ISSN : 0974 - 7486 Volume 7 Issue 5

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(5), 2011 [297-301]

Studies and characterization of bentonite clay obtained from Gulbarga, Karnataka region

Sridhar Pande[1], Mahesh D.Bedre[2], C.D.Madhusoodana[3], A.Venkataramana[1]*
[1]Materials Chemistry Laboratory, Department of Materials Science,
Gulbarga University, Gulbarga - 585 106, Karnataka, (INDIA)
[2]Gurukul College of Science, Gulbarga - 585 102, Karnataka, (INDIA)
[3]CTI, Bharat Heavy Electricals Ltd. Bangalore, Karnataka, (INDIA)
E-mail: raman_chem@rediffmail.com

Received: 18th February, 2011 ; Accepted: 28th February, 2011

ABSTRACT

Bentonite clay mineral from the Gulbarga region belonging to the smectite group having a wide range of industrial uses was activated by different methods (such as water, chemically and thermally activated). The acid activation of the investigated bentonite increased three times the surface area and volume. This activated clay is characterized for chemical analysis (XRF). Surface area determination indicates increase in surface pore diameter. Thermal Gravimetric analysis (TGA) and Differential thermal analysis indicates the decomposition of carbonates. X-ray diffraction (XRD) patterns indicate the increase in the calcium phase.

KEYWORDS

Acid activation;
Bentonite clay;
XRD;
TGA.

INTRODUCTION

Clays, whose basic mineral is montmorillonite, or smectite, are generally called bentonites. Bentonites, which are employed is prevalent among most industrial raw materials[1]. Acid activated bentonites are used as adsorbents in the bleaching of edible oils[2], in the production of carbonless copy paper[3], and in the preparation of pillard clays[4], orgnaoclays[5], and heterogeneous catalysts[6-9].

The surface acidity and the porous structure of bentonites can be changed to some extent by acid activation[10-12]. These changes depend on the smectite minerals, other clay minerals and non-clay minerals contained in the bentonite as well as the chemical composition, the type of cations between the layers, the type of acid, the mass percent of the acid in the bentonite-acid mixture, the process temperature and the process period.

Bentonite can be used in cement, adhesives and ceramics. Bentonite is also used as a binding agent in the manufacture of taconite pellets used in the steelmaking industry. Fuller's earth, an ancient dry cleaning substance, is finely ground bentonite, typically used for purifying transformer oil. Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Bentonite clay is also used in pyrotechnics to make end plugs and rocket nozzles[13].

The ionic surface of bentonite has a useful property in making a sticky coating on sand grains. When a small proportion of finely ground bentonite clay is added to hard sand and wetted, the clay binds the sand particles into a moldable aggregate known as green sand used for making molds in sand casting. Some river deltas mix or make naturally just such a blend of such clay silt and sand, creating a natural source of excellent molding sand that was critical to ancient metal working technology. Modern chemical processes used to modify the ionic surface of bentonite greatly intensify this stickiness, resulting in remarkably dough-like yet strong casting sand mixes that stand up to molten metal temperatures[14].

MATERIALS AND METHODS

The processing clay sample is collected from Gulbarga district. The operations like clay crushing, air-drying and grinding by ball mill and passing through different meshes are carried out. The clay fraction was purified and the surface area measurement is carried out by the classical method[16].

The chemical analyses were obtained by using X-ray diffraction studies (Philips goniometer, PW 1730/10, using the Kα radiation of copper). The infrared spectra obtained by using KBr pellets were recorded with a Perkin Elmer 783 dispersive from 4000 to 400 cm^{-1}. Thermo gravimetric (TG) and differential thermal analysis (DTA) experiments were performed using NETZSCHSTA 409 PC. TG and DTA data were obtained at a heating rate of 10^{0}C/min up to 900^{0}C under Argon atmosphere.

EXPERIMENTAL

Treatment of raw clay

In the preparation of raw clay, the bentonite is taken from locally available units in Gulbarga which is obtained in the form of lumps. The lumps were fed into ball mill with 150 alumina balls and milling was carried out for 10 min to 15 min.

The raw clay obtained after milling was screened in the sieve shaker to get desired particle size without fine particles. The raw materials retained at different sieve were collected in different containers.

Preparation of washed clay

100 gm of bentonite clay is taken in a volumetric flask; about 1000 ml of distilled water is added to it. The mixture was thoroughly stirred. It was left for about 2 hours for sedimentation. The water was decanted slowly. The procedure was repeated for about 3 times. Finally the clay was dried at 100 ^{0}C.

Preparation of thermally activated clay

The 100 g prepared raw material of different size is taken and mixed properly. Then the prepared mixture is placed in 6 fireclay crucibles, these crucibles are placed in the furnace and heated at a temperature of about 750 ^{0}C, two crucibles are taken out at zero hour soaking, and two more crucibles are taken out at 1 hour soaking again two more crucibles is taken out after two hour soaking. This thermally activated clay is kept in air tight box.

Preparation of chemically activated clay

The 40 g of raw clay is taken from fraction in a flask then 10 ml of concentrated H_2SO_4 is added along with 800 ml of water.

This set up is taken for 6 hour for heating until the small bubbles rise up and care must be taken so that it boils continuously during heating, then allow it to cool for 2 to 3 hours after cooling the chemically activated clay is washed with distilled water for 4 to 5 times to remove excess water from it. This washed clay is kept for drying for 24 hours at 100 ^{0}C then removed from furnace and kept it in air tight box.

Preparation of thermo-chemically activated clay

Thermally activated clay which is heated at 750 ^{0}C soaked for 1 hour is taken about 40 gm of this clay and placed in round bottomed flask then 10 ml of concentrated H_2SO_4 is added along with 800 ml of water.

This set up is kept for 6 hours for heating until the small bubbles raises up and care must be taken so that it boils continuously during heating, then allow it to cool for 2 to 3 hours after cooling the chemically activated clay is washed with distilled water for 4 to 5 times to remove excess water from it. This washed clay is kept for drying for 24 hours at 100 ^{0}C then remove from furnace and kept in air tight box.

RESULT AND DISCUSSION

X-ray fluorescence (XRF)

From the table (TABLE 1) it is clear that the elements such as, SiO_2, CaO and Al_2O_3 in major percentage except in the chemically activated clay.

TABLE 1

Analyses	Bentonite Raw clay	Bentonite Washed clay	Bentonite Chemically activated	Bentonite Thermo Chemically activated	Bentonite Thermally activated
MgO	3.252	3.154	3.116	3.352	2.897
Al_2O_3	8.607	8.249	6.998	8.932	8.520
SiO_2	57.810	55.219	66.791	58.573	66.859
K_2O	2.612	2.504	2.700	2.645	2.007
CaO	21.810	25.008	14.175	20.735	13.756
TiO_2	1.355	1.257	1.744	1.382	1.685
Mn_2O_3	0.043	0.043	0.056	0.043	0.054
Fe_2O_3	4.325	4.434	4.219	4.220	4.067
Total	100	100	100	100	100
LOI	21.4	22.58	17.92	21.28	17.9

From this table is observed that, Al_2O_3 leached out in chemically activation. SiO_2 decreased by washing, some free quartz removed. CaO reduced in activation, more by thermal & chemically activation. No changes or small change in other oxides.

FTIR spectra

Identification of clay minerals the absorption band due to structural OH and Si-O groups plays frequently an important role in the differentiation of clay minerals from each other. Infrared spectra (Figure 1) are the evident in the frequency range 4000-400 cm^{-1}. The peak at 3620-915 cm^{-1} confirms the dominant presence of smectite with [Al, Al-OH] stretching and bending bands. The adsorption bands at 3750-3250 cm^{-1} and 1750-1250 corresponds to OH frequencies for the water molecule adsorbed on the clay surface[16]. Bands at 490, 500, 900 cm^{-1} can be assigned to [Si-O-Al], [Si-O-Fe], [SiO] and [Si-O-Si]. The (Si-O) bands are strongly evident in the silicate structure and can be readily recognized in the IR spectrum by the very strong absorption bands in the 1250-900 cm^{-1} region[17].

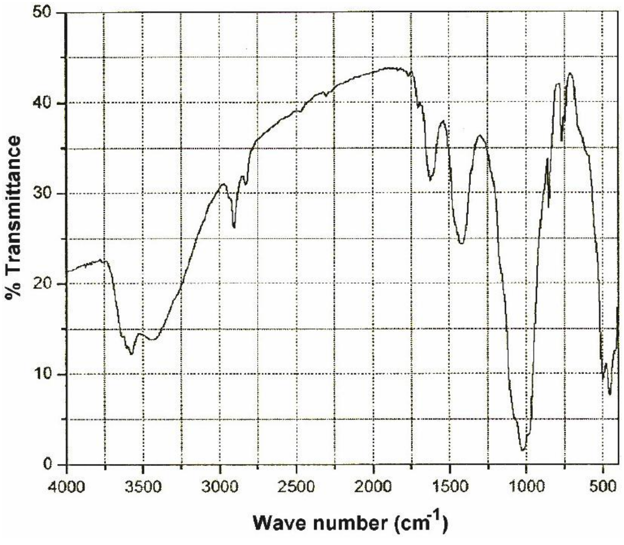

Figure 1 : FTIR spectra of clay sample

Surface area determination

The surface area of the clay adsorbents were estimated according to Scars method. A sample containing 0.5g of clay was acidified with 0.1 N HCl to a p^H 3 to 3.5. The volume was made up to 50 ml with distilled water after addition of 10g of NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298 k to p^H 4 and then to p^H 9. The volume 'V' required to raise the p^H from 4 to 9 was noted and the surface area was computed from the following equation,

Surface area (m^2/g) = 32 V-25

Clay	BRC	BWC	BTA	BCA	BTC
Surface Area (m^2/g)	103	77.4	119	631	733.4

Data shows that sulpuric acid activation of the bentonite increased three times then the surface area and volume values

Thermal analysis (TGA/DTA)

The thermal decomposition of Clay shows a three step weight loss. (Figure 2) The first weight loss of 10-12% from 30 ^{0}C to 130 ^{0}C is due to the loss of adsorbed and interlayer water from the clay mineral.

A second weight loss of 5-6% from 130 to 630 ^{0}C, is due to the removal of water composition from the clay mineral. The third loss of weight 3-4% appears only at 620 to 800 ^{0}C this can be attributed to the carbonate decomposition. This total loss is equal to the LOI values.

A significant endothermic peak between 120 to 180 ^{0}C, these transformation are due to the removal of adsorbed and inter layer water from the removal of the first peak confirm the clay presence of a swelling phase interstratified with non swelling clay.

A DTA trace (Figure 2) of the crude sample corresponding to the transformation of the quartz, at 630 ^{0}C and other endothermic peak at 731 ^{0}C can be attributed to the carbonate decomposition.

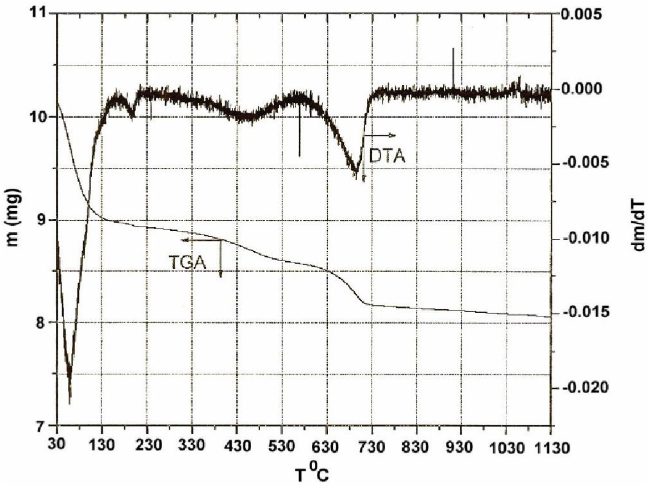

Figure 2 : TGA/DTA analysis of clay sample

X-ray diffraction (X-ray)

The XRD spectrum of all these samples (Figure 3) XRD shows SiO_2 peak and montrmorillnite peak in raw and washed clays. This SiO_2 peaks is due to free quartz in the minerals. But in the activated clays only free quartz peaks is seen and crystalline clay peaks disappears. This suggests that activation makes clay amorphous. This is the reason why the surface area increased drastically after activation.

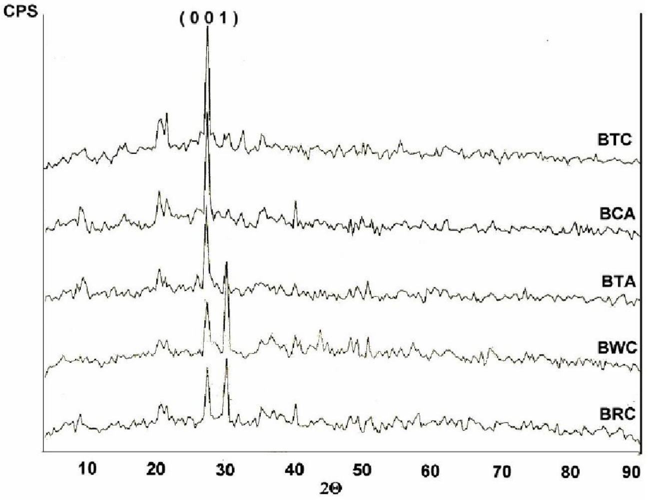

Figure 3 : XRD of clay sample

The edges of crystals are opened and the Al^{3+} and Mg^{2+} cations of octahedral sheet are exposed to the acid and then become soluble. The surface pore diameter expands the specific surface area of the smectite increases to maximum.

CONCLUSION

Important information was obtained about the effect of thermal and acid activation on some of the physico-chemical properties of bentonite clay by using chemical analysis. TGA and DTA analysis suggests that the thermal stability of sample. FTIR and XRF show the bonding nature and the presence of ions in the sample. In addition to this the proportion of the destroyed crystal structure was employed by using the raw clay found by the normalization of the regularly decreasing XRD. During the acid activation, the partial loss of Mg^{2+}, Fe^{3+} and Al^{3+} cations of the octahedral are exposed to the acid and become soluble as a result, increased the porosity considerably. The sulpuric acid activation of the investigated bentonite increased three times the surface area and volume values. The activation realized at constant temperature and period; it was possible to obtain bentonite samples of required properties.

ACKNOWLEDGEMENT

Authors thank to the Department of Science and Technology (DST), India (Grant No. SR/S1/ PC-10/ 2005) New Delhi & UGC Innovative Programme in Materials Chemistry, New Delhi (D.O.No.F.14-4/2001 (Innov.Policy/ASIST)) for their financial assistance.

REFERENCES

[1] H.H.Murray; Appl.Clay Sci., **5**, 379 **(1987)**.
[2] E.P.Gonzales, M.S.Villatrance, A.C.Gallego; J.Chem. Technol.Biot. **87**, 213 **(1993)**.
[3] M.Takashima, S.Sano, S.Ohara; J.Imaging, Sci.Tech., **37**, 163 **(1993)**.
[4] J.M.Adams; Appl.Clay Sci., **2**, 309 **(1978)**.
[5] C.Breen, R.Watson, J.Madejova, P.Komadel, Z.Klapyta; Langmuir, **13**, 6473 **(1997)**.
[6] P.Laszlo; Science, **235**, 1473 **(1983)**.
[7] T.J.Pinnavaia; Science, **220**, 365 **(1983)**.
[8] S.R.Chitnis, M.M.Sharma; React.Funct.Polym., **32**, 93 **(1997)**.
[9] F.Kooli, W.Jones; Clay Sci., **6**, 59 **(1991)**.

[10] N.Javanovic, J.Janackovic; Appl.Clay Sci., **6**, 59 **(1991)**.
[11] M.A.Vicente, M.Suarez, J.de D.Lopez-Gonzalez, M.A.Banares-Munoz; Langmuir, **12**, 566 **(1996)**.
[12] J.Ravichandran, B.Sivasankar; Clays & Clay Miner., **45**, 854 **(1997)**.
[13] D.L.Sparks; Environmental Soil Chemistry, Academic Press, Inc, California, **(1995)**.
[14] S.D.Faust, O.M.Aly; Adsorption Processor for Water Treatment, Butterworth Publishers, Boston, **(1987)**.
[15] H.Van Olphon; An Introduction to Clay Colloid Chemistry, Interscience Publishers, NY, London, **(1963)**.
[16] V.C.Farmer; Spectrochim.Acta A, **56**, 927 **(2000)**.
[17] V.C.Farmer, in: V.C.Farmer (Ed); Infrared Spectra of Minerals, Mineralogical Society, London, UK, **(1974)**.