Indian Journal of Engineering & Materials Sciences
Vol. 30, February 2023, pp. 65-72
DOI: 10.56042/ijems.v1i1.64836

Beneficiation of Clays from Ramgarh-Naudiha Region of Sonbhadra District Uttar Pradesh, Impart Improved Properties for Ceramic Industries

Debiprasad Karmakar[a,d], Vartika Singh[b], Shetru Mallappa Veerabhadrappa[a], Raghvendra Singh[a], Lalit Kumar Sharma[c], & Swapankumar Ghosh[c,e]*

[a]Amity Institute of Geo Informatics & Remote Sensing, Amity University, Noida 201 303, India
[b]Amity Institute of Global Warming & Ecological studies, Amity University, Noida 201 303, India
[c]CSIR-Central Glass & Ceramic Research Institute, Khurja 203 131, India
[d]CSIR-Recruitment and Assessment Board, CSIR Complex, Library Avenue, New Delhi 110 012, India
[e]Department of Chemistry, West Bengal State University, Berunanpukuria 700126, India

Received: 25 July; Accepted: 13 December 2022

Chemical and physical properties of clay samples collected from the deposits in the Ramgarh-Naudiha of Sonbhadra district, Uttar Pradesh were examined for their utilisation in ceramic industry. The raw clays from the deposits were found to be siliceous ball clays, contained less kaolinite, non-plastic and were unsuitable for making ceramic items. These clays have been subjected to standard beneficiation techniques which removed the free quartz. The beneficiated clays were less siliceous, had improved properties that can be used as partial replacement material in making ceramic items

Keywords: Ball clay, Beneficiation, Ceramics, Calcareous, Geology

1 Introduction

Clay minerals are the weathering products of continental rocks. The composition of clay minerals primarily depends on the source rock composition, climate and topography of the drainage basin of the river. The parent rocks in the humid tropical regions undergo weathering and release clay minerals, which are transported to the estuary by rivers. The fine grained nature of the clay might be due to the attrition among particles while being transported by flowing water before depositing in to the basin and the water demand for such fine ball clays is higher than for most china clays. In an estuarine environment, clay minerals undergo modifications by physical and bio-geochemical processes and get accumulated in sediments[1].

The minerals that are found to be rich in Kaolinite are identified as Kaolin or china clay[2]. Kaolinite is a common 1:1 dioctahedral phyllosilicate (clay) mineral found in soils across the world, particularly in highly-weathered environments, as well as scattered monomineralic deposits that are mined for industry. Being a 1:1 mineral, each kaolinite layer has one silica tetrahedral sheet and one alumina octahedral sheet. Individual layers are held together in a crystal by hydrogen bonding between the octahedral sheet of one layer and the tetrahedral sheet of the adjacent layer[3].

Kaolinite minerals may be expressed by chemical formula $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$.[4] In ancient times, sources of clays were widely available, between them soils or surface sediments have been the proper sources for ceramics without further treatment, due to their natural mixture of plastic and non-plastic components[5]. Kaolin is used extensively in the ceramic industry, where its high fusion temperature and white burning characteristics make it particularly suitable for the manufacture of white ware, refractories[6], sanitary wares, crockeries, cement, paper coating, extender pigment[7] etc. Special grade china clays are used as fillers in pharmaceutical industries[8]. The purity of clay determines its' suitability in ceramic industry. Pure kaolinite is white in colour and its chemical composition is ca. SiO_2–46.54 wt%, Al_2O_3–39.50 wt% and H_2O–13.96 wt%.[9] The clays formed by the weathering of siliceous rocks in *in situ* condition are considered primary clays and are the purest forms in terms of composition, whereas, secondary clays are formed by deposition of the particles by water or air along with presence of impurities like quartz, anatase, rutile, pyrite, siderite, feldspar, depending on the provenance and

*Corresponding authors
(E-mail: swapankumar.ghosh2@mail.dcu.ie)

depositional environment[10]. Iron usually exists as iron oxides or hydroxides and occasionally as pyrite, siderite, illmenite or as a minor component in mica, etc. Iron may also substitute for aluminium in the kaolinite structure[11]. The non-structural Fe in iron-stained kaolinite generally exists as a fine coating of goethite, non-crystalline gel on kaolinite plates[12,13]. In India, Gujarat was the leading producing state of kaolin accounting for 64% of the total production in 2014–15 followed by Rajasthan (16%), Kerala (15%) and West Bengal (2%). The remaining 3% was shared by Andhra Pradesh, Jharkhand, Karnataka and Madhya Pradesh[14].

In globalisation and world-wide competitive market, the revenue generated by industries is going down and manufacturing resources are getting costly[15]. Reserves of quality china clays in India are exhausting and with the spiraling rise in the cost of the raw materials and increasing cost of production, have made the existence of the Indian ceramic industries very difficult in this competitive world. At this juncture, search for other sources of raw materials like clays within India can be made use and substitute the expensive or imported clays.

As per the reported data, the estimated reserve of Clay in the Ramgarh-Naudiha and surrounding area is 165 lakh tonnes (2006) in Sonbhadra district[16,17] in the south-eastern part of Uttar Pradesh. This district occupies a geographical area of about 6800 sq km[17]. A thick clay zone of about 30–38 m has been encountered in Kuldiwa Kon and Bilwara-Sonjhar Blocks. In this area, opencast mining is adopted which can have significant impact on the environmental status of the district[17]. Though there are few reports in the recent past for utilising the low grade Indian clays by beneficiation[18–21] and partial substitution of the expensive clays, no systematic study has been made on the clay deposits of the south eastern Uttar Pradesh for use in ceramic industries.

With this background, clay samples 10 kg each were systematically mined in the Ramgarh-Naudiha region of Sonbhadra district from 15 locations based on the appearance and visible properties. Samples were tagged properly and used for further investigation to assess their suitability in ceramic industry. The geological and geomorphological details were photographed using digital camera. The quality of the raw clays was tested physico-chemically. The presence of poorly crystalline kaolinite in the clay was confirmed by X-ray diffraction. Beneficiation, utilising standard methods by sieving and magnetic separation techniques[22], resulted considerable improvement in the quality of the clays. The raw and beneficiated clays were air dried at 110°C and fired in the temperature range 1200°C to 1350°C to evaluate the green and fired properties which showed substantial improvements in the beneficiated clays, matching Grade 3 of Type 1–Unwashed plastic clay, IS:4589-2002.

2 Materials and Methods

2.1 Geology of the study area

Son, Rihand, Kanhar, Karmanasha, Gaghar and Belan rivers and their tributaries constitute the drainage in the area. Near Kalighat, Son enters the area, flows nearly 60 km towards east and leaves the area about 15 km north-east of Kon and enters Bihar (Fig. 1). The river Son forms a deep cut valley of about 12-15 km width. This tableland forms a part of the Kaimur plateau with little undulations and a sharp line in the south which separates it from the Valley of Son River. The altitude of the plateau is about 250-400 m above mean sea level (MSL), whereas, the valley of Son river lying south of the tableland has altitude from 150-200 m above MSL. The area south of Son valley is marked by ridges, valleys and forests with an altitude 200-400 m above MSL[16] (for stratigraphy see Supplementary material and Table S1).

An impure variety of chert, called porcellanite is abundant in the area and is present on the right bank of Son River in the Semri Group of the Lower Vindhyan Supergroup (Panel B in Fig. 2). Due to its abundance, most of the Middle Palaeolithic artifacts are made on this particular type of chert, while the upper palaeolithic and microlithic tools are made on cryptocrystalline siliceous materials like quartz, agate and chalcedony[17].

The clay deposits of Ramgarh-Naudiha area lies in between latitude 24°25'N-24°27'N and longitude 83°15'E–83°21'E in the Survey of India toposheet No. 63P/7 and 63P/3. The clay deposits are exposed and overlain by sandstone or covered with topsoil and ferruginous sandstone. The clay deposit occurs in sedimentary feldspathic sandstone. In the western portion of Harwariya nala (Panel a in Fig. 4), calcareous sediments like limestone are found flanked by phyllitic rocks and followed by quartzites. East of this nala, mostly porcellinites are present in the north and quartzite beds in the southern part which contains fine grained clay deposits with calcareous nodules. Harwariya nala form a topographically lower basin in the eastern part where clay is deposited.

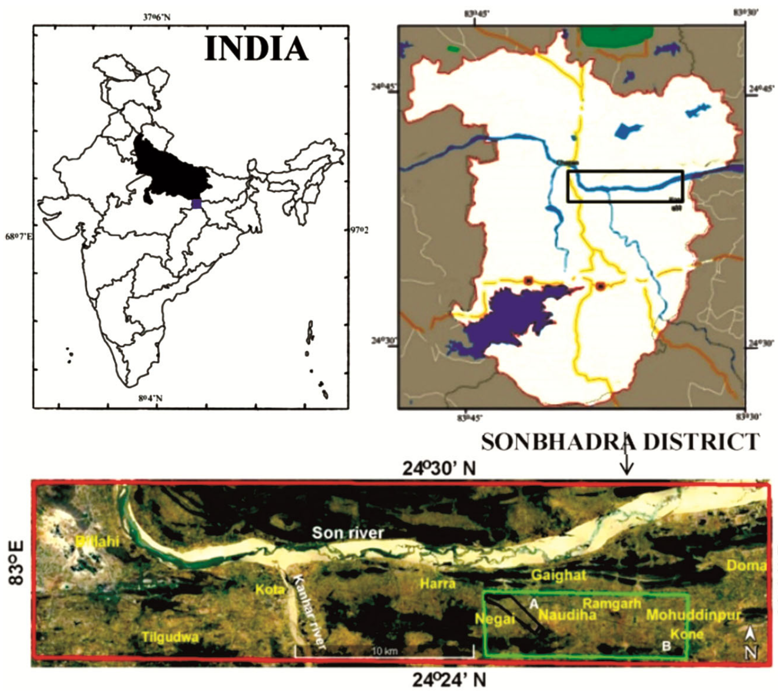

Fig. 1 — Location map of the study area in Sonbhadra district, U.P. The green rectangle with A and B indicates the locations of clay samples.

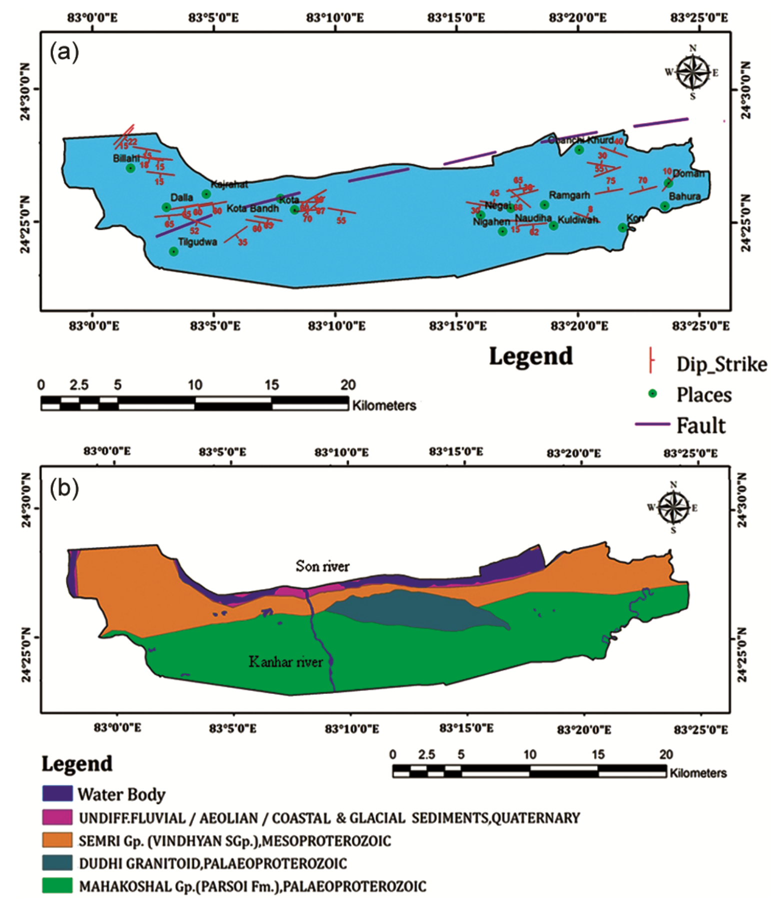

Fig. 2 — Map of study area of Ramgarh-Naudiha, Sonbhadra district, UP showing (a) Fault and Dip-Strike, and (b) Stratigraphy of the rock formation.

2.2 Lithology

Bedded limestones occur in the Billahi, Dala and Obra striking mostly NW-SE from Chopan to Dala and swings to E–W near Dala, then extends upto Kotabandh. The limestones are thick bedded upto Kanhar river. South of this area bedded limestones are flanked by phyllitic schist (Fig. 3).

East of Kanhar river, bedded limestones continue along the banks of Son river. In the North and South, is bounded by coarse grained intrusive granitic body. The granitic body is bordered by porcellinites dipping north showing east-west strike. In the southern portion, east of the Harwariya Nala, Nigahen, Kuldiwah and Kon areas are soil covered; and at places clay patches are located which are indicated by old mining pits. In the southern area, clay zone is flanked by bedded quartzites trending east-west dipping south which are occurring as ridges. Structurally the central belt starting from Naudiha to Bahura is flanked by the porcellanites in the north, trending E-W are northerly dipping and the quartzites are southerly dipping, indicating a probable anticlinal structure where the crust would have been subjected to long period of erosion and deposition of clay minerals. The granitic body clearly shows the presence of inclusions in it and remains as vestiges on the top surface (Fig. 3). This indicates that the granitic intrusion is younger than the metasedimentary rocks in the area. A fault, running WNW-ESE from Chanchi Khurd to Doman in the eastern portion of the area, shows strong structural disturbance (Panel A in Fig. 2 and Fig. S1 in Supplementary material).

The maps of the study area were prepared in Google Earth Pro and ArcGIS V10.4. Fifteen clay samples were collected from the marked spots A and B (Fig. 4) from Ramgarh-Naudiha area of Sonbhadra district. The clays at locations 31, 32A and 32B (Panel b in Fig. 5) showed presence of spherical (dia 1–1.5 cm) calcareous nodules, may be the result of eroded particles transported from the nearby limestone deposits by flowing water into the basin. The clays were analysed physically and chemically to ascertain their suitability for ceramic industries as per Indian Standard Specifications [IS 2840-1965, IS 4589-2002].

2.3 Beneficiation

The clay samples were beneficiated using aqueous sedimentation method which consists of the following operations, e.g., (i) crushing, (ii) slaking, (iii) blunging,

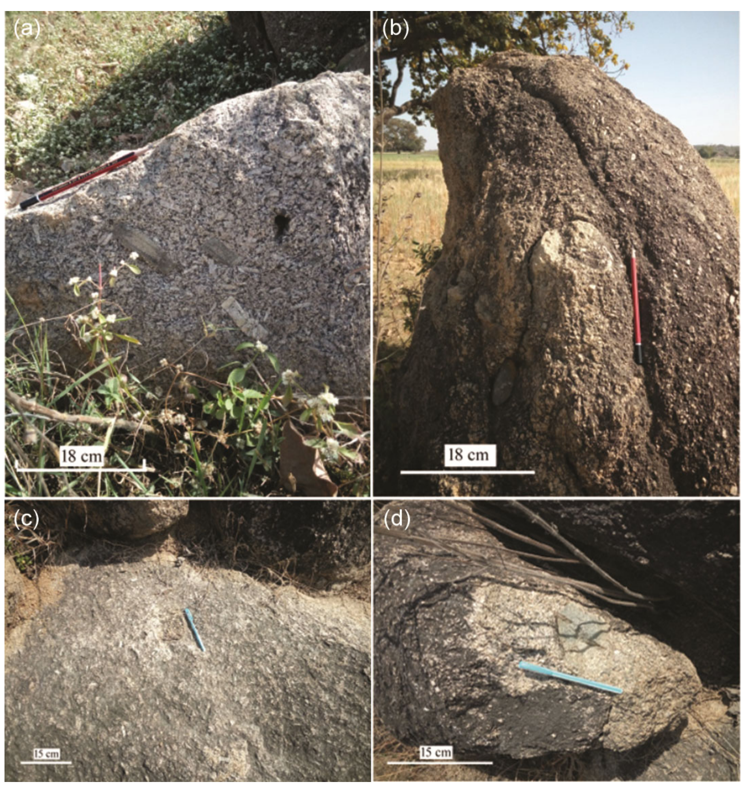

Fig. 3 — Granitic bodies show inclusions of feldspars, and metasedimentary rocks, (a) Coarse grained granite show lamellar phenocrysts of feldspar, (b) Large xenocrysts of other rocks in the weathered granitic body, (c) Coarse grained granite show lamellar phenocrysts of feldspar, (d) Large phenocryst of feldspar in the coarse grained granite.

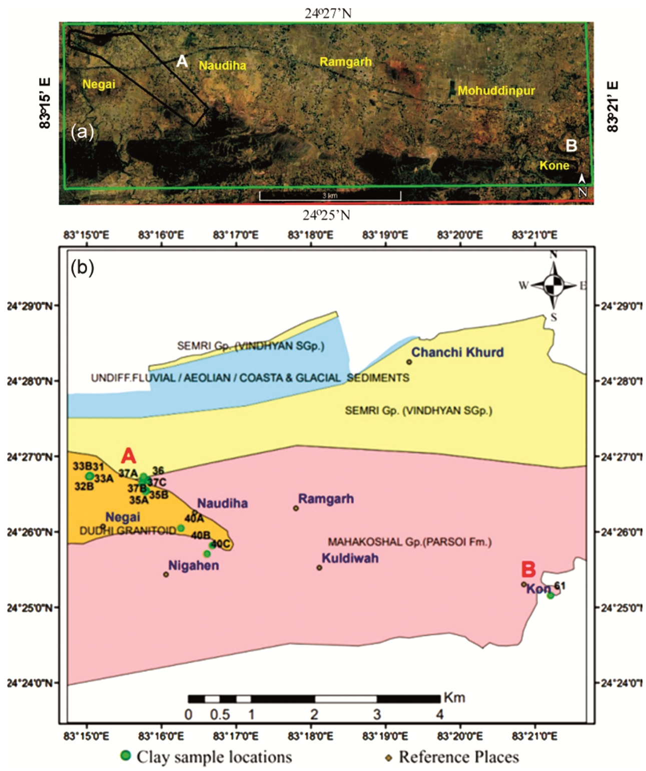

Fig. 4 — (a) Clay sample location A and B in goole earth, and (b) the same in ARCGIS map.

(iv) settling the impurities, and finally (v) recovering the clay. Each of the above operations may, however, need some adjustments depending upon the individual characteristics of the clay undergoing washing[25,26]. Mined clays which were dry, hard, and lumpy were crushed using a small jaw crusher (Retsch, Germany). Powdered clays of 1 kg batch were slaked in 10 l water overnight. The clay was then mechanically stirred vigorously using a Remi ½ hp overhead stirrer for 30 min to disperse the clay in suspension. The suspension was passed slowly through a sand box followed by zig-zag channel to screen off ~53 µm fraction and then it was collected in the final settling tank. In order to maximise the clay recovery, sand box fraction and zigzag channel fractions were collected and re-passed through a levigation unit following the earlier sequence twice. On blunging the raw material, the fine clay will go in suspension and the accessory minerals like quartz, mica, feldspar and others as well as the undispersed crude, settle at the bottom. Certain difficult clays can be brought in suspension, to some extent, with the help of electrolytes as well as by adjusting the concentration of the crude clay in the suspension[25]. The levigated clay fraction collected in the final settling tank was passed through a magnetic field (1500 G) until no

Fig. 5 — Optical photographs of (a) clay deposit, and (b) clay deposit showing presence of calcareous nodules.

trace of magnetic material was seen on the magnet. The demagnetised clay suspension was dried and marked as levigated clay and reserved for further investigations.

2.3.1 Fired colour

The samples of dry test pieces were fired in an oxidising atmosphere in an electric muffle furnace at 1400°C (cone 14 down) with half an hour soaking. The fired colour of the discs was visually examined and the colours were assigned, as far as possible, on the basis of the colour chart given in IS:5-1969 for ready mixed paints.

2.3.2 Fired linear shrinkage

The 30 mm dia and 10 mm thick discs made for determination of dry linear shrinkage were fired at 1400°C and the total fired shrinkage was measured similarly as done for determining dry linear shrinkage.

2.3.3 Water absorption

Water absorption of fired samples was determined by boiling the fired test specimens in distilled water for 2 h and allowing them to soak for 24 h. The weight of such a 'saturated' specimen in air was taken as W; the weight of a dry specimen was taken as D; and the water absorption (%) was given by the equation,

$$\text{Water absorption (\%)} = \frac{W - D}{D} \times 100$$

The clays were subjected to the following tests like water of plasticity, dry linear shrinkage, grit content, particle size distribution and rational analysis to ascertain its quality as per Indian Standards Specifications (IS 2840-1965, IS 4589-2002) (For details see Supplementary material and Fig. S2).

2.3.4 Chemical analysis

The method adopted for the ultimate chemical analysis of the -100 mesh material was similar to that given in the IS:4589-2002 standard for wet chemical analysis of ceramic whiteware clays. The alkali oxides Na_2O and K_2O were determined by the Flame photometry[27,28].

2.3.5 X-Ray Diffraction

X-ray diffraction (XRD) patterns of the raw clay were recorded between the 2θ range of 10°–70° (2θ) with a step size of 0.02° using a Philips X'pert PRO X-ray diffractometer (Almelo, the Netherlands), using Ni-filtered Cu-Kα radiation of wavelength 1.5406 Å.

3 Results and Discussions

The area across Negai–Ramgarh–Naudiha–Barwadih–Mohiuddinpur–Doma, forming roughly a triangular space tapering towards Doma could have been a basin which would have acted as receptacle for deposition of clays at places. The exposure, along the Harwariyanala, exhibits clay deposits occasionally mixed with calcareous nodules (panel b in Fig. 5) and many sporadic clay deposits in the basin spread all through which is indicated by old clay mine workings. The sources of clay material are likely the granitic bodies which were altered by the forces of nature and get deposited to contribute to form the clay material. The calcareous nodules present in the clay are mostly from the carbonate rocks (mostly limestones) from the northern beds flanking the basin.

The raw clays collected in the study area are found to be siliceous (Fig. 7) and less plastic in nature (Panel A in Fig. 6). They are much inferior in quality with respect to loss on ignition (LOI) (2.07–6.01%), SiO_2 (67.33–87.67%), and Al_2O_3 (8.10–19.81%) contents as per the Indian Standards for the China Clays and ball clays for ceramic industries. The kaolinite content in these clays was found to be very low (Fig. 9). The impurities like CaO (0.02–1.74%), MgO (0.08–4.86%) contents are found on the higher side (Table S2 in Supplementary material). Presence of calcareous nodules was noted in the clay samples of locations 31, 32A and 32B (see Supplementary material and Table S3).

Often, mineral impurities present in the primary deposit are left behind during the transport. However, other impurities such as TiO_2 and Fe_2O_3 are often picked up during transport[23]. Because of the fine particle size, the water demand for these clays is higher than for most china clays. The SiO_2 content of these clays are higher due to its deposition from the adjoining areas. In the raw state, ball clays range in colour from light brown to nearly black, depending on the organic content. After firing, the higher Fe_2O_3 and TiO_2 contents give an ivory to buff colour.

The clays after beneficiation showed reduction of SiO_2 content to 63.07–70.10%, Al_2O_3 to 18.21–22.77% (Fig. 7) and LOI increased to 5.77–7.69% (Fig. 8) which imparted enhancement oftheir plasticity (panel

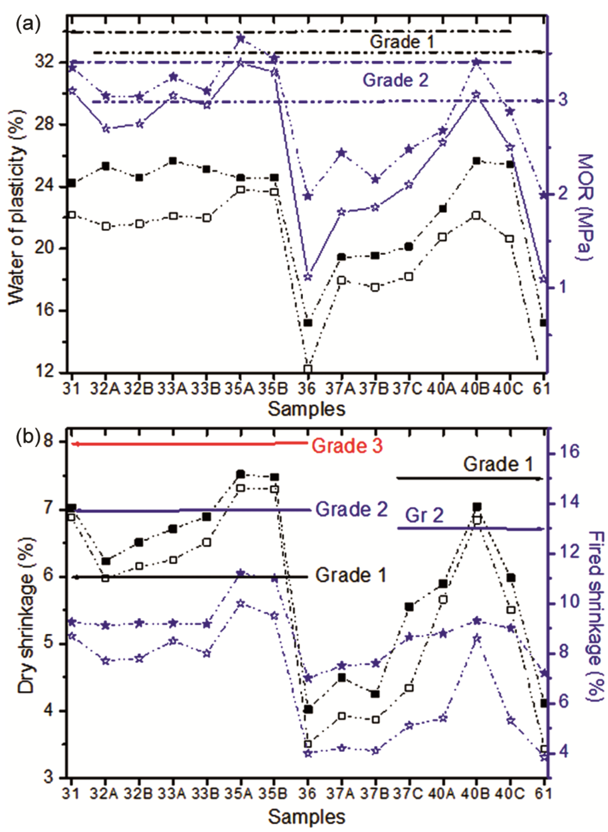

Fig. 6 — Physical properties of the raw and beneficiated clays (a) Water of plasticity (WOP), (square box) with MOR (star), and (b) Linear shrinkage (LS) (square box), plotted with fired shrinkage (star symbols).

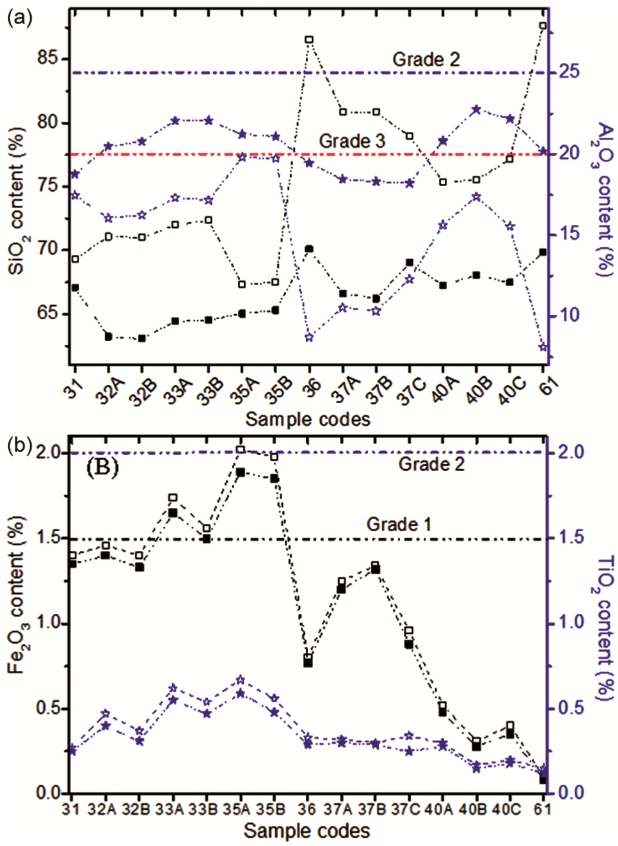

Fig. 7 — Chemical analysis data on (a) SiO_2 (square box) and Al_2O_3 content (star) with the empty symbols represent raw and filled symbols represent washed clay data. The horizontal lines indicate the clay grades based on alumina content, and (b) Plot of Fe_2O_3 (square box) and TiO_2 contents (star) with the empty symbols representing raw and filled symbols as washed clay data. The horizontal lines indicate the clay grades based on both Fe_2O_3 and TiO_2 contents.

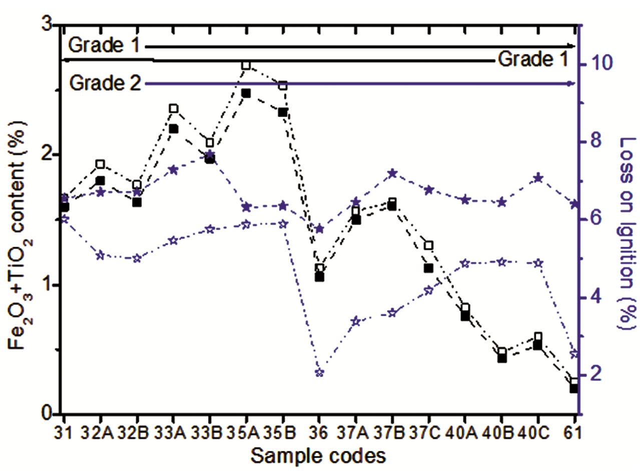

Fig. 8 — Plot of Fe_2O_3+TiO_2 content (square box) and LOI (star) against samples with the empty symbols representing raw and filled symbols as washed clay data. The horizontal lines indicate the clay grades

A in Fig. 6). The LOI value suggests presence of more kaolinite in the beneficiated clay. Wet sieving, therefore, removes almost all the quartz impurity from the clay (Fig. 7 and Table S4 in Supplementary material).

The X-ray diffractograms of the representative samples collected from Ramgarh-Naudiha area of Sonbhadra district, U.P. (Fig. 9) show mainly siliceous associated impurity in the unwashed clay as indicated by the presence of (100) and (101) peaks of low quartz at 20.5 and 26.66° 2θ (ICDD card 5-490) respectively. The physical appearance and X-ray patterns revealed that associated minerals and impurities present in the crude clay are quartz, feldspar, mica, coloured minerals, soluble salts and scattered organic matter. Presence of poorly crystallised kaolinite clays (ball clay) have been confirmed by the presence of reflections from (001), (002), and {(202), (131)} planes as indicated by the presence of X-ray peaks at 12.4, 24.94 and 38.5 degree 2θ (ICDD card 5-143) respectively.

Due to the higher content of silica, the clays of the study area were of relatively low plastic in nature and thus unsuitable for direct use in the ceramic industries. But on beneficiation, some clays (31, 32A, 32B, 33A, 33B, 35A, 35B, 40A, 40B and 40C) showed improved properties in terms of reduced SiO_2, TiO_2 and Fe_2O_3 contents, and enhanced Al_2O_3, LOI contents and improved LS, FS, WOP and MOR. These beneficiated clays were found close to the Grade II and Grade III ball clays as per Indian Standards (IS 2840-1965, IS 4589-2002). These clays may be utilised as a partial replacement of the

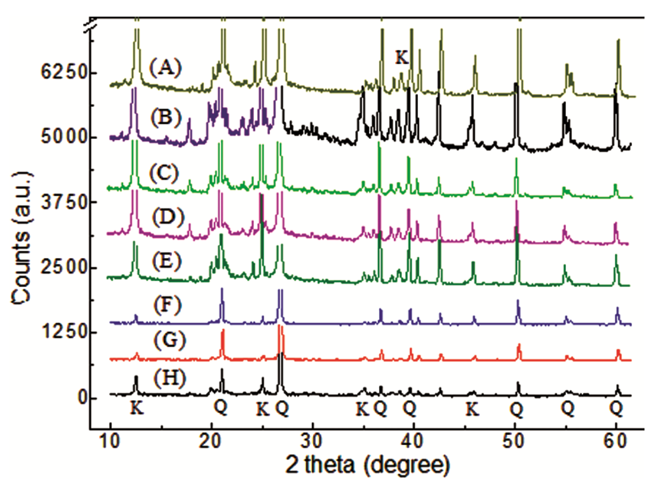

Fig. 9 — X-ray diffraction patterns of clay samples (a) 40A, (b) 35A, (c) 33A, (d) 40B, (e) 37C, (f) 37B, (g) 36, and (h) 31. The Y-axis is scaled to avoid overlapping of layers.

expensive / imported clays for making ceramic wares. However the clays 36, 37A, 37B, 37C and 61 were found to be of the poorest quality.

4 Conclusion

The nature of the clay deposits show that they might have been formed by the weathering and decomposition of the granitic rocks in one location and then transported and deposited by the fluvial action of water into the enclosing basin and are called ball clays. The fine grained nature of the clay might be due to the attrition among particles while being transported by flowing water before depositing in to the basin and the water demand for such fine ball clays is higher than for most china clays. The outcrops of the clay deposit showed presence of nodules eroded from the nearby limestone deposits and transported by flowing water into the basin. The SiO_2 content of these clays are higher due to the deposition of the silica from the adjoining areas. In the raw state, ball clays range in colour from light brown to nearly black, depending on the organic content. After firing, the higher Fe_2O_3 and TiO_2 contents give an ivory to buff colour.

The beneficiated clays, as such, were not suitable for use in manufacture of high grade ceramics. The LOI, Al_2O_3 and Fe_2O_3+TiO_2 contents, shrinkage and firing characteristics show tht the deposits are suitable as grade II and III clays for making ceramic products. Particle size distribution and water of plasticity however do not strictly meet the industry requirements. The clay deposits under the study could be useful as a partial substitute of the imported, expensive clays in the ceramic industries, thus contributing reduction in production cost.

Acknowledgements

The authors (DPK, LKS and SG) are extremely thankful to Director, CSIR-Central Glass & Ceramic Research Institute for permitting the study and using its laboratory facilities. Technical staffs helped the testing of samples. The Geology Department, Aligarh Muslim University, provided facilities for carrying out the XRD analysis. Thanks are also to the Directorate of Geology and Mining, Government of Uttar Pradesh for giving important guidance about the clay deposits in the area. We are thankful to AIGIRS, Noida for facilities provided and advise in preparation of this article.

References

1 Nasnodkar M R & Nayak G N, *Indian J Geo-Mar Sci*, 48 (3)(2019) 379.
2 Perry D L, *Handbook of Inorganic Compounds* (2nd ed. CRC Press, Boka Raton, USA), 2011.
3 https://virtual-museum.soils.wisc.edu/display/kaolinite/
4 https://www.britannica.com/science/clay-mineral
5 Barden L & Sides G R, *J Soil Mech Found Div,* 97 (1971) 1708.
6 https://www.britannica.com/science/kaolin
7 Ghosh S, Warrier K G K & Damodaran A D, *J Mater Sci Lett*, 9 (1990) 1046.
8 Murray H H, *Appl Clay Sci*, 17 (2000) 207.
9 Cruz M D R, Fernando N & Juan J, in *Crystal structure of clay minerals and their X-ray identification,* edited by Brindley G W & Brown G (Mineralogical Society, London SW7 5HR), 1980.
10 https://www.britannica.com/science/silicon
11 Levy G J & Shainberg I, in *Encyclopedia of Soils in the Environment*, edited by Hillel D (Academic Press, New York), 2005.
12 Grimshaw R G, *Physics and Chemistry of Clay*, (Ernest Benn, London), 1971.
13 Malden P & Meads R, *Nature*, 215 (1967) 844–846.
14 Randive K, Raut T & Jawadand S, *Miner Econ,* 34 (2021) 371.
15 Bhadu J, Bhamu J & Singh D, *Indian J Eng Mater Sci*, 28 (2021) 271.
16 Srivastava V & Srivastava H, *J Sci Res India*, 56 (2012) 1.
17 Mishra A & Pandey V K, *J Appl Nat Sci*, 5 (2)(2013) 361.
18 Ghosh S N & Guha S K, *T Indian Ceram Soc*, 1 (1981) 40.
19 Saikia N J, Bhrali D J, Sengupta P, Bordoloi D, Goswamee R L, Saikia P C & Borthakur P C, *Appl Clay Sci*, 24 (1-2)(2003) 93.
20 Chandrasekhar S & Ramaswamy S, *Investigations on Selected Indian Kaolins for their Possible Value Addition*, paper presented at Proceedings of the International Seminar on Mineral Processing Technology, Chennai, India, 2006.
21 Kar B, Sahoo H, Rath S S, Rao D S & Das B, *Clay Miner*, 48 (2013) 759.
22 Amarascriwardena D, Grove E D & Bowen L, *Clay Clay Miner*, 34 (3)(1986) 250.
23 Maharana C & Tripathi J K, *District Survey Report,* Sonbhadra (2016; 2018).
24 Mehra S B, *Herit: J Multidiscip Stud Archaeology*, 6 (2018) 148.
25 Sen S, *T Indian Ceram Soc*, 23 (1)(1964) 1.
26 Sen S & Guha S K, *T Indian Ceram Soc*, 27 (1)(1968) 19.
27 Bennet H & Reed R A, *Chemical Methods of Silicate Analysis*, Academic Press, London, UK (1971).
28 Dasgupta S & Roy S K, *Chemical Analysis of Ceramic and Allied Materials* (Indian Institute of Ceramics, Kolkata, India), 1985.
29 Andrews A I, *Ceramic Tests and Calculations* (John Wiley & Sons Inc, London), 1945.