MINERALOGICAL ANALYSIS OF DUNAÚJVÁROS PLEISTOCENE DRILLED SAMPLES

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During the reconstruction following the 1964 embankment collapse at Dunaújváros, I had opportunity to test samples from some borings made by the Civil Engineering Design Enterprise. Mineralogy tests have led to some conclusions pointing out the importance of mineralogy tests on similar regions.

Geology conditions

In the period preceding the design of the Danube Steel Works, the geology of the Dunaújváros region was rather poorly known. Few old tests data were available for supporting expertizes on this territory (VOGL 1925, BULLA 1936). Detailed geomorphology and geology surveys were only published after the Danube Steel Works have been constructed (ÅDÁM-MAROSI-SZILÁRD 1959, PÉCSI 1959), while no detailed mineralogical and petrological analysis has been made earlier than in 1964 (SCHMIDT 1966, Reports of Civil Engineering Design Enterprise (Mélyépterv) and of Survey and Soil Exploration Enterprise (FTV)).

Publications and reports are unanimous in that the loess plateau at the high embankment on the Danube right bank is crossed by NW-SE faults. The loess is stratified by clay and fossile soil stripes. The loess substratum comprises Pannonian sand, superposed by pleistocene clay, then by sandy clay. Thereupon comes the loess stratum.

Mineralogy exploration of rocks of the Hungarian loess regions has been begun with in the 1930-s. VENDL and his co-workers made systematic mineralogical, chemical and grading tests on several loess samples (1933, 1935), among them on a sample from the Dunavecse region. Recent tests have been made by FÖLDVÁRI-VOGL (1953) and MIHÁLYI-LÁNYI (1953). Unfortunately, however, the detailed tests did not reckon with the loess stratification and the eventually divergent mineralogy composition between strata, and samples were not identified as to which stratum they came from. A deficiency of the research made in the '30-s was to include only minerals detectable by microscopy, while in lack of an appropriate instrument, clay minerals and minerals of the clay particle fraction could not be examined.

The first detailed description of a loess stratum series is due to KRIVÁN (1955). He published also some clay mineral tests. A complete, detailed study on the Hungarian loess strata series. documented by clay mineral tests, has been elaborated by Pŕcsi (1966).

Origin of the samples

Samples originated from the borings of the MÉLYÉPTERV. Borings were located on the plateau top, almost aligned, depths ranging to 50 to 52 m. Samples of the soil categories of clay, silt and fine sandy silt, were taken from depths below 30 m (Fig. 1).

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Test method

Two methods lent themselves to determine the mineralogy composition of the samples. Well crystallized materials were advisably tested by the X-ray diffraction method, while thermal analysis methods suited to test clay minerals.

Minerals ready to detect by X-ray diffraction methods are quartz, calcite, dolomite, feldspar, and clay minerals in important occurrences. These latter are rather hard to detect, as even the well crystallized kaolinite can only be detected beside quartz if it occurs in at least 10 to 15 per cent. This ratio is even less favourable for less crystallized minerals (BIDLÓ 1963).

Thermal analyses are favourable by permitting clay minerals to be identified and assessed in rather small quantities. Their drawback is, however, to detect quartz poorly and feldspar not at all, beside a clay mineral, and not to decide the crystalline form of $CaCO_3$ (whether calcite or aragonite). It is thus advisable to combine both test methods.

X-ray tests had been done in a Müller Micro 60 equipment using $\operatorname{FeK}_{z,\beta}$ radiation in a chamber of 57.4 mm dia. Unfortunately, this instrument makes only quality determinations, with the outlined restrictions. Thermal analyses have been made using the Paulik—Paulik—Erdey derivatograph produced by MOM. This instrument is much more expedient than the ordinary thermal analyser in that it both weighs and records the decomposition and the weight loss of one and the same sample.

Identification of the minerals has been made either using our own photos on pure materials, or on the basis of literature data (MIHEEV 1957, BROWN 1961, and MACKENZIE 1957).

Minerals in the soil samples

According to their importance for soil physics, sample minerals can be classified as:

- a) inert soil minerals
- b) active soil minerals.

The first group includes minerals affecting soil properties only in that their presence reduces the proportion of active minerals but these are not determinant for the physical characteristics. The most typical of them is quartz, occurring in any sedimentary rock in lesser or greater quantity, even in clay fractions of the soil. Besides, minerals like rutile, zircone, apatite etc. belong to this group, present in the soil in rather small quantities and demonstrable in the "heavy minerals" part of the samples.

The group of active soil minerals includes, beside clay minerals, calcite, feldspar, as well as organic and inorganic non-crystalline materials. The role of dolomite, occurring in some samples, is not cleared yet.

Classification of calcite and feldspar among the active soil minerals needs further explication. Earlier microscope tests already demonstrated members of the feldspar group to be present in clay and clayey rocks (VENDL 1932), in the clay size range X-ray diffraction tests often exhibited a line at 3.18 Å, coincident with that of plagioclase feldspar. Weathering of members of the feldspar group is known since long to produce clay minerals. Hence, feldspar acts as a clay mineral reserve, to be classified among the active soil minerals.

Also the role of calcite is known to affect the physical properties of soils. Finely distributed, it is a component of several sedimentary clay mineral rocks, meriting thereby a special consideration.

Determination of mineral proportions

Sample tests much relied upon the determination of the component quantities. This was done by means of a derivatograph and mineral quantities had been calculated from sample weight losses. Since this method is not generally known, it is advisable to present it.

Thermal analyses are advantageous by continuously recording sample weight losses and permitting thereby to determine the quantity of each component. This is of special importance for clay minerals, namely in course of X-ray diffraction methods, clay minerals in rocks are not always well crystallized, thereby X-ray contours are dim and peaks difficult to determine. Upon heating, clay minerals give off water in two steps. The first step ranges from 95-100 °C to 200-250 °C, depending on the mineral features. The absorbed water quantity to leave depends on the mineral character and on how long and at what relative humidity the mineral was stored prior to testing. Thus, this peak can only be applied to determination after a previous calibration. Another disadvantage is that gypsum as well as organic and inorganic colloids also give off water, disturbing thereby the quantity determination.

During the second step, water begins to leave about 450°C and continues to almost 700°C. In this range, clay minerals loose their constitutional water. The water loss is anyhow characteristic for each mineral, since its quantity depends on the lattice structure and the decomposition temperature differs for each mineral (MACKENZIE 1957). Quantity determination is disturbed by the ealcite contained in the sample alone, its decomposition curve fusing with that of the clay minerals, making delimitation difficult.

To ease quantity determination, an intermediary method has been introduced to the analysis of the Dunaújváros samples.

Clay mineral taken from the reddish-brown clay stratum 42 m below ground level was neatly prepared using the Buzágh-Szepesi method (1955) and scrutinized. The sample was found to consist exclusively of clay minerals, i.e. of two ones, montmorillonite and palygorskite (Table 1).

Test results explain for the rather poor physical properties of clay, palygorskite (attapulgite) being still poorer than montmorillonite.

Characteristics of the neat clay mineral sample preparate have been determined by thermogravimetry, and the weight loss during the second range has been applied to determine the clay mineral content of the samples.

Sample		Palyg	Palygorskite		Montmorillonite		
d _{hkl} À	1	dhhi À	I	d_{hkl} Å	I		
1.90	w	·		4.89	3		
4.37	s	4.35	10				
3.68	w	3.69	2				
3.28	s	3.26	10				
3.02	w	3.03	3				
2.80	W	2.81	$\overline{2}$	2.81	3		
2.55	m	2.55	10	2.55	$\overline{7}$		
1.986	vw				illite		
1.803	vw	1.80	2				
1.653	vw	1.66	2	1.652	5		
1.498	m	1.49	4	1.495	10		
1.368	vw			1.368	1		
1.291	VW.			1.292	<u>.</u>		

Table	I
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X-ray test results of a clay sample from Dunaújváros

I = line intensity; vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

Other mineral quantities have also been determined from weight losses. Weight loss at the characteristic decomposition temperature delivered mineral percentage by weight from the stoichometric ratio corresponding to the composition.

From among carbonate minerals, the decomposition of calcite depends on many circumstances (PAULIK – LIPTAY – ERDEY 1963; ADONYI 1967). The determination is rather difficult since its decomposition curve coincides with that of the clay minerals, keeping, however, its typical endotherm peak. Dolomite is manifest by its double endotherm peak, the first one marking the decomposition of MgCO₃ and the second one that of CaCO₃. Quantity determination is based on the weight loss at decomposition peaks. Eventual magnesite content can be detected even in presence of dolomite and calcite, since it is decomposed at a lower temperature than MgCO₃ in the dolomite.

Thermal analysis cannot detect quartz in the presence of clay minerals. The peak at 575°C, indicating polymorphous transformation, is all superposed by the endotherm peak of clay minerals. Quartz has been detected from X-ray powder photographs. No quantities are tabulated here, since these could only be determined by indirect calculation. Approximate percentage is obtained by deducing the indicated results from 100 per cent. This quantity includes of course feldspar and other minerals present in low proportions. A more exact determination is possible by confronting intensity of the lines of calcite of known quantity to that for quartz.

Sometimes, samples exhibit an endotherm peak about 320° C, due to gibbsite or goethite. Their decomposition temperature differs by only 5°C, hence they cannot be distinguished. In case of greater quantities, lines appear also on X-ray powder photographs, so they can be distinguished. Tabulated weight losses were attributed partly to gibbsite and partly to goethite.

Exotherm domain from 250°C to 450°C and related weight loss is but partly due to organic matter, since here also amorphous silica gels crystallize (SiO₂ gel). The two processes can but seldom be distinguished, so the entire weight loss had to be attributed to organic matter.

Sample test results

Sample test results are compiled in Table 2.

Data permit some conclusions on bedding conditions of the region. Strata succession of borings Nos. 4 and 5 can well be related on the bases of both soil characteristics and minerals. Borings Nos. 1, 2 and 3, — in spite of their relative proximity — cannot be paralleled. Dolomite appears in borings Nos. 4 and 5 about the same depth, and aragonite at 37.0 m level. Presence of aragonite generally indicates a living organism in cases where no hydro-thermal effects have to be reckoned with (BIDLÓ 1960 and 1964).

Mineral composition of bored samples

Sample No.	Depth m	Туре	H ₂ O %	Organic %	Clay mineral %	Calcite %	Other
1	36.5 39.0 45.3 48.0 54.0	Yellow clay Yellow silt Yellow silt Yellow clay Yellow poor clay	$3.3 \\ 2.6 \\ 0.9 \\ 1.0 \\ 1.0$	$1.0 \\ 0.6 \\ 0.2 \\ 0.5 \\ 0.5$	33.0 27.6 11.0 28.0 25.0	$\begin{array}{r} 6.5 \\ 36.5 \\ 21.8 \\ 25.0 \\ 20.9 \end{array}$	Feldspar, gibbsite Dolomite Dolomite
2	$\begin{array}{c} 33.0\\ 37.0\\ 38.0\\ 43.0\\ 45.0\\ 48.0\\ 50.0\\ 51.0\\ 52.0\end{array}$	Sandy clay Brown clay Yellow clay Sand flour Grey silt Sand flour silt Yellow clay Yellow clay Yellow clay	$2.6 \\ 4.9 \\ 5.6 \\ 1.0 \\ 2.7 \\ 2.0 \\ 2.7 \\ 2.3 \\ 2.3$	$\begin{array}{c} 0.6 \\ 0.9 \\ 0.8 \\ 0.5 \\ 0.7 \\ 1.0 \\ 0.3 \\ 1.3 \\ 0.3 \end{array}$	$ 19.0 \\ 30.0 \\ 31.0 \\ 15.0 \\ 30.0 \\ 28.0 \\ 42.0 \\ 35.0 \\ 30.0 \\ $	$13.6 \\ 2.5 \\ 12.7 \\ 17.2 \\ 27.2 \\ 24.0 \\ 28.0 \\ 38.5 \\ 27.2$	Feldspar Dolomitic Dolomitic
3	$\begin{array}{c} 31.0\\ 36.5\\ 37.0\\ 39.7\\ 41.0\\ 42.0\\ 43.5\\ 49.0 \end{array}$	Sandy silt Yellow clay Sandy silt Sandy silt Yellow clay Yellow clay Yellow clay Yellow clay Yellow lime clay	$2.3 \\ 3.0 \\ 4.0 \\ 2.6 \\ 2.6 \\ 8.1 \\ 7.0 \\ 3.6$	$\begin{array}{c} 0.6 \\ 0.7 \\ 0.6 \\ 0.5 \\ 0.4 \\ 1.0 \\ 0.6 \\ 0.3 \end{array}$	$16.7 \\ 21.6 \\ 16.8 \\ 18.1 \\ 19.0 \\ 45.0 \\ 27.6 \\ $	$19.5 \\ 21.6 \\ 16.8 \\ 15.0 \\ 15.8 \\ 0.0 \\ 16.4 \\ 27.2$	Feldspar Clay rubble Goethite
4	33.5 36.0 39.0 42.0 44.5 50.0	Yellow silt Yellow silt Yellow clay Stone rubble clay Yellow clay Yellow clay	$1.7 \\ 2.0 \\ 3.0 \\ 2.0 \\ 4.8 \\ 6.0$	$0.4 \\ 0.4 \\ 0.5 \\ 0.6 \\ 0.8 \\ 0.6$	$13.5 \\ 55.0 \\ 24.5 \\ 30.0 \\ 68.0 \\ 33.0$	$20.0 \\ 15.6 \\ 15.2 \\ 15.8 \\ 2.1 \\ 0.6$	Dolomitic. Aragonite, dolomite Feldspar Gibbsite
5	$35.0 \\ 37.0 \\ 47.0$	Sandy silt Yellow clay Yellow clay	$2.0 \\ 3.3 \\ 5.2$	$\begin{array}{c} 0.4\\ 0.8\\ 1.0\end{array}$	16.7 28.0 27.6	$15.2 \\ 13.4 \\ 10.6$	Aragonite

Hence, presumably, at this depth a fossile soil level exists, the once plants of which secreted aragonite.

Dolomite occurs in several samples (at 51.0 m and at 36.0 m in borings No. 2, and No. 4, resp.). No unambiguous explanation has been found as to its origin, it may be due to simultaneous sedimentation but might form after sedimentation.

Presence of quartz and calcite in the samples is customary. Sedimentary rocks always contain quartz, resistant to weathering, to handling, therefore likely to pile up. Also calcite may be a conveyed or locally formed material, its presence being common in sedimentary rocks, even if lesser than quartz.

From among clay minerals, the appearance of palygorskite acted as a novelty. Its occurrences up to now are either of hydrothermal or of sedimentary (lagoon) origin. Its physical and physico-chemical features vary for each deposite. It resembles montmorillonite by the ability of base exchange, its chainlike structure is, however, different. Its appearance is by no means isolated since it could be detected in several bored samples from Transdanubia.

The presence of montmorillonite in the samples explains for the poor soil characteristics.

Relationship between soil characteristics and the mineral composition

After detailed mineralogy tests, relations had been sought for between mineral composition and physical characteristics. Tests were facilitated by a study resulting in the deduction of relations between characteristics (JÁRAY-BIDLÓ 1967), permitting also the liquid limit to be determined.

Boring No.	Depth m	Туре	Clay mineral %	Calcite %	F _{lest}	F _{eale}
1	$36.5 \\ 39.0 \\ 45.3 \\ 48.0 \\ 54.0$	Light yellow clay Yellow silt Yellow silt Yellow clay Yellow clay	33.0 27.6 11.0 28.0 25.0	6.9 36.5 21.8 25.0 20.9	$44 \\ 27 \\ 26 \\ 40 \\ 40$	$\begin{array}{r} 65\\ 24\\ -\\ 36\\ 34\end{array}$
2	$\begin{array}{c} 33.0\\ 37.0\\ 38.0\\ 43.0\\ 45.0\\ 48.0\\ 50.0\\ 51.0\\ 52.0\end{array}$	Sand flour clay Light brown clay Grey poor clay Sand flour Grey clay Sand flour silt Yellow clay Yellow clay Yellow clay	$19.0 \\ 30.0 \\ 31.0 \\ 15.0 \\ 30.0 \\ 28.0 \\ 42.0 \\ 35.0 \\ 30.0 \\ $	$13.6 \\ 2.5 \\ 12.7 \\ 17.2 \\ 27.2 \\ 24.0 \\ 28.0 \\ 38.5 \\ 27.2 \\ 2$	$32 \\ 57 \\ 57 \\ -44 \\ 38 \\ 63 \\ 40 \\ 40 \\ 40$	$ \begin{array}{r} 30 \\ 64 \\ 56 \\ \\ 39 \\ 38 \\ 64 \\ 39 \\ 30 \\$
3	$\begin{array}{c} 31.0\\ 36.5\\ 37.0\\ 39.7\\ 41.0\\ 43.5\\ 49.0 \end{array}$	Sand flour silt Yellow clay Sandy silt Sand flour silt Yellow clay Yellow clay Yellow lime clay	16.7 21.6 16.8 18.1 19.0 27.6 27.6	$19.5 \\ 21.6 \\ 16.8 \\ 15.0 \\ 15.8 \\ 16.4 \\ 27.2$	$30 \\ 30 \\ 28 \\ 43 \\ 43 \\ 56$	27 25 42 44 43 Dolomite !
4	$33.5 \\ 39.0 \\ 41.0 \\ 50.0$	Yellow silt Yellow clay Stone rubble clay Yellow clay	$13.5 \\ 24.5 \\ 30.0 \\ 33.0$	20.0 15.2 15.8 0.6	35 35 28 57	
5	$35.0 \\ 37.0 \\ 47.0$	Sandy silt Yellow clay Yellow clay	$16.7 \\ 28.0 \\ 27.6$	$15.2 \\ 13.4 \\ 10.6$	$41 \\ 42 \\ 51$	$\begin{array}{c} 37\\47\\50\end{array}$

Table 3

F values calculated from the mineral composition

SKEMPTON (1950, 1953) established a relationship between the liquid limit (F value) and the mineral composition:

$$F = 2 M \% + 1 I \% + 0.6 K \%$$
.

where M, I and K are percentages by weight of montmorillonite, illite and kaolinite in the sample, respectively. From this relationship the palygorskite "equivalent" missed, therefore "equivalents" have been recalculated from some empirical F values to obtain the other values. There was a rather fair agreement in cases where the sample contained no CaCO₃. A satisfactory agreement was possible between experimental and theoretical clay and silt samples by modifying the formula:

$$F = 2.2$$
 (montmorillonite + palygorskite) $\% - CaCO_3\%$.

In some cases the calculated and the experimental values were not in agreement, awaiting to be explained for (Table 3).

Deviations could be attributed partly to the fact that mineralogy tests were made on other samples than used for soil characteristics, and partly, that for stone or crushed stones samples, only fine fractions had been tested. In a few cases, deliberately, the adhering clay crumbles have been tested.

Summary

Samples from borings made in Dunaújváros after 1964 have been tested and their mineral composition determined by X-ray diffraction and by derivatography. Most frequent minerals in the samples are quartz, calcite: dolomite and aragonite are less common. Clay minerals are montmorillonite and palygorskite. Mineral composition was applied to calculate the soil physical characteristics, exhibiting a fair agreement with test values.

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