# THE EFFECT OF ZEOLITIC BY-PRODUCT WITH CaCl₂ ADMIXTURE AS SUPPLEMENTARY CEMENTITIOUS MATERIAL ON THE PROPERTIES OF HARDENED CEMENT PASTE

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Recently, supplementary cementitious materials are widely used in cements systems. One of these materials could be a zeolitic by-product. The present study carried out experiments with the aim to find out the impact of zeolitic by-product with incorporated CaCl<sub>2</sub> on the main features of hardened cement paste. A zeolitic by-product is the cracking catalyst of a fluidized bed. It was treated with saturated CaCl<sub>2</sub> solution. Specimens were produced from Portland cement paste with a zeolitic by-product as supplementary cementitious material. It was determined that according to the X-ray the modified zeolitic by-product resulted in the formation of substantial amounts of hydrocalumite (Ca<sub>4</sub>Al<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>·10H<sub>2</sub>O). The results indicate that the addition of small amounts of this additive can increase the compressive strength of the early and late hydration ages as well. In Portland cement systems the zeolitic by-product with inserted CaCl<sub>2</sub> behaved as a hydration accelerator, had the filler effect at early-ages, and acted as a pozzolanic material at later-ages.

Keywords: zeolitic by-product, hardened cement paste, Portland cement hydration, supplementary cementitious material, CaCl<sub>2</sub> accelerator

#### 1. Introduction

It is common knowledge that due to big amounts of reactive SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> zeolites can act as pozzolanic materials and can be used as supplementary cementitious materials. Radeka et al. [1] carried out the experiment on the effect of clinoptilolite as the supplementary material to cement and presented the results. It was cured for 28 days, and the results of the compressive strength values indicate that pastes with 10% and 20% clinoptilolite have a higher compressive strength in comparison to the reference specimen. After 60 days, the compressive strength fell down in comparison to the strength of the reference paste. Another study shows [2] that the use of clinoptilolite in the mortars resulted in the increase of the compressive strength values, the decrease of water absorption and porosity of the mortars. The mortars with clinoptilolite can endure more than the control mortar. Ramezanianpour et al. [3] concluded that the use of natural zeolite remarkably decreased water permeability and capillary absorption concerning all the water-to-cementitious materials ratios. As natural zeolite was used as a supplementary cementing material, the calcium hydroxide content remarkably decreased. Secondary C-S-H could be manufactured as a result of it. Rudžionis et al. [4] suggested explaining the increase of the self-compacting concrete strength values due to the pozzolanic effect of zeolitic waste. As the hydration process takes place, the zeolitic waste binds portlandite to the secondary calcium silicate hydrates. This investigation shows that it is indeed possible to save cement and reuse the waste material. The study indicated [5] that 10% of natural zeolite in self-compacting concrete can be considered as a proper and economic substitute.

Lately, the industrial by-products in concrete production are reused, which is becoming more and more popular. Fluidized bed cracking catalyst residue can be used as supplementary cementitious material (SCM). It also agglomerates zeolite (faujasite) crystals. Pacewska et al. [6, 7] research indicated that the compressive strength of concrete is positively affected by the fluidized bed cracking catalyst integrated up to 20 wt. % in cement systems. Instead of cement or sand, the spent catalyst of catalytic cracking in fluidized bed (FBCC) was used for mortars, and the compressive strength was measured and evaluated after that. In case the fluidized bed cracking catalyst was used instead of sand, it was noticed that the compressive strength increased (in comparison to reference specimens). However, in the case of the cement replacement, the compressive strength did not increase or even decreased. FBCC can be used in hydrated cementitious mixtures, which can act as the active micro filler. The pozzolanic activity of FBCC has been the object of many studies. Carolina et al. [8] have confirmed that pozzolanic activity is induced in the beginning of the type II cement hydration by the spent catalyst. It also makes setting start faster. The study examined [9] the FBCC catalysts, i.e. equilibrium catalyst (Ecat), and electrostatic precipitator catalyst (Epcat), and compared their

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pozzolanic activity. The results of the study show that both Ecat and Epcat, like silica fume, display good pozzolanic activity and are reactive with CH. Monzó et al. [10] found interesting data how FBCC reactivity and compressive strength behave with regards to FBCC-concrete. Fly ashes (FA) had to increase the hydration degree of cement particles for low water/binder ratio in the early stages. On the other hand, FBCC acts as a very reactive pozzolan in cement/FA/FBCC mixtures.

We still do not know how the acceleration of CaCl<sub>2</sub> takes place. Peterson et al. [11] found out that due to CaCl<sub>2</sub>, the amount of total hydration product was increased during early hydration. He also observed the increase in the permeability of the hydration products, which is closely related to the increased rate constant. Singh et al. [12] analyzed the hydration of tricalcium silicate at the temperature of 30° C with and without 2 wt. % CaCl<sub>2</sub> in water: solid ratio of 0.8. The results show that the higher is the diffusivity of chloride ions [12], the bigger is the acceleration action of CaCl<sub>2</sub>. The ways how CaCl<sub>2</sub> accelerates were analyzed in the study [13] carrying out experiments of thermodynamic modeling. The results showed that the acceleration period of ordinary Portland cement hydration was brought forward by the filler materials. Super saturation is caused by calcium chloride, as is shown by thermodynamic modeling, with regards to pure calcium-silicate-hydrate.

Actually, there are many sources in literature on the aspects related to the accelerating effect of CaCl<sub>2</sub> and the pozzolanic effect of zeolitic residues. However, the topic how these factors have joint effects is quite a new idea. The aim of this work is to study the effect of zeolitic by-product with CaCl<sub>2</sub> chemical admixture as an activator on the main properties of hardened cement paste.

## 2.Materials and methods

#### 2.1 Experimental techniques

The materials were analyzed with regards to their X-ray diffraction by the X-ray diffractometer

"Bruker D8 Advance". CuK $\alpha$  radiation and Ni filter were used. The PDF-2 data base included references that were used to identify the power Xray diffraction patterns (PDF – 2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA 19073-3273 USA).

The laser granulometric "Cilas 1090LD" helped to determine the particle size distribution of Portland cement and zeolitic by-product.

Calorimetric analysis was conducted according to the temperature measurements of cement paste hydration. They were performed with 8-channel USB "TC-08 Thermocouple Data Logger" (temperature measurement ranges from –270 °C to +1820 °C). The setting time of the Portland cement pastes were determined according to the standard EN 196-3.

The electronic microscopy scanned the structure of hardened cement paste and studied it. The high-resolution scanning electron microscope "FEI Quanta 200 FEG" with a Schottky field emission *gun (FEG)* was also used.

The compressive strength of hardened cement paste was measured by EN 196-1[14]. The compressive strength of the hardened cement paste was measured by using the automated and computerized ToniTechnik 2020 press after 3, 7 and 28 days.

### 2.2 Raw materials

The ordinary Portland cement (a CEM I 52.5R with mineral composition  $C_3S = 50.7$  %;  $C_2S = 18.5$  %;  $C_4AF = 14.2$  %;  $C_3A = 9.7$  %) was used in the study.

Synthetic modified zeolitic by-product was used as a cement substituting material. Granulometric composition curves of cement and zeolitic by-product are presented in Fig. 1. According to the results of granulometric analysis, it was established that the particles of zeolitic by-product disperse between diameters ranging from 0.63  $\mu$ m to 239  $\mu$ m, with the peak at 79.43  $\mu$ m with 10.25% of all particles in the histogram, the specific particle surface being equal to the 0.1403 m<sup>2</sup>/cm<sup>3</sup>



Fig. 1 - The cumulative values (a) and histograms (b) of particle sizes distributions for zeolitic by-product and Portland cement.



Fig. 2 - X-ray diffractions patterns of unmodified and modified with CaCl<sub>2</sub> solution zeolitic by-product. Note: Y is zeolite Al<sub>60.352</sub>·Si<sub>139</sub>·O<sub>371·52</sub>·H<sub>5.984</sub> (73-2313).

(Figure 1). For the time being the size of the Portland cement particle varied more evenly from  $0.05\mu m$  to 52.5  $\mu m$ , forming two peaks at 1.8  $\mu m$ (1.75% of all particles) and at 19.42  $\mu$ m (2.14% of all particles) in the distribution histogram. The specific surface of Portland cement was equal to 0.599 m<sup>2</sup>/cm<sup>3</sup>. In conclusion, the particles of Portland cement are almost four times finer than the particles of zeolitic by-product.

During the production process in oil treatment plants, catalyst waste remains. Petroleum refining company, which processes around 5 million tons of oil per year, produces about 200 tons of catalyst waste annually, and almost half of this amount is hauled to dump. In other countries, this waste is increasingly disposed in concrete containing Portland cement, in asphalt production, etc.

In this study zeolitic by-product was modified with saturated CaCl<sub>2</sub> solution. In the unstirred suspension CaCl<sub>2</sub> solution was filled up with zeolitic by-product. At 50 °C, the treatment time lasted for about 5 minutes. Finally, the ultimate product underwent filtration and was dried at the temperature of 60 °C.

Fig. 2 illustrates the X-ray diffraction of used zeolitic by-product. This mineral has similar peaks close to that of Faujasite. The diffraction peaks with interplanar distances of (d): 1.399; 0.857; 0.731; 0.556; 0.429; 0.367, as is indicated by the first X-ray diffraction curve, are characteristic of zeolite.

Therefore, after treatment of zeolitic by-product with CaCl<sub>2</sub> solution, the main peak of this zeolite remained the same (Fig. 2, 2 curve). This could be

explained by the fact that XRD analysis captures only the diffraction reflections of crystalline compounds. In water, CaCl<sub>2</sub> completely dissociates into Ca2+ and Cl- ions, which are likely to be sorbed at different sites in the zeolite (in the pores or channels and on the surface of zeolites), but without the changing of structure for the zeolite crystal lattice. Therefore, the X-ray diffractions patterns were almost identical. In the study [15], it was found that in zeolites that absorbed less than 10% CaCl<sub>2</sub>, XRD analysis also did not detect any changes in the X-ray diffractions patterns of zeolites. Authors stated that nanosized CaCl<sub>2</sub> could be formed.

XRD pattern of the composite with 4 wt.% and 10 wt.% of calcium chloride did not show any reflections of calcium chloride, which could be explained with the presence of highly dispersed calcium chloride with nanosized dimensions that are located on the surface and within the pores.

Table 1 shows the chemical composition of zeolitic by-product calcined at 105 °C temperature after treatment with CaCl<sub>2</sub> solution. With regards to the amount of aluminum and silicon oxides (up to 78.02 %), this by-product belongs to the aluminosilicate material group with a crystalline structure. The saturated CaCl<sub>2</sub> solution was used for the treatment of zeolitic by-product. Almost 17.69% of CaCl<sub>2</sub> was left after treatment of zeolitic by-product.

In the hardened cement paste specimen, modified zeolitic by-product (0, 5, 15, 20 and 30 wt%) was used as the cement supplementary material.

Table 1

xide composition of modified and unmodified zeolitic by-product, wi
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Oxide composition of modified and unmodified zeolitic by-product, wt%											
Type*	SiO <sub>2</sub>	$AI_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	CaO	Na <sub>2</sub> O	SO3	$P_2O_5$	CI
I	38.68	39.33	0.86	0.71	1.63	0.6	8.11	0.28	0.38	0.76	8.21
11	46.47	47.25	1.03	0.85	1.96	0.72	0.00	0.34	0.46	0.91	0.00

\*I - modified; II - unmodified

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Portland cement	Modified zeolitic by- product	The amount of CaCl₂ in Portland cement specimen	W/S*	Setting time, min	
				Initial	Final
100	0	0	0.354	203	405
95	5	0.88	0.354	185	297
85	15	2.65	0.354	141	208
80	20	4.01	0.354	91	109
70	30	5.31	0.354	92	111

\*- water and solid material ratio



Fig. 3. X-ray diffraction patterns of hardened cement paste after 28 days having 0% (1), 10% (2), 20% (3), and 30% (4) of modified zeolitic by-product. Notes: CH – portlandite Ca(OH)<sub>2</sub> (84-1265); A – alite Ca<sub>54</sub>MgAl<sub>2</sub>Si<sub>16</sub>O<sub>90</sub> (13-272); D – larnite Ca<sub>2</sub>(SiO<sub>4</sub>) (83-461); K – calcium silicate hydrate Ca<sub>1.5</sub>Si O<sub>3.5</sub> x H<sub>2</sub>O (33-306); E – ettringite Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O (41-1451); CC – calcite CaCO<sub>3</sub> (24-27); H – hydrocalumite Ca<sub>4</sub>Al<sub>2</sub>O<sub>6</sub>Cl<sub>2</sub>·10H<sub>2</sub>O (19-202).

Respectively, CaCl<sub>2</sub> consisted of 0, 0.88, 2.65, 4.01 and 5.31 wt. % in the Portland cement mixtures. Five series of specimens were formed with modified zeolitic by-product (Table 2).

Water and solid materials ratio (W/S = 0.354) remained the same in all the cases. The hardening of the produced test samples ( $2 \times 2 \times 2$  cm size cubes) lasted for 3, 7, and 28 days.

#### 3.Results and discussions

The hydrates formed during the hydration process are similar in all the specimens with or without zeolitic by-product. As the substitutes increased from 0 to 30% (Fig. 3), the portlandite decreased significantly, as was shown by hardened cement paste specimens in the X-ray diffraction. After comparing all five curves, we can say that the highest typical peak of portlandite (0.493 nm) is the most intense in the reference specimen (Fig. 3, 0%), i.e. when the zeolitic by-product is not used. The insertion of zeolitic by-product in the cement paste specimens caused the decrease of the portlandite peaks. Apart from the aforementioned portlandite, there can be also ettringite, calcium silicate hydrate and clinker minerals identified in these systems: alite and belite (larnite). Hydrocalumite formed only on that specimen where zeolitic by-product was used (Fig. 3, 5%, 15%, 20%, 30%).

Zeolite has not been identified. It was due to the fact that in the course of hydration of Portland cement with zeolitic by-product, the high level of pH of the zeolite made the aluminosilicate frame disintegrate and depolymerize:

 $n[\equiv Si-O-Al\equiv] + 7nOH^- \rightarrow [-O-Si-(OH)_3]_n + + [Al-(OH)_4]_n$  (1)

As the depolymerization takes place,  $[SiO(OH)_3]^-$  and  $[Al(OH)_4]^-$  ions enter solution and react with  $Ca^{2+}$  ions, and the result of that is hydrated calcium silicates and calcium aluminates formed that are very similar to those compounds that develop during the hydration of the ordinary Portland cement. According to the XRD analysis, the reaction product has the formula of hydrocalumite  $Ca_4Al_2O_6Cl_2\cdot 10H_2O$ . Other authors [16, 17] stated that hydrocalumite form during Portland cement with  $CaCl_2$  hydration, too.

In order to explain the influence of the modified zeolitic by-product on the hydration of Portland cement, the calorimetric analysis was carried out. Fig. 4 shows the effect that is made by



Fig. 4 - The effect of modified zeolitic by-product on the hydration heat of Portland cement paste

modified zeolitic by-product on the hydration heat of Portland cement paste. In all the binder's systems, this zeolitic by-product decreased the period of induction (123 min - 296 min) and increased the rate of hydration in the acceleration period if compared to the pure Portland cement system (407 min). It is evident that the calcium chloride from modified zeolitic by-product can act as Portland cement accelerator. Actually, these results and the ones gained from blended cement pastes prepared with calcium chloride admixture [18] are very similar. All the cases showed (except the case with 30 wt. % of zeolitic by-product) the increase of the temperature along with the increase of zeolitic byproduct, as compared to the reference specimen temperature. The filler effect accounts for the fact of the increase of these temperatures. The present particles help the hydration of the clinker phases. The outcome is called the filler effect, which accounts for the increase of the number of

nucleation sites provided by the extra surface from the particles [19]. The setting times were close related to the hydration heat of Portland cement paste (Table 2). Both initial and final setting times were shorter for the specimens with modified zeolitic by-product. In this way, a synergistic effect was observed with filler and calcium chloride.

The development of the compressive strength of the hardened cement paste specimen as far as the content of zeolitic by-product is concerned is shown in Figure 5. The compressive strength of specimens with unmodified zeolitic by-product slightly decreased by compared with specimens without zeolitic by-product after 2 and 7 days of hydration. This could be related with dilution effect of Portland cement. After 28 days of hydration by using from 5 until 20 % of unmodified zeolitic by-product the compressive strength increased, and this increase could be related with the pozzolanic effect of zeolite. According to Salain, et al. [20] the



Fig. 5 - The compressive strength of hardened cement paste after 2, 7 and 28 days. Zeolitic by-product content accounts for 0 %; 10 %; 20 %; and 30 %. Constant W/S=0.354 was.

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reaction between pozzolan (in this case zeolitic byproduct) and calcium hydroxide which form during Portland cement hydration is relatively slow and the rate of strength development is slow too.

Different situation was when modified zeolitic by-product was incorporated in Portland cement specimens. It was noticed that the compressive strength of the specimen increased after 2 days of hydration when 5% of Portland cement consisted of zeolitic by-product modified with CaCl<sub>2</sub>. In the case when the zeolitic by-product exceed, 5%, the compressive strength decreased as compared to the control specimen (Fig. 5). Presumably, CaCl<sub>2</sub> acceleration accounts for the increase of the compressive strength, and the binder dilution could be the reason of the decrease (Portland cement). Some researchers stated [21, 22] that the strength of Portland cement is positively affected by the addition of CaCl<sub>2</sub> at early hydration stages. As the CaCl<sub>2</sub> additive increases the rate of C-S-H formation, the early stage strength (the first day of

hydration) is also increased. Chloride combines with calcium aluminate hydrates are responsible for the decrease of chloride concentration in the pore solution forming Friedel's salt (in this case hydrocalumite).

After the periods of 7 days and 28 days of hydration, the compressive strength of specimens shows different trends. Here the compressive strength increased in the hardened cement paste as far as the Portland cement replacement level for the modified zeolitic by-product is regarded. At the end of the period of 28 days of hydration, the results of the compressive strength values indicated that specimens containing 15% and 20% of zeolitic by-product had higher compressive strengths that increased by 11.9 % and 7.0%, respectively, as compared to the reference specimen. If the amount of substituted material was higher, i.e. 30%, the compressive strength starts decreasing. Radeka et al. [1] also gained similar results stating that an



Fig. 6 - SEM images of hardened cement paste. Zeolitic by-product content accounts for 0 % (a, c) and 30 % (b, d).

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increase of zeolite content (10% and 20%) is responsible for the higher compressive strength of the paste specimen after 28 days of curing in comparison to the reference specimen. Zeolite is one of pozzolanic materials such as fly ash and silica fume. Zeolites show perfect pozzolanic activity despite their crystalline structure [23]. Calcium silicates hydrates and calcium aluminates hydrates are formed by the combination of the calcium hydroxide as a cement hydration product and zeolite consisting of reactive SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. So, the longterm strength of cement systems was increased by zeolite through the pozzolanic reaction and the early-age strength was decreased due to dilution of Portland cement [24, 25].

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The compressive strength of specimen is also influenced by the microstructure of hardened cement paste, and therefore it should be investigated. The SEM images of specimen without zeolitic by-product are shown in Fig. 6 (a and c). The cementing matrix consists of a heterogeneous mixture of phases that formed as a result of the hydration process. The particles of needle crystals are linked to ettringite, very small formations that are like needles or plate are related to C-S-H and column aggregate is characteristic to portlandite (Fig. 6, a) [24, 26]. According to XRD analysis, significant amounts of ettringite as well as clearly visible needle-like particles linked to ettringite (Fig. 6, c) are found. After hardened cement paste structure included 30 % of zeolitic by-product (Fig. 6 (b and d)), different particle morphology as compared to the reference specimen appeared. Transformations of portlandite into solid forms, and needle forms of C-S-H into "honey comb" structures [26] respectively were detected. Zeolitic by-product influenced the formation of hydrocalumite-type particles and its particles could be revealed by almost hexagonal plate-like crystals (Fig. 6, d) [27].

The chloride could be the cause of corrosion of reinforcement in concrete. This corrosion risk could be determined and evaluated additionally in our next study.

# 4.Conclusions

The summary of the study has the following points:

- Due to this zeolitic by-product, the length of the induction period decreased and the temperature of hydration (except the case with 30 wt. % of zeolitic by-product) of the acceleration period increased as compared to the pure Portland cement system. The synergistic effect of zeolitic by-product was observed with filler and calcium chloride.
- 2. The increase of the early (after 2 days) compressive strength could be associated to CaCl<sub>2</sub> acceleration influence. Gradually the chloride combined with calcium

aluminate hydrates and forms Friedel's salt (in this case hydrocalumite).

- 3. After 28 days the compressive strength of specimen containing 15% and 20% of zeolitic by-product have had the increase in the compressive strength by 11.9 % and 7.0%, respectively, then the reference specimen. This increase is related with zeolitic by-product pozzolanic activity.
- 4. In Portland cement systems the zeolitic byproduct with inserted CaCl<sub>2</sub> accelerated hydration and affected the filler at earlystages as well as acted as a pozzolanic material at later-stages. By using zeolitic by-product with CaCl<sub>2</sub> accelerates the hydration process and improves the compressive strength of hardened cement paste as well.

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