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Peculiarities of hydration of cement paste with addition of hydrosodalite

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A synthetic zeolite – hydrosodalite was used as a hydraulic additive for hardened cement paste, and the influence of this additive on the hydration and other properties of the system was determined. Hydraulic activity of zeolite has been examined, X-ray diffraction, DTA and IR analysis of the hardened cement paste with zeolite additive have been carried out. The results have shown that the additive has a high hydraulic activity (the content of bound CaO – 370 mg/g). The addition of hydrosodalite reduces the content of $Ca(OH)_2$ in hardened cement paste which transforms into calcium zeolite – gismundite. The density of the hardened cement paste with the addition of hydrosodalite after 3, 7 and 28 days of curing decreases by about 11%. This predetermines a decrease in the compressive strength of the hardened cement paste. The compressive strength after 3 days of curing decreases by about 70%, after 7 days of curing – by 66%, and after 28 days of curing – by about 65%.

Key words: *hydrosodalite; hydraulic activity; hardened cement paste*

1. Introduction

Puzzolanic additives, micro silica, fly ash and other substances have been used in Portland cement mortars and concretes for a long time. Micro silica and fly ash similar to other puzzolanic substances can improve the strength of concrete when $Ca(OH)_2$ reacts with puzzolans. Zeolites are alkaline and ground alkaline metal hydroaliumosilicates and contain large amounts of active SiO_2 and Al_2O_3. This investigation was carried out to estimate the influence of zeolites on the hydration process and the properties of hardened cement paste.

Investigations of Canpolat, Yilmaz and Köse show that natural zeolites behave like other puzzolanic substances in cement paste and improve concrete strength. Zeo-

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lites also encourage the origination of such undesirable compounds as alkalis and other complex compounds [1].

The influence of mineral admixture on the compressive strength of concrete containing natural zeolite and powdered inorganic substances were investigated by Feng, Yang and Zu [2]. Upon blending 450 kg/m^3 of Portland cement with 50 kg/m^3 of this mineral additive, the concrete showed a compressive strength of 80 MPa and upon addition of 500 kg/m^3 of Portland cement – 70 MPa. Using such mineral additive (5–10% of cement content) together with superplasticizer at $W/C = 0.31–0.35$, the concrete strength increased by 10–15%. Super-high-strength concrete can be obtained by adding some zeolites to cement, by shortening the time of hydration of cement, so that the concrete shows higher initial compressive strength. Zeolites and cement can undergo the Puzzolanic reaction which results in less void content and higher final compressive strength, so a super high strength concrete is obtained [3]. Antimicrobial cement compositions have many dental applications, including fillers, adhesives, and medical applications such as bone cements, implant components and substitutes. A particularly preferred cement is an antimicrobial glass ionomer cement composition for dental use, comprising a polyelectrolyte, glass ionomer particles, and antimicrobial zeolite particles [4]. The acidic resistance of mortars made from blended cement with 35% by weight of zeolite and zeolite sand as well as Portland cement mortar attacked for 365 days by 0.5%, 1.0% and 1.5% solution of hydrochloridic acid was studied by Janotka. The result shows that zeolite increases acid resistance of cement. Zeolite sand neutralizes HCl solutions, thus contributing to the increased acidic resistance of zeolite mortar [5, 6]. Addition of zeolite to Portland cement contributes to the significant decrease of the arising solids volume and evident elimination of damaging expansion relative to that of alone Portland cement when exposed to the sulphate solution [7].

Zeolites have low bulk densities and high porosities. Natural zeolites can be used to prepare lightweight concrete for construction. Natural zeolite has a high ion exchange capacity and a particular affinity of cations. It can absorb, e.g., strontium 90, cesium 137, and other isotopes from solution, and hold them in the crystal frame. The adsorption, cation exchange, biotechnical properties of zeolitic materials can be used for new materials with special properties [8]. Hydrosodalite, as a hydraulic admixture to Portland cement, was used in our investigation. The basic formula of hydrosodalite is $Na_{6+x}(SiAlO_4)_6(OH)_x\cdot nH_2O$. This synthetic zeolite was obtained through low-temperature synthesis (under 100 °C). The aim of the work was to determine the influence of addition of hydrosodalite on hydration processes and microstructures of hardened cement paste.

2. Materials and methods

Pure reagents have been used for analysis of hydrosodalite synthesis: silicagel $SiO_2\cdot nH_2O$ (loss on ignition – 23.5%, SiO_2 – 76.5%); $Al(OH)_3$; NaOH and water. Portland cement CEM I 42.5 R and superplasticizer Rebaflow 202 (FM) on the basis of polycarboxylate resins were used for the preparation of cement pastes. *W*/*C* ratio of cement paste was 0.38 in all mixtures. The addition of superplasticizer into cement paste accounted for 2.0% of the cement mass in all mixtures. Cement was blended with powdered hydrosodalite (5–15% of the cement mass) and mixed with an appropriate amount of water to obtain a paste. The X-ray diffraction analysis was conducted using DRON-6 diffractometer (2Θ angle 4–60°, Ni-filtered CuK_α radiation). The degree of hydration was determined based on specimen mass losses on ignition and the ratio of the water requirement for fully hydrated hardened cement paste. Thermographic investigations have been carried out using a differential scanning calorimeter STA 409 PC (Netzsch). Maximum temperature was 1500 °C, and the rate of temperature increase was 10 °C/min. The products of hydration were investigated with the scanning electronic microscope JSM–5600 (JEOL). The electron emitter of the microscope (cathode) was made of wolfram, the resolution power was 3.5 nm, enlargement 18–300000×, voltage accelerating electron flux was 0.5–30 kV.

The consistency of the paste was determined using Suttard viscometer. The density and compressive strength of cubes of hardened cement paste ($20\times20\times20$ mm^3) were tested 3, 7 and 28 days after preparation.

3. Results and discussions

The consistency of cement pastes is presented in Table 1. With the increasing content of hydrosodalite, the fluidity of cement paste decreases which may be explained by high surface area and porosity of the hydrosodalite additive.

Table 1. The consistency of cement pastes with various contents of hydrosodalite

Content of hydrosodalite [%]	Consistency of cement paste [mm]
0	28
5	24
10	15
15	9

The X-ray diffraction patterns of hydrosodalite are given in Fig. 1 (lower curve). First, hydraulic activity of hydrosodalite was determined. X-ray diffraction patterns of hydrosodalite after chemisorption of CaO from saturated $\mathrm{Ca(OH)_2}$ solution are also shown in Fig. 1 (upper curve).

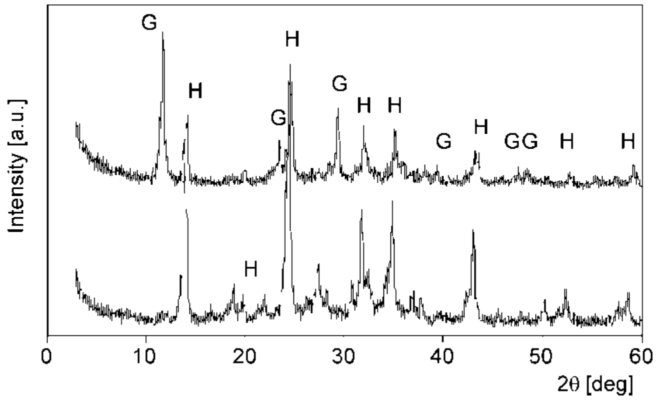

Fig. 1. X-ray diffraction patterns of hydrosodalite: lower curve – pure hydrosodalite; upper curve – after hydraulic activity test; G – gismundite, H – hydrosodalite

After 28-day chemisorption, a part of hydrosodalite reacted with the $Ca(OH)_2$ contained in water and was transformed into calcium zeolite – gismundite ($CaAl_2Si_2O_8 \cdot 4H_2O$), which formed hydrosodalite upon replacement of Na with Ca. In this case, an ion exchange typical of zeolites takes place [9]. It was also established that during chemisorption the volume of the solid phase (volume of deposits) increases nearly 4 times. Volume expansion may have a negative effect on the strength of the hardened cement paste. Volume expansion was also noticed when zeolites were formed in cement hardened paste [9]. Hydrosodalite under investigation has a fairly high hydraulic activity (370 mg/g), higher than that of opoca (281 mg/g) and microsilica (352 mg/g) but lower than that of tripolite (401 mg/g) [10] rather due to the presence of SiO_2 and Al_2O_3 than the content of SiO_2 or specific surface.

The investigation of X-ray diffraction patterns of hardened cement paste with hydrosodalite admixture shows that when the content of hydrosodalite increases from 0 to 15%, the content of $Ca(OH)_2$ in the mineralogical composition of hardened cement paste decreases. $Ca(OH)_2$ peaks of 0.493 nm interplane distances in Fig. 2 are more intensive without hydrosodalite admixture, and when hydrosodalite is added (5, 10 or 15%), lower intensities of the peaks are observed (Fig. 2b).

Upon increasing duration of curing (Fig. 2, curves 1 and 2), the content of $Ca(OH)_2$ rises, and more $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ converts into calcium hydrosilicate and calcium hydroxide. This tendency is still more distinct when the specimens are steam-cured in a steam-curing chamber (Fig. 2a, curve 3).

When 5 and 10% of hydrosodalite was added to the hardened cement paste, the X-ray diffraction patterns of the hydration products did not reveal the presence of the mentioned additive but part of the non-reacted hydrosodalite remains after 3, 7 and 28 days of curing when using 15% of hydrosodalite. After steam-curing, hydrosodalite reacted and the X-ray diffraction patterns did not show any peaks of hydrosodalite (Fig. 2b, curve 3).

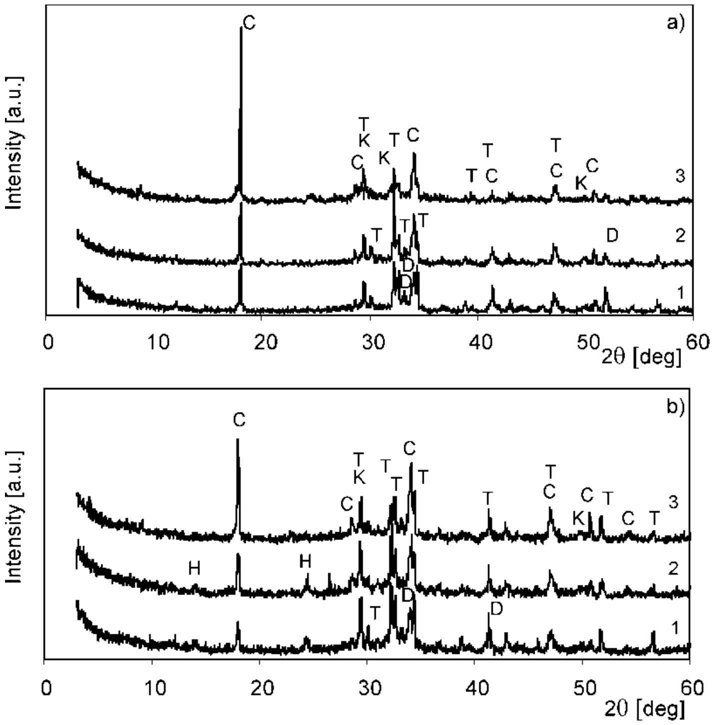

Fig. 2. X-ray diffraction patterns of hardened cement paste with 0% (a) and 15% (b) of hydrosodalite: 1 – after 3 days; 2 – after 28 days; 3 – after steam curing at 90 °C for 24h; C – $Ca(OH)_2$; T – $3CaO \cdot SiO_2$; K – C–S–H(II); D – $2CaO \cdot SiO_2$; H – hydrosodalite

The secondary processes take place among the clinker hydration products and hydraulic admixtures. First of all this is the reaction between $Ca(OH)_2$ and hydrosodalite. Hydrosodalite reacts with $Ca(OH)_2$ and passes into gismundite. In the X-ray diffraction patterns, it is difficult to identify the peaks typical of gismundite because hydrosodalite was blended into the mix as admixture (up to 15% of cement mass) and the peaks of other main compounds cover the peaks characteristic of this mineral. At typical conditions and a typical temperature, the C–S–H(I) type compound $(0.8\text{-}1.5)CaO–SiO_2–(0.5\text{-}2.5)H_2O$ is formed and its basicity depends on the concentration of $Ca(OH)_2$ in the liquid medium. After hydrosodalite reacts with $Ca(OH)_2$, NaOH is released and alkali, which reduce the concentration of $Ca(OH)_2$, emerge in the liquid phase. The most frequent compound is $3CaO \cdot 2SiO_2 \cdot 3H_2O$ ($C_3S_2H_3$) which depends on C-S-H(II) type for calcium hydrosilicates. Taking into consideration the fact that the structures of calcium hydrosilicates are similar to the structure of natural tobermorite $5CaO \cdot 6SiO_2 \cdot 5H_2O$ ($C_5S_6H_5$), they are called minerals of the tobermorite group.

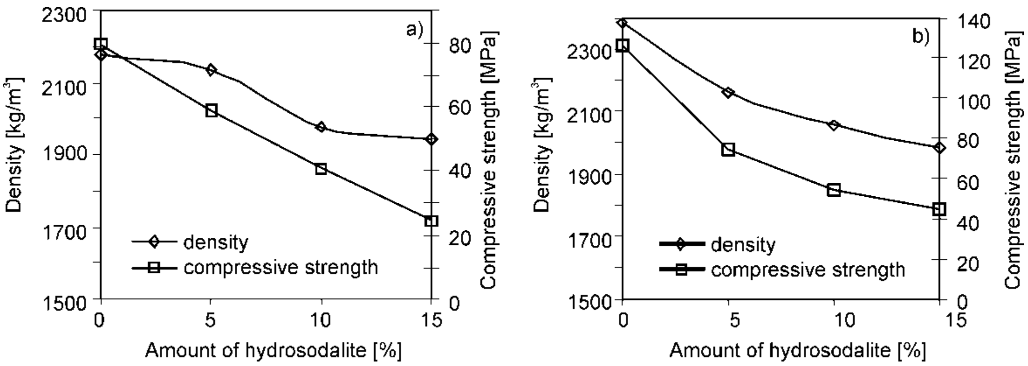

Fig. 3. Dependence of density and compressive strength of hardened cement paste on the additive amount after 3 days (a) and after 28 days (b)

The density and compressive strength of hardened cement paste decreases with increasing hydrosodalite amount (Fig. 3). The density of hardened cement paste after 3–7 days of curing decreases from 2160–2180 kg/m^3 to 1920–1950 kg/m^3, i.e. by about 11% (Fig. 3a). The density decreases proportionally to the content of hydrosodalite. This determines a decrease in the compressive strength of the hardened cement paste. After 3 days of curing it decreases by about 70%; after 7 days of curing – 66% and after 28 days of curing – about 65% (Fig. 3b).

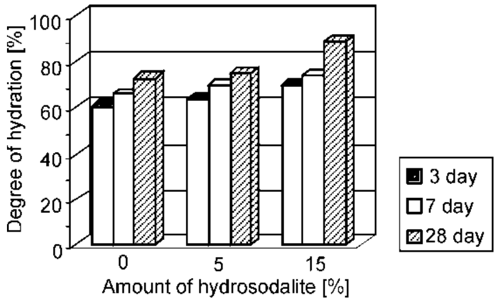

Fig. 4. Influence of additive amount on the hydration degree of hardened cement paste

The degree of cement hydration increases when the content of hydrosodalite increases (Fig. 4) but the strength of hardened cement paste decreases (Fig. 3b). The reduction of the strength of hardened cement paste is caused by different microstructure of the hardened cement paste but not by the retardation of cement hydration process.

Microscope inspection of the hardened cement paste was carried out, revealing large hexagonal crystals of calcium hydroxide and their adhesions in hardened cement paste without hydrosodalite (Fig. 5a). Upon the addition of 15% of hydrosodalite, smaller hexagonal crystals of calcium hydroxide, which are more distant from one another, as well as larger amount of amorphous mass, are obtained (Fig. 5b). Multimineral products of cement hydration are nearly amorphous compounds forming from C–S-H needles and their network, and the gaps are filled with the substance of undefined structure as well as with $Ca(OH)_2$ crystals and non-hydrated cement phases. A disordered arrangement of these structures is observed.

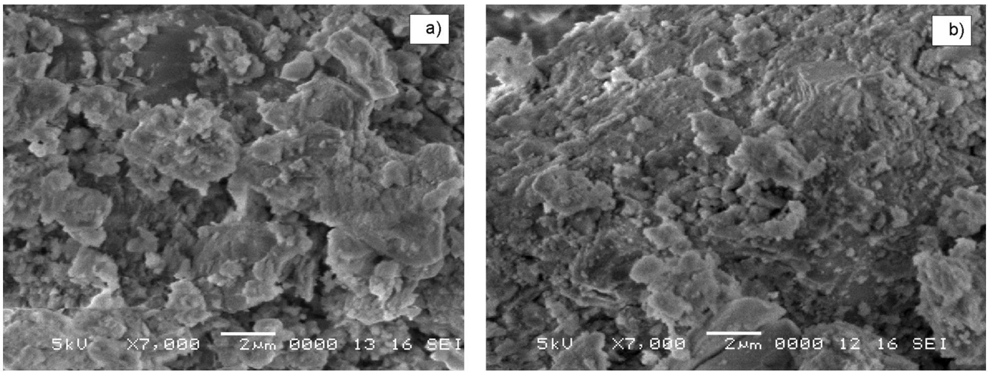

Fig. 5. Microscope photos: hardened cement paste without hydrosodalite (a) and hardened cement paste with 15% of hydrosodalite (b)

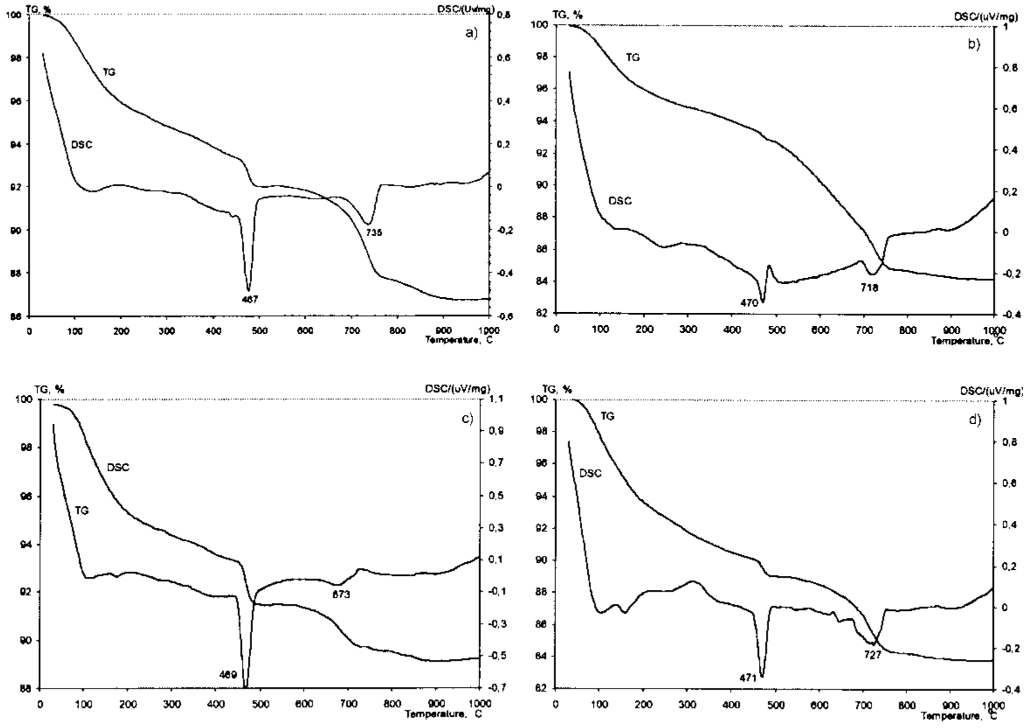

Fig. 6. DTA curves: hardened cement paste without hydrosodalite after 3 days (a); hardened cement paste with 15% hydrosodalite after 3 days (b); hardened cement paste without hydrosodalite after 28 days (c) and hardened cement paste with 15% hydrosodalite after 28 days (d)

In order to supplement the results of X-ray diffraction analysis, thermal analysis of the tested hardened cement paste specimens was performed. It is considered that endothermal peaks in the 100–200 ºC temperature range display water loss from the tobermorite gel phase. Another intense endothermal peak, visible in all the DSC curves (Fig. 6), within the temperature range of 467–481 ºC corresponds to the decomposition of $Ca(OH)_2$. Peaks within the temperature range of 718–735 ºC are linked with water loss from calcium hydrosilicate $(1.5–2.0)CaO·SiO_2·nH_2O$ similar to tobermorite. Belite $2CaO·SiO_2$ forms at this temperature [11].

Based on TG curves, it can be stated that the content of $Ca(OH)_2$ in the hardened cement paste with hydrosodalite admixture decreases upon increasing amount of the hydrosodalite. In Figure 6, TG curves a) and c) show a higher calcination loss than b) and d) curves (1.33 and 1.82%, vs. 0.68 and 1.10%). As the duration of specimen curing increases, the content of $Ca(OH)_2$ also increases because calcination loss related to $Ca(OH)_2$ increases from 1.33% to 1.82%, without using hydrosodalite admixture, and increases from 0.68 to 1.10%, when applying 15% of the admixture. The thermal analysis results confirm those of X-ray diffraction analysis.

4. Conclusions

- The additive of hydrosodalite can be used as a puzzolanic admixture for Portland cement due to its high hydraulic activity.
- The additive of hydrosodalite reduces the content of $Ca(OH)_2$ in the hardened cement paste when it forms some amount of calcium zeolite gismundite, and NaOH, as it is demonstrated by X–ray diffraction and thermal analysis results.
- Reduction of $Ca(OH)_2$ content influences the formation of hydrosilicates $3CaO·2SiO_2·3H_2O$ of lower alkalinity in the hardened cement paste with hydrosodalite.
- The density of the hardened cement paste containing hydrosodalite after 3, 7 and 28 days of curing decreases by about 11%. This determines a decrease in the compressive strength of the hardened cement paste. The compressive strength after 3 days of curing decreases by about 70%, after 7 days of curing – by 66%, and after 28 days of curing – by about 65%.

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