

PREPARATION AND CHARACTERISATION OF ANALCIME POWDERS

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Previous studies have showed that analcime $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ is a potential precursor for the preparation of leucite – the major crystalline component of a new generation of dental porcelains having high fracture toughness. The purpose of this study was to investigate the synthesis of analcime and the effect of principal factors influencing its crystallisation. Analcime powders were prepared by hydrothermal synthesis in a Teflon lined stainless steel autoclave. The role of the gross composition of the reaction mixture (source materials, silica/alumina ratio, OH^- concentration, and water concentration), reaction temperature and time was studied.

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1. Introduction

Analcime is a zeolite (and feldspathoid) having a complex aluminosilicate framework that is common to all leucite-type feldspathoids. The framework is based on corner sharing $(\text{Al},\text{Si})\text{O}_4$ tetrahedra, arranged in fourfold, sixfold and eightfold rings. The sixfold rings are arranged axially, forming structural channels parallel to $\langle 111 \rangle$ [1]. Such a channel arrangement shows many possibilities for structural modification, including framework distortion, channel collapse, and ionic mobility.

This is due to the similarities in structure; analcime was designed as a potential precursor for the synthesis of leucite [2], essential component of composite dental material retaining high fracture toughness.

In this paper we report the synthesis of analcime in hydrothermal conditions. The attention was paid to the investigation of the reaction parameters: composition of the reaction mixture (source materials, silica/alumina ratio, OH^- concentration, and water concentration), reaction temperature and time, with the aim to enable controlling the synthesis procedure, i.e. phase composition of the reaction product, its particle size and particle size distribution.

2. Experimental

As the source materials were used amorphous silica powder (SiO_2 , Polskie Odczynniki Chemiczne Gliwice, PL), sodium hydroxide solution (NaOH , Lachema, CZ) and either metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, calcinated kaolin Sedlec Ia, CZ, at 700°C 1h) or aluminium powder (Al, Lachema, CZ). The starting sols were made up by mixing aluminate and silicate solutions, which were prepared separately by dissolving silica and aluminium sources in a sodium hydroxide solution under the permanent stirring.

Thoroughly homogenized synthesis mixtures were treated hydrothermally in a Teflon-lined stainless steel autoclave. Source materials, silica/alumina ratio, molarity of NaOH solution,

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water/silica ratio, reaction temperature and time were modified to investigate the influence of particular reaction parameters on the synthesis procedure.

After the hydrothermal treatment, the content of the autoclave was washed with boiling distilled water, vacuum filtered and dried in an oven at 100 °C.

Phase composition was identified by X-ray powder diffraction method (XRD, Philips). Particle size and their distribution were observed by optical microscopy (Olympus BX 51) and determined by image analyser (LUCIA). Particle size and morphology analysis were completed by scanning electron microscopy (SEM, Philips XL 30 CP). Energy dispersive X-ray analysis (EDAX) was used to measure chemical composition of single grains.

3. Results and discussion

Table 1. Compositions of starting sols and resulting phase compositions and particle sizes.

No.	Source materials	SiO ₂ /Al ₂ O ₃ ratio	NaOH molarity	H ₂ O/SiO ₂ ratio	Reaction time	Reaction temper.	Phase composition	Particle size
1	SiO ₂ Al	4,8	1M	16	24h	200°C	amorphous	~ 9µm
2	SiO ₂ Al	4	2M	16	24h	200°C	analcime	~ 6µm
3	SiO ₂ Al ₂ O ₃ .2SiO ₂	4	2M	16	24h	200°C	analcime	~ 7µm
4	SiO ₂ Al	4,8	2M	16	24h	200°C	analcime	~ 7µm
5	SiO ₂ Al ₂ O ₃ .2SiO ₂	4,8	2M	16	24h	200°C	analcime	~ 5µm
6	SiO ₂ Al	4,8	3M	16	24h	200°C	analcime	~ 6µm
7	SiO ₂ Al	4,8	4M	16	2h	100°C	amorphous	~ 9µm
8	SiO ₂ Al	4,8	4M	16	24h	100°C	Na _{3,6} Al _{3,6} Si _{12,4} O ₃₂ .14H ₂ O	~ 10µm
9	SiO ₂ Al	4,8	4M	16	1h	150°C	amorphous	~ 9µm
10	SiO ₂ Al	4,8	4M	16	2h	150°C	Na _{3,6} Al _{3,6} Si _{12,4} O ₃₂ .14H ₂ O	~ 10µm
11	SiO ₂ Al	4,8	4M	16	3h	150°C	analcime Na _{3,6} Al _{3,6} Si _{12,4} O ₃₂ .14H ₂ O	~ 6µm
12	SiO ₂ Al	4,8	4M	16	4h	150°C	analcime	~ 5µm
13	SiO ₂ Al	4,8	4M	16	24h	150°C	analcime	~ 5µm
14	SiO ₂ Al	4,8	4M	16	2h	200°C	analcime	~ 4µm
15	SiO ₂ Al	4	4M	12	24h	200°C	analcime	~ 6µm
16	SiO ₂ Al ₂ O ₃ .2SiO ₂	4	4M	12	24h	200°C	analcime	~ 5µm
17	SiO ₂ Al	4,8	4M	12	24h	200°C	analcime	~ 5µm
18	SiO ₂ Al	4	4M	16	24h	200°C	analcime	~ 4µm
19	SiO ₂ Al ₂ O ₃ .2SiO ₂	4	4M	16	24h	200°C	analcime	~ 5µm
20	SiO ₂ Al	4,8	4M	16	24h	200°C	analcime	~ 4µm
21	SiO ₂ Al	4,8	4M	20	24h	200°C	analcime	~ 3µm
22	SiO ₂ Al	4,8	5M	16	24h	200°C	analcime faujasite-Na	~ 3µm
23	SiO ₂ Al	4,8	6M	16	24h	200°C	faujasite-Na	~ 1µm

The compositions of starting sols, resulting phase compositions and particle sizes are listed in Table 1. Source materials, silica/alumina ratio, OH⁻ concentration, water/silica ratio, reaction temperature and time were modified to obtain the optimal conditions for the analcime synthesis and to enable controlling of the synthesis procedure.

Compositions based on SiO₂, Al and SiO₂, Al₂O₃.2SiO₂ respectively were used to follow the effect of source materials. Pairs of samples no. 2-3, 4-5, 15-16, 18-19 were compared. The results showed that both these compositions are suitable for the synthesis of analcime. Differences were observed only in the morphology of the analcime particles. While using SiO₂ and Al as source materials, homogenous product formed of spherical particles of the uniform size was obtained (Fig. 1-A). On the other hand in samples prepared from SiO₂ and Al₂O₃.2SiO₂ two forms of particles – spherical and cubical, were observed (Fig. 1-B).

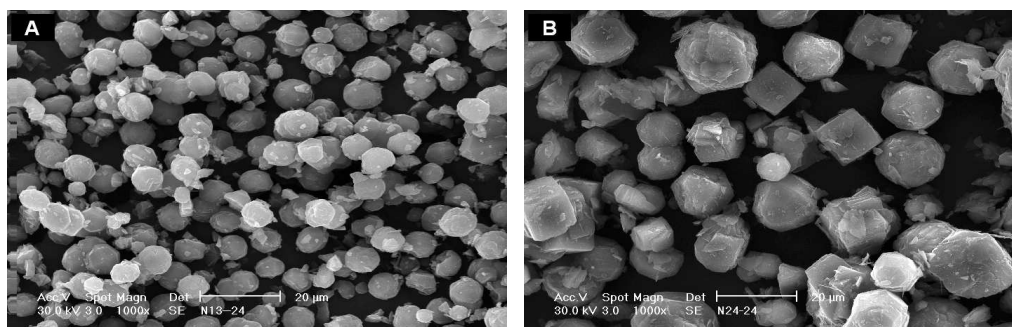


Fig. 1. SEM images of analcime grains – A: prepared from SiO₂, Al, - B: SiO₂, Al₂O₃.2SiO₂.

Silica/alumina ratio has an influence especially on the phase composition of reaction product. However rates of 4 and 4,8 reported in this paper were both found suitable for the synthesis of analcime.

The role of initial molarity of sodium hydroxide solution was monitored in samples no. 1, 4, 6, 20, 22 and 23. From the results it is perceptible that NaOH molarity significantly effects both phase composition and particle size of the resulting product. It was proved that the particle size decreases with increasing molarity of the solution. Fig. 1 represents XRD spectra of above-mentioned samples, i.e. spectrum of amorphous substance prepared from 1M NaOH, next of analcime synthesized from 2-4M NaOH, in the sample using 5M NaOH two different crystalline phases were identified – analcime, faujasite-Na (Na₁₄Al₁₂Si₁₃O₅₁·6H₂O), and the last is the spectrum of faujasite-Na prepared from 6M NaOH.

Water/silica ratio in the entering reaction mixture was found to influence resulting particle size – the higher H₂O/SiO₂ ratio gives rise to smaller particles.

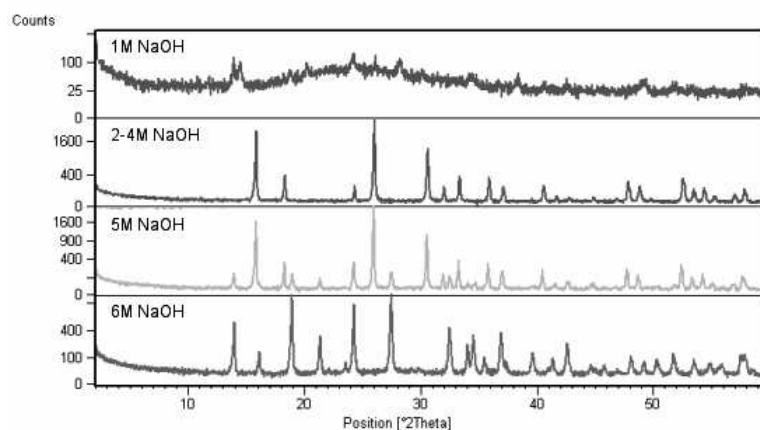


Fig. 2. XRD of samples no. 1, 4, 6, 20, 22, 23 illustrating the role of NaOH molarity in the synthesis.

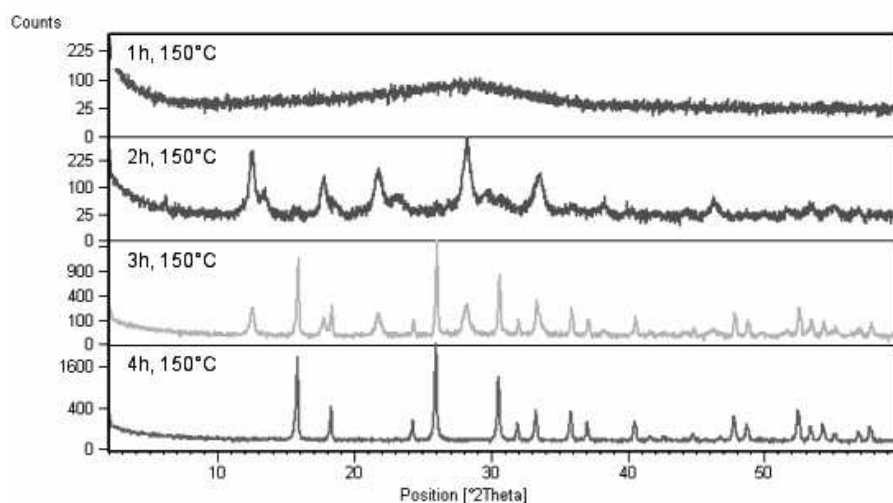


Fig. 3. XRD spectra of samples no. 9, 10, 11, 12, representing crystallization process at 150 °C.

Long reaction time as well as higher temperature enhances the analcime crystallisation. At temperature of 200 °C only two hours were required to synthesize pure analcime. On the other hand at 150 °C required reaction time was four hours and at 100 °C crystallization of analcime was not observed even after 24 hours. Fig. 3 illustrates crystallization process at temperature of 150 °C. After one-hour treatment no crystalline phase was identified in the reaction product. As the first arose zeolite P – sodium aluminium silicate hydrate ($\text{Na}_{3,6}\text{Al}_{3,6}\text{Si}_{12,4}\text{O}_{32}\cdot 14\text{H}_2\text{O}$). This metastable phase later gradually dissolved and analcime started to crystallize. After four hours of the hydrothermal reaction only analcime was presented in the product.

In terms of particle size, it was observed that the particle size increases with increasing reaction time and decreasing temperature.

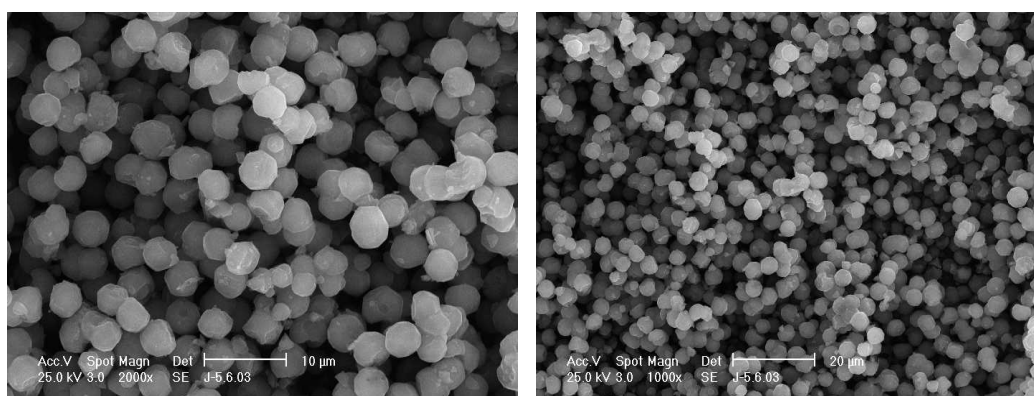


Fig. 4. SEM images of analcime grains prepared by 2h hydrothermal synthesis at 200 °C.

4. Conclusions

Analcime powders were prepared by hydrothermal synthesis in a Teflon lined stainless steel autoclave. Results of this investigation showed that all the studied variables: composition of the reaction mixture (source materials, silica/alumina ratio, OH^- concentration, and water concentration), reaction temperature and time, have substantial effect on results of the hydrothermal synthesis. The

choice of source materials and silica/alumina ratio effects especially phase composition and homogeneity of the reaction product. Initial molarity of sodium hydroxide solution significantly effects both phase composition and particle size. It was proved that the particle size decreases with increasing molarity of the NaOH solution and water/silica ratio. Long reaction time as well as higher temperature enhances the analcime crystallisation. The particle size increases with time and decreasing temperature.

Detailed investigation of the reaction variables made possible to control the synthesis of analcime, i.e. phase composition of the reaction product, its particle size and particle size distribution. On account of this knowledge we were able to prepare homogenous analcime powders (Fig.4) with the particle size of 2 μm being a suitable precursor for the synthesis of leucite.

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