

Determination of the CEC and carbonate content of bentonites: Methods and accuracy

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Introduction

Bentonites that are used for geo-barriers are required to meet a number of stringent Standards. These Standards, usually set by State Environmental Protection Agencies, are, in broad terms, to ensure low hydraulic conductivity. Consequently many of the Standards are related to the swelling properties of the bentonites and also to factors that effect swelling properties. Essentially the Standards specify that the bentonite must have a high Na-exchanged montmorillonite content and that the content of phases that might affect the swelling properties of the bentonite (such as calcite and dolomite that can release divalent cations) are below acceptable levels. Although the Standards vary from authority to authority, commonly accepted criteria for bentonites suitable for geo-barriers are a montmorillonite content of greater than 70wt.%, a CEC greater than 80 cmol_c/kg, an exchangeable sodium percentage (ESP) greater than 80% and total carbonates less than 2wt.%.

The imposition of Standards necessitates repeated testing of batches of bentonite used in geo-barriers. There is therefore a genuine need for tests that are simple enough to be carried out with basic equipment whilst at the same time maintaining a reasonable degree of accuracy. Many of the tests used for characterising bentonites are extensions of tests developed for measuring the properties of soils. These soil-based tests do not always extrapolate to bentonites.

Carbonates

Three methods are in common use for the determination of carbonates in bentonites.

1. Rietveld analysis of XRD patterns gives quantitative data for both the amounts and types of carbonates present. However, the method does have several drawbacks. One drawback is that the accuracy of the technique is limited to roughly ± 0.2 wt.% which may not be sufficient when the carbonate content of the bentonite is close to the limit set by a given Standard. The second drawback is the overall cost of the XRD instrument and associated Rietveld software and, equally importantly, the high level of skill required by the operator of the XRD system and Rietveld software.

2. Gravimetric methods determine carbonate content by dissolving the carbonates with acid and measuring the associated weight loss. Often two dissolution experiments are carried out: one using a weak acid (e.g. acetic acid) and another using a strong acid (e.g. HCl). The weak acid dissolution gives a value for the amount of readily soluble carbonates (e.g. calcite and dolomite) while the strong acid gives a value for the total amount of acid soluble material present in the bentonite. The total acid soluble material will include the readily soluble carbonates, carbonates whose dissolution kinetics are slow (e.g. siderite) and other materials including some organic matter. The amount of the organic carbon dissolved can be reduced by adding an antioxidant (e.g. FeCl₂) to the acid solution.

The only specialised equipment required for gravimetric determination of carbonates is a reasonably high-precision balance (e.g. a four figure balance when working with a sample weight of 5 to 10g). The disadvantage of the gravimetric method is that in order to measure the weight loss the system must remain open to allow the CO₂ to escape. The escaping CO₂ carries off water causing an overestimation of the carbonate content but this is compensated to some extent by CO₂ that remains trapped in the bentonite slurry. As gravimetric methods cannot determine carbonate species the final step in these methods is to convert the measured weight loss caused by the evolution of CO₂ to an equivalent content of a given carbonate mineral (e.g. calcite or dolomite).

3. The third method is similar to gravimetric methods in that the carbonates are dissolved using acid but rather than allowing the CO₂ to escape the acid dissolution is carried out in a sealed vessel and the pressure

build up in the vessel caused by the CO₂ evolved is measured using a suitable pressure gauge. As a closed system is used there are no extraneous losses. The system is calibrated using pure carbonates and the content of carbonate in the bentonite is determined against the carbonate used for calibration.

CEC and exchangeable cations

Methods for determining CEC and exchangeable cations are, in general, based on exchange with a cation not generally found in bentonites (e.g. NH₄⁺ or Ba²⁺). The standard method (as used for soils) is to completely exchange the bentonite with NH₄⁺ and measure the cations released by the exchange to determine exchangeable cations and, in doing so, ESP. The overall CEC is then measured by completely exchanging the bentonite with a cation such as Na⁺ and determining the NH₄⁺ released. The operative word here is “completely” because it has become increasingly obvious that, in the standard experimental setup, the NH₄⁺ is not completely re-exchanged from bentonites with a high CEC. As the NH₄⁺ method requires the measurement of reasonably low concentrations of cations it necessitates the use of somewhat expensive equipment such as atomic absorption spectrometers or inductively-couple plasma optical-emission spectrometers.

Ba exchange for CEC determination is most often used in conjunction with XRF. This method can be applied to both bulk material and thin films. The major problem with this method is that insoluble Ba-carbonate will form during the exchange process if any carbonates (e.g. calcite) are present in the bentonite being tested. The formation of Ba-carbonate thus causes the method to significantly over estimate CEC.

A XRF method that overcomes the problem of carbonate formation measures the elemental composition of the bentonite in the as-received state and after several distinct washing and exchange treatments. This method potentially gives an accurate measurement of soluble salts, acid soluble material, exchangeable cations and CEC. The method is however too involved to apply on a routine basis in most laboratories.

A method for CEC determination that has found widespread use for drilling muds and has been successfully applied to soils is exchange with methylene blue. Exchange with methylene blue is probably the simplest of all methods in terms of experimental setup and requirements. When the methylene blue exchange method is applied to bentonites it has been found to significantly over estimate the CEC. For this reason exchange capacity determined by methylene blue is generally referred to as the MBC (methylene blue capacity). Despite its shortcomings, the simplicity of the methylene blue method makes it very useful in comparing bentonites. The method can be tuned to give a good estimate of the CEC by running the test against a standard material of well known CEC (e.g. Wyoming bentonite). The use of a standard material as a “calibration” applies not only to the methylene blue method but to all methods of determining CEC and is recommended practice.