

Solubility and Migration Ability of Rhodium in Natural Conditions: Model Experimental Data

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Abstract—The contents of dissolved rhodium species in the near-neutral environments have been studied for the first time and data on the interaction of Rh with organic matters of natural waters and its sorption behavior during contact with the components of geochemical barriers were obtained. The solubility method was used to analyze the behavior of rhodium hydroxide in the $\text{Rh}(\text{OH})_x\text{-H}_2\text{O}$ and $\text{Rh}(\text{OH})_x\text{-H}_2\text{O-FA}$ (fulvic acids) systems. The possible contents of inorganic species of rhodium and its compounds with humic organic ligands were determined within the pH range typical of surface waters. The solubility of rhodium shows a two-order-of-magnitude increase in the presence of humic matters (FA). The sorption interaction of the soluble rhodium species with the main components of geochemical barriers such as iron oxyhydroxides (III), (including fulvic-acid modified ones), aluminosilicates, and precipitates of humic acids in contact with natural waters was studied. It was revealed that rhodium has the high affinity to all studied materials; its species are sorbed by ferrihydrite within several hours. It is suggested that rhodium is mainly transferred as colloid with suspended particulate matters of waters and then is accumulated in bottom sediments. The differences revealed in the sorption behavior of Pt(IV), Pd(II) and Rh(III) may be used to predict the distribution of the considered platinum group elements between the components of ecosystems.

Keywords: rhodium, solubility of rhodium hydroxycompounds, migration ability, sorption behavior on geochemical barriers

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INTRODUCTION

Platinum group elements (PGE) are characterized by the low natural contents and weak migration ability (Perelman, 1989). Their behavior in natural systems and the degree of ecological hazard for a long time have remained weakly studied. The increasing industrial demand for these metals in recent decades has led to the increase of anthropogenic influx of platinum and other PGE into environment at mined ore deposits, near metallurgic plants, and in large towns. The background PGE levels in soils, bottom sediments, and surface waters have considerably increased in recent decades (Moldovan, 2007; Ek et al., 2003; Cobelo-Garsia et al., 2008). In addition to mining, metallurgical, and radiochemical activities, the sources of anthropogenic PGE influx in ecosystems are also motor and industrial catalytic agents. Most part of the anthropogenic PGE, including rhodium, are supplied in an environment as finely dispersed metallic particles, which in contact with water, oxygen, and organic matters are transformed into the dissolved species. The fraction of dissolved PGE significantly increases in weakly acid environments, as well

as in the presence of natural complexing agents (Whiteley and Murrey, 2003; Kubrakova et al., 1988).

There is very limited opportunity to study the transfer and accumulation of PGE in natural conditions. Thereby, experimental data on speciation and solubility of PGE compounds in aqueous solutions, as well as their redistribution between a solution and a solid phase play significant role in study of their behavior. Sorption is one of the most important geochemical processes, which define the migration ability of elements in natural and natural–anthropogenic environments. For this reason, the experimental simulation of the behavior of elements using individual model sorbents (components of geochemical barriers) acquires especial significance.

The speciation of PGE migration was mainly studied for platinum and palladium. In spite of the coexistence of these elements in primary (rocks, ores) and secondary (transformation products, catalytic agents) sources of environmental pollution and the apparent similarity of their physicochemical properties, they show significant difference in the behavior during accumulation and transfer under diverse natural conditions, in particular, in oceanic and fresh-water envi-

ronments (Kubrakova et al., 2010; Kubrakova et al., 2012). Of special interest in this regard is the study of behavior of one more PGE, rhodium, whose contents, solution speciations, sorption and migration ability in natural systems have been weakly studied. The aim of this work is to obtain data on the solubility of rhodium hydroxycompounds in near-neutral environments, their interaction with humic organic matters of natural waters and sorption behavior of rhodium during contact with components of geochemical barriers, as well as the comparison of results obtained for rhodium(III) with analogous data on platinum(IV) and palladium(II) from previous works.

EXPERIMENTAL

Rhodium hydroxide (III) was obtained by precipitation during neutralization of rhodium chloride solution (red species $\text{H}_3[\text{RhCl}_3(\text{OH})_3]$) with sodium hydroxide solution. Suspension of obtained precipitate was subdivided into four equal portions in the volumetric flasks, and filtered through ultrafilters with pore size of 450 nm. Precipitates on the filters were washed to remove chloride ions and then in a wet state were transferred into 100-mL Teflon beakers and filled with 40 mL of distilled water. The solubility of the precipitate in the $\text{Rh}(\text{OH})_x\text{-H}_2\text{O}$ system was studied by ICP-AES within pH range of 3.0–9.0. The dependence of element concentration on the experimental time was analyzed by its measurement after 0.1, 1, 4, 5, 6, 7, 8, and 13 days. Then, equilibrium rhodium(III) solubility values versus pH were plotted for each studied pH value (3.0, 5.0, 7.0, 9.0).

In order to evaluate the effect of organic ligands such as humic acids on the rhodium solubility within a wide isoelectric range (pH 4.5–7.5) with constant concentration of neutral rhodium(III) complexes, the interaction of rhodium hydroxide with FA extracted from concentrate of the Moscow River headwaters using known technique (Varshal et al., 1973) was studied by the example of neutral environments (pH 7.0). For this purpose, around 10 mg of synthesized rhodium(III) hydroxide (the time of precipitate ageing from the beginning of synthesis is three days) were brought in contact with 40 mL of FA with concentration of 120 μg and pH 7.0. Equilibrium in “the rhodium hydroxide(III)-FA” system was attained sufficiently rapidly, during few hours, while element concentration in the solution increased by two orders of magnitude as compared to its concentration in the absence of FA, remaining constant during entire experiment (15 days).

In order to study the distribution of dissolved Rh(III) species between solution and components of suspended particulate matter or bottom sediments in natural conditions, we analyzed the sorption of rhodium from aqueous solutions with starting concentration of the element of 0.05–5.0 $\mu\text{g}/\text{mL}$. For this pur-

pose, we prepared a series of solutions with equal concentrations of the element and pH varying from 4.0 to 8.0, which were established using 1 M and 0.1 M NaOH solutions. The variable pH values were corrected as required with time, daily controlling environmental acidity, up to the attainment of equilibrium (constant pH values of the solutions), and already equilibrium solutions with different rhodium concentrations were brought in contact with sorbent. The experiment was performed on a humic acid (HA) precipitate, aluminosilicates (by the example of shale), iron (III) oxyhydroxides of diverse composition, as well as on ferrihydrite modified by FA (Kubrakova et al., 2011). Ferrihydrite $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ was obtained using technique (Jambor and Datrızac, 1998) and used in experiments after three-day ageing. It is characterized by two XRD-bands (2.54 and 1.97) and applied in a wet state, which most resembles natural colloids. Ferrihydrite covered by FA was obtained by interaction with FA for one day. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) was synthesized at 225°C and characterized by XRD-bands of 2.70, 3.68, and 2.52. Magnetite (Fe_3O_4) displays XRD-bands at 2.53 and 2.97.

The HA was extracted from peat using known technique (Varshal et al., 1996). The role of aluminosilicate suspended particulates in the migration behavior of rhodium was studied by the example of sorption of its dissolved inorganic species on a shale having the following composition (wt %): SiO_2 —60.24, TiO_2 —0.94, Al_2O_3 —20.6, Fe_2O_3 —0.91, FeO —5.43, MnO —0.05, MgO —1.4, CaO —0.30, Na_2O —1.31, K_2O —3.85, CO_2 —1.129, P_2O_5 —0.095.

RESULTS AND DISCUSSION

Migration behavior and the style of accumulation of PGE in natural and anthropogenic environments are mainly determined, on the one hand, by metal speciation in solution, and on the other hand, by sorption behavior of dissolved compounds at geochemical barriers of different composition.

Dissolved rhodium species in aqueous environments.

Data on the platinum and palladium speciations in natural waters are briefly summarized in (Sassani and Shock, 1998; Wood et al., 1992; Kubrakova et al., 2012; Turner, 2007). It is shown that these PGE in near-neutral environments exist mainly as aquatic and hydrolyzed chlorine complexes. In the absence of organic ligands, the minimum solubility under these conditions is typical of palladium hydroxides $\text{Pd}(\text{OH})_2 \cdot m\text{H}_2\text{O}$. Unlike palladium and platinum (II), the platinum hydroxide(IV) $\text{Pt}(\text{OH})_4 \cdot m\text{H}_2\text{O}$ demonstrates the higher solubility, which sharply increases with pH growth from 4 to 11 (Kubrakova et al., 1988). This substantiates the conclusion that hydroxyl ion was the main inorganic complexing agent for platinum in the waters. The coordination chemistry of rhodium is characterized by the diversity of its complex species,

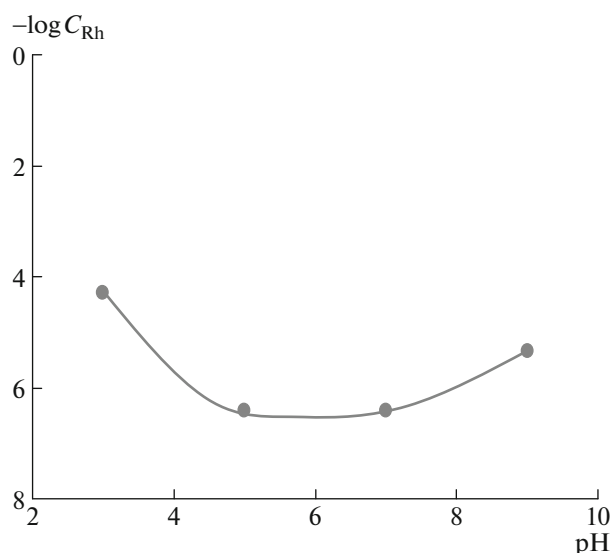


Fig. 1. Solubility of $Rh_2O_3 \cdot nH_2O$ as a function of pH (equilibrium time of 13 days; $[C_{Rh}]$ -mol/L).

which are simultaneously present in solution in response to the aquation, hydrolysis, isomerization, and (in alkaline environments) polymerization. Hydrolysis of aqua-chloride complexes of rhodium starts at pH 3.3–4.5. In this case, hydrolytic processes are not accompanied by a change in oxidation state of central nuclei, while acid dissociation proceeds with low rate. In a general view, the rhodium speciation in natural environments, including both anionic and cationic species, may be designated as $[RhCl_x(OH)_y(H_2O)_z]^{3-x-y}$, where $x + y \leq 6$, $z = 6 - x - y$ (Buslaeva and Simanova, 2003). The rhodium species in the near-neutral environments are practically unstudied. There are data (Pechenyuk, 1991) that sulfate–chloride environments, which are typical, for example, of surface waters of some sulfide deposits, are likely dominated by weakly charged aquatic complexes.

The study of rhodium (III) solubility performed in this work at 25°C, atmospheric pressure, and pH 3–9 in the $Rh(OH)_x-H_2O$ system showed that equilibrium was reached in solutions after 8–13 days. Rhodium shows the maximum solubility of 5×10^{-5} M (5.15 µg/mL) at pH 3.0. In the isoelectric region dominated by neutral complexes (pH 5.0–7.0), rhodium has minimum solubility of 4×10^{-7} M (0.041 µg/mL), increasing by an order of magnitude to pH 9.0 (Fig. 1). The comparison of the solubility of rhodium hydroxide in the isoelectric region with data on platinum (IV) and palladium (IV) hydroxycomplex species shows that their relative solubility is $Pt > Rh > Pd$, accounting for, respectively, 1.5×10^{-6} M (Kubrakova et al., 1988), 4×10^{-7} M (this work), and 3.5×10^{-8} M (Van Middlesworth and Wood, 1999).

In the presence of organic matters in surface waters, most of PGE form strong complexes with organic ligands (Morel et al., 2003). This is confirmed by the experimental data on platinum interaction in solutions with model organic compounds and with humic acids extracted from highly colored waters (Kubrakova et al., 1988; Wood, 1990), as well as by thermodynamic calculations using stability constants of hydroxy- and fulvate complexes of palladium and platinum (Kubrakova et al., 2011). Data on rhodium are only inferred from (Turner, 2007). We established that, by analogy with palladium and platinum, the solubility of rhodium hydroxide in the presence of natural fulvic acids shows a sharp increase by two orders of magnitude from 0.04 µg/mL in the absence of FA up to 5.01 µg/mL rhodium(III) in the presence of FA (at pH 7.0); this is caused by the formation of complex compounds of rhodium with FA in the solution.

Interaction of dissolved rhodium species with components of natural geochemical barriers. Dissolved element species formed during leaching from rocks or soils, while entering surface waters, interact with their components to form new dissolved compounds (primarily, with organic matter), and/or to precipitate on colloid particles or in bottom sediments. These phases are composed of iron oxides of different mineral composition, as well as clay minerals and humic matter. For this reason, we analyzed sorption of platinum, palladium, and rhodium on iron oxides of known structure (ferrihydrite, hematite, and magnetite), organomineral precipitates prepared on their basis (iron oxides modified by fulvic acids), aluminosilicates, as well as humic acids extracted from peat in a wide pH range of natural waters.

The experimental study of the interaction of dissolved inorganic rhodium, platinum, and palladium species with HA in neutral and weakly alkaline environment (with pH from 5.0 to 8.0 and higher) is peculiar in the appearance of well soluble FA, the products of HA destruction, in the Me–HA solution system. Fulvic acids contain complexing functional groups and have the high ability to form soluble complex compounds with ions of many metals. The presence of dissolved FA in the system follows from the coloration of solutions (starting from pH 5.0), which becomes more intense in experiments with higher pH (6.0, 7.0, 8.0). This suggests proceeding the differently directed processes in the considered “Rh(III)–FA” system starting from pH 5.0. On the one hand, Rh(III) complexes may interact with surface of HA (by mechanism of ion exchange and/or complexing with functional groups on the sorbent surface), and, on the other hand, rhodium may form complexes with FA in a solution. Quantitative proportions of these reactions for three studied PGE are different, which is explained (Fig. 2) by the different affinity of metal ions to the considered sorbents. Figure 2 and Table 1 (tables show the initial and final concentrations of metal ions for each element in the solution) demonstrate sorption

behavior of three PGE (platinum, palladium, and rhodium) on HA depending on solution pH. Among these elements, rhodium(III) possesses the highest affinity to HA and is completely extracted from solutions at pH 6.0, 7.0, and 8.0. Palladium is sorbed on HA only in weakly acid environments. At higher pH, it begins to interact with dissolved humic matters (FA) and is completely retained in solution presumably as complexes with FA at pH 7.0. The behavior of platinum in the Pt(IV)–HA system differs from that of rhodium and palladium in the above described systems. Only 25–35% of inorganic platinum complexes are sorbed by HA surface in the pH region of 3.5–6.0; with the growth of pH values, the efficiency of platinum extraction from solutions by HA precipitates increases only up to 55%. Thus, platinum, palladium, and rhodium show quite different behavior on HA within the pH range from 4 to 8: rhodium(III) is completely extracted from solution, platinum is redistributed between phases of solution–HA system, while palladium at pH > 5.0 again sharply passes in solution presumably due to the formation of well soluble complexes with FA.

Another important components of natural colloids are aluminosilicates. Unlike iron(III) oxyhydroxides, aluminosilicates do not interact with dissolved humic matter of waters (FA), which was confirmed by studying the interaction at their contact with montmorillonite (Dudarchik, 1993) and in our investigations of FA sorption on shale and clinoptilolite. The sorption of metal ions on the surface of clay minerals proceeds in two directions: ion exchange on basal and interlayer planes and specific chemical absorption (surface complexing) on amphoteric groups ($>Al-OH$, $>Si-OH$) of the edge faces (Gaskova, 2009). Specific sorption of anions (anionic form is typical of PGE in a weakly alkaline environment) is driven by their incorporation in the coordination sphere of metal oxyhydrate (sorber) (Pechenyuk, 1991).

The interaction of rhodium(III) hydroxycomplexes with aluminosilicates was simulated by the example of its sorption on a shale within pH range from 5.0 to 8.0. Figure 3 illustrates the dependence of rhodium sorption on time for indicated pH values. It is seen that the element extraction was 80–100%, and equilibrium in the Rh(III)–H₂O–shale was attained after 11–12 days. For palladium (II) and platinum(IV) under similar conditions, equilibrium was reached after 21 days, while sorption of their ions within pH range of 5.0–8.0 was 50–80% and 78–80%, respectively. Figure 4 and Table 2 demonstrate the dependence of sorption of inorganic complex species of platinum, palladium, and rhodium (chloride, hydroxychloride, and hydroxycomplexes) on a shale on the pH value of solution. Figure 4 illustrates that the highest degree of extraction at the contact with a shale is observed for rhodium. Obtained experimental data suggest the higher solution–precipitate partition coefficients for rhodium in natural systems of solu-

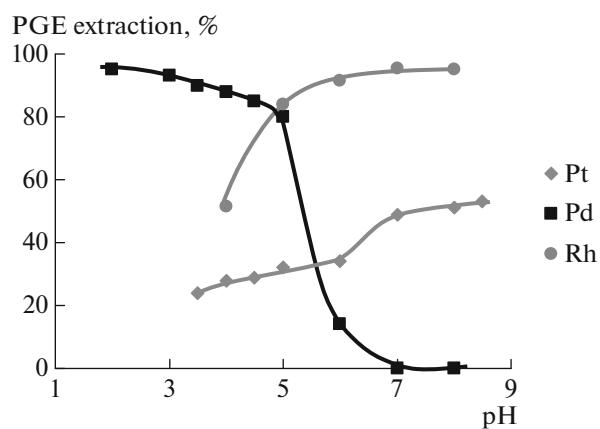


Fig. 2. Sorption of inorganic complex PGE species on HA precipitate as a function of pH. Starting concentrations of metal ions, $\mu\text{g/mL}$: $C_{Rh} = 1.39$; $C_{Pt} = 1.27$; $C_{Pd} = 1.05$.

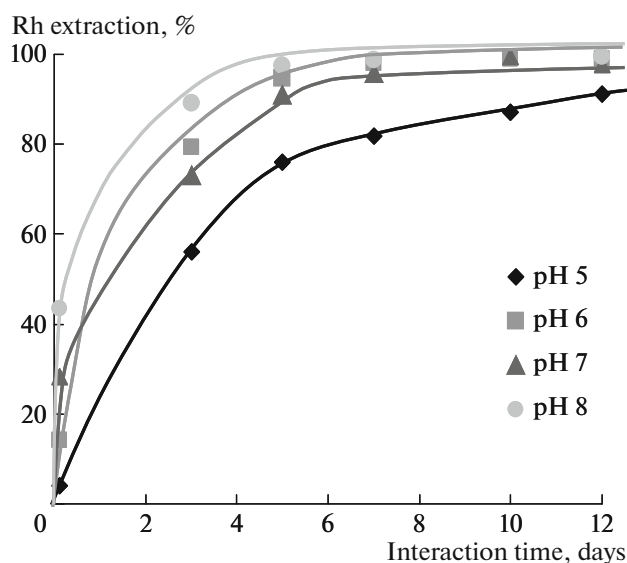


Fig. 3. Sorption of Rh(III) on a shale as a function of time at different pH values of solutions.

tion–aluminosilicate mixtures, which is confirmed by studies (Turner, 2007).

As was established, ferrihydrite precipitate exhibits intense absorption of Rh inorganic complex species from solution. Figure 5 demonstrates that the interaction is characterized by sufficiently rapid kinetics: equilibrium in the Rh(III)–H₂O–ferrihydrite system is reached after 2–3 hours, while rhodium extraction does not depend on pH and is quantitative. Such a Rh(III) behavior is consistent with concepts about significant acceleration of sorption processes passing through hydrolysis stage at the contact with oxyhydroxide surface, and possibly, is related to the acceleration of hydrolysis of aquatic rhodium species on the errihydrite surface (Pechenyuk, 1991). In the Pd(II)–

Table 1. Sorption of Rh(III) (1), Pt(IV) (2), Pd(II) (3) on humic acids (HA) as a function of pH 1. $M_{HA} = 50$ mg, $V = 40$ mL; 2. $M_{HA} = 20$ mg, $V = 40$ mL; 3. $M_{HA} = 20$ mg, $V = 40$ mL

1. Sorption of Rh(III) ions				2. Sorption of Pt(IV) ions				3. Sorption of Pd(II) ions			
pH	time of Rh interaction with HA	Rh content in solution, $\mu\text{g/mL}$	Rh extraction from, %	pH	time of Pt interaction with HA	Pt content in solution, $\mu\text{g/mL}$	Pt extraction from, %	pH	time of Pd interaction with HA	Pd content in solution, $\mu\text{g/mL}$	Pd extraction from, %
4.0	0	1.39	–	3.5	0	1.27	–	2.0	0	2.05	–
	15 days	0.67	51.6		21 days	0.96	24.4		14 days	0.10	95.3
5.0	0	1.34	–	4.0	0	1.30	–	3.0	0	1.92	–
	15 days	0.22	83.7		21 days	0.93	28.5		14 days	0.14	92.7
6.0	0	1.33	–	4.5	0	1.23	–	3.5	0	1.93	–
	15 days	0.11	91.4		21 days	0.87	29.3		14 days	0.19	90.2
7.0	0	1.08	–	5.0	0	1.25	–	4.0	0	1.89	–
	15 days	0.05	95.5		21 days	0.85	32.6		14 days	0.23	87.8
8.0	0	0.93	–	6.0	0	1.06	–	4.5	0	1.78	–
	15 days	0.05	94.7		21 days	0.70	34.0		14 days	0.26	85.4
				7.0	0	0.94	–	5.0	0	1.66	–
					21 days	0.48	48.9		14 days	0.34	79.7
				8.0	0	0.91	–	6.0	0	0.14	–
					21 days	0.45	50.8		14 days	0.12	14.3
				8.5	0	1.11	–	7.0	0	0.14	–
					21 days	0.52	53.1		14 days	0.14	0
				8.0				8.0	0	0.15	–
					14 days	0.15	0		14 days	0.15	0

At interaction time equals "0", the concentrations of metal ions in a solution correspond to starting ones.

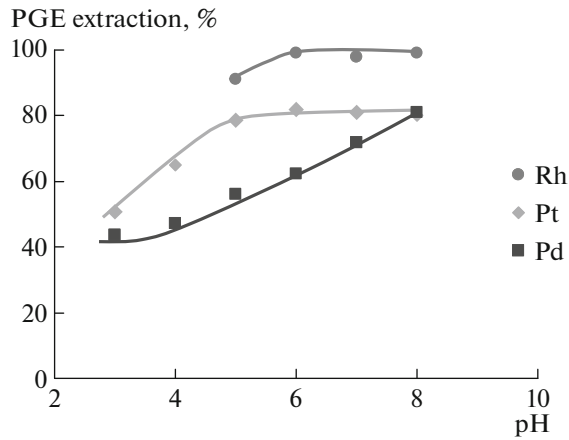


Fig. 4. Sorption of inorganic PGE complex species on a shale as a function of pH. Starting concentrations of metal ions, $\mu\text{g/mL}$: $C_{\text{Rh}} = 1.15$; $C_{\text{Pt}} = 0.045$; $C_{\text{Pd}} = 2.58$.

H_2O -ferrihydrite and $\text{Pt(IV)}-\text{H}_2\text{O}$ -ferrihydrite systems, the equilibrium was achieved after 6 and 21 days, respectively, while the metal extraction varied from 80 to 88% for Pd(II) and from 70 to 90% for Pt within pH range from 4.0 to 8.0. Figure 6 illustrates obtained data on sorption of the studied PGE on the iron hydroxide(III) precipitate versus pH solution. It is seen that rhodium shows the highest affinity to iron hydroxide(III) among the three elements.

Under equal conditions, equilibrium was attained on humus-covered ferrihydrite after 6 days for palladium and after 14 days for platinum. Experimental study of Rh extraction on the iron hydroxide preliminarily brought in contact with FA (1g of freshly precipitated amorphous iron hydroxide(III) extracts 50 mg FA after 1 day) demonstrated practically complete extraction of rhodium after 30 min. It is seen that iron

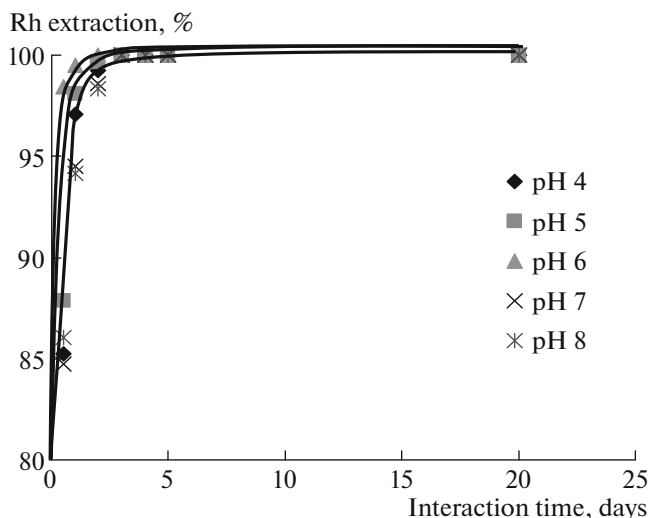


Fig. 5. Sorption of Rh(III) on ferrihydrite as a function of the interaction time at different pH values.

hydroxide(III) and FA-modified hydroxide are sorption phases, which provide intense absorption of all three studied elements from solution, differing only in sorption kinetics; with almost instant absorption of rhodium. We may suggest that rhodium will exhibit the similarly high sorption activity on the other types of sorbents bearing varieties of iron oxides(III).

Quantitative sorption on hematite was noted in the pH range of 4.0–8.0 for palladium and within 5.0–8.0 for platinum. The study of sorption behavior of platinum on magnetite in the absence or presence of humic matters showed that the style of sorption of chloride and hydroxychloride platinum complexes on both the sorbents is almost identical: the low sorption within pH range from 3.0 to 6.0 (within 40–65%) and sufficiently significant sorption at pH 7.0 and 8.0. Extraction of platinum from solutions in this pH interval is 75–85% for magnetite sorbent and 80–95% for modified sorbent.

Thus, all studied varieties of iron oxides that are typical of natural conditions in near-neutral and weakly alkaline environments may serve as sufficiently efficient reservoirs for inorganic PGE. Note that the kinetics and degree of metal extraction and pH range significantly increase in the presence of humic matters, which modify the surface of the considered mineral phases. The most efficient PGE reservoirs are organomineral phases based on the ferrihydrite—natural mineral sorbent dominating in aquatic systems. This sorbent is formed, in particular, during drainage of overburden and waste rocks of sulfide deposits by water and accounts for significant part of colloids and suspended particulate matter of surface waters (Baken et al., 2013). It is known that precisely natural colloids provide transfer and accumulation of trace elements in natural environments.

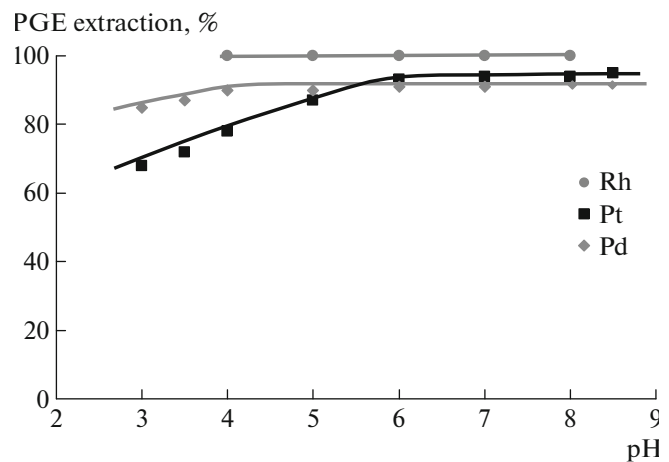


Fig. 6. Sorption of inorganic complex PGE species on ferrihydrite precipitate as a function of pH. Starting concentrations of metal ions, $\mu\text{g/mL}$: $C_{\text{Rh}} = 1.20$; $C_{\text{Pt}} = 1.23$; $C_{\text{Pd}} = 0.117$.

Table 2. Sorption of Rh(III) (1), Pt(IV) (2), and Pd(II) (3) on a shale as a function of pH $m_{\text{sorp}} = 50$ mg; $V = 40$ mL

1. Sorption of Rh(III) ions			2. Sorption of Pt(IV) ions			3. Sorption of Pd(II) ions					
pH	interaction time of Rh with sorbent	Rh content in solution, $\mu\text{g/mL}$	Rh extraction from solution, %	pH	interaction time of Pt with sorbent	Pt content in solution, $\mu\text{g/mL}$	Pt extraction from solution, %	pH	interaction time of Pd with sorbent	Pd content in solution, $\mu\text{g/mL}$	Pd extraction from solution, %
5.0	0	1.15	—	3.0	0	0.045	—	3.0	0	2.58	—
	12 days	0.11	91.0		21 days	0.022	50.6		21 days	1.45	43.6
6.0	0	1.03	—	4.0	0	0.045	—	4.0	0	2.50	—
	12 days	0.012	99.0		21 days	0.016	65.0		21 days	1.32	47.1
7.0	0	0.86	—	5.0	0	0.042	—	5.0	0	2.47	—
	12 days	0.026	97.8		21 days	0.009	78.7		21 days	1.08	56.1
8.0	0	0.68	—	6.0	0	0.030	—	6.0	0	2.36	—
	12 days	0.007	99.4		21 days	0.006	80.1		21 days	0.89	62.3
				7.0	0	0.038	—	7.0	0	1.12	—
					21 days	0.007	81.0		21 days	0.31	71.9
				8.0	0	0.039	—	8.0	0	1.83	—
					21 days	0.008	79.5		21 days	0.35	80.9

At interaction time of element with sorbent equal "0", the concentrations of metal ions in a solution correspond to starting ones.

Presented data obtained using individual sorption phases as well as thermodynamic calculations (Kubrakova et al., 2011) are well consistent with experimental results on the distribution of dissolved PGE species between solution and natural particulate matter of waters (Kubrakova et al., 2010; 2012; Turner, 2007). In particular, the potential ability of natural colloids to accumulate platinum was studied by us by the example of suspended particulate matters of different size of the White Sea, the main mineral components of which are iron oxyhydroxides and clay particles. IR spectroscopic study showed that the organic matter of colloid fractions contains carboxyl, phenol, and ester functional groups that are capable of complexing with metals. It was established that these natural colloids serve as efficient sorbents of platinum (up to 70%), although kinetics of its extraction is retarded as compared to the freshly precipitated iron hydroxides, which may indicate the preferential interaction of platinum with mineral surface of iron oxyhydroxide and the predominant coprecipitation and accumulation of its complex species with iron oxyhydroxide during its formation (Kubrakova et al., 2010).

Similar results (Kubrakova et al., 2012; Koshcheva et al., 2012) were obtained in the model experiments on the distribution of dissolved PGE species (platinum and palladium) between riverine water and native particulate matter, which represents clay matter with admixture of humus and iron oxides. This study revealed the absence of sorption palladium species and the possibility of platinum accumulation by particulate and/or sedimentary matter, which is confirmed by sorption experimental data (Fig. 2). The experimental evaluation of the mobility of anthropogenic platinum, palladium, and rhodium (in particular, from road dust) (Turner, 2007) showed that palladium has the highest potential for the distal transfer and bioaccumulation in an aqueous environment, being practically completely retaining in solution; platinum is almost equally partitioned between solution and particulate matter. Rhodium suffered intense interaction with natural colloids; its partition coefficients between water and particulate matter are few times higher than those of platinum and palladium. The same conclusion was drawn from our study during PGE sorption on the components of geochemical barriers.

Thus, data on the composition of aqueous solutions, the type of suspended particulate matter, speciations of the studied elements in these systems, and behavior of their predominant species at contact with sorption phases of different nature may be used to predict the migration behavior and transport of platinum, palladium, and rhodium that entered the environment from secondary sources (overburden and waste rocks in the mining zones, road dust near highways, and others), as well as to infer the possible ecological pollution due to the accumulation of these elements. The proportions of contribution of PGM transfer and accumulation in natural environments are defined by

the metal nature (significant differences in the metal behavior), by the presence of iron hydroxides in the particulate and sedimentary matters, as well as by the content of humic matters in a solution (FA) and a precipitate (HA). Obtained data indicate that the order of the decreasing migration ability of the studied PGE is $\text{Pd} > \text{Pt} \gg \text{Rh}$.

CONCLUSIONS

The migration behavior of platinum group elements, especially rhodium, in natural and natural–anthropogenic environments is poorly studied. At the same time, the further study of their geochemical behavior, in particular, obtaining data on the sorption ability of the components of geochemical barriers typical of natural settings relative to the dissolved species of these elements, is required for solving ecological problems and developing the geochemistry of this element.

Obtained data on the solubility of rhodium hydroxycompounds within pH range typical of surface waters and the interaction of rhodium with natural organic ligands of humic nature, as well as with main components of natural geochemical barriers make it possible to suggest the efficient migration of this element with suspended particulate matter of natural waters and its accumulation by sedimentary matter. The most efficient reservoirs for rhodium and other PGE are organomineral ferrihydrite-based sorption phases, which provide the colloid transport and serve as geochemical barrier in natural and natural–anthropogenic settings; rhodium is characterized by the highest sorption and the lowest migration ability in a dissolved state.

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