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The synthesis of hydrosodalite and its use in mortar technology

V. SASNAUSKAS, D. PALUBINSKAITĖ*

Faculty of Chemical Technology, Kaunas University of Technology,
Radvilėnų str. 19, 50254 Kaunas, Lithuania

Conditions for the low-temperature hydrothermal synthesis of zeolites from AlF_3 production waste – technogenic silica gel polluted with admixtures of fluorides – were analysed. It was determined that an AlF_3 admixture encourages the formation of hydrosodalite. When using technogenic silica gel, crystal zeolite – hydrosodalite was synthesised. The reaction was conducted under hydrothermal conditions and atmospheric pressure (90 °C for 0.5, 1, and 2 hours). The best molar ratio of the components Na_2O, Al_2O_3, SiO_2, H_2O was 2 : 0,02 : 1 : 10. Lignosulphonic plasticiser (LST) was modified with synthesised hydrosodalite. The binding duration of cement paste of normal consistence with modified LST plasticiser decreased up to 40/395 min. (at 0.25% content of admixture) and 80/150 min. (0.75%) as compared to that of unmodified mortar, for which the binding duration was 65/475 min. (0.25%) and 105/150 min. (0.75%). A larger compression strength was obtained for cement grout with modified LST plasticiser after 3, 7, and 28 days of hardening – 12.61; 21.52; 25.49 MPa (at 0.25% content of the addition) as compared to that off mortar with non-modified LST plasticiser – 6.04; 9.63; 22.69 MPa.

Key words: *hydrosodalite; lignosulphonic plasticiser; mortar*

1. Introduction

Hydrosodalite belongs to the group of zeolites, widely spread natural minerals. In comparison to natural zeolites, however, the synthetic ones are better suitable for research and better meet the requirements of industry due to their purity and homogeneity. Natural zeolites are practically not used for these purposes. As a rule, they are polluted with extraneous minerals, and it is difficult to prepare adsorbent granules of corresponding sizes, since it is impossible to control the diameter of the pores within natural zeolites. On the other hand, in agriculture natural zeolites are widely applied to improve soil structure [1–3].

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[*] Corresponding author e-mail: danute.palubinskaite@ktu.lt

Synthetic zeolites are obtained by heating suspensions of alkaline alumosilicate mixtures composed of SiO_2, Al_2O_3, alkali and water. They may be synthesised from amorphous or crystalline materials, alumosilicate gels of alkaline metals, and from clays. The initial formation of zeolite structure occurs only in the presence of water. Under hydrothermal conditions in alkaline alumosilicate suspensions (R_2O–SiO_2–Al_2O_3–H_2O) and at a certain temperature, the crystallization of zeolites depends not only on the ratios and concentrations of components but also on their nature and state, the conditions of preparation, mixing, the initiation of crystallization, and other properties of the reagents forming the initial alumosilicate mixtures [4, 5]. The reactants for the synthesis of zeolites are gels or solid amorphous substances. The reactions proceed at high pH values, since hydroxides of alkaline metals or other strong bases are used, at low temperatures and autoclave pressures of saturated water vapour.

The properties of zeolites and possibilities for their application have been examined in numerous branches of science and, in fact, all fields of chemical technology. They are efficient catalysts in many organic and inorganic chemistry reactions. Zeolites are also used for cleaning harmful atmospheric pollutants. Upon harmonizing the cleaning and drying processes in one-phase gaseous adsorptive processes, the treatment of emitted gas is simplified. By heating zeolites within a certain interval of temperatures it is possible to remove (reversibly) the constitutional water while not destroying the frame. Channels and cavities appear within the structure, therefore zeolites are used as molecular sieves and filters in adsorptive processes [6–8].

The synthesis of low-temperature zeolites is presented in the paper. In this synthesis it is possible to use technogenic AlF_3 production waste aggressive to the environment instead of reagent silica gel. Amorphous SiO_2 is the basis of such a raw material. In the Kėdainiai chemical plant Lifosa, several thousand tons accumulate each year.

Lignosulphonates (LST) are most widely used as hydrophilic-plasticifying admixtures in mortar technology. Their presence in cement-water suspensions predetermines the slowdown of the hardening of the mineral-binding agents in the initial period of hydration. In order to decrease the slowing impact of technical lignosulphonates on cement hydration, they are modified. As a rule, this plasticifying admixture is used in fat mortar or concrete mixtures, i.e. in mixtures with a large content of binding agents [9–11].

The principle of activity of zeolites as molecular sieves was applied to modify the LST plasticiser. This paper analyses the impact of modified LST plasticisers on the water content in cement paste of normal consistence, duration of cement paste binding, technological qualities of mortar, and the density and strength of hardened mortar.

The aim of this paper is to investigate the possibilities and conditions of synthesising zeolites from AlF_3 production waste of Lifosa, which is polluted with admixtures of fluoride compounds. After performing the synthesis of synthetic zeolite – hydrosodalite, there exists a possibility of using it for to modify technical lignosulfonatic (LST) plasticisers.

2. Experimental

AlF_3 production waste was used as the source of SiO_2 and Al^{3+}. By chemical analysis, the following content of AlF_3 waste-silicagel was determined:

I) H_2O, 70.24%; SiO_2, 93.6%; Al_2O_3, 2.88%; Fe_2O_3, 1.78%; CaO, 1.49%; F, 0.25%.

II) H_2O, 73.46%; SiO_2, 93.10%; Al_2O_3, 2.11%; CaO, 1.68%; Fe_2O_3, 2.10%; F, 1.01%.

Solutions of NaOH were also applied as well as portland cement CEM I 42.5; plasticiser LST, plasticiser LST modified with hydrosodalite; sand (coarseness module MS = 2.11, apparent density $\rho_p = 1.540$ kg/m^3).

X-ray diffraction analyses have been conducted using a DRON-6 diffractometer. The investigation was carried out with the 2Θ angle range of 4–60, with Ni-filtered CuK_α radiation. Thermographic analyses were conducted with a differential scanning calorimeter Du-Pont 990. The maximum temperature was 1000 °C, and the temperature increase velocity was 10 ^{o}/min. IR spectrograms were recorded with a specord M-80 (C. Zeiss Jena), and the source of light was a Ni-Cr electrode.

The hydrothermal crystallization of sodium-bearing zeolites was carried out using alkali alumosilicate mixtures. A calculated amount of technogenic silica gel was added to caustic soda dissolved in the required amount of water. Low-temperature (90 °C) crystallization occurred in glass vessels resistant to alkali put into thermostats. The obtained suspension was poured into the vessel and mixed (60 r/min). The crystallization lasted for 1, 2 or 3 hours. Upon the end of crystallization the precipitates were filtered. Apart from the main product, the admixture of sodium fluoride (NaF) formed up, which was washed away with distilled water. The obtained products of synthesis were dried at the temperature of 100 °C.

3. Results and discussion

3.1. Synthesis of hydrosodalite

It is more economical to synthesize hydrosodalite from technogenic raw materials than to synthesize it from reagents. Different contents of sodium oxide (0.5, 1, 2, and 3 mol) were used to determine the best conditions of crystallization. A constant amount of silica gel was used. In the technogenical silica gel, the fluorine content was 12 mol.

In accordance with X-ray diffraction analysis in the specimen whose initial mixtures contained 0,5 mol sodium oxide, non-reacting amorphous SiO_2 was predominant after 3 hours of crystallization, irrespective of the amount of water used. In the specimen where Na_2O content amounted to 2 or 3 mol, hydrosodalite crystallized after one hour; water amount did not have a major impact on the synthesis of the product. When using 1 mol Na_2O and 20 or 30 mol water, non-reacting amorphous SiO_2 was predominant in the products of the reaction. Upon reducing water content down to 10 mol, however, hydrosodalite (Fig. 1) crystallized. The peaks typical of hydrosodalite were: 0.365; 0.628; 0.256; 0.290; 0.210; 0.175; 0.158 nm. This can be explained by the conditions of hydrosodalite crystallization.

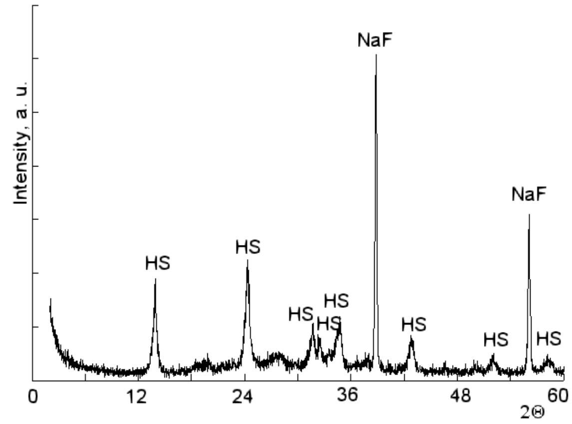

Fig. 1. The X–ray pattern of the specimen synthesised at 90 °C for 1 hour. The initial molar ratio of Na_2O : Al_2O_3 : SiO_2 : H_2O was 2 : 0.02 : 1 : 10. The hydrosodalite (HS) and sodium fluoride admixture formed up

Table 1. The synthesis of low-temperature hydrosodalite by using AlF_3 production waste

No.	Molar ratio Na_2O : Al_2O_3 : SiO_2 : H_2O	Conditions of synthesis		Product of synthesis
		t, °C	τ, h	
1	1 : 0.026 : 1 : 30	90	1	amorph.
2	2 : 0.026 : 1 : 30	90	1	HS
3	1 : 0.026 : 1 : 30	90	2	amorph.
4	2 : 0.026 : 1 : 30	90	2	HS
5	1 : 0.026 : 1 : 20	90	1	amorph
6	2 : 0.026 : 1 : 20	90	1	HS
7	1 : 0.026 : 1 : 20	90	2	amorph
8	2 : 0.026 : 1 : 20	90	2	HS
9	1 : 0.026 : 1 : 10	90	1	HS
10	2 : 0.026 : 1 : 10	90	1	HS
11	1 : 0.026 : 1 : 10	90	2	HS
12	2 : 0.026 : 1 : 10	90	2	HS
13	2 : 0.026 : 1 : 10	90	1	HS
14	2 : 0.026 : 1 : 30	90	0.5	HS
15	2 : 0.018 : 1 : 10	90	1	HS

With 2 and 3 moles of Na_2O, hydrosodalite formed up when using different amounts of water (10, 20, and 30 moles). The results are given in Table 1.

The effect of fluorides is explained by the fact that when the components containing an active admixture of fluorides having a mineralising effect, react within the system of sodium alumosilicagel, HF associates with water (H_2O+ HF = H_3O^+ + F^-) and hydrogen bonds are formed: H_2F_2, H–F… H–F (for ions : HF_2, F^-… H – F), and complexes of fluorine silicates form up in the alkali medium [5]. Similar results (Table 1 No. 15) were obtained when using a silica gel of (II) composition for synthesis.

The obtained synthetic zeolites were investigated by IR spectroscopy. Based on this research method it is possible to decide about the structure of the zeolite (X-ray characteristics are insufficient), the way water molecules are associated with cations, oxygen ions, and other hydroxyl groups.

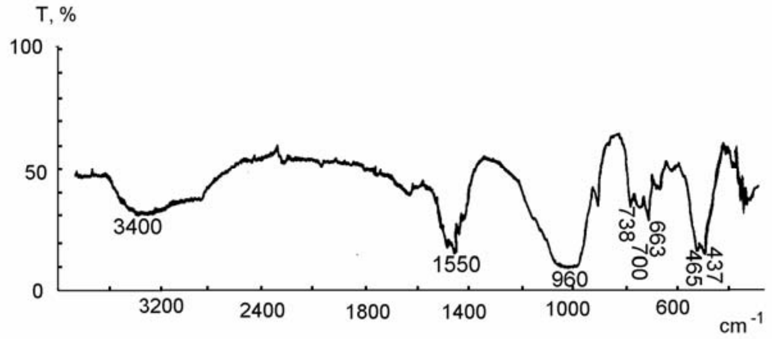

Fig. 2. IR spectra of the specimen synthesised at 90 °C for 2 hours.
The initial molar ratio of Na_2O : Al_2O_3 : SiO : H_2O was 3 : 0.026 : 1 : 30

IR spectra testify the predominance of hydrosodalite in the products of the reaction. The absorption bands characteristic of hydrosodalite are: 960 cm^{-1} within the ranges of asymmetrical stretching vibrations, 738, 700, and 663 cm^{-1} within the ranges of symmetric stretching vibrations, and 465 and 437 cm^{-1} Si(Al) within the ranges of O deformation fluctuations.

Absorption bands located in the 3400 cm^{-1} area are observed in the IR spectra, which can be ascribed to the vibrations of OH hydroxyl groups interconnected by hydrogen bonds. Absorption bands in the 1550 cm^{-1} range show deformation fluctuations of simple water molecules. No isolated OH groups connected with hydrogen bonds were detected in hydrosodalite since the absorption band at 3700 cm^{-1} has not been observed (Fig. 2).

The obtained products of synthesis were analysed thermographically. As a rule, the emission of water from zeolites ends between 300 and 400 °C. The exothermal point, fixed at 667 °C, reflects the transformation of dehydrated zeolite into anhydrous alumosilicate (Fig. 3). After a partial dehydration, water molecules shift to positions where they are more firmly bound with the (Si, Al, O) frame [4]. DTA curves and other physical and chemical methods confirm the predominance of hydrosodalite with an NaF admixture in the products of the reactions.

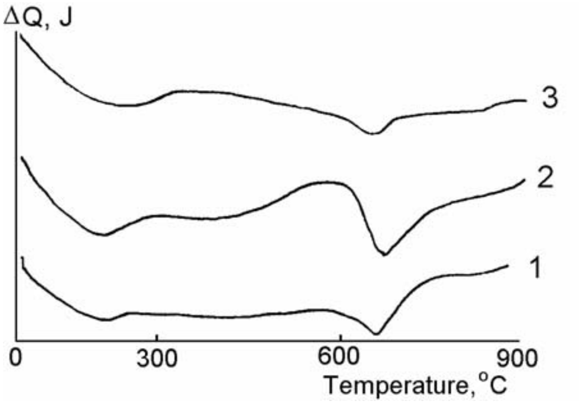

Fig. 3. Thermograms of specimen synthesised at 90 °C. Initial substances: technogenical silica gel and NaOH. The initial molar ratio of $Na_2O : Al_2O_3 : SiO_2 : H_2O$ 1 – 2 : 0,026 : 1 : 20; $\tau = 2$ h; 2 – 2 : 0,026 : 1 : 30; $\tau = 3$ h; 3 – 2 : 0,026 : 1 : 30; $\tau = 1$ h

3.2. Modification of the LST plastifying admixture with synthesized hydrosodalite

In this part of the research, we have analysed the efficiency of the LST plastifying admixture modified with synthetic hydrosodalite on the hydration processes of cement paste and mortar. An anhydrous non-modified admixture of lignosulfonic plasticiser was used. In comparison to cement mortar with unmodified LST plasticiser, the duration of binding of cement mortar modified with LST plasticiser of normal density becomes shorter (Table 2).

The lignosulphonates introduced into cement mortar change the rate and intensity of hydration of cement clinker minerals as well as the crystalline structures of newly formed elements. Also, they influence the temporal and final strength of cement stone. The ability of dispergation and drawing air by lignosulphonates depends on the surface tension at the liquid–air interface. The surface tension of water solutions of lignosulphonates depends on their molecular mass and cation valence. Hence, bearing in mind these regularities, it is feasible to change the lignosulphonate properties that determine their polymolecular structure and valence.

The modification of lignosulfonic plasticiser was performed in three ways under normal conditions: by filtering LST plasticiser via a respective layer of synthesized hydrosodalite, by filtering plasticiser via a hydrosodalite layer in a vacuum filter, or by mixing hydrosodalite with plasticiser and, after a certain time, separating the hydrous solution of plasticiser by decanting. The synthesized hydrosodalite adsorbed reducing substances when large molecules or sugary substances were present in the lignosulfonic plasticiser (hydrogen, organic acids, and related compounds). Owing to this, the slowing effect of technical lignosulfonates on the hydration processes of cement minerals decreased.

Table 2. Initial and final durations of binding of normal density cement paste

No.	Additives	The amount of additive, %	W/C	The duration of binding, min	
				Initial	Final
1	Without additives	–	25.0	240	330
2	LST unmodified	0.25	22.1	65	475
		0.75	21.7	105	150
3	LST mod. self flowing	0.25	22.1	45	420
		0.75	21.7	100	150
4	LST mod. vacuum filtering	0.25	22.1	50	415
		0.75	21.7	90	150
5	LST mod. adsorption	0.25	22.1	40	395
		0.75	21.7	80	150
6	Plastiment BV 60	0.25	23.1	30	340
		0.75	21.9	75	290

The effect of unmodified and modified LST plasticisers on the duration of cement paste binding beginning and binding end was investigated; for the sake of comparison, the binding durations with commercial plastifying admixtures applied in mortar technology (from the companies Sika and MC Bauchemie) were determined. The amount of plasticiser was 0.25% (calculating dry substances), 0.75% from cement mass. The results are presented in Table 2.

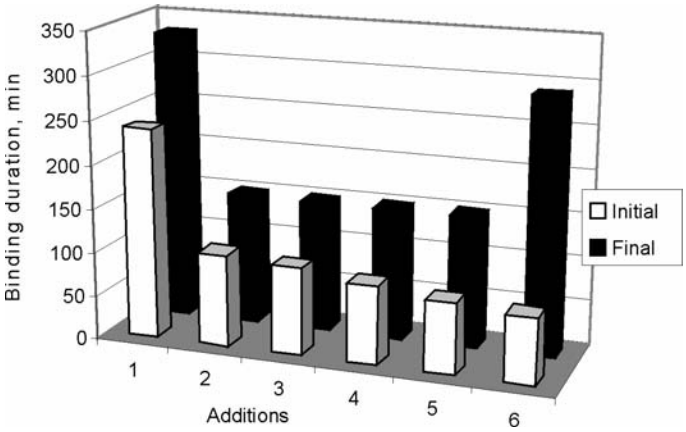

Fig. 4. Binding durations of cement slurry of normal consistence. Different admixtures were used (0.75 % from cement mass): 1 – without admixtures; 2 – LST unmodified; 3 – LST modified by discharge; 4 – LST modified by vacuum dessication; 5 – LST modified by adsorption; 6 – plastiment BV 60

When modified LST plasticiser was used, the binding duration of Portland cement decreased (Fig. 4). Consequently, the slowing effect of modified LST plasticiser on the hydration process of cement paste and mortar is lower than that of non-modified lignosulfonatic plasticiser at the same admixture content.

The strength qualities were determined, i.e. densities and compression strengths after 3, 7, and 28 days of mortar hardening with unmodified and modified LST plasticifying admixtures (Fig. 5).

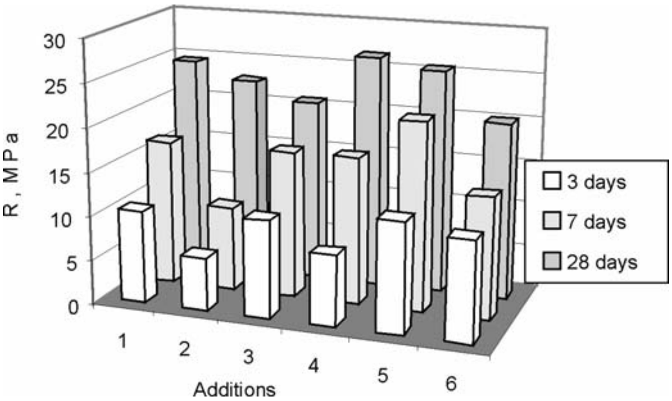

Fig. 5. Strength characteristics of normal consistence cement grout. Various admixtures were used (0.25 % from cement mass): 1 – without admixtures; 2 – LST unmodified; 3 – LST modified by discharge; 4 – LST modified by vacuum dessication; 5 – LST modified by adsorption; 6 – plastiment BV 60

The compression strength of mortar specimens after 3, 7, and 28 days of hardening, with LST plasticiser, when its content accounts for 0.2% of the cement mass, was larger than for specimen with unmodified LST plasticiser (Fig. 5). The strength characteristics of mortar specimens with modified LST plasticiser as compared specimens with plasticifying Plastiment BV 60 and Muraplast NN (FM) admixtures are similar. Therefore, research findings allow us to draw the conclusion that the zeolite way of modifying lignosulfonatic mortar plasticisers is perspective.

4. Conclusions

AlF_3 admixture stimulates the formation of hydrosodalite. When using technogenic silica gel, crystal zeolite – hydrosodalite has been synthesized. The reaction was performed under atmospheric pressure at the temperature of 90 °C for 0.5, 1 and 2 h. The molar ratio of $Na_2O : Al_2O_3 : SiO_2 : H_2O$ was (1–3): 0.026: 1 : (10–30). The best molar ratio was 2 : 0.02 : 1 : 10.

LST plasticiser was modified with synthesized hydrosodalite. The binding duration of normal consistence cement paste with modified LST plasticiser decreased up to 40/395 min. (at 0.25% content of admixture) and 80/150 min. (0.75%), as compared to cement paste with unmodified LST plasticiser, for which binding durations were 65/475 min. (0.25%) and 105/150 min. (0.75%).

Higher compression strengths for mortar with modified LST plasticiser after 3, 7, and 28 days of hardening were obtained: 12.61, 21.52, 25.49 MPa (at 0.25% content of admixture), as compared to those of mortar with unmodified LST plasticiser (the compression strengths of these were: 6.04, 9.63, 22.69 MPa).

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