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EXTRACTION OF AMORPHOUS SILICA FROM WASTE DUST OF ELECTROWINNING OF ILMENITE CONCENTRATE

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Preliminary Note – Prethodno priopćenje

The paper presents research on the processing of waste dust from the electrical smelting of ilmenite concentrates with the removal of silicon from them by the fluoride method. The optimum conditions for fluorination of electric smelting dust were determined, at which the degree of silicon fluoride sublimation was 84,2 %. The silicon-containing sublime obtained in the presence of an ammonia agent has been studied. Based on the results of thermal analysis and studies on the effect of process duration the optimum pyrolysis modes that provide the separation of fluoride and silicon oxide: temperature 530 - 560 °C and duration of 60 - 80 min have been determined. The content of silicon oxide in the obtained product was 96,3 %.

Keywords: extration, amorphous silica, dust, phase analysis, X-ray research

INTRODUCTION

At Ust-Kamenogorsk Titanium-Magnesium Plant JSC (UKTMK), one-stage electric smelting of ilmenite concentrates to produce titanium slag and cast iron is applied; the furnace charge is supplied to smelt in a loose condition, accompanied by high dust entrainment. During melting of ilmenite concentrates at temperatures of 1600 - 1700 °C, silica contained in the furnace charge is sublimed and together with the gases is carried into the gas duct system; in scrubbers, it condenses as amorphous silica SiO2 and enters the thin bag filters. The high silica content provokes boiling of the melt and when titanium slag is chlorinated, the silica converts to titanium tetrachloride and worsens the grade of the titanium sponge.

Every year thin bag filter dust is deposited together with order solid waste in landfills. Under the influence of natural precipitations and wind, the waste is eroded and dispersed, polluting water and soil basins [1]. The enterprise has to pay huge fines to keep the stored waste.

Many works on waste processing of titanium-magnesium production are devoted to hydrometallurgical methods [2-5], research on dust processing includes works related to the improvement of operating conditions [6].

For the decomposition of silicon-containing phases and separation of silicon impurity from titanium, a study using high-temperature fluoroammonium processing, which can fit organically into the existing titanium-magnesium production, is of interest. It has been demonstrated, that the hydrodifluoride technologies of mineral raw material processing allow to extract all valuable components in the form of final oxides or fluorides with similar low-operational closed-loop schemes in similar apparatuses with high yield [7,8].

The work is devoted to the processing of electric smelting dust of ilmenite concentrates of "UKTMK" JSC with the removal of silicon from them and their return to the technological process, as well as the production of amorphous silica from fluorides.

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MATERIALS AND METHODS

In experiments were used: pure ammonium fluoride GOST 9546-72, 10 and 25 % ammonia, the dust of bag filters for electrical melting of ilmenite concentrates of UKTMK JSC (Republic of Kazakhstan).

The methodology of the experiment was as follows. A sample with thoroughly mixed ammonium bifluoride and dust in a certain ratio was transferred into an alundumina boat which was placed in a steel tube located in a horizontal tubular furnace. Argon was fed through the steel tube and the furnace was heated to a predetermined temperature within a certain time interval. At the end of the experiment the outgassed ammonium hexafluorosilicate was collected at the end of the steel tube and the gas-air mixture was captured in a flask with ammonia water. The ammonium hexafluorosilicate and the remaining sludge in the boat were subjected to ammonia alkaline hydrolysis.

After alkaline hydrolysis, the amorphous silica was pyrolyzed to distill the remaining fluorine. The components content was determined by chemical and X-ray fluorescence methods.

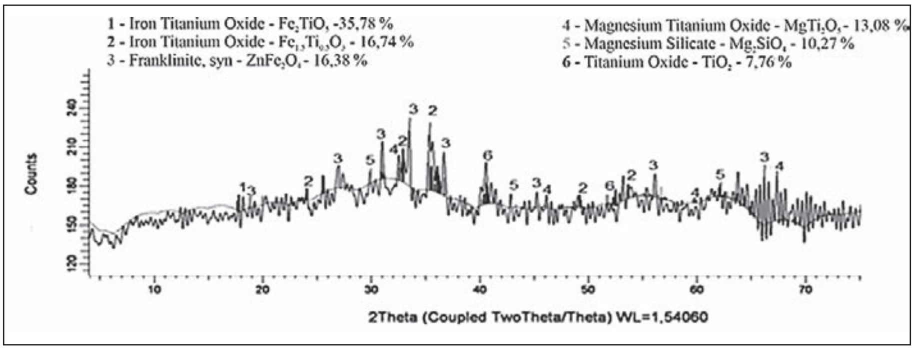

Figure 1 Diffractogram of electric smelting dust of ilmenite concentrate

Chemical analysis of the samples was performed on an atomic emission spectrometer Optima 8300 DV Rerkin Elmer (USA), flame photometer PFP7 “Jenway” (England). X-ray fluorescence analysis was performed on a Venus 200 spectrometer – by – PANalyticalB.V. (PANalyticalB.V., Holland), X-ray phase analysis was carried out on BRUKERD8 ADVANCE X-ray diffractometer (Germany). Thermal analysis was performed on a TG-DTA/DSC synchronous thermal analyzer with a Jupiter STA 449 F3 quadrupole mass spectrometer (Germany).

RESULTS AND DISCUSSION

The electric smelting dust was homogenized and dried with a moisture content of 50 % before physical and chemical analyses.

X-ray fluorescence and chemical analyses were carried out to determine the quantitative material composition of electric smelting dust of ilmenite concentrate. According to the results of these analyses the composition of electric smelting dust of ilmenite concentrate was determined / wt.%: 27,53 SiO_2, 34,29 TiO_2, 0,79 Cr_2O_3, 4,17 MnO, 18,19 FeO.

The results of X-ray phase analyses are shown in Figure 1 and indicate that the substance of the dust sample is in an X-ray amorphous state and the background of the diffractogram is high. It should be noted that iron in the dust is present in a trivalent state and the harmful impurity of silicon is connected with magnesium.

Experiments on fluorination of electric smelting dust of ilmenite concentrate were carried out on the installation shown in Figure 2.

As a result of this work, the optimum conditions for fluorination of electrowinning dust of ilmenite concentrate were found: temperature 260 °C, duration 6 hours, the mass ratio of dust to ammonium bifluoride was 1:1. Under these conditions, the degree of sublimation of silicon fluoride is 84,2 %.

According to X-ray phase analysis, the silica-containing substrate is represented by oxonium hexafluorosilicate and to a minor extent ammonium hexafluorosilicate (Table 1).

Ammonium and oxonium hexafluorosilicates are highly soluble in water at room temperature. For silicon oxide precipitation an alkali, e.g. ammonia, has to be acted upon by the reactions:

Figure 2 Installation for laboratory tests

$$(NH_4)SiF_6 + 4\ NH_4OH = SiO_2 + 6\ NH_4F + 2\ H_2O \qquad (1)$$

$$(H_3O)_2SiF_6 + 6\ NH_4OH = SiO_2 + 6\ NH_4F + 6\ H_2O \qquad (2)$$

Precipitation of amorphous silicon oxide according to thermodynamic calculations should be carried out in the temperature range of 25 – 100 °C [9]. In a solution containing hexafluorosilicate ion heated to 40 °C in the first case 10 % and in the second case 25 % ammonia solution with active stirring were added to pH 7,5 - 8.

In a course of investigation of the influence of ammonia solution concentration on the precipitation efficiency of amorphous silicon oxide, it was noted that a given pH value is obtained in 20 - 30 min. However, silicon oxide flake formation and precipitation require suspension residence time.

When using 25 % ammonia solution, about 80 min; and when using 10 % ammonia solution, 90 min (Figure 3).

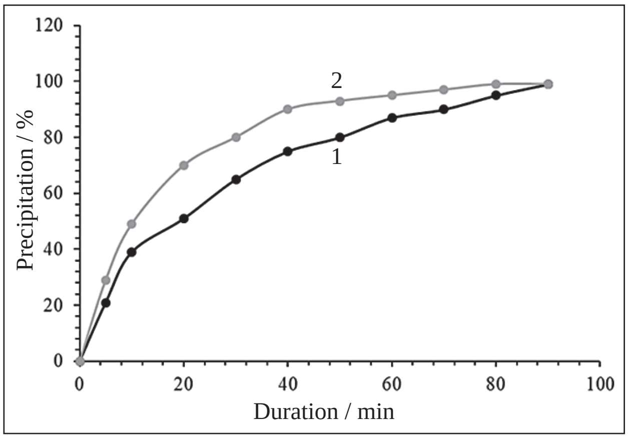

Figure 3 Dependence of amorphous silicon oxide precipitation on the duration of the process (1 – 10 % NH_4OH; 2 – 25 % NH_4OH).

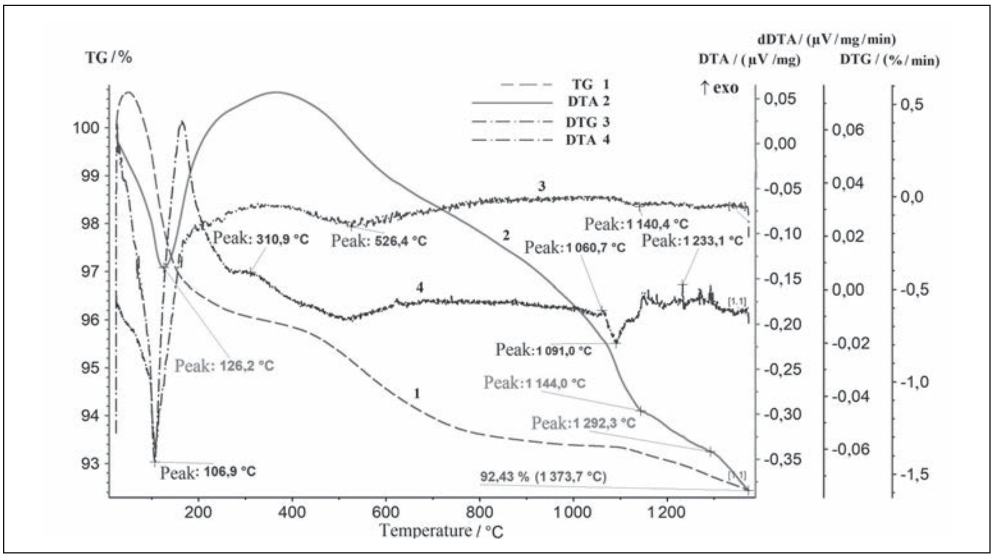

Figure 4 Derivatogram of amorphous silicon oxide (sample size 0,088 g

Table 1 **Phase analysis of silica-containing sublime (260 °C, 6 hours, dust: NH_4HF_2 = 1:0,9)**

Component	Formula	Content in the sample / %
Ammonium hexafluorosilicate	$(NH_4)_2SiF_6$	1,9
Oxonium hexafluorosilicate	$(H_3O)_2SiF_6$	98,1

The composition of the precipitated amorphous product is shown in Table 2.

The data in Table 2 show that the product does not contain any heavy metals or arsenic. The presence of ammonium fluoride is due to its absorption by amorphous particles and cannot be removed by washing the sludge with water. Ammonium fluoride is known to decompose if heated. In this connection, a thermal analysis of the obtained amorphous silicon oxide was carried out. The result is shown in Figure 4. The combination of exothermic effects with peaks at 310,9 °C and 1 060,7 °C on the DTA (Differential thermal analysis) curve is an indication of amorphous silica. The combination of endothermic effect with extremum at 126,2 °C and exothermic effect with a peak at 1 233,1 °C on the DTA curve characterizes the melting of FeF_2 impurity. The endothermic effect with the extremum at 1 144 °C on the DTA curve shows the release of previously adsorbed gases. The slight endothermic effect with the extremum at 1 292,3 °C on the DTA curve reflects the sublimation of aluminum fluoride impurity.

The analysis of the DTA curve showed that at temperature 526,4 °C the increase of sample weight loss is observed that is connected with hydrogen fluoride removal. Therefore the temperature of 530 - 560 °C is adopted for the pyrolysis of the product, the composition of which is shown in Table 3. The effect of duration was studied in the range of 20 - 80 min. The results are shown in Figure 5.

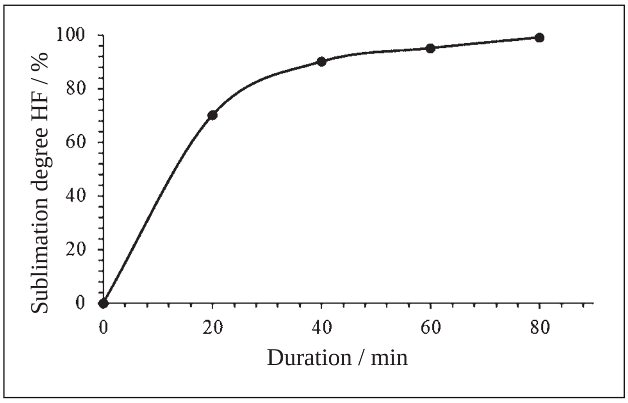

Figure 5 Effect of pyrolysis duration on the degree of hydrogen fluoride sublimation

The curve in Figure 5 shows that the pyrolysis process duration of 60 - 80 min provides the purification of silicon oxide from fluorine at 95 – 99 %.

Table 3 shows the composition of the amorphous silica obtained.

X-ray phase analysis of the obtained product showed amorphous silicon dioxide monophase. Thus, the optimum pyrolysis regime for the separation of fluoride and silicon

Table 2 **Contents of main components and impurities in the precipitated amorphous product / wt. %**

SiO_2	NH_4F	Fe	Cu	Zn	As	Sr	Pb	Others
81,6	12,9	0,045	0,005	0,025	0,014	0,003	0,017	5,4

Table 3 **Contents of main components and impurities in amorphous silica / wt. % (converted into oxides)**

SiO_2	F	Fe_2O_3	Al_2O_3	ZnO	CaO	TiO_2
96,3	n/o	0,14	0,16	0,02	0,03	0,15

oxide should be considered as 530 – 560 °C and a duration of 60 - 80 min. The investigations have shown the possibility of obtaining commercial amorphous silica from waste dust of electric smelting of ilmenite concentrate.

After alkaline hydrolysis of the residue in a boat, a titanium-containing product was obtained with the composition, wt. %:54,0 TiO_2, 32,0 Fe_2O_3, 7,6 MnO_2, 1,4 SiO_2, 1,5 Al_2O_3, 0,36 K_2O, 1,2 ZnO, 0,14 ZrO_2, 0,9 PbO.

The product can be returned to smelting together with ilmenite concentrate.

CONCLUSION

The process of silicon sublimation from fine specks of dust of electrical melting of ilmenite concentrates was studied. The optimum conditions for the fluorination of electrical smelting dust of ilmenite concentrate were determined: temperature 260 °C, duration 6 hours, the mass ratio of dust to ammonium hydrofluoride = 1:1. Under these conditions, the degree of silicon fluoride sublimation was 84,2 %.

The conditions of amorphous silica precipitation from the process duration at a concentration of 25 % ammonia were studied. An amorphous product with 81,6 % SiO_2, 12,9 % NH_4F was obtained.

Optimum pyrolysis conditions that provide the separation of fluoride and silicon oxide: temperature 530 - 560 °C and duration 60 - 80 min were determined. The content of silicon oxide in the product obtained was 96,3 %.

After alkaline hydrolysis of the cinder, a titanium-containing product containing 54,0 % TiO_2, 32,0 % Fe_2O_3 was obtained, which is returned to the technological process.

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Note: The responsible translator for English languages is Kurash Anastasia Alekseyevna, Almaty, Kazakhstan.