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# STUDIES ON THERMAL TRANSFORMATIONS AND POZZOLANIC ACTIVITIES OF CLAY FROM JAMMU REGION (INDIA)

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Clay from the Nagrotta area of Jammu (J & K State, India) was calcined at various temperatures. The products were analysed by X-ray diffraction. The mode of loss of hydroxyl group from the structure with respect to temperature is discussed. The results were supplemented by differential thermal analysis. The calcined products were subjected to lime reactivity tests and the data obtained were correlated with those of the above study to investigate the pozzolanic activity at various temperatures.

Numerous thermal activation studies have been performed on clay for its use in pozzolanic cements [1–4]. Although a large number of Indian clays from various regions have been investigated for use in pozzolanic cements [5, 6], this work has not extended to the clay from the Nagrotta area of Jammu (J&K State), India. The main aims of the present investigation are to study this clay, to establish the thermal transitions as revealed by X-ray diffraction and DTA, and also to correlate the results with the pozzolanic activity in the light of lime reactivity tests.

## Experimental

The bulk representative sample of clay for this work was collected from the Nagrotta area (J&K State), lattitude 32° 48′, longitude 74° 48′. The clay occurs in the form of beds, interbedded with sandstone dipping towards the west and exposed at the slope of the hill. The total exposed thickness of these beds is nearly 10 feet. Nagrotta clay on the whole is brown in colour, with buff-coloured graios in the matrix. This clay is plastic in nature and looks like a volcanic stuff; it has a specific gravity of 2.7. Its plastic index, physical properties and the results of chemical analysis (performed in the laboratory by conventional methods) are given in Tables 1 and 2.

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The representative clay sample of < 1 cm size was heated in silica dishes inside an electric furnace in the laboratory. The temperature was raised to the desired particular value within 2 h and maintained there for another 2 h with a temperature variation of ±5 deg, and the furnace was then brought to room temperature. The calcined clay was taken out, powdered and passed through a 200 mesh BSS.

**Table 1** Properties of Nagrotta clay

| | Property |
|---|---|
| Colour | Brown |
| Plasticity by feel | Good |
| Liquid limit | 26.6 |
| Plasticity index | 10.38 |
| pH of clay suspension (2% S/L) | 9.55 |

**Table 2** Chemical analysis of Nagrotta clay

| Constituent | Percentage |
|---|---|
| $SiO_2$ | 61.92 |
| $Al_2O_3$ | 15.60 |
| $Fe_2O_3$ | 7.60 |
| $TiO_2$ | 1.40 |
| CaO | 4.20 |
| MgO | nil |
| $K_2O$ | 2.00 |
| $Na_2O$ | nil |
| L.O.I. | 6.70 |

DTA was carried out on an MOM derivatograph Model (OD–103) at a heating rate of 10 deg/min. The X-ray analyses of the samples were carried out by a powder diffraction technique using a Philips PW 1350 X-ray powder diffractometer with nickel-filtered $CuK_\alpha$ radiation (30 kV, 15 mA). The samples were scanned with a scanning speed of 1° in $2\theta$ per minute. The rate meter and chart speed were kept constant for all runs. The lime reactivity test was carried out as per Indian Standard specification IS 1727.

## Results and discussion

Figure 1A depicts the X-ray powder diffractogram of the raw clay sample. The interplanar spacings and the peak intensities calculated from the diffratogram are given in Table 3. From a comparison of the *d* value and intensities with those on the standard ASTM data cards [7] (following the method of Hnawalt and Fink, it was found that the clay is illitic in nature and also contains silica in the form of quartz. According to Bradly and Grim [8], several types of illites, e.g. muscovite, biotite etc. exist in nature. They can best be identified on the basis of X-ray diffraction data. The (001) reflection with *d* value in the vicinity of 10 Å can be taken as the basis for identification. A slightly lower value of the (001) reflection may give rise to a different structure. Our diffraction data compare well with the diffraction data on muscovite and illite (Gilead) on the basis of Grim, Bray and Bradley [9]. The most intense line with a *d* value of 3.35 Å may be attributed to quartz.

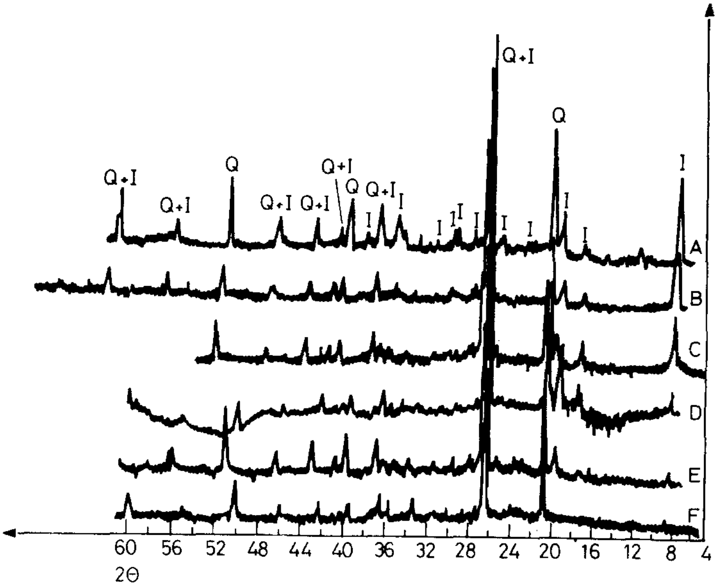

**Fig. 1** X-ray powder diffractograms of different samples. I – Illite, Q – Quartz, A – Raw sample; Samples calcined: B – at 600; C – at 800; D – at 850; E – at 900; F – at 1000 °C

The most recent survey of illite compositions by Weager and Pollard [10] indicates that average illite, with a *d* value of 10 Å, contains about half as much tetrahedral Al as ideal muscovite; about 1/8 of its octahedral cations are in the form of $Mg^{2+}$ or $Fe^{2+}$ and it has a total layer charge of about $-0.75$ per formula unit. It

**Table 3** Interplanar spacings and peak intensities of raw sample and samples calcined at different temperatures

| Raw | | 600 °C | | 800 °C | | 850 °C | | 900 °C | | 1000 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* | *d*, Å | *I* |
| 10.05 | 35 | 10.05 | 25 | 10.06 | 22 | 10.05 | 10 | 10.05 | 5 | 10.05 | 4 |
| 7.08 | 10 | | | | | | | | | | |
| 4.48 | 4 | 4.93 | 6 | | | | | | | | |
| 4.48 | 18 | 4.46 | 9 | 4.48 | 13 | 4.48 | 25 | 4.48 | 12 | | |
| 4.25 | 46 | 4.21 | 27 | 4.23 | 30 | 4.25 | 47 | 4.25 | 53 | 4.27 | 30 |
| 3.98 | 4 | | | | | | | | | | |
| 3.49 | 3 | | | | | | | | | | |
| 3.35 | >100 | 3.32 | >100 | 3.33 | >100 | 3.32 | >100 | 3.32 | >100 | 3.34 | >100 |
| 3.21 | 5 | | | 3.30 | 7 | | | | | | |
| 3.04 | 10 | | | 3.04 | 4 | | | | | | |
| 2.99 | 6 | | | | | | | | | | |
| 2.87 | 2 | | | | | | | | | | |
| 2.69 | 5 | | | 2.69 | 4 | | | | | 2.68 | 8 |
| 2.56 | 11 | 2.58 | 4 | 2.58 | 5 | | | | | 2.51 | 5 |
| | | | | 2.53 | 6 | | | | | | |
| 2.46 | 16 | 2.44 | 11 | 2.45 | 12 | 2.45 | 9 | 2.46 | 13 | 2.46 | 7 |
| 2.37 | 6 | | | | | | | | | | |
| 2.27 | 19 | 2.27 | 3 | 2.28 | 11 | 2.27 | 7 | 2.27 | 14 | 2.28 | 9 |
| 2.23 | 7 | 2.22 | 6 | 2.23 | 7 | | | 2.23 | 7 | 2.23 | 4 |
| 2.13 | 13 | 2.12 | 6 | 2.13 | 9 | 2.13 | 7 | 2.13 | 11 | 2.13 | 7 |
| 1.98 | 11 | 1.98 | 5 | 1.98 | 7 | | | 1.98 | 29 | 1.98 | 5 |
| 1.82 | 25 | 1.81 | 13 | 1.82 | 18 | 1.82 | 11 | 1.82 | 23 | 1.82 | 15 |
| 1.67 | 8 | 1.67 | 6 | 1.67 | 9 | | | 1.67 | 9 | | |
| 1.54 | 18 | 1.54 | 9 | 1.54 | 17 | 1.54 | 6 | 1.54 | 15 | 1.54 | 9 |

*d*, Å = Interplanar spacing
*I* = Peak intensity.

is quite clear from Table 2 that Mg is not present in the clay. The presence of iron emphasizes the fact that 1/8 of the octahedral cation sites are occupied by $Fe^{2+}$. The illite is predominantly dioctahedral, but differs from ideal muscovite in having on average more Mg and interlayer water [11]. From the chemical analysis (Table 2) it is seen that the loss on ignition is about 6.7 percent. This leads to the conclusion that interlayer water is absent and the loss is due to structural water. Moreover, the absence of magnesia confirms the muscovitic nature of the samples.

Figure 2 shows the DTA curve of the clay. There is an endotherm at about 150°; this initial endotherm corresponds to the loss of interlayer water. There are two more endothermic reactions, one at 550° and the other at 850°. The third endothermic reaction is slight. The second endothermic peak corresponds to a

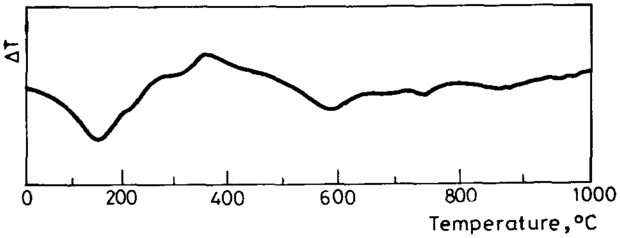

Fig. 2 DTA curve of clay sample

slight loss of OH lattice water, and the third endotherm may be attributed to the subsequent abrupt loss of hydroxyl group. Thus, it can be conjectured that water is lost in three stages, at 150°, at 550° and finally at 850°. The dehydration curves of Roy [12] also show that muscovite undergoes a slow and relatively gradual loss of water up to 800°, without any particular interval involving a large water loss.

The DTA results were supplemented with X-ray data on calcined samples. Figure 1 (b–f) present X-ray diffractograms of clay calcined at 600, 800, 850, 900 and 1000°, respectively. It is clear from the diffractograms that the loss of OH water from the illite is not accompanied by the loss of structure [13]. Only a very slight change is observed in the diffractograms due to a slight decrease in the intensities of the muscovite basal reflection. In fact, the continuous decrease in intensity of the reflections when the samples are heated from 600° to 800° shows that the well-oriented structure is in the process of transformation to a poorly crystalline structure [14]. Appreciable structural change was observed at about 850°. According to Grim and Bradley [15], the structure of the illite group is not destroyed until at least 850°. The intensities of the lines with a *d* value of 10.048 Å are not distinct and they merge with the background. Maegdafrau and Hofmann [16] reported that the illite structure continues up to 1000°, even after the complete loss of OH water beyond 850°. However, this is a rare phenomenon. The 10 Å line in the diffractogram of the sample heated to 1000° is not well resolved and almost diffuse, leading to a spinel form, which is in agreement with the findings of Grim and Kulbacki [17].

Srinivasan [18] reports that, on heating clays, generally first release their surface and interlayer water. Further heating brings about a continuous loss of the hydroxyl ions in the structure, followed by collapse of the structure, yielding a very intimate mixture of the amorphous oxides or a solid solution. Further heating results in the interaction of these oxides to form a spinel structure and finally mullite.

As regards the pozzolanic activity of clay minerals, Milenz et al. [19] showed that clay minerals have an optimum temperature of calcination at which they exhibit maximum pozzolanic activity. Srinivasan [18] extended this idea and suggested that

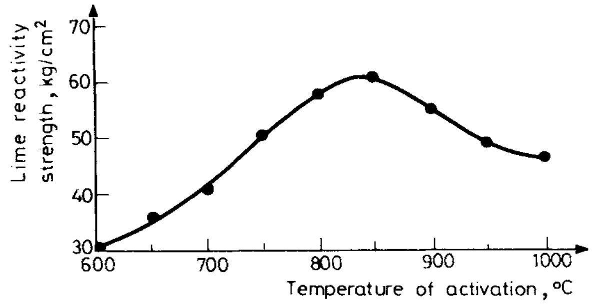

**Fig. 3** Lime reactivity strengths of clay samples calcined at various temperatures

**Table 4** Lime reactivity values of Nagrotta clay at different temperatures of activation

| Sample no. | Temperature of activation, °C | Lime reactivity kgs/cm$^2$ |
|---|---|---|
| 1 | 600 | 30 |
| 2 | 650 | 35 |
| 3 | 700 | 40 |
| 4 | 750 | 50 |
| 5 | 800 | 57 |
| 6 | 850 | 60.60 |
| 7 | 900 | 54 |
| 8 | 950 | 48 |
| 9 | 1000 | 46.6 |

the pozzolanic activity is the highest when the collapse of the structure has just begun, resulting in nascent and microcrystalline oxides and the reminiscent structure with high strains in the bonds. The above phenomenon is in agreement with the results of X-ray and DTA studies on Nagrotta clay. This is further confirmed by lime reactivity tests carried out as per IS 1727 on the calcined clay samples. The results are reported in Table 4 and Fig. 3. The graph of temperature of calcination *vs.* lime reactivity strength indicates that the optimum temperature of calcination for maximum compressive strength is about 850°.

## Conclusion

Thus, from the DTA, X-ray and lime reactivity studies on Nagrotta clay, it appears that the clay is illitic (muscovite) in nature, with an appreciable quartz content; the structural water is lost in three stages. The structure of the clay becomes disordered at about 850°, which is the optimum temperature for maximum activation of the clay. The clay calcined at this temperature is most suitable for making pozzolanic cements.

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**Zusammenfassung** — Tonerde, stammend aus dem Gebiet Nagrotta in Jammu (Staat J&K, Indien) wurde bei verschiedenen Temperaturen kalziniert und die Produkte mittels Röntgendiffraktion untersucht. Die Art und Weise des Verlustes an Hydroxylgrouppen in Abhängigkeit von der Temperatur wurde besprochen. Die Untersuchungsergebnisse wurden mittels Differentialthermoanalyse ergänzt. Die Kalzinierungsprodukte wurden Kalkreaktivitätsuntersuchungen unterzogen und die Ergebnisse mit denen der obigen Untersuchungen verglichen, um die Puzzolan-aktivität bei verschiedenen Temperaturen zu untersuchen.

**Резюме** — Глина из месторождения Джамму (Индия) была подвергнута обжигу при различных температурах, а продукты обжига были изучены рентгенофазовым анализом. обсужден ход реакции дегидроксилирования в зависимости от температуры. Результаты были дополнены дифференциальным термическим анализом. Продукты обжига были подвергнуты тестовым испытаниям с известью. Полученные при этом данные были скоррелированы с вышеприведенными исследованиями спекаемости при различных температурах.