Double layers in pyrometamorphosed bentonite: index properties and complex permittivity

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Abstract

Index properties such as grain size distribution, specific gravity, and plasticity index, and measurements of complex permittivity between 10 MHz and 1.3 GHz showed that pyrometamorphosed bentonites had larger grain size, lower specific surface, high electrolyte concentration, decreased double layer phenomena, increase in the ratio of free to adsorbed water for a given moisture content, and reduced plasticity. These transformations have important implications for phenomena such as swelling, permeability, diffusion and adsorption, which affect the performance of bentonite as an engineering and industrial material.

1. Introduction

Clays with high plasticity, such as bentonite, have unique hydraulic, mechanical and chemical properties. From an engineering point of view, these properties have both positive and negative consequences. For example, bentonite is suitable for the construction of low permeability, self-healing barriers and buffer zones. However, bentonite is an unwanted foundation or backfill material due to the exceptionally high swell potential. Clays may be subjected to high temperatures while functioning as barriers, for example in the disposal of high-level radioactive waste, where expected temperatures may exceed 100°C, or during earth material improvement programs designed to alter the properties of the clay. Clays are also exposed to high temperatures in natural geothermal events, and in many industrial processes.

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1.1. Pyrometamorphosed clays—index properties

Progressive heating of clays leads to the removal of free, adsorbed and structural water, which is followed by the formation of new minerals. The progressive effects of heating bentonite in open atmospheric conditions include reversible dehydration of loosely bound water when dry-heated between 100°C and 300°C; irreversible removal of interlayer water and loss of swell potential at temperatures above 400°C; de-hydroxylation or the release of hydroxyl groups from the crystal structure between 500°C and 1000°C; silicate recrystallization and the formation of new minerals above 800°C. Finally, increased heating causes melting and the formation of fused materials (Mitchell, 1976; Allen and Wood, 1988; Wang et al., 1990; Alther, 1991; Kühnel et al., 1993). Alther (1991) concluded that the thermal stability of bentonite is affected by its surface chemistry, and that Na-exchanged Ca-bentonite is more thermally stable than naturally occurring Na-bentonite.

Pusch and Güven (1990) heated water-saturated Na-bentonite in an autoclave at 150°C and 200°C for 0.5 years and examined samples by analytical electron microscopy. At 150°C they observed a regrouping of montmorillonite flakes into fewer and denser branches, which created larger voids. More extensive microstructural changes occurred at 200°C including the precipitation of silica in the form of hydrated amorphous silica gels.

Allen and Wood (1988) reported results from several studies conducted with bentonite–basalt mixtures which examined the effects of both *dry-heating* and *hydrothermal-heating*. Hydrothermal-heating in an autoclave allowed control of the vapor–liquid balance at high temperature. Dry-heating was carried out at temperatures between 250°C and 500°C for periods of 1 to 365 days. Samples were analyzed by X-ray diffraction (XRD), thermogravimetric analysis and differential scanning calorimetry. Results indicate no permanent change in the dry-heated bentonite sample at a temperature of 370°C for 340 days. Hydrothermally-heated materials were analyzed using XRD, scanning electron microscopy and transmission electron microscopy. In general, they observed small changes for temperatures below 200°C; however, significant changes took place at 300°C. These changes included montmorillonite dissolution and reprecipitation, ion replacement and partial conversion of montmorillonite to illite (Allen and Wood, 1988). Since illite is a non-swelling phase, the swelling potential of bentonite was irreversibly reduced. In addition, when subjected to water vapor at temperatures of 200°C or greater, permeability increased several orders of magnitude (Couture, 1985).

In the context of soil stabilization, the effect of increased temperature on index properties (i.e., specific gravity, plastic index, grain size distribution) and mechanical properties (i.e., swell and strength) of bentonite was examined by Wang et al. (1990). They heated Na-montmorillonite in an electric furnace for 24 h at five different temperatures: 100°C, 200°C, 400°C, 500°C and 600°C, and observed a small reduction in grain size at 200°C. Further heating caused the grain size to increase, probably due to the aggregation of fine particles. A drastic increase of more than one order of magnitude in grain size was observed between 500°C and 600°C (measured at 50% passing). After heating, the specific gravity increased slightly, from 2.76 to 2.79. The liquid limit varied significantly more than the plastic limit, decreasing from 430% to 210% when the temperature of the heat treatment increased from 100°C to 500°C, at higher temperatures the bentonite became non-plastic. The swelling

potential was unaffected until temperatures reached 500°C, suddenly vanishing at 600°C. Also, an increase of frictional strength with higher heating temperatures was observed.

1.2. Complex permittivity

Examination of the complex permittivity at different frequencies can yield fundamental insight into the nature of a material. When a solid–water mixture is considered as an electrical component, resistance and capacitance can be determined. The physical interpretation of these parameters leads to the complex permittivity. Frequency sweep measurements of the complex permittivity show spectral features such as relaxation and resonance. The real component of the permittivity characterizes the polarizability of the medium in the presence of an applied electric field, and the imaginary component indicates the presence of losses, including DC-ohmic, and polarization losses. Ohmic losses decrease with frequency. Polarization losses manifest around the characteristic frequency of the polarization phenomenon under study: they increase as the frequency approaches the characteristic frequency, and decrease afterwards. The higher the frequency, the smaller the size of the "polarizable unit" that is excited. For example, molecular polarization is observed in the microwave range, ionic polarization in the infrared range, and electronic polarization in the ultraviolet range (Von Hippel, 1954 and de Loor, 1968).

In the case of mixtures, such as soil and water, additional relaxation mechanisms take place. These relaxations reflect the entropy of the system, such as geometric structure, electromagnetic variations and changes in activation energies of different monolayers around particles. The Maxwell–Wagner anomalous dispersion is the inherent response of two different materials, each free of polarization, when they are mixed together. Furthermore, if the mixture is a fine particle phase and a polar fluid, such as wet clays, the resulting double layer that forms on the clay surface can be polarized in the presence of an electric field. This polarization can be observed in the radio frequency range. Several theoretical models have been formulated that take into consideration the formation of these double layers and thereby explain the high electric dispersion of clays (O'Konski, 1960; Schwarz, 1962; Schurr, 1964; Lyklema et al., 1983).

Early permittivity measurements on heat-treated kaolinite, halloysite, and montmorillonite were conducted in the late 1950s and are reported in Grim (1968). The frequency range for these measurements was 30 kHz to 3 MHz, and the preheating temperatures varied between 75°C and 220°C. Samples were measured at room temperature. Results for montmorillonite showed a reduction of the dielectric constant, with increased temperature, from 15.3 to 4.27 at 1 MHz. These experimental results in Grim (1968) may illustrate the effect of interlayer water, however, the potential absorption of moisture from air during the cooling stage was not documented.

This study resembles the one performed by Wang et al. (1990), modified by the additional measurement of the complex permittivity. The goals of this study are the verification of their results, and the collection of information that will further elucidate the effect of pyrometamorphosis on the formation of double layers.

2. Experimental procedures

2.1. Samples

A commercially available Na-bentonite, produced in Southern Saskatchewan, was used in this study. The important properties of the material include: 79% smectite (10% illite); cation exchange capacity, 82 meq/100 g; surface area, 631 m^2/g; and fusion temperature, 1225°C (Quigley, 1984; Oscarson and Dixon, 1989; Graham et al., 1992). Three samples of this bentonite were dry-heated in an electric furnace at 200°C, 400°C and 600°C. After heating for 24 h, they were cooled for 24 h in a convection oven at 100°C. For comparison, testing also was performed on samples of unheated bentonite.

2.2. Index properties

Grain size distribution, specific gravity, liquid limit and plastic limit were measured for the four samples. Procedures followed in these determinations are the same as those used by Wang et al. (1990) in their study; the corresponding ASTM guidelines were: Method for Particle Size Analysis of Soils (D 422-63), Method for Specific Gravity of Soils (D 854-83), Method for Liquid Limit, Plastic Limit and Plasticity Index of Soils (D 4318-84). The procedure for the hydrometer analysis was altered to reduce the effects of swelling and viscosity, so that only 25 g of sample were used. Two tests for the measurement of specific gravity were performed for each sample. Results were averaged, except for the 200°C sample where one measurement was discarded.

2.3. Complex permittivity

The spectral variation of the complex permittivity between 10 MHz and 1.3 GHz was measured with a Hewlett Packard network analyzer HP-8752-A, driven through a PC computer. A coaxial termination probe (HP-85070A) was used as soil–device interface. All four bentonite samples were mixed with de-ionized water at the same moisture content of 50%. Additional tests were conducted on samples with similar liquidity index. The bentonite–water mix was placed in small plastic cells, by thin layers to avoid trapping air bubbles. The probe was pressed lightly onto the top of the sample until the entire surface of the probe was in contact with the soil mix.

3. Results and discussion

3.1. Grain size

Grain size slightly decreased for the bentonite heated to 200°C compared to the unheated sample (Table 1). However, grain size increased significantly for the 400°C and 600°C samples. According to Wang et al. (1990), the mechanisms that cause this change in grain size include de-hydroxylation, followed by oxidation of freed iron and aluminum ions, and reprecipitation of oxides at interparticle contacts, which bonds smaller particles into larger

Table 1
Summary of geotechnical index properties

Temperature (°C)	Grain size distribution (%)			Specific gravity (G_s)	Liquid limit	Plastic limit	Plasticity index (PI)	Activity	Color (wet)
	< 1mm	< 2mm	< 10mm						
Room	79	87	95	2.6	240	46	194	2.23	Gray-Green
200	69	82	92	2.67	190	44	146	1.78	Gray-Green (lighter)
400	40	52	75	2.68	114	41	73	1.40	Light-Brown
600	2	5	22	2.73	< 30	0	< 30	N/A	Amber

ones. Oxidation was confirmed by color change, particularly noticeable in the 400°C and 600°C samples, which became brown and amber respectively when wet, as compared to the characteristic gray-green of the wet, unheated bentonite.

3.2. Specific gravity

Results shown in Table 1 indicate a gradual increase in specific gravity at all heated temperatures, reaching a maximum 5% increase for the 600°C sample. This variation reflects internal changes in the composition and/or structure of the clay mineral.

3.3. Consistency limits

The liquid limit decreased in all heated samples, becoming increasingly lower with higher heating temperature. The plastic limit remained almost unchanged until the 600°C sample, which showed no plasticity.

Consistency limits reflect the combined effects of specific surface S_s [m²/g] and double layer thickness t [m]. For a given thickness t, the corresponding moisture content w of the material that is affected by the double layer can be estimated as

$$w = S_s \cdot t \cdot \gamma_w \tag{1}$$

where subscript w is the unit weight of water [g/m³]. According to the Gouy–Chapman theory, the thickness of the double layer is proportional to the temperature T, the dielectric constant ε', and inversely proportional to the valence v and the concentration η (Mitchell, 1976)

$$t \propto \sqrt{\frac{\varepsilon' \cdot T}{\eta \cdot v^2}} \tag{2}$$

Assuming that heating did not affect concentration or valence, the decrease in liquid limit could be the result of a reduction in specific surface (this assumption is further discussed in the sequel). This interpretation is compatible with the observed increase in grain size and the decrease in activity with higher heat-treatment temperatures (Table 1). However, the input of mechanical energy required to perform consistency tests and the high level of interparticle effects restrict the quantitative interpretation of results, particularly for plastic limit.
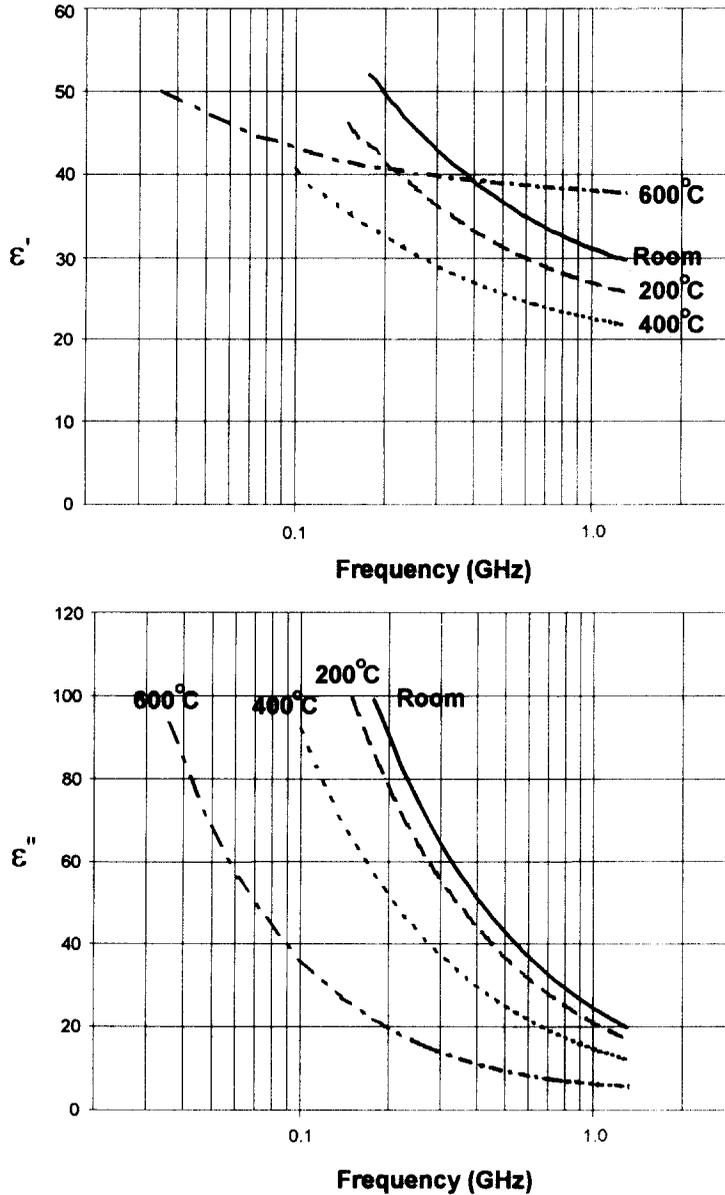
Fig. 1. Complex permittivity at 50% moisture content. As-received sample (''room'') and samples preheated for 24 h (200°C, 400°C, and 600°C). Real component, ε', and imaginary component, ε''.

3.4. Complex permittivity

The real and imaginary components of the permittivity are shown in Fig. 1. Only data for $\varepsilon'' < 100$ are presented because the calibration of the probe with a KCl aqueous solution
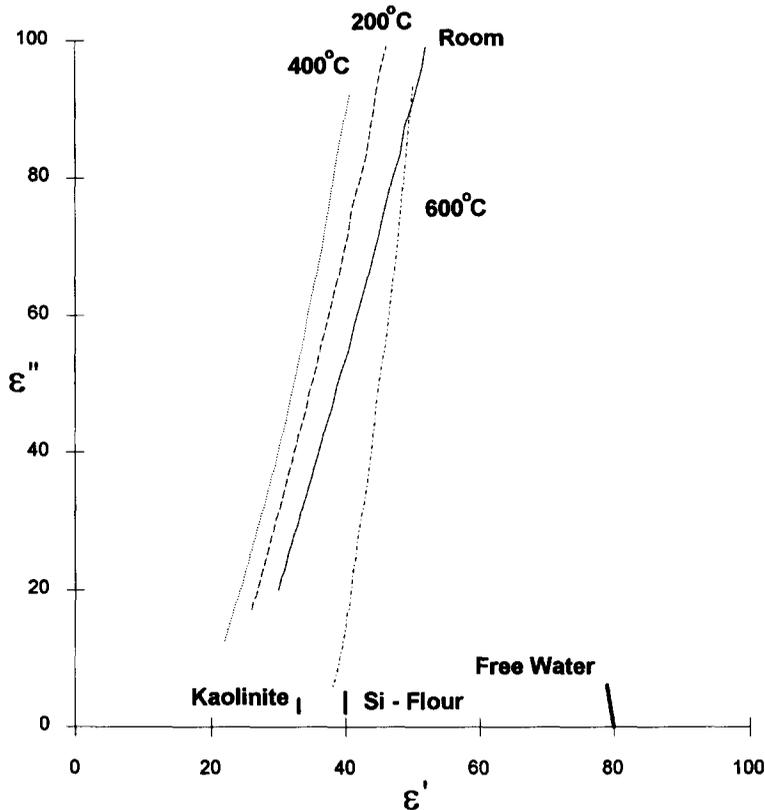
Fig. 2. Cole–Cole plot: real component ε' vs imaginary component ε''. Samples at 50% moisture content.

showed that measurements of permittivity were unreliable for higher losses. The same results are presented in Fig. 2, in a Cole–Cole diagram where ε'' is plotted vs ε' (ε'' was not corrected for DC losses). Data for non-plastic silica flour at 52% moisture content, kaolinite at 50% moisture content, and water are also shown. The orientation polarization of free water plots as a circle in a Cole–Cole plot, and the polarization of mixtures with double layers plots as skewed circles. Only a small part of these circles can be observed in Fig. 2 due to the limited frequency range used in these tests. Within this range, we observed the end of radio frequency polarizations and the beginning of the orientational polarization of the free water.

The gradual decrease of the dielectric constant and loss factor with the increase in heat-treatment temperature up to 400°C indicates a reduction in double layer polarization. This decline is in agreement with the observed increase in grain size and decrease in activity. For the 600°C sample, double layer effects were very weak, as shown by the gradual decline of the real permittivity at low frequencies. At the high frequency end, the real permittivity was higher for the 600°C sample than in the other three cases. This region was primarily affected by the polarization of the free water. In fact, as shown in Fig. 2, the dielectric constant was about the same as for silica flour at the same moisture content. The drastic

change in behavior after heating at 600°C indicates the loss of most double layer effects in this sample, and the ensuing increase in the ratio of free to adsorbed water for a given moisture content.

The loss factor, ε'', was lower than in the other three samples, yet, higher than the loss in kaolinite (Fig. 2). Kaolinite is finer and has much higher specific surface than the 600°C sample. Therefore, DC losses must prevail over polarization losses; this indicates high electrolyte concentration even after heating at 600°C. Summarizing, these pyrometamorphosed bentonites had larger grain size, lower specific surface, high electrolyte concentration, decreased double layer phenomena, and reduced plasticity.

4. Conclusions

Index properties and the complex permittivity of as received and preheated samples of bentonite were measured. Data showed that, even after a short period of heating, pyrometamorphism permanently changed the properties of the bentonite, resulting in coarser particle size, lower plasticity, lower activity, and loss of double layer effects. Although these changes were more apparent at temperatures that exceeded 500°C, they were already detectable in samples heated at 200°C. Plasticity is lost in samples heated to 600°C. These phenomenological changes explained the decrease in swelling potential and the increase in permeability of heated bentonites that were observed by other researchers.

Acknowledgements

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