

SULPHUR COMPOUNDS IN A HYDRAULIC ASH-DISPOSAL SYSTEM

Leevi MÖLDER^{a, b}, Alfred ELENURM^a, and Hindrek TAMVELIUS^a

^a Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

^b Tallinna Tehnikaülikool (Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

Received 16 March 1995; accepted 20 March 1995

Abstract. In the retorting process of Estonian "kukersite" oil shale over half of the sulphur occurring in the feed shale remains in the solid residue. Sulphide in the form of iron and calcium sulphides is environmentally the most dangerous. This paper discusses the mechanism and the rate of hydrolysis and oxidation reactions of sulphur compounds in the hydraulic ash-disposal system.

Key words: calcium and iron sulphides, oxidation, hydrolysis, ash-disposal system.

In the retorting process of Estonian "kukersite" oil shale more than 50% of the sulphur occurring in the feed shale remains in the solid residue (spent shale or the so-called black ash) and it is deposited in ash fields and dumps.

In the fresh solid residue sulphur occurs mainly in the form of calcium and iron sulphides, and, to a smaller extent, as corresponding sulphates. CaS is formed at the retorting process. FeS originates from pyrites occurring in the feed oil shale. Sulphate sulphur is formed mainly as a result of the oxidation of other sulphur forms [1–3].

Sulphides are the most noxious form of sulphur in the environment.

In this paper the mechanism and the rate of hydrolysis and oxidation reactions of sulphur compounds in the hydraulic ash-disposal system are investigated.

EXPERIMENTAL PART

Iron sulphide (FeS) needed for the experiments was synthesized by the direct reaction of sulphur with iron powder at a high temperature [4]. Calcium sulphide (CaS) was received by conducting gaseous hydrogen sulphide over hot (600 °C) calcium oxide.

The mechanism and kinetics of oxidation of solid iron sulphide in water were studied in experiments where air was bubbled through a mixture of

powdered FeS and water at a constant temperature in the presence of KOH (pH of the solution 12.8–13.5).

The kinetics of hydrolysis of calcium sulphide was studied in experiments where solid CaS was exposed in air-free distilled water in hermetically closed reaction vessels. The mechanism and kinetics of oxidation of hydrosulphide ions SH^- formed were studied in experiments where the mixture of solid calcium sulphide and water at a constant temperature was bubbled with air.

In all experiments the sulphur forms present in the water were determined after fixed time intervals.

For determining the total sulphur content of the water solutions all sulphur compounds were oxidized to sulphate with hydrogen peroxide. The sulphate sulphur formed was determined by gravimetric analysis as barium sulphate. Sulphide (hydrosulphide), sulphite, and thiosulphate sulphur were determined from one and the same sample. After the precipitation of sulphides as cadmium sulphide the precipitate was removed and determined iodometrically.

The content of thiosulphate and sulphite sulphur in the filtrate was at first determined jointly. After binding the sulphite sulphur with formaldehyde the determination of thiosulphate sulphur was carried out separately.

All analytical results are presented in moles per volume unit.

OXIDATION OF IRON SULPHIDE

In the iron sulphide oxidation experiments it was established that the formation of both thiosulphate and sulphate sulphur forms begins immediately from the outset. The concentration of hydrosulphide in the water solution is negligible. Practically no sulphite is formed either. These facts allow us to suppose that FeS practically does not hydrolyze and its oxidation occurs only in the solid phase. Thiosulphate and sulphate are formed from solid iron sulphide by two simultaneous reactions of the first order.

From experimental data the rate constants of thiosulphate (k_1) and sulphate (k_2) formation reactions were calculated (Table).

Rate constants of reactions, h^{-1}

k_1 , thiosulphate formation; k_2 , sulphate formation; k_3 , CaS hydrolysis; k_{31} , hydrosulphide oxidation to thiosulphate; k_{32} , hydrosulphate oxidation to sulphate

Temperature, °C	$k_1 \cdot 10^4$	$k_2 \cdot 10^4$	$k_3 \cdot 10^4$	$k_{31} \cdot 10^4$	$k_{32} \cdot 10^4$
20	7.3	1.9	465	272	119
40	8.2	4.3	936	402	209
60	9.1	8.9	1730	569	342
80	10.0	17.0	2990	770	530

HYDROLYSIS AND OXIDATION OF CALCIUM SULPHIDE

Calcium sulphide hydrolyzes in the water so rapidly that its oxidation in the solid phase is negligible. The hydrolysis also may be considered as a first order reaction (Fig. 1) having the rate constant k_3 .

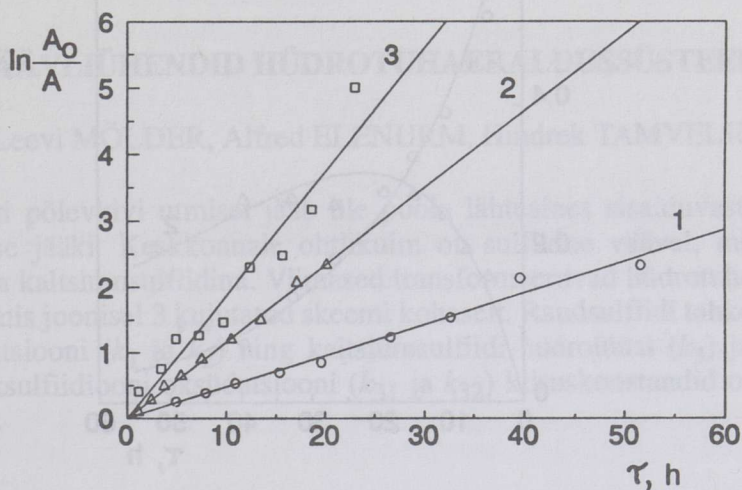


Fig. 1. Hydrolysis of solid CaS in water (A , concentration of solid CaS, kg/m^3 ; τ , reaction time). 1, at 20°C; 2, 50°C; 3, 60°C.

The forming hydrosulphide SH^- ion (Fig. 2) oxidizes to thiosulphate and sulphate. These oxidation reactions are also of the first order (rate constants k_{31} and k_{32} , respectively), and they proceed simultaneously, not consecutively. The further oxidation of thiosulphate to sulphate is very slow and can be disregarded.

A principal transformation scheme of sulphur compounds in the hydraulic ash-disposal system is presented in Fig. 3.

Using this scheme and experimentally determined rate constants from the Table, a simplified mathematical model of the hydraulic ash-disposal system can be composed, supposing that from the viewpoint of the transformation of sulphur compounds the hydraulic ash-disposal system represents a reactor of ideal stirring. It is valid in case the temperature and the concentration of the reactants and reaction products are constant and stable in time in the whole system. Using this model the dependence between the concentration of the sulphur compounds in the circulating water and system parameters can be prognosticated.

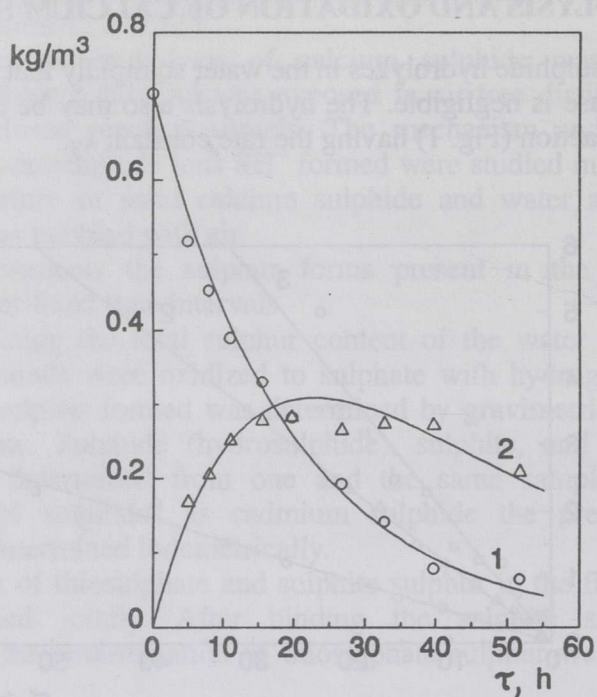


Fig. 2. Concentration of solid CaS (1) and hydrosulphide ion (2) at 20°C.

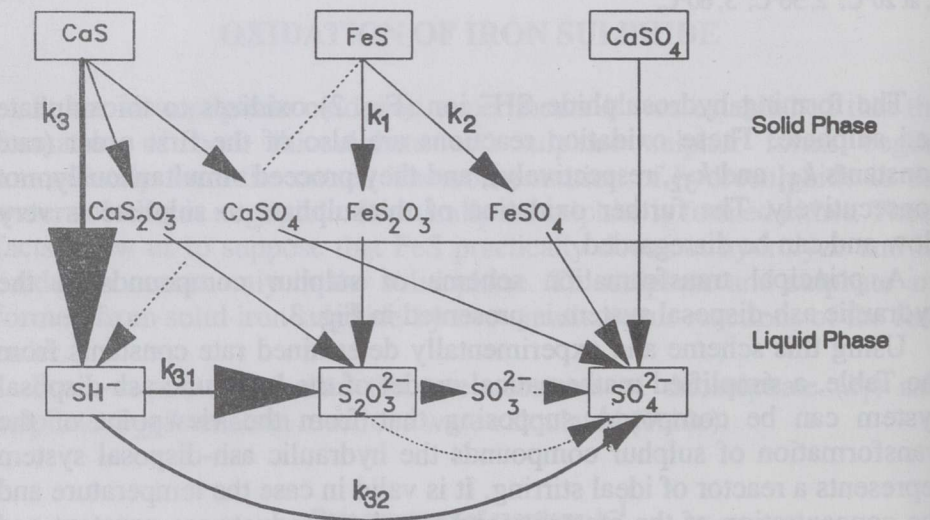


Fig. 3. A principal transformation scheme of sulphur compounds in an ash-disposal system.

REFERENCES

1. Ефимов В. М., Дойлов С. К., Лезпер Р., Соо М. Возможности предотвращения образования водорастворимой сульфидной серы при переработке сланца в газогенераторах. – Горючие сланцы, 1984, 1, 2, 179–188.
2. Эленурм А. А., Рохтла И. И., Маргусте М. А., Вескюя Т. И.-В., Мильк А. А., Стельмах Г. П., Чикул В. И., Верещака С. А. Сернистые соединения в твердых остатках

термической переработки сланца-кукерсита в установках с твердым теплоносителем. – Горючие сланцы, 1988, 5, 3, 285–296.

3. Эленурм А., Маргусте М., Рохтла И., Вескюя Т., Губергриц М., Чикул В., Тягунов Б. Распределение серы при термической переработке кукерсита в установках с твердым теплоносителем. – Изв. АН ЭССР. Хим., 1988, 37, 2, 57–64.

4. Карякин Ю. В., Ангелов И. И. Чистые химические вещества. Химия, Москва, 1974.

VÄÄVLIÜHENDID HÜDROTUHAERALDUSSÜSTEMIS

Leevi MÖLDER, Alfred ELENURM, Hindrek TAMVELIUS

Eesti põlevkivi utmisel jääb üle poole lähteaines sisalduvast väävlist tahkesse jääki. Keskkonnale ohtlikum on sulfiidne väävel, mis esineb raud- ja kaltsiumsulfiidina. Viimased transformeeruvad hüdrotuhaeraldussüsteemis joonisel 3 kujutatud skeemi kohaselt. Raudsulfiidi tahkefaasilise oksüdatsiooni (k_1 ja k_2) ning kaltsiumsulfiidi hüdrolüüsi (k_3) ja tekkiva vesiniksulfiidiooni oksüdatsiooni (k_{31} ja k_{32}) kiiruskonstandid on toodud tabelis.

СЕРНИСТЫЕ СОЕДИНЕНИЯ В СИСТЕМАХ ГИДРОЗОЛОУДАЛЕНИЯ

Лееви МЕЛЬДЕР, Альфред ЭЛЕНУРМ, Хиндрек ТАМВЕЛИУС

При термической переработке сланца-кукерсита более половины серы исходного сланца остается в твердом остатке. Сульфидная сера, наиболее опасная для окружающей среды, содержится в твердом остатке в виде сульфидов железа и кальция. В системе гидрозолоудаления эти соединения преобразуются согласно схеме на рис. 3. Константы скорости реакции твердофазного окисления сульфида железа (k_1 и k_2), гидролиза сульфида кальция (k_3) и окисления образующегося гидросульфид-иона (k_{31} и k_{32}) приведены в таблице.