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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Stability of Calcium and Magnesium Phosphate Sorbents in Solution of Calcium Chloride and Complexing Agents

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Abstract—The study of the stability and physicochemical transformations of calcium and magnesium phosphate sorbents in a solution of calcium chloride and complexing agents: disodium salt of ethylenediaminetetraacetic acid and oxyethylidenediphosphonic acid established that calcium phosphates undergo no significant changes in aqueous systems under study, while magnesium phosphates (trimagnesium phosphate and magnesium hydrogenphosphate) are converted into calcium phosphates in solutions of $CaCl_2$, therewith the introduction of ethylenediaminetetraacetic acid (EDTA) into the solution of $CaCl_2$ has no significant effect on the magnesium phosphate conversion process, and introduction of oxyethylidene diphosphonic acid (OEDP) inhibits crystallization of calcium phosphate formed. Observed conversions should be considered when using magnesium and calcium phosphates as sorbents.

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Sorbents obtained earlier based on calcium and magnesium phosphates have shown high efficiency in purification of aqueous solutions from various metal ions (Zn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, etc.), including ions of stable and radioactive strontium [1, 2]. An efficiency of sorption purification is largely determined by both the nature of the sorbent and sorption process conditions (composition of a solution, a ratio of the solution volume to weight of the sorbent, pH, etc.) [3–5]. Researching the sorption of ions of various metals was performed by means of model solutions in the absence of any other impurities, while the actual wastewater and liquid radioactive waste contain substantial quantities of dissolved calcium salts and organic compounds: surfactants and chelating agents [usually ethylenediaminetetraacetic acid (EDTA), oxyethylidenediphosphonic (OEDP) acid [6].

Given that phosphate sorbents contain calcium and magnesium cations, which form stable complexes with EDTA and OEDP a possible interaction in systems chelating agent–sorbent can be propose, and in the solutions of $CaCl_2$ calcium and magnesium phosphates may undergo chemical and phase transformations. However, the reports on the interaction of calcium and magnesium phosphates with aqueous solutions of chelating agents are reduced to the study of the interaction of hydroxyapatite with EDTA [7, 8].

In the study researching the stability, chemical and physical processes occurring in the interaction of calcium and magnesium phosphate sorbents with calcium ions and chelating agents (EDTA and OEDP) was performed for effective practical use of calcium and magnesium phosphates in the sorption purification of real wastewater and liquid radioactive waste.

EXPERIMENTAL

Calcium and magnesium synthetic phosphates of different composition were used as objects of study: acidic $CaNPO_4$ (calcium hydrogen phosphate, CHP) and $MgHPO_4{\cdot}3H_2O$ (magnesium hydrogen phosphate trihydrate, MHPTH); medium $Ca_3(PO_4)_2{\cdot}2H_2O$ (tricalcium phosphate dihydrate, TCPDH) and $Mg_3(PO_4)_2{\cdot}10H_2O$ (trimagnesium phosphate decahydrate, TMPDH) with a small admixture of $MgNH_4PO_4{\cdot}H_2O$ and $Mg_2PO_4OH{\cdot}4H_2O$; and also basic $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite, HA). All phosphates were prepared by chemical precipitation from solutions according to standard methods [9].

$CaCl_2$ (pure grade), disodium salt of EDTA (chemically pure), and OEDP (commercial-purity) were used to study the effect of Ca^{2+} and chelating agents on phosphate sorbents in solution. The content of Ca^{2+} in the sample solutions was 0.05, that of chelating agents was 0.001 M. When conducting experiments using chelating agents the prepared mixture of $CaCl_2$ with an addition of EDTA or OEDP was adjusted to pH 5.0 with solutions of HCl or KOH, and then aged for 1 day, afterwards, if necessary, pH was further adjusted. The selection of pH 5.0 of initial solutions was due to the creation of suitable conditions for the preferential formation of the metal–ligand complexes and to minimize the formation of hydroxo complexes [8]. To the solution (50 mL) a weighted portion of the sorbent (0.050 g) was placed controlling changes in solution pH over time.

XRD was carried out on an installation DRON-3 using CuK_α-radiation. Phase identification of the samples was carried out using X-ray powder standard base JCPDS PDF2. Analysis of sizes of the crystallites was performed using a Size/Strain software complex WinXpow in accordance with the Scherrer and Wilson equations. IR spectra were recorded on a FTIR spectrometer of firm Midac (tablets with KBr, weighted portions 1.5 mg).

RESULTS AND DISCUSSION

Analysis of changes in the solutions pH vs. a time of contact with the sorbent allows indirect suggestion on the processes occurring simultaneously on the surface the sorbent and in the bulk of the solution: hydrolysis of ions, formation of complexes, partial dissolution of the solids. According to Fig. 1 the interaction of phosphate sorbents with all aqueous solutions is accompanied by a marked change in pH, while equilibrium is set for 2 h. When equilibrium reached, in the aqueous suspensions of calcium phosphate practically neutral medium occurs, therewith minimal changes are observed in the suspension of HA. For aqueous suspensions containing magnesium phosphate, pH of solutions is significantly higher, and curves of pH variation differ by the presence of inflection on them. The observed increase in pH in aqueous systems (Fig. 1a) is due to reactions of protonation–deprotonation of surface groups according to chemical model of HA dissolution [10] and hydrolysis of phosphate and partially hydrogen phosphate ions released during the partial dissolution of the solids.

In introduction of phosphate sorbents into solutions containing Ca^{2+} (Fig. 1b), there is a minimal change in pH of the solutions compared to a suspension in distilled water that is due to reducing their solubility. In addition, the observed changes in pH curves for systems with TMPDH and MHPTH.

The nature of the pH curves variation of suspensions of phosphate sorbents containing chelating agents essentially varies depending on a solution composition. Adding EDTA to a solution of the sorbents leads to a decrease in equilibrium values of pH relative to the aqueous solution. In this case, in the onset time for HA and CPH a strong decrease in pH occurs and then a gradual increase in pH is observed (Fig. 1c), while the inflections on pH curves for both magnesium phosphates disappear. For OEDP-containing solutions a relatively small increase in pH is observed after the interaction with the phosphate sorbents at little difference between them by the form of curves as well as by the equilibrium values of pH (Fig. 1d): about 7 for magnesium phosphate, and about 6, for calcium phosphates.

Addition of EDTA to a solution of $CaCl_2$ virtually does not vary the nature of the pH curves for all the sorbents relative to the solution of $CaCl_2$ (Fig. 1d). Unlike EDTA in systems containing OEDP against the background of $CaCl_2$, pH curves of solutions undergo a fundamental change (Fig. 1f). For TMPDH and MHPTH there is a relatively weak growth in pH in the absence both of inflections of the curves and an increase in the time for reaching equilibrium for MHPTH. For systems containing calcium phosphates pH decreases monotonically throughout the entire period of observation, therewith curves of all three sorbents coincide.

For interpretation of the processes occurring in the solutions XRF of products of phosphate sorbents transformation obtained under equilibrium conditions. Calcium phosphates virtually retain their original structure in aqueous solutions without any additives and in the presence of ions Ca^{2+} (Figs. 2a, 2b). HA in contact with aqueous solutions of different composition undergoes no phase changes, so, diffraction patterns of products of its interaction with solutions was not listed.

Adding EDTA to the solution enhances dissolution processes, as evidenced by a decrease in intensity and resolution of the reflexes in the diffraction patterns of

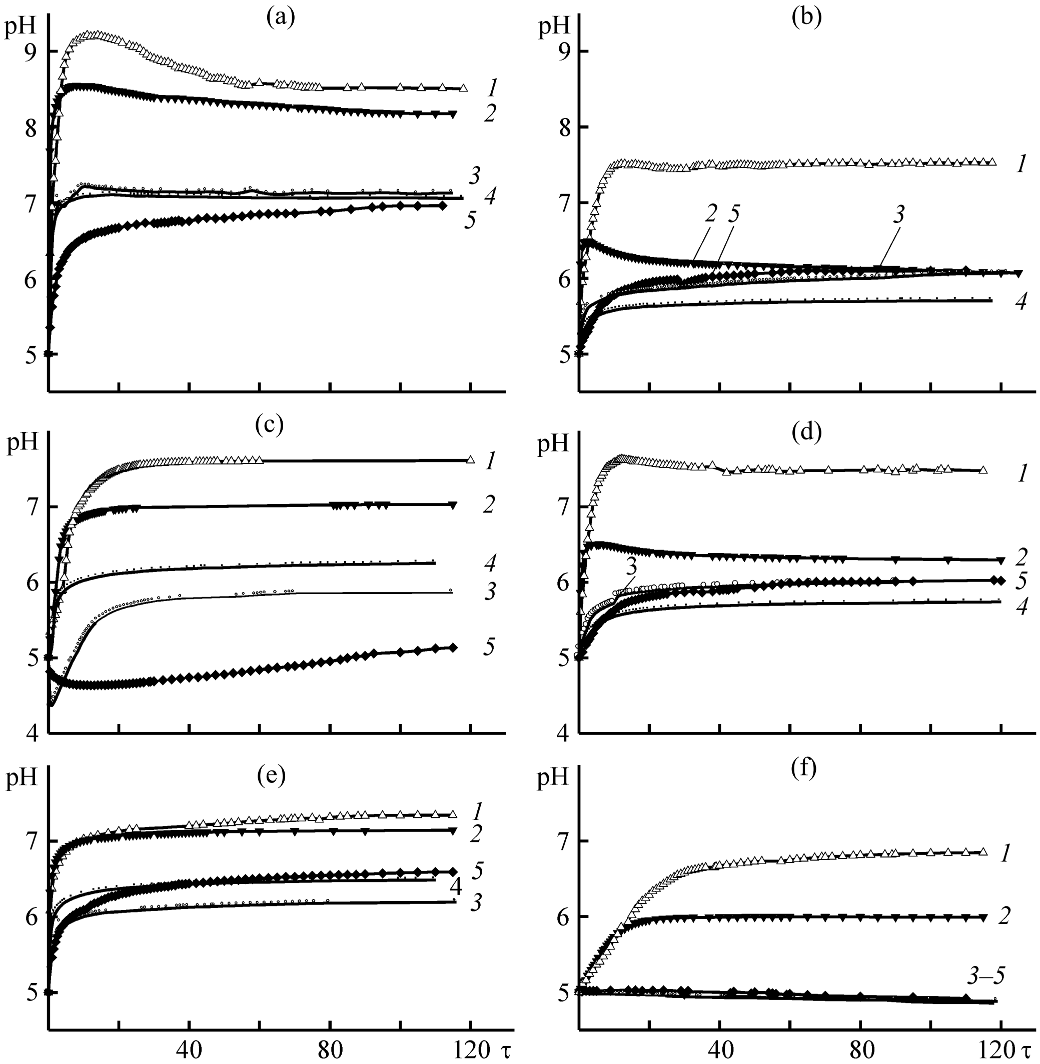

Fig. 1. pH variation curves of (a) aqueous solutions, (b, d, f) calcium-, (c, d) EDTA-, and (e, f) OEDP-containing solutions in the presence of Ca- and Mg phosphate sorbents. (τ) the contact time (min). (*1*) TMPDH, (*2*) MHPTH, (*3*) CHP, (*4*) TCPDH, (*5*) GA.

main phases of TCPDH and CHP (Figs. 2a, 2b). Products after contact with the solutions of EDTA + $CaCl_2$ are almost identical to those obtained after the reaction with a solution of $CaCl_2$. The difference consists in the fact that in the TCPDH after treatment with a solution of EDTA + $CaCl_2$ weakly crystallized mixture was found, which may be calcium complexonate, for which the main reflex is observed at $2\theta = 10.968°$ (file 28-1583) (Fig. 2a).

IR spectra of these products also showed the presence of EDTA anion, bands in the region of 2855–2940 cm^{-1}, which are not characteristic of calcium phosphates (Fig. 3). According to the reference data they may be attributed to the stretching, symmetric (2855–2870 cm^{-1}) and asymmetric (2923–2940 cm^{-1}) vibrations of methylene groups that are part of EDTA [11]. Deformation vibrations of these groups as well as vibrations of carboxyl groups are related to the same region with vibrations of the phosphate anion and, therefore, can not be identified. It can be assumed that, despite the formation of stable complexes of EDTA with cations of calcium soluble in water, a part of the chelating agent remains on the surface of the sorbent forming weakly crystallized phase. In the presence of OEDP the formation of a new well crystallized phase is observed, whose intensity of the reflexes is increased by adding the solution of $CaCl_2$. In the available databases there no data on a substance characterized

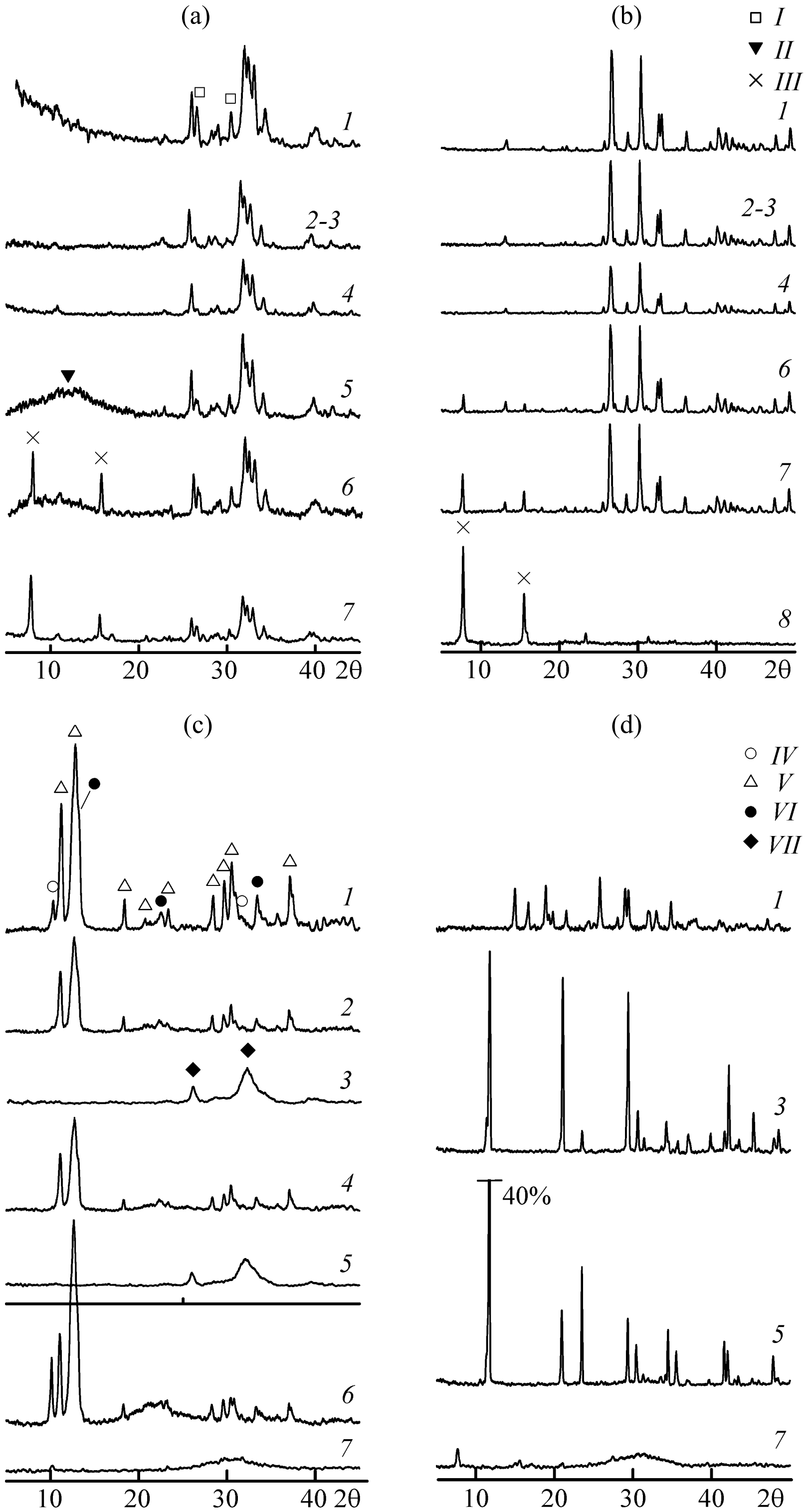

Fig. 2. Diffraction patterns of (a) TCPDH, (b) (CHP), (c) TMPDH, and (d) MHPTH before treatment with solutions (*1*) and of the formed products after their exposing in a solution (*2*) without additives, with additives of (*3*) $CaCl_2$, (*4, 5*) EDTA, and (*6, 7*) OEDP of a concentration 0.001 M (*4, 6*) without a salt background and (*5, 7*) against background of 0.05 M $CaCl_2$ solution and also (*8*) a precipitate formed in the system Ca–OEDP. (2θ) Bragg angle (deg). Designation of phases: (*I*) $CaHPO_4$ (file 70-359), (*II*) $Ca_2(C_{10}H_{12}N_2O_8)\cdot 7H_2O$ (file 28-1583), (*III*) not identified phase, (*IV*) $MgNH_4PO_4\cdot H_2O$ (file 20-663), (*V*) $Mg_3(PO_4)_2\cdot 10H_2O$ (file 35-330), (*VI*) $Mg_2PO_4OH\cdot 4H_2O$ (file 44-774), (*VII*) $Ca_3(PO_4)_2\cdot xH_2O$ (file 18-303).

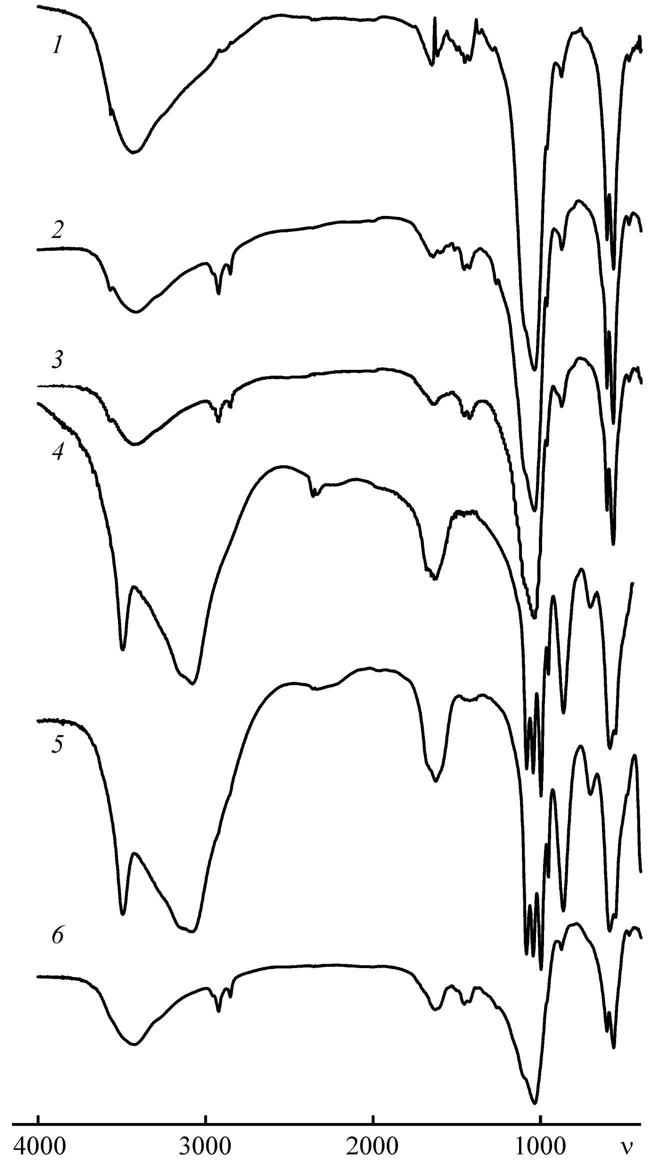

Fig. 3. IR spectra of (*1*) TCPDH and (*4*) TMPDH and of products of their interaction with solutions of EDTA without additives calcium chloride and (*3, 6*) against salt background. (ν) Wavenumber (cm^{-1}); the same for Fig. 4.

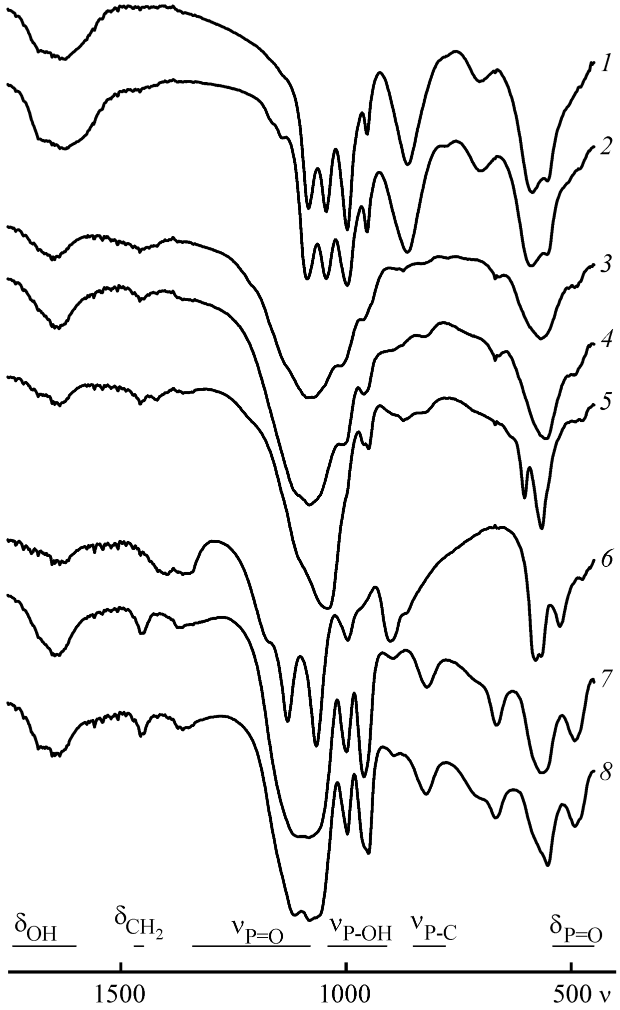

Fig. 4. IR spectra of (*1*) original TMPDH and (*8*) OEDP, and the products of interaction of (*2, 3*) TMPDH, (*4*) MHPTH, (*5*) TCPDH, (*6*) CHP with solutions of OEDP (*2*) without additives of calcium chloride and (*3–6*) against salt background, and also (*7*) OEDP with $CaCl_2$.

by diffraction pattern with interplanar spacings 11.440 and 5.718 Å. IR spectrum of this phase coincides with the spectrum of OEDP (Fig. 4). The presence of OEDP in the composition of calcium phosphates is confirmed by a weak band in the region of 820 cm^{-1} related to the stretching vibrations of P–C bond [11].

Magnesium phosphates undergo a significant transformation, including recrystallization. In $CaCl_2$ solution, including in the presence of EDTA, the dissolution of magnesium phosphate is accompanied by the formation of calcium phosphate of suitable composition due to the lower solubility of the latter. In the case of TMPDH the formation of weakly crystallized CPT occurs, and instead of MHPTH, of calcium hydrogen phosphate dihydrate (CHPDH) (Figs. 2c, 2d). The proceeding transformation of TMPDH in CPT also is confirmed by IR spectroscopy (Fig. 3). Furthermore, in a composition of products of TMPDH the presence of methylene groups is also evident according to the bands of different intensity in the region 2855–2940 cm^{-1}. Processes of magnesium phosphate conversion into the corresponding calcium phosphates in the solutions of calcium background evidently proceed in two stages that explains the presence of inflections in the curves of pH variation (Figs. 1b, 1d): as a result of protonation of phosphate ions dissolution of magnesium phosphate accompanied by raising pH followed by crystallization of the less soluble calcium phosphates and, respectively, by deprotonation of phosphate ions. In a joint action of $CaCl_2$ and OEDP an active transformation of the initial phases of MHPTH and TMPDH into X-ray amorphous compound occurs. According to Fig. 4 it is amorphous calcium phosphate [12]. This fact may mean that the introduction of OEDP prevents the formation of CHPDH and CPT, for which the formation of amorphous calcium phosphate is an intermediate stage [13]. In these spectra there is also weak band at 820 cm^{-1} indicating the presence of OEDP in the composition of the product. This agrees well with the ability of OEDP to be adsorbed on the surface, thereby acting as crystallization inhibitor [14].

The effect of the chelating agents on processes of recrystallization may be considered mostly completely by phases formed in processing of MHPTH as the most soluble among the studied phosphate by solutions in the presence of excess cations Ca^{2+}. In all cases CHPDH formed, which is characterized by different diffraction patterns (Fig. 2d). However, for samples treated with solutions of $CaCl_2$ without chelating agents and in the presence of EDTA, the reflex intensity corresponding to the plane {020} was significantly superior to the others. This fact means that morphologically the particles are in the form of plates preferentially oriented along the plane that is typical of CHPDH particles according to [15]. The diffraction pattern of the sample treated with a solution with the addition of OEDP demonstrates redistribution of the intensities of the diffraction peaks, which suggests under these conditions a variation of the lamellar morphology of the particles by bulk. Moreover, both chelating agents cause a decrease in the size of the crystallites. For example, if in the absence of chelating agents the crystallite size reaches 177 nm, in the presence of EDTA and OEDP it consists of 156 and 117 nm, respectively.

CONCLUSIONS

(1) It was demonstrated that calcium phosphates [$Ca_3(PO_4)_2 \cdot 2H_2O$, $CaHPO_4$, hydroxyapatite] show high stability both in aqueous solutions of $CaCl_2$ and in the joint presence of ethylenediaminetetracetic acid or oxyethylenediphosphonic acid and only insignificantly dissolve in the presence of the chelating agents. Magnesium phosphates [$Mg_3(PO_4)_2 \cdot 10H_2O$ and $MgHPO_4 \cdot 3H_2O$] transform into calcium phosphates in the solution of $CaCl_2$, therewith the introduction in the solution of $CaCl_2$ of ethylenediaminetetracetic acid has no essential effect on the magnesium phosphate transformation while injection of oxyethylenediphosphonic acid inhibits crystallization of calcium phosphate formed.

(2) It was found that the action of ethylenediaminetetracetic acid and oxyethylenediphosphonic acid on calcium and magnesium phosphate sorbents is due to both their effect on a state of calcium ions in the solution and the formation of complexes with surface calcium ions. In the case of ethylenediaminetetracetic acid this fact leads to partial dissolving the sorbents while in the presence of oxyethylenediphosphonic acid, to inhibition of crystallization of calcium phosphates formed in interaction of magnesium phosphates with calcium-containing aqueous solutions.

(3) The obtained data on stability and physicochemical transformations of calcium and magnesium phosphates in the aqueous solutions of $CaCl_2$ in the presence of ethylenediaminetetracetic acid and oxyethylenediphosphonic acid should be accounted for their application in sorption processes in purification of real wastewater and liquid radioactive waste.

REFERENCES

1. Ivanets, A.I., Kitikova, N.V., Shashkova, I.L., et al., *J. Environ. Chem. Eng.*, 2014, vol. 2, no. 2, pp. 981–987.
2. Ivanets, A.I., Shashkova, I.L., Kitikova, N.V., et al., *Radiochemistry,* 2014, vol. 56, no. 1, pp. 32–37.
3. Zakutevskii, O.I., Psareva, T.S., and Strelko, V.V., *Russ. J. Appl. Chem.*, 2012, vol. 85, no. 9, pp. 1366–1370.
4. Tin'gaeva, E.A., Glushankova, I.S., Zil'berman, M.V., et al., *Russ. J. Appl. Chem.*, 2012, vol. 85, no. 9, pp. 1371–1375.
5. Asabina, E.A., Lukuttsov, A.A., and Pet'kov, V.I., *Russ. J. Appl. Chem.*, 2012, vol. 85, no. 6, pp. 867–871.
6. Ryabchikov, B.E., *Ochistka zhidkikh radioaktivnykh otkhodov* (Purification of Lquid Radioactive Waste), Moscow: DeLi print, 2008.
7. Smiciklas, I., Dimovic, S., Plecas, I., et al., *Water Res.*, 2006, vol. 40, no. 12, pp. 2267–2274.

8. Tõnsuaadu, K., Viipsi, K., and Trikkel, A., *J. Hazard. Mater.,* 2008, vol. 154, nos. 1–3, pp. 491–497.
9. Shchegrov, L.N., *Fosfaty dvukhvalentnykh metallov* (Phosphates of Bivalent Metals), Kiev: Naukova Dumka, 1987.
10. Dorozhkin, S.V., *World J. Methodol*., 2012, vol. 2, no. 1, pp. 1–17.
11. *Atlas IK-spektrov fosfororganicheskikh soedinenii* (Atlas of IR spectra of Organo-Phosphorus Compounds), Shagidullin, R.R., et al., Moscow: Nauka, 1984.
12. Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., *Kompleksony i kompleksonaty metallov* (Chelating Agents and Metal Complexonates), Moscow: Khimiya, 1988.
13. Christoffersen, J., Christoffersen, M.R., Kibalczyc, W., and Andersen, F.A., *J. Crystal Growth.* 1989, vol. 94, no. 3, pp. 767–777.
14. Nowack, B., *Water Research*, 2003, vol. 37, no. 11, pp. 2533–2546.
15. Plokhikh, N.V., Filippov, Ya.Yu., Putlyaev, V.I., et al., *Russ. J. Inorg. Chem*., 2013, vol. 58, no. 10, pp. 1152–1159.