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ScienceDirect

Applied Clay Science 34 (2006) 47–57

Applied CLAY Science

www.elsevier.com/locate/clay

Cation exchange capacity methodology III: Correct exchangeable calcium determination of calcareous clays using a new silver–thiourea method

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Received 3 June 2005; accepted 13 February 2006
Available online 6 September 2006

Abstract

Cation exchange capacity (CEC) is a fundamental property of clays and soils. Determination of CEC for samples that contain Ca-carbonate minerals, such as calcite and dolomite, is problematic because Ca^{2+} released by dissolution of carbonates during CEC determinations interferes with the accuracy of CEC values. This paper describes a new method for the determination of correct exchangeable Ca^{2+} values of calcareous clays and soils. For the method, a silver–thiourea exchange solution is saturated with Ca^{2+} by treatment with fine-grained calcite prior to the start of the exchange procedure. Using this exchange solution, calcite in the sample can no longer be dissolved but exchangeable Ca^{2+} is desorbed quantitatively. The case for dolomite is similar, because dissolution of dolomite is minimised. However, the determination of reasonable exchangeable Ca^{2+} values for samples containing gypsum is not possible because gypsum is soluble in the exchange solution.

Keywords: Exchangeable calcium; Silver thiourea method; Calcareous clays; Calcareous soils

1. Introduction

The aim of this study is to present a new silver thiourea method for the correct determination of CEC and exchangeable cations in calcareous clays, bentonites, and soils. For many scientific investigations it is important to know what exchangeable cations are present on the exchanger surfaces. In soil science, exchangeable nutrients are essential for plant growth and in geotechnical engineering the stability of a building foundation may depend on the nature of exchangeable cations in the soil. In host rocks of radioactive waste disposals sites, the chemistry of the exchangeable cations and cations in the porewater must to be determined exactly to evaluate the potential for fluid flow pathways through the barrier (Nagra, 2002).

Numerous publications deal with methods for extraction of exchangeable cations, the most widely accepted being the ammonium acetate method (Lewis, 1949). As long as the sample under investigation only contains clay minerals and relatively insoluble phases like quartz, mica or feldspar the ammonium acetate method should provide accurate results. Problems arise, however, when minerals are dissolved or partially dissolved during the course of the experiment (Kick, 1956; Deller, 1981). In those cases non-exchangeable cations are added to the extracted exchangeable cations.

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doi:10.1016/j.clay.2006.02.010

The result is a significant overestimation of exchangeable cations.

Calcite is one of the most common mineral phases in sediments and soils. During cation exchange capacity (CEC) experiments calcite is partially dissolved and the released Ca^{2+} will lead to highly erroneous CEC results. Dissolution can be minimised by short reaction times but this may cause other problems because some clay minerals like vermiculite and illite do not exchange their adsorbed cations instantaneously (Walker, 1959; Graf von Reichenbach, 1966; Malcolm and Kennedy, 1969). Neal (1977) tried to solve the exchangeable Ca^{2+} problem by using ethanolic mixtures of LiCl–CsCl. He investigated mixtures of pure clay with pure calcite and magnesite. However, because of possible changes in layer charge density due to diffusion of Li^{+} into the crystal lattice, exchange solutions containing Li^{+} should not be used for CEC determination (Eckstein et al., 1970). A different approach involves a double leaching procedure (Hissink, 1923) and alcoholic solutions that reduce the solubility of the carbonates with a double leaching procedure (Tucker, 1954). During the first step of a double leaching procedure, it is assumed that all exchangeable calcium will be desorbed and that a distinct portion of calcite will be dissolved. For the second extraction step which is performed using identical experimental conditions, the assumption is that exactly the same portion of calcite is dissolved but no additional exchangeable calcium is extracted. The first assumption is not valid because very fine-grained minerals will dissolve rapidly during step 1 and may be depleted from the sample during step 2. The second assumption is also wrong because cation exchange using this kind of anorganic cations is not complete using only one extraction step (McBride, 1979). Our analyses show that only 80–95% of the exchangeable cations will be desorbed in the first extraction step. The extent of desorption depends on the sample type, reaction temperature, solid/solution ratio and on the type and concentration of cations and anions present in suspension. Furthermore, after centrifugation or percolation there is always a small amount of the first extraction solution retained by the sample, which will violate the implicit assumption that exactly the same amount of extracting solution is used in steps 1 and 2. This can be corrected by a time-consuming reweighing procedure but reweighing introduces another source of potential error.

One approach that should be avoided when the mineralogical composition is unknown is to calculate exchangeable Ca^{2+} by the difference between CEC and the sum of other exchangeable cations as in the following equation: $\mathrm{CEC}-Mg^{2+}-Na^{+}-K^{+}=Ca^{2+}$. If for example the barium chloride method is used there is always a reaction of calcite or dolomite with the exchange solution leading to a precipitation of witherite (Kick, 1956). Witherite ($BaCO_3$) will be dissolved during the reexchange steps with magnesium chloride solution (Lippmann, 1973) leading to superelevated CEC values. This source of error can be circumvented by using the compulsive exchange method (Bascomb, 1964). For the compulsive exchange method, a sample is initially saturated with Ba^{2+}, washed free of excess salt, then a $MgSO_4$ solution ($c=0.05$ M) with known Mg^{2+} concentration is added to the slurry and equilibrated for 2 h. After centrifugation of this slurry, Mg^{2+} concentration is measured in the clear supernatant. The assumption of this compulsive exchange is that all desorbed Ba^{2+} cations precipitate immediately as baryte ($BaSO_4$) once they enter the sulphatic exchange solution. This forces Mg^{2+} for Ba^{2+} exchange in one-step because exchange competition is prevented. The decrease in solution Mg^{2+} is used to calculate the CEC (Bascomb, 1964). However, the measurement of solution Mg^{2+} has to be performed with great accuracy and precision. In most of the commonly used procedures the CEC results may be affected by specific interactions of the exchange solution with carbonates.

The aim of this paper is to propose a new method for the correct determination of exchangeable calcium values of calcareous clays and soils. To achieve this goal, the exchange solution first must be saturated with exactly the mineral that causes the problems during the exchange experiment, calcite. But the procedure must be compatible with a calcite saturated exchange solution. Use of metal-organic cations (Cremers and Pleysier, 1973) such as silver–thiourea (AgTU) for the exchange could be the key. Exchange sites on clays and soils are highly selective for AgTU cations relative to typical index cations like ammonium or barium (Chhabra et al., 1975; Pleysier and Cremers, 1975). According to Lewis acid/base theory (Pearson, 1963) most acceptor molecules or cations are either hard or soft, and “hard acids bind strongly to hard bases and soft acids bind strongly to soft bases” whereas bindings between soft acids and hard bases and between hard acids and soft bases are unstable. The AgTU complex is stabilised by the soft character of the silver cation and the uncharged thiourea. Complexes of hard cations like sodium, potassium, magnesium or calcium with thiourea are unstable. Therefore during a cation exchange reaction there is negligible competition between calcium or any of the other released inorganic cations and silver thiourea. Keeping this in mind it now is possible to develop a method where the exchange solution can contain several different cations but where