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## DISTRIBUTION OF SULPHUR IN SOME HUNGARIAN OIL SHALES (ALGINITES)

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*The most promising use of the products from oil shale mines opened in 1984 in Gércé and in 1986 near Pula (Transdanubia, Hungary) is to be expected in agriculture as a raw material for soil amelioration. This is due to the high organic, lime, potassium, and macro- and micro-element content of these products. Alternatively, they could play an important role in Hungarian coal-dust briquetting. Experiments on this option are currently in progress. Because of the high sulphur content of the Hungarian coals, it is very important that the sulphur emitted during combustion be minimized. Therefore, knowledge of the sulphur distribution in Hungarian oil shales (which have relatively low sulphur content) is important for the effective decrease of coal environmental pollution.*

*The data about sulphur distribution demonstrate that processes of its dissolution and oxidation in soil have taken place through the years.*

### Introduction

During geological mapping in the Transdanubian Central Range during 1973, a borehole was drilled west of Pula Village. This hole intersected 30 meters of greenish-coloured, unconsolidated, microlaminated sedimentary rock. This formation was found between Upper Pannonian basalts and Pleistocene loessic, gravely sediments. This sedimentary rock was strikingly light and ignitable with a lit match [1].

As a result of subsequent Hungarian oil shale exploration performed since 1973, five oil shale deposits have been discovered, along with an additional seventeen indications of additional resources. Four deposits (Pula, Gércé, Várkesző, Egyházaskesző) were formed in contemporaneous maar-type volcanic basalt craters, and one deposit (Várpalota) originated in a contemporaneous intramontane lagoon. The organic matter in the maar type oil shale derives from the remains of *Botryococcus braunii* Kützing algae, being, in fact, alginites. (The term "alginite" was suggested by Hevia [2].) The alginite deposits are of relatively small size with about 8 to 100·10<sup>9</sup> kg of reserves that can be mined under favourable conditions. Although some intervals of the deposits are of top quality (20-30 % tar content as determined by the Fischer probe), their bulk is of an average oil shale with oil content of 4 to 8 %. In Hungary, these alginites cannot be

regarded as potential energy resources. Technical experiments have verified possibilities for their use in the silicate industry (concrete, thermal and sound insulators etc.). The most promising uses, however, are to be expected in agriculture [3]. The presentations of the Alginite Conference dealt with the possibilities of this agricultural use [4-13].

Some data about the sulphur content of Hungarian oil shales can be found in the analyses presented in several sources. The total sulphur content in borehole Put-7 ranges from 0.1 to 1.1 %. It varies from 0.1 to 0.9 % at Gércse [1] and from 0.45 to 0.6 % at Pula [6]. Furthermore, it was established that about 10 % of the sulphur content in the alginites of Gércse is soluble sulphur. The sulphur content of alginites is interesting from an agricultural point of view, because additional amounts of sulphur could become soluble as a result of post-application oxidation. This has a pH-decreasing effect, but that can be offset by the carbonate content of alginites.

Knowledge of the sulphur distribution became important during Hungarian coal-dust briquetting experiments, that are currently in progress. The sulphur content of Hungarian coal is extremely high [14]. During the combustion of these brown coals, a large part of the sulphur is emitted into the atmosphere. For reasons of environmental protection, the amount of sulphur dioxide emitted should be reduced (a small amount of SO<sub>2</sub> is further oxidized to SO<sub>3</sub>). It is also important to know the distribution of pyritic and organic sulphur, if the coal is used as an energy resource.

Table 1. Markings Connected with the Samples from Gércse and Pula

Symbol	Feature	Notes
G é r c s e		
G-1	Stratified	Bottom of mine
G-2	Stratified	Bottom of mine
G-3	Stratified	Bottom of mine; aleuritic alginite
G-4	Stratified	Bottom of mine
G-5	Stratified	Commercial product from 1993
P u l a		
P-1	Unstratified; "massive" type	Bottom of mine
P-2	"Massive" type	Bottom of mine
P-3	"Massive" type	Bottom of mine
P-4	Boundary of the massive and stratified alginite type	Bottom of mine; limonitic alginite
P-5	Stratified	Bottom of mine
P-6	Thin-stratified	Bottom of mine; "paper" type
P-7	Stratified	Bottom of mine; "shoe sole" type
P-8	Stratified	Bottom of mine
P-9	Stratified	Bottom of mine + 5 m
P-10	Stratified	Bottom of mine + 5 m
P-11	Stratified	Bottom of mine + 5 m
P-12	Mixed	Commercial product from 1993
P-1928		Average samples of the bore Put-7

One of the most widely accepted theories for the origin of syngenetic pyrite is that the pyrite was incorporated into sediments by the action of bacterial colonies [15-17]. The amount of pyrite that may form in a sediment under anoxic conditions (absence of measurable dissolved oxygen) is limited by the rates of supply of decomposable organic matter, interstitial dissolved sulphate, and reactive detrital iron minerals. Organic matter appears to be the major control on pyrite formation in normal (non-euxinic) terrigenous marine sediments where dissolved sulphate and iron minerals are abundant. By contrast, pyrite formation in non-marine, freshwater sediments is severely limited by low concentrations of sulphate. As a result the sulphate content is rapidly and totally consumed via sulphate reduction within the sediment, leaving behind little pyrite and much organic matter [18].

According to the most widespread theory of diagenetic pyrite formation, the direct products from the reaction between hydrogen-sulphide ( $H_2S$ ) and  $Fe^{3+}$ -minerals are the acid volatile sulphides. (This attribute refers to the fact that these iron-sulphide minerals, in contrast with the pyrite, react instantly with the HCl while  $H_2S$  is evolved.) In this case, the elemental sulphur and polysulphide are produced in the reduction of sulphate [19]. Laboratory experiments proved that pyrites could be produced from the reaction of the  $H_2S$  and acid volatile sulphides [20].

## Samples and Analytical Methods

Eighteen oil shale samples from Pula and the Gércse Mines (Table 1) were examined. Samples were ground to grain size  $d \leq 60 \mu m$ .

The total carbon content was measured at 1000 °C under intense oxygen flow by combusting in a Carmograph-8 (Wösthoff).

Determination of calcite and dolomite by gasometry is based on the fact that, after a certain exposure time, 1:1 hydrochloric acid dissolves calcite at room temperature. Dolomite remains undissolved under the same conditions. Both calcite and dolomite dissolve after boiling for 5 minutes in the same solution [21].

The determination of the total sulphur was made using the Eschka procedure. The Eschka method consists of thoroughly mixing the powdered alginite sample with Eschka mixture (two parts calcined  $MgO$  and one part anhydrous  $Na_2CO_3$ ) and then ashing the mixture in a muffle furnace at 800 °C. The ashed alginite is leached with hot water and filtered. The sulphate is precipitated with  $BaCl_2$  and measured by gravimetric analysis as barium sulphate.

The sulphur content of disulphide in alginite samples was reduced by nascent hydrogen to hydrogen sulphide in the presence of Cr(II)-ions. The hydrogen sulphide formed from this reduction was bubbled through a cadmium acetate solution and the disulphide sulphur content was determined by iodometry.

The sulphate sulphur is measured by extraction of minus 60 mesh alginite with hydrochloric acid, followed by precipitation with barium chloride and weighing as barium sulphate.

In every case, the organic sulphur is determined by the difference between the total sulphur and inorganic sulphur, as indicated below.

$$\text{organic S} = \text{total S} - (\text{pyritic S} + \text{sulphate S})$$

Table 2. Distribution of Sulphur in Samples at Gérce and Pula, Including Data for Moisture, Ash, Total Carbon and Carbon Dioxide Content, %

Symbol	$W^w$	$A^d$	$C_t$	$CO_2$	$S_t^a$	$S_p^a$	$S_{SO_2}^a$	$S_{org}^a$ (diff.)	$S_t^{dif}$	$S_p^{dif}$	$S_{SO_2}^{dif}$	$S_{org}^{dif}$ (diff.)
G-1	3.3	22.3	5.1	9.4	0.1	<0.1	<0.1	<0.1	0.13	<0.1	<0.1	<0.1
G-2	2.7	28.9	5.3	7.8	0.5	0.4	<0.1	<0.1	0.73	0.6	0.1	<0.1
G-3	3.4	23.0	5.0	7.7	0.1	<0.1	<0.1	<0.1	0.14	<0.1	0.0	<0.1
G-4	3.1	25.4	7.5	6.7	<0.1	<0.1	0.0	<0.1	0.14	<0.1	0.0	<0.1
G-5	3.2	22.7	5.7	10.4	0.4	0.4	<0.1	<0.1	0.54	0.5	<0.1	<0.1
P-1	2.4	64.6	42.9	4.8	0.3	<0.1	<0.1	-0.1	0.91	0.3	0.3	-0.3
P-2	2.4	62.6	39.8	4.4	0.3	<0.1	<0.1	-0.1	0.89	<0.3	<0.3	-0.3
P-3	3.6	32.3	10.2	16.3	0.2	0.1	0.1	0.0	0.31	0.15	0.15	0.0
P-4	3.8	32.0	10.0	7.1	3.6	1.1	2.3	0.2	5.60	1.7	3.6	0.3
P-5	2.9	47.4	24.0	16.6	0.4	0.1	0.1	0.2	0.80	0.2	0.2	0.4
P-6	4.1	50.7	26.1	9.7	0.3	0.1	<0.1	-0.1	0.66	0.2	0.2	-0.2
P-7	5.2	35.7	13.3	3.6	0.1	0.0	0.0	0.1	0.17	0.0	0.0	-0.2
P-8	5.1	41.7	12.3	34.5	<0.1	0.0	0.0	<0.1	~0.17	0.0	0.0	-0.2
P-9	4.9	41.8	20.3	5.3	0.2	<0.1	<0.1	<0.1	0.38	~0.15	~0.15	<0.1
P-10	3.6	50.2	25.8	8.7	0.2	<0.1	<0.1	<0.1	0.43	0.2	0.2	<0.1
P-11	3.4	28.6	7.9	1.8	0.2	<0.1	<0.1	<0.1	0.42	0.2	0.2	<0.1
P-12	3.8	50.7	28.0	7.9	0.6	0.2	0.2	0.2	1.32	~0.4	~0.4	-0.4
P-1928	2.2	49.9	30.0	9.5	0.4	0.1	<0.1	-0.2	0.84	0.2	<0.2	-0.4

$W^w$  - analytical moisture, wt%;  $A^d$  - ash (air dried sample), wt%;  $C_t$  - total carbon content, wt %;  $CO_2$  - mineral carbon dioxide content, wt%;

$S_t^a$ ,  $S_p^a$ ,  $S_{SO_2}^a$ ,  $S_{org}^a$  - total, pyritic (+ sulphide), sulphate, organic (by difference) sulphur content in air dried sample;

$S_t^{dif}$ ,  $S_p^{dif}$ ,  $S_{SO_2}^{dif}$ ,  $S_{org}^{dif}$  - total, pyritic (+ sulphide), sulphate, organic (by difference) sulphur content in dry, ash-free basis.

## Results and Discussion

The results of experiments are summarized in Table 2.

The samples from Gércse are macroscopically uniform and there are no significant divergences in the total sulphur content. The samples from Pula are of two types. There is no significant difference in the total sulphur content in either type, but at the dividing line of the two types (Put-4) the sulphur content is extremely high.

In the samples from Gércse, the distribution of sulfur types is as follows:  $S_p^a \geq S_{SO_4}^a + S_{org}^a$ . In the samples from the Pulaian Mine none of the sulphur types has dominance within the total sulphur content, except in the case of P-4. In the average samples of Borehole Put-7, certain differences can be found.

The carbonate content of the samples from Gércse and Pula is usually about 20 %. Mezősi and Mucsi draw attention to the fact that in Borehole Put-7, aragonite can be found, in addition to calcite and dolomite [22].

## Conclusions

The total sulphur content of the examined oil shale samples is low, being on average  $\leq 0.5$  %. This is due to their occurrence in freshwater sediments.

The low amount of pyrite and organic sulphur in the oil shale "attenuates" the high sulphur content of Hungarian coals when the oil shale is used as a supplement in coal-dust briquets. The carbonate content also favourably influences the  $SO_2$  emission during the combustion of the briquets.

In the agricultural use of the alginite, it immediately supports the supply of sulphur to the soil as soluble sulphur and, in the long run, adds additional sulphur as a result of pyrite oxidation. At the same time, the average 20 % content of carbonate inhibits the soil pH from becoming more acidic at the place of fertilization.

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