

Immobilization of Chromium from Liquid Waste of Electroplating Home-Industries by Fly Ash Geopolymerization

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Abstract. Immobilization is one of methods that can be used to overcome the problem of water pollution by heavy metals, such as chromium, which is possibly produced in an electroplating home-industry. One method that can be used to immobilize heavy metals is by using the waste water as a reactant in a geopolymerization process. The resulting geopolymer will contain such heavy metals and keep them from being dispersed into the environment. In this research, the immobilization was carried out by geopolymerization of fly ash from PT. IPMOMI (International Power Mitsui Operation and Maintenance) in Probolinggo, Indonesia, which pass through 60 (FA 60), 100 (FA 100), and 200 (FA 200) mesh sieve and using wastewater from electroplating home-industries in Ngingas Village, Sidoarjo-Indonesia, or a solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as one of its reactants. The composition of the geopolymerization follows the results of previous research, i.e using the ratio of Solid to Liquid (S/L) = 3.59, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.67$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 3.33$ and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 6.46$. Experimental results show that the compressive strength of geopolymers without heavy metals addition increases when the particle size decreases. Geopolymer made of FA 100 has the highest compressive strength i.e 35.05 MPa. The addition of a chromium-containing wastewater in FA 100 geopolymerization produce a geopolymer with a lower compressive strength i.e 26.42 MPa while the addition of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution produce geopolymer with compressive strength of 24.47 MPa. The SEM-EDX photo shows that chrome was evenly dispersed in the geopolymer. Leaching test with TCLP method (Toxicity Characteristic Leaching Procedure) on the geopolymer product showed that no chrome content in the leachate was found. This suggests that chromium is immobilized by geopolymers very well.

Keywords. geopolymer, immobilization, chrome waste, and fly ash.

1. Introduction

Ngingas village in Sidoarjo, East Java, Indonesia is well known as a center for metal-plating home industry. The metal plating is started with cleaning the metal using acid solutions and followed by plating process. Chrome electroplating is one of important metal-plating processes in the area to produce various chrome plated metals [1].



Chromium, especially in the form of Cr(VI), is very toxic and it is an agent that can cause cancer, cell mutation, and malformation [2]. It also can cause cancer of skin and respiratory system [3]. Therefore, although Cr(VI) concentration in a normal chrome plating waste is small, its release to the environment must be controlled cautiously.

Immobilization of chrome by geopolymerization is a promising method to control chromium release to the environment. Immobilization of Cr³⁺ by geopolymerization using fly ash of PT. IPMOMI in Probolinggo, Indonesia can hold almost 100 % Cr³⁺ in the geopolymer when tested by TCLP method [4]. Other researcher reported that 96 % of chromium in the form of Cr⁶⁺ ion remains in the geopolymer after leaching [5].

Although it has been reported that chromium can be excellently immobilized by geopolymerization, the chromium ion was introduced to the geopolymer mixture in the form of its salt [5]. The effect might be different if the source of chromium is a homogenous solution of chromium salts (such as Cr(NO₃)₆·9H₂O) or from the waste water of a chrome-electroplating home industry because it might also contain other components which may alter the immobilization of chromium ion by geopolymerization process. Therefore, it is interesting to study the immobilization of chromium ion in the waste water of chrome-electroplating home industry. This paper reports our effort to immobilize chromium in waste water of chrome-electroplating home industry in Ngingas village, Sidoarjo, Indonesia by using geopolymerization of fly ash of PT. IPMOMI.

2. Materials and methods

The chemicals that were used in this research are fly ash, demineralized water, technical grade waterglass (2SiO₂·Na₂O) and p.a. grade sodium hydroxide (NaOH), aluminum hydroxide (Al(OH)₃), and acetic acid glacial. The ashes were taken from PT. IPMOMI power plant in Probolinggo, East Java, Indonesia.

The chemical composition of the fly ash was characterized by XRF and the result is shown in Table 1. The composition of waterglass has been reported elsewhere [6] and it was comprised of 19.16 wt.% SiO₂, 37.99 wt.% Na₂O, and 28.07 wt.% H₂O.

Table 1. Elemental composition of PT. IPMOMI fly ash

Element (reported as its most stable oxide)	% mass	Element (reported as its most stable oxide)	% mass
SiO ₂	50.67	CaO	12.7
Al ₂ O ₃	13.76	MgO	0.19
Na ₂ O	0.19	K ₂ O	1.28
TiO ₂	0.76	Fe ₂ O ₃	11.99
MnO ₂	0.14	SO ₂	0.63
Se ₂ O ₃	0.12	P ₂ O ₅	0.08
LOI	1.42		

2.1. Preparation of Al(OH)₃ and Activating Solution

The activating solution is a mixture of NaOH solution and waterglass. The NaOH solution was prepared by dissolving 28 g of NaOH in demineralized water so that the total volume was 50 mL. After leaving the resulted solution at room temperature for 24 h, 80 g waterglass was added and stirred well and then left at room temperature for 6 h. Meanwhile, Al(OH)₃ solution was prepared by dissolving 3.4 g Al(OH)₃ in 15 g of demineralized water.

2.2. Preparation of Geopolymer

The geopolymer was prepared by mixing 260 g of FA60, FA100 or FA 200 with the activating solution and then stirred well using a mixer for 40 s. After that, Al(OH)₃ solution was added and the mixture was stirred again for another 2.5 min. The resulted paste was then poured into a 2 cm height

and 4 cm tall PVC cylindrical mold and left at room temperature for 24 h. The geopolymer was then taken out of the mold and put into a plastic bag and sealed before cured in an oven at 55 °C for 24 h. The compressive strength of the geopolymer was measured in the 7th day of curing. The mixture had solid/liquid (S/L) = 3.59; Na₂O/SiO₂ = 0.67; Na₂O/Al₂O₃ = 4.31; and SiO₂/Al₂O₃ = 6.46. The geopolymer is called chromium free-geopolymer.

2.3. Preparation of Geopolymer to Immobilize Chromium in the Waste Water

The preparation of geopolymer to immobilize chromium in the waste water was carried out by the same procedure as the preparation of the strongest chromium free-geopolymer. However, the concentration of sodium hydroxide was increased to reduce its volume while maintaining the same amount of sodium ion in the geopolymer paste mixture. To avoid the precipitation of chrome due to high alkaline concentration, the addition of waste water was carried out just after the addition of Al(OH)₃ solution. The geopolymer is denoted as chrome containing-geopolymer.

2.4. Leaching Test

Leaching test was carried out for the chrome containing-geopolymer. The geopolymer paste was immersed in 2.5% acetic acid solution and stirred by a magnetic stirrer for 24 h. The ratio of volume of acetic acid solution to the mass of geopolymer paste was 1:20. At 1, 2, 4, 8, 16 and 24 h, 10 mL of the immersing solution was taken out to be analyzed by Atomic Absorption Analyzer (AAS) to determine the concentration of leached chromium from the geopolymer.

2.5. Characterization

Compressive strength of all geopolymer pastes were measured using Universal Testing Machine (UTM). SEM-EDX analyses were carried out using Zeiss EVO MA 10 on Au-Pd coated polished cross-section of the geopolymer samples.

3. Results and discussion

3.1. Characteristics of the Waste Water and Fly Ash

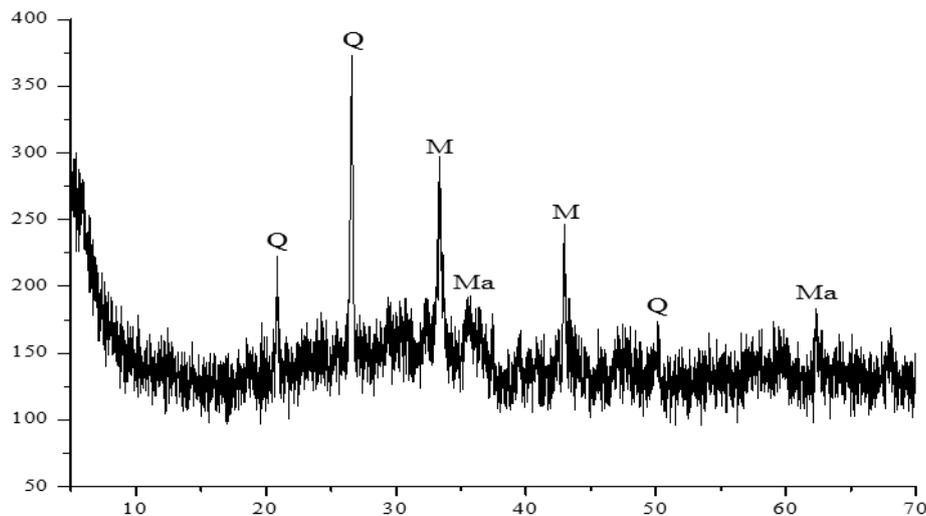
Concentration of total chromium content in the waste water, which was analyzed by an AAS, is shown in Table 2. Sample L1 and L2, which were taken from the unprocessed waste water, contain relatively high chromium concentration. The other two (L3 and L4), which were taken from waste water treatment plants, contains no chromium.

The maximum allowable chromium content, in the form of Cr⁶⁺, in surface water is 0.1 mg/L (0.1 ppm) [7]. Although the analysis method (AAS) could not differentiate the chromium species whether it is in the form of Cr³⁺ or Cr⁶⁺, the chromium content in L1 and L2 are very high (6.0 and 28.8 ppm, respectively). Therefore, the waste water is suitable for the study of immobilization by geopolymer and the highest one (L2) was used in the geopolymerization experiments.

The mineral composition of the fly ash was determined by XRD and the diffractogram is shown in Figure 1. The diffractogram shows peaks of quartz at $2\theta = 20.58^\circ$, 26.61° and 50.04° , mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or $2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) at $2\theta = 33.44^\circ$ and 42.95° , and magnetite at $2\theta = 35.56^\circ$ and 62.40° . The fly ash also contains amorphous phase of aluminosilicate which is shown by a hump at 2θ between 20° and 40° [8]. The diffractogram also shows that major elements as in Table 1 (Si, Al and Fe) are distributed in crystalline and might also be found in the amorphous phases in the fly ash.

Table 2. Concentration of chromium in the waste water

Sample ID	Cr _{total} (ppm)
L1	6.0
L2	28.8
L3	0.0
L4	0.0

**Figure 1.** X-ray diffractogram of fly ash of PT. IPMOMI. Q = quartz, M = Mullite and Ma = Magnetite.

According to Supriadi, *et al.* [6], the amorphous phase is the most reactive component of fly ash and reacted completely in geopolymerization process while the crystalline phase only partially reacted. However, Atmaja, *et al.* [7] reported that although the crystalline phases are only partially reacted, their existence do not have significant effect to the overall strength of geopolymer. Therefore, it is assumed that all silicon and aluminum content in the fly ash will be involved in the geopolymerization process and counted in the calculation of Si/Al ratio.

Before the preparation of the geopolymer, fly ash of PT. IPMOMI was sieved through 60 (FA 60), 100 (FA 100) and 200 (FA 200) mesh sieve to get a uniform particle size and to study the effect of particle size to the compressive strength of the resulting geopolymer. The sieve opening of each mesh is 0.250 mm, 0.149 mm and 0.074 mm respectively. According to Wang, *et al.* [8], particle size affected the reactivity of the ash to alkaline activator during the geopolymerization process. Fly ash with smaller particle size is more reactive in the geopolymerization process than fly ash with larger particle size.

Table 3 shows the compressive strength of chromium free-geopolymer. The test was carried out in the day 7 of curing. The table shows that the strongest geopolymer was made of FA 100, which is the intermediate particle size of fly ash. The result seems contradict to Wang *et al.* [8] who reported that the strength of geopolymer was inversely proportional to the geopolymer strength.

In our case, particle size of FA 100 was larger but more uniform than FA 200. The uniformity of fly ash comes from the sieving process where fly ash particles smaller than 0.149 mm but larger than 0.074 mm will be stay in 100 mesh sieve while the smaller particles will pass through the 200 mesh sieve. Therefore, although smaller particle will produce stronger and better geopolymer, there is a possibility that the uniformity, in combination with small particle size of the fly ash, also has an

important role in the geopolymerization process. Based on the results in Table 3, FA 100 was then used to make chromium containing-geopolymer.

Table 3. Compressive strength of chromium free-geopolymer

Trial No	Compressive Strength (MPa)		
	FA 60	FA 100	FA 200
1	25.00	33.95	31.45
2	21.45	36.18	33.00
3	22.55	35.00	32.24
Average	23.00	35.05	32.20

3.2. Immobilization of Chromium by the Geopolymer

Table 4 shows the compressive strength of chromium containing-geopolymer made of FA 100. It is shown that the geopolymer strength was reduced from 35.05 MPa to 24.47 MPa – 26.42 MPa when it contains chromium. The results seem contradict to a report by Fatmawati [4] where compressive strength of fly ash geopolymer increased at increasing chromium content up to 6,860 ppm (the concentration of chromium is relative to the mass of fly ash used in the synthesis of geopolymer) before it drastically decreased at higher chromium content. However, in Fatmawati's reports the strength of chromium containing-geopolymer at low chromium content was about 29 MPa, which was close to our results. Therefore, the strength of chromium containing geopolymer in this research is in agreement with low chromium content geopolymer in Fatmawati's report [4].

Figure 2 shows SEM-EDX images of cross section of chromium containing-geopolymer. Although concentration of chromium was very low, the SEM-EDX image shows the existence of the metal and its distribution across the cross section.

Table 4. Compressive strength (in MPa) of chromium containing-geopolymer made of FA 100

Chromium from waste water	Chromium from $\text{Cr}(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$ Solution
26.42	24.47

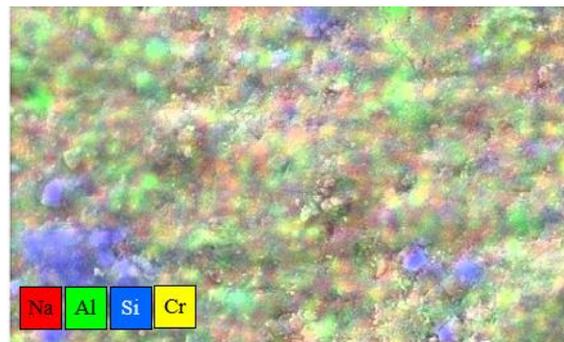


Figure 2. SEM-EDX photo of the cross section of chromium containing geopolymer

Leaching test results of chromium containing geopolymer are listed in Table 5. In the table, the name of “with waste water” means that the geopolymer was prepared by using the waste water while number in “Geo-2000” means that the geopolymer was prepared with the addition of 2000 ppm chromium, relative to total fly ash used in the preparation. The table shows that no chromium was leached out from geopolymers that were prepared with waste water.

When the geopolymer was made with chromium $\text{Cr}(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$ solution, a small amount of chromium (1 % for Geo-2000 to 3 % Geo-8000) was leached out. It means that more than 97%

chromium was immobilized by the geopolymer. The percentage of immobilized chromium is slightly lower than the result that was reported by Zhang, *et al.* [9]. However, Zhang, *et al.* [9] converted all chromium ion to Cr^{3+} before the geopolymer preparation, which was not done in this research.

The immobilization of chromium by the geopolymer can also be seen from SEM-EDX results in Figure 3. The figure shows that the chromium content stayed in the geopolymers after leaching process.

Table 5. Leaching test results of chromium containing geopolymer

No	Geopolymer	t _{.Leaching} (h)	[Cr] _{leached} (%)
1	with waste water	1	0
2	with waste water	2	0
3	with waste water	4	0
4	with waste water	8	0
5	with waste water	16	0
6	with waste water	24	0
7	Geo-2000*	24	1
8	Geo-4000*	24	1
9	Geo-8000*	24	3

*Geo-2000: chromium content = 2000 ppm relative to total fly ash used in the geopolymer preparation

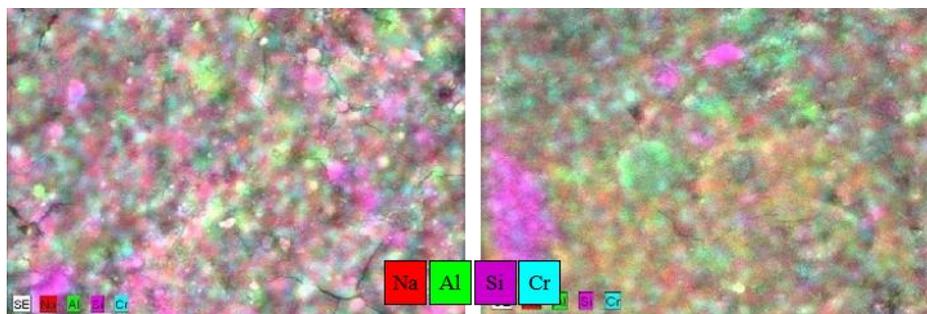


Figure 3. SEM-EDX photo of the cross section of chromium containing geopolymer: (a) before and (b) after leaching

4. Conclusions

Experimental results showed that the highest compressive strength of chromium free-geopolymer (35.05 MPa) was given by the geopolymer made of PT. IPMOMI fly ash with particle size between 0.074 mm and 0.149 mm (FA 100). The results indicated that uniformity of the particle size of fly ash may also play an important role in the geopolymerization process. The addition of a chromium-containing waste water and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution reduced compressive strength of the resulted geopolymer to 26.42 MPa and 24.47 MPa, respectively. SEM-EDX images showed that chromium was evenly dispersed in the geopolymer. Leaching test result showed that no chromium was found in the leachate when the source of chromium was waste water from Ngingas village with the highest chromium concentration. When using higher chromium solution, which was made of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, up to 3% of chromium was leached out of the chromium containing-geopolymer. This suggests that chromium is immobilized by geopolymers very well and geopolymerization can immobilize chromium in the waste water from electroplating home-industry in Ngingas village, Sidoarjo.

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