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Physico-chemical characteristics of Nagar Parkar kaolin deposits, Thar Parkar district, Sindh, Pakistan

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Abstract

Nagar Parkar kaolin deposits lie parallel to Runn of Kutch area, aligned in a belt trending NW–SE. The present study examines the physico-chemical characteristics of the raw and washed Nagar Parkar kaolin deposits. It compares them with world's best kaolin deposits and provides the basis for detailed studies on the development and value added utilization. The Nagar Parkar kaolin deposits are formed by chemical weathering of Precambrian granite. The Nagar Parkar raw kaolin has medium compressibility, moderate toughness, medium plasticity and acceptable moulding properties. The processing of Nagar Parkar kaolin was being done by simple water washing instead of elutriation. After washing the kaolin SiO_2 content was reduced by 10% and the Al_2O_3 content increased by up to 15%. Present study shows that the raw and washed kaolin of Nagar Parkar is of good quality and comparable with world's known kaolin deposits. Due to lack of processing by elutriation, the consistency in quality of the Nagar Parkar kaolin is not maintained. Hence, its utilization is restricted to limited low cost sanitary and crockery products in the country.

Keywords: Kaolin; Physico-chemical properties; Thermal characteristics; Nagar Parkar; Pakistan.

1. Introduction

In Pakistan, with the growing ceramic table and sanitary ware industry and fast developing paper, plastic and rubber industries, the demand for kaolin raw material is increasing. Kaolin (China clay) deposits of economic significance occur in Shah Dheri, Swat, (34°53′30″N; 72°53′30″E) and Nagar Parkar district Thar Parkar, Sindh (24º 15' to 24º 30'N, 70º 37' to 71º 07' E). The Shah Dheri kaolin is processed by elutriation, which produces three grades of kaolin based on the physico-chemical properties and particle size for making high quality ceramic products. In contrast, the Nagar Parkar kaolin is mined and processed by untrained manpower and by unscientific methods. Although these kaolin deposits have been mined in hundreds of pits and utilized by the local sanitary ware industry for about two decades, detailed physico-chemical studies for their value added utilization are still lacking.

The Nagar Parkar kaolin deposits were first reported by Geological Survey of Pakistan in 1961. Detailed exploration studies were carried out by Pakistan Mineral Development Corporation (PMDC) during 1976-79. Based on a large number of exploratory and drilling pits, bulk sampling, physical tests and chemical analysis, 3.634 million tons of reserves were estimated (Kella, 1983). Present study examines the physical and chemical characteristics of Nagar Parkar kaolin (raw and washed) with emphasis on comparing them with other kaolin deposits in Pakistan and some other countries.

2. Geology of the study area

The Nagar Parkar area lies in Thar Parkar district of Sindh province of Pakistan ~400 km south east of Karachi at 24º 15' to 24º 30'N, 70º 37' to 71º 07' E (Fig. 1). Detailed geological map of Nagar Parkar area was prepared by Muslim (1997). Nagar Parkar is the only other area in Pakistan, apart from the Kirana hills in Punjab with Precambrian outcrops of the Indian Shield (Table 1).

The Nagar Parkar kaolin was formed by deep chemical weathering of Precambrian granite (Ismail, 2011). Kaolin deposits occur as medium to large size pockets or lenses mostly covered by soil or laterite cap rock. The thickness of the deposits varies from 1.5 to 10 m and average overburden thickness is 2.1 m (Ismail, 2011). There are dozens of localities in Nagar Parkar, where hundreds of open pits have been dug to exploit kaolin by artisanal mining methods. This study is focused on the six large deposits of Nagar Parkar area, namely Viravah, Ramji jo Vandio, Karkhi, Parodhro, Dhedvero and Moti jo Vandio (Fig. 2).

3. Processing of Nagar Parkar kaolin

The raw kaolin collected from Nagar Parkar deposits is sent to the processing plant. In the first step, raw kaolin is introduced into rotating machine

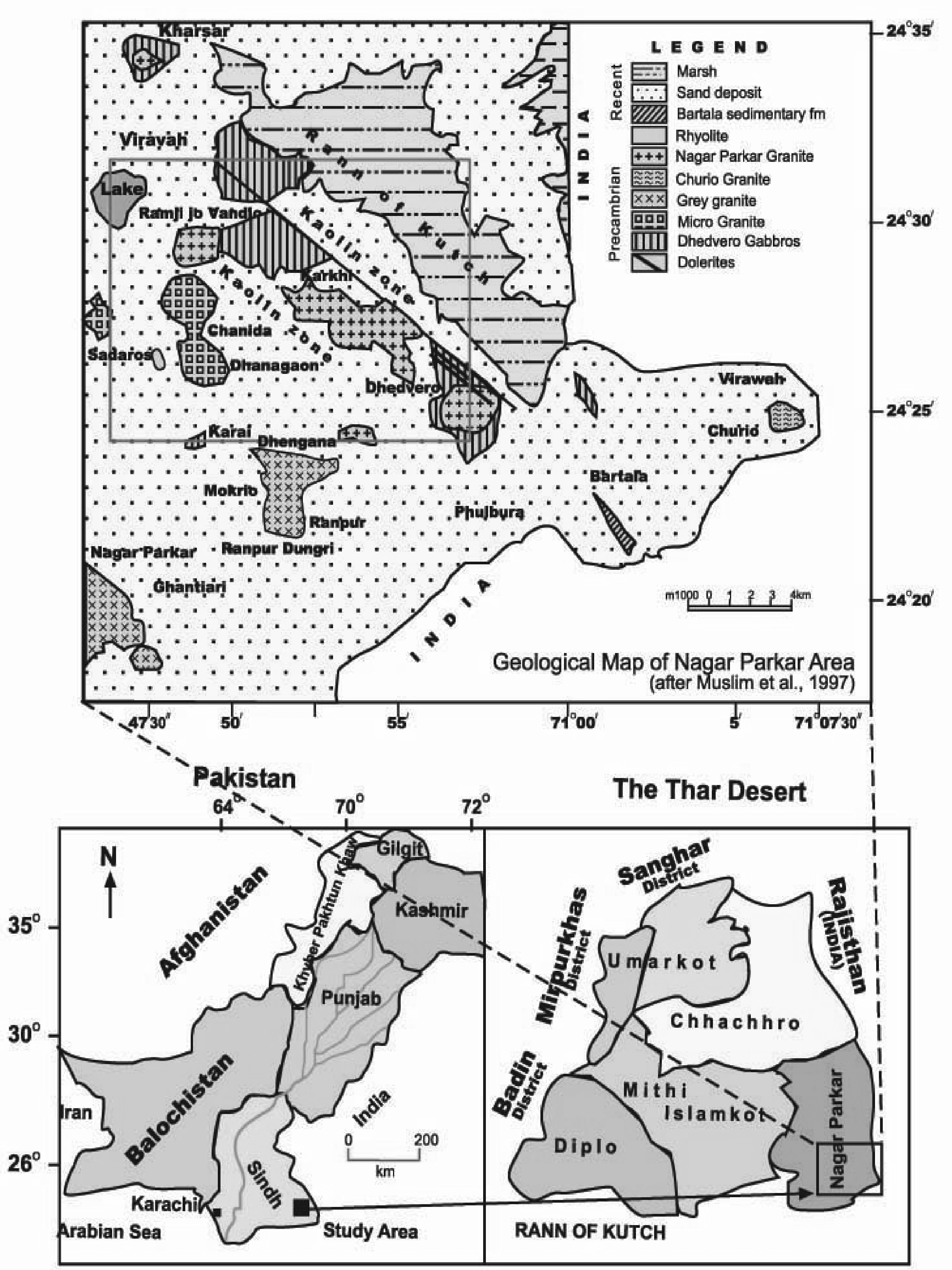

Fig. 1. Location and Geological map of Nagar Parkar, Thar Parkar district Sindh.

Table 1. General stratigraphic succession in Nagar Parkar area (After Kazmi and Khan, 1973; Kella, 1983).

AGE	GROUP	ROCKS/ DEPOSITS
Early Recent to Recent	Unconsolidated Quaternary deposits	Stream sandstone and flood plain deposits, Playa and evaporite deposits Outwash deposits, piedmont and sub-piedmont deposits.
UNCONFORMITY		
Cretaceous to Eocene	Sedimentary rocks	Aeolian sand deposits, Rann of Kutch mud deposits Residual deposits: Laterite/kaolin Bartala Sedimentary unit
UNCONFORMITY		
Precambrian	Nagar Parkar Igneous complex	Basement (metabasites) with acidic basic dykes and pink/ grey granite.

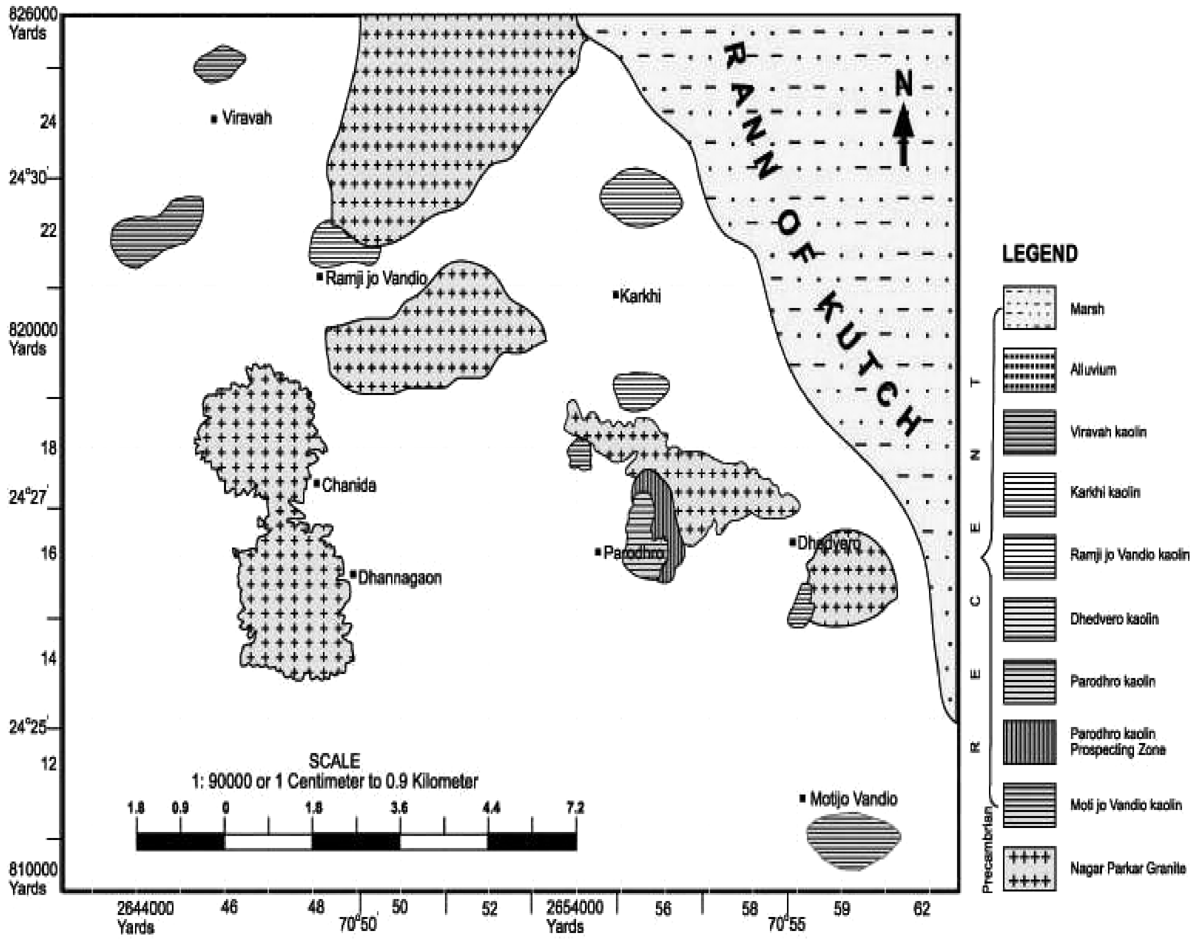

Fig. 2. Geological map of Nagar Parkar Kaolin deposit, Thar Parkar district, Sindh (after Ismail, 2011)

in which water is added and mixed well to form slurry, which is passed into 250 mesh sieves. The sieved slurry of kaolin is then pumped into open tank for settling. After two days, water mixed with impurities is pumped into another tank for recycling and the settled kaolin is pumped into a tank, from where the washed kaolin is filled into filter pressing unit. As a result, the slurry of water and kaolin are converted into washed kaolin cakes. These cakes are exposed to sunlight for drying and then broken into pieces. The broken pieces of processed (washed) kaolin are filled in the bags for sending mostly to the local kaolin based industries.

4. Methods and materials

About seventy clay samples were collected from six kaolin deposits and some kaolin processing (washing) plants located in Nagar Parkar area. At every pit and sample location, detailed morphological description, longitude, latitude, overburden thickness, depth of kaolin horizon, length and of width deposit were recorded.

The Atterberg limits (plastic limit, liquid limit and Plasticity index) were determined by Casagrande method in accordance with ASTM D 4318 (2012). The shrinkage limit was determined in accordance with ASTM D 4943. The specific gravity was determined by the Pycnometer method (ASTM D 854, 2012). The bulk density was measured according to ASTM D1556 (2012). In order to determine the screen residue percentage 100 g of sample was thoroughly mixed and dispersed with water. After carefully determining the weight percent solids of the dispersed slip, the amount of residue retained on the 300 mesh screen was accurately weighted and the percentages were calculated. Changes in kaolin color after firing were determined by the method used by IMERYS. This is a visual test in which kaolin sample is fired at 1360ºC and the colour is compared to that of a standard. The thermal properties of Nagar Parkar kaolin deposits were determined by Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA). The DTA and TGA were carried out using a Mettler Toledo TGA/SDTA 851 and 20 mg powdered sample with heating up to 1000ºC at the rate of 10ºC/min. Chemical analysis of raw and processed kaolin samples were carried out by X-ray Fluorescence Spectroscopy (XRF). Loss on ignition for each sample was also determined.

5. Results and discussion

5.1. Physical properties

The test to find out physical and firing properties conducted on representative samples from Nagar Parkar kaolin deposits and processing (washing) plants included plasticity limits (PL), plasticity index (PI), liquid limits (LL), shrinkage limit (SL), firing shrinkage, firing color, screen residue percentage, specific gravity (sp.gr) and bulk density (Table 2).

The physical characteristics of each Nagar Parkar kaolin deposit have been compared with international standards and specifications required by the kaolin based value added industries. According to Plasticity Chart (Casagrande, 1948) and clay identification chart (Bain, 1971) all the six kaolin deposits are inorganic in nature having medium plasticity, low to medium toughness, medium compressibility and their major mineral is kaolinite (Fig. 3a and 3b), which is comparable with good quality kaolin deposits of the world (Holts and Kovacs, 1981; Bain, 1971).

Firing color and firing shrinkage are the major properties of fired kaolin products, which provide additional information on the potential of clay for use in ceramics. The fired shrinkage of Nagar Parkar kaolin deposit ranges from 6 to 13% at 1360°C with no indication of black spots and cracks. The firing behavior of Nagar Parkar kaolin is similar to the Deopani kaolin of western Cameroon with firing shrinkage ranging between 13 and 15% (Saikia, 2003).

Table 2. Physical properties of kaolin (raw) samples of Nagar Parkar

S.No	Locality name	No. of samples	Density g/cm^3	Sp.gr.	PL%	LL%	PI%	SL%
1	Viravah	23	0.53-2.04 1.27avg.	2.4-2.68 2.57avg.	14.85-34.94 25.53avg.	30-49 39.39avg.	7.47-22.25 13.85avg.	0.14-3.20 1.05avg.
2	Parodhro	14	1-2.75 1.53avg.	2.4-2.65 2.55avg.	18-29.50 23.23avg.	30-42 36.28avg.	9.54-19 13.07avg.	0.16-2.92 1.100avg.
3	Moti Jo Vandio	7	0.96-2.81 1.75avg.	2.5-2.66 2.60avg.	18.65-32.08 24.36avg.	30-46 35.85avg.	9.6-16.63 11.50avg.	0.16-1.42 0.88avg.
4	Ram ji jo Vandio	4	1.14-1.98 1.51avg.	2.46-2.65 2.55avg.	19.55-23 20.86avg.	32-38 35.5avg.	11.0-16.0 14.5avg.	0.68-2.51 1.191avg.
5	Dhedvero	5	1-1.969 1.70avg.	2.55-2.63 2.6avg.	22-30 27.5avg.	35-48 46avg.	13-20 18. 50avg.	0.22-0.69 0.605avg.
6	Karkhi	12	1.22-2.75 1.79avg.	2.51-2.68 2.57avg.	15.98-32.44 22.64avg.	30-48 38.08avg.	9.79-26.63 15.47avg.	0.16-2.46 1.04avg.

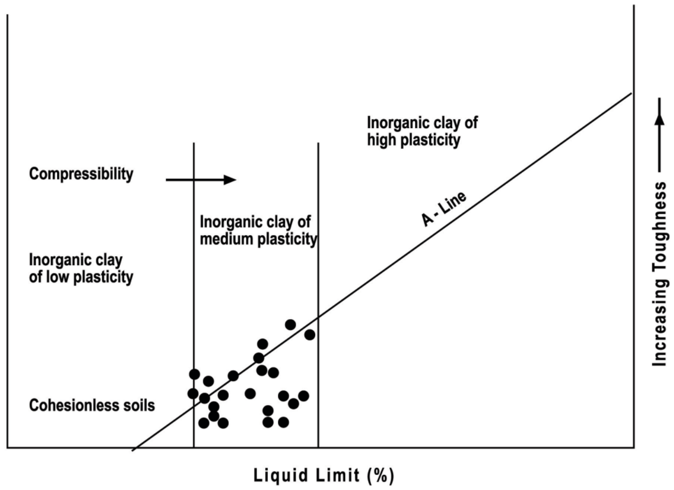

Fig. 3a. Plasticity chart for the classification of Nagar Parkar Kaolin deposit (after Casagrande, 1948).

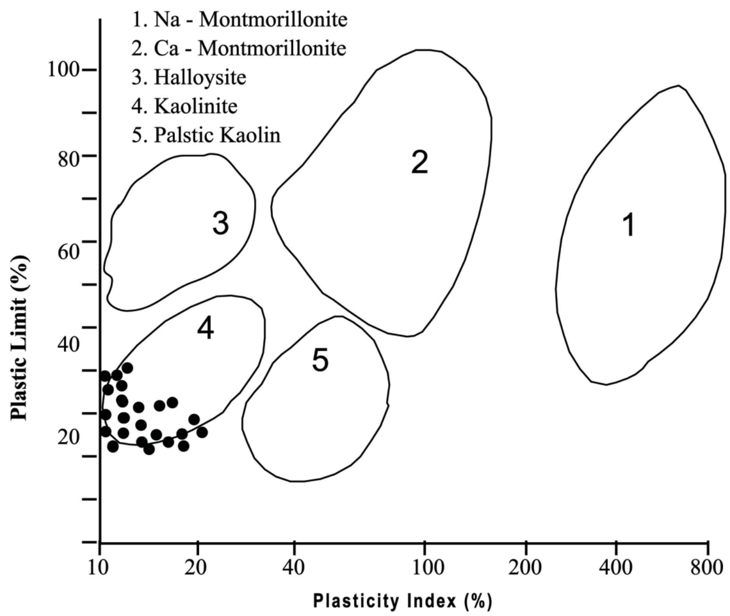

Fig. 3b. Clay identification chart of Nagar Parkar Kaolin deposit (after Bain, 1971).

The screen residue of the kaolin samples from all the deposits of Nagar Parkar, retained on the 300 mesh sieve ranges from 23.5 to 30%. After washing, the grit content is reduced to 6.6%, which can further be removed, if processing of Nagar Parkar kaolin is performed by elutriation. Average densities of raw kaolins dried at 110°C range from 1.273 to 1.797 g/cm³. The specific gravity of Nagar Parkar kaolin ranges from 2.40 to 2.69, which is very close to the specific gravity of pure kaolinite (2.62-2.66) according to Lambe and Whitman, 1979.

5.2. Thermal properties

Raw kaolin: The DTA curves of the Viravah, Parodhro, Karkhi, Moti jo Vandio, Dhedvero and Ramji jo Vandio kaolin samples show that first endothermic event, due to dehydration, i.e. loss of adsorbed water is observed at 150-250ºC (Fig. 4). The second endothermic peak which corresponds to dehydroxylation of kaolinite is associated with a well-defined endothermic peak in DTA curve at 500 - 550°C (McConville and Lee, 2005; McConville et al., 1998; Ekosse, 2001).

The weight loss in the temperature range 500-600°C obtained from the TGA curves varies between 7.04 and 8.48%. Considering that the weight loss due to dehydroxylation of pure kaolinite is 14% (Eslinger and Peaver, 1988), the calculated kaolinite content in the Nagar Parkar kaolin is 50.3-61.7%. This kaolinite content is comparable to that of the English kaolin (51.89%, after Haq et al., 2009).

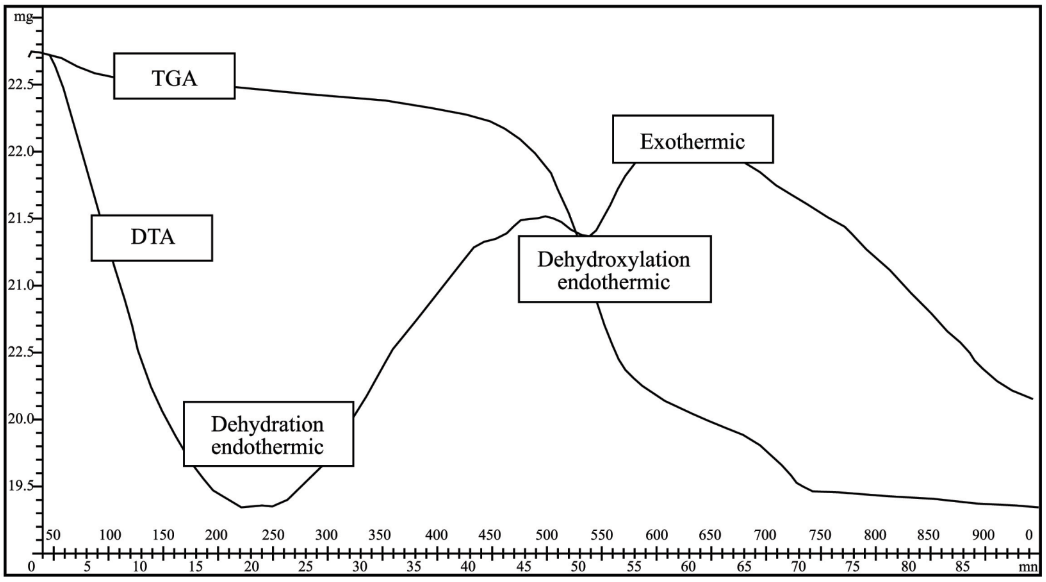

Fig. 4. DT and TGA graph of kaolin (raw) sample of Nagar Parkar deposit.

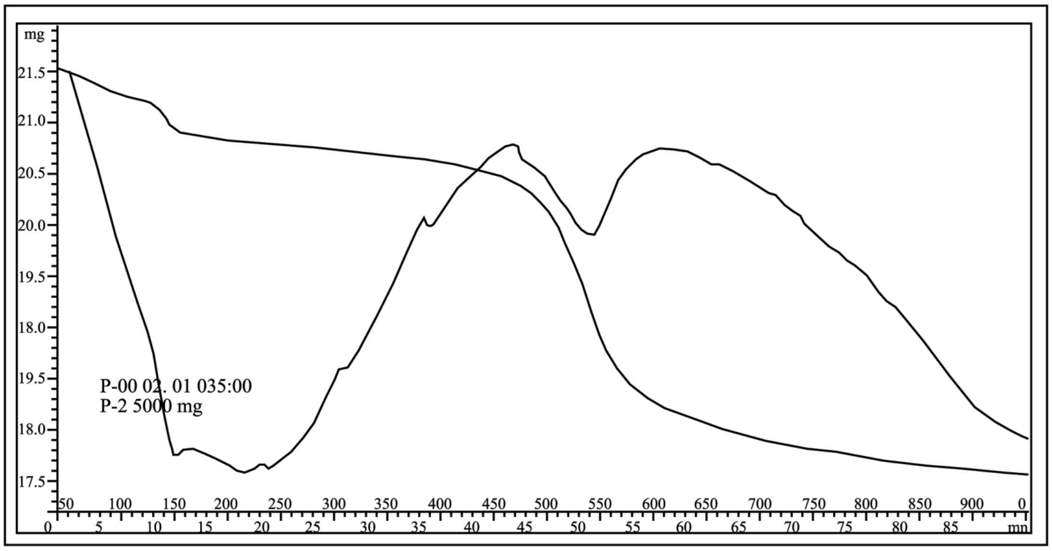

Fig. 5. DT -TGA curve of kaolin (washed) sample of Nagar Parkar

The first endothermic event of the washed kaolins, which is attributed to dehydration, is observed between 170 and 270ºC (Fig. 5). The endothermic peak is followed by an exothermic peak at ~500ºC, which can be attributed to the oxidation of impurities. The second endothermic peak of washed Nagar Parkar kaolin appears at ~560ºC and is attributed to dehydroxylation (Todor, 1976). The dehydroxylation temperature of washed Nagar Parkar kaolinite is comparable with English and Botswana kaolinite, with dehydroxylation temperature 500-600ºC (McConville and Lee, 2005, 1998; Ekosse, 2001). The exothermic effect appearing between 600-700ºC can be attributed to the oxidation of ferrous iron. The mass loss of the washed Nagar Parkar kaolinite was 8.52% at 500-600ºC. With further increase in temperature i.e. from 650 to 950ºC, mass loss was not observed.

6. Chemical characteristics

Raw kaolin: Thirty representatives (raw) kaolin samples from Viravah, Pardhro, Karkhi, Moti jo Vandio, Dhedvero and Ramji jo Vandio deposits of Nagar Parkar were analyzed by XRF for their major and minor element oxides (Table 3). The SiO_2 content of raw kaolin ranges from 48.7 to 59.2%. The raw Nagar Parkar kaolin has higher $S_iO_2$content than the ideal kaolin (46.6%), due to presence of quartz (Sei, 2004). The Al_2O_3 content of Nagar Parkar kaolin is lower (21.3-26.8%) than in the ideal kaolinite (39.5%) due to presence of quartz and clay mineral impurities. The Al_2O_3 content of clays depends upon the intensity of kaolinization. Incomplete kaolinization indicates lesser amount of kaolin minerals, and thus lowers Al_2O_3 content (Sayin, 2007; Visser and Young, 1990).

The loss on ignition (LOI) of kaolinitic clays allows estimation of the kaolinite content (Searle and Grimshaw, 1959). The LOI at 1000ºC of the raw Nagar Parkar kaolin ranges from 11.1 to 13.7%; hence it is comparable to other important kaolin deposits of the world. The Fe_2O_3 content of the Nagar Parkar kaolin ranges from 0.29 to 1.62%, which is close to the maximum allowed limit of 1% Fe_2O_3 (Highley, 1984). Presence of iron oxide in these kaolin deposits can be attributed to the breakdown of biotite and other ferromagnesian minerals of the source rock (Olaolorun and Oyinloye, 2001).

However, the Fe_2O_3 is not the only factor affecting the colour of the ceramic wares. Other constituents such as CaO, MgO, TiO_2 and MnO can also appreciably modify the color of the fired clay (Kreimeyer, 1987). The CaO content in these kaolin samples is relatively high (2-9.8%) as compared to other world kaolin deposits (Table 4) (Murray and Keller, 1993; Ekosse, 2000). Moreover, MgO and TiO_2 contents of the Nagar Parkar kaolin are 0.2 - 0.6%, and 0.4 - 1.3% respectively, which are quite similar to the kaolin deposits of Morocco, Southeastern Botswana and Georgia, USA (Ekosse, 2000; Murray and Keller, 1993).

Table 3. Average oxide composition (%) of Nagar Parkar raw and processed (washed) kaolin.

Oxides	Viravah (Raw)	Parodhro (Raw)	Karkhi (Raw)	Moti jo Vandio (Raw)	Ramji jo vandio (Raw)	Dhedvero (Raw)	Washed kaolin
SiO_2	52.9	59.2	58.2	53.7	48.7	58.8	45.1
TiO_2	1.3	0.4	0.7	0.4	0.6	0.4	0.7
Al_2O_3	24.7	24.4	23.8	21.3	26.8	24.1	35.1
$^*Fe_2O_3$	0.7	0.6	0.9	0.9	1.0	0.7	0.7
MnO	0.0	0.0	0.0	0.0	0.0	0.0	0.0
MgO	0.2	0.2	0.2	0.4	0.6	0.3	0.6
CaO	4.8	2.0	3.1	9.8	5.4	2.4	1.8
Na_2O	1.4	1.7	1.1	0.8	1.7	1.1	1.2
K_2O	0.3	0.2	0.3	0.6	0.3	0.1	0.2
P_2O_5	0.0	0.1	0.1	0.0	0.1	0.0	0.0
LOI	13.7	11.9	11.4	12.1	15.1	11.1	14.8

LOI (loss on ignition) at 1000ºC

$^*Fe_2O_3$ as total Iron

Table 4. Comparison of Nagar Parkar kaolin with other kaolin deposits of the world (wt %).

Oxides	NAGAR PARKAR KAOLIN (Raw) DEPOSITS							I	U.S.A.	UK	Ideal kaolin	Pakistan	
	Viravah (Raw)	Parodro (Raw)	Karkhi (Raw)	Moti jo Vandio (Raw)	Ramji jo vandio (Raw)	Dhedvero (Raw)	Washed kaolin		II	III	IV	V	VI
SiO_2	52.9	59.2	58.2	53.7	48.7	58.8	45.1	51.1	45.3	46.8	46.6	43.7	45.3
TiO_2	1.3	0.4	0.7	0.4	0.6	0.4	0.6	1.5	1.4	nd	nd	0.6	0.5
Al2O3	24.7	24.4	23.8	21.3	26.8	24.1	35.1	32.0	38.4	37.8	39.5	37.2	36.8
$^*Fe_2O_3$	0.7	0.6	0.9	0.9	1.0	0.7	0.7	1.8	0.3	0.4	nd	1.4	0.8
MnO	nd	nd	nd	nd	nd	nd	nd	0.0	nd	nd	nd	nd	nd
MgO	0.2	0.2	0.2	0.4	0.6	0.3	0.6	0.2	0.3	0.2	nd	0.2	0.5
CaO	4.8	2.0	3.1	9.8	5.4	2.4	1.8	0.1	0.1	0.1	nd	2.8	2.0
Na_2O	1.4	1.7	1.1	0.8	1.7	1.1	1.2	0.1	0.3	0.2	nd	nd	1.0
K_2O	0.3	0.2	0.3	0.6	0.3	0.1	0.2	0.1	0.0	1.5	nd	nd	0.2
P_2O_5	nd	0.1	0.1	nd	0.1	nd	nd	0.1	nd	nd	nd	nd	nd
LOI	13.7	11.9	11.4	12.1	15.2	11.1	14.8	12.0	14.0	13.0	14.0	14.3	nd

I. Makoro kaolin, South eastern Botswana (Ekosse, 2000).

II.Georgia kaolin (Murray and Keller, 1993).

III. Cornwall kaolin (Murray and Keller, 1993).

IV. Ideal kaolin (Newman and Brown, 1987).

V. Islamkot kaolin (Jafery, 2001).

VI. Shah Dheri, Swat (Siddiqui, et al., 2005).

Table 5. Chemical analysis of kaolin (washed) samples of Nagar Parkar (wt %).

Oxides	W1	W2	W3	W4	W5
SiO_2	45.48	44.89	44.95	45.11	45.19
TiO_2	0.77	0.65	0.81	0.74	0.71
Al_2O_3	34.45	35.55	35.22	35.07	35.00
Fe_2O_3	0.50	0.90	0.67	0.69	0.70
MnO	0.01	0.02	0.02	0.02	0.02
MgO	nd	0.46	0.74	0.60	0.46
CaO	1.80	1.90	1.81	1.84	1.85
Na_2O	1.83	0.27	1.47	1.19	1.05
K_2O	0.16	0.27	0.21	0.21	0.22
P_2O_5	0.04	0.05	0.04	0.04	0.05
SiO_2/Al_2O_3	1.32	1.26	1.28	1.29	1.29
LOI	15.00	15.04	14.05	14.70	15.02

Washed kaolin: The SiO_2 content of washed kaolin samples ranges from 44.89 to 45.48%, i.e. it is reduced significantly compared to the raw kaolin by about 15% due to removal of quartz (Table 5). Similarly, the Al_2O_3 content ranges from 34.45 to 35.55% showing increase by about 10% compared to the raw kaolin due to elimination of impurities by washing.

The Al_2O_3 and SiO_2 contents of processed kaolin of Nagar Parkar approach those of theoretical kaolinite (39.5% Al_2O_3 and 46.6% SiO_2, after Murray and Keller, 1993). The loss on ignition of processed Nagar Parkar kaolin ranges from 14.05 to 15.04% which shows that it is high grade kaolin because the weight loss percentage is quite similar to the ideal kaolinite (14%). The Fe_2O_3 (0.5 - 0.9%) and CaO (1.80 - 1.90%) contents are also lower in the processed kaolin, indicating elimination of Fe-oxide and calcite impurities during washing. Finally the abundance of MnO, MgO, K_2O and P_2O_5 are also reduced significantly in the processed Nagar Parkar kaolin.

6. Conclusion

Physical tests show that Nagar Parkar kaolin has medium plasticity, medium toughness and medium compressibility. The plasticity of Nagar Parkar kaolin is quite comparable with the kaolin deposits of Georgia (USA) and Makoro (Botswana). The Nagar Parkar (raw and washed) kaolin has low shrinkage limit ranging from 0.15 to 3.20%. The fired shrinkage ranges from 6 to 13% at 1360°C with no indication of black spots and cracks. The firing behavior of Nagar Parkar kaolin is as good as Deopani kaolin of western Cameroon with fired shrinkage ranging between 13 to 15%.

Chemical studies show that silica content of Nagar Parkar kaolin (raw) ranges from 48.7 to 59.2%, which is much higher than in the ideal kaolin (46.6%). After washing, silica content is reduced to about 45.1%. However, the alumina content of raw kaolin is lower (21.3-26.8%) than the ideal kaolin (39.5%) but after washing, the alumina content is enriched to 35.1%. Most of the chemical parameters of Nagar Parkar kaolin are comparable to the world known kaolin deposits except its Al_2O_3, CaO and Fe_2O_3 contents. The weight loss of 14.8% at 1000 ºC of kaolin (washed) from Nagar Parkar is also quite similar to other important kaolin deposits of the world.

These kaolin deposits are good in quality, but uniformity in its quality, which is first demand of kaolin based industries, is lacking due to unscientific processing practices. This consistency can be obtained by processing through modern Elutriation plant, which produces three grades of kaolin based on its physical and chemical properties as well as particle size. Therefore, more technical and financial inputs, in exploring, mining and processing of Nagar Parkar kaolin deposits, should applied to make them suitable for more diversified and value added industrial uses.

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