

# Mineralogical changes and geotechnical properties of an expansive soil interacted with caustic solution

Puvvadi Venkata Sivapullaiah · Gullapalli Sankara · Mehter M. Allam

Received: 4 May 2009 / Accepted: 10 July 2009 / Published online: 31 July 2009  
© Springer-Verlag 2009

**Abstract** The type and amount of clay mineral plays an important role in the behaviour of fine-grained soils. Clay minerals are the primary source and moisture is often the external agent of swelling in soils. Also soils may exhibit increased/reduced swelling due to interaction with chemicals. Alkalis used in industrial operations are one such example. Concentrations of alkali and mineral type are the key factors in such interactions. The present paper reports the changes in the properties of an expansive Black Cotton soil containing a mixed layer mineral, rectorite upon interaction with high concentration caustic solutions. X-ray diffraction studies have shown that the rectorite present in the soil undergoes changes with increase in the concentration of alkali. Saponite gets transformed to nantronite. Small amount of kaolinitic mineral present in the soil also reacts with alkali producing some changes in its mineralogy. Many hydroxides are produced. Differential thermal analysis studies have been supportive of these changes. Consequent of these changes, the soil-specific surface increases, changes its Atterberg limits and free swell volume increases. The results have been supported by the characteristics and behaviour of samples contaminated in the field with alkali from an alumina extraction plant.

**Keywords** Alkali · Atterberg limits · DTA · Index properties · Rectorite · X-ray diffraction

## Introduction

The term expansive soil is associated with soils that are sensitive to changes in the moisture regime. These soils swell and shrink due to seasonal moisture content variation and pose problems to structures founded on them. The extent of swell and shrink varies from soil to soil depending on the presence of certain minerals. Thus, the type and amount of different minerals present in a given expansive soil assumes a great importance in their behaviour. Also, the response of soils to chemical additives for controlling/altering their properties depends on the mineralogical composition (Mitchell 1993).

## Mineralogy and properties of expansive soils

Soils containing smectite, vermiculite, and some mixed layer minerals behave as expansive soils. Many of these clay minerals occur as the dominant mineral in some areas and often occur as minor constituents with other clay minerals.

The inherent swelling potential of aggregates of clay minerals is closely related to the total external and internal surface areas of clay-mineral particles. Some clay minerals, such as montmorillonite and beidellite of the smectite group, are capable of absorbing appreciable amounts of water between the individual silicate layers, which results in a high swelling potential. Vermiculite, attapulgite, nontronite, and degraded mica (illite) and chlorite, though less common, are also capable of absorbing appreciable amounts of water. These expandable clay minerals consist of sheets or ribbons bound together by atomic physicochemical forces. The strengths of these forces vary with the types of clay minerals and with the water-retention properties of the cations that occur between the lattice layers (Olive et al. 1989).

P. V. Sivapullaiah (✉) · G. Sankara · M. M. Allam  
Indian Institute of Science, Bangalore, India  
e-mail: siva@civil.iisc.ernet.in

Mixed layer minerals present in the soil can also cause swelling in expansive soils. Montmorillonite–illite is most common mixed layer mineral present in expansive soils (Mitchell 1993). In interstratified minerals, clay crystals may consist of alternating layers of two or more different layer types. These mixed layer materials can be composed of expanded water bearing layers and contracted non-water bearing layers. Common combinations contain the expandable clay mineral montmorillonite or beidelite, interlayered with chlorite or with mica. One such mixed layer mineral was noticed in Black Cotton soils of India.

#### *Indian Black Cotton soils*

In India, over 20% of the land area is covered by Black soils, locally known as Black Cotton soils (BC soil). Usually, they are associated with basalt but their occurrence on granite, gneiss, shale, sandstone and slate, and limestone has also been reported. These clays are of medium to high compressibility and form a major soil group. They are predominantly smectite and black or blackish grey in colour. Interstratified smectite–kaolinite was identified in the fine clays of vertisols of Deccan Plateau of India (Bhattacharya et al. 1993). Black Cotton soils contain abundant iron and fairly high quantities of lime, magnesia and alumina. They are characterized by high shrinkage and swelling properties (IS 1498-2002).

#### *Scope of the study*

Soils often get contaminated with a variety of chemicals due to improper disposal of waste or inadequate design of waste containment and industrial facilities. Several studies have shown that geotechnical failures such as tilting of storage tanks, ground soil heave below industrial structures can occur due to changes in soil properties (Ass'ad 1998; Lukas and Gnaedonger 1972; Sridharan et al. 1987). Alkali contamination of the soil and its effects on geotechnical properties is a cause for concern in caustic soda manufacture industry and other industries using alkali (Rao and Reddy 1997; Rao and Rao 1994). There are reports that some of the hydroxides can increase the swelling of some soils. Alkali at lower concentration (up to  $0.10 \text{ mol/dm}^3$ ) can cause changes in the soil structure. At higher concentration (higher than  $0.40 \text{ mol/dm}^3$ ), clay–alkali interaction can produce changes due to formation of new compounds and/or mineralogical changes (Mohnot and Bae 1985; Sivapullaiah and Manju 2005). Also it is known that soil–alkali interaction at relatively lower concentrations (about  $0.10 \text{ mol/dm}^3$ ) are pronounced in terms of changes on charges on clay particles and consequent fabric changes

(Jozefaciuk 2002; Jozefaciuk and Bowanko 2002). Thus, in this paper, the interaction of expansive soil with alkali of different concentrations and changes in their basic properties are investigated. Also for comparison, the soil contaminated in situ with alkali spills from an alumina extraction plant has been studied.

## **Materials and methods**

### **Soil**

Naturally occurring Black Cotton soil from Belgaum, Karnataka, India (vertisol as per soil survey classification) was used in this study. The Black Cotton soil was collected by open excavation, from a depth of 1 m below natural ground level. The soil was air dried, powdered and used after sieving through Indian Standard 425- $\mu\text{m}$  sieve.

Further, the same soil contaminated in situ with an approximately 4 N sodium hydroxide solution containing alumina (called liquor) was collected from the foundation soil in digester plant, thickener plant and precipitator plant locations in an alumina extraction plant. This plant extracts alumina from bauxite ore by the Bayer process. The alkali solution used for digesting alumina spilled in to the foundation soil in all the three major units, viz., digester, thickener and precipitator.

### **Preparation of solutions**

The fluids used in this study are as follows: (1) distilled water, (2) 1 N sodium hydroxide and (3) 4 N sodium hydroxide. To verify some of the reaction mechanisms, solutions of sodium chloride were utilized. The sodium hydroxide and sodium chloride solutions of 1 and 4 N were prepared by dissolving the required amount of Analar Reagent Grade Chemicals in distilled water. Liquor from the alumina extraction plant was also used.

### **Treatment of soil with alkali**

The method of treatment of soil varied depending on the subsequent tests to be carried out.

For X-ray, differential thermal analysis (DTA), pH, conductivity and specific surface area, the air-dried Black Cotton soil was thoroughly mixed with alkali solutions using spatulas in batches of 50 g (solid:solution ratio of 1:2.5) and were equilibrated with 1 N NaOH, 4 N NaOH and liquor solutions for 3 days at room temperature. The samples were air dried and powdered.

For Atterberg limits, the required quantity of solution is directly added to the soil and stored in desiccators to attain equilibrium moisture contents.

### *X-ray diffraction studies*

The X-ray diffractometer used in this study was a Philips PW 3710 automated powder diffractometer with a generator settings of 40 kV and 40 mA and Cu K $\alpha$  radiation. Samples were scanned from  $2\theta$  of 3° to 70°, at a scanning rate of 2°/min at room temperature. The output data were received in the form of a .RD file. Philips X'Pert HighScore software (version 1.0a) was used to plot the X-ray patterns of the samples and to output lists of the  $d$  values, angle of diffraction and intensities, etc. To separate clay (<2  $\mu\text{m}$ ) from fine silt, the freshly dispersed suspension of the untreated Black Cotton soil passing through 75  $\mu\text{m}$  was left to stand 8 h for every 10 cm of its depth. The suspended material (clay fraction) was decanted leaving the fine silt on the bottom of the beaker. Oriented sample slides prepared from clay fraction without and with glycol treatment were used to find out the initial mineral composition (Poppe et al. 2003). Oriented preparations of the clay fractions were obtained by vacuum filtration of the clay suspension and transferred to glass plates (Filter-Peel technique). The fraction of Black Cotton soil less than 75  $\mu\text{m}$  samples treated with 1, 4 N NaOH and liquor as well as field-contaminated samples were also studied.

### *Differential thermal analysis and thermo-gravimetric studies*

Differential thermal analysis and thermo-gravimetric (TG) studies were performed on 15 mg air-dried powder samples using TA Instruments Q600 Simultaneous DSC/TGA (SDT) thermal analyser. The temperature was measured with platinum sensors. The analyses were carried out at a heating rate of 10°C/min in nitrogen atmosphere.

### *Atterberg limits*

The soil is mixed with varying amounts of moulding fluid and packed in polyethylene bags and stored in airtight container in order to achieve equal distribution of moisture, prior to testing. Liquid limit was determined according to cone penetration method because of its simplicity, quickness and reproducibility of test results, especially with high concentration of alkali solution (BS: 1377-part 2 1990). The plastic limit test was performed according to the conventional 3 mm thread method (ASTM D4318) and shrinkage limit of uncontaminated and contaminated soil specimen was determined as outlined in the ASTM procedure (ASTM D427).

### *Specific gravity*

The specific gravity value of untreated samples was determined using standard test method (ASTM D854) in which an average of three test results is reported. Individual determinations differed from the mean by less than or equal to 0.01. The specific gravity of Black Cotton soil is 2.79.

### *Particle size distribution*

The particle size distribution of untreated Black Cotton soil was conducted in accordance with ASTM D422. The coarser fraction, i.e., the fraction larger than 0.075 mm was analysed by dry sieving method, while the fraction passing 0.075 mm sieve (No 200 sieve) was analysed by sedimentation process using hydrometer. The Black Cotton soil consists of by weight: fine sand 6%, silt 54% and clay fraction 40%.

### *Specific surface area*

The procedure involves determination of the number of molecules of gas required to form a monolayer on the surface of the clay material. Though nitrogen gas is more commonly used, water adsorption is preferred for plastic clays as both external and internal area is covered by water unlike nitrogen where only external surface is covered (Gillot 1968). In this study, water adsorption has been used to measure specific surface area. The amount of water adsorbed at 52% relative humidity has been used to calculate the specific surface of the soils. It is generally considered that a mono layer of water is adsorbed at this humidity (Puri and Murari 1963). Adsorption of water at 23°C at different humidities is determined using 2 g of dry sample (untreated and treated) over saturated solutions in the desiccators. To maintain the relative humidity of 0, 52 and 100%, dry phosphorus pentoxide, saturated solution of sodium dichromate and distilled water, respectively, were used in the bottom of the desiccators. The soil samples were kept in desiccators till equilibrium was reached as indicated by constant weight. The specific surface area was calculated as detailed by Lowell (1979).

### *Free swell test*

The testing procedure adopted for determining free swell was as follows: 10 g oven-dried powder samples were submerged in 40 ml of distilled water or other alkali solvents in 100 ml, standardized graduated cylinders. The suspensions were repeatedly stirred for thorough mixing and allowed to equilibrate for 24 h to ensure thorough

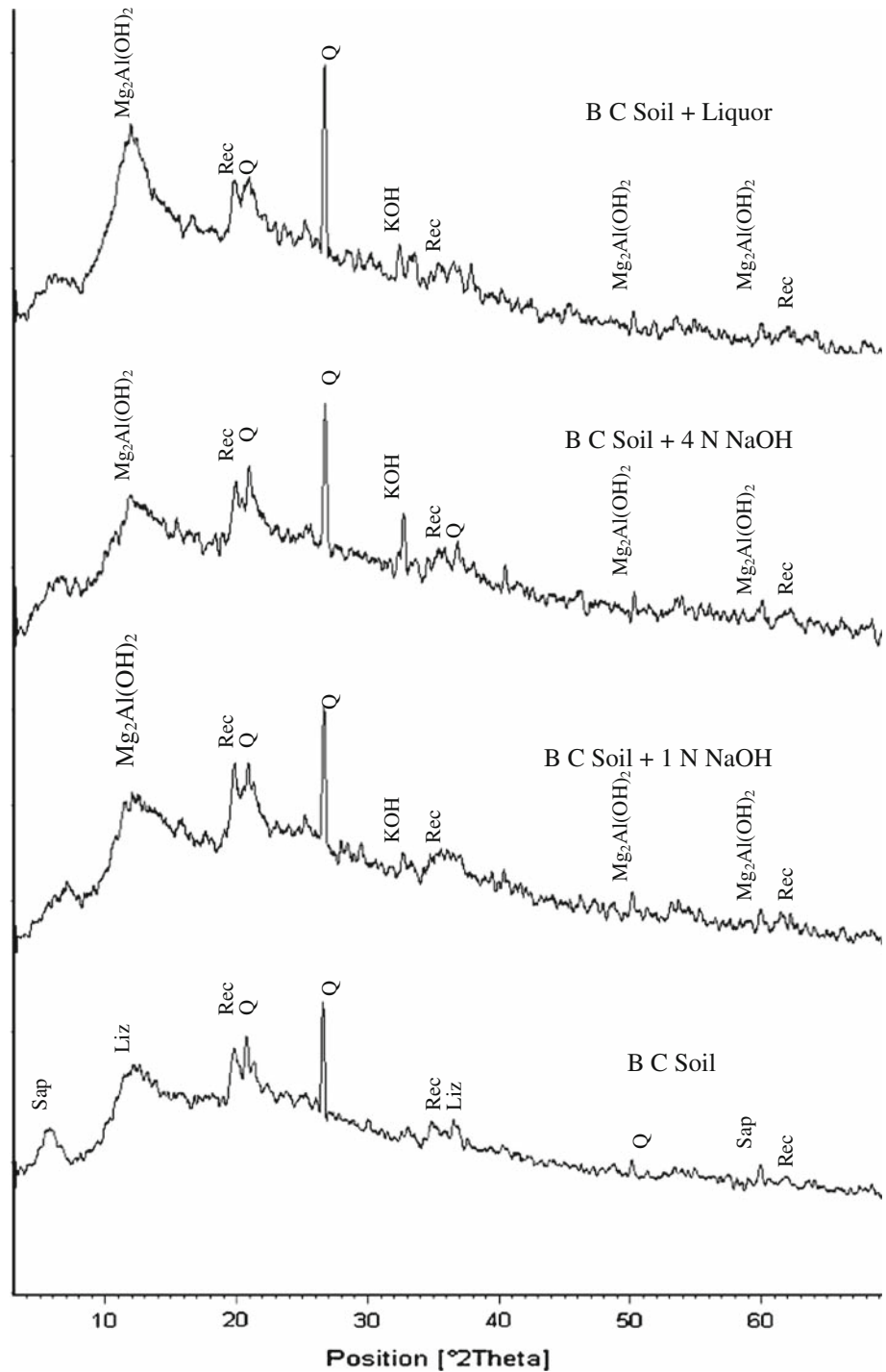
wetting of the samples. The suspensions were then made up to the 100 ml mark with the respective solvents, with stirring. The cylinders were covered and left undisturbed for a further period of 24 h at which time the volume occupied by sample particles on settling was noted. Free swell index is expressed as sediment volume per gram of soil (Rao and Sridharan 1985).

## Results and discussion

### Identification of minerals

From Fig. 1 and Table 1, it can be noticed that the peaks corresponding to  $d$  values pertaining to interstratified clay mineral rectorite, viz., 4.45, 2.56 and 1.49 Å (PDF

**Fig. 1** XRD pattern for uncontaminated soil and samples treated with various fluids



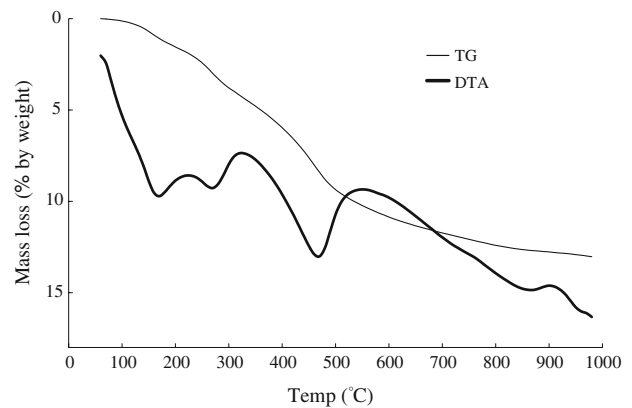
**Table 1** XRD data for Black Cotton soil samples treated with various pore fluids

<i>d</i> value (Å)	Mineral/compound	Relative intensity			
		BC soil	BC soil + 1 N NaOH	BC soil + 4 N NaOH	BC soil + liquor
15.00	Saponite	29.17			
7.76	Lizardite	24.11			
7.50	Mg <sub>2</sub> Al(OH) <sub>7</sub>		26.66	21.54	37.93
4.48	Rectorite	47.53	54.82	36.58	28.84
4.26	Quartz	59.19	47.65	47.73	27.55
3.35	Quartz	100.00	100.00	100.00	100.00
2.74	KOH		15.42	40.13	18.74
2.56	Rectorite	18.67	15.42	15.36	14.54
2.45	Q/Lizardite	24.41		23.49	
1.81	Q/Mg <sub>2</sub> Al(OH) <sub>7</sub>	14.8	16.62	14.96	8.83
1.54	Saponite/Mg <sub>2</sub> Al(OH) <sub>7</sub>	17.73	13.16	10.93	9.63
1.49	Rectorite	7.61	10.09	8.04	9.65

Rectorite: K<sub>0.6</sub>Al<sub>2</sub>SiO<sub>10</sub>(OH)<sub>2</sub>·XH<sub>2</sub>O (PDF 29-1495); saponite: Ca<sub>0.5</sub>(Mg,Fe)<sub>3</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·XH<sub>2</sub>O (PDF 13-0305); lizardite: Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (PDF 86-0403)

29-1495) in order of decreasing intensities are present in the uncontaminated soil. Peaks corresponding to *d* values of smectite group mineral, saponite (15.4, 1.54 Å; PDF 13-0305), lizardite, a serpentine mineral (7.29, 2.49 Å; PDF 86-0403), and quartz are also noticed as per PCPDFWIN (1999). Shift in the peaks position of samples with glycol saturation is negligible. In India, most Black Cotton soils have di-octahedral smectite–montmorillonite as the principal clay mineral. However, in this soil, saponite ferroan, a tri-octahedral smectite mineral containing iron, has been identified as a clay mineral. Parthasarathy et al. (2003) reported the occurrence of ferrous saponite in Deccan Plateau of India. The mixed layer clay mineral of mica–smectite, rectorite, consists of pairs of di-octahedral 2:1 layers; alternate interlayers are mica-like and montmorillonite-like (Bailey et al.; 1982). Rectorite is normally found as an intermediate in the transformation of mica to smectite or vice versa (Terzaghi et al. 1996).

The DTA and TG curves for untreated Black Cotton soil are shown in Fig. 2. There are two endothermic peaks at 150 and 250°C due to removal of hygroscopic and adsorbed water, respectively (Mitchell 1993). As the natural moisture content of the air-dried sample is in the range of 6–8% and as the samples were not oven dried, high dehydration peaks are noticed at these temperatures. There is a strong endothermic peak at about 475°C. This is due to dehydroxylation. The weight loss corresponding to this peak as indicated from TGA is about 4%. An exothermic peak in the range of 850–950°C can also be noticed. DTA peaks for regular interstratifications of mica and montmorillonite fall in three temperature regions (Sudo and Shimoda 1970): (a) the low-temperature sorbed-water region, 100–300°C; (b) the dehydroxylation region, 500–



**Fig. 2** DTA and TG plots for uncontaminated Black Cotton soil

600°C; and (c) the region representing breakdown of structure and recrystallization, 800–1,000°C. The dehydroxylation peak of the soil at 475°C slightly below the range of 500–600°C may be due to the presence of iron in the soil. The presence of iron depresses the temperature of endothermic dehydroxylation peak (Meyers and Speyer 2004). The presence of rectorite indicated by the XRD patterns can be conformed from the DTA analysis.

Soil–alkali interactions

X-ray diffraction studies

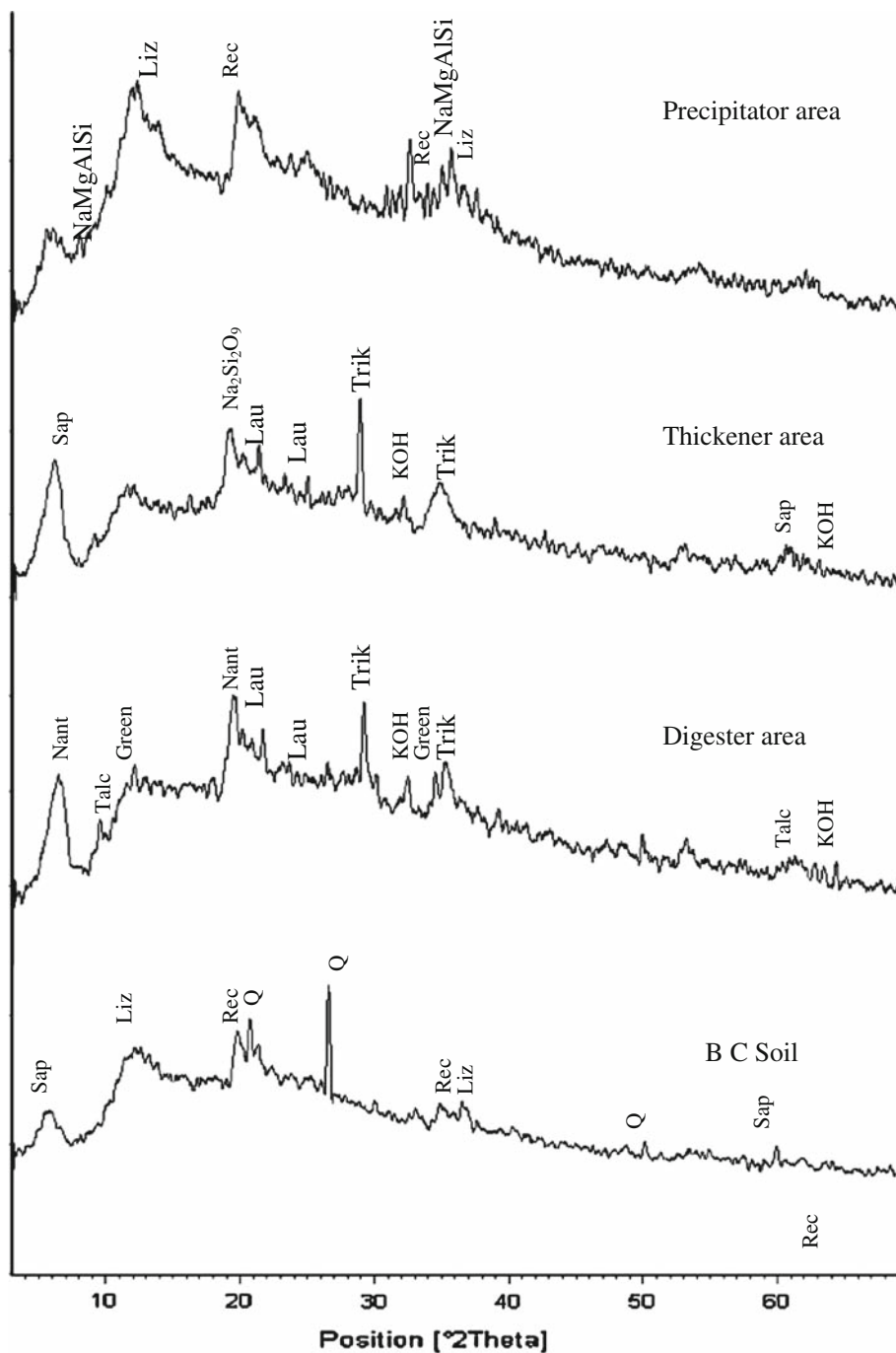
On interaction with alkali, mineralogical changes are noticed in the Black Cotton soil (Fig. 1; Table 1). The intensity of peak due to saponite at 15 Å is reduced. The peak due to rectorite is not affected. Further, the peaks due to hydroxides of potassium and magnesium appear.

The reduction in the intensity of saponite peak and the increase in the intensity of the peaks of hydroxide generally increase with the concentration of alkali solution.

More mineralogical changes appear in the field-contaminated soils (Fig. 3; Table 2). The mineral saponite is transformed to nontronite. The peaks due to rectorite almost vanish in the samples collected from digester and thickener units and present in low intensity in the sample from precipitator area. The peak due to quartz disappears. It is known that silica dissolves at higher alkali

concentrations. The extent of dissolution varies depending on the crystallinity and size of the quartz particles. Hydroxides of potassium and iron appear in all the field samples. Qafoku et al. (2004) observed that K and Fe were released from soil minerals upon interaction with NaOH solutions. Complex minerals of sodium, aluminium, potassium, iron, silica and zeolite appeared to have been formed as these elements are present in soil in the form of rectorite, saponite and lizardite, etc. These minerals are nontronite,  $(Ca,Mg)_{0.5}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot xH_2O$ ; Talc,

**Fig. 3** XRD pattern for field-contaminated samples





**Table 2** XRD data for Black Cotton soil samples contaminated in the field

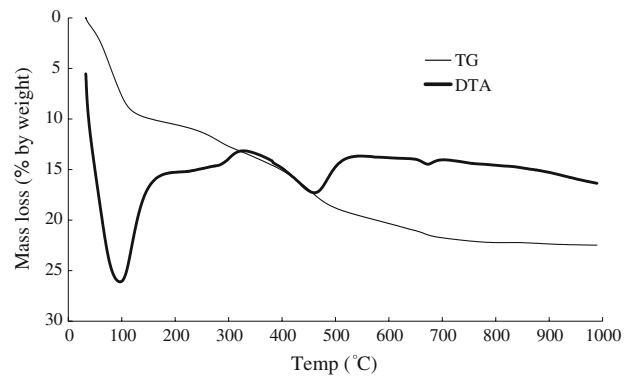
<i>d</i> value (Å)	Mineral/compound	Relative intensity		
		Digester area	Thickener area	Precipitator area
15.38	Saponite		92.57	
15.19	NaMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ·5H <sub>2</sub> O			53.87
13.74	Nontronite	98.14		
9.29	Talc	31.07		
7.76	Lizardite			87.59
7.30	Greenalite	47.03		
4.62	Na <sub>2</sub> Si <sub>2</sub> O <sub>9</sub>		65.75	
4.54	Nantronite	100.00		
4.48	Rectorite			100.00
4.15	Laumontite	62.9	43.97	
3.55	Na <sub>2</sub> Si <sub>4</sub> O <sub>9</sub> /Laumontite		22.32	26.22
3.08	Na <sub>3</sub> Mg <sub>4</sub> AlSi <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>		100.00	
3.05	Trikalsilite	95.69		
2.75	KOH	35.41	27.04	
2.74	Na <sub>2</sub> Mg <sub>6</sub> Si <sub>3</sub> O <sub>22</sub> (OH) <sub>2</sub>			86.32
2.59	Greenalite	44.37		
2.54	Trikalsilite	53.92		
2.51	Rectorite/Na <sub>2</sub> Mg <sub>6</sub> Si <sub>3</sub> O <sub>22</sub> (OH) <sub>2</sub>			84.89
2.39	NaMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ·5H <sub>2</sub> O			42.99
1.54	Saponite		17.91	
1.51	Talc	20.31		
1.44	KOH	23.77	11.66	

Nontronite: (Ca,Mg)<sub>0.5</sub>Fe<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·XH<sub>2</sub>O (PDF 34-0842); Talc: Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> (PDF 74-1036); Greenalite: Fe<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (PDF 39-0348); Trikalsilite: K<sub>0.7</sub>Na<sub>0.3</sub>AlSiO<sub>4</sub> (PDF 12-0197); Laumontite: CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O (PDF 26-1047)

Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>; Greenalite, Fe<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>; Trikalsilite, K<sub>0.7</sub>Na<sub>0.3</sub>AlSiO<sub>4</sub>; and Laumontite (zeolitic mineral), CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O. The precipitation of these hydroxides depends on their solubility product. It is known that under high alkaline and reducing conditions in areas of restricted drainage nontronite is formed (Harder 1976). Thus, the mineral, nontronite, is observed only in the field-contaminated sample obtained below the digester unit where the leaked solution was relatively hotter and highly concentrated. Formation of many hydroxides and dried salts could have lead to reduction in the porosity of the soil leading to poor drainage. These major changes may be due to interaction of soil with alkali for very long period in the field.

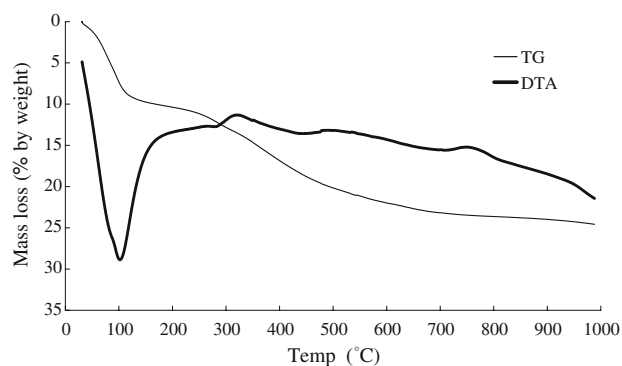
*Thermal analysis*

The exothermic peak at 850–950°C range is missing and a small endothermic peak developed at about 700°C in the soil treated with 1 N alkali (Fig. 4). This may be due to formation of various hydroxides upon treating the soil with alkali. Both DTA and TGA curves have undergone significant changes for soil treated with 4 N alkali solution (Fig. 5). The DTA curve for soil treated with 4 N solution shows one major endothermic peak due to removal of hygroscopic water. This indicates that the new compounds formed holds lot of free water. This is supported by nearly 9% of weight

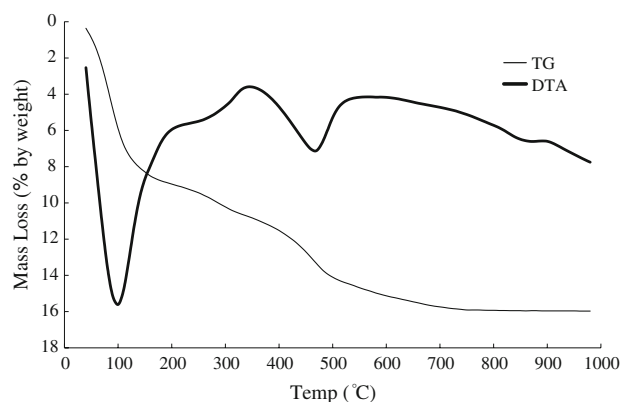


**Fig. 4** DTA and TG plots for BC soil sample treated with 1 N NaOH

loss in the TGA curve. The strong endothermic peak at about 475°C is absent in this treated soil. This is probably due to transformation of primary mixed layer minerals present in the soil. Identical changes were noticed in sample treated with liquor and field-contaminated soil from digester area where the contamination is high and also liquor enters the soil at high temperature. However, the peak at 450°C is slightly reduced in the soil from thickener area (Fig. 6). This is due to lesser contamination in this area. But there is a new peak at about 700°C. This may be due to formation of new minerals, such as Trikalsilite (K<sub>0.7</sub>Na<sub>0.3</sub>AlSiO<sub>4</sub>) and Laumontite (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·4H<sub>2</sub>O), observed in the sample from



**Fig. 5** DTA and TG plots for BC soil sample treated with 4 N NaOH



**Fig. 6** DTA and TG for soil sample from thickener area

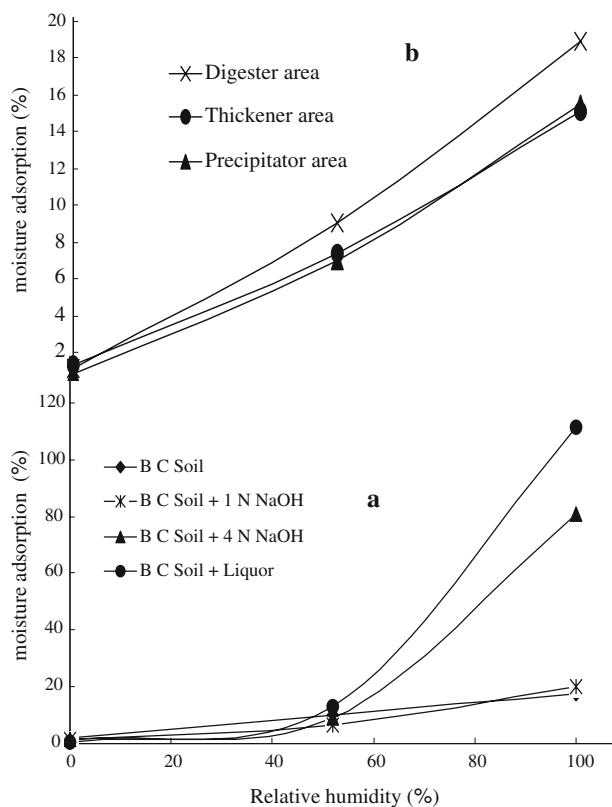
this place. The soil from precipitator area, where the contamination is least, the peak due to rectorite at 450°C is not at all affected.

#### Water adsorption and specific surface area

Table 3 shows the moisture content at different percentages of relative humidity and specific surface area of Black Cotton soil, treated Black Cotton soil and field-contaminated soils. These variations are represented in the form of moisture adsorption isotherms in Fig. 7. The water adsorption isotherm relates the equilibrium amount of water sorbed on a solid and the water activity at constant temperature and pressure. The amount of water associated with a solid at a particular relative humidity and temperature depends on its chemical affinity for the solid and the number of available sites for interaction. The samples examined exhibited transformation from a linear sorption isotherm in untreated soil to an isotherm approaching type III of Brunauer classification in treated and field-contaminated samples. Type III isotherm is characteristic of weak, non-specific interaction between adsorbate and solid (Gregg and Sing 1982). The moisture adsorbed at relative humidity greater than 60% accounted for much of the total

**Table 3** Moisture adsorption and Specific Surface area

Soil sample	Moisture adsorption (%) at a relative humidity of			Specific surface area (m <sup>2</sup> /g)
	100	52	0	
BC soil	17.4	9.9	1.8	357.3
BC + 1 N NaOH	19.9	6.7	1.3	240.6
BC + 4 N NaOH	80.9	6.2	1.3	223.7
BC + liquor	111.4	11.2	0.5	405.5
Digester area	18.9	9.1	1.2	327.3
Thickener area	15.1	7.4	1.4	266.6
Precipitator area	15.5	7.0	0.9	254.3



**Fig. 7** Moisture adsorption isotherms for **a** samples treated with various pore fluids and **b** field-contaminated samples

uptake. The increased uptake at high relative pressures may be due to adsorption of water forming the second layer.

The specific area of samples is calculated from the amount of water adsorbed at 52% humidity. Hence, the reasons for change in specific surface area are similar to those given for water adsorption.

#### Index properties

The liquid limit, plastic limit, plasticity index and shrinkage limit values of Black Cotton soil treated with water,



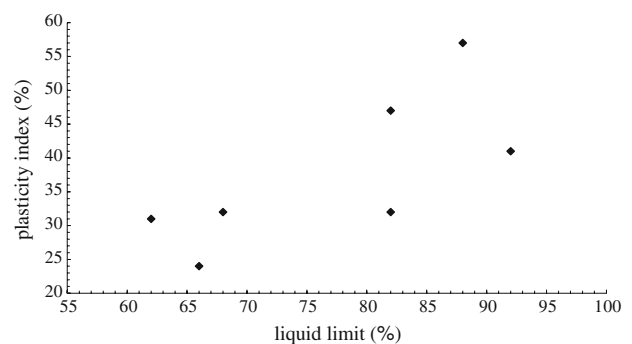
**Table 4** Atterberg limits

Soil sample	Liquid limit (%)	Plastic limit (%)	Plasticity index (%)	Shrinkage limit (%)
BC soil + water	82	35	47	11
BC soil + 1 N NaOH	92	51	41	10
BC soil + 4 N NaOH	82	50	32	Became friable material
BC soil + liquor	66	42	24	Became friable material
BC soil + 1 N NaCl	68	36	32	Became friable material
BC soil + 4 N NaCl	62	31	31	Became friable material
Thickener plant area	88	31	57	9

1 N NaOH, 4 N NaOH, liquor solution, 1 N NaCl, 4 N NaCl solutions are presented in Table 4. It can be observed that the liquid limit with water is greater than 50 and plasticity index falls above ‘A’ line in plasticity chart. Hence, the soil can be classified as fat clay (CH). Fat clays are highly plastic or expansive in nature. To understand the effect of varying concentration of alkali on Atterberg limits of soil, three concentrations of alkali solutions are used. It is known that for Black Cotton soil containing smectite mineral, the changes in diffuse double layer thickness of clay mineral as brought out by electrolyte concentration assume important (Mitchell 1993). Thus for Black Cotton soil, to understand and separate the effect due to electrolyte concentration, two electrolyte solutions of 1 N NaCl and 4 N NaCl are used. It can be seen from Table 4 that the liquid limit of soil reduced drastically on treatment with 1 N NaCl solution. This is clearly due to reduction in the thickness of double layer due to increased electrolyte concentration as given in Table 4. However, with 1 N NaOH solution, there is considerable increase in the liquid limit of Black Cotton soil. It has been shown in the previous sections that no major mineralogical changes occur in Black Cotton soil on treatment with 1 N NaOH solution. Thus, the increase in liquid limit is essentially due to increase in the alkalinity of the pore fluid. It is well known that increase in pH of the soil increases negative charges on clay particles (Mitchell 1993). This in turn will increase the thickness of diffuse double layer of clay particles. With further increase in electrolyte concentration with 4 N NaCl solution, the liquid limit of soil further reduces. However, with increase in sodium hydroxide concentration, a change in the direction of change in liquid limits is noticed. While with 1 N NaOH, the liquid limit has increased, with 4 N NaOH, the liquid limit decreased. Thus, with increase in pH with 1 N solution, the effect of increase in negative charge dominates. With further increase in concentration of alkali solution, the effect of increase in electrolyte concentration controls the liquid limit of Black Cotton soil. However, with liquor, the liquid limit of Black Cotton soil has significantly reduced. This is predominantly due to mineralogical changes after interaction with liquor. It has been shown earlier that saponite and rectorite present in the

soil undergo changes after reactions with alkali. Reduction in the amount of saponite mineral will reduce the liquid limit of soils. Also the electrolyte concentration is fairly high. The liquid limit of contaminated Black Cotton soil from thickener area has increased. This is due to lower concentration of contaminating fluid. The concentration of alkali is actually lower than that of 1 N NaOH. However, the concentration might have been slightly reduced due to interactions between soil and alkali solution.

It can be seen from Table 4 and Fig. 8 that there is no good relationship between liquid limit of treated soil and their plasticity index. The Black Cotton soil, which is CH soil as per Casagrande (1932) classification chart, lies on A line. But it is clear that treated soil undergoes drastic changes in their basic properties and there is scatter in the relationship between liquid limit and plasticity index. It has been shown earlier that the changes in Black Cotton soil occur due to change in the thickness of diffused double layer, charges on clay surface and mineralogical changes due to soil–alkali interaction. The interaction changes with concentration of alkali. The shrinkage limit of treated soil could not be determined accurately in most cases as the precipitates/dried salts formed on the soil after treatment with alkali solutions. The effect of ageing on Atterberg limits has been reported in Table 5. It can be noticed that the alkali–mineral reactions are fast and ageing does not alter the behaviour.



**Fig. 8** Variation of plasticity index with liquid limit for treated and field-contaminated BC soil samples

**Table 5** Variation in Atterberg limits with time

Consistency limit	Curing time	With 1 N NaOH	With liquor
Liquid limit (%)	1 day	92	66
	3 months	94	65
Plastic limit (%)	1 day	51	42
	3 months	48	43
Shrinkage limit (%)	1 day	10	Became friable material
	3 months	11	Became friable material

**Table 6** Free swell index of BC soil in various pore fluids

BC soil in	Sediment volume (ml/10 g)
Water	22
1 N NaOH	23
4 N NaOH	27
Liquor	34
1 N NaCl	20
4 N NaCl	18

Normally, good correlation exists between the liquid limit and free swell index of soil as they are predominantly controlled by similar mechanisms. But as seen from Tables 4 and 6, there are differences between the trends of variations in liquid limit and free swell index of treated soil. This is because the concentration of alkali in the soil is different during these tests because of change in the water content due to the standard procedures adopted in the respective test.

## Conclusions

Based on the detailed results presented in the paper, the following conclusions can be drawn:

1. Black Cotton soil used in this study is a swelling soil based on its high liquid limit and plasticity index.
2. Fewer common interstratified clay mineral such as rectorite has been identified as a predominant mineral in this Black Cotton soil.
3. Black Cotton soil undergoes mineralogical changes on reactions with NaOH, the reaction products varying with concentration of alkali. From X-ray and diffraction and thermal scanning electron microscopic studies, it was confirmed that, with high concentration of the alkali used for treatment, the minerals present in the soil such as rectorite, saponite and quartz have undergone transformations. Formation of new minerals and compounds is noticed.

4. Depending on the type of mineralogical products formed due to interaction with alkali, the specific surface and water holding capacity of the soil changes. The higher is the concentration of alkali used for treatment of the soil, the higher is the increase in moisture adsorption with humidity.
5. The mineralogical alterations bring out considerable variations in the geotechnical properties of soil. Changes in the liquid limit of soil on treatment with 4 N solution are mainly due to these changes. Further with 4 N solution, the liquid limit has decreased due to the effect of increase in electrolytes concentration.
6. There is no definite relationship between liquid limit and plasticity index or free swell index in the treated and contaminated soil due to changes in the mineralogy of the soil.

## References

- Ass'ad A (1998) Differential upheaval of phosphoric acid storage tanks in Aqaba, Jordan. *ASCE J Perform Constr Facil* 12:71–76
- ASTM D427 (1998) Test method for shrinkage factors of soils by the mercury method. American Society for Testing and Materials, West Conshohocken, PA
- ASTM D422-63 (2002) Standard test method for particle-size analysis of soils. American Society for Testing and Materials, West Conshohocken, PA
- ASTM D4318 (2000) Standard test methods for liquid limit, plastic limit, and plasticity index of soils. American Society for Testing and Materials, West Conshohocken, PA
- ASTM D854 (2002) Standard test methods for specific gravity of soil solids by water pycnometer. American Society for Testing and Materials, West Conshohocken, PA
- Bailey SW, Brindley GW, Kodama H, Martin RT (1982) Report of the clay minerals society nomenclature committee for 1980–1981. *Clay Clay Miner* 30:76–78
- Bhattacharya T, Pal DK, Deshpande SB (1993) Genesis and transformation of minerals in the formation of red (Alfisols) and black (Inceptisols and Vertisols) soils on Deccan basalt in the Western Ghats, India. *J Soil Sci* 44:159–171
- BS: 1377-1990 British Standard methods of test for soil for engineering purposes. Part 2. Determination of liquid limit, preferred method using the cone penetrometer
- Casagrande A (1932) Research of Atterberg limits of soils. *Public Roads* 13(8):121–136
- Gillot JE (1968) *Clay in engineering geology*. Elsevier, New York
- Gregg SG, Sing KSW (1982) *Adsorption, surface area and porosity*. Academic Press, London
- Harder H (1976) Nontronite synthesis at low temperatures. *Chem Geol* 18:169–180
- IS 1498-2002 Indian Standard Classification and identification of soils for general engineering purposes. Bureau of Indian Standards, New Delhi, India
- Jozefaciuk G (2002) Effect of acid and alkali treatments on surface-charge properties of selected minerals. *Clay Clay Miner* 50:647–656
- Jozefaciuk G, Bowanko G (2002) Effect of acid and alkali treatments on surface areas and adsorption energies of selected minerals. *Clay Clay Miner* 50:771–783

- Lowell S (1979) Introduction to powder surface area. Wiley, New York
- Lukas RG, Gnaedonger RJ Jr (1972) Settlement due to chemical attack of soils. In: Proceedings of ASCE specialty conference on performance of earth and earth supported structures, vol 1. Purdue University, Lafayette, Louisiana, pp 1087–1104
- Meyers KS, Speyer RF (2004) Thermal analysis of clays. In: Brown ME, Gallagher PK (eds) Handbook of thermal analysis and calorimetry, vol 2: applications to inorganic and miscellaneous materials. Elsevier B.V., Amsterdam, pp 261–303
- Mitchell JK (1993) Fundamentals of soil behaviour. Wiley, New York
- Mohnot SM, Bae JH (1985) A study of alkali–mineral reactions. Part II. International symposium on oil field and geothermal chemistry, Phoenix, AZ, SPE 13576
- Olive WW, Chleborad AF, Frahme CW, Schlocker J, Schneider RR, Shuster RL (1989) Swelling clays map of the conterminous United States. US Geological Survey Publication, USGS, USA
- Parthasarathy G, Choudary BM, Sreedhar B, Kunwar AC, Srinivasan R (2003) Ferrous saponite from the Deccan Trap, India, and its application in adsorption and reduction of hexavalent chromium. *Am Miner* 88:1983–1988
- PCPDFWIN (1999) JCPDS-ICDD, USA
- Poppe LJ, Paskevich VF, Hathaway JC, Blackwood DS (2003) A laboratory manual for X-ray powder diffraction. US Geological Survey Open-File Report 01-041. <http://pubs.usgs.gov/of/0f01-041/html/docs/methods.html>, Aug
- Puri BR, Murari K (1963) Studies in surface area measurements of soils. 1. Comparison of different methods. *Soil Sci* 96:331–336
- Qafoku NP, Ainsworth CC, Szecsody JE, Qafoku OS (2004) Transport-controlled kinetics of dissolution and precipitation in the sediments under alkaline and saline conditions. *Geochim Cosmochim Acta* 68(14):2981–2995
- Rao SM, Rao KSS (1994) Ground heaving from caustic soda solution spillage—a case study. *Soil Found (Japanese Society of Soil Mechanics and Foundation Engineering)* 34(2):13–18
- Rao SM, Reddy PMR (1997) Laboratory studies on the volume change characteristics of Kaolinite contaminated with sodium phosphate/sulphate. *Geotechn Test J ASTM* 20(3):362–367
- Rao SM, Sridharan A (1985) Mechanism controlling the volume change behaviour of kaolinite. *Clay Clay Miner* 33(4):323–328
- Sivapullaiah PV, Manju (2005) Kaolinite–alkali interactions and effects on basic properties: geotechnical and geological engineering. Kluwer, Netherlands
- Sridharan A, Rao SM, Gajarajan VS (1987) Influence of fluoride on the compressibility of montmorillonites. *Geotechnique* 37(2): 197–206
- Sudo T, Shimoda S (1970) Interstratified phyllosilicates. In: Mackenzie RC (ed) Differential thermal analysis, vol 1. Academic Press, London, pp 539–551
- Terzaghi K, Peck RB, Mesri G (1996) Soil mechanics in engineering practice. Wiley, New York