The research of sulfuric acidic recycling of aluminum industry fluorine-containing waste products

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Abstract

The article presents the method of recycling aluminum industry fluorine-containing waste products to produce hydrogen fluoride. We carried out the estimate of the thermodynamic parameters of sulfuric acidic recycling of fluorine-containing waste products. We considered the necessity of waste products preliminary oxidizing roast stage to reduce carbonic constituent due to the interaction between carbonic constituent blocks of the sulfuric acid and waste products. We also carried out the researches for kinetic characteristics and to determine the optimal conditions for the to recycle sulfuric acidic in the fluorine-containing waste products.

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Keywords: hydrogen fluoride; aluminum industry; fluorine-containing waste products; sulfuric acidic recycling; complex recycling; oxidizing roast; thermodynamic parameters; kinetics descriptions

1. Introduction

Here introduce the paper, and put a nomenclature if necessary, in a box with the same font size as the rest of the paper. The paragraphs continue from here and are only separated by headings, subheadings, images and formulae. The section headings are arranged by numbers, bold and 10 pt. Here follows further instructions for authors.

Primarily, aluminum industry fluorine-containing waste products are interesting as alternative source for hydrogen fluoride production. The primary raw material for HF production nowadays is still fluorite (flour-spar) – CaF₂. Forecast for the flour-spar ores resources in Russia are evaluated in 148.2 million tons1. But ore quality of

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Russian fluor-spar deposits is much lower than that abroad: average content of CaF₂ in Russian stocks – 38.9 % whereas the average content in the analogous stocks in China is higher than 60%. There are no large-scale deposits in Russia with high qualified ores and there is little amount of deposits where possibility to mine lump fluorite exists. The lack of quality fluor-spar production in the Russian Federation leads to the following problems:

- unprofitability of hydrogen fluorate production in Russia;
- dependency of the Russian industry on imported raw materials.

At the same time, aluminum industry bears fluorine at the rate of about 18 kg per 1 ton of producing metallic aluminum. So, about 400 thousand tons of solid fluorine-containing waste products are dumped into the mud fields every year. Such accumulation of dumps severely complicates ecological conditions. Besides fluorine, such waste products contain sufficient amount of other substances, which can be regenerated and returned to technological repartitions: carbon, alumina, cryolite, sodium sulfate, and carbonate. Therefore, the research on complex recycling technologies targeted at scientific bases and fluorine-containing waste products are not only of ecological but of large economic interests.

The electrostatic precipitator dust of aluminum producing electrolyzers from Irkutsk Aluminum Factory was selected for the researches among all kinds of fluorine-containing waste products. The phase composition of such dust is (% mass): Na₃AlF₆ (cryolite) – 25.08; Na₅Al₃F₁₄ (chiolite) – 4.73; Al₂O₃ – 19.53; C – 35.23; Na₂SO₄ – 13.31; Fe₂O₃ – 1.04; SiO₂ – 1.08.

2. Experimental Stage

The purpose of this research work is to determine the possibility of raw material change in HF production – fluor-spar to aluminum industry fluorine-containing waste products. To research the mechanism of sulfuric acid recycling for the aluminum industry fluorine-containing waste products, we carried out the thermodynamic calculation of possibility of sulphatization of the main components.

The calculation shows that reactions of cryolite and chiolite sulfuric acid decomposition are endothermic and demand added heat. These reactions passing probability to products forming side increases with temperature increase. The temperatures for the direct reactions to begin are 81°C (for cryolite) and 236°C (for chiolite). Interactions of aluminum oxide, sodium sulfate and iron (III) oxide with sulfuric acid are exothermic and pass with heat emission to products forming side at room temperature.

To estimate the optimal time and temperature of reaction mixture interaction in static conditions, we carried out the kinetic experiment. This experiment has been carried out by continuously weighing the reacting mixture with automatic mass registration. The interaction degree has been determined by mass loss, which has been stipulated by formation of gaseous hydrogen fluoride and water. Sulfuric acid 98% (based on stoichiometric quantity) was used for the experiment mixture consisting of 1 g fluorine-containing waste products and 2.7 g.

The experiment results show that the degree of interaction of the mineral constituent is only 15-20%. After the analysis of additional literature, we made a data assumption that the low interaction degree of fluorine-containing waste products mineral constituent is stipulated by the presence of carbon constituent superfluous amount, which blocks interaction between fluorine-containing components and leachant. The carbon envelops fluorine-containing particles blocking penetration of sulfuric acid to the interaction surface. Such structure of waste products forms as a result of condensation of flying fluorine-containing fallows in carbon developed surface during electrolytic aluminum production in electrolyzers dry and wet dust collecting systems. Moreover, carbonic dust with developed surface is an excellent adsorbent of liquid and gaseous substances. So, sulfuric acid and the produced hydrogen fluoride must be adsorbed by carbon. To move off the carbon and to activate the surface of fluorine-containing particles the stage of preliminary oxidizing roast has been used before sulfuric acid recycling.

To determine the effectiveness of oxidizing roast by removing the carbon constituent from fluorine-containing waste products, we carried out the thermogravimetric and differential thermal analysis. Fig. 1 presents the results of thermogravimetric and differential thermal analysis. Fig. 1 presents the results of thermogravimetric and differential thermal analysis. Fig. 1 presents the results of thermogravimetric and differential thermal analysis.

By gradually heating up the waste products we first remove the hygroscopic moisture (endoeffect at 100 °C). The following sample mass decrease at until 363 °C is the consequence of desorption of the gaseous impurities (CO, CO₂, HF, SO₂ etc.) from dust particles as well as the evaporation (and burning) of resinous substances inspissated on dust. The mass loss at the end of such processes is about 4 %. Exoeffect appearing at the temperature range of 360-
750 °C is the consequence of intensive burning of carbon. The mass loss in this case is about 26 %. The endoeffect at 496 °C is caused by cryolite polymorphous transformation process. Over the range of 750-1200 °C the mass loss and the endoeffect are caused by pyrohydrolysis of the fluorine-containing components (cryolite and chiolite) of the waste products. The mass decrease by pyrohydrolysis is about 11 %. The maximum total mass loss in the oxidizing roast (till 750 °C) of aluminum industry waste products is 30-35 %. The liquid phase formation (melting of mineral constituent) doesn’t appear in researching range of temperatures (till 1200 °C). That is explained by absence of corresponding endothermic effect of the phase transformation.

To determine if the carbon constituent is completely removed at different temperatures, we carried out the following experiments. We placed the waste on pallet (layer no thicker than 1cm), then put the pallet into a muffle furnace where the roast has been carried out at the temperature range of 400-900 °C with the step of 50 °C; the roast time was 1 hour. The experiments results are presented as dependence of carbon maintenance in sample from roast temperature (Table 1).

Table 1 - Dependency of carbon maintenance in sample on the roast temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>300</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>550</th>
<th>600</th>
<th>650</th>
<th>700</th>
<th>750</th>
<th>800</th>
<th>850</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon maintenance, %</td>
<td>32.50</td>
<td>28.11</td>
<td>22.63</td>
<td>17.36</td>
<td>11.04</td>
<td>5.19</td>
<td>1.94</td>
<td>0.54</td>
<td>0.21</td>
<td>0.09</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The oxidizing roast is most effective at 850-900 °C: carbon content in samples at these temperatures is 0.04 %. However, according to the results of thermogravimetric researches, these temperature activate the collateral process of fluorine-containing components pyrohydrolysis: it triggers the loss of hydrogen fluoride. Therefore, to identify optimal temperature for the oxidizing roast, which would minimize carbon maintenance and maximize fluorine content while producing concentrate as the result of the roast at the same time, we carried out the experiments to determine fluorine content in concentrates.

We put the cryolite-alumina concentrate produced at specific roast temperatures (150 g) into the reactor; then added the sulfuric acid 98% with 10% surplus. Then reactor cover was set, reactor was heated on electric stove to 250 °C and the temperature was maintained stable for 3 hours; the temperature was measured by thermocouple and controlled by microprocessor-based temperature time-pattern controller. The constant mixture agitation in reactor was provided by electric motor with impeller mixer. The gases produced in the course of interaction of cryolite-alumina concentrate were moved to absorber, where they were absorbed by soda solution on fluorplastic chips-nozzle. The concentration of soda solution was 20 g/L, the solution volume – 5l. The continuous irrigation of reaction gases and nozzle was implemented by pump and sprinkler. The gases that weren’t absorbed moved through
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absorber and were utilized by ventilation system. The time of experiment was 4 hours total: 3 hours – heating to 250 °C and interaction; 1 hour – mixture cooling. Gases absorption was implemented throughout the entire experiment.

After the experiment we took a sample from absorber (sample volume – 50 ml) and determined the concentration of fluorine in solution by potentiometric method.

We carried out the researches of the samples produced at roast temperature range of 450-900 °C. The experiment results are presented in the form of dependencies of fluorine make on the oxidizing roast temperature (Fig. 2). The fluorine make value was determined as ratio of fluorine quantity established experimentally to the possible quantity estimated theoretically. The theoretically possible quantity means that fluorine quantity, which could be in sample in condition of absence of fluorine-containing components pyrohydrolysis process.

Fig. 2. The dependence of fluorine make from roast temperature

The fluorine make spike in the range of 450-700°C is the result of carbon constituent negative effect decreasing due to the decrease of carbon maintenance. The fluorine make decrease in the range of 700-900°C is the result of the activated pyrohydrolysis process and, consequently, the result of fluorine loss. The maximum fluorine make is observed after sulfuric acidic recycling of sample roasted at 700 °C. The make is 93.79 %.

Thus, according to the experimental data, the optimal temperature for fluorine-containing waste products oxidizing roast is 700 °C; the time of roast is 1 hour. The averaged phase composition of concentrate produced at 700 °C is (% mass): Na3AlF6 (cryolite) – 38.51; Na5Al3F14 (chiolite) – 7.26; Al2O3 – 29.99; C – 0.54; Na2SO4 – 20.44; Fe2O3 – 1.60; SiO2 – 1.66.

Fig. 3 presents the dependency of degree of interaction between cryolite-alumina concentrate and sulfuric acid on time.

Fig. 3. The dependency of the degree of concentrate interaction on time
This kind of dependency in the first 20 minutes linearizes at «reducing sphere» equation most6,7. This equation describes the model of “melting ball”, i.e. it can be used to describe processes of burning and dissolution, when particle of reacting substance losing mass is diminishing in its size. Usually the “reducing sphere” equation describes processes running in kinetic reaction area really well.

As a result of calculations and manipulations the apparent energy required for the process activation has been determined. The energy value is 38.258 kJ/mol. In addition, we formulated the equation of dependency of cryolite-alumina concentrate interaction degree on time:

\[ \alpha = 1 - (1 - 1.281 \cdot \exp\left(-\frac{38258}{RT}\right) \cdot t)^3 \]  

The concentrate sulfurization process takes course in transitional reacting area. The limiting stages of the process are both the chemical interaction of reactants and the diffusion of sulfuric acid from volume to fluorine-containing particle surface.

According to the experimental data carried out in static rate, we can conclude that to gain maximum degree of interaction of cryolite and to minimize the loss of acid, the process must be carried out at 240-250 °C for 2–3 hours with intensive agitation to renew cryolite reacting surface.

3. Summary

1. In the course of research we’ve established the possibility of fluorine-containing waste products use as raw material for hydrogen fluoride production.
2. As a result of thermodynamic calculation we have determined the possibility of waste products sulfatisation process running at temperature higher than 236 °C.
3. We’ve identified the necessity to introduce the waste products preliminary oxidizing roast stage. The optimal roast conditions have been detected: temperature – 700 °C, time – 1 hour, the sample layer thickness – 1cm.
4. As a result of kinetic research we determined the apparent energy necessary to activate the process. It is 38,258 kJ/mol. In addition, we formulated the equation of dependency of cryolite-alumina concentrate interaction degree on time. The concentrate sulfurization process takes course in transitional reacting area.
5. Kinetic research revealed that the optimal conditions for cryolite-alumina concentrate sulfuric acidic recycling: temperature – 250 °C (concentrate interaction degree is 97%), reacting time – 3 hours with intensive agitation to renew cryolite reacting surface.

References