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Determination of the clay index of limestone with methylene blue adsorption using a UV-VIS spectrophotometric method☆

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Abstract

The clay index values of limestone samples were spectrophotometrically determined using the absorbance value at 630 nm of a known concentration of methylene blue. The applicability of this approach to and the advantages over currently used methods in the cement industry is demonstrated by the results summarized in this report.

Keywords: Characterization; Spectroscopy; $CaCO_3$; Clay index

1. Introduction

Limestone is an important extender often used in Portland cements. New European standards adopted by the South African cement industry require the determination of the clay index of limestone [1]. The South African Bureau of Standards (SABS) tested and adopted the determination of the clay index by means of a methylene blue adsorption process in a similar fashion as stated in the European Cement Specifications (Norm No. ENV 196:2, 1995), and will be further detailed in the experimental part of this paper. The clay index is of particular importance if several different sources of limestone are used. The clay index is related to the clay content of the limestone, provided the type of clay is known. The clay index is usually expressed in terms of the amount (g) of methylene blue adsorbed by the clay fraction of 100 g of the limestone material. An elaborate wet chemical method is described for this measurement (see Methods). The purpose of this investigation was to develop an easy, alternative method by which the methylene blue adsorption and thus the clay index could be determined. Methylene blue is well known to adsorb on a number of substances [2].

2. Methods

Pure calcium carbonate and the limestone samples were wet ground with hexane in a ring mill for 3 min and then dried at 105°C for 60 min to ensure that they have comparable surface areas for the adsorption of methylene blue.

Concentrations of 1.0 to 25.0 mg/L of methylene blue were made up and their absorbance measured at 630 nm on a Spectronic 601 ultraviolet-visible light (UV-VIS) spectrophotometer (Spectronic Instruments Inc., Rochester, NY, USA). The maximum absorbance of methylene blue is obtained at 630 nm [3]. A calibration curve of absorbance against concentration of methylene blue is given in Fig. 1, which indicates that the Beer-Lambert law is obeyed up to a concentration of 20 mg/L. The Beer-Lambert law describes a linear relationship between the concentration of a solution and the absorbance measured at a constant wavelength [4]. Beyond this concentration, a deviation from the linear relationship between concentration and absorbance is observed.

To determine the adsorption of methylene blue on limestone containing no clay, 1.0049 g of pure calcium carbonate added to solution of 100 mL of 20 mg/L methylene blue was stirred on a magnetic stirrer. Aliquots were taken at intervals during a 2-h period and the absorbance of the suspensions determined. An absorbance value of 2.22 $\pm$ 0.02 was obtained for all the samples, indicating that no adsorption of the methylene blue on calcium carbonate (or limestone) occurred. This indicated that the clay fraction of the limestone samples is responsible for the methylene blue adsorption.

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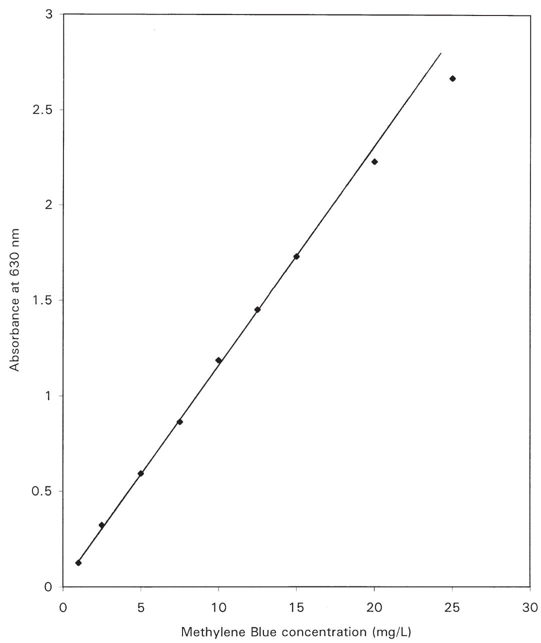

Fig. 1. Methylene blue calibration curve.

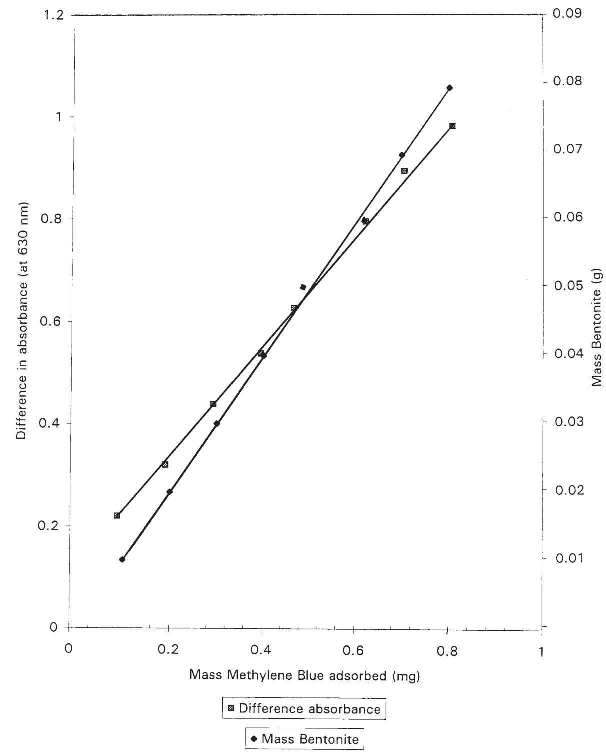

Fig. 2. Adsorption of methylene blue on bentonite clay samples of different masses.

It was decided to use a bentonite clay to investigate the adsorption of methylene blue on clay samples since adsorption may differ for different types of clay [5,6]. To investigate the influence of clay mass on the adsorption of methylene blue, 10 g of a bentonite clay was added to 250 mL of distilled water to form a gel. Volumes of this gel containing masses of bentonite that differ between 0.01 and 0.08 g were stirred for 90 min with 100 mL of a solution of 16 mg/L of methylene blue. The absorbance at 630 nm of these solutions was determined. The amount of unadsorbed methylene blue is calculated and the value used to determine the mass adsorbed on the bentonite clay samples.

The adsorption values of methylene blue on various limestone samples containing different amounts and types of clay from different quarries were measured. Each limestone sample (1 g) was stirred for 90 min with 100 mL of a solution of 16 mg/L of methylene blue. Stirring was done on a magnetic stirrer at a speed of 700 rpm. The solutions were then centrifuged for 3 min and the absorbance at 630 nm measured as described earlier. The clay index and the clay content were determined using this method.

The SABS standard method, involving a methylene blue titration (described below) was also performed on the centrifuged samples. The clay index and the clay content were calculated from this value and compared to the value obtained from the spectrophotometric method.

For the methylene blue titration method, 5.0 g of the limestone sample with 5 mL of distilled water was stirred

Table 1
Adsorption of the methylene blue solution on different masses of the bentonite clay

Bentonite clay mass (g)	Absorbance	Absorbance difference[a]	Unabsorbed methylene blue (mg)	Absorbed methylene blue (mg)[b]
0.01	1.67	0.22	1.5	0.10
0.02	1.57	0.32	1.4	0.20
0.03	1.45	0.44	1.3	0.30
0.04	1.35	0.54	1.2	0.40
0.05	1.26	0.63	1.13	0.47
0.06	1.09	0.80	0.98	0.62
0.07	0.99	0.90	0.9	0.7
0.08	0.90	0.99	0.8	0.8

[a] Absorbance of methylene blue solution before bentonite was added minus absorbance after bentonite was added.
[b] Mass of methylene blue in solution added to bentonite minus mass of methylene blue remaining in solution (unadsorbed).

Table 2
Absorbance data of methylene blue in contact with different limestone samples

Source of limestone	Absorbance of methylene blue	Absorbance sample	Absorbance difference	Mass of methylene blue adsorbed
Riebeeck W (Western Cape)	1.89	0.93	0.96	0.74
Lime Acres (Northern Cape)	1.89	1.75	0.14	0.04
Beestekraal (North West Province)	1.89	1.30	0.59	0.43
De Hoek (Western Cape)	1.89	0.99	0.90	0.70

Table 3
Clay index for different limestone samples as determined by titration and spectrophotometric methods

Source of limestone	Clay index with titration method (g Methylene blue/100 g sample)	Clay index with spectrophotometric method (g methylene blue/100 g sample)
Riebeeck West (Western Cape)	0.070	0.074
Lime Acres (Northern Cape)	0.030	0.004
Beestekraal (North West Province)	0.064	0.043
De Hoek (Western Cape)	0.074	0.070

on a magnetic stirrer. Two mL of a 3.2 g/L methylene blue solution was added, the solution stirred for 1 min, and a drop of the suspension then transferred to filter paper. A dark spot surrounded by clear liquid is formed on the paper. As long as no pale blue ring formed around the dark spot, futher aliquots of 2 mL of the methylene blue solution were added and the suspension stirred for 1 min before testing. The whole procedure was then repeated, using smaller aliquots of methylene blue near the titration end point. The amount of methylene blue added to obtain the pale blue ring was determined and the titration value expressed as g methylene blue adsorbed per 100 g limestone (clay index).

3. Results and discussion

To obtain a calibration curve for methylene blue adsorption of a clay sample, the difference in absorbance of 100 mL of the solution of 16 mg/L methylene blue, added to 250 mL of distilled water, and the samples containing different masses of the bentonite clay were plotted against the mass of methylene blue adsorbed (Table 1, Fig. 2).

A linear relationship is obtained for the mass of methylene blue adsorbed against the mass of the bentonite clay samples. A linear plot is also obtained for the differences in absorbance plotted against the mass of methylene blue adsorbed (Fig. 2).This implies that a direct quantification of the amount of bentonite clay in the sample can be obtained by a fast measurement of the difference in absorbance of the solutions of methylene blue with and without the sample.

Table 2 summarises the absorbance measured for various limestone samples. Using Fig. 2, the mass of methylene blue adsorbed by the clay in the limestone samples was determined and the values compared to the values obtained using the titration method as described in the Methods section (Table 3). Table 3 indicates an excellent agreement between the methods in the case of the two Western Cape limestone samples that contain mainly a bentonite-type clay. However, the other two samples gave lower adsorption values, indicating that only part of the clay in the samples is bentonite clay or clay of a different type. The adsorption behaviour of different types of clay may differ [5,6] and a calibration curve for each type of clay should be obtained.

4. Conclusions

The results obtained during this investigation indicate that the amount of methylene blue adsorbed on a limestone sample containing clay can be determined by a spectrophotometric method, on the condition that the type(s) of clay is known and the calibration curve for that type(s) of clay is obtained. A great advantage of this method over the conventional titration method is that the spectrophotometric method involves objective measurements, while the titration method asks for the subjective determination of a pale blue ring, making it much more prone to operator error and bias. Further advantages of the ultraviolet spectrophotometric method are that much smaller clay contents can be determined and that it is faster than the titration method.

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