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Sulphuric acid decomposition of kaolin clays of the Chovdar Deposit (Azerbaijan)

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Abstract

Increased demand for aluminium around the world is promoting interest in developing alternative technologies for producing aluminium oxide (alumina) from non-bauxite sources, especially from clay. The sulphuric acid decomposition of kaolin clay of the Chovdar deposit (Azerbaijan) has been investigated with the aim of aluminium recovery using the aqueous solution of sulphuric acid as a leaching agent. Before leaching, kaolin clay was calcined at a temperature of 700–750 °C for 2 h. This process involves dehydration of kaolinite, which is the main mineralogical phase of kaolin, and its transformation into metakaolin, an amorphous Al-Si structure from which aluminium is readily leached. The optimal conditions for iron oxide and aluminium oxide leaching by sulphuric acid have been determined, and the degree of recovery was determined for these metals. It has been revealed that kaolin clay leaching to extract aluminium and iron oxides is achieved using kaolin clay samples calcined under the above-mentioned conditions, by treating them with 40 % sulphuric acid for 120 min at a temperature of 95 °C. The degree of Al_2O_3 and Fe_2O_3 extraction under these conditions is 95.6 and 85.2 %, respectively.

Keywords: kaolin clay, calcination, sulphuric acid, alumina, leaching

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INTRODUCTION

At present, much attention is attracted all over the world to aluminium-containing raw materials processing to obtain aluminium oxide (Al_2O_3, alumina), as well as the products for various applications [1, 2]. Clays are considered to be among the most widespread kinds of these materials. Clay deposits are rather widespread, mining causes no difficulties, and aluminium oxide content in them reaches 25–40 % [3, 4]. The use of clay as a primary raw material makes it possible to produce hundreds of thousands of metallurgical alumina per year, which fully covers the needs of the main metallurgical combines receiving metal aluminium [5].

Clays are the rocks containing such minerals as the oxides of aluminium, iron, and alkaline metals [6, 7]. One of the sources of obtaining aluminium oxide (alumina) is kaolin (or white clay), a rock composed mainly of the two-layered silicate mineral kaolinite with chemical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. The main contaminants of kaolin are quartz and mica (10–45 %), as well as ferric oxide (1–10 %) [8]. Kaolin may also contain large amounts of siallites, pyrophyllite, montmorillonite, dickite, illite and other minerals [9–11], which forms its difference from other kinds of raw materials used to produce alumina, and brings about definite difficulties for processing. However, the major difficulty in processing is kaolinite, possessing a certain structure which prevents easy recovery of aluminium oxide from the rock [10], and a substantial proportion of silicon-containing compounds present as admixtures [11].

Researchers propose a number of acid- and alkali-based hydrometallurgical processes to recover alumina from kaolin [12–18]. The use of the acid method provides integrated waste-free processing of the raw material and can turn out to be environmentally favourable for processing low-grade rocks [19]. The studies [17] have shown that the sulphuric acid method can be used for any kind of high-silica raw materials. The studies aimed at leaching the high-silica aluminium-containing raw material in sulphuric acid and physicochemical modelling if this process are not only of practical interest but also significant for scientific investigation in the area of chemistry and technology of aluminium.

The goal of the present work was to determine the optimal conditions for maximal sulphur acid recovery of the oxides of aluminium and iron into solution from kaolin clays of the Chovdar deposit.

EXPERIMENTAL

Object of investigation

The Chovdar deposit of kaolin clay is situated in the northern part of the Dashkesan District of Azerbaijan, not far from Chovdar settlement. The position of the Chovdar deposit on the map is shown in Fig. 1.

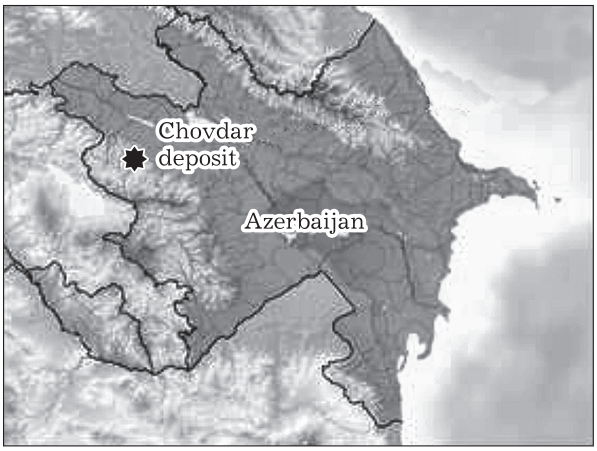


Fig. 1. Map showing the position of the Chovdar deposit of kaolinite clay (Azerbaijan) [20].

Methods of investigation

The phase composition of clay samples and their phase transformations were studied by X-ray diffraction (XRD) analysis with a D2 PHASER diffractometer (Bruker, Germany) using CuK_α-radiation (λ = 1.54 Å, nickel filter).

The chemical composition of kaolinite clays from the Chovdar deposit was studied by X-ray fluorescence method using an Universal S8 TiGER spectrometer (Bruker, Germany) with CuK_α-radiation (λ= 1.54 Å, nickel filter).

Experimental procedures

To provide maximum isolation of the useful components, the samples of kaolin clay were ground in a mortar to the particle size of 0.1 mm, and dried at a temperature of 110 °C. The necessity of clay sample calcination at 700–750 °C, leading to kaolinite dehydroxylation with its transformation into metakaolin has been previously demonstrated by us [21] and by other authors [22–24]. For this reason, kaolin clay was calcined at 700–750 °C for 2 h in a muffle furnace SNOL (Russia).

Investigation of the stages of clay leaching was carried out in a thermostatic reactor equipped with a mixer and a backflow condenser. Initial raw material was placed in the required proportions in the reactor and heated to a definite temperature. After the process was over, the pulp was filtered. The solid residue was washed, dried, and weighted. The oxides of aluminium and iron that passed into solution were determined using physicochemical methods of analysis (gravimetric, titrimetric).

RESULTS AND DISCUSSION

To determine the optimal conditions of efficient use of kaolin clays, it is necessary to study their phase and chemical composition, as well as structure phase transformations within the temperature range under investigation. Results of the chemical analysis of kaolinite clay from the Chovdar deposit before and after thermal treatment are presented in Table 1. One can see that in both cases, the major components of the samples are aluminium and silicon oxides.

Analysis of the diffraction patterns of initial sample has shown [21] that the material under investigation contains a substantial amount of the mineral kaolinite ($Al_2Si_2O_5(OH)_5$), as well as

TABLE 1

Chemical composition of kaolinite clay from the Chovdar deposit before and after thermal treatment

Experimental conditions	Component, wt%											
	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	MgO	K_2O	SO_3	CaO	TiO_2	V_2O_5	SrO	LC*
Before thermal treatment	25.67	62.97	0.23	0.08	0.01	0.12	1.02	0.15	0.40	0.06	0.45	8.84
After thermal treatment	27.60	67.71	0.25	0.09	0.11	0.13	1.10	0.16	0.43	0.07	0.48	1.86

* Loss on calcination.

quartz (SiO_2) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). Calcined sample does not contain reflections corresponding to kaolinite (Fig. 2, *a*); it is known [22] that under these conditions the mineral kaolinite is not transformed into metakaolin, which is more readily dissolved in acids.

The effect of the temperature of sample treatment (T = 25–105 °C), sulphuric acid concentration ($C_{H_2SO_4}$ = 20–60 %) and process duration (t = 30–150 min) on the yield of Al_2O_3 and Fe_2O_3 in solution during leaching the sample of kaolinite clay has been studied.

One of the main factors affecting the recovery of components is temperature. The effect of temperature on the degree of aluminium oxide and iron oxide recovery from calcined kaolin is shown in Fig. 3. One can see that the maximum recovery of the components is observed at a temperature of 95 °C, when the degree of $A1_2O_3$ and Fe_2O_3 recovery reaches 79.6 and 57.6 %, respectively.

Then the effect of the duration of kaolin clay decomposition by sulphuric acid on the degree of aluminium and iron oxide recovery was studied for constant process parameters: $C_{H_2SO_4}$ = 40 %; T = 95 °C. The results are presented in Fig. 4.

One can see that treatment duration has a strong effect on the degree of $A1_2O_3$ and Fe_2O_3 recovery. For instance, the degree of aluminium and iron oxide recovery from calcined clay increases with an increase in treatment time; for process duration equal to 120 min, it is 95.6 and 85.2 %, respectively. Further increase in process time did not have a significant effect on the degree of components recovery.

The effect of sulphuric acid concentration on ore decomposition was studied within the concentration range from 20 to 60 % (Fig. 5) at constant process parameters: T = 95 °C and t = 120 min.

With an increase in acid concentration from 20 to 60 %, the degree of components recovery increased to reach the maximum at 40 %. The maximum yield for Al_2O_3 and Fe_2O_3 was 95.6 and 85.2 %, respectively. With a further increase in acid concentration, the degree of components recovery from the ore decreases. With an increase in acid concentration, Al^{3+} ions hinder the diffusion of H^+ ions into the solid phase, which is most probably due to the destruction of kaolin structure [23].

So, the optimal conditions for leaching the oxides of aluminium and iron from the calcined sample are as follows: decomposition temperature is 95 °C; treatment time is 120 min; H_2SO_4 concentration is equal to 40 %.

Under the conditions determined as optimal, the concentration of Al^{3+} in solution is 13.96 g/L, and Fe^{3+} – 0.15 g/L. In addition, the solution from leaching contains the following ions as admixtures, g/L: Na^+ 0.126, K^+ 0.21, Ca^{2+} 0.023, Mg^{2+} 0.13, Ti^{4+} 0.036. After purification of the sulphate solution from iron (by reduction in solution), aluminium remaining in the solution is precipitated

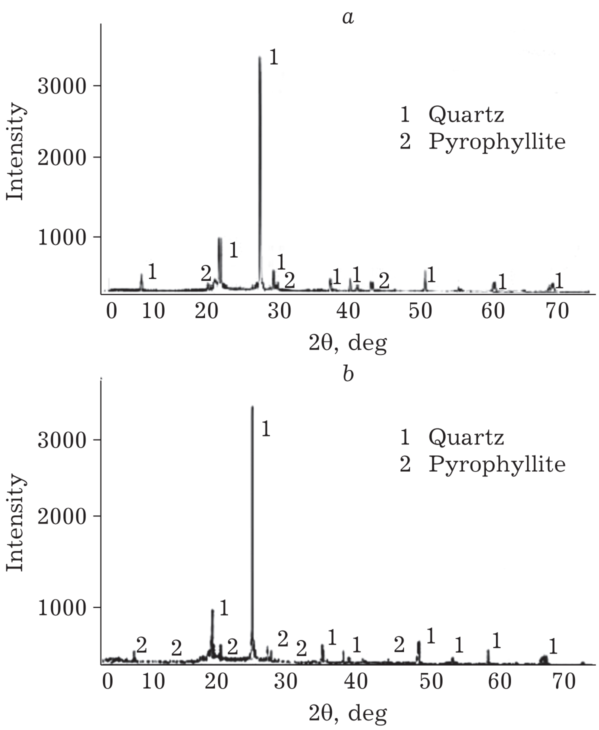


Fig. 2. Results of XRD analysis of the Chovdar kaolinite clay sample calcined at 750 °C (*a*) and the solid residue treated in sulphuric acid solution (*b*).

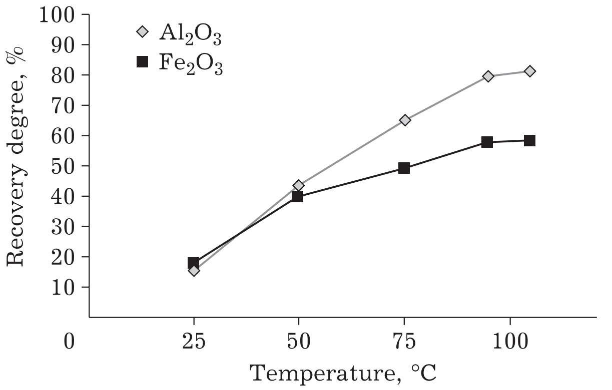


Fig. 3. Effect of the temperature of sulphuric acid decomposition of kaolin on the degree of aluminium and iron oxide recovery (t = 1 h, $C_{H_2SO_4}$ = 40 %, S/L = 1 : 5).

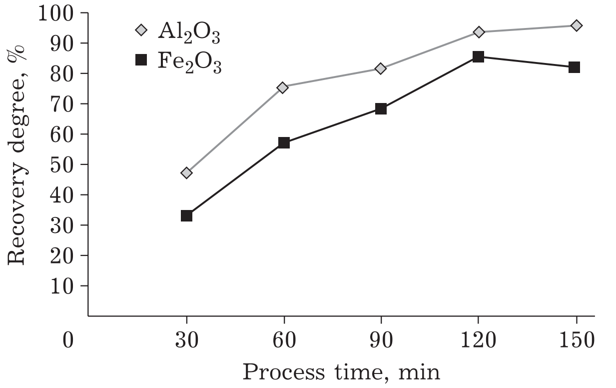


Fig. 4. Effect of process time on the degree of aluminium and iron oxide recovery ($C_{H_2SO_4}$ = 40 %, T = 95 °C, S/L = 1 : 5).

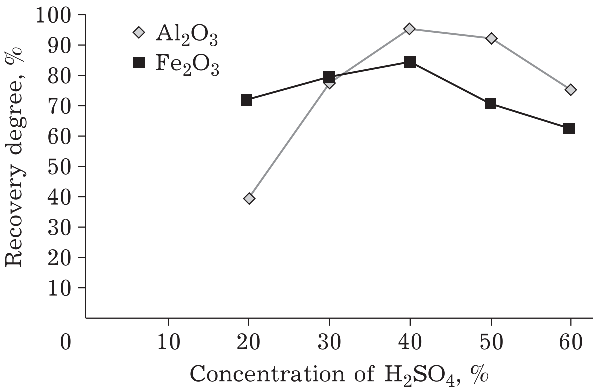


Fig. 5. Effect of sulphuric acid concentration on the degree of aluminium and iron oxide recovery from kaolin clay (t = 120 min, T = 95 °C, S/L = 1 : 5).

by ammonia in the form of $Al(OH)_3$, which is used to obtain alumina.

Results of the XRD analysis of solid residue after leaching are presented in Fig. 2, *b*. Comparison of the diffraction patterns recorded before and after leaching (see Fig. 2, *a* and *b*) shows that they are almost completely identical. This is associated with the amorphous structure of metakaolin, which is readily leached, so aluminium passes completely into solution. The chemical composition of the solid residue is, wt%: SiO_2 95.35, Al_2O_3 1.73, Fe_2O_3 0.052, K_2O 0.0014, V_2O_5 0.0092, SrO 0.682, CaO 0.204, TiO_2 0.569, SO_3 1.39. Correspondingly, sodium and magnesium completely pass into solution in the form of ions. The degree of K^+ recovery is 99 %, Ca^{2+} – 9 %, Ti^{4+} – 6.7 %. Silicon dioxide (silica), strontium and vanadium remain in the solid residue.

Chemical interaction between sulphuric acid and the major components of kaolin clay can be described by the following reactions:

$$Al_2O_3 \cdot 2SiO_2 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 2SiO_2\downarrow + 3H_2O \quad (1)$$

$$Fe_2O_3 \cdot 2SiO_2 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2SiO_2\downarrow + 3H_2O \quad (2)$$

$$CaO \cdot 2SiO_2 + H_2SO_4 \rightarrow CaSO_4 + 2SiO_2\downarrow + H_2O \quad (3)$$

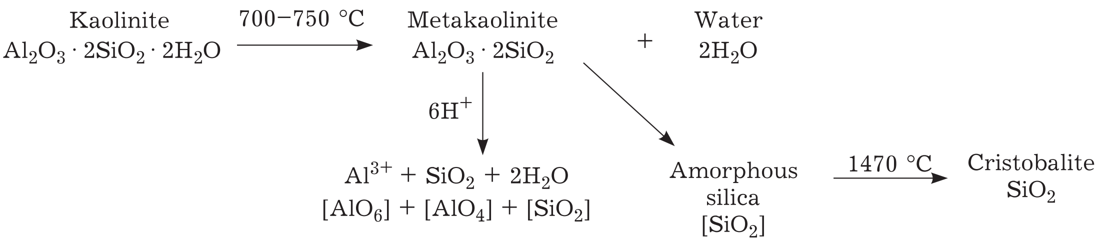
$$MgO \cdot 2SiO_2 + H_2SO_4 \rightarrow MgSO_4 + 2SiO_2\downarrow + H_2O \quad (4)$$

$$K_2O \cdot 2SiO_2 + H_2SO_4 \rightarrow K_2SO_4 + 2SiO_2\downarrow + H_2O \quad (5)$$

$$Na_2O \cdot 2SiO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2SiO_2\downarrow + H_2O \quad (6)$$

Aluminium leaching out from kaolinite during the sulphuric acid treatment of the products of thermal processing (calcination) of alumina-containing raw material can be represented schematically as follows (Scheme 1).

The solid residue in which silica can account for up to 90 wt% has a broad application range. For instance, silica can be used in the cement industry [25], in manufacturing ceramics and glass,



Scheme 1.

etc. [26]. Possible routes and conditions for processing admixture metals are the subject of further investigation.

CONCLUSION

1. Kaolin from the Chovdar deposit can be processed using the sulphuric acid method after calcination of initial clay at a temperature of 700–750 °C for 2 h.

2. The degree of Al_2O_3 and Fe_2O_3 recovery is 95.6 and 85.2 %, respectively, for sulphuric acid decomposition of kaolin clay under the following conditions: sulphuric acid concentration 40 %, process duration 120 min, process temperature 95 °C.

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