SOLUBILIZATION REACTION OF THE ALUMINA FROM KAOLIN BY SOLID STATE REACTION

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ABSTRACT

In this paper we have studied the solubilization of alumina from kaolin by solid state reaction between the kaolin and sodium bisulphate.

We prepared mechanical mixtures with a molar ratio of alumina to bisulphate of $1:6$. These mixtures were studied by thermogravimetry (TG) and differential thermal analysis (DTA). X-Ray diffraction was used to identify the residues of calcination at temperatures established on the TG and DTA curves. At $500\,^{\circ}$C the double salt aluminium sodium sulphate, $Na_3Al(SO_4)_3$, and α-quartz were formed. At this temperature the reaction of solubilization had finished.

The efficiency of the reaction is ≈ 70–80% expressed as alumina obtained/alumina contained in the kaolin.

INTRODUCTION

The world demand for aluminium grows constantly, while the reserves of bauxite, the only mineral from which alumina (the raw material for obtaining aluminium) is currently extracted, are limited. This situation encourages the search for new techniques of producing alumina from non-bauxite minerals, for example, kaolin and other forms of clay of which the world reserves are practically inexhaustible.

In this paper we give a method of solubilization of the alumina from kaolins by solid state reaction with sodium bisulphate. There are numerous earlier papers which describe procedures for extracting alumina from clays, using sodium bisulphate reagent, but satisfactory results have not been achieved [1–4]. In the majority of these procedures, the reagent is employed in concentrated solution, and is generally used in great excess.

In U.S. Patents [5,6] and in Spanish Patents [7–9] an industrial procedure is given for solubilization of the metallic elements of phyllosilicates by solid

state reaction between the phyllosilicate and sodium or potasium bisulphate or ammonium sulphate reagents. After the reaction the major metallic element is found in the form of a compound soluble in water that responds to the following general formulae: $M'_a M_b(SO_4)_c$ and $M'_2 M(SO_4)_2 \cdot x H_2O$, where M is a di- or trivalent cation; M' is a monovalent cation originating from the reagent; $a = 1, 2$ or 3; $b = 1$ or 2; $c = 2$ or 3.

EXPERIMENTAL

Products

Kaolin; $NaHSO_4 \cdot H_2O$ was from Merck, AR quality.

Preparation of samples

We prepared mechanical mixtures having a $1:6$ molar ratio of alumina to bisulphate. The grain size of the kaolin and sodium bisulphate used was > 0.062 mm and > 0.200 mm respectively.

The mixtures prepared were studied by thermogravimetry and differential thermal analysis, and X-ray powder diffraction was used to identify the residue obtained as a result of calcination at temperatures established in the TG and DTA curves.

The amount of alumina extracted from kaolin was measured in the following way. When the solid state reaction had finished, the residue consisted of an aluminium–sodium double salt, silica, and the rest of the unreacted kaolin. The double salt of aluminium was separated from the other components by dissolution in water, and aluminium in the aqueous solution was determined by complexometric titration using dithizone as indicator [10].

Apparatus

Thermogravimetry
A Mettler TA3000 thermobalance was used, at a heating rate of $10\,°C$ min^{-1}.

Differential thermal analysis
A home-made system incorporating a vertical furnace and a temperature regulation system, both from Adamel, was used, fitted with a differential chromel–alumel thermocouple. The heating rate was $5\,°C$ min^{-1}.

X-ray powder diffraction
A Philips PW 1130 diffractometer was used, with a Ni filter and Cu $K\alpha_1$ radiation.

RESULTS AND DISCUSSION

We achieved solubilization of the alumina from kaolin by a solid state reaction. The reaction that took place between the kaolin and the hydrated sodium bisulphate was as follows

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6NaHSO_4 \cdot H_2O \rightarrow 2Na_3Al(SO_4)_3 + SiO_2$$

A double salt of aluminium and sodium was obtained as a result of the reaction, together with silica and the rest of the unreacted kaolin. This double salt is not an alum; it is very soluble in cold water.

In Fig. 1 we give the TG and DTA curves of the kaolin–bisulphate 1 : 6 mixtures. The TG curve (Fig. 1.1) shows three steps; the first corresponds to the loss of the hydration water of the kaolin and the bisulphate, the second is due to decomposition of the bisulphate that has not reacted with the kaolin, and the third, between 680 and 1000°C, corresponds to the decomposition of the aluminium–sodium double salt formed.

The DTA curve (Fig. 1.2) exhibits three endothermic peaks that correspond to the three steps of the TG curve, as is shown by X-ray powder diffraction analysis, although in the DTA curve the temperatures of the peaks are lower than the temperatures of the steps of the TG curve.

In view of the thermal results, we used X-ray powder diffraction to study samples taken at predetermined points of the DTA and TG curves.

In Fig. 2 we give the X-ray diagrams corresponding to samples taken at 280°C, 500°C and 700°C.

The X-ray diagram for the sample taken at 280°C (Fig. 2a) indicates that the double salt $Na_3Al(SO_4)_3$ is beginning to form. The X-ray diagram for the sample taken at 500°C (Fig. 2b) corresponded to the double salt and an α-quartz. The reaction was complete. The X-ray diagram for the sample taken at 700°C (Fig. 2c) shows the double salt beginning to decompose. In the diagram the lines of sodium sulphate and aluminium sulphate appear.

In view of the results obtained by X-ray powder diffraction and to establish the optimum conditions of solubilization of alumina in the kaolin–bisulphate reaction, we made a study of the efficiency/temperature
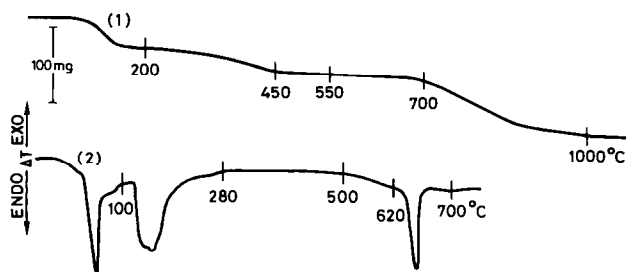

Fig. 1. TG and DTA curves: curve (1) TG; curve (2) DTA. Sample weight 394.0 mg.
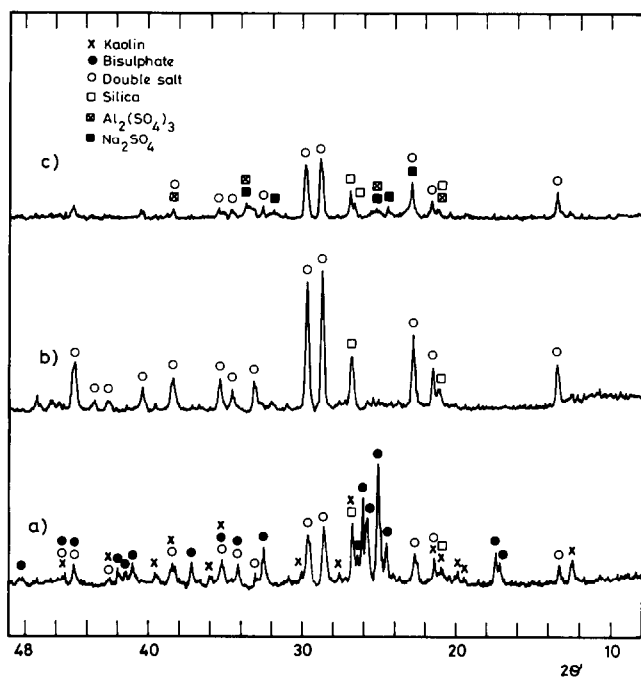
Fig. 2. X-ray diagrams at different temperatures of heating. (a) 280°C; (b) 500°C; (c) 700°C.

ratio over a constant time (75 min). The study was carried out using open and closed vessels.

In Fig. 3 we can see that, up to 400°C, the efficiency of the extraction of alumina in closed vessels was superior to that attained in open vessels. From 500–600°C the efficiencies were very similar in open and closed vessels. At low temperatures, for example at 150°C, the closed vessels gave approximately twice the efficiency obtained with open vessels.

Subsequently, to find the lowest temperature of reaction which gave a good efficiency of extraction of alumina, we studied, in the low temperature range, the efficiency/temperature ratio over a constant time (3 days).

In Fig. 4 we can see that between 140°C and 160°C, and with a reaction time of 3 days, an efficiency between 80 and 90% was obtained.

Once the interval of optimum reaction temperature had been established, we studied that efficiency/time ratio at constant temperature (160°C); see Fig. 5. In this figure we observe that the efficiency of alumina extracted increases in line with increases in the reaction time. With a reaction time of 5.5 h an efficiency of ≈ 70% was obtained, and after this reaction time the efficiency slowly increased; for a reaction time of 3 days the efficiency was 88%.

At low temperature and in a closed vessel, a hydrated double salt of aluminium and sodium was formed, $Na_3Al(SO_4)_3 \cdot 1.5H_2O$; this salt is also soluble in cold water.
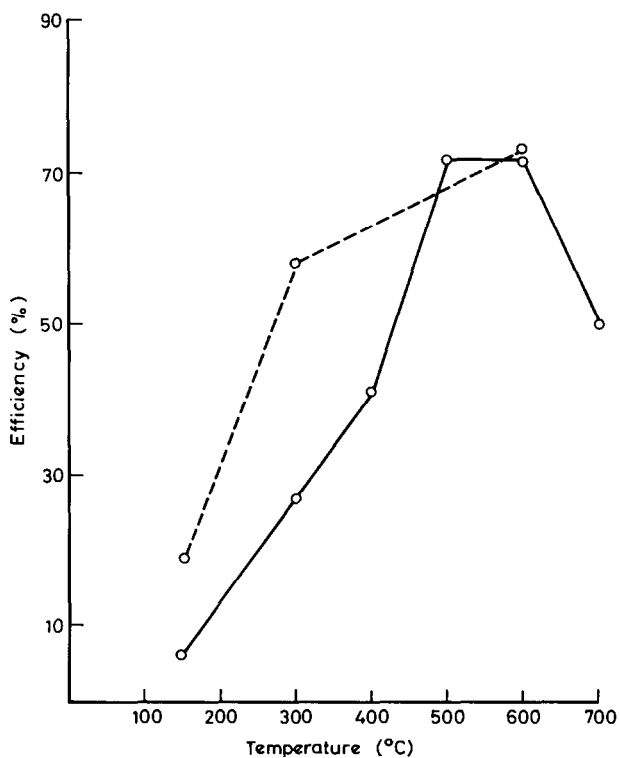
Fig. 3. Efficiency/temperature ratio at constant time (75 min) (———) open vessel; (- - - - - -) closed vessel.

We can conclude that the solubilization of alumina from kaolin is possible by solid state reaction between kaolin and sodium bisulphate at a low reaction temperature and with a short reaction time. The amount of sodium
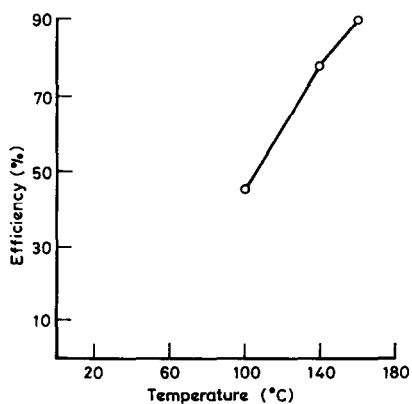

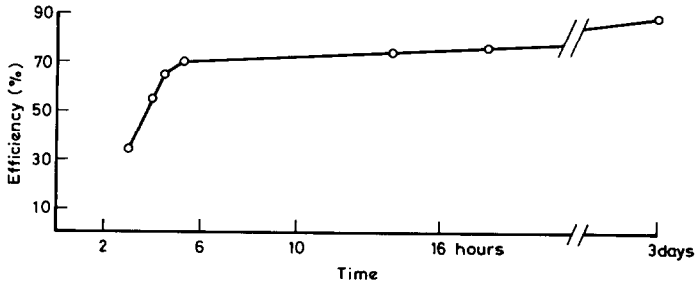Fig. 4. Efficiency/temperature ratio at constant time (3 days).

Fig. 5. Efficiency/time ratio at constant temperature (160 °C).

bisulphate employed in the reaction is the stoicheiometric amount by which the aluminium–sodium double salt is formed.

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