ON A POSSIBILITY TO DETERMINE THE CONTENT OF CLAY MINERALS HYDRATION WATER IN SOLID FOSSIL FUELS

Kaarli UROV and Mihkel KOEL

Keemia Instituut (Institute of Chemistry), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

Abstract. It has been demonstrated that it is possible to determine the constitutional water content in organogenous rocks by means of high-resolution thermogravimetry. The content of hydration water in the non-carbonate mineral portion of solid fuels is not constant and has a tendency to decrease with increasing content of this material in a caustobiolith.

Key words: thermogravimetry, fossil fuels, clays, crystal-hydrates water, organic matter content.

The lack of trustworthy methods for estimating the water contained in minerals, in the first place aluminosilicates, present in fossil solid fuels causes the most considerable error in the determination of their organic matter content. It is, of course, true that quite an adequate picture can be obtained on the basis of the results of a full mineralogical analysis of the inorganic part of the rock. However, this procedure is very labour-consuming and besides it, there is always a portion of amorphous mineral material not registered by such an analysis. Separating the mineral part by removing the organic portion by its complete oxidation [1] is also quite time-consuming and is associated with several side reactions. Therefore, in routine analysis the presence of hydrates water is usually ignored, though the mistake in estimating the organic content of a fuel can reach in this case 20–30% and more, especially when analysing ash-rich rocks such as oil shales. Attempts have been made to approach the problem with more accuracy.

Thus, it has been assumed that all clay minerals or those present in various layers of a certain deposit have practically the same composition and, consequently, the same mineral water content. According to [2, 3] aluminosilicates and gypsum present in solid fuels contain on the average 8–10% of hydrates water, for kukersite shale its content is estimated to be 2.5–3% [4, 5], for Turovo oil shale (Belarus) about 3.6% [6], and for Dictyonema shale (Estonia) 2.3% [7]. As to the graphical methods [8], also only average values can be estimated with their help.

In the present work, it has been established that in the case of high-resolution thermogravimetric analysis the constitutional water of solid fuels forms a well defined peak in the region of 520–580°C (Figs. 1 and 2). The work was carried out in Duke University, North Carolina, USA; a Perkin-Elmer Series 7 thermograph was used (heating rate 10°C/min, N_2 as carrier gas). All in all, 39 solid fuel samples, most of them oil shales, have been analysed, 25 of these as most representative were investigated
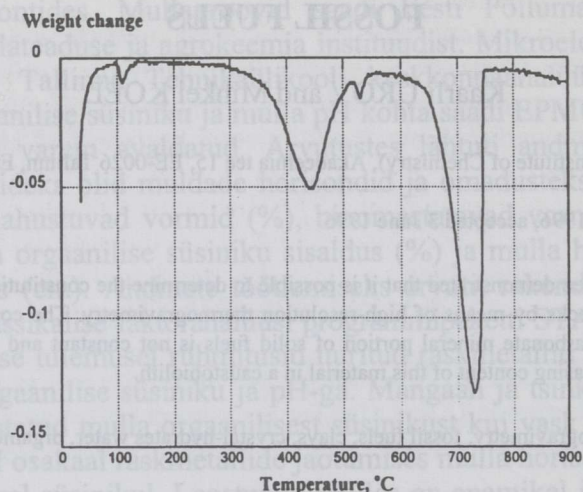

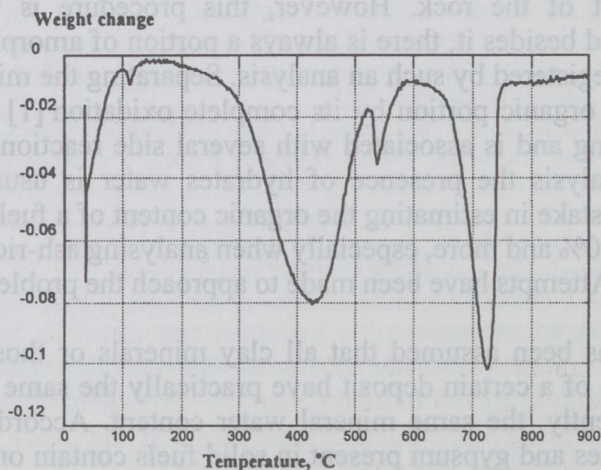Fig. 1. DTG curve for Lyuban oil shale, layer Ia (Belarus).

Fig. 2. DTG curve for Chagansk oil shale (Orenburg District, Russia).

more thoroughly (repeated experiments with the same sample); see the Table. Among the samples analysed some young sediments (sapropelic mud of Lahepera Lake, Estonia, and balkhashite of Lake Balkhash, Kazakhstan), a brown coal of Novo-Dmitrovo, Ukraine, and Riphean graphitic rocks of East Siberia, Irkutsk District, Russia, were also represented. More detailed characteristics of the fuels investigated can be found in [9].

It is evident from Figs. 1 and 2 that, besides constitutional water, carbonates derived carbon dioxide also forms a well separated peak on thermograms in the region of 620–770 °C.

As it is sometimes difficult to obtain reliable quantitative data by thermogravimetry (very small sample size combined with problems in collecting a representative portion of a solid heterogeneous mixture, possible entrainment of the material by carrier gases, etc.), it seems to be more convenient and exact to proceed from the thermogravimetrically determined ratio of the amount of the hydrates water to that of carbon dioxide derived from carbonates, and from the total carbon dioxide content of the sample, measured by the standard laboratory procedure (via decomposition of carbonates by an acid). The crystal-hydrate water content of the rock, W_M^d, is then found as follows:

$$W_M^d = \left[\frac{W_M^d}{(CO_2)_M^d} \right]_T \times \left[(CO_2)_M^d \right]_S, \tag{1}$$

where $\left[\dfrac{W_M^d}{(CO_2)_M^d} \right]_T$ – ratio of constitutional water content and carbonates derived carbon dioxide content determined by thermogravimetry;

$\left[(CO_2)_M^d \right]_S$ – content of the carbonates carbon dioxide determined by the standard laboratory procedure.

The results obtained are given in the Table, the content of hydrates water in the samples investigated varies in quite large limits (from 0.1 to 4.9%). If the rock contains, for example, 20% of organic matter and 4% of constitutional water, the relative error in estimating the content of the former, if one ignores the water presence, will be 20%. Proceeding from the data obtained we also examined the above-mentioned hypothesis about various fossil fuels having similar composition of clays contained in them, at least as to the content of hydrates water. Actually, it is obvious from the table that the minerals water content in the non-carbonate portion of mineral matter varies in the case of rocks investigated from 0.2 to 9.4%.

Content of constitutional water in fossil fuels investigated, wt.-%

Deposit, outcrop	Geological age	Content of constitutional water	
		in dry sample	in the non-carbonate portion of mineral matter
Graphitic argillite, Irkutsk, Russia	Riphean	4.93	5.70
Dictyonema shale, Maardu, Estonia	Ordovician	0.16	0.24
Selennyakh, Yakutia, Russia	Devonian	0.62	6.32
Lyuban, Belarus: layer Ia	Devonian	0.97	1.84
layer Ib	Devonian	0.76	1.72
layer IIa	Devonian	0.65	1.12
layer IIb	Devonian	0.86	1.92
Turovo, Belarus	Devonian	4.85	8.98
Ukhta, Komi, Russia	Devonian	0.64	1.35
Kenderlyk, Kazakhstan	Carboniferous	0.51	0.69
Edge, Spitzbergen Archipelago	Triassic	0.81	1.13
Levyi Kedon, East Siberia	Triassic	0.24	0.24
Kashpir, Volga basin, Russia: layer I	Jurassic	2.17	9.42
layer II	Jurassic	2.20	4.61
layer III	Jurassic	1.93	3.28
Syssol, Komi, Russia	Jurassic	1.05	1.75
Chagansk, Orenburg, Russia	Jurassic	1.60	6.16
Ukhta, Komi, Russia	Jurassic	1.56	4.73
Borov Dol, Bulgaria	Eocene	1.25	1.70
Krasava, Bulgaria	Eocene	1.14	1.97
Baisun, Uzbekistan	Eocene	2.37	5.08
East Urtabulak, Uzbekistan	Eocene	2.03	4.41
East Chandyr, Uzbekistan	Eocene	1.90	4.84
Novo-Dmitrovo, Ukraine: oil shale	Tertiary	0.78	1.16
brown coal	Tertiary	0.13	1.30

Therefore, it is certainly not correct to use some kind of average values as a base for calculations.

It is interesting to note that the minerals water content in the non-carbonate mineral material depends to some extent on the content of this material in the rock (Fig. 3). This correlation seems to be inversely proportional. According to the results of statistical analysis

$$W_M^{(sil)} = -0.061 \left[A^d - 1.27 \left((CO_2)_M^d \right) \right] + 6.436, \qquad (2)$$

where $W_M^{(sil)}$ — content of hydrates water in the non-carbonate part of mineral matter, %;

A^d — ash, dry sample basis, %;

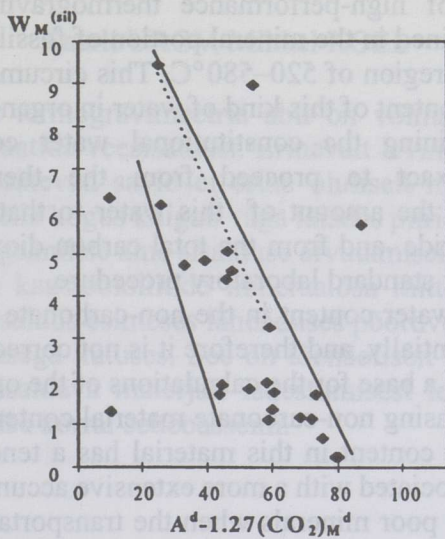$(CO_2)_M^d$ — carbonates derived carbon dioxide, %.

Fig. 3. Dependence of the hydrates water content in the non-carbonate mineral material, $W_M^{(sil)}$, on the latter's content in the rock $\left[A^d - 1.27\left((CO_2)_M^d \right) \right]$. The dotted line designates Kashpir shale.

The correlation coefficient $R = 0.480$ and the level of confidence $P > 0.98$. This tendency is revealed especially well in the case of Kashpir shale (dotted line in Fig. 3).

If we exclude from the samples examined those four rocks that are outside the main pathway in Fig. 3 and are prevailingly not typical oil shales (brown coal, graphite rock, thermally very profoundly transformed Selennyakh shale, and Turovo shale), we will have:

$$W_M^{(sil)} = -0.095 \left[A^d - 1.27\left((CO_2)_M^d \right) \right] + 7.789 \qquad (3)$$

with $R = 0.872$ and $P > 0.99$.

This means that, as a general rule, the more there is non-carbonate material in a solid fuel the lower is the constitutional water content in this material. We are of the opinion that this phenomenon is connected with a relatively more extensive accumulation of coarser, free from hydrate water or low in it minerals (quartz, feldspar, etc.) in the case of a large scale transportation of terrigenous material into the sedimentation basin.

CONCLUSIONS

1. In the case of high-performance thermogravimetry the crystal-hydrate water contained in the mineral portion of fossil fuels forms a well defined peak in the region of 520–580°C. This circumstance can be used for estimating the content of this kind of water in organogenous rocks.

2. When determining the constitutional water content it is more convenient and exact to proceed from the thermogravimetrically determined ratio of the amount of this water to that of the carbonates derived carbon dioxide, and from the total carbon dioxide content of the sample measured by standard laboratory procedure.

3. The hydrates water content in the non-carbonate portion of mineral matter varies substantially, and therefore it is not correct to use some kind of average values as a base for the calculations of the organic content.

4. With the increasing non-carbonate material content in solid fuels the constitutional water content in this material has a tendency to diminish. This is probably associated with a more extensive accumulation of coarser, constitutional water poor minerals when the transportation of terrigenous material into the sedimentation basin takes place on a large scale.

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ÜHEST VÕIMALUSEST SAVIDE HÜDRAATVEE SISALDUSE MÄÄRAMISEKS TAHKEKÜTUSTES

Kaarli UROV, Mihkel KOEL

On näidatud, et termogravimeetria abil on võimalik määrata tahke-kütuste kristallhüdraatide veesisaldust. Erinevalt levinud oletusest, et fos-siilsetes kütustes esinevad savid ei erine oluliselt hüdraatvee sisalduse poolest, selgus, et selle kogus kõigub väga laiades piirides, mistõttu mingit keskmist suurust orgaanilise aine sisalduse arvutamisel aluseks võtta ei ole õige. Seejuures on kaustobioliitide mineraalosa mittekarbonaatse frakt-siooni kristallvee sisaldus esimeses lähenduses pöördvõrdeline selle mine-raalaine osa sisaldusega kütuses. See on tõenäoliselt tingitud jämedama, hüdraatvett vähe sisaldava materjali ladestumisest terrigeense materjali intensiivse kandumise korral settebasseini.