Influence of metakaolin on chemical resistance of concrete

L. Mlinárik, K. Kopecskó
Department of Construction Materials and Engineering Geology, Budapest University of Technology and Economics, Budapest 1111, Hungary
E-mail: lilla.mlinarik@gmail.com

Abstract. Nowadays the most suitable and widely used construction material is concrete. We could develop concrete for every request in connection with the properties of fresh concrete and the quality of hardened concrete, too. The demand is rising in application of special concretes, like high performance and ultra high performance concretes (HPC, UHPC). These are usable in extreme natural circumstances or in very corrosive surroundings (for example: sewage farm, sewer, cooling tower, biogas factories). The pH value of the commercial sewage is between 7-8, but this value is often around 4 or less. The concrete pipes, which transport the sewage, are under corrosion, because above the liquid level sulphuric acid occurs due to microbes. Acidic surroundings could start the corrosion of concrete. When the pH value reduces, the influence of the acids will increase. The most significant influence has the sulphuric acid. The pH value of sulphuric acid is about 1, or less. Earlier in the cooling towers of coal thermal power stations used special coating on the concrete wall. Recently application of high performance concrete without polymeric coating is more general. Cementitious supplementary materials are widely used to protect the concrete from these corrosive surroundings. Usually used cementitious supplementary materials are ground granulated blastfurnace slag (GGBS), flying ash (FA) or silica fume (SF). In the last years there has been a growing interest in the application of metakaolin. Metakaolin is made by heat treatment, calcinations of a natural clay mineral, kaolinite. In our present research the chemical resistance of mortars in different corrosive surroundings (pH=1 sulphuric acid; pH=3 acetic acid) and the chloride ion migration were studied on series of mortar samples using rapid chloride migration test. Cement paste and mortar samples were made with 17% metakaolin replacement or without metakaolin. The following cements were used: CEM II/A-S 42.5 N, CEM I 42.5 N-S. We concluded that the replacement of cement by metakaolin results in significant increases in compressive and tensile strengths and it prevents the infiltration of harmful substances.

1. Introduction

The additional cementing materials are essential in the production of high-strength/ ultra-high-strength concrete (HSC/UHSC) and high-performance/ultra-high performance concrete (HPC/UHPC) without coating. The reason is that the cost of coating could reach the 40% of the total costs of the investment. It could be high rate, and that is why the developers try to solve this problem with concrete structure. The aim is to make a compact and resistant structure, which gives the same properties, like the coating. The main scopes of application: sewage plants, cooling towers, biogas production. On these fields, the acidic corrosion is very significant, because of the rate of the biological sulphuric acid in the atmosphere is very high. The pH could reach the value 1. Why biological sulphuric acid corrosion is harmful? When the concrete react with the sulphuric acid, the alkali and the acid will form a water-soluble sulphate-salt. Because of water solubility the structure could lose strength.

The process has a microbial indicator: Thiobacillus concretivorus [1]. This bacterium is growing especially in severe condition on concrete surfaces. Thiobacillus concretivorus consumes sulphur and produces sulphuric acid. At the end of the chemical process sulphates will increase the amount of...
ettringite or gypsum in the cement stone, which could form microcracks in the structure. Due to cracks harmful particles could introduce the structure. It could decrease with more compact fitting. What is the solution to make more compact fitting? Researchers try to find with the application of supplementary cementing materials (fly ash, blast furnace slag, silica fume, metakaolin). These are commonly, simple and easily available materials because they are industrial by-products.

2. Properties of metakaolin

Metakaolin is an artificial pozzolanic material, one species of alumina-silicates. The structure of metakaolin is lamellar with white colour. The silicate-chemical formula of metakaolin is \( \text{AS}_2 (\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_3) \). The average grain size is about 3 \( \mu \)m. This grain size is between the grain size of cement and micro silica. The specific area of metakaolin is approximately 15000 \( \text{m}^2/\text{kg} \) [2].

The raw material of metakaolin is kaolinite. The method of the preparation is thermal activation or calcination. The preparation has three steps. The phase transformation could be followed and explained by thermoanalytical (TG/DTA) methods. In the first change (between 60-160 °C) the physically absorbed water gets away. The second step is the dehydration of chemically bound water (between 450-650 °C). On the third step (about 900 °C) occurs the collapse of the structure, and the formation of metakaolin (figure 1.). Under the preparation we have to be careful, because if the temperature is higher, other phase, mullite, will form. Mullite has absolutely different properties, which are not useful as supplementary cementitious material. There is a new method of preparation: this is flash calcination. In this process the dehydroxilation of powdered kaolin clay is much faster (several tenths of a second) [3].

![Figure 1. Phase transformation by thermoanalytical (TG/DTA) measurement [3]](image-url)

One of the most significant properties of metakaolin is pozzolanic activity. This mean that metakaolin reacts with \( \text{Ca(OH)}_2 \) and produces CASH (calcium-aluminate-silicate-hydrate) gel as well as, alumina containing phases, including \( \text{C}_4\text{AH}_{13}, \text{C}_2\text{ASH}_8, \) and \( \text{C}_3\text{AH}_6 \) at ambient temperature [4]. Pozzolanic activity index determined by the strength activity index as prescribed by ASTM C311 [5]. The main advantages of application of metakaolin are the increased strength of concrete (both compressive and tensile strengths); reduced permeability, reduced alkali-silica reactivity; higher resistance against chemical attack and durability [6].
3. Experimental

3.1. Applied materials
In the experiments two types of cement were used: a sulphate resistant Portland cement (SRPC, CEM I 42.5-N-S), and blasted furnace slag Portland cement (GGBSPC, CEM II/A-S 42.5 N). The supplementary material was metakaolin (the replacement of cements was 17 m %). The additive materials were standard sands with different grain size. Superplasticizer was added to reach the same plasticity.

Experiments were made on cement paste specimens (gas adsorption) or on mortar specimens (standard tests of strength, SEM observation, rapid chloride migration method).

3.2. Methods
The following experimental methods were used:
- a, standard tests of strength (both compressive and tensile strength)
- b, SEM (scanning electron microscopic) observation
- c, rapid chloride migration method (HTC)
- d, gas absorption (on cement paste specimens)

Parts of the evaluations of the results are still running.

3.3. Experimental program
The specimens were made with and without metakaolin (the replacement of cements was 17 m %). The samples were cured in standard circumstances for 28 days (7 days in water, then 21 days under air-conditioned laboratory), and then the specimens were treated: immersed in sulphuric acid (pH=1), acetic acid (pH= 3) parallel for further 28 days (table 1.).

| Samples                  | Curing (7 days) | Curing (21 days) | Treatment (28 days)   |
|--------------------------|----------------|------------------|-----------------------|
| CEM I 42.5 N-S + MK      | water          | climatic chamber | pH=1 sulphuric acid  |
|                          |                | (T= 20-21 °C, RH= 65%) | pH=3 acetic acid      |
| CEM I 42.5 N-S (ref.)    | water          | climatic chamber | pH=1 sulphuric acid  |
|                          |                | (T= 20-21 °C, RH= 65%) | pH=3 acetic acid      |
| CEM II/A-S 42.5 N + MK   | water          | climatic chamber | pH=1 sulphuric acid  |
|                          |                | (T= 20-21 °C, RH= 65%) | pH=3 acetic acid      |
| CEM II/A-S 42.5 N (ref.) | water          | climatic chamber | pH=1 sulphuric acid  |
|                          |                | (T= 20-21 °C, RH= 65%) | pH=3 acetic acid      |

4. Results and discussion

4.1. Effect of metakaolin on strength
The tests of strength were made according to European standards [7]. The 28-day compressive strengths were measured on mortar specimens made with different types of cements. The specimens were made with or without metakaolin (references). The strength values (both tensile and compressive) are highly depending on the volume of CSH formed during hydration, so the tests were made on specimens in the same ages. The results of strength tests are summarized in figure 2. and figure 3. It could be seen that the samples made with metakaolin have higher strength values, than the references. The reason could be that the grain size of metakaolin is smaller than the grain size of cement. The smaller particles of metakaolin and its hydration products will result more compact structure.
Using the strength values, we could determine the pozzolanic activity. The pozzolanic activity of metakaolin is the ratio between compressive strengths of mortars made with or without metakaolin. The measured pozzolanic activity is well corresponding to the references. We have studied the pozzolanic activity and the calculated value is 1.26 (120%) [8].

4.2. Influence of corrosive circumstances on mortar sample

After acidic treatment we detected changes in the physical appearance. In case of samples which were treated in sulphuric acid (pH=1) the colour of the surfaces changed into dark brown. A layer has formed on the surface, which came from the reaction with sulphate ions. On the surface of samples stored in acetic acid a similar layer was not detected.

To get more details about the surface of specimens scanning electron microscope (SEM) observations were obtained. On the surface of the samples, which were treated in sulphuric acid, ettringite crystals formed. This is a product of the reaction between mortar compounds (aluminate-hydrates and sulphate ions) (figure 4.). In case of treatment with acetic acid crystals did not formed (figure 5.).
4.3. Examination of the resistivity against chloride ions

To study the diffusion characteristics HTC methode was used [9]. It is a fast electric migration method which is usable for determination of the diffusion coefficient (D_{nssm}, non-steady state migration coefficient). Under this examination we could determine the rate of the chloride ion migration with colorimetric analysis using AgNO_3 solution. The diffusion coefficients were calculated using the measured data. From the diffusion coefficient we can deduce for the permeability of the structure. Our results indicate that chloride ion diffusion coefficients are smaller in case of samples containing metakaolin replacement of cement (figure 6).

The diagram shows a relative big differences between the samples which made with or without MK. The main reason of this differences, that MK and its hydration products could cause a more compact structure, than the references, and that is why the chloride ions could not penetrate deep into the structure. This is a more compact fitting of the total volume.

![Figure 6. Diffusion coefficients in corrosive circumstances (specimens with or without MK)](image)

4.4. Results of gas adsorption measurement

The aim of the gas adsorption experiments was to determine the total pore volume. The total pore volume was smaller in case of samples made with metakaolin. Cement paste samples without sand aggregate were made using two different metakaolin products (M or C). The measurements were made on cement paste samples. The replacement of cement was 17%. Experiments were made on two different types of MK. Sample 0 is the reference sample, and numbers are the signs for cements (2 = CEM I 42.5-NS, 3 = CEM II/A-S 42.5 N. Letters are signs for the different metakaolin products (M and C). Similarly to the results of chloride migration results of gas adsorption measurement refer more compact structure (figure 7).

![Figure 7. Total pore volume (specimens with or without MK)](image)
5. Conclusion
The aim of the study was to analyze the influence of a supplementary material, metakaolin (MK) on the chemical resistance of concrete. For this reason acidic treatments were made on mortar samples from the age of 28 days to 56 days. Agents were sulphuric acid (pH=1) or acetic acid (pH=3). Our experimental results (pozzolanic activity, increased compressive and tensile bending strengths) indicated that the application of MK provide better performance against severe chemical conditions.

The structure of samples containing MK became more compact, and the migration of harmful particles or ions are restricted. Results both of the chloride ion migration and the gas adsorption measurements indicated the more compact structure in case of metakaolin containing samples. SEM observations show that reaction products on the treated surface are depending on the composition of acidic agents. In case of treatment with sulphuric acid ettringite crystals are formed on the mortar surface.

To determine the influence of metakaolin on chemical resistance of concrete long-term experiments are needed, respectively.

6. Acknowledgments
The work reported in this paper has been developed in the framework of the project „Talent care and cultivation in the scientific workshops of BME” project. This project is supported by the grant TAMOP-4.2.2.B-10/1--2010-0009. Authors are appreciated to the company MC Bauchemie Hungary for the support of materials.

References
[1] Hillemeier B, Hüttl R 2000 Säureresistenter Beton mit einstellbarer Festigkeit für den höchsten Kühlturm der Welt Proc. Ulmer Beton- und Fertigteil-Tage (Ulm) L142-157
[2] Moulin E, Blanc P and Sorrentino D 2001 Influence of key cement chemical parameters on the properties of metakaolin blended cement Cement & Concrete Composites 23 L463-469
[3] Ilić B R, Mitrović A A and Mišić L R 2010 Thermal treatment of kaolin clay to obtain metakaolin Hemijska Industrija 64 L351–356
[4] Said-Mansour M, Kadri E-H, Kenai S, Ghrici M, Bennaceur R 2011 Influence of calcined kaolin on mortar properties Construction and Building Materials 25 L2275-2282
[5] ASTM C311 - 11b Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete
[6] Siddique R, Klaus J 2009 Influence of metakaolin on the properties of mortar and concrete: A review Applied Clay Science 43 L392–400
[7] MSZ-EN 1015-11:2000 Methods of test for mortar for masonry. Determination of flexural and compressive strength of hardened mortar
[8] MSZ EN 450-1:2005 Fly ash for concrete. Definition, specifications and conformity criteria
[9] Tang L, Nilsson L O 1992 Chloride diffusivity in high strength concrete Nordic Concrete Research, 11 L162-170.