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# Immobilization of heavy metal ions $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ in the structure of cement-based materials

## ABSTRACT

*Natural zeolite and bentonite were utilized as mineral additives in the mix-design of environmentally safe cement-based building materials. The adsorptive abilities of these two clayey raw materials, i.e. their affinity to immobilize heavy metal ions $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ were investigated. Single- and multi-solutions of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ were prepared for the experiment. The obtained results were submitted to analysis via pseudo-first and pseudo-second order kinetic models. Langmuir and Freundlich isotherms were analyzed. Bentonite exhibited better adsorption affinity than zeolite towards all four investigated cations. As a proof, a leaching test was conducted on seven different cement binders with different mineral additives (fly ash, zeolite, bentonite). The leachates obtained on the samples of cement with addition of fly ash and clay (either zeolite or bentonite) contained lower concentrations of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ ions than leachates obtained on the samples of cement binder with fly ash solely as a result of adsorption and hydration mechanisms that immobilized heavy metals within cementitious composites.*
*Keywords: Ion-exchange; Kinetics; Clayey adsorbents; Leaching control; Cement.*

## 1. INTRODUCTION

The prerequisite for immobilization of heavy metals became extremely important due to the rapid increase of pollution degree in the nature. Different techniques have been developed to prevent the release of toxic metals into the environment. One of a frequently used technique is solidification, i.e. stabilization, of toxic metals by cementitious binders [1]. Use of fly ash as bonding agent instead of cement is one of the solutions for decreasing its quantities [2-4]. Fly ash has relatively high concentration of heavy metals in its composition [2]. Clayey materials such as zeolite and bentonite are also used as mineral additives in cementitious binders due to their pozzolanic properties [5-7], however they are more commonly used as adsorbents for heavy metals [8].

Natural zeolites are hydrated aluminosilicate minerals with an open three dimensional framework of silicon oxygen $[SiO_4]^{4-}$ and aluminium oxygen $[AlO_4]^{5-}$ tetrahedral and a micro porous crystalline structure intersected by with maze of small pores and channels [9-11]. Bentonite has layered structure with a framework composed of two $[SiO_4]^{4-}$ tetrahedra enclosing an octahedral sheet of $[AlO_4]^{5-}$ ions. The piled layers of basic units are tied together by Van der Waals forces [6]. Adsorption of targeted heavy metal ions using zeolite and bentonite as low-cost ion-exchangers is technologically simple and low-cost procedure [12]. During preparation of a cement based binder heavy metals from fly ash are dissolved in the added water. The ions adhere onto surfaces of additives (i.e. zeolite or bentonite) due to their ion-exchange ability. Two adsorption mechanisms are possible: 1) the formation of a surface complex (mono) layer; 2) development of a thick precipitate layer. A coordinate covalent bond is formed between adsorbent surface and ion, i.e. either inner-sphere complex or electrostatic attraction between hydrated ion and adsorbent outer-sphere complex [5].

Adsorption of heavy metals within structure of cement binder can prevent their leaching into the

environment [13-16]. In this study de-ionized water was applied as a leaching agent. Adsorption experiments were conducted using single- and multi-solutions of Zn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ ions. Adsorption and leaching of Zn$^{2+}$, Ni$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$, as cations commonly comprised within fly ash structure, were investigated on the pulverized samples of cement binders with added mineral raw materials (fly ash, zeolite and bentonite).

## 2. EXPERIMENTAL

### 2.1. Materials

Zeolite (Z) and bentonite (B) were obtained by standard ore refinement treatment. Namely, the crude samples from the ore deposit were acquired by standard sampling campaign. Prior to the laboratory analyses, the samples were to crushed and grinded to be finally pulverized in an agate stone mill. Both used clayey raw mineral materials were aluminosilicates. Fly ash (FA) was sampled directly from the filter of power-plant "Kolubara" (Serbia). The samples were randomly taken and preserved in hermetically sealed boxes. As a product of lignite combustion, fly ash was also an aluminosilicate. The base raw material for all composites was standard Portland cement CEM I 42.5R (Lafarge). The chemical reagents used as adsorbates were: Pb(NO$_3$)$_2$ (purity 98.5 %; V/0 SOJUZCHIMEXPORT), Ni(NO$_3$)$_2$·6H$_2$O (purity 99.8 %, Chemistry), Cu(NO$_3$)$_2$·3H$_2$O (purity 99.8 %, Chemistry) and Zn(NO$_3$)$_2$·6H$_2$O (purity 98.5 %, V/0 SOJUZCHIMEXPORT). Stock solutions containing 1000 mg dm$^{-3}$ of Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ or Zn$^{2+}$ were prepared using mentioned 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.

### 2.2. Adsorption - kinetic study

The adsorption experiments in which Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ concentrations were used in single and multi-solutions were performed at 25 °C in duplicate. The mass of adsorbent ($m_{sorb}$) = 0.01 g was dispersed in 50 ml of 0.1 mmol adsorbate solution and shaken for established contact time (10, 20, 60, 120, 180 and 1440 min). Two testing routes were employed in order to quantify the adsorption ability of the sample (zeolite or bentonite): 1) individual Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ or Zn$^{2+}$ ions; 2) the combination of Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Zn$^{2+}$ ions.

The experiments were carried out in a magnetic stirrer (INTLLAB). After conducted adsorption, solid and liquid phases were separated by centrifugation for 10 min at 1700 rpm (Heittech Eva 21). The concentrations of ions in thus obtained solutions were measured by inductively coupled plasma -

optical emission spectrometry (ICP-OES, SPECTRO GENESIS) at $\lambda_{Pb}$=220.4 nm. $\lambda_{Ni}$=231.6 nm $\lambda_{Cu}$=324.7 nm i $\lambda_{Zn}$=213.8 nm. The amount of adsorbed ions with time, $q_t$ (mg/g) was calculated using the mass balance correlation:

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

Where: $C_0$ and $C_e$ are the initial and equilibrium concentrations of cations in the solution, respectively [16].

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

$$\log\left(Q_e - Q_t\right) = \log Q_e - k_1 \cdot t \qquad (2)$$

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 the pseudo-first order adsorption (min$^{-1}$).

Pseudo-second order rate is expressed as:

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

Where: $k_2$ is the pseudo-second order rate constant (g/mg min) [17].

### 2.3 Adsorption - isotherm study

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 and multi-solutions in different concentrations 0.10, 0.15, 0.20, 0.25 and 0.30 mmol/dm$^3$ were interpreted via Langmuir and Freundlich adsorption isotherms. The Langmuir equation model is given as (Eq. 4):

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

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

The linear form of Freundlich equation (Eq. 5) is:

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

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 Freundlich constant related to the adsorption capacity; and $1/n$ is an empirical parameter related to adsorption intensity, which varies with heterogeneity of the material.

## 2.4. Leaching test

Seven cement binders with different mix-designs were prepared. $M_0$ binder was based on Portland cement (PC) solely. $M_1$, $M_2$, $M_3$, $M_4$, $M_5$ and $M_6$ binders contained PC and various amounts of mineral additives (fly ash – FA, zeolite – Z and bentonite –B). 30 mass % of fly ash was added to the $M_1$ binder's mix-design. $M_2$, $M_3$, $M_4$ and $M_5$ binders contained two mineral additives - fly ash and either zeolite or bentonite: ($M_2$ – 20 mass % of FA + 10 mass % of Z, $M_3$ – 10 mass % of FA + 20 mass % of Z, $M_4$ – 20 mass % of FA + 10 mass % of B, and $M_5$ – 10 mass % of FA and 20 mass % of B). $M_6$ binder was prepared with the equal quantity (10 mass %) of all three mineral additives.

Cement binders used in the leaching test were prepared in accordance with the Standard SRPS EN 12457-4:2008 [18]. Dry components were homogenized in a laboratory pan mixer for 120 s. The water content needed for a self-flowing consistency was added during mixing. Green mixtures were poured into steel molds (2 × 2 × 2 cm) and preserved sealed in polyethylene bags for 48 hours (20 ± 2 °C, 95 ± 5 % humidity). After removing from the molds, the samples were kept under same conditions for the next 5 days. Then samples were stored at 20 ± 2 °C and 65 ± 5 % until 28th day.

The hardened samples were crushed and ground in order to reduce the grain size to less than 10 mm (mean diameter of thus obtained grain was 2 mm). The leachability of heavy metals for each binder was investigated on the mixtures of the testing samples and deionized water. The mixing ratio was 1:10 (liquid to solid). The prepared mixtures were placed in a laboratory mixer at room temperature and continuously stirred for the next 24 hours. Afterwards the leachate was filtered over a membrane filter (0.45 μm). Metal concentrations in leachates were determined using by ICP-OES.

## 2.5. Microstructural analysis

The morphology of the crushed mortar samples was characterized by scanning electron microscopy (JEOL JSM-IT300). The samples were covered with gold using a sputter machine, type BALTEC-SCD-005, for improvement of the conductivity prior to the imaging.

# 3. RESULTS AND DISCUSSION

## 3.1. Adsorption isotherms

$Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ adsorption isotherms were obtained by calculating and subsequently plotting the adsorbed amount of the observed ion ($q_e$, mmol/g) versus the equilibrium $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ concentrations (C, mmol/dm). The obtained adsorption isotherms are shown in Fig. 1a-d.

The shapes of all obtained isotherms are highly similar regardless of applied adsorbate - zeolite or bentonite. In Fig. 1a, $Cu^{2+}$ and $Pb^{2+}$ isotherms obtained on bentonite sample show a relatively higher slope at lower initial concentrations than $Ni^{2+}$ and $Zn^{2+}$ isotherms obtained on the same adsorbent. Adsorption maximums for $Cu^{2+}$ and $Pb^{2+}$ are recorded at concentration of 0.3 mmol/dm$^3$. Adsorption procedures for $Ni^{2+}$ and $Zn^{2+}$ exhibit a somewhat slower rate, but the maximum is also achieved at 0.3 mmol/dm$^3$. The increasing adsorption trend for the single solution tested on bentonite sample is: Zn < Ni < Pb < Cu. $Pb^{2+}$ isotherm obtained on zeolite sample shows that the slope was relatively low at higher concentrations as it can be seen in Fig. 1b. This isotherm also has a defined plateau for the adsorption maximum. $Ni^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ isotherms are similar, but they do not have a defined plateau for the adsorption maximum. The increasing adsorption trend for single solution obtained on zeolite sample is Ni < Zn < Cu < Pb. In Fig. 1c, $Cu^{2+}$ and $Pb^{2+}$ isotherms have a higher slope than $Ni^{2+}$ and $Zn^{2+}$ isotherms, which is similar to disposition of isotherms previously seen in Fig. 1a. The difference between the single solution (Fig. 1a) and the multi solution (Fig. 1b) on bentonite sample was higher adsorption capacity for all HM in single solutions compared to capacities in the multi solution is that the adsorptions are higher for the single solution for all ions than for the multi solution. The adsorption for $Cu^{2+}$ was highest for both types of solutions (single and multi). Besides previously mentioned, the $Cu^{2+}$ and $Pb^{2+}$ isotherms intersect within the single solutions, while the isotherms of $Cu^{2+}$ and $Pb^{2+}$ in multi solution are completely separated. The increasing adsorption trend for multi solution on bentonite sample is same as in the case of single solution on bentonite. Fig. 1d illustrates the adsorption maximum for $Pb^{2+}$. The increasing adsorption trend for multi solution obtained on zeolite is: Ni < Zn < Cu < Pb, which is the same as the trend recorded on the single solutions in combination with zeolite adsorbent. The difference is in the adsorption capacity. Adsorption maximums for all investigated ions are higher for single solutions than for multi-solutions. Also, it is evidenced that bentonite exhibits the highest affinity towards $Cu^{2+}$. Zeolite shows the highest affinity towards for $Pb^{2+}$.
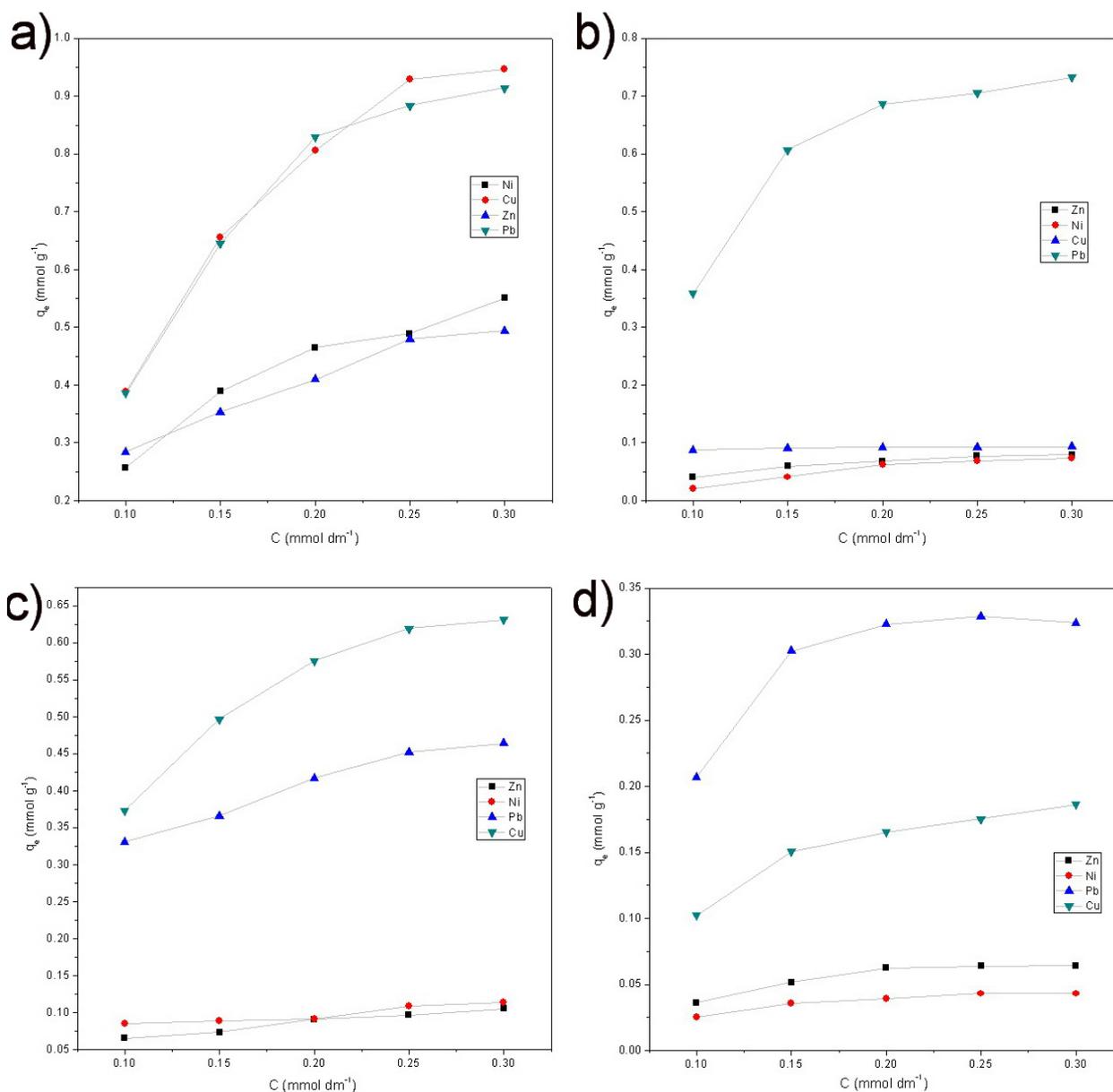
*Figure 1. Adsorption isotherms: a) single component solution on bentonite sample;
b) single component solution on zeolite sample; c) multi-component solution on bentonite sample;
d) multi-component solution on zeolite sample*

*Slika 1. Adsorpcione izoterme: a) jednokomponentnih rastvora na uzorku bentonita;
b) jednokomponentnih rastvora na uzorku zeolita; c) više-elementarnih rastvora na uzorku bentonita;
d) više-elementarnih rastvora na uzorku zeolita*

Langmuir and Freundlich isotherms were used for the evaluation of the adsorption capacities of the adsorbents (zeolite and bentonite) [19]. Dependencies of $C/q_e = f(C)$ and $log\ q_e = log\ C$ are given in Tab. 1 and 2 as a data derived from the

linear forms of Langmuir (constants *b* and *k*) and Freundlich (constants n *and log* k) equations for $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ adsorption in single and multi-solutions onto zeolite and bentonite.

*Table 1. Linear forms of Langmuir equations for single and multi solutions tested on zeolite and bentonite samples*

*Tabela 1. Linearni oblici Langmuir-ove jednačine za pojedinačne i multi-elementarne rastvore testirane na uzorcima zeolita i bentonita*

| Sample | Equation | $k^*$ (mmol dm$^{-3}$) | $b^*$ (mmol g$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| Zeolite/ single $Ni^{2+}$ | y = 1.780x + 0.604 | 2.947 | 0.562 | 0.966 |
| Bentonite/single $Ni^{2+}$ | y = 1.117x + 0.216 | 5.171 | 0.895 | 0.976 |
| Zeolite/single $Cu^{2+}$ | y = 3.065x + 0.044 | 69.659 | 0.326 | 0.999 |
| Bentonite/ single $Cu^{2+}$ | y = 0.569x + 0.137 | 4.153 | 1.757 | 0.945 |
| Zeolite/single $Zn^{2+}$ | y = 2.718x + 0.334 | 8.138 | 0.368 | 0.987 |
| Bentonite/single $Zn^{2+}$ | y = 1.220x + 0.234 | 5.214 | 0.820 | 0.985 |
| Zeolite/ single $Pb^{2+}$ | y = 1.033x + 0.076 | 13.592 | 0.968 | 0.995 |
| Bentonite/ single $Pb^{2+}$ | y = 0.656x + 0.123 | 5.333 | 1.524 | 0.932 |
| Zeolite/multi $Ni^{2+}$ | y = 15.12x + 2.179 | 6.939 | 0.066 | 0.955 |
| Bentonite/multi $Ni^{2+}$ | y = 6.325x + 0.978 | 6.467 | 0.158 | 0.975 |
| Zeolite/multi $Cu^{2+}$ | y = 3.384x + 0.566 | 5.979 | 0.296 | 0.954 |
| Bentonite/multi $Cu^{2+}$ | y = 1.110x + 0.152 | 7.303 | 0.901 | 0.980 |
| Zeolite/multi $Zn^{2+}$ | y = 9.754x + 1.539 | 6.338 | 0.103 | 0.921 |
| Bentonite/multi $Zn^{2+}$ | y = 7.005x + 0.600 | 11.675 | 0.143 | 0,950 |
| Zeolite/ multi $Pb^{2+}$ | y = 2.301x + 0.197 | 11.680 | 0.434 | 0.940 |
| Bentonite/ multi $Pb^{2+}$ | y = 1.664x + 0.145 | 11.476 | 0.601 | 0.994 |
| $K^*$ = slope/intercept; $b^*$ =1/slope | | | | |

*Table 2. Linear forms of Freundlich for single and multi solutions tested on zeolite and bentonite samples*

*Tabela 2. Linearni oblici Freundlich-a za pojedinačne i multi-elementarne rastvore testirane na uzorcima zeolita i bentonita*

| Sample | Equation | n (g dm$^{-3}$) | *log* k (mmol g$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| Zeolite/ single $Ni^{2+}$ | y = 1.107x + 0.052 | 0.903 | 1.127 | 0.900 |
| Bentonite/single $Ni^{2+}$ | y = 0.669x + 0.108 | 1.495 | 1.282 | 0.951 |
| Zeolite/single $Cu^{2+}$ | y = 0.078x - 0.464 | 12.82 | 0.343 | 0.988 |
| Bentonite/ single $Cu^{2+}$ | y = 0.553x + 0.283 | 1.808 | 1.919 | 0.948 |
| Zeolite/single $Zn^{2+}$ | y = 0.385x - 0.376 | 2.597 | 0.421 | 0.942 |
| Bentonite/single $Zn^{2+}$ | y = 0.522x - 0.020 | 1.916 | 0.955 | 0.988 |
| Zeolite/ single $Pb^{2+}$ | y = 0.097x - 0.082 | 10.309 | 0.828 | 0.936 |
| Bentonite/ single $Pb^{2+}$ | y = 0.792x + 0.422 | 1.263 | 2.642 | 0.915 |
| Zeolite/multi $Ni^{2+}$ | y = 0.280x - 1.209 | 3.571 | 0.062 | 0.942 |
| Bentonite/multi $Ni^{2+}$ | y = 0.280x - 0.810 | 3.571 | 0.155 | 0.840 |
| Zeolite/multi $Cu^{2+}$ | y = 0.302x - 0.571 | 3.311 | 0.268 | 0.998 |
| Bentonite/multi $Cu^{2+}$ | y = 0.487x + 0.080 | 2.053 | 1.202 | 0.948 |
| Zeolite/multi $Zn^{2+}$ | y = 0.310x - 1.014 | 6.338 | 0.103 | 0.769 |
| Bentonite/multi $Zn^{2+}$ | y = 0.454x - 0.739 | 3.226 | 0.182 | 0.974 |
| Zeolite/ multi $Pb^{2+}$ | y = 0.104x - 0.427 | 9.615 | 0.374 | 0.708 |
| Bentonite/ multi $Pb^{2+}$ | y = 0.327x - 0.156 | 3.058 | 0.698 | 0.982 |

The values of the adsorption capacities for Langmuir and Freundlich models with coefficient of determination ($R^2$) are listed in Tab. 1 and 2. High coefficients of determinations ($R^2$) from Tab.1 suggest that Langmuir models are better than Freundlich (Tab. 2) for description of adsorption of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ in single and multi-solutions on zeolite and bentonite. Langmuir model of adsorption isotherms shows that adsorption takes place at specific homogeneous sites at adsorbent. This model is generally successfully applied in cases of monolayer adsorption [20].

Maximum adsorption data (*b*, mmol/g) (Tab. 1) showed that bentonite is over-all better adsorbent than zeolite for all elements in either single or multi-solutions. The following decreasing array regarding

adsorption capacity can be established: BS $Cu^{2+}$; BS $Pb^{2+}$; ZS $Pb^{2+}$; BM $Cu^{2+}$; BS $Ni^{2+}$; BS $Zn^{2+}$; BM $Pb^{2+}$; ZS $Ni^{2+}$; ZM $Pb^{2+}$; ZS $Zn^{2+}$; ZS $Cu^{2+}$; ZM $Cu^{2+}$; BM $Ni^{2+}$; BM $Zn^{2+}$; ZM $Zn^{2+}$; and ZM $Ni^{2+}$ (where Z is zeolite, B is bentonite, S is single and M is multi). The comparison of binding strengths ($k$ in mmol/dm³) given in Tab. 1 resulted in the following decreasing array: ZS $Cu^{2+}$; ZS $Pb^{2+}$; ZM $Pb^{2+}$; BM $Zn^{2+}$; BM $Pb^{2+}$; ZS $Zn^{2+}$; ZM $Ni^{2+}$; BM $Cu^{2+}$; BM $Ni^{2+}$; ZM $Zn^{2+}$; ZM $Cu^{2+}$; BS $Pb^{2+}$; BS $Zn^{2+}$; BS $Ni^{2+}$; BS $Cu^{2+}$; and ZS $Ni^{2+}$.

Results presented in Fig. 1a-d and Tab. 1 and 2 highlighted that the particular amounts of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ in single solutions adsorbed by bentonite and zeolite are higher than the amount of

adequate element in the multi-solution. Adsorption isotherms for multi-solutions showed that the presence of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ influenced the decreased in adsorption of all ions due to a significant competition effect [21]. The zeolite was more selective towards $Pb^{2+}$ than towards $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$, unlike the bentonite which was most selective towards $Cu^{2+}$ rather than $Pb^{2+}$, $Zn^{2+}$, and $Ni^{2+}$.

### 3.2. Kinetic models

The effect of adsorption contact time on the concentration of adsorbed metal ions ($Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$) on bentonite and zeolite used as adsorbents in single and multi-solutions is illustrated in Fig. 2a-d.
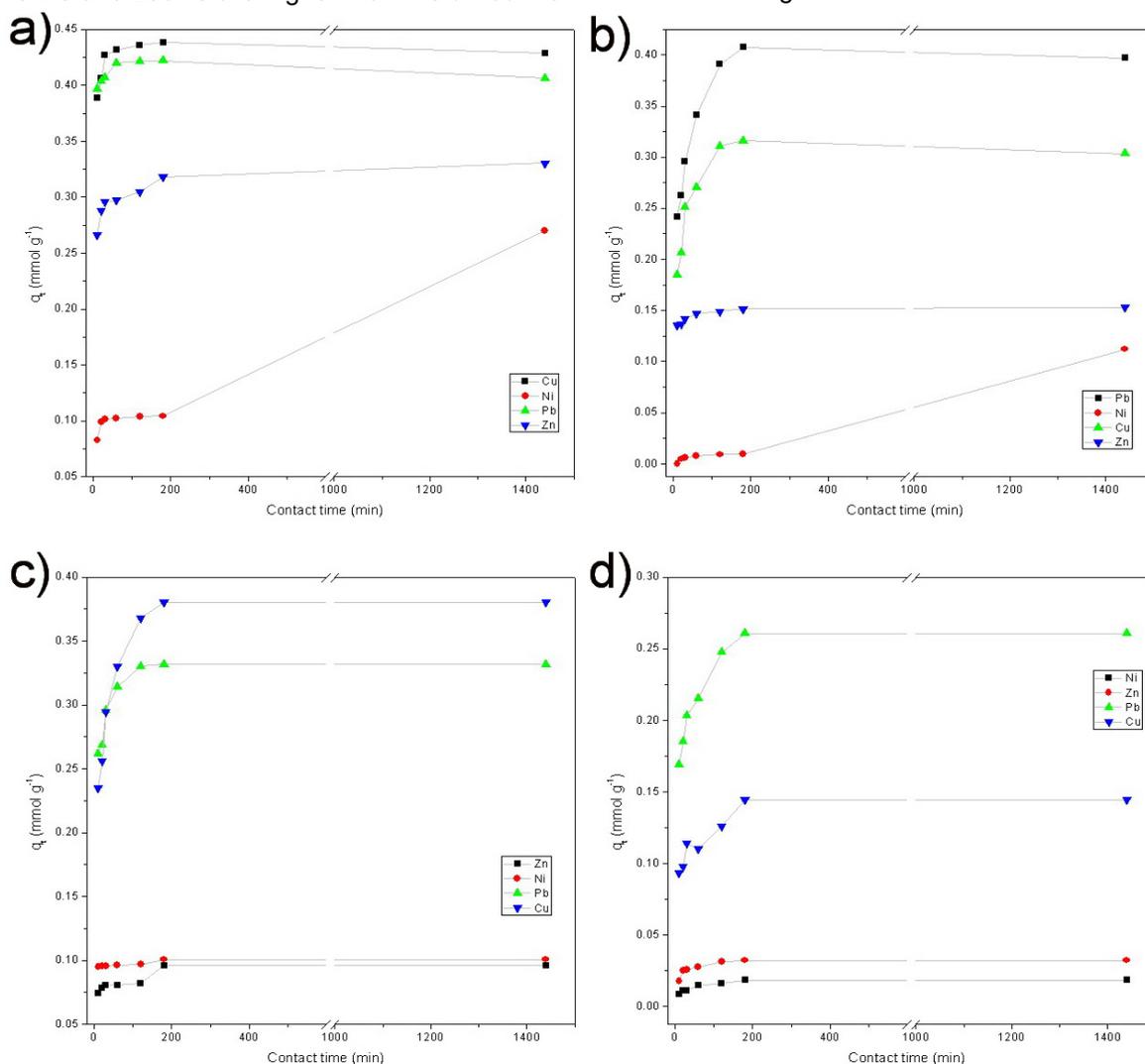


*Figure 2. Influence of contact time on adsorption of Zn²⁺, Ni²⁺, Pb²⁺ and Cu²⁺ from: a) single component solution on bentonite; b) single component solution on zeolite; c) multi-component solution on bentonite; d) multi-component solution on zeolite*

*Slika 2. Uticaj vremena kontakta na adsorpciju Zn²⁺, Ni²⁺, Pb²⁺ i Cu²⁺ iz: a) jednokomponentnog rastvora na bentonitu; b) jednokomponentni rastvori na zeolitu; c) više-elementarni rastvori na bentonitu; d) više-elementarni rastvori na zeolitu*

In the Fig. 2a-d a neat difference in the adsorption behavior onto bentonite and zeolite can be observed. The adsorption affinity in the single component solution can be arranged in the increasing array as follows: $Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+}$ for bentonite and $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$, for zeolite). The observed adsorption affinity sequence in multi component solutions was $Cu^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+}$ for bentonite and $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ for zeolite.

Fig. 2a shows that adsorption of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ in single component solutions on bentonite uptake were found to increase with the increase in contact time and maximum percentage of adsorptions occurred at 30 min where after they became constant. After a constant adsorption of $Ni^{2+}$, there was a sharp increase in amount of adsorption at the contact time of 1440 min. For $Zn^{2+}$, after contact time achieved at 60 min, there was a gradual increase in amount of adsorption. Fig. 2b shows similar the behavior of the ions, but contact time was achieved at 180 min for maximal adsorption of $Pb^{2+}$ and $Cu^{2+}$ in single component solutions on zeolite. For $Zn^{2+}$ and $Ni^{2+}$ in this case contact time of adsorption was acquired at 30 min, but the maximum of adsorption occurred at 1440 min. Fig. 2c and 2d show different contact times of

maximum adsorption for different ions. Contact times of maximum adsorption in multi component solution on bentonite were: for $Cu^{2+}$ at 180 min, for $Pb^{2+}$ at 120 min, for $Ni^{2+}$ at 180 min and for $Zn^{2+}$ at 30 min. There are two folds in $Zn^{2+}$ adsorption, the first at 30 min and the second at 180 min. Contact times of maximum adsorption in multi component solution on zeolite were: for $Pb^{2+}$ and $Cu^{2+}$ at 180 min., for $Ni^{2+}$ and $Zn^{2+}$ at 30 min. There are two folds in $Cu^{2+}$ adsorption, the first at 30 min and the second at 180 min.

Equilibrium time was reached after 30 min, 120 min or 180 min in both single and multi-component solutions. Both adsorbents showed somewhat different trends in affinity toward investigated cations depending on whether the adsorption was performed from single component or multi-component solution. The 1440 min was adopted as the equilibrium time for all processes, although for some experiments the equilibrium was reached after significantly shorter times.
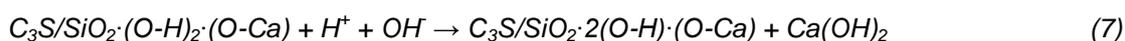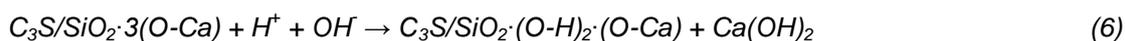
The adsorption rate constants and coefficient of determinations were obtained from the plot $\log(Q_e - Q_t)$ versus $t$ for pseudo-first kinetic model (Model I). Constants and coefficient for pseudo-second-order model (Model II) were derived from the plot $t/Q_t$ versus $t$. Results are given in Tab. 3.

*Table 3. Adsorption kinetic model equations with different parameters for adsorption of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ on bentonite and zeolite in single and multi solutions*

*Tabela 3. Jednačine kinetičkih modela adsorpcije sa različitim parametrima za adsorpciju $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ i $Cu^{2+}$ na bentonitu i zeolitu u pojedinačnim i multi-elementarnim rastvorima*

| Adsorption kinetic model | | | Model I | | Model II | | |
|---|---|---|---|---|---|---|---|
| Parameter | | | $R^2$ | $Q_{ecal}$ (mmol·g$^{-1}$) | $R^2$ | $Q_{ecal}$ (mmol·g$^{-1}$) | $Q_{eexp}$ (mmol·g$^{-1}$) |
| $Ni^{2+}$ | single | bentonite | 0.924 | 63 | 0.999 | 0.25 | 0.27 |
| | | zeolite | 0.964 | 111 | 0.999 | 0.11 | 0.11 |
| | multi | bentonite | 0.791 | 67 | 0.988 | 0.09 | 0.10 |
| | | zeolite | 0.951 | 200 | 0.998 | 0.033 | 0.032 |
| $Cu^{2+}$ | single | bentonite | 0.977 | 58 | 1.000 | 0.42 | 0.41 |
| | | zeolite | 0.975 | 83 | 0.998 | 0.33 | 0.30 |
| | multi | bentonite | 0.584 | 111 | 0.996 | 0.32 | 0.33 |
| | | zeolite | 0.980 | 142 | 0.988 | 0.15 | 0.14 |
| $Pb^{2+}$ | single | bentonite | 0.889 | 90 | 1.000 | 0.44 | 0.43 |
| | | zeolite | 0.996 | 111 | 0.998 | 0.42 | 0.40 |
| | multi | bentonite | 0.604 | 100 | 0.997 | 0.37 | 0.38 |
| | | zeolite | 0.863 | 333 | 0.836 | 0.25 | 0.26 |
| $Zn^{2+}$ | single | bentonite | 0.783 | 250 | 0.998 | 0.31 | 0.33 |
| | | zeolite | 0.956 | 142 | 0.999 | 0.15 | 0.15 |
| | multi | bentonite | 0.978 | 100 | 0.988 | 0.09 | 0.09 |
| | | zeolite | 0.950 | 200 | 0.992 | 0.019 | 0.018 |

As it can be seen from the results presented in Tab. 3, high $R^2$ values suggest that the adsorption is ruled by pseudo-second order model. The pseudo-second order kinetics model describes the adsorption system more precisely, since the squares of the correlation coefficients ($R^2$) were close to 1. Calculated values for the equilibrium adsorption capacity ($q_{ecalc}$) for the pseudo-second order model were close to experimentally obtained adsorption capacity ($q_{eexp}$) which confirms that the adsorption of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ on bentonite and zeolite in single and multi-solutions match criteria of the pseudo-second-order kinetics model.

$$C_3S/SiO_2 \cdot 3(O\text{-}Ca) + H^+ + OH \rightarrow C_3S/SiO_2 \cdot (O\text{-}H)_2 \cdot (O\text{-}Ca) + Ca(OH)_2 \qquad (6)$$

$$C_3S/SiO_2 \cdot (O\text{-}H)_2 \cdot (O\text{-}Ca) + H^+ + OH \rightarrow C_3S/SiO_2 \cdot 2(O\text{-}H) \cdot (O\text{-}Ca) + Ca(OH)_2 \qquad (7)$$

When fly ash is available in the cement aqueous mixture, some of $Ca^{2+}$ ions are being adsorbed on the surfaces of fly ash particles. Lower cement content leads to the decrease in $Ca^{2+}$ concentration in the liquid phase. The pozzolanic activity of fly ash consumes the quantity of $Ca(OH)_2$ due to the pozzolanic reaction (Eq. 8) [26]:

$$3Ca(OH)_2 + 2\ SiO_2 + H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O\ (i.e.\ secondary\ ettringite,\ CSH) \qquad (8)$$
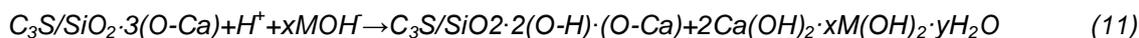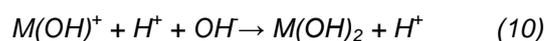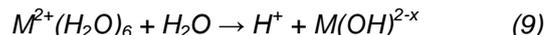
Presence of heavy metal ions can affect the reaction rate of cement, the precipitation of portlandite, polymorphism of calcium carbonate, formation of calcium aluminate hydrate phases and polymerization of calcium silicate hydrate, final amorphous hydration product of cement, as it can be found described in literature [25]. The hydration of heavy metals (M) takes place according to the following reactions (Eq. 9-11):

$$M^{2+}(H_2O)_6 + H_2O \rightarrow H^+ + M(OH)^{2-x} \qquad (9)$$

$$M(OH)^+ + H^+ + OH^- \rightarrow M(OH)_2 + H^+ \qquad (10)$$

$$C_3S/SiO_2 \cdot 3(O\text{-}Ca) + H^+ + xMOH \rightarrow C_3S/SiO2 \cdot 2(O\text{-}H) \cdot (O\text{-}Ca) + 2Ca(OH)_2 \cdot xM(OH)_2 \cdot yH_2O \qquad (11)$$

M is the symbol of heavy metal. In this case M could be Pb, Ni, Cu and Zn

As hydration proceeds, pH of the mixture increases to the pH of saturated solution of portlandite ($Ca(OH)_2$). As a result, portlandite precipitates from solutions [25].

$$C_3S/SiO_2 \cdot 3(O\text{-}Ca)/SiO2 \cdot 2(O\text{-}H) \cdot (O\text{-}Ca) + H^+ + OH + M(OH)_2 \rightarrow C_3S/2(SiO_2)_3 \cdot (O\text{-}H) \cdot 2(O\text{-}Ca) \cdot M(OH)_2 +$$
$$+\ 2Ca(OH)_2 \cdot xM(OH)_2 \cdot yH_2O + 2Ca(OH)_2 \cdot M(OH)_2 \qquad (12)$$

Natural zeolite used as an additive in cementitious material also alters the pozzolanic reaction. Furthermore, the alternations in pozzolanic reactions of a cement binder with zeolite addition have different route than those of cement binder with fly ash addition. Reasons behind these changes in the chemical reactions that take place between standard cement minerals are: additional amount of water absorbed within zeolite structure, negatively charged zeolite framework which obstructs the diffusion of hydroxyl ions into the zeolite pore, and exchangeable properties of cations from zeolite structure [11]. Namely, zeolite can absorb relatively great amount of water in its pore structure. When this absorbed

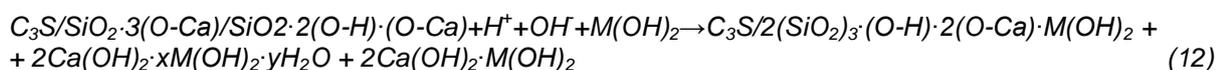## 3.3. Additional ion immobilization mechanisms

The immobilization of heavy metals can be conveyed during the hydration process that takes place within cementitious material [16]. Namely, during hydration, the structures of cement minerals undergo certain changes which enable immobilization of heavy metals ions within newly formed crystalline grid [22-24]. Mineral additives - fly ash, zeolite and bentonite can be considered as pozzolanic materials which means that they influence and participate in the process of hydration [6]. Namely, the hydration of alite ($3CaO \cdot SiO_2$) is normally expressed with the following reactions (6) and (7) [25]:

water gets released during ongoing pozzolanic reaction it has double function. The function effect is a decrease of pH value as dilution effect. The second function is to contribute with additional amount of water when the water level within pores of cement decreases due to the hydration process.

Bentonite shows comparatively lesser pozzolanic abilities than fly ash and zeolite. Furthermore, bentonite can slow down the process of cement hydration [26]. Reaction between cement and bentonite (i.e. smectite minerals and any secondary minerals such as quartz, etc.) are in risk of degradation via dissolution-precipitation reactions. At high pH, the cementitious products (portlandite, calcium silicate hydrate gel (CSH),

calcium aluminium silicate hydrates (CASH), etc.) are chemically stable, but with reducing pH the cementitious products will dissolve and reform as other products. For example: portlandite will degrade below a pH of 12.4 and the CSH gel will degrade below a pH of 10 [27]. On the other side, the smectite minerals within the bentonite are likely to experience degradation at higher pH levels. Although, bentonite is not good pozzolanic material, bentonite is very good adsorbent and this affect on good immobilization of heavy metals.

## 3.4. Microstructural analysis of experimental mortars

Differences in the microstructural and mineralogical composition of zeolite and bentonite are very important for their adsorption behavior when applied in composite materials [6, 21]. The surface morphology of the experimental cementitious binders $M_{0-6}$ with addition of fly ash, bentonite and/or zeolite was examined by SEM and the obtained microphotographs are presented in Figure 3.
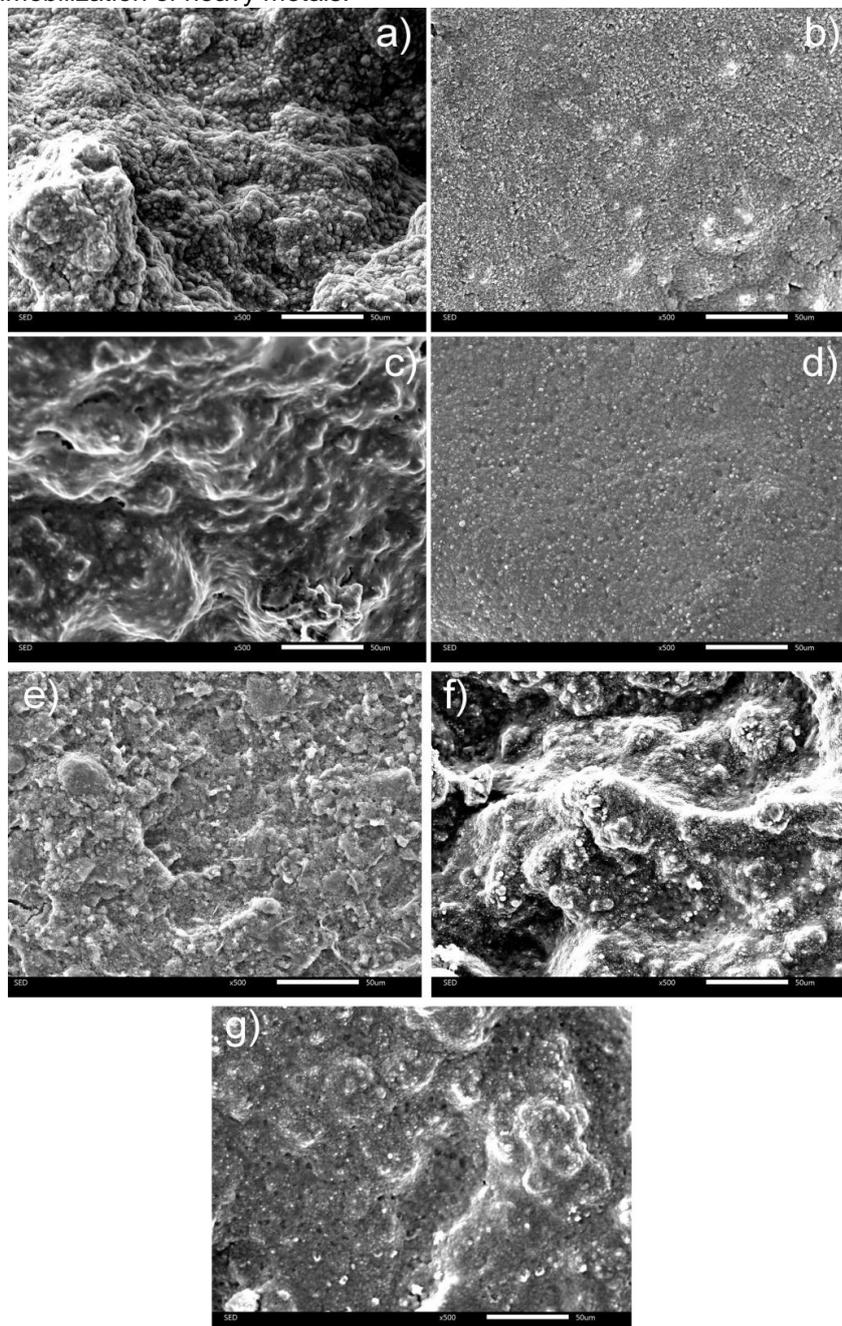


*Figure 3. SEM microphotographs of experimental binders: a) $M_0$; b) $M_1$; c) $M_2$; d) $M_3$; e) $M_4$; f) $M_5$; g) $M_6$*
*Slika 3. SEM mikrofotografije eksperimentalnih veziva: a) $M_0$; b) $M_1$; c) $M_2$; d) $M_3$; e) $M_4$; f) $M_5$; g) $M_6$*

Scanning electron microscopy indicated that each of the analyzed binders comprises mixture of particles with average diameter is varying from 1 μm to 30 μm. Also, numerous voids and pores of micron sizes are visible on the surface of the recorded samples (Fig. 3a-g). The cement matrix is predominant component in the microstructure of investigated binders. This matrix is formed during hydration and therefore it is composed of various cement minerals (alite, belite, etc.) [28]. Hydrated cement grains are merged together closely into a stiff base. Unbound hydration debris which appears in form of "lumps and platelets" on top of merged cement grains is usually identified as hydration products such as tricalcium aluminate, brownmillerite, portlandite [6]. At the end of hydration process newly formed layer of hydration products is merged with cement grains into a solid

structure [28]. Microstructure of the binders with mineral additives (M₁₋₆) is characterized by smaller number and size of the pores in comparison with hardened Portland cement. The combination of fly ash and zeolite as mineral additive used in the $M_2$ mortar produced a very dense structure with very small randomly scattered pores (Fig. 3c).

### 3.5. Leaching analysis

The concentrations of heavy metals $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ leached from the cement binders are presented graphically in Fig. 4. The leaching limit is given as LIM value obtained from Waste Acceptance Criteria regulation [15]. The leaching limit values for Zn, Ni, Pb and Cu are proposed in order to classify a waste material as hazardous or non-hazardous.
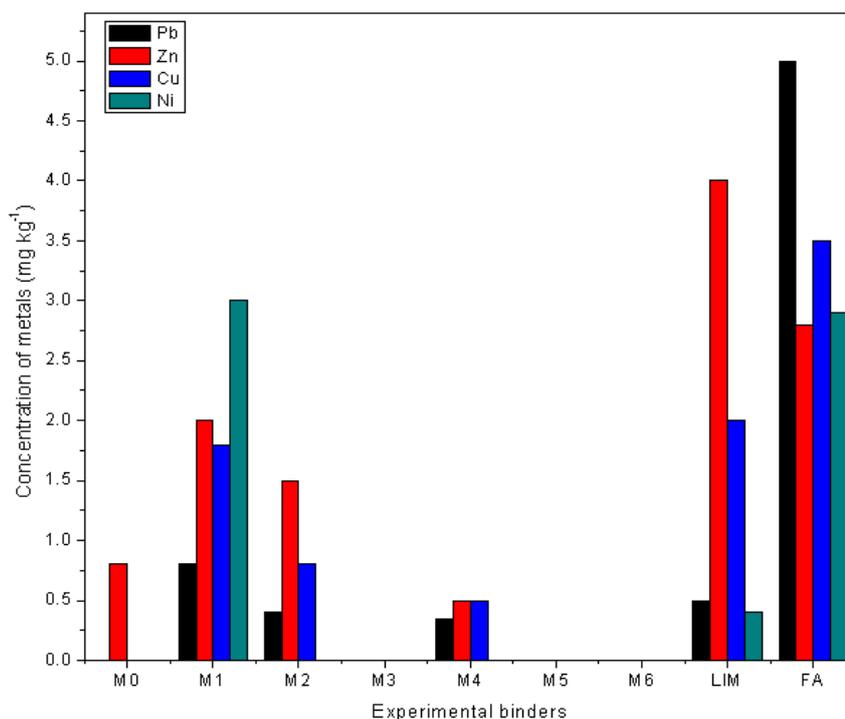


*Figure 4. Concentrations of metal ions in leachates obtained on cement binders*

*Slika 4. Koncentracije jona metala u eluatima dobivenim na cementnim vezivima*

As it can be seen in Fig. 4, the leachate obtained from the binder which is composed of cement and of fly ash ($M_1$) contains the highest concentration of heavy metals ($Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$). On the other hand, the addition of natural zeolite in the mixtures $M_2$ and $M_3$ effectively reduces the leaching amounts of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$. Better results of immobilization of the mentioned heavy metals were acquired by addition bentonite in the mixture $M_4$, $M_5$ and $M_6$. As it was proved in adsorption experiments zeolite absorbs

more $Pb^{2+}$ ions, but bentonite absorbs more $Cu^{2+}$ ions. Difference in the concentration of ions in the leachate obtained on fly ash sample solely and leachate obtained on the mixture of cement, ash, and zeolite are: 80 % for $Pb^{2+}$, 30% for $Zn^{2+}$, 50 % for $Cu^{2+}$ and 10 % for $Ni^{2+}$. Difference in the concentration of ions in the leachate obtained on fly ash sample solely and leachate obtained on the mixture of cement, ash, and bentonite are: 80 % for $Pb^{2+}$ and $Cu^{2+}$, 50 % for $Zn^{2+}$ and 90% for $Ni^{2+}$. The concentrations of of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ in all

obtained leachates, with an exception leachate obtained on $M_1$ binder, were lower than the LIM value provided Waste Acceptance Criteria.

## 4. CONCLUSION

The zeolite and bentonite were successfully applied as adsorbents for $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ ions contained in fly ash. Langmuir isotherm fully describes the adsorption process for both tested of adsorbents. The adsorption affinity in single component solution was as follows: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. In multi component solution, the acquired adsorption affinity was: $Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$. The adsorption of $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ on bentonite and zeolite samples in both single and multi-solutions complied with the pseudo-second order kinetics model. The concentrations of metal cations in all leachates, with an exception of leachate obtained on binder $M_1$, were lower than the limit of leachability value specified in the Waste Acceptance Criteria. SEM microphotographs showed that the additions of fly ash, zeolite and bentonite separately or mutually influenced in the process of cement hydration by behaving as pozzolanic materials. Also, during the cement hydration heavy metals were bound and immobilized within the crystalline structure of newly formed cement minerals. Adsorption experiments showed that bentonite and zeolite are efficient adsorbents for $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ and $Cu^{2+}$ ions.

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## IZVOD

### IMOBILIZACIJA TEŠKIH METALNIH JONA $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ I $Cu^{2+}$ U STRUKTURI MATERIJALA NA BAZI CEMENTA

*Prirodni zeolit i bentonit korišćeni su kao mineralni dodaci u mešavinskom dizajnu ekološki sigurnih građevinskih materijala na bazi cementa. Ispitane su adsorptivne sposobnosti ove dve glinene sirovine, tj. njihov afinitet da imobiliziraju jone teških metala $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ i $Cu^{2+}$. Za eksperiment su pripremljeni pojedinačni i multi-rastvori $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ i $Cu^{2+}$. Dobijeni rezultati su analizirani pomoću kinetičkih modela pseudo prvog i pseudo drugog reda. Analizirane su izoterme Langmuira i Freundlicha. Bentonit je pokazao bolji adsorpcioni afinitet od zeolita prema sva četiri ispitivana katjona. Kao dokaz, ispitano je ispitivanje ispiranja na sedam različitih veziva za cement sa različitim mineralnim dodacima (leteći pepeo, zeolit, bentonit). Eluati dobijeni na uzorcima cementa sa dodatkom letećeg pepela i gline (bilo zeolita ili bentonita) sadržavale su niže koncentracije jona $Zn^{2+}$, $Ni^{2+}$, $Pb^{2+}$ i $Cu^{2+}$ u odnosu na eluat dobijen na uzorcima cementnog veziva sa letećim pepelom. Razlog za dobijanje ovakvih rezultata su adsorpcioni i hidratacioni mehanizmi koji imobiliziraju teške metale u cementnim kompozitima.*
**Ključne reči:** *Jon-razmena; kinetika; glineni adsorbenti; izluživanje; cement.*