ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 13, pp. 2596–2602. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © P.S. Gordienko, S.B. Yarusova, A.P. Suponina, A.A. Yudakov, I.G. Zhevtun, 2014, published in Ekologicheskaya Khimiya, 2014, Vol. 23, No. 2, pp. 102–109.

Effect of Hydration and Air Exposure on Sorption Properties and Phase Composition of Calcium Silicate Hydrate

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Received April 25, 2014

Abstract—The research results on stability of amorphous calcium silicate hydrate samples in air medium with high humidity and some of their sorption characteristics obtained for low concentrations (from 0.34×10^{-2} to 0.17 mmol L^{-1}) of cobalt ions in an aqueous medium were presented. It was shown that the sorption capacity of calcium silicate hydrate is affected by the phase composition change, caused by interaction with carbon dioxide to form two calcium carbonate polymorphs, calcite and aragonite, and amorphous silica.

Keywords: calcium silicate hydrate, hydration, phase composition, calcite, aragonite, sorption, cobalt ions

DOI: 10.1134/S1070363214130179

INTRODUCTION

Environmental pollution by heavy metals resulting from various industrial activities is a topical problem whose solving requires development of environmentally friendly inexpensive sorption materials for detoxification of contaminated sites.

Among the variety of inorganic sorbents used for treatment of aqueous media to remove heavy metal ions, a special group is constituted by natural and synthetic silicates, as well as by composite sorbents prepared therefrom.

In particular, calcium silicates $n\mathrm{CaO}\cdot m\mathrm{SiO_2}$ and calcium silicate hydrates (CSHs) $n\mathrm{CaO}\cdot m\mathrm{SiO_2}\cdot p\mathrm{H_2O}$ are effective environmentally friendly sorbents for removing heavy metal ions from aqueous solutions, as demonstrated by numerous domestic and foreign research works in this sphere.

A number of studies sought to elucidate the mechanism of interaction of $\mathrm{Co^{2+}}$ ions with various calcium silicates {tobermorite $\mathrm{Ca_{10}[Si_{12}O_{31}](OH)_6\cdot 8H_2O}$, xonotlite $\mathrm{Ca_6[Si_6O_{17}](OH)_2}$, and wollastonite $\mathrm{Ca_6Si_6O_{18}}$} and to assess their sorption properties [1–5].

For example, the interaction of $\mathrm{Co^{2+}}$ ions with xonotlite and tobermorite [1, 2] and with wollastonite [2] was studied. In [2], the mechanisms of the reactions of various metal ions, including $\mathrm{Co^{2+}}$, with tobermorite, xonotlite, and wollastonite at the solid to liquid phase ratio S : L = 1 : 400 (as well as at S : L = 1 : 100 for wollastonite), pH ~ 6.5, and room temperature were described. In that study, cobalt nitrate solutions with $\mathrm{Co^{2+}}$ ion concentrations of 100, 200, 500, and 1000 mg L^{-1} were used. It was found that the reaction results in replacement of virtually all the $\mathrm{Ca^{2+}}$ ions in tobermorite and xonotlite by $\mathrm{Co^{2+}}$ ions, leading to structural changes and amorphization of these minerals. The reaction of $\mathrm{Co^{2+}}$ with wollastonite proceeds to a lesser extent. It was shown that the reaction of the cobalt ions with calcium silicates is irreversible.

In [3], a sorbent based on 11 A tobermorite derived from newsprint recycling residues was used. Its maximum sorption capacity for cobalt ions in acidic solutions at S : L = 1 : 20 and 20°C was estimated at 10.47 mg g^{-1} (or 0.177 mmol g^{-1}).

The static exchange capacity toward Co^{2+} ions at S : L = 1 : 250, pH = 8.0, and 25°C, calculated in [4] for calcium silicate sorbents (xonotlite and wollastonite) prepared from industrial waste and natural components, was 0.2–0.5 and 0.25–0.4 mmol g^{-1} for xonotlite and wollastonite, respectively.

Previously [5] we examined the sorption properties of amorphous CSH with respect to cobalt ions at concentrations within 4×10^{-3}–1.02×10^{-1} M, S : L = 1 : 40, and room temperature and, based on the sorption isotherm, estimated the limiting sorption capacity at ~4.1 mmol g^{-1}.

It should be noted that optimized application of calcium silicates for Co^{2+} sorption requires that the influence of various conditions on the efficiency of the above-mentioned compounds be considered.

The reaction with water vapor and sorption of atmospheric CO_2 are known to cause partial decomposition of calcium silicates into $CaCO_3$ and amorphous silica, as confirmed by previous studies [6]. Thereby, the sorption characteristics of these compounds can be affected. The resistance to external factors (moisture, temperature, atmospheric CO_2) will determine the performance characteristics and the range of applications of calcium silicates.

In this context, studies into stability and changes in the sorption properties of calcium silicates when exposed to humid air are of certain practical interest. Here, we examined how the humid air exposure affects the phase composition and sorption properties of calcium silicate hydrate $CaO{\cdot}SiO_2{\cdot}1.3H_2O$ obtained from a $CaCl_2$–Na_2SiO_3–H_2O multicomponent system (hereinafter, model CSH) with respect to Co^{2+} ions at concentrations from 0.34×10^{-2} to 0.17 mM, S : L = 1 : 1000, and 20°C.

EXPERIMENTAL

The components used for CSH synthesis were “chemically pure” grade sodium silicate (silicon content 22.4%; silicate module $SiO_2/Na_2O = 1$) and calcium chloride $CaCl_2{\cdot}2H_2O$ [TU (Technical Specifications) 2152-069-00206457-2003, $CaCl_2{\cdot}2H_2O$ content no less than 98.3%], which were mixed in an aqueous medium in open vessels, as described in [7]. The resulting bulky white precipitate was thoroughly rinsed until Cl^- ions were completely removed (as checked by the reaction between the rinsate and an $AgNO_3$ solution), filtered through “blue tape” filter, and dried at 85°C.

Stability of the resulting model CSH under exposure to water vapor and atmospheric CO_2 was determined under exposure to air at 100% humidity. To this end, the tested CSH samples in Petri dishes were placed on a grating with holes in a desiccator filled with water up to the grating and loosely covered with a lid. The time of the experiment ranged from 60 to 120 days.

The stability of the CSH samples was checked by the moisture content and the amount of $CaCO_3$, %. The moisture content was calculated by the formula:

$$W = \frac{g_1 - g_2}{g_1} \times 100\%, \qquad (1)$$

where g_1 and g_2 are the weights of the weighed portions before and after drying at 105–120°C, respectively [8].

Carbonates (dry basis) were determined quantitatively using the gas-volumetric method, by measuring the volume of the gas released from a solid weighed portion [9].

The X-ray diffraction patterns of the precipitates were recorded on a D8 ADVANCE automatic diffractometer by rotating the samples under CuK_α irradiation. The X-ray diffraction analysis was performed using EVA searching software with PDF-2 powder diffraction file databank.

Specific surface areas of the samples were determined by the low-temperature nitrogen adsorption technique using a Sorbtometr-M instrument.

Sorption was carried out under static conditions at 20°C from aqueous solutions of cobalt chloride $CoCl_2{\cdot}6H_2O$ while stirring on a 358 S (Poland) laboratory shaker (shaking frequency 200 cycles min^{-1}) for 1 h. The cobalt chloride solutions with preset concentrations were prepared by dissolving an accurately weighed portion of “chemically pure” grade $CoCl_2{\cdot}6H_2O$ in distilled water.

For studying the sorption properties of the model CSH, 0.05-g weighed portions of the sorbent were placed in a set of test tubes, poured with 50 mL of an

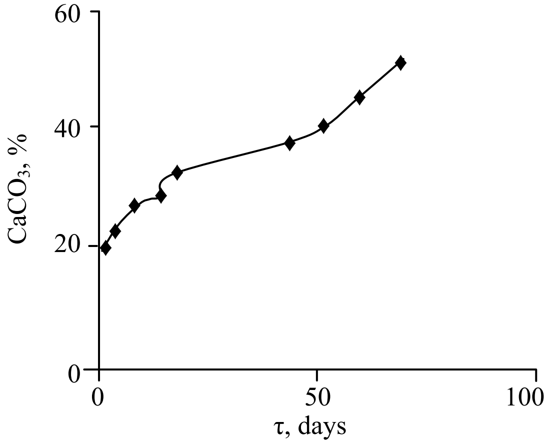

Fig. 1. Calcium carbonate content, %, in the model calcium silicate hydrate sample as a function of the time of humid air exposure.

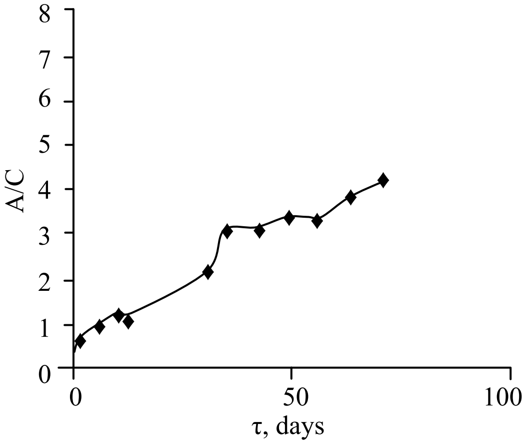

Fig. 2. Time dependence of the intensity ratio of the X-ray diffraction peaks of the aragonite (A) and (C) calcite phases formed in the model calcium silicate hydrate.

aqueous solution of cobalt chloride with the initial concentration ranging from 0.34×10^{-2} to 0.17 mM, and shaken for 1 h. In a blank experiment, a weighed portion of the sorbent was placed in a vessel with distilled water, and the resulting mixture was stirred concurrently with the test samples. Also, experiments with "pure" grade calcite $CaCO_3$ and "analytically pure" grade silica $SiO_2 \cdot nH_2O$ were run in parallel under the above-described conditions. Next, the solutions were separated from the sorbents by filtration, and the concentration of Co^{2+} ions was determined.

The sorption capacity, A_s, mmol g^{-1}, of the test samples was calculated using the formula:

$$A_s = \frac{C_i - C_{eq}}{m} V, \tag{2}$$

where C_i is the initial concentration of the cobalt ions in solution, M; C_{eq}, equilibrium concentration of the cobalt ions in solution, mM; V, solution volume, L; and m, sorbent mass, g.

Influence of pH on the sorption properties of the test samples was assessed from the change in the cobalt ion percentage removal from the solutions with controlled pH (pH was adjusted with 0.1 N solution of either NaOH or HCl).

The percentage removal of Co^{2+} ions α was calculated by the formula:

$$\alpha = \frac{C_i - C_{eq}}{C_i} \times 100\%. \tag{3}$$

Atomic absorption spectrometry with a Solaar 6 M spectrometer using the analytical line at 240.7 nm was applied to determine the content of the cobalt ions in the solutions. The detection limit for cobalt in aqueous solution is 0.15 μg mL^{-1}, and the relative errors in determination of cobalt in the 0.001–1.0 μg mL^{-1} and 1.0–10 μg mL^{-1} concentration ranges, 25 and 10%, respectively.

The hydrogen ion concentration was monitored in all the experiments using an IPL-102 Multitest pH-meter/ion-meter with an ESK-10601/7 glass electrode standardized by means of buffer solutions with known acidity.

Raman spectra of the samples were recorded on a BRUKER RFS 100/S Fourier transform Raman spectrometer with an Nd:YAG laser (wavelength 1064 nm, laser power 100 mW, spectral resolution 0.2 cm^{-1}).

The morphological characteristics of the samples were examined using a LEO EVO-50XVP scanning electron microscope (SEM) equipped with an INCA Energy-350 energy dispersive X-ray spectrum analyzer (Carl Zeiss, FRG).

RESULTS AND DISCUSSION

According to the X-ray diffraction analysis data, the calcium silicate synthesized in the $CaCl_2$–Na_2SiO_3–H_2O system was X-ray amorphous, but the sample contained a crystalline phase of calcium carbonate in the calcite modification. The specific surface area of the resulting sample was estimated at 108.6 m^2 g^{-1}. The main factor in the $CaCO_3$ formation is carbonation of calcium hydroxide, which in turn is yielded by the reaction of amorphous calcium silicate with water and carbon dioxide dissolved therein: $CaO{\cdot}SiO_2{\cdot}nH_2O + CO_2 > CaCO_3 + SiO_2{\cdot}nH_2O$. Using the technique described in [9], the $CaCO_3$ amount was estimated at ~30%. Consequently, the initial sample was originally composed of calcium silicate, calcium carbonate, and amorphous silica. The stability of this composition under exposure to external factors (humidity, temperature, atmospheric CO_2) will be a determinant factor for its performance and applications.

Figure 1 demonstrates how the percentage of the calcium carbonate formed in the model CSH sample exposed under the above-described conditions varies with the time of experiment.

As seen from Fig. 1, the $CaCO_3$ amount in the sample tends to increase with increasing time of the calcium silicate hydrate exposure in humid air and reaches 50% in the final stage of the experiment. This is paralleled by an increase in the proportion of hygroscopic moisture from 3.13 in the initial sample (before exposure to humid air, hereinafter, sorbent I) to 16.81% in the sample after 65 days of exposure to humidity with access of air (hereinafter, sorbent II). It should be noted that, after 120 days of exposure to humidity with access of air, the specific surface area of the CSH sample decreases to 89.6 $m^2\,g^{-1}$.

Our experiments revealed formation of an orthorhombic aragonite phase (A), along with the hexagonal calcite phase (C), upon exposure of the CSH sample in 100% humidified atmosphere with access of atmospheric CO_2. As known [10], stable calcite and aragonite are calcium carbonate polymorphs, and aragonite (density 2.94 g cm^{-3}), in turn, is a solid form of calcite (density 2.72 g cm^{-3}).

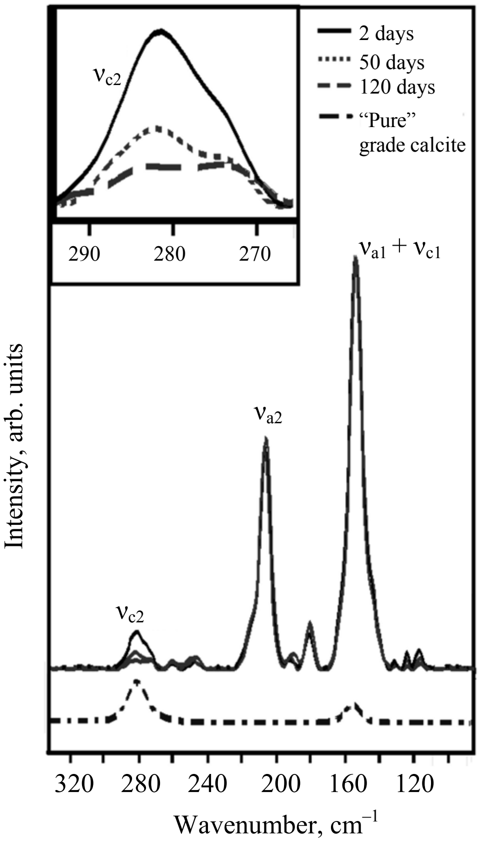

Fig. 3. Raman spectra of the calcium silicate hydrate samples after different times of humid air exposure (2, 50, and 120 days) and of "pure" grade calcite.

Considering the uniform sample preparation technique and identical reflection character, the ratio of intensities of the X-ray diffraction peaks from the different phases of calcium carbonate allows judging approximately the content ratio of the aragonite and

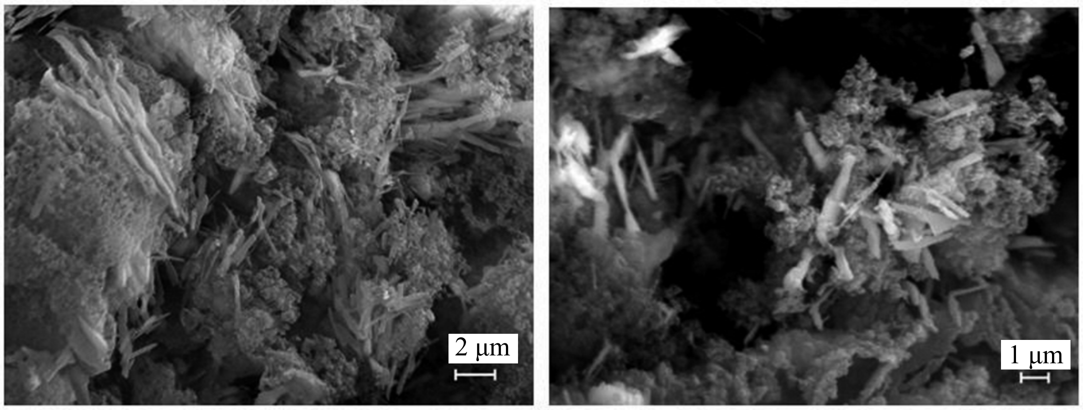

Fig. 4. SEM images of the calcium silicate hydrate sample exposed in humid air for 120 days.

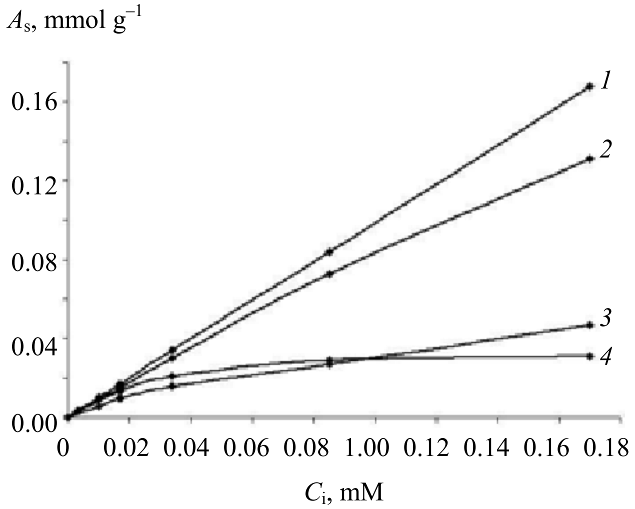

Fig. 5. Variation of the sorption capacity with the initial concentration of Co^{2+} ions: (*1*) sorbent I, (*2*) sorbent II, (*3*) “pure” grade $CaCO_3$, and (*4*) “analytically pure” grade $SiO_2 \cdot nH_2O$.

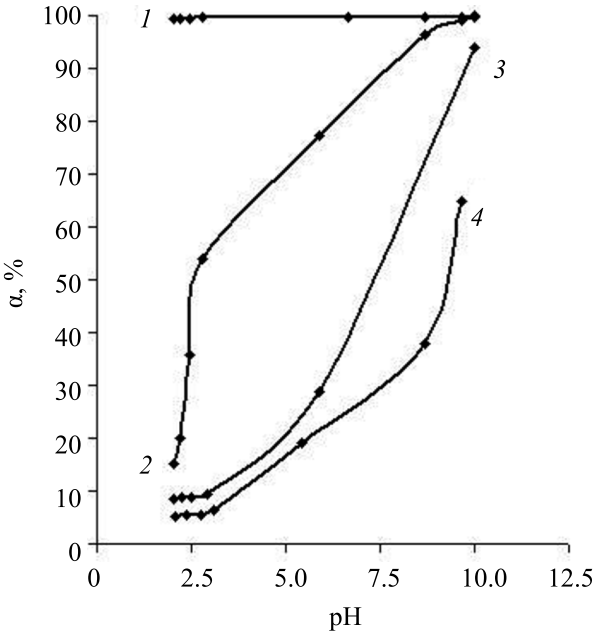

Fig. 6. pH dependence of the percentage removal α of Co^{2+} ions: (*1*) sorbent I, (*2*) sorbent II, (*3*) “pure” grade $CaCO_3$, and (*4*) “analytically pure” grade $SiO_2 \cdot nH_2O$.

calcite phases formed. Figure 2 shows how the aragonite to calcite intensity ratio ($I_{A/C}$) varies with the time of experiment.

As seen from Fig. 2, the aragonite proportion in the sample tends to increase with increasing time of experiment, as evidenced by an increase in the peak intensity of aragonite and a decrease in that of calcite.

The observed trend was confirmed by the results of a Raman spectroscopic examination. Figure 3 presents the lattice mode region of the $CaCO_3$ compound in the Raman spectra recorded.

It follows from analysis of the spectra in this region that the CSH samples contain two $CaCO_3$ polymorphs: calcite and aragonite. As demonstrated in [11], the peak intensity ratio of the lattice vibrations characteristic for the different $CaCO_3$ modifications provides highly accurate information on their quantitative contributions to the composition of the sample. The intensity normalization of the peaks in the Raman spectra to the aragonite peaks ν_{a1} and ν_{a2} shows that an increase in the humidity exposure time causes the intensity of the peak of the lattice mode of calcite ν_{c2} to decrease, thereby indicating that its content in the samples decreases with increasing time.

Figure 4 presents the SEM images of the CSH sample after 120 days of exposure to humidity with access of air. It is seen that the sample contains particles in the form of bundles of needle-shaped crystals characteristic for aragonite [12]. Also, there are individual needle-shaped crystals. The length of the needle-like particles ranges from 1 to 5 μm, and thickness, from 0.1 to 0.5 μm. It should be noted that, according to the SEM data, such bundles of needle-shaped crystals were lacking in the as-synthesized initial sample.

Thus, the calcium silicate hydrate obtained from a $CaCl_2$–Na_2SiO_3–H_2O multicomponent system and subsequently used in this study for sorption of Co^{2+} ions from aqueous solutions is a multicomponent system based on calcium silicate hydrate, calcium carbonate, and amorphous silica. Therefore, the contribution made by each component in the system studied to sorption of Co^{2+} ions should be taken into account.

Using the experimental Co^{2+} ion sorption data that we obtained, the sorption capacities of the initial CSH (sorbent I), the CSH after exposure to humidity with access of air for 65 days (sorbent II), calcium carbonate (“pure” grade), and silica $SiO_2 \cdot nH_2O$ (“analytically pure” grade) were plotted versus the initial concentration of the Co^{2+} ions (Fig. 5).

As seen from Fig. 5, the sorption capacities of sorbent I and sorbent II differ insignificantly, and at

<0.02 mM Co^{2+} concentrations in solution they are virtually identical. A slight decrease in the sorption capacity of the CSH sample after 65 days of exposure to humidity with access of air is associated with formation of $CaCO_3$ and amorphous silica, which, as follows from Fig. 5, also contribute to the sorption of the cobalt ions, but are strongly exceeded in sorption capacity by the initial CSH.

Figure 6 shows the pH dependences of the percentage removal of the Co^{2+} ions by the initial CSH (sorbent I), CSH after exposure to humidity with access of air for 65 days (sorbent II), calcium carbonate ("pure" grade), and silica $SiO_2{\cdot}nH_2O$ ("analytically pure" grade). It is seen that, for the initial CSH, the percentage removal α of the Co^{2+} ions does not change significantly over a broad pH range from 2.0 to 10.0, being close to 100%. For the CSH after 65 days of exposure to humidity with access of air the percentage removal of Co^{2+} ions significantly decreases in the acidic region (pH from 2.0 to 2.8) and increases to 99.9% with pH increasing from 5.9 to 10.0. Calcium carbonate and silica demonstrated similar trends: Over the pH range from 2.0 to 2.8, calcium carbonate removes no greater than 8.5–9.0% of Co^{2+} from a solution containing 10 μg mL^{-1} cobalt, and silica, no greater than 6.5%. At pH 5.9 to 10.0 the percentage removal of cobalt tends to gradually increase from 28.8 to 93.8 (for $CaCO_3$) and from 19 to 65% (for $SiO_2{\cdot}nH_2O$).

CONCLUSIONS

(1) Calcium silicate hydrate obtained from the $CaCl_2$–Na_2SiO_3–H_2O model system, under exposure to air and as a result of interaction with water vapor and absorption of atmospheric CO_2, undergoes partial decomposition into $CaCO_3$ and amorphous silica. With the time of humidity exposure of calcium silicate hydrate increased to 70 days the amount of $CaCO_3$ in the sample reaches 50%; in parallel, the proportion of hygroscopic moisture in the sample increases from 3.13 to 16.81%. After 120 days of exposure to humidity with access of air the specific surface area of the calcium silicate hydrate sample decreases from 108.6 to 89.6 $m^2\,g^{-1}$ due to the calcium carbonate formation.

(2) The exposure of the initial samples containing calcium silicate hydrate, calcite (up to 30%), and amorphous silica to 100% humidified atmosphere with access of air for 60–120 days results in that, along with the calcite phase having a hexagonal structure, an aragonite phase with orthorhombic configuration is formed, and its content in the samples tends to increase with increasing exposure time.

(3) The initial calcium silicate hydrate sample (before exposure to humid air) and that after 65 days of exposure to humidity with access of air were tested for sorption properties with respect to cobalt ions (at Co^{2+} ion concentrations ranging from $0.34{\cdot}10^{-2}$ to 0.17 mM, solid to liquid phase ratio S : L = 1 : 1000, and 20°C). The tests showed that the sorption capacities of these samples differed insignificantly and were virtually identical at Co^{2+} ion concentrations in the solution under 0.02 mM. A minor decrease in sorption capacity of the calcium silicate hydrate sample after 65 days of exposure to humidity with access of air is associated with formation of $CaCO_3$ and amorphous silica, which also contribute to the sorption of cobalt ions but are significantly exceeded in sorption capacity by the initial calcium silicate hydrate sample.

(4) The percentage removal α of the Co^{2+} ions by the initial calcium silicate hydrate sample does not change significantly over a broad pH range from 2.0 to 10.0, being close to 100%. For the calcium silicate hydrate sample exposed to humidity with access of air for 65 days the percentage removal of Co^{2+} ions significantly decreased in the acidic region (over pH range from 2.0 to 2.8) and increased to 99.9% with pH increasing from 5.9 to 10.0. Similar trends were revealed for calcium carbonate and silica.

(5) The data on stability of amorphous calcium silicate hydrate samples in air with high humidity and their sorption properties with respect to Co^{2+} ions, obtained from this study, are of practical interest in assessing their performance characteristics and selecting the applications.

ACKNOWLEDGMENTS

This study was financially supported by the Ministry of Education and Science of the Russian Federation according to Russian Federation Government Decree P 218 (contract № 02.G25.31.0035-225 of February 12, 2013, between Dal'nevostochnyi Zavod "Zvezda" Open Joint Stock Company and the Ministry of Education and Science of the Russian Federation.

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