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TECHNOLOGY OF INORGANIC SUBSTANCES AND MATERIALS

Effect of Ultrasonic Treatment on the Kinetics of the Formation of Calcium Hydrosilicate from Boron-Containing Technogenic Wastes

P. S. Gordienko, S. B. Yarusova, A. P. Suponina, Yu. V. Sushkov, and V. A. Stepanova

Institute of Chemistry, Far East Branch, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia
e-mail: yarusova_10@mail.ru

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Abstract—This work presents some results of studying the effect of ultrasonic treatment on the kinetics of the formation of calcium hydrosilicate from boron-containing mineral feedstock processing wastes, namely, borogypsum. Kinetic parameters and rate constants were determined for the synthesis reactions of calcium hydrosilicate from borogypsum under ultrasonic treatment conditions and conventional stirring.

Keywords: calcium hydrosilicate, wollastonite, borogypsum, ultrasonic treatment

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INTRODUCTION

Calcium silicates of different compositions and structures have found wide applications in the production of building materials, paper, paints, plastics, polymer composites and cermets, and water purification sorbents. In some cases, they are high-quality substitutes of talcum, kaolin, chalk, and titania. In the whole variety of silicates, calcium silicates $n\mathrm{CaO} \cdot m\mathrm{SiO_2}$ and hydrosilicates $n\mathrm{CaO} \cdot m\mathrm{SiO_2} \cdot p\mathrm{H_2O}$ are of the greatest practical interest. The valuable physicochemical and engineering properties of calcium hydrosilicates and wollastonite $\mathrm{Ca_6Si_6O_{18}}$ cause a wide spectrum of their application in different industry branches. There are currently a large number of methods for synthesizing calcium silicates made from different calcium- and silicon-containing compounds, including melt syntheses of wollastonite, hydrothermal (autoclave) synthesis of calcium hydrosilicates, and high-temperature synthesis via direct solid-phase reactions [1–4].

It is known [5] that ultrasound is widely applied to intensify many chemical processes, including the synthesis of hydrosilicates [6, 7]. In the earlier work [8], the possibility of synthesizing calcium hydrosilicates and wollastonite from boron-containing technogenic wastes (borogypsum) under ultrasonic treatment conditions has been shown, and the chemical and phase composition, morphology, and thermal behavior of obtained compounds were studied. However, the time dependence of the yield of a target product has not been studied.

The objective of this study is to perform the synthesis of calcium hydrosilicate from borogypsum and to study the effect of ultrasound on the kinetics of the formation of this compound.

EXPERIMENTAL

Synthesis of Calcium Hydrosilicate

The feedstock used for the synthesis of calcium hydrosilicate was boric acid production wastes, namely, borogypsum, with the following content of major components (wt %): $\mathrm{SiO_2}$, 32.2; CaO, 28.4; $\mathrm{SO_3}$, 31.3; $\mathrm{Fe_2O_3}$, 2.7. In addition, the wastes contained 0.9–2.2 wt % of $\mathrm{B_2O_3}$. The mass of borogypsum per ton of synthesized boric acid is 5–5.5 t. The total amount of borogypsum in the Russian Far East exceeds 50 million tons.

Borogypsum portions were mixed with a solution of potassium hydroxide of chemically pure for analysis grade at a stoichiometric ratio. Synthesis was performed at 20°C in tightly closed 100-mL plastic vessels placed into a LABIMEX UNITRA-UNIMA UM-1 washer bath (Poland) with ultrasonic treatment of a reaction mixture for the following time intervals: 10, 15, and 30 min, 1, 3, 5, 7, 9, 12, 24, 48, 72, and 96 h. Synthesis without ultrasonic treatment was performed simultaneously at the same ratios, temperature, and time intervals under stirring on a 358 S laboratory shaker (Poland) (at a shaking frequency of 200 cycles/min). After the specified time interval had ended, precipitates were separated from a solution by filtration, washed with distilled water, and dried at a temperature of 85–90°C for several hours. The reaction rate was monitored by the residual concentration of potassium hydroxide in a solution.

Methods of Analysis

The concentration of potassium hydroxide was determined by acid–base titration using a 0.1 N HCl solution prepared from fixanal as a titrant.

The X-ray fluorescent analysis of borogypsum was performed using a Bruker AXS S4 Pioneer X-ray fluorescent spectrometer (Germany). The relative measurement error was ±2%. The samples for analysis were pellets 40 mm in diameter manufactured by pressing the studied powders ground to an average particle size of less than 10 μm and mixed with several drops of a polyvinyl alcohol aqueous solution on a boric acid substrate at a pressure of 30 t on an Herzog HTP-40 semi-automatic press.

The X-ray diffraction patterns of precipitates were recorded on a D8 ADVANCE automatic diffractometer able to rotate a sample in CuK_α radiation. X-ray diffraction analysis was performed using the EVA search software with a PDF-2 powder databank.

The quantitative estimation of the elemental composition of samples was performed by energy-dispersive X-ray fluorescence using a Shimadzu EDX 800 HS spectrometer (Japan). A sample portion with a mass of 1 g was ground in an agate mortar with polytetrafluoroethylene with a mass of 0.5 g and placed into a press mold of 20 mm in diameter. A pellet was pressed for 2 min under a pressure of 20 MPa. The measurement time was 200 s, and the excitation source was a rhodium-anode X-ray tube. Light elements were not taken into account when performing the analysis. The concentration of determined elements was calculated by the method of fundamental parameters using the spectrometer software. The relative measurement error did not exceed ±2%.

The IR spectra of samples were recorded in the region of 400–2000 cm^{-1} using a Shimadzu Prestige-21 FT-IR Fourier-transform IR spectrometer at room temperature. Samples for recording were ground in an agate mortar to a finely dispersed state and deposited onto a CsJ substrate as Nujol mulls.

RESULTS AND DISCUSSION

The time dependences of the yield of a target product in the synthesis of calcium hydrosilicate from borogypsum with the use of ultrasonic treatment and conventional stirring in the process of synthesis are plotted in Fig. 1.

The positive effect of the ultrasonic treatment on the reaction rate and the target product yield can be seen from the obtained dependence. Thus, the yield of calcium hydrosilicate in 96 h of synthesis under ultrasonic treatment conditions was 86%, compared to 74% with conventional stirring at the same temperature. It should be noted that no considerable differences between the yields of a target product under conventional stirring and ultrasonic treatment were observed within initial time intervals of synthesis (10 min to 3 h). In 3 h, the target product yield is 67% with conventional stirring and 66% with ultrasonic treatment.

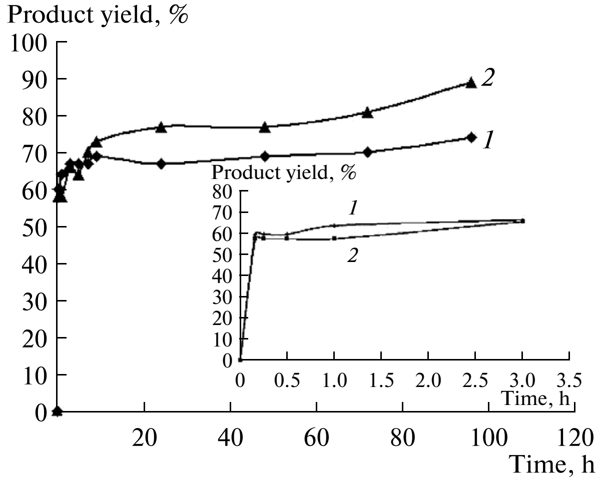

Fig. 1. Target product yield under (*1*) conventional stirring and (*2*) ultrasonic treatment versus time.

The obtained experimental data on the yield of calcium hydrosilicates were used to calculate constants that characterize the rate of reactions under ultrasonic treatment conditions and conventional stirring.

The calculation was performed using the generalized chemical Kolmogorov–Erofeev equation [9]

$$\alpha = 1 - e^{-kt^n}, \tag{1}$$

where α is the fraction of substance converted by the time moment t and n and k are constant, which are determined graphically and characterize the order and rate constant of a reaction.

The logarithmic time dependence on the target product yield degree in the synthesis of calcium hydrosilicate under ultrasonic treatment conditions and conventional stirring is plotted in Fig. 2.

The linear dependence observed in the logarithmic coordinates indicates the constancy of n within the given time intervals. The kinetic data processed by the generalized topochemical equation are listed in the table.

It should be noted that the rate constant for the reaction between borogypsum and potassium hydroxide is formally determined from the dependence

$$k = \frac{1}{K^n}, \tag{2}$$

Reaction order (n) and rate constant (k) for the synthesis of calcium hydrosilicate from borogypsu

Synthesis conditions	n	k	R^2
Ultrasonic treatmen	0.1292	0.9569 h$^{-0.1292}$	0.8475
Conventional stirring	0.0498	0.997 h$^{-0.0498}$	0.8694

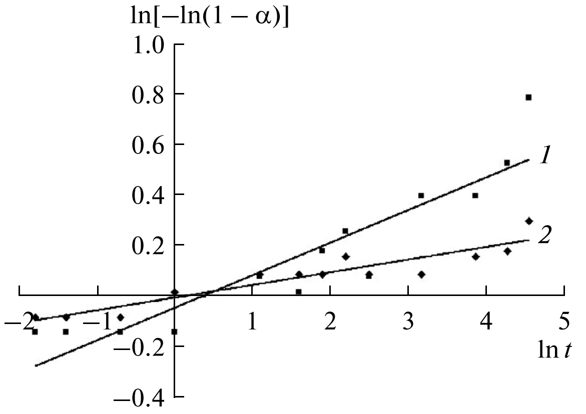

Fig. 2. Target product yield degree logarithm ln[−ln(1−α)] versus time logarithm ln*t* for the formation of calcium hydrosilicate under (*1*) ultrasonic treatment conditions and (*2*) conventional stirring.

where K is the reaction rate constant measured in hours (as follows from Eq. (1)), n is the reaction order, and k is a constant that is graphically determined from the logarithmic dependence. Hence, for the reaction between borogypsum and potassium hydroxide,

$$K^n = 1.408^{0.1292}[\mathrm{h}^{0.1292}],$$

under ultrasonic treatment and

$$K^n = 0.047^{0.0498}[\mathrm{h}^{0.0498}],$$

under conventional stirring without ultrasonic treatment.

It can be seen from the data given in the table that, in both cases, the reaction order is <1, which indicates that the synthesis of calcium hydrosilicate from borogypsum occurs in the diffusion region.

The X-ray diffraction analysis of the obtained precipitates indicates the existence of an amorphous phase and admixture calcium carbonate $CaCO_3$ and silicon dioxide SiO_2 in all of the samples synthesized under ultrasonic treatment and conventional stirring conditions. The presence of calcium carbonate may be due to the reaction that occurs between calcium sulfate and potassium hydroxide in the process of synthesis with the formation of calcium hydroxide $Ca(OH)_2$, which in turn intensively reacts with atmospheric CO_2 to yield $CaCO_3$. Moreover, the formed calcium hydrosilicate partially decomposes to yield $CaCO_3$ and amorphous alumina due to the reaction with water vapor and the absorption of CO_2 from the atmosphere, as confirmed by the earlier studies [10]. It should be noted that the calcium sulfate dihydrate $CaSO_3 \cdot 2H_2O$ phase is present in all the samples synthesized under conventional stirring conditions (from 10 min to 96 h). In the case of ultrasonic treatment, the $CaSO_4 \cdot 2H_2O$ phase is only present in samples synthesized within time intervals of 10 min to 12 h. There is no calcium sulfate phase in the X-ray diffraction patterns of the samples synthesized within time intervals of 24 to 96 h.

After annealing at 1000°C for 40 min, the phase composition of the samples synthesized under both ultrasonic treatment and conventional stirring conditions for 9 h is characterized by the presence of the triclinic wollastonite modification (Fig. 3).

The quantitative estimation of elemental composition shows that the content of sulfur in the samples after synthesis variates from 0.9 to 3.2 wt % for ultra-

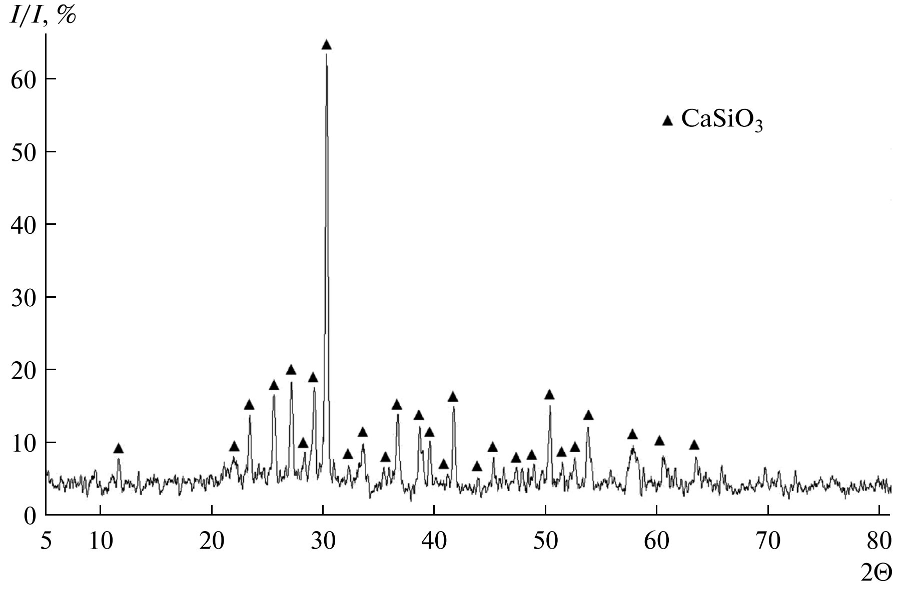

Fig. 3. X-ray diffraction pattern of the sample synthesized under ultrasonic treatment conditions for 9 h after annealing at 1000°C for 40 min.

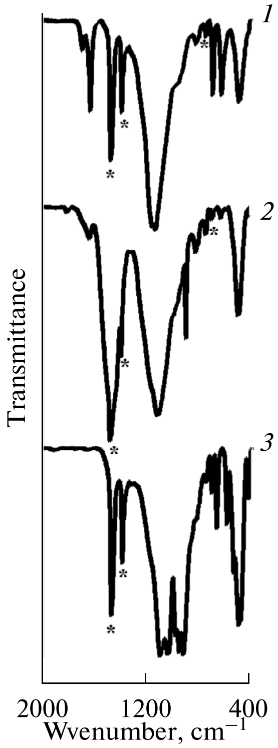

Fig. 4. IR spectra of samples: (*1*) borogypsum (reference sample), (*2*) synthesized calcium hydrosilicate after drying at 85°C, (*3*) synthesized calcium hydrosilicate after annealing at 1000°C, (*) Nujol peaks.

sonic treatment and from 1.5 to 5.3 wt % for conventional stirring depending on the time of synthesis.

The data on the IR spectroscopic analysis of initial borogypsum and synthesized calcium hydrosilicate samples indicate the formation of calcium silicates (Fig. 4).

According to [11–13], it can be seen from the given IR spectra that synthesized calcium silicates (spectra *2* and *3*) are characterized by an intense absorption band produced by the asymmetric vibrations of bridging Si–O–Si bonds and the asymmetric and symmetric vibrations of terminal Si–O bonds in the region of 850–1100 cm^{-1}. When the annealing temperature is increased to 1000°C, amorphous calcium silicate is observed to transition into the crystalline wollastonite phase (spectrum *3*). A set of bands in the region of 550–750 cm^{-1} is assigned to the symmetric vibrations of bridging Si–O–Si bonds in [SiO_4] tetrahedra. The absorption bands in the low-frequency region of 400–550 cm^{-1} are due to the bending vibrations of terminal O–Si–O bonds and the vibrations of Ca–O bonds in [CaO_6] octahedra [11–13]. Moreover, the absorption bands, which belong to calcium carbonate [14, 15] and disappear after annealing (spectrum *3*), are identified in spectrum *2* at 1430 and 880 cm^{-1}. The absorption bands produced in the region of 1190–1020 and 650–470 cm^{-1} by the stretching and bending vibrations of SO_4^{2-} are typical for borogypsum containing up to 70% of calcium sulfate dihydrate (spectrum *1*) [14]. The absorption band at 1600 cm^{-1} (spectra *1* and *2*) is due to the bending vibrations of crystallization water [14].

It should be noted that the IR spectra of calcium silicates synthesized under conventional stirring are identical to corresponding spectra *2* and *3* shown in Fig. 3 for the ultrasonic treatment of borogypsum.

CONCLUSIONS

The possibility of synthesizing calcium hydrosilicates made from borogypsum under ultrasonic treatment and conventional stirring conditions was shown. The annealing of synthesized samples at 1000°C was established to result in the formation of triclinic wollastonite modification.

The effect of ultrasonic treatment on the kinetics of the formation of calcium hydrosilicates has been established. Kinetic parameters and rate constants were determined for the reactions of the synthesis of calcium hydrosilicate from borogypsum under ultrasonic treatment conditions and conventional stirring. The application of ultrasonic treatment was found to increase the yield of a target product up to 89%. The yields of a target product in the case of conventional stirring and ultrasonic treatment were shown to demonstrate no significant difference between each other within initial time intervals of synthesis (from 10 min to 3 h).

The performed studies will make it possible to optimize the complex processing of borogypsum with the production of calcium hydrosilicates, wollastonite, potassium fertilizers, silicate sorbents, and additives for producing building materials.

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