Application of Mechanochemical Treatment to Disintegration of Kaolinite with Sulphuric Acid

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Abstract

It is demonstrated that combined mechanochemical treatment (CMCT) of a mixture of kaolinite and sulphuric acid may be used for extracting aluminum from layered aluminosilicates. X-ray phase analysis showed that aluminum sulphate crystalline hydrate is formed in the products of CMCT of kaolinite. The effect of CMCT of kaolinites on the degree of aluminum extraction into the liquid phase has been studied in apparatuses with different levels of power supply. The highest degree of aluminum extraction was achieved in an AGO-2 centrifugal planetary mill.

INTRODUCTION

Substantial growth of aluminum consumption and the emergence of the problem of raw materials for aluminum production caused increased interest in acidic methods for processing low-grade bauxites and kaolinites with low contents of iron. The main products of the acidic processing techniques are aluminum salts widely used in chemical industry and in industrial water and sewage cleansing processes [1, 2]. A number of sulphuric-acid methods for processing kaolinites have been developed in Russia and abroad [3–5].

Kaolinite falls under the category of layered silicates. A peculiarity of its structure is the existence of two-layer packages, each containing silicon-oxygen tetrahedra and an octahedral layer composed of aluminum atoms, oxygen atoms, and hydroxyl groups. Networks of silicon-oxygen tetrahedra $[SiO_4]$ combined into six-membered rings are connected with the $[Al(O,OH)_6]$ octahedral layer on the free-top side of tetrahedra. The chemical composition of kaolinite corresponds to the formula $Al_4[(OH)_8Si_4O_{10}]$ [6–8]. The shielding of alumi-num cations by the silicon-oxygen network and the presence of Al–O–Si bonds results in low solubility of kaolinite in acids. Therefore, all methods for acidic processing of kaolinites involve a stage of activation. Activation of kaolinites may be performed in a variety of ways [3–5]: thermoactivation, thermoactivation combined with chemical activation, etc. The limitations of the thermal methods of activation are high temperature of the process, and the necessity to use special (heat- and acid-resistant) equipment.

Mechanical methods of kaolinite activation followed by kaolinite treatment with an acid hold much promise. However, in traditional grinding machines, complete extraction of aluminum may be achieved by prolonged (for at least 12–15 h) activation of kaolinite [9]. Application of higher stress planetary, centrifugal mills allows the activation time to be reduced to 10–15 min, but again treatment of activation products with concentrated H_2SO_4 with heating is needed for complete aluminum extraction [10]. Thus, it is of interest to improve the mechanochemical methods of disintegration of kaolinite.

TABLE 1

Chemical composition of kaolinite raw material from Puzlinskoye deposit (based on higher oxide forms)

Oxide	Content, mass %	Oxide	Content, mass %
Al_2O_3	37.2	MgO	0.17
SiO_2	43.4	CaO	0.28
TiO_2	2.50	Na_2O	0.16
Fe_2O_3	0.56	K_2O	0.03
FeO	0.04		

To solve this problem, combined mechanical treatment (CMCT) of kaolinite mixed with concentrated H_2SO_4 is suggested in this work. It is assumed that this type of mechanochemical treatment will increase the degree of extraction of aluminum due to the high activity of the "fresh" surface, resulting from destruction of kaolinite, and mechanically stimulated chemical interaction of an acid with kaolinite.

EXPERIMENTAL

The white variety of kaolinite from Puzlinskoye deposit (Komi Republic) was used as a feed stock. The kaolinite stocks of Puzlinskoye deposit originated by redeposition (secondary stock). The results of chemical analysis for the white species of kaolinite is presented in Table 1. The mass fraction of kaolinite in the raw material amounts to 37 %; the content of the iron and titanium oxide impurities is low. The results of particle size analysis of the raw material listed in Table 2 suggest that the clay fraction of kaolinite is represented by particles ≤1−5 mm in size.

Prior to CMCT, a kaolinite sample was mixed with a required quantity of H_2SO_4. Combined mechanochemical treatment of a mixture of kaolinite with acid was performed at first in a porcelain mortar and then in an SMBM triturating machine, in a LE-102/2 type vibration mill (ball diameter 10 mm, ball charges/sample = 20 : 1), and in an AGO-2 centrifugal-planetary mill [11] (ball diameter 8 mm, ball charge/sample = 20 : 1). When CMCT was performed with a deficiency of H_2SO_4, the products were extracted with a calculated volume of a 20 % acid solution with up to stoichiometric quantity of the acid. The extraction time was 30 min in all cases; the temperature of water and sulphuric acid solution was 25 °C, and the solid phase/fluid phase ratio = 1 : 2 (by mass). The solid and fluid phases were separated by filtering with a "blue tape" filter. The amount of aluminum extracted in the form of salt was calculated from the results of photometric measurement for the solution. Analysis was performed using aluminon on a KFK-3 photocolorimeter. X-ray phase analysis of the solid products of CMCT was accomplished on a DRON-3M diffractometer (CuK_α radiation).

RESULTS AND DISCUSSION

X-ray phase analysis (XRPA) of the starting kaolinite showed several groups of dif-

TABLE 2

Results of particle size analysis of a suspension of the raw material from Puzlinskoye deposit

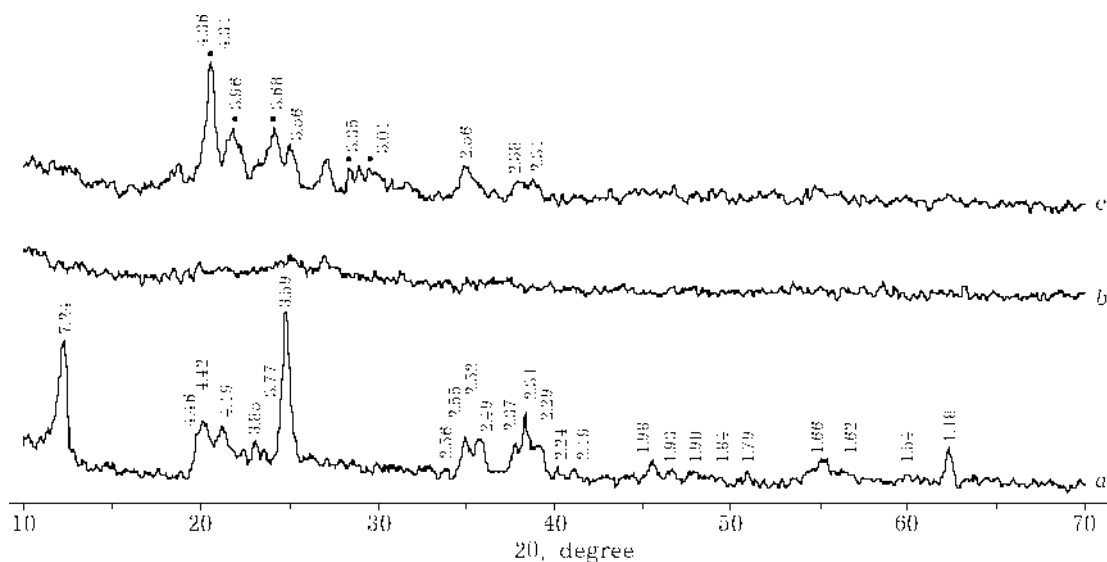| Sand		Silt		Clay	
Diameter, mm	Content, mass %	Diameter, mm	Content, mass %	Diameter, mm	Content, mass %
2.0−1.0	5.2	0.10−0.05	14.9	0.01−0.005	5.2
1.0−0.5	4.1	0.05−0.03	2.9	0.005−0.001	13.5
0.5−0.25	3.5	0.03−0.01	9.7	<0.001	38.9
0.25−0.10	1.2				

Fig. 1. Diffractograms of the kaolinite raw material (*a*), the product of mechanical treatment of kaolinite (*b*), and the product of CMCT of kaolinite (*c*). Activation conditions: *b* − activation time 6.5 min, acceleration 40 *g*; *c* − the same, content of acid is 100 mass %; • alunogen.

fraction lines on the X-ray diffractogram corresponding to a kaolinite structure (Fig. 1, *a*). The strong lines in the ranges of 2θ angles 12° and 25° are typical for the majority of kaolinite species; localization of lines in the ranges $\theta \approx 34-36^{\circ}$, $38-42^{\circ}$, $45-50^{\circ}$, and $54-60^{\circ}$ may vary for kaolinites from different deposits. Calculation of the Hinckley crystallinity index [8] from the main diffraction lines for a nonactivated kaolinite sample gave 1.16, which corresponds to a regular structured typomorphic species. According to the classification suggested by B. B. Zvyagin [8], which is based on the degree of perfection of a kaolinite structure, kaolinite from Puzlinskoye deposit used in this work belongs to type IV, *i.e.* kaolinite with a triclinic and pseudomonoclinic unit cell and with a strict *c* parameter. The degree of approximation of the unit cell to the triclinic or monoclinic cell was estimated from a conventional quantitative parameter, namely, the triclinicity factor K_t, which can vary from 1 (extreme triclinic case) to 0 (extreme monoclinic case). The calculated triclinic factor for kaolinite of Puzlinskoye deposit was, on the average, 0.85.

The diffractograms of the product of mechanical treatment and CMCT of kaolinite are presented in Fig. 1, *b* and *c*. The product obtained by mechanical treatment of kaolinite has a distinct amorphized structure. In all ranges of 2θ angles on the diffractogram, the kaolinite

lines are very weak and diffuse. The product of CMCT is characterized by the absence of kaolinite lines from the (2θ) angle ranges 12°, $45-50^{\circ}$, $54-60^{\circ}$ and by a significant decrease in intensity of kaolinite lines in the (2θ) ranges of angles 25°, $34-36^{\circ}$, $38-42^{\circ}$. At the same time, strong lines have appeared on the diffractogram of the product, indicating that an alunogen phase (aluminum sulphate crystalline hydrate) formed as a result of treatment.

The results of aluminum extraction from the product obtained by treatment of kaolinite by CMCT in devices differing strongly in the amount of mechanical energy applied to the substance (triturating machine, vibrating mill, centrifugal planetary mill) (treatment time 10 min, mass fraction of acid 25 % of the stoichiometric quantity) showed that the maximum yield is achieved in centrifugal planetary mills (Fig. 2). Aluminum sulfate is formed in reasonably short periods of time. Thus the relatively short treatment time in AGO-2 (2.5 min, 40 *g*) results in a high (65 %) degree of aluminum extraction in solution.

With a low degree of conversion of the starting kaolinite after treatment with H_2SO_4 in experimental conditions (1−2 %), it can be inferred that mechanochemical activation of kaolinite (KA) occurs at the first stage to form an active phase of the product (KA*), which then reacts with H_2SO_4. It was shown [12] that
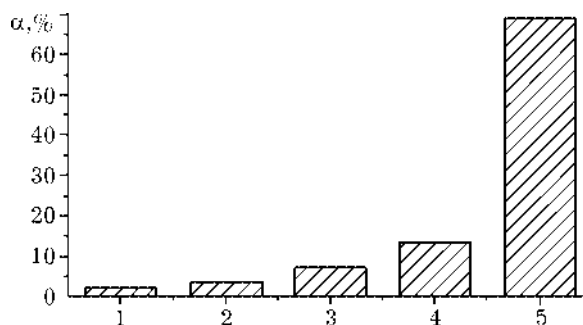
Fig. 2. Degree of aluminum extraction (based on aluminum oxide) into the fluid phase from crude kaolinite (1) and the products of CMCT of kaolinite obtained in various devices: porcelain mortar (2), vibrating mill (3), triturating machine (4), and AGO-2 centrifugal planetary mill (40 *g*) (5). Activation conditions: time − 10 min, content of acid − 25 mass %.

Al−O bond cleavage in the Al−O−Si fragment is the limiting stage, determining the solution rate of kaolinite in acids. Mechanical treatment leads to structural distortions in kaolinite, including cleavage of Al−O−Si bonds [10]. Therefore, one can assume that partial cleavage or weakening of these bonds during activation accelerates aluminum sulphate formation by reaction with sulphuric acid.

CONCLUSION

Thus, combined mechanochemical treatment of kaolinite with sulphuric acid followed by hydrochemical treatment increases the degree of aluminum extraction in the form of its sulphate, which is certainly of interest from the viewpoint of practical applications [13]. It seems that practical realization of this method is quite possible because the drums and balls are made of corrosion-resistant steel and are therefore stable in concentrated sulphuric acid.

REFERENCES

1 Yu. A. Lainer and V. A. Reznicheko, *Khim. tekhnologiya*, 2 (2000) 22.
2 Tekhnologiya koagulyantov, in K. V. Tkachev (Ed.), UNIKHIM, Khimiya, Leningrad, 1974.
3 A. K. Zapolskii, Sernokislotnaya pererabotka vysokokremnistogo alyuminiyevogo syr'ya, Nauk. dumka, Kiev, 1981.
4 A. Yu. Lainer, Kompleksnaya pererabotka alyuminiysoderzhashchego syr'ya kislotnymi sposobami, Nauka, Moscow, 1982.
5 V. I. Zakharov, V. T. Kalinnikov, V. A. Matveev and D. V. Maiorov, Khimiko-tekhnologicheskiye osnovy i razrabotka novykh napravleniy kompleksnoy pererabotki i ispolzovaniya shchelochnykh alyumosilikatov, vol. 1: Kratkaya kharakteristika syr'evoi bazy. Obzor sposobov pererabotki. Azotnokislotnye metody, Izd-vo KNTs, Apatity, 1995.
6 T. Penkalya, Ocherki kristallokhimii, Khimiya, Leningrad, 1974.
7 W. L. Bragg and G. F. Claringbull, Crystal Structures of Minerals, Bell, London, 1965.
8 Rentgenografiya osnovnykh tipov porodoobrazuyu-shchikh mineralov (sloistye karkasnye silikaty), in V. A. Frank-Kamenetskiy (Ed.), Nedra, Leningrad, 1983.
9 R. Schrader, H. Kutzer and B. Hoffmann, *Tonind. Zeit.*, 94 (1970) 410.
10 E. S. Lapteva, T. S. Yusupov and A. S. Berger, Phiziko-khimicheskiye izmeneniya sloistykh silikatov v protsesse mekhanicheskoy aktivatsii, Nauka, Novosibirsk, 1981.
11 Patent 975068 USSR, 1982.
12 J. Ganor, J. L. Mogollon and A. C. Lasaga, *Geochim. Cosm. Acta.*, 59 (1995) 1037.
13 Application No. 2003126945, Sposob pererabotki sloistykh alyumosilikatov (varianty), B. N. Dudkin, I. V. Loukhina, V. P. Isupov and E. G. Avvakumov, priority of 03.09.2003.