THE DURABILITY PROPERTIES OF CONCRETE INCORPORATING ZEOLITIC TUFF

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ABSTRACT

The corrosion resistance of concrete containing zeolitic tuff in different aggressive environment was investigated in the article. Objective of this work was investigation of the behaviour of concretes incorporating 10% by mass of zeolitic tuff and superplasticizer, as well as 10% by mass of the zeolitic tuff, a superplasticizer and an air-entraining agent as well as concretes without zeolitic tuff, which contain only a superplasticizer and an air-entraining agent in Na₂SO₄ and MgCl₂ solutions. The chemical composition of the zeolitic tuff and Portland cement used in this research was determined using X-ray spectrometer ARL 9800 XP. The results of the research show that fresh concrete mixture incorporating zeolitic tuff due to its porous structure and high surface area demands a higher amount of superplasticizer to obtain the targeted slump flow. The results also reveal the effectiveness of the zeolitic tuff use to improve corrosion resistance of concretes exposed to Na₂SO₄ and MgCl₂ solutions.

Key words: zeolitic tuff, pozzolanic reaction, corrosion resistance, durability.

INTRODUCTION

The durability properties of concrete structures play an important role in the infrastructure of cities. The properties of concrete depend on different factors, such as type of Portland cement, correctness of concrete mix design, placement and curing. It is well known that the use of pozzolans instead of cement results in an increase of the concrete durability in different aggressive environments depending on the exposure classes [1,2].

Zeolitic tuff as a natural pozzolanic material possesses unique properties, which makes it possible to use it in some regions of the world in the construction industry, because of its lower cost and accessibility. In spite of the zeolitic tuff being crystalline, it is characterised by proper pozzolanic activity [3,4]. The lime reactivity of the zeolitic tuff (clinoptilolite type) is comparable to silica fume (SF) and higher than fly ash (FA) [3-5]. Calcium hydroxide, which has been produced during period of cement hydration reacts with the reactive SiO₂ and Al₂O₃ of zeolitic tuff producing calcium hydrosilicates. Therefore, concretes containing zeolitic tuff become more durable due to higher resistance to the expansion caused by sulphate attack and lime leaching by flowing waters as a result of the reduction of free Ca(OH)₂ in the hardened concrete [6,7]. Many researchers concluded that zeolitic tuff improves the compressive strength of concrete if its content is less than approximately 10% by mass [8,9]. A higher amount of zeolitic tuff can result in the reduction of the compressive strength. The particle size distribution also plays very important role [10].

Some researchers also reported that concrete incorporating zeolitic tuff has improved durability properties such as higher resistance to freezing/thawing cycles, drying shrinkage and water penetration depth, but various types, structures and purities can have different influence on the concrete strength and durability [11-13].

The aim of the article is to study the influence of zeolitic tuff (Sokyrnytsia, Ukraine) on the behaviour of concrete exposed to different aggressive environments.

EXPERIMENTAL

The zeolitic tuff of clinoptilolite type and Portland cement CEM I 42.5R were used in this study. The chemical composition of the zeolitic tuff and Portland cement was determined using X-ray spectrometer ARL 9800 XP and presented in Fig. 1. Zeolitic tuff in comparison with Portland cement has a higher content of silica, alumina and iron oxides. Namely these oxides are responsible for the pozzolanic activity of zeolitic tuff.

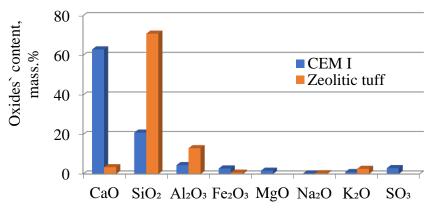


Figure 1. Chemical composition of Portland cement (CEM I) and natural zeolitic tuff.

The properties of Portland cement were determined according to EN 196. The specific surface of Portland cement was $425 \text{ m}^2/\text{kg}$. The water demand was 27%, initial and final setting time were 200 and 260 min, respectively. The compressive strength of cement CEM I 42.5R after 2 and 28 days was 30.5 and 55.0 MPa, respectively.

The properties of aggregates were tested according to PN-EN 1097 and conform to the requirements of European norms. Polycarboxylate-based superplasticizer and an air-entraining agent, based on abietate salts, were used in this study. Four concrete mixtures, as in previous research [11], were prepared, namely the control concrete mixtures without zeolitic tuff, which contained 1.22% by mass of superplasticizer (Z0P), 1.22% by mass of superplasticizer and 0.3% by mass of air-entraining agent (Z0PA) as well as two mixtures incorporating 10% by mass of the zeolitic tuff instead of Portland cement and 1.64% by mass of superplasticizer (Z10P) and 1.64% by mass of superplasticizer and 0.3% by mass of air-entraining agent (Z10PA).

Nominal mixture proportions of fine-grained concretes were cement:sand = 1:1.88 and (cement + zeolite):sand = 1:1.88, except that coarse aggregate was not used. The use of zeolitic tuff results in a decrease of the workability of the concrete mixture. It was compensated by using an extra amount of superplasticizer. The higher water demand of concrete mixtures containing zeolitic tuff is caused by its porous microstructure. An air-entraining agent was used to increase the durability properties of concretes.

The corrosion resistance was determined using 40x40x160 mm prisms. Three samples for each test were prepared, demolded 24 h after casting, and stored 6 and 12 months in the different environment, namely in a water, Na₂SO₄ solution with a concentration of SO₄²⁻ 10 g/l and MgCl₂ solution with a concentration of Mg²⁺ 10 g/l. Then the coefficient of corrosion resistance (CR) was determined as the ratio of the strength of the samples in an aggressive environment to the strength of similar samples in water.

The morphology and chemical composition of main mineral components of the studied materials were determined using scanning electron microscope SEM FEI Quanta 250 FEG, equipped with EDS.

RESULTS AND DISCUSSION

The durability properties of concrete are one of the key factors on the way to the sustainable development of construction industry. Some of them were studied in the previous research [11]. It was established that zeolitic tuff used in an optimal amount (10% by mass) in spite of its pores structure was an effective component of concrete. It results in the increase of the resistance to freezing and thawing damage, the decrease of drying shrinkage and the water penetration depth. The study of corrosion resistance revealed that the coefficient of corrosion resistance of concretes incorporating 10% by mass of zeolitic tuff is higher in both MgCl₂ and Na₂SO₄ aggressive environments. The coefficient of CR is higher for concrete specimens exposed to Na₂SO₄ solution by approximately 1.5 times in comparison with concretes exposed to MgCl₂ aggressive environment (Fig. 2).

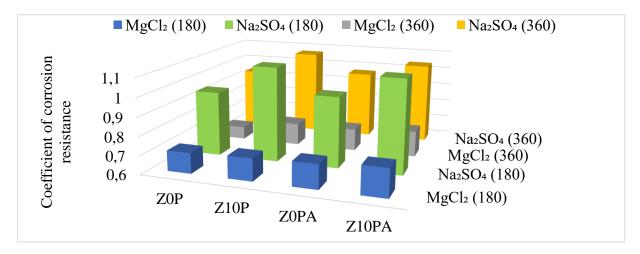


Figure 2. Coefficients of corrosion resistance of fine-grained concrete, determined by the results of compressive strength tests.

According to the scanning electron microscopy data, the microstructure of fine-grained concrete without zeolitic tuff, exposed for 180 days to MgCl₂ solution, exhibited a separate polyhedral block shape, which was cemented closely with other hydration products as indicated in Fig. 3 a. Loose formations of Mg(OH)₂, which is formed as a result of chemical reaction between calcium hydroxide (Portlandite) and magnesium chloride in an aggressive environment, is observed on the surface of concrete. These formations accumulate in the pores of the fine-grained concrete and do not interfere with the diffusion of Ca^{2+} ions from the deep layers to the surface. As the concentration of Ca(OH)₂ decreases, high calcium hydrosilicates and hydroaluminates begin to break down, leading to the loss of concrete durability properties. The microstructure of fine-grained concrete without mineral additions (Fig. 3 c), exposed for 180 days to Na₂SO₄ solution, is characterized by a fine-crystalline structure, long prismatic crystals of the ettringite. The crystallization of the ettringite is accompanied by an increase in volume by 2.5-2.86 times. The rapid growth of ettringite crystals with prolonged exposure to sulphates causes the destruction of the concrete structure. The formation of substances, such as Mg(OH)₂, ettringite, which are produced in aggressive environments was confirmed by the results of microprobe analysis. If zeolitic tuff is added, the surplus SiO₂ reacts with calcium hydroxide producing progressively more low calcium C–S–H and as a result more refined and compact structure resulting in the improvement of the concrete durability in both aggressive environments (Fig. 3, b, d).

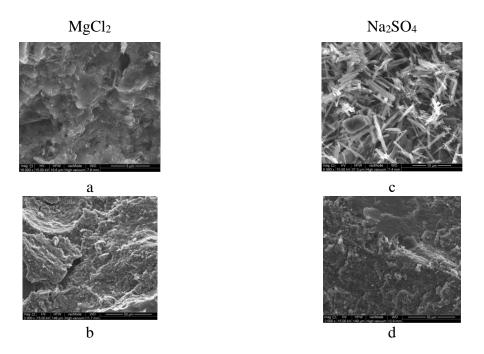


Figure 3. Microstructure of specimens ZOP without mineral additions (a, c) and with 10 % by mass of zeolitic tuff Z10P (b, d), which were exposed to $MgCl_2$ and Na_2SO_4 solutions, respectively.

CONCLUSION

This paper considers the issues of development of effective concrete containing zeolitic tuff. The most important conclusions are that incorporation of cement replacement materials, such as zeolitic tuff in spite of its pores structure allows to improve the resistance of such concrete against aggressive environments such as Na₂SO₄ and MgCl₂ solutions improving the durability properties of concretes.

REFERENCES

- [1] Y. Kocak, E. Tasci and U. Kaya, Constr. Build. Mater., 2013, 47, 720–727.
- [2] Kh. Sobol, T. Markiv, V. Terlyha and W. Franus, Bud. Archit., 2015, 14(1), 105-113.
- [3] W. Franus and K. Dudek, Geol Carpath., 1999, 50, 23-24.
- [4] M. Najimi, J. Sobhani, B. Ahmadi and M. Shekarchi, Constr. Build. Mater., 2012, 35, 1023–1033.
- [5] B. Uzal and L. Turanli, Cem. Concr. Compos., 2012, 34, 101–109.
- [6] M. Sanytsky, Kh Sobol and T. Markiv, "Modified composite cements", Lviv Polytechnic National University Publishing House, Lviv-Ukranian, 2010, 132.
- [7] D. Caputo, B. Liguori and C. Colella, Cem. Concr. Compos., 2008, 30, 455-462.
- [8] D. Jana, in: Proceedings of the twenty-ninth conference on cement microscopy Quebec City, PQ, Canada, 2007.
- [9] T. Markiv, O. Huniak and Kh. Sobol, Theory Pract. of Build., 2014, 781, 116-121.
- [10] M. Sanytsky, A. Usherov-Marshak, T. Kropyvnytska and I. Heviuk, *Cem. Wapno, Beton.*, 2020, 25(5), 416-427.
- [11] T. Markiv, Kh. Sobol, M. Franus and W. Franus, Arch. Civ. Mech. Eng., 2016, 16, 554– 562.
- [12] F. Sabet, N. Ali and M. Shekarchi, Constr. Build. Mater., 2013, 44, 175–184.
- [13] B. Ahmadi and M. Shekarchi, Cem. Concr. Compos., 2010, 32, 134–141.