The Methylene Blue adsorption test applied to geomaterials

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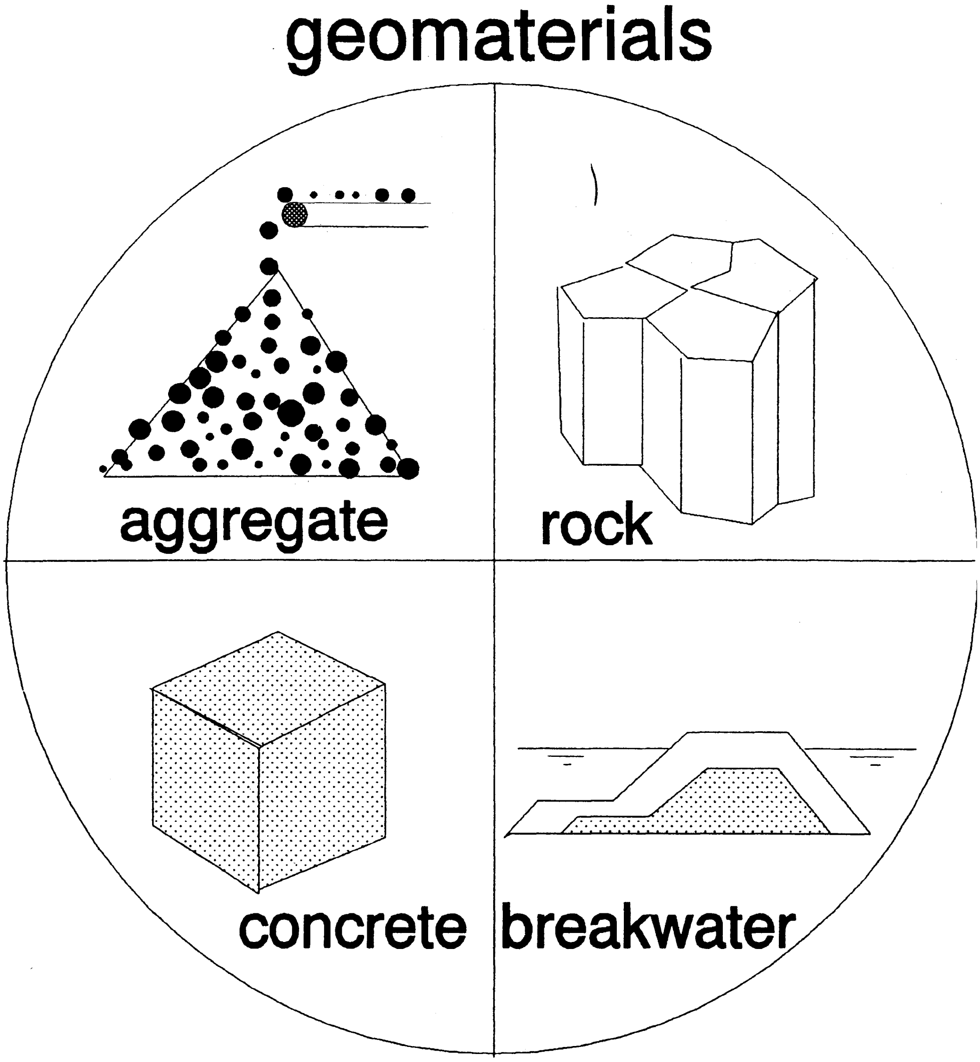
The Methylene Blue Adsorption test applied to Geomaterials

Drs. P.N.W. Verhoef



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Directoraat-Generaal Rijkswaterstaat

Dienst Weg- en Waterbouwkunde

TU Delft
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Faculteit der Mijnbouwkunde en Petroleumwinning
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15. Opmerkingen
De projectbegeleiders bij de Dienst Weg- en Waterbouwkunde zijn Ir. P.M.C.B.M. Cools (projectleider), H.A. Rijnsburger en Ing. G.J. Laan.

16. Referaat

In dit rapport wordt een overzicht gegeven van een eenvoudige chemische methode om de kation uitwisselings capaciteit (CEC) van fijnkorrlig of fijngemalen aggregaat te bepalen. Deze uitwisselingscapaciteit is zeer groot voor die kleimineralen die als zwellend bekend staan. De door een ruwe titratieproef bepaalde methyleen blauwwaarde (MBA) correleerd lineair met het zwellend vermogen van kleimineralen. De adsorptie van methyleen blauw aan dergelijke kleimineralen is orden van grootte hoger dan enig ander mineraal.

De methode is sneller en betrouwbaarder dan standaard röntgen diffractie methoden die gewoonlijk gebruikt worden voor de identificatie van kleimineralen. Gespecialiseerde röntgendiffractie blijft noodzakelijk voor de mineraal-determinatie van klei.
Geotechnisch is de methode interessant voor de klassificatie van grond. De MBA correleert met de plasticiteitsindex en de Atterbergse grenzen. Bovendien is de MBA methode sneller en waarschijnlijk ook betrouwbaarder dan de klassieke Atterbergse grenzen. In Frankrijk gebruikt het LCPC een klassificatie van wegenbouw granulaten en zanden gebaseerd op MBA bepalingen.

Voor de vaststelling van de duurzaamheid van gesteenten en granulaten toegepast in de weg- en waterbouw is de test ook interessant. In steen kan vrij eenvoudig de aanwezigheid van minieme hoeveelheden zwellende klei aangetoond worden. Met behulp van het kleuren van slijpplaatjes met MB kan de positie van de adsorberende mineralen vastgesteld worden. Hieruit kunnen conclusies getrokken worden over de duurzaamheid van het gesteente.

De methode is een krachtig hulpmiddel bij de vaststelling van de te verwachten geotechnische eigenschappen van zowel grond als gesteente.

17. Trefwoorden
Kleimineralen, Bentoniet, Waterbouwsteen, Steengranulaat
Zwellende grond, Duurzaamheid steen

18. Distributie systeem

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19. Classificatie

20. Classificatie deze pagina

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Project "Geomaterials Characterisation and Testing"

Contractnummer DWW 402
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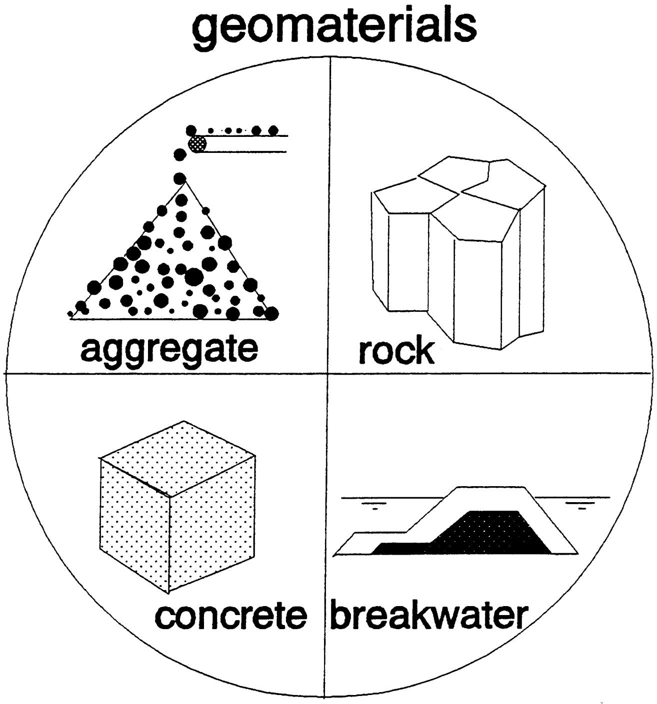

Het project wordt uitgevoerd door de Technische Universiteit Delft, Faculteit Mijnbouwkunde en Petroleumwinning (sectie Ingenieursgeologie; Prof. D.G.Price, Eur.Eng., C.Eng), de uitvoerende onderzoekers zijn:
Drs. P.N.W. Verhoef (ingenieursgeoloog, projectleider); Drs. W. Pieters (petrograaf, hoofdonderzoeker); Drs. M. van Tooren (petrograaf); Ir. H. Houwink (geofysicus, tot december 1990).

De projectbegeleiders bij de Dienst Weg & Waterbouwkunde zijn Ir. P.M.C.B.M. Cools, Ing. H.A. Rijnsburger en Ing. G.J. Laan (adviseur).

Project "Geomaterials characterisation and testing".

Contractnummer DWW 402
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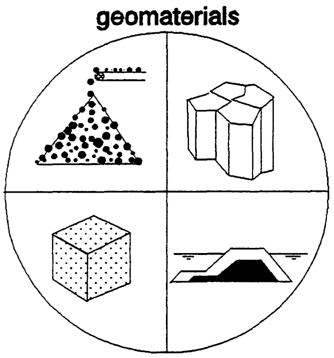
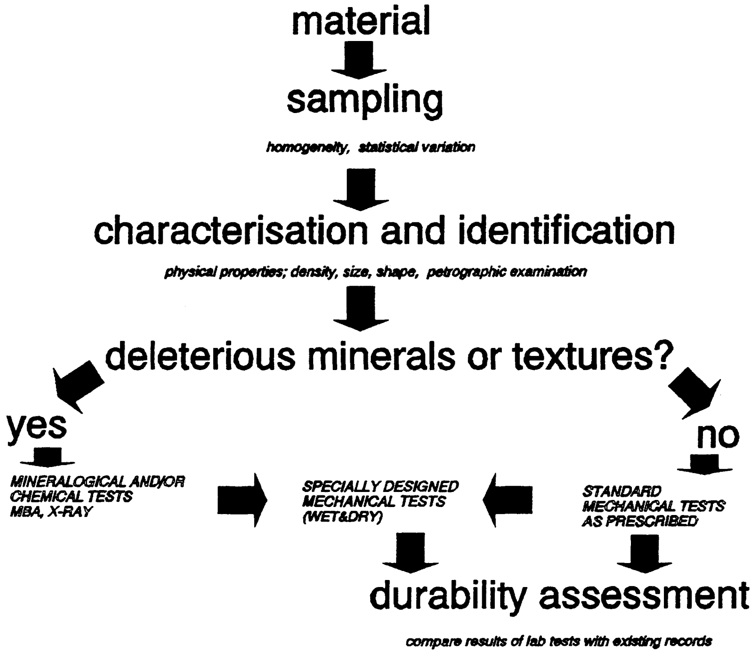


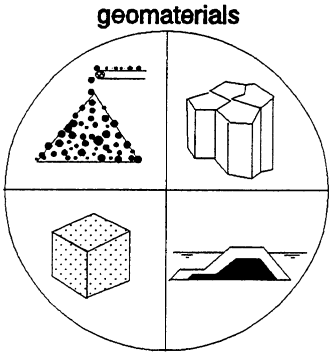
Dit onderzoekprogramma omvat de studie naar de technische eigenschappen van steenachtige granulaten die gebruikt worden voor civiel-technische doeleinden. Hierbij kan gedacht worden aan aggregaten in losse vorm of in gebonden vorm (fundering wegen: aarde baan; gebruik van steenachtige materialen in ophogingen; gebruik van breuksteen bij kustbeschermingswerken; toeslag voor beton of asfalt beton).

Het doel van het onderzoekprogramma is het ontwikkelen van een geintegreerde opzet van het laboratoriumonderzoek van deze materialen. Hierbij ligt de nadruk op het petrografisch onderzoek van de gesteenten, dat vooraf gaat aan het beproevingsprogramma. De duurzaamheid (de mate waarin de technische eigenschappen behouden blijven tijdens de levensduur van de constructie waarin het materiaal gebruikt wordt) is voor een groot deel afhankelijk van de mineraalsamenstelling en microscopische structuur van het gesteente. Is de petrografie bekend, dan kan aan de hand hiervan een gericht testprogramma opgesteld worden. Deze testmethodologie is samengevat in onderstaand diagram.



De hoofdmoot van het onderzoek omvat het ontwikkelen en beschrijven van de petrografische technieken en parameters en de correlatie van deze laatste met al of niet aangepaste aggregaatproeven. Verder wordt nog aandacht besteed aan het schaaleffect wat speciaal optreedt bij grote steenblokken voor de waterbouw, waarbij (verborgen) scheuren op groter dan microscopische schaal invloed uitoefenen op de mechanische eigenschappen.

THE METHYLENE BLUE ADSORPTION TEST APPLIED TO GEOMATERIALS



Peter N.W. Verhoef.
June 1992

GEOMAT.02

Memoirs of the Centre of Engineering Geology in the Netherlands, 101

THE METHYLENE BLUE ADSORPTION TEST APPLIED TO GEOMATERIALS

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Content

THE METHYLENE BLUE ADSORPTION TEST APPLIED TO GEOMATERIALS

1. INTRODUCTION

In recent years it has become clear that the methylene blue adsorption test is a reliable and simple method to obtain information on the presence and properties of clay minerals in soils and rock. The test was first described in the fifties (Fairbairn and Robertson, 1957). Several methods have been used to measure the adsorption of methylene blue by hydrophillic and cation-exchanging substances, some of which have been rather complicated. For example, Orchard (1976) describes how the test was done in the School of Highway Engineering in Australia. A suspension of finely ground rock or soil was mixed with a solution of methylene blue, left over for a few days, and then on a diluted solution the optical density was measured by a spectrophotometer, from which the amount of methylene blue adsorbed by the clay was determined. Because this method is quite involved and despite the fact that one could determine the MB adsorption by comparing the colours of the test solution with a standard set of solutions of varying MB concentration, this method was not universally accepted. In many papers where the method is applied, no mention is made of the concentration of the methylene blue solution used, and the adsorption is given in ml MB taken up by the soil. Without knowing the MB concentration used, nothing can be done with such data. Possibly also for this reason the method has not gained widespread popularity. In most geotechnical literature the concentration is reported in grams MB adsorbed by 100 g of soil. Also this way of reporting the concentration is basically incorrect; it should be reported in milli-equivalents per 100 g of soil [meq/100g], because the molecular weight of MB is dependent on its water content (it is hygroscopic).

The "spot method" developed by Jones (1964) was applied in the oil industry, to check the quality of bentonite drilling mud. This method is essentially a titration technique which determines the amount of MB adsorbed by a suspension of fines. The "spot method" is very simple, convenient and sufficient for the purpose of estimating geotechnical properties of geomaterials. The spot method has been applied both to rock and soil materials. The Laboratoire Central des Ponts et Chaussées (LCPC) has done a continuous investigation of the method over the past 15 years and applied it on soils, rocks and aggregates. Much of this research is summarized in the report "Essai au bleu de méthylène" (LCPC, 1990). One of the important conclusions that can be drawn from this report is that with help of the methylene blue method a more convenient way is available to obtain information on the nature and activity of clay substances in soil and rock and probably the method may be even more reliable than the traditional geotechnical tests performed.

LCPC has found that:

1. There are good correlations between the methylene blue adsorption (MBA) and plasticity index and liquid limit of soils. The method is easier to perform and probably more accurate than the classical determination of Atterberg limits.
2. Clay activity can be expressed by MBA values.
3. MBA can be used conveniently in soil classifications.

Both in soils and rock a good idea of the nature of the clays present may be obtained using

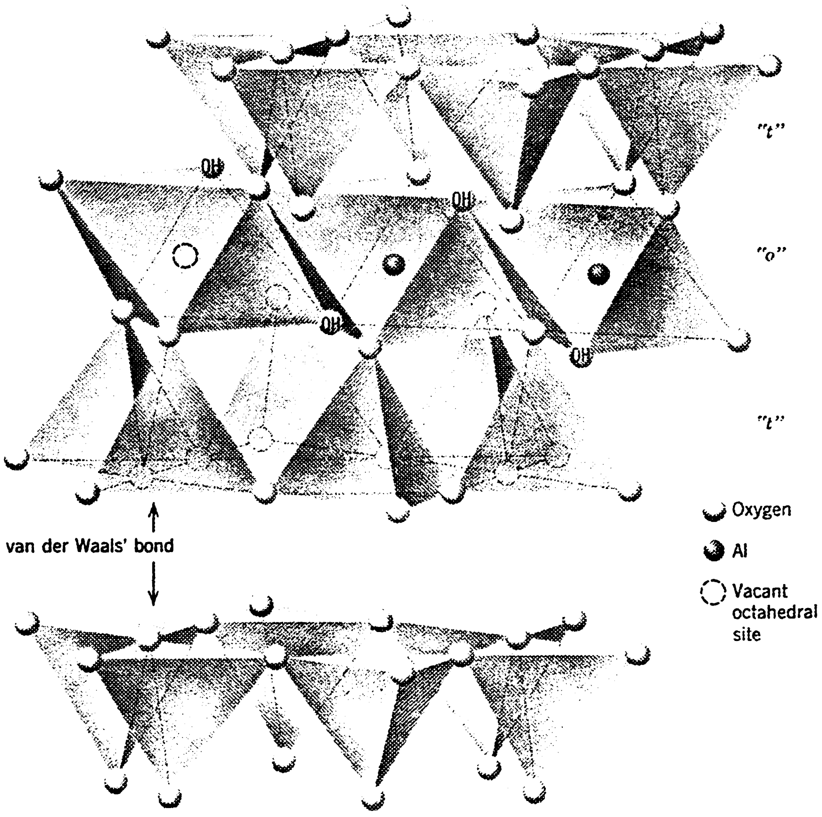


Figure 1. Diagrammatic sketch of a t-o-t sandwich structure as in pyrophyllite (Hurlbut & Klein, 1977, Dana's Manual of Mineralogy, Wiley, New York)

methylene blue in the characterisation phase of geomaterial investigations. In this report the major findings by LCPC are summarized and the results of our own investigations into the application of the method to the study of rock material are presented. From our own findings we may add:

4. MBA is a reliable method to identify potential deleterious swelling clay in rock and an educated guess of the nature of the clay present in the rock can be made.

It appears that for geotechnical engineering purposes the MBA method gives sufficient information on the nature of clay minerals present in soil or rock.

2. METHYLENE BLUE ADSORPTION: THEORY

2.1. Clay minerals

Clay minerals belong to the phyllosilicate mineral group. Phyllosilicates (sheet silicates) are characterized by a platy, sheet-like, crystal structure. The understanding of clay minerals and their classification is mainly based on crystallographic examination by X-ray diffraction and electron diffraction studies. Linus Pauling was the first to unravel the structure of clays (1930). The principal building elements of clay minerals are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of oxygen-hydroxyl octahedra. In most clay minerals sheets of tetrahedra and of octahedra are superimposed in different fashions. Clay minerals can be divided broadly into two groups:

a. t-o structure (kaolinite-group).
b. t-o-t structure (e.g. smectite-group).

The t-o structure consists of one octahedra layer (o) and one tetrahedra layer (t). The t-o-t structure consists of one octahedra layer and two tetrahedra layers (Fig. 1). These two main groups can each be subdivided into two subgroups on the basis of the infilling of trivalent Al in the octahedral positions: if two of the three positions are occupied: dioctahedral, if all three positions are occupied: trioctahedral.

When examining the crystal structures of clay minerals, of which more than 300 different types have been described, two ideal electroneutral structures have been realized in nature. These are shown in Figure 2 and 3 and represent the t-o-t mineral pyrophyllite (dioctahedral; the trioctahedral electroneutral variety is talc) and the t-o mineral kaolinite. These minerals are in fact stacks of the crystal structures depicted in Figures 2 and 3. The cohesive force between the layers is primarily electrostatic, amplified by Van der Waals attraction. Cleavage parallel to the layers is relatively easy.

The different clay minerals are derived from the prototypes by introducing more or less atom substitutions in the crystal structure, like Si^{4+} <-> Al^{3+} and Al^{3+} <-> Mg^{2+}, $Fe^{2+,3+}$ (Figure 4). Table 1 gives a classification of clays.

Kaolinite has the t-o structure, with the chemical formula $Al_2Si_2O_5(OH)_4$. The structural building

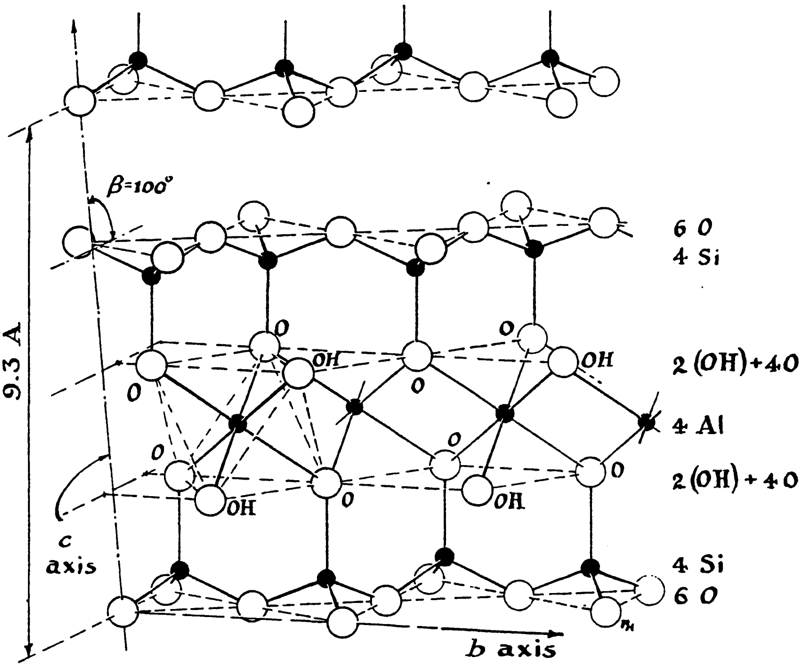


Figure 2. Atom arrangement in the unit cell of a t-o-t mineral (Mason & Berry, 1968, Elements of mineralogy, Freeman, San Francisco)

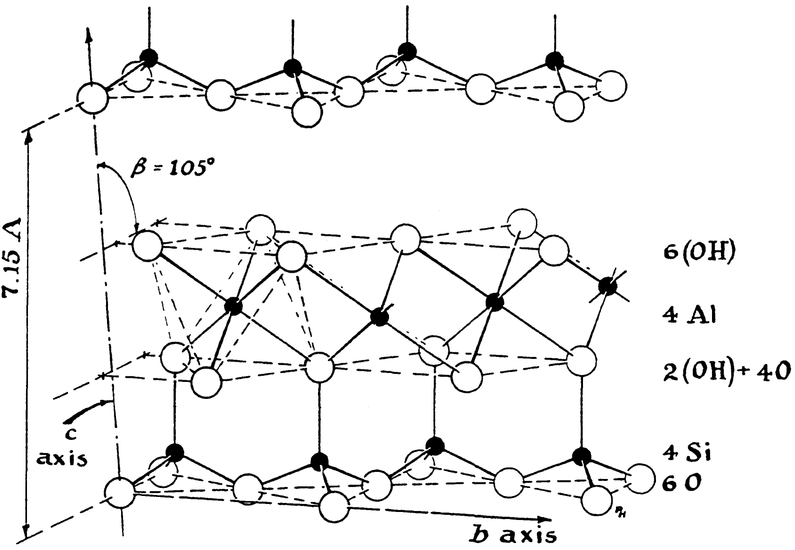


Figure 3. Atom arrangement in the unit cell of a t-o mineral (Mason & Berry, 1968, Elements of mineralogy, Freeman, San Francisco)

is formed by the t-layer: $(Si_2O_5OH)^{3-}$ plus the o-layer: $Al(OH)_3$. The electroneutrality is obtained by leaving one of the three octahedral cation seats vacant. The mineral kaolinite is formed by the stacking of the molecule units: t-o/t-o/t-o etc.

The electroneutral t-o-t minerals pyrophyllite and talc form rather thick and large crystals and do not disintegrate to a size normal for clay minerals. They are therefore not classified as clay minerals proper, but belong to the mica-like minerals. The clay minerals which belong to the t-o-t structural group are the smectite and illite clay groups.

Illite has a t-o-t structure in which two t-o-t layers are connected by a shared K-ion (Figure 4). This results in a strong crystal structure. Formula: $(K,Ca,Na,H_2O)_x(Al,Mg,Fe)_2(Si_{4-x}Al_x)O_{10}(OH)_2$

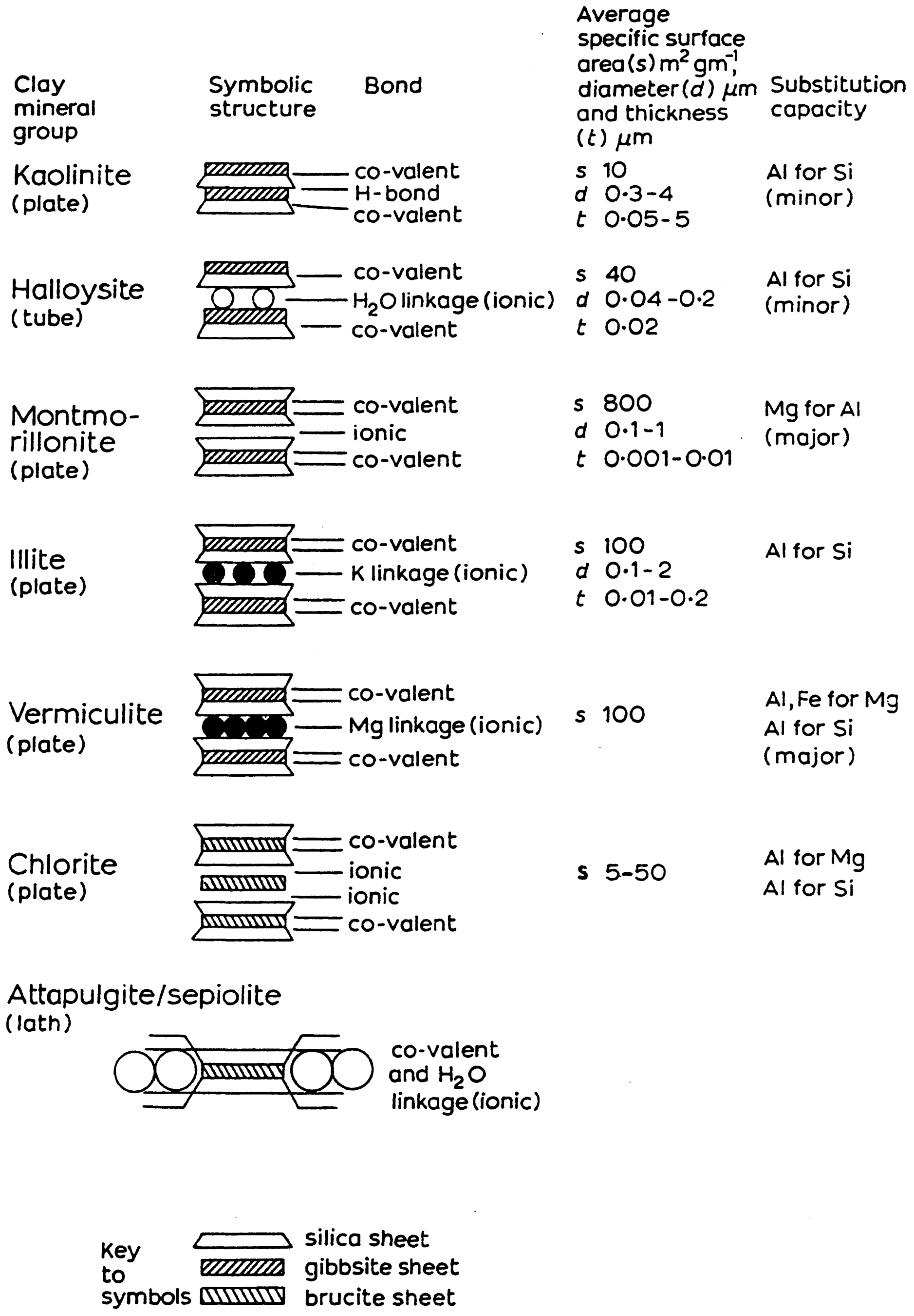
Smectite clay minerals are characteristically very fine grained and chemically very active. Much ion substitution is possible in the octahedral layer. A typical smectite mineral is montmorillonite, $Al_2Si_2O_5(OH).xH_2O$ (no good stacking of t-o-t units; Figure 4). Montmorillonite-like minerals can easily adsorb and release water (swelling and shrinking clay).

Crystal structure	Prototype	Common clay minerals	Remarks
1:1	Kaolinite		non-swelling
2:1 dioctahedral	Pyrophyllite	Montmorillonite	Smectite Group
2:1 trioctahedral	Talc	Vermiculite	
2:1	Muscovite	Illite	non-swelling
2:1	Chlorite		
needle structure	Attapulgite		
	Mixed-layer clays		

Table 1. Clay mineral crystallographic classification (Van Olphen, 1977)

From a geotechnical point of view the ability to swell and shrink and the possibility of clays to be chemically active by exchanging ions is important. Therefore some emphasis is placed on the smectite group of clays, which are very active in this respect. Before describing the smectites in some more detail (following Van Olphen, 1977), some remarks on nomenclature are made. In literature sometimes with the terms *smectite*, *montmorillonite* and *bentonite* the same swelling clay is meant. Montmorillonite is the principal clay mineral of bentonite rock. "Bentonite" is a soil or rock (when indurated) that originates from volcanic ash. Thus, properly speaking, bentonite is the name of a montmorillonite-bearing rock and smectite refers to the clay mineral group to which the mineral montmorillonite belongs.

The structure of the minerals of the smectite group of clay minerals is derived from that of the prototypes pyrophyllite and talc by substitution of certain atoms for other atoms. The following types of atom substitutions have been observed in representative minerals of this group.



Clay mineral group	Bond	Average specific surface area (s) $m^2 gm^{-1}$, diameter (d) μm and thickness (t) μm	Substitution capacity
Kaolinite (plate)	co-valent H-bond co-valent	s 10 d 0·3-4 t 0·05-5	Al for Si (minor)
Halloysite (tube)	co-valent H_2O linkage (ionic) co-valent	s 40 d 0·04-0·2 t 0·02	Al for Si (minor)
Montmorillonite (plate)	co-valent ionic co-valent	s 800 d 0·1-1 t 0·001-0·01	Mg for Al (major)
Illite (plate)	co-valent K linkage (ionic) co-valent	s 100 d 0·1-2 t 0·01-0·2	Al for Si
Vermiculite (plate)	co-valent Mg linkage (ionic) co-valent	s 100	Al, Fe for Mg Al for Si (major)
Chlorite (plate)	co-valent ionic ionic co-valent	s 5-50	Al for Mg Al for Si
Attapulgite/sepiolite (lath)	co-valent and H_2O linkage (ionic)		

Figure 4. Schematic crystallographic classification of clay minerals. Gibbsite refers to octahedral sheet consisting of $Al(OH)_3$, Brucite consists of $Mg(OH)_2$. (From Attewell and Farmer, 1976, Principals of Engineering Geology, Chapman and Hall, London)

In the tetrahedral sheet, tetravalent Si is sometimes partly replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg without complete filling of the third vacant octahedral position. Al atoms may also be replaced by Fe, Cr, Zn, Li, and other atoms. The small size of these atoms permits them to take the place of the small Si and Al atoms; therefore, the replacement is often referred to as isomorphous substitution. In many minerals an atom of lower positive valence replaces one of higher valence, resulting in a deficit of positive charge, or, in other words, an excess of negative charge. This excess of negative layer charge is compensated by the adsorption on the layer surfaces of cations which are too large to be accommodated in the interior of the crystal. This interpretation of the results of the analysis of the chemical composition of the clay minerals was first proposed by Marshall in 1935 (Van Olphen, 1977).

In the presence of water, the compensating cations on the layer surfaces may be easily exchanged by other cations when available in solution; hence they are called "exchangeable cations". The total amount of these cations may be determined analytically. This amount, expressed in milli-equivalents per 100 g of dry clay, is called the cation exchange capacity (CEC) of the clay.

Since the exchangeable cations compensate the unbalanced charge in the interior of the layers due to isomorphous substitutions, the CEC is a measure of the degree of substitution. If the CEC and the chemical composition of the clay are known from a chemical analysis, it is possible to assign the substituting ions to the tetrahedral and the octahedral sheets, and derive the chemical formula of the clay (Van Olphen, 1977).

In the stack of layers which form a smectite particle, the exchangeable cations are located on each side of each layer in the stack; hence they are present not only on the external surfaces of the particle but also in between the layers. Their presence causes a slight increase of the basal spacing as compared with that of pyrophyllite from about 9.13Å to at least 9.6Å (for the dry clay) or slightly higher when the compensating cations are larger. The difference between the basal spacing of pyrophyllite and that of a smectite is much less than the diameter of the compensating cations. Apparently, these cations are partly sunk in the holes of the tetrahedral sheet.

When smectite clays are contacted with water or with water vapour, the water molecules penetrate between the layers. This so called interlayer swelling, or (intra-)crystalline swelling, of smectites is evident from an increase of the basal spacing of the clays to definite values of the order of 12.5-20 Å, depending on the type of clay and the type of cation. A more or less stable configuration of the hydrated clay is obtained, corresponding with the presence of one to four monomolecular layers of water between the layers. In a water-vapour-adsorption isotherm, a stepwise hydration with one, two, three, and four water layers could be observed in some clays by taken X-ray diffraction patterns of a flake of the clay at different water-vapour pressures. Cations, water, and other materials between layers are referred to as the interlayer.

The importance of the presence of the interlayer cations for the interlayer swelling process can be demonstrated by the following possibility to reduce the surface charge. By heating of dioctahedral lithium-smectites, lithium ions diffuse through the layers and occupy vacant octahedral positions, thus reducing the layer charge. The mineral then looses its swelling ability with the charge reduction, and the layers "collapse".

Smectites also admit organic compounds of a polar or ionic character between the layers. The adsorption of the organic compounds leads to organo-complexes of montmorillonites. The basal spacings of these complexes depend on the size and the packing of the organic molecules. The change in the basal spacing caused by the formation of such complexes is often used to detect the presence of montmorillonites in natural clay mixtures. Commonly, the complexing with ethylene glycol is used for this purpose. Methylene blue complexing also belongs to this category.

Interlayer swelling leads to, at most, a doubling of the volume of the dry clay when four layers of water are adsorbed. The much larger degree of swelling which is observed for many smectite clays is due to another mechanism, osmotic swelling. Osmotic swelling is related to the repulsive forces between two clay molecule platelets, in the so-called "diffuse-ion-layer". The osmotic pressure is a result of concentration differences of dissolved ions or molecules in different parts of the clay-fluid system. It is possible to calculate osmotic pressures from the theoretically derived distribution of ions in the double layers between the clay plates and the surrounding fluid. The calculated osmotic pressure was found to be equal to measured swelling pressures, and both are a function of water content (or platelet distance) (Van Olphen, op.cit. p.156).

The 'specific surface' is that surface of the clay mineral which is accessible to water. In smectites this total layer surface area per gram of clay represents both the external and the internal surface area which is accessible to exchange ions and to water or other polar molecules. For clays with platy-like particles, the internal and external surface areas per gram of clay may be calculated from the dimensions of the unit-cell of the crystal structure, as determined by X-ray diffraction analysis. The total external area of the flat part of the surface per gram of clay is found by dividing the total layer surface by the number of layers which are stacked in the particles. This number may be derived from the thickness of particles obtained by electron microscope or other techniques (Van Olphen, op. cit., p.87). Determination of surface area by adsorption data is also possible. The external surface area may be determined by the method of Brunauer, Emett and Teller (BET), from the adsorption isotherm of nitrogen gas on powdered clay. To determine the total internal and external surface area other methods can be used, which are based on the adsorption of polar organic compounds, such as glycol and glycerol from the liquid phase, or of cationic compounds (such as methylene blue) from hydrous solution (Table 2).

Method used	Specific surface (m^2/g)			Type of surface measured
	kaolinite	illite	montmorillonite	
BET	22	113	82	external
Ethylene-glycol	45	90	750 800	external - internal
MBA	48	74	860	external - internal

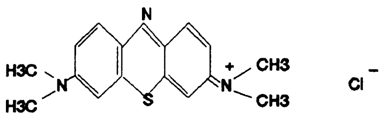
Table 2: Specific surface of clay minerals (Denis et al, 1980)

2.2. Methylene blue

Methylene blue (3.9 bis Dimethylamino phenazothium chloride) is an organic molecule which is built up of benzene rings.

Molecular formula: $C_{16}H_{18}N_3ClS$

Structural formula:



Looking at the structural formula it can be seen that the molecule actually contains a negatively charged (Cl^-) ion and a large positively charged ion.

It can be regarded as a rectangular volume of dimensions 17.0x7.6x3.25 Å^3. The projected area of the molecule is about 130 Å^2 (= 17.0x7.6). The molecular weight is 319.9. Methylene blue hydrochloride (trihydrate) has a molecular weight of 373.9.

Hang and Brindley (1970) have investigated the mechanisms by which MB is adsorbing on the clay minerals kaolinite, Na- and Ca- montmorillonite and illite. X-ray diffraction was used to clarify the adsorption behaviour in Na- and Ca- montmorillonite. Their study was specifically undertaken to examine the determination of surface areas and cation exchange capacity (CEC) by methylene blue adsorption. Careful experimenting with clay suspensions showed that the clay suspensions started to flocculate at a specific concentration of MB. This point was interpreted as the amount of MB needed to cover the clay surfaces with MB cations. The specific surface area could be calculated as follows:

$$S_s = M_f \times A_m \times 6.02 \times 10^{-2} \quad [m^2/g] \tag{1}$$

S_s = specific surface
M_f = amount of MB adsorbed per 100 g clay [meq/100g]
A_m = area per molecule on the surface = 130 Å^2

Maximum adsorption of methylene blue, corresponding to complete exchange of the inorganic by the organic ions, occurs with larger amounts of MB than required for optimum flocculation. The results of the MB adsorption experiments on montmorillonite are given in Figure 5. Here the arrow indicates the optimum flocculation point, the plateaux give the CEC for Na- and Ca- montmorillonite respectively.

Hang and Brindley emphasize that high concentrations of MB solutions are needed to complete the exchange reactions. They also note that the "correct", maximal, exchange capacity of montmorillonite is obtained only when the Na-form is used. The exchange reaction is far from complete when Ca-montmorillonite is used. Under wet conditions the X-ray diffraction measurements showed that the basal spacing of the Ca-clay, normally 19.0 Å, diminished to 15.9 Å with a small adsorption of MB and to 15.7 Å as the adsorption increased to the limit of about 90 meq/100 g clay. The basal spacing of the Na-clay in water remained very large or very irregular even after full exchange of the Na^+ by MB cations; under aqueous conditions no basal reflections were observable.

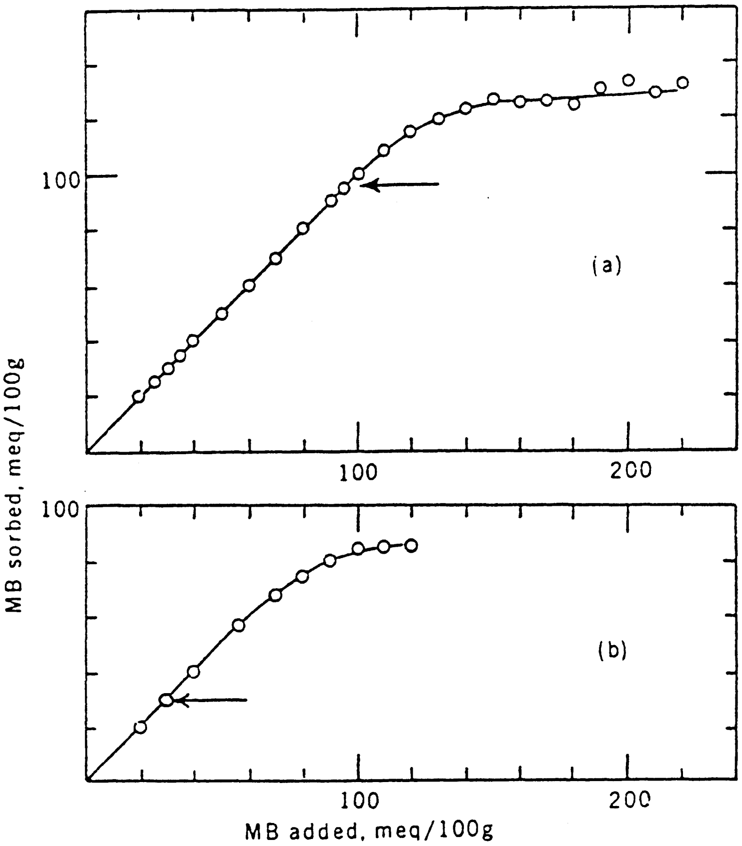


Figure 5. Methylene blue adsorption by (a) Na-montmorillonite, (b) Ca-montmorillonite. Arrows indicate conditions for optimum flocculation and probably mark the end point of the spot test (Hang and Brindley, 1970).

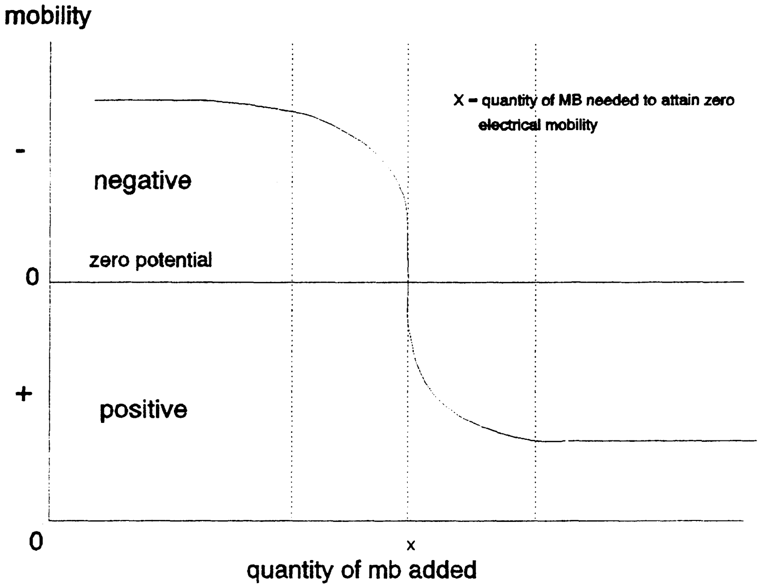


Figure 6. Electrophoresis diagram showing mobility of clay particles in a suspension. The change of electro-negative to -positive charge is clearly related to MB addition (Lautrin, 1990).

In Figure 5 is shown that the optimum flocculation point occurs in the region where the curve begins to deviate from the initial 45° slope, i.e., where adsorption is no longer 100 %. This corresponds to the end point given by the spot test (Hang and Brindley, op. cit., p.207).

From the work of Hang and Brindley (1970) we may conclude:

1. For determination of specific surface, the amount of MB leading to optimum flocculation of the clay should be used. This point is determined by the spot test.
2. The maximum amount of MB adsorbed corresponds to the "effective" CEC, i.e. the cation capacity also available for water molecules.

Summarizing, the mechanism is rather simple. When a methylene blue solution is added to a watery clay mixture the positive methylene blue ion will drive away the positive ions of the above described diffuse-ion-layer. This process will continue until all the other positive ions have been expelled. Up to that point all the methylene blue will attach to the clay mineral surfaces. Then MB ions will replace the positive ions of the interlayers. From then on the remaining methylene blue ions will stay in solution. There is a distinct point in the process, the point where the clay minerals become electroneutral. This point can also be measured by electrophoresis techniques (Figure 6). Further adsorption gives the clay molecules a positive charge. Maximum adsorption corresponds with the CEC. Another way of interpreting the process can be found in the LCPC reports: As there are actually two surfaces, the external and the internal, there are also two stages in the attachment process: a fast and a slow one. Methylene blue will first attach to the external surface, the fast process, and then slowly attach to the internal surface.

2.3. Test methods

Two methods have been used extensively at the Laboratoire des Ponts et Chaussées (LCPC 1990); the "spot method" and the "turbimetric method". The spot method is a simplified titration technique. A certain concentration of MB solution is used (normally 10 g/l or 3 g/l dry MB), which is added in definite volumes (0.5 ml) to a suspension of fine grained soil or ground rock particles. About 2 g of particles suspended in 20 ml water is sufficient. Drops of the suspension are placed on filter paper. When MB is adsorbed, the fluid migrating in the filter paper from the droplet outwards is colourless. MB is added to the suspension again, while the suspension is thoroughly shaken (by a magnetic rod stirrer, for example). Another droplet is placed on the filter paper and the migrating halo around the droplet is examined. This process is continued until the migrating fluid is blue coloured by the excess MB resting in solution when all MB is adsorbed. It was found that, when using this method, the MB that is adsorbed by the clay minerals corresponds with total coverage of the surface areas of the clay layers. When titrating a pure clay suspension the amount adsorbed would relate to the cation exchange capacity of that clay. (Otherwise it would relate to the CEC of the soil or rock under study). The procedure of the spot method is described in Appendix 1. Appendix 2 gives the latest French norm for the spot test performed on sand aggregate. This procedure differs from the procedure described in Appendix 1, which was applied for this study. Much larger quantities of sample suspension are used with the latter method.

The methylene blue adsorption value is calculated in grams MB adsorbed by 100 g of sample:

$$MBA = (c \times p) / (A/100) \quad [g/100\ g], \tag{2}$$

MBA = methylene blue adsorption value (V_B in French literature)
c = concentration methylene blue solution [g/ml]
p = amount of MB adsorbed [ml]
A = weight of soil or rock powder

The adsorption expressed in milli-equivalents (M_f; see equation 1) can be calculated as follows:

$$M_f = (100 \times N \times p) / A \quad [meq/100\ g] \tag{3}$$

N = normality of the MB solution [meq/l]

In the reports of LCPC and the papers of the French authors the results of the adsorption tests are always reported in MBA values (noted as "V_B"; la valeur de bleu), with the units g/100g or g%. This is not really good practice, because of the fact that methylene blue turns out to be hygroscopic. Because of this its molecular weight may vary. As has been noted above, the molecular weight of dry MB is 319.9, that of trihydrate 373.9. To determine the hygroscopic water content of the MB, a sample of the crystalline dye is dried at 105 °C and the loss of the weight determined (a typical weight loss is about 12.34 %). The normality of a MB solution can then be calculated:

$$N = (c \times 1000)/319.9 \times (100.00 - 12.34)/100 \quad [meq/l] \tag{4}$$

c = concentration methylene blue solution [g/ml]

When dried methylene blue crystals are used to prepare the MB solution (Appendix 1), M_f = 3.13 MBA [meq/100g]; when saturated trihydrate is used, M_f = 2.67 MBA [meq/100g]. It is desirable to report MB test results in meq/100g, to prevent misunderstanding. In this report MBA is reported in g/100g and where possible M_f is given as well. For the experiments in Delft always dried MB was used to prepare the solutions. The older French values might relate to MB solutions prepared from trihydrate.

The turbimetric method was developed by LCPC, because it was found necessary to have a more precise test method available, to measure very minute contaminations of clay, for example in sands used for concrete manufacture. The second reason given was that the spot method would measure the total, external and internal, surface adsorbing MB and cannot distinguish the two. Tourenq and Tran Ngoc Lan (1990) think that this distinction may, in some cases, be of geotechnical significance. A distinction between short-term and long-term geotechnical behaviour is made. An analysis of quite a number of studies seems to indicate that:

1. In the long term it is the total specific surface (internal and external) of clays that determines the maximal risk (here the result of the "spot test" is significant).
2. In short term only the external surface may determine the mechanical behaviour of clays. This may relate to laboratory tests with a duration of less than 7 days.

The turbimetric method allows one to determine adsorption only on the external surface. It appears that, also in France, the turbimetric method is only rarely used (Mishellany, 1990).

2.4. MBA measurements on minerals

On a suite of minerals MBA spot measurements have been made, to observe whether some adsorption would take place (Table 3). The reason for this survey was that it could be observed that some minerals, like hornblende and chlorite sometimes would take some stain (as observed under the microscope). It was done also to check whether other minerals than clays would adsorb some MB, or would act inert. Table 4 gives values obtained for clay minerals. Both tables give also the M_f value and the specific surface derived from the MBA results.

Mineral	MBA [g/100g]	M_f [meq/100g]	S_s [m^2/g]
23 Analcite	0.59	1.8	14
29 Anhydrite	0		
38 Antigorite	0.15	0.47	3.7
39 Apatite	0		
48 Asbestos	0.14	0.5	3.9
49 Asbestos	0.23	0.7	5.5
66 Baryte	0		
79 Biotite	0.15	0.5	3.9
92 Calcite	0.09	0.3	2.3
100 Cancrinite	0		
112 Chamosite	0		
137 Dolomite	0		
142 Epidote	0		
152 Garnierite	5.4	16.9	132
156 Gypsum	0		
165 Hornblende	0.15	0.5	3.9
172 Kaolinite	1.4	4.4	34
186 Lazurite	0		
189 Magnesite	0		
198 Monticellite	0.10	0.3	2.3
199 Muscovite	0.15	0.5	3.9
203 Nephelinite	0		
236 Sepiolite	7.2	22.5	176
237 Sericite schist	0.15	0.5	3.9
238 Serpentinite	0.18	0.6	4.7
239 Serpentinite	0.15	0.5	3.9
246 Scapolite	0.15	0.5	3.9
256 Talc	0.38	1.2	9.4
284 Wavellite	0.5	1.8	14

Table 3: MBA values for minerals and rocks from the collection of the Faculty of Mining Engineering, Delft.

Mineral	MBA [g/100g]	M_f [meq/100g]	S_s [m^2/g]
Li-montmorillonite[1]	11	29.4	230
Na-montmorillonite	9.5	26.1	204
Na-montmorillonite[2]		126.0[2]	
K- montmorillonite	22.9	62.6	490
Rb-montmorillonite	11.4	31.1	243
Cs-montmorillonite	4.7	12.9	101
Mg-montmorillonite	22.0	60.2	471
Ca-montmorillonite	21.2	57.8	452
Ca-montmorillonite[2]		90.0[2]	
Sr-montmorillonite	20.3	55.4	434
Ba-montmorillonite	17.5	47.8	374
Montmorillonite[3]		64.3	503
Palygorskite	14.6	39.9	312
Chlorite	0.6	2.0	16
Illite	2.5	6.7	52
Oswego Illite[2]		13.2[2]	
Kaolinite	2.4	6.6	52
Florida kaolinite[2]		7.2[2]	
Serpentine	1.2	3.3	26
Halloysite	1.3	3.4	27
Ball clay[3]		12.3	96
London clay[3]		25.2	197

[1] homoionic fractions of montmorillonite were prepared from Wyoming bentonite
[2] data from Hang and Brindley (1970), CEC (maximum adsorption) obtained by spectrophotometer measurements (see Fig. 5).
[3] data from Kühnel (Delft)

Table 4: MBA values of some clay minerals (Stapel & Verhoef, 1989)[o].

2.5. Interpretation of MBA adsorption data

There are two problematic issues related to the interpretation of MBA data.

1. Does the spot test actually measures cation exchange capacity (CEC)?
2. The units of measure of MBA

The first point is related to Figure 5. If we follow the interpretation of Hang and Brindley (1970), the MB spot test would indicate the concentration at which some MB remains in solution. This relates to the flocculation point for pure clays. It appears that the clay is capable of adsorbing more MB, the maximum amount is the cation exchange capacity (Fig. 5). As noted earlier (section 2.2), it depends on the chemical composition of the clay, i.e. the type of cation, how much exchange can occur. Table 3 and 4 and data in literature show that CEC values vary also for the same clay mineral, even with identical chemical composition. According to the above, the MBA spot test probably underestimates CEC. There is ample evidence, however, that MBA results (M_f) correlate very well with, and are near to, CEC values measured with other methods (e.g. Sweere and Galjaard, 1987; LCPC, 1990). In fact, "cation exchange capacity" is a term which should be regarded in relation to the method by which it is determined. How much exchange will take place is a function of the environment (pH, type of clay, type of exchanging cation etc.) If the method by which CEC is determined is given, there is no objection to replace "M_f" by "CEC".

Specific surface can be determined without problem from the MBA spot test data. The accuracy of the spot method can be illustrated with the minimum surface area that can be determined, which is 2 to 3 m^2. This would correspond with 0.1 % kaolinite or 0.002% montmorillonite present in the rock or soil. The calculated S_s values in Table 4 are generally lower than theoretically possible (compare with Table 2). This may relate to a systematic underestimation by the MBA test, but probably also is a real effect. As for CEC, also specific surface will be dependent on experimental conditions and method of determination used.

More important than the fact whether the MBA method gives theoretically correct values of CEC and S_s is its relationship with chemical activity and water adsorption, which both determine geotechnical properties (swelling and shrinking, shear strength etc.). Figure 7 shows the results of a comparative study on homoionic fractions of Wyoming Bentonite, where the methylene blue adsorption has been compared with the result of Foster's swell test (Foster, 1953; Stapel and Verhoef, 1989).

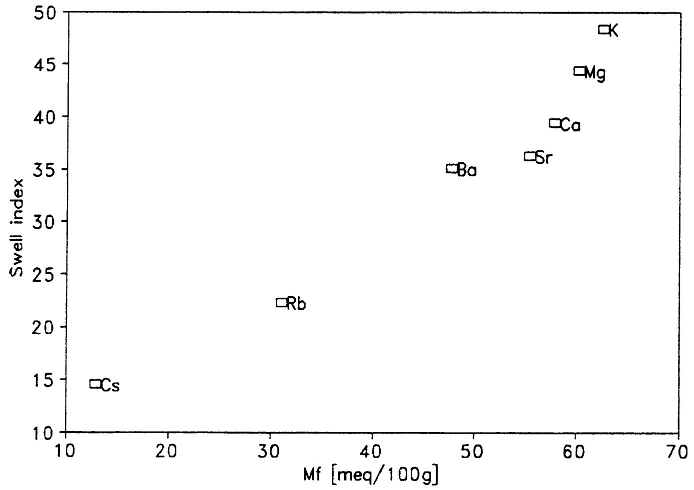


Figure 7. Swell capacity of different montmorillonite clays and MB adsorption

Since the LCPC has already assembled a large data base, we have chosen in this report to follow the procedures adopted by LCPC. The MBA value will be given in g/100g or g%, based on the result of a determination with a solution of dry MB. The more correct usage of giving the data in meq/100g is advocated, however. Therefore M_f, when possible, is given as well. As discussed above, M_f is nearly equal to the CEC. The French "V_B" data should be multiplied with 2.67 [meq] to obtain M_f.

Class	Description	Identification parameters and boundary values				Sub class
A	Finegrained soils	D_{max} < 50 mm Fraction passing 80µm >35%	MBA_s[1] < 2.5			A_1
			12 < I_p < 25 or 2.5 < MBA_s <6[2]			A_2
			25 < I_p < 40 or 6 < MBA_s <8[2]			A_3
			I_p > 40 or MBA_s >8[2]			A_4
B	Sandy and gravelly soils with fines	D_{max} < 50 mm Fraction passing 80µm <35% MBA_s > 0.1	Fraction passing 80µm < 12%	Fraction passing 2 mm > 70%	MBA_s < 0.2	B_1
					MBA_s > 0.2	B_2
				Fraction passing 2 mm < 70%	MBA_s < 0.2	B_3
					MBA_s > 0.2	B_4
			Fraction passing 80µm: 12 - 35%	MBA_s < 1.5		B_5
				MBA_s > 1.5		B_6
C	Soils with fines and coarse material	D_{max} > 50 mm MBA_s > 0.1	Fraction passing 50 mm > 60-80% (material of low workability)			C_1
			Fraction passing 50 mm < 60-80% (material of high workability)			C_2
D	Soil not sensitive for water	Fraction passing 80µm <12% MBA_s < 0.1	D_{max} < 50 mm	Fraction passing 2 mm > 70%		D_1
				Fraction passing 2 mm < 70%		D_2
			D_{max} > 50 mm			D_3

(1) MBA_s = methylene blue adsorption value of the soil
(2) For these soils identification using I_p is preferred.

Table 5. New French proposal for road stone classification, including MBA test (LCPC, 1990)

3. MBA AND GEOTECHNICAL PROPERTIES OF SOILS (LCPC, 1990)

3.1. Soil classification

The Laboratoire des Ponts et Chaussées has published the results of numerous tests on soils and rock in their special publication "Essai au blue de méthylène" (1990). In this chapter a short summary of their results is given. For more details one is referred to the papers in the LCPC report. The MB method has many advantages over the usual tests to classify soils. For example Tourenq and Tran Ngoc Lan (1990) point to the usual identification methods applied for sandy and gravelly soils; the Atterberg limits and the sand equivalent test. The two tests measure different properties on certain size fractions of the soils under study. Figure 8 shows the results obtained by LCPC on the relationship between plasticity index I_p and the sand equivalent value ES with V_B (MBA). If the test is carried out on a (fine) size fraction (o/d), then the MBA of the total soil (o/D) can be found by:

$$MBA_{o/D} = MBA_{o/d} \times C_d/100 \qquad (5)$$

C_d = the weight percentage of size fraction o/d in the soil with size distribution o/D

The $MBA_{o/D}$ therefore can act as an index which quantifies the effect of clay present in the soil.

Table 5 is a classification for road base materials applied in France, where the advantage of using MBA values is clearly illustrated. From table 5 can be seen that the MBA test can replace the determination of sand equivalent value (ES) and the Atterberg limits. Especially for the determination of Atterberg limits quite some laboratory work is needed. The determination of the percentage of fines ($< 80\ \mu m$) can be done with the simple "densitometer" method (LCPC, 1990, p. 16). The MBA can be determined on the fine fraction. Compared with the Atterberg limits determination and the sand equivalent test, the MBA test is the only one which obeys the law of additivity: the amount of MB adsorbed by a mixture is exactly equal to the sum of the amounts adsorbed by the masses of clays present in the mixture. This does not hold for the other two tests (Tourenq and Tran Ngoc Lan, op. cit.). From Figure 8 can be deduced that the MBA test can replace the determination of plasticity index Ip without problem. The sand equivalent test should be kept to describe soil with ES > 60. For sands with ES < 60, the MBA test can distinguish between soils with kaolinite clay, which adsorb little and soils with smectite clay, which adsorb much.

For fine grained soils, which normally are classified with use of the Atterberg limits, the following correlations have been found (for soils without carbonates):

For: $0 < MBA < 1.9$

$$W_L = 17.8\ MBA + 6; \qquad (6)$$
$$I_p = 14.65\ MBA - 11; \qquad (7)$$

for $1.9 < MBA < 2.4$

$$W_L = 17.4\ MBA - 5; \qquad (8)$$
$$I_p = 9\ MBA - 7.6; \qquad (9)$$

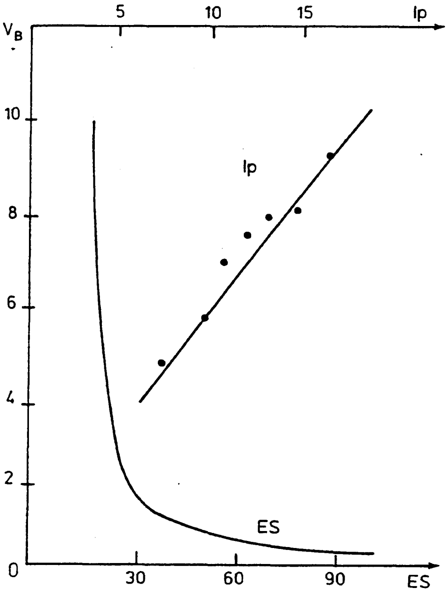


Figure 8. Variation of plasticity index I_p and sand equivalent value ES with MBA value V_B.

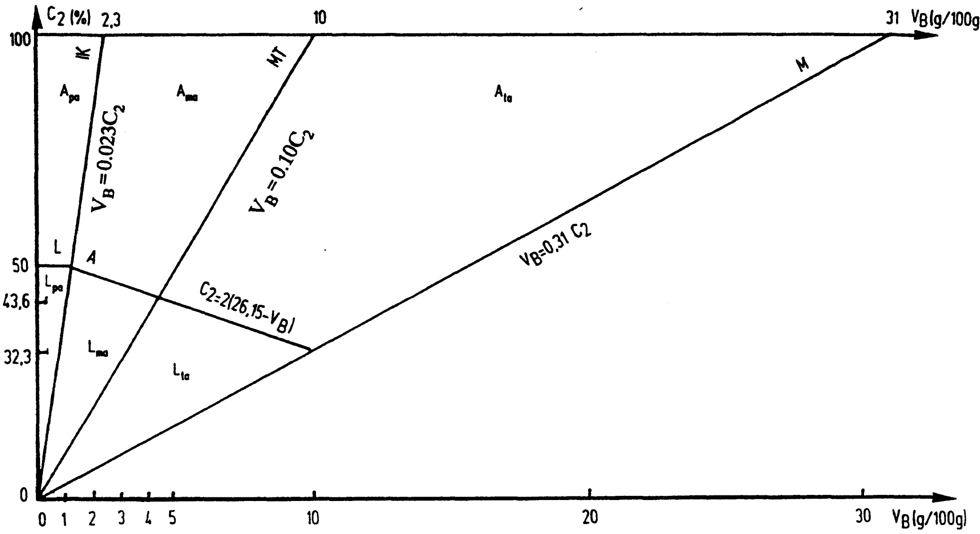


Figure 9. New classification for fine grained soils (LCPC 1990), according to MBA value and clay (< 2 μm) content.

for MBA > 2.4

W_L = 7.53 MBA + 10.2; (10)
I_p = 5.23 MBA - 5.4; (11)

Figure 9 gives the classification of fine grained soils as proposed by LCPC, where the percentage of clay (C_2 = content of particles < 2 μm in the soil) is compared with the MBA (V_B) value. Fine grained soils are soils with more than 50% fines (size ≤ 80μm). The line MT in Figure 9 corresponds to a soil with about 25% of montmorillonite in the clay fraction. This line separates "moderately active" soils from "very active" soils. The following classification has been proposed:

A_{pa} = argile peu active = non active clay
A_{ma} = argile moyennement active = moderately active clay
A_{ta} = argile très active = very active clay
L_{pa} = limon peu active = non active silt
L_{ma} = limon moyennement active = moderately active silt
L_{ta} = limon très active = very active silt.

A similar diagram is developed for sands and gravels, Figure 10. These granular soils have less than 50% fines.
The symbols in this diagram are given below.

SA = clayey sand
SL = silty sand
GA = clayey gravel
GL = silty gravel
b = bien gradués = well graded
m = mal gradués = badly graded

The distinction between gravel and sand is made according to the diagram of Figure 11, where C_{80} signifies the percentage of fines < 80 μm in the soils and C_{2000} the percentage of sands < 2 mm in the soil (LCPC, 1990, p. 22, 23).

3.2. Geotechnical properties of soils

The activity of clay minerals in a soil was defined by Skempton (1953) as follows:

$$A_c = \frac{I_p}{C_2} \qquad (12)$$

I_p = plasticity index
C_2 = percentage of clay-size fraction (< 2 μm) in the soil.

For pure clays the following activities were found:

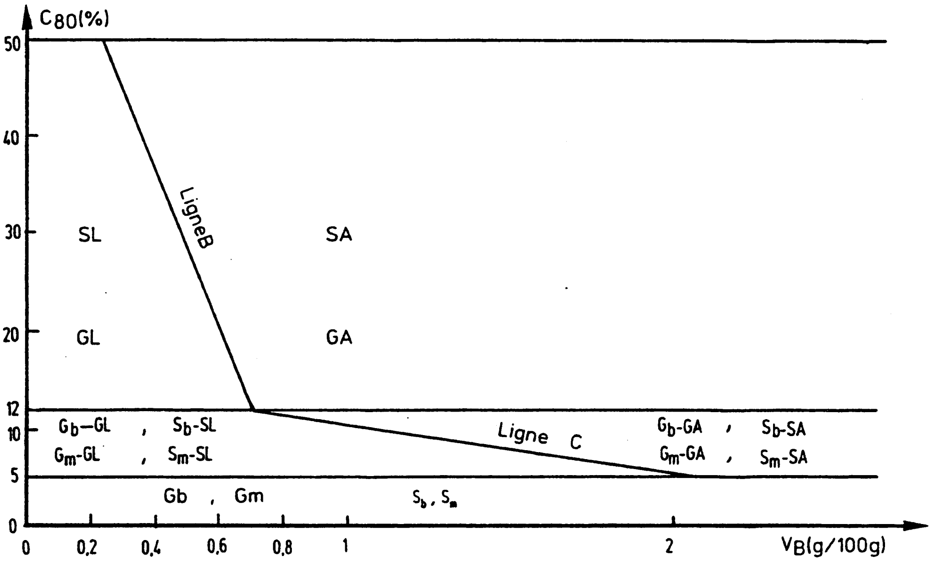


Figure 10. Distiction between clayey and silty granular soils, based on MBA (V_B) value and fines fraction (< 80 µm).

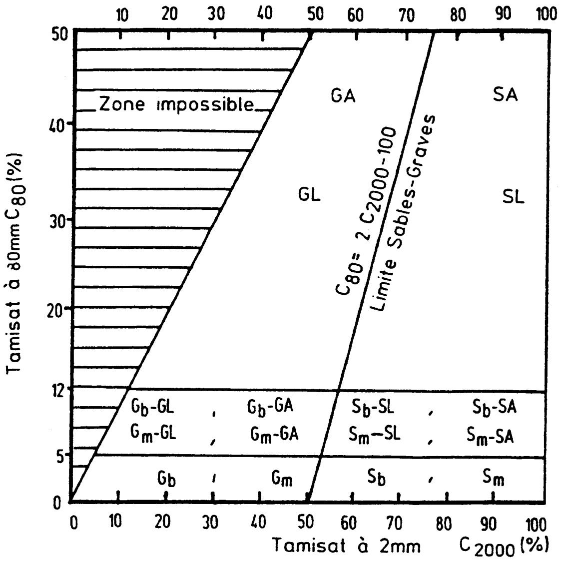


Figure 11. Distinction sand and gravel according to LCPC, based on percentage fines (< 80 µm) and percentage sand (< 2 mm).

Clay mineral	A_c
Kaolinite	0.33 - 0.46
Illite	0.90
Ca-montmorillonite	1.50
Na-montmorillonite	7.20

Skempton (1963) proposed the following soil classification:

CLASS	A_c
1. inactive soil	< 0.50
2. inactive soil	0.50 - 0.75
3. normal soil	0.75 - 1.25
4. active soil	1.25 - 2
5. very active soil	> 2

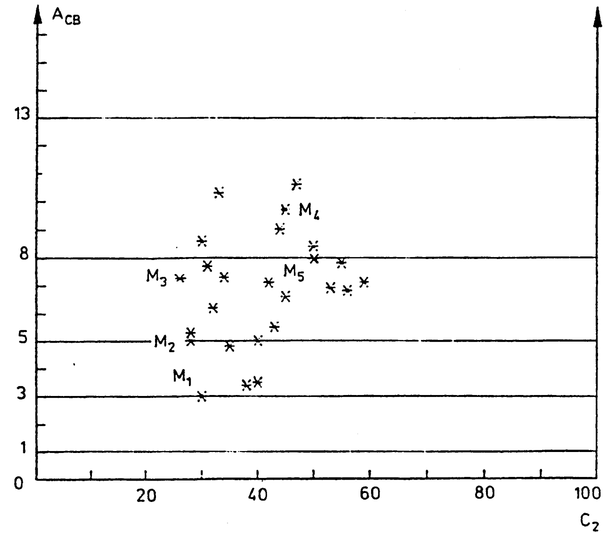
Using the relationships (5), (7), (9), (11) we can obtain A_c from the MBA test, and the result of a sieve analysis.

LCPC (1990, p. 36) has proposed an activity index based on MBA:

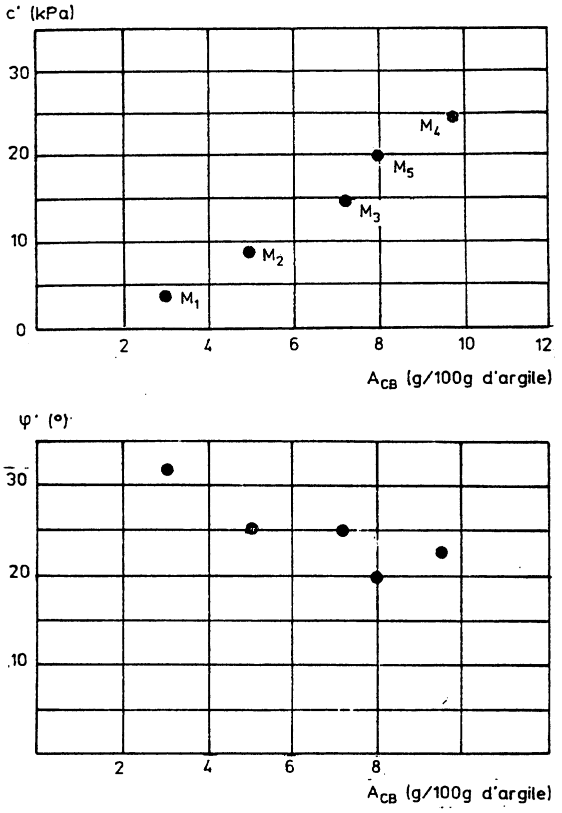
$$A_{CB} = \frac{100\ MBA}{C_2} \tag{13}$$

The following classes are proposed:

CLASS	A_{CB}
1. Non-clay soil	< 1
2. Inactive soil	1 - 3
3. Slightly active soil	3 - 5
4. Normal soil	5 - 8
5. Active soil	8 - 13
6. Very active soil	13 - 18
7. Noxious soil	> 18



a) Diagramme d'identification des sols.



c) Relations entre la cohésion, l'angle de frottement interne et l'activité de bleu.

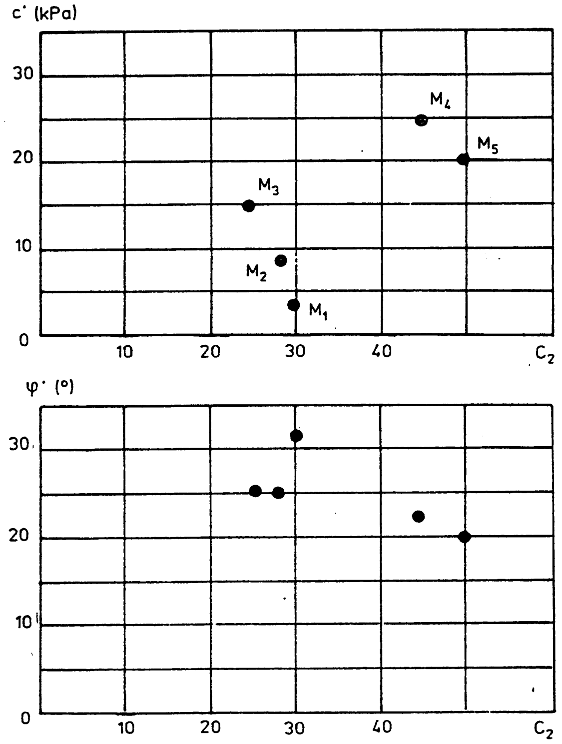


Fig. 9

b) Relations entre la cohésion, l'angle de frottement interne et le pourcentage d'éléments inférieurs à 2 μm.

TABLEAU VIII

Caractéristiques géotechniques et minéralogiques des échantillons d'argile du Miocène

	C_2 (< 2 μm) (%)	A_{cB} (g/100 g d'argile)	Composition minéralogique de la fraction < 2 μm				c' (kPa)	φ' (degré)
			K (%)	I (%)	M (%)	Interstratifiés chlorite-vermiculite (%)		
M_1	30	3	20	55		25	4	32
M_2	28	5	20	65		15	9	25
M_3	25	7,2	20	40	40		15	25
M_4	45	9,7	20	80			25	23
M_5	50	8	25	50	25		20	20

Figure 12. Results of tests on Miocene clay (Lautrin, 1990). K = Kaolinite, I = Illite, M = Montmorillonite.

A Miocene clay from the Aquitaine basin was classified this way and consolidated non drained triaxial tests were performed. The results of this study are reproduced as Figure 12 (Lautrin, 1990). As expected, clay activity is related to shear strength.

4. MBA AND DURABILITY OF ROCK

The MB test can also be performed on crushed rock aggregate or stone. This requires crushing the rock to a size where the clay particles become exposed. Normally a size < 100 μm will be sufficient. From a batch of aggregate commonly 1 kg is crushed and the test is performed on 2 g of the finely ground rock (Appendix 1).

Wimpey Laboratories (UK) has given guidelines to assess soundness of rock aggregate (Table 6).

Class	MBA [g/100g]	M_f [meq/100g]
Acceptable	< 0.7	< 1.9
Marginal	0.7 - 1.0	1.9 - 2.7
Unsound	> 1.0	> 2.7

Table 6. Indication of rock durability (Wimpey Laboratories, UK)

The MBA values determined on rock aggregate are a function of clay mineral content and clay type. If the percentage of clay present is known, the clay type may be inferred. Typical values for the three major clay types are given in Table 7.

Clay mineral	range MBA [g/100g]	range M_f (CEC) [meq/100g]
Kaolinite	2 - 5	5 - 15
Illite	5 - 15	15 - 40
Montmorillonite	15 - 40	40 - 100

Table 7. Typical range of adsorption values for the common clay minerals

To appreciate the effect of swelling clay in rock, two examples of deterioration that can occur in practice are given.

1. Limestone from a rock quarry near Tunis was used as rip-rap to protect the slopes of Lake Tunis. The quarry is in strong limestone, locally layered and laminated. The climate in the area is arid. When the rock blocks became exposed to wetting and drying conditions, about 30% of them deteriorated to rock powder within a few months of time. Four rock samples were provided for study. The rocks were partly crushed and the MBA test was performed on the rock powder. Four thin sections were prepared for microscopic study. These were stained in a MB solution. By staining, the adsorbing minerals are coloured blue. The results of the

MB test are given in Table 8.

Sample No.	M_f [meq/100 g]	Sample description
1	6.6	Laminated Calcilutite, stained clay in layers + patches
1	6.1	
2	1.9	stained clay highly dispersed
3	0.9	local stained parts, in high concentrations
3	1.9	
4	0.9	

Table 8. Results of MBA test on limestone blocks from Lake Tunis rip rap.

Parts of the rocks were ground and the clay fraction was concentrated, to perform an X-ray examination. The following minerals were identified in the clay-size fraction: quartz, kaolinite, montmorillonite and possibly chlorite.

It is obvious that the swelling clay montmorillonite was the cause of the problem. When wetting and drying of the rock occurs, the layers and laminae of clay will act as small pumps: expanding when wet and shrinking when dry. This may lead to crack growth, with resulting enlargement of the areas in the interior of the rock that will be wetted and disintegration of the blocks.

2. Another way that rock may disintegrate for the same reason is possibly less obvious. If rock which contains some swelling clay (for example argillaceous mudstones) is used for road base aggregate, which - when the road is well constructed - is normally well drained and dry, deterioration has been reported by the following mechanism. Due to the dynamic loading by the traffic, pressure differences within the rock particles cause water to migrate from pore to pore. If swelling clay comes into contact with this water it will start to expand and may cause crack growth. It is known that swelling pressures up to 2 MPa can occur due to clay swelling (Fookes et al, 1988). Due to this mechanism the rock particles start to degrade and fines may concentrate between the road base and black top, with subsequent failure of the road structure.

The two examples given above illustrate that, when swelling clay is present, the following factors determine the durability of the rock.

1. clay activity (MBA and percentage of clay present)
2. microstructural position of the clay
3. a wetting- and drying mechanism.

The above made us suspicious that probably not only the MBA value of the crushed rock is sufficient to predict durability, but the microstructural position had to be evaluated as well.

Therefore microscopic examination is recommended.

A suite of rock aggregate used as ballast for railway tracks was examined this way. Apart from determining MBA also the percentage of stained mineral in the rock was obtained by estimating volume percentage present in thin section. The following formula allows one to obtain an impression of the MBA of the "adsorbing mineral" (this will be an average value for all adsorbing mineral types present).

$$MBA_{min} = \frac{MBA_{rock}}{vol.\%} . \frac{\rho_{min}}{\rho_{rock}} .100 \qquad (14)$$

If we would know the density difference between mineral and rock, the MBA_{min} can be derived. Table 9 gives a list of common densities of minerals. From the table we can deduce that commonly the clay minerals have more or less the same density as the minerals in the rock powder used for the MBA_{rock} determination. However, when smectites are present, they will be present in the expanded state and will have a low density. If this is the case, the ρ_{min}/ρ_{rock} ratio will be about 1.7/2.6 = 0.7. This means that the derived estimate of MBA_{min} will be lower if a swelling clay mineral occurs. If we assume that the densities of rock and mineral are equal, we have a conservative guess of the MBA of the mineral (i.e. the values will be high).

Mineral	Density [Mg/m^3]
Kaolinite	2.6 - 2.7
Illite	2.6 - 2.9
Smectites	1.7 - 2.7
Serpentinites	2.4 - 2.7
Chlorites	2.6 - 3.3
Talc	2.6 - 2.8
Glauconite	2.2 - 2.8
Muscovite	2.8 - 2.9
Biotite	3.0 - 3.1
Quartz	2.5 - 2.8
Plagioclase	2.6 - 2.8
Kalifeldspar	2.5 - 2.6
Amphibole	3.1 - 3.3
Pyroxene	3.2 - 3.6

Table 9. Densities of minerals

rock type	Vol.% stained	MBA (g%)	MBA min (g%)	0.7*MBA min (g%)	Deval (wet)
andesite *	1	0.35	35.1	24.6	9.7
andesite *	1	0.59	58.5	41.0	9.1
andesite *	5	1.29	25.7	18.0	6.0
andesitic basalt *	1	0.35	35.1	24.6	9.6
andesitic basalt *	1	0.82	81.9	57.3	9.0
basalt	5	0.35	7.0	4.9	14.9
dacite *	20	2.11	10.5	7.4	7.8
granite	3	0.35	11.7	8.2	14.6
granite *	4	0.70	20.1	14.0	12.1
granite *	18	0.94	5.2	3.6	8.7
granodiorite	10	0.59	5.9	4.1	15.0
quartz diorite	22	0.35	1.6	1.1	20.1
dolomite *	1	0.35	35.1	24.6	18.2
limestone *	1	0.23	23.4	16.4	6.2
limestone *	1	0.23	23.4	16.4	10.3
limestone	5	0.35	7.0	4.9	9.3
limestone	15	0.59	3.9	2.7	5.9
quartz arenite	10	0.35	3.5	2.5	10.5
quartz arenite *	1	0.47	46.8	32.8	6.2
quartz arenite *	15	0.82	5.5	3.8	7.4
graywacke	8	0.70	8.8	6.1	10.6
metabasalt	5	0.47	9.4	6.6	13.7
metagabbro *	45	1.17	2.6	1.8	5.5
gneiss *	1	0.35	35.1	24.6	9.3
gneiss *	1	0.59	58.5	41.0	21.5

*Table 10. Results of petrographic examination, MBA test and Deval test on railway ballast aggregate. Rocks indicated by * were considered suspect after petrographic examination of MB stained thin sections.*

Apart from the microscopic examination and the MBA test, also the wet Deval attrition test has been carried out (Table 10). It can be seen that using formula (14), and applying a density ratio of 1, unrealistically high values of MBA_{min} are obtained. Using the above mentioned ratio of 0.7, the estimated MBA_{min} values approach realistic values for smectite. In this example, the following criteria were used to indicate potential durability problems with regard to swelling clays:

1. MBA > 0.7 g/100g for the aggregate
2. MBA_{min} > 10 if present in vol.% > 5 *(MBA_{min} determined with eq.14; $\rho_{min}/\rho_{rock} = 1$)*
3. MBA_{min} > 20

If either of these criteria were met, the rock was considered suspect. These rocks are indicated in Table 10, and are plotted as filled squares in Figure 11. In Figure 11 the results of the MBA test and the wet Deval test are plotted. The result of the Deval attrition test is given in Deval numbers. A higher number indicates better performance. The MBA test results are plotted against the vertical axis. An MBA value > 0.7 is considered marginal, > 1 indicates unsound rock. It is thought that the wet Deval test indicates also degradation due to the action of the clay. The result shows that most of the rocks considered suspect performed badly in the Deval test, including rocks which would pass the MBA < 0.7 criterion (sound rock; Table 6).

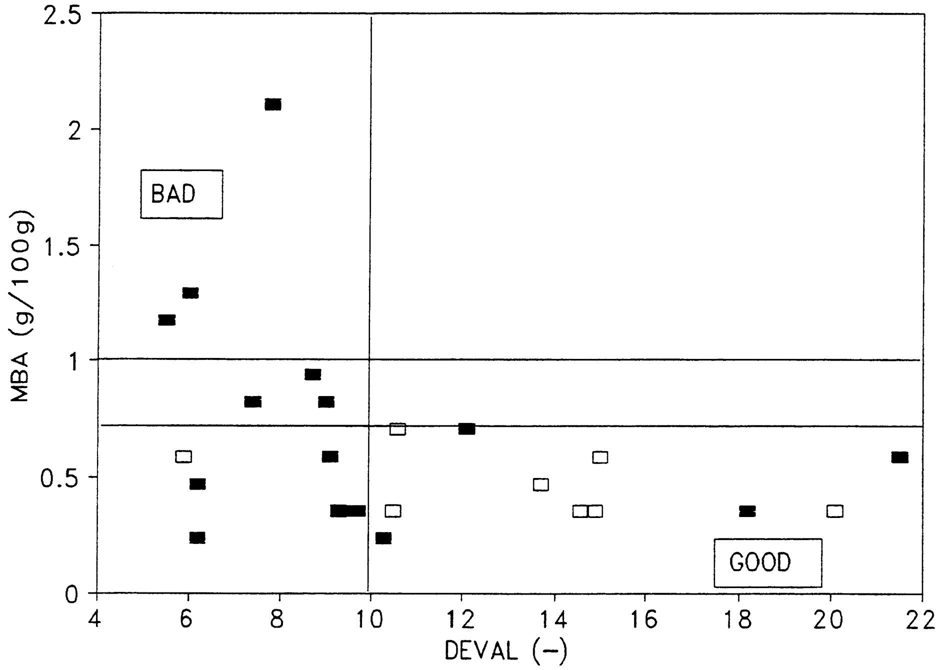


Figure 11. The filled squares indicate rock considered suspicious after petrographic examination of stained thin sections and the MBA test. The wet Deval coefficient < 10 indicates poor attrition resistance.

Only by this method of staining rock thin sections, minute amounts (around 1 vol.% or less) of smectites can be detected and potentially deleterious rock indicated. It is thought that this method should be included in the routine petrographic examination of rock construction materials, because swelling clays can occur in any weathering grade of rock, including fresh.

Figure 11 also shows four rocks that were suspect, but performed well in the Deval test. Most of these have 1 vol.% (or less) clay. It should be noted that petrographic examination has the function of indicating potential hazard. In this example only vol.% and MBA values were considered, not microstructural position. The one sample which was considered sound, both by the MBA test and the petrographic MBA test, but with Deval coefficient 5.9, is a limestone with 15 % clay, were the clay is surrounding the calcite grains. This rock shows microstructural weakness, which also bears out in the Deval test.

5. CONCLUSION

This survey has shown that the methylene blue method is a very useful aid in the study of geotechnical properties of geomaterials. The MBA test gives direct information of the activity of clays present in the soil or rock. MBA is directly related to swelling potential of clays, which is the property that determines mechanical behaviour. The experience of LCPC shows that MBA can reliably and comfortably be used for geotechnical classification of soils. Also in the study of rock intended for construction purposes MB is very valuable. If the spot test on ground rock is done in combination with a study of stained thin sections, a very good impression can be gained of the potential soundness of the rock.

A source of error lies in the different ways that methylene blue adsorption is reported. The best way of reporting MB adsorption is in milli-equivalents adsorbed by 100 g of soil or ground rock [meq/100g]

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APPENDIX 1: THE METHYLENE BLUE ADSORPTION SPOT TEST
JUNE 1992

1. Scope of the test

This test is used to quantify the adsorption of clay mineral (smectite group) present in an aggregate and hence to indicate the soundness of the aggregate. If a significant amount of methylene blue is adsorbed by the soil or ground rock material, this may indicate the presence of swelling clay minerals, although there exist substances that also may adsorb methylene blue. Further study, for example using specialised X-ray diffraction techniques suitable to identify smectite clay minerals, is necessary to assess the true nature of the adsorbing substance. Low MBA (methylene blue adsorption) values, however, nearly always indicate absence of significant amounts of swelling clay minerals. If a petrographic study is carried out concurrently, the adsorbing minerals may be stained, by immersing the thin sections with the methylene blue solution. In this way the volumetric amount of adsorbing minerals can be estimated and an educated guess of the nature of the clay mineral may be made. The methylene blue test is an alternative way to determine the cation exchange capacity of a soil or finely ground rock.

2. Apparatus and reagents

- 25 ml burette mounted on stand
- 250 ml Erlenmeyer flasks
- 100 ml volumetric flask and stopper
- 250 ml beakers
- glass stirring rod
- magnetic stirrer
- small clock glasses
- sample containers
- spatula
- Whatman No. 40 filter papers (12.5 cm diameter)
- distilled or de-ionised (demineralized) water
- Methylene Blue
- chemical waste tank
- analytical balance; aggregate crusher; grinding apparatus; riffle boxes; scoop; metal trays; an oven.

3. Preparation of the Methylene Blue solution

The crystalline Methylene Blue (3.9-bis-dimethylamino-phynazothionium-chloride; $C_{16}H_{18}N_3ClS$) has to be oven-dried for several hours at 105 degrees C to expel water, because it is hygroscopic. A 0.0094 N solution is prepared by dissolving 3.0 g of the oven-dried Methylene Blue crystals in 250 ml destilled water. The solution is cooled and diluted to 1 l. Alternatively, the solution can be prepared by dissolving a certain weight of methylene blue crystals in destilled water and determine the normality of the solution. To determine the hygroscopic water content of the MB, a sample of the crystalline dye is dried at 105 °C and the loss of the weight, x, is determined (a typical weight loss is about 12.34 %). The normality of a MB solution can then be calculated:

$$N = (c \times 1000)/319.9 \times (100.00 - x)/100 \quad [\text{meq/l}]$$

c = concentration methylene blue solution [g/ml]
x = weight loss of crystalline dye by drying, in percentages [%]

4. Preparation of the aggregate suspension

If the MBA value of a soil has to be prepared, the soil has to be sieved. The test has to be performed on the fine fraction of the soil (at least smaller than 63 micrometer: silt and clay fraction). The fines content "f" of the soil has to be determined.

If the MBA content of a rock has to be determined, a representative portion of the rock has to be ground down to
smaller than 0.063 mm.

Prepare from the rock or soil aggregate a very fine grained powder by drying, crushing and sieving, as described above. The powder must be representative of the aggregate or rock composition or the fines fraction of the soil. The grainsize must be less than 63 micrometer.

Take a part of the sample, weigh it, and dry it in the oven at 105 degrees Celcius to determine the water content of the sample. (Remember that the MBA test has to be performed at least twice; keep enough undried sample for this purpose).

Make a suspension of the undried aggregate powder (the amount should correspond to about 2 g dried aggregate powder) in the Erlenmeyer flask with 30 ml distilled or demineralized water.

The crushed rock or soil may come from a small sample or handspecimen. If a representative aggregate sample is available, the following procedure is recommended (Wimpey Laboratories, UK, see Higgs, 1986).

To prepare the test sample, riffle the sample of aggregate down to a portion of about 1 kg and crush it in a jaw crusher to passing the 6.3 mm sieve. Then riffle the portion down to about 100 g and, using the jaw crusher, crush it as finely as possible (say passing 0.425 mm). Follow this by grinding it in a mechanical pestle and mortar until nearly all of it passes the 0.063 mm sieve. The material retained on the 0.063 mm sieve is ground to passing this sieve using a hand agate pestle and mortar. A portion of the sample has to be used for the determination of the watercontent (see above).

5. Procedure of the test

From the Methylene Blue solution 0.5 ml is added to the aggregate suspension by means of a 25 ml burette. Shaking during the addition is necessary, for which a magnetic stirrer may be used. To perform the titration, add successive volumes of 0.5 ml of the methylene blue solution to the Erlenmeyer flask. After each addition, agitate the flask for 1 min. and remove a drop of the dispersion with the glass rod and dab it carefully on a sheet of filter paper. Initially, a circle of dust is formed which is coloured dark blue and has a distinct edge, and is surrounded by a ring of clear water.

When the edge of the dust circle appears fuzzy and/or is surrounding by a narrow light blue halo, agitate the flask for 1 more min. and do another spot test. If the halo has disappeared, add more blue. If there is still a halo, agitate the flask for a further 2 min. and do another spot test. Whatever the outcome of this test, add more blue, agitate for 2 min. do a spot test, then agitate for a further 2 min. and do another spot test. This sequence, with a total of 4 min. of agitation is repeated until there is a definite light blue halo. It is recommended to note down the sample number and the amount of methylene blue added below each spot on the filter paper.

To determine the end-point, hold the filter paper up to daylight while it is still damp, and compare the dust circles made after 4 min. of agitation. It should then be possible to see where the halo first appears and thus where the end-point is. The corresponding volume of methylene blue solution added is noted down.

This procedure is called the 'spot' method. After completing the test, pour the remaining methylene blue solution and the titrated suspension in a chemical waste container, specially determined for this purpose.

6. Calculation of MBA and CEC

The Methylene Blue Adsorption value is - in the literature -normally expressed in grams Methylene Blue adsorpted by 100 grams of sample material, given as g% or g/100g.

$\text{MBA} = \{(X\ \text{g} / Y\ \text{ml}) \times p\ \text{ml MB}\} / (A\ \text{g} / 100\ \text{g});\ [\text{g\%}]$

It is preferred to express the MBA in milliequivalents adsorbed per 100 grams of sample material.

$M_f = (100 \times n \times p\ \text{ml MB}) / A\ \text{g};\ [\text{meq/100g}]$

X = weight of dried methylene blue crystals
Y = volume of diluted methylene blue solution
p = volume of methylene blue solution added
A = weight of **dry** soil or rock powder i.e. a correction for the water content of the sample should be made (see section 4)
n = normality of the MB solution (0.0094 meq/l for a 3 g/l methylene blue solution)

If a soil sample is tested, the MBA and M_f are determined as follows: When the test is carried out on a (fine) size fraction (o/d), then the M_f of the total soil (o/D) can be found by:

$Mf_{o/D} = Mf_{o/d} \times C_d/100$
C_d = the weight percentage of size fraction o/d in the soil with size distribution o/D

The $Mf_{o/D}$ or the similarly determined $MBA_{o/D}$ can act as an index which quantifies the effect of clay present in the soil.

M_f can be regarded as a good approximation of cation exchange capacity (CEC).

7. Reporting of results

At least two determinations of the MBA adsorption value should be done on each sample; the average is reported.

The M_f value should be reported; the cation exchange capacity should be given with an accuracy of 0.1 meq/100g. To compare the data with literature also the MBA value should be calculated with an accuracy of 0.1 g/100 g.

It is advisable to keep record of
- the amount of soil or ground rock used (with 0.01 g accuracy)
- the water content of the sample
- the amount of methylene blue solution added (with accuracy of 0.5 ml)

Together with the result of the calculations, the filter paper, on which the sample number and the amounts of MB (in ml) are noted down, should be kept in the laboratory files.

8. Interpretation of results

Limiting values used in the UK (Wimpey Lab., see Higgs, 1986) are 1.0 for basaltic rock and 0.7 for coarse grained sandstone. Cole and Sandy (1980) also give a boundary for unsound basaltic aggregate, which (recalculated) is 1.5 g/100 g MB. That value is also given as a boundary value for rock by Tran Ngog Lan (1985). The values of Wimpey Lab. are given in the following table.

Indication of durability	MBA (g/100g)	M_f (meq/100g)
Acceptable	< 0.7	< 1.9
Marginal	0.7 - 1.0	1.9 - 2.7
Unsound	> 1.0	> 2.7

Some characteristic MBA values for soils and rocks are given in the following table.

Mineral	MBA (g/100g)	M_f (meq/100g)
Montmorillonite	19 - 36	50 - 96
Bentonites	5 - 23	13 - 61
Chlorite	0.6	1.6
Kaolinite	2 - 5	5 - 13
Illite	1.8 - 2.5	4.8 - 6.7
Halloysite	1.3	3.5
Palygorskite	14.6	39.0
Ferrihydrite	<0.6	< 1.6
Serpentine	1.2	3.2
Basalt	0.11-0.4	0.3 - 1
Granite	0.11-0.4	0.3 - 1
Weathered basalt	18.7	50
Bauxite	1.2	3.2
Organic limestone	0.9	2.4
Marble	<0.6	<1.6

Data from Stapel and Verhoef (1989).

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APPENDIX 2: NEW LCPC PROCEDURE FOR THE SPOT TEST

1. Introduction

The LCPC has developed a test procedure which ensures a satisfactory concentration whilst performing the test. This is accomplished by testing larger quantities of soil or ground rock aggregate; in stead of about 2 g, about 30 g of sample is tested. To attain higher accuracy, a given quantity of kaolinite clay of known MB value is added to the sample. Also it is avoided to dry the test sample. The test procedure is presently considered for standardization as Euro norm. The following text is kindly provided by Mr. A. Mishellany of LCPC, acting also as secretary of CEN working group TC 154/TG 6.

The preparation of the MB solution is not described. On a video tape made by LCPC to illustrate the method the following points are noteworthy:

1. The MB solution is prepared using MB crystals of known water content: the molecular weight of dry methylene blue is used to obtain a solution of 10 g/l.

2. Also in the new procedure the MB value is reported in g MB absorbed by 100 g of sample. But this time, contrary to what can be deduced from earlier literature, the value is referring to solution of dry methylene blue.

3. The solution is kept for a period of maximally 1 month, in special plastic bottles.

2. Preparation of test portion

Knowing the water content w and the fines content f (see NF P 18-597), the mass of sand 0/2 mm, at its raw water content, which has to be washed to extract the fines, is given by the formula:

$$Mh = f' \cdot \frac{w + 100}{f}$$

adjusted to the nearest gram; f' representing the quantity of fines, in grams, which it is desirable to have in the test portion (approx. 30 g).

The mass of sand Mh shall not exceed 300 g.

3. PROCEDURE

3.1 Preparation of the test portion

Place 500 ml of distilled water in the wash bottle.
Place the sand in the platics container and using the wash bottle, add around 100 ml of demineralized or distilled water to cover the material.
Stir well with the spatula.
Poor the contents of the container onto the (0,063 mm) sieve above which is the 0,5 mm discharge sieve, placed over the 3 litres beaker, in several portions so as not to clog the (0,063 mm) sieve; rinse then pour through all the material remaining in the container with the remaining water in the wash bottle. Dry and weigh the oversize from the two sieves, this mass being M. The actual mass q of the fines tested is given by the formula:

$$q = \frac{100Mh}{100+w} - M$$

Having isolated the fines, add to the beaker 30 g of kaolinite, dried to 105°C ± 5°C to a constant mass, of known blue value V_{btak} between 0,5 and 3 g per 100 g of kaolinite. The volume v', expressed in ml, of solution adsorbed by this kaolinite is given by the formula:

$$v' = 30\ V_{btak}$$

The combination of water + fines + kaolinite is agitated for 5 minutes at 600 rev/min, and then continuously at 400 rev/min for the duration of the test using the agitator, with the impellers 1 cm above the base of the container.

3.2 Determination of the quantity of blue adsorbed

3.2.1 Definition of the stain test

After each injection of blue (see 3.2.2), this test consists in taking a drop of suspension by means of the glass rod and depositing it on the filter paper. The stain which is formed is composed of a central deposit of material, of a generally solid blue colour.
The drop taken shall be such that the diameter of the deposit is between 8 and 12 mm.
The test is deemed to be positive if, in the wet zone, a persistent light blue ring appears around the central deposit.

3.2.2 Determination

Using the burette, inject a dose of 5 ml of blue solution into the container, this being followed by the stain test on the filter paper.
The test continues thus until it becomes positive. At this point, without adding anything, the adsorption of blue, which is not instantaneous, is left to proceed while carrying out tests minute by minute.
If the light blue ring disappears on the fifth stain, further elementary additions of 2 ml of blue are made. Each addition is followed by tests always carried out every minute.
These operations are repeated until the test remains positive for five consecutive minutes: the determination is then regarded as completed.
The apparatus is cleaned thoroughly with water. If detergent products have been used, end by rinsing with plenty of water.

4.EXPRESSION OF RESULTS

4.1. Blue value

The blue value of the fines V_{bta} expressed in grams of blue per 100 g of fines is given by the formula.

$$V_{bta} = \frac{V1 - v'}{q}$$

V_1 being the final volume of solution injected, in ml.

4.2. Test of conformity in relation to a specified value

The specification is expressed as a blue value per 100 g of fines, this value being s.
The volume of blue solution to be injected in one go is then: $V_2 = q.s + v'$
The stain test is carried out after eight minutes of stirring. If it is positive, the sand conforms to the specification; if it is negative, add a volume of blue solution equal to qs/10
If the test is still negative, after five minutes, the determination described in 4.2 is carried out. If the test is positive, the sand is deemed to conform to the specification.

APPENDIX 3

POINT COUNTING THIN SECTIONS OF APHANITIC ROCKS STAINED WITH METHYLENE BLUE.

W.E.Pieters

GENERAL.

At the department of Engineering Geology, Delft Technical University, thin sections stained with methylene blue are often used for geotechnical assessment. The methylene blue is applied to the rock surface by submerging the uncovered thin section a short time (up to a few minutes) in a methylene blue solution. Surplus dye is wiped off and the thin section is then covered according to standard procedures.

Some questions arose concerning the nature of staining and the accuracy of point counting, specifically in relation with very fine grained rock. To clarify these matters hypotheses were formulated that were subsequently tested by statistically evaluating differences between observed and expected (on the basis of hypotheses) results of point counting. Point counting was performed on selected thin sections, of which one was especially prepared for this purpose. Statistical evaluation was carried out using the Chi-square test.

QUESTIONS.

Study of thin sections of aphanitic rocks stained with methylene blue raised two questions:

(1) does methylene blue permeate the thin sections and stain deeper situated adsorbing grains apart from those on the surface, and if so, to what extent?

(2) does point counting of the stained minerals record the correct volume percentages?

An affirmative answer to question (1) is suspected to have a direct bearing on the results of point counting (see (2)). A negative answer might have implications for the interpretation of the methylene blue adsorption test, spot method (Stapel & Verhoef, 1989), as might have incomplete permeation.

IMPLICATIONS.

The spot method of methylene blue adsorption uses soil or ground rock material passing 0.15 mm (or passing 0.006 mm, see Appendix 1). If no permeation takes place, the potentially adsorbing minerals in the interior of the grains will remain unstained and will not be taken into consideration in calculations. Similar reasoning applies when permeation is incomplete. In those cases methylene blue adsorption values measured would be functions of, among other things, the grain size distribution of the material passing the delimiting sieve.

If no permeation occurs, question (2) can be answered in a straightforward way. The surface of stained minerals is proportional to their percentage by volume. If, however, deeper situated grains are stained too, they may upset the results of point counting. This would happen when they lie in focus, which is dependent on the distance from the upper surface, the magnification used and optical properties of the microscope (and on refractive indices of the material surrounding the stained minerals). The result could be that a too large amount of grains is recorded and that the volume of methylene blue adsorbing minerals is overestimated (a similar problem is known to occur in the case of small opaque minerals in thin section).

SAMPLE DESCRIPTION.

In order to find an answer to these questions point counting was undertaken on two thin sections prepared from the same plaquette. One is a wedge shaped thin section, especially prepared for this occasion. The thickness variation is from 30 - 0 μm. A line was drawn on the sample separating a zone with thickness 30 - ±15 μm and a zone ±15 - 0 μm thick. Its surface is roughly 3 x 2.5 cm^2. The other is standard 30 μm thick, planparallel, its surface is about 2 x 3 cm^2. Both thin sections were stained with methylene blue.

The thin sections derive from a homogeneous, aphanitic, sparsely phyric ignimbrite. The grain size of the matrix is less than 0.02 - 0.03 mm. Methylene blue adsorbing minerals are dispersed in this matrix. For a description see Table 1.

EQUIPMENT.

Observations were made with a ZEISS polarisation microscope, type UNIVERSAL. Counting was performed with a SWIFT automatic point counter model F 415C.

COUNTING PROCEDURE.

Counting was performed with a stage interval of 1/6 mm in 7 or 8 parallel lines separated about 3 mm from each other and evenly distributed over the sample. These spacings ensured at least 1000 points to be counted. In the case of the wedge shaped sample counting went from the thick to the thin end. Separate record was kept of the counts in the two zones.

Counting was performed at two magnifications (625X and 250X) and on both the top surface and bottom surface.

One operator performed the counting (present author).

DATA.

Measurements were set up to test for influence of depth of field of view, and to test for difference in depth or extent of permeation of methylene blue. To this end the following series of measurements were made (Scheme 1). The data can be found in the appendices indicated in this Scheme.

sample nr.	shape	magnific.	surface	data
1	wedge	625X	top	Table 2.1
		250X	top	Table 2.2
		250X	bottom	Table 2.3
	planparallel	625X	top	Table 4.1
		250X	top	Table 4.2
		250X	bottom	Table 4.3

Scheme 1. Series of measurements.

HYPOTHESES AND THEIR TESTING.

Testing of the hypotheses was executed by means of the Chi-square test of hypothesis, with a 5% level of significance.

HYPOTHESIS 1: only the top surface is stained.

Test 1: varying the position of the focal point between the upper and lower surface.

Result: microscopic observation shows stained minerals at lower levels.

Conclusion: MB did permeate down from the top surface. The hypothesis is invalid.

HYPOTHESIS 2: given that MB permeated to some depth, point counting results are not influenced by depth of field of view.

Test 2.1: observation of differences in counted MB stained minerals between the thick and thin zones and test against expected frequencies. This was done for the wedge shaped sample on the top surface at 625X and 250X and on the bottom surface at 250X.

Result: computed Chi-square values (appendices 3.1.A, 3.1.B, 3.1.C) are smaller than the critical value at the 5% significance level (which is 3.84 for $\nu = 1$).

Conclusion: point counting results are not influenced by depth of field of view.

Comment: a significant difference would indicate permeation of MB and counting of deeper situated stained grains. The difference would be caused by a shallowing of the observable MB stained zone in the first two cases (with a concomitant reduction in MB stained grains recorded) and a surfacing of this zone in the third case with the opposite effect) towards the thin end (Figures 1-4).

The computed Chi-square value for the top surface at 250X (Table 3.1.B) is close to zero: 0.003. In fact it is smaller than the critical value at the 95% significance level (which is 0.0039 for $\nu = 1$), which should lead us to conclude that the agreement is too good at the 5% confidence level (Spiegel, 1981, p202). However, since the count at 625X yields a similar low value, 0.007, but greater than the critical value, it is considered that the lower value is above suspicion.

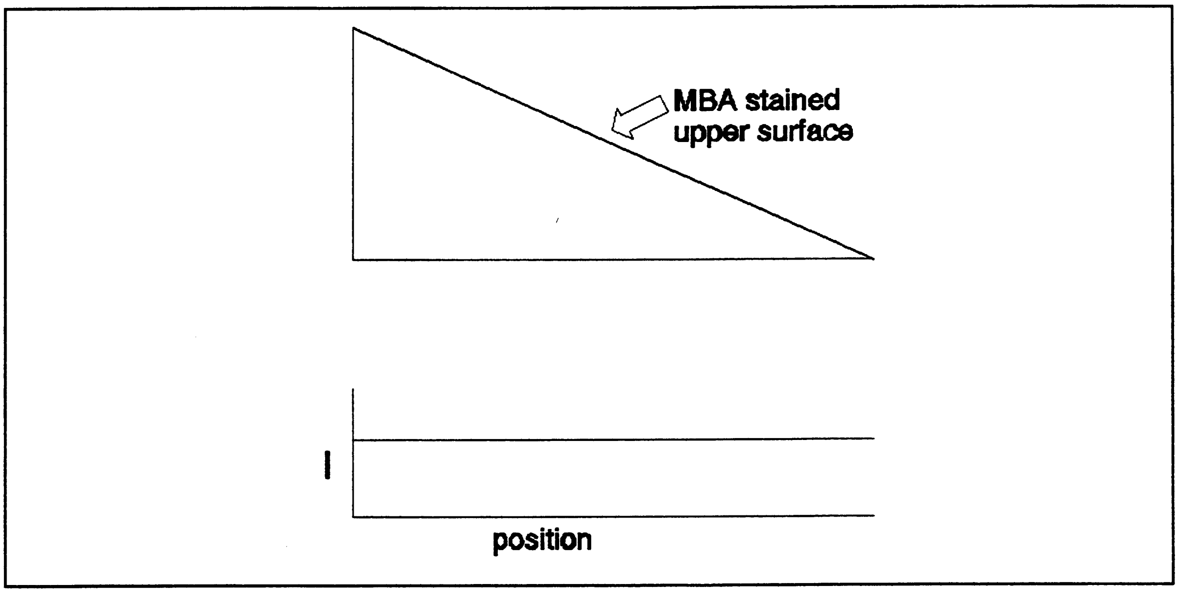

Figure 1 Sketch of wedge shaped thin section, dimensions not to scale. Only upper surface is stained with MB. Depth of field of view is of no importance. Intensity of staining (I) is constant through entire range.

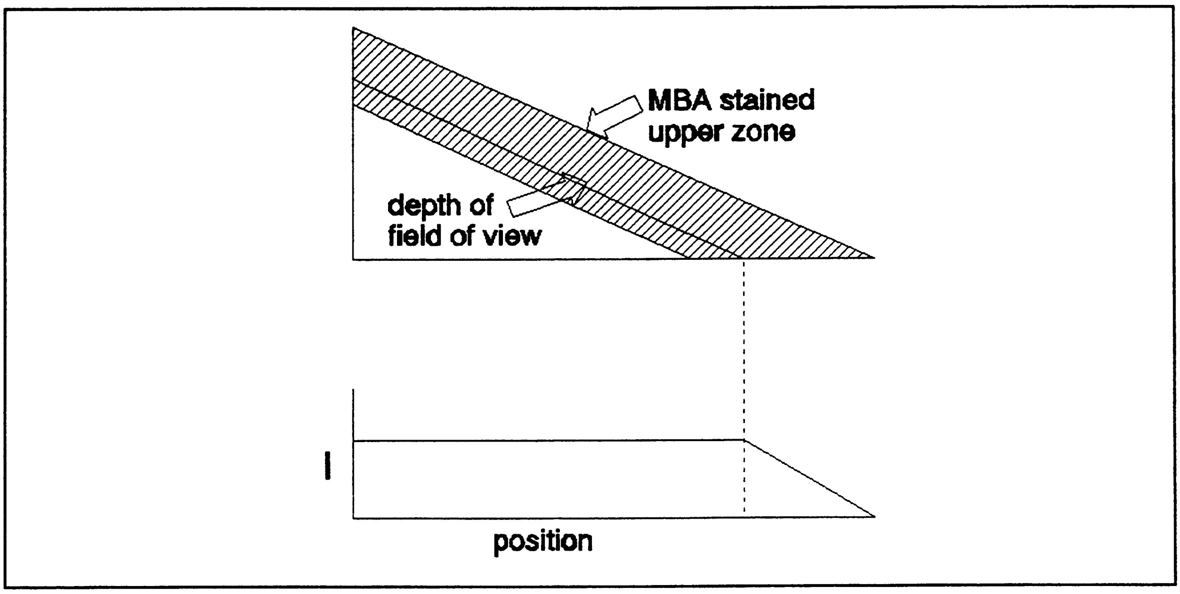

Figure 2 Effect of permeation of MB together with depth of field of view on observed intensity (I) of staining. Possible shielding effects and gradients in staining to deeper levels not taken into account.

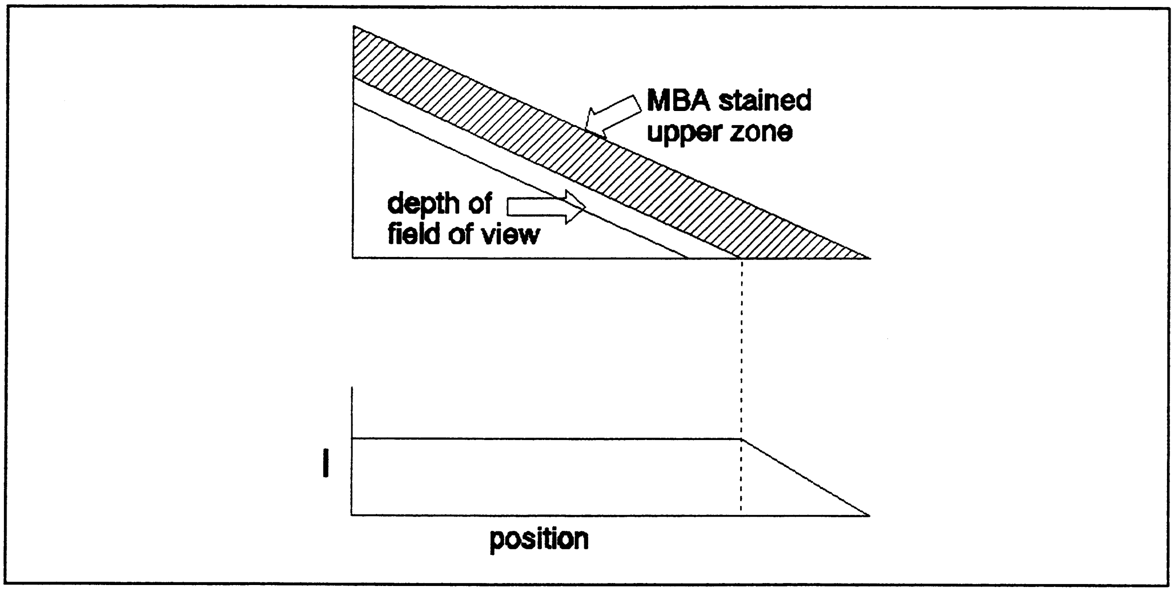

Figure 3 As in Fig. 2. Here depth of field of view extends beyond zone of staining. Diminution of I commences where bottom of zone of staining touches glass plate. In Fig. 2 this occurs where depth of field of view touches glass.

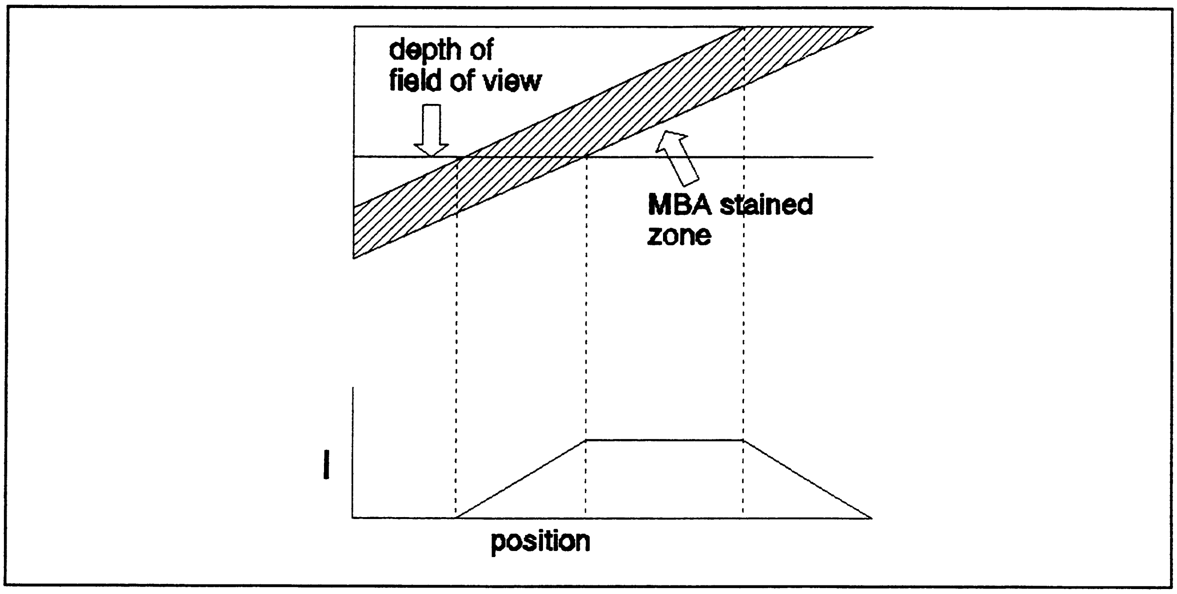

Figure 4 When the lower surface of the wedge-shaped thin section is observed, surfacing of the MB stained zone causes higher I in the thin part, and depending on the depth of field of view, a lowering at the extreme end.

Test 2.2: observation of differences in counted MB stained minerals between two magnifications and test against expected frequencies. This was done for the wedge shaped sample on the top surface between 625X and 250X, for the entire sample, the thick end and the thin end.

Result: computed Chi-square values (Table 3.2.A, 3.2.B, 3.2.C) are smaller than the critical values at the 5% significance level (3.84 for ν = 1).

Conclusion: point counting results are not influenced by differences in depth of field of view at high magnifications.

Comment: a significant difference could be due to the expected greater depth of field of view at the lower magnification, causing more MB stained grains to be recorded. This does not seem to be the case. This effect is possibly partly counteracted by not recording the smallest of grains at the lower magnification.

Because of the geometry of the thin section the effect of shallowing of the MB stained zone towards the thin end is included in two of these tests. Comparison of the outcome of these three and the foregoing test however, lead to the conclusion that this has no significant effect.

HYPOTHESIS 3: permeation of MB caused a homogeneous staining of adsorbing minerals throughout the volume of the sample.

Test 3.1: observation of differences in number of MB stained minerals between top and bottom surfaces of treated sample and test against expected frequencies. This was done for the wedge shaped sample at 250X magnification. The total surface, the thick end and the thin end were tested separately.

Result: computed Chi-square values (Table 3.3.A, 3.3.B, 3.3.C) are greater than the critical values at the 5% significance level (3.84, ν = 1) for the entire surface and the thick end. For the thin end the value is smaller.

Conclusion: permeation of MB is not homogeneous throughout the volume of the sample. There is a marked difference in the degree of staining between the thick and thin ends of the bottom surface.

Comment: The farther away from the top surface the less staining occurs. This explains the difference in number of stained minerals between the two zones.

ADDITIONAL TESTING.

Some additional tests of the foregoing hypotheses were carried out on a planparallel thin section. This was prepared from the same plaquette as the wedge shaped sample. In the following tests the effect of thinning of the sample at one end is ruled out.

Test 2.3: (analogous to test 2.2) observation of differences between counted MB stained minerals at two magnifications and test against expected frequencies. This was done for the entire top surface of planparallel sample 1 at 625X and 250X.

Result: the calculated Chi-square value (Table 5.1) is greater than the critical value at the 5% significance level (3.84, ν = 1).

Conclusion: point counting results are influenced by differences in depth of field of view at high magnifications.

Comment: the result of this test contradicts the outcome of test 2.2.

Test 3.2: (analogous to 3.1) observation of differences in number of MB stained minerals between top and bottom surfaces of treated sample and test against expected frequencies. This was done for the planparallel sample at 250X magnification.

Result: the calculated Chi-square value (Table 5.2) is greater than the critical value at the 5% significance level (3.84, $\nu = 1$).

Conclusion: permeation of MB is not homogeneous throughout the volume of the sample. The bottom surface is markedly less stained than the top surface.

Comment: this outcome corroborates the conclusion of test 3.1. In fact, the high value of Chi-square (greater than the critical value at the 1% significance level) indicates that this is a *highly significant* outcome (Spiegel, 1981, p174).

CONCLUSIONS.

The present investigation is not sufficiently extensive enough to conclude whether the depth of field of view (read magnification) influences the accuracy of point counting of thin sections of aphanitic rock.

Methylene blue dye applied to the uncovered surface of a thin section of a crystalline, aphanitic rock permeates imperfectly to lower levels. This is already noticeable on a scale of 30 μm.

This imperfect permeation has consequences for the interpretation of the methylene blue adsorption test, spot method. The grain size of crystalline, aphanitic material in the sample to be tested, be it ground rock or soil, must be such that complete permeation of MB in the grains occurs. Thus all adsorbing minerals can be stained.

The present investigation suggests that the maximum depth of permeation at which no statistically significant differences are detectable lies around 15 μm. At a depth of 30 μm permeation is notably imperfect.

RECOMMENDATIONS.

The systematic error introduced by counting not only the upper surface, but also a deeper zone of a sample, should theoretically decrease with decrease in depth of field of view. The depth of field of view decreases with increasing magnification. It is therefore recommended that the maximum magnification practicable be used in point counting when high accuracy is required.

Further investigation of the role of depth of field of view on point counting results may be justified to find out if it is warranted to use lower magnifications, which is more agreeable.

This investigation suggests that there is a maximum grain size that can be used in the methylene blue adsorption test, spot method, to ensure staining of all potentially adsorbing minerals present. This size lies around a diameter (spherical particle) of 30 μm (radius 15 μm). A diameter of 60 μm would certainly be too large. Therefore a maximum diameter of grains in the test portion of 30 μm is recommended.

A repeat investigation with an immersion time of the thin section corresponding to the time a ground rock sample stays in the methylene blue solution during the MBA test spot method, could shed some light on the time dependency of permeation in both thin sections and rock particles.

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Spiegel, M.R. 1981. Schaum's outline of theory and problems of STATISTICS SI (Metric) Edition. *McGraw-Hill Book Co.*, vii + 359 pp.

Stapel, E.E. & Verhoef, P.N.W. 1989. The use of the methylene blue adsorption test in assessing the quality of basaltic tuff rock aggregate. *Engineering Geology*, **26**, 233-246.

Table 1.

Petrographic description of sample 1, planparallel.

LABORATORY OF ENGINEERING GEOLOGY, DELFT UNIVERSITY OF TECHNOLOGY

PETROGRAPHIC DESCRIPTION

name : W. E. Pieters
date : 19-6-1991

Project :
location : Sinsy, Korea
coordinates :
spec. no. : 1
thin section no. : 1
collection :

Rock name :

petrographic classification :
rhyolite/rhyodacite/dacite

geological formation :

MACROSCOPIC DESCRIPTION

Greenish grey, extremely fine grained rock with white feldspars.

		mineral	**vol. %**	**grain size**	**description / microstructure**
MINERALOGY	matrix 98.4%	quartz and/or feldspar	68 ± 5.5	0.03 mm	anhedral-subhedral
		quartz	3.0 ± 1.5		
		opaques	4.0 ± 2	0.006 mm	anhedral
		calcite	2.0 ± 1.5	0.03 mm	anhedral
		chlorite	13.3 ± 4	0.02 mm	sub-anhedral
		MB-ads	8.0 ± 3	0.02 mm	anhedral
	pheno-crysts 1.6%	plagioclase altered to:		1.5 mm	euhedral-anhedral, broken
		calcite	0.6		
		MB-ads	acc		
		opaques	acc		
		brown material	1.0		
		opaques	acc	0.2 mm	
		accessories			

GENERAL REMARKS

Abbreviation: MB-ads = methylene blue adsorbing minerals. QF = quartz and/or feldspar.

Phenocrysts in very fine grained matrix. Some flow banding in matrix around phenocrysts. Rest of matrix composed of more or less circular QF domains, partly surrounded by rings of finely divided opaques and MB-ads. This is suggestive of devitrified or recrystallised glass with former perlitic cracks. Plagioclase is sometimes broken. Rock is possibly an ignimbrite.

Volume percentages determined by point counting, 300 points. When applicable 95% confidence interval is given.

Table 2.1.

Data from sample 1, wedge shaped, studied at (12.5 x 1.25 x 40) 625X magnification, top surface.

COUNTS	rest	MB ads	totals
thick	516	25	541
thin	572	27	599
totals	1088	52	1140

VOL. % PER ZONE	rest	MB ads	totals
thick	95.4	4.6	100.0
thin	95.5	4.5	100.0

Table 2.2.

Data from sample 1, wedge shaped, studied at (12.5 x 1.25 x 16) 250X magnification, **top surface**.

COUNTS	rest	MB ads	totals
thick	505	29	534
thin	566	32	598
totals	1071	61	1132

VOL. % PER ZONE	rest	MB ads	totals
thick	94.6	5.4	100.0
thin	94.6	5.4	100.0

Table 2.3.

Data from sample 1, wedge shaped, studied at (12.5 x 1.25 x 16) 250X magnification, **bottom surface**.

COUNTS	rest	MB ads	totals
thick	584	17	601
thin	668	26	694
totals	1252	43	1295

VOL. % PER ZONE	rest	MB ads	totals
thick	97.2	2.8	100.0
thin	96.3	3.7	100.0

Table 3.1.

A. Chi-square test on thick and thin part of sample 1, wedge shaped, at 625X, top surface.

OBSERVED	rest	MB ads	totals
thick	516	25	541
thin	572	27	599
totals	1088	52	1140

EXPECTED	rest	MB ads	totals
thick	516.3	24.7	541.0
thin	571.7	27.3	599.0
totals	1088.0	52.0	1140.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.007.

Table 3.1.

B. Chi-square test on thick and thin part of sample 1, wedge shaped, at 250X, **top surface**.

OBSERVED	rest	MB ads	totals
thick	505	29	534
thin	566	32	598
totals	1071	61	1132

EXPECTED	rest	MB ads	totals
thick	505.2	28.8	534.0
thin	565.8	32.2	598.0
totals	1071.0	61.0	1132.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.003.

C. Chi-square test on thick and thin part of sample 1, wedge shaped, at 250X, **bottom surface**.

OBSERVED	rest	MB ads	totals
thick	584	17	601
thin	668	26	694
totals	1252	43	1295

EXPECTED	rest	MB ads	totals
thick	581.0	20.0	601.0
thin	671.0	23.0	694.0
totals	1252.0	43.0	1295.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.869.

Table 3.2.

A. Chi-square test on the whole of sample 1, wedge shaped, at 625X and 250X, top surfaces.

OBSERVED	rest	MB ads	totals
625X	1088	52	1140
250X	1071	61	1132
totals	2159	113	2272

EXPECTED	rest	MB ads	totals
625X	1083.3	56.7	1140.0
250X	1075.7	56.3	1132.0
totals	2159.0	113.0	2272.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.823.

Table 3.2.

B. Chi-square test on thick part of sample 1, wedge shaped, at 625X and 250X, top surfaces.

OBSERVED	rest	MB ads	totals
625X	516	25	541
250X	505	29	534
totals	1021	54	1075

EXPECTED	rest	MB ads	totals
625X	513.8	27.2	541.0
250X	507.2	26.8	534.0
totals	1021.0	54.0	1075.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.384.

C. Chi-square test on thin part of sample 1, wedge shaped, at 625X and 250X, top surfaces.

OBSERVED	rest	MB ads	totals
625X	572	27	599
250X	566	32	598
totals	1138	59	1197

EXPECTED	rest	MB ads	totals
625X	569.5	29.2	599.0
250X	568.5	29.5	598.0
totals	1138.0	59.0	1197.0

Chi-square = Σ [(observed - expected)^2/expected] = 0.446.

Table 3.3.

A. Chi-square test on the whole of sample 1, wedge shaped, at 250X, top and bottom surfaces.

OBSERVED	rest	MB ads	totals
top	1071	61	1132
bottom	1252	43	1295
totals	2323	104	2427

EXPECTED	rest	MB ads	totals
top	1083.5	48.5	1132.0
bottom	1239.5	55.5	1295.0
totals	2323.0	104.0	2427.0

Chi-square = Σ [(observed - expected)^2/expected] = 6.307.

Table 3.3.

B. Chi-square test on thick part of sample 1, wedge shaped, at 250X, top and bottom surfaces.

OBSERVED	rest	MB ads	totals
top	505	29	534
bottom	584	17	601
totals	1089	46	1135

EXPECTED	rest	MB ads	totals
top	512.4	21.6	534.0
bottom	576.6	24.4	601.0
totals	1089.0	46.0	1135.0

Chi-square = Σ [(observed - expected)^2/expected] = 4.981.

C. Chi-square test on thin part of sample 1, wedge shaped, at 250X, top and bottom surfaces.

OBSERVED	rest	MB ads	totals
top	566	32	598
bottom	668	26	694
totals	1234	58	1292

EXPECTED	rest	MB ads	totals
top	571.2	26.8	598.0
bottom	662.8	31.2	694.0
totals	1234.0	58.0	1292.0

Chi-square = Σ [(observed - expected)^2/expected] = 1.964.

Table 4.1.

Data from sample 1, planparallel, studied at (12.5 x 1.25 x 40) 625X magnification, top surface.

	rest	MB ads	totals
counts	1057	71	1128
volume %	93.7	6.3	100.0

Table 4.2.

Data from sample 1, planparallel, studied at (12.5 x 1.25 x 16) 250X magnification, **top surface**.

	rest	MB ads	totals
counts	1019	108	1127
volume %	90.4	9.6	100.0

Table 4.3.

Data from sample 1, planparallel, studied at (12.5 x 1.25 x 16) 250X magnification, **bottom surface**.

	rest	MB ads	totals
counts	1079	65	1144
volume %	94.3	5.7	100.0

Table 5.1.

Chi-square test on sample 1, **planparallel**, at 625X and 250X, top surfaces.

OBSERVED	rest	MB ads	totals
625X	1057	71	1128
250X	1019	108	1127
totals	2076	179	2255

EXPECTED	rest	MB ads	totals
625X	1038.5	89.5	1128.0
250X	1037.5	89.5	1127.0
totals	1076.0	179.0	2255.0

Chi-square = Σ [(observed - expected)^2/expected] = 8.307.

Table 5.2.

Chi-square test on sample 1, **planparallel**, at 250X, top and bottom surfaces.

OBSERVED	rest	MB ads	totals
top	1019	108	1127
bottom	1079	65	1144
totals	2098	173	2271

EXPECTED	rest	MB ads	totals
top	1041.1	85.9	1127.0
bottom	1056.9	87.1	1144.0
totals	2098.0	173.0	2271.0

Chi-square = Σ [(observed - expected)^2/expected] = 12.224.

Appendix 4: **A STUDY OF A WEATHERING PROFILE**

M. van Tooren

1. INTRODUCTION

Weathering is a very common geological phenomena. It is defined as a process that occurs at or near the surface of the earth and which leads to the degradation of the geological material present. This process takes place under the influence of atmospheric conditions and includes chemical and physical weathering. Physical weathering finally leads to the formation of particles. Chemical weathering processes lead to decomposition of the rock. During the chemical weathering secondary minerals are formed which have a negative effect on the durability of the rock. Physical and chemical weathering often take place simultaneously and even enhance each other.

When naturally occurring rocks are used as construction material this geological definition is not accurate enough. For engineering purposes the engineering time scale becomes important as well as the degradation of the material caused by man. For engineering purposes the definition by Fookes et all ('88) is appropriate. They define the weathering of construction material as : "the degradation or deterioration of naturally occurring construction material under the direct influence of the atmosphere, the hydrosphere and the activities of man, within an engineering time scale".

To enlarge the knowledge about weathering processes a series of rocks with different stages of weathering is studied. The studied series comprise degradation stages of a rhyolite, a porphyritic volcanic rock which has its origin near Dobritz, 30 km. northwest of Dresden, Germany.

The study includes a petrographic examination, the Methylene Blue Adsorption test and the Water Drop Absorption test. The samples were too small too carry out mechanical tests.

2. PETROGRAPHIC EXAMINATION

The weathering profile consists of eight rock pieces. Sample number 1 represents a relatively fresh rock and sample number 8 represents the most weathered product. No further information is available about the fieldrelations of the samples. The samples in which the original rock is visible consist of a rhyolite in which phenocrysts of quartz and feldspar are clearly visible.
Table 1 gives a macroscopic description of the samples.

From each sample two thin sections were prepared which were studied microscopically. In table 2 a summarized description is given. Appendix 1 gives the complete description of the samples.

3. METHYLENE BLUE ADSORPTION

Of each sample one thin section is stained with a solution of methylene blue. Minerals able to swell are coloured blue by this solution. The volume percentage of the swelling minerals present is determined with the aid of a pointcounter. These values are given in table 2.

A powdered piece of rock was used to determine the absolute MBA-value. This determination was carried out twice for each sample and the average values are given in table 2. With the aid of the volume percentage of the swelling minerals and the absolute MBA-value the average swelling potential of the minerals can be estimated (table 2).

4. THE WATER DROP ABSORPTION TEST

This absorption test is a simple and quick test to get some rough information about the water absorption behaviour of the rock. A drop of water is placed on a clean, airdried surface of a particle . The time at which the wet film disappears gives information about the water absorption rate of the rock. The water drop test was carried out thrice. Average results are given in table 3.

5. DISCUSSION AND CONCLUSIONS

Petrographic examination.

Samples 1 to 5 are rhyolites according to the petrographic examination. The mineralogy of these samples is more or less identical. However the texture of these samples varies. Some samples have fragments, others have obviously a flow structure. To be able to study a weathering profile a homogeneous parent rock is necessary. In other words, this series is not appropriate.

Sample no. 1 should represent a fresh rhyolite. Petrographic examination and examination of methylene blue adsorption behaviour reveals that sample no. 1 is not a fresh rhyolite at all, but a rhyolite weathered to a certain degree already. This is also shown by the relatively high absorption rate of a water drop. Thus, the first weathering features of this rhyolite cannot be studied in this profile. X-ray diffraction indicates clay in this sample, probably montmorillonite.

However, some weathering features could be studied.

Which clay mineral formed during the weathering of this rhyolite depended on the amount and the distribution of K-feldspar and glass-spherulites. In the red parts an alteration of K-feldspar into a Methylene Blue adsorbing clay mineral is present. This swelling clay mineral later on changes into kaolinite, a clay mineral with a relatively low swelling potential. In the grey parts K-feldspar is absent, but aggregates of glass-spherulites parallel to the flow structure are present. These spherulites show different stages of crystallisation into K-feldspar and quartz. However, during the weathering kaolinite was formed directly. In these areas no methylene blue, or only a minor amount was adsorbed. The inhomogeneity in the distribution and the amount of K-feldspar and glass spherulites makes a comparison difficult.

Methylene Blue adsorption.

During weathering secondary minerals form. Many secondary minerals have a high swelling potential. An increase in the vol.% of MB-adsorbing minerals in the thin sections of samples 1 to 6 was expected, as well as an increase in the MBA-rock values. However, no such trend is visible (table 2). The inhomogeneous parent rock and the interaction between the reactions

K-feldspar ---> swelling clay mineral ---> kaolinite, and
glass ---> kaolinite

is responsible for this absence.

The high value of MBA-mineral in sample no.1 is due to the presence of montmorillonite, a clay mineral with a high swelling potential. It illustrates the weathering-degree of this sample.

Water drop absorption rate

From the results (table 3) can be concluded that the absorption rate in the greyish parts of the rocks is higher than in the red parts of the rock. Although swelling minerals are present in the red parts the water is quicker absorbed in the grey parts were pores and micropores were formed during weathering. The red parts are relatively impermeable with the exception of sample 1 in which a clay mineral is present with a relatively higher swelling potential.

Durability.

The high MBA-rock values demonstrate that all samples of the series are moderately unsound to unsound.

References

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Fookes, P.G., Gourly, C.S., Ohikere, C. : Rockweathering in engineering time. Quat.Jour.Eng.Geol. London, 1988, Vol.21, pp 33-57

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TABLE 1 : MACROSCOPIC DESCRIPTION OF SAMPLES 1-8

no	colour	texture	cracks	phenocr.	name
1	pinkish-red	cemented fragments	open + filled	quartz feldspar	rhyolite
2	pinkish and greyish	flow structure	filled	quartz feldspar	rhyolite
3	pinkish and white	white rounded fragments in a pinkish matrix	-	quartz feldspar	rhyolite
4	red and grey	flow structure	filled	quartz feldspar	rhyolite
5	grey, some red spots	cemented fragments, in which a flow structure	open	quartz	rhyolite
6	grey	broken into many small particles (4 cm)	open	quartz	claystone
7	white	homogeneously finegrained	-	-	kaolinite
8	white	homogeneously finegrained			kaolinite

TABLE 2 : MICROSCOPIC DESCRIPTION OF SAMPLES 1-8

vol. %	1	2	3	4	5	6	7	8
phenocrysts	2	11	4	8	5	1		
quartz	*	*	*	*	*	*		
plagioclase	*	*	*	*	*	*		
calcite		*	*	*	*	*		
biotite		*	*					
matrix	97	87	95	91	92	60		
glass								
quartz								*
K-feldspar								
plagioclase								
opaque min.								
clay	*							*
open cracks and pores	1	2	1	1	3	39		
MBA vol%	12	31	23	35	22	53		
MBA g%	1.05	1.23	0.97	1.40	1.32	0.84		
MBA min.(average)	8.8	4.0	4.2	4.0	6.0	1.6		

The volume percentages of the minerals were determined with the aid of a pointcounter.

Samples no. 1 and 8 were determined with the aid of X-ray diffraction :
sample 1 : albite, quartz and probably montmorilloniet
sample 8 : quartz and kaolinite

* = minerals present as phenocryst. The matrix was too finegrained to determine the volume percentages of the minerals present.

TABLE 3 : WATERDROP ABSORPTION RATE

sample	minutes	$\sqrt{(x-\bar{x})^2}$
1 - red	8	1.4
2 - red	31	1.4
- grey	20	1.7
3 - red	12	1.4
- grey	7	1.4
4 - red + grey	28	1.7
5 - red	22	1
- grey	9	1.4
6 - grey	1.5	0.5
7 - white	0.1	
- white	0.15	

APPENDIX 1 : MICROSCOPIC DESCRIPTION OF SAMPLES 1-8

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 31-05-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 1
thin section no. : 1 : +MB
collection : 1a: pores blue

Rock name :

petrographic classification :
rhyolite (ignimbritic ?)

geological formation :

MACROSCOPIC DESCRIPTION

pinkish to red fine grained inhomogeneous rock in which fragments can be recognized within a matrix. In both phenocrysts can be recognized. Cracks are visible.

MINERALOGY

mineral	vol. %	grain size mm	description / microstructure
PHENOCRYSTS:	2	0.3-1.5	in fragments and matrix identical.
plagioclase			oligoclase; alteration into fine grained chlorite and sericite.
quartz			hypidiomorphic to rounded with resorption features ; also broken crystals and crystals with deformation lamellae.
MATRIX :	97	0.01-0.2	in fragments and matrix identical. present : quartz, K-feldspar, plagioclase sericite, opaque (goethite or hematite), glass and clay (montmorillonite)
cracks and pores	1		see general remarks.
MBA	12±3.5		see general remarks
accessories			

GENERAL REMARKS

microscopic overview : fine grained fragments with a varying grain size are imbedded in a coarser matrix. Within the fragments a fluidal layering is present.

cracks : - open
- filled with - iron(hydr)oxides and quartz
  - fine grained volcanic material and chlorite

pores : - micropores within or in between the minerals.
- pores due to the weathering of phenocrysts.

MBA : - in clay particles (according to X-ray diffraction this is probably montmorillonite).
- in chlorite.

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 03-06-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 2
thin section no. : 2 : +MB
collection : 2a: pores blue

Rock name :

petrographic classification :
rhyolite - weathered
geological formation :

MACROSCOPIC DESCRIPTION

This sample contains an alternation of red and grey layers - this is a fluidal layering. In the centre of the grey layers white material is present which can be removed by a fingernail. This is probably kaolinite.

MINERALOGY

mineral	vol. %	grain size mm	description / microstructure
PHENOCRYSTS:	11		
quartz		0.1-3	see description of thin section 1
biotite		≤0.3	
plagioclase		0.1-1.8	alteration into chlorite and sericite
calcite		0.1-2	pseudomorph to plagioclase probably due to alteration; contains quartz inclusions
MATRIX :	87	≤0.1	
quartz			
K-feldspar			dusty, due to alteration into clay.
plagioclase			
glass			in spherulites, these can be solitary or can form aggregates; crystallisation into quartz and K-feldspar.
clay			
cracks and pores	2		see general remarks
MBA	31±5.5		see general remarks
accessories			

GENERAL REMARKS

microscopic overview : the red and the grey colours result the distribution of iron(hydr)oxides.
red (20%) : iron(hydr)oxides and solitary glass spherulites.
grey (80%): the glass spherulites are concentrated in aggregates; in the centre are sometimes open spaces visible.

cracks : one crack (width 0.08mm), lately formed, partly filled with iron(hydr)oxides and quartz.

MBA : - the alteration product of K-feldspar = clay
- chlorite

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 05-06-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 3
thin section no. : 3 : +MB
collection : 3a : pores blue

Rock name :

petrographic classification :
rhyolite - weathered

geological formation :

MACROSCOPIC DESCRIPTION

light-pinkish rock in which white spots - no fragments or layers visible.

MINERALOGY

mineral	vol %	grain size mm	description / microstructure
PHENOCRYSTS:	4		see description of thin section 1 and 2
quartz		≤1	
plagioclase		≤1.3	
biotite			
MATRIX :	95	≤0.04	quartz, K-feldspar, plagioclase, glass, opaque, clay
cracks and pores	1		
MBA	23±5		
accessories			

GENERAL REMARKS

MBA : adsorbed by clay particles

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 04-06-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 4
thin section no. : 4 : +MB
collection : 4a: pores blue

Rock name :

petrographic classification :
rhyolite - weathered

geological formation :

MACROSCOPIC DESCRIPTION

This sample resembles sample 2 : red and grey layers alternate, this represents a fluidal layering. In the centre of the grey layers is again a white, soft material visible.
1 crack : filled with red material.

MINERALOGY

mineral	vol. %	grain size mm	description / microstructure
PHENOCRYSTS:	8	0.2-2	
quartz			see description thin section 1
plagioclase			" " " " "
calcite			the calcite seems to replace the plagioclase, intermediate stages are present
MATRIX :	91	≤0.2	
glass			A large part of the red layers consists of glass spherulites. This is also in the grey layers, but here the spherulites are more clustered. Goethite and hematite are alteration products of the K-feldspar but they occur as well in the spherulites.
opaque			
quartz			
biotite			
cracks and pores	1		see general remarks
MBA	35±5.5		see general remarks
accessories			

GENERAL REMARKS

cracks : there are no cracks in the thin sections

pores :
- in the centre of the grey layers
- micro pores in and in between the minerals
- pores due to degassing during lithification

MBA :
- alteration products (clay) of K-feldspar
- chlorite

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 04-06-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 5
thin section no. : 5 : +MB
collection : 5a: pores blue

Rock name :

petrographic classification :
brecciated rhyolite - weathered

geological formation :

MACROSCOPIC DESCRIPTION

Greyish rock with some light-pinkish spots (no sharp boundaries). Fragments visible with a variable size and a variable orientation of the fluidal layering. 1 open crack visible.

MINERALOGY

mineral	vol. %	grain size	description / microstructure
PHENOCRYSTS	5		see description thin section 2 and 4
MATRIX	92		" " " " " " "
cracks and pores	3		
MBA	22±4		
accessories			

GENERAL REMARKS

microscopic overview : the rock resembles sample 2 and 4, but brecciation took place after the solidification of the rock. The fragments were cemented by comparable volcanic material.

differences compared to sample 4 :
- variable orientation of the fluidal texture
- many cracks present, randomly distributed
  - filled with volcanic material; iron (hydr)oxides: quartz or combinations
  - open, width up to 0.01 mm
  - no calcite phenocrysts

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 05-06-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 6
thin section no. : 6 : +MB
collection : 6a : pores blue

Rock name :

petrographic classification :
claystone (weathered rhyolite)

geological formation :

MACROSCOPIC DESCRIPTION

The sample broke into several small fragments. The main size is now less than 1/½/½ cm. The rock has a greyish colour and feels very soft due to the high clay content. No original texture visible.

MINERALOGY

mineral	vol. %	grain size	description / microstructure
PHENOCRYSTS:	1		
quartz			
plagioclase			altered in sericite and clay
MATRIX :	60		
clay			
cracks and pores	39		
MBA	53±5.5		
accessories			

GENERAL REMARKS

microscopic overview : the original red and grey layers can be distinguished :
red : many unrecognizable particles of dust size
a relatively high %MBA
not so many pores
grey : no dust
many pores
a relatively low %MBA

PETROGRAPHIC DESCRIPTION

name : M.M. van Tooren
date : 07-91

Project : Weathering
location : Dobritz
coordinates :
spec. no. : 7 and 8
thin section no. : -
collection :

Rock name :

petrographic classification :
claystone

geological formation :

MACROSCOPIC DESCRIPTION	

mineral	vol. %	grain size	description / microstructure
accessories			

GENERAL REMARKS	No thin sections of these samples were prepared. The mineral composition of sample 8 was identified with the aid of X-ray diffraction. Found were : α-quartz kaolinite

Appendix 5. French norm: P-18-592. Granulats: Essai au blue de méthylène, méthode à la tache.

ISSN 0335-3931

normalisation française

P 18-592
Décembre 1990

Granulats

Essai au bleu de méthylène

Méthode à la tache

E : Aggregates — Methylene blue test — Spot test
D : Granulate — Methylenblau verfahren — Fleck-Methode

Norme expérimentale publiée par l'afnor en décembre 1990.

Les observations relatives à la présente norme expérimentale doivent être adressées à l'afnor, avant le 31 décembre 1992.

Remplace la norme expérimentale de même indice, de juillet 1980.

correspondance À la date de publication de la présente norme, il n'existe pas de norme européenne ou internationale sur le sujet.

analyse Dans la série des normes P 18-... qui concerne les granulats, cette norme définit un essai d'évaluation de la quantité d'argiles présentes dans les fines d'un sable.

descripteurs **Thésaurus International Technique : granulat, propriété, argile,** sable, fines.

modifications Par rapport à la précédente édition, cette norme précise que l'essai doit se faire sur les fines séparées du sable.

corrections

éditée et diffusée par l'association française de normalisation (afnor), tour europe cedex 7 92049 paris la défense — tél. : (1) 42 91 55 55

1^er tirage 90-12

Granulats

BNSR **GRA**

Membres de la commission de normalisation chargée de l'élaboration du présent document

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M	LEROUX	CIMENTS LAFARGE
M	LOT	SOC. DES CARRIERES DE LA MEILLERAIE
M	MAUGET	ENTREPRISE LEFEBVRE
M	PARRIAUD	CONSEIL GENERAL DES PONTS ET CHAUSSEES
M	PARTHENAY	CIMENTS LAFARGE
M	PIKETTY	PIKETTY FRERES
M	TAVANTI	SNCF
MLLE	VINCENSINI	AFNOR

1 OBJET

La présente norme a pour objet de décrire la méthode permettant de déterminer la «valeur de bleu» des fines contenues dans un sable ou une grave. Elle décrit également une méthode rapide de contrôle de conformité des fines par rapport à une «valeur de bleu» spécifiée.

2 DOMAINE D'APPLICATION

La présente norme s'applique aux sables et aux graves d'origine naturelle ou artificielle, utilisés dans les domaines du bâtiment et du génie civil.

3 RÉFÉRENCES

P 18-553	Granulats — Préparation d'un échantillon pour essai.
P 18-595	Granulats — Valeur de bleu de méthylène — Méthode turbidimétrique.
P 18-597	Granulats — Détermination de la propreté des sables — Équivalent de sable à 10 % de fines.

4 GÉNÉRALITÉS

4.1 But de l'essai

Cet essai permet de mesurer la capacité des éléments fins à adsorber du bleu de méthylène.

Le bleu de méthylène étant adsorbé préférentiellement par les argiles, les matières organiques et les hydroxydes de fer, cette capacité rend compte globalement de l'activité de surface de ces éléments.

On appelle «valeur de bleu» des fines, la quantité exprimée en grammes de bleu de méthylène adsorbée par 100 g de fines.

4.2 Principe de l'essai

On injecte successivement des doses élémentaires d'une solution de bleu de méthylène dans le bain aqueux contenant la prise d'essai. On contrôle l'adsorption du bleu après chaque ajout, en effectuant une tache sur un papier filtre (test de la tache, voir paragraphe 7.2.1).

Pour un simple contrôle de conformité, la quantité de bleu spécifiée est injectée en une seule fois.

5 APPAREILLAGE

5.1 Appareillage d'usage courant

Balance dont la portée limite est compatible avec les masses à peser et permettant de faire toutes les pesées avec une précision relative de 0,1 %.

Chronomètre au 1/10 s.

Matériel nécessaire pour effectuer l'échantillonnage du matériau (voir la norme expérimentale P 18-553).

Tamis de 0,08 mm et 0,5 mm ayant un diamètre de 150 mm.

Pissette de 500 ml.

Bécher plastique de 3 l ayant un diamètre intérieur de 155 mm.

Spatule.

5.2 Appareillage spécifique

Une burette de capacité 100 ml ou 50 ml et de graduation 1/10 ml ou 1/5 ml ou une micropipette de 5 ml et une de 2 ml.

Papier filtre : quantitatif et sans cendre (< 0,010) ; grammage : 95 g/m^2 ; épaisseur : 0,20 mm ; vitesse de filtration 75 ; rétention : 8 micromètres.

Une baguette de verre : longueur 300 mm ; diamètre 8 mm.

Un agitateur à ailettes, tournant entre 400 et 700 tr/min. Le diamètre des ailettes est compris entre 70 mm et 80 mm.

Un bac carré en matière plastique de 150 mm de côté et 60 mm de hauteur.

5.3 Produits utilisés

Solution de bleu de méthylène de qualité médicinale à 10 g/l ± 0,1 g/l (voir la norme expérimentale P 18-595, paragraphe 5.3).

La durée maximale d'utilisation de la solution est de un mois. Elle doit être conservée à l'abri de la lumière.

Eau déminéralisée ou distillée.

Kaolinite séchée à 105 °C.

6 PRÉPARATION DE L'ÉCHANTILLON POUR ESSAI

Connaissant les teneurs en eau w et en fines f (voir la norme expérimentale P 18-597), la masse de sable 0-2 mm, à sa teneur en eau en l'état, qu'il faut laver pour en extraire les fines est donnée par la formule :

$$M_h = f' \frac{w + 100}{f}$$

ajustée au gramme près ; f' représentant la quantité de fines, en grammes, qu'il est souhaitable d'avoir dans la prise d'essai (environ 30 g).

La masse de sable M_h ne doit pas dépasser 300 g.

7 EXÉCUTION DE L'ESSAI

7.1 Mise en place de la prise d'essai

Mettre 500 ml d'eau distillée ou déminéralisée dans la pissette.

Placer le sable dans le bac plastique, ajouter à l'aide de la pissette environ 100 ml d'eau déminéralisée ou distillée pour recouvrir le matériau. Bien agiter l'ensemble avec la spatule.

Verser en plusieurs fois le contenu du bac sur le tamis de 0,08 mm surmonté du tamis de décharge de 0,5 mm, l'ensemble étant placé au-dessus du bécher de 3 l. Rincer, pour faire passer la totalité du matériau restant dans le bac avec l'eau qui reste dans la pissette.

Sécher et peser les refus des deux tamis, soit M cette masse.

La masse réelle q de fines soumises à l'essai est donnée par la formule :

$$q = \frac{100\ Mh}{100 + w} - M$$

Après avoir isolé les fines ajouter dans le bécher 30 g de kaolinite de valeur de bleu connue V_{BtaK}.

Le volume v', exprimé en ml, de solution de bleu adsorbée par cette kaolinite est donné par la formule :

$$v' = 30\ V_{BtaK}$$

L'ensemble eau + fines + kaolinite, est soumis à une agitation de cinq minutes à 600 tr/min, puis permanente à 400 tr/min, pendant toute la durée de l'essai à l'aide de l'agitateur, les ailettes étant situées à 1 cm au-dessus du fond du récipient.

7.2 Détermination par dosage de la quantité de bleu adsorbée

7.2.1 Définition du test à la tache

Après chaque injection de bleu (voir paragraphe 7.2.2), ce test consiste à prélever, à l'aide de la baguette de verre, une goutte de suspension que l'on dépose sur le papier filtre. La tache ainsi formée se compose d'un dépôt central de matériau, coloré d'un bleu généralement soutenu, entouré d'une zone humide incolore.

La goutte prélevée doit être telle que le diamètre du dépôt soit compris entre 8 et 12 mm.

Le test est dit positif si, dans la zone humide, apparaît autour du dépôt central une auréole bleu clair persistante. Il est dit négatif si l'auréole est incolore.

7.2.2 Dosage

À l'aide de la burette, injecter v' millilitres de solution de bleu dans le récipient. Après 2 min, ajouter une dose de 5 ml de solution de bleu, cette addition étant suivie du test de la tache sur le papier filtre.

On procède ainsi jusqu'à ce que le test devienne positif. A ce moment, sans rien ajouter, on laisse s'opérer l'adsorption du bleu, qui n'est pas instantanée, tout en effectuant des tests de minute en minute.

Si l'auréole bleu clair disparaît à la cinquième tache on procède à de nouvelles additions élémentaires de bleu de 2 ml.

Chaque addition est suivie de tests effectués toujours de minute en minute.

Renouveler ces opérations jusqu'à ce que le test demeure positif pendant cinq minutes consécutives : le dosage est alors considéré comme terminé.

On procède au nettoyage de l'appareillage dès que l'on a terminé les essais, les dépôts de bleu se détachant facilement quand ils sont récents.

Le matériel se nettoie très bien à l'eau. Si l'on a utilisé des produits détergents, on doit terminer par un rinçage abondant à l'eau.

8 EXPRESSION DES RÉSULTATS

8.1 Valeur de bleu

La valeur de bleu des fines V_{Bta} exprimée en grammes de bleu pour 100 g de fines est donnée par la formule :

$$V_{Bta} = \frac{V_1 - v'}{q}$$

V_1 étant le volume final de solution injectée, en ml,

v' volume de solution de bleu kaolinite,

q masse réelle de fines soumises à l'essai.

8.2 Contrôle de conformité par rapport à une spécification donnée

La spécification est exprimée en valeur de bleu pour 100 g de fines, soit s cette valeur.

Le volume de la solution de bleu à injecter en une seule fois est alors :

$$V_2 = q.s + v'$$

Le test de la tache est effectué après huit minutes d'agitation. S'il est positif, le sable est conforme à la spécification ; s'il est négatif, on ajoute un volume de solution de bleu égal à :

$$\frac{qs}{10}$$

Si le test est toujours négatif, après cinq minutes, on effectue le dosage conformément à l'article 7.2. Si le test est positif, on considère que le sable est conforme à la spécification.

9 PRÉCISION

La répétabilité r a été mesurée sur des niveaux de valeur 0,3 à 1,5. Elle est de 0,28.