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PHYSICS AND CHEMISTRY OF THE HYDROGEN FLUORIDE PRODUCTION PROCESS FROM FLUORINE-CONTAINING WASTE

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Abstract. The impact of the aluminum industry wastes on the environment is established. The resource efficient method of aluminum industry fluorine-containing wastes processing, which includes wastes oxidizing roasting to remove carbon component and the interaction of fluorine-containing particles with sulfuric acid in order to produce hydrogen fluoride, is considered. The economic and environmental effect of the proposed processing method is substantiated.

1. Introduction

Metallic aluminum world production is steadily increasing. At the end of 2015 it has increased by 15.5 % and has amounted to 56 134 tons, as compared to 48 578 tons in 2014 [1]. Russian aluminum industry is the most prosperous among national steel industries, and it is the one of the biggest world exporters of metallic aluminum. The national production capacity of primary aluminum is about 4.2 million tons per year. More than 75 % of Russian aluminum is produced by plants located in Krasnoyarsk, Irkutsk, Kemerovo, and Sverdlovsk regions.

Due to aluminum practical design characteristics and working properties, the use of metallic aluminum is increasing in all sectors of the global industry: mechanical engineering, aerospace engineering, packaging printing, shipbuilding, industrial and civil construction. Aluminum is without a rival because of its technical, technological, and economic parameters. However, the aluminum industry is characterized by significant amounts of pollutants fluxing into the environment [2].

Aluminum production loses about 18 kg of fluorine per produced metallic aluminum ton in the form of gaseous hydrogen fluoride (HF), electrofilter dust, gas purification slimes, skim flotation tailings, etc. [3].

According to the available data, the content of hydrogen fluoride in the air of a aluminum factory production building reaches nearly 0.3 mg/m^3. At the same time the maximum permissible concentration of HF in the air of the working area is 1 mg/m^3 [4].

The annual hydrogen fluoride concentration increase in cities producing metallic aluminum is as follows: Bratsk – 2-8 $\mu g/m^3$, Volgograd – 5 $\mu g/m^3$, Novokuznetsk – 5-6 $\mu g/m^3$, Pervouralsk – 6-10 $\mu g/m^3$.

It has been determined that the impact of fluorine compounds on vegetation is among the most toxic. Fluorine-containing substances pollute the atmosphere in the form of gaseous compounds (hydrogen fluoride) or the dust of fluorinated substances mainly because of the metallic aluminum production, fertilizers, glass, and fluoroorganic compounds [5].

Large-scale mapping of the Krasnoyarsk Aluminium Smelter zone (suburban area of Krasnoyarsk) has shown that the area of soils with extremely and highly hazardous contamination with fluorine of grasslands and pastures amounts to 8.1 thousand hectares or 25.7 % of the surveyed area [6].

Modern industrial production should combine the principles of resource efficiency and environmental safety, which implies the full recycled use of most reagents and the regulation of industrial emissions. Such term as "production waste" should not be present in the production vocabulary.

The so-called natural protective forest areas, mostly "dead" taiga, will extend for many hundreds of kilometers if decisive measures on the disposal of the aluminum industry waste are not taken.

The greatest harm is inflicted by solid production wastes, as the formation of liquid waste is minimal and the main portion of gaseous emissions is captured and neutralized on special gas-cleaning units comprising the steps of dry and wet cleaning of anode gases [7]. To solve this problem it is necessary to develop an effective method for processing of solid fluorine-containing wastes from the aluminum production.

The problem of waste management lies in the fact that there are no industrially implemented technologies of its processing. All wastes differ in their physical properties and chemical composition, and often require an individual approach in the selection of processing options. The main areas in the processing technology are: leaching, flotation, pyrohydrolysis, heat treatment.

2. Theoretical part

The concept of the proposed method consists in the use of solid fluorine-containing wastes of the aluminum industry as a raw material for production of HF. The schematic diagram of processing of the fluorine-containing wastes of the aluminum industry to produce hydrogen fluoride is shown in Fig. 1.

The main reactions in the production of HF are the interaction of sodium fluoroaluminates (Na_3AlF_6, $Na_5Al_3F_{14}$) with sulfuric acid:

$$2Na_3AlF_6+9H_2SO_4=12HF+6NaHSO_4+Al_2(SO_4)_3 \quad (1)$$

$$2Na_5Al_3F_{14}+19H_2SO_4=28HF+10NaHSO4+3Al_2(SO_4)_3\ Na_2SO_4+H_2SO_4+2NaHSO_4 \quad (2)$$

Sodium sulfate, present in slag as a result of capturing sulfur dioxide by soda solution in the wet gas cleaning system, also reacts with sulfuric acid to form sodium hydrosulfate:

$$Na_2SO_4+H_2SO_4=2NaHSO_4 \quad (3)$$

Aluminum and iron oxides are among main components in almost all types of wastes occurring in the aluminum production. Typically, oxides pass into a highly soluble sulfate form. The presence of silicon dioxide has a negative impact on the process of sulfuric acid decomposition of fluorine-containing wastes, because silicon dioxide interacts with the produced hydrogen fluoride and, thereby, affects the yield and the purity of HF. The pollution of production gasses by silicon tetrafluoride takes place:

$$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O \quad (4)$$

$$Fe_2O_3+3H_2SO_4=Fe_2(SO_4)_3+3H_2O \quad (5)$$

$$SiO_2+4HF=SiF_4+2H_2O \quad (6)$$

To investigate the possibility of the process of sulfuric acid decomposition of aluminum production wastes, an equilibrium thermodynamic calculation of the equilibrium of chemical reactions of slag components has been carried out using the Temkin – Schwartzman method. The results of thermodynamic calculations are presented in Table 1.

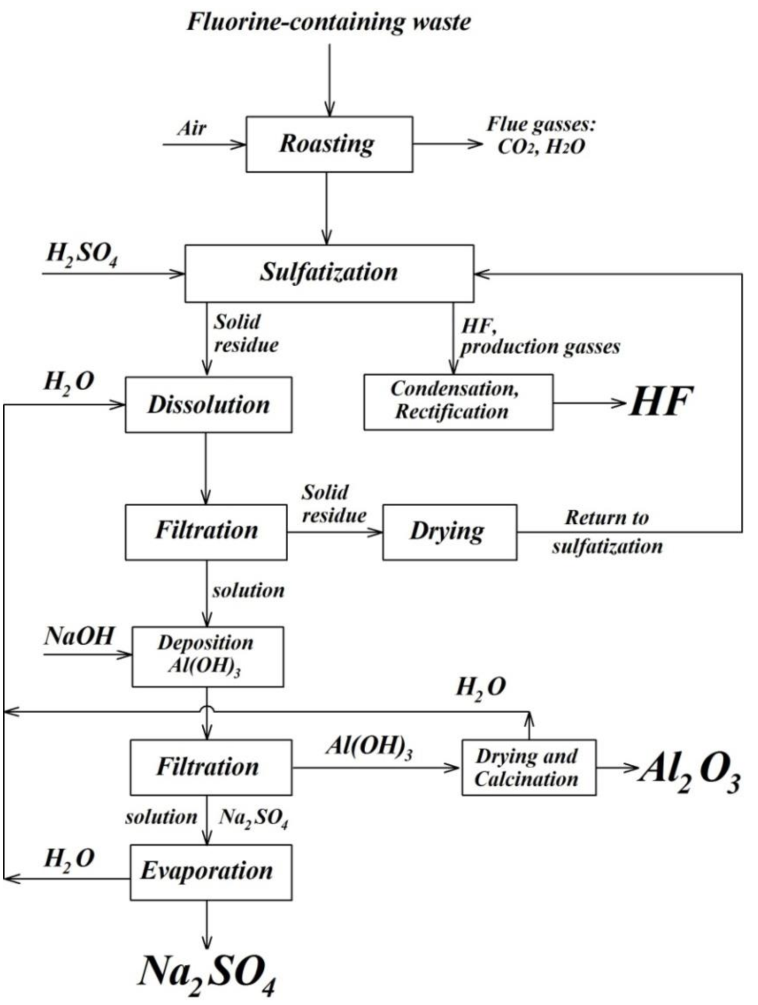

Figure 1. The schematic diagram of the fluorine-containing waste processing.

Reactions of the sulfuric acid decomposition of cryolite and hyolite are endothermic and require heat input. The probability of their occurrence towards the formation of reaction products increases with an increase in the temperature. The onset temperatures of direct reactions are 81 °C and 236 °C, respectively. The interaction reactions of aluminum oxide, sodium sulphate, and iron oxide (III) with sulfuric acid are exothermic and proceed with the evolution of heat towards the formation of reaction products even at room temperatures.

3 Practical Part

The kinetic experiment was carried out using the method of continuous weighing of the reaction mixture with an automatic mass registration at different process temperatures. The conversion degree was determined based on the weight loss which was caused by the formation of gaseous reaction products – hydrogen fluoride and water vapor. A chemically pure mixture (GOST 4204-77) consisting of 5 g of slag and 7.7 g of sulfuric acid, with regard to acid excess of 10% from the stoichiometrically required, was used in the course of the experiment. Based on the research findings, a dependency graph of the conversion degree on time was built (shown in Fig. 2).

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Table 1. Gibbs energies, equilibrium constants, and thermal effects of reactions of slag component sulphatization.

T, K	298	300	400	500	600
			$2Na_3AlF_6+9H_2SO_4=12HF+Al_2(SO_4)_3+6NaHSO_4$		
ΔH, KJ/mol	420.24	420.59	443.99	477.83	521.23
ΔG, KJ/mol	66.437	64.061	-57.999	-187.21	-324.14
K_P	$2.26\cdot10^{-12}$	$7.02\cdot10^{-12}$	$3.75\cdot10^{7}$	$3.61\cdot10^{19}$	$1.65\cdot10^{28}$
			$2Na_5Al_3F_{14}+19H_2SO_4=28HF+3Al_2(SO_4)_3+10NaHSO_4$		
ΔH, KJ/mol	1366.0	1366.3	1385.6	1419.0	1466.6
ΔG, KJ/mol	524.51	519.86	278.53	23.265	-243.77
K_P	$1.16\cdot10^{-92}$	$3.06\cdot10^{-91}$	$4.25\cdot10^{-37}$	$3.71\cdot10^{-3}$	$1.67\cdot10^{21}$
			$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O$		
ΔH, KJ/mol	-181.33	-181.35	-63.024	-76.261	-89.409
ΔG, KJ/mol	-159.71	-159.41	-153.67	-170.84	-185.94
K_P	$9.87\cdot10^{27}$	$5.69\cdot10^{27}$	$1.17\cdot10^{20}$	$7.04\cdot10^{17}$	$1.54\cdot10^{16}$
			$Na_2SO_4+H_2SO_4=2NaHSO_4$		
ΔH, KJ/mol	-68.880	-68.584	-51.894	-32.300	-10.390
ΔG, KJ/mol	-52.413	-52.303	-49.297	-50.863	-56.598
K_P	$1.54\cdot10^{9}$	$1.28\cdot10^{9}$	$2.74\cdot10^{6}$	$2.06\cdot10^{5}$	$8.46\cdot10^{4}$
			$Fe_2O_3+3H_2SO_4=Fe_2(SO_4)+3H_2O$		
ΔH, KJ/mol	-182.00	-182.05	-63.651	-73.809	-80.554
ΔG, KJ/mol	-161.75	-161.62	-163.16	-186.80	-208.70
K_P	$2.25\cdot10^{28}$	$1.38\cdot10^{28}$	$2.03\cdot10^{21}$	$3.27\cdot10^{19}$	$1.48\cdot10^{18}$

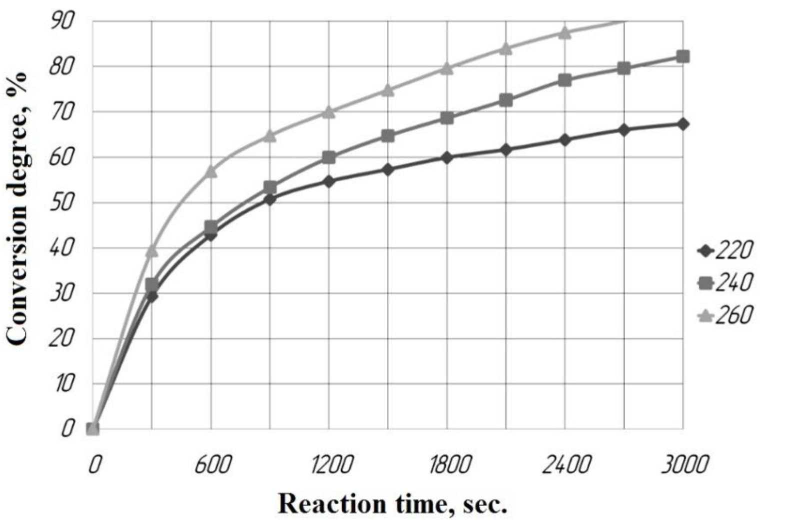

Figure 2. The dependence of the conversion degree on time.

This kind of dependence is mostly linearized under the Crank-Gistling-Braunstein equation [8]:

$$1-{}^{2}/_{3}\,\alpha-(1-\alpha)^{1/3}=kt$$

The values of the rate constant (k_0 = 6.05 c^{-1}) and the value of the activation energy (E = 50.2 KJ/mol) were determined based on the dependency built in coordinates of the Arrhenius equation. Thus, the general form of dependence is:

$$1 - {}^{2}/_{3}\,\alpha - (1-\alpha)^{1/3} = 6.5 \cdot \exp\left(\frac{-50258}{RT}\right) \cdot t$$

In the temperature range of 220-260 °C the activation energy of the process was 50.2 kJ/mol. The process proceeds in the outer-kinetic reaction area. The limiting stage of the process is the interaction of reagents. An increase in the temperature accelerates the process.

The proposed method for processing of aluminum industry wastes has both the environmental and the economic benefit. According to preliminary calculations, the use of fluorine-containing wastes will allow reducing the cost of the produced hydrogen fluoride by 20% due to the reduction in the cost of raw materials and the sale of popular on the market by-products – aluminum oxide and sodium sulfate [9].

4 Conclusions

1. The studies have proved the possibility of the use of fluorine-containing wastes as raw materials for the production of hydrogen fluoride.
2. The use of aluminum industry wastes as raw materials for the production of hydrogen fluoride will solve the problem of its processing, and will allow manufacturers of hydrogen fluoride to give up the procurement of costly raw materials – fluorspar.
3. The possibility of the sulfuric acid processing of fluorine-containing wastes from the aluminum production has been determined in the course of thermodynamic calculations. The value 220-260 °C has been selected as the operating temperature range.
4. The activation energy of the process – 50.2 kJ/mol and the rate constant k_0= 6.05 c^{-1} have been determined as a result of the kinetic study. The dependency equation of the reaction degree on time in the temperature range of 220 – 260 °C has been established. The process takes place in the outer-kinetic reaction area. The limiting stage of the process is the interaction of reagents. An increase in the temperature accelerates the process.
5. The use of fluorine-containing wastes will allow reducing the cost of the produced hydrogen fluoride by 20 % due to the reduction in the cost of raw materials and the sale of popular on the market by-products.

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