



LEACHABILITY OF CHROMIUM FROM COAL BOTTOM ASH USING CONTINUOUS COLUMN TEST

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Abstract: Bottom ash is one of the by-products of coal combustion from circulating fluidized bed boiler which contains 22 ppm of chromium that can be leached and recovered. The study aims to determine the effects of pH and type of leachant on the leaching of chromium using continuous leaching test. Results show that acetic acid at pH 2 has the highest cumulative amount of chromium leached with 3.224 ppm and reddish-orange leachant and followed by sulfuric acid at pH 6 with 0.170 ppm and translucent color leachant. Moreover, the amount of chromium mobilized was 27.11% and 1.43% for acetic acid pH 2 and sulfuric acid pH 6 respectively.

Key words: leaching; bottom ash; chromium; column test

1. INTRODUCTION

Coal is the cheapest raw material for the production of energy. In the Philippines, 80% of coal utilization is being used by the power generating industry. Upon the combustion of coal, approximately 80% of the coal solid residue leaves the boiler as fly ash and 20% as bottom ash in the flue gas (Asilo et al., 2004).

Based on the study of Gallardo et al. (2012), the Semirara bottom ash contains trace metals such as arsenic and chromium. However, using the Serial Batch Leaching Procedure (SBLP) it was found out that only chromium can be readily leached as compared with arsenic. This is due to the attachment of arsenic to hematite which is also present in the bottom ash (Ronquillo and Salido, 2012).

Chromium compounds are widely distributed in nature and are commonly used in industry. The main application of chromium is in metallurgy, dyes and pigments, wood preservative, tanning, catalyst and other chemical industry. Due to its wide industrial application, possible leaching and recovery of chromium from secondary waste material is necessary.

The main focus of this research was the leachability of chromium using Semirara bottom ash. Moreover, the leachant that were used was sulfuric acid and acetic acid which are produced by bacteria and fungi in the process of bioleaching. Future researches may be done using bioleaching in the recovery of valuable metals as a sustainable solution for coal ash utilization.

2. METHODOLOGY

The Semirara bottom ash came from the industry partner coal-fired power plant that uses circulating fluidized bed (CFB) boiler in the production of electricity. For the experiment a fabricated acrylic column was used (Figure 1). It has a dimension of 55 cm height with 5.08 cm inside diameter. Semirara bottom ash was sieved using particle size passing #20 sieve or 850 microns (0.0331 in). The particle size used was fixed throughout the experiment.

For the purpose of this study, 16 cm height of the ash was used approximately 390 grams and an outlet port of 20 cm. The selection of the height of the sample was based on the Standard Dutch Colum Test NEN 7343 wherein the height should be 4 times greater than the inner diameter of the column.

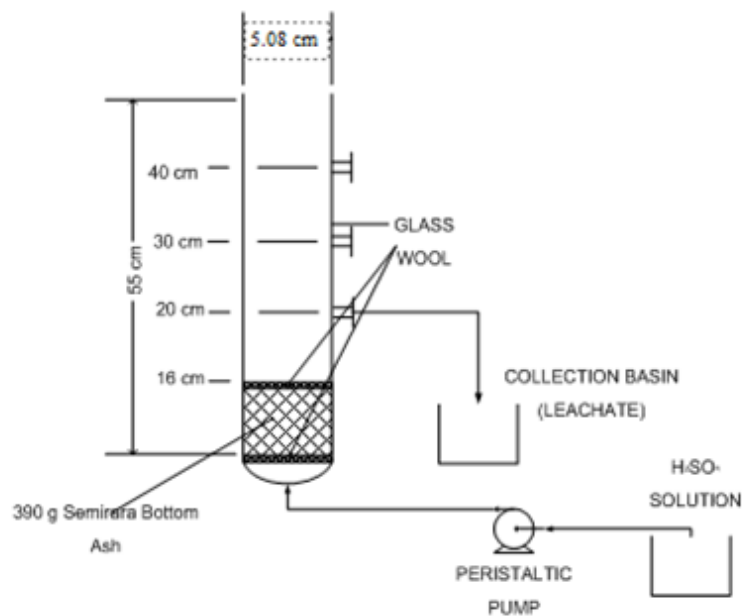


Figure 1. Schematic Diagram of the Column Test

The leaching solution was prepared using concentrated sulfuric acid and glacial acetic acid in de-ionized water using sequential dilution process to achieve the desired pH which is 2



and 6. For pH 10, 0.1 M sodium hydroxide was used to adjust the pH of the solution to achieve the desired value.

The bottom ash was manually packed. The leaching solution was passed through a peristaltic pump in an upflow motion with a constant flowrate of 2 mL/min. The sampling was done for 6 hours taking one fraction, 10 mL of the sample per hour and filtered using Whatman filter. The procedure was carried out using sulfuric acid, acetic acid and sodium hydroxide at the initial pH of 2, 6 and 10. The experiment was done in duplicate runs.

X-Ray Diffraction Analyzer and X-Ray Fluorescence Analyzer were used to determine the mineralogical and elemental composition of the ash respectively; Atomic Absorption Spectrometer was used to determine the concentration of chromium from the leached solution.

To calculate for the maximum chromium that can be leached and percent chromium leached using the formula:

$$\text{max. Cr leached} = \text{max. Cr conc (ppm)} \times \frac{\text{amount of ash (g)}}{\text{amount of leachate (ml)}}$$

The maximum chromium that can be leached is 11.92 ppm (Salido and Ronquillo, 2012).

$$\% \text{ Cr leached} = \frac{\text{max conc} - \text{cumulative conc}}{\text{max conc}} \times 100\%$$

3. RESULTS AND DISCUSSION

Based on the XRD results, Semirara bottom ash has a mineral content of Stratlingite, α Quartz – SiO₂, Melilite, Belite, Lime-CaO, Mullite, Hematite, Magnetite, Tricalcium aluminate, Thenardite and Periclase. The XRF results show that the highest elemental contents are calcium (52.5%), silicon (20.2%), iron (18.9%) and sulfur (3.3%), thus, the Semirara bottom ash is basic in nature. Table 1 shows the final pH value versus the cumulative chromium concentration leached from the Semirara bottom ash.

Table 1. Summary of final pH, Cumulative Cr concentration and % leached Cr

Type of Leachant and initial pH Value	Final pH Value	Cumulative Cr Conc. (ppm)	% Leached Cr
Sulfuric Acid pH = 2	12.13	0.144	1.21
Sulfuric Acid pH = 6	12.16	0.170	1.43
Sulfuric Acid pH = 10	12.15	0.168	1.41
Acetic Acid pH = 2	3.65	3.244	27.11
Acetic Acid pH = 6	12.07	0.158	1.33
Acetic Acid pH = 10	12.13	0.135	1.14
De-ionized Water pH = 5.6	12.03	0.150	1.26

The acetic acid (leachant) with an initial pH of 2 has the highest cumulative chromium concentration of 3.224 ppm and the final pH value of 3.65 (leachate) after 6 hours. As pH decreases, metal desorption increases therefore the solubility of the metal is higher under these conditions. With this, metal may have the possibility to form soluble metal oxides in acidic environment. The leachability of trace elements is indeed strongly influenced by pH (Van Hullebusch, 2011; Izquierdo and Querol, 2012).

Figure 2 and 3 show the pH measurements for 6 hours at one hour interval for sulfuric acid, acetic acid and de-ionized water. It shows that there is an increase in pH value every hour. This may be accounted for the inert basic pH of the Semirara bottom ash that was used.

Figures 4 and 5 show the cumulative chromium concentration leached from the bottom ash using sulfuric acid, acetic acid and de-ionized water with initial pH of 2, 6, 10 and 5.6 for de-ionized water.

Based on Figure 2, the leached solution is alkaline in nature. In sulfuric acid with an initial pH of 6 the range of the pH over time varies from 12.11 to 12.16 and the alkaline

solution with an initial pH of 10 are almost similar with varying pH from 12.14 to 12.16. On the other hand, sulfuric acid with an initial pH of 2 has lower pH values over time varying from 12.11 to 12.13. Comparing it with de-ionized water with an initial pH of 5.6, the pH value increases over time from 11.84 to 12.03.

Based on the study of Izquierdo and Querol (2012), the alkalinity of the ash is due to the high calcium oxide (CaO) content of the ash which conforms with the XRD and XRF analysis that was conducted. Moreover, the use of limestone (CaCO₃) from the combustion process of the power plant can be accounted for the high alkalinity of the ash.

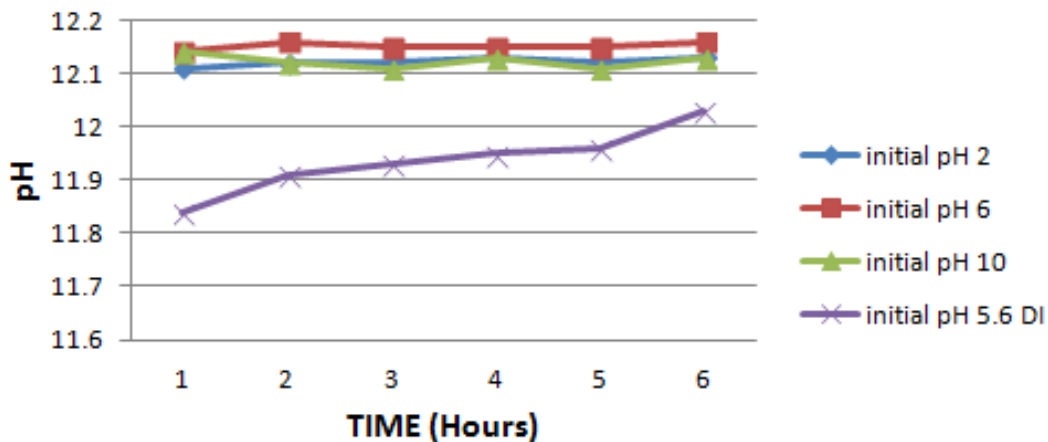


Figure 2. pH values versus Time for Sulfuric acid and De-Ionized Water

Based on Figure 3, the initial pH values of 6 in acetic acid and alkaline solution with an initial pH of 10 are relatively the same pH values over time ranging from 12.03 to 12.14. However for acetic acid with the initial pH of 2 the leaching solution was acidic and the color is reddish-orange as compared with other solution which has a clear solution after filtration. The pH values decreases over time varying from 4.03 to 3.86.

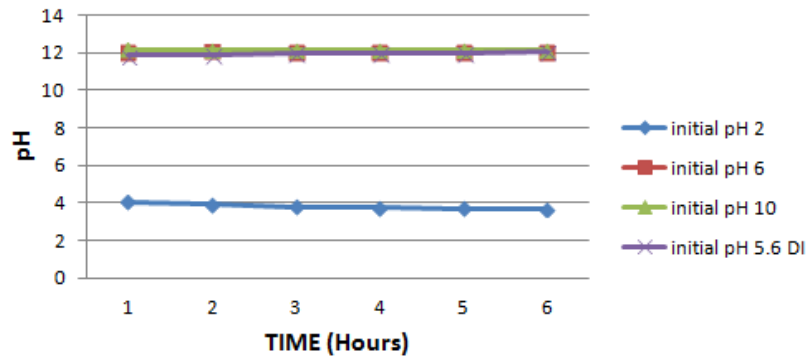


Figure 3. pH values versus Time for Acetic acid and De-Ionized Water

Based on the Figure 4, sulfuric acid at pH 6 has the highest cumulative chromium concentration of 0.170 ppm followed by pH 10 with 0.168 ppm and lastly is pH 2 with a cumulative chromium concentration of 0.144 ppm.

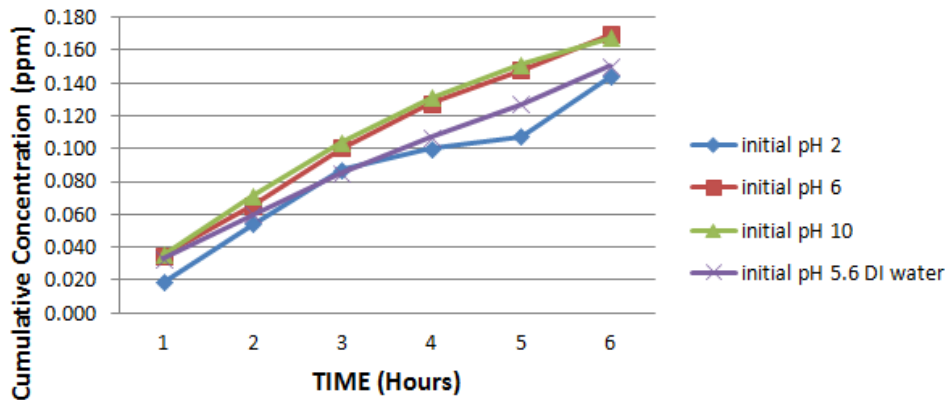


Figure 4. Cumulative Leaching Concentration of Chromium using Sulfuric Acid and DI Water

Since acetic acid can form complexes with chromium (III), the latter can polymerize into higher order polyacids. The reaction involves proton consumptions (or hydroxyl release). The complexation process is enhanced by the acidic condition leading to the formation of complexes (Mandich, 1995). Also at low pH, the solubility of chromium (III) is enhanced by these conditions.

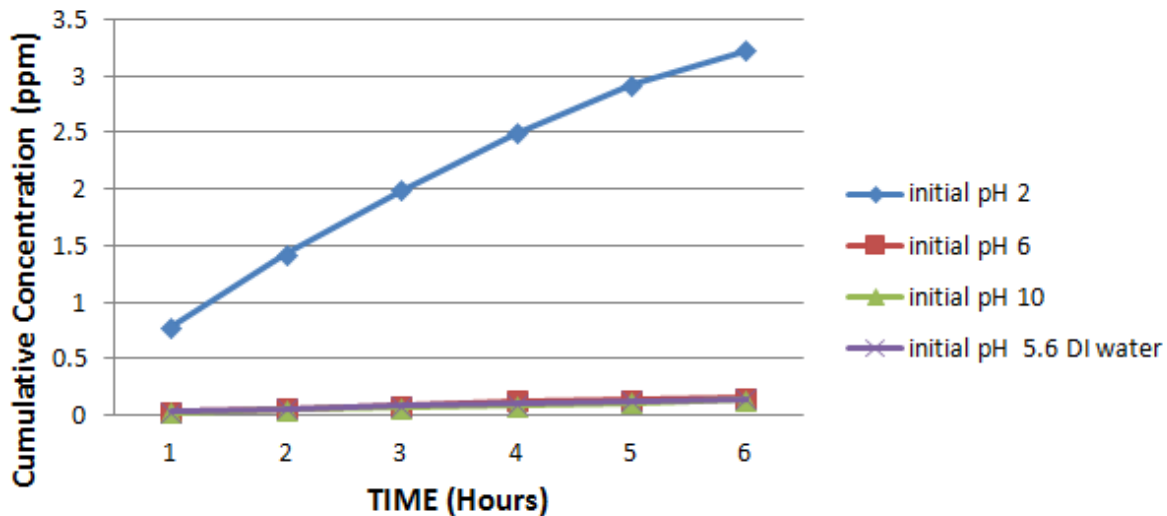


Figure 5. Cumulative Leaching Concentration of Chromium using Acetic Acid and DI water

Furthermore, the conversion of chromium (III) via anion penetration for the production of oxyanion chromium favors the acetate ions compared to sulfate ions (Mandich, 1995). Moreover, the reddish orange leached solution may be explained by the presence of polyacid of chromium (Shupak, 1991). It was recently showed that both chromium oxidation could co-exists in coal bottom ashes (Huggins et al., 1991; Shah et al., 2012), however, chromium (IV) only contribute 1.5% of the total chromium present.



4. CONCLUSIONS

Based on the results of the experiment, that acetic acid at pH 2 has the highest cumulative chromium concentration leached with 3.224 ppm and was evident in the reddish orange solution of the leached solution and followed by sulfuric acid at pH 6 with 0.170 ppm with a translucent color leachant. Moreover, the amount of chromium mobilized was 27.1% and 1.4% for acetic acid pH 2 and sulfuric acid pH 6, respectively.

5. ACKNOWLEDGEMENT

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