

TRANSFORMATION OF SULPHUR COMPOUNDS IN A HYDRAULIC ASH-DISCHARGE UNIT

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Abstract. The state of sulphur compounds formed as a result of hydrolysis and oxidation of iron sulphide and calcium sulphide in ash-discharge units of oil shale retorting plants is analysed. A simplified model is used, assuming that water temperature and the amount of the reacting compounds are stable with respect to time and the volume within the entire basin and that the end products of the reaction are continuously removed from the active zone of the basin. Formulae for predicting the equilibrium concentration of hydrogen sulphide as well as the amount of thiosulphate and sulphate formed depending on the unit's parameters were constructed.

Key words: iron sulphide, calcium sulphide, hydrolysis, oxidation, ash-discharge unit.

In our previous papers [1, 2], the kinetics of hydrolysis reactions of calcium sulphide and iron sulphide was analysed. It is known that these compounds are present in the solid residue of retorting (so-called black ash) of the Kukersite oil shale. Calcium sulphide and iron sulphide are also the main source of environmentally harmful sulphur compounds, found both in rainwater draining from spent shale piles and the water circulating in the hydraulic ash-discharge unit.

This paper provides a mathematical description of the state of sulphur compounds present in the circulating water of the hydraulic ash-discharge unit, and in so doing, gives a prognosis of the equilibrium concentration of hydrogen sulphide for the unit working in a stationary regime.

SOURCE MODEL

All the following equations were arrived at assuming that the transformation of sulphur compounds takes place according to a diagram given in our previous

paper [1, Fig. 3]. In accordance with this diagram, the main path for the transformation of solid calcium sulphide is hydrolysis along with the oxidation of hydrogen sulphide ions formed in the liquid phase into thiosulphate and sulphate. Oxidation reactions take place simultaneously, not in sequence. Both thiosulphate and sulphate are stable in an alkaline solution (pH approx. 13) and practically no oxidation of thiosulphate into sulphate takes place.

Iron sulphide that is present in the incoming solid residue does not hydrolyze on contact with water, instead it oxidizes in the solid phase upon contact with oxygen. Thiosulphate and sulphate formed as a result of oxidation dissolve in circulating water. It is possible that calcium sulphide oxidizes also in the same way. However, compared to the hydrolysis reaction, the rate of the oxidation of calcium sulphide in the solid phase is insignificantly low.

We regard the hydraulic ash-discharge unit working in a stationary regime as a chemical reactor of ideal stirring. That is, we presume that the temperature and the concentration of the reacting substances in the basin's working (active) volume are constant both temporally and topologically, and that the products of the reaction are continuously removed from the active zone.

It is apparent that the assumption that the products of the reaction are continuously removed from the basin's active zone is more or less true only for solid material. After a certain period of time it turns into a tight layer covering the bottom of the basin. This layer is almost waterproof and thus, after a period of time, the material becomes harder and separates completely from the active volume of the basin.

Dissolved sulphur compounds, regardless of their origin, accumulate in water. An equilibrium is attained in the system only after the saturation concentration is achieved. Only the concentration of hydrogen sulphide originating from calcium sulphide is derived not by the saturation concentration but by the condition that in the stationary regime the amount of the reaction products forming and the amount of the hydrogen sulphide oxidizing are equal.

Kinetic equations for reactions of sulphur compounds taking place in a hydraulic ash-discharge unit are written as follows:

1. Oxidation of solid FeS, which results in the formation of thiosulphate and sulphate:

$$-\frac{d[A_F]}{d\tau} = (k_1 + k_2)[A_F], \quad (1)$$

$$\frac{d[B_F]}{d\tau} = k_1[A_F], \quad (2)$$

$$\frac{d[C_F]}{d\tau} = k_2[A_F]. \quad (3)$$

2. Hydrolysis of solid CaS:

$$-\frac{d[A_C]}{d\tau} = \frac{d[A_L]}{d\tau} = k_3[A_C]. \quad (4)$$

3. Oxidation of dissolved hydrogen sulphide SH^- , which also results in the formation of thiosulphate and sulphate:

$$-\frac{d[A_L]}{d\tau} = (k_{31} + k_{32})[A_L], \quad (5)$$

$$\frac{d[B_L]}{d\tau} = k_{31}[A_L], \quad (6)$$

$$\frac{d[C_L]}{d\tau} = k_{32}[A_L]. \quad (7)$$

Integration of Eq. (1) reveals the transformation degree for iron sulphide (φ_F) and the concentration of iron sulphide sulphur ($[A_F]$) that is present in the solid residue after the residue has been in contact with water for τ hours:

$$\varphi_F = \frac{(k_1 + k_2)\tau}{1 + (k_1 + k_2)\tau} \quad (8)$$

and

$$[A_F] = \frac{[A_F]_0}{1 + (k_1 + k_2)\tau}, \quad (9)$$

where the subscript 0 represents the moment when the solid residue enters the unit.

The amounts of thiosulphate (B_F) and sulphate (C_F) sulphur that form from $A_{F,0}$ kilograms of iron sulphide sulphur after being in contact with water for τ hours are

$$B_F = k_1 F \quad (10)$$

and

$$C_F = k_2 F, \quad (11)$$

where

$$F = A_{F,0} \tau [1 + (k_1 + k_2)\tau]^{-1}. \quad (12)$$

Analogously, we derive from Eq. (4) the degree of hydrolysis for calcium sulphide (φ_C), and the concentration of calcium sulphide sulphur ($[A_C]$) after the solid residue has been in contact with water for τ hours. These are:

$$\varphi_C = \frac{k_3 \tau}{1 + k_3 \tau} \quad (13)$$

and

$$[A_C] = \frac{[A_C]_0}{1 + k_3 \tau}. \quad (14)$$

If the unit is working in a stationary regime, all the hydrogen sulphide SH^- must oxidize into thiosulphate B_L and sulphate C_L . The amounts of thiosulphate and sulphate sulphur which originate from $A_{C,0}$ kilograms of calcium sulphide sulphur after the solid residue has been in contact with water for τ hours is expressed as follows:

$$B_L = k_{31}L(k_{31} + k_{32})^{-1} \quad (15)$$

and

$$C_L = k_{32}L(k_{31} + k_{32})^{-1}, \quad (16)$$

where

$$L = A_{C,0}k_3\tau(1 + k_3\tau)^{-1}. \quad (17)$$

The total amounts of sulphur as thiosulphate (ΣB) and sulphate (ΣC) which form from $A_{F,0}$ kilograms of iron sulphide sulphur and $A_{C,0}$ kilograms of calcium sulphide sulphur are expressed as follows:

$$\Sigma B = B_F + B_L, \quad (18)$$

$$\Sigma C = C_F + C_L. \quad (19)$$

The equilibrium concentration of hydrogen sulphide SH^- in circulating water is derived from assessing the condition of equality of the forming and oxidizing hydrogen sulphide within a unit of time:

$$[A_L] = \frac{k_3\tau[A_C]}{k_{31} + k_{32}}. \quad (20)$$

It is obvious that if the ash-discharge unit is working in a stationary regime, the amount of sulphur present in the end products which forms during τ hours from the material entering the system within a unit of time, and the amount of sulphur transformed to the final products within the same unit of time, must be equal. Thus, the amounts of thiosulphate and sulphate sulphur, which form from both source substances within a period of 1 hour can be calculated using, respectively, Eqs. (10)–(12) and (15)–(17), providing that

$$[A_F]_0 = A_{F,0}/V = Gp_{F,0}/100V \quad (21)$$

and

$$[A_C]_0 = A_{C,0}/V = Gp_{C,0}/100V. \quad (22)$$

TRANSFORMATION OF IRON SULPHIDE AND CALCIUM SULPHIDE IN THE HYDRAULIC ASH-DISCHARGE UNIT

Using the described model and rate constants taken from our previous article [2], we analysed the state of sulphur compounds in the hydraulic ash-discharge unit depending on the unit's parameters.

From Eqs. (10)–(12) and (18) it can be deduced that if both the temperature and time of the transformation of solid residue in the active zone of the basin are constant, then the amounts of thiosulphate (B_F) and sulphate (C_F) sulphur are proportional to the amount of the solid residue entering the ash-discharge unit (G) and to the concentration of iron sulphide sulphur in the incoming solid residue ($p_{F,0}$). An increase in the time the residue is in contact with water increases also the degree of the transformation of iron sulphide (φ_F). However, these variables are related in a more complicated way (Fig. 1). An increase in temperature accelerates the formation of both B_F and C_F (Fig. 2).

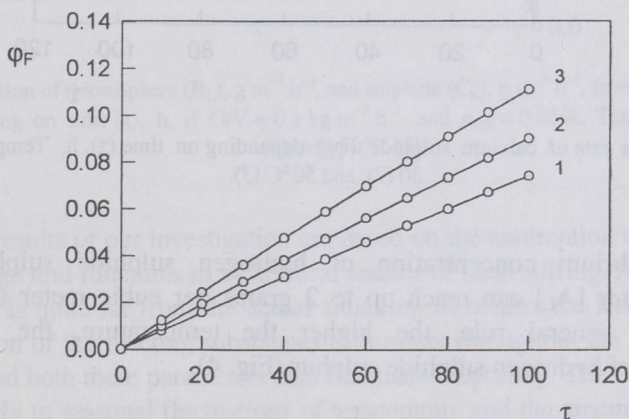


Fig. 1. Degree of transformation of iron sulphide (φ_F) depending on time (τ), h. Temperature: 10 (1), 30 (2), and 50°C (3).

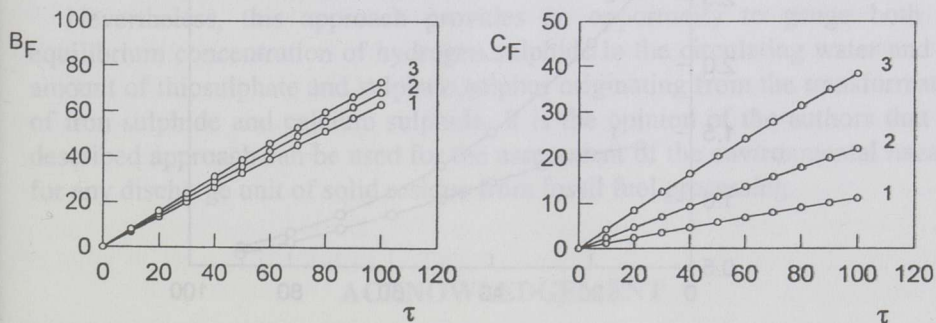


Fig. 2. Formation of thiosulphate (B_F), $\text{g m}^{-3} \text{h}^{-1}$, and sulphate (C_F), $\text{g m}^{-3} \text{h}^{-1}$, from iron sulphide depending on time (τ), h, if $G/V = 0.1 \text{ kg m}^{-3} \text{h}^{-1}$ and $p_{F,0} = 0.5\%$. Temperature: 10 (1), 30 (2), and 50°C (3).

The degree of the hydrolysis of calcium sulphide (φ_C) increases both with a rise in the temperature and an increase in the length of time that the solid material is staying in the working zone of the basin. When τ reaches 100 hours, calcium sulphide hydrolyzes almost completely (Fig. 3).

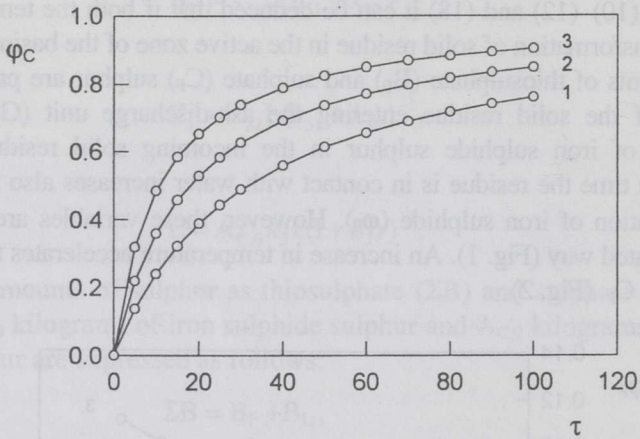


Fig. 3. Hydrolysis rate of calcium sulphide (φ_C) depending on time (τ), h. Temperature: 10 (1), 30 (2), and 50°C (3).

The equilibrium concentration of hydrogen sulphide sulphur SH^- in circulating water $[A_L]$ can reach up to 2 grams per cubic meter of water and above. As a general rule, the higher the temperature, the smaller the concentration of hydrogen sulphide sulphur (Fig. 4).

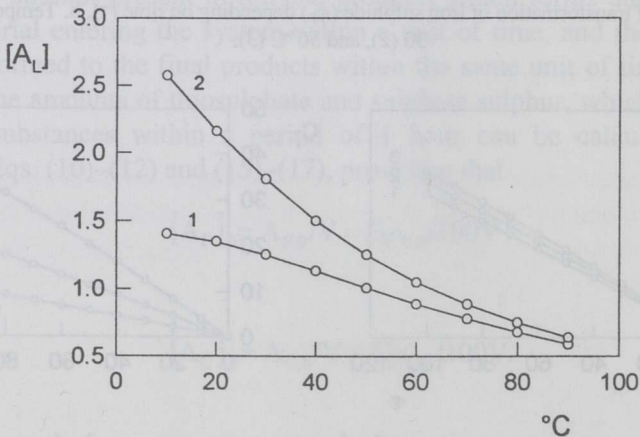


Fig. 4. Concentration of hydrogen sulphide ($[A_L]$), g m^{-3} , in the circulating water depending on temperature, $^{\circ}\text{C}$, if $G/V = 0.1 \text{ kg m}^{-3} \text{ h}^{-1}$ and $p_{C,0} = 0.05\%$. Time (τ): 24 (1) and 72 h (2).

If temperature and the time that the solid residue is staying in the active zone of the basin are both constant, then the amounts of thiosulphate (B_L) and sulphate (C_L) sulphur originating from hydrogen sulphide SH^- are proportional to the amount of the solid residue entering the unit (G) and to the concentration of calcium sulphide sulphur in the solid residue ($p_{C,0}$). An increase in τ increases the amount of B_L and C_L . With the rise in temperature, the formation of both B_L and C_L accelerates (Fig. 5).

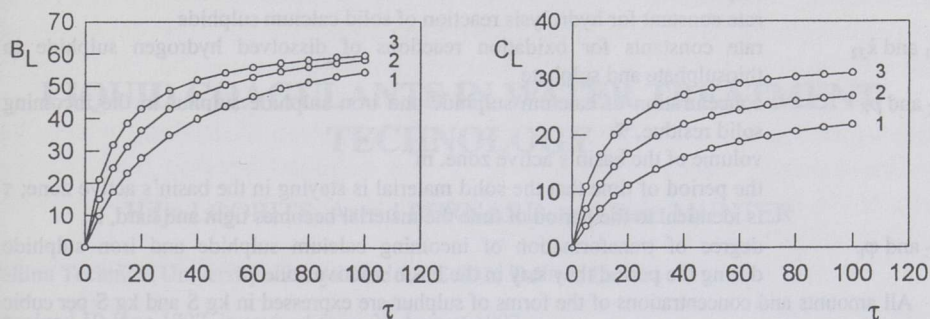


Fig. 5. Formation of thiosulphate (B_L), $\text{g m}^{-3} \text{h}^{-1}$, and sulphate (C_L), $\text{g m}^{-3} \text{h}^{-1}$, from hydrogen sulphide SH^- , depending on time (τ), h, if $G/V = 0.1 \text{ kg m}^{-3} \text{h}^{-1}$ and $p_{C,0} = 0.05\%$. Temperature: 10 (1), 30 (2), and 50°C (3).

All the results of our investigation are based on the assumption that the hydraulic ash-discharge unit functions as a chemical reactor of ideal stirring. Naturally, such an assumption is quite far from the actual situation, as neither the temperature nor the concentration of the reacting substances is constant throughout the active volume of the basin and both these parameters also fluctuate temporally. The fluctuation in time is due mostly to seasonal fluctuations of temperature and the amount of water in the basin, but also to conditions of dissolution of oxygen in the water. The amount of water in the basin fluctuates seasonally depending on the amount of rainfall and the amount of water lost through evaporation.

Nevertheless, this approach provides an opportunity to gauge both the equilibrium concentration of hydrogen sulphide in the circulating water and the amount of thiosulphate and sulphate sulphur originating from the transformation of iron sulphide and calcium sulphide. It is the opinion of the authors that the described approach can be used for the assessment of the environmental hazards for any discharge unit of solid residue from fossil fuel processing.

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EXPLANATION OF NOTATION

A, B, C	sulphide, thiosulphate, and sulphate sulphur
A _C , A _F , and A _L	calcium sulphide, iron sulphide, and dissolved hydrogen sulphide sulphur
B _F and B _L	thiosulphate sulphur that originates from A _F and A _L
C _F and C _L	sulphate sulphur that originates from A _F and A _L
G	amount of solid residue that enters the hydraulic ash-discharge unit, kg h ⁻¹
k ₁ and k ₂	rate constants for oxidation reactions of solid iron sulphide to thiosulphate and sulphate
k ₃	rate constant for hydrolysis reaction of solid calcium sulphide
k ₃₁ and k ₃₂	rate constants for oxidation reactions of dissolved hydrogen sulphide to thiosulphate and sulphate
p _C and p _F	concentration of calcium sulphide and iron sulphide sulphur in the incoming solid residue, %
V	volume of the basin's active zone, m ³
τ	the period of time that the solid material is staying in the basin's active zone; τ is identical to the period of time the material becomes tight and hard, h
φ _C and φ _F	degree of transformation of incoming calcium sulphide and iron sulphide during the period they stay in the basin's active zone

All amounts and concentrations of the forms of sulphur are expressed in kg S and kg S per cubic meter of water. Rate constants for liquid phase reactions are expressed in (Mol S) m⁻³/(Mol S) m⁻³ h = h⁻¹. Rate constants for solid phase reactions are expressed in (Mol S)/(Mol S) h = h⁻¹.

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VÄÄVLIÜHENDITE TRANSFORMEERUMINE HÜDRAULILISES TUHAERALDUSSÜSTEEMIS

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On analüüsitud raud- ja kaltsiumsulfiidi hüdrolyüsil ja oksüdatsioonil tekkivate väävliühendite seisundit Eesti põlevkivi utteseadmete hüdraulilistes tuhaeraldussüsteemides. On kasutatud lihtsustatud mudelit, eeldades, et vee temperatuur ja reageerivate ainete kogused on püsivad nii ajas kui ka kogu basseini ruumala ulatuses ning reaktsiooni lõppsaadused eemaldatakse pidevalt basseini aktiivsest tsoonist. On saadud võrrandid, mis võimaldavad prognoosida vesinik-sulfiidiooni tasakaalukontsentratsiooni ning tekkiva tiosulfaadi ja sulfaadi kogust sõltuvalt süsteemi tööparameetritest.