Impact of metakaolin - a new supplementary material - on the hydration mechanism of cements

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Abstract

Nowadays environmental problems are more and more significant. The industrial area produces lots of waste materials and CO_2, respectably. One of the most effective ways to solve these problems is the utilization of these waste materials. One choice of the usage of the waste materials is in the construction industry. The most common and widely used building material is concrete. Scientists and engineers are continuously working for better concrete properties from strength to durability standpoint with the help of innovative chemical admixtures and supplementary cementing materials. Waste materials are used as replacement of common aggregates or cements. The most significant and indispensable part of concrete is cement. The production process of cements from its raw material produces a lot CO_2. The most effective way to decrease the CO_2 emission of cement industry is the substitution of a proportion of cement with supplementary cementing materials (SCM's). SCM's are often used in concrete mixes to reduce cement contents, improve workability, increases strength and enhanced durability through hydraulic or pozzolanic activity. Utilization of these - usually industrial - by-products in cement/mortar/concrete not only prevents them from being land-filled but also enhances the properties of concrete in the fresh and hardened states. Usually used supplementary cementing materials are: ground granulated blastfurnace slag, flying ash, silica fume, trass or metakaolin. The aim of our research is to get acquainted with one of SCM's, especially with metakaolin, and to find some other advantageous features. The most interesting feature could be how will influence metakaolin (MK) the hydration of cements. The examinations focus on the effect of replacement of cements by MK in cement paste or mortar samples.

Keywords: supplementary cementing materials, metakaolin, cement hydration, chloride ion migration, gas adsorption, SEM

1. Introduction

The most commonly used supplementary cementing materials (SCM's) are ground granulated blastfurnace slag (GGBS), flying ash (FA) or silica fume (SF). These materials are widely used and studied in concrete technology because of their advantageous properties. The aim of recent research is to study the hydration mechanism of SCM's, especially in case of metakaolin.

Nowadays the interest is more and more intensive in connection with application of metakaolin. There are promising results with concrete applications made with metakaolin in corrosive

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surroundings.

In our recent experiments the examined properties are: hydration of cements partly replaced with metakaolin; determination the influence of MK on diffusion coefficients by chloride ion migration tests; examination of pore structure and texture with gas adsorption; observation of surface and microstructure of samples with scanning electron microscope.

2. Supplementary cementing materials

The usage of additional cementing materials are the essentials in the production of high/ultra high-strength concrete (HSC/UHSC) and high/ultra high-performance concrete (HPC/UHPC).

Supplementary cementing materials - through hydraulic or pozzolanic activity - contribute the properties both of fresh and hardened concrete. The supplementary cementing materials can be used individually with Portland or blended cements or in different combinations [1].

These materials react chemically with calcium hydroxide released from the hydration of Portland cement to form cement hydrates. These materials are often added to concrete to make concrete mixtures more economical, reduce permeability, increase strength, or influence other concrete properties.

Fly ash, the most commonly used pozzolan in concrete, is a finely divided residue that results from the combustion of pulverized coal and is carried from the combustion chamber of the furnace by exhaust gases. Commercially available fly ash is a by-product of thermal power generating stations [2].

Blast-furnace slag, or iron blast-furnace slag, is a non-metallic product consisting essentially of silicates, aluminosilicates of calcium, and other compounds that are developed in a molten condition simultaneously with the iron in the blast-furnace.

Silica fume, also called condensed silica fume and microsilica, is a finely divided residue resulting from the production of elemental silicon or ferro-silicon alloys that is carried from the furnace by the exhaust gases. Silica fume, with or without fly ash or slag, is often used to make high-strength concrete. Silica fume can give significant benefits to concrete including reduced construction times, improved pumpability, enhanced early strength development and excellent durability, particularly resistance to abrasion, impact and chemical attack.

Trass is the name of a volcanic tuff. The first application was in hydraulic mortar. It is a grey or cream-coloured fragmental rock, largely composed of pumiceous dust, and may be regarded as riolitic or a trachytic tuff. Mixed with lime and sand, or with Portland cement, it is extensively employed for hydraulic work, while the compact varieties have been used as a building material and as a fire-stone in ovens [3].

Metakaolin is a mineral material of aluminosilicate. The formula of metakaolin in the silicate chemistry is AS_2 ($Al_2O_3.2SiO_2$). Grain size of metakaolin is between cement and microsilica, and the specific surface is about 15000 m^2/kg. The MK is made from kaolinite with thermal activation. The cement industry does not produce cements with MK, just blend subsequently.

3.   Materials

Three types of cements, CEM I 42.5 N ordinary Portland cement, CEM I 42.5 N-S sulphate resistant Portland cement and CEM II/A-S 42.5 N blast-furnace slag Portland cement were involved in the experiments.

Metakaolin samples were used as replacement of cement content. Three different types of metakaolins were products of two producers. Two of them are powder form materials (signed by M

and C), and one is a liquid form product (suspension, signed by S). Metakaolins with sign C (powder) and S (suspension) originated from one producer.
The mineralogical composition of metakaolins was investigated by X-ray powder diffraction (XRD) *(Figure 1).*
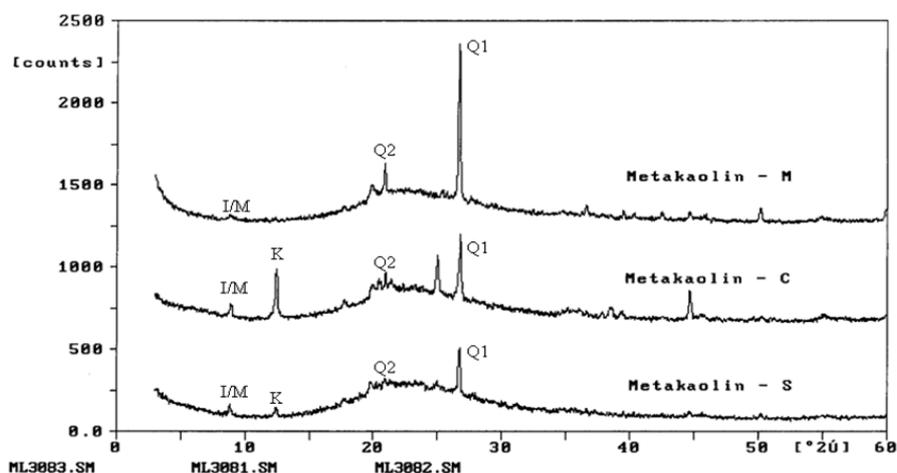
Figure 1. XRD patterns of the used metakaolins
(Notations: Q1, Q2: quartz 1st and 2nd most intensive peaks; K: kaolinite 1st most intensive peaks; I/M: illite/muscovite 1st most intensive peaks)

Table 1. Chemical composition of metakaolins

Chemical composition m%	C	M
MgO	0.022	0.182
Al_2O_3	41.738	39.676
SiO_2	52.962	55.620
P_2O_5	0.365	0.352
SO_3	0.855	0.418
K_2O	0.487	0.875
CaO	2.983	1.486
TiO_2	0.040	0.411
Fe_2O_3	0.525	0.960
ZnO	0.003	0.005
Cl	0.004	0.001

X-ray patterns indicated that in two types of metakaolins (C, S) there is a considerable part of the original clay minerals. This means that the dehydration process during metakaolin production was not completed. From the determination of chemical composition of powder form metakaolins (C and M type) we could notice, that the most significant components are Al_2O_3, SiO_2, CaO. The measurement was made by X-ray Fluorescence Spectroscopy (XRF) *(Table 1).* Remarkable differences are between some minor components of metakaolins, e.g. in case of TiO_2 or Fe_2O_3. These data are confirmed by references.

X-ray patterns proved that the part of SiO_2 originated from crystallic quartz (SiO_2) *(Figure 1.)* The most intensive phase in metakaolin M was quartz. The remaining part of SiO_2 in the chemical composition is the product of dehydration of clay minerals.

As a result of XRD and XRF measurements we can see, that the mineralogical and chemical composition of metakaolins are slightly different. The type C and S metakaolin contains kaolinite yet, which means that in this case the dehydration process was not completed. In metakaolin M quantity of kaolinite is the less and quantity of quartz is the highest. In addition all samples contain a substantial amount of amorphous materials [4]. After dehydration process the kaolin loses its crystal structure and become mainly amorphous material.

The chemical compositions of cements were analyzed also by XRF method, too *(Table 2)*. The elemental compositions of cements deviate in main components. The most important components, which determine the quality of cements through the clinker composition, are: SiO_2, CaO, Al_2O_3, Fe_2O_3.

Table 2**.** Chemical composition of cements

Chemical composition m%	CEM I 42.5 N	CEM I 42.5 N-S	CEM II/A-S 42.5 N
MgO	0.900	0.792	1.504
Al_2O_3	3.705	2.217	3.497
SiO_2	15.982	15.411	17.225
P_2O_5	0.270	0.236	0.282
SO_3	4.137	3.283	4.184
Cl	0.076	0.000	0.035
K_2O	0.819	0.382	0.538
CaO	69.283	69.957	68.515
Ti	0.219	0.139	0.225
Mn	0.340	0.091	0.638
Fe_2O_3	4.207	7.243	3.320
Zn	0.009	0.218	0.008

4.   Experimental program

In these recent experiments cement paste and mortar specimens were investigated. On the mortar samples we tested the chloride ion migration, which give information about the resistivity of cement stone against chloride penetration. For this reason cylindrical specimens were made, and the chloride migration coefficients were determined by Rapid Chloride Migration (RCM) test. From measured data we could calculate the non-steady state diffusion coefficient (D_{nssm}), which is used for determining the permeability of the specimen. Experiments were taken on mortar samples at the age of 28 days. Duration of tests was 8 hours and the employed DC was 30 V.

Cement paste samples were using to follow the hydration process. Two series of cement paste samples were made for the experiments: i) with and ii) without metakaolin. Cement paste samples contain cement or cement and metakaolin in the required ratio. The metakaolin replacement of cements was 17 m%. Binders were mixed with the required water amount to reach the standard consistency (semi-plastic) and then casted in standard size moulds (10x10x50 mm). After demoulding specimens were stored in humid conditions 22°C±2 and RH~100%. Measurements were taken on samples at the ages of 1, 7, 28, 120, 180 days.

The hydration rate in cement paste samples was followed by X-ray powder diffraction (XRD) and

thermoanalytical methods (TG/DTG/DTA). Morphological observations were carried out on the cement paste specimens with scanning electron microscope (SEM). The pore size and shapes were determined by gas adsorption method.

5.   Results and Discussion

5.1 Cement hydration

The hydration could be followed by the changes of the quantity of the cement components. The other way is to follow the formation of hydrate phases. Some of the clinkers decrease or later disappear, and form a new hydrate phase. We observed the speed of disappearance of the present phases, as well as we were able to follow the formation of different hydrate phases. The expected changes are the formation of portlandite and the increasing amount of CAH (calcium-aluminate-hydrate) and CSH (calcium-aluminate-hydrate) phases, respectably. The changes of quantity of ettringite, $C_3A \cdot 3CaSO_4 \cdot H_{32}$ and portlandite, $Ca(OH)_2$ have been considered.
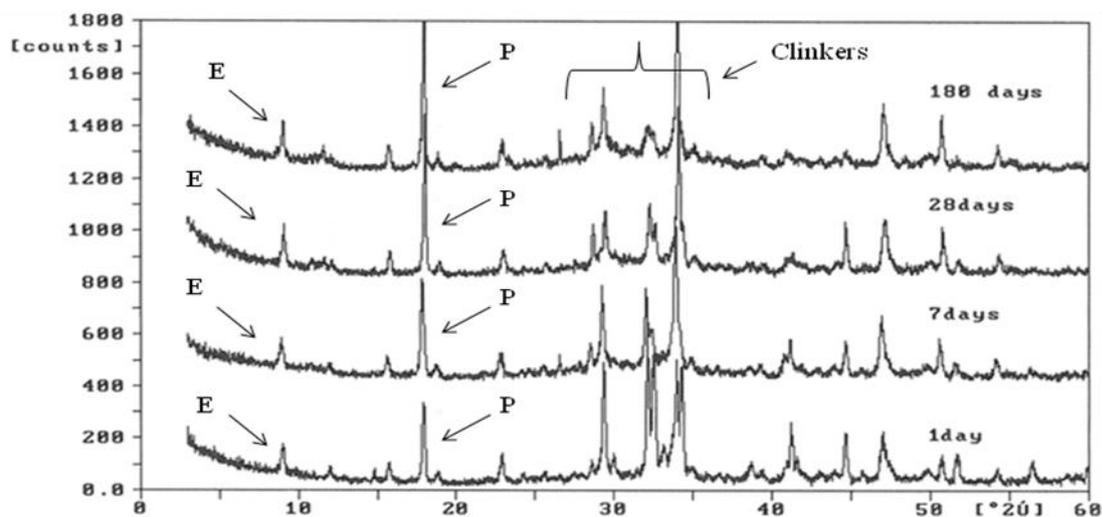
Figure 2. XRD pattern of cement pastes CEM I 42.5 N ordinary Portland cement without metakaolin, at the ages of 1 day, 7 days, 28 days and 180 days
(Notations: E: ettringite; P: portlandite)

Figure 2 shows the XRD results of cement paste samples made without metakaolin. First we compared the X-ray patterns of reference samples in different ages. It could be seen, that ettringite and portlandite (the two of the most important phases because of their well-crystallinity) are attended. In case of samples at the age of 180 days the hydrations of clinker minerals are still running. This is indicated by the decreasing relative intensity of the peaks of clinker minerals. In the cement paste samples made without metakaolin this process is connected with an increasing amount of portlandite ($Ca(OH)_2$). We also examined the hydration of samples where 17m% of cement was substituted by metakaolin. In case of samples mixed with certain amount of metakaolin, the increase of portlandite with the age of samples is negligible or very small. This means that up to the age of 180 days the hydration of metakaolin (the pozzolanic reaction between metakaolin and portlandite) persists furthermore with low rate. In the case of reference samples (without metakaolin) the hydration of silicate clinkers indicated by the increasing intensity of portlandite *(Figure 3)*.
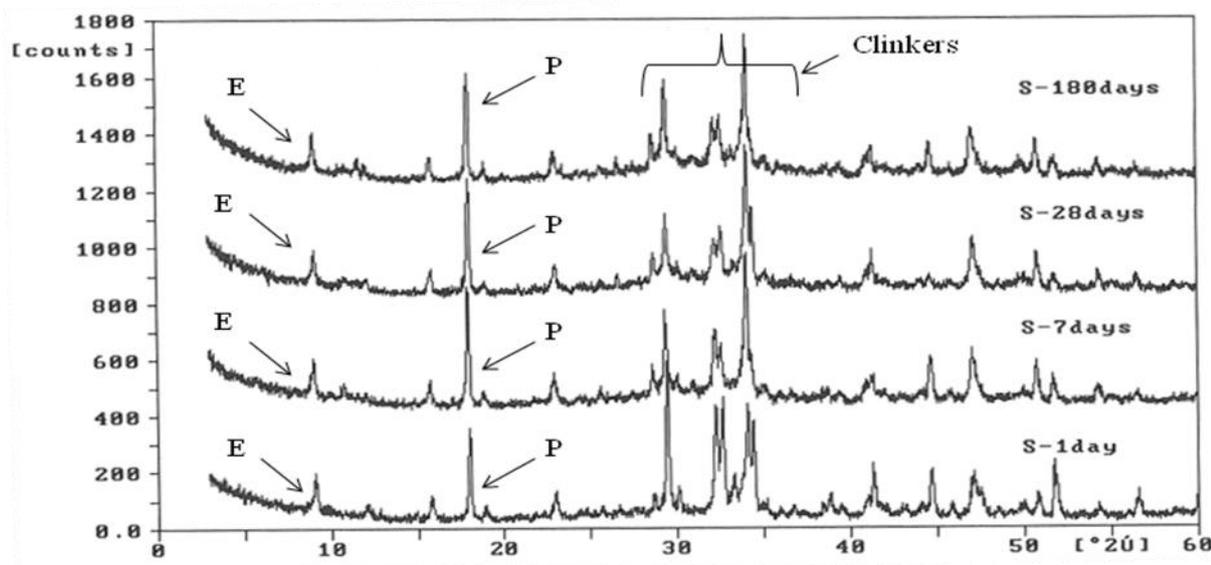
Figure 3. XRD pattern of cement pastes, CEM I 42.5 N ordinary Portland cement with
metakaolin (S), at the age of 1 day, 7 days, 28 days and 180 days
(Notations: E: ettringite; P: portlandite, S: suspension)

To get quantitative information, thermoanalytical methods were used. TG/DTG/DTA patterns indicate the presence of portlandite as well as the presence of CAH and CSH phases due to dehydration reaction during test conditions *(Figure 4-5)*.
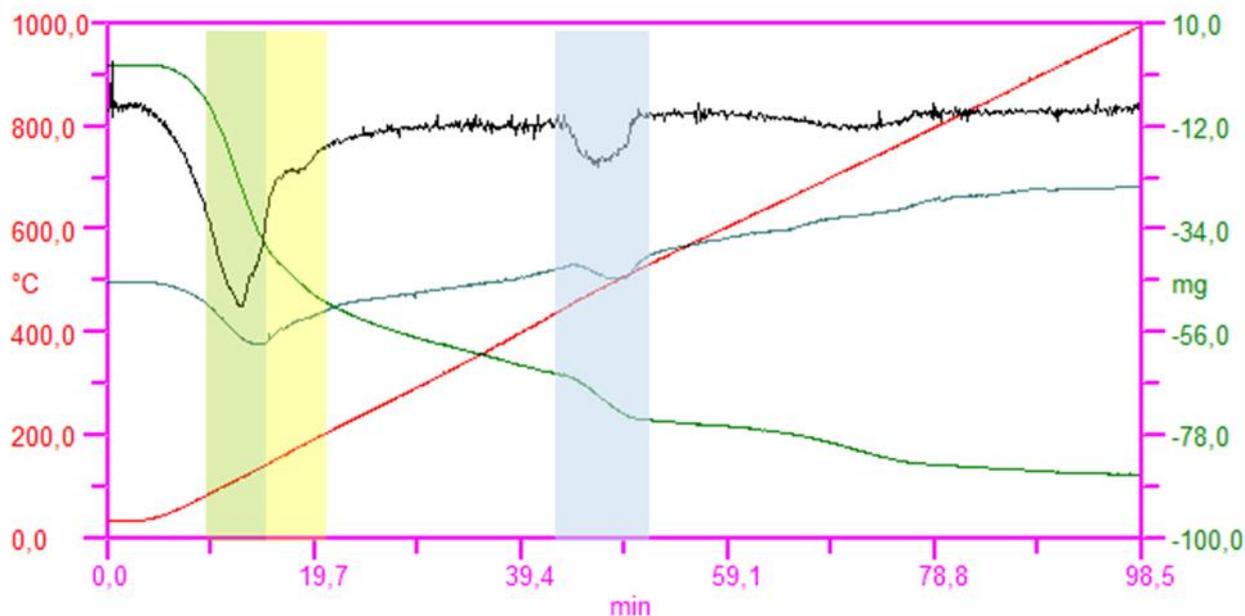
Figure 4. TG/DTG/DTA patterns of cement paste, CEM I 42.5 N ordinary Portland cement
without metakaolin at the age of 180 days
(Notations: green: ettringite; yellow: monosulphate; blue: portlandite)
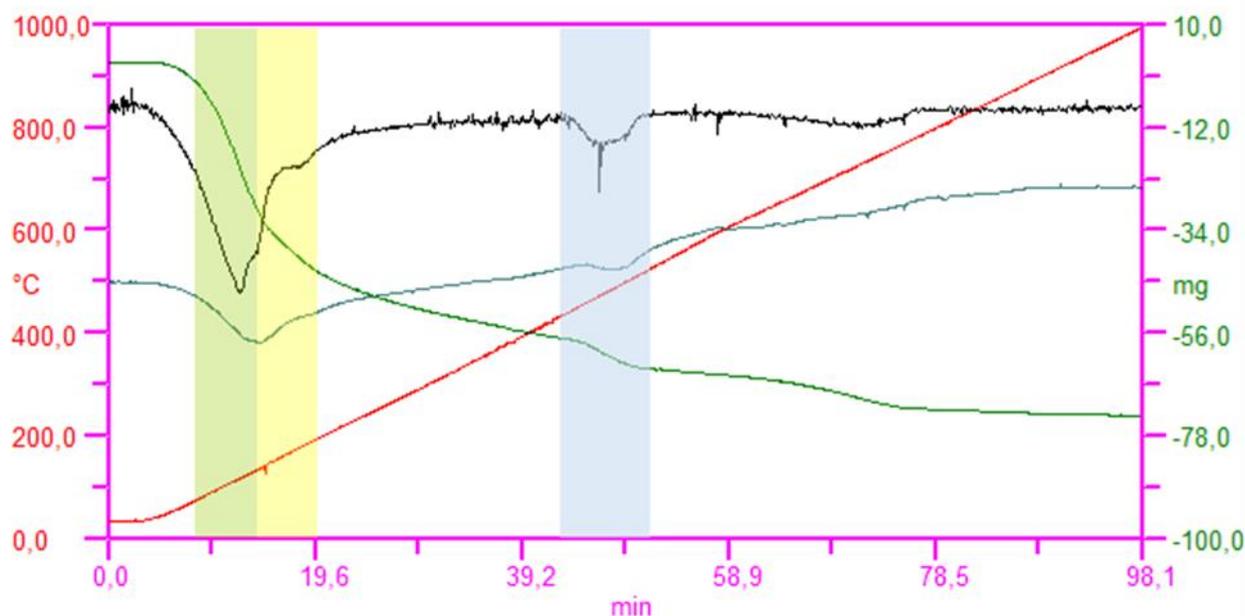
Figure 5. TG/DTG/DTA patterns of cement paste CEM I 42.5 N ordinary Portland cement
with metakaolin (S) at the age of 180 days
(Notations: green: ettringite; yellow: monosulphate; blue: portlandite, S: suspension)

The comparison of the amounts of portlandite in different samples could be seen at *Table 3*. The amounts of portlandite in ordinary cement paste samples increased with the ages, while the amounts in samples made with metakaolin decreased.

Table 3. The amounts of portlandite in cement paste samples made with or without metakaolin at the age of 28 days and 180 days

Ordinary Portland cement (CEM I 42.5 N) without metakaolin	Amount of portlandite (m%)	Ordinary Portland cement (CEM I 42.5 N) with metakaolin	Amount of portandite (m%)
28 days	12,81	*28 days*	9,02
180 days	13,03	*180 days*	8,43

5.2 Chloride ion migration

The non-steady state chloride diffusion coefficient was calculated and the formula was obtained from Fick 2nd law [5]. From the measurement data with the following formula could be quantify the diffusion coefficient. This coefficient suggests to the permeability of the samples with or without MK.

$$D_{nssm} = \frac{0,0239(273+T)L}{(U-2)t}\left(x_d - 0,0238\sqrt{\frac{(273+T)Lx_d}{U-2}} \right)$$

D_{nssm} = diffusion co-efficient, x 10^{-12} [m^2/s]
U = direct voltage [V]
T = average temperature [°C]
L = average thickness of the sample [mm]
x_d = average penetration of depth [mm]
t = testing time [hour]

Before testing the chloride ion migration, mortar samples were stored for 28 days in acidic solutions to study the resistivity of specimens against acidic circumstances. Solutions were sulphuric acid (H_2SO_4) with pH value 1 as well as acetic acid (CH_3COOH) with pH value 3. The changes were followed first by visual appearance and also by testing the chloride ion permeability. On the surface of specimens stored in sulphuric acid, needle-shape crystallic phase, ettringite ($C_3A \cdot 3CaSO_4 \cdot H_{32}$) was found. This hydration phase could react with chloride ions originated from the anodic solution of chloride migration test, forming Friedel's salt [6]. This can block the chloride ions while the chloride migration test was performed due to its chloride ion binding ability. Samples stored in acetic acid similar formation did not result, because the acetate ions ($COOH^-$) could not change the chloride ions (*Figure 6*) [7].

Figure 6. shows that the non-steady-state chloride diffusion coefficients of the samples made with MK are smaller as the diffusion coefficients of the references. This means, that textures of the specimens with MK are more compact or the porosity is not permeable; and that is why the chloride ions could not penetrate in the mortar sample so deep. The permeability of the samples with MK is about one fifth as for the references.

Measurements proved that the penetration of chloride ions in MK containing samples did not changed significantly by the different corrosive environments.
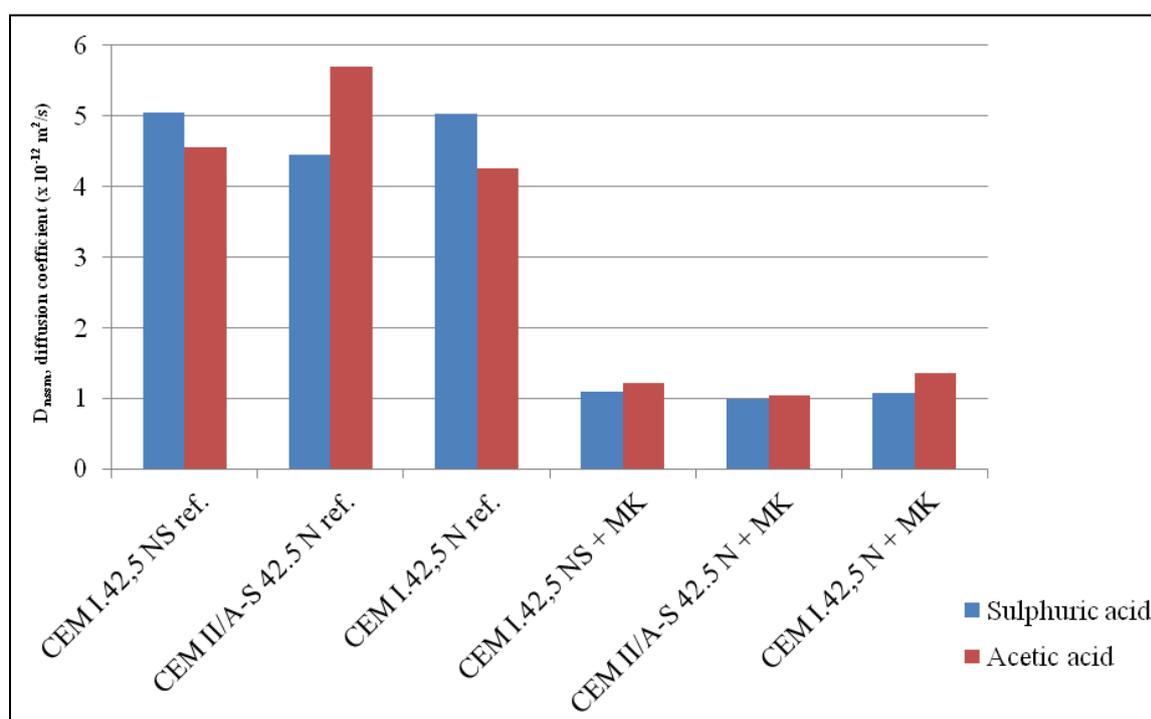
Figure 6. The non-steady state chloride ion diffusion coefficients of mortar specimens after immersed in acidic solutions at the age of 28 days for other 28 days.

5.3 Gas adsorption

The aim of the gas adsorption experiments was to determine the quantity and the shapes of pores in cement paste samples made with or without metakaolin *(Figure 7)*.

Figure 7. shows the typical hysteresis loops: H1: opened, cylindrical shaped pore type; H2: between different pore systems; H3: leak shaped pores with lamellar structures; H4: structures with lots of micropores. For these measurements automatic volumetric gas adsorption equipment was used. The lower limit of determination is 0,05 m^2/g. The adsorbate was nitrogen gas, and the temperature of measurement was 77 K.
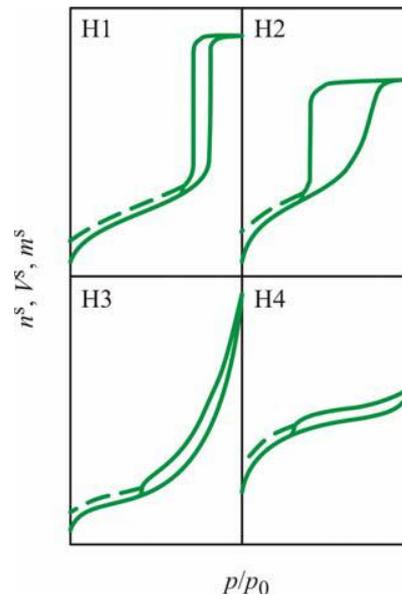
Figure 7. Classification of the hysteresis loop according to the IUPAC [8].

We defined the hysteresis loops, which can be classified by the forms of curves *(Figure 8)* [8]. From the shape we could indentify, that the gas adsorption in the pore structure of our samples resulted H3 type of hysteresis loop. This mean, that the pores are leak shaped which formed by particles bounded with lamellar structure.
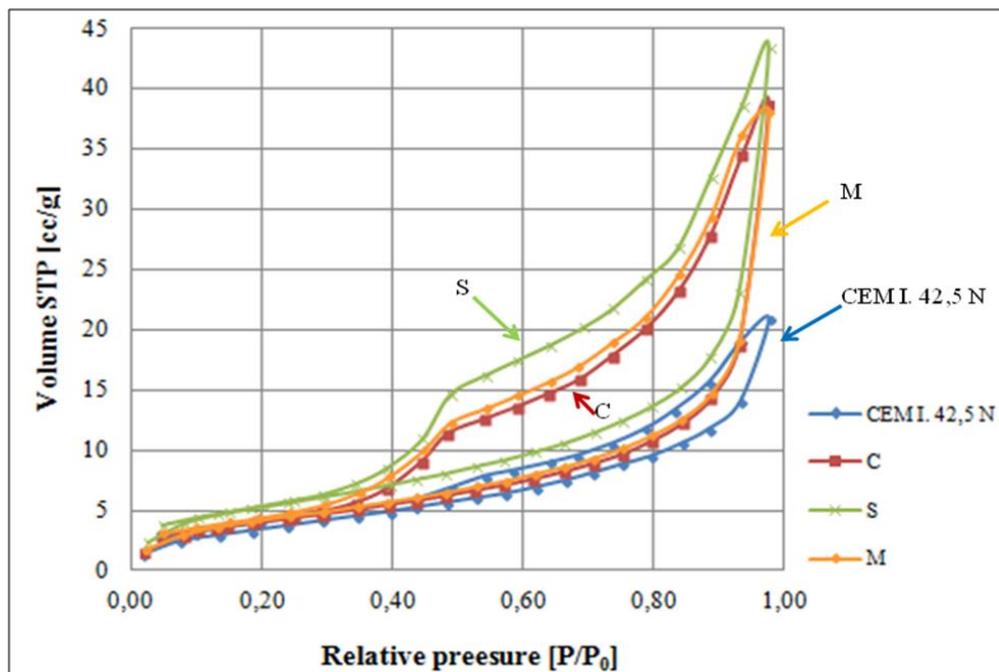
Figure 8. The hysteresis loops of adsorption and desorption mechanism of cement paste samples CEM I 42.5 N ordinary Portland cement with or without metakaolin (type: C, M, S) at the age of 28 days

Additional result of gas adsorption measurement is the total pore volume of cement paste samples *(Figure 9.)*. Sample 0 is the reference sample; letters are signs for the different metakaolin products (M, C, and S).
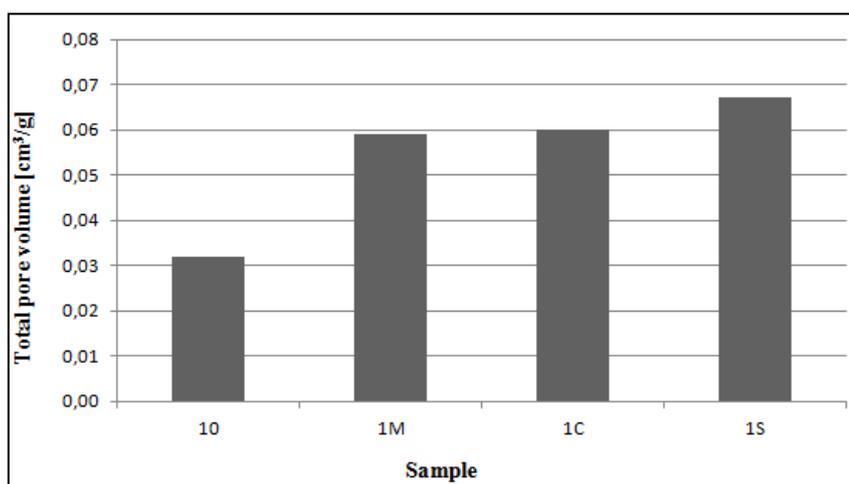
Figure 9. Total pore volume of cement paste samples without MK, CEM I 42.5 N ordinary Portland cement (reference sign: 10), and with MK (signs: 1M, 1C, 1S)

The total pore volumes of the samples with MK are higher. To analyze the connection between the decrease of diffusion coefficient and the increase of total pore volume of MK containing samples, further tests are required. Our explanation is, that metakaolin consumed the early crystallic hydration product, the portlandite phase due to pozzolanic reaction. Portlandite usually has big hexagonal plates and after pozzolanic reaction the initial volume of portlandite is not completely filled by CASH (calcium-aluminate-silicate hydrate) phases by this age.

5.4 Scanning electron microscope observations

To determine the morphology of the samples scanning electron microscope (SEM) observations were made. With this method we could see the differences between the formations of crystals in the structure. With the help of these information we could observe, that the formation of portlandite from clinkers into calcite ($CaCO_3$, calcium-carbonate) is faster in case of samples which were made without MK. On the other hand we can also observe the decreasing quantity of portlandite in the samples containing MK.
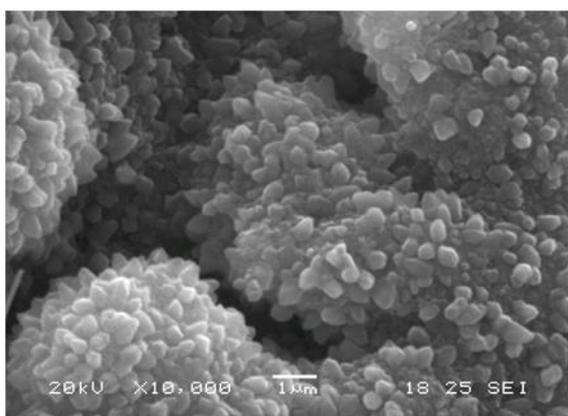
Figure 10. SEM observations: CEM I 42,5 N Portland cement samples without MK at the age of 28 days
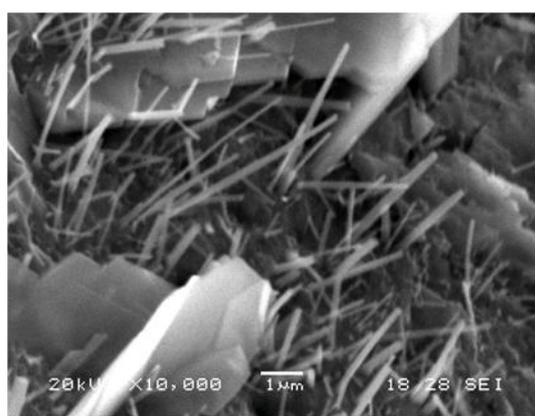
Figure 11. SEM observations: CEM I 42,5 N Portland cement samples with S type MK at the age of 28 days

Figure 10. shows the surface of the samples without metakaolin. We can notice the growing of calcite ($CaCO_3$) crystals from the portlandite phase due to the airborn CO_2. The other observation shows ettringite crystals (pin shape particles) and the transformation into monosulphate (lamellar

shape particles) *(Figure 11.)*. Both pictures were taken at the age of 28 days.

6.   Concluding remarks

In the last years there has been a growing interest in the application of metakaolin. There are promising results with concrete applications in corrosive surroundings made with metakaolin.
In our recent experiments the hydration mechanism of metakaolin in cement paste circumstances was followed. The most important conclusion of X-ray diffraction measurement is the evidence, that MK decreases the amount of portlandite due to the pozzolanic reaction. These are confirmed also by thermoanalytical (TG/DTA/DTG) measurements and it can follow by SEM observations, too.

The non-steady state diffusion coefficient was determined by the rapid chloride ion migration test. The diffusion coefficients of the samples made with MK are smaller as the diffusion coefficient of the references (without MK). This means that the mortar specimens made with MK are more compacted or their pore structure is not permeable than samples made without MK: that is why the chloride ions could not penetrate in the concrete so deep.

The results of gas adsorption investigation show, that the total pore volume is increasingin samples made with MK. This is contradictory with the conclusion of chloride ion migration test. Increase in micropores does not result higher permeability if the pores are mainly closed by the further hydration (formation of CASH phases).

For further conclusions other investigations and measurements are needed. Supplementary cementing materials could be the most important parts of concrete in the future, that is why necessary to study them.

7.   References

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