TOXICOLOGY TEST ON COAL ASH FROM ASAM-ASAM COAL FIRED POWER PLANT, TANAH LAUT - SOUTH KALIMANTAN

SITI R. UNTUNG
R & D Centre for Mineral and Coal Technology
Jalan Jenderal Sudirman 623 Bandung 40211,
Ph. 022 6030483, fax. 022 6003373
e-mail: sruntung@tekmira.esdm.go.id

ABSTRACT

The utilization of coal at Asam-asam Coal Fired Power Plant produces a by-product of ash waste that consists of either coal ash or bottom ash. The power plant produces 720 tons of coal ash each year that threatens the environment due to pollution to surrounding waters. Based on the Government Regulation No. 85/1999, coal produces hazardous and toxic wastes. Due to that situation, toxicology test has been conducted on coal ash using Cyprinus carpio L. The research also analyzed chemical composition of the ash, Toxicity Characteristic Leaching Procedure (TCLP) test as well as determined the acute characteristic by setting Lethal Concentration 50 (LC50).

Chemical analysis shows that the almost 90% of coal ash and bottom ash are comprise SiO₂, Al₂O₃, and Fe₂O₃. The TCLP test using atomic absorption spectrophotometer shows that heavy metals with in the coal ash filtrate were Pb (3.1 ppm), Zn (4.3 ppm), Cd (0.2 ppm), Cu (2.2 ppm), but As and Cr were not detected; in the bottom ash. there were Zn (3.1 ppm), Cu (0.2 ppm), while Pb, Cd, As and Cr were not detected. It suggests that the power plant heavy metals with in the coal ash was still the quality standard as regulated by the Government Decree No. 85/1999 and US EPA. Therefore the coal ash is not categorized as hazardous and poisonous waste. Moreover, the result of acute toxicity test conducted by examining the number of dead fish, shows that the LC concentration values of fly ash and bottom ash are 20.564% (205,640 ppm) and 11.637% (116,370 ppm). Referring to the Association of Australian Petroleum Energy criteria of LC50 toxicity, the coal ash from Asam-asam is a non toxic waste.

Keywords : coal ash, toxicology test, TCLP test, coal fired plant

INTRODUCTION

Coal Fired Power Plant Asam-asam or known as PLTU Asam-asam utilizes coal as its energy source. The capacity of the PLTU is 2 x 65 megawatt and requires 2,000 tons coal per day. The coal is supplied by, among others, PT. Arutmin and PT. Jorong Barutama Greston. Besides produces electricity, PLTU Asam-asam also produces wastes that consists of fly and bottom ashes. In one day, coal ash waste produced by coal combustion reaches 8 - 10% or 160-200 tons of coal ash. To solve the problem, there are some alternatives to utilization the ashes namely using them as mixing material in cement and brick makings. However, those two alternatives have not been obtaining interests from community and entrepre-

neurs due to some reasons like high transportation and production costs. Consequently, there is an excessive piling of coal ash at the storing area that will threaten the environment as the rain water can leach the material and flow it to the. Water pollution result from coal ash due to the heavy metals such as Cu, Pb, Cd, As and Hg enter the river. During dry season, the ash can also cause air pollution as it is blown by the wind and spreads to the nearest housing, creating infection to precipitation system.

Referring to the Government Decree No. 85/1999 pertaining to Hazardous and Toxic Waste Management with the waste code of 223 and activity code of 4010, coal ash is categorized as hazardous and toxic waste, so its utilization has to go
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through TCLP (Toxicity Characteristic Leaching Procedure) and acute toxicity bio-test LD50 (Lethal Dose) or LC50 (Lethal Concentration). The LD50 is provision of single dose of substance that can cause death to 50% experimental animals within 24-96 hours time while the LC50 is concentration of substance in the air/water that can cause death to 50% of experimental animals within certain period of time (CCOHS, 2008). From various experiments, the safety level of coal ash towards the environment and living creature can be identified in a short time.

This paper presents the research on the impact of coal ash towards surrounding environment. The LC50 bioassay has been conducted using *Cyprinus carpio L.* By identifying the toxicity value, it can be identified the impact of PLTU Asam-asam coal ash to the environment and the possible utilization to eliminate the impacts.

**MATERIAL AND TEST PROCEDURE**

**Material**

Materials used in this research were coal ash (fly ash and bottom ashes) from PLTU Asam-asam, glacial acetate acid, HCl 1 N solution, HNO₃ 1 N solution, NaOH 1 N solution, malachite green oxalate 0.1 ppm, formalin 25 ppm, aquades and fish feed. The *Cyprinus carpio L.* was obtained from a spawning centre of Ciparay Seed Bureau of District Fishery Office with weight of 3 gram/unit and uniformed age.

**Method**

The test consisted of 3 phases, namely:

- chemical Analysis
  The test was conducted to identify the composition of chemical substance contained in the coal ash.

TCLP Test

TCLP test is a method to determine toxic character of waste by measuring the toxic rate of a substance, inorganic and organic polluting substances contained in solution, solid matter, or a mixture of waste. The test was conducted based on the EPA 1311 method using coal ash sample from PLTU Asam-asam. Then, the obtained filtrate was collected to be used as the basic material for bioassay;

- bioassay
  Bioassay consisted of 2 phases, namely object acclimatization and acute toxicity test;

- acclimatization
  Acclimatization is an object adaptation to a new environment. The used object was *Cyprinus carpio L.* as the fish has high economic value and is sensitive to pollution. The fish used had the same age, size, and shape. In the test, the fish was adapted to the new environment. Prior to acclimation, the fish was put into malachite green oxalate 0.1 ppm and formalin 25 ppm for ± 10 – 15 minutes to clean any fungi and flea available within fish. The acclimation is 8 days;

- acute toxicity test
  The acute toxicity test on the fish consisted of 2 phases, namely a preliminary test to determine the critical range concentration and a real test. The real test was conducted by storing 10 fishes into 4 liters of treatment media. As comparison, control containing dilution liquid or 0% treatment concentration was provided. The test was carried on for 96 hours by examining the total dead fishes every 24 hours. The total dead fishes were then calculated to determine LC50 value using probity analysis method. Examination on environmental condition was also conducted through physical parameter measurement and tested solution chemicals, i.e. pH degree, temperature (T), dissolved oxygen content (DO), electric conductivity (DHL), and turbidity. Measurement of environmental condition is conducted before and after the test.

**RESULT AND DISCUSSION**

**Coal Ash Composition**

PLTU Asam-asam adopts pulverized system which produces fly ash and bottom ash. The chemical composition of PLTU Asam-asam can be seen in Table 1. Based on the analysis result, the biggest component in fly ash and bottom ash was silica (SiO₂). Table 1 shows silica, iron (Fe₂O₃), K₂O, P₂O₅ and loss of ignition of bottom ash was higher than that of fly ash; while mineral content of Al₂O₃, TiO₂, CaO, MgO, Na₂O,
SO\textsubscript{3}, MnO was higher in the fly ash.

**Result of Trace Element Analysis and TCLP test**

Result of trace element analysis can be seen in Table 2. Trace element is inorganic element (metal) affluence of coal in very low concentration. Rollinson (1993) stated that the trace element is counted when the concentration is < 1000 ppm (0.1%). Table 2, it shows that both types of coal ashes did not contain Hg element. Metal content in bottom ash was less than that in coal ash. In the bottom ash there were only 3 types of metal that can be analyzed (Cu, Zn and Cr), while in the coal ash there were 6 types of metal (Cu, Pb, Zn, Cd, Cr and As). This was probably due to the combustion system. At combustion temperature around 1000-1600°C, metal oxides with melting point below those figures will evaporate and be accumulated in the coal ash.

Results of TCLP test can be seen in Table 3 which exhibits that the arsenic (As) and chromium (Cr) were undetected in both types of coal ash. Besides those two metals, in the bottom ash, lead (Pb) and cadmium (Cd) were not detected either. The undetected heavy metals are probably caused by the absence of bond between the metal ions and extractive solution or because both metals did not exist with in the ash. The measured metal concentration of lead, zinc, cadmium, and copper

<table>
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<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lead (Pb)</td>
<td>3.1</td>
<td>ud</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Zinc (Zn)</td>
<td>4.3</td>
<td>3.2</td>
<td>50</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Arsenic (As)</td>
<td>ud</td>
<td>ud</td>
<td>5</td>
<td>5</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Chromium (Cr)</td>
<td>ud</td>
<td>ud</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>Cadmium (Cd)</td>
<td>0.2</td>
<td>ud</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Copper (Cu)</td>
<td>2.2</td>
<td>0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Khaerunisa et.al (2006)
Note: ud = undetected
in coal ash were 3.1, 4.3, 0.2 and 2.2 ppm respectively, while in the bottom ash, measured zinc and copper concentration were 3.1 and 0.2 ppm. It proves that those measured metals were contained in both coal ashes and can be indicated by extractive solution. The metal concentrations were also still below the concentration standard regulated by the Government Decree No. 85/1999 and US-EPA.

**Acute Toxicity Bio Test on Cyprinus carpio L**

Result of acute toxicity bio test on PLTU coal ash is stated by LC50 for 96 hours on *Cyprinus carpio L*. Measured parameters were temperature, pH, DO, DHL, and turbidity. Normally, fish lives in temperature around 20 – 28 °C and see tolerated pH between 5.0 – 9.0 but ideally between 6.5 – 8.2. DO must be above 6 ppm. Therefore during the experiment aeration must always be took place using an aerator with oxygen supply to maintain the DO above 6 ppm. DHL is used to predict the total content of electrolyte substances that are ionized in water. The higher the concentration of testing solution, the higher the DHL will be. Turbidity is a parameter that states clarity of liquid through calculating the amount of sediment or suspended particles in water. Turbidity in fish water habitat creates damage to fish organs.

The result of acute toxicity test (LC50) on *Cyprinus carpio L* can be seen in Table 4 and compared to the Australian Petroleum Energy Association criteria (Swan et al, 1994, in Cobby and Craddock, 1999) of toxicity rate as stated in Table 5.

Table 4 shows that the LC50-96 hours of the tested coal ash sample give different values. Compared to the toxicity criteria standard (Table 5), it shows that the fly ash is categorized as almost non toxic (LC50=20,564 ppm) and bottom also as almost non toxic (LC50= 11,6370 ppm).

Referring to a research conducted by Khaerunisa et al (2006), LD50-96 hours test used *Mus musculus* as experimental animal towards fly ash was 62,025.7 mg/ bw and bottom ash was 29,855.6 mg/kg bw. From the result of LD50 test, coal ash of PLTU Asam-asam is claimed to be relatively harmless as its LD50 value is higher than 15,000 mg/kg bw. It is in line with waste characteristic criteria of the Government Decree No. 74/2001 pertaining to hazardous and toxic waste that categorizes a substance as toxic waste (Khaerunisa, et al, 2006). From the two results mentioned above, the coal ash of PLTU Asam-asam is relatively safe to be utilized for various needs.

<table>
<thead>
<tr>
<th>No</th>
<th>Test Solution</th>
<th>Value of LC50 (%)</th>
<th>Value of LC50 (ppm)</th>
<th>Toxicity Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fly ash</td>
<td>20.564</td>
<td>205,640</td>
<td>Almost Non Toxic</td>
</tr>
<tr>
<td>2</td>
<td>Bottom ash</td>
<td>11.652</td>
<td>116,370</td>
<td>Almost Non Toxic</td>
</tr>
</tbody>
</table>

**Table 4. Value of LC50-96 hours of PLTU Asam-asam coal ash on cyprinus carpio L**

**Table 5. Toxicity rate criteria of LC50**

<table>
<thead>
<tr>
<th>No</th>
<th>Toxicity Criteria</th>
<th>Value (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Very toxic</td>
<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>Toxic</td>
<td>1-100</td>
</tr>
<tr>
<td>3</td>
<td>Moderately toxic</td>
<td>100- 1,000</td>
</tr>
<tr>
<td>4</td>
<td>Slightly toxic</td>
<td>1,000-10,000</td>
</tr>
<tr>
<td>5</td>
<td>Almost Non-Toxic</td>
<td>10,000-100,000</td>
</tr>
<tr>
<td>6</td>
<td>Non Toxic</td>
<td>&gt; 100,000</td>
</tr>
</tbody>
</table>
CONCLUSION AND SUGGESTION

Conclusion

The result of this research shows the following: coal ash of PLTU Asam-asam contains several types of metal. However, the metal content of bottom ash is less than that of fly ash. The bottom ash contains 3 types of metal (Cu, Zn and Cr), while the fly ash contains 6 types of metal (Cu, Pb, Zn, Cd, Cr and As).

The TCLP test shows that the metals concentration in fly ash and bottom ash are also still below the concentration standard regulated by the Government Decree No. 85/1999 and US-EPA. Moreover, based on Association of Australian Petroleum Energy criteria of LC50 toxicity test using Cyprinus carpio L. shows that both ash types and bottom ash are categorized as almost non toxic materials. The LC50 of fly ash and bottom ash and LC50 is 20,5640 and 11,6370 ppm respectively. Refering to the Government Decree No. 85/1999 and Association of Australian Petroleum Energy, the Asam-asam coal ash can not be categorized as hazardous and poisonous waste.

Suggestion

Based on its characteristics and toxicity data, the coal ash of PLTU Asam-asam can be used to solve the environmental problems in mining industry, such as acid mining neutralization, soil amendments and building materials. However, to utilize the PLTU’s Asam-asam in commercial scale, TCLP test, LD 50 or LC 50 should be repeated in accordance with government regulations.

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