

Effect of Hydroxyl Ion on Immobilization of Oxyanions Forming Trace Elements from Fly Ash-based Geopolymer Concrete

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ABSTRACT

Geopolymer is an amorphous three dimensional aluminosilicate binder that is developed from the alkali activation of an aluminosilicate material such as fly ash. This binder has excellent physical properties which makes it a good replacement for cement as binder in various applications. It also has the tendency to immobilize toxic elements from waste materials. The hydroxyl ion supplied by the alkali activating solution acts as catalyst in the dissolution and condensation process of the geopolymer synthesis, and can affect the way elements are immobilized. In this investigation, geopolymer concrete was produced from coal fly ash, aggregates and an activating solution which contains sodium hydroxide and sodium silicate. In order to study the effect of hydroxyl ion on the immobilization of oxyanions forming trace elements, NaOH added during preparation were 10%, 13%, and 16% by mass of the fly ash used. The concrete was tested for the 28 days compressive strength and leaching tests conducted to determine the concentration of oxyanion trace elements. Oxyanions concentration measured in the leachates from the availability test are selenium (Se), chromium (Cr), and arsenic (As), which were determined using an inductively coupled plasma mass spectrometer (ICP-MS). The concentration of the hydroxyl ion leached from the sample was also determined from the pH and temperature of the leachate. The investigation shows that the highest compressive strength was obtained with geopolymer made with the 13% NaOH mix, and that the concentration of Se and Cr leached from the geopolymer were much lower than that of the fly ash which indicates the geopolymer was effective at immobilizing the elements. The measured As concentration in the geopolymer leachate far exceed the amount leached out of the fly ash, which might suggest that As became more available due to the geopolymer synthesis. The amount of NaOH used in this study for geopolymer synthesis was observed to have no effect on the immobilization or leaching of the elements. Increased amount of NaOH does not seem to result in increased leaching of the elements.

INTRODUCTION

Apart from the excellent physical properties of geopolymer such as its high compressive strength, low shrinkage and excellent acid/heat resistance that makes it a good alternative for replacing cement as binder in concrete^{5,6}, it also possesses the ability to immobilize toxic elements from leaching¹⁻⁴. Geopolymer are amorphous three dimensional (3-D) aluminosilicate materials that comprise of three classes of inorganic polymeric units depending on the ratio of the silica to alumina⁶. The material has a basic silicon-oxygen-aluminum framework called silicate⁸ (silicon-oxo-aluminate) having a structural formula Si-O-Al that are linked together to form the different polymeric units. The polysialate (PS) is the simplest polymeric unit with structural formula Si-O-Al-O, formed from silicon and alumina tetrahedra linked by the sharing of all oxygen atoms^{7, 8}. For high silica to alumina ratio, polysialatesiloxo (PSS) with structure Si-O-Al-O-Si-O and polysialatedisiloxo (PSDS) with structure Si-O-Al-O-Si-O-Si-O are formed⁶⁻⁸.

Materials used in the synthesis of geopolymer include coal fly ash, blast furnace slag, metakaolinite and kaolinite^{6, 8-12}. Due to ease of availability and little or no cost associated with fly ash, its use as feedstock material in geopolymer has been growing¹³. No matter the material used in geopolymer synthesis, the reaction mechanism is assumed to be the same⁶. Swanepoel and Stydom reported that this reaction mechanism is not fully understood but it is generally agreed upon that it occurs through a series of steps that take place simultaneously¹⁴. The reaction mechanism involves the dissolution of the silicon and aluminum from the aluminosilicate material through the action of hydroxyl ions supplied by the alkali hydroxide, followed by the hydrolysis of the silicon and aluminum to form silicate and aluminates species, the final step is the condensation of the silicate and alumina species to form the polymeric framework^{10,11,14,15}. Depending on the concentration of the silicate in the system (indicated by the silica to alumina ratio), condensation can occur between the aluminate and silicate species or between silicate species to form the different class of polymeric unit (PS, PSS and PSDS)^{15, 16}. In some cases, alkali silicate is added to the system to increase the silicate available for geopolymerization^{8, 18}.

The hydroxyl ions in the system are responsible for the dissolution of the silicates and aluminates, and also act as catalysts during the condensation reaction¹⁷. During the condensation step, hydroxyl ions from neighboring molecules condense to form an oxygen atom that link the silicate and aluminate species, and releases a molecule of water. High amount of hydroxyl ions in the system accelerates the chemical dissolution of the aluminosilicate material, and would lead to a greater likelihood of having higher strength geopolymer^{8,17}. It was also observed that an excess of hydroxyl ion in the system might lead to reduction in the strength of the matrix¹⁷. The added NaOH may leach out in the same amount as it was added because it only acts as a catalyst for the dissolution and condensation process¹⁷.

Immobilization of hazardous waste, trace and heavy elements is a technique that has been achieved by the use of geopolymer^{1-4, 8, 13, 20}. Several studies are in agreement that the mechanism of waste immobilization is either through physical encapsulation or

chemical bonding into the geopolymer structure or a combination of both^{17, 19, 20}. The efficiency of the immobilization is influenced by factors such as the pH of the material, concentration of the alkali activator and type of element to be immobilized. Geopolymer might not be effective at immobilizing elements that show increased solubility at high pH conditions³. Such elements are the oxyanions forming trace elements, which are negatively charged species containing oxygen that are formed by arsenic(As), chromium (Cr), molybdenum (Mo), selenium (Se), vanadium (V), antimony (Sb) and tungsten (W)²¹.

The immobilization of these elements would be a great challenge under the highly alkaline condition of geopolymerization. The basic method of evaluating the immobilization efficiency of elements within a geopolymer matrix is by carrying out metal extraction using leaching test^{1, 8} such as TCLP and NEN 7341.

The objective of this study is to investigate the efficiency of fly ash-based geopolymer in immobilizing trace elements such as Cr, As and Se, and also assess the effect of hydroxyl ion on the immobilization of the oxyanions forming trace elements. The Dutch availability test²² (NEN7341) was employed to assess the leaching and immobilization of these elements from pulverized fly ash-based geopolymer concrete.

EXPERIMENTAL

Materials

The fly ash used in this study was obtained from a coal fired power plant and the silica fume from Elkem materials. The material's chemical composition as determined by X-Ray Fluorescence (XRF) analysis is shown in Table 1 and the fly ash can be categorized as a class F fly ash according to the American Society for Testing and Materials (ASTM C618-03) specification²³. The sodium silicate solution used was prepared by dissolving silica fume (98.6% amorphous silica content) in hot concentrated sodium hydroxide solution (NaOH, 98% pure), and the solution allowed to equilibrate in the oven at 75 °C for at least 24hrs.

Table 1: Chemical composition of the fly ash and silica fume used (wt %)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅	LOI
Fly ash	56.20	28.00	5.22	1.52	1.00	0.02	1.46	2.74	0.21	0.18	3.32
Silica fume	98.6	0.15	0.01	0.02	0.09	-	-	0.11	0.11	0.02	0.51

Concrete mix design

The geopolymer concrete comprised of sand, coarse aggregate, fly ash and the alkaline activating solution that contains a mixture of sodium hydroxide and the produced sodium silicate solution. As in ordinary Portland cement concrete, sand and aggregates make up about 70% by weight of the geopolymer concrete. Superplasticiser was added to the concrete to aid workability. The mix design as presented in Table 2 was such that

the amount of NaOH in the three mixes was 10%, 13% and 16% by mass of fly ash used.

Table 2: Mix proportions for the geopolymer concrete

Mix #	Fly ash(kg)	Water (kg)	Silica fume(kg)	NaOH (kg)	Coarse Aggregate (kg)	Sand (kg)	Super plasticizer(ml)
1	495	163	37.1	49.5	793	793	50.00
2	474	163	46.2	61.6	793	793	50.00
3	455	163	54.5	72.7	793	793	50.00

Based on 1 m³ of concrete

Geopolymer concrete synthesis

The geopolymer concrete was prepared by mixing the different components according to the mix design; the aggregates are first dry mixed with the fly ash for about 2 minutes before adding the activating solution and superplasticiser. The mixture was further mixed for an additional 5 minutes, after which the concrete was cast into 76 mm X 152 mm cylindrical mold in three layers and vibrated to remove air bubbles. The molds were labeled according to a nomenclature that includes the Mix #, aging time at room temperature and the curing time at elevated temperature in the oven. Each sample was subjected to aging at room temperature and curing at 75°C as specified in the aging and curing regime presented in Table 3.

Table 3: Aging and curing regime for the concrete

	Description	Designation
Mix	#1 – 10% by mass NaOH	J1
	#2 – 13% by mass NaOH	J2
	#3 – 16% by mass NaOH	J3
Aging	0 hr at room temp.	0
	24 hrs at room temp.	1
	48 hrs at room temp.	2
Curing	24 hrs in oven at 75°C	24
	48 hrs in oven at 75°C	48

The notation J3-1-48 designate a Mix # 3 sample that was aged for 24hrs at room temperature before being cured in the oven for 48hrs at 75°C. After oven curing, the samples were removed from the oven, demolded, and allowed to cure at room temperature for a period of 28 days.

Compressive strength testing

In order to confirm that a geopolymer with high strength has been produced, the samples were subjected to compressive strength testing, which was performed on three samples of each mix in accordance with the ASTM C39 specification²⁴.

Leaching sample preparation

The aggregates and all the concrete samples were crushed, ground to fine powder using a ring grinder, and then sieved to pass a 150µm sieve. The moisture content of all the samples including the fly ash was determined by heating in the oven at 105°C for 24hours.

Leaching test

In this study, the Dutch availability test, NEN 7341²² was used to assess the leachability. Unlike the Toxicity Characteristic Leaching Procedure (TCLP) performed only at pH of 2.88 which cannot correctly evaluate leaching from alkaline materials such as geopolymer concretes with pH close to 12, NEN test is used mainly to determine the maximum leachable amount of a constituent that can be available for released under aggressive condition. The test predicts the constituent availability and is performed at two pH levels consisting of two extraction step on finely ground sample with a liquid to solid ratio (L/S) of 100. In the first step, the pH was maintained at pH 7.0 ± 0.5 for 3 hrs using 1M HNO₃ after which the suspension was filtered using 0.45µm membrane filter. The second step of the leaching was done on the residue from the first filtration using the same acid to maintain pH 4.0 ± 0.5 for additional 3hrs. After filtration, the two filtrates were combined and acidified with 5M HNO₃ to reduce the pH to less than 2.0.

Determination of hydroxyl ion content in the geopolymer leachate

Since it was assumed that not all the hydroxyl would take part in the geopolymerization process, the hydroxyl ion in the system after leaching the material in deionized water was determined. The finely ground geopolymer concrete samples were extracted using the water leach test in accordance with ASTM D3987²⁷ for 18 hrs. After filtration, the pH and temperature of the leachate was measured. The hydroxyl ion concentration in the leachates was calculated from the sample's initial pH. Equation 1 below is used to obtain the hydroxyl ion concentration by determining the acid dissociation constant for water (K_w) as a function of temperature (K)²⁸.

$$\text{OH}^- [\text{mg/l as OH}^-] = 17007 * K_w * 10^{\text{pH}} \text{-----} 1$$

RESULTS AND DISCUSSION

Compressive strength results

The compressive strength results are presented in Figure 1. The J1, J2 and J3 are the concrete mixes with respectively 10%, 13% and 16% NaOH of the amount of fly ash. The concrete gained strength from 37 MPa to 67 MPa as the amount of NaOH increases from 10% to 13%, but strength reduction was observed for the 16% NaOH mix. The J2 mix with 13% NaOH has the highest compressive strength. The figure represents the compressive strength values for all the mixes at the different aging-curing regime. Aging the geopolymer before oven curing, increases the compressive

strength. For the 24hrs curing period, there is a strength gain from 51 MPa to 57 MPa for the J2 mix, while the 48hrs curing gave a strength increase from 55 MPa to 67 MPa. The other mixes also follow the same trend. A general observation from the compressive strength result is that the 13% NaOH mix is the optimal mix that gave the highest strength for the entire aging-curing regime²⁹.

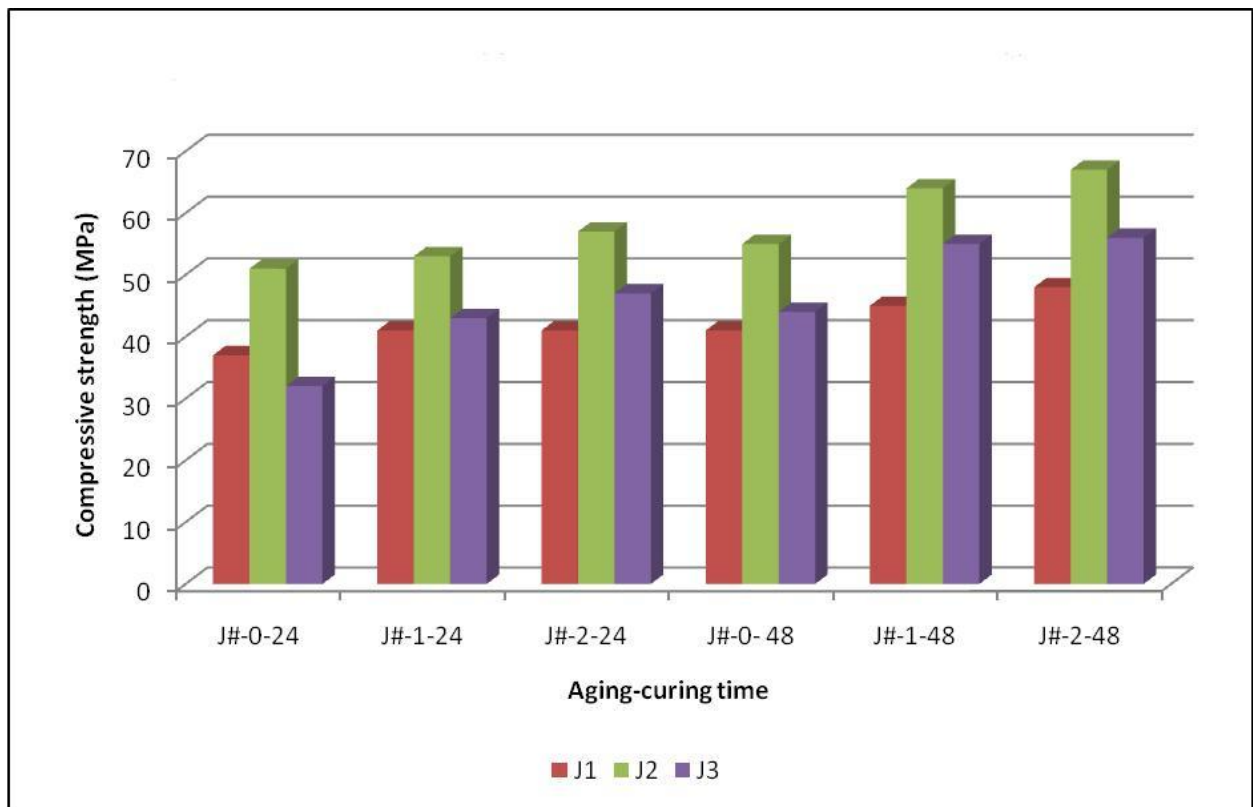


Figure 1: Compressive strength of the geopolymer concrete samples

Leaching test

The analysis of the leachate samples was done using an inductively coupled plasma mass spectrometer (ICP-MS) to determine the concentration of As, Se and Cr at the ppb ($\mu\text{g/l}$) level. Table 4 shows the pH, concentration and amount of each elements available for leaching from the geopolymer concrete mix and aggregate materials used. CFA in the table denotes the fly ash, AGG is the coarse aggregate and SAND denotes the sand used.

Table 4: pH, concentration and element availability in leachate

	Concentration ($\mu\text{g/l}$)			Available amount (mg/kg)			Material pH
	Se	As	Cr	Se	As	Cr	
SAND	< 2	< 2	2.62	10	10	18	5.75
AGG	< 2	< 2	< 1	10	10	7	8.42
CFA	74.4	17	27.6	644	147	239	5.05
J1-0-24	42	138	5.94	314	1031	44	11.39
J1-0-48	40.9	127	5.64	249	773	34	11.17
J1-1-24	42.9	138	5.33	244	786	30	11.38
J1-1-48	39.7	128	4.84	313	1009	38	11.11
J1-2-24	51.5	176	3.49	319	1090	22	11.42
J1-2-48	46.5	150	2.94	322	1040	20	11.45
J2-0-24	39	132	5.66	226	766	33	11.34
J2-0-48	38.3	130	2.66	224	762	16	11.46
J2-1-24	40.3	137	3.8	241	818	23	11.60
J2-1-48	35.8	114	6.11	269	858	46	11.25
J2-2-24	37.2	126	2.96	190	644	15	11.41
J2-2-48	41.5	141	2.76	275	935	18	11.43
J3-0-24	45.2	158	3.72	302	1057	25	11.94
J3-0-48	33	110	11.2	208	692	70	11.84
J3-1-24	31	99.6	5.54	206	661	37	11.59
J3-1-48	34.2	113	2.92	219	724	19	11.74
J3-2-24	27.9	79.4	11.1	188	534	75	11.65
J3-2-48	28.2	91.1	2.68	171	553	16	11.18

The pH of the fly ash and geopolymer concretes are plotted in Figure 2 . It can be seen from the figure that the pH of the fly ash is 5.05 but that of the geopolymer range from pH 11.18 to pH 11.94. This shows that the material is alkaline and in the pH range for Portland cement concrete.

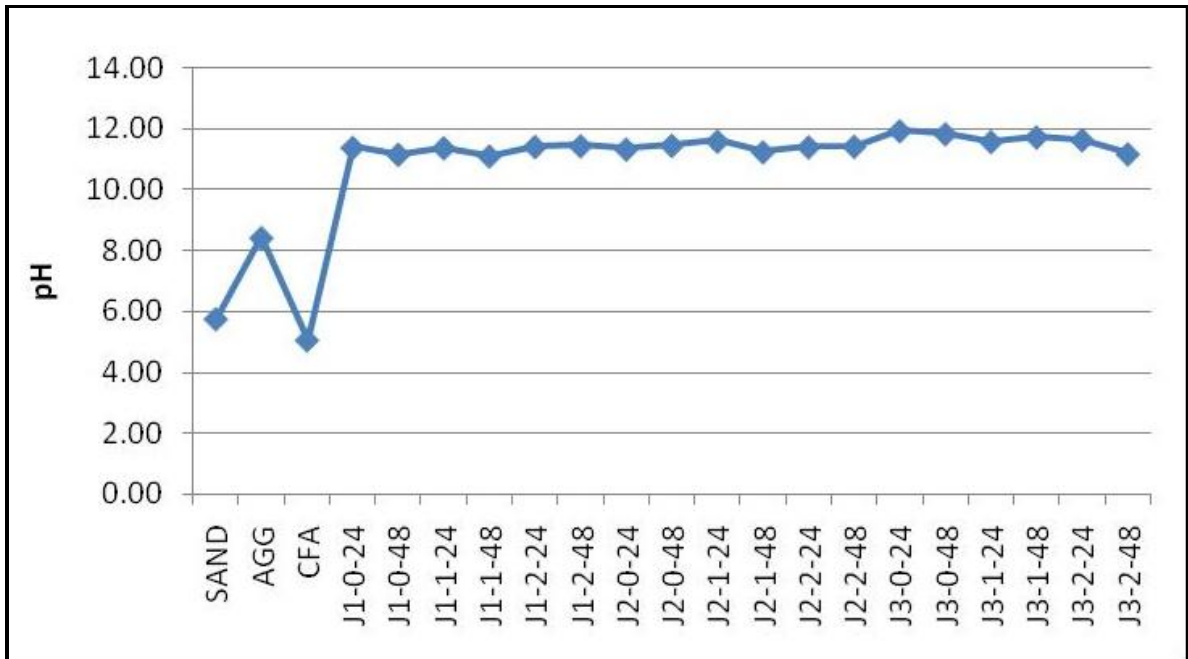


Figure 2: Stabilized pH measurements of the leachates

The leaching results for the As, Cr and Se are presented in Figure 3. It shows the concentration of the elements measured in the leachate as determined by ICP-MS.

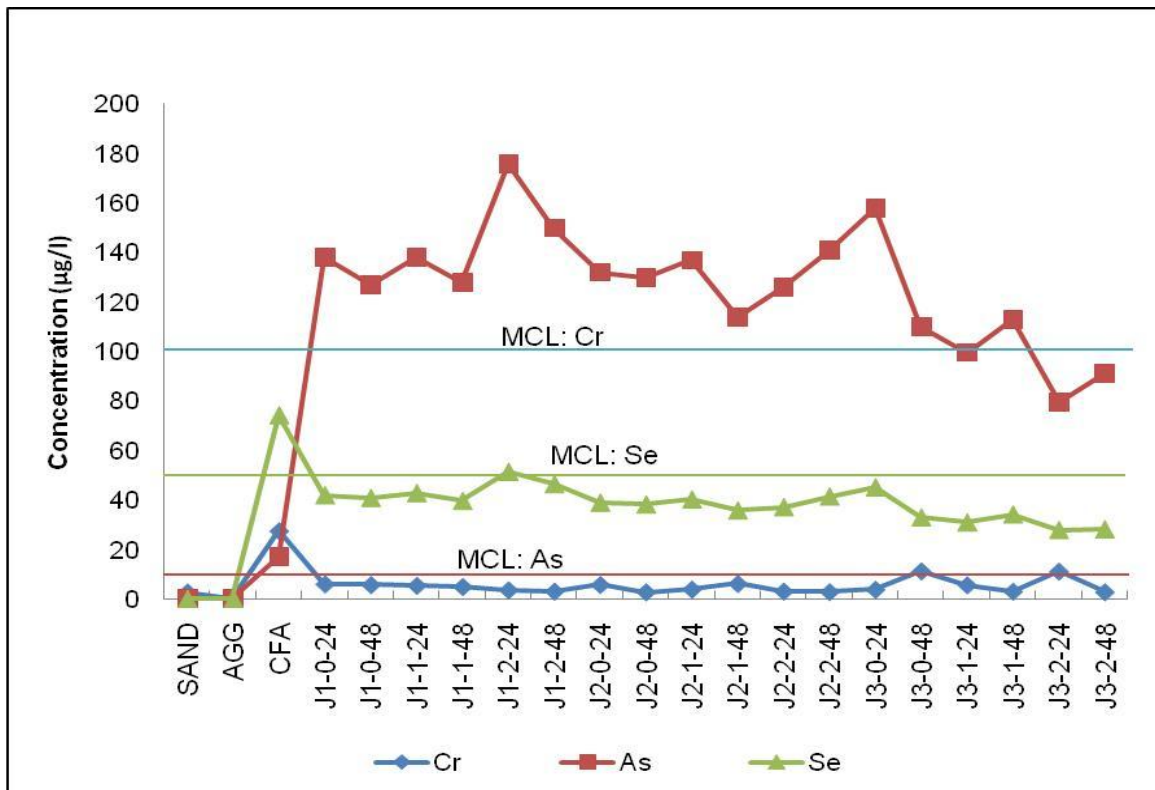


Figure 3: Concentration of the oxyanions measured in the leachates

The concentration of Cr measured in the leachates is lower than the US EPA maximum contaminant level(MCL) for drinking water. In the case of Se, the concentration in the fly ash is above the MCL, but the measured concentration in the geopolymer falls below the MCL. On the other hand, As concentration measured in all the leachates is much higher than the regulatory limits . The US EPA maximum contaminant level for As, Cr and Se are respectively 10 µg/l,100 µg/l and 50 µg/l²⁵.

For a better comparison of the leaching results, the concentration of the elements measured in the fly ash were compared with that measured in the geopolymer concrete samples, and the results are presented in Figures 4, Figure 5 and Figure 6.

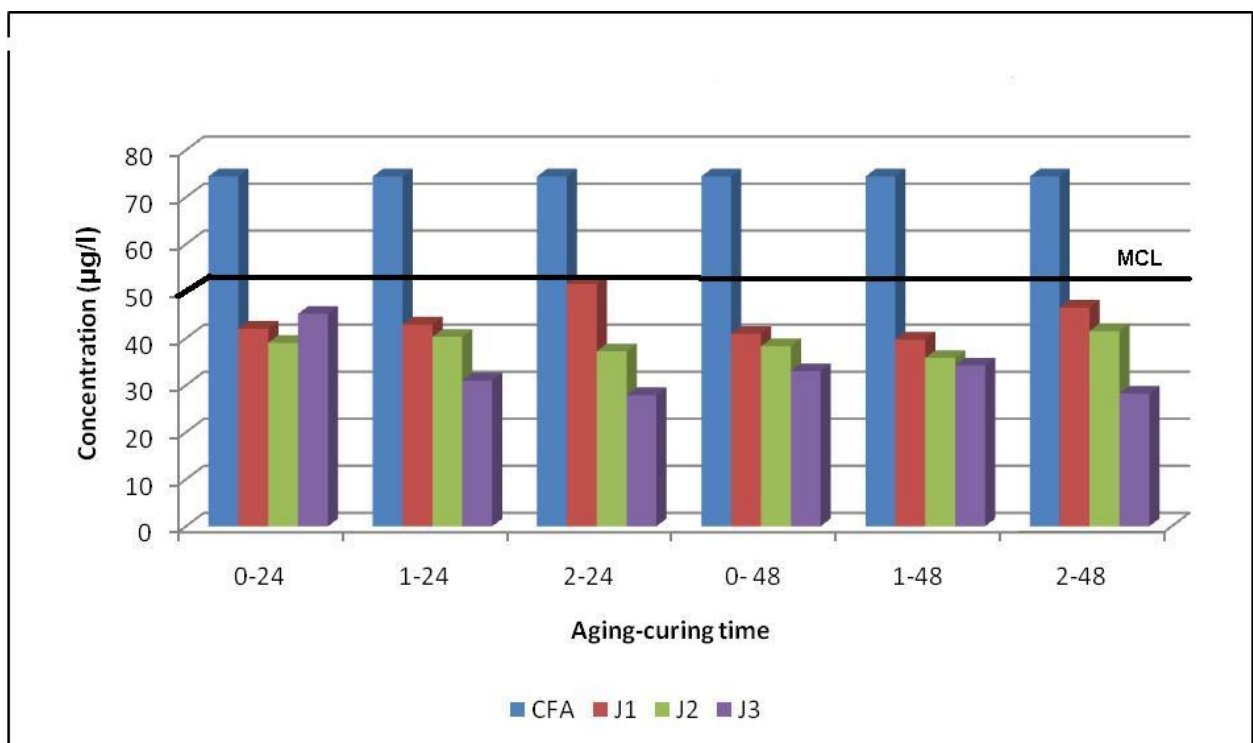


Figure 4: Concentration of Se measured in the leachates

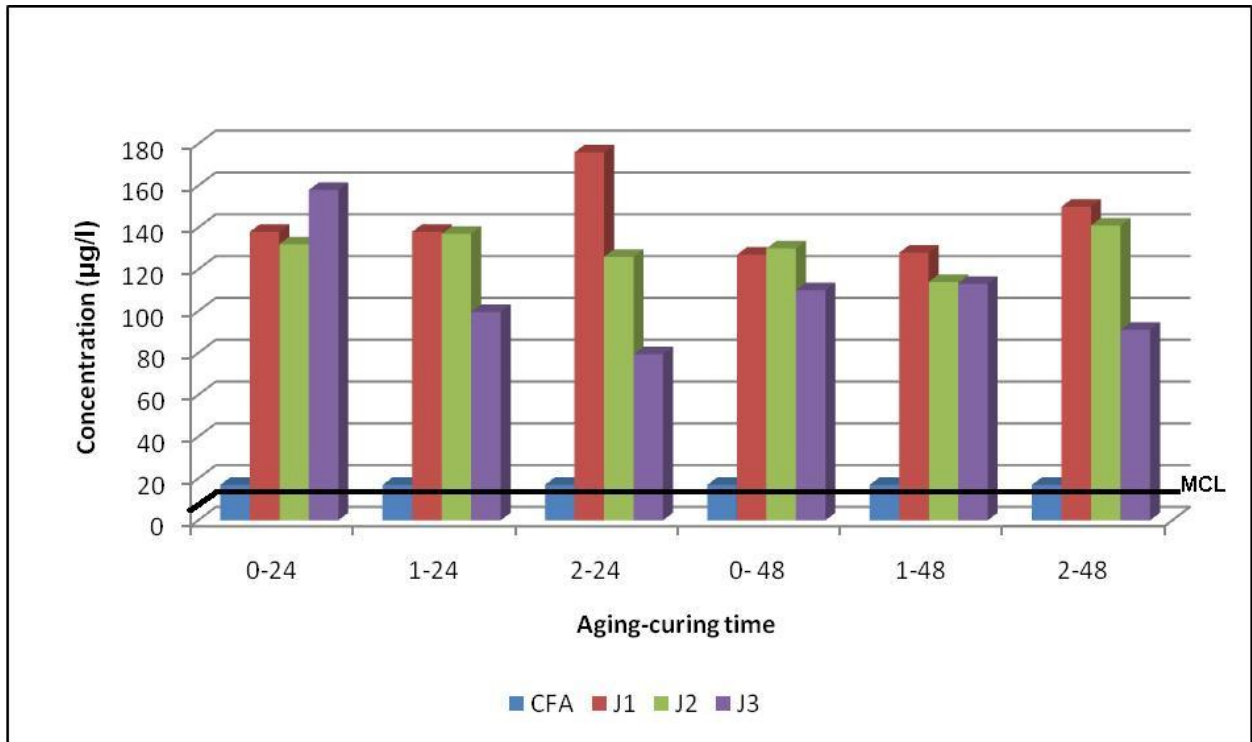


Figure 5: Concentration of As measured in the leachates

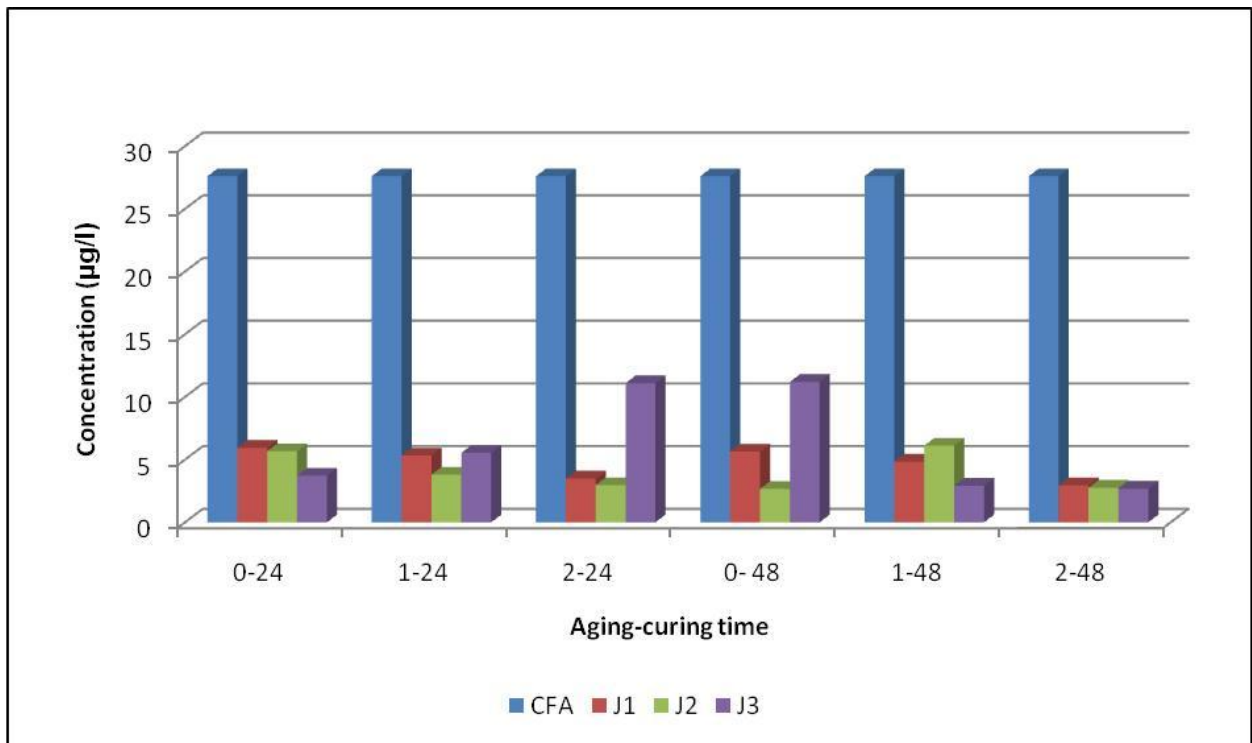


Figure 6: Concentration of Cr measured in the leachates

As shown in Figure 4, the geopolymer concrete was able to immobilize the release of Se since the concentration measured in the geopolymer leachate is lower than the fly ash concentration. It was observed that an increased amount of NaOH used during geopolymer synthesis does not result in increased leaching of Se from the geopolymer; the only exception is the sample cured for 24hrs without aging that showed an increase in Se concentration when the NaOH content was increased from 13% to 16%.

The As leached out of the geopolymer samples far exceed the concentration measured in the coal fly ash (Figure 5). Authors have reported in other study that oxyanions especially As show this type of behavior¹¹. This leaching pattern might be attributed to the high alkaline nature of the geopolymer (pH 11) compared to the acidic fly ash (pH 5) used in their synthesis, which might have caused the higher release since oxyanions tend to be released more at higher pH. Bankowski et al.²⁶ reported a reduction in As leaching from geopolymer made from coal fly ash, therefore it is necessary to investigate why the concentration of As was higher in the geopolymer. The As leaching trend from the different geopolymer mixes shows a similar pattern to that observed for Se; increasing the NaOH amount does not increase the leaching of the element.

The Cr leaching results in Figure 6, clearly show that the element was effectively immobilized in the geopolymer. The response of Cr leaching to increased NaOH content is different from that observed for As and Se. For NaOH content above the 13% mix, there is increased leaching of Cr. This suggest that increasing the NaOH content above the optimal alkali concentration (13% for this investigation) would result in higher leaching for Cr.

Availability of the elements in the geopolymer concrete

The amount of each elements available for leaching in the geopolymer concrete was based on the amount available in the fly ash, and the result is expressed as the percentage of the total available in the fly ash as presented in Figure 7. The results shows that the availability of Cr is between 7% and 30% of the total available in the fly ash, while Se availability range from 26% to 50%. The observed As availability was between 363% and 740% of amount available in the fly ash. The results clearly indicate that Cr with minimum availability was effectively immobilized in the geopolymer while Se was also immobilized, but the result for As suggest that there maybe an introduction of the element through an external source or the availability in the fly ash was underestimated. Future investigation would focus on the silica fume used in the geopolymer synthesis, and also on the pH at which the fly ash and the geopolymer was leached since they both have different pH (fly ash has pH of 5.05 while the geopolymer has pH of 11.94), and should provide conclusive reasons why the leaching of As was more in the geopolymer concrete than in the fly ash. The leaching of oxyanions would definitely be underestimated at the pH of the fly ash.

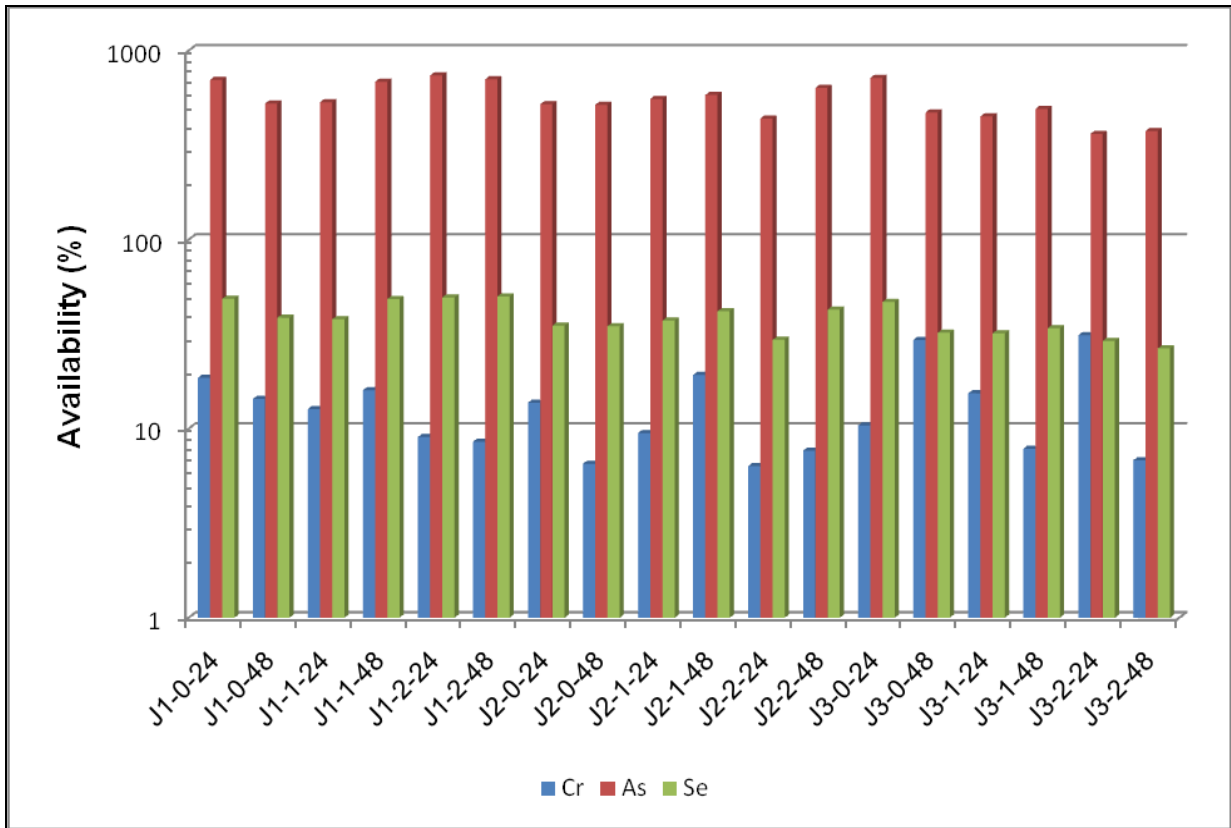


Figure 7: Availability of the elements in the geopolymer concrete samples

Hydroxyl ion concentration in the leachate

Figure 8 shows the concentration of hydroxyl ion measured in the geopolymer concrete leachates. The result shows that there is no relationship between the concentration of hydroxyl ion in the leachate and the amount of NaOH used in the geopolymer mix, this suggest that the hydroxyl ion does not leach out in the same amount added during geopolymer synthesis. On the other hand, the trend observed from the hydroxyl ion concentration result is similar to the compressive strength result. This might be an indication that there exist a relationship between the compressive strength and the amount of hydroxyl ion that leach out of the geopolymer. The J2 mix with 13% NaOH and the highest compressive strength has the highest hydroxyl ion concentration.

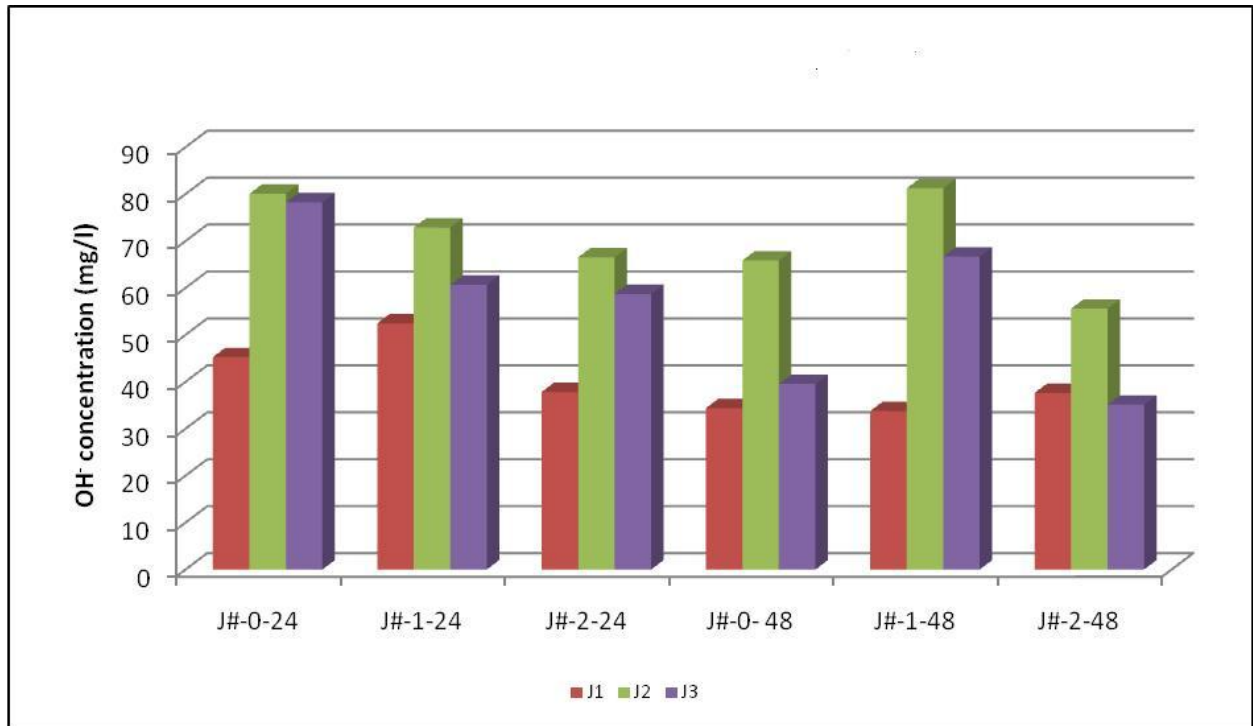


Figure 8: Hydroxyl ion concentration in the geopolymer leachates

CONCLUSIONS

In this study to investigate the effect of hydroxyl ion on immobilization of As, Cr and Se, fly ash-based geopolymer concrete was developed using an activating solution that contains NaOH and silica fume, the amount of NaOH added during the geopolymer synthesis was such that it contains three mixes with 10%, 13% and 16% NaOH per fly ash used.

The compressive strength result indicate that the 13% NaOH mix has the highest compressive strength, and that increasing the NaOH content above the 13% mix would lead to reduction in the concrete strength.

Results from the Dutch availability test (NEN 7341) shows that the measured concentration of Se and Cr in the geopolymer leachate tends to be lower than the USEPA maximum contaminant levels (MCL) for these elements in drinking water, but that of As far exceed the regulatory limit.

The availability of Cr and Se based on the result of the availability test indicate that the geopolymer was able to immobilize these two elements. The observed availability of As suggest that effective immobilization of As was not achieved in the geopolymer concrete which might be a result of additional As introduction during the geopolymer synthesis or an underestimation of the total available in the fly ash.

The results also showed that increased amount of NaOH used in the geopolymer mix during geopolymerization does not lead to increase in concentration of the elements in the geopolymer leachates, this suggest that as the percentage of NaOH increase in the different mix, the concentration of the elements in the geopolymer generally reduces. The water extraction test result shows that the concentration of hydroxyl ion measured in the geopolymer leachates does not have a relationship with the amount added in the different geopolymer mix, but on the other hand, the hydroxyl ion concentration trend looks similar to the result for the compressive strength of the geopolymer concrete which might be an indication that there is a relationship between the compressive strength and the amount of hydroxyl ion that is available for leaching from the geopolymer.

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