

A. SUMBERG, K. UROV

## INFLUENCE OF ANHYDRITE AND GYPSUM ON THE YIELD AND COMPOSITION OF KUKERSITE SEMICOKING PRODUCTS

Usually not being a preponderant ingredient of fossil fuels mineral part, calcium sulfate is nevertheless its quite common constituent. The effect of sulfates on the kaustobioliths thermal decomposition has not been, to our knowledge, investigated except few cases [1-3]. In this work, natural anhydrite and its hydration product were used as representatives of sulfates characteristic of fossil fuels. One can assume that interaction of anhydrite with water results in considerable desintegration of the former accompanied by a growth of its specific surface not achievable by mechanical pulverizing. It is an interesting possibility to get information on the influence of mineral matter dispersion degree on thermal destruction of the fossil fuels organic matter. Gypsum loses its hydration water on heating at temperatures below 200 °C and owing to that water as such cannot essentially interfere with kerogens thermal decomposition processes normally starting at 300-350 °C.

Characteristics of the kukersite-shale concentrate used in this work are presented in Table 1. Sample of anhydrite originated from the Kustin seam (East Siberia, region of the river Nižhnyia Tunguzka) contained (wt. %): CaO 38.5, SO<sub>3</sub> 54.6, H<sub>2</sub>O 0.13; its mineralogical composition, according to X-ray analysis\* data, was (wt. %): anhydrite 92.8, gypsum about 0.8. The analytically dry material obtained from anhydrite (grain size up to 0.1 mm) after its storing under water for two months contained (wt. %): CaO 36.3, SO<sub>3</sub> 51.8, H<sub>2</sub>O 11.9; anhydrite 43.1, gypsum 56.9.

Thermal decomposition of model mixtures prepared from kerogen concentrate, anhydrite and its hydration product ("gypsum") was performed in Fischer retort using the standard procedure. Since the effect of anhydrite desintegration resulting from its hydration on the kerogen thermal degradation is probably more pronounced in the region of high concentrations of mineral additive in the initial mixture for semicoking, experiments with gypsum were carried out mostly in this region. The shale oils obtained were dephenolized using a 10 % aqueous sodium hydroxide solution and thereupon separated into chemical group compounds by thin layer chromatography on silica gel with *n*-hexane as an eluent. Thin layer fractions as well as gaseous products were analyzed by gas chromatography in columns of different polarity.

It became evident that gypsum is indeed much more active in depressing oil formation than anhydrite: with decreasing kerogen content in the mixture with anhydrite and gypsum from 50 to 10 % shale oil yield, kerogen basis, decreases correspondingly by 2.5 and 11.2 % or by 5 and 23 % relatively to oil yield from fifty-fifty mixtures (Fig. 1). The same applies to the yield of the oil chemical group compounds (Fig. 2) determined on the ground of data on group composition of the oils obtained (Table 2). Thus, with decreasing kerogen content in the initial mixture

\*Carried out by K. Utsal.

Table 1. Characteristics of Initial Mixtures of Kukersite Concentrate with Anhydrite and its Hydration Product (Gypsum<sup>1</sup>), Yield of Semicoking Products, wt. %

Index	Kukersite concentrate	Kukersite + anhydrite						Kukersite + gypsum			
		Sample number									
		1	2	3	4	5	6	7	8	9	10
Initial model mixtures											
Analytical moisture W <sup>a</sup>	1.6	1.6	1.4	1.1	0.8	0.6	0.5	4.6	7.7	9.2	
Ash A <sup>d</sup>	9.3	22.3	36.7	49.9	64.5	79.1	89.8	47.4	72.8	88.3	
Organic matter (100 - A <sup>b</sup> ) <sup>2</sup>	90.7	77.7	63.3	50.1	35.5	20.9	10.2	52.6	27.2	11.7	
Semicoking products yield, dry material basis:											
Shale oil	49.0	42.4	33.3	26.8	19.2	10.5	5.2	26.0	12.8	4.6	
Pyrogenetic water	4.9	4.6	3.7	3.0	1.7	1.2	1.1	5.7	2.8	1.5	
Pyrogenetic water	21.2	27.6	39.7	54.5	73.3	85.3	92.0	58.9	78.9	90.9	
Solid residue (semicoke)	24.9	25.4	23.3	15.7	5.8	3.0	1.7	9.4	5.5	3.0	
Gas and losses (by difference)											

<sup>1</sup> Partially hydrated anhydrite.

<sup>2</sup> Only traces of mineral carbon dioxide have been detected.

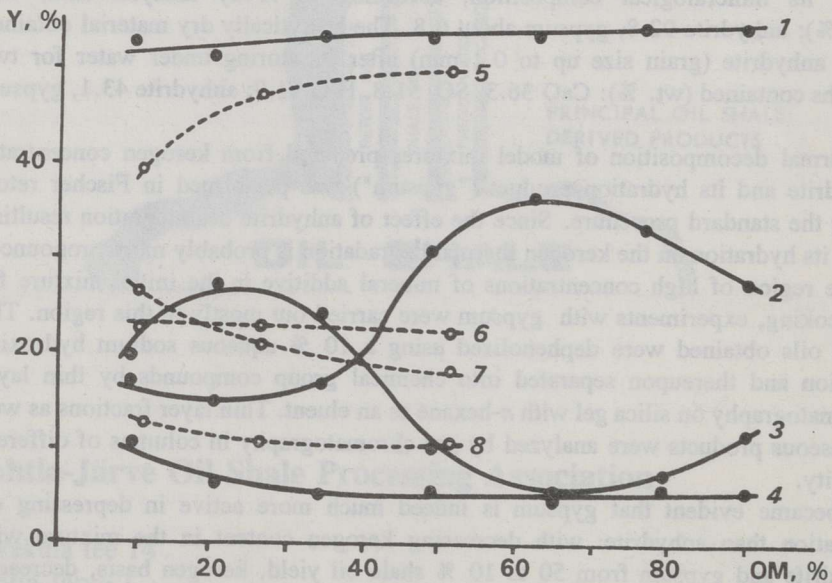


Fig. 1. Dependence of the kukersite semicoking products yield, kerogen basis (Y), on the content of the latter (OM) in the mixtures with anhydrite (1-4) and gypsum (5-8); 1 and 5 - shale oil; 2 and 7 - gaseous products; 3 and 6 - non-volatile residue (semicoke); 4 and 8 - pyrogenetic water

from 50 to 10 % the yield of the oil neutral heteroatomic compounds on the kerogen basis drops by 1.7 % (relative) in the case of anhydrite and by 10.3 % when using gypsum, that of aliphatic and naphthenic hydrocarbons correspondingly by 3.6 and 24.1 %.

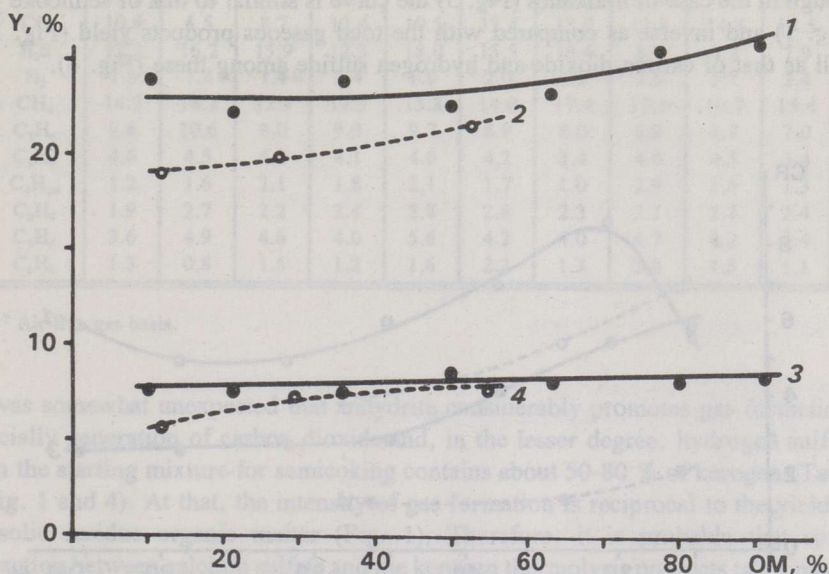


Fig. 2. Influence of the kerogen content in starting mixtures (OM) with anhydrite (1 and 3) and gypsum (2 and 4) on the yield, kerogen basis (Y), of neutral heteroatomic compounds (1 and 2) and non-aromatic hydrocarbons (3 and 4) contained in shale oil

Table 2. Characteristics of Semicoking Oils

Index	Sample number according to Table 1									
	1	2	3	4	5	6	7	8	9	10
Density $\rho_4^{20}$	0.966	0.966	0.964	0.966	0.967	0.969	0.971	0.966	0.967	0.963
Chemical group composition, wt. %:										
Hydrocarbons:										
Aliphatic and naphthenic	15.8	14.7	15.0	17.0	13.2	14.5	14.7	15.0	16.2	14.7
Aromatic	26.5	26.7	26.4	26.2	25.6	25.9	25.0	25.2	27.7	26.9
Heteroatomic compounds:										
Neutral and basic	45.4	46.1	43.2	41.7	45.4	43.7	46.1	43.8	42.8	48.8
Acidic (mainly phenols)	12.3	12.5	15.4	15.1	15.8	15.9	14.2	16.0	13.3	9.6

As to the individual chemical composition of oils on the basis of their gas chromatographic analysis data, there are no considerable qualitative changes in connection with mineral additive concentration variations in model mixtures but some quantitative changes take place. It is typical that the ratio of low-boiling compounds to the heavier ones increases with increasing the content of mineral compounds in the starting mixture (more extensive secondary reactions of oil transformation) though in the case of *n*-alkanes (Fig. 3) the curve is similar to that of semicoke yield (Fig. 1) and inverse as compared with the total gaseous products yield (Fig. 1) as well as that of carbon dioxide and hydrogen sulfide among these (Fig. 4).

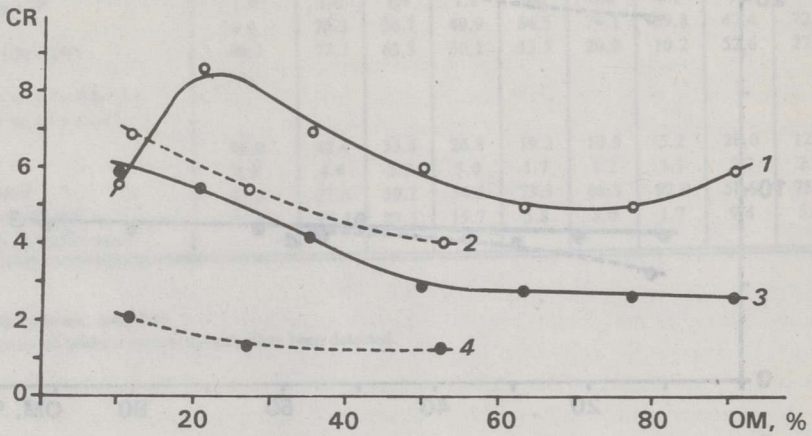


Fig. 3. Influence of the kerogen content in starting mixtures (OM) with anhydrite (1 and 3) and gypsum (2 and 4) on the concentration ratios (CR) of *n*-alkanes ( $C_{10}-C_{17}$ ) : *n*-alkanes ( $C_{18}-C_{25}$ ) (1 and 2) and 2-methylnaphthalene : phenanthrene (3 and 4) in the oils obtained

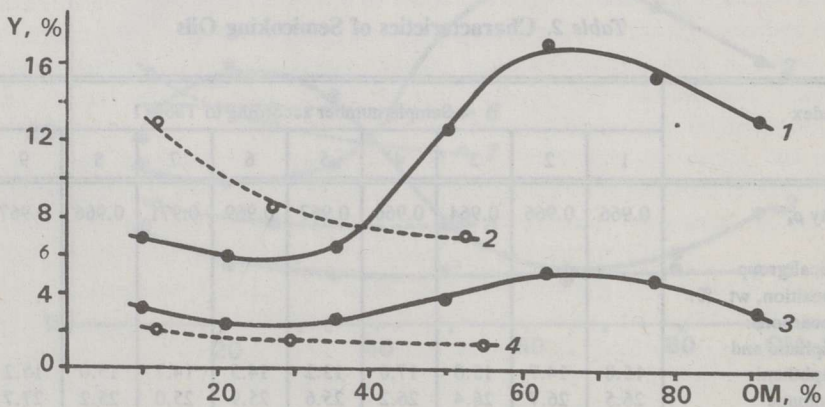


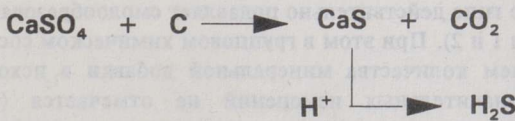
Fig. 4. Dependence of some gaseous products yield, wt. % kerogen basis (Y), on the latter content (OM) in mixtures with anhydrite (1 and 3) and gypsum (2 and 4); 1 and 2 -  $CO_2$ ; 3 and 4 -  $H_2S$

Table 3. Composition of Gaseous Products<sup>a</sup>, vol. %

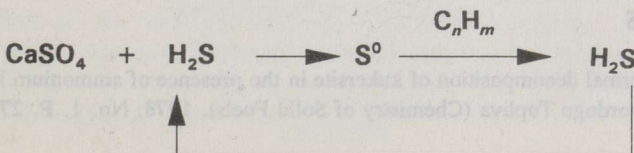
Com- pound	Sample number according to Table 1									
	1	2	3	4	5	6	7	8	9	10
CO <sub>2</sub>	39.3	37.6	36.9	32.9	29.4	31.4	30.1	32.8	31.9	39.2
CO	10.6	5.5	8.7	12.4	10.5	12.4	13.0	13.8	14.8	14.5
H <sub>2</sub> S	12.2	16.2	15.9	12.3	18.0	15.5	18.4	8.7	8.2	7.9
H <sub>2</sub>	1.5	1.4	1.4	2.4	1.9	2.0	1.1	2.5	1.7	2.4
CH <sub>4</sub>	14.2	14.2	12.9	17.5	13.8	14.9	17.4	17.1	19.7	15.4
C <sub>2</sub> H <sub>6</sub>	9.6	10.6	9.0	9.0	9.7	8.9	8.0	8.9	8.7	7.0
C <sub>3</sub> H <sub>8</sub>	4.6	4.5	4.8	4.1	4.6	4.2	3.4	4.0	4.5	3.4
C <sub>4</sub> H <sub>10</sub>	1.2	1.6	2.1	1.8	2.1	1.7	1.0	2.6	1.6	1.3
C <sub>2</sub> H <sub>4</sub>	1.9	2.7	2.2	2.4	2.8	2.6	2.3	2.1	2.7	2.4
C <sub>3</sub> H <sub>6</sub>	3.6	4.9	4.6	4.0	5.6	4.2	4.0	4.7	4.7	5.4
C <sub>4</sub> H <sub>8</sub>	1.3	0.8	1.5	1.2	1.6	2.2	1.3	2.8	1.5	1.1

<sup>a</sup> Air-free gas basis.

It was somewhat unexpected that anhydrite considerably promotes gas formation, especially generation of carbon dioxide and, in the lesser degree, hydrogen sulfide when the starting mixture for semicoking contains about 50-80 % of kerogen (Table 3; Fig. 1 and 4). At that, the intensity of gas formation is reciprocal to the yield of the solid residue organic matter (Fig. 1). Therefore, it is probable that some interaction between calcium sulfate and the kerogen thermolysis products takes place; these reactions seem to be favoured in the region of a certain optimal organic matter to mineral additive ratio. For example, it is known that carbon dioxide and calcium sulfide are formed when calcium sulfate is heated with coal. As a result of the reaction of calcium sulfide and acidic compounds of oil, hydrogen sulfide can be generated:



It has been also established [4] that interaction between anhydrite and hydrogen sulfide leads to formation of elemental sulfur that is known as an effective dehydrogenation agent for organic substances (Vesterberg's reaction); this in its turn results again in hydrogen sulfide formation:



Thus, if there is enough organic hydrogen in the system, extensive calcium sulfate transformation is expected. Indeed, by determining the sulfates sulfur content in solid residues (in the case of samples 3 and 4 correspondingly 6.7 and 7.3 %) it has been shown that a considerable portion (here 62-63 %) of calcium sulfate is converted into some non-sulfate products.

It is quite possible that there are also other pathways of sulfates transformation in presence of thermally decomposing organic material, mechanism of these processes obviously needs further investigation.

To sum up, the above-described experiments confirmed that the dispergation degree is of considerable importance in determining the shales mineral matter influence on the yield and composition of its semicoking products. Likewise it became evident that the anhydrite effect on the kerogen thermolysis process is of specific character as compared with that of a series of other minerals; calcium sulfate itself is transformed in these conditions to a remarkable extent.

**А. И. СУМБЕРГ, К. Э. УРОВ**

### **ВЛИЯНИЕ АНГИДРИТА И ГИПСА НА ВЫХОД И СОСТАВ ПРОДУКТОВ ПОЛУКОКСОВАНИЯ КУКЕРСИТА**

#### *Резюме*

В продолжение серии работ по изучению влияния минеральной части горючих сланцев на термическую деструкцию их органического вещества с применением модельных смесей (табл. 1) исследовано воздействие природного ангидрита и полученного его обводнением гипса на выход и состав продуктов полукоксования керогена кукерсита. Поскольку при гидратации ангидрита можно ожидать его заметной дезинтеграции, сопровождающейся ростом удельной поверхности, представляется интересная возможность изучить влияние степени дисперсности минерального материала на термолиз керогена.

Установлено, что гипс действительно подавляет смолообразование сильнее, чем ангидрит (рисунки 1 и 2). При этом в групповом химическом составе полученных смол с увеличением количества минеральной добавки в исходной смеси для полукоксования значительных изменений не отмечается (табл. 2), но в индивидуальном химическом составе содержащихся в смолах углеводородов возрастает роль низкокипящих соединений (рис. 3).

Ангидрит обуславливает усиленное газообразование в области 50—80 %-ного содержания керогена в модельной смеси (табл. 3; рис. 4), чему сопутствует превращение части сульфата в продукты, не содержащие сульфат-иона. Высказано предположение, что это вызвано взаимодействием сульфата кальция с продуктами термодеструкции керогена, в частности с сероводородом.

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*Estonian Academy of Sciences*  
*Institute of Chemistry*  
*Tallinn, Estonia*

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