



“Gheorghe Asachi” Technical University of Iasi, Romania



---

## EFFECT OF TEMPERATURE ON BUFFERING CAPACITY OF CARBONATED AND DECARBONATED KAOLINITE IN COPPER CONTAMINATED SOIL

Vahid Reza Ouhadi<sup>1,2\*</sup>, Raymond Yong<sup>3</sup>, Hanieh Hejazifar<sup>4</sup>,  
Omid Bahadorinezhad<sup>4</sup>

<sup>1</sup>Faculty of Engineering, Bu-Ali Sina University, University Blvd., Hamedan, Iran

<sup>2</sup>School of Civil Engineering, University of Tehran, Enghelab Ave., Tehran, Iran

<sup>3</sup>Emeritus, McGill University, 11349 Redbud Place, North Saanich, British Columbia, V8L 5J9, Canada

<sup>4</sup>Faculty of Engineering, Bu-Ali Sina University, University Blvd., Hamedan, Iran

---

### Abstract

Even though carbonate fraction of soils significantly influences soil contaminant retention, there are few reports in the literature on the influence of temperature on contaminant retention of carbonated soils. Therefore, this study was conducted to investigate the effect of temperature on buffering capacity in carbonated and decarbonated kaolinite and on changes in intensity of x-ray diffraction for major peak of kaolinite. To achieve this aim, samples of kaolinite containing 2.5% carbonate and also the decarbonated samples were assessed using various tests such as X-ray diffraction, titration analysis, buffering capacity, and pH in a temperature ranges of 25 to 1000°C. Results showed that, in order to use buffering capacity of carbonate phase through its interaction with contaminants, temperature should be kept below 500°C. At temperatures above than 500°C, decomposition of calcium carbonate was found to be associated with a pH increase, which is responsible for an increase in the soil buffering capacity. At a temperature ranges from 800 to 1000°C, major peak of kaolinite completely disappeared and its buffering capacity was close to that of the control sample. Results indicate that, by adding copper nitrate, intensity of major peak of kaolinite for all the samples containing carbonate was larger than that of the decarbonated samples. At high concentrations of copper nitrate, pH levels of the kaolinite and decarbonated kaolinite samples became almost equal attributing to neutralization role of carbonate in soil buffering capacity at presence of copper ions.

**Keywords:** buffering capacity, carbonate, contaminant, kaolinite, temperature

*Received: April, 2019; Revised final: August, 2019; Accepted: November, 2019; Published in final edited form: June, 2020*

---

### 1. Introduction

Existence of clay minerals dates back to ancient times in most parts of the world, and their use in engineering projects has had a long history (Zhou et al., 2016). In many civil engineering projects such as slope stability and selection of waste disposal sites, identifying types and percentages of clay minerals in soil is of great importance. In several important projects worldwide, in spite of assessment of engineering parameters of materials, lack of

determining types of clay minerals present in such materials has led to failure of engineers in correctly predicting performance of materials (Moore and Reynolds, 1987). Quantitative mineral evaluation of clayey soils and their structure changes using X-ray diffractometry is an essential step needed to provide reliable soil recognition and behavior (Ouhadi and Goodarzi, 2003). Many of properties of clay minerals and other clay-size materials are related to water attached to edges and to (001) surfaces of clay minerals (Moore and Reynolds, 1987). Diffracted

---

\* Author to whom all correspondence should be addressed: e-mail: vahidouhadi@yahoo.ca; phone: +98 912 1072042; Fax: +98 813 824 6132

intensity of any hkl reflection from any crystalline material can be related to its composition, soil matrix, instrumental characteristics (Alexander and Klug, 1948; Norrish and Taylor, 1962) and geotechnical structure and microstructure of soil matrix (Mitchell and Soga, 2005; Pusch and Yong, 2006; Ouhadi et al., 2014a). In waste disposal sites, it is desirable to construct liners from material, which does not easily change in different environmental conditions (Ringwood, 1985).

For clayey soil remediation, various researches have applied heat treatment at temperatures between 800 to 1000°C to decontaminate soils from radioactive and toxic substances (Yilmaz et al., 2004). Thermal treatment alters physical and mechanical properties of clays. When clayey soils are stabilized with heat treatment, they can have important permanent properties (Tan et al., 2004). Heat treatment of clayey soils at temperatures up to 700°C causes physical and chemical changes in microstructure of soils (Abu-Zreig et al., 2001). For instance, experimental results revealed that heating and contaminating clays at 600°C decreased size fraction of soil particles, liquid limit and plastic limit; however, it increased silt size fraction and caused an increase in the compressive strength of soil (Yilmaz et al., 2004). Besides, the effects of thermal treatment on behavior of clays are important at places where clay is exposed to elevated temperatures over a long period of time (Yilmaz, 2011). Therefore, soil stabilization by means of heating has been widely applied to a large variety of engineering projects conducted to improve properties of problematic clayey soil. For instance, kaolinite has been shown to become non-plastic when treated under a temperature of 400°C (Yilmaz, 2011). It is known that kaolinite transforms into metakaolinite at about 500°C due to loss of structural water (Mittra and Bhattacharjee, 1969). Metakaolinite is an amorphous alumino-silicate (Siddique and Klaus, 2009). As heating proceeds, a spinel-type phase crystallizes within metakaolinite, beginning at around 900°C (Onike et al., 1986). Mullite also begins to form at this stage, and development of these phases continues to 1000°C (McConville and Lee, 2005).

Generally, thermal treatment strongly influences behavior of clays by influencing free and adsorbed water. Thermal strain occurs in clay structures mainly due to expansion of free water and changes in adsorption forces. Magnitude of thermal changes in clay body largely depends on mechanical and mineralogical makeup of clay mass, besides temperature of exposure and its duration, fabric of clay mass, and inter-particle separations (Bhatnagar and Goel, 2002). Therefore, understanding the effect of temperature on changes in properties and behavior of clay minerals is of great importance.

On the other hand, most countries intend to dispose their wastes by converting them into a solidified form and burying them underneath the earth. Fine-grained clay material is considered a suitable liner in disposal of waste, because it significantly restricts movement of aqueous fluids, and thus

contributing in retaining toxic elements over significant periods of time (Warr and Berger, 2007; Yao et al., 2012). In this regard, enormous quantity and complexity of metal-contaminated soils constitute an important challenge for clay soil remediation (Adriano, 2001; Yu et al., 2017). Thus, efficiency of remediation methods is dependent on recognition of mineral types. During identification of clay minerals in soils and sediments, identification of kaolinite in presence of chlorite has been one of the most frequent problems, and there is a need for a reliable procedure in order to distinguish between these minerals (Vivaldi and Gallgo, 1961). Among different methods, a combination of thermal and X-ray methods has been generally accepted as a method for distinguishing kaolinite and chlorite (Kodama and Oinuma, 1963).

Regarding remediation of contaminant soils, thermal treatment of soils contaminated with organic and heavy metal contaminants is a common and proven technology for remediation of contaminated soils (Lighty et al., 1990; Yong, 2001). As a matter of fact, while several parameters have been found to be important and influence desorption of contaminants from soil, heat treatment is the most effective method (Lighty et al., 1990). Because of this, some researchers have devoted their research to study remediation of contaminated soils through heating (Abu-Zreig et al., 2001; Tan et al., 2004). Previous research suggested that, sufficient durations and temperatures of treatment can provide energy required for remediation. Therefore, soil temperature, treatment time, and heating rate have been recognized to influence decontamination processes (Piña et al., 2002; Yao et al., 2012). However, there has been lack of attention in the literature on the influence of temperature on buffering capacity variations in soils.

Among clay minerals, kaolinite is a common mineral generally considered to be in a size range of 2 to 4 micron. Depending on pH, kaolinite particles have either positive or negative charges on their edge surfaces (Cruz et al., 2015). In spite of low adsorption of kaolinite, due to stability of its structure in interaction process with heavy metal contaminants, the use of kaolinite in multilayer systems has been recommended (Abu-Zreig et al., 2001). Numerous researches showed that, other clay minerals like kaolinite can be used as a less sensitive component for landfill layers with low permeability (Koch 2002). In such a case, bentonite-enriched layers and kaolinite-enriched layers are built up to multi-mineral barriers with appropriate adsorption behavior, low permeability, and low sensitivity against contaminant attack (Koch, 2002). This has spurred up the need for more investigation on the process of heavy metal interaction with kaolinite.

Generally, several studies have been conducted to investigate the effect of temperature on engineering behavior of contaminated soils. Moreover, behavior of these soils has always been studied with respect to remediation. Hence, to determine capability of thermal method in remediation of contaminated soil and also to identify clay minerals in soils and

sediments, it is necessary to identify mineral types and their percentage and buffering capacity variations. Accordingly, this study was carried out to evaluate changes in buffering capacity of kaolinite at temperatures between 25 and 1000°C, and to evaluate the effect of temperature on alterations in intensities of peaks heights of kaolinite and decarbonated kaolinite in X-ray diffraction.

## 2. Material and methods

### 2.1. Physical and chemical characteristics of materials

The clay sample used in this research was obtained from northwestern Iran, in which its dominant fraction is kaolinite mineral (Table 1). Physical characteristics of the kaolinite under study were determined according to the ASTM standard (ASTM, 2017). Also, chemical analysis was performed according to laboratory manual of the Geotechnical Research Center of McGill University and EPA (USEPA, 2008). Some properties of the soil under study are presented in Table 1.

**Table 1.** Some of physical and geo-environmental properties of kaolinite

<i>Physical properties</i>	<i>Kaolinite</i>
Liquid Limit (LL), %	35
Plasticity Index (PI), %	20
Soil Classification	CL
pH (1:10, Soil:Water)	9.3
Carbonate percentage	2.5
Cation Exchange Capacity (Cmol/Kg-Soil), (CEC)	9
Specific Surface Area (SSA), (m <sup>2</sup> /g)	28
Basal Spacing of Kaolinite mineral, A	7.13
Percentages of minerals present in soil, based on XRD analysis	Kaolinite 91%, Quartz 3%, Calcite 2.5%, Chlorite 2%, Illite 1.5%

### 2.2. Sample preparation and experimental methods

To determine carbonate percentage of the soil, titration method (Eltantawy and Arnold, 1973) was used. In addition, kaolinite sample was decarbonated using Hesse's decarbonation method (Hesse, 1971). To achieve the objectives stated in this study, in preparing the samples, kaolinite and decarbonated kaolinite samples were first heated at 50, 100, 200, 300, 500, 550, 600, 650, 700, 800, and 1000 °C for 30 minutes.

Samples contaminated with heavy metals were obtained by adding copper nitrate at concentrations of 4, 10, and 20 cmol/kg-soil to samples of kaolinite and decarbonated kaolinite. Copper nitrate was used in the study with the following chemical formula (Cu(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O), and was provided from Merck company (Germany).

pH of the samples was measured in soil-water suspensions at ratio of 1:10 using HANNA-Hi 9321 pH meters. Buffering capacity of the soil was measured by performing titration experiment and by adding different concentrations of nitric acid (HNO<sub>3</sub>) to the samples (ASTM, 2017; EPA, 1983; Hendershot and Duquette, 1986). Acid solutions with different concentrations were added to the soil at a ratio of 1:10 (soil-acid solution). Then, acquired suspension was shaken using an electric shaker. To obtain homogeneous samples and to have the required cation exchange, they were kept for 96 hours. Finally, pH values were measured using a pH meter device. Prepared X-ray samples were provided and analyzed using the method proposed in previous studies (Moore and Reynolds, 1987; Ouhadi and Yong, 2003). To prepare X-Ray Diffraction samples (XRD), 0.5 g of dry soil was weighed with a precision of 0.0001 grams, and was taken from all the samples, and then was placed in a 15-mL centrifuge tube. After adding 10 mL of distilled water to the soil, suspension was shaken by an electric shaker for 3 hours. After keeping the samples for 24 hours to ensure that equilibrium conditions are achieved, suspension was shaken with an electric shaker for another 3 hours, and the samples were kept for additional 120 hours to become homogeneous. Finally, 7 drops of suspension were placed on a glass slide using an automatic pipette, and after drying, the samples were analyzed by a D8-Advance Diffractometer. X-ray diffraction was analyzed in a range of  $2\theta = 4 - 60^\circ$  using CuK<sub>α</sub> radiation.

As mentioned previously, in order to obtain the decarbonated sample, Hesse's decarbonation method was used based on pH adjustment of soil-water-acid suspension. Two experiments, titration and X-ray diffraction (XRD), were performed, respectively on the decarbonated kaolinite samples to determine amount of carbonate in soil and to check initial structure of soil (from geotechnical aspect) maintained after carbonate removal. As shown in Fig. 1, since differences between intensities of major peaks of kaolinite in XRD diffractometry of carbonated and decarbonated kaolinite are less than 1%, it can be concluded that structure of the soil sample remains similar. Generally, variation in the position and intensities of major peaks of kaolinite is due to at least one of the following four mechanisms: cation exchange, clay mineral disintegration, formation of new minerals, or change in soil structure (soil matrix) (Ouhadi and Amiri, 2014). Lack of change in the peak position and intensities of X-ray diffraction of clay fraction in the decarbonated kaolinite samples compared to results of X-ray diffraction on kaolinite implies that none of above mechanisms occurred in decarbonation process. In other words, decarbonation process occurred without any change in the mineralogical characteristics and geotechnical properties of kaolinite. Besides, pH of the sample was measured as 8.3 after decarbonation. Considering a 1-unit decrease in the pH of sample relative to initial pH of sample and also based on results obtained from X-ray diffraction and stability of intensity and position

of kaolinite peak (Fig. 1), it can be concluded that structure of clay part was retained without any change as well. Remaining of pH in alkaline range indicates no changes in soil matrix (Norrish and Taylor, 1962). In other words, very small change was observed in pH of soil sample after decarbonation process. Besides, according to results presented in Fig. 1, peak of carbonate was omitted in the decarbonated sample, indicating consistency of results obtained from chemical decarbonation with the results of X-ray diffraction experiment.

Generally, thermal transformation has been reported to be a function of clay mineral type and thermal processing conditions (McConville and Lee, 2005). On the other hand, in this paper, the clay mineral type and thermal processing conditions were similar for all samples. Therefore, in this paper, extent of clay mineral transformation was not discussed.

### 3. Results and discussion

#### 3.1. Effect of temperature on intensities of peaks of kaolinite and decarbonated kaolinite

To evaluate the effect of temperature on transformation and distortion of carbonate in soil, percentages of carbonate in heat-treated kaolinite samples were measured using titration experiment. Fig. 2 illustrates changes in the amount of carbonate in soil with respect to heat variations from 25 to 1000°C. Results revealed that, there were no changes in the amount of carbonate for the samples heated under temperatures from 25 to 500°C; consequently, percentage of carbonate was retained at 2.5% for all tested samples. For the samples heated under temperatures from 550 to 600°C, carbonate percentage decreased to 2% and, then from 650 to 1000°C, as calcium carbonate started to decompose (Cultrone et al., 2004; Ouhadi et al., 2011), carbonate percentage of the samples reached zero. As carbonate percentage of soil remained unchanged up to 500°C, it can be inferred that in order to use buffering capacity of carbonate phase in soil through its interaction with

different contaminants to form insoluble components, temperature should be kept below 500°C.

Furthermore, in order to interpret observed behavior from a microstructural perspective, X-ray diffraction of the kaolinite and decarbonated kaolinite samples was obtained and analyzed at different temperatures, and results are presented in Fig. 3. As shown in Fig. 3, three areas were distinguishable on this graph. Analysis of results in each area was performed with respect to two aspects: 1) the effect of temperature on changes in intensity of major peak of kaolinite considering loss of adsorbed water and dehydroxylation, and 2) the effect of temperature on changes in intensity (peak height) of major peak of kaolinite both in presence or absence of carbonate in soil. As illustrated in Fig. 3, in area 1, corresponding to temperatures from 25 to 300°C, with loss of pore water and free water, intensity of major peak of kaolinite shows a very minor reduction.

Previous studies showed that, if the soil is in alkaline conditions, it will retain its alkalinity if heated to temperatures from 25 to 300°C (Hejazifar, 2016; Ouhadi et al., 2010). Accordingly, changes in temperature do not cause microstructure to change considerably with regard to pH. In addition, decreases in the intensities of major peaks of the kaolinite and decarbonated kaolinite samples at 300°C relative to 25°C were equal to 4% and 16%, respectively. Due to relative stability in intensities of peaks, it can be suggested that resultant interaction forces are repulsive, and from geotechnical point of view, the samples have dispersed structures.

Therefore, because of lack of change in the soil structure and also negligible change in the macropores of the soil, behavior of the soil is a function of distribution and amount of initial micro-pores in the soil. In other words, manner of distribution and changes of micro-pores controls behavior of the soil (Yong et al., 2009). This is in agreement with very low exchangeable cations on kaolinite particles, in which removal of pore water and adsorbed water does not cause any significant change in its initial geotechnical structure.

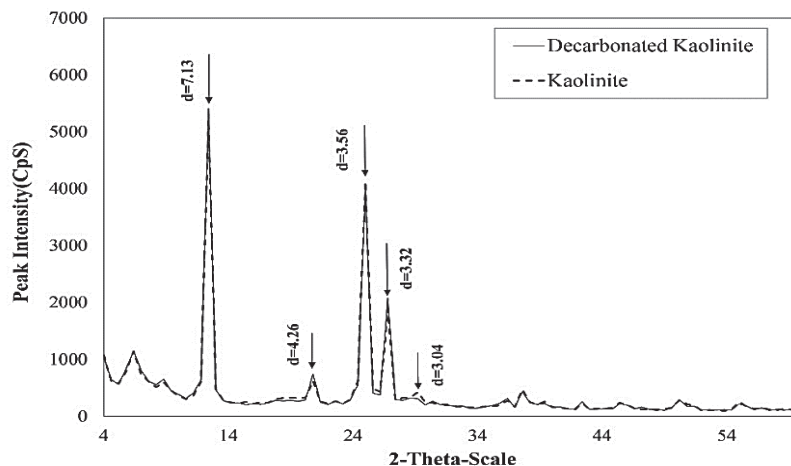


Fig. 1. Comparison between X-ray diffraction (XRD) of kaolinite and decarbonated kaolinite

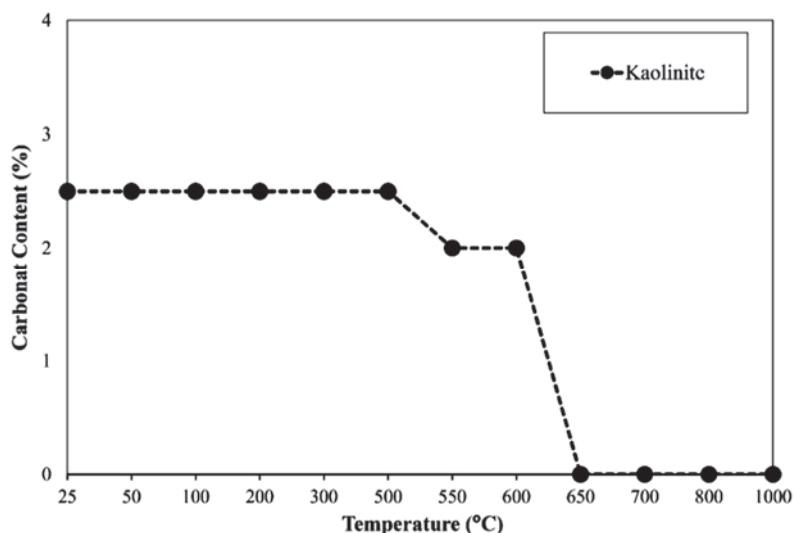


Fig. 2. Changes in carbonate percentages of the heated kaolinite samples

At temperatures above 500°C and at a temperature range from 500 to 1000°C, dehydroxylation of clay minerals occurs. In these conditions, with removal of hydroxyl ion from crystal structure of kaolinite, concentration of hydrogen ion increases and pH of the soil decreases (Mitchell and Soga, 2005). As indicated in Fig. 3, in area 2 (at a temperature range of 500 to 550°C), with commencement of de-hydroxylation, a decrease occurred in the intensities of peaks at a greater rate, so a 31 and 76% decrease was observed in the intensities of peaks for kaolinite sample at temperatures from 500 and 550°C, respectively. Decreasing trend in intensity of peak caused by the increase in the heat in this range of temperature can be attributed to kaolinite dehydroxylation and transformation to metakaolinite (McConville and Lee, 2005).

The results presented in Fig. 3 showed that 41 and 78% decrease in the intensity of major peak of the

decarbonated kaolinite sample, respectively at temperatures from 500 to 550°C. As a matter of fact, in the two types of soils mentioned above (carbonated and decarbonated kaolinite), intensities of the major peaks of kaolinite had a 2-fold decrease at 550°C relative to a temperature of 500°C. In other words, since an increase in the temperature results in dehydroxylation process, it causes an increase in the concentration of hydrogen ions around clay particles. Therefore, as a result of pH drop, repulsive forces also decrease. Consequently, it is expected that, formation of micro-pores is dominant on behavior of the soil (Yong et al., 2009). Furthermore, as can be seen in Fig. 3, in the second area, a noticeable change is observed in peak intensity of major basal spacing peak of kaolinite in the kaolinite and decarbonated kaolinite samples. Since, the temperature of initiation of dehydroxylation is about 500°C (Mitchell and Soga, 2005; McConville and Lee, 2005).

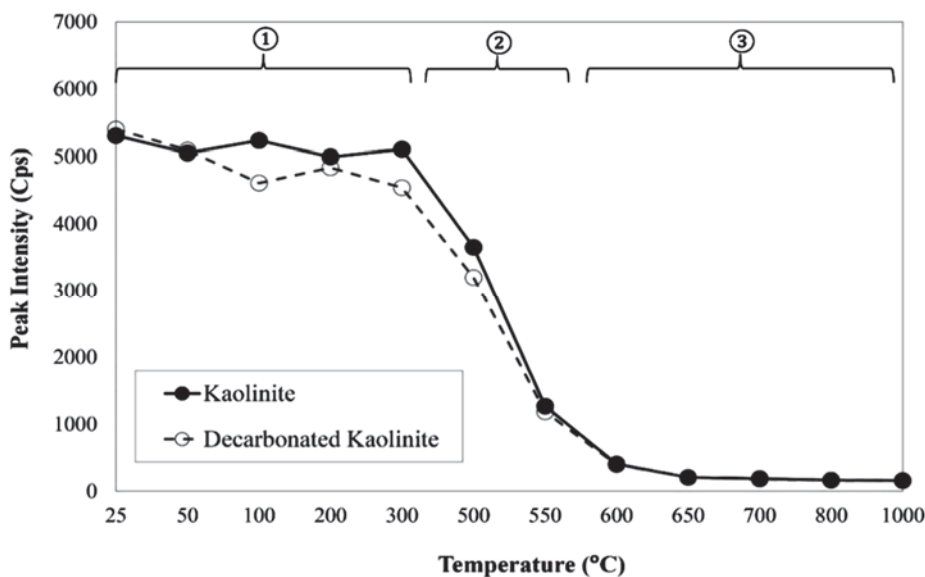


Fig. 3. Changes in the intensity of the major basal spacing peak of the kaolinite and the decarbonated kaolinite at different temperatures

It seems that, noticeable change in kaolinite peak intensity in this area relative to areas 1 and 3 is indicative of high change in soil structure due to commencement of de-hydroxylation, alterations of de-hydroxylation percentages in this temperature range, and destruction of basic structures of kaolinite particles. Moreover, as shown in Fig. 3, at temperatures above than 500 °C and with decomposition of calcium carbonate in kaolinite soil intensities of peaks of the kaolinite and decarbonated kaolinite samples converge towards a similar value. It can be concluded that, at this range of temperature, soil microstructure of kaolinite and decarbonated kaolinite samples inclines toward each other.

On the other hand, results presented in Fig. 3 indicated that, in area 3 involving a temperature range of 600 to 1000°C, intensities of peaks of carbonated and decarbonated kaolinite samples decreased by about 90% from intensities at a temperature of 25 °C. In other words, destruction of basic structures of kaolinite particles started, and at temperatures above than 600°C, formation of macro-pores commenced at a greater rate (Yong et al., 2009). In addition, at temperatures above than 600°C and with decomposition of calcium carbonate, the effect of presence of carbonate on changes in the intensity of major basal spacing peak of kaolinite disappeared, and intensities of peaks converged. With the increase in the temperature and with decomposition of calcium carbonate in soil and release of CO<sub>3</sub> and CaO at temperatures above than 600°C, two mechanisms occur: 1) reaction of CO<sub>2</sub> with water (H<sub>2</sub>O) and formation of weak acid H<sub>2</sub>CO<sub>3</sub>, and 2) reaction of CaO with water(H<sub>2</sub>O) and formation of calcium hydroxide Ca(OH)<sub>2</sub>. Whereas the first reaction causes a decrease in the pH of the soil's environment, and occurrence of the second reaction, due to hydration of lime increases pH of the soil's environment. Therefore, there is a need to investigate pH variation in soil and its effect on soil buffering capacity.

### 3.2. Effect of temperature on pH values and buffering capacity of kaolinite and decarbonated kaolinite

Due to importance of buffering capacity of clay materials in industrial waste disposal sites, buffering capacities of kaolinite and decarbonated kaolinite samples were studied before and after heating (25 to 1000 °C), and results are presented in Figs. 4-5.

Considering results presented in Fig. 4, and regarding decarbonated samples, it can be concluded that when no acid was added to the samples, an increase in the temperature, with release of hydroxyl ions(OH<sup>-</sup>) in form of water, called de-hydroxylation caused an increase in the concentration of H<sup>+</sup> ions. The increase in the acidity due to formation of this weak acid caused a decrease in the pH of the samples, so this decrease in the pH intensified with the increase in the temperature from 550 °C and with de-hydroxylation of the soil. On the other hand, due to absence of carbonate in soil and thermal treatment of the samples, there was low buffering up to 20 cmol/kg-soil of concentration for HNO<sub>3</sub>. With increase in the concentration of added acid from 60 to 100 cmol/kg-soil, graphs of pH values converged. In fact, it can be suggested that when the soil does not contain carbonate, temperature has no significant effect on buffering capacity. Moreover, despite relative difference in initial pH of samples, with an increase in the temperature and de-hydroxylation of the samples, buffering capacities of the decarbonated samples converged, especially at temperatures above than de-hydroxylation.

Behavioral similarity of curves for decarbonated kaolinite and distilled water containing HNO<sub>3</sub> acid (Blank) showed dominance of carbonate controller on buffering capacity of kaolinite soil. Furthermore, behavioral convergence of above samples is indicative of appropriateness of Hesse's decarbonation method for removal of carbonate from kaolinite sample.

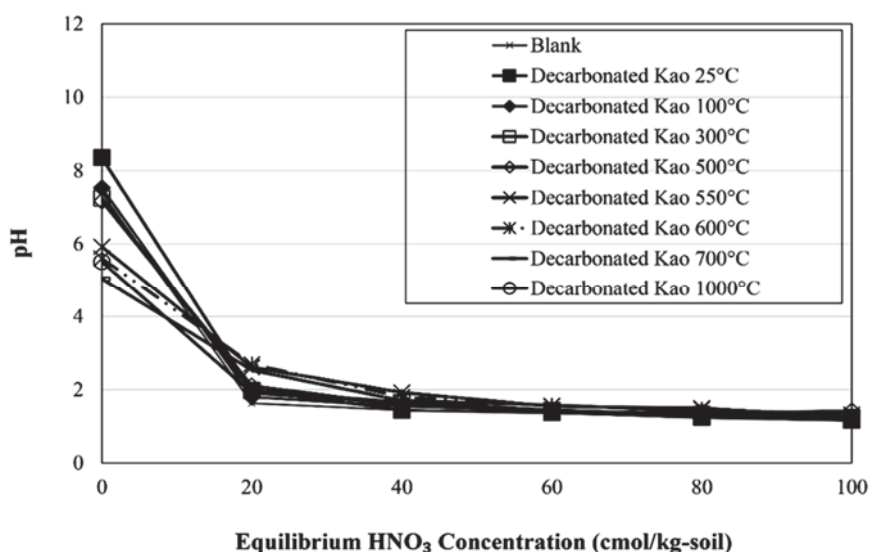


Fig. 4. Buffering capacity of decarbonated kaolinite samples heated at different temperatures

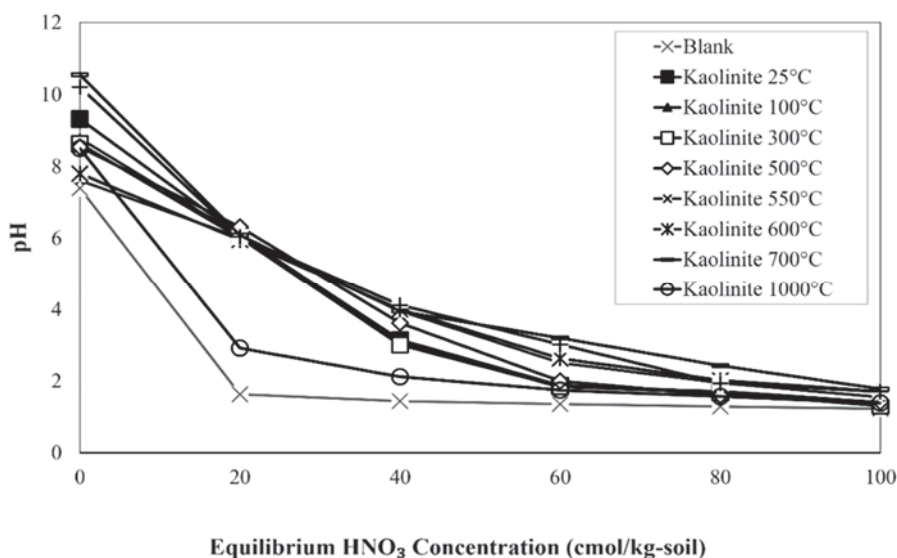


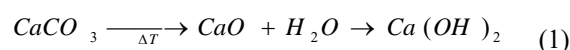
Fig. 5. Buffering capacity of Kaolinite samples heated at different temperatures

Previous studies have also stated existence of carbonate phase as one of the most important phases of contaminant retention in soils (Ouhadi et al., 2014a). As depicted in Fig. 5, when no acid was added to kaolinite samples, the increase in the temperature to 600°C, through formation of weak acid caused a decrease in the pH from 9.3 to 7.8. With the increase in the temperature to more than 600°C, decomposition of calcium carbonate caused formation of quicklime. Quicklime is prone to slake when exposed to moisture in soil's environment, and this increases pH value up to 10.5. In general, carbonates contribute in preventing transmission of contaminant in soils through three mechanisms: 1) through neutralization of soil acidity, 2) through an increase in the pH level of pore fluid of soil, and 3) through reaction with different contaminants to form insoluble components (Ouhadi et al., 2014b).

At temperatures above 650°C and with decomposition of some parts of calcium carbonate of the soil, the influence of calcium carbonate decreases in neutralization of acidity of environment. Results presented in Fig. 5 showed that, at concentration of 20 cmol/kg-soil of HNO<sub>3</sub> acid, pH graphs of the samples heated at temperatures below 1000°C and the sample heated at 1000°C and the control sample (acid and distilled water) were highly different (about 3 units), attributing to performance of carbonate present in the soil through the three explained mechanisms. However, with the increase in the concentration of acid and ineffectiveness of the first mechanism, buffering capacity of the samples decreased. At concentration of 100 cmol/kg-soil of acid, pH values became equal to that of the control sample. For kaolinite sample heated at 1000°C, due to formation of new structures and phase transitions, buffering capacity was almost non-existent and equal to that of the control sample. Comparing Fig. 4 and Fig. 5, it can be inferred that, for the decarbonated samples, with removal of carbonate from the soil, pH graphs of the

samples at acid concentrations of 60, 80 and 100 cmol/kg-soil matched each other, and pH values of the samples were almost equal to pH of the control sample. However, in case of the carbonated samples, because of role of carbonate in increasing buffering capacity of the soil and preventing the decrease in the soil's pH, up to acid concentrations of 60 and 80 cmol/kg-soil, the soil still exhibited some buffering capacity, and its pH was higher than pH of the control solution (acid and distilled water).

To investigate the effect of temperature on pH changes of the kaolinite and decarbonated kaolinite samples, pH levels of these samples were measured at temperature ranges of 25 to 1000°C, and results are shown in Fig. 6. Results showed that, concerning the carbonated kaolinite samples, with commencement of thermal treatment up to 500°C and with loss of adsorbed water of the soil and de-hydroxylation, concentration of H<sup>+</sup> ion increased, and as a result, pH levels decreased to about 8%. At temperatures of 550 to 600°C and with de-hydroxylation of kaolinite mineral, trend of pH reduction also decreased. With continuous increase in the temperature and at temperatures of 650 to 800°C and with commencement of decomposition of calcium carbonate, soil's pH increased by 31% relative to 600°C. Based on Eq. (1), decomposition of calcium carbonate, beginning from about 650°C caused release of quicklime. Consequently, when samples were exposed to water and also reacted with water, Ca(OH)<sub>2</sub> and finally OH ion were released (Cultrone et al., 2004). This stage is in fact the second mechanism of decomposition of calcium carbonate, which is associated with a pH increase in soil's environment. This pH increase was not observed for decarbonated kaolinite. Therefore, in the decarbonated kaolinite sample, pH continuously decreased with an increase in the temperature.



In addition, to confirm results obtained from experiments on the kaolinite samples containing carbonate, after heat treatments, x-ray diffraction experiment was performed on above samples and alterations in intensity of peak of carbonate in the samples were measured. Results obtained from XRD in a spacing of 3.04 (belonging to carbonate mineral) for heat-treated samples are presented in Fig. 7. As illustrated in Fig. 7, with thermal treatment of the kaolinite samples up to 600°C, intensity of peak of calcium carbonate was almost invariable.

However, with the increase in the temperature from 650°C to 1000 °C and commencement of decomposition of soil calcium carbonate, intensity of peak of calcium carbonate decreased. Results presented in Fig. 7 show a significant correspondence with results presented in Fig. 6.

3.3. Effect of addition of heavy metal contaminant on aggregation and flocculation of kaolinite and decarbonated kaolinite

Process of soil-contaminant interaction, through influence on forces between clay particles causes a change in the microstructure of clayey soils

from geotechnical point of view. To evaluate the effect of heavy metal contaminant on microstructure of the kaolinite and decarbonated kaolinite samples, X-ray diffractions were obtained from some samples. In this part of this experimental study, copper nitrate was used as a heavy metal contaminant.

Results of X-ray diffraction experiment for the kaolinite and decarbonated kaolinite samples at concentrations of 4, 10, and 20 cmol/kg-soil of copper nitrate are shown in Fig. 8. By adding 4 cmol/kg-soil of copper nitrate as heavy metal contaminant, intensity of peak of X-ray diffraction decreased by 564 Cps (10.6 percent) for the kaolinite sample. In addition, by increasing concentration of contaminant up to 10 cmol/kg-soil, intensity of peak decreased by 1395 Cps (26%).

At concentration of 20 cmol/kg-soil, and by more increasing concentration, formation of flocculated structure increased, and due to formation of flocculated structure in the soil, and a reduction in the reflection of rays striking the soil, intensity of major peak of kaolinite mineral reached a value of 2564 Cps, showing a decrease of about 50% from intensity of major peak of kaolinite mineral before interaction with heavy metal contaminant.

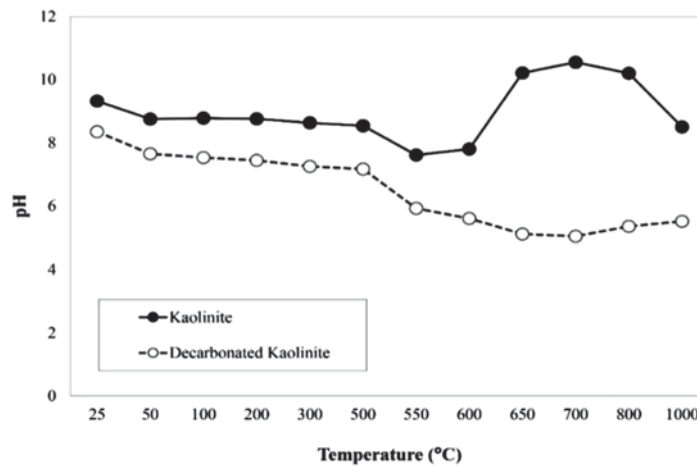


Fig. 6. pH changes for kaolinite and decarbonated kaolinite at different temperature

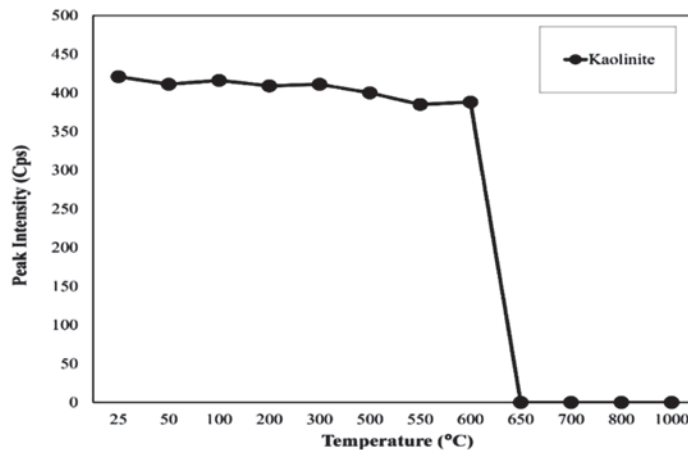


Fig. 7. Alterations in intensity of major basal spacing peak of calcium carbonate in heat-treated kaolinite samples



In fact, an increase in the concentration of heavy metal contaminant caused aggregation of clay particles, and creation of a number of large pores in the soil. In other words, due to the cation exchange caused by replacement of copper ions with alkaline cations of adsorbed ions, repulsion force among particles decreased, implying that with an increase in the concentration of copper ion in electrolyte, a considerable amount of negative charges of clay are neutralized by these cations, leading to the reduction of the repulsive forces of clay particles, closeness of clay particles and creation of aggregated structure. Results indicated that, when no contaminant was yet added to the soil, difference between intensities of peaks of the kaolinite and decarbonated kaolinite samples was equal to 1.8%, which is very low. By adding heavy metal contaminant to the samples, in the samples containing carbonate, the interaction of heavy metal ion with carbonate resulted in decomposition of a part of carbonate (Yong et al., 1993). Therefore, due to initial interaction of heavy metal contaminant with carbonate fraction of sample, there was a decrease in the possibility of interaction between heavy metal contaminant and clay particle. Thus, in presence of copper ions, intensity of major peak of kaolinite was more for all the samples containing carbonate than that of the decarbonated samples.

Difference between intensities of peaks was equal to 17% at concentration of 4 cmol/kg-soil of HMs. By increasing contaminant concentration and due to the increase in the role of carbonate in the interaction with copper ions and prevention of interaction between metal ion and clay particle, difference between intensities of peaks increased for the carbonated and decarbonated samples (about 30% difference at concentration of 10 cmol/kg-soil). On the other hand, by further increasing contaminant concentration up to 20 cmol/kg-soil, due to consumption of carbonate in the interaction with added copper nitrate, intensities of peaks of the carbonated and decarbonated kaolinite samples became closer to each other and their difference decreased to about 27%.

In addition, results obtained from pH experiment on these samples showed that, by adding contaminant to the samples, a decrease was found in the pH levels. Presence of heavy metal contaminant reduces system pH for two reasons: 1) when metal contaminant dissolves in water, because of production of hydrated ion and hydrolysis of metal, and acidification of solution, pH of water-soil system decreases. 2) Adsorption of metal ions to clay surfaces causes release of  $H^+$  ion and reduction of pH. Results obtained from measurement of pH showed that, whereas pH of pure kaolinite sample was about 9.3, presence of 4 cmol/kg-soil of heavy metal contaminant caused a decrease in the pH of the sample to 8.2.

Results presented in Fig. 8 showed that, not all the phases of soil retention have yet been filled and the soil has a dispersed structure. However, by increasing contaminant concentration to 20 cmol/kg-soil, pH of reaction environment reached 5, indicating possibility of formation of flocculated structure and domination of macro-pores. At a concentration 20 cmol/kg-soil of heavy metal copper, pH levels of the kaolinite and decarbonated kaolinite samples became almost equal, indicating lack of function of carbonate as a major controller in soil buffering capacity against pH alterations in the carbonated kaolinite sample.

#### 4. Conclusions

- Behavioral similarity of curves for decarbonated kaolinite and distilled water containing  $HNO_3$  acid (Blank) showed dominance of carbonate controller on buffering capacity of kaolinite soil.
- In the decarbonated kaolinite sample, temperature was found to have no significant effect on buffering capacity. Moreover, despite relative difference in initial pH of heat-treated samples, with an increase in the temperature and de-hydroxylation of the samples, buffering capacities of the decarbonated samples heated at different temperatures converged, especially at temperatures above than de-hydroxylation.

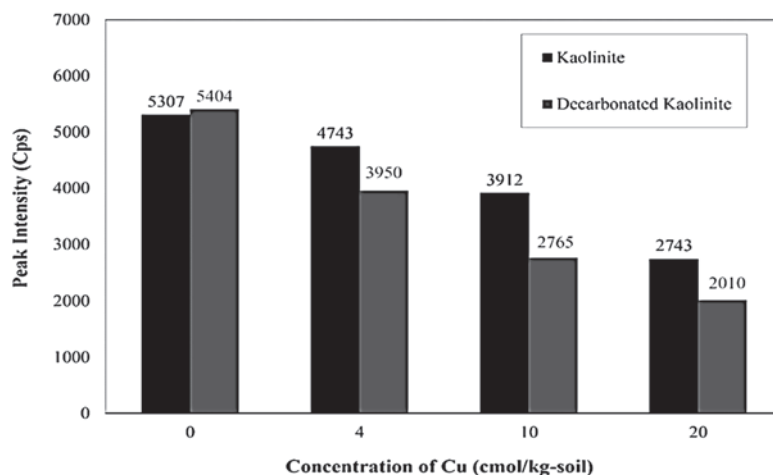


Fig. 8. Alterations in intensities of major basal spacing peaks of kaolinite and decarbonated kaolinite containing contaminant copper

At temperatures of 800 to 1000 °C, peak of kaolinite completely disappeared and its buffering capacity also became very close to buffering capacity of the control sample. It can be concluded that buffering capacity of the carbonated kaolinite sample is noticeably pH-dependent.

- Results of this paper indicated that mechanism of calcium carbonate contribution to soil buffering capacity is different at temperatures below and above than 500°C. At temperatures below than 500°C, carbonate contributes to soil buffering capacity through reaction with different contaminants to form insoluble components. Whereas, at temperatures above than 500°C, decomposition of calcium carbonate is associated with a pH increase in the soil's environment, resulting in an increase in the soil's buffering capacity.

- Addition of copper nitrate (as a source of heavy metal contaminant) to clay soil resulted in hydration of metal ion and release of H<sup>+</sup> ion, and as a result reduces pH level. It can be concluded that, at high concentrations of copper ion, soil structure became flocculated and intensity of major peak of kaolinite decreased.

- Results of this paper indicated that by adding copper nitrate, intensity of major peak of kaolinite was more for all the samples containing carbonate than that of the decarbonated samples, attributing to more interaction of copper ions and kaolinite in the decarbonated kaolinite sample. It can be concluded that, in the carbonated kaolinite sample, due to initial interaction of heavy metal contaminant with carbonate fraction of sample, a decrease was found in the possibility of interaction between heavy metal contaminant and clay particle.

### Acknowledgements

This research work was part of the master's thesis of the third author. The contribution of the fourth author (Mr Bahadorinezhad) is limited to the experimental setup training for the third author, which is highly appreciated by other authors.

### References

Abu-Zreig M.M., Al-Akhras N.M., Attom M.F., (2001), Influence of heat treatment on the behavior of clayey soils, *Applied Clay Science*, **20**, 129-135.

Adriano D.C., (2001), *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metals*, 2nd Edition, Springer, New York.

Alexander L.E., Klug H.P., (1948), Basic aspect of X-ray absorption in quantitative diffraction analysis of powder mixtures, *Analytical Chemistry*, **20**, 886-889.

ASTM, (2017), *Soil and Rock (I): D420-D5876*, In: *Annual Book of ASTM Standards*, vol. 4.08, American Society for Testing and Materials, West Conshohocken PA.

Bhatnagar J.M., Goel R.K., (2002), Thermal changes in clay products from alluvial deposits of the Indo-Gangetic plains, *Construction and Buildings Materials*, **16**, 113-122.

Cruz N., Peng Y., Wightman E., Xu N., (2015), The interaction of pH modifiers with kaolinite in copper-

gold flotation, *Minerals Engineering*, **84**, 27-33.

Cultrone G., Sebastián E., Elert K., José M., Cazalla O., Rodríguez C., (2004), Influence of mineralogy and firing temperature on the porosity of brick, *Journal of European Ceramic Society*, **24**, 547-564.

Eltantawy I.N., Arnold P.W., (1973), Reappraisal of ethylene glycol mono-ethyl ether (EGME) method for surface area estimation of clays, *Soil Science*, **24**, 232-238.

EPA, (1983), *Process Design Manual, Land Application of Municipal Sludge*, Municipal Environmental Research Laboratory, EPA-625/ 1-83-016, U.S. Government Printing Offices, New York.

Hejazifar H., (2016), *Effect of temperature changes on the kaolinite peak intensity in clayey soils and contaminated clayey soil*, MSc Thesis, Bu-Ali Sina University, Hamedan, Iran.

Hendershot W.H., Duquette M., (1986), A simple barium chloride method for determining cation exchange capacity and exchangeable cations, *Soil Science Society of America Journal*, **50**, 605-608

Hesse P.R., (1971), *A Textbook of Soil Chemical Analysis*, William Clowes and Sons, London.

Koch D., (2002), Bentonites as a basic material for technical base liners and site encapsulation cut-off walls, *Applied Clay Science*, **21**, 1-11.

Kodama H., Oinuma K., (1963), Identification of kaolin minerals in the presence of chlorite by X-ray diffraction and infrared absorption spectra, *Clays and Clay Minerals*, **11**, 236-249.

Lighty J.S., Silcox G.D., Pershing D.W., (1990), Fundamentals for the thermal remediation of contaminated soils, Particle and bed desorption model, *Environmental Science and Technology*, **24**, 750-757.

McConville C.J., Lee W.E., (2005), Microstructural development on firing Illite and smectite clays compared with that in kaolinite, *Journal of the American Ceramic Society*, **88**, 2267-2276.

Mitchell J.K., Soga K., (2005), *Fundamentals of Soil Behaviour*, 3rd Edition, John Wiley and Sons Inc., Hoboken, New Jersey.

Mitra G.B., Bhattacharjee S., (1969), X-ray diffraction studies on the transformation of kaolinite into metakaolin: I. Variability of interlayer spacings, *The American Mineralogist*, **54**, 1409-1418.

Moore D.M., Reynolds R.C., (1987), *X-ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford University Press, New York.

Norrish K., Taylor R.M., (1962), Quantitative analysis by X-ray diffraction, *Clay Minerals Bulletin*, **5**, 98-109.

Onike F., Marti G.D., Dunham A.C., (1986), Time-temperature transformation curves for kaolinite, *Materials Science Forum*, **7**, 73-82.

Ouhadi V.R., Goodarzi A.R., (2003), *Pore Fluid Characteristics Effect on the Dispersivity Behaviour of Soils from Macro and Micro Structure Aspects*, Proc. of the 2nd International Symposium on Contaminated Sediments, 200-206.

Ouhadi V.R., Yong R.N., (2003), Impact of clay microstructure and mass absorption coefficient on the quantitative mineral identification by XRD analysis, *Applied Clay Science*, **23**, 141-148.

Ouhadi V.R., Yong R.N., Goodarzi A.R., Safari-Zanjani, M., (2010), Effect of temperature on the re-structuring of the microstructure and geo-environmental behaviour of smectite, *Applied Clay Science*, **47**, 2-9.

Ouhadi V.R., Yong R.N., Rafiee F., Goodarzi, A.R., (2011), Impact of carbonate and heavy metals on micro-

- structural variations of clayey soils, *Applied Clay Science*, **53**, 228-234.
- Ouhadi V.R., Amiri M., (2014), Interaction of nano-clays and Cu contaminant in geo-environmental projects, *Journal of Environmental Science and Technology*, **16**, 75-87.
- Ouhadi V.R., Bahadori Nezhad O.R., Amiri M., (2014a), Lead retention of carbonated kaolinite in the adsorption and electrokinetics processes, *Modarres Journal*, **14**, 17-30.
- Ouhadi V.R., Yong R.N., Amiri M., Ouhadi, M.H., (2014b), Pozzolanic consolidation of stabilized soft clays, *Applied Clay Science*, **95**, 1111-1118.
- Piña J., Merino J., Errazu A.F., Bucalá V., (2002), Thermal treatment of soil contaminated with gas oil: influence of soil composition and treatment temperature, *Journal of Hazardous Materials*, **94**, 273-290.
- Pusch R., Yong R.N., (2006), *Microstructure of Smectite Clays and Engineering Performance*, Taylor and Francis, London and New York.
- Ringwood A.E., (1985), Disposal of high-level nuclear wastes: a geological perspective, *Mineralogical Magazine*, **49**, 159-176.
- Siddique R., Klaus J., (2009), Influence of metakaolin on the properties of mortar and concrete: A review, *Applied Clay Science*, **43**, 392-400.
- Tan Ö., Yilmaz L., Sahin Zaimoğlu A., (2004), Variation of some engineering properties of clays with heat treatment, *Materials Letters*, **58**, 1176-1179.
- USEPA, (2008), *Fate, Transport and Transformation Test Guidelines OPPTS 835.1230 Adsorption/Desorption (Batch Equilibrium)*, Office of Prevention, Pesticides and Toxic Substances U.S. Environmental Protection Agency-USEPA, Washington, DC.
- Vivaldi J.L., Galgo M., (1961), Some problems in the identification of clay minerals in mixtures by X-ray diffraction. I. chlorite-kaolinite mixtures Granada, Spain, 288-292.
- Warr L., Berger J., (2007), Hydration of bentonite in natural waters: Application of "confined volume" wet-cell X-ray diffractometer, *Physics and Chemistry of the Earth*, **32**, 247-258.
- Yao Z., Li J., Xie H., Yu C., (2012), Review on remediation technologies of soil contaminated by heavy metals, *Procedia Environmental Sciences*, **16**, 722-729.
- Yong R.N., Galvez-Cloutier R., Phadungchewit Y., (1993), Selective sequential extraction analysis of heavy metal retention in soil, *Canadian Geotechnical Journal*, **30**, 834-847.
- Yong R.N., Ouhadi V.R., Goodarzi A.R., (2009), Effect of Cu<sup>2+</sup> ions and buffering capacity on smectite microstructure and performance, *Journal of Geotechnical and Geoenvironmental Engineering*, ASCE, **135**, 1981-1985.
- Yong R.N., (2001), *Geoenvironmental Engineering, Contaminated Soils, Pollutant Fate and Mitigation*, CRC Press New York.
- Yu R., Xu J., Hu G., (2017), Application of fly ash-stabilized municipal sewage sludge of growth of *Brassica Chinensis* and heavy metal transfer in pot experiment with a barren soil, *Environmental Engineering and Management Journal*, **16**, 2803-2812.
- Zhou C.H., Zhao L.Z., Wang A.Q., Chen T.H., He H.P., (2016), Current fundamental and applied research into clay minerals in China, *Applied Clay Science*, **119**, 3-7.