride. During the tests, the maximum degree of extraction of sodium fluoride from scrubbing solutions was established as 92 %. The duration of mixing of the purified solutions with alumina was 45 minutes. From slurry field water, 87 % of sodium fluoride was extracted in the first minute of the experiment. The parallel adsorption of sodium sulfate with a recovery rate of 31 % for scrubbing solutions and 13 % for slurry field water was obtained. In addition, the optimal time of contact with alumina in the extraction of sodium fluoride from waste waters and scrubbing solutions should not exceed 3 minutes since, in this case, the degree of extraction of sodium sulfate (18-19 %) is minimal. The use of slurry field water for the adsorption process is more promising due to the stable chemical composition and more efficient extraction of sodium fluoride. Scrubbing solutions which were purified in this way are suitable for sodium sulfate extraction, and waste waters could be used in scrubbing solution production. This reduces the consumption of fresh water for these purposes.

Keywords: Sodium fluoride, fluorinated alumina, solutions, adsorption, soda.

1. Introduction

The usage of dry gas cleaning method in aluminum plants reduced the sodium fluoride content to 5–8 g/dm^3. The decreasing of the content limited the cryolite production. However, in the waste waters, a total of 4.5 thousand tons of sodium fluoride are contained, which it is desirable to return to aluminum production.

Currently, the following methods for purifying industrial wastewaters from fluoride are known:

- Chemical;
- Electrochemical;
- Adsorption / ion exchange;
- Membrane processes.

Chemical methods consist of adding to the solutions containing fluoride-ions chemical compounds that form insoluble precipitates with fluorine. As chemical reagents, generally calcium chloride, oxides of magnesium and calcium, milk of lime, aluminum salts are used. Chemical methods are widely used throughout the world because of their relative simplicity. The disadvantages of the methods are insufficient precipitation of sodium fluoride, about 74 – 77 % [1], and the need for chemicals and containers for their storage and preparation.

Membrane wastewater treatment technology is universal, allowing most of the dissolved impurities and solid particles to be removed from the water in a single stage. Reverse osmosis, nanofiltration, electrodialysis can be used to remove fluoride ions. Despite the high cleaning efficiency, about 99% [2, 3], the use of membrane methods in the aluminum industry is impractical because of the looped cycle of using scrubbing solutions. In addition, membrane cleaning methods are not of commercial interest due to the high cost of their implementation.

Electrochemical methods are divided into electrocoagulation and electrosorption. The former is based on the electrochemical dissolution of the electrode, followed by the formation of insoluble hydroxide, on the surface where fluoride ion adsorption occurs [4]. The process is carried out using soluble and insoluble electrodes (aluminum, iron, lead, titanium) [5]. During the electrosorption, the removal of fluoride is carried out by the adsorption of fluoride ions on the surface of the electrode. As an electrode, a column filled with activated alumina or carbon is generally used [6]. The disadvantages of electrochemical methods are associated with serious energy consumption and a fairly long duration of the processes, which casts doubt on the economic efficiency of their use in industrial plants.

Adsorption methods are among the most convenient, flexible and widely used for wastewater treatment processes due to the wide choice of adsorbents, their variability and availability: clay, bone or activated carbon, activated alumina, ion exchange resins. Technologically, the principle of adsorption is based on chemical or physical interaction of molecules of a substance (adsorbate) dissolved in a solution with a solid active surface of an adsorbent.

In the adsorption process, the interaction of the adsorbate with the surface of the adsorbent occurs at the interface liquid-solid in the presence of a solvent. The adsorption level will be determined by the surface functional groups. Upon contact of the adsorbent with water, the formation of hydroxyl ions (OH-) on the surface occurs, which is associated with the chemisorption of hydrolyzing water molecules.

The charge on the surface of the sorbent in this case is determined by the pH of the aqueous solution. Under acidic conditions, an excess of protons accumulates in the surface layer, which leads to the formation of a positively charged surface [7]:

$$\underset{\text{Low pH}}{XOH_2^+} \leftarrow XOH \rightarrow \underset{\text{High pH}}{XO^-} \quad (1)$$

The effectiveness of adsorption is influenced by various factors: the pH of the solutions to be purified, the concentration of the adsorbent and dissolved salts, the sorption capacity of the material, the temperature and pressure at which the process is carried out.

The use of clay materials is limited by the contact time of the adsorbent with the solution. The maximum efficiency of fluorine removal in the first 2 hours of contact will be 50 % and 94 % after 7 days of contact, which makes their use in industrial environment not economically justifiable [8]. Despite the low price of bone coal and its high efficiency in the treatment of wastewater from fluorine, in the order of 96 %, the use of this material in aluminum production is questioned, as there is a need to dispose of the product [9].

The disadvantages of using activated carbons include their strong dependence on the pH of the solution being purified [10] and the need to heat the solution to increase the adsorption capacity, which requires additional energy costs. In addition, in the future, there is a need to process the spent adsorbent, which requires additional material costs.

The efficiency of using alumina, as it is the case with other adsorbents, depends on the pH of the medium [11] and the sorption capacity of the material; but, the degree of purification of wastewater from fluorine can reach 97 % [12].

Today, one of the promising technologies for the extraction of sodium fluoride is adsorption by alumina. The technology allows to produce alumina saturated with fluoride salts. After drying of excess moisture, it can be used in the electrolytic production of aluminum, thus reducing the consumption of fresh cryolite and aluminum fluoride.

The purpose of this work is to study the process of extracting sodium fluoride from alumina from solutions of gas cleaning and waste waters of electrolytic aluminum production.

2. Trials on Sodium Fluoride Extraction Adsorption Technology

For laboratory trials, the solutions with compositions similar to the ones used in sodium sulfate extraction galvano-coagulation technology were tested [13,14].

Table 1. Chemical composition of tested solutions.

Content, g/dm^3			
NaF	Na_2SO_4	Na_2CO_3	$NaHCO_3$
Scrubbing solutions			
18.6	116.4	6.7	27.2
Waste waters			
13.1	88.0	11.5	18.0

For research, alumina with an average α-Al_2O_3 content of 15.36 wt.% and a granulometry of 28.29 % -45 μm and 7.65 % +150 μm was used [15]. For chemical composition analysis of solutions, the titrimetric analysis methods were applied; and for the analysis of solid residue, the X-ray fluorescence method was used. The sodium fluoride and sodium sulfate extraction degree from scrubbing solutions are presented in Figure 1.

The data presented in Figure 1 demonstrates the linear variation of sodium fluoride and sodium sulfate extraction degree from scrubbing solutions. The extraction degree is 67 and 13 % at the minimum experiment duration (1 min.), but 92 and 31 % at maximum duration (45 min.).

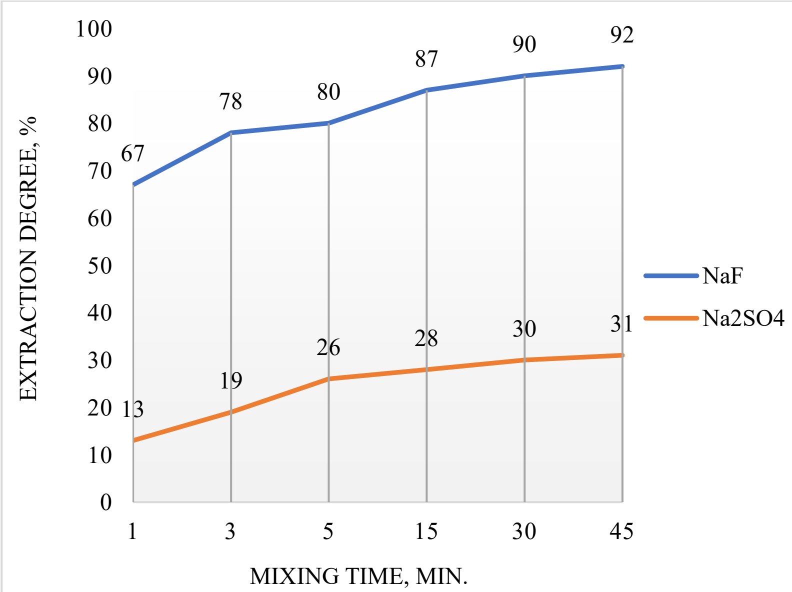

Figure 1. Dependence of the extraction degree of scrubbing solutions for sodium fluoride and sodium sulfate on the mixing time with alumina.

The sodium fluoride and sodium sulfate extraction degree from waste waters are presented in Figure 2. The data presented in Figure 2 shows that the highest sodium fluoride extraction degree of 87 % from waste waters is reached in the first minute of experiment, and it remains at the same with time. However, the sodium sulfate extraction degree increases from 17.7 to 22.5 %.

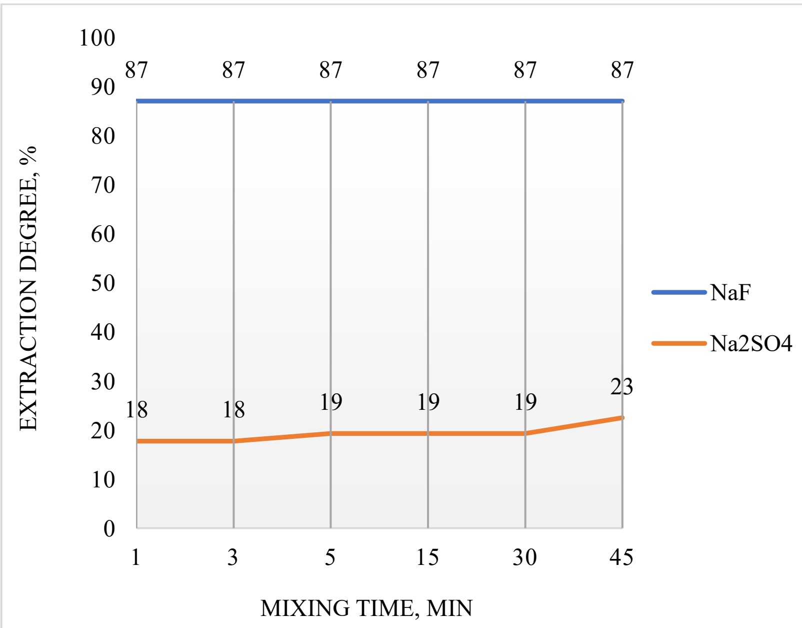

Figure 2. Dependence of the extraction degree of waste waters for sodium fluoride and sodium sulfate on the mixing time with alumina.

The amount of sodium fluoride and sodium sulfate adsorbed on alumina is 2.63 and 0.54 wt. %. The results of x-ray fluorescence analysis are presented in Table 2. The yield was 87 % for the total content of fluorine ion in solution. The loss of 4.1 % is because of residual alumina on the surface of the empty flask, and 8.9 % are the losses at the drying.

Table 2. The results of x-ray fluorescence analysis of dried alumina.

Sample	Content, wt.%					
	Al	Na	F	S	K	P
4/19 Ш	44.82±1,02	2.66±0,31	2.63±0,36	0.54±0,13	0.2±0,04	0.025

The increase of soda content in scrubbing solutions was observed during the experiment from 6.7 g/L to 18.9…43.0 g/L (2.3…6.7 times), in waste waters from 11.5 g/L to 13.6…22.0 g/L (1.1…1.9 times). At the same time, the bicarbonate content in scrubbing solutions decreased from 27.2 g/L to 2.8…13.3 g/L (2.1…9.6 times), in waste waters from 18.0 g/L to 1.4…15.6 g/L (1.1…12.9 times).

3. Conclusions

The technology tested under the laboratory conditions allows to extract more than 90 % of sodium fluoride from scrubbing solutions and waste waters for one extraction cycle. However, this extraction degree may be reached after a long mixing time (about 45 min.) of the treated solutions with alumina. Therefore, the mixing time less than 3 minutes is more promising, allowing to reach the sodium fluoride extraction degree of more than 80 %.

4. References

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