

# PRODUCTION OF ALUMINIUM SULPHATE AND UTILIZATION OF CLAY RESIDUE FROM KAOLINITE CLAY

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Preparation of aluminium sulphate from Kaolinite clay has been studied by calcinations with sodium chloride followed by sulphuric acid extraction. The calcination was carried out at 850-900°C for 3 h. The maximum recovery of alumina extracted as aluminium sulphate has been determined both on laboratory and pilot plant scale. The utilization of clay residue as an active pozzolanic material is discussed in this investigation.

**Key words:** Kaolinite, Aluminium sulphate, Clay residue.

## Introduction

A clay may be a good source of alumina and hence of aluminium compounds. It is essentially a fine-grained argillaceous material. Chemical analysis had shown that such materials were composed in general of alumina, silica and water, with iron, alkalies and alkaline earths also some times present in varying amounts (Ingerson 1960). All the clayey minerals are hydrated alumino-silicates with alumina content varying from 20 ~ 76% (Gillott 1968). By the action of intense heat these hydrated alumino silicates in argillaceous sediments may be dehydrated and converted into anhydrous alumino-silicates or into corundum ( $Al_2O_3$ ) or other mixed oxides with a resulting increase in the alumina content of the rock (Grim 1953). In addition to the clay minerals some clays contain varying amount of so-called non-clay minerals such as quartz, calcite, feldspar and pyrite (Bates 1960). Also many clay materials contain organic material and water soluble salts.

High alumina clays are mostly found in the province of Punjab mainly in Mianwali, Sargodha and Attock Districts (Shah 1980; Moosvi *et al* 1974). These deposits are extensive and quite suitable for alumina extraction. In Kala Chitta range, high alumina clay deposits from Bagh Nilab, Chhoi, Surg, Boota and Akhori (all in district Attock) have been estimated to be about 47 million long tons (Moosvi *et al* 1974). This estimate is based on the outcrop of clay and no drilling to any notable depth had been made.

The theoretical composition of kaolinite minerals  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$  expressed as oxide is  $SiO_2$ , 46.54%  $Al_2O_3$ , 39.50% and  $H_2O$ , 13.96%. Much research has been carried out on a variety of processes for extracting alumina from clay. There

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are five major processes that have been investigated extensively for extracting aluminium from clays (1). Acid process (2) Ammonium Sulphate process (3) Lime-sinter process (4) Lime-soda-sinter process (5) and Electro thermal process (Grim 1962). The evaluation of some Pakistani clays has already been done (Ahmad *et al* 1964). Some details of the DTA and X-ray techniques have been reported in early papers (Faruqi *et al* 1965; Faruqi 1966).

The chemical analysis, mineralogical composition, DTA and X-ray properties of the raw and the washed representative samples of kaolinite have been determined (Faruqi *et al* 1967). Hjrja *et al* (1989) studied preparation of alumina from bauxite by calcinations with sodium carbonate but these studies were confined to the bench level. Shah Alam *et al* (1995) prepared commercial grade aluminium sulphate from indigenous Bauxite by sulphuric acid using lead lined vessel. The presence of objectionable quantities of free acid and iron were a problem.

A number of studies have since then been conducted on the extraction of alumina from clay by sulphuric acid treatment. Results of such investigations are mostly covered by patents (Mellor 1917; Erwine *et al* 1928; Lewis 1936). However, information regarding the basic line of treatment of clays with sulphuric acid is available in literatures (Dodoner *et al* 1970; Dubnil 1947; Walthal *et al* 1945; Biswas *et al* 1965).

The present work was therefore undertaken to provide relevant information to prepare aluminium sulphate from kaolinite type clays. Where other studies have been based on direct acid leaching or lime/soda lime sintering prior to leaching, our approach lies on sodium chloride sintering before acid extraction. This has the advantage due to sodium chloride being more efficient flux than lime and cheaper than soda ash. Moreover, utilization of clay residue obtained as a by-product of

the process has also been studied successfully. Both the above aspects are supported by pilot scale trials.

## Experimental

The alumina-bearing ore (kaolinite clay) was ground into fine powder.

*Production of aluminium sulphate on laboratory scale.* 100g kaolinite clay was mixed with 100g sodium chloride in two china / porcelain dishes and placed in muffle furnace at 850 - 900°C for 3 h. Natural gas was then passed in order to keep the atmosphere in a reducing form.

After heating, the material was ground into fine powder, treated with warm water and filtered in order to remove sodium chloride. The material thus obtained was treated with 500ml of 20% sulphuric acid. The mixture was diluted with warm water and filtered. Alumina was determined in the filtrate.

5g roasted kaolinite clay was treated with conc.sulphuric acid and 15ml distilled water and refluxed for 1 h. After refluxing the mixture was filtered and alumina determined in the filtrate.

*Production of aluminium sulphate on laboratory scale.* 100kg each of kaolinite clay and sodium chloride was mixed moulded into 2" dia balls and fired at 850 - 900°C for 3 h in a gas fired furnace. After heating, the material was crushed and treated in the usual manner as mentioned previously. Alumina was determined in the filtrate and the clay residue obtained was washed with warm water and thus recovered.

**Table 1**

Chemical analysis of Kaolinite Clay

SiO <sub>2</sub>	=	44.76%
Al <sub>2</sub> O <sub>3</sub>	=	40.05%
Fe <sub>2</sub> O <sub>3</sub>	=	1.27%
CaO	=	0.46%
MgO	=	0.54%
L.O.I	=	12.68%
Total	=	99.76%

**Table 2**

Extraction of alumina from clay mineral with sulphuric acid

Clay mineral	Alumina extracted (% total alumina present)		Commercial scale
	Reducing atmosphere	Under reflux	
Kaolinite clay	72.03	91.52	62.42

## Results and Discussion

The clay used in this investigation is siliceous kaoline. The chemical composition of clay mineral is given in Table 1. The data of alumina extracted from clay mineral is presented in Table 2. Table 3 gives the characteristics of extracted aluminium sulphate. Chemical analysis of clay residue is given in Table 4 whereas Table 5 shows the comparison of compressive strength of lime-clay residue with ordinary Portland cement mortar.

Series of experiments were conducted and optimum conditions for the extraction of alumina from kaolinite clay were established in this study. Kaolinite clays are favored as sources of alumina because they possess the highest amount of alumina and moderate calcining renders the alumina soluble,

**Table 3**

Characteristics of extracted aluminium sulphate

Appearance	White crystalline
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .18H <sub>2</sub> O	98.70%
Free acid (H <sub>2</sub> SO <sub>4</sub> )	0.25%
CaO	0.10%
MgO	0.12%
Na <sub>2</sub> O	0.08%
Cl	0.10%

**Table 4**

Chemical analysis of clay residue

SiO <sub>2</sub>	=	44-55%
R <sub>2</sub> O <sub>3</sub>	=	12-22%
Na <sub>2</sub> O	=	2-09%
SO <sub>3</sub>	=	5-20%
CaO	=	1-02%
L.O.I	=	10-18%

**Table 5**

Comparison of compressive strength of lime-clay residue with ordinary portland cement-sand mortar

Age	3 days	7days	28 days
Mix proportion	1330 Psi	1471 Psi	1584 Psi
Lime: Clay residue: Sand			
1 : 2.3 : 6.6			
*OPC : Sand	1349 Psi	1956 Psi	3036 Psi
1 : 3			

\*OPC = Ordinary portland cement.

and also they do not contain any iron, alkalies or alkaline earths as essential components, which would go into solution in acids along with the aluminium.

In the present investigations an attempt has been made to attack alumina from the kaolinite clay with sulphuric acid. After the acid attack, the leach liquors are concentrated in order to obtain aluminium sulphate. As a by-product of the process large quantity of silica residue is produced. This silica residue has cementitious properties and can be used as a building material. The combination of utilizing the clay residue as building material and alumina extraction from clay could be feasible economically.

It is clear from Table 2 that alumina found on pilot plant scale was 62.42% which can be feasible for the production of aluminium sulphate. Under reducing atmosphere, the alumina extract observed was 72.03% whilst under reflux the alumina extract came out to be 91.52%. Although the alumina obtained in both these determinations is high but both the methods applied are on laboratory scale.

On pilot plant scale, pure aluminium sulphate crystals free from impurities are obtained by concentrating the solution. The mother liquors obtained after crystallization is mixed with fresh extracts and aluminium sulphate is recovered from the mixture. These experiments favorably indicate that the process of preparation of crystalline aluminium sulphate can be made commercially feasible.

The average alumina content in the original clay is 40%, out of which 25% was extracted on the semi pilot plant scale. If these conditions are maintained on a commercial scale plant, from one ton clay, extraction of aluminium sulphate (anhydrous) equivalent to 1632kg of hydrated aluminium sulphate  $Al_2(SO_4)_3 \cdot 18H_2O$  (tested by X-ray in the laboratory) could be produced leaving 750kg of silica rich clay residue which can be utilized as cementitious material.

#### *Utilization of clay residue as a building material.*

During heating the structure of the clay alters and the partial extraction of alumina creates cavities in the structure. These cavities have a tendency to be filled in with basic ions. The extraction of alumina from clay leaves silica ( $SiO_2$ ) in a reactive form. This active silica (acidic in character) has the capability of combining with lime to form calcium silicate hydrates at ordinary temperature. This type of clay residue was added to cement and it was noted (Dzizin *et al* 1978; Ghosh *et al* 1967) that it produced accelerated hardening. The active silica combined rapidly with the lime liberated during cement hydration (Ponomarev *et al* 1978; Lea 1956).

Keeping in view the above property of active silica the clay residue was mixed with hydrated lime and pressed into

cylinders. The development of strength was characteristic of lime puzzolana reaction but the rate of development of strength was more rapid. Thus a mix of hydrated lime, clay residue and silica sand in the ratio 1:2.3:6.6 was moulded into test cylinders which were cured under water like cement blocks and tested for compressive strength at different time intervals.

It is interesting to note that three days strength of lime clay residue mix is almost equivalent to 1:3 cement-sand mortars, but the rate of further development of strength is slower than O.P.C. In the case of lime clay residue reaction, almost 80% of ultimate strength is developed in 3 days. Thus the by-product silica residue in the process of alumina extraction from clay could easily be used as a building material, which has considerable strength and useful weather resisting properties. This utilization of clay residue will ultimately improve the economics of process.

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