Assessment of hexavalent chromium release in Malaysian electric arc furnace steel slag for fertilizer usage

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Abstract. This study investigates the leaching of hexavalent chromium (Cr (VI)) from electric arc furnace steel slag as Cr (VI) is classified as human carcinogen. Batch leaching tests were performed for 16 days. The lixiviants used were alkaline, de-ionized and rain water. After 16 days, Cr (VI) was found to be highest in alkaline water (0.03 mg/L) and lowest in de-ionized water (0.01 mg/L). Besides the lixiviants used, slag stirring speed and liquid to solid ratio also affect Cr (VI) released. The experimental work was complimented with slag characterization using XRF, XRD and SEM/EDX analysis. The leaching process was also simulated via FactSage software to calculate isothermal pourbaix diagrams. The Cr (VI) released was low and below the threshold of 0.1 mg/L set for public water systems. Recycle the slag as fertilizer should be considered safe as it does not exceed the safety limit set for Cr (VI) dissolution.

1. Introduction

Steelmaking in Malaysia is mostly produce using electric arc furnace (EAF) and about 8 million tons of steel is being consumed per year [1]. As a result of steel production, 10-15% of EAF steel slag is being generated as by-product [2]. This by-product contains valuable metals which have facilitated its utilization as aggregate in road and water-way construction, cement production, metallurgical fluxes and as soil amendment [3]. Currently in Malaysia, there is no utilization of EAF steel slag except being disposed in landfill [4]. The main concern is that slag recycling as soil amendment and fertilizer will pose a serious environmental problem due to the leachable heavy metals and contamination of the soil environs, surface and ground water.

Cr is one of the heavy metal contained in EAF steel slag and its presence may be due to the use of scrap metal with high Cr content in the EAF during steelmaking. Cr exists in the most stable form as Cr (III) and (VI) in the environment. Cr (III) is an essential element in human metabolism at low dose, relatively immobile and low in reactivity [5]. However, Cr (VI) is more toxic at moderate doses, highly mobile, soluble in water and classified as human carcinogen with negative health effects ranging from skin irritation to lung cancer [6-8]. The toxic effects of Cr (VI) are consequence of its readily penetrating into cell membrane and its strong oxidizing power. It forms a number of anions which are soluble and mobile in the environment [9]. They are weakly sorbed to soil under alkaline to slightly acidic condition leading to high mobility in the subsurface [10]. Thus, the maximum concentration of Cr (VI) allowed in drinking water is 0.1 mg/L due to Cr (VI) toxic nature and the potential oxidation of Cr (III) to (VI) [11].

Cr leaching have been studied extensively [3, 12-15], however, steel slag originating from various localities may differ in terms of leaching behaviour, mineralogy, extraction process and scraps
charging process. In this study, modified European batch leaching test was employed to determine the release of Cr (VI) in Malaysian EAF steel slag. The leaching experiment was complemented with slag characterization and the leaching process also simulated via Factsage software using the EpH module. The results of this study will provide further understanding of Cr (VI) leaching from EAF steel slag and assist in further predicting the risk toxicity effect to the soil, surface and ground water.

2. Experimental

2.1. Slag sample characterization
EAF steel slag samples were ground in an agate mortar to avoid contamination and sieved to gain powder of less than 75μm. The -75μm powder were then sent for characterization. The chemical composition was determined by Rigaku XRF spectrometer, model RIX 3000. The mineralogical phases were identified using Bruker AXS diffractometer D8 Advance machine. The diffractometer were conducted at 40 mA and 40 kV using diffracted beam graphite-monochromatic with Cu radiation at a step size of 0.0340. The XRD patterns were measured in a 20 range of 0–80° intervals and the analysis performed at room temperature. Qualitative analysis of XRD patterns were conducted using the Eva software and its database reference patterns. The morphology of the EAF slag was studied on polished sample using SEM coupled with EDX microprobe for in-situ chemical analysis. The SEM was a Zeiss Gemini Supra 35VP coupled with EDAX equipment.

2.2. Leaching test
Modified European batch leaching test EN 12457-2 [16] were performed for a period of 16 days. The lixiviant used were de-ionized (DI), alkaline and rain water. Particle sizes of the EAF slag was set at 1-4 mm. Each batch leaching experiment contained 50 g of EAF steel slag in bottles filled with the lixiviant solution corresponding to liquid solid (L/S) ratio of 20 at varying speed. Another set of leaching experiment were conducted at zero (0) rpm for 8 days at varying L/S ratio. Small samples of the leachate were taken every 24 hours and filtered through Whatman 42 filter paper. The filtered leachates were analyzed for Cr (VI) using UV-Vis spectrophotometer and the pH values measured using digital pH meter. XRD analysis were also performed on the residue slag samples after leaching for 30 days at 0 rpm with L/S ratio of 10 in DI water, to identify any new phases formed.

2.3. Simulation of leaching process
The EpH module was used to simulating the leaching process and plots isothermal pourbaix diagrams [17]. The leaching simulation parameters depend on the Cr (VI) ions concentration from the leaching experiment and slag chemical composition from the XRF analysis. The EpH module carries out calculations using pure stoichiometric substances and the simulation was performed at room temperature based on the FactSage database.

3. Results and Discussion

3.1. Slag sample characterization
The chemical composition of the EAF steel slag sample was shown in table 1. The slag mainly composed of Fe₂O₃, CaO, SiO₂, Al₂O₃, MgO, MnO, Cr₂O₃ and some minor metal oxide constituents. The basicity index of the slag calculated based on \( \frac{(CaO+MgO)}{(SiO₂+Al₂O₃)} \) works out to be 1.065. This basicity index has effect on the leaching of EAF steel slag due to dissolution and hydrolysis of basic oxides compare to the soluble acidic oxide. Besides, the chemical composition plays an
important role in the leaching mechanism of Cr and the pH of the leachate [18]. The higher amounts of basic oxide in the slag samples, contributed to the slight increase in the pH values observed in solution. This gives high alkalinity and favourable to Cr (VI) leaching.

Table 1. Chemical composition of EAF steel slag by weight (%).

| Slag  | Fe₂O₃ | CaO  | SiO₂ | Al₂O₃ | MgO  | MnO  | Cr₂O₃ | ZnO  | TiO₂ | P₂O₅ | SO₃ |
|-------|-------|------|------|-------|------|------|-------|------|------|------|------|
| EAF   | 33.3  | 27.5 | 19.3 | 9.40  | 3.07 | 3.55 | 1.54  | 0.80 | 0.57 | 0.49 | 0.42 |

The XRD analysis of the raw EAF steel slag and the leached samples were shown in Figure 1. The diffraction patterns were heterogeneous consisting of a mixture of crystalline phases. The analysis shows the presence of Calcium silicate oxide, Magnesium iron oxide, Wustite and Magnetite. Cr was not detected from the XRD as it was observed in the XRF and SEM/EDX analysis. This may be due to low intensity of their diffraction lines and the complexity of the diffractograms. Any other minor constituent phases were very difficult to assign as well. The XRD analyses after the leaching experiment indicate that the calcium silicate oxide phase was not dissolved in solution after the leaching for 30 days. This shows that this mineral phase was more tightly bonded together.

The SEM micrograph show distinct mineral phases as shown in figure 2. The presences of light and dark areas in this figure are explained by variable Fe, Ca, Si, Mg, Mn, Al and Cr contents as revealed by the EDX analysis. The EDX analyses revealed that light areas contained higher proportion of Fe, Mg, Mn, Cr and Al, while the dark area contained higher proportion of Ca and Si. Cr was associated within the light area as revealed by the EDX. The dissolution of this moderately-to-sparingly soluble phase (spinel phase) [19] will have effect on the leaching of the Cr from the EAF steel slag.

The EDX results also confirm the presence of minor constituent phases such as titanium already observed by XRF spectrometer. With the coupled EDX, the EAF steel slag shows predominant presence of Fe, Ca, Si, Mg, Mn, Al and Cr. The EDX points 1, 2 and 3 are shown in table 2.
Table 2. EDX point 1, 2 and 3 of EAF slag sample by weight [%].

| EDX point | O   | Mg | Al | Si  | Ca  | Ti  | Cr  | Mn | Fe |
|-----------|-----|----|----|-----|-----|-----|-----|----|----|
| Point 1   | 27.04 | -  | -  | 18.68 | 50.36 | -  | -  | -  | -  |
| Point 2   | 16.64 | 4.13 | 0.51 | 0.22 | 2.33 | 0.50 | 1.64 | 9.17 | 61.93 |
| Point 3   | 24.85 | 5.15 | 5.33 | -   | -   | -   | 42.61 | -  | 18.53 |

3.2. Leaching test

3.2.1. Effect of different lixiviant. Figure 3 shows the effect of different lixiviant on Cr (VI) leaching at 0 rpm. After 16 days, Cr (VI) was found to be highest in alkaline water (0.03 mg/L) and lowest in DI water (0.01 mg/L). In alkaline water, the pH was high, thus Cr (VI) was steadily leached. After 13 days, the leaching chemical reaction still continues with the alkaline water due to slow rate of initial reaction. Besides, Cr (VI) was favourable to form at high pH as shown in the pourbaix diagram (Figures 9 and 10), which also corroborate the leaching result. The pH reading in the different lixiviant shows similar trend but the DI water has the lowest pH value as shown in Figure 4. The leachates pH was alkaline and these were generated within the first 24 hours of contact with the lixiviant.

![Figure 3](image1.png)  ![Figure 4](image2.png)

Figure 3. Effect of lixiviant on Cr (VI) leaching.  Figure 4. Effect of lixiviant on leachate pH.

The increases in the amount of Cr (VI) leached and later decreased, could be interpreted as the reduction of Cr (VI) by precipitation of reductant mineral. Fe (II) could act as a reductant to Cr (VI) and more soluble acidic oxide will also oxidize Fe (II) to Fe (III), leading to a lower potential for Cr (VI) reduction, thus more Cr (VI) will remains in solution [6, 20, 21]. Cr (VI) leaching is thereby related to redox reactions taken place in the leaching process.

3.2.2. Effect of stirring speed. Figure 5 shows the effect of stirring speed on Cr (VI) leaching using DI water. Cr (VI) was found to be highest at 50 rpm within the first seven days. Increase in stirring speed leads to an increase in the concentration of Cr (VI) leached from 0.006 mg/L at 0 rpm to 0.032 mg/L at 50 rpm within the first 24 hours. The pH at 30 and 50 rpm shows similar trend and both falls within the same values as shown in Figure 6. As the speed was increasing, there was more contact between the slag samples and the lixiviant. It was found that the highest concentration of Cr (VI) was leached within the first 24 hours at 30 and 50 rpm. Thus, increase in stirring speed indicates that the release of Cr (VI) may be controlled by diffusion.

![Figure 5](image3.png)  ![Figure 6](image4.png)

Figure 5. Effect of stirring speed on Cr (VI) leaching.  Figure 6. Effect of stirring speed on pH of the leachate.
3.2.3. Effect of liquid to solid ratio. Figure 7 shows the effect of L/S ratio on Cr (VI) leaching at 0 rpm using DI water. Cr (VI) was found to be highest at L/S ratio of 5. The concentration of Cr (VI) leached increases as the L/S ratio decrease. At L/S ratio 20, 10 and 5, the concentration of Cr (VI) leached increases from 0 to 0.017, 0.023 and 0.032 mg/L respectively at the end of the leaching experiments. The highest pH was also recorded when the L/S ratio was 5 within the first 48 hours of the leaching experiment as shown in Figure 8. The volume of the lixiviant could affect the concentration of leached slag into the solution due to the dilution factor.

![Figure 7. Effect of liquid to solid ratio on Cr (VI) leaching.](image1)

![Figure 8. Effect of liquid to solid ratio on pH of the leachate.](image2)

3.3. Simulation of leaching process

The simulated leaching process for slag system predicted was shown in Figures 9 and 10. From the SEM/EDX analysis, substantial fraction of the Cr content was contained in the phase detected by XRD as magnesium iron oxide. This phase was regarded as a possible source of the Cr leaching. Pourbaix diagram for the Fe-Mg-Cr-H2O and Ca-Si-Cr-H2O system containing 2 wt % Cr at 25°C was analyzed to verify the most suitable leaching condition for the Cr to dissolves into solution. The concentration of Cr (VI) ions in the leachate reaches 0.03 mg/L (0.6e-6 mol/Kg) from the leaching experiment. This value was used in the simulation and weight percent ratio of the elements contained in the EAF slag.

The simulation shows that Cr (VI) species (HCrO$_4^-$) is thermodynamically favourable when the redox potential (Eh) is within 0.7 to 1.4 at acidic pH range. In the neutral and caustic solutions, Cr$_2$O$_3$ is stable near zero potential. It dissolves as chromate (CrO$_4^{2-}$) in anode conditions and as the solution becomes more caustic in the cathode conditions. Under oxidizing conditions, Cr (III) will be converted into Cr (VI), resulting in the toxic and more mobile form of Cr. Thus stabilization of aqueous Cr (III) requires strong reductant concentration. From the pourbaix diagram, Cr (VI) is favourable to form at any environmental condition at higher redox potential and when the solution is more caustic. At high potential (Eh > 0), the system tends to remove electrons from the species (oxidizing condition), and at low potential (Eh < 0), the system is able to supply electrons to the species (reducing conditions). Thus, redox potential is a measure of the tendency of a chemical species to gain or loss electrons.

![Figure 9. Pourbaix diagram of Fe-Mg-Cr-H$_2$O system containing 2 wt % Cr.](image3)

![Figure 10. Pourbaix diagram of Ca-Si-Cr-H$_2$O system containing 2 wt % Cr.](image4)
4. Conclusion

Cr (VI) leaching was found to be highest in alkaline water and lowest in de-ionized water. Besides the different lixiviant used, increase in stirring speed leads to an increase in the concentration of Cr (VI) leached from 0.006 mg/L at 0 rpm to 0.032 mg/L at 50 rpm within the first 24 hours. Also, the concentration of Cr (VI) leached increases as the L/S ratio decrease. At L/S ratio 20, 10 and 5, the concentration of Cr (VI) leached increases from 0 to 0.017, 0.023 and 0.032 mg/L respectively at the end of the leaching experiments. The slag characterization shows that Cr (VI) leaching was related to the mineral components bounded within stable mineral phases detected by XRD as magnesium iron oxide, where Cr was situated as observed in the EDX analysis, and also the relative amounts of the soluble basic and acidic oxides in the EAF slag. From the pourbaix diagrams, Cr (VI) is favourable to formed when the solution is more caustic and at higher redox potential. Slag recycling as fertilizer usage in the environment does not have any negative effect and is safe, as the maximum Cr (VI) concentration released from the leaching experiment was low and does not exceed the safety limit set for Cr (VI) dissolution in the soil environs, surface and ground water.

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