Looking for Expansive Minerals in Expansive Soils; Experiments with Dye Absorption Using Methylene Blue

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1 INTRODUCTION

According to Chen (1975, p.16) there are three different approaches to the problem of classifying potentially expansive soils. The first, mineralogical identification, can be useful in the evaluation of the material but is not sufficient in itself when dealing with natural soils. The second includes the indirect methods such as the index property, the PVC method and the activity method which are valuable tools in evaluating the swelling property; and the third is direct measurement which offers the most useful data for a practicing engineer.

Chen lists five techniques for mineral identification; these are X-ray diffraction, differential thermal analysis (DTA), dye adsorption, chemical analysis and electron microscopy. He comments that the test results require expert interpretation and the specialised apparatus required is costly and often not available in soil testing laboratories.

The purpose of this paper is to report on some investigations which bear on Chen's claim of impracticality for the mineral identification methods. In particular we have studied the information which can be produced by dye adsorption tests on soils. The dye adsorption method did get some approval from Chen, and he stated that "the relatively simple testing procedure and speed of dye staining tests compared with X-ray diffraction and DTA justify wider application of the colour method." One of the contending dyes for use in the method is methylene blue and this does seem very suitable for investigations on soils for engineering purposes.

The dye adsorption method gives a measure of the surface area (S.A.) of the soil, and it appears that there is a very good correlation between surface area and swelling behaviour, although the presence of allophane may disturb this assertion. The clay minerals which are really dangerous from a swelling point of view are the high surface area smectites or montmorillonites, and these can be difficult to detect and measure. We investigated eight soils: four smectite-containing soils from north Greece (Gr1-Gr4); a black cotton soil from Kenya supplied by the Transport and Road Research Laboratory, England; two soils from the Adelaide area (Modbury & Adelaide) supplied by R. Martin and P. Peter of CSIRO Applied Geomechanics Division, and a vertisol from Transvaal, South Africa (Mngazi soil) supplied by Dr R.W. Fitzpatrick of Natal University. The swelling minerals content of these soils ranges from 10 to 60% of the whole soil. The last four soils are known to be highly expansive soils.

2 METHYLENE BLUE ADSORPTION METHOD

When methylene blue dye is adsorbed by clay, the dye molecules first form an irreversibly adsorbed monolayer over all the accessible clay surface (internal and external). Dye continues to be adsorbed from solution until this monolayer is formed, leaving a clear solvent on sedimentation of the clay. Further adsorption is reversible and the dye molecules superimposed on the monolayer are in equilibrium with the dye molecules in solution, leaving a coloured solution on sedimentation of the clay. (The actual technique used in the test is described in the appendix.)

When a monolayer has just been formed, any excess of dye will give a colouration to the supernatant liquid; the 'end-point' is considered to have been reached when enough dye has been added to a given amount of clay in suspension to produce this first permanent colouration. This is a little higher than the 'optimum flocculation point' used by Hang and Brindley (1970).

We need to relate the amount of dye used to reach the end-point to the surface area of the clay in the soil under test. The total area of the dye molecules at the end-point can be calculated by taking the effective area of the dye molecule as 107 $Å^2$. This area is defined as the 'Apparent Surface Area' (ASA) of the clay; the units are m^2g^{-1} clay. The value of 107 $Å^2$ is a compromise between the theoretical site area of a dye molecule and the fact that the dye behaves slightly differently with respect to the various types of clays (see Xidakis, 1979 for some discussion and justification).

The dye used was methylene blue hydrochloride, supplied by Hopkin and Williams Ltd, Chadwell Heath, Essex, England. The ASA of the clay or soil is calculated from the formula:

$$ASA = \frac{Vd}{C} \times N \times Ad \times 10^{-25}\ m^2/g \qquad (1)$$

where Vd is the volume of 0.01 M methylene blue standard solution required to reach the end-point, in cm^3; C is the mass of clay or soil present in the test-tube in grams; N is Avogadro's Number (6.02×10^{23}) and Ad is the effective area of the dye molecule in $Å^2$.

Substituting for N and Ad in formula (1) it reduces to:

$$ASA_{107} = \frac{Vd}{C} \times 6.45\ m^2/g$$

3 SUPPORTING TESTS AND RESULTS

To provide data for the important correlations a set of supporting tests was carried out on the eight soils. We report here tests on liquid and plastic limits, free swelling of dry disaggregated soil and linear shrinkage. The free swelling test was considered to give an indication of the expansiveness of the soil (and thus a measure of the geotechnical hazard) and this was related to the dye adsorption measurements and to the more conventional soil properties indicated by Atterberg limit and shrinkage determinations. To show how the methylene blue method relates to other methods of surface area determination some comparative tests were carried out with ethylene glycol and glycerol, on the fine clay (<1 µm) fractions of the eight soils. Table 1 shows the results of the surface area determinations.

methylene blue dye method. It represents the dye adsorption by the untreated soil and not the true surface area of the soil i.e. the apparent surface area (ASA). When the surface area of the treated soil (i.e. after the removal of carbonates and organic matter) was used, the correlations were lower (data not shown).

This is not unexpected since in principle the treated soil must behave differently from the untreated one in which the carbonates and organic matter can act as cementing agents and reduce the surface area of the clay. The treated soil is expected to swell more (Rimmer & Greenland, 1976). However the use of the ASA or dye adsorption value of the untreated soil is preferable because firstly it simplifies the dye adsorption method since no pretreatment of the soil is required, and secondly it possibly simulates more closely the water

TABLE I

SURFACE AREA (m^2g^{-1}) OF CLAY FRACTIONS OF EIGHT EXPANSIVE SOILS
(SIMPLIFIED FROM XIDAKIS, 1979)

Method \ Soil	Gr1	Gr2	Gr3	Gr4	Kenya	Adelaide	Modbury	Mngazi
Ethylene glycol	485	530	490	437	674	589	610	575
Glycerol	384	514	480	430	670	616	607	615
Methylene Blue (ASA_{107})	426	480	440	414	656	574	571	585

Table 2 is a matrix of correlation coefficients between the various properties of the eight soils. It should be noted that the ASA value has a correlation coefficient of 0.991 with respect to the free swelling capacity (although it must be admitted that the number of specimens is rather meagre).

adsorption system in a natural soil which is responsible for the swelling. In this case, where the soil is aggregated, part of the soil surface accessible to water molecules may be inaccessible to dye ions which are up to ten times as large (Lafleur, 1972). Nevertheless this difference is believed to be small and may be neglected.

TABLE II

MATRIX OF CORRELATION COEFFICIENTS BETWEEN VARIOUS PROPERTIES
OF EIGHT EXPANSIVE SOILS
(SIMPLIFIED FROM XIDAKIS, 1979)

		1 LS	2 LL	3 PL	4 PI	5 Cf	6 Fr.Sw	7 ASA
1	LS	1						
2	LL	0.992	1					
3	PL	0.527*	0.606*	1				
4	PI	0.985	0.983	0.449*	1			
5	Cf	0.794	0.862	0.754*	0.794	1		
6	Fr.Sw	0.989	0.998	0.617*	0.978	0.854	1	
7	ASA	0.968	0.989	0.623*	0.957	0.895	0.991	1

Significance level (S) <0.01 except values with asterisk (*); LS = linear shrinkage (%); LL = liquid limit; PL = plastic limit; PI = plasticity index; Cf = % fine clay (< 1 µm); Fr.Sw = % free swelling; ASA = surface area of untreated whole soils (m^2/g - determined by methylene blue adsorption).

4 SURFACE AREA

It is apparent from the correlation matrix that the measured surface area of the untreated soil is reasonably well correlated with most of the other properties of the soils examined (r >0.95). The surface area used for the correlations was that obtained on the untreated natural soils, by the

The high correlation of the ASA with the liquid limit and plasticity index (r >0.95) means that the ASA (or dye adsorption value) may possibly be useful in determining the latter in soils and clays, after proper calibration or redefinition. Thus the plasticity of clays and soils might be defined by an intrinsic and not an arbitrary property. Many authorities have obtained good correlations between surface area and Atterberg limits (Fairbairn & Robertson, 1956, Farrar & Coleman, 1967, Warkentin, 1972) or surface area and swelling properties (De Bruyn *et al.*, 1956, Greene-Kelly, 1974, Ross, 1978).

From the above results it appears that the best parameters for an indirect determination of the swelling potential of expansive soils are the Atterberg limits (LL and PI), linear shrinkage and the ASA of the untreated soil.

5 THE USE OF SURFACE AREA FOR CLASSIFYING SOILS

Some advantages of using surface area as an indicator of soil properties are presented below:

(a) The ASA appears to be as good as the other parameters often used for this purpose, i.e. LL, PL, etc.

(b) It is a basic and well defined property of the soil or clay and not an empirical one like the Atterberg limits.

(c) It can be determined in a much shorter time than even the consistency limits. For example, using the methylene blue dye method the time required for a test on a natural untreated soil is less than an hour, compared with the 48 hours necessary to complete the Atterberg limit tests.

(d) The methylene blue dye method appears to have a greater reproducibility than the consistency tests. The precision of the dye method is ±5-8% (Xidakis, 1979) whereas with the Atterberg limits it hardly exceeds ±10%. The effect of the operator's judgement can be more pronounced in the consistency limits operation than in the dye test. The method has possible application for soil classification in road works where there is the need for quality control of large amounts of earth-works. Also it could be used during site investigation for quick evaluation of soil samples obtained as drill cores.

(e) Surface area is an indicator of many other properties of a soil or clay, such as CEC, mineralogy, clay content, water adsorption, retention of phosphates and nutrients, green sgrength, etc. Thus it can be used in the evaluation of clays and soils for agricultural, engineering and ceramic purposes. It also provides information for soil genesis and evolution in pedological studies, for oil genesis and migration in the petroleum industry, and for catalyst preparation in the chemical industry.

(f) It can be shown by theoretical considerations that the surface area is directly related to both swelling pressure and volume change of soils (Xidakis, 1979).

However there are also some shortcomings to the dye method. For example, the dye adsorption is influenced by the nature of the surface, charge density, exchangeable ions, particle aggregation and other factors which have been discussed in more detail by Xidakis (1979). Nevertheless all these disadvantages are believed to be of minor importance when the method is employed for engineering purposes, where absolute accuracy is not of paramount importance.

6 DISCUSSION & CONCLUSIONS

The surface area is a basic soil property, directly related to swelling and other properties of soils, and can be adequately determined by dye adsorption methods. Therefore it can be used for evaluation and classification of expansive soils, and for the grading of such soils we suggest the boundaries: <100, 100-150, 150-200, >200 m^2g^{-1} as demarcating the low, medium, high and very high expansiveness classes.

The methylene blue dye method is a simple and versatile method of looking for expansive minerals in expansive soils, and it is also possible that the same method after proper calibration may be used to determine the Atterberg limits of expansive soils.

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APPENDIX

Outline of the methylene blue dye method (for laboratory use or field test).

1. Take a few grams of <2 mm air dry soil and disaggregate it carefully to give about 5 g passing a BS 200 sieve (74 μm). Dry the soil in an oven at 105°C to give dry mass.

2. Make a suspension (2-5% by weight) preferably with distilled water. The concentration of the suspension should be adjusted depending upon the kind and amount of the clays in the soil; i.e. the greater the amount of swelling minerals in the soil the more dilute the suspension should be. This can easily be determined by a trial test.

3. Add 'Calgon' or Na_4EDTA solution to give 0.5-1.5 me Na per gram of dry soil. Excess of dispersing agent, within reasonable limits, does not affect the results.

4. Stir the suspension with a commercial stirrer for about 15 min. If no stirrer is available shake vigorously for 2-3 mins by hand. If the soil contains no more than small amounts of carbonates and/or soluble salts it will disperse easily by hand shaking.

5. Prepare a standard 0.01 M methylene blue dye solution (dissolve 3.65 g of dye in a litre of distilled water). Keep the standard dye solution away from the direct sunlight and in a polythene bottle to avoid fading of the solution.

6. Pipette an aliquot of the soil suspension (10-20 cm^3) into a Pyrex test-tube or a conical flask with stopper. The initial suspension can be prepared directly in a conical flask (200 cm^3 recommended). Avoid the use of soda glassware since it absorbs the dye. Perform the 'spot' test (Jones 1964): i.e. titrate the standard 0.01 M methylene blue dye solution by burette. For field tests a 2-10 cm^3 disposable plastic medical syringe without needle can be used both for pipetting the soil suspension and titrating the dye solution. The dye should be added to the suspension 1 cm^3 at a time; after each 1 cm^3 dye addition shake the container vigorously for a few seconds; then, using a glass rod, place one drop of suspension on a medium soft filter paper (e.g. Whatmans No. 1 or 40).

7. The 'end-point' is indicated when excess dye appears as a sky-blue (possibly greenish) colouration radiating away from the normally deeply dyed solid in the centre. This is confirmed as the true end-point if the titrated suspension still shows excess dye when the spot test is repeated after a two minute period.

8. With the spot-test an accuracy of ±0.5 cm^3 of dye can easily be obtained under normal conditions and this is quite satisfactory for engineering purposes. Having found the end-point from the spot test the ASA is obtained from the formula:

$$ASA_{107} = \frac{Vd}{C} \times 6.45 \ m^2/g \ soil$$

where Vd is the volume of the 0.01 M methylene blue standard solution required to reach the end point; C is the mass of the soil in the test container in grams.