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SEDIMENT VOLUME OF THE HUNGARIAN OIL SHALES IN ORGANIC SOLVENTS

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INTRODUCTION

Sediment volume of the Hungarian oil shales from Pula (Balaton Highland area) was determined in organic solvents of different polarity.

The purpose of the work was to find a quick and simple method to choose samples coming to detailed examinations.

Therefore, connections were looked for between the sediment volume and the amount of organic and inorganic components of the oil shales.

The structure and the volume of the sediments formed from suspensions are determined by the type of the dispersed material, the dispersing medium, the size, the shape and the surface quality of the dispersed particles, as well as by the temperature.

OSTWALD and HALLER [cited by SZÁNTÓ *et al.* 1971] studying the sediment volume of powders in organic solvents found that the sediment volume decreases with increasing dielectric constant of dispersing medium. The sediment volume is influenced by the wetting power of the medium by BLOM and it is influenced by the adhesive power between the particles by BUZÁGH [see SZÁNTÓ *et al.*, 1971]. The higher the adhesion the looser the structure of the sediment, consequently, the sediment volume becomes higher.

Adhesion is determined by the character of the adsorption layer, i. e. in water and in solutions of electrolytic conductors by the change and depth of the adsorption layer and in non-electrolyte by the structure and depth of the lyosphere, respectively. So, the sediment volume of hydrophylic powder is fairly high in apolar liquids because of the thin lyosphere and strong adhesion but it is small in polar liquids because of the thick lyosphere and weak adhesion.

Mixing a polar solvent into the system the sediment volume of polar powders decreases monotonously in apolar liquids. According to OSTWALD and HALLER [see SZÁNTÓ *et al.*, 1971] this fact can be explained by the oriented adsorption of the polar molecules.

The sediment volume in organic solvents is strongly influenced by the presence of water even in small amount.

The conditions in swelling systems capable of peptization are different from those of compact-grained systems.

In swelling systems the number of the particles is important regarding to the sediment volume, so the sediment volume is increased by the peptization and disaggregation.

The adsorption of organic material changes the surface conditions and therefore it influences strongly the sediment volume.

MATERIALS

Samples were collected from the borehole Put—7 from 38,5 to 4,8 m depth. Mineral components determined by X-ray diffractometry by MEZŐSI (personal communication) are calcite, dolomite, aragonite, quartz, feldspar, clay minerals, olivine and pyrite.

The organic material content of the samples is fairly high. Organic material consists of soluble and insoluble organic components.

The short description of the geological section by MUCSI (personal communication) see in Table 1.

TABLE 1

Short description of the samples

Depth (m)	Number of the sample	Characterization of the samples
39,3—30,0	73—55	Lime-marl rich in alginite with coalified plant remnants.
30,0—26,0	54—47	Alginite with high content of lime-marl, clayey laminae and coalified plant remnants. The porosity of the sample is various.
26,0—24,5	46—44	Alginite with lime-marl.
24,5—19,6	43—34	Alginite with lime-marl. The amount of the organic material is increased.
19,6—13,4	33—22	Aleurolite with significant clay content. The porosity of the sample is high.
13,4—13,0	21	Aleurolitic fine sandstone.
13,0— 8,0	20—11	Alginitic aleurolite, aleurolitic alginite and lime-marl with coalified plant remnants.
8,0— 6,0	10— 7	Lime-marl with coalified plant remnants.
6,0— 5,4	6	Clay marl, clayey aleurolite with few plant remnants.
5,4— 4,8	5	Lime-marl, clayey aleurolite.

EXPERIMENTAL PART

The samples were air-dried, they were ground in ball mill and sieved. The grain size used is under 0,1 mm. Experiments were carried out in test-tube of 20 ml. 0,8 g material was suspended in 10 ml solvent. Sediment volume was measured about one week later when it did not show any changes.

The soluble organic material was extracted by chloroform to obtain bitumen-A (Bit-A) then by the mixture of benzene-acetone-methanol to obtain BAM bitumen-A (BAM Bit-A).

The carbonate contents were measured by gas volumetric method and the organic carbon contents by burning.

Four solvents of different dielectric constant were chosen to determine the sediment volume:

	dipole moment	dielectric constant
benzene	0	2,2
chloroform	1,15	5,1
methanol	1,69	33,7
nitrobenzene	4,00	36,4

Sample	Depth (m)	Metha ml
5	4,8— 5,4	1,5
6	5,4— 6,0	1,4
7	6,0— 6,5	1,6
8	6,5— 7,0	1,8
9	7,0— 7,5	1,6
11	8,0— 8,5	2,0
14	9,5—10,0	1,9
15	10,0—10,5	2,0
17	11,0—11,5	1,9
18	11,5—12,0	2,0
20	12,5—13,0	1,8
21	13,0—13,4	1,2
22	13,4—14,0	1,8
24	14,5—15,0	2,3
25	15,0—15,5	2,3
26	15,5—16,0	2,7
27	16,0—16,5	2,4
29	17,0—17,5	2,1
30	17,5—18,0	2,1
31	18,0—18,5	2,1
33	19,0—19,6	1,8
34	19,6—20,0	2,4
35	20,0—20,5	2,2
38	21,5—22,0	2,3
39	22,0—22,5	2,5
40	22,5—23,0	2,2
42	23,5—24,0	2,5
43	24,0—24,5	2,4
45	25,0—25,5	2,3
47	26,0—26,5	2,1
48	26,5—27,0	2,3
52	28,5—29,0	2,8
58	31,5—32,0	2,5
59	32,0—32,5	2,3
62	33,5—34,0	2,4
66	35,5—36,0	2,7
67	36,0—36,5	2,6
69	37,0—37,5	2,4
71	38,5—39,0	2,0
72	39,0—39,3	2,0

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Table 2 contains the depth of the samples, the values of sediment volumes, the carbonate and total organic carbon contents.

Sediment volumes in the more polar methanol are lower than in the less polar chloroform, in benzene and nitrobenzene they are between those of methanol and chloroform.

It can be supposed that there is an adsorption layer on the surface of the particles and this absorption layer consisting of organic material is fairly polar. This is support-

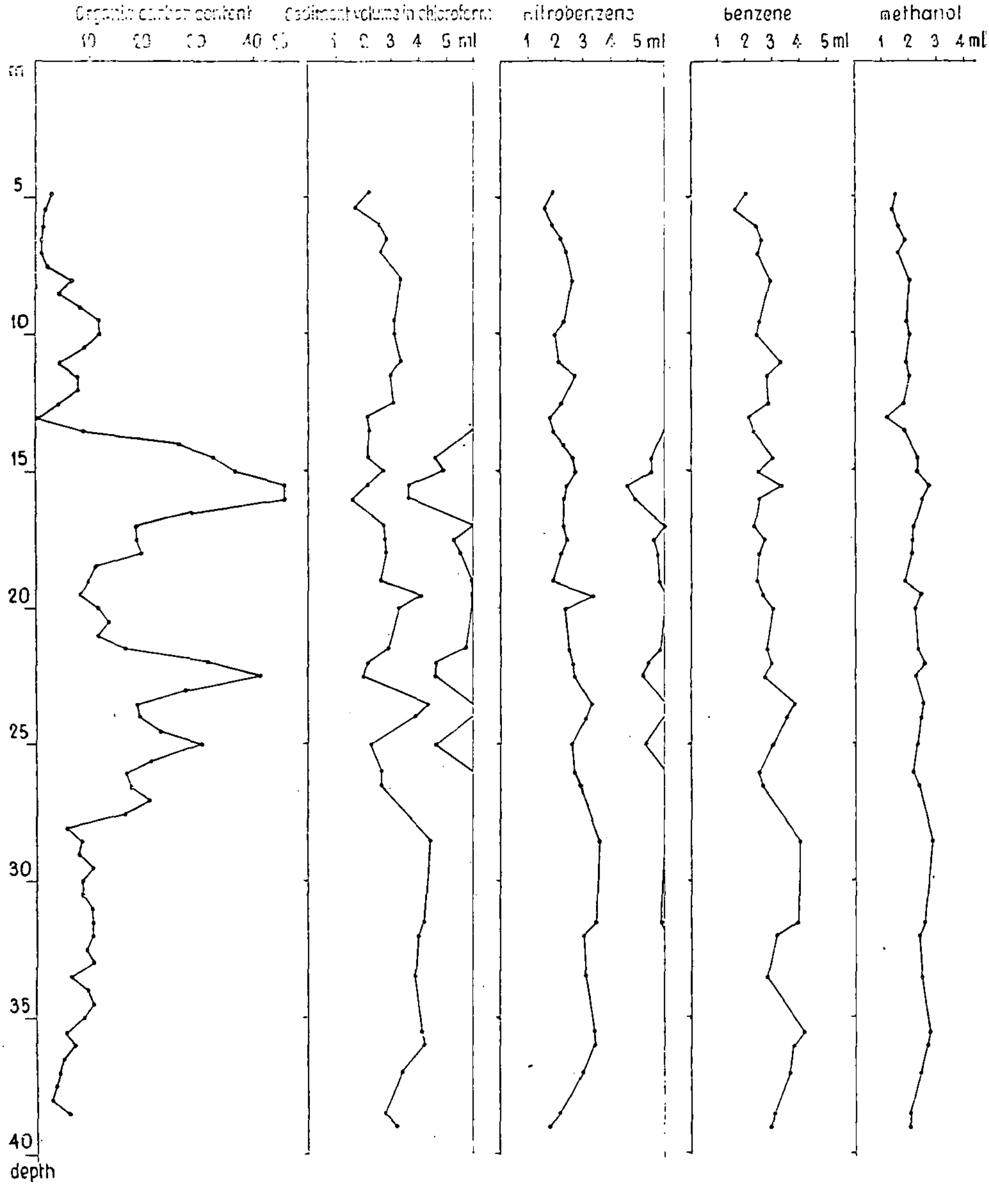

Fig. 1. Organic carbon content and sediment volume as a function of depth.

ed by the fact that the particles are flocculated and settled like floccules in the apolar benzene and chloroform.

The sediment volume and organic carbon contents as a function of depth are shown in *Fig. 1.*

Particles of several samples were separated into two phases, an upper and a lower one. As it can be seen on *Fig. 1* samples of very high organic carbon contents are separated. Organic carbon content was measured in upper and lower phases of sample No 27. Organic carbon content of the upper phase is 65,6 per cent and that of the lower phase is 19,3 per cent. So, this separation can be attributed to the difference of specific gravity between organic and inorganic components of the samples.

Of course separation took place only in chloroform (specific gravity 1,5) and nitrobenzene (sp. gr. 1,2) but it did not occur in benzene (sp. gr. 0,9) and methanol (sp. gr. 0,8). Maximum amount of the upper phase of the separated samples coincides with the maximum of the organic carbon contents.

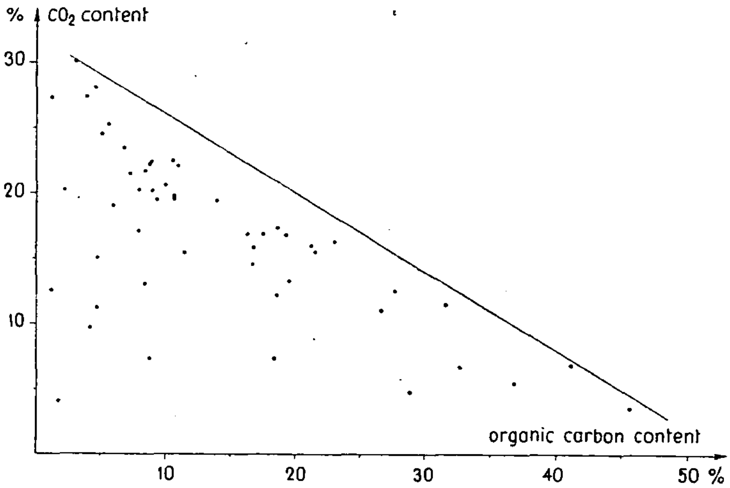

Fig. 2. Connection between CO_2 and organic carbon content.

A direct connection between the depth and the sediment volume could not be established because factors influencing the sediment volume are altered in a different way with the depth.

Considering the sediment volume depending on the carbon dioxide they do not show any connections.

The CO_2 and organic carbon contents are shown by *Fig. 2.* As it can be seen CO_2 contents decreases with increasing organic carbon contents, but in several samples these two factors seem to be independent of each other because of other minerals present in the samples.

To study the organic carbon contents and the sediment volume the amount of the organic carbon was recalculated into 100 g of the inorganic mineral components *(Figs. 3* and *4).*

In each solvent the sediment volume changes according to a maximum curve. The maximum is at about 10 per cent organic carbon contents. Reaching the maximum the curve declines but over 25 per cent organic carbon contents the sediment volume becomes independent of the quantity of the organic carbon.

Effect of the soluble organic material on the sediment volume was also studied. Bit-A and BAM Bit-A are shown in Table 3 [GRASSELLY *et al.*, 1975].

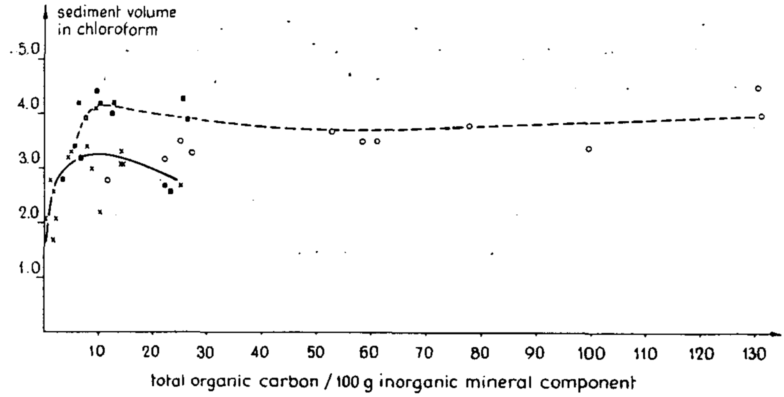

Fig. 3. Sediment volume in chloroform depending on total organic carbon content.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.
○ Samplex with high organic carbon content from 39,0 to 20,0 m depth.

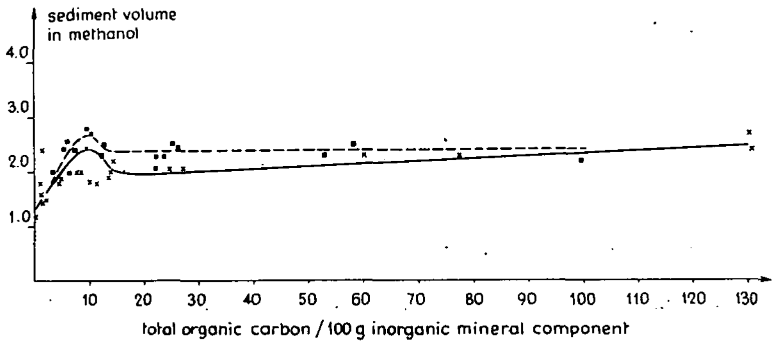

Fig. 4. Sediment volume in methanol depending on the total organic carbon content.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.

The sediment volumes determined in benzene and in chloroform depending on the amount of the soluble organic material are shown by *Figs. 5* and *6*.

These curves show also a maximum similarly to *Figs. 3* and *4*. In this case maximum is at about 1 per cent of soluble organic material. This fact suggests that the sediment volume is influenced rather by the soluble organic material than by the insoluble one.

Samples were extracted by chloroform and by the mixture of benzene-acetone-methanol then dried at 60 °C. Sediment volume of these samples were determined in chloroform, benzene and methanol (Table 4).

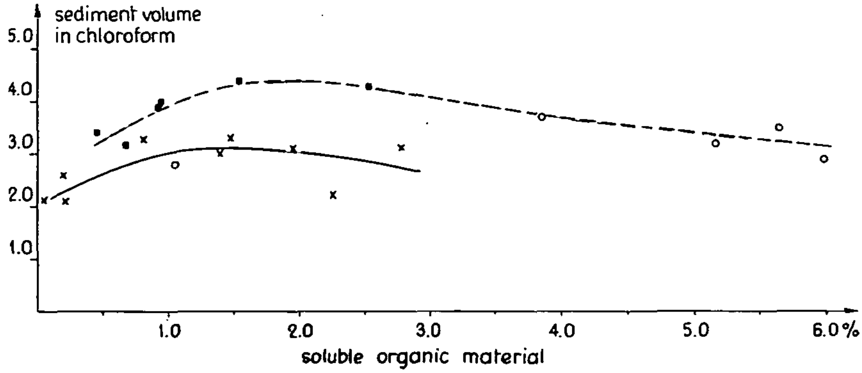

Fig. 5. Sediment volume in chloroform depending on the soluble organic material.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.
○ Samples with high organic carbon content from 39,0 to 20,0 m depth.

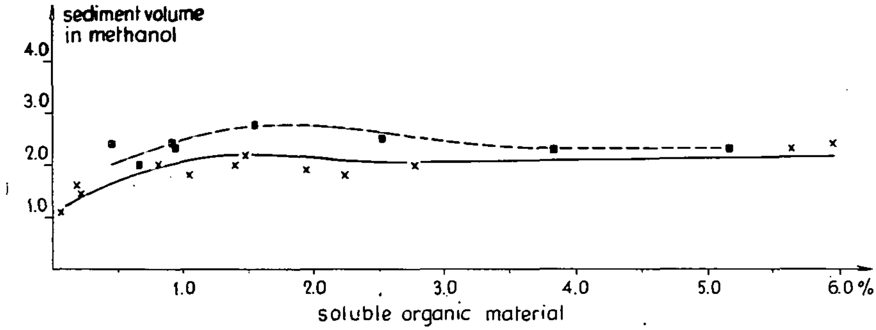

Fig. 6. Sediment volume in methanol depending on the soluble organic material.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.

In methanol and chloroform values show a saturation curve and in benzene they give a maximum, but this maximum is not so intensive as the values obtained before extraction *(Figs. 7.* and *8).*

The sediment volume obtained after extraction are lower than before extraction but the types of the curves are similar in both cases. It may be assumed that soluble organic material is adsorbed on the surface of inorganic mineral components. In all probability the sediment volume is influenced by adsorbed soluble organic material. Since the shape of the curves is similar before and after extraction this adsorption may be considered partly a chemical and partly a physical one.

The organic material bound by physical adsorption can be extracted by organic solvents, but the organic material bound by chemical adsorption remains on the surface even after extraction. This chemically adsorbed layer results the similar shape of the curves before and after extraction.

On the basis of *Figs. 3* and *5* it can be seen that samples can be grouped into three types. One of the types contains organic material in a fairly great amount. This type separates into two phases in chloroform and nitrobenzene. Sediment volume of the

TABLE 3

Bit-A, BAM Bit-A and total soluble organic material contents of the samples

Sample No	Bit-A %	BAM Bit-A %	Total soluble organic material %
5	0,14	0,07	0,21
7	0,11	0,08	0,19
11	0,61	0,19	0,80
14	1,40	0,54	1,94
15	2,34	0,43	2,77
18	0,84	0,55	1,39
21	0,05	0,01	0,06
22	1,80	0,43	2,23
24	3,61	2,04	5,65
26	5,12	1,73	6,85
27	3,95	2,01	5,96
33	0,55	0,49	1,04
35	1,15	0,32	1,47
38	3,99	1,18	5,17
42	1,56	0,95	2,51
45	2,99	0,85	3,84
52	1,06	0,48	1,54
59	0,67	0,27	0,94
62	0,53	0,38	0,91
69	0,28	0,17	0,45
72	0,43	0,23	0,66

TABLE 4

Sediment volume and insoluble organic carbon contents of the samples after extraction

Sample N⁰	Sediment volume in Methanol (ml)	Benzene (ml)	Chloroform Lower phase	Upper phase	Insoluble organic carbon/100 g mineral component
5	1,4	1,7	1,9		2,17
7	1,5	2,0	2,0		1,35
11	1,8	2,2	2,2		6,98
14	1,8	2,0	2,3		11,47
15	1,8	2,0	2,1		11,18
18	1,7	1,9	1,9		7,34
21	1,2	1,7	1,7		0,17
22	1,7	1,7	1,7		8,11
24	2,4	2,3	1,5	1,6	48,30
27	2,5	2,8	1,0	2,5	101,00
32	2,0	1,9	1,9	0,3	11,58
33	1,4	1,8	1,8	0,3	10,50
35	1,7	2,2	2,4	0,4	12,63
38	2,2	2,6	1,4	1,7	15,90
42	2,5	2,4	2,2	0,7	22,99
45	2,2	2,4	1,5	1,4	44,62
52	2,1	2,6	2,9		7,20
59	1,9	2,4	2,9		11,45
72	1,9	2,4	2,4		6,15

samples belonging to the second type gives a maximum curve, the value of the sediment volume is fairly high. The curve of the third type is under the curve of the second type.

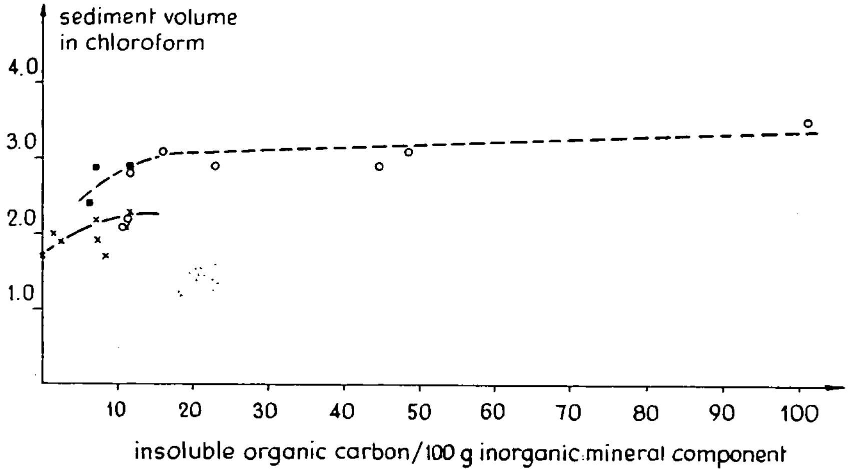

Fig. 7. Sediment volume of the extracted samples in chloroform.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.
○ Samples with high organic carbon content from 39,0 to 20,0 m depth.

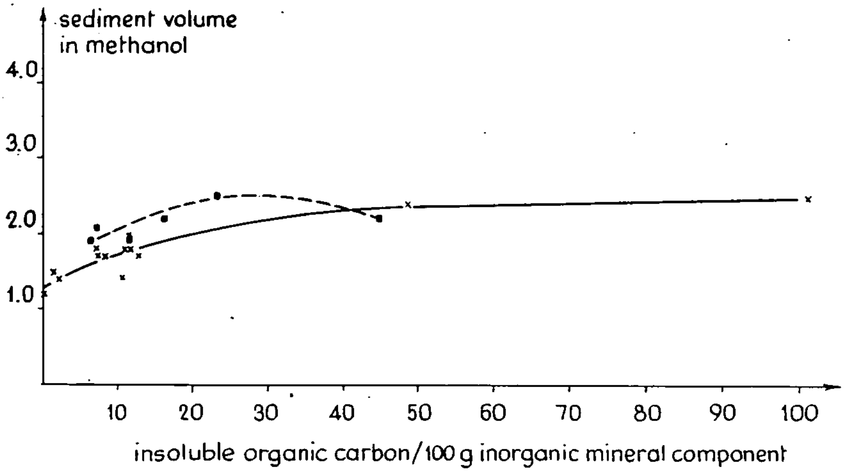

Fig. 8. Sediment volume of the extracted samples in methanol.
■ Samples from 39,0 to 20,0 m depth.
× Samples from 20,0 to 4,8 m depth.

According to MEZŐSI (personal communication) within the Püt—7 borehole two cycles can be distinguished, samples below 20,0 m depth contain more carbonate, aragonite prevails among the carbonates, the quantity of the quartz and the feldspar is negligible. Above 20,0 m depth the quantity of the quartz and the feldspar is more significant and the carbonate contents of the samples decreases.

The two types represented by the two curves mentioned above coincide with the samples belonging to the two sedimentation cycles.

Samples with high organic material contents belonging to the third type can be inserted into both sedimentation cycles.

SUMMARY

Sediment volume of Hungarian oil shales was measured in organic solvents and it was compared with the organic carbon and soluble organic material contents. The accumulation of the organic material in oil shales can be detected by measuring sediment volume in organic solvents of 1,2 to 1,5 specific gravity. The organic material concentrates in an upper solid phase on the top of the solvent due to its low specific gravity.

Considering connections between the total and soluble organic material as well as the sediment volumes it was supposed that the sediment volume is influenced rather by the soluble organic material. One part of this „soluble" organic material can be removed indeed by extraction, however, "soluble" organic material adsorbed by chemical force remains on the surface. In this case "soluble" organic material means chemical type and not the amount of organic material which is really extracted.

The sediment volume is influenced by the mineral components, too. Samples with higher carbonate and lower quartz contents have higher sediment volume than samples with lower carbonate and higher quartz contents. The samples from 39,0 to 20,0 m depth represent the type of low quartz and high carbonate contents with aragonite and the samples from 20,0 to 5,0 m depth contain quartz and feldspar, small carbonate without aragonite.

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