PARAMETERS OF EARLY HYDRATION OF CEMENT SYSTEMS AS INDICATORS OF SUCCESSFUL SOLIDIFICATION AND STABILIZATION OF WASTE ZEOLITE FROM A ZINC-PLATING PLANT

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INTRODUCTION

For solidification and stabilization of harmful waste materials to be successful, the addition should affect the hydration of the cement component of the system as little as possible and the harmful component should not be eventually released from the cement stone. Hydration of clinker minerals is accompanied with a series of reactions that cannot be traced individually. It is necessary to block hydration at certain times and determine the amount of un-reacted clinker mineral in the system or the amount of products formed. Such discontinuous methods of tracing reactions are time consuming and require costly analytic equipment (XRD, XRF, TA,.etc.). The course of hydration can be traced by monitoring the effects due to hydration reactions, such as hydration heat, changes in the pH value and specific conductivity of the cement paste, development of strength etc. Hydration is often traced by recording released heat developed in hydration reactions in clinker minerals, added gypsum, free CaO and MgO, yielding a result curve well described in literature. By analysing the hydration heat curves it is possible to determine the intensity and duration of individual processes, and kinetic parameters of hydration, rate and degree of hydration at specific moments. One of methods for continuous tracing of heat released during hydration of cement constituents is microcalorimetry. Continuous determination of specific conductivity of hydrating cement paste indicates the start of binding, which is an important practical parameter for determination of the effect of the addition on hydration of cement composite[1].

Replacement additions to cement additionally complicate the hydration processes, especially if the addition is active and if interactions between the addition and cement take place forming various reaction products. The products formed affect the dynamics and kinetics of cement hydration and the solidification process, modifying both the composition and the properties of the cement gel formed in the composite[2-5].

EXPERIMENTAL

Experiments were performed with samples of industrial Portland cement with the addition of natural zeolite in the amount of w = 10 – 50 mass % and zeolite saturated by zinc ions in the amount of w = 10 – 50 mass %. Portland cement is a commercial product of CEMEX-Dalmacijacement, Kaštel Sućurac, Croatia, marked CEM I according to the EN-197 standard. After 28 days of hydration, it develops a compressive strength of 42.5 MPa. The cement composition was determined by an EDXRF device TWIN-X, Oxford Instruments. The following composition of basic constituents was obtained (mass %): SiO2 22.82, Al2O3 4.82, Fe2O3 2.78, CaO 65.26, SO3 2.55, MgO 1.60, Na2O 0.18. The natural zeolite tuff came from the Donje Jesenje deposits, Croatia. The main mineral was clinoptilolite with more than 50%, with admixtures of muscovite, ilite, feldspar, quartz, and sepiolite. The chemical composition of zeolite expressed in mass percents was: SiO_2 64.93, Al_2O_3 13.66, Fe_2O_3 2.03, K_2O 1.88, Na_2O 3.66, CaO 2.99, MgO 1.10 and loss of heat 9.84. Zeolite saturated by Zn^{2+}- ions was also used as replacement addition. After saturation with Zn^{2+}- ions, the zeolite was dried at 105 °C, ground and sieved through the standard 4900 mesh/cm2 sieve, so that its particles had the size similar to those of Portland cement used.

Samples used to determine hydration heat were prepared from cement mixtures with the corresponding content of addition (of natural zeolite or saturated zeolite, *w* = 0-50 %) with the total mass of 4,0000 g. Measurements were made at the temperature of 20 ^{o}C with the constant water / solid ratio (W/S) of 0.5.

Cement pastes used in conductometrical measurements were prepared from cement and different additions of natural and saturated zeolite with the total mass of 100 g. Measurements were performed at the temperature of 20 ^{o}C with the constant water / solid ratio (W/S) of 0.5.

The microcalorimetrical measurements used to determine the effect of admixtures the hydration and solidification process parameters were carried out by means of a differential microcalorimeter[6] of the conduction-isoperibolic type. An ALMEMO 2290-8 data logger was used to record the thermal effects of the hydration processes in the microcalorimeter, tracing the change of voltage dU = $f(t)$, due to the change of temperature in the sample examined as a result of the hydration processes. The recorded values for dU = $f(t)$ were processed by a computer program on a PC, yielding the values of the hydration heat, the relative reaction degree, and the heat-release rate for the given hydration conditions.

The conductometrical measurements[7] used to determine the specific conductivity in the cement-paste composites were carried out by means of an ISKRA MA 5964 microprocessor conductometer connected to a PC via an RS 232 C digital output. The conductometrical cell electrode is metal, made of stainless steel with a constant CC = 0.2950 cm^{-1}.

RESULTS AND DISCUSION

Preliminary examinations have shown that the addition of natural zeolite to cement pastes affects the rheology, as the paste loses its plasticity with the increased addition of zeolite, and shows typical signs of false binding. In order to determine the effect of addition of zeolite on early cement hydration, specific conductivity of cement pastes was continuously determined with the aim to determine conductivity maximums, which are indicators of time of binding of cement pastes, and to compare them with the results of microcalorimetrical measurements.

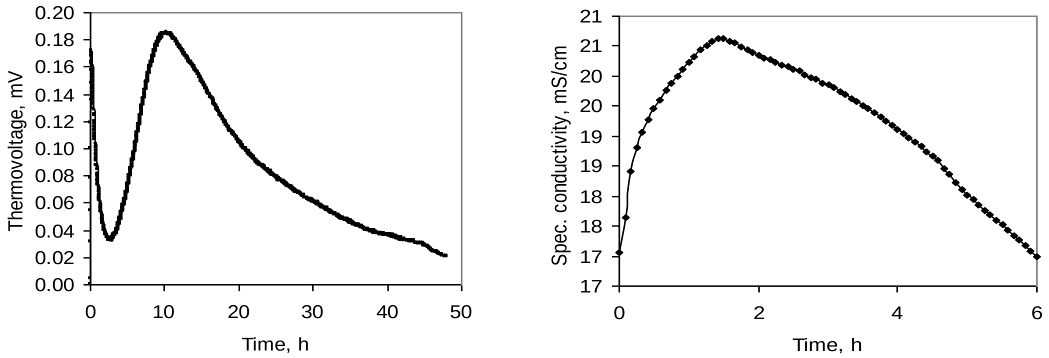

Figure 1. Microcalorimetrical (a) and conductometrical (b) curves for cement CEM I determined at W/C = 0.5 and t = 20 °C

Figure 1 shows a typical microcalorimetrical curve (a) and a specific conductivity curve (b) for CEM I without additions. The addition of zeolite in the cement system does not change the hydration mechanism (Figure 2), the shape of curves remains the same, but it affects the appearance of maximums and minimums on the curves, and their intensity.

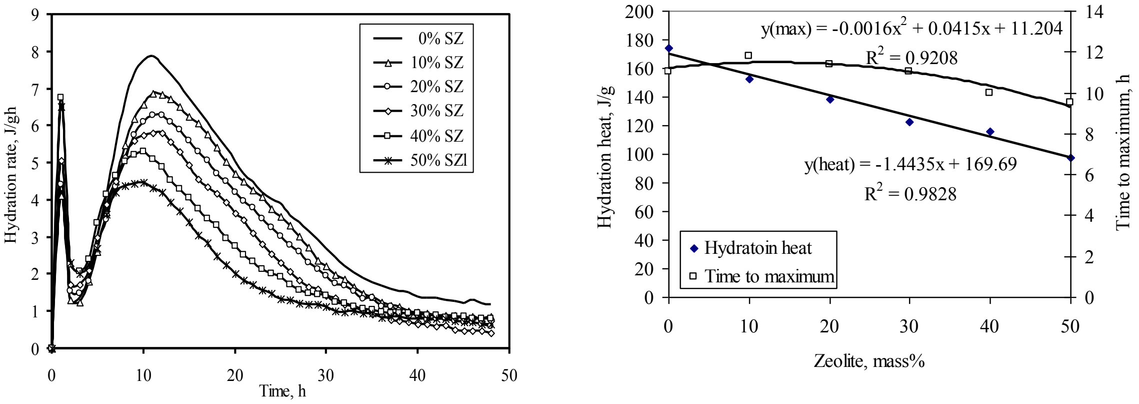

Figure 2. Hydration rate curve for CEM I with the addition of saturated zeolite, (SZ) and hydration heat and time needed to reach the maximum relative to the mass part of zeolite.

Values for hydration heat, rate and degree are significantly lower, and maximums on hydration curves appear sooner. Figure 2 shows the mathematical relationship of hydration heat and the time of appearance of the main maximum vs. addition of saturated zeolite. The following expression can be used to estimate the hydration heat released in CEM I with the addition of saturated zeolite in the amount of w = 0-50 %:

$$y(heat) = -1.44x + 169.7, \qquad (J/g) \qquad (1)$$

where y (heat) – hydration heat in J/g, and x – amount of saturated zeolite expressed in mass %. The same Figure shows the mathematical relationship of the time of appearance of the maximum on the hydration curve vs. added saturated zeolite:

$$y(max) = -0.0016\ x2\ -0.0415x + 11.204\ , (h) \qquad (2)$$

where y(max) represents the time of appearance of the main maximum in hours, (h), and x is the mass part of the saturated zeolite.

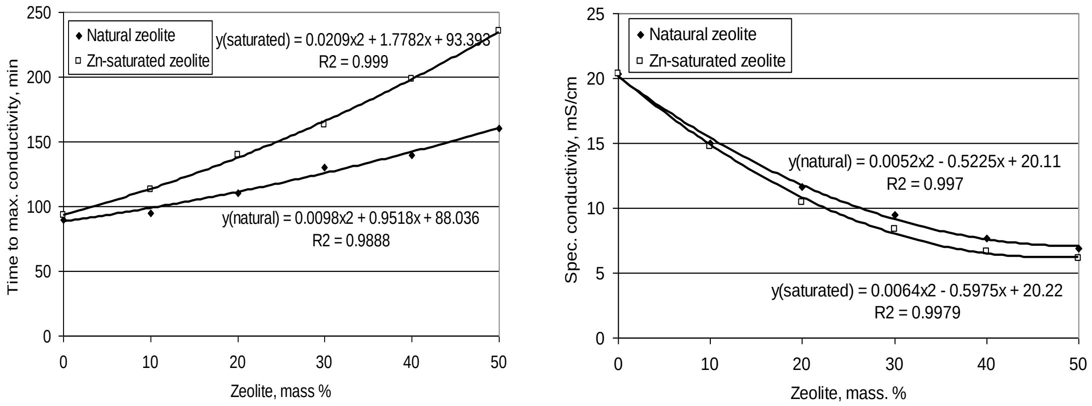

Figure 3. Determination of mathematical relationships of time needed to reach maximum conductivity and the value of specific conductivity vs. the amount of natural and Zn-saturated zeolite.

An important parameter in solidification and stabilization in practice is the time of binding of the cement composite. The Vicat device can be used to determine the time of binding of the cement paste in an discontinuous manner, while the electrochemical method, conductometry, continuously follows the changes in specific conductivity of the cement paste. The appearance of maximum specific conductivity indicates the start of binding of the cement paste[8].

The mathematical expressions (Figure 3) obtained make it possible to estimate the time of binding and the value of specific conductivity for any addition of zeolite in the w = 0-50 % range.

CONCLUSION

The microcalorimetrical method provides for continuous tracing and determining of effects of various additions of saturated zeolite on hydration processes. The higher the amount of saturated zeolite, the lower the values of total heat released, and the sooner the maximums appear. Determination of specific conductivity in cement pastes that contain additions of saturated zeolite from a zinc-plating plant may be used to estimate the effect of such additions on hydration processes. The increased addition of zeolite to cement composites retards the time of binding of the composite, more significantly in the case of saturated zeolite, while the specific conductivity values decrease. Zeolite additions to cement do not affect the hydration process mechanism, but affect the kinetic parameters and dynamics of the cement hydration process.

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PARAMETRI RANE HIDRATACIJE CEMENTNOG SUSTAVA KAO POKAZATELJ USPJEŠNE PROVEDBE SOLIDIFIKACIJE I STABILIZACIJE OTPADNOG ZEOLITA IZ POGONA POCINČAVANJA

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SAŽETAK

Za uspješnu solidifikaciju i stabilizaciju štetnih otpadnih materijala treba poštovati uvjet da dodatak što manje utječe na procese hidratacije cementne komponente sustava te u kanačnici da se štetna komponenta ne oslobađa iz cementnog kamena. Tijek hidratacije moguće je dekonvoluirati praćenjem efekata, koji su posljedica reakcija hidratacije, kao što su toplina hidratacije, promjene pH vrijednosti i specifične provodnosti cementne paste, razvoj čvrstoća i drugo. Često se hidratacija prati registriranjem oslobođene topline, koja nastaje pri reakcijama hidratacije u prvom redu minerala klinkera, dodanog gipsa, slobodnog CaO i MgO, gdje se dobije rezultantna krivulja koja je u literaturi dobro opisana. Analizom krivulja topline hidratacije moguće je odrediti intenzitet i trajanje pojedinih procesa, te kinetičke parametre hidratacije, brzinu i stupanj hidratacije u pojedinom trenutku. Jedna od tehnika za kontinuirano praćenje oslobađanja topline tijekom procesa hidratacije konstituenata cementa, je mikrokalorimetrija. Kontinuirano određivanje specifične provodnosti hidratizirajuće cementne paste ukazuje na početak vezanja, što je važan praktičan parametar za utvrđivanje utjecaja dodatka na hidrataciju cementnog kompozita.

Zamjenski dodatci cementu dodatno usložnjavaju hidratacijske procese, naročito ako su to aktivni dodatci te dolazi do interakcija između dodatka i cementa uz stvaranje različitih reakcijskih produkata. Nastali produkti utječu na dinamiku i kinetiku hidratacije cementa te na procese solidifikacije, mijenjajući kako sastav tako i karakteristike nastalog cementnog gela u kompozitu.

Ključne riječi: otpadni zeolit, solidifikacija/stabilizacija, hidratacija cementa, toplina hidratacije, specifična vodljivost.