



## Research paper

## Characterization of kaolinitic clays subjected to alkali contamination



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## ABSTRACT

Differential settlements due to alkali contamination in the foundation soil and the deformations in super-structures were well documented. The influence of alkalis on clay minerals has been the subject of many studies for decades. However, studies on the role of mineral content, type of alkali and volume of the interacting solution on the dissolution of clay minerals and formation of new minerals at hydrothermal condition are scanty for a particular duration and concentration of alkali. Thus, in this paper micro level investigations were carried out to clearly understand the influence of alkalis with the varying volume of interaction on the new mineral formation along with the dissolution of the actual mineral. Two soils, namely, natural red earth and commercial kaolin with varying kaolinite content were selected for this study. The mineralogical and the morphological aspects involved in alkali treatment of these soils have been investigated using XRD, SEM, FTIR, and TG-DTA. The results showed that both red earth and kaolin treated with alkali solutions (4N NaOH and 4N KOH) at 110 °C showed the complete dissolution of mineral at higher volume of interaction. However, at given thermal condition, complete dissolution of mineral in red earth occurred at a lesser volume of interaction compared to kaolin. Furthermore, the dissolution of the original mineral and the intensity of new mineral formations varied with mineral content, volume of interacting solution and the type of alkali. Thus, the detailed analysis of the results clearly brought out that the disintegration of the actual mineral and the formation of new minerals greatly depend on the mineral content and volume of interaction

## 1. Introduction

Improper disposal of waste or inadequate design of waste containment systems often leads to contamination of soil. Soils exhibit unforeseen behavior upon interaction with contaminants and lead to various geotechnical problems. Contaminants can be mainly divided into organic and inorganic. Many researchers have focused on geotechnical properties of soil due to the effect of organic contaminants (Meegoda and Ratnaweera, 1994; Singh et al., 2008; Moavenian and Yasrobi, 2008; Olgun and Yildiz, 2010; Khosravi et al., 2013), whereas in recent times, researchers have shown interest focusing on the effect of inorganic contaminants on soil properties. One such inorganic contaminant which has a significant impact on soil properties is Caustic Soda (Maltsev, 1998; Jozefaciuk, 2002; Mulyukov, 2008; Gratchev and Sassa, 2009; Gratchev and Sassa, 2013; Ponnareddy et al., 2017). Primary utilization of alkalis was mainly found in dyes, paper and pulp, aluminum and ceramic industries, etc. The formation of hydrated salt crystals due to alkali contamination leads to increase in number of instances of structural failures (Sokolovich and Troitskii, 1976; Kabanov et al., 1977; Sibley and Vadgama, 1986; Chumikhin et al., 1988; Shekhtman et al., 1995). On this basis, several researchers conducted

laboratory investigations to understand the influence of alkali on clay minerals (Cuadros and Linares, 1996; Bauer and Berger, 1998; Bauer and Velde, 1999; Taubald et al., 2000; Wang and Siu, 2006a; Wang and Siu, 2006b; Elert et al., 2008; Jiang et al., 2008; Alshaer, 2013; Elert et al., 2015; Boussen et al., 2015). A very low concentration (0.1 N) of caustic soda solution can alter the soil structure (Mitchell, 1993 and Mulyukov, 2008) whereas, higher alkali concentration alters the mineralogy of clay and lead to new mineral formations (Sivapullaiah and Manju, 2007; Chavali et al., 2016). Moreover, it is worth noting that dissolution of kaolinite does not necessarily imply new mineral formation, particularly when the contact solution contains chemical species that can form soluble complexes with  $Al^{3+}$  released cations (Bidwell et al., 1970; Yuan et al., 1998; Zaman and Mathur, 2004; Andreola et al., 2007).

Based on the studies mentioned, it can be summarized that the soil-alkali interaction affects the crystal lattice owing to the dissolution of aluminosilicate portion of the mineral along with the formation of new minerals resulting in soil deformation which eventually leads to structural failure. Hence, micro-level investigations play an important role in understanding the behavior of soils. The minerals formed under high pH conditions in soil environment comprise zeolite and other clay

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minerals (Barrer et al., 1959; Barrer, 1982; De Kimpe, 1976; Breck, 1974). Numerous researchers have explored that kaolin interaction with alkali solutions leads to the origination of zeolite (Madani et al., 1990; Rocha and Klinowski, 1991; Gualteri et al., 1997; Akokelar et al., 1997; Demortier et al., 1999; Sivapullaiah and Manju, 2005; Reddy and Sivapullaiah, 2010). It is established that alkalinity loss in kaolinitic clays was dominated by chemical reactions (Mohnot et al., 1987). Further, studies on soils containing interstratified and montmorillonite minerals (Reddy and Sivapullaiah, 2010) revealed that soils with interstratified minerals showed the formation of zeolite P at lower concentrations of alkali and transformed to *sodalites* at higher concentration whereas soil with montmorillonite mineral showed no severe mineralogical changes. From the above studies, it can be inferred that the loss of alkalinity due to soil alkali reactions would be the greatest for kaolinite compared to that of montmorillonite. Overview of the literature summarizes the fact that the type of clay minerals and the concentration of alkali play a remarkable role in the synthesis of new mineral. In addition to this, focus of researchers in late 90's shifted to mineral transformations of soils at very high temperatures in the presence of alkalis by varying the temperature.

Experimental investigations have been carried out on the mineralogy of Opalinus shale at low temperatures to examine the effect of NaOH and KOH solutions (Chermark, 1992, 1993). New formations observed were Analcime, followed by vermiculite precipitation, and finally Na-rectorite formations were observed in the presence of NaOH whereas new minerals like Phillipsite, K-feldspar + K-rectorite were formed in the presence of KOH. Phillipsite which is a metastable intermediate finally changes to K-feldspar at higher concentration. Thereafter, Bauer and Berger (1998) conducted a series of batch experiments to evaluate the dissolution rate of kaolinite and smectite in KOH solution at 35 °C and 80 °C. XRD and SEM analysis reveals that no new minerals were formed during the dissolution phase. Rate limiting step in kaolinite was the dissolution of an octahedral layer and in smectite was the dissolution of the tetrahedral sheet. Later, Bauer et al. (1998) continued work on the transformation of kaolinite in high molar KOH solutions and highlighted the sequence of reaction products formed at 35 °C and 80 °C. It is also observed that crystallization restricts the concentration of Al and Si in solution and the perseverance of the varied metastable phases is temperature dependent (Bauer et al., 1998). Further the effect of concentration of alkali, temperature and type of alkali on the formation of zeolites was investigated by Kawano and Tomita (1997). New minerals formed in KOH medium were different to that formed in NaOH medium. Boehmite, smectite, phillipsite, and rhodochite were formed in NaOH whereas smectite, merlinoite and sanidine were formed in KOH medium. However, conclusions from the above mentioned experimental investigations were unclear since the nature of synthesized products altered with experimental conditions like starting material, solid/liquid ratio as well as solution composition and reaction temperature. In aforementioned studies, concentrations under which studies were carried out were in the range of 0.001–0.5 M both in case of NaOH and KOH medium. But, in practice, concentrations which many industry processes such as Aluminum extraction plant (Whittington and Cardile, 1996) and nuclear weapons industry (Qafoku et al., 2004) use are approximately 4N. When there is any leakage at these industrial sites, soils at closer surrounding become contaminated with such high concentrated alkalis. It is also noticed in many case studies (Rao and Rao, 1994; Sibley and Vadgama, 1986; Sivapullaiah et al., 2004) that the concentration of alkalis in soils due to accidental spillages, where deformations observed to a higher degree of extent, was high. So, in the present study to replicate the field contamination condition, higher concentration of alkali solutions were selected. To highlight the influence of type of alkali, mineral content and volume of interaction on the mineral dissolution and new mineral formations set of laboratory studies were carried out with two types of kaolinitic clays interacted with 4N NaOH and 4N KOH solutions of varying volume at 110 °C. The mineralogical changes and micro

structural variations were monitored using XRD and SEM which are supported by FTIR and TG/DTA.

## 2. Materials and methods

### 2.1. Clays used

In the present study, two kaolinitic clays with varying mineral content were used for the experimental investigation. One is a natural red earth soil possessing kaolinite was collected at one meter depth from natural ground level from Warangal (Latitude: 17.9689° N, Longitude: 79.5941° E), Telangana, India. The other is commercially available kaolin obtained from Godavari Mines and Minerals, Visakhapatnam (Latitude: 17.6868° N, Longitude: 83.2185° E), Andhra Pradesh, India. Both soils were air dried and soil passing through Indian Standard 425- $\mu$ m sieve was prepared before its usage.

### 2.2. Solution used

4N NaOH and 4N KOH solutions were considered for experimental investigation. These solutions were made by dissolving the necessary mass of sodium hydroxide pellets and potassium hydroxide pellets of Analar Grade in distilled water as per standard procedures. The physical properties of clays are summarized in Table 1. All the physical properties tests were performed as per ASTM standards. The chemical composition of clays is presented in Table 2.

### 2.3. Experimental investigation

The aim of the experimental investigation is to simulate the long-term effects of alkali on complete mineral dissolution and new mineral formations of kaolinitic clays (Chavali et al., 2016), which subsequently may influence the geotechnical properties of soils. Due to slow reaction rates at normal temperature under alkaline environment, engineering properties (mainly swelling behaviors and strength characteristics) of soils could not be able to notify unless the scenario becomes dangerous i.e. complete mineralogical transformation occurring due to continuous exposure to alkali solution. In the mineral transformation process volume of interacting solution plays an important role. The following experimental procedure was adopted to identify the conditions favorable for the complete mineral dissolution and new mineral formations.

Soils used in the present study were air dried and passed through 425- $\mu$ m sieve. Soils weighing 30 g were taken and mixed with 4N NaOH and KOH solutions thoroughly without any air bubbles at respective varying volume of interacting solutions. Volume of interacting solution to be added was calculated based on liquid limit times of given soil and allowed to interact for 24 h in a desiccator for attaining uniformity in soil-alkali interaction. Liquid limit is the minimum water content at which the soil changes from plastic state to liquid state and is an important property of fine grained soil which gives information regarding the state of consistency of soil on site. Initially sample was mixed for

**Table 1**  
Physical properties of kaolinitic clays.

Properties	Red earth	Kaolin
Specific gravity	2.62	2.70
Liquid limit (LL), %	38	42.9
Plastic limit (PL), %	22.64	29.72
Plasticity index (PI), %	15.36	13.18
Free swell index (ml/g)	1.0	1.1
Max. dry unit weight (kN/m <sup>3</sup> )	18.3	17.0
Optimum water content (%)	20.74	27.05
Clay content (%)	26	32
Silt content (%)	38	68
Fine sand content (%)	36	–
Cation exchange capacity (meq/100 g)	9.39	5.62

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