

Aging of Oxyhydroxide Sorbents Saturated with the Cations of Nonferrous Metals

SOPHIA I. PECHENYUK, VASILIIY V. SEMUSHIN and TATIANA G. KASHULINA

Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Sources, Kola Scientific Centre of the Russian Academy of Sciences, Ul. Fersmana 26a, Murmanskaya obl., Apatity 184209 (Russia)

E-mail: pechenyuk@chemy.kolasc.net.ru

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Abstract

The aging of freshly precipitated and immediately saturated with a sorbate (Cu(II), Ni(II), Cr(III), Pb(II) and Cd(II) cations) oxyhydroxides of Fe(III), Cr(III), Al(III), Zr(III) and Ti(IV) in 0.25 M solution of NaCl at room temperature is studied. It is established that the aging is accompanied by spontaneous acidification of the oxyhydroxide suspension and by partial desorption of the sorbate, which is to the highest extent exhibited with aluminium oxyhydroxide with Cd sorbed, and by the lowest extent with Cr(III) oxyhydroxide. It is concluded that acidification is a consequence of oxolation of the oxyhydroxides, while desorption is a consequence of acidification. Using the equation for the 1st order reaction, we calculated oxolation rate constants for oxyhydroxides, which are of the order of 10^{-6} – 10^{-8} s⁻¹.

INTRODUCTION

The distribution of substance between phases in the system composed of a solution and a solid is common both in biogeochemical and in technological systems. Such versions of the inter-phase distribution as co-precipitation and sorption of the components of solution in the systems with the participation of oxyhydroxide sorbents (collectors) belong to the most widely spread heterogeneous processes that occur in nature. The same processes attract attention of chemists and ecologists as the means of collective and selective concentrating of substances in analytical practice, technology and ecology, in particular, for burying toxic and radioactive wastes [1].

Oxyhydroxides of Fe(III), Al(III), Ti(IV) and Zr(IV) are most frequently used to obtain inorganic sorbents with different properties strongly depending on synthesis method [2, 3]. We showed previously in our investigations that freshly precipitated gel-like oxyhydroxides

(OX) of these metals exhibit the best sorption properties; however, they are thermodynamically unstable and undergo a series of transformations with time [6, 7]. Researchers are usually interested in the capacity of the sorbent, in kinetics and mechanism of sorption, retention degree, but they rarely consider further transformations of the used sorbents. Meanwhile, it was shown [1] that the strength of holding sorbate by the sorbent is very important because the used sorbents are stored in one way or another or are to be buried and can be the source of secondary pollution of the environment as a result of spontaneous desorption of the sorbed substances, which can occur during the aging of the sorbents. Because of this, we investigated the aging of freshly precipitated and immediately saturated with nonferrous metals (NM) oxyhydroxides of Fe(III), Al(III), Ti(IV) and Zr(IV), to which we added the oxyhydroxide of Cr(III) possessing very unusual sorption properties [8, 9]. Aging proceeded at room temperature for 1–2

years in the aqueous solution of NaCl, which is the electrolyte most widely spread in nature.

EXPERIMENTAL

Systems for investigation of aging processes were prepared as follows: 62.5 ml of 4 M NaCl solution (background electrolyte), an aliquot of sorbate solution calculated so that the cation concentration in the sorbent + sorbate system was 15–30* mg/l, water till the volume of 0.75 l, and 250 ml of suspension containing 0.02 mol of the sorbent were sequentially added into a vessel. The solutions of salts: CuSO_4 , NiSO_4 , $\text{Pb}(\text{NO}_3)_2$, $\text{KCr}(\text{SO}_4)_2$, $\text{Cd}(\text{NO}_3)_2$ were used as sorbates. The 0.75 l of sorbate solution was every time sampled for precise determination of sorbate concentration in the system.

In order to obtain sorbents, rapid alkaline hydrolysis of the solutions of metal salts was used [10]. Reagents of the “kh.ch.” and “ch.d.a.” grades were used. The initial substances to obtain ferro-, alumino- and chromo-gels were aqueous solutions of $\text{Fe}(\text{NO}_3)_3$ (53.3 g Fe/l), $\text{Al}(\text{NO}_3)_3$ (48.75 g Al/l), CrCl_3 (38.93 g Cr/l), zircon-gel was obtained using crystal $\text{ZrO}(\text{NO}_3)_2 \cdot 2.3\text{H}_2\text{O}$, titanium-containing titano-gel was obtained using commercial TiCl_4 (from Merck-Schuchardt) with a density of 1.728 g/l. Aliquots or weighed portions of initial substances, corresponding to 0.02 moles, were diluted with water till ~50 ml and neutralized with a solution of 2 M NaOH under mixing and pH control till pH 8.5 stable for ~5 min. The precipitated OX were separated from mother solutions and washed three times by decanting with H_2O and centrifuging each time for 5 min with $n = 2000$ rpm. The washed precipitates were suspended in water to the volume of 250 ml. Sorbent suspension was introduced into sorbate solution, and pH was corrected to 8.5. The reference sample was taken to determine completeness of sorbate precipitation by the sorbent. The resulting suspension was poured into another vessel, which was tightly closed to avoid evaporation and placed onto a shaker; after that, the system was kept

at room temperature ($(18 \pm 5)^\circ\text{C}$) under mixing from time to time without correcting pH for 1–2 years. For comparison, similar experiments were performed to study aging of sorbent free of sorbate.

During the whole time of exposure, a sample of 30–50 ml was taken from each system after definite intervals increasing with time. In these samples, pH (pH_c) was measured under mixing; then the solid phase was filtered and pH of the filtrate was measured (pH_f). The filtrate was analysed by means of atomic absorption to determine amounts of sorbate cations and central cations of sorbents (Table 1).

RESULTS AND DISCUSSION

It is known that oxyhydroxide sorbents are very selective with respect to NM cations [12]. We discovered that they are able to retain the latter in sorbed state for a long time. In all the systems, both with sorbate and without it, except Cr gel/ Cd^{2+} and Ti gel/ Cd^{2+} , spontaneous acidification of suspension occurs with time.

To explain the mechanism of acidification of the system during aging and desorption of NM cations from sorbent surface, a very limited number of processes can be proposed. Since the systems under investigation contain only NM cations and Na^+ , OH groups, Cl^- anions and water molecules, we may consider the formation of ol and oxo bridges (olation and oxolation) between central atoms of OH as the main reactions responsible for all the changes in the systems under consideration [13]. These processes can be schematically represented by the following equations in two versions:

a) Without the participation of additional alkali – spontaneous ololation and oxolation, sorption and desorption due to hydroxyl groups of OH (eqns. (1) and (2)), with the participation of M^{n+} (sorbate) (eqns. (3)–(5));

b) With the participation of additional OH groups of the negatively charged surface of sorbent (for ololation stage, see eqn. (1)) (eqns. (6)–(8)).

Acidification degree is strongly dependent on the nature of both the sorbent and sorbate.

*Some exceptions from this rule are given in Table 1.

TABLE 1

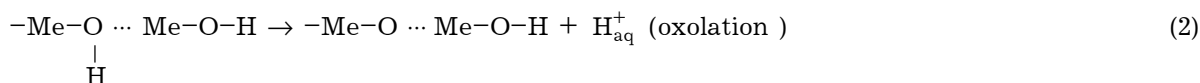
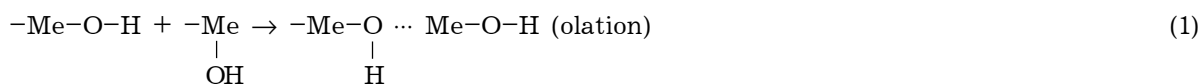
Changes in the systems sorbent + sorbate + electrolyte occurring during aging

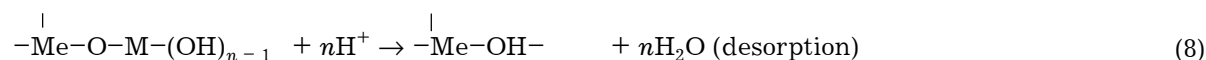
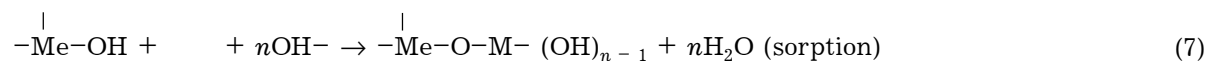
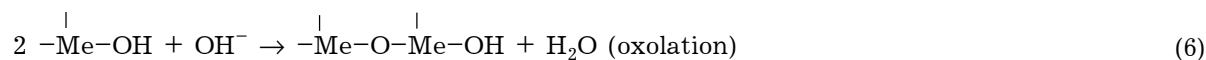
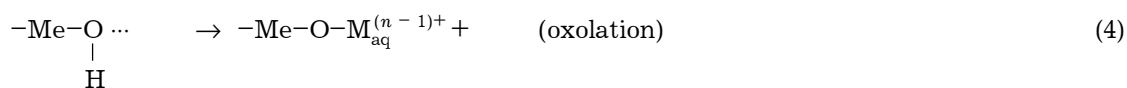
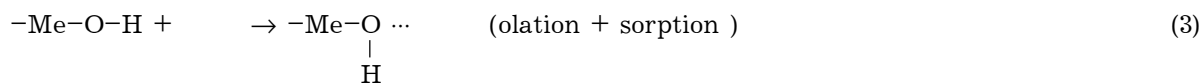
Sorbent	Sorbate	pH _e	pH _{1f}	Composition of filtrate, mg/l; sorbate desorption degree, %
Fe gel	-	8.50→7.16	6.81→7.00	-
	Cu ²⁺	8.50→6.79	7.04→6.49	13.4→0.03; <1
	Ni ²⁺	8.50→7.29	7.18→6.18	20.0→0.51; 1→3
	Pb ²⁺	8.50→7.04	7.35→6.91	18.3→0.2; 0.7→1
	Cr ³⁺	8.50→7.39	7.49→6.89	18.4→<0.5
	Cd ²⁺	8.50→6.63	7.51→6.64	17.3→8.7; 5→49
Al gel	-	8.50→5.84	5.47→5.53	-
	Cu ²⁺	8.50→6.15	6.01→6.12	17.6→0.17; 1.7→1
	Ni ²⁺	8.50→4.95	8.04→5.37	18.4→7.8; 1.6→42
	Pb ²⁺	8.50→6.86	8.40→5.46	10.4→3.24; 3→31
	Cr ³⁺	8.50→6.60	8.23→6.21	14.3→<0.1
	Cd ²⁺	8.50→6.95	8.2→6.56	16.9→12.5; 6→74
Cr gel	-	8.50→7.21	6.15→6.33	-
	Cu ²⁺	8.50→8.21	7.36→7.04	15.5→<0.1
	Ni ²⁺	8.50→7.98	6.33→7.56	19.6→0.1; 1.4→0.5
	Pb ²⁺	8.50→8.08	6.75→6.45	368.0→<0.5; 0.1→0
	Cd ²⁺	8.50→8.76	6.26→6.46	188.0→0.4; 1.1→ 0.2
Zr gel	-	8.50→6.61	5.22→6.10	-
	Cu ²⁺	8.50→7.39	5.53→6.63	18.0→<0.1
	Ni ²⁺	8.50→7.5	5.81→5.73	390.0→0.2; 18→0.05
	Pb ²⁺	8.50→7.17	5.37→6.17	20.0→<0.5
	Cr ³⁺	8.50→6.77	6.16→6.59	15.5→<0.5
	Cd ²⁺	8.50→7.23	6.24→5.59	195.0→31; 5→16
Ti gel	-	8.50→6.91	7.04→6.94	-
	Cu ²⁺	8.50→7.59	7.39→7.35	18.0→<0.1
	Ni ²⁺	8.86→7.60	7.26→6.63	20.0→<0.1
	Pb ²⁺	8.50→7.37	7.10→7.11	17.0→<0.1
	Cr ³⁺	8.50→7.56	7.36→7.43	10.0→<0.1
	Cd ²⁺	8.50→8.53	7.09→7.97	43.5→<0.2

Acidification degree in the systems containing no sorbate depends on the nature of the central cation of OH as follows: Al > Zr > Ti > Fe ≥ Cr. In the systems containing the same sorbate the acidification degree also depends on the nature of central cation of OH. For Cu²⁺, this dependence looks as follows: Al > Fe > Zr > Ti > Cr; for Ni²⁺, Al > Fe > Zr ≥ Ti > Cr; for Pb²⁺, Al ≥ Fe > Zr > Ti > Cr; for

Cr³⁺, Al > Zr > Fe > Ti; for Cd²⁺, Fe ≥ Al > Zr > Ti > Cr (Ti, Cr - alkalisation).

One can see that, independently of sorbate nature, the intensity of acidification depends in almost similar manner on the nature of central cation of OH; in all the cases, maximal acidification is observed for Al gels, minimal one for Cr gels, and Zr gels are acidified stronger than Ti gels.





Finally, in the systems containing one and the same sorbent, acidification degree depends on sorbate nature as follows for the Al gel: Ni > Cu > Cr > Pb, Cd; for Fe gel: Cd > Cu > Pb > Ni > Cr; for Cr gel: Ni > Pb > Cu > Cd (alkalisation). In this case, no clear regularity for all the sorbents can be observed.

One can see that no substantial changes in pH are observed in systems containing no sorbate. In the systems containing sorbate, all changes in pH_f are within 7.0 ± 1 in the majority of cases (see Table 1). It should be noted that a distinct trend of approaching is observed for pH_f and pH_s (Fig. 1). In fact, aging of sorbent suspensions leads to a decrease or even disappearance of the suspension effect*.

According to the definition of the suspension effect [14], this fact can be evidence of the loss of charge by the sorbent surface with time.

It is interesting that a very small deviation between pH of suspensions and filtrates is observed in all the systems with Fe, Al, Ti gels and NM cations as sorbates. Since the sign of suspension effect is positive in all the systems investigated by us, and suspension effect is maximal for the systems without sorbate, we may assume that the NM cations getting absorbed on the positively charged OX surface cause a decrease in the charge of this

surface. This agrees with the schemes of OX oxolation reactions (eqns. (2), (4)). Though cation adsorption should increase the positive charge of the surface, it should be stressed that in all cases we observed acidification of suspension at the very beginning of experiment while sorbate cations got sorbed on the OX; this was neutralized by additional introduction of an alkali (eqn. (7)).

The most substantial changes occur in the systems with Al and Fe gels (see Table 1). In some cases, spontaneous acidification of the system is accompanied by partial desorption of the sorbed cations; however, one cannot say that maximal desorption corresponds to maximal acidification. This is likely to be explained by the fact that protons released during oxolation are consumed for desorption (eqns. (5), (8)). The Cd^{2+} cation gets desorbed most easily. It noticeably desorbs from the surface of ferro-, alumino- and zircono-gels (see Table 1). In addition, noticeable desorption from the surface of Al gel is observed for Pb^{2+} and Ni^{2+} . This agrees with pH of complete precipitation of the hydroxides of Cd^{2+} , Ni^{2+} and Pb^{2+} : 9.7, 9.5 and 7.2–10.3, respectively [15, 16]. So, our assumption that the oxyhydroxide sorbents saturated with NM ions on aging can be the source of the secondary contamination of the environment was confirmed. At the same time, it should be noted that Cr, Ti and Zr gels on aging tightly hold all the sorbates investigated herein. Among all sorbates, only cadmium cations are poorly retained by the Zr gel.

*Suspension effect involves substantial difference between pH of suspension and pH of its filtrate $\Delta\text{pH}_{\text{se}} = \text{pH}_s - \text{pH}_f$. The sign of $\Delta\text{pH}_{\text{se}}$ coincides with the sign of the charge of the surface [14].

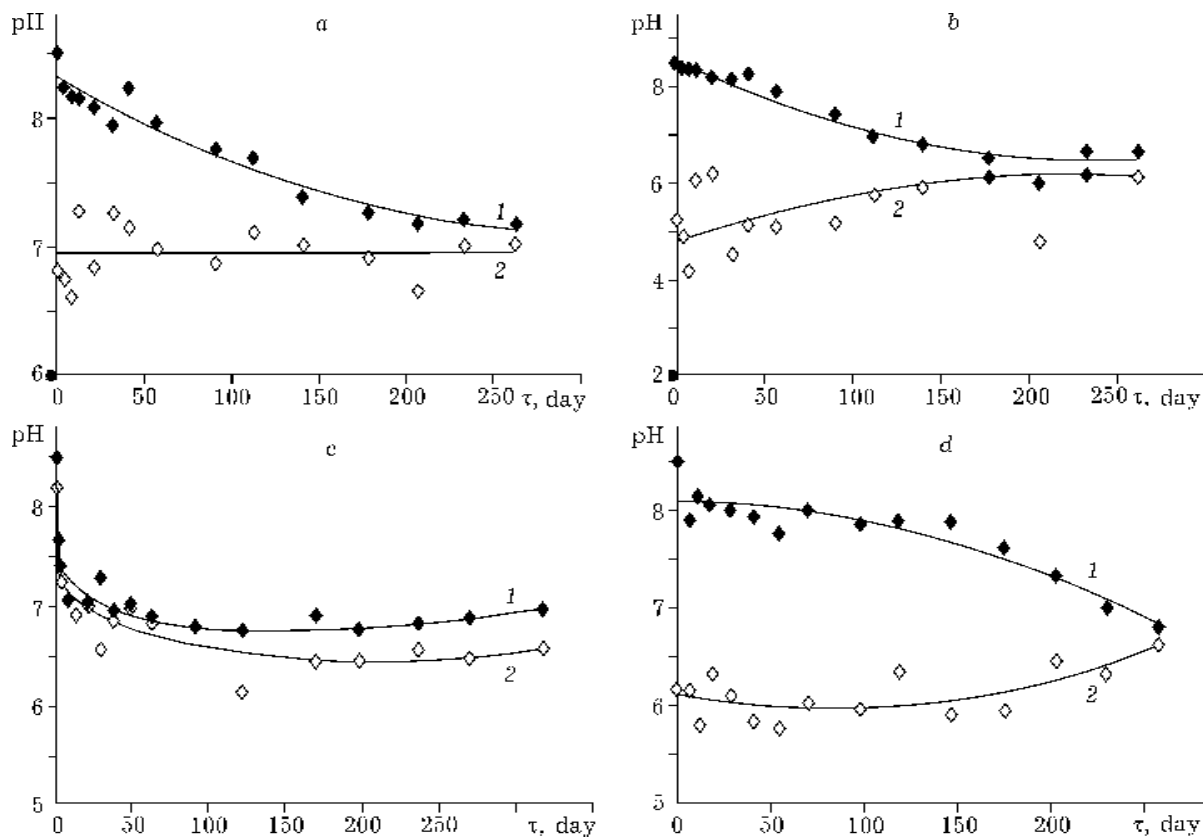


Fig. 1. Changes in the acidity of suspension (1) and filtrate (2) during aging of oxyhydroxides in 0.25 M solution of NaCl at room temperature: a - Fe gel; b, d - Zr gel; c - Al gel; a, b - in the absence of sorbate; c, d - with Cd^{2+} and Cr^{3+} as sorbate, respectively.

In both cases, the formation of ol bridges does not cause changes in pH, while the formation of oxo bridges is conjugated with acidification. The authors of [17] using changes in pH of mother solution determined mean rates of olation ($6.4 \cdot 10^{-2} \text{ l}/(\text{mol s})$) and oxolation ($5.0 \cdot 10^{-5} \text{ s}^{-1}$) of zirconium (IV) OX at room temperature. However, not acidification but alkalisation of the system was observed at the first stage of aging [17]. Some increase in pH_s and pH_r , observed by us in most stable systems with Cr and Ti gels (see Table 1) can be explained by some decrease in specific surface of gel during aging, which is accompanied by partial desorption of OH groups [9].

Using the semilogarithmic dependence of on time (Fig. 2), we determined that the aging process in the systems under investigation is usually split into two stages with different rates; we calculated acidification rate constants according to the equation for the 1st order reaction with respect to proton concen-

trations (Table 2). In some systems (see Table 2) the process occurred in one stage; these systems did not have enough time to reach the state of pseudoequilibrium within the time of experiment, though the major part of the investigated systems acquired constant pH, that is, came to the pseudoequilibrium state within ~ 1 year.

The rate constant of the first stage of aging (K_I) which lasts 10 to 70 days was about two orders of magnitude higher in the investigated systems than the rate constant of the second stage (K_{II}). Maximal $K_I = (1-3) \cdot 10^{-6} \text{ s}^{-1}$ is observed for Al gels; for Fe, Zr and Ti gels, the corresponding values are about 10^{-7} s^{-1} ; the slowest transformations are those occurring in systems with Cr gel. Anomalous behaviour of Cr gel was also observed by us earlier [4, 6, 9]. The K_{II} values are close to each other in all the systems investigated; they are equal to $(1-4) \cdot 10^{-8} \text{ s}^{-1}$. The nature of sorbate cation has no effect on K_I for Fe, Zr and Ti gels. For Al

TABLE 2

Rate constant (K , 10^{-7} s^{-1}) of acidification of the investigated suspensions

Sorbent	Sorbate	K^*	Duration of stages, day
Fe gel	–	0.75/0.11	160/>100
	Cu^{2+}	1.62/0.37	50/115
	Ni^{2+}	1.78/0.45	50/110
	Pb^{2+}	1.62/0.2	48/>300
	Cr^{3+}	2.02/0.18	38/160
	Cd^{2+}	3.93/0.45	26/180
Al gel	–	14.9/1.76	8/59
	Cu^{2+}	7.4/0.16	15/>300
	Ni^{2+}	34.7/0.88	9/83
	Pb^{2+}	8.45/0.24	19/>300
	Cr^{3+}	2.66/0.06	35/>280
	Cd^{2+}	10.46/0.58	10/63
Cr gel	–	0.51	>320
	Cu^{2+}	~7.4**	>900
	Ni^{2+}	0.12**	>860
	Pb^{2+}	0.07**	>780
	Cd^{2+}	0.69/0.35***	53/>710
Zr gel	–	1.44	157
	Cu^{2+}	0.01/1.16	186/>100
	Ni^{2+}	0.19	300–400
	Pb^{2+}	0.41	300–400
	Cr^{3+}	0.15/1.18	149/100–200
	Cd^{2+}	0.42	300–400
Ti gel	–	1.03	150
	Cu^{2+}	0.81/0.1	37/>260
	Ni^{2+}	0.23	>300
	Pb^{2+}	1.0/0.12	39/>260
	Cr^{3+}	0.64/0.05	47/>250
	Cd^{2+}	0.94/0.3***	50/280

*Numerator: K_I , denominator: K_{II} .

**For the period 0–320 days.

***Alkalisiation of suspension occurs during the second stage of aging.

gels, the rate of acidification increases in the row $\text{Cr}^{3+} < \text{Cu}^{2+} \leq \text{Pb}^{2+} \leq \text{Cd}^{2+} < \text{Ni}^{2+}$. One can see in Table 2 that acidification rate in systems containing sorbate is somewhat higher than that in the absence of the latter, but is of the same order of magnitude. It is evident that the acidification rate depicts the overall process of the release of H^+ ions during oxolation and their absorption during desorption of NM ions.

Numerical data are almost absent from literature, except [17, 18]. The rate of oxolation of Zr(IV) OH determined by us is 2 orders of magnitude lower than that determined in [17]. The authors of [18] estimated half-life of ferric oxyhydroxide aging at room temperature to be 2–3 years. According to our data, half-life of ferric oxyhydroxide in NaCl medium is about 1 year. It should be noted that the authors of [17, 18] investigated aging in water

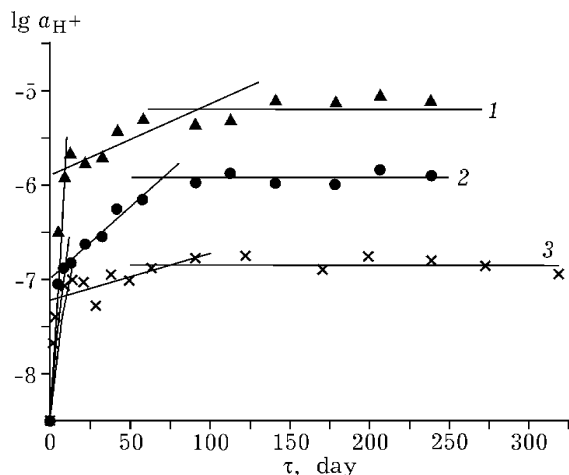


Fig. 2. Semilogarithmic anamorphisms of the rate of acidification of suspensions during aging of Al gel in solution of 0.25 M NaCl at room temperature with sorbate Ni^{2+} (1), Cd^{2+} (3) and without sorbate (2).

but not in a solution of electrolyte with fixed concentration. The presence of electrolyte is likely to affect the rates of aging processes of OX of different metals in different manners.

CONCLUSION

Thus, the investigations demonstrated that oxyhydroxide sorbents saturated with nonferrous metal ions during aging can be the source of secondary pollution of the environment due to desorption of previously sorbed cations. Desorption occurs under the action of protons released by the sorbent during its oxolation. Oxolation reactions are of the first order with respect to the concentration of the released protons. Oxyhydroxides of chromium (III) and titanium (IV) are most stable to aging. The higher is pH of complete precipitation, the higher is the ability of the cations of sorbates to be desorbed.

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