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Comparison of the sorption properties of crystalline and amorphous samarium(III) oxohydroxides

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The influence of the pH of precipitation (pH_1) and the ionic medium on the sorption properties of as-precipitated samarium(III) oxohydroxides, *i.e.*, the pH of zero charge point and the rate of heterogeneous hydrolysis of the $IrCl_6^{2-}$, $RhCl_6^{3-}$, and $PtCl_4^{2-}$complexes, was studied. The composition of precipitates was studied by the drop titration of solutions of samarium nitrate and thermography. It was found that as-precipitated samarium oxohydroxides are amorphous and the substitution of NO_3^- ions by OH^- is not complete even at pH_1 11. Heterogeneous hydrolysis occurs on the surface of samarium oxohydroxide, and its rate increases with increasing pH_1. The as-precipitated samarium oxohydroxides have much higher sorption activities than crystalline Sm_2O_3, and their activities are similar to those of ferrogels.

Key words: sorption properties, zero charge point, indicator reaction rate, samarium oxohydroxide, heterogeneous hydrolysis.

Poorly soluble metal oxohydroxides are of interest as sorbents for both chemical and environmental technologies.[1,2] The previous studies of the properties of iron,[1] rare-earths (RE),[1] titanium,[3] zirconium,[4] indium,[5] chromium, and zinc oxohydroxides have shown that amorphous and crystalline oxohydroxides are markedly different in their sorption properties and the crystalline compounds are significantly inferior in this property to amorphous and especially as-precipitated compounds. The difference is so high that the mechanism of adsorption changes: for instance, heterogeneous hydrolysis of hematite, anatase, crystalline zirconium, and chromium oxides does not occur, but electrostatic sorption (non-exchange sorption on a charged sorbent surface) takes place that is accompanied by some hydrolysis of the sorbate in the sorbent phase (for titanium and zirconium[6]). The crystalline RE oxides exhibit high sorption activity, which allows one to identify the heterogeneous hydrolysis.[1]

It was of interest to compare the sorption properties of the crystalline and amorphous Sm^{III} oxohydroxides. A great body of data on the kinetics of heterogeneous hydrolysis are available, and the pH values of zero charge points (pH_{ZCP}) in various ionic media have been determined.[7] The preparation procedure for the samarium oxohydroxide and the methods of its study are precisely the same as those used in the previous studies of the oxohydroxides of other metals.[1,3–5]

In this work, a series of samples of samarium oxohydroxide was obtained and their sorption properties were studied by the methods of zero charge point (ZCP)[8] and the indicator reactions of heterogeneous hydrolysis of

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Table 1. Calculation of the OH : Sm ratio for drop titration of $Sm(NO_3)_3$ with a solution of NaOH

Starting solution*	pH_1	pH_2	V_2 /mL	pH_s	pH_3	OH : Sm ratio**		
						α	β	γ
1	7	7.25	320	9.42	5.70	0.94	0	0.94
	9	7.90	390	9.55	5.95	2.40	0	2.40
	11	10.64	395	11.05	10.62	2.57	0.032	2.54
2	7.5	6.20	380	8.7	6.5	2.235	0	2.235
	9	6.60	385	9.5	8.9	2.73	0	2.73
	11.05	9.40	375	10.9	10.6	2.888	0.03	2.858

* **1** is a solution of $Sm(NO_3)_3$, 1.68 *M* HNO_3, **2** is a stoichiometrically neutral solution of $Sm(NO_3)_3$.
** α is the sum of OH/Sm introduced, g-equiv./g-at., β is the sum of H/Sm attached during washing off or removed OH/Sm, g-equiv./g-at., γ is OH/Sm in the precipitate, g-equiv./g-at.

complex anions ($IrCl_6^{2-}$, $RhCl_6^{3-}$, and $PtCl_4^{2-}$).[1,3–5] The sorption properties mean the capability of an oxohydroxide (a dispersed phase) to exrtract a sorbate from the bulk of a solution (a dispersion medium) rapidly and to a high extent, close to 100%. As a sorbent is a highly dispersed phase far from equilibrium, the kinetic parameters (the rate constants of indicator reactions) are more suitable for characterization. The sorption of H_3O^+ and OH^- ions studied by the ZCP method is pseudo-equilibrium in its nature; this is used for determination of the sign and value of the surface charge of a sorbent.

Experimental

A solution of $Sm(NO_3)_3$ obtained by dissolution of a weighed portion of Sm_2O_3 (CMo-E, monoclinic) in 1.68 *M* HNO_3 (chemically pure grade) was used to prepare the samples of samarium oxohydroxide; the concentration of the solution was 85.2 (g Sm) L^{-1}. An aliquot of the solution containing 0.008 g-at. Sm was diluted with distilled water and neutralized by a solution of NaOH (chemically pure grade) under stirring and pH-metric control until establishment of a specified pH of precipitation (pH_1) in a ~50 mL suspension that was constant during ~5 min. The precipitate was separated by centrifuging, triply washed by decantation with H_2O, and centrifuged again. The samples obtained were suspended in 50 mL of water and used for experiments. For some comparative experiments, crystalline salt $Sm(NO_3)_3 \cdot 6\,H_2O$ synthesized from the same oxide and recrystallized from a solution in acetone was used. The content of Sm_2O_3 was 33.4 wt.% (28.8 wt.% Sm).

The composition of samarium oxohydroxides. The compositions of the samples obtained at various pH_1 was estimated by drop titration with NaOH, as in previous works[3–5] (Fig. 1). Both acidified solution of samarium nitrate (0.024 g-mol of the starting salt in 175 mL of water) and a stoichiometrically neutral solution (0.017 mol in 150 mL of water) of the crystalline salt were titrated. The samples (0.008 mole or 0.0057 mole Sm^{III}), corresponding to pH_1 7.5, 9, and 11, were washed with water as described above and introduced to 200 mL of 0.5 *M* KNO_3. The precipitate was filtered off, and the pH values of the washing liquor (pH_2), the suspension in 0.5 *M* KNO_3 (pH_s), and the filtrate (pH_3) were measured. To calculate the OH/Sm ratio in the samples, the amounts of the alkali washed off and displaced by the electrolyte were determined (Table 1).

After washing, the samples were dried in a vacuum desiccator over concentrated H_2SO_4 at ~20 °C for 6—7 days and then studied by the DTA—TG and X-ray diffraction techniques. The thermal analysis was carried out with the ~0.2 g sample at a heating rate of 10 deg min^{-1} on an NTR-70 instrument combined with a PRT-1000 and a Pt—PtRh thermocouple and a PP-63 instrument combined with a VT-1000 torsion balance. X-ray diffraction study was performed on a DRON-2 diffractometer with the use of Cu-Kα-radiation (graphite as a monochromator). Thermograms and diffractograms are presented in Figs. 2 and 3.

Determination of the pH of the zero point was performed by the Parks method[8] modified by us for gels[1] and by the potentiometric titration of samples on a pH-121 pH-meter in an argon atmosphere in a half-open type quartz cell with an ESL-43-07 glass electrode and an EVL-1M1 accessory electrode immersed in the slurry of oxohydroxide (pH_s) or in a reference solution (pH_0). Prior to titration, argon was purged for ~1.5 h through the oxohydroxide slurry washed as described above and a solution of the electrolyte to remove dissolved CO_2. Then the slurry (50 mL) was introduced to 150 mL of a

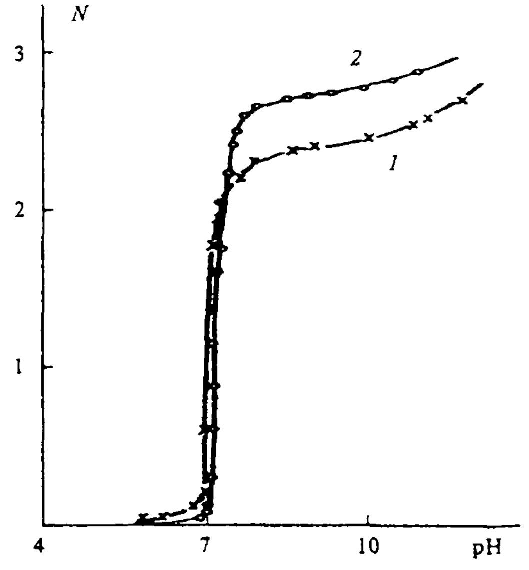

Fig. 1. The curves of drop titration of the solutions of samarium(III) nitrate with a solution of NaOH: *1*, an acid solution, *2*, a stoichiometrically neutral solution, *N* is the OH : Sm ratio.

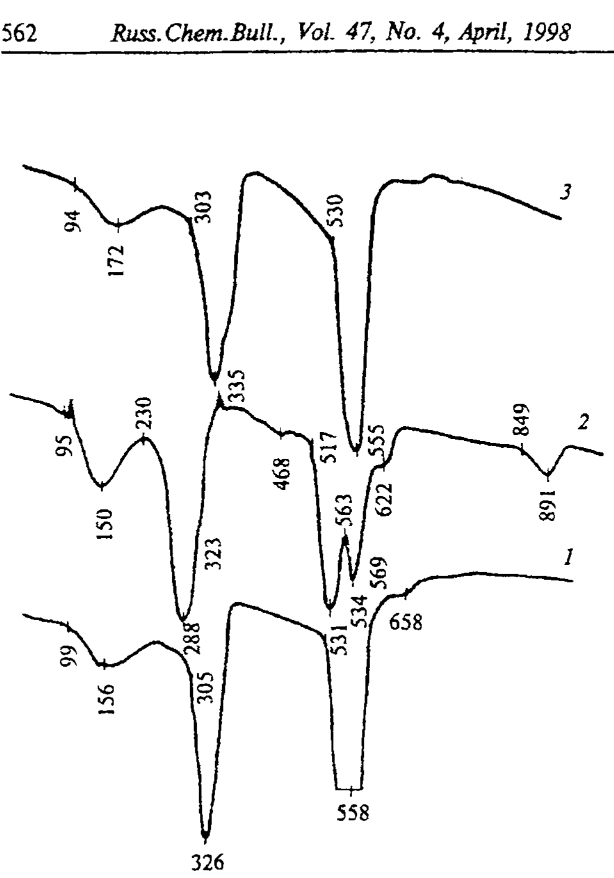

Fig. 2. Thermograms of the xerogels of samarium(III) oxohydroxide at pH_1 = 7.5 (*1*); 9 (*2*); 11 (*3*). The heating rate is 10 deg min^{-1}.

solution of the electrolyte prepared in such a way that the concentration of the electrolyte was 1.0, 0.1, or 0.01 mol L^{-1} in the final volume of the slurry. To estimate the initial pH or the pH_0 values, a 0.123 mol L^{-1} solution of carbonate-free NaOH (5 mL) was added, then the slurry was titrated by a solution of the acid (0.1 mol L^{-1}, fixanal) whose anion corresponds to the anion of the electrolyte at the rate of 0.4 mL min^{-1}. Recrystallized NaCl and Na_2SO_4 were used as the supporting electrolytes. The amount of excess OH^- (H_3O^+) ions sorbed was determined by comparing pH_s and pH_0 during the blank experiment at the specified volume of the titrant. The pH_{ZCP} can be found graphically as the intersection of the titration curve for the gel sample and the curve from the blank experiment. The results of the determination of pH_{ZCP} are presented in Table 2.

Indicator reactions of heterogeneous hydrolysis. As in the other works,[1,3–5] the reaction rates of heterogeneous hydrolysis of the $IrCl_6^{2-}$, $RhCl_6^{3-}$, and $PtCl_4^{2-}$ complexes were used to characterize the surface properties. K_2IrCl_6, $Na_3RhCl_6 \cdot 2H_2O$, and K_2PtCl_4 obtained according to the known procedures[9] and characterized by elemental microanalysis and X-ray diffraction were used. The initial concentrations of Ir, Rh, and Pt were (2—3) · 10^{-4} mol L^{-1}, and the volumes of the reaction mixtures were 200 mL; the measurement and calculation procedures have been described previously in Ref. 1. The contents of Ir, Rh, and Pt were determined according to the known procedures.[10]

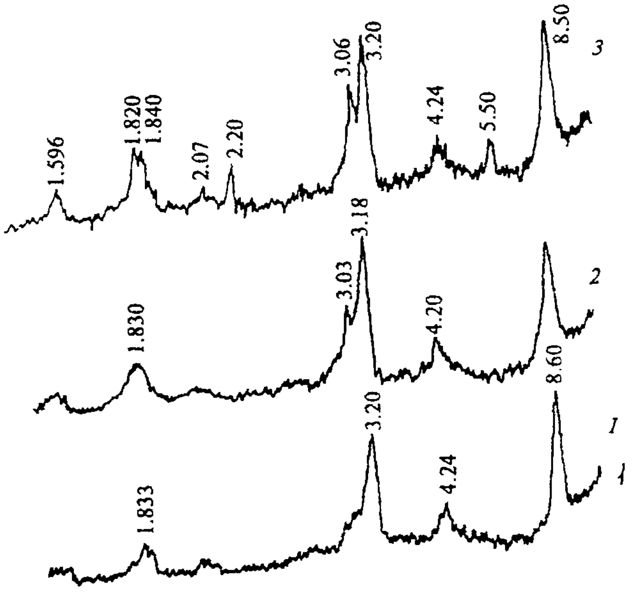

Fig. 3. Diffractograms of the xerogels of samarium(III) oxohydroxide at pH_1 = 7.5 (*1*); 9 (*2*); 11 (*3*).

Results and Discussion

Drop titration of the $Sm(NO_3)_3$ solutions (see Fig. 1, Table 1) with alkali showed that Sm^{3+} cation is titrated as a strong acid and almost complete precipitation of the metal from a solution occurs at pH_1 ~7; the OH : Sm ratio reaches 2.3 for the stoichiometrically neutral solution and ~2 for the acid solution. The titration curves exhibit a typical inflection point in the pH_1 9 region, which is also observed during the titration of solutions of iron and chromium salts and corresponds to OH : Sm ratios of 2.7 and 2.4, respectively. The replacement of anions for OH groups during titration under the conditions mentioned is not complete even at pH_1 11 (see Table 1). The thermal analysis confirms the presence of the unsubstituted NO_3 groups in the dried samples obtained at pH_1 7.5, 9, and 11. The compositions of these samples were calculated from the TG curves:

Table 2. The pH_{ZCP} values for samarium oxohydroxides in a solution of NaCl at various pH_1 values (7—11)

C_{NaCl} /mol L^{-1}	pH_{ZCP}				
	7*	8*	9*	10*	11*
1.0	7.78	8.25	8.58 (9.75)**	9.47	—
0.1	7.84	7.92	8.02	8.87	9.68
0.01	7.60	7.89	7.80	8.20	—

*pH_1. ** The sample is obtained from a stoichiometrically neutral solution of $Sm(NO_3)_3$.

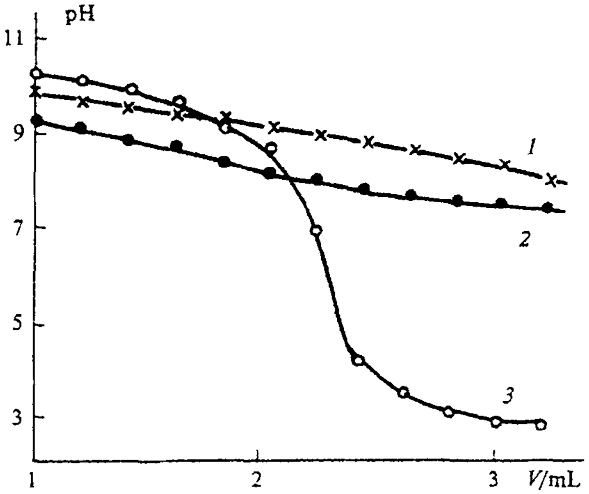

Fig. 4. Potentiometric titration of the as-precipitated samarium(III) oxohydroxide in a 1 *M* solution of NaCl at pH_1 = 10 (*1*) and 8 (*2*), as well as the blank experiment (*3*). *V* is the titrant volume.

$[Sm(OH)_{2.4}(NO_3)_{0.6}] \cdot 0.5H_2O$*,
$[Sm(OH)_{2.55}(NO_3)_{0.45}] \cdot H_2O$, and
$[Sm(OH)_{2.65}(NO_3)_{0.35}] \cdot 0.5H_2O$, respectively. These compositions do not suggest that samarium oxohydroxide is polymerized during the precipitation and drying, as was observed for titanium, zirconium, and chromium oxohydroxides.[3,4] The OH : Sm ratios calculated from the titration curve (see Table 1) practically coincide with those found by TG. The diffractograms of the dried samples (see Fig. 3) show that the samples are poorly crystalline even after drying. We failed to identify the diffractograms of this type under the data base.[11] These are likely the basic salts of the compositions mentioned.

The behavior of as-precipitated samples in the course of titration (to estimate pH_{ZCP}) is typical of gelatinous oxohydroxides (Fig. 4). The titration is reversible. A comparison of the pH_{ZCP} values obtained (see Table 2) and the pH_{ZCP} values at pH_1 9 in 0.05 and 0.005 *M* solutions of Na_2SO_4, which are equal to 10.75 and 7.97 respectively, shows that in the presence of SO_4^{2-} ions, the pH_{ZCP} of the amorphous Sm oxohydroxide increases, as in the case of the crystalline sample.[7] The curves of the dependence of pH_{ZCP} on pH_1 in NaCl solutions intersect at pH_{ZCP} 7.6 and pH_1 7 (Fig. 5), as has been observed for iron, titanium, zirconium, chromium, and indium oxohydroxides.[3,4,12] Previously we suggested[12] that this intersection point corresponds to the true pH_{ZCP} of an amorphous oxohydroxide in a given ionic medium. Interestingly, the value obtained is close to pH_{ZCP} of the crystalline Sm_2O_3 in a chloride medium that is equal to 7.45,[7] although, as the data mentioned above show, the composition of the helium phase at this value of pH_1 corresponds to $Sm(OH)_{2.3}(NO_3)_{0.7} \cdot n\ H_2O$. It can also be seen (see Table 2) that pH_{ZCP} of the gel depends directly on the extent of replacement of the acid residues for OH groups.

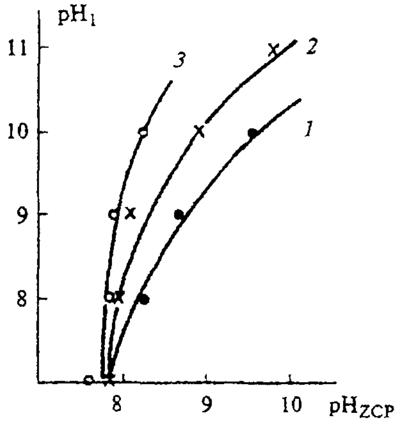

Fig. 5. Dependence of pH_{ZCP} on pH_1 for as-precipitated samarium(III) oxohydroxides in solutions of NaCl of concentrations 1.0 (*1*); 0.1 (*2*); 0.01 (*3*) mol L^{-1}.

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* The sample is obtained from a stoichiometrically neutral solution of $Sm(NO_3)_3$.

Table 3. The rate constants of heterogeneous hydrolysis on the surface of samarium oxohydroxides and comparative data for crystalline oxides

Complex	pH_1 (Crystalline oxide)	Ionic background (*C*/mol L^{-1})	$k_{obs} \cdot 10^4/s^{-1}$ at various temperatures (20—80 °C)							E_a /kJ mol^{-1}
			80	70	60	50	30	25	20	
$IrCl_6^{2-}$	7	NaCl (2)	14.7	5.8	1.37	—	—	—	—	119.7
	(Y_2O_3)		4.7	1.7	0.4	—	—	—	—	122.5
	(Sm_2O_3)		6.3	—	—	—	—	—	—	—
$PtCl_4^{2-}$	9	Na_2SO_4 (0.5)	—	14.6	6.8	2.05	—	—	—	95.8
$RhCl_6^{3-}$	9	NaCl (1) + Na_2SO_4 (0.5)	—	—	832*	250*	21.3	9.14	5.15	102.2
	(Sm_2O_3)				55*	20.7	2.0	—	—	95.0

* Obtained by extrapolation.

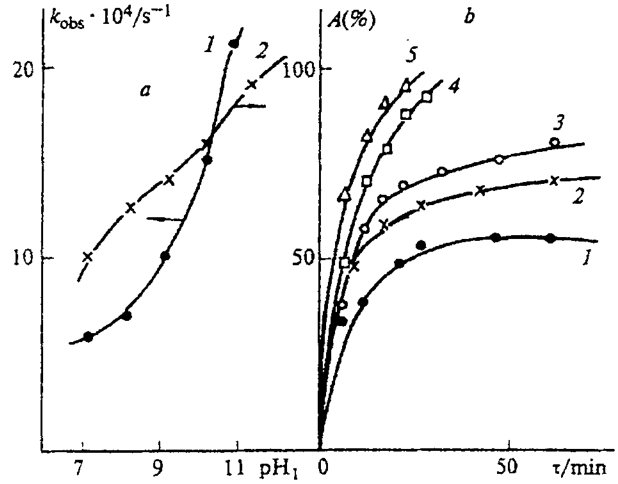

Fig. 6. *a*. Dependence of the rate constant (k_{obs}) of heterogeneous hydrolysis of $IrCl_6^{2-}$ (*1*) and $PtCl_4^{2-}$ for 20 min (*2*) on the as-precipitated samarium(III) oxohydroxide on pH_l at 70 °C. The ionic background is NaCl (2 mol L^{-1}).
b. Dependence of the extent of precipitation of Pt (*A*) on time (τ) during the heterogeneous hydrolysis of $PtCl_4^{2-}$ on the as-precipitated samarium(III) oxohydroxides at 60 °C and at pH_l = 7 (*1*); 8 (*2*); 9 (*3*); 10 (*4*); 11 (*5*). The ionic background is NaCl (0.5 mol L^{-1}).

In addition to determination of the observed rate constants of heterogeneous hydrolysis over samarium oxohydroxides at various temperatures shown in Table 3, the dependences of the rate constants on pH_l as well as on the concentration and nature of the ionic background were studied. The comparative data for Sm_2O_3 and ferrogels are presented here. In those cases where comparative data for Sm_2O_3 are absent, the data for the crystalline Y_2O_3 are presented, whose sorption activity is in fact equal to that of Sm_2O_3.[1]

The values of the rate constants of heterogeneous hydrolysis of $IrCl_6^{2-}$ over the amorphous samarium oxohydroxide in a 2 *M* solution of NaCl at 70 °C are given below:

pH_l	7	8	9	10	10.5
$k_{obs} \cdot 10^4/s^{-1}$	5.8	6.75	10.1	15.1	21.3

For the heterogeneous hydrolysis of $IrCl_6^{2-}$ on the surface of crystalline Sm_2O_3 in a 2 *M* solution of NaCl at 70 °C, $k_{obs} = 1.8 \cdot 10^{-4} s^{-1}$.

A similar dependence was obtained for the heterogeneous hydrolysis of $PtCl_4^{2-}$ over amorphous samarium oxohydroxide in a 0.5 *M* solution of NaCl at 60 °C. The shapes of the kinetic curves were shown to change with increasing pH_l (Fig. 6). At $pH_l < 10$ the kinetic curves are not described by the first-order kinetic equation but resemble the corresponding kinetic curves for ferrogels.[12] With increasing pH_l their shapes approach the first of the curves mentioned and at pH_l 10 and 11, the dependence of log*C* on time is rigorously described by a straight line and k_{obs} are equal to $18.3 \cdot 10^4$ and $24.0 \cdot 10^4 s^{-1}$, respectively. As can be seen in Fig. 6, the rate of the heterogeneoos hydrolysis of the complex increases with increasing pH_l. The rates of the heterogeneous hydrolysis of $PtCl_4^{2-}$ at the same pH_l (equal to 9) are nearly the same in 0.5 *M* solutions of NaCl and Na_2SO_4 and are significantly higher in a 1 *M* solution of $NaClO_4$ ($1.5 \cdot 10^{-3} s^{-1}$ at 50 °C).

Table 4. Comparative data on the rates of indicator reactions on the surfaces of samarium oxide and ferrogels

Sorbent	Ionic background (C/mol L^{-1})	T/°C	$k_{obs} \cdot 10^4$ /s^{-1}
	$PtCl_4^{2-}$		
Sm_2O_3	$NaClO_4$ (1.0)	50	2.1
	Na_2SO_4 (0.5)	75	25.0
	NaCl (0.5)	75	0.45
Ferrogel $Fe(NO_3)_3$/NaOH, pH_l = 7	$NaClO_4$ (1.0)	50	9.6
	Na_2SO_4 (0.5)	60	8.9
	$RhCl_6^{3-}$		
Sm_2O_3	NaCl (1.0)	40	1.9
	NaCl (1.0) + Na_2SO_4 (0.5)	40	6.2
Ferrogel $Fe(NO_3)_3$/NaOH, pH_l = 7	NaCl (1.0) + Na_2SO_4 (0.5)	60	290
Ferrogel $Fe(NO_3)_3$/NaOH, pH_l = 9	NaCl (1.0) + Na_2SO_4 (0.5)	35	23.3

For the heterogeneous hydrolysis of $RhCl_6^{3-}$ on the surface of amorphous samarium oxohydroxide in a 1 *M* solution of NaCl at 30 °C, $k_{obs} \cdot 10^4$ are equal to 7.5 and 35 s^{-1} at pH_l 7 and 9, respectively.

Comparative data for the heterogeneous hydrolysis of $PtCl_4^{2-}$ and $RhCl_6^{3-}$ on the surfaces of crystalline Sm_2O_3 and ferrogel (Table 4) show that the character of the dependence of the rate on the nature of the ionic background for all indicator reactions is the same as that for the reaction over crystalline samarium oxide, but the rates of heterogeneous hydrolysis over as-precipitated amorphous samarium oxohydroxides at all pH_l values are markedly higher than those over the crystalline oxide. With few exceptions, the rates differ by a factor of 2—3 and even 1—2 order for $RhCl_6^{3-}$, as has been observed for ferrogel and hematite[1] or chromogel and crystalline chromia. It can be seen from the comparison with ferrogel obtained under similar conditions that the kinetic parameters are very close and even higher in the case of amorphous samarium oxohydroxides.

One can suggest that gelatinous oxohydroxides of almost all metals will be the more active in heterogeneous hydrolysis than the corresponding crystalline oxides. The following tendency is seen: the higher activity of crystalline oxides, the lower difference between the sorption activity of amorphous and crystalline modifications.

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References

1. S. I. Pechenyuk, *Sorbtsionno-gidroliticheskoe osazhdenie platinovykh metallov na neorganicheskikh sorbentakh* [*Sorption Hydrolytic Precipitation of Platinum Metals on Inorganic Sorbents*], Nauka, Leningrad, 1991, 245 pp. (in Russian).
2. S. I. Pechenyuk, *Proc. Int. Congress on Waste Solidification—Stabilization Processes, 28 November—1 December 1995, Nancy, France*, Grenoble, France, 1997, p. 191.
3. S. I. Pechenyuk and E. V. Kalinkina, *Zh. Fiz. Khim.*, 1993, **67**, 1251 [*Russ. J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
4. S. I. Pechenyuk and E. V. Kalinkina, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2653 [*Russ. Chem. Bull.*, 1996, **45**, 2512 (Engl. Transl.)].
5. S. I. Pechenyuk, S. I. Matveenko, E. V. Kalinkina, and N. L. Mikhailova, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 242 [*Russ. Chem. Bull.*, 1998, **47**, 237 (Engl. Transl.)].
6. S. A. Simanova and E. S. Boichinova, *Ionnyi obmen i ionometriya* [*Ion Exchange and Ionometry*], LGU, Leningrad, 1988, Issue 6, p. 3.
7. S. I. Pechenyuk, *Zh. Fiz. Khim.*, 1987, **61**, 165 [*J. Phys. Chem.*, 1987, **61** (Engl. Transl.)].
8. G. A. Parks and P. L. de Bruyn, *J. Phys. Chem.*, 1962, **66**, 967.
9. *Sintez kompleksnykh soedinenii metallov platinovoi gruppy* [*Synthesis of Complex Compounds of the Platinum Group Metals*], Spravochnik (Handbook), Ed. I. I. Chernyaev, Nauka, Moscow, 1964, 339 pp. (in Russian).
10. S. I. Ginzburg, N. A. Ezerskaya, I. V. Prokof'eva, V. I. Shlenskaya, and N. K. Bel'skii, *Analiticheskaya khimiya platinovykh metallov* [*Analytical Chemistry of the Platinum Metals*], Nauka, Moscow, 1972, 613 pp. (in Russian).
11. *ASTM Diffraction Data Cards and Alphabetical and Grouped Numerical Index of X-ray Diffraction Data*, Philadelphia, 1046—1969.
12. S. I. Pechenyuk, E. V. Kalinkina, L. F. Kuz'mich, and S. I. Matveenko, *Koordinats. Khim.*, 1997, **23**, 768 [*Russ. J. Coord. Chem.*, 1997, **23** (Engl. Transl.)].

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