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EFFECTIVE REMOVAL OF THE HEAVY METAL ION CD²⁺ FROM THE STRUCTURE OF CEMENTITIOUS MATERIALS WITH MINERAL ADDITIVES

EFIKASNO UKLANJANJE JONA CD²⁺ IZ STRUKTURE CEMENTNIH MATERIJALA SA MINERALNIM DODACIMA

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Abstract

Natural zeolite and bentonite were used as mineral additions to create cement-based building materials that are safe for the environment. This research focuses on the adsorptive qualities of these two clay raw materials, i.e., their propensity to immobilize heavy metal ions like Cd^{2+}. The acquired results were examined using kinetic models of pseudo-first and pseudo-second order. The isotherms of Langmuir and Freundlich were examined. Zeolite and bentonite had different adsorption affinities for Cd^{2+} cations. Seven cement binders with various mineral additions (fly ash, zeolite, bentonite) underwent a leaching test. The adsorption and hydration mechanisms that immobilized heavy metals within cementitious composites caused leachates obtained on cement samples with the addition of fly ash and clay (either zeolite or bentonite) to contain lower concentrations of Cd^{2+} ions than leachates obtained on cement samples with fly ash alone.

Izvod

Prirodni zeolit i bentonit korišćeni su kao mineralni dodaci za pripremu građevinskih materijala na bazi cementa koji su bezbedni za životnu sredinu. Ovo istraživanje se fokusira na adsorpcione kvalitete ove dve glinene sirovine, odnosno, njihovu sklonost ka imobilizaciji jona teških metala poput Cd^{2+}. Dobijeni rezultati su ispitani korišćenjem kinetičkih modela pseudo-prvog i pseudo-drugog reda. Ispitivane su Langmirove i Frojndlihove izoterme. Zeolit i bentonit su imali različite adsorpcione afinitete za katjone Cd^{2+}. Sedam cementnih veziva sa različitim mineralnim dodacima (leteći pepeo, zeolit, bentonit) je podvrgnuto ispitivanju luženja. Mehanizmi adsorpcije i hidratacije koji su imobilisali teške metale unutar cementnih kompozita doveli su do toga da eluati dobijeni na uzorcima cementa sa dodatkom letećeg pepela i gline (bilo zeolita ili bentonita) sadrže niže koncentracije Cd^{2+} jona od eluata dobijenih na uzorcima cementa samo sa elektrofilterskim pepelom.

INTRODUCTION

Due to the fast rise in the level of environmental pollution, the precondition for immobilizing heavy metals has taken on a role of utmost significance. Various methods have been devised to stop the leakage of harmful metals into the environment. One of the most commonly used methods is stabilizing hazardous metals by solidifying cementitious binders, /1/. The leaching of heavy metal ions can be reduced if fly ash is used as a substitute for cement in concrete, /2-5/. Heavy metals are present in relatively high concentrations in fly ash, /2/. Due to their pozzolanic characteristics, clayey minerals like zeolite and bentonite are also utilized as mineral additives in cementitious binders /5-7/. They are, however, more frequently used as heavy metal adsorbents, /8/.

Natural zeolites are hydrated aluminosilicate minerals with a microporous crystalline structure and an open three-dimensional framework of silicon-oxygen $[SiO_4]^{4-}$ and aluminum oxygen $[AlO_4]^{5-}$ tetrahedral with a network of tiny pores and channels /9-11/. The layered structure of bentonite is made up of two $[SiO_4]^{4-}$ tetrahedra that surround an octahedral sheet of $[AlO_4]^{5-}$ ions. Van der Waals forces bind the

basic unit layers together, /6/. Zeolite and bentonite can be used inexpensive ion exchangers to quickly and affordably adsorb specific heavy metal ions, /12/. Heavy metals from fly ash are dissolved in the extra water to create a cement-based binder. The ions adhere to the surfaces of the additives (such as zeolite or bentonite) because of their ion-exchange characteristics. There are two possible adsorption mechanisms: 1) the creation of a surface complex (mono) layer, and 2) the establishment of a thick precipitate layer. A coordinating covalent bond is formed between the adsorbent surface and the ion due to an inner-sphere complex or electrostatic attraction between the hydrated and adsorbent outer-sphere complex, /5/.

Cadmium naturally occurs in the environment as a pollutant derived from agricultural and industrial sources. As the green revolution, urbanization, and industrialization speed up, cadmium concentrations in soil are rising worldwide. Exposure to cadmium primarily occurs through ingesting contaminated food and water and, to a significant extent, through inhalation. The biggest issue with Cd-toxicity in the ground is currently seen in the world's south and southeast /13/. Another cause of Cd contamination is industrial waste-

INTEGRITET I VEK KONSTRUKCIJA
Vol. 23, Specijalno izdanje (2023), str. S19–S24

S19

STRUCTURAL INTEGRITY AND LIFE
Vol. 23, Special Issue (2023), pp. S19–S24

water dumped into rivers and canals, contaminating irrigation water, /14/.

Heavy metal adsorption inside the cement binder's structure can stop the metals from leaching into the environment /15-18/. In this study, Cd^{2+} adsorption and leaching were investigated on pulverized samples of cement binders with added mineral raw materials (fly ash, zeolite, and bentonite). Cadmium is selected for the investigation as a cation frequently contained within the fly ash structure. De-ionized water was used as a leaching agent in the experiment.

EXPERIMENTAL

Materials

Bentonite (B) and zeolite (Z) were produced using the conventional ore refinement technique. A routine sampling operation was used to collect the unprocessed samples from the ore deposit. The samples were crushed and milled prior to the pulverization in Herzog (Germany) vibration disk mill. Pulverized aluminosilicates were used in laboratory experiments. Fly ash (FA) originated from the 'Kostolac' power plant filter. Chemical composition of fly ash was determined using energy-dispersive X-ray fluorescence (EDXRF) spectrometry technique. The results are given in Table 1.

Table 1. Chemical composition of fly ash.

LOI at 1000 °C (%)	Si_2O (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)
3.15	50.30	22.32	12.14	8.96	1.88
K_2O (%)	Na_2O (%)	SO_3 (%)	Pb (mg/kg)	Cd (mg/kg)	Zn (mg/kg)
0.60	0.35	0.30	20.67	2.52	50.02
Cu (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	As (mg/kg)	Hg (mg/kg)	Ba (mg/kg)
39.32	80.13	805.72	62.65	0.00	68.66

Similar to the study of the immobilization of Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} /19/, the samples were chosen at random and kept in hermetically sealed containers. Fly ash, a byproduct of lignite combustion, is also an aluminosilicate. All composites were made using conventional Portland cement CEM I 42.5R as their base raw material (Lafarge). The chemical reagent used as adsorbate was $Cd(NO_3)_2$ (Carlo Erba, pro analysis > 99 %). Stock solutions containing 1000 mg·dm⁻³ of Cd^{2+} were created using the aforementioned analytical reagents. The diluted solutions obtained 0.10, 0.15, 0.20, 0.25 and 0.30 mmol·dm⁻³ concentrations of observed metal ions. Deionized water (18 MΩ·cm) was used for the solution preparation.

Kinetic study of adsorption

Duplicate adsorption tests were performed at 25 °C, with varying Cd^{2+} concentrations in single solutions. 0.01 g of adsorbent was dispersed in 50 ml of 0.1 mmol adsorbate solution. The mixture was shaken for the designated contact periods (10, 20, 30, 60, 120, 180, and 1440 min).

The experiments were carried out on a magnetic stirrer (INTLLAB). Following adsorption, the solid and liquid phases were separated by centrifugation at 1700 rpm for 10 minutes (Heittech Eva 21). These resulting solutions' ion concentrations were assessed using inductively coupled plasma-optical emission spectrometry (ICP-OES, SPECTRO GENESIS) at $\lambda_{Cd} = 226.502$ nm. The amount of adsorbed ions with time, q_t (mg/g), was calculated using the mass balance equation:

$$q_t = \frac{(C_0 - C_e)v}{m_{ads}}, \qquad (1)$$

where: C_0 and C_e are initial and equilibrium concentrations of cations in the solution, respectively, /18/.

The rates of ion adsorptions were evaluated using pseudo-first and pseudo-second kinetic models. The pseudo-first-order rate is provided by the Lagergren equation:

$$\log(Q_e - Q_t) = \log Q_e - k_1 t, \qquad (2)$$

where: Q_e is the amount of metal ions adsorbed in mg/g at equilibrium (min); Q_t is the amount of metal ions adsorbed in mg/g at time t (min); and k_1 is the rate constant of pseudo-first order adsorption (min⁻¹).

Pseudo-second order rate is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}, \qquad (3)$$

where: k_2 is pseudo-second order rate constant (g/mg·min) /20/.

Adsorption isotherm analysis

The period of 1440 min was adopted as the equilibrium time for all processes. The equilibrium amount of the adsorbate was denoted as q_e. All adsorbates prepared as single solutions in different concentrations of 0.10, 0.15, 0.20, 0.25, and 0.30 mmol/dm³ were interpreted via Langmuir and Freundlich adsorption isotherms. The Langmuir equation model is given as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{b Q_{max}}, \qquad (4)$$

where: q_e is adsorption capacity (mg/g); C_e is equilibrium concentration (mmol/dm³); Q_{max} is the maximum possible amount of ions that can be adsorbed per unit dry weight of adsorbent; and b is Langmuir constant (l/mg),

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \qquad (5)$$

where: q_e is the equilibrium ions concentrations adsorbed in adsorbent (mmol/g); C_e is the equilibrium concentrations of ions in the solution (mmol/dm); K_f is the Freundlich constant related to the adsorption capacity; and $1/n$ is an empirical parameter related to adsorption intensity, which varies with the heterogeneity of the material.

Leaching control

Seven cement binders were created using various mix patterns. S_0 binder was based on Portland cement (PC) solely. Binders S_1, S_2, S_3, S_4, S_5, and S_6 contained PC as well as varying amounts of mineral additives (fly ash - FA, zeolite - Z, and bentonite - B). Fly ash participated in the mix design of the S_1 binder with 30 wt%. Fly ash and either zeolite or bentonite were used as combined mineral additions in the S_2, S_3, S_4, and S_5 binders (S_2: 20 wt% FA + 10 wt% Z, S_3: 10 wt% FA + 20 wt% Z, S_4: 20 wt% FA + 10 wt% B, and S_5: 10 wt% FA and 20 wt% B). The S_6 binder was made with an equal amount of all three mineral additives (10 wt%).

INTEGRITET I VEK KONSTRUKCIJA
Vol. 23, Specijalno izdanje (2023), str. S19–S24

S20

STRUCTURAL INTEGRITY AND LIFE
Vol. 23, Special Issue (2023), pp. S19–S24

Cement binders were prepared according to the standard SRPS EN 12457-4:2008, /21/, for the leaching test. Dry components were homogenized in a lab pan mixer for 120 s. During mixing, the water required for a self-flowing consistency was added. Green mixes were sealed in polyethylene bags for 48 hours (20 ± 2 °C, 95 ± 5 % humidity), after being poured into steel molds (2×2×2 cm). Samples were stored in the same conditions for the following five days after they were taken out of the molds. The samples were then stored at 20 ± 2 °C and 65 ± 5 % humidity until the 28th day.

The hardened samples were crushed and pulverized into particles smaller than 10 mm (mean diameter of the resulting grain was 2 mm). The testing samples and combinations of deionized water were examined to determine the leachability of heavy metals for each binder. 1:10 was the liquid to solid mixing ratio. For the following 24 hours, the produced combinations were continuously mixed in a lab mixer at room temperature. After that, a membrane filter (0.45 μm) was used to filter the leachate. ICP-OES technique was employed to calculate the metal concentrations in leachates.

Instrumentation

EDXRF Spectro Xepos (Germany) and the ICP-OES analyzer Spectro Genesis (Germany) were the tools employed in this work.

The binary cobalt/palladium alloy thick-target anode X-ray tube (50 W/60 kV) and combined polarized and direct excitation are features of the EDXRF equipment. A novel silicon drift detector (SDD) design serves as the detector for Spectro Xepos. This detector uses air as part of its cooling system. The Spectro XRF Analyzer Pro, Xepos C Software manages the EDXRF.

A plasma generator operating at 27.12 MHz is included with the ICP-OES analyzer, enabling the 'robustness' of plasma. The generator has a 1.700 KW output. 16 l/min of argon is used up during the analysis. The plasma has a wavelength range of 175-775 nm and is positioned radially. For plasma initiation, as a carrier gas, and to cool the quartz system where the plasma forms, high purity argon (99.9999 %) is employed. Software called Smart Analyzer Vision is used by the instrument system.

RESULTS AND DISCUSSION

Adsorption isotherms

By computing and graphing equilibrium Cd²⁺ concentrations, C (mmol/dm³) versus the adsorbed amount of detected ion q_e (mmol/g), Cd²⁺ adsorption isotherms are discovered. The obtained adsorption isotherms are presented in Fig. 1.

The shapes of both obtained isotherms are highly similar regardless of the applied adsorbent - zeolite or bentonite. Adsorption maximums for Cd²⁺ are recorded at a concentration of 0.3 mmol/dm³. The maximum of adsorption for the Cd²⁺ solution tested on bentonite sample is 0.91 mmol/g, while adsorption maximum on the zeolite sample is lower and amounts to 0.73 mmol/g. Cd²⁺ isotherms obtained on zeolite and bentonite samples are similar and show that the slope was relatively low at higher concentrations, as can be seen in Fig. 1. These isotherms also have a defined plateau for the adsorption maximum. The main difference between

isotherms of Cd²⁺ on bentonite and zeolite was the higher adsorption capacity for bentonite adsorbent compared to capacities in samples where the adsorbent was zeolite.
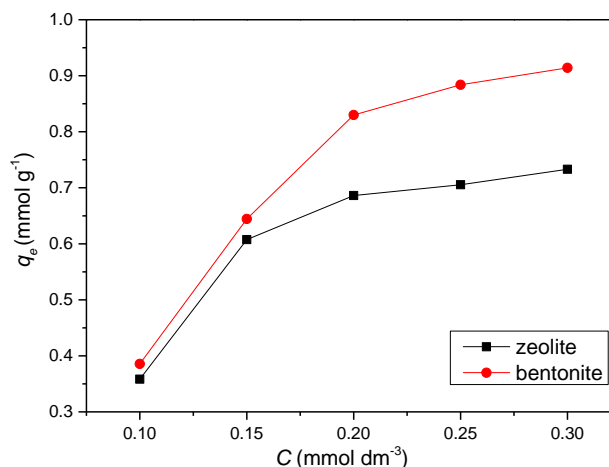

Figure 1. Adsorption isotherms of Cd²⁺ solution on zeolite and sample.

Langmuir and Freundlich isotherms were used for evaluating adsorption capacities of zeolite and bentonite adsorbents, /22/. Tables 2 and 3 present data derived from linear forms of Langmuir (constants b and k) and Freundlich (constants n and log k) equations for Cd²⁺ adsorption in solutions onto zeolite and bentonite, respectively.

With coefficients of determination (R^2), the values of the adsorption capacities for Langmuir and Freundlich models are presented in Tables 2 and 3. High coefficients of determination (R^2) imply that Langmuir is preferable to Freundlich models for the description of Cd²⁺ adsorption on zeolite and bentonite. The Langmuir model of adsorption isotherms demonstrates that the adsorbent homogenous sites are where the adsorption occurs. When dealing with monolayer adsorption, this model is typically successfully implemented, /23/.

Table 2. Linear forms of Langmuir equations for Cd²⁺ tested on zeolite and bentonite samples.

Sample	Equation	k^* (mmol/dm³)	b^* (mmol/g)	R^2
Zeolite	$y = 1.15x + 0.15$	7.66	0.86	0.97
Bentonite	$y = 0.61x + 0.12$	5.08	1.64	0.91
K^* = slope/intercept; b^* = 1/slope				

Table. 3. Linear forms of Freundlich for Cd²⁺ solutions tested on zeolite and bentonite samples.

Sample	Equation	n (g/dm³)	log k (mmol/g)	R^2
Zeolite	$y = 0.11x + 0.06$	0.70	1.14	0.63
Bentonite	$y = 0.73x + 0.43$	3.01	0.65	0.71

The maximum adsorption data, b (mmol/g) (Table 2) shows that bentonite is over-all better adsorbent than zeolite for Cd²⁺. The result of comparing the binding strength, k (mmol/dm³), is that the value is higher in the solution with zeolite than when the adsorbent is bentonite. According to maximal adsorption data, b (mmol/g) in Table 2, bentonite is often a more effective adsorbent for Cd²⁺ than zeolite.

Results presented in Fig. 1 and Tables 2 and 3 highlight that particular amounts of Cd²⁺ adsorbed by bentonite are

INTEGRITET I VEK KONSTRUKCIJA
Vol. 23, Specijalno izdanje (2023), str. S19–S24

S21

STRUCTURAL INTEGRITY AND LIFE
Vol. 23, Special Issue (2023), pp. S19–S24

higher than the amount of Cd²⁺ adsorbed by zeolite. The bentonite is more selective towards Cd²⁺ than zeolite.

Kinetic models

The effect of adsorption contact time on the concentration of adsorbed metal ions of Cd²⁺ on bentonite and zeolite used as adsorbents is illustrated in Fig. 2.
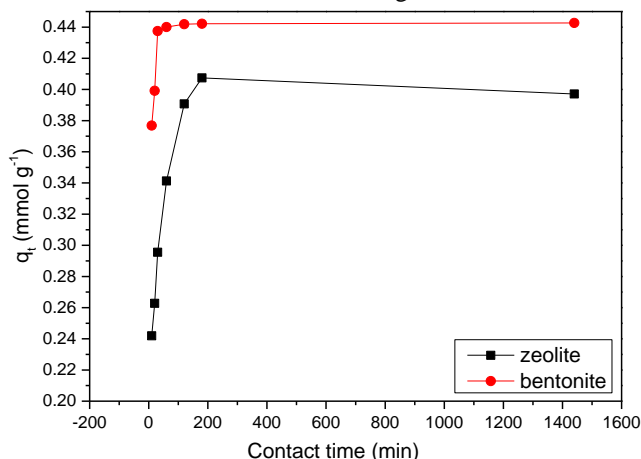

Figure 2. Influence of contact time on adsorption of Cd²⁺ from solution on bentonite and zeolite.

In Fig. 2, a net difference in the adsorption behavior onto bentonite and zeolite can be observed. The adsorption of Cd²⁺ on bentonite uptake were found to increase with increase in contact time and maximal percentage of adsorptions occurred at 30 min, and afterwards they became constant. Adsorption of Cd ions on zeolite shows similar behavior, but contact time is achieved at 180 min for maximal adsorption of Cd²⁺ on zeolite.

The $\log(Q_e - Q_t)$ versus t in the pseudo-first kinetic model provided the adsorption rate constants and coefficient of determination (Model I). The plot of t/Q_t against t is used to develop constants and coefficients for a pseudo-second-order model (Model II). Results are displayed in Table 4.

As evident from the outcomes displayed in Table 4, high R^2 values imply that a pseudo-second order model governs the adsorption. The adsorption system is described more precisely by the pseudo-second order kinetics model since the squares of correlation coefficients (R^2) are near to 1. The adsorption of Cd²⁺ on bentonite and zeolite confirms the criteria of the pseudo-second order kinetics model because calculated values for the equilibrium adsorption capacity (q_{ecalc}) for the pseudo-second order model were close to the experimentally obtained adsorption capacity (q_{eexp}).

Table 4. Adsorption kinetic model equations with different parameters for adsorption of Cd²⁺ on bentonite and zeolite.

Adsorption kinetic model		Model I		Model II		
Parameter		R^2	Q_{ez} (mol/g)	R^2	Q_{ecal} (mmol/g)	Q_{eexp} (mmol/g)
Cd2+	bentonite	0.92	63	0.99	0.25	0.27
	zeolite	0.79	67	0.98	0.09	0.10

Hydration process - a mechanism of immobilization

During the hydration process that occurs inside cementitious materials, heavy metals are being immobilized, /19/. The structure of cement minerals changes specifically during hydration, allowing for the immobilization of heavy metal ions within a newly formed crystalline grid, /24-26/. Fly ash, zeolite, and bentonite are examples of pozzolanic materials, which implies they have an impact on, and take part in the hydration process, /6, 19/.

Some Ca²⁺ ions are adsorbed on fly ash particle surfaces when fly ash is present in the cement-aqueous mixture. Ca²⁺ concentration in the liquid phase decreases with decreasing cement content. Due to the pozzolanic reaction, fly ash pozzolanic activity consumes a significant amount of Ca(OH)₂ /19, 27/.

According to literature /19, 28/, heavy metal ions can have an impact on the reaction rate of cement, portlandite precipitation, calcium carbonate polymorphism, formation of calcium aluminate hydrate phases, polymerization of calcium silicate hydrate, and the final amorphous hydration product of cement.

The pH of the mixture increases until it reaches the saturation point of the portlandite solution (Ca(OH)₂).

The pozzolanic reaction is also changed by the addition of natural zeolite to cementitious materials. Additionally, a cement binder with zeolite addition undergoes pozzolanic reactions in a different manner than a cement binder with fly ash addition. The additional water absorbed within the zeolite structure, the negatively charged zeolite framework that prevents the diffusion of hydroxyl ions into the zeolite pore, and the exchangeable properties of cations from the zeolite structure are the causes of these changes in chemical reactions that occur between standard cement minerals, /11, 19/. In particular, the pore structure of zeolite allows for rather significant water absorption. This absorbed water serves two purposes when it is released during the ongoing pozzolanic reaction. A lowering in pH as a result of dilution is the function effect. The second purpose is to provide extra water when the amount of water in the cement pores drops as a result of hydration.

In comparison to fly ash and zeolite, bentonite has lesser pozzolanic activity. Additionally, the hydration of cement can be slowed down by bentonite, /19, 28/. The dissolution-precipitation reactions that occur when cement and bentonite (i.e., smectite minerals and any secondary minerals like quartz, etc.) react, run the danger of degrading the material. The cementitious materials, such as portlandite, calcium silicate hydrate gel (CSH), calcium aluminum silicate hydrates (CASH), and others, are chemically stable at high pH, but at low pH, they dissolve and then reform as different materials. For instance, below a pH of 10.4, the CSH gel will disintegrate and portlandite will degrade, /19, 28/. On the other hand, higher pH levels are probably going to cause the smectite minerals in bentonite to degrade. Bentonite is a highly good adsorbent, which contributes to the effective immobilization of heavy metals even if it is not a good pozzolanic material.

Leaching analysis

In Fig. 3, a graphic representation of the concentrations of heavy metals (Cd²⁺) leached from cement binders is shown. The LIM value derived from the Waste Acceptance Criteria rule is used as the leaching limit, /17/. The suggested leach-

ing limit values for Cd are used to determine whether a waste material is harmful or not.

As can be seen in Fig. 3, the leachate made of cement and fly ash (S_1) used as binders, showed the highest Cd^{2+} concentration. On the other hand, mixtures S_2 and S_3 with natural zeolite effectively minimized the leaching levels of Cd^{2+}. The addition of bentonite to binders S_4, S_5, and S_6 improved the outcomes of the immobilization of the afore-mentioned heavy metal. Additionally, bentonite exhibited higher adsorption of Cd^{2+} ions than zeolite. For Cd^{2+}, there is a 70 % difference in ion concentration between the leach-ate obtained on a fly ash sample alone and the leachate col-lected on a cement, ash, and zeolite mixture. For Cd^{2+}, there is an 80 % difference in ion concentration between the leachate obtained on a sample of fly ash and that of mixture of cement, ash, and bentonite. All obtained leachates had Cd^{2+} concentrations significantly lower than the LIM limit specified by the waste acceptance criteria.
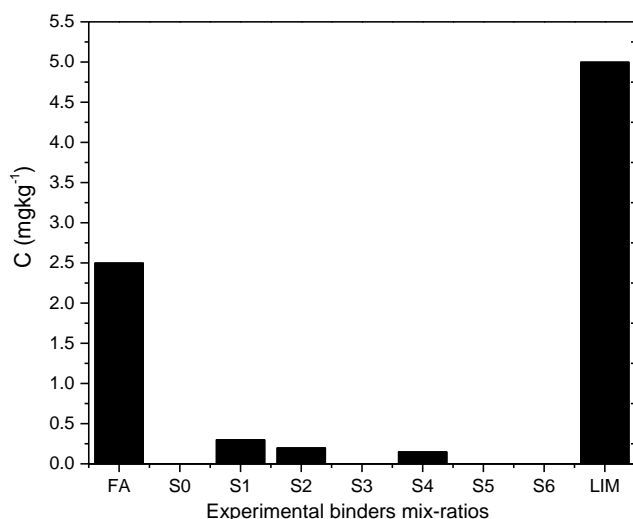

Figure 3. Concentrations of Cd ions in leachates obtained on cement binders.

CONCLUSION

The results of adsorption studies demonstrated the effec-tiveness of bentonite and zeolite as Cd^{2+} ion adsorbents. Namely, zeolite and bentonite were successfully employed as adsorbents for Cd^{2+} ions in fly ash-and-cement-based bonding agents. Both adsorption processes - on zeolite and bentonite, can be fully described by the Langmuir isotherm. The pseudo-second-order kinetics model was equally sup-ported by Cd^{2+} adsorption on bentonite and zeolite samples. All investigated leachates exhibited Cd^{2+} concentrations significantly lesser than the limit of leachability outlined in the waste acceptance criteria. Additionally, as the newly created cement minerals are crystallizing during cement hydration, heavy metals are being bound and immobilized in the cementitious structure.

ACKNOWLEDGEMENT

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INTEGRITET I VEK KONSTRUKCIJA
Vol. 23, Specijalno izdanje (2023), str. S19–S24

S24

STRUCTURAL INTEGRITY AND LIFE
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