Influence of Caustic Alkalis on Mineral Transformations in Red Earth

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Abstract

Clay minerals exhibit mineralogical transformations when interacted with chemicals. Alkalis used in industries are one such example. Understanding the mechanism of change in plasticity properties of soils due to alkali interaction would be of great use to explain the variations in their geotechnical properties, as plasticity properties are always an indicative of engineering properties. Type and concentrations of alkali, duration of interaction and type of the mineral are the prime factors causing mineral transformations. So, in the present study efforts are made to understand the influence of alkali solutions on the plasticity properties and also on the mineralogy of red earth possessing kaolinite mineral at different periods of interaction. Two types of alkalis namely sodium hydroxide and potassium hydroxide of 8N have been selected in this study. Duration of interaction maintained was 7, 14, 28 and 56 days. The results showed that changes in the plasticity properties of red earth in the presence of NaOH are comparatively more than that of KOH. The changes observed have been explained with the help of new mineral formations by X-ray diffraction studies. Detailed XRD analysis revealed that sodalite at all curing periods are majorly formed in NaOH where as in KOH muscovite (hydrogen aluminum potassium silicate), microcline (potassium aluminum silicate) and rectorite (potassium aluminium silicate hydroxide hydrate) are formed. Effect of 8N NaOH on mineralogical transformations is predominant when compared to 8N KOH. Thus the type and intensity of new mineral formations largely depend on type of alkali and the duration of interaction period.

Keywords: Alkali, Red earth, Plasticity properties, Interaction period, Mineralogy.

1. INTRODUCTION

The failure of industrial structures due to accidental spillage or leakage of highly concentrated caustic soda with differential settlements of foundation bed soils have been reported by several researchers (Maltsev 1998; Rao and Rao 1994; Sivapullaiah et al 2004). Industries such as Paper and pulp, cotton and aluminum are some, where NaOH is released into soil environment. Soils exhibit swelling upon interaction with hydroxides was reported by Ingles (1970). Formation of heavily hydrated salt crystals due to alkali contamination was reported by Sokolovich and Troitskii (1976), which resulted in increase in the number of instances of geotechnical failures. In the above mentioned studies, in case of alkali medium, concentrations under which studies were carried out were in the range of 0.001- 4M. But, there are instances where in the concentrations of NaOH, $NaNO_3$, and $NaNO_2$ can reach 5 molar (Serne et al 1998; Lichtner and Felmy 2003) and as high as 10 mol L^{-1} (Qafoku et al 2004) as a result of accidental discharge from high level radioactive waste into the sediments that leads to high pH environments (Serne et al 1998; Lichtner and Felmy 2003 and Qafoku et al 2004). When such high concentrated solutions with high pH reach subsurface environment, minerals may partially or completely gets affected. Therefore, in order to replicate such high pH environment conditions, in the present study, attempts were made by considering higher concentration (i.e., 8N) of alkali solutions. The present work investigates the influence of high concentrations of sodium hydroxide and potassium hydroxide solutions on the plasticity properties and mineralogy of red earth under different interaction periods to understand their effect on volume change behavior.

2. MATERIALS

2.1. Red Earth (*RE*)

Naturally available red earth was used in this laboratory investigation. The physical properties of soil are presented in Table 1. The XRD pattern of red earth showed the presence of quartz and kaolinite. The soil was collected around NIT Warangal campus at one meter depth from ground and passed through 425 micron sieve prior to its usage.

Table 1 Physical properties of Red earth

Property	Red Earth
Liquid limit (LL), %	38.0
Plastic limit (PL), %	22.64
Plasticity index (PI), %	15.36
Specific gravity	2.62
Optimum water content (%)	20.74
Max. dry unit weight (g/cc)	1.83
Clay content (%)	26
Silt content (%)	38
Fine sand content (%)	36
Cation exchange capacity meq/100 g	9.39

2.2. Solutions used

To understand the influence of type of alkali, two fluids were used in this study. The fluids are (1) 8N NaOH and (2) 8N KOH

2.3. XRD Studies

Mineralogical variations in soils were assessed using PAN analytical X-ray diffractometer. The samples were scanned between 6° to 70° theta values with a step size of 0.01°.

3. METHODS

3.1. Treatment with alkali

250 g of 425 micron passing soil was mixed with 8N NaOH and 8N KOH with 1.5 times liquid limit of soil and stored in dessicator for desired periods.

3.2. Atterberg limits

Liquid limit of soil specimen mixed with solutions were determined according to Cone penetration method (BS: 1377 – part 2, 1990). The plastic limit test is performed by adopting the test procedure mentioned in ASTM, 1976c.

4. RESULTS AND DISCUSSIONS

4.1. Plasticity properties

The plasticity properties (L.L and P.L) are basic measure of the critical water contents of a fine-grained soil. Plasticity properties are used for identifying the soil's classification, which also helps to understand the engineering properties of soil. Table 2 presents the results of liquid limit, plastic limit and plasticity index of the red earth and contaminated red earth specimens for different period of interactions.

Table 2. Plasticity Properties of red earth contaminated with different alkali solutions after curing for different periods

Curing Period (days)	8N NaOH			8N KOH		
	L.L	P.L	P.I	L.L	P.L	P.I
0	38	22.64	15.36	38	22.64	15.36
7	59.51	32.48	27.03	33.72	28.8	4.92
14	63.16	34.3	28.86	57.54	33.5	24.04
28	63.55	32.92	30.63	58.58	33.88	24.7
56	63.09	32.08	31.01	60.94	35.15	25.79

Soil contaminated with different type of alkali shows an increase in liquid limit as compared to water (Figure 1a). The two basic mechanisms that affect the properties of alkali treated soil are: i) increased pH which raises the negative charge on clay particles leading to repulsion of clay particles, ii) electrolyte concentration reducing the diffuse double layer repulsion and brings the particles closer. But for red earth, with fewer amounts of clay and the primary mineral being kaolinite which has lower CEC, above mentioned effects are negligible and the improvements in plasticity properties are presumed to be mainly due to alteration in the mineralogy of soil due to alkali interaction. Increase in the liquid limit of red earth is very high in 8N NaOH at 7 days interaction. This is mainly due to the formation of sodium aluminum silicate hydroxide hydrate (NASH) in 8N NaOH, which are discussed in section 4.2. Further for higher duration of interaction, the values almost remain constant. When it comes to 8N KOH, though the liquid limit value for 7 days interaction showed marginal decrease, the higher liquid limits values with increase in the interaction period is attributed to the type of new mineral formations that have taken place in the soil, which are discussed in section 4.3. Similarly, plastic limit values of red earth increased with both NaOH and KOH interactions (Figure 1b).

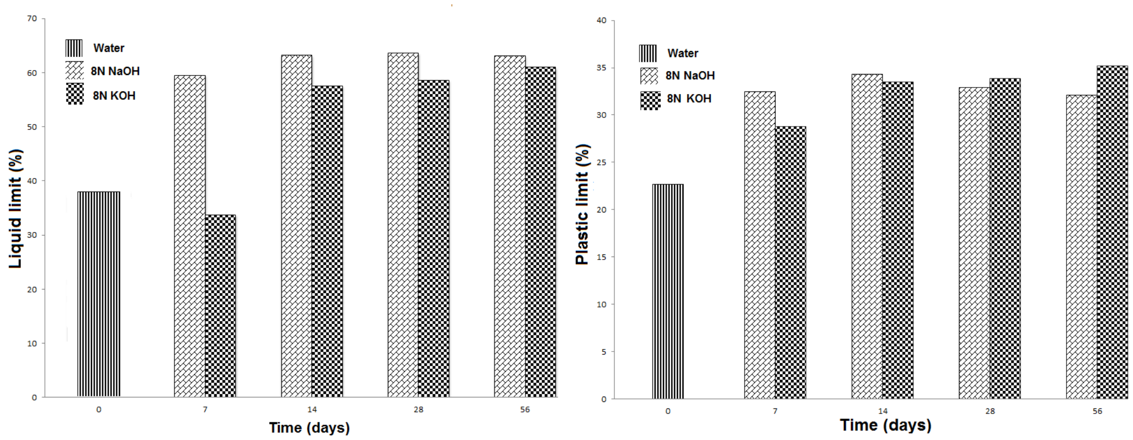

Figure 1. Plot showing (a) liquid limit (b) plastic limit variations with curing period when mixed with 8N NaOH and KOH solutions

4.2. Mineralogical Changes in Red Earth Interacted with 8N NaOH

Red earth mainly comprises of very intense peaks of quartz (4.24, 3.340, 1.819 and 1.366 [Å]) and peaks pertaining to kaolinite (7.14 [Å], 4.45 [Å], 3.59 [Å] and 2.56 [Å]) and hematite (2.69 [Å] and 2.51 [Å]) (Figure 2a). XRD patterns of red earth samples interacted with 8N NaOH (Figure 2a) for 7 days and 14 days interaction period had shown new peaks which can be assigned to *sodalite* ($Na_8(AlSiO_4)_6(OH)_2.4H_2O$). These new peaks at 6.314[Å], 3.645[Å], 2.10[Å] are attributed to sodium aluminum silicate hydroxide hydrate. These are formed when alumina and silica from kaolinite dissolution reacts with 8N NaOH solution. XRD analysis indicates a significant drop in the kaolinite peak intensities has taken place after interacting with 8N NaOH at both 7 and 14 days interaction period. With further increase in the interaction period to 28 days, new peaks pertaining to *albite* (Sodium aluminum silicate) have appeared with its intensity at 3.21[Å]. Severity in the intensity of sodalite peaks was observed at 56 days interaction periods. Peaks pertaining to kaolinite were completely out of sight at 56 days interaction period, which can be clearly visualized. Sodalite peak intensities increased with duration of interaction, but the intensity changes neither influenced the liquid limit values nor plastic limit values. Further investigations are required to clearly understand the influence of mineralogy on plasticity properties in alkali contaminated soils.

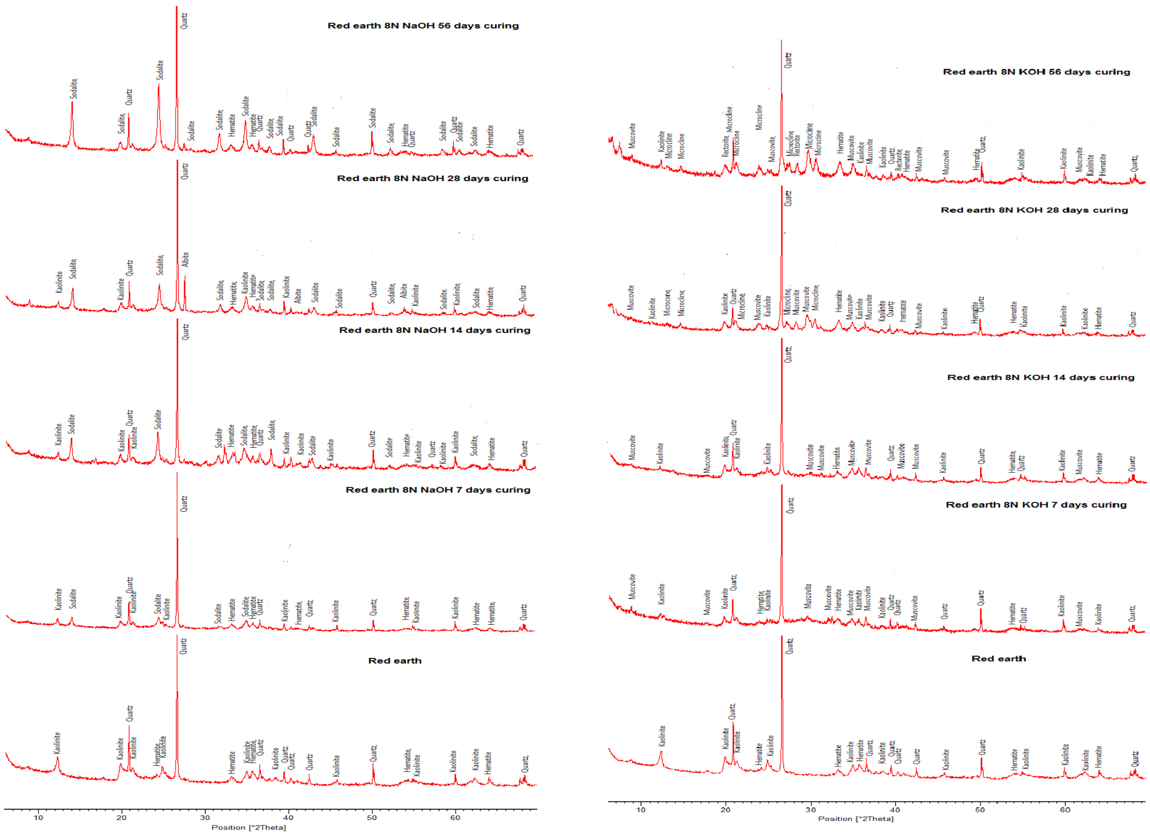

Figure 2. XRD patterns of red earth interacted with (a) 8N NaOH and (b) 8N KOH solution at different interaction periods.

4.3. Mineralogical Changes in Red Earth interacted with 8N KOH

Figure 2b shows the XRD analysis of red earth interacted with 8N KOH solution at different interaction periods. XRD patterns of red earth samples interacted with 8N KOH for 7 days and 14 days interaction period had shown new peaks pertaining to *muscovite* ($H_2KAl_3Si_3O_{12}$). These new peaks at 9.92 [Å], 3.06 [Å] and 2.576 [Å] are attributed to potassium hydrogen aluminum silicate, which is formed as a reaction product when silica and alumina from kaolinite dissolution interact with 8N KOH solution. With increase in interaction period to 28 days, besides muscovite, a new mineral named *microcline* ($KAlSi_3O_8$) has been observed. These new peaks at 4.22 [Å] and 3.26 [Å] are attributed to potassium aluminum silicate. With further increase in interaction period to 56 days, in addition to muscovite and microcline, new peaks pertaining to *rectorite* ($K_{1.2}Al_4Si_8O_{20}(OH)_4 \cdot 4H_2O$) have been observed. These new peaks at 4.45 [Å] and 2.55 [Å] are attributed to potassium aluminum silicate hydroxide hydrate. Kaolinite peak intensities reduced at all interaction periods when compared to that of actual soil. The reduction in the intensity of kaolinite peaks indicates that dissolution of silica and alumina has taken place in the presence of alkali solutions at all interaction periods. Complete dissolution of kaolinite mineral is not observed in 8N KOH even at 56 days interaction period unlike 8N NaOH. Thought the type of new mineral formations varied with increase in duration of interaction the effect on plasticity properties is minimal. In order to distinctly comprehend the influence of KOH on plasticity properties, additional studies need to be carried out in detail.

5. CONCLUSIONS

- Liquid limit and plastic limit increased with both NaOH and KOH solutions.
- In red earth, new mineral peak intensities increased with duration of interaction with NaOH. Whereas with KOH, type of new mineral formations varied with duration of interaction. Thus the disintegration of the actual mineral and the formation of new minerals greatly depend on the type of alkali solution and duration of interaction.
- Though intensity of peaks and mineralogical changes increased with increase in duration of interaction, but the effect is minimal on the plasticity properties (Liquid limit and plastic limit values are almost same). So, direct prediction of engineering properties on the basis of plasticity properties cannot be true in case of alkali-contaminated soils (where conventional correlations cannot be applied). Therefore, micro level investigation plays a crucial role in understanding the engineering properties of alkali contaminated soils

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