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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Study of the Kinetic Aspects of Formation of Calcium Monosilicate in the Model System $CaSO_4 \cdot 2H_2O$–$Na_2O \cdot SiO_2$

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Abstract—The possibility and kinetic aspects of formation of X-ray amorphous calcium monosilicate in the model system $CaSO_4 \cdot 2H_2O$–$Na_2O \cdot SiO_2$ at room temperature were studied.

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Owing to valuable physicochemical, physicomechanical, and thermal properties, xonotlite and wollastonite, belonging to calcium monosilicates, are widely used in various industrial areas [1].

Borogypsum waste formed in preparation of boric acid from datolite concentrate, containing anhydrous, semi-hydrated, and dihydrated gypsum as well as amorphous silica, is used as a raw material for xonotlite and wollastonite synthesis.

It was of interest to study the kinetic aspects of synthesis of calcium monosilicates from borogypsum wastes.

This study is concerned with the kinetics of formation of silicates in the model system $CaSO_4 \cdot 2H_2O$–$Na_2O \cdot SiO_2$.

EXPERIMENTAL

The components for synthesis of calcium monosilicates, anhydrous gypsum (10 g) and liquid glass (pure grade, silicate modulus $SiO_2/Na_2O = 1$), were mixed at a stoichiometric ratio 1:1 in aqueous medium.

The synthesis was performed in an UM-1 UNITRA–UNIMA water bath (LABIMEX, Poland) ensuring ultrasonic treatment of the reaction mixture in air at room temperature for a certain time, 0.5, 1.0, 3.0, 5.0, and 7.0 h. The volume of the water bath was 1.0 dm^3 and its dimensions were 120×120×100 mm. Additionally, a 48-h synthesis with mixing of the reaction mixture with a magnetic stirrer was performed. As was established previously, it is reasonable to synthesize calcium monosilicate in an ultrasonic installation.

The precipitate was separated from the solution by filtration onto a paper white tape with a water-jet pump and washed 2–3 times with distilled water warmed to boiling temperature, at which the solubility of gypsum in water is minimal (0.1619 g/100 g) [2]. Under these conditions, the additional amount of sulfate ions passed into the solution is small and contributes negligibly into the total amount of sulfate ions present in the aqueous phase of the mixture after the synthesis.

A solution containing 4.0 mg ml^{-1} of barium chloride was prepared by dissolving a precise weighed portion of chemical purity grade barium chloride in distilled water.

The barium content was determined by flame atomic absorption spectroscopy [(AA-780 "Nippon Jarrell Ash" spectrometer, 535-nm line, acetylene-air ratio 2.5:6.75)].

The reaction was monitored by the X-ray phase and IR spectroscopic analyses of deposits dried at room temperature. The deposits annealed at 850 and 1000°C for 1 h were also analyzed by the same methods.

The diffraction patterns of the deposits were recorded on a D8 ADVANCE automated diffracto-

Results of sulfur determination by (*I*) atomic absorption and (*II*) gravimetric methods and the formation kinetics of calcium monosilicate (yield of product)

Synthesis time, h	Gravimetric method, x % (n = 3)	Atomic absorption method			Yield of product, %	
		n	x, %	S_g	**I**	**II**
0.5	5.75	8	6.10±0.26	0.045	30.91	32.80
1.0	6.22	5	6.50±0.21	0.038	33.50	34.90
3.0	7.55	3	7.70±0.15	0.042	40.60	41.40
5.0	8.70	4	8.71±0.06	0.010	46.77	46.72
7.0	11.65	5	11.70±0.10	0.021	62.60	69.90
48.0	12.44	6	12.60±0.14	0.032	66.90	67.74
control	22.41	5	22.85±0.37	0.040	99.42	101.0

meter able to rotate sample in CuK_α radiation and were analyzed using Powder Diffraction File PDF-2 (EVA search program).

The IR absorption spectra of samples (finely dispersed compositions in the form of mineral oil suspension on KBr) in the range 350–4000 cm^{-1} at room temperature were recorded on a SHIMADZU-IR Prestige 21 spectrophotometer.

The thermal analysis of the deposits was done on a MOM G-1500 D derivatograph (Hungary). Samples were annealed in open platinum crucibles in air at a rate of 5 deg min^{-1}.

The kinetic aspects of the formation of calcium monosilicates in the model system proposed are determined by the rate of passage of sulfate ions into the solution. Therefore, the product yield at a quantitative level was determined from the amount of sulfate ions (sulfur) present in the filtrates after the synthesized material was separated, as obtained by indirect atomic absorption determination of barium (*I*) and by traditional gravimetry (*II*).

The method *I*, indirect determination of sulfur by atomic absorption of barium in barium sulfate solution [4, 5], is express analysis suitable for technological objects of complex composition [6]. In addition, with this method, test gravimetric analysis may be performed in shorter time, because calculation of the amount of precipitant for sulfate ions, whose concentration in solutions is unknown, is made difficult.

From the filtrate solutions, silicon was preliminarily removed by traditional procedures [7, 8], and then the amount of sulfate ions in solutions was analyzed by the above-described methods.

In indirect determination of sulfur by barium atomic absorption, from the obtained solution, aliquots (2–20 ml) were taken into a 50-ml graduated cylinder and its pH ~ 3 was adjusted with methyl orange indicator (1–2 drops), then a solution of barium chloride was added to 400 μg ml^{-1}, and distilled water was added to a total volume of 50 ml. After sedimentation, the solutions were analyzed by atomic absorption method. The amount of sulfur in the test samples was determined from the $A = f(c)$ calibration graph constructed for solutions containing 100, 200, 300, and 400 μg ml^{-1} Ba^{2+}, where A is absorption (%) and c, barium concentration (μg ml^{-1}). The graph is the linear dependence to Ba^{2+} concentrations of 400 μg ml^{-1} Ba^{2+}. The sulfur content x (%) was calculated by formula:

$$x = 2.334\times10^{-5}(400 - c)kV/a,$$

where x is sulfur concentration in analyzed object (%); c is the concentration of barium in solution, found from calibration graph (μg ml^{-1} Ba^{2+}.); k is dilution coefficient; V is the total volume of analyzed solution (ml); a sample weigh (g).

Then, from the obtained data on the sulfur concentration in a working solution the amount of barium chloride necessary for precipitation of sulfate ions by method *II* was calculated, its amount in excess of about 1.5 of calculation was taken to cause crystalline and amorphous deposits to precipitate, and a control gravimetric determination of sulfur was done.

Results of the sulfur determination by two independent methods are in satisfactory agreement, with standard deviation S_g within 5–20% sulfur not exceeding 0.045 (Table 1).

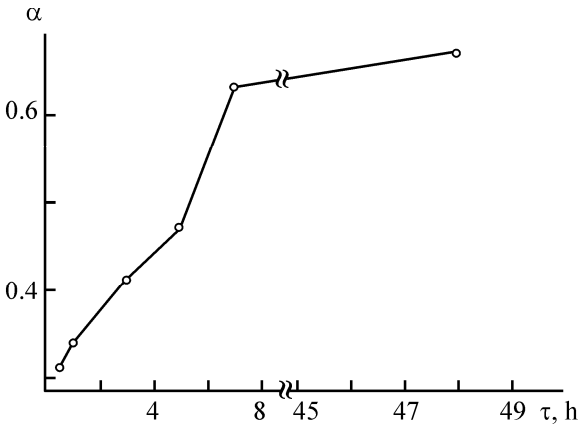

Fig. 1. Product yield α vs. time τ for the formation of calcium monosilicate in the model system.

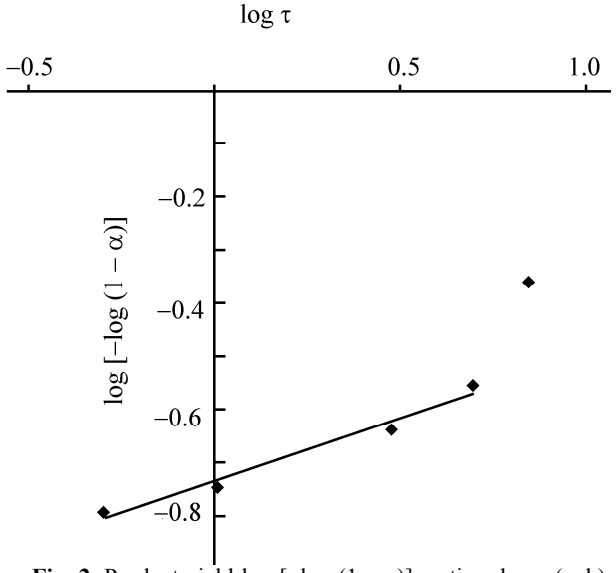

Fig. 2. Product yield log [–log (1 – α)] vs time log τ (τ, h) plot for the formation of calcium monosilicate in the model system.

The yield of product, as calculated from results of the gravimetric determination of sulfur, is shown in Fig. 1 as a function of the synthesis time of calcium monosilicate in the model system at room temperature.

The kinetic curve demonstrates an increase in the product yield to a value of 62.6% after 7 h of synthesis. The experiments showed that it is inappropriate to increase further the time of concentration of the final product, because its yield with time increases inconsiderably, for example, to 67% after 48 h of synthesis.

The reaction order *n* and the rate of the reaction of $CaSO_4 \cdot 2H_2O$ with $Na_2O \cdot SiO_2$ were calculated based on experimentally obtained data on the formation of calcium monosilicate under the given conditions. We used in the calculation the generalized Kholmogorov–Erofeev topochemical equation [9].

Figure 2 presents the product yield vs. time graph for calcium monosilicate synthesis. The linear dependence in the logarithmic coordinates observed to a synthesis time as high as 5 h with a reaction product yield of up to 47% confirms applicability of the Kholmogorov-Erofeev equation for processing the experimental data obtained.

Processing of the kinetic data by the generalized topochemical equation yields a value of 0.23 for the reaction order *n*. Because the reaction order formally characterizes the kinetic dependence of reaction rate on the reagent concentration, this experimentally determined value of the reaction order may result from the diffusion limitation of the processes under study. The rate constant of calcium monosilicate formation in the model system at room temperature does not exceed 0.0057 h^{-1}.

Increase in the calcium monosilicate yield at a synthesis time of 7 h is likely due to some warming of an ultrasonic water bath in the course of exploitation, which, in turn, causes calcium sulfate concentration in the solution to increase and kinetic characteristics of the process to change.

The X-ray phase analysis of deposits, which were obtained by a model synthesis of dihydrated gypsum and a liquid glass and dried at room temperature, revealed only $CaSO_4 \cdot 2H_2O$.

At the same time, the IR spectra of the above deposits contain absorption bands attributable to certain functional groups, which show that calcium monosilicate is also present in the synthesized material. The bands in the regions 1090–800 and 650–470-cm^{-1} are due to the stretching and bending vibrations of SiO^- group, respectively [10]. At the same time, the spectra of the reference samples prepared from authentic $CaSiO_3$ synthesized by technology [11] contain a band around 970 cm^{-1} before annealing and bands at 956, 931, and 898 cm^{-1} after annealing. In the spectrum of the deposit obtained after 48 h of synthesis, intense band peaking at 970 cm^{-1} is present. The same absorption band is present in the synthesized material annealed at 850°C. From the results obtained, SiO_2 group was identified in the materials under study (Fig. 3a).

In the spectrum of the $CaSO_4 \cdot 2H_2O$ reference sample, absorption bands in the regions 1190–1020

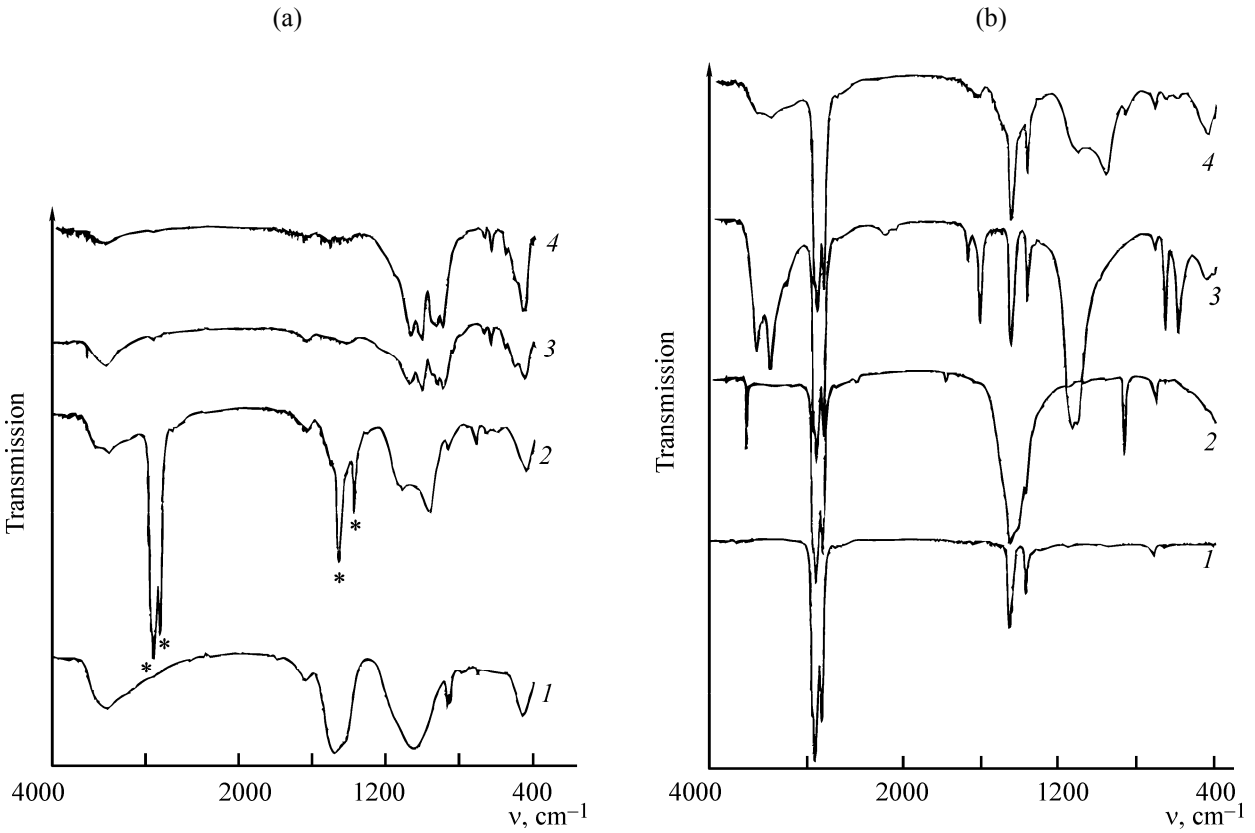

Fig. 3. IR spectra of the synthesized materials and test samples; (ν) wave number, cm^{-1}. (a) (*1*) authentic $CaSiO_3$; (*2*) deposit obtained after 48 h of synthesis, (*3*) authentic $CaSiO_3$ annealed at 850°C; and (*4*) synthesized material annealed at 850°C. (b) (*1*) mineral oil; (*2*) CaO; (*3*) $CaSO_4 \cdot 2H_2O$; and (*4*) deposit obtained after 48 h of synthesis.

and 650–470 cm^{-1} are due to the stretching and bending vibrations of SO_4^{2-} group [10, 12] and correlate with the same bands in the spectra of deposits, which confirms once again presence of unreacted dihydrated gypsum in the latter compounds (Fig. 3b).

Presence of anhydrous calcium sulfate and wollastonite, a crystalline phase of X-ray amorphous calcium monosilicate, in the annealed material synthesized during 0.5–7 h was confirmed by XPA and IR spectroscopy. With synthesis time increased to 48 h, a phase of CaO is present in the deposit by the data of XPA, which is likely due to the formation of $CaCO_3$ at prolonged agitation of the reaction components with a magnetic stirrer in air. The IR spectrum of the synthesized material has weak absorption bands in the region 875–711 cm^{-1} due to the stretching vibrations of Ca–O bond (Fig. 3b).

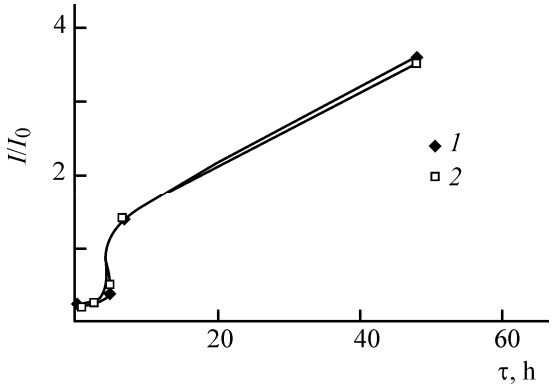

Fig. 4. Relative intensities *I* of the formed phases of calcium monosilicate and I_0 of residual calcium sulfate vs. time τ for annealing temperature (*1*) 850 and (*2*) 1000°C.

In its turn, increasing the synthesis time increases a portion of calcium monosilicate in the obtained product: the intensities of $CaSiO_3$ peaks increase, whereas the intensities of $CaSO_4$ peaks decrease sharply owing to consumption of dihydrated gypsum in the course of the reaction.

As known [13], wollastonite is commonly obtained by calcination of a stoichiometric mixture of $CaCO_3$ and SiO_2 at 950–1200°C.

From relative intensity of the reflections belonging to different phases formed in the obtained deposits,

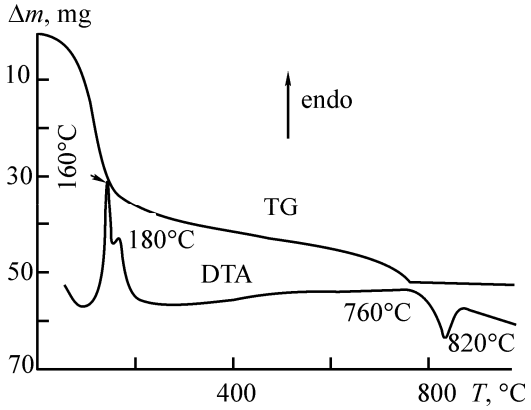

Fig. 5. DTA and DTG curves of the calcium silicate sample synthesized for 48 h; (Δm) mass loss, (T) temperature.

with sample preparation and its reflectivity character the same, it may be judged to a certain extent on the relative amount of crystalline phases. Figure 4 presents the dependence of the relative intensity (I/I_0) of the $CaSiO_3$ and $CaSO_4$ reflections vs. the time of synthesis of the model samples. With sintering temperature increased to 1000°C, the relative reflection intensity in the diffraction patterns of the synthesized material is increased inconsiderably. Consequently, we confirm once again that a synthesis temperature of 850°C is optimal, which in its turn decreases the energy expenditure for sintering.

The temperature intervals of conversion of X-ray amorphous calcium silicate into wollastonite were determined by the DTA. The DTA curves contain endothermic peaks at 160–180°C (loss of adsorption water) and at 690–760°C (loss of crystallization water and $CaCO_3$ decomposition). Trace amounts of the latter compound in the form of CaO were found by IR spectroscopy. Exothermic effect at 820°C confirms formation of crystalline calcium monosilicate (Fig. 5).

CONCLUSIONS

(1) The results of the performed study confirmed formation of calcium monosilicate in the model system $CaSO_4 \cdot 2H_2O$–$Na_2O \cdot SiO_2$ in aqueous medium at room temperature in air.

(2) Presence of wollastonite, crystalline phase of X-ray amorphous calcium monosilicate, in the synthesized material after sintering was confirmed by the X-ray phase and differential thermal analyses and by IR spectroscopy.

(3) The kinetic aspects of formation of calcium monosilicates in the model system proposed are determined by the rate of departure of sulfate ions into the solution. As the time of synthesis of the reaction mixture components increases the yield of calcium monosilicate increases, attains a value of about 70% at a synthesis time of 7 h, and then the rate decreases owing to diffusion limitation. Consequently, it is inappropriate to increase further the synthesis time.

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