

## The Kinetics of Cd<sup>2+</sup> and Pb<sup>2+</sup> Leaching from Fly Ash Geopolymers

Hamzah Fansuri<sup>a,\*</sup>, Subaer<sup>b</sup>, Warih Supriadi<sup>a</sup>, Djoko Hartanto<sup>a</sup>, Nurul Widiastuti<sup>a</sup>

<sup>a</sup>Department of Chemistry, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

<sup>b</sup>Department of Physics, Universitas Negeri Makassar, Jalan Mallengkeri, Parang Tambung, Makassar 90224, Indonesia  
[h.fansuri@chem.its.ac.id](mailto:h.fansuri@chem.its.ac.id)

This research is aimed to reveal the kinetics of Cd<sup>2+</sup> and Pb<sup>2+</sup> leaching from fly ash geopolymer as a promising and sustainable method to solve the problems of heavy metals contamination. The geopolymer was made by using fly ash of PT. IMPOMI in East Java, Indonesia and the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 6.5, Solid/Liquid (S/L) = 3.59 and Na<sub>2</sub>SiO<sub>3</sub>/NaOH = 2.5. A solution of Cd (NO<sub>3</sub>)<sub>2</sub> or Pb(NO<sub>3</sub>)<sub>2</sub> were added at 1,000, 4,000, 8,000 or 16,000 ppm relative to the weight of fly ash. Compressive strength test of geopolymers was carried out at the end of day 7 after curing the geopolymer mixture at room temperature. Leaching tests for the kinetics and mechanisms studies were carried using TCLP method by immersing the resulted geopolymers into 0.01 M acetic acid solution. The ratio of geopolymer mass to the volume of acetic acid solution was 1:25. ICP-OES was used to measure the leached Cd<sup>2+</sup> and Pb<sup>2+</sup> while SEM-EDS was used to study the morphology and heavy metal distribution on the polished geopolymer cross section. It was found that the compressive strength of Cd<sup>2+</sup> geopolymer was slightly higher than those of Pb<sup>2+</sup>-geopolymer. The strength of geopolymer decreased at higher concentration of heavy metal cations. The maximum strength (24.4 MPa) was shown by 4,000 ppm Cd<sup>2+</sup> geopolymer while SEM-EDX images showed that Cd<sup>2+</sup> and Pb<sup>2+</sup> were distributed uniformly from the surface to the core of geopolymers. The leaching test reveals that more than 99.5 % of Cd<sup>2+</sup> and Pb<sup>2+</sup> were retained by geopolymer while in depth kinetics investigation of both Cd<sup>2+</sup> and Pb<sup>2+</sup> leaching shows that the leaching rate follows the first order rate law with two step leaching processes. The first originates from cations at the surface followed by cations from the bulk of geopolymer.

### 1. Introduction

Geopolymer has several advantages over ordinary cement that is more durable in high salinity environment, resistant to high temperature and to acidic and alkaline environments. Furthermore, carbon footprint of geopolymer is much lower than Ordinary Portland Cement (OPC). Turner and Collin (2013) reported that concretes comprising geopolymer have 10 % less carbon foot print compare to 100 % of OPC. In addition, geopolymers are also capable to retain metal ions in them as reported by Phair and van Deventer (2004). The durability and ability of geopolymers to captive heavy metal ions can be utilized for the treatment of heavy metals waste, hereinafter referred to as immobilization (Zhang et al., 2008). Leaching test to alkali activated slag binder (Deja, 2002) and geopolymer (Zhang et al., 2008) revealed that 99.3 to 99.9 % of immobilized Pb<sup>2+</sup> was retained. The interaction between heavy metal ions and the geopolymer matrix is different depending on the element and its oxidation number. van Jaarsveld and van Deventer (1999) suggested that larger size metal cations tend to be better immobilized in geopolymers and the greater the ratio of valence to radii the greater the bonded strength of the metal ions in the geopolymer matrix. The Cs<sup>2+</sup> ion is immobilized in geopolymer chemically and its presence does not cause significant changes to the mechanical strength of the geopolymer (Fernandez-Jimenez et al., 2004). As<sup>2+</sup> ions are only slightly bound by geopolymers (Fernandez-Jimenez et al., 2005) whereas Cr<sup>3+</sup> chromium ions are immobilized very well while Cr<sup>6+</sup> does not even immobilized by geopolymers (Zhang et al., 2008). However, the immobilized heavy metal ions in geopolymers may reduce the geopolymer performance (Xu et al., 2006). Palomo and Palacios (2003) reported that the addition of Pb(NO<sub>3</sub>)<sub>2</sub> reduce the geopolymer compressive strength by 30 %. Similar strength reduction is also reported by Deja (2002) in immobilization of Cd<sup>2+</sup>.

Paper Received: 18 April 2018; Revised: 24 September 2018; Accepted: 09 December 2018

Please cite this article as: Fansuri H., S., Supriadi W., Hartanto D., Widiastuti N., 2019, The kinetics of cd<sup>2+</sup> and pb<sup>2+</sup> leaching from fly ash geopolymers, Chemical Engineering Transactions, 72, 235-240 DOI:10.3303/CET1972040

It has also been reported that the immobilization can be performed by encapsulation and/or cation neutralization of the geopolymer matrix (Fansuri et al., 2016). There is still not enough information regarding how the ions are leached out from geopolymer structure. The existing informations are generally limited to the amount of ions (in percentage) that were leached out of geopolymers in a given period of time and conditions but the kinetic model has not been fully discussed so far. The model is a very important tool in designing geopolymers as heavy metal ion immobilizers in real applications in order to predict the leaching out mechanism from the geopolymers and how to improve the immobilization strength of the geopolymers in the long run.

This paper is intended to reveal the mechanisms and kinetics of heavy metal ions leaching from fly ash geopolymer. In this study, fly ash from PT. IPMOMI in Probolinggo, East Java, Indonesia was used as a source of aluminosilicate in geopolymer synthesis while  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were used as models of heavy metal ions. The geopolymers were made according to our previous reports (Fansuri et al., 2016) while TCLP methods and SEM-EDX analyses were used to collect leaching data for mechanisms and kinetics study.

## 2. Experimental

### 2.1 Materials

The materials used in this research are: fly ash from PT IPMOMI power plant in East Java, Indonesia; industrial grade sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and demineralized water. Other pro analyses grade chemicals i.e. NaOH pellet,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , acetic acid ( $\text{CH}_3\text{COOH}$ ),  $\text{HNO}_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Pb}(\text{NO}_3)_2$  from SIGMA-ALDRICH were used in the synthesis of geopolymers.  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  content in the  $\text{Na}_2\text{SiO}_3$  are 19.16 and 37.99 % while the chemical compositions of fly ash has been reported by Supriadi et al. (2016).

### 2.2 Preparation of fly ash, alkaline solution and nitrates solution

Before being used, the fly ash was dried for 1 h at 105 °C. The dried ash was sieved using a 120 mesh test sieve to get more uniform particle size and remove unnecessary contaminants. The alkaline solution was made by dissolving 4 g of NaOH into 8.8 mL demineralized water. The solution was allowed to stand for 24 h before being used in geopolymer synthesis. Heavy metal solutions were made by dissolving their respective nitrate salts in demineralized water. The solution was diluted by demineralized water to get the suitable concentration for immobilization.

### 2.3 Preparation and characterization of geopolymer pastes

Geopolymer samples were made by mixing fly ash with 8.8 mL alkaline solution using a hand held mixer. 5 min after mixing,  $\text{Na}_2\text{SiO}_3$ ,  $\text{Al}(\text{OH})_3$  and 2.2 mL  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  solution were added to the stirred mixture. The ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of the final mixture was 6.5 and solid to liquid ratio (S/L) was 3.59. The concentration of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  solution was varried to get a concentration of 1,000; 4,000; 8,000 or 16,000 ppm, relative to the weight of fly ash that was used in the production of geopolymer paste. Although fly ash contains several heavy metals as reported by Colangelo et al. (2017), the concentration of heavy metals is considered negligible compared to heavy metals added in geopolymer preparation in this study.

The mixture was stirred for 5 min to form a homogenous paste. The paste was poured slowly into a cylindrical mold with a size of 20 mm in diameter and 40 mm in high, vibrated to reduce bubbles and then allowed to form solid geopolymer for 24 h in a plastic bag to keep the moisture. Geopolymer paste was then taken out from its mold and was put in a sealed container for 7 days at 60 °C to cure in an electric oven.

Compressive strength of the cured geopolymers were measured by a Universal Testing Machine using pressure increment of 100  $\text{kg}\cdot\text{s}^{-1}$ . The pressure (in MPa) was calculated by Eq(1).

$$P = \frac{F}{A} = \frac{m \cdot g}{\pi \cdot r^2} \quad (1)$$

$g$  = gravitation force ( $10 \text{ m}\cdot\text{s}^{-1}$ ),  $m$  = pressure force (in kg),  $\pi=3.14$  and  $r$  = radius of geopolymer paste (m). Cross section of geopolymer cuts which have been polished and coated with carbon using sputtering method were used in SEM and SEM-EDX analyses.

### 2.4 Leaching test

Leaching test was carried out for geopolymers after being cured for 7 days using TCLP method as reported by Yusheng et al. (2007). In this test, 38 g of each geopolymer was soaked in 1 L 0.01 M acetic acid solution. The mass ratio of geopolymer to acetic acid solution was 1:25. The acetic acid solution was stirred at 300 rpm for 32 h. At 1, 2, 4, 8, 16 and 32 h, 10 ml of each leaching solution was taken for analysis of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  concentration and 2 drops of concentrated nitric acid were added to preserve the solution. The concentration of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in the leachate was measured by ICP-OES.

### 3. Results and discussion

#### 3.1 Compressive strength of Cd<sup>2+</sup> and Pb<sup>2+</sup>-containing geopolymers

Figure 1 shows the strength of Cd<sup>2+</sup> and Pb<sup>2+</sup>-geopolymer which is stronger than that reported by Supriadi et al. (2016) for smaller SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (3.0 and 1.6) but similar to those observed by Fansuri et al. (2016) which used similar molar ratio as this work. In addition, the strength of geopolymer is clearly affected by the concentration of Cd<sup>2+</sup> and Pb<sup>2+</sup> presence in the geopolymer. At low concentration (less than 5,000 ppm), the addition of Cd<sup>2+</sup> and Pb<sup>2+</sup> improve geopolymer strength but the opposites occurs at higher concentration. It is also apparent that the strength of Cd<sup>2+</sup>-geopolymers are higher than Pb<sup>2+</sup>-geopolymer when the heavy metals concentration are between 1,000 and 16,000 ppm.

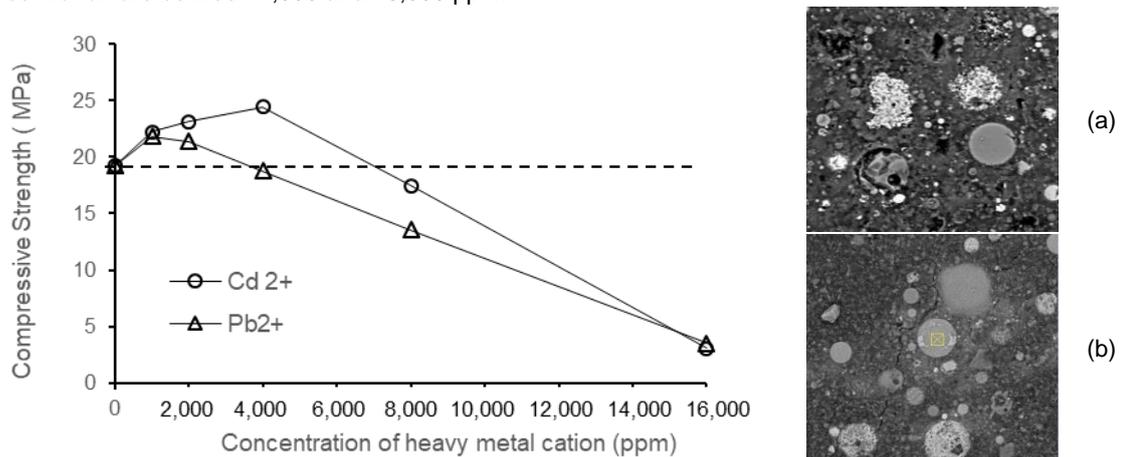


Figure 1: Compressive strength of Cd<sup>2+</sup> and Pb<sup>2+</sup>-geopolymers at different concentration of heavy metal cations and polished surface of (a) Cd<sup>2+</sup> and (b) Pb<sup>2+</sup>-geopolymers

SEM analysis results show that the addition of Cd<sup>2+</sup> and Pb<sup>2+</sup> revealed slightly different morphology where Cd<sup>2+</sup>-geopolymer did not show any crack development while Pb<sup>2+</sup>-geopolymer showed a small cracks propagation. It is well known that cracks reduce the strength of the geopolymer. Further SEM analysis of geopolymer using EDS detector shows that both Cd<sup>2+</sup> and Pb<sup>2+</sup> are concentrated mostly in the inner part of geopolymer rather than at the edge (outer part) as shown in Figure 2. The distribution indicated that the Cd<sup>2+</sup> and Pb<sup>2+</sup> cations are well immobilized by the geopolymer.

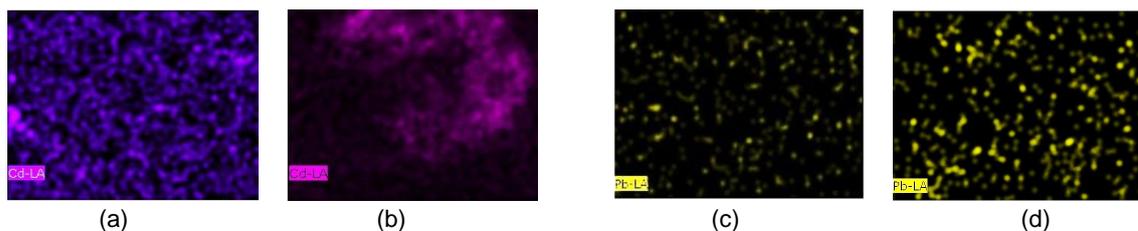


Figure 2: Distribution of Cd<sup>2+</sup> in the (a) edge and (b) inside part; Pb<sup>2+</sup> in the (c) edge and (d) inside part of fly ash geopolymer

#### 3.2 Cd<sup>2+</sup> and Pb<sup>2+</sup>- leaching

Leaching test results are shown in Figure 3. Cd<sup>2+</sup> was leached out of the geopolymer when its concentration is 4,000 ppm while Pb<sup>2+</sup> was only leached out of the geopolymer when its concentration is 16,000 ppm. At 16,000 ppm, Cd<sup>2+</sup> is leached out since the beginning of soaking (at 1 h) while Pb<sup>2+</sup> 16,000 ppm was leached out at 4 h and Cd<sup>2+</sup> 4,000 ppm at 8 h of soaking in 0.01 M acetic acid solution.

The leaching pattern as shown in Figure 3 indicates that there are two types of cations (Cd<sup>2+</sup> or Pb<sup>2+</sup>) in the geopolymer. The first was leached out immediately when the geopolymer was soaked in the acetic acid solution and the second takes longer time to be leached out. When it is compared to Figure 2, the first type of cation is located at the the surface or outer part of the geopolymer while the second is from the inner part (core) of the geopolymer as schematically shown in Figure 4. The two steps of leaching is shown clearly by Cd<sup>2+</sup>-geopolymer

at concentration of 16,000 ppm where at 0 h of soaking,  $\text{Cd}^{2+}$  has already been leached out of the geopolymer. After the number of  $\text{Cd}^{2+}$  leached was reduced drastically at 4 h, it increase again and reach a peak at 8 h. The second peak is might be due to the leaching of inner  $\text{Cd}^{2+}$  that was leached when the acetic acid solution penetrates the inner part of geopolymer, dissolve and carry the  $\text{Cd}^{2+}$  into the acetic acid solution.

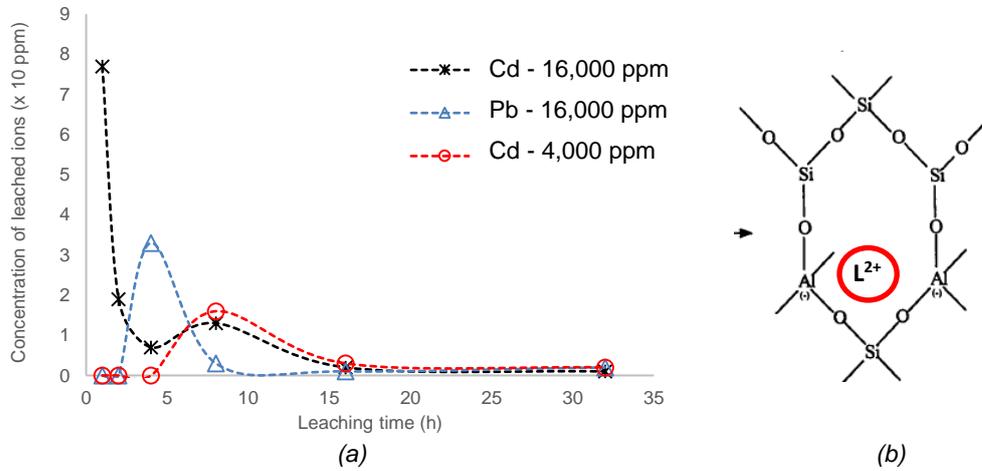


Figure 3: (a) Leaching rate of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from the geopolymer and (b) cation in the geopolymer matrices

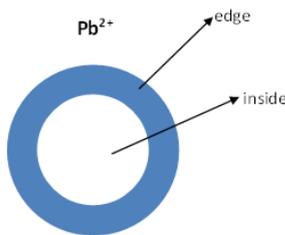


Figure 4: Schematic model of  $\text{Pb}^{2+}$  leaching from  $\text{Pb}^{2+}$ -geopolymer

Although some  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were leached out of the geopolymer, most of them are still retained. The percentage of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  that were retained by the geopolymer is called as immobilization effectivity in this case and it is shown in Table 1. The table shows that eventhough  $\text{Cd}^{2+}$  and/or  $\text{Pb}^{2+}$  were leached out, the percentage of them that were remain in the geopolymer is till high, i.e. more than 99.5 % which is comparable to the report by Zhang et al. (2008). The concentration of leached  $\text{Pb}^{2+}$  out of the geopolymer (less than 0.4 ppm) is also lower than the standard limit that was reported by Rafieizonooz et al. (2017). It means that some of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are still bonded strongly to the geopolymer matrix due to encapsulation or the geopolymers are impenetrable by the acid solution.

Table 1: Immobilization effectivity (%)

Leaching time	$\text{Cd}^{2+}$ 1,000 ppm	$\text{Cd}^{2+}$ 4,000 ppm	$\text{Cd}^{2+}$ 16,000 ppm	$\text{Pb}^{2+}$ 1,000 ppm	$\text{Pb}^{2+}$ 4,000 ppm	$\text{Pb}^{2+}$ 16,000 ppm
1 h	100	100.00	99.78	100.00	100.00	100.00
2 h	100	100.00	99.73	100.00	100.00	100.00
4 h	100	100.00	99.69	100.00	100.00	99.77
8 h	100	99.28	99.55	100.00	100.00	99.74
16 h	100	99.00	99.51	100.00	100.00	99.71

Zhang et al. (2008) also mentioned that the cations may be encapsulated or simply trapped in the geopolymer matrix. However, there is also a possibility that the cations are acted as an exchangeable cations as shown in Figure 3b. The exchangeable  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are easily leached out of the geopolymer by the acetic acid solution while encapsulated/trapped  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are not leached which explain the high  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  retention by the geopolymer. In addition to the difference in heavy metal immobilisation process, the size different of  $\text{Cd}^{2+}$  ( $r = 0.92 \text{ \AA}$ ) and  $\text{Pb}^{2+}$  ( $r = 1.12 \text{ \AA}$ ) seem to affect the leaching of both ions. The exchangeable  $\text{Pb}^{2+}$  is retained

stronger than the exchangeable  $\text{Cd}^{2+}$ . Due to its larger size,  $\text{Pb}^{2+}$  is more difficult to diffuse to the geopolymer surface while smaller  $\text{Cd}^{2+}$  is easily diffused to the surface. These results are in good agreement with those reported by Yunsheng et al. (2007).

Figure 5 shows the leaching rate of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  from their respective geopolymer, based on leaching test results (Figure 3). The rate was calculated using Eq(2):

$$v[\text{L}^{2+}] = \frac{d[\text{L}^{2+}]}{dt} \quad (2)$$

where  $v[\text{L}^{2+}]$  is rate of cation leaching from the geopolymer,  $d[\text{L}^{2+}]$  is the concentration of heavy metal ions and  $dt$  = is the change in unit time.

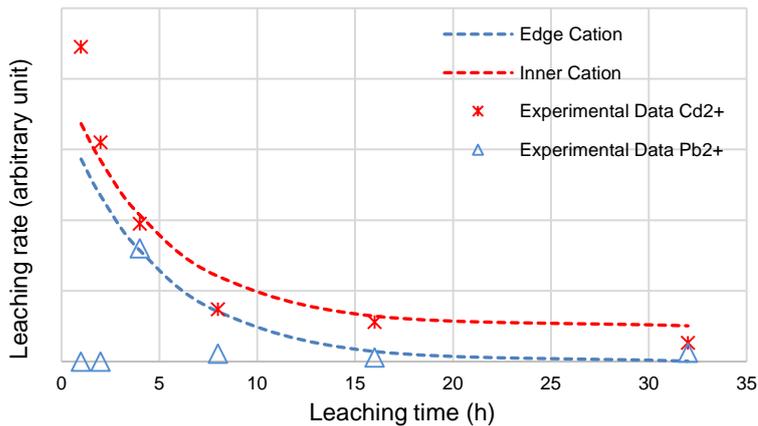


Figure 5: First order modelling of leaching kinetics of cation leaching

Distribution of  $\text{Pb}^{2+}$  before and after leaching (Figure 6) shows that the ion is homogeneously distributed in the geopolymer matrix. Its concentration, especially on the edge, is relatively unchanged after leaching which indicates that  $\text{Pb}^{2+}$  is not easily leached from the geopolymer.

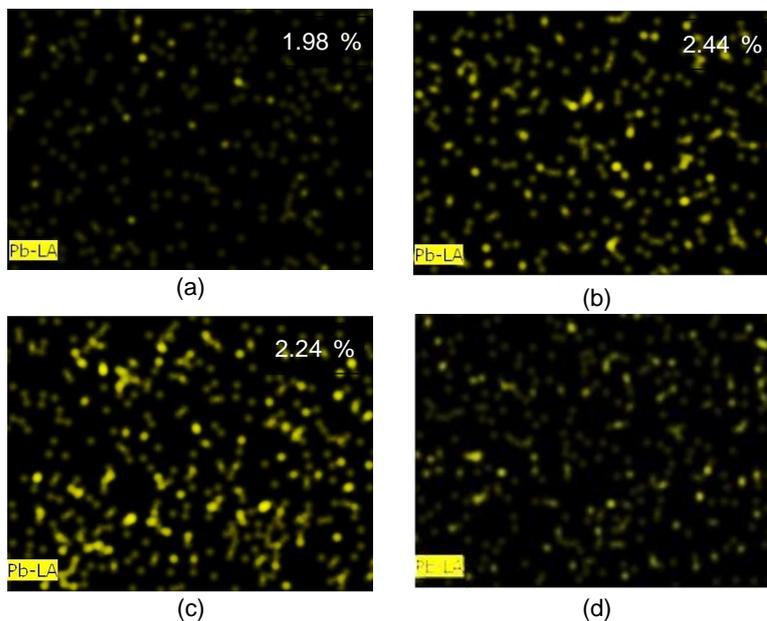


Figure 6: The distribution of  $\text{Pb}^{2+}$  (a) inside; (b) edge of geopolymer matrices before leaching test; (c) inside; (d) edge of geopolymer matrices after leaching test

By using the first order of reaction as in Eq(2) and the two type of exchangeable cation on the geopolymer, a trend line was fitted on the experimental leaching data. The line shows very good fit between data from simulation and data from the experiment. The fit lead to the conclusion that the leaching mechanisms can be modelled by calculating the contribution of the two type of heavy metal cations in the geopolymer. Again, the simulation shows that  $\text{Cd}^{2+}$  is easier to be leached out than  $\text{Pb}^{2+}$ .

#### 4. Conclusions

Based on the experimental results, it can be concluded that the existence of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  affect the strength of the geopolymer where  $\text{Cd}^{2+}$ -geopolymer was slightly stronger than  $\text{Pb}^{2+}$ -geopolymer. In addition to the strength, SEM-EDX analysis show that  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  are distributed uniformly from the surface to the core of geopolymer. The leaching test reveals that more than 99.5 % of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  was retained by geopolymer. This might be due to the mechanism in which the cations attached to the geopolymers. Easily leachable cations are located in the surface geopolymer where it is penetrable by the acetic acid solution. By using this notion, it is found that leaching of both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  follows first order rate law with two steps leaching process according to the ions position in the geopolymer. The first step was surface cation leaching followed by inner cations leaching.

#### Acknowledgments

The authors acknowledge financial supports from Indonesian Ministry of Research, Technology and Higher Education for this work under the decree of the directorate general of research strengthening and development No. 1/E/KPT/2018 and contract No 885/PKS/ITS/2018.

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