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Research paper

Identification of clay minerals in mixtures subjected to differential thermal and thermogravimetry analyses and methylene blue adsorption tests

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ABSTRACT

The study of identification methods for clay minerals is very important because of the very fine particle size (less than 2 μm) of these materials, which makes it difficult to recognize them with the naked eye. Because they consist of electrically charged particles, clay minerals exhibit distinct and dynamic behavior. From geotechnical standpoint, clay minerals are present in a wide variety of rocks and soils. Because their behavior is difficult to predict, careful consideration is necessary because they exert great influence on the design and construction of roads, tunnels, foundations, slopes, and many other types of infrastructure. Their characteristics may have a positive effect, e.g., when acting as clay liners, or a negative one, e.g., when their swelling characteristic causes buildings to lose their stability. In this context, the purpose of this work was to compare the reliability of two clay mineral identification methods: combined differential thermal analysis and thermogravimetry (*DTA-TG*) and the methylene blue adsorption test (*MBAT*). Proportional mixtures of kaolinite and bentonite were prepared in order to investigate the two methods. These two types of clay were chosen due to their distinct behaviors: kaolinite is a 1:1 clay mineral, and bentonite is composed mostly of montmorillonite, a 2:1 clay mineral. The two methods showed a positive and highly significant correlation. Moreover, the *MBAT* is a lower cost test that requires only ordinary chemistry laboratory equipment. Correlations revealed that the *MBAT* can provide thermal information related to *DTA-TG* tests.

1. Introduction

Clay minerals have been used extensively in the production of building materials and ceramics due to their unique properties. More recently, they have become an important element in the composition of plastics, paints, rubbers, and even cosmetics. In geotechnical terms, clays are part of the Earth's substrate and are present in a wide variety of rocks and soils. Therefore, it is of great importance to identify them properly because they exert great influence in the design and construction of many types of buildings. Clays may be used in a positive way, e.g., as barriers against contaminant percolation ("clay liners"). However, if they are part of a soil mass, their swelling properties can lead to slope instability.

Numerous methods have been devised to identify clay minerals, including the methylene blue adsorption test (*MBAT*) and combined differential thermal analysis and thermogravimetry (*DTA-TG*). These methods do not provide the exact mineral composition but offer indirect information about its behavior, allowing for an interpretation of possible minerals. These methods are inexpensive and can be completed in a short time and may therefore be of interest, depending on the type of clay minerals involved.

The aim of this study was to analyze and compare the two identification methods: the *MBAT* and *DTA-TG*, through the recognition of proportional mixtures of kaolinite and bentonite because the geotechnical behavior of the soil depends on the ratios of different types of clay.

The methylene blue (*MB*) test has long been employed to determine the cation exchange capacity (CEC) and surface area of clay minerals (Fairbairn and Robertson, 1957; Johnson, 1957; Phelps and Harris, 1967; Kahr and Madsen, 1995; Neumann et al., 2002; Chiappone et al., 2004; Yukselen and Kaya, 2006; Petkovsek et al., 2010) but was only fully standardized by Tran Ngoc Lan in 1977. This methodology is based on the measurement of the amount of *MB* adsorbed by or exchanged on clay from an aqueous solution (Pham Thi and Brindley, 1970), considering that each type of clay mineral has a given range of *MB* adsorption. According to Stapel and Verhoef (1989), *MB* is a positively charged organic polymeric molecule ($C_{16}H_{10}N_3ClS$) that is used in the *MBAT* in an aqueous solution; thus, all clays capable of swelling are in an expanded state. Therefore, all the external and internal crystal surfaces of the clay minerals are accessible to the *MB*, which replaces the exchangeable cations. As stated in Appelo and Postma (1994), sorption may be defined as an alteration of the concentration of a solute as a result of mass transfer between the solution and the solids.

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Table 1
Characteristics of the samples: columns 2 and 3 describe the proportion of kaolinite and bentonite in each sample; columns 4, 5, and 6 describe the mass used in the methylene blue adsorption test (*MBAT*), the differential thermal analysis (DTA), and thermogravimetry (*TG*), respectively.

Sample	*Kaolinite (%)*	*Bentonite (%)*	*MBAT (g)*	*DTA (g)*	*TG (g)*
1	100	0	1	1	6.83
2	90	10	1	1	6.83
3	80	20	1	1	6.85
4	70	30	1	1	6.83
5	60	40	1	1	6.83
6	50	50	0.5	1	6.84
7	40	60	0.5	1	6.83
8	30	70	0.5	1	6.83
9	20	80	0.5	1	6.83
10	10	90	0.5	1	6.84
11	0	100	0.5	1	6.84

Table 2
Calculated parameters of *MBAT*.

Sample	*Mass (g)*	*Volume* (cm^3)	*A (g/100g)*	*Vb (g/100g)*	*SSA* (m^2/g)	*CEC* ($cmol^+/kg$)
1	1	10.5	1.58	1.58	38.54	4.92
2	1	35	5.25	5.25	128.45	16.41
3	1	59	8.85	8.85	216.53	27.67
4	1	81	12.15	12.15	297.27	37.99
5	1	106.5	15.98	15.98	390.86	49.95
6	0.5	64	19.2	19.2	469.76	60.03
7	0.5	76.5	22.95	22.95	561.51	71.75
8	0.5	88.2	26.46	26.46	647.39	82.73
9	0.5	101	30.3	30.3	741.34	94.73
10	0.5	117	35.1	35.1	858.78	109.74
11	0.5	133	39.9	39.9	976.22	124.75

Numerous studies have focused on analyzing the efficiency of the *MBAT* applied to soils with widely different mineralogy (Brindley and Thompson, 1970; Higgs, 1988; Kahr and Madsen, 1995; Çoçka, 2002), some of them related to soil expansivity (Fityus and Smith, 2000; Yukselen and Kaya, 2008). Erguler and Ulusay (2003) stated that the *MBAT* is a good tool in order to predict the swelling properties of soils. An interesting application of the *MBAT* is in the assessment of the quality of rock aggregates (Stapel and Verhoef, 1989; Yool et al., 1998) used in concrete and mortar. Because these rock aggregates may contain swelling clay minerals that have deleterious effects on buildings, the recognition of these types of minerals is very important.

The thermal analysis is based on the observation of the responses of materials to changes in temperature. While DTA curves show the effect of energy changes (endothermic and exothermic reactions), *TG* curves show weight changes during heating (Guggenheim and Van Groos, 2001). Because clay minerals are highly susceptible to significant compositional changes in response to subtle changes in their environmental conditions, *TG* curves provide interesting information about the reactions that occur during this test because each clay mineral exhibits distinct behavior.

Like the *MBAT*, general studies involving the thermal analyses of clay behavior are also long-standing (Bradley and Grim, 1951; Greene-Kelly, 1957; Grim and Kulbicki, 1961; Mackenzie, 1970; Balek and Murat, 1996; Guggenheim and Van Groos, 2001; Costa et al., 2004; Manoharan et al., 2012; Arsenovic et al., 2014; Tajeddine et al., 2015). Studies related to construction, which consider the effect of various components in cement and concrete composition, are also common (Wild et al., 1996; Stroeven and Dau, 1999; Kakali et al., 2001), as are several works on the composition and strength of ceramics (Brindley and Maroney, 1960; Kingery, 1974; Ramesh et al., 1998; Seifert et al., 2001).

The interpretation of *DTA-TG* curves alone is not sufficient to accurately identify mineralogical species, but it allows for a broad classification of the main clay minerals, particularly of monomineralic clays (Mackenzie, 1970). The *DTA* provides basic information for the identification of the main clay minerals, and *TG* indicates which reactions are associated with mass losses.

According to the typical thermal behavior of kaolinite, it starts to lose both moisture and adsorbed water at a temperature of 100 °C. Subsequently, a dehydroxylation reaction occurs in the range of 450 °C and 650 °C, represented by a second endothermic peak in its curve. At this point, the clay mineral loses its plasticity, and as temperature increases, it forms an amorphous kaolinite known as metakaolinite (Grim, 1953). The vitrification phase starts at temperatures higher than 900 °C, where mullite and high temperature silica polymorphs crystallize.

In smectites, the loss of adsorbed and coordinated water occurs between 100 °C and 250 °C. These clay minerals have a high CEC, so the shape of their peaks depends on the nature of the adsorbed cations (Hendricks et al., 1940). Dehydroxylation occurs between 400 °C and 700 °C, with Fe-rich smectites showing an endothermic peak at approximately 500 °C, while Fe-poor smectites show the same peak at approximately 700 °C. Smectites lose their structure at 900 °C, whereupon the vitrification phase begins with the crystallization of mullite, tridymite, and cristobalite.

2. Materials and methods

2.1. Materials

Kaolinite and bentonite were chosen because these materials behave quite differently. While kaolinite has a 1:1 structure, bentonite is a commercial designation for a clay blend composed predominantly of montmorillonite, which has a 2:1 structure, characterizing it as a swelling type mineral. This study involved clay mixtures; hence, the choice of completely different clay minerals favored a better comparative analysis of the two methods under analysis.

Eleven mixtures were prepared in pre-established proportions, as shown in Table 1, which also describes the mass quantities used in each test. Both materials were characterized by x-ray diffraction with oriented specimens and a copper-target tube as showed in Fig. 1.

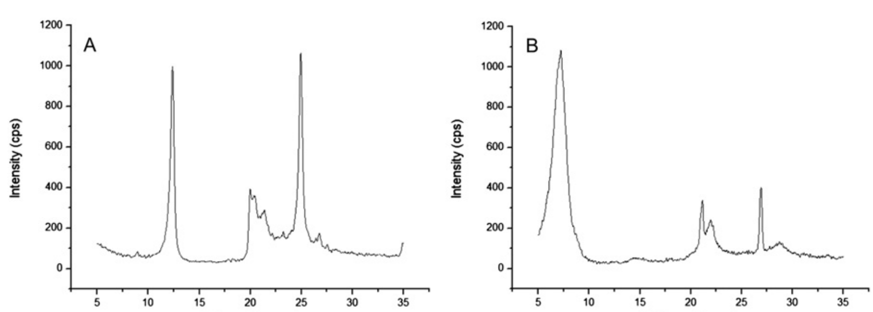

Fig. 1. Diffractograms of (A) kaolinite and (B) bentonite.