IMBIBOMETRY—A NEW METHOD FOR THE INVESTIGATION OF CLAYS

J. KONTA, *Institute of Petrology, Charles University, Prague, Czechoslovakia.*

ABSTRACT

A method for rapid identification of clay minerals in natural clays or in artificial aggregates prepared by elutriation and sedimentation of clay particles is described. The behavior of a drop of water and a drop of ethylene glycol on the surface of a smoothed section is observed. The section is easily prepared on glass- and emery-cloth. The following physical properties are decisive: (1) total surface area of the particles, (2) marked swelling of montmorillonite and "open" illite and no swelling of kaolinite and "closed" illite, (3) small wettability of aggregates of the kaolinite group minerals and greater wettability of illite and montmorillonite aggregates. The speed of imbibition of the liquid by the clay aggregate is regulated by the absorption equation. The method is explained on the basis of the experimental data, obtained by the investigation of eleven clays from Central Europe.

ORIGIN AND DEVELOPMENT OF THE METHOD

The method of observing the behavior of drops of water and of ethylene glycol on sections of unconsolidated clay rocks was worked out in our laboratory (Konta, 1956). Two polar liquids, differing considerably in their viscosity, were used.

It was expected that water and ethylene glycol would be quickly imbibed by the unconsolidated clay rocks, in which the particles of clay minerals are large and thick. The imbibition ought to be slower for aggregates in which the clay particles are rather small and thin. The less viscous water should be imbibed more quickly and cause a greater intermicellar swelling of montmorillonite clays than the more viscous ethylene glycol. During the experimental work it was found that in addition to the speed of imbibition and the extent of swelling, a further highly important diagnostic property of clay aggregates was noted, namely the wettability.

Until now no special name has been given to the new method (Konta, 1959 *a,b*). In the present paper there is applied to this new method the name of *imbibometry*. The investigation of water and ethylene glycol imbibition on sections of unconsolidated clay aggregates can be quantitatively measured and is reliable for the rapid identification of clay minerals. Besides, this method has a wider use in the investigation of some clay-rock properties which are important in geology and technical practice.

BASIS OF THE METHOD

The method is based on certain physical properties of clay minerals and clay aggregates in the presence of polar liquids. They are:

(1) The total surface area of the particles.
(2) Marked swelling of montmorillonite and "open" illite and none
     for kaolinite and normal illite.
(3) Wettability of the aggregates.

These physical properties become apparent simultaneously during the imbibition of a drop of water or a drop of ethylene glycol on sections of clay aggregates and therefore it is necessary to observe and record simultaneously the phenomena caused by all three properties.

The *total surface area* of the clay particles is fully characteristic for each chief group of clay minerals and is the chief physical property affecting the speed of imbibition of a drop of water and of ethylene glycol by the surface of the clay sections. Crystals of the kaolinite group minerals, which form the thickest plates of all the clay minerals, have the smallest total surface area, usually in several $m.^2/g.$ up to several tens $m.^2/g.$; their highest value reaches about 40–60 $m.^2/g.$ Minerals of the illite group have crystals essentially thinner and a total surface area several times larger, usually in many tens $m.^2/g.$ most often from 70 to 150 $m.^2/g.$; and "open" illite more than 200 or 300 $m.^2/g.$ Finally, minerals of the montomorillonite group have the thinnest crystals and their total surface area is usually in hundreds $m.^2/g.$, most often between 500 $m.^2$ and 800 $m.^2/g.$

The *swelling* of montmorillonite and of "open" illite (van der Marel 1960) makes possible a quick and easy determination of the presence of these minerals in a clay. It is necessary, while applying the imbibometric method, to note on the sections of the clay not only the swelling itself but also the speed of imbibition (in seconds) and the wettability.

The *wettability* of unconsolidated but coherent aggregates of clay minerals represents a very important property and makes it possible to distinguish the kaolinite clays from illite and montmorillonite. Kaolinite clays have the smallest wettability. On sections of kaolinite, a drop of water or ethylene glycol always takes up a relatively small circular area (Fig. 1 *a,b*). On illite (Fig. 1 *c,d*) or on montmorillonite (Fig. 2) a drop of water or ethylene glycol spreads over a considerably larger area. When ethylene glycol is used, and in some cases even with water, characteristic small spurs are formed. The imbibition ratio is the area occupied by one drop of ethylene glycol divided by the corresponding area for water. This ratio is less than 1 for kaolinite, but always above 1 for illite, and especially so for montmorillonite.

MATHEMATICAL EXPRESSION

The rate of imbibition depends both on the physical properties of the clay aggregate and on the character of the liquid. The purity of the
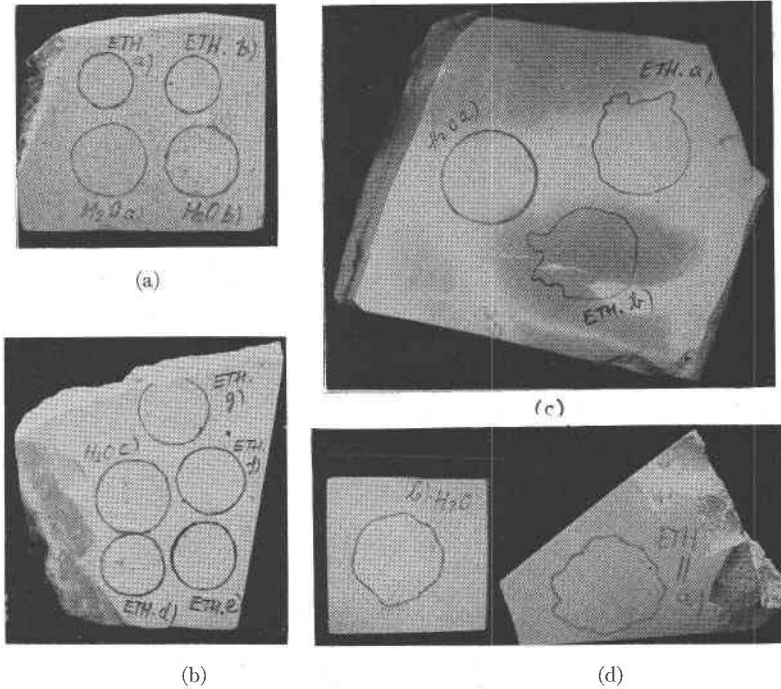
(a)

(c)

(b)

(d)

Fig. 1. (a) Characteristic small circular areas taken by drops of water and of ethylene glycol. Kaolin from Sedlec near Karlovy Vary, western Bohemia.

(b) Silty kaolinite clay from Jarov near Plzeň, western Bohemia.

(c) Greater areas taken up by a drop of water and a drop of ethylene glycol, with characteristic small spurs if ethylene glycol is used. Illite clay from Chlum near Beroun, central Bohemia.

(d) Greater areas taken up by a drop of water and a drop of ethylene glycol, with characteristic small spurs. Illite clay from Füzerradvany, Hungary.

liquid, and the temperature can be controlled, and atmospheric pressure should be normal.

The speed of imbibition of the liquid by the clay aggregate is regulated by the absorption equation:

$$ t = \frac{s \cdot \eta}{\epsilon^3 \cdot \sigma \cdot k} \left(\frac{q}{A} \right)^2, $$

where:

t = the time of the complete imbibition of the liquid in seconds,

s = the effective surface area of mineral particles (in cm^2/cm^3 of the substance),

η = the viscosity (in poises at 20° C.),

ϵ = the effective porosity (in %:100),

$\sigma =$ the surface tension of the liquid (in dynes/cm²; in the value the gravity acceleration is, therefore, included),

$k =$ the constant including the shape of the particles and the tortuosity of pores in the clay aggregate (in the majority of clays its value remains constant; it depends, however, on the direction of imbibition, i.e. whether it is for instance parallel or perpendicular to the lamination of the rock),

$q/A =$ the amount of the liquid (q in cm³) sorbed on the area (A, in cm²) during a known time.

An analogous equation has been used to express the sorption property of hardened Portland cement paste (Powers and Brownyard, 1948).

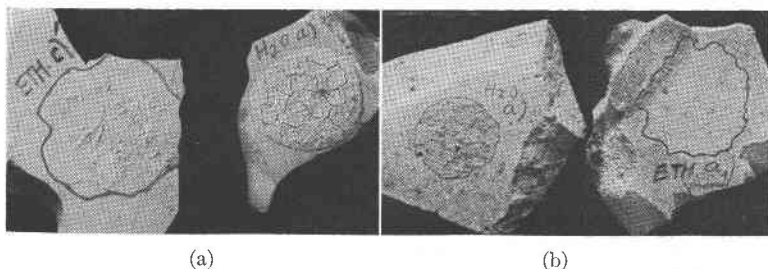(a)   (b)

FIG. 2 (a) Swollen areas taken up by a drop of water (right) and ethylene glycol (left). Montmorillonite clay from Istenmezö, Hungary. (Sample No. 10.)

(b) Swollen area after imbibition of a drop of water (left) and less evident swelling on bentonite section if ethylene glycol is used (right). Braňany near Most, northern Bohemia. (Sample No. 9.)

From this equation it follows that for the imbibition rate of a known constant amount of polar liquid on a known area and under a constant temperature and constant conditions of purity of the liquid, as well as an unchanging direction of the imbibition, only two properties of clay are decisive, namely, the total surface area of the particles (s) and the effective porosity (ϵ). The time of imbibition of the liquid by a clay aggregate is in direct proportion to the effective surface area of the particles and inversely proportional to the effective porosity of this aggregate.

The *effective porosity* of the clay aggregate is a further important physical property which also has an influence on the imbibition speed of the liquids, as follows from the equation given above. In the majority of unconsolidated, yet coherent kaolinite and illite clays, the values of the effective porosity varies between 25–50% under laboratory conditions of humidity and temperature. In montmorillonite rocks the effective porosity is still smaller, usually between 10–20% under laboratory humidity and temperature conditions. The experimental work has shown that the imbibition speed on the sections of clays of different mineral

composition is mainly influenced by the total surface area of the particles, which value varies with the chief groups of clay minerals, *i.e.* kaolinite, illite and montmorillonite. The differences in the speed of the imbibition of liquids by clays of approximately identical mineral composition and of not considerably different values of the total surface area of the particles, are mainly caused by differences in effective porosity.

This important finding is represented by several diagrams drawn up on the basis of data obtained from the study of eleven samples of unconsolidated clay rocks of different mineral composition. The approximate quantitative mineral composition of these rocks had been given in the author's articles (Konta, 1959 *a,b*). Since the values obtained are necessary for the understanding of the following four figures, they will be repeated here in the abbreviated form of a triangular diagram (Fig. 3).
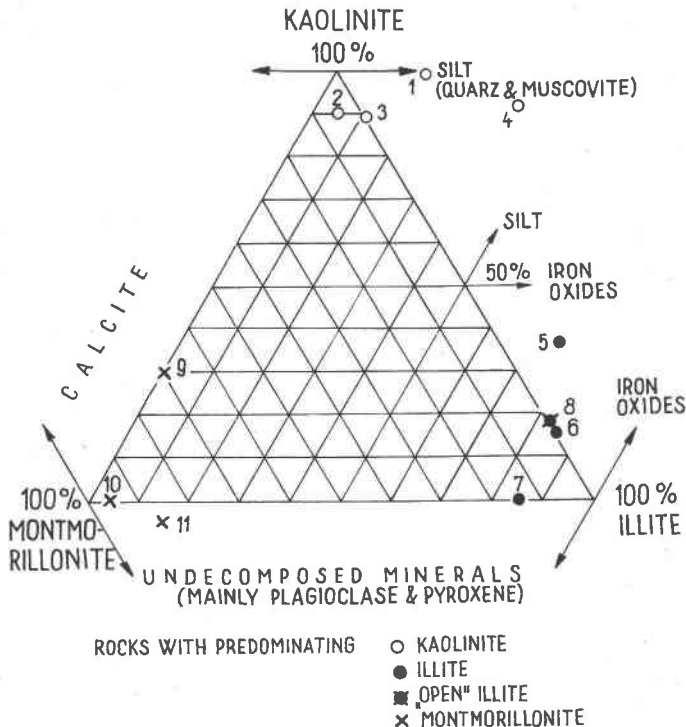

FIG. 3. The approximate semiquantitative mineral composition of eleven clay rocks studied. The data were obtained by evaluation of the results of these methods: investigation under polarizing microscope, *x*-ray analysis, DTA, gravimetric thermal analysis and imbibometry. The numbers of the points in the triangular diagram correspond to the numbers in all other diagrams and tables.

In Table I, data are given concerning the effective porosity, density and the total surface area of the particles of eleven samples investigated. The last values have been found by the absorption method according to Dyal and Hendricks (1950), namely in all cases with finely powdered samples sieved through 200 mesh with aperture of 0.074 mm.

In Fig. 4 the values of effective porosity expressed in $(\%:100)^3$ are given. On the horizontal axis, the times during which one drop of water is imbibed by the sections are plotted. The times found are related to a uniform basic area (cf. Konta, 1959 a,b). The method of calculating of the imbibition times are illustrated in Tables II and III. Figure 5 is similar to Fig. 4, but for ethylene glycol. Here too, the values of the imbibition times have been related to a uniform basic area.

From Figs. 4 and 5 this main conclusion follows: The effective porosity has little decisive influence upon the speed of imbibition of water and ethylene glycol by the unconsolidated but coherent clay aggregates. However, in samples of nearly identical mineral composition, which do not differ greatly in the values of the total surface area of the particles, the differences in effective porosity have a marked influence upon the speed of imbibition. This can be best seen in kaolinite clays.

In addition to the effective porosity and the total surface area of the

TABLE I. EFFECTIVE POROSITY, DENSITY AND TOTAL SURFACE
AREA OF ELEVEN CLAY SAMPLES

Sample	Effective porosity (approximate data)	Total surface in m.²/g.	Densities of samples dried at 110° C.	Total surface in cm.²/cm.³ $\times 10^4$
Kaolinite clays				
1. Vonšov-Nová Ves, w. Bohemia	43.8	41.1	2.64	108.50
2. Staré Sedlo near Loket, w. Bohemia	31.5	45.5	2.59	117.85
3. Sedlec near Karlovy Vary, w. Bohemia	37.0	33.9	2.68	90.85
4. Jarov, near Plzeň, w. Bohemia	35.5	58.5	2.68	156.78
Illite clays				
5. Chlum, near Beroun, c. Bohemia	33.6	79.3	2.75	218.08
6. Chlum, centr. Bohemia	35.1	72.7	2.70	196.29
7. Füzerradvany, Hungary	44.4	148.8	2.78	413.66
Clays with predominating montmorillonite and "open" illite				
8. Vonšov near Cheb, w. Boh.	13.8	358.2	2.83	1013.71
9. Braňany near Most, n. Bohemia	17.7	348.7	2.75	958.93
10. Istenmezö, Hungary	19.6	730.0	2.60	1898.00
11. Komloska, Hungary	11.4	667.5	2.80	1869.00

particles, another important factor appears in montmorillonite clays or in clays containing the "open" illite, which considerably influences the speed of imbition of the polar liquids into the sections. This important factor is the phenomenon of swelling. Especially during imbibometric tests with water such a strong swelling takes place, that immediately after the contact of water and clay on the surface of a polished section the original effective porosity grows several times. This is the cause of a considerably quicker imbition of water than would correspond only to the value of the effective porosity of the aggregate and the total surface

IMBIBITION TIME OF 1 DROP OF WATER
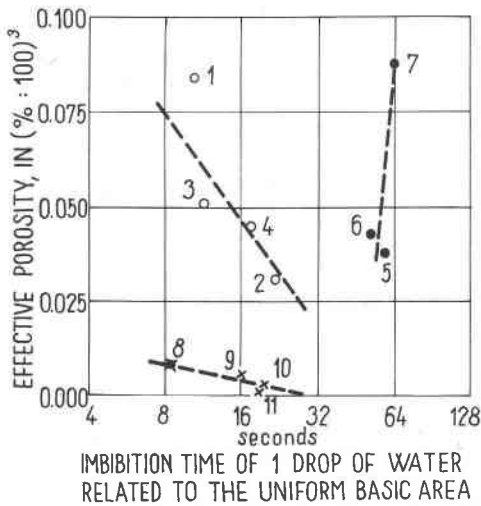RELATED TO THE UNIFORM BASIC AREA

Fig. 4. Dependence between effective porosity and imbibition speed of one drop of water.

area of the particles (cf. Fig. 4). An especially strong swelling took place in both the montmorillonite rocks from Hungarian localities.

The relation between the total surface area of the clay particles and the speed of imbibition of water and ethylene glycol are shown in Figs. 6 and 7. In Table I, in the fourth column are given the values of the total surface area of eleven clay rocks investigated, expressed in $cm.^2/cm.^3$ of the substance $\times 10^4$. From these figures this main conclusion follows: The speed of imbibition of a drop of water and ethylene glycol by sections of unconsolidated clay rocks is chiefly determined by the value of the total surface area of the particles. The other physical properties of clay particles and their aggregates are of smaller import. This is only valid for the use of polar liquids with nonswelling or slightly swelling clays. In strongly swelling clays, instead of remaining constant, the ef-
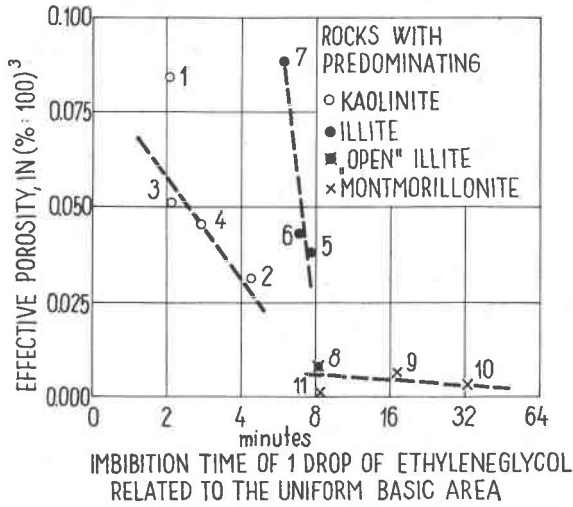
FIG. 5. Dependence between effective porosity and imbibition speed
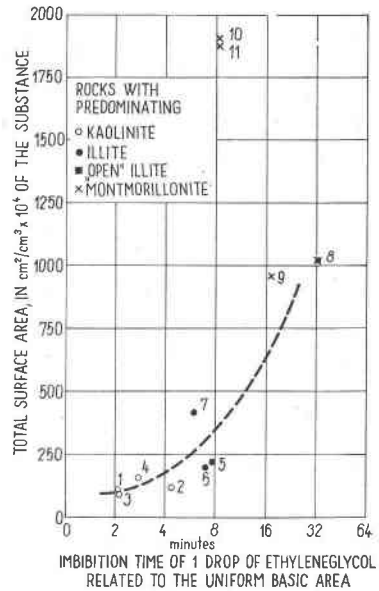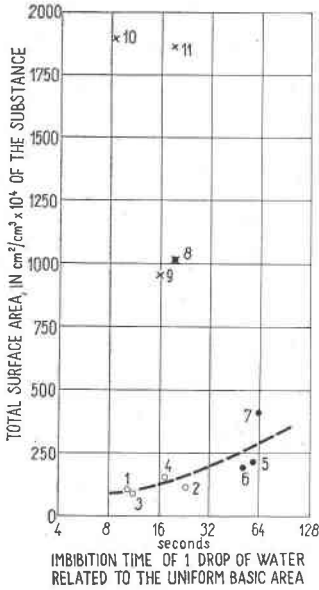of one drop of ethylene glycol.

FIG. 6. (left) Dependence between total surface area and imbibition speed of one drop
of water.

FIG. 7. (right) Dependence between total surface area and imbibition speed of one drop
of ethylene glycol.

TABLE II. CALCULATION OF THE RESULTANT IMBIBITION TIME OF A DROP OF
WATER AND A DROP OF ETHYLENE GLYCOL ON THE POLISHED SECTION OF
THE NATURAL KAOLIN FROM SEDLEC NEAR KARLOVY VARY, BOHEMIA

Real area occupied by a drop, in mm.²	Recorded imbibition time, in seconds	$\dfrac{\text{Real area}}{\text{Uniform basic area}}$	Resultant imbibition time, in seconds
Water:			
(a) 85	13	$\dfrac{85}{89}=0.955$	$0.955 \times 13 = 12$ sec.
(b) 102	10	$\dfrac{102}{89}=1.146$	$1.146 \times 10 = 11$ sec.
(c) 91	12	$\dfrac{91}{89}=1.022$	$1.022 \times 12 = 13$ sec.
(d) 80	14	$\dfrac{80}{89}=0.899$	$0.899 \times 14 = 13$ sec.
358:4 = 89 mm.², is the uniform basic area			Average = 12 sec.
Ethylene Glycol:			
(a) 56	121	$\dfrac{56}{55}=1.018$	$1.018 \times 121 = 123$ sec.
(b) 59	134	$\dfrac{59}{55}=1.073$	$1.073 \times 134 = 144$ sec.
(c) 55	119	$\dfrac{55}{55}=1$	$= 119$ sec.
(d) 59	115	$\dfrac{59}{55}=1.073$	$1.073 \times 115 = 123$ sec.
(e) 55	139	$\dfrac{55}{55}=1$	$= 139$ sec.
(f) 53	127	$\dfrac{53}{55}=0.964$	$0.964 \times 127 = 122$ sec.
(g) 55	135	$\dfrac{53}{55}=0.964$	$0.964 \times 135 = 130$ sec.
(h) 53	133	$\dfrac{55}{55}=0.964$	$0.964 \times 133 = 128$ sec.
443:8 = 55 mm.², is the uniform basic area			Average = 129 sec.

fective porosity on the surface of the section is increased many times
with a polar liquid, and hence the liquid imbibes rather quickly. There-
fore it is necessary for the determination of the effective surface area of

TABLE III. CALCULATION OF THE RESULTANT IMBIBITION TIME OF A DROP OF
WATER AND A DROP OF ETHYLENE GLYCOL ON THE SMOOTHED SECTION OF
KAOLINITE CLAY FROM JAROV NEAR PLZEŇ, BOHEMIA

Real area occupied by by a drop, in mm.²	Recorded imbibition time, in seconds	Real area / Uniform basic area	Resultant imbibition time, in seconds
Water:			
(a) 96	16	$\frac{96}{89}=1.079$	$1.079\times16=17$ sec.
(b) 95	17	$\frac{95}{89}=1.067$	$1.067\times17=18$ scc.
(c) 89	17	$\frac{89}{89}=1$	$1\times17=17$ sec.
(d) 99	18	$\frac{99}{89}=1.112$	$1.112\times18=20$ sec.
			Average$=18$ sec.
Ethylene Glycol:			
(a) 68	151	$\frac{68}{55}=1.236$	$1.236\times151=187$ sec.
(b) 75	111	$\frac{75}{55}=1.364$	$1.364\times111=151$ sec.
(c) 78	124	$\frac{78}{55}=1.418$	$1.418\times124=176$ sec.
(d) 65	134	$\frac{65}{55}=1.182$	$1.182\times134=158$ sec.
(e) 71	131	$\frac{71}{55}=1.291$	$1.291\times131=169$ sec.
(f) 72	120	$\frac{72}{55}=1.309$	$1.309\times120=157$ sec.
(g) 77	129	$\frac{77}{55}=1.400$	$1.400\times129=181$ sec.
(h) 88	131	$\frac{88}{55}=1.600$	$1.600\times131=210$ sec.
(i) 87	121	$\frac{87}{55}=1.582$	$1.582\times121=191$ sec.
			Average$=176$ sec.
			$=2$ min. 56 sec.

the particles or of the effective porosity to use nonpolar liquids. For the purpose of identification of clay minerals, the procedure of the imbibometric method here described, has proved to be a fully satisfactory one.

Preparation of Sections

The clay is roughly ground by circular movements on glass-paper no. 50, and then the surface of the section is smoothed on emery-cloth no. 240 or finer. Thus the preparation of a section requires no more than 2–4 minutes. By using the same type of emery cloth sections of equal quality can be obtained.

During the preparation of sections it is important to observe the following rules:

(1) The grinding is always done in dry state.

(2) Sections which should serve for the identification of clay minerals or for the determination of the relative age of clay rocks are always made parallel to the stratification. In clay aggregates without stratification a number of sections should be prepared, and in various directions.

(3) On the section or in the area where the liquid is imbibed, there should be no pores or cracks visible by eye or by lens.

(4) When the grinding is finished it is necessary to remove carefully the loosened clay powder on the surface of the polished section by means of a soft brush.

(5) The surface of the prepared section is always dull and it should not glisten in any case (as required by metallographic microscopy).

(6) The surface of the section must be free from grease.

For other purposes sections can be made perpendicular to the stratification, or with varying orientations.

Smooth sections of sandy or silty-sandy clays are for the most part difficult to prepare. For imbibometric identification of clay minerals in these rocks it is necessary to prepare artificial solid plates, by elutriation and sedimentation of dispersed particles. The natural sample of the rock is pulverized and elutriated in a tall beaker filled with water. After thorough stirring and dispersion of clay particles, adding a suitable dispersive solution, the suspension in the beaker is left to settle in a quiet place. Care must be taken so that the orientation of clay particles is not changed during the drying of the sediment. The dried sediment ready for the preparation of the section has the form of a solid disc about $\frac{1}{2}$ to 1 cm. thick.

Imbibometric Tests

The working process during imbibometric tests is quite simple:

(1) The section is fixed on plasticine in a horizontal position.

(2) On the surface of the polished section a drop of water is dropped from a vertically held pipette (constant size) from a height of about 4 to 6 mm. Simultaneously, we observe and ascertain:

(a) The size and the shape of the area occupied by the drop.

(b) The time during which the drop gets entirely imbibed.

(c) The changes on the surface of the section during the imbibition and mainly after the imbibition of the liquid.

(3) This complex observation must always be carefully registered, and the area in which the drop was imbibed, copied on a transparent paper.

Then the same process is used in the case of a drop of ethylene glycol, which is more viscous and is imbibed by all aggregates more slowly than water. It is recommended that all the observations be entered in a card index.
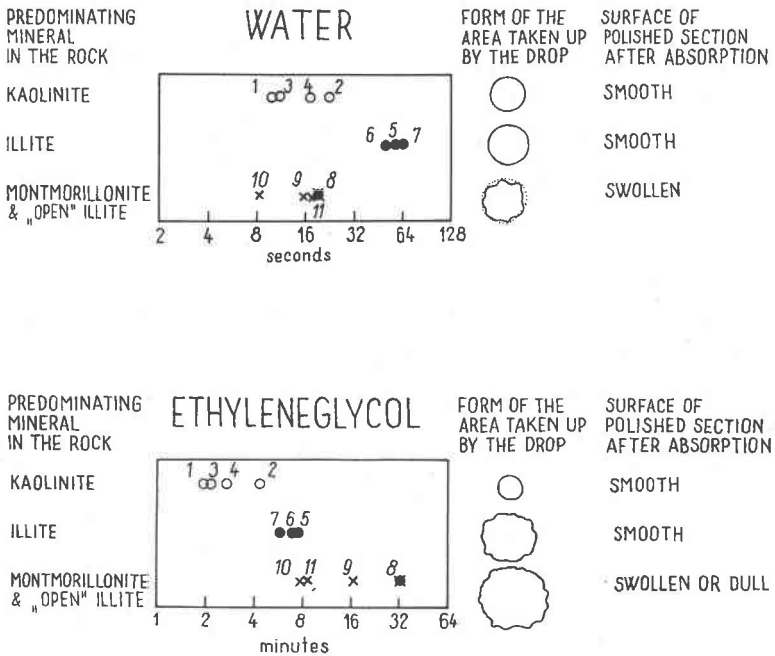

Fig. 8. Identification table serving for entering observations obtained during the imbibometric tests.

The Use of Imbibometry for Identification of Clay Minerals

The relation of the size of the area occupied by the drop on the section to the speed of imbibition is best evident from the mathematical equation previously given. The larger the area occupied by the drop, the shorter is the time of imbibition. Every area on the section occupied by the drop is carefully traced on a transparent millimeter-lined paper and thus its size is ascertained with relative precision. Even quicker is the determination of the size of the irregularly shaped area by a suitable planimeter.

The actual measured time of a complete imbition of a drop of water and a drop of ethylene glycol has then to be transferred to a uniform basic area and the resultant imbition time is obtained. It is the time during which the drop should be imbibed if it occupied on every section such an area as it occupies on the section of the natural pure kaolin from Sedlec near Karlovy Vary, Bohemia. A drop of water let down from the pipette from the height of 4–6 mm. on the natural pure kaolin from Sedlec near Karlovy Vary occupies a circular area of average size 89 mm.^{2} (computed from four measurements). A drop of ethylene glycol under the same conditions occupies an area of average size of 55 mm.^{2} (computed from eight measurements). In Table II the manner of calculation of the resultant imbition times for the pure kaolin sample from Sedlec is given. In both cases the measured values are related to a uniform basic area for water and ethylene glycol. In Table III the calculation for the section of silty kaolinite clay from Jarov near Plzeň, Bohemia, is given.

The resultant values giving the imbition times are entered in a table (Fig. 8). In the upper part of the table the resultant imbition times of a drop of water related to a uniform basic area with regard to the wettability and to the surface change of the section after imbition are entered. In the lower part the corresponding times for ethylene glycol are listed.

ANOMALOUS SHORTENING OR PROLONGATION OF THE IMBIBITION TIME

In some cases the imbition speed of water and ethylene glycol may be essentially shorter or longer than might be expected, considering the clay minerals present in the sample. The character of the predominating clay mineral can be determined, however, on the basis of mere wettability, and swelling or nonswelling of the sample. These properties can be recognized on the *smoothed* section by the different size of the area occupied by a drop of water or a drop of ethylene glycol, further by a characteristic contour of the area, and finally by a change of the surface of the polished section upon imbition.

The *shortening* of the imbition time of the liquid which does not correspond to the size of the effective surface area of the clay particles can be the result of different factors. Of these the most important are:

(a) Presence of a greater number of clastic grains.
(b) Swelling of montmorillonite or of "open" illite.
(c) Placing drop in the direction of the preferred orientation of the clay particles in samples without evident stratification.
(d) Presence of admixture of carbonate minerals.

(e) Presence of soluble salts, especially of halite.
(f) Formation of cracks on the section during imbibition.

The *prolongation* of the imbibition time of the liquid is most often influenced by:

(g) A greater consolidation of the clay rock and a total porosity under 25 per cent.
(h) Presence of finely dispersed organic substance (enlargement of the effective surface area).

It is therefore always important before and in the course of imbibometric tests to determine for every rock studied if the imbibition will be influenced by some of these factors. The majority of these unfavorable factors can be eliminated in imbibometry by the making of artificial solid plates of the clay. Thus can be eliminated the factors given above under a, c, d, e, and g.

GENERAL USE OF IMBIBOMETRY

First, it is possible to identify clay minerals on sections of unconsolidated but coherent clay aggregates by a drop of water and of ethylene glycol. These aggregates can be either natural, or artificial if the natural clay is not suitable for the making of the section required. It is further possible to determine, imbibometrically, the value of effective porosity, if the total surface area of the particles is determined beforehand (e.g., by a simple method according to Dyal and Hendricks, 1950). By means of imbibometry it is possible in clays to determine the direction of the maximum imbibition by making sections of various orientations. Imbibometry also quickly reveals the extent of swelling in argillaceous rocks containing montmorillonite or "open" illite. The results are of relative nature only when using polar liquids. When using a polar and a nonpolar liquid on the same section the results begin to have a quantitative character.

The imbibometric method can also, in some cases, be applied to problems connected with the determination of the relative age of clay rocks in a definite uniform geologic area. In clay rocks of relatively earlier geologic age the suitable liquid will imbibe more slowly than into later rocks which in most cases are less consolidated, i.e. of greater total porosity. At the same time, the mineral composition of clay rocks must be approximately the same.

On the basis of recent experimental work we can say that in the future other liquids, polar and nonpolar, will be used in imbibometry.

ACKNOWLEDGMENTS

REFERENCES

DYAL, R. S., AND HENDRICKS, S. B. (1950): Total surface of clays in polar liquids as a characteristic index. *Soil Sci.*, **69,** 421–432.

KONTA, J. (1956): Schnelle petrographische Identifikation der Tonminerale in den Anschliffen mittels Wasser und Ethylenglykoll. *Chemie der Erde*, **18,** 179–193.

——— (1959*a*): Porosity of clay rocks and their imbibition capacity. *Silicates Industriels*, **24,** 133–136 (Bruxelles).

——— (1959*b*): Porosita a nasákavost nezpevněných jílovitých hornin. (Porosity and imbibition capacity of unconsolidated clay rocks.) *Acta Univ. Carolinae, ser. Geologica*, 25–43 (Praha).

MAREL VAN DER, H. W. (1960): Verband tussen het uiterlijk van de kleideeltjes en de grondmechanica. *LGM Mededelingen, Orgaan van het Laborat. voor Grondmechanica*, **4,** p. 1–28. (overdruk).

POWERS, T. C., AND BROWNYARD, T. L. (1948): Studies of the physical properties of hardened Portland cement paste. Auth. reprint from *Journ. Amer. Concr. Inst., Michigan*, 101–992. (*Portland Cement Assoc., Bull.* **22,** Chicago.)