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THE INFLUENCE OF AGING PHENOMENON IN SILICA HYDROGEL DERIVED FROM A SERPENTINE-GROUP MINERAL ON THE YIELDS OF CALCIUM SILICATE SPECIES

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In the paper the interaction between silica hydrogel species recovered from serpentine minerals $(Mg(Fe))_6[Si_4O_{10}](OH)_8$ and calcium hydroxide $Ca(OH)_2$ in aqueous medium by stirring in air at ambient pressure has been studied. The present research was aimed to investigate the effect of stirring time and the silica hydrogel aging on the yield of β -wollastonite produced by the heat-treatment of intermediates which had been precipitated in the boiling aqueous suspension prepared from the mentioned reagents. The data derived from the experiments have revealed that the portion of β -wollastonite in the products is variable and depends on the stirring time and the silica hydrogel aging. The replacement of the freshly synthesized silica hydrogel with the same one aged for six months' time leads to increase in stirring time from 15 min up to 120 min in order to achieve the higher yields of β -wollastonite.

Figs. 4, references 10.

A novel nontraditional approach to the chemical processing of dehydrated serpentinites¹ has allowed producing a silica hydrogel containing about 7 % of amorphous silicon dioxide SiO₂ [1]. The silica hydrogel is synthesized by the polycondensation of silicic acids formed from ortho- $[SiO_4]^{4-}$, di- $[Si_2O_7]^{6-}$,

¹ Serpentinite is a rock largely composed of serpentine group minerals $(Mg(Fe))_6[Si_4O_{10}](OH)_8$ belonging to phyllosilicate group, layer-type silicates or sheet silicates in other words.

 $[Si_3O_{10}]^{8-}$, $[Si_4O_{13}]^{10-}$ and other silicate anions less polymerized and having oligomeric dimension which have been leached from the dehydrated silicate sheets of serpentine minerals [2].

Recent studies have shown that this silica hydrogel can not only be successfully used as a raw material for the production of a number useful silicate materials such as strontium and barium silicates but it also essentially simplifies the first stage of intermediates precipitation and decreases the temperatures of intermediates crystallization into final products on heating thereby streamlining the whole procedure of their syntheses [3, 4].

These findings suggest that the involvement of the silica hydrogel in the precipitation process which will be performed by stirring of the boiling aqua solution prepared from the silica hydrogel and calcium hydroxide Ca(OH)₂ is likely to facilitate the technology for calcium silicates production, particularly β -wollastonite (β -CaSiO₃), which is an interesting material for various domains of a modern engineering [5, 6].

For β -wollastonite synthesis, two routes are traditionally applied: (i) the solid state reaction between calcium carbonate CaCO₃ or dolomite CaCO₃·MgCO₃ and silicon dioxide SiO₂ within the temperature range of 1100–1350°C and (ii) the hydrothermal treartment. In the hydrothermal method, in the first stage, calcium silicate hydrates are produced by an hours-long hydrothermal treatment (2–7 *hours*) of an aqueous mixture of a source of CaO and SiO₂; in the second stage, these calcium silicate hydrates are transformed into β -CaSiO₃ by annealing in the temperature range of 800-1150°C for hours (2–8 *hours*) [7, 8]. All these methods suggest either high temperature or autoclave treatment as well as a long process duration, and thus are great energy consuming.

It is well known that because of some structural redistributions and arrangements taking place between silica monomers, oligomers or particles in silica constituting gels during aging, silica gels are considered to be unbalanced systems [9, 10]. For this reason, balance disturbance of vulnerable gels during aging and the relation between the state of amorphous species and the crystalline phase depending on aging must be determined. Despite the industrial relevance and high commercial interest there has not been much progress in this field up to now. Hence, understanding of aging processes in the silica hydrogel on a scientific basis is essential in preparing a wide range of silicate compounds.

The present research is aimed to study the effect of structural changes in the aged silica hydrogel derived from serpentine minerals on the yields of calcium silicate species synthesized by the heat treatment of intermediates which had been previously precipitated via stirring of the boiling aqueous suspension prepared from the silica hydrogel and $Ca(OH)_2$.





Fig. 1. XRPD patterns of the specimens which were produced by the heat treatment at 850°C of the precipitate samples prepared from Gel Sample №1 and Ca(OH)₂ by stirring for different times. ■– β-CaSiO₃; □– Ca₂SiO₄.

Fig. 2. XRPD patterns of the specimens which were produced by the heat treatment at 850°C of the precipitate samples prepared from Gel Sample №2 and Ca(OH)₂ by stirring for different times. ■–β-CaSiO₃; □–Ca₂SiO₄; ●–CaO.



Fig. 3. Relative phase concentrations of the components in the products synthesized by the heat treatment at 850°C of the precipitate samples which were produced from Ca(OH)₂ and Gel Sample №1 (a) and Gel Sample №2 (b) by stirring for different times.

Experimental

A serpentinite sample located in Shorja (Armenia) was used as a precursor for the silica hydrogel production using the method described in the work [1].

Reagent grade CaO 98% (248568 Sigma-Aldrich) previously annealed at 1000°C for 0.5 h was used as a raw material for Ca(OH)₂ production.

For the intermediates precipitation two samples of suspension with liquid/solid ratio of 15 were prepared from the primary mixtures of Ca(OH)₂ and silica hydrogel with the CaO and SiO₂ molar ratio of 1:1. The frist sample was prepared from the silica hydrogel freshly synthesized (Gel Sample N $ext{el}$ 1), the second one – from the same silica hydrogel aged for six months (Gel Sample N $ext{el}$ 2). When the silica hydrogel was metered, SiO₂ content in the silica hydrogel that is 5.8% was taken into consideration in order to guaranty the molar ratios CaO to SiO₂. Each of the prepared samples was put into a vessel and stirred with mechanical stirrer for a certain time which is 15, 30, 60, 90 and 120 *min* in air at ambient pressure while being heated up to the temperature of 95°C (boiling point). Then each of the suspensions produced in the mixer was filtered. A gellike mass remained on the filter was washed by distilled water and dried at the temperature of 100°C for 24 *h* in a dryer type KBC G – 100/250 manufactured by Premed (Warszawa, Poland). As a result, a white precipitate powder was produced.

Each of the ten precipitates produced was annealed at 850°C for 30 *min* and subjected to XRD analysis. Of the ten precipitate samples the two were selected for DTA from room temperature up to 1000°C.

X-ray powder diffraction (XRPD) measurements were made on a Dron-3 diffractometer (Russia) equipped with nickel filter, under the following conditions: CuK α -radiation; power supply 25 *kV*/10 *mA*; angular range 20=8°-70° at the room temperature in air. The mass of each test specimen was 250 mg. All the reflections were identified and interpreted using the ICDD-JCPDS database of crystallographic 2004.

DTA, thermogravimetry (TG) and DTG (differential thermogravimetric) measurements were performed by using a Derivatograph Q–1500D equipment manufactured by the MOM company (Hungary) in air at a heating rate of 10° C min⁻¹. The samples of equal mass were investigated in platinum crucibles.

Results and Discussion

The XRPD patterns of the heated precipitate specimens produced from the suspension samples which were prepared from the silica hydrogel and Ca(OH)₂ with the SiO₂: CaO molar ratio of 1:1 demonstrate that two species of calcium silicate, namely β -wollastonite (Card N₂84–0655) and larnite Ca₂SiO₄ (Card N₂33–0302) are precipitated (Fig. 1 and 2). A detailed analysis of the diffraction peaks recorded for all the samples has revealed that the portion of each phase in the final product depends on the two factors: stirring time and gel aging. β -CaSiO₃ and Ca₂SiO₄ peaks of different intencities are observable depending on

the stirring time and the aging of the silica hydrogel involved in the precipitation stage.

Based on the fact that the diffraction line intensity is proportional to the phase volume content, the relative concentration of each phase in the synthesized mixtures was estimated from the diffraction peaks intensities by the nonstandard method measuring the ratio of intensities of the different phases. The calculations were graphically represented in Fig. 3.

The higher yields of β -wollastonite are produced on heating up to 850°C in the intermediates prepared from Gel Sample №1 that is proved by the intensive peaks β -CaSiO₃ discovered in the corresponding patterns (Fig. 1). The highest concentration of β -wollastonite is fixed in the samples produced by stirring for 15 and 120 *min* (Fig. 3a). The increase in stirring time up to 90 min inclusive leads to a slight decrease of β -wollastonite amount (Fig. 3a).

Unlike the previous samples produced from Gel Sample N°1, besides the reflections of wollastonte and larnite the ones of calcium oxide CaO (Card No 82–1690) are traceable in the XRPD patterns of the final products produced from Gel Sample N°2 via stirring within the range of 15-90 *min* (Fig. 2). The appearance of CaO reflections indicates that as distinct from the previous samples Ca(OH)₂ is partly involved in the reaction with the SiO₂, which is a constituent part of the silica hydrogel, and the fifteen-minute stirring is not sufficient for the complete interaction between the initial reagents in the system (Fig. 3b). Only increase in stirring time up to 120 *min* provides the complete (Fig. 3b).

The DTA curves of the two precipitate samples prepared from Gel Samples $N_{2}1$ and 2 by the fiftten-minute stirring were considered. They display noticeable exothermic peaks of high intensities within the temperature range of 750-850°C with the maxima at 827 and 839°C (Fig. 4).



Fig. 4. Differential thermal curves for the precipitate samples produced from Ca(OH)₂ and Gel Sample №1 (a) and Gel Sample №2 (b) by the 15-minute stirring. TG thermogravimetric or weight loss curve, DTA differential thermal analysis curve. DTG differential thermal thermogravimetry curve. The vertical axis label applies to the DTA curve.

These exotherms are preceded by endothermic events with the minima at 775 and 812°C which are accompanied by mass loss that is proved by the trend

of the TG curves (Fig. 4). These endotherms are most likely produced by dehydroxylation – hydroxyl water formation and removal from the intermediates – and indirectly indicate chain-like calcium hydroxosilicate species formation during precipitation because only this type of Ca-containing silicate compounds can be easily transformed into such a calcium silicate species as wollastonite on heating. The intermediate calcium hydro- and hydroxosilicates can not be identified by XRD analysis because they were all produced in an amorphous state. Naturally, the mild conditions of the treatment (95°C, ambient pressure) can not provide the formation of any chain-like crystalline compounds easily trasformed into wollastonite configuration on heating up to 850°C. Crystalline compounds production such as tobermorite (Ca₅Si₆O₁₆(OH)₂·4H₂O or Ca₅Si₆(O,OH)₁₈·5H₂O) or xonotlite (Ca₆Si₆O₁₇(OH)₂) which are distinguished by chain-like structure and therefore considered the best intermediates for wollastonite synthesis is only achieved via hydrothermal treatment.

An endothermic event with the minimum at 491°C set on the DTA curve of the precipitate sample produced from Gel Smaple No2 is caused by the process of unreacted Ca(OH)₂ decomposition with the formation of H₂O and CaO (Fig. 4b) the reflections of which (Card No82–1690) are seen in the XRPD patterns of the same specimens produced after the heat treatment of the corresponding precipitates (Fig. 2).

Another endotherm barely detectable over 600°C on the DTA curve of the precipitate sample prepared from Gel Smaple No1 must have been caused by the decomposition of calcium carbonate CaCO₃ resulting in the formation of CO₂ and CaO (Fig. 4a). The lower intensity of this effect indicates a negligiable amount of CaCO₃ formed by CO₂ absorption from the air. But CaO reflections are not traceable in the XRPD patterns of the corresponding sample. It is quite logical to suggest that on heating up to 600°C CaO released by CaCO₃ decomposition immidiatedly reacts with the SiO₂ that remained in an amorphous state inside the intermediate, producing calcium silicate species and CO₂ and causing the endotherm barely detectable over 600°C on the DTA curve of the precipitate sample. As for the exothermic event that should be seen over 600°C and evidence the calcium silicate species formation, it is most likely overlapped by the endothermic process of CO₂ releasing that requires energy input more than the heat released by the reaction of calcium silicate species formation.

Both the intensive diffraction peaks of β -wollastonite and larnite fixed in the diffraction patterns of the heated specimens point to the fact that the strong exothermic peaks are originated by both β -wollastonite and larnite formation (Fig. 4).

The knowledge of the structural particularities of the silica constituting the silica hydrogel has allowed to gain an insight into the process occurring in the silica hydrogel during aging.

Recall that the structure of the silica is made up of mono- $[SiO_4]$, one-, twodimensional and oligomeric silicate units bound with each other by unsaturated, i.e. comparably weak bonds that distinguishes it from all other species of traditional silicon dioxide. In spite of the fact that the Si–O(Si) bonds arisen between the silicate anions during the polycondensation are less saturated, i.e. weaker, than the primary Si–O(Si) ones intrinsic in the silicate oligomers formed in magma prior serpentinization, they must have been marginally strengthened during the silica hydrogel aging. Naturally, more energy input is required for the cutting of siloxane bonds slightly strengthened by aging and thus silicate anions releasing. As a result, the stirring time must be prolonged so as to supply this extra energy needed for the Si–O(Si) bonds weakening, thereby insuring β -wollastonite high yields.

Conclusion

These studies have shown that a new species of silica hydrogel derived from serpentine minerals can be successfully used in the system SiO_2 -CaO-H₂O as a source of silica for the development of a new route to β -wollastonite synthesis based on the heat treatment of the intermediates precipitated via stirring of the initial reagents without involving autoclave treatment and additional reagents.

The information obtained by collating the data has revealed that the stirring time and the silica hydrogel aging essentially affect the concentration of β -wollastonite in the final product. In order to guarantee the complete interaction between the SiO₂ and Ca(OH)₂ via a short-term procedure (fifteen-minute stirring) thus providing higher yields of β -CaSiO₃, the freshly synthesized silica hydrogel derived from serpentine minerals must be involved as a source of SiO₂ in the first stage of precipitation. If the aged silica hydrogel is used as a raw materal in the same system, higher yields of β -wollastonite are expected in the case of stirring time prolonging (up to 120 *min*). The Si–O(Si) bond's strength arisen between various silicate units in the silica during the polycondensation is the main factor playing a major role in the complete interaction of the silica with Ca(OH)₂. The cutting of the Si–O(Si) bonds partly strengthened by the silica hydrogel aging requires more energy that is provided by more prolonged stirring.

As can be seen from the experimental data, the investigations of aging mechanisms and their influence on the final products are quite challenging. These studies are of great interest and practical value for the further development of a new simplified technology for the low-temperature production of β -wollastonite.

ՍԵՐՊԵՆՏԻՆԱՅԻՆ ԽՄԲԻ ՄԻՆԵՐԱԼԻՑ ՍՏԱՑՎԱԾ ৲ՒԴՐՈՍԻԼԻԿԱԺԵԼԻ ԾԵՐԱՑՄԱՆ ԱԶԴԵՑՈԻԹՅՈԻՆԸ ԿԱԼՑԻՈԻՄԻ ՍԻԼԻԿԱՏԻ ԵԼՔԻ ՎՐԱ

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Ուսումնասիրվել է սերպենտինային միներալներից ((Mg(Fe)) $_6[Si_4O_{10}](OH)_8)$ առաջացած Հիդրոսիլիկաժելի և կալցիումի Հիդրօքսիդի (Ca(OH)₂) փոխազդեցուԹյունը։ Այս աշխատանքի նպատակն է ուսումնասիրել ելային նյուԹերի խառնման տևողուԹյան և Հիդրոսիլիկաժելի ծերացման ազդեցուԹյունը β-վոլաստոնիտի ելքի վրա։ Այն ստացվում է միջանկյալ նյուԹերի ջերմամշակման ընԹացքում։ Միջանկյալ նյուԹերը նստեցվել են ելանյուԹերի սուսպենդիայի մԹնոլորտային ճնչման և եռման պայմաններում։ ՈւսումնասիրուԹյունների արդյունքում ցույց է տրվել, որ վերջնական նյուԹի մեջ β-վոլաստոնիտի բաժինը փոփոխվում է կախված խառնման տևողուԹյունից և Հիդրոսիլիկաժելի ծերացումից։ Թարմ պատրաստված Հիդրոսիլիկաժելի փոխարինումը նույն Հիդրոսիլիկաժելի Հետ, որը պաՀվել է կես տարի, բերում է խառնման տևողուԹյան մեծացմանը՝ 15 րոպեից մինչև 120 րոպե, որպեսգի ստացվի մեծ ելքերով β-վոլաստոնիտ։

ВЛИЯНИЕ ПРОЦЕССА СТАРЕНИЯ В ГИДРОГЕЛЕ КРЕМЕНЗЕМА, ВЫДЕЛЕННОГО ИЗ МИНЕРАЛА ГРУППЫ СЕРПЕНТИНА, НА ВЫХОДЫ СИЛИКАТОВ КАЛЬЦИЯ

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В статье изучено взаимодействие в водной среде между гидрогелем кремнезема, выделенном из серпентиновых минералов (Mg(Fe))₆[Si₄O₁₀](OH)₈, и гидроксидом кальция Ca(OH)₂, осуществляемое посредством перемешивания при атмосферном давлении. Целью настоящего исследования являлось изучить влияние длительности перемешивания и старения гидрогеля кремнезема на выход β -волластонита, получаемого термической обработкой промежуточных соединений, которые были предварительно осаждены в кипящей водной суспензии, приготовленной из упомянутых реагентов. На основе экспериментов выявлено, что доля β -волластонита в конечном продукте варьирует и зависит от длительности перемешивания и старения гидрогеля кремнезема. Замена свежесинтезированного гидрогеля кремнезема тем же гелем, но выдержанном в течение полугода, приводит к увеличению длительности перемешивания от 15 до 120 *мин* для того, чтобы обеспечить высокие выходы β -волластонита.

REFERENCES

- Zulumyan N.O., Isaakyan A.R., Ovsepyan T.A., Kazanchyan A.M., Terzyan A.M. Method for complex processing of serpentinit. RF patent 2 407 704 C2. 2010.
- [2] Zulumyan N., Isahakyan A., Beglaryan H., Melikyan S. // J. Therm. Anal. Calorim., 2018, v. 131, №2, p. 1201.
- [3] Terzyan A.M., Melikyan S.A., Beglaryan H.A., Isahakyan A.R., Zulumyan N.H. // Chem. J. of Armenia, 2018, v. 71, №4, p. 517.
- [4] Beglaryan H.A., Melikyan S.A., Zulumyan N.H., Terzyan A.M., Isahakyan A.R. // J. Mol. Liq.; 2019, DOI: 10.1016/j.molliq.2019.111263.
- [5] Ding Q., Zhang Z., Wang C., Jiang J., Li G., Mai K. // J. Therm. Anal. Calorim., 2014, p. 115.
- [6] Morsy R., Abuelkhair R., Elnimr T. // Silicon, 2017, v. 9, No4, p. 489.
- [7] Ismail H., Shamsudin R., Abdul Hamid M.A. // Mater. Sci. Eng., C, 2016, v. 58, p. 1077.
- [8] Wu H., Yang J., Ma H.W., Wang M.W. // Integrated Ferroelectrics, 2013, v. 146, №1, p. 144.
- [9] Iswar S., Malfait W.J., Balog S., Winnefeld F., Lattuada M., Koebel M.M. // Microporous Mesoporous Mater., 2017, v. 241, p. 293.
- [10] Wijnen P.W.J.G., Beelen T.P.M., Rummens K.P.J., Saeijs H.C.P.L., van Santen R.A. // J. Appl. Crystallogr., 1991, v. 24, №5, p. 759.