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Formation and Sorption Behavior of the Palladium Thiosulfate Complexes under Natural Conditions (Model Experiments)

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Abstract—The formation of significant amounts of thiosulfate ion (up to 42 mg/L) was established in experiments on the interaction of sulfide-bearing rocks with water. The possibility of the formation of palladium compounds with thiosulfate ion $[Pd(S_2O_3)_2]^{2-}$ was demonstrated. The stability constant of the complex is 3.7×10^9, which may provide intense migration of this palladium species in ecosystem. The study of the behavior of palladium thiosulfates during interaction with inorganic and organic components of geochemical barriers showed that around 50–55% of thiosulfate-bound palladium is extracted by humic acid in the pH range typical of natural waters. Under these conditions, ferrihydrite sorbes palladium quantitatively, and may serve as efficient barrier to the interaction of palladium compounds with particulate matters of waters and bottom sediments.

Keywords: composition and stability constant of the thiosulfate palladium complexes, sorption behavior under natural conditions

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INTRODUCTION

The transfer and accumulation of platinum group elements (PGE) in natural environments are mainly determined by solubility, chemical transformations, and sorption behavior of PGE compounds that prevail in aquatic systems. In particular, the geochemical behavior of dissolved Pd species in the surface waters is dictated by properties of its coordination compounds containing inorganic ligands and humic organic matter. The main inorganic palladium species in natural aquatic systems are chloride and hydroxy-chloride compounds (Kubrakova et al., 2012). The behavior of these species in ocean as well as in the aquatic systems of the mining zones of ore deposits have been studied by us previously (Kubrakova et al., 2012). In addition to the hydroxy-chloride complexes, the palladium migration in scattered water flows in PGE deposits area under conditions of bacterial oxidation of sulfides with participation of diverse microorganisms may be essentially controlled by interaction with sulfoanions (Mountain and Wood, 1998; Anthony and Williams, 1993; Rohwerder et al., 2003; Schippers et al., 1999), including thiosulfate ion. In addition, thiosulfate could be formed under weak reducing environments, for instance, in the anoxic sulfate-bearing zones due to the activity of sulfate-reducing bacteria (Fitz and Cypionka, 1990).

It is known that the finely dispersed metallic gold (Aylmore and Muir, 2001) and platinum (Wood, 2002) can be dissolved and remain stable in neutral and weakly alkaline media in the presence of thiosulfate ions and air oxygen, while forming Au-bearing complex is characterized by the high stability ($\log K_{st} = 26.5–28.0$). The possibility to form complex compounds of thiosulfate ions with palladium was mentioned, for instance, in (Anthony and Williams, 1993), but these compounds have been weakly studied and their parameters were not quantified.

The aim of this work was to study in detail the Pd complexation with thiosulfate ion under circum-neutral-neutral conditions, which is typical of the mining zones of sulfide deposits, to establish the composition of forming compounds, to calculate their stability constants, and to explore the sorption behavior of Pd(II)-thiosulfate complexes during their interaction with main organic and inorganic components of natural geochemical barriers.

EXPERIMENTAL

The formation of sulfoanions was studied in the water–rock model experiments under static and dynamic conditions. Experimental conditions are described in (Kubrakova et al., 2011a). In static experiments, less than 150-g sample with grain size of 75 μm was mixed with deionized water (<18.2 MΩ) in proportion 1: 3 and shaken for 23 hours at room temperature. Then, the solution was filtered through a 0.45-μm membrane filter (Celulose Nitrate Membrane Filters, Whatman). In this work, we used data obtained for different sulfide-bearing rocks from the Fedorova Tundra

Composition of rock and example of composition of experimental solution after water-rock interaction (by the example of sulfide-bearing carbonaceous shale)

Rock composition	Olimpiada	Composition of aqueous extract, mg/L	
Al_2O_3, %	11.14	pH	5.66
CaO, %	1.06	HCO_3^-	5.4
Fe_2O_3, %	5.48	CO_3^{2-}	<0.2
K_2O, %	2.08	SO_4^{2-}	345
MgO, %	1.27	Cl^-	<0.2
MnO, %	0.013	F^-	6.25
Na_2O, %	0.47	$S_2O_3^-$	31.8
P_2O_5, %	0.74	Al	0.03
TiO_2, %	0.23	Ca	47.9
S, %	3.29	Fe	84.3
As, μg/g	3.4	K	43.2
Co, μg/g	44.1	Mg	11.0
Cr, μg/g	73.7	Na	4.26
Cu, μg/g	53.6	Mn	3.99
Ni, μg/g	268	Zn	0.18

and Olimpiada deposits. The chemical composition of aqueous extract obtained from the quartz–sericite–coal shale with disseminated pyrite and pyrrhotite from the Olimpiada deposit is shown as an example in table.

To study the leaching kinetics under dynamic conditions, 500-g sample with grain size < 5 mm was loaded in a special cell, mixed with 200 mL deionized water, and held for 2 hours. Then, the solution was poured out and the system was blown down by air for 22 hours. The cycle was repeated during 30 days. Data on composition of solutions obtained in the model experiments for the overburden of the Fedorova Tundra deposit (by the example of gabbronorite with disseminated pyrite and pyrrhotite) are reported in (Kubrakova et al., 2011a).

Sulfoanions in solutions were measured by anion exchange chromatography using conductometric titration (LC-20 Prominence Shimadzu chromatograph, Japan) on an IC I-524A column with 0.7 mM potassium hydrogenphthalate and 0.3 mM tris(hydroxymethyl) aminomethane as eluents, flow of 1 mL/min, at column temperature of 45°C. An example of typical chromatograms of the experimental solution after water–sulifde-bearing rock interaction is shown in Fig. 1.

Palladium hydroxide $Pd(OH)_2$ was synthesized from HCl solution of palladium chloride, which was obtained by dissolution of 99.95% metallic palladium in a aqua regia, with subsequent transformation into chloride form and precipitation by sodium hydroxide at pH 11–12. Brown precipitate was thoroughly rinsed with distilled water up to the complete removal of chloride ions.

The palladium thiosulfate complex was obtained by interaction of palladium hydroxide precipitate with sodium thiosulfate solution. Formation kinetics of the complex and its composition were studied at pH 6.3 within sodium thiosulfate concentration range from 0 to 158 μg/mL for 14 days, with periodical sampling of the solution using a 45 μm syringe filter (Millipore Millex-HV).

The palladium concentrations in the solutions were measured by AES-ICP (Iris Interpid II Duo, Thermo Electron Corp., United States) and ETAAS (Solaar MQZ, Thermo Electron Corp., United States).

Electron absorption spectra were recorded on a Shimadzu UV-1800 two-beam scanning spectrophotometer in a spectral range from 190 to 1100 nm.

Mass spectra were obtained on a high-resolution Thermo Scientific Exactive TM spectrometer equipped with heated electrospray ionization source, and Orbitrap^{TM} orbital ion trap.

The behavior of formed dissolved thiosulfate palladium species on the geochemical barriers was simulated in sorption experiments during interaction with precipitates of ferrihydrite and humic acids in the pH range of 6–8 using solutions containing 1–4 μg/mL Pd, with continuous shaking for 28 days. The bottom phase weighed 50 mg. The Pd concentration was analyzed by AES-ICP. A specimen of humic acids was extracted from peat using technique (Varshal et al., 1988). Ferrihydrite was obtained from a Fe(III) nitrate solution using technique (Jambor and Dutrizac, 1998). To reach maximum structural and compositional correspondence of the bottom phase to natural particulate matters, the obtained ferrihydrite precipitate was used in a wet state.

RESULTS AND DISCUSSION

The formation of thiosulfate ions during water–rock interaction. The interaction of sulfide-bearing rocks with water and oxygen leads to the oxidation of sulfide minerals and formation of sulfur compounds with different degrees of oxidation (Fig. 2). The interaction of some of these ligands with metal ions may lead to the formation of strong complexes and affect the migration behavior of elements. In particular, neutral and alkaline media are very favorable for the existence of strong thiosulfate complexes of Au (I). In this work, the formation kinetics of thiosulfate ion was analyzed by the example of different sulfide-bearing rocks from the Fedorova Tundra and Olimpiada deposits. It was established that the thiosulfate ion has been formed in the solution already in the first day of the interaction (Fig. 3).

It was found that practically all analyzed experimental solutions obtained both in static and dynamic conditions contain both sulfate and thiosulfate in concentrations of 2.5–285 and 0.2–42 mg/L, respectively. Thus, it was experimentally proved that the drainage of overburden and waste ores in the mining zone of sulfide

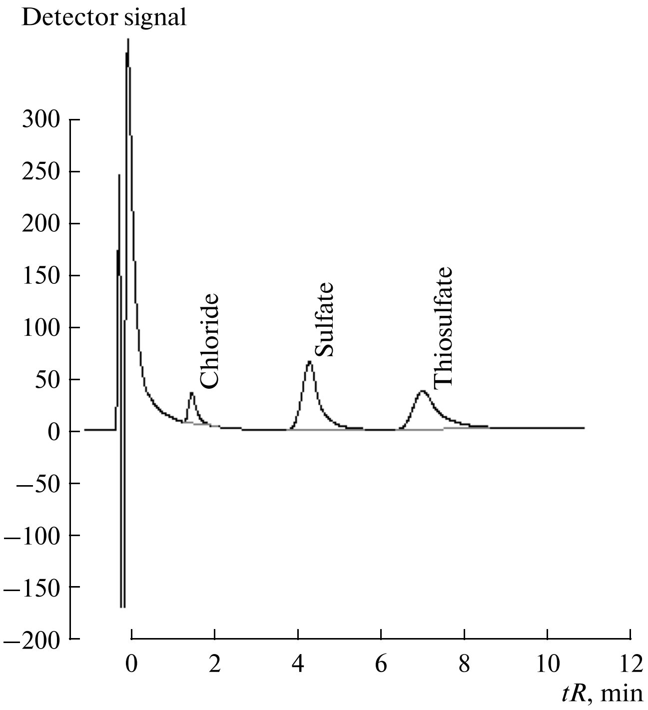

Fig. 1. Typical chromatogram of solution after water–sulfide-bearing rock interaction.

deposits by atmospheric precipitates may result in the formation of technogenic solutions with sufficiently high content of thiosulfate ions.

Formation, composition, and stability of the palladium thiosulfate complex. Formation kinetics and composition of palladium thiosulfate compounds were studied in model experiments at pH 6.3. Below, we demonstrate a change of palladium concentration in solution with increase of the sodium thiosulfate content:

$C_{Na_2S_2O_3}$	0	18.9	39.6	79.6	158
C_{Pd}	0.00375	3.41	4.57	6.78	9.07

Thus, intense dissolution of palladium hydroxide is observed in the presence of thiosulfate ions, concentration of which in the solution approximately corresponds to that in technogenic solutions.

Experimental data obtained under equilibrium conditions ($t = 14$ days) were plotted on a $\log(C_{\mathrm{Pd\,tot}} - C_{\mathrm{Pd\,in}})$ versus $\log C_{Na_2S_2O_3}$ diagram (Fig. 4) to define a linear dependence $y = 2.114x + 5.595$ with a slope of 2.114, which indicates the formation of complex compound of 1 : 2 composition.

In order to confirm the existence of the palladium thiosulfate complex and to establish the composition of this compound, we performed mass-spectral studies of

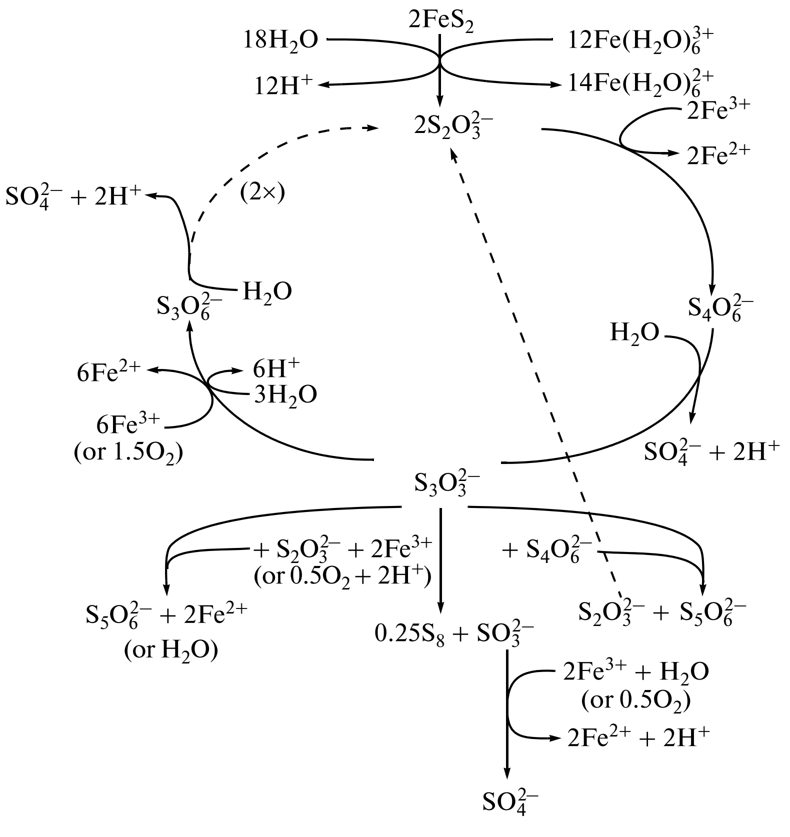

Fig. 2. A scheme of sulfide oxidation (by the example of pyrite, Schippers et al., 1999).

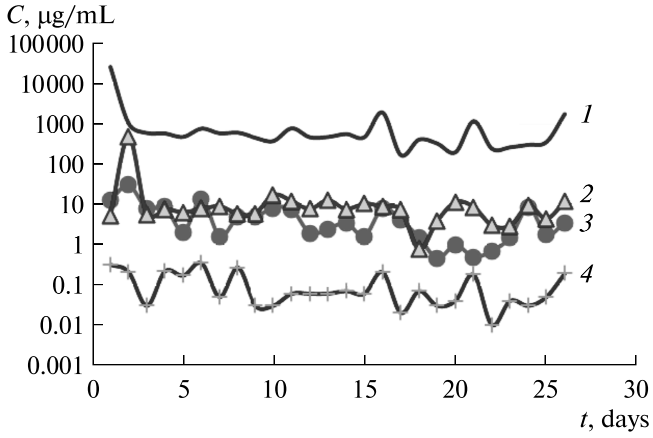

Fig. 3. Variations of the solution components for gabbronorite sample with disseminated pyrite and pyrrhotite (Fedorova Tundra) with time:
(*1*) SO_4^{2-}, (*2*) Fe^{2+}, (*3*) Cu^{2+}, (*4*) $S_2O_3^{2-}$.

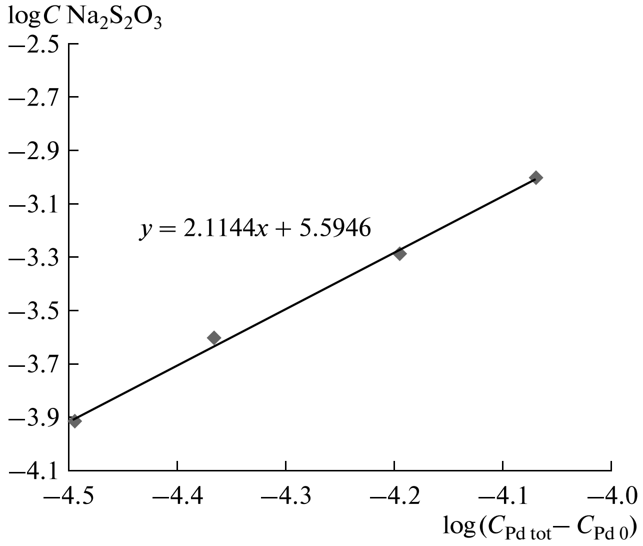

Fig. 4. Variations of $\log C_{Na2S2O3}$ versus $\log(C_{Pdtot} - C_{Pdinit})$.

obtained solutions. Characteristic relations of isotope peaks made it possible to unambiguously identify Pd-containing ions formed under experimental conditions. All recorded mass spectra contain two main groups of isotope peaks of Pd-containing ions. Figure 5a shows the mass spectrum region containing the first group. The measured mass to charge ratios *m*/*z*, as well as observed characteristic ratio of isotope peaks make it possible to identify this group as corresponding to doubly charge ions of complex $[Pd(S_2O_3)_2]^{2-}$. The calculated isotope distribution for $[Pd(S_2O_3)_2]^{2-}$ ion is shown for comparison in Fig. 5b. It is seen that the observed isotope distribution is well consistent with calculated one. The second group of isotope peaks of Pd-bearing ions is shown in Fig. 5c and corresponds to the singly-charge ions of composition $[Pd(S_2O_3)_2]^{-}$, while Fig. 5d shows the calculated isotope distribution of the same ion.

Thus, the results of mass-spectrometric studies unambiguously confirm the formation of the inner-sphere Pd complex with thiosulfate ion of (1 : 2) in composition; this fact may be regarded as reliably established.

In addition to mass spectral data, Figure 6 demonstrates an absorption data onf Pd thiosulfate solution with characteristic maximum at $\lambda = 365$ nm.

An important characteristics of the compounds that are considered as migration species of elements is their stability. Based on obtained experimental data on the solubility of aqueous palladium hydroxide [1], as well as its increase in the presence of thiosulfate ion, the apparent stability constant of the inner sphere complex $[Pd(S_2O_3)_2]^{2-}$ was calculated:

$$Pd(OH)_{2sol} + H_2O \rightarrow [Pd(OH)_2(H_2O)_2]_{sol}, \qquad (1)$$

$$\begin{aligned}&[Pd(OH)_2(H_2O)_2]_{sol} + 2S_2O_3^{2-}\\&\rightarrow [Pd(S_2O_3)_2]^{2-} + 2H_2O,\end{aligned} \qquad (2)$$

$$K_{st} = \frac{[Pd(S_2O_3)_2]^{2-}}{[Pd(OH)_2(H_2O)_2][(S_2O_3)^{2-}]^2} = 3.66 \times 10^9, \qquad (3)$$

where equilibrium concentrations (in M) were calculated based on Pd concentration in solution:

$$C_{Pd(OH)_2} = 3.5 \times 10^{-8}\text{ M};\ C_{[Pd(S_2O_3)_2]^{2-}} = 8.56 \times 10^{-5}\text{ M};$$

$$C_{[S_2O_3]^{2-}} = 8.29 \times 10^{-4}\text{ M}.$$

The value of the stability constant of the Pd thiosulfate complex shows that this compound is sufficiently stable under neutral conditions. Palladium does not form complexes with carbonate- and sulfate ions; while complexes with chloride ions exist only if its contents reach 10^{-3} M and pH < 4; at pH 8 chlorides are absent in the inner coordination sphere (Polotnyanko and Khodakovsky, 2012). As shown by thermodynamic calculations (Kubrakova et al., 2011a), in the absence of thiosulfate ions and under conditions typical of surface waters, palladium forms complexes with fulvic acid, the logarithm of the apparent stability constants of which at pH 5.3 is 7.3 (Kubrakova et al., 1988). Thiosulfate complexes are characterized by even greater stability ($\log K_{st} = 9.56$), which makes it possible to qualify the state of palladium under studied conditions and propose that coordination inner sphere compounds of palladium with thiosulfate could be one of its main migra-

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[1] Obtained solubility of amorphous palladium hydroxide in water at room temperature (pK 7.45) is close to value presented in (Polotnyanko and Khodakovsky, 2012) (pK 7.24).

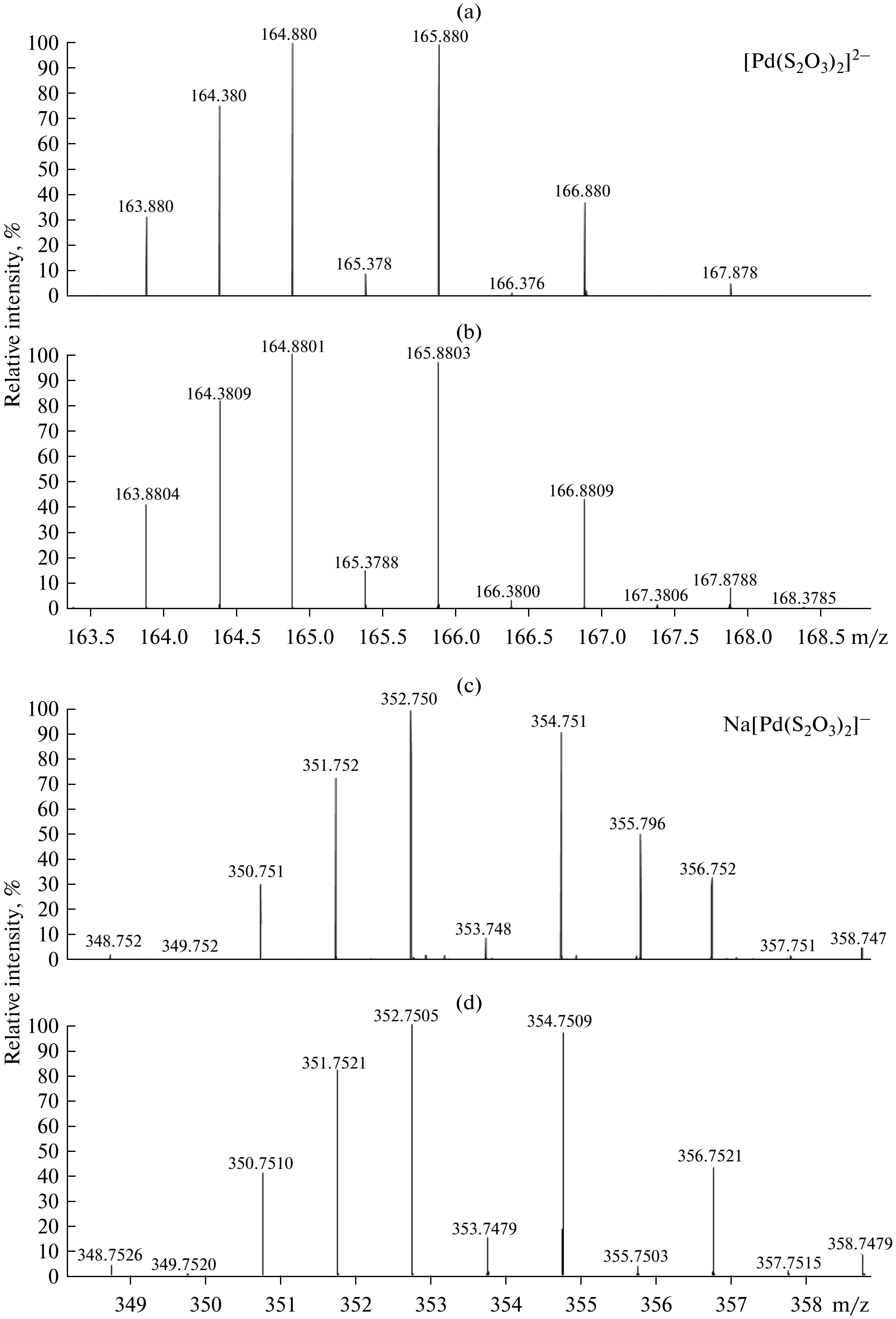

Fig. 5. Mass spectra of palladium thiosulfate ions $[Pd(S_2O_3)_2]^{2}$—(a, b) and $[Pd(S_2O_3)_2]$—(c, d).
(a, c) experimental spectra; (b, d) theoretically calculated spectra.

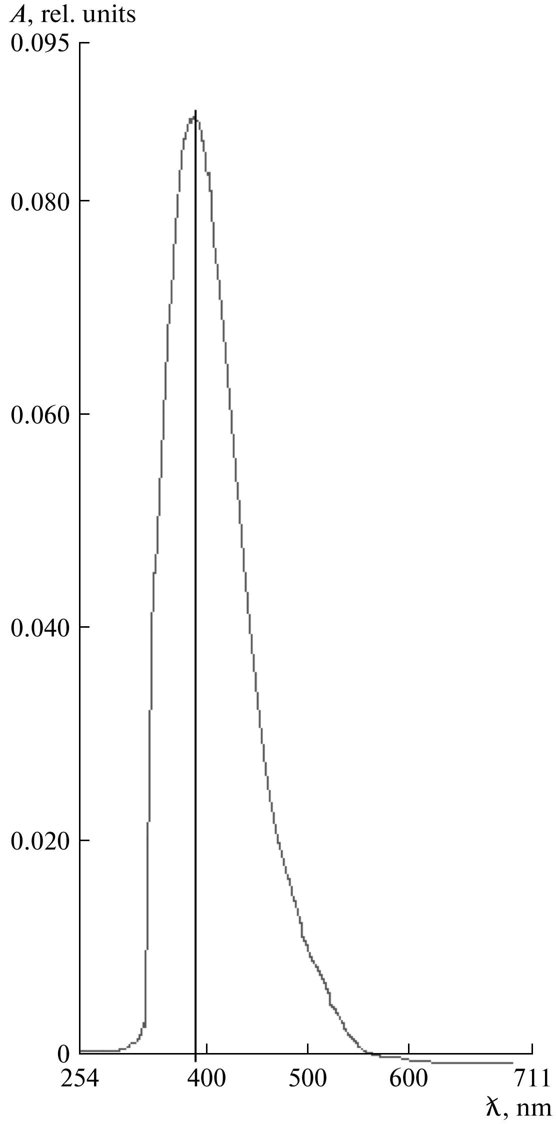

Fig. 6. Electron absorption spectra of the palladium thiosulfate solution.

tion species, which provides a transfer of palladium in a dissolved state. Thiosulfate ion also plays significant role in the gold migration (Kubrakova et al., 2011b), whereas platinum under these conditions does not form strong coordination compounds with thiosulfate.

Interaction of palladium thiosulfate with iron oxyhydroxide and humic matter. The behavior of formed dissolved thiosulfate Pd species on the geochemical barriers was modeled in sorption experiments on interaction with precipitates of ferrihydrite and humic acids in the pH range typical of natural waters (pH 6–8) (Fig. 7). It was shown that no more than 55% palladium thiosulfate, like gold thiosulfate (Kubrakova et al., 2011b), is sorbed by humus within the considered pH range. It was previously shown (Kubrakova et al., 2011a) that in the absence of thiosulfate ions, the hydroxy-chloride palladium species that are dominant in near-neutral media interact with HA to produce well soluble humic complexes and are completely retained in solution, if a system does not contain another (in addition to HA) sorption phases.

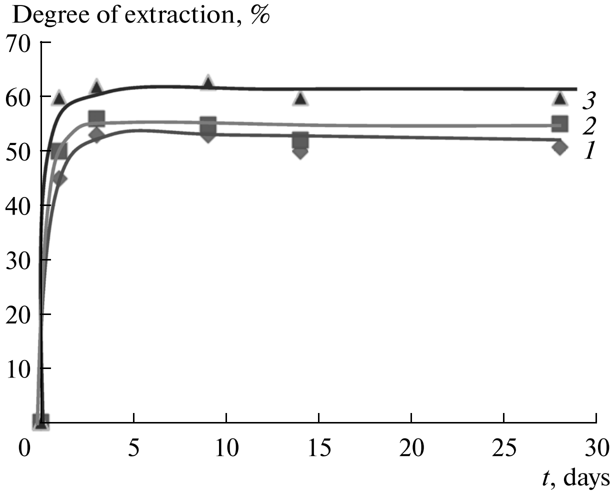

Fig. 7. Sorption of the palladium thiosulfate complex by humic acid (HA): (*1*) pH 6, (*2*) pH 7, (*3*) pH 8.

The study of sorption of palladium thiosulfate complexes on ferrihydrite at the same pH, sorbent masses, and solution volumes as in the systems with HA revealed significant Pd bonding during few hours of interaction between solution and sorbent (Fig. 8). The degree of extraction of hydroxyl-chloride palladium species is also high and reaches 90% (Kubrakova et al., 2011a), however, shows even worse kinetics. Thus, inorganic, primarily, thiosulfate species of palladium in the oxidation zone will be bonded mainly with iron oxyhydroxide-based particulate matter of waters and migrate as pseudocolloids or are accumulated by bottom deposits.

CONCLUSIONS

Experiments on oxidizing leaching of the rocks from noble metal sulfide deposits revealed the formation of thiosulfate anion. It was established that palladium thiosulfates may exist under conditions typical of natural-technogenic sulfide oxidation zones.

The presence of complex of palladium ion with thiosulfate ion [$Pd(S_2O_3)$] and its composition were established on the basis of obtained data on the solubility of amorphous palladium hydroxide in the near-neutral media and its change in the presence of thiosulfate ion of variable concentration and mass spectrometric analysis of formed compounds. The stability constant of this complex $K_{stab} = 3.66 \times 10^9$ ($\log K_{stab} = 9.56$) determined for the first time testifies its high stability.

The migration behavior of the palladium thiosulfate complexes in the aqueous systems of mining zones of

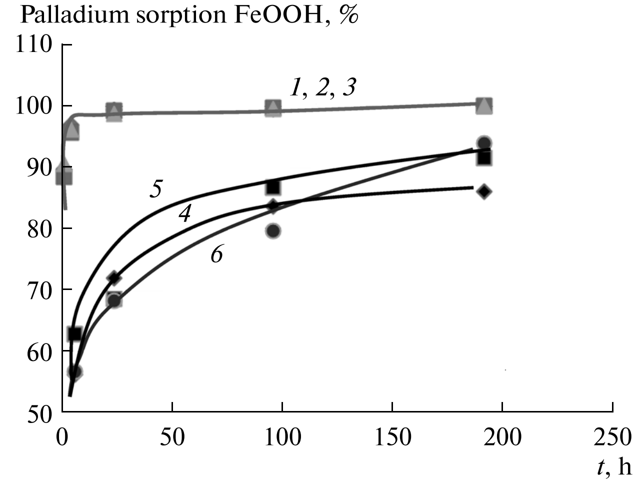

Fig. 8. Kinetics of palladium extraction by iron oxyhydroxide from model solutions of thiosulfate (*1–3*) and hydroxy chloride (*4–6*) complexes:
(*1, 4*) pH 6, (*2, 5*) 7, (*3, 6*) pH 8.

sulfide deposits was experimentally studied. It was shown that these previously unstudied species are characterized by the elevated migration ability as compared to hydroxy-chloride complexes and are able to interact with main components of natural particulate matters in the near-neutral media, thus providing a transfer and accumulation of palladium by pseudocolloid transport. Undoubtedly these species becomes dominant under conditions of slow sulfide oxidation (for instance, during formation of scattered water flows in sulfide deposits area in the permafrost landscapes); at low content of particulate matter in such waters, the thiosulfate compounds of palladium, as well as gold, can be transferred also in a dissolved state.

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