

THE STABILIZATION OF HAZARDOUS ZEOLITE WASTES IN CEMENT COMPOSITES AND ITS EFFECT ON HYDRATION PROCESSES

STABILIZACIJA NEVARNEGA ZEOLITNEGA ODPADKA V CEMENTNIH KOMPOZITIH IN NJEGOV VPLIV NA HIDRATACIJSKE PROCESSE

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This study presents the results of an investigation into the effect of adding hazardous wastes in the form of zeolite tuff saturated with Zn^{2+} ions on hydration processes via the solidification of cement binding composites. The samples were prepared as cement pastes with a variety of zeolite contents (0.0–50.0%) relative to the mass of the solid (cement + zeolite addition) at a defined water/solid (W/S) ratio and a constant content of the admixture-type plasticizer. The processes of stabilizing hazardous wastes by the solidification of binding composites were analyzed by microcalorimetric, conductometric and UV/Vis spectrophotometric methods. The results obtained indicate a certain correlation between the quantity of zeolite waste added to the cement composite and the developed hydration heat, the relative reaction degree of the cement composite, and the Zn^{2+} -ion content in the eluates obtained by rinsing the cement composites after stabilization and solidification have taken place for a determined time of hydration.

Keywords: cement composite, cement hydration, stabilization/solidification, hazardous waste

V delu so prikazani rezultati raziskovanja vpliva dodatka škodljivih odpadkov v obliki zeolitnega tufa, nasičenega z Zn^{2+} -ioni na hidratacijske procese s solidifikacijo cementnih vezivnih kompozitov. Vzorci za raziskovanje so pripravljani v obliki cementnih past z različnim deležem zeolitnega dodatka (0,0–50,0 %) v odnosu na maso trdega (cement + zeolitni dodatek) in z določenim razmerjem voda/trdo (V/T) ter s konstantnim deležem plastifikacijskega aditiva. Procesi stabilizacije škodljivega odpadka s solidifikacijo nastalih vezivnih kompozitov so bili spremljani z mikrokolorimetrijsko, konduktometrijsko in UV/Vis spektrofotometrijsko analizo. Dobljeni in obdelani rezultati kažejo na povezavo med deležem dodanega zeolitnega odpadka v cementnem kompozitu in vrednostjo razvite toplote hidratacije, relativne stopnje reakcije cementnega kompozita ter vsebine Zn^{2+} -ionov v eluatih, ki se dobijo z izpiranjem cementnih kompozitov po izvedeni stabilizaciji in solidifikaciji, ki je trajala določen čas hidratacije.

Ključne besede: cementni kompozit, hidratacija cementa, stabilizacija/solidifikacija, škodljivi odpadki

1 INTRODUCTION

Waste materials containing Pb, Cd, Cr, Zn and other ions hazardous to the environment, as well as materials receiving these ions through various physical and chemical processes (ion exchange, etc.) must not be deposited in the environment without some form of control^{1,2}. They must be stabilized and taken care of in such a way as to prevent them from releasing into the environment hazardous ions in excess of the amount allowed, even when exposed to possible agents (atmospheric conditions and other aqueous electrolytes) over a long period of time. Studies of the stabilization processes in industrial waste and similar materials containing harmful ions indicate that they can be successfully stabilized by solidifying them in cement binding composites¹⁻³. Stabilization by solidification in cement composites immobilizes the hazardous waste components both physically and chemically^{2-4,5}.

The basic processes that successfully stabilize hazardous wastes in cement composites are the hydration

processes of the cement itself, acting as a hydraulic binder. Through these processes the cement binder undergoes a physical and chemical transformation over time, passing from the state of a paste into the state of a hydrated cement gel, with the properties of the solid state showing a certain strength. The cement hydration process is very complex; it can, however, be represented in a simplified manner through the hydration of its main components: clinker minerals such as C_3S , C_2S , C_3A and C_4AF . In hydration conditions, these components, together with gypsum ($CaSO_4 \cdot 2 H_2O$) as the binding regulator, become hydrate compounds, developing the final structure of a strengthened hydrated binder – cement gel of a specific strength^{6,7}. The cement gel that is formed surrounds the distributed particles of added waste material containing harmful ions (Zn^{2+} , etc.), and in this way immobilizes them by a process of solidification¹⁻⁷. The possibility of the harmful addition migrating from the hardened cement composite mass to its surface, and then back to the environment, is defined by a series of equilibrium conditions, resulting from a

series of interactions and possible Zn^{2+} -ion exchanges with ions from the cement binder and, of course, diffusion that governs the mass transport rate to the surface of the cement composite in the solidified system¹⁻⁸.

2 EXPERIMENTAL

Materials

Cement

Industrial Portland cement, PC-45B, a product of the Dalmacijacement-RMC Group, Kaštel Sućurac, Croatia, was used in this study. Its basic physical and chemical properties are shown in **Table 1**.

Zeolite waste with Zn^{2+} ions

Zeolite tuff saturated with Zn^{2+} ions, obtained by saturation with a solution containing 9.0 mmol/dm³ of $ZnSO_4$, was used in this study. The zeolite tuff originated from the Donje Jesenje deposit, Croatia, containing the clinoptylolite mineral, whose formula is $(NaK)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$. The exchange capacity of the zeolite tuff (granulation from 0.04–0.10 mm), established by means of the Kjeldal method, was 1.12 mmol/g. The saturated zeolite tuff was dried at 105 °C and sieved through a mesh 4900 cm⁻² sieve, so that its particle size matched that of the cement particles.

Admixture

An admixture, AD, of the water-reducing type of plasticizer, was used to reduce the quantity of water needed to prepare the cement composite pastes of specified consistency. It was used in a constant-mass addition of 0.3 %, compared to the mass of the cement + zeolite addition mixture.

Hydration water

Distilled water was used for the hydration and solidification processes.

Sample preparation and measurements

The cement pastes used for the microcalorimetric measurements were prepared by mixing the PC-45B industrial cement and zeolite waste saturated with Zn^{2+} ions. The quantity of the zeolite waste was 0.0 %, 10.0 %, 20.0 %, 30.0 %, or 50.0 % relative to the solid (cement + zeolite waste) mass. The solid mass was constant and amounted to 4.000 g. A constant amount of 0.3 % of the AD admixture relative to the solid was introduced into the reaction system together with the hydration water. The water/solid (W/S) ratio was constant and amounted to 0.5. The hydration and solidification were carried out in a microcalorimeter at 20 °C.

The cement pastes for the conductometric measurements were prepared by mixing the PC-45B industrial cement and zeolite waste saturated with Zn^{2+} ions. The quantity of the zeolite waste was 0.0 %, 10.0 %, 20.0 %, 30.0 %, or 50.0 % relative to the solid (cement + zeolite waste) mass. The solid mass was constant and amounted to 150.000 g. A constant amount of 0.3 % of the AD admixture relative to the solid was introduced into the reaction system together with the hydration water. The water/solid (W/S) ratio used to prepare the cement composite pastes varied and was exactly that needed to obtain a paste of normal consistency. The specific conductivity of the prepared cement pastes was determined in a thermostat at 20 °C.

The cement pastes for the UV/Vis spectrophotometric analysis were prepared by mixing the PC-45B industrial cement and zeolite waste saturated with Zn^{2+} ions. The quantity of the zeolite waste was 15.0 % or 30.0 % relative to the solid (cement + zeolite waste) mass. The solid mass was constant and amounted to 150.000 g. A constant amount of 0.3 % of the AD admixture relative to the solid was introduced into the reaction system together with the hydration water. The water/solid (W/S) ratio used to prepare the cement pastes was 0.5. The cement pastes formed were moulded in plastic vessels, so that the resulting shape of the samples for measurement was a cylinder of constant height and diameter. The pastes were left to hydrate for 24 h in air,

Table 1: Physical, chemical and mechanical properties of the PC-45B cement

Tabela 1: Fizikalno-kemijske in mehanične karakteristike cementa PC-45B

Component	Component content, %	Physical property and measure	Value
SiO ₂	20.50	Specific surface according to Blaine, cm ² /g	3300
Al ₂ O ₃	4.82	Standard consistency, %	26
Fe ₂ O ₃	2.82	Start of binding, min	85
CaO	65.43	End of binding, min	150
MgO	1.63	Average bending strength, MPa	
Na ₂ O	0.20	at 3 d	6.26
K ₂ O	0.78	at 28 d	8.44
		Average compressive strength, MPa	
		at 3 d	33.5
Total	99.26	at 28 d	50.7

and then immersed (isolated contact of cement paste and water) in thermostatically controlled water at 20 °C. The hydration and solidification processes for the pastes prepared in this manner took place for 1, 3, or 7 d in a thermostat. After solidification, the cement composite pastes were subjected to rinsing with a specific quantity of rinsing agent (water or 0.5 mol/dm³ HAc) on an automatic vibrator for a specific rinsing time from 0 to 24 h. After rinsing, the samples of eluates obtained were spectrophotometrically analyzed for their Zn²⁺-ion content.

Equipment and examination methods

The microcalorimetric measurements used to determine the effect of zeolite wastes on the hydration and solidification process parameters were carried out by means of a differential microcalorimeter of the conduction-isoperibolic type⁹. An ALEMO 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 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 $CC = 0.5673 \text{ cm}^{-1}$.

The UV/Vis spectrophotometrical analysis used to determine the quantity of Zn²⁺ ions in the eluates after the rinsing of the solidified cement composites was carried out in a PERKIN ELMER, Lambda EZ201 UV/Vis spectrophotometer. The content of Zn²⁺ ions in the eluates was expressed in mg/dm³.

3 RESULTS AND DISCUSSION

The results of the microcalorimetric analysis of the effect of different quantities of added zeolite waste on the hydration processes in the stabilization of the cement composites by solidification are shown graphically in **Figures 1, 2, and 3**.

The analysis of the results obtained for the change $dU = f(t)$ shown in microcalorigrams, **Figure 1**, shows that during hydration the calorimetric curve reaches a maximum that lasts for a short time and ends in a minimum. This early hydration period represents the so-called induction period of hydration, in which the initial dissolving and hydrolysis reactions take place. After that, the system enters the accelerated hydration

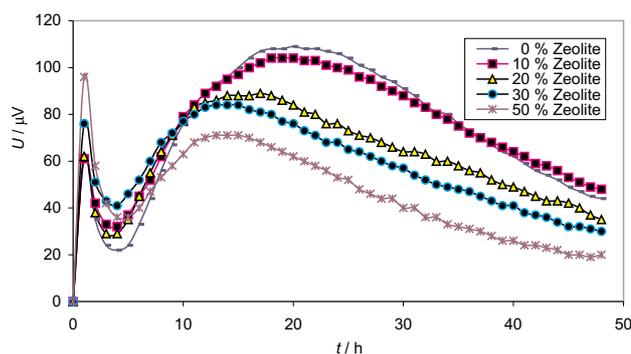


Figure 1: Change in thermo-voltage relative to the duration of the hydration and solidification of PC-45B cement pastes with differing quantities of zeolite waste saturated with Zn²⁺ ions

Slika 1: Odvisnost spremembe termonapetosti od časa hidratacije in solidifikacije cementnih past PC-45B z različnim deležem zeolitnega odpadka, zasičenega z Zn²⁺-ioni

period, when the reaction system binds and starts to harden, achieving the maximum values for the heat-release rate. After its maximum, the heat-release rate decreases, the system keeps hardening, and control of the hydration process rate is taken over by diffusion^{6,11,12}. The position and magnitude of the main maximum depends on the quantity of zeolite waste in the cement composite. The higher the content of zeolite waste, the lower the value of the maximum, and the earlier in the hydration process the maximum is recorded. These results are in accordance with expectations, as the increased content of zeolite tuff saturated with Zn²⁺ ions in the reaction system increases the quantity of Zn²⁺ ions that, under hydration conditions – high pH and Ca(OH)₂ – slow down the hydration of the C₃S, as the main component of silicate cement. The hydration slows down due to the formation of a surface layer of CaZn₂(OH)₆ · 2H₂O that prevents water transport to the C₃S phase^{5,7}.

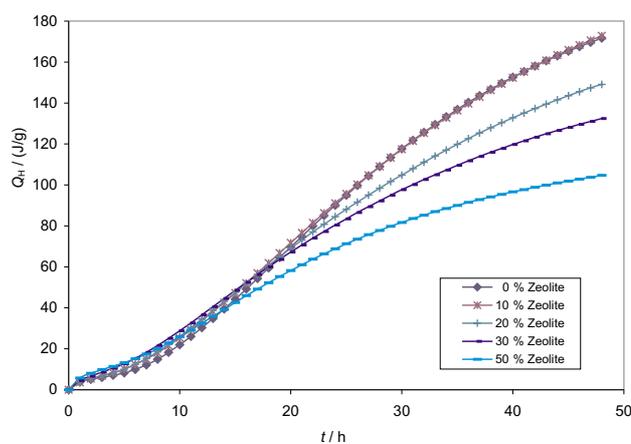


Figure 2: Developed hydration heat for PC-45B cement pastes with differing quantities of zeolite waste saturated with Zn²⁺ ions

Slika 2: Odvisnost razvite hidratacijske toplote cementnih past PC-45B z različnim deležem zeolitnega odpadka, zasičenega z Zn²⁺-ioni

The hydration heat of the cement composites developed during solidification, **Figure 2**, shows the direct effect of the quantity of zeolite waste added to the reaction system. When the zeolite waste content increases in cement composites, the final heat decreases during 48 hours of hydration. The composite without zeolite waste shows a hydration heat of 171.696 J/g, the composite containing 30 % of zeolite waste has a hydration heat of 132.463 J/g, and the composite containing 50 % of zeolite waste has a hydration heat of 104.714 J/g. The results obtained are in accordance with expectations, as the content of cement as the active component that releases heat during hydration is reduced in composites with an increased content of zeolite waste.

The analysis of the relative reaction degree relative to the content of zeolite waste in cement composites, **Figure 3**, indicates a similarity with the results obtained for the hydration heat in **Figure 2**. The relative reaction degree, α , was determined from microcalorimetric measurements¹² using the expression:

$$\alpha = \frac{Q(t)}{Q_{UK}}$$

where:

$Q(t)$ is the hydration heat at time t , J/g,

Q_{UK} is the hydration heat at the final hydration time, J/g

The analysis of the reaction-degree curves for cement composites indicates that the reaction rate changes during the hydration, depending on the content of zeolite waste in the composite. When the zeolite-waste content increases in the composites, the values of the reaction degree during 48 hours of hydration become increasingly lower. The composite without any waste addition shows a relative reaction degree of 59.3%, the one with 30% of zeolite-waste addition shows a value of 47.3%, and the one with 50% of zeolite-waste addition shows a value of 37.4%. The dynamics of change of the reaction degree, especially in the early hydration period, depends on the

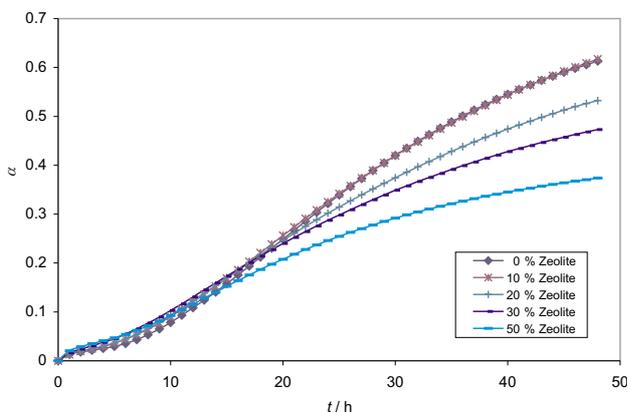


Figure 3: Relative hydration degree for PC-45B cement pastes with differing quantities of zeolite waste saturated with Zn^{2+} ions

Slika 3: Odvisnost relativne stopnje proaktivnosti cementnih past PC-45B z različnim deležem zeolitnega odpadka, nasičenega z Zn^{2+} -ioni

quantity of added zeolite waste and the actual water/cement ratio. The W/C ratio increases with decreasing cement content in the composite, with the consequence being an increased cement reaction degree. Because of this, the curves of samples containing increased quantities of zeolite waste in the early hydration phase up to approximately 15 hours lie above the curves of samples of cement paste without the addition. The results obtained agree with expectations as the balance shifts to the product side under the given solidification conditions^{5,6,7}.

Figure 4 shows graphically the results of the conductometrical measurements determining the specific conductivity of cement pastes, of the consistency corresponding to the normal one for each addition of zeolite waste.

The analysis of the conductograms indicates that the specific conductivity changes during hydration. Curves $\kappa = f(t)$ show the abrupt initial increase in specific conductivity and the reaching of the so-called first maximum, after which the specific conductivity falls to a minimum. This initial, very early period, is characterized by initial dissolution and hydrolysis reactions in which the aqueous phase of the cement composite paste fills with ionic species, reaching certain equilibria. After this, the dissolution and transfer of ionic species from the cement base and the zeolite waste slow down, which is recorded as a characteristic minimum on the curve. This hydration period can be characterized as the induction period. After the induction period, which lasts until the more abrupt change in the specific conductivity, the accelerated hydration period takes place, lasting for a certain period in which the conductogram records the second or the main maximum^{12,13}. The shape of the curve and the position of the main maximum and the measured value of the specific conductivity at this maximum depend on the content of zeolite waste in the cement

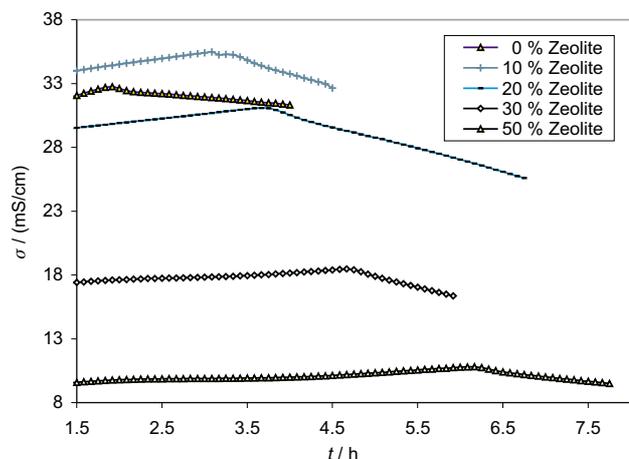


Figure 4: Conductivity relative to the duration of hydration of PC-45B cement pastes with different contents of zeolite waste

Slika 4: Odvisnost prevodnosti σ od časa hidratacije za cementne paste PC-45B z različnim deležem zeolitnega odpadka

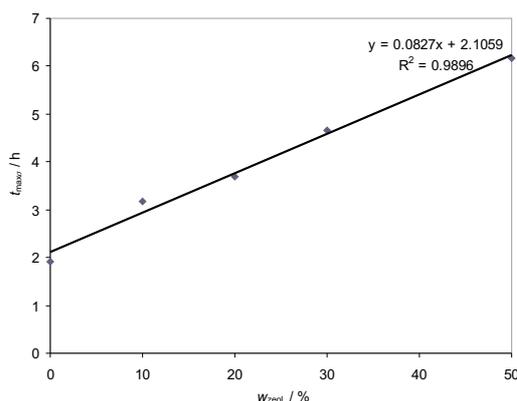


Figure 5: The position of the main maximum of the specific conductivity relative to the zeolite-waste content in cement composites

Slika 5: Odvisnost časovne pojave glavnega maksimuma prevodnosti od deleža zeolitnega odpadka v cementnih kompozitih

composite. If the zeolite-waste content increases, the position of the main maximum shifts to later times and the value of the specific conductivity becomes increasingly lower. The results obtained are due to interactions and equilibriums realized in the reaction system when the addition containing Zn²⁺ ions is introduced^{5,7}.

Figure 5 shows graphically the position of the main maximum on the temporal axis and the specific conductivity for cement composites on conductograms of cement composites relative to the content of zeolite tuff saturated with Zn²⁺ ions.

Figure 5 shows a linear dependence of the position of the specific-conductivity maximum on the zeolite-waste content in cement composites. This dependence can be described mathematically by a linear equation of the general form, $Y = ax + b$, in which $a = 0.0827$ and $b = 2.1059$, and x represents the content of zeolite tuff

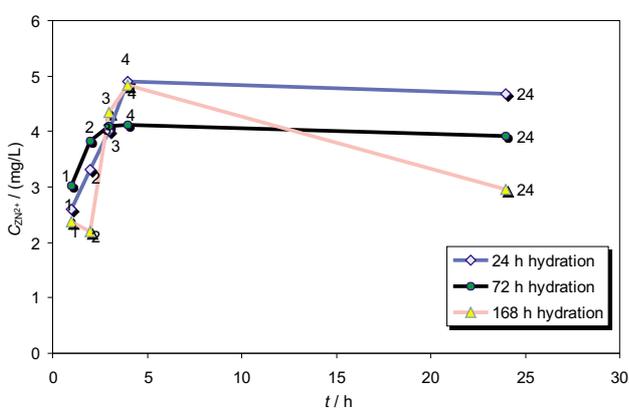


Figure 6: Concentration of Zn²⁺ ions in eluates relative to the time of rinsing with 0.5 M HAc and the time of solidification of cement composites with 15 % zeolite waste

Slika 6: Odvisnost koncentracije Zn²⁺-ionov v elutih od časa izpiranja z 0,5 M HAc in časa solidifikacije cementnih kompozitov s 15 % zeolitnega odpadka

saturated with Zn²⁺ ions relative to the mass of the solid (cement + zeolite waste).

Figures 6 and 7 show graphically the results of the spectrophotometrical measurements by analyzing the Zn²⁺-ion content in the eluates obtained by rinsing the cement composites solidified for a specified hydration time with 0.5M HAc.

The analysis of the results shown in **Figures 6 and 7** indicates that the concentration of Zn²⁺ ions decreases with longer solidification times. If the zeolite-waste content increases, the content of eluted Zn²⁺ ions increases for the same solidification time. These results agree with expectations as the solidification goes on in the hydration process with the formation of hydration products and the development of the final structure with densification of the reaction system^{5-8,14,15}. The content of Zn²⁺ ions in the eluates with 15 % and 30 % of zeolite waste shows low concentration values, even though the electrolyte is 0.5 M HAc. The results obtained by using the distilled water to rinse the cement composites with the same content of zeolite waste showed that the Zn²⁺ ions are found in traces in their eluates. These results were expected and agree with the results of the study of the applicability of the process of stabilization of hazardous wastes by solidification in cement composites¹⁻⁸.

4 CONCLUSION

This study shows that the content of zeolite tuff saturated with Zn²⁺ ions added to cement composites affects the hydration and solidification processes. This effect is observed by measurements of specified properties. It modifies the dynamics of the cement hydration process, thereby emphasizing the measured values to a greater or lesser degree. Hazardous wastes and the interaction in the reaction system result in changes of intensity of the resulting effect and changes of its position on the temporal axis representing the time

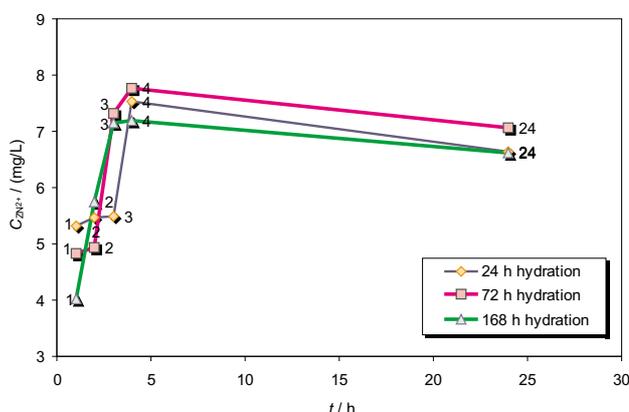


Figure 7: Concentration of Zn²⁺ ions in eluates relative to the time of rinsing with 0.5 M HAc and the time of solidification of cement composites with 30 % zeolite waste

Slika 7: Odvisnost koncentracije Zn²⁺-ionov v elutih od časa izpiranja z 0,5 M HAc in časa solidifikacije cementnih kompozitov s 30 % zeolitnega odpadka

of solidification for the cement composite. With an increased zeolite addition in the cement composite, the hydration heat and the relative reaction degree assume lower values. The maximum heat-release intensity observed in calorigrams $dU = f(t)$ shifts to earlier times with an increased content of the zeolite addition. Also, the specific conductivity of the cement pastes assumes lower values with maximums occurring later on the temporal axis when the zeolite content increases. Leaching tests of cement composites containing the zeolite addition show lower values of Zn^{2+} ions in the eluates with an increased solidification time. The low Zn^{2+} -ion content in the eluates of rinsed, solidified cement composites indicates that they can be successfully used for the stabilization of hazardous wastes.

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