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Hydrochemical Oxidation of Sulfonated Derivatives of Lignin

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Abstract—Kinetics of oxidation of low and high molecular weight sulfonate derivatives of lignin in the presence of oxygen and Fe^{2+}, Fe^{3+}, or Cu^{2+} ions has been studied; the oxidation products have been characterized by physicochemical methods.

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Liquid elemental sulfur is a side product of oxidative autoclave leaching of zinc; sulfur immediately spreads over the unreacted sulfide particles thus reducing the metal recovery. Surfactants are usually used to remove liquid sulfur from the inorganic particles surface [1]. Sulfonate derivatives of lignin (so-called technical lignosulfonates) are the most widely used surfactants for metallurgy applications. However, lignosulfonates efficiency can significantly differ depending on their source and production batch; furthermore, deterioration of the surfactant efficiency in the course of the leaching process or due to variation of the crushed ore or raw material composition is a general problem [2]. Information on lignosulfonates chemical properties reported so far has been contradictory, and their changes in the course of redox reactions in the presence of oxygen and redox-active ions (Fe^{3+}, Fe^{2+}, or Cu^{2+}) virtually has not been discussed in the literature. Identification of the oxidation products is important for theoretical as well as applied tasks; in particular, this information can be used for optimization of technology parameters of oxidative leaching of crude zinc-containing material and subsequent autoclave operations.

In view of the above, we studied kinetics of oxidation of two lignosulfonate materials: the low molecular weight fraction (LMF) and the high molecular weight fraction (HMF); their compositions are reported in Table 1. The oxidation conditions were chosen close to those commonly used in industry.

Composition of the oxidation products was evaluated by IR spectroscopy, conductometry, and potentiometry; the analysis results were further used to elucidate the features of the oxidation process.

The lignosulfonate–Fe^{3+}–H_2SO_4 system. Rate of the LMF and HMF lignosulfonates oxidation as function of temperature, Fe^{3+} concentration, and sulfuric acid concentration is shown in the figure. Temperature had more pronounced effect on oxidation of the HMF sample: the calculated apparent activation energies were 200.5 kJ/mol (HMF) and 115.9 kJ/mol (LMF). From the activation energy values, oxidation of both lignosulfonates occurred under the kinetic control conditions.

The LMF oxidation rate order with respect to Fe^{3+} concentration was 2.0. The rate of HMF oxidation was almost independent of Fe^{3+} concentration up to 7.1×10^{-4} mol/L ($V_{sp} = 4\times10^{-6}$–5×10^{-6} mol/s); however, further increase of Fe^{3+} concentration significantly accelerated the reaction, and the rate order with respect to metal ions concentration was about 10.

Increase of sulfuric acid concentration slowed down the lignosulfonates oxidation. The partial reaction rate order with respect to sulfuric acid was of –1.0 in the cases of both LMF and HMF. Temperature and sulfuric acid concentration being the same, the reductive activity of the HMF lignosulfonate was higher than that of the LMF one. From the data on Fe^{3+} consumption, complete oxidation of lignosulfonates required at least 32.5 mol of Fe^{3+} per 1 mol of LMF and 87 mol of Fe^{3+} per 1 mol of HMF. The Fe^{3+} consumption ratio

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† Deceased.

Table 1. Elemental analysis of the lignosulfonate samples (wt %)

Sample	C	O	S	Na	K	Mg	Ca	Other elements
LMF, $\bar{M}$ 16900	33.9	46.8	9.5	5.7	0.18	0.80	–	3.12
LMF, $\bar{M}$ 46300	41.7	38.2	5.4	0.8	–	–	3.0	10.9

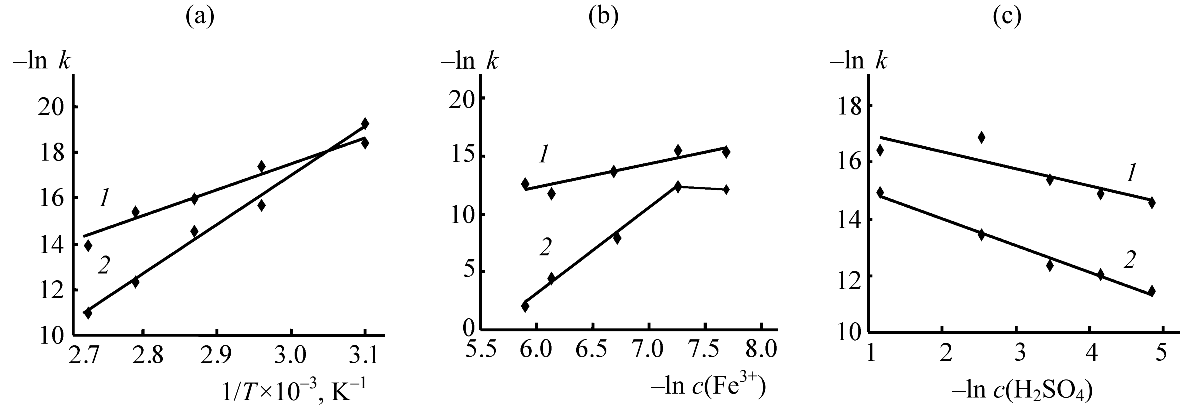
equaled the ratio of the lignosulfonates molecular weight [*M*(HMF) : M(LMF) ≈ 2.7].

The lignosulfonate–Cu^{2+}–Fe^{3+}–O_2 system. Oxidation of the lignosulfonates with Fe^{3+} in the presence of Cu^{2+} was studied at feeding 2 L/min of technical grade oxygen as well as under oxygen-free conditions. The experiments were performed under isothermal conditions ($T = 368$ K) and at fixed concentrations of sulfuric acid (0.025 mol/L) and of Fe^{3+} (3.57×10^{-4} mol/L). The varied parameters were concentrations of copper (0–3.13×10^{-4} mol/L) and of the lignosulfonates (0–4.1×10^{-5} mol/L). At Fe^{3+} to LMF molar ratio $\beta = 18.86$, practically complete iron(III) reduction (95–96%) was reached in the absence of copper. Introduction of molecular oxygen had almost no effect on the reduction parameters. Other conditions being the same, addition of copper ions decreased the concentration of the reduced iron form by 5–8%, especially at the initial stage of the process (3–5 min). Doubling of Fe^{3+} to the lignosulfonate ratio (to reach β of 37.7) led to the decrease in Fe^{3+} reduction degree by 60%, it did not exceed 27–35%. As was mentioned previously, the complete reduction of Fe^{3+} with the LMF lignosulfonate required $\beta \leq 32.5$. Hence, the incomplete reduction of Fe^{3+} by the limited quantity of the lignosulfonate was due to faster and quantitative oxidation of the latter with Cu^{2+}. Similar trend was observed in the case of the HMF lignosulfonate oxidation with the mixture of Fe^{3+} and Cu^{2+}.

The impact of molecular oxygen on the oxidation process was enhanced in the presence of copper ions and it was accompanied with a slight increase in the concentration of the oxidized iron form in the solution (by 10%). Additional experiments on iron ions oxidation with molecular oxygen (353 K, 2100 s) demonstrated that the degree of Fe^{2+} oxidation in the absence of copper ions did not exceed 2% and decreased with increasing lignosulfonates concentration. Basing on the results collected in Table 2 and the scarce published data, high oxidation efficiency of Fe^{3+} towards lignosulfonates and negligibly low degree of Fe^{2+} oxidation with molecular oxygen (without copper as well as in its presence) could be ascribed to the formation of stable Fe^{2+} chelate complexes with lignosulfonates [3].

In order to study the lignosulfonates oxidation with molecular oxygen, severe autoclave conditions should have be used. Activated forms of both HMF and LMF lignosulfonates were obtained.

Solutions of lignosulfonates (concentration was kept constant at 13.3 g/L) were treated in titanium autoclave (Vishnevski type, 1.0 L) equipped with agitator, oxygen feeding, and sampling units. Lignosulfonates



Rate constant of lignosulfonates oxidation as a function of temperature (a), iron ions concentration (b), and sulfuric acid concentration (c). [(*1*) LMF, (*2*) HMF). (a) $c(Fe^{3+}) = 7.05\times10^{-4}$ mol/L, $c(H_2SO_4) = 3.14\times10^{-2}$ mol/L; (b) $T = 358$ K, $c(H_2SO_4) = 3.14\times10^{-2}$ mol/L; (c) $T = 358$ K, $c(Fe^{3+}) = 7.05\times10^{-4}$ mol/L.

Table 2. Parameters of Fe^{2+} oxidation in the presence of lignosulfonates (LS) and sulfuric acid at 358 K during 2100 s

c_{LS}, mol/L×10^{-5}	$c(Fe^{2+})$, mol/L×10^{-3}	$c(H_2SO_4)$, g/L	pH	E, mV	$c(Fe^{3+})$, mol/L×10^{-5}	Degree of oxidation, %
	3.57		3.35	345	5.0	1.4
	3.57	0.05	1.60	360	6.2	1.7
0.19	3.57		2.80	360	2.9	0.8
0.47	3.57		2.50	365	2.3	0.6
1.89	3.57		3.80	330	1.9	0.5
0.47	3.57	0.05	1.70	370	3.7	1.0
0.69	3.57	0.05	1.85	360	4.6	1.3

were activated under conditions of hydrothermal oxidation with molecular oxygen. The varied parameters were temperature (393–423 K), oxygen partial pressure (0.2–0.8 MPa), and the treatment duration (0.5–3 h). The products of oxidation of the LMF and HMF lignosulfonates were designated as oxLMF and oxHMF, respectively.

Identification of oxidation-activated lignosulfonates and physicochemical properties of their solutions. IR studies of the lignosulfonates oxidation products revealed the appearance of intense absorption bands at 1720 cm^{-1} (stretching vibrations of non-conjugated carbonyl groups) and 1640 cm^{-1} (stretching vibrations of C=O conjugated with benzene ring); simultaneously, of stretching vibrations hydroxy groups band at 3420 cm^{-1} was weakened.

Under more stringent oxidation conditions (higher temperature, higer oxygen pressure, and longer oxidation duration), the spectra of oxidized samples contained no bands of aromatic rings skeletal vibrations (at 1510 cm^{-1}).

Thus, the collected IR data confirmed the appearance of carboxy, carbonyl, and *o*-quinoid groups upon lignosulfonates oxidation; under more severe conditions benzene rings were chemically decomposed, and low molecular weight carboxyl derivatives were formed. The spectra were assigned using the ASTM database and the data published in [4–6].

Two pairs of the oxidized lignosulfonates were chosen for detailed studies: those treated under milder conditions [383 K, $p(O_2)$ = 0.3 MPa, 1 h] – oxLMF-A and oxHMF-A, and those oxidized under more severe conditions [428 K, $p(O_2)$ = 0.7 MPa, 3 h] – oxLMF-B and oxHMF-B. The measured properties of samples are reported in Table 3. Except for the mildly oxidized high molecular weight lignosulfonate oxHMF-A, increasing of the oxidation products concentration in the 0.01 to 0.64 g/L range resulted in pH decrease (from 4.3–5.4 to 3.4–3.5), redox potential increase (from 185 to 385 mV), and specific conductivity increase (from 12–20 to 370–440 μS/cm); the most significant change of the determined characteristics were observed in the cases of oxLMF products. In the case of oxLMF-A, increasing its concentration led to increase in pH and ж, and to decrease in the redox potential.

In summary, the studies reported in this work led to the following conclusions.

– Lignosulfonates oxidation with Fe^{3+} occurred under conditions of kinetic control. The lignosulfonates conversion was slowed down with increasing sulfuric acid concentration. When both Cu^{2+} and Fe^{3+} were present in the solution, lignosulfonates were predominantly oxidized with copper ions.

– Lignosulfonates oxidation with molecular oxygen under autoclave conditions [403–423 K, $p(O_2)$ = 0.2–0.8 MPa] resulted in the decrease in hydroxy groups content, simultaneously, more carbonyl groups were formed. Under severe oxidation conditions [423–433 K, $p(O_2)$ = 0.8 MPa, 3 h], the lignosulfonates were chemically destructed into low molecular weight carboxyl derivatives.

– One of the reasons of decreasing lignosulfonates efficiency in the course of autoclave leaching of zinc concentrates could be the side reactions of lignosulfonates oxidation into less efficient products.

Table 3. Physicochemical parameters of the oxidized lignosulfonates (LS) solutions

c_{LS}, g/L		æ, μS/cm		pH		*E*, mV	
		A	B	A	B	A	B
LMF	0.01	16	12	5.1	5.4	185	185
	0.04	49	34	4.4	5.1	200	215
	0.16	150	104	4.0	4.2	245	245
	0.64	440	379	3.5	3.5	265	385
HMF	0.01	15	20	6.4	4.3	300	310
	0.04	46	36	6.8	4.1	255	315
	0.16	130	116	7.0	3.8	250	345
	0.64	400	400	7.5	3.5	235	340

EXPERIMENTAL

Oxidation of two types of lignosulfonates was studied at varied conditions: temperature (293–368 K), the lignosulfonate concentration (4.1×10^{-6}–4.1×10^{-5} mol/L), sulfuric acid concentration (0.007–0.32 mol/L), and Cu^{2+}, Fe^{3+}, or Fe^{2+} ions concentration (4×10^{-4}–4×10^{-3} mol/L); the metal ions were introduced in the form of the corresponding sulfates. All experiments were run in the 0.5 L reactor (filling coefficient of 0.7) equipped with the agitator, sampling, technical oxygen feeding, and oxygen dispersion units.

In the kinetic experiments, lignosulfonate should have been isolated from other chemicals until thermal equilibrium was reached. To do so, lignosulfonate solution was introduced in the reactor in the sealed ampule. Then, after the desired temperature had been reached, oxygen feeding and stirring was turned on, and the ampule was broken; that moment was regarded as the reaction start. The reaction mixture was sampled at regular intervals, and the oxidation state of the reactants was evaluated from the changes in the metal oxidized and reduced forms, pH, and redox potential. Degree of Fe^{3+} reduction and its consumption were calculated with respect to 1 mole of lignosulfonate.

Kinetic data were fitted with

$$c_\tau = k\tau^n \qquad (1)$$

with c_τ, Fe^{2+} concentration (mol/L) at time τ (s); k and n, fitting coefficients.

The specific rate of lignosulfonates oxidation was calculated at constant Fe^{2+} concentration of 0.0003 mol/L using the following equation.

$$V_{\mathrm{sp}} = c_{\mathrm{Fe}} n \left\{ \frac{c_{\mathrm{Fe}}}{k} \right\}^{-1/n}. \qquad (2)$$

Structure and physicochemical properties of the oxidation products were studied in the separate experiments.

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