Experimental processing of some of the Indian clays for chemical purposes

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INTRODUCTION

Clays are of various types viz., fire clays ball clays, stoneware clays, pipe clays, brick clays, bentonite, kaolin etc. Excepting the last, the rest are available in sufficient purity and no dressing is usually necessary. Kaolin is to be washed free of gritty material in suitably designed washers.

Uses and specifications :

The specifications of clay for commercial purposes, vary according to the users and unlike many other mineral substances, it is not possible to give general specifications for the purity of clay, as this depends largely upon the purpose for which it is to be used.

(1) Paper industry :

China clay which is used for paper manufacture, is normally judged by its colour brightness, which is generally rated as a General Electric Brightness number between 65 and 90.

(2) Cement industry :

For cement making, the iron content in the limestone or clay or in both (the mix) shall be below 0.42 % Fe after ignition i. e., the clinker should not contain more than 0.42% Fe (0.6% Fe_2O_3). This may be taken as a suggestive guideline.

(3) Foundry purposes :

Bentonite, which is most widely used as a bonding agent in foundry moulding sands, should have very high plasticity and bonding power. The fineness of bentonite is also important. Use of bentonite as a pellet binder for iron ore is also gaining importance.

Besides the above, clays find extensive use in ceramics, rubber, plastics, paints and pigments, oil cloth, insecticides, fertilisers, textiles and other industries also.

Bench scale experiments at N.M.L. on processing of some of the Indian clays :

Experiments by way of systematic studies had been carried out at N.M.L. on the beneficiation or processing of some of the clay samples received, on sponsored basis, so that the beneficiated product meet the requirements of specific industrial users. A brief account of some of the typical projects undertaken at N.M.L. are briefly presented.

Recovery of sulphur from sulphur-bearing clays :

Three samples of clays containing elemental sulphur of bio-chemical origin, assaying 21.8%, 4.5% and 0.4% sulphur (dry basis) were received from Kona village, near Masulipatnam (A.P.) at N.M.L. for investigation purposes. Besides sulphur, the samples also contained quartz, organic matter and soluble salts of sodium and potassium chlorides and sulphates of magnesium and calcium. Detailed experimental studies were carried out with the first sample of clay only for the reason, that the other two samples were too poor by themselves to be economically exploited, but they could however be treated along with the rich sample by the same process for separation of sulphur.

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Sulphur in all the samples existed in the ree state as well as interlocked with clay, quartz, nd organic matter. The chemical analysis of he first clay sample investigated at N.M.L. is iven in Table—1.

Table—1 Chemical analysis (dry basis)

Constituent	Percent
SiO_2	42.3
Fe_2O_3	11.4
CaO	2.0
MgO	1.8
Free S	21.8
Combined S as SO_3	8.2

Net sieve analysis :

A sieve analysis of the sample was carried ut to determine the sulphur contents in the lifferent sieve fractions and the results are jiven below in Table—2.

Table—2 : Wet sieve analysis

Size in mesh	Wt %	Free sulphur %
+ 35	2.6	21.5
− 35 + 48	7.0	21.6
− 48 + 65	6.7	22.7
− 65 + 100	12.1	19.8
− 100 + 150	10.2	22.6
− 150 + 200	9.5	25.9
− 200	51.9	24.3
Feed	100.0	22.5

The above results indicated that the sulphur contents of the different sieve fractions were nearly the same as in the clay sample, thereby indicating that desliming as a preliminary step in beneficiation, would result in heavy loss of sulphur in the slime.

Flotation :

Next attempts were made to float off the sulphur from the clay sample, employing different reagent combinations and optimum conditions were arrived at.

Cresylic acid or pine oil alone as frother-collector was not found effective as coarser particles could not be floated. Reagent combination consisting of light diesel oil with cresylic acid gave good results. Under optimum conditions, flotation at pH of 4.6, gave a rougher concentrate assaying 52.2 % sulphur with 80.9% recovery. The grade could be improved further by reflotation to 66.0% S for a lower recovery of 59.0 % in it.

Flotation at pH 7.2, using soda ash and sodium meta silicate improved the sulphur recovery to 94.1%, but the grade was lowered to 42% sulphur.

Effect of pH on concentrate grade and recovery :

The results of flotation tests conducted at different pH are presented in Table—3, which indicates the effect of varying the pH on the grade and recovery of sulphur.

Table—3 : Effect of pH

Sl. No.	pH during flotation	Wt% of float	Grade % S	Recovery % S
1.	4.6	35.3	52.2	80.9
2.	6.4	38.4	45.7	81.9
3.	6.6	45.8	46.0	91.5
4.	7.1	49.5	44.9	93.3
5.	7.2	52.6	42.0	94.1

It was observed from the above results, that under optimum conditions, the recovery of S improved steadily with increase in pH 4.6 to 7.2 with a gradual lowering of the grade. Also, flotation was faster at higher pH.

Lowering iron content in a clay sample received from M/s. A.C.C. Ltd., for cement manufacture :

A sample of slate clay, which constituted 15% of the dry mix (mixture of limestone and clay) for cement mixture was investigated at N.M.L. for lowering the iron content in the sample to specified limits by dry processing methods only. M/s. A.C.C. had specified that the iron in the clinker produced by calcining the above mix should be less than 0.42% Fe (0.6% Fe_2O_3).

The sample of clay, as received, was greyish black in colour, possibly due to the presence of organic matter and assayed 1.22% Fe. On roasting in air, the main sample turned white and ocherous minerals, which turned red, were finely disseminated in the clay. Due to the fine association of the ocherous material with the sample, straight tabling and magnetic separation did not yield any satisfactory results.

Reduction roast followed by magnetic separation lowered the iron in the non-magnetic fraction to 1.18% Fe. Magnetic separation of the sample after heating in oxidising atmosphere also gave a non-magnetic product assaying high in iron (1.23 % Fe).

Electrostatic separation and flotation experiments were also attempted but not with encouraging results. Hence it could perhaps be concluded that lowering of iron content in the sample could not be achieved by physical ore dressing methods, on account of the fine dissemination of iron in the clay sample.

Improving the colour – brightness of washed china clay for use in paper, textile and procelain industries :

Experimental work on a sample of washed china clay sample from Chaibasa, Bihar was undertaken at N.M.L., with a view to investigating the possibility of improving the quality of the clay for use in paper, textile and porcelain industries. The sample of clay which was reported to have been obtained from crude clay after treatment in their clay washing plant, had the following chemical analysis given in Table—4.

Table—4 : Chemical analysis

Constituents	Percent
SiO_2	44.37
Al_2O_3	37.50
Fe_2O_3	2.49
LOI	11.28

Mineralogy :

The clay consisted of kaolinite and hydromuscovite as principal clay minerals in fine crystalline form. Colloidal ferruginous matter accounted for the gangue minerals Mineralogical and spectrochemical analysis indicated that there was no other element other than iron, which could be responsible for the off-colour of the clay.

Experimental results :

Mere sizing or classification did not improve the colour of the products, because of the colloidal nature of ferruginous gangue in the sample. Hence attempts were next made to leach out the iron by chemical methods followed by removal of the leached iron by filtration or other suitable methods. Another possibility which might be considered and investigated is "Ultra-flotation", but it needs extensive studies and was not attempted.

Leaching :

The ferric iron (Fe_2O_3 content) which was responsible for the off-colour of the clay was reduced to ferrous state by using a suitable reducing/leaching agent. For this purpose, a few leaching tests were performed by taking 50 gm of the sample agitating with 200 gm of raw water for about one hour, using varying concentrations of reagent and the clay slip was washed three times. The slurry was then filtered and dried at low temperatures. The results are recorded in Table—5.

Table—5 : Results

Additive %	Fe_2O_3 % in the leached clay
0.6	2.13
1.0	2.14
2.0	2.04
4.0	2.06
6.0	2.00
8.0	2.02

It is seen from the results that the Fe_2O_3 content could be lowered to about 2.0% and a 2% solution would be sufficient. But the colour of the leached clay was still not satisfactory probably due to the fact that the iron salts had not been completely eliminated and also due to subsequent re-oxidation during drying etc. Hence the use of an ion-exchange resin for removal of soluble iron salts was tried.

Use of ion-exchange resin :

In this experiment, after reducing the ferr-iciron present in the sample to the ferrous state subsequent elimination of these reduced iron ions from the solution, was achieved by introducing a resin "Zeo carb 225" as an ion exchange material. The resin which was available in sodium form was found to be very rapid in action. Using different amounts of the reducing agent, the leached clay pulp was agitated with the resin for about half an hour and the resin was removed by repeated washing with water and the clay slip filtered and dried. The results are shown in Table—6.

Table—6 : Results

Additive %	% Fe_2O_3 in the product
2.0	1.8
3.0	1.7
4.0	1.7

Hence it was observed that leaching followed by ion-exchange could lower the Fe_2O_3 content to about 1.7. The colour brightness of the clay, by this method had improved considerably and compared well with the standards supplied by the sponsors.

The ion-exchange resin could be regenerated by passing through 2.5 times its volume of a 10 % brine solution followed by washing with water several times.

However, further detailed studies on a large scale should be carried out, before commenting about the economic viability of this process.

Bonding effect of bentonite :

Bentonite, which is widely used as a bonding agent in foundry moulding sands, has very high plasticity and bonding power. Normally this does not require any dressing. After mining, it is dried in rotary kilns and ground dry in ball or roller mills in closed circuit with cyclone collectors to yield very fine powder of about 200 mesh size. For use as a binder the swelling index and base exchange capacity is also made use of. For pelletisation of iron ore fines, a higher figure is generally proposed. However, actual application trials in comparison to other known bentonite samples are taken as a guide.

Pelletisation of iron ore fines :

A sample of bentonite from Kutch was investigated at N.M.L. for studying its suitability as binder in the pelletisation of iron ore fines. Two samples of iron ore fines (−6 mesh classifier sand) were chosen for experimental work. The samples were separately wet ground to about 75% −325 mesh and pellets were prepared using 0%, 0.5% and 1.0% bentonite. It was observed from the test results that pellets prepared without bentonite were of poor strength. The physical property of the green pellets as well as heat hardened pellets, using 1.0% bentonite as binder, showed marked improvement in the quality of pellets and in general satisfied the specifications for their use in a blast furnace. Therefore, it was concluded that this bentonite sample could be used as a binder for pelletisation of iron ore fines.

Bentonite clays for foundry purposes :

Excellent facilities exist in the foundry section of the NML, for evaluating the properties of bentonite clays. Lot of work has been carried out in the laboratory on several bentonite samples received from industries in different parts of the country, for assessing their suitability in foundry use and the results published in the monograph entitled "Indian Foundry Sands and Bentonite Clays". Further R & D work on the behaviour of indigenous bentonites as well as activation of clays, have also indicated that indigenous lean bentonite clays could be successfully upgraded for foundry moulding purposes.

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