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A Search for New Use of Clay Mineral

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A search for some more applications of clay mineral has been discussed.

Key Words: **Clay mineral.**

INTRODUCTION

The term clay is used in three ways: (i) As a diverse group of fine grained crystalline minerals (ii) as a type of rock and (iii) as a particle size term. Clay is a natural earthy, fine-grained material largely composed of crystalline substances that make up the group of clay minerals. The clay minerals are hydrous aluminum silicates usually containing alkalis, alkaline earth's and iron in appreciable quantities[1].

Classification: Clay mineralogists have classified the clay minerals in different groups known as:

1. **Illite group**: These clay minerals are similar to but not identical to white micas. This group of mineral has less percentage of potash and more of water as compared to white micas. They also differ in physical properties. These were formerly known as mica like clay mineral ore and potash bearing clay minerals, but all these were included in a single group. Illites contain almost no iron but most of them contain replacement of aluminium by iron and magnesium.

2. **Montmorrilonite group:** In this mineral group, the aluminium is partly replaced by magnesium or iron. All the members of this group (seponite, nontronite and bedilite) have expanding lattice. Some other minerals of this group halloysite, alltapolgite, allophane and chlorites mica are the minerals of minor importance. Among these the commercially important minerals are bentonite and fuller's earth.

3. **Kaolinite group:** Kaolinite is the main member of this group. However dickite, nacrite and anauxite are also important members of this group. Ball clay, china clay, fire clay, white clay and terracota minerals are commercial names of the kaolin mineral group. Indian kaolinites contain 43-49% SiO_2, 34–40% Al_2O_3, 0.6–2.0 Fe_2O_3, 0.1–1.0% TiO_2 and minor amount of Na_2O, K_2O, CaO and MgO.

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Commercial grade of Kaolinites:

China Clay: A good quality of china clay should be free from grit, *i.e.* should be free from silica and unaltered feldspar. It should also be free of lime. The physical properties are also important for rubber industries, it should be free from copper and should be light, *i.e.*, with specific gravity of the order of 2.5 and should have good reinforcing properties. To meet the requirement of electrical and insulating industries it is essential that iron content should be very low. However, for good glaze on paper and textiles, it is desired that colour reflectance should be less than 88.

Ball clay: Ball clay is another grade of kaolinites. Although its refractory value is less than of china clay or fire clay, but plasticity is higher. The higher plasticity is due to the fineness of the grains where 85% particles are of less than one micron in diameter. It is therefore used to blend non-plastic or semi plastic clays for increasing the plasticity, workability and strength to the bodies on drying. The important industrial sector using ball clay are the manufacturers of vitreous, sanitary ware, bath tubs, hotel china ware, floor and wall tiles, porcelain and spark plugs.

Fire clay: Fire clay has higher fusion point which is of the order of 1515°C. It is further classified according to fusion temperature, *i.e.*, low duty (1515–1615°C), high duty (upto 1700°C) and super duty (upto 1775°C). It is used for firebricks and as mortar for construction of furnaces and also as acid refractories in different industries. This clay is graded by their alumina content that varies between 30–60% and high alumina clays are preferred.

Occurrence

The principal producers of china clay are Rajasthan, West Bengal, Kerala, Bihar, Delhi and Andhra Pradesh. These together account for 86% of the total production. Ball clay is produced from Andhra Pradesh, Kerala and Rajasthan. The state of Rajasthan alone contribules about 40 % production of ball clay. Other important deposits of fire clay are located in the states of Bihar, West Bengal and Madhya Pradesh. The lignite fields of Tamilnadu and Rajasthan also contain clay along with coal.

In Rajasthan:

About 260 mining leases of ball clay and fire clay were reported in operation during January 2000. Ball clay is mainly found in the district of Bikaner and minor occurrences are located in Pali, Nagour and Jaisalmer districts. Fire clay mainly occurs in Bikaner, Alwar and Jhunjhnu districts, where as such type of clays are also found in Sawai Madhopur and Bharatpur districts. The occurrences of china clay and white clay are mainly located in the districts of Chittorgarh, Bhilwara and Bikaner. Minor deposits are also located in Jaipur, Udaipur, Sawai Madhopur, Bundi and Pali districts.

In Gujarat

There is good number of deposits located at various places in this state. The total number of leases is nearly 200. The major deposits of china clay are in Sabarkantha and Mehsana districts of north Gujarat.

Geology of clay deposits

Geology of clay deposits serve as a useful guideline for development of appropriate technology for beneficiation. The most of the clay deposits area of western India (Gujarat and Rajasthan) are covered with sand and sandy alluvium of quaternary period. Tertiary rock-exposures are found only in certain places as detached outcrops. Almost all these rock types are either ferruginous or having iron stains. Sandstone's are in general, current bedded. The basal part of this formation contains some dieotyledonous angiosperm leaf impressions preserved in siltstones. In some deposits there are clay horizons alternated with sandstones and siltstones.

The ferruginous nature of sediments has wide variations in texture from clay to grit. The occurrences of leaf impressions indicate a shallow water continental (deltaic) to marginal marine (littoral) condition of their deposition of clay in quieter environment. Such conditions can be related to relatively small oscillations of the strand line. The depositions of clay appear to be accelerated due to salinity of water, as the clay particles quickly coagulate and precipitate in saline medium.

Uses of clay

The different types of kaolinite minerals have their specific uses in a large number of industries.

China clay: It is mainly used in ceramics, refractory, paper, rubber, paints, insecticides, cements, textiles and fertilizers. Minor consumption of china clay is reported in abrasives, asbestos, pharmaceuticals, chemicals, electrodes, battery and similar industries.

Ball clay: The important industrial sectors using ball clay are the manufactures of vitreous, sanitary ware, bath tubs, hotel china ware, floor and wall tiles, porcelain and spark plugs.

Fire clay: It is used for firebricks and as mortar for construction of furnaces in refractories in different industries.

Need of beneficiation of clays:

These clay deposits in general yield about 20 % high grade, 40 % each of medium grade and low-grade clay. The main deleterious materials responsible for the price and quality of the marketable product are the presence of,

(i) Ferruginous sandstone
(ii) Free silica and
(iii) Anatase

The most of the clay deposits in this part of country (States of Rajasthan and Gujarat) are being exploited to the extent of 50–80% of reserves. However, a significant percentage of reserve is going waste or being sold at lower prices as inferior material.

Analysis of Clay

The determinative methods used to study clay minerals, chemical analysis is the oldest and most established. Before the development of the earliest instrumental techniques, such as X-ray diffraction and thermal methods, the identification of clay-mineral phases was accomplished by chemical analysis, supplemented where possible by optical data and physical characteristics such as specific gravity, colour and hardness.

Analysis of clay is, in fact, a silicate analysis, but there are special problems associated with clays that are not encountered with some other types of silicate materials and particular attention is paid to overcome these problems.

Sampling of clay minerals for analysis

The representative sampling is by far the most important for chemical analysis of clay minerals. If the sample of interest is available in bulk, then it must be reduced to a smaller representative amount, which is statistically equivalent to the whole sample. The size of a representative sample is influenced by the size of the particles in the materal. Jackson has shown that for samples containing particles up to 100 micron in diameter the optimum sample weight is about 5 mg, so that precautions are not necessary to ensure a representative sample for clay-size material (< 2 micron). If, however, the sample contains very coarse particles, the sample may be split (after grinding, if necessary) in an unbiased manner using a simple splitter or riffler. This should be used, repeatedly if necessary, on the subdivided portions, until the desired quantity is obtained. Allen and Khan[2] have critically evaluated several sampling techniques, and concluded that the spinning riffler is by far the best technique for sub sampling powders.

Methods of clay analysis

Major elemental analysis methods have changed dramatically over the last fifty years. Initially, the 'Classical Scheme' of analysis was adopted, as devised by Lundell and Hoffiman, Groves and Hillebrand. These methods consisted of a decomposition step, followed by gravimetric determination of the constituent elements and although recognized by many analysts to be accurate, the procedure is tedious, very time-consuming and requires quite a large sample (1 g), which in many cases is not available. The development of calorimetric methods has led to their introduction into more rapid analytical schemes, whereby much smaller sample weight (0.1 g) can be utilised.

More recently, techniques such as flame photometry, atomic emission and absorption and X- ray fluorescence spectroscopy have resulted in greatly reduced analysis times and sample weights of course, at the expense of a small reduction in accuracy which however can be minimised by replication.

EXPERIMENTAL

The elements normally analysed and reported in the form of oxides are SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO, MgO, K_2O, Na_2O, TiO_2, MnO, P_2O_5 and CO_2. The summation should result in a total in the range 99.75–100.50% for 'classical analyses' and 99.0–101.0% for 'rapid' techniques for an acceptable analysis. Chalmers and Page have recommended that reports of elemental analyses should include an estimate of the precision and accuracy of the results. Carrying out a complete analysis of mineral or rock of similar known composition should always monitor the latter.

Instrumental methods of analysis

A wide range of analytical techniques is currently available to quantify the elemental composition of clays. The methods are numerous, the main methods in use are listed below:

UV/visual spectroscopy, atomic absorption, flame emission inductively coupled plasma (ICPS), X-ray fluorescence (XRF) and neutron activation analysis (NAA).

The choice of method depends on a number of factors, such as availability of equipment, size of sample, adequate sensitivity and accuracy of the required analysis. UV/visual methods are cheap and fairly simple to use, but suffer from interference effect. Conventional atomic-absorption and flame-emission spectrometry have the disadvantage of being single-element techniques but the advantages of easy sample preparation and low cost. Inductively coupled plasma (ICP) has several advantages when dealing with clay samples. It has a linear dynamic range over several orders of magnitude and can analyse small samples. However, the inherent high sensitivity of ICP is lost in the dilution process. All these techniques are solution-analysis methods, and consequently, are prone to losses and contamination during the process of clay dissolution. X-ray fluorescence (XRF) and neutron activation analysis (NAA) are multi element techniques for solid samples. XRF can be non-destructive, but for major elemental analysis it is usually advisable to fuse the sample and dilute with flux to reduce interrelate effects. It is very accurate, but can not differentiate between ferrous and ferric iron. NAA can also be non-destructive, has high sensitivity and accuracy, but suffers the major drawback of requiring a nuclear reactor[3].

Use of Kaolinite

With a theme of investigating new uses of kaolinite presently the emphasis has been laid on utilizing these clay samples in newer areas of value-added products:

(i) Transformation into product with good ion exchange properties.

(ii) Exploring the possibilities of its use in cement industries.

Technical evaluation of ion exchange properties:

For this ten samples were selected from the samples of different areas of Rajasthan and Gujarat. All these ten samples were evaluated for ion exchange properties. The method used for the purpose is detailed below:

Method:

25 g clay sample of (–)200 mesh was taken and spherical balls of 2–3 mm diameter were manually prepared by using 5 mL of 0.01% sodium silicate slurry

in distilled water. These balls were heated in muffle furnace for 3 h in temperature range of 800–900°C. The clay balls were allowed to cool at room temperature and stored in a desicator. Clay material was transformed into H^+– form by dipping in 1 N HCl for 24 h. The balls were then separated from acid and washed with water till washing were free from chloride ions. 20 g balls of each samples were packed in 1 cm diameter column. 1 L of 4% sodium chloride solution was passed through this column at the rate 100 mL per 3 minute and collected in a 2 L beaker, the column was further washed with distilled water and volume was made upto 1500 mL. 200 mL of this effluent solution was taken in 500 mL volumetric flask and titrated against 0.1 N NaOH solution using phenolphthalein indicator and exchange capacity was calculated. The ion exchange capacity of the samples is given in Table-1.

TABLE-1
CATION EXCHANGE CAPACITY OF CLAY

Sample No.	Volume of titre 0.1 N NaOH for 200 mL	Cation Exchange Capacity (meq/100g) on dry basis
1.	0.1	0.375
2.	0.3	1.125
3.	0.3	1.125
4.	0.1	0.375
5.	1.2	4.500
6.	1.1	4.125
7.	0.7	2.625
8.	0.5	1.875
9.	0.3	1.125
10.	0.4	1.500

RESULTS AND DISCUSSION

The results in almost all cases were not encouraging. None of the sample came upto expectation with good ion exchange properties.

Development of kaolinite as blending material in high magnesium portland cement (HMPC)

One of the most important potential uses of china clay that can be visualised for the 21st century is its use in blending with cement.

Cement is a very important building material and no construction activity can be thought of without use of Portland cement. Many countries in the world are manufacturing cement. The basic requirement in cement grade limestone is that it should not contain more than 5% magnesium carbonate. However in many parts of the world the limestone is not available whereas dolomatical limestone is available in plenty. This dolomatic limestone can produce HMPC. This HMPC is technically unsound as the magnesia present forms free hard burnt crystalline MgO (periclase) causes the disruption in cement during hydration. Poddar *et al.*[4]

have reported the improvement of hydraulic activity HMPC by blending it with kaolinite. These workers have blended 30% kaolinite in three typical HMPC in which MgO varies from 9.40 to 18.01% and have reported that this cement is comparable with the ordinary Portland cement in setting propeties *viz.* setting time, compressive strength and Le-Chatilier expansion. The relevant data given are summarises and the initial and final setting time with expansion rate of ordinary portland cement (OPC), HMPC and 30% kaolinite blend if HMPC are given in Table-2.

TABLE-2
SETTING TIME OF DIFFERENT CEMENTING MATERIALS

Sample No	Setting time (min.)		Expansion result
	Initial	Final	
OPC	60	240	—
HMPC	165	365	0.94
HMPC with 30% Kaolinite	165	310	0.41

The compressive strength of HMPC with different percentage of kaolinite at varying interval of hydration are given Table-3.

TABLE-3
THE COMPRESSIVE STRENGTH OF HMPC WITH DIFFERENT PERCENTAGE OF KAOLINITE AT VARIOUS INTERVAL OF HYDRATION PERIOD

Hydration period (days)	Compressive Strength (Kg/sq.cm)			
	0%	25%	30%	35%
3	31	10	35	116
7	55	10	48	155
14	166	18	107	230
28	194	42	174	273
180	271	218	232	350

In our present investigation our object have been to improvise the properties of china clay and also to explore the utilization of finished product. We have largely been successful in our mission to recommend two of our china clay suitable for blending with HMPC. Sample No. 4 and 8 are the suggested kaolinite for HMPC blending.

Economics of blending clay with HMPC: In remote areas where cement grade limestone is not available, the cost of a 50 kg bag of OPC is not less than Rs. 100. The cost of production of HMPC with 30% kaolinite shall be Rs. 77.50 showing the net reduction in cost by 22.50%. This can be shown by the simple calculation based on the basic assumption that,

1. The production cost of OPC and HMPC are same, amounting Rs. 100/- per 50 kg bag.

2. The cost of beneficiated kaolinite is about Rs. 0.50 per kg

A blend of 70 HMPC: 30 kaolinite gives the cost of 50-kg bag as follows:

(i)	Cost of 35 kg HMPC @ Rs. 2.00 per kg	Rs. 70.00
(ii)	Cost of 15 kg kaolinite @ Rs. 0.50 per kg	Rs. 7.50
	Total cost	Rs. 77.50

Conclusion

The beneficiated china clay samples were considered for blending with HMPC. The chemical properties of all the ten samples were compared and on the basis of identical desired composition for the purpose of blending sample No. 4 and sample No. 8 are recommended. The composition of OPC, HMPC, Rajmahal kaolinite recommended clay for blending along with our kaolinite samples is reported in Table No. 4.

TABLE 4
CHEMICAL COMPOSITION (%by wt.) OF CEMENT SAMPLES AND ADDITIVES

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	LOI
OPC	62.00	22.14	5.80	2.44	3.80	0.81
HMPC	51.22	19.81	5.80	3.00	18.01	0.87
Rajmahal Kaolinite	Trace	53.89	45.01	0.49	Trace	Trace
Kaolinite Sample 4	0.34	62.67	32.19	1.26	0.40	Trace
Kaolinite Sample 8	0.29	53.79	41.87	1.02	0.20	Trace

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