

## QUALITY REDUCING PROPERTIES OF HUNGARIAN BROWN COALS

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### ABSTRACT

Hungarian brown coals of different ages and from different mines were examined. On the basis of elementary analysis it can be established that the maturity of Hungarian brown coals is lower and their total sulfur content is higher than that of foreign coals. A part of the total sulfur is included in pyrite form but it is very likely that the larger part of the sulfur content is organic sulfur. During combustion of these coals the largest part of the organic sulfur and a part of the pyrite sulfur gets into atmosphere as combustible sulfur. For reasons of environmental protection the experiments should be contained to reduce the amount of the sulfur dioxide getting into the atmosphere to minimum value.

### INTRODUCTION

On the basis of archival documents the coal mining was started in Hungary in the April of 1759 from the coal bed could be found in the neighbourhood of Wansdorf village (today is Brennbergbánya) was attached to Sopron (BÁN, 1936). Since that time Jurassic black coal, Eocene-Oligocene and Miocene brown coal and Pliocene lignite have been being mined. In the first place the exploited coals are used up as the source of energy. Therefore from the point of view of environment protection the sulfur content of mineral coals is an important information.

The total sulfur content is usually combined from inorganic and organic sulfur. The sources of inorganic sulfur content is the elemental sulfur occurring in little quantities, the frequent pyrite or marcasite, melnikovite, pyrrhotine some rarely occurring sulfid minerals (chalcopyrite, arsenopyrite, etc.).

The sulfate sulfur content is originated mainly from gypsum and anhydrite. The organic sulfur can be determined as the difference between the total sulfur and the sum of pyritic-, metallic-sulfid and sulfate sulfur content.

According to previous views concerning the sulfur content of mineral coals, it is mainly originated from the proteins (cystein, cystine, methionine) and from other organic compounds. Recently the researchers' opinion it that the sulfur content in the fossil organic matter is predominantly of secondary origin. Namely, is has come from the sulfates through the reduction performed by *Desulfovibrio desulfuricans* bacteria under anaerobic circumstances. Organic material of sediments is oxidised by the bacteria using up oxygen of the sulfates to the reaction while sulfates are being reduced into hydrogen sulfide.

In the presence of iron pyrite has been formed. Without iron hydrogen sulfide in practice other sulfuric compounds, even elemental sulfur have been formed (KLESMENT *et al.*, 1985).

The common paludal microflora does not proliferate in the acid water of swamps so most of the "normal" mineral coals do not contain much sulfur. The paludal bacteria have been proliferated only in alkaline waters. The water of the swamps can be turned into alkaline in three different ways:

1. The reaction of the water of deeper sapropelic swamps is usually more alkaline because of the lower humus content (jüttja pH=6—7, sapropel pH=8—8.5);
2. Acidity of marshes effected on by the saline water is lost because of the sea water (pH=8);
3. The water of swamps turns to alkaline in consequence of dissolution of the carbonate content of surrounding limestones.

In Hungary this third case is the most important. It is effective on several areas. The peat or coals surrounded by limestone usually contain organic sulfur in large quantity (SZÁDECZKY-KARDOSS, 1952).

In laboratory investigations catalytic effect of carbonates on petroleum and sulfur reaction wered determined (VALITOV, 1978).

It was established on the basis of oil shales' elementary analysis (KLEMENT, 1985) that the organic material contained much sulfur if the mineral component of the oil shale was carbonate, and the sulfur content could be found in the form of pyrite if the mineral component were argillaceous. The sulfur content of the fossil matter is influenced by the rock-type and even by its iron content which is only 0.5% or lower in the carbonate rocks, while 6.5% ( $\text{Fe}_2\text{O}_3 + \text{FeO}$ ) in the argillaceous rocks (VOYTKEVITSH *et al.*, 1977).

More than half part of the total sulfur content of brown coals consists of organic sulfur. Its distribution is shown in Table 1 in case of American and Australian brown coals (SMITH and BATTS, 1974; SCHOBERT, 1984).

Forms of sulfur in Texas lignites and Australian brown coals

TABLE 1

	Total sulfur (%)	Pyritic sulfur (%)	Sulfate sulfur (%)	Organic sulfur (%)	Description
<b>Texas USA</b>					
Wilcox mean	0.9	0.26	0.02	0.62	
Jackson east	1.29	0.40	0.02	0.87	
Yegus east	0.99	0.50	0.02	0.47	
<b>Gippsland Basin Victoria Australia</b>					
	7.9	0.07	0.44	7.41	Brown coals with high organic sulfur contents
	6.5	0.09	0.42	6.01	
	6.8	0.01	0.17	6.65	
	7.2	0.12	1.83	5.23	
<b>Yallourn</b>					
	0.2	0.00	0.01	0.19	Coals with low sulfur contents
	1.2	0.09	0.42	0.65	

In addition to brown coals measurements on soils and peats also were performed, and two forms of organic sulfur were reported:

1. A carbon-bounded sulfur such as in amino acids and heterocyclics; and

2. A carbon-oxygen bounded sulfur as in choline sulfate or sulfated polysaccharides.

The latter sulfur form is referred to as estersulfate and in many cases accounts for over half of the organic sulfur (TABATABAI and BREMNER, 1972).

The fact that the organic sulfur content in different peats is higher than it is could be expected from original vegetable matter, and that only less than 40% of organic sulfur content is originated from amino acids called researchers' attention to clear up how the sulfur built into the organic fraction of peat and what is the source of the main part of the organic sulfur (CASAGRANDE *et al.*, 1979). It was established on the basis of experiments with elemental sulfur ( $^{35}\text{S}$ ) and  $\text{H}_2^{35}\text{S}$  that the elemental sulfur and the sulfur of hydrogen sulfid built into the organic material. Hydrogen sulfide has already able to react with peat at room-temperature and the largest part of the organic sulfur can be found in humin and humic acids.

There are in the peat swamps elemental sulfur and hydrogen sulfid which may be originated microbiologically, i.e. the laboratory experiments can be carried out in the nature, too.

The intricacy of the processes proceeding in the nature is shown by the fact that different sulfur compounds were produced from sulfur-free amino acids with the aid of elemental sulfur (MARTIN and HODGSON, 1973). In addition, carbohydrates react with hydrogen sulfid at low temperature (100—200 °C) yielding variety of organosulfur compounds including thinphenes, thiols, sulfids and sulfones (MANGO, 1983), finally sulfate ions oxidize the methyl group to carboxyl in the presence of hydrogen sulfide (TOLAND, 1960).

#### SAMPLES AND ANALYTICAL METHODS

57 coal samples from different mines (*Fig. 1*) were examined. The determination of carbon was carried out by Carmhograph 8 (Wösthoff) in oxygen flow at 1000 °C.

The hydrogen content was determined by CHN—1 analysator.

The nitrogen determination was carried out by the Kjeldahl-method. Measurements were carried out after destruction in concentrated sulfuric acid in form of ammonium ion, using ion-selective electrodes in an equipment of OP—264 type.

The determination of the total sulfur was carried out with Eschka-mixture (2 parts by weight MgO and 1 part by weight anhydrous  $\text{Na}_2\text{CO}_3$ ) at 800 °C. The sulfate precipitated with barium chloride was determined by gravimetric analysis as  $\text{BaSO}_4$ .

#### RESULTS

Data of some Hungarian brown coals analysed by us are shown in Table 2. In Table 3 the total sulfur content data of some Hungarian brown coals are summarized in chronological succession on the basis of published data and our measurements. The name of analyst or informant is marked.

For comparison some total sulfur content data of measured brown coal occurrences of the world are presented in Table 4.

Elementary analyses of Hungarian brown coals

TABLE 2

Coal fields	Mines	Number of samples	Age	C	H (wt %)	N	S	O dif.	Dry, ash-free basis				
									C	H	N	S	O dif.
Tatabánya basin	Nagyegyháza	8	Eocene	59.0	4.7	0.2	5.3	30.8	72.1	5.7	0.3	6.5	15.4
	Csordakút	6		54.0	4.4	0.7	4.0	36.9	70.6	5.7	0.9	5.3	17.5
Veszprém area	Balinka	5	Eocene	50.0	3.9	0.3	5.7	40.1	70.9	5.6	0.4	8.3	14.8
	Dudár	8		48.7	4.1	0.2	5.3	41.7	69.2	5.8	0.3	7.7	17.0
Dorog basin	Lençsehegy	11	Eocene	55.7	4.9	0.1	5.3	34.0	70.9	6.3	0.2	6.3	16.3
	Mogyorósbánya	3		Oligocene	56.3	4.5	0.2	3.8	35.2	70.9	5.6	0.3	4.8
Borsod basin	Kurityán	5	Miocene	48.9	4.3	0.3	3.0	43.5	69.0	6.0	0.5	4.3	20.2
	Putnok	11		51.1	4.2	0.3	2.4	42.0	70.6	5.8	0.4	3.1	20.1

The total sulfur content data of some Hungarian brown coals summarized in chronological succession on the basis of published data and our measurements

TABLE 3

Coal fields	Mines	GRITNER	VARGA—	KÁPLÁR	BALÁZS—	MOLNÁR		PÁPAY	PÁPAY
		S(%) 1906	NYÜL S+(%) 1937	S(%) 1968)	JUHÁSZ S(%) 1969	1970	1981	S(%) 1985—86	S+(%) 1985—86
Borsod basin		3.51			0.5—3.5 mean 2.6			2.6	3.4
Veszprém area	Balinka			4.0		5.1	5.04	5.7	8.3
	Dudár			3.2		4.4	5.00	5.3	7.5
Tatabánya basin		3.74	4.5	3.3		4.5	4.20	4.7	6.0
Dorog basin		1.10—3.41	4.8	3.5		3.7		4.9	6.0

\* dry, ash-free basis

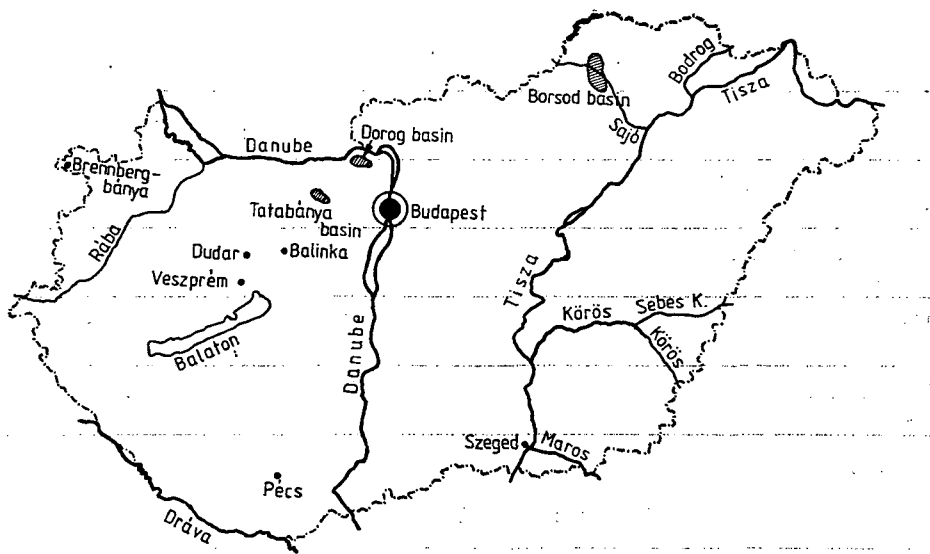


Fig. 1. Geographical setting of the studied region.

### CONCLUSIONS

The average carbon content of Hungarian brown coals studied is 10–15% lower than that in foreign coals. On the other hand, the total sulfur content is higher than those. The total sulfur content of 57 brown coal samples was found to be 4.4% (On dry, ash-free basis: 5.7%).

According to our own measurements the total sulfur content of Miocene brown coals of Borsod basin is the lowest among the Hungarian occurrences. Examining chronologically the sulfur data of some brown coals exploited in different mining districts, an increasing tendency can be established with a certain oscillation during the last 80 years.

If the qualitative distribution of total sulfur content is examined — on the basis of published data and the available pyritic sulfur data of informing character — the conclusion can be drawn that the pyritic sulfur content is low in the Eocene brown coals of Lencsehegy and Duder. The pyritic sulfur content is 10% or higher in the coals from Nagygyháza, Csordakút, Balinka and partly in the course of Oligocene age from Mogyorósbánya, respectively. The major part of Miocene coals of Borsod basin is characterized by low pyritic sulfur content, nevertheless, the pyritic sulfur content of the brown coal mined out from Putnok is higher than the average.

Presuming that the sulfate sulfur is not a significant quantity in Hungarian coals, it can be made probable that the sulfur is bounded in organic compounds in the samples of low pyritic sulfur content.

During combustion of these coals the major part of sulfur bounded in organic compounds and partly the pyritic sulfur get into the atmosphere as combustible sulfur. The sulfur content data of different Hungarian brown coals are published in Table 5 (TARJÁN, 1981; FEJÉR—OSWALD, 1988).

On the basis of above mentioned establishments the sulfur content of brown coals must be decreased to minimum value in one of the possible manners — before

TABLE 4

*Some total sulfur content data of major brown coal occurrences of the world*

Coal fields	S (wt %)	Moisture ash free or dmif (wt %)
Victorian brown coal Australia		0.14—5.36
Rhenish brown coal Germany	0.25 <sup>+</sup>	
Norther Great Plains lignites USA	0.6—0.8 mean 0.7	0.9—1.1 mean 1.0
Texas lignite USA	0.9—1.29 mean 1.05	1.35—2.25 mean 1.79

<sup>+</sup> S(org)

TABLE 5

*Forms of sulfur in Hungarian brown coals*

Mines	Total sulfur (wt %)	Pyritic sulfur (wt %)	Combustible sulfur (wt %)
Lencsehegy II	6.5	0.8	5.0
Nagyegyháza	4.4	1.1	3.7
Balinka	4.6	1.1	3.6
Dudar	4.7	0.8	3.4
Borsod	2.5		1.8

combustion, during combustion or from flue gas — before using up in thermal power-station in order to reduce the amount of air polluting sulfur dioxide. Or course, the ideal solution of this question would be giving up the combustion of coals in thermal power-station.

In Hungary experiments have been continued for years to reduce the amount of sulfur dioxide in order to satisfy our international engagement i.e. by 1993 the quantity of sulfur dioxide emitted into the atmosphere will have been decreased by 30%.

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