Study on the Potential Rare Earth Elements in Coal Combustion Product from Banjarsari Power Plant, South Sumatera

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Abstract. Coal combustion product (CCP) from Banjarsari power plant, both fly ash and bottom ash are numerous and have not been utilized optimally. CCP contains rare earth elements so that the potential needs to be assessed as a resource and reserve of rare earth elements (REE) in the future. The stages of this research were sample preparation and testing of grain size distribution using the wet and dry sieving method. Grain morphology was observed under a microscope and the determination of mineralogical content with XRD, oxide content with XRF and elemental content with ICP-MS. Fly ash grain size distribution of 76.15% passed 200 mesh sieve (0.074 mm) while the bottom ash was only 0.2%. Grain morphology is sub-rounded and there are still coal that has not been completely burned. The dominant mineral content is quartz, mica mineral (muscovite), clay mineral (kaolinite), lime, siderite, magnetite and hematite. The dominant oxides are SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\) and CaO. Based on ICP-MS test results, 16 elements of REE were detected. The total REE contents for each sample, FA and BA were 264.97 ppm and 49.22 ppm, respectively. REE of CCP from Banjarsari power plant which has the potential to be extracted is the content of cerium 80.5 ppm, neodymium 42.9 ppm, yttrium 41.8 ppm and lanthanum 31.4 ppm from fly ash while at the bottom ash there is no potential to be extracted.

Keywords: Banjarsari, bottom ash, CCP, fly ash and REE

1. Introduction

The rare earth elements (REEs) in nature consists of 17 elements [1]. REE is 15 elements from the lanthanide group (atomic number 57-71) and two transition metal elements, namely scandium and yttrium [2]. Lanthanide groups are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. REE is known as an important material source at this time, is a determining material for hybrid cars, health identification devices (MRI, X-Ray, scanners, contrast agents, etc.), LCD, computer hard drives, wind power generation facilities, green technology, magnets, battery alloys, ceramics, equipment with high accuracy, night vision devices, radar systems and military equipment [3][4][5]. Coal combustion product (CCP) in the form of fly ash can contain relatively high concentrations of REE. For example from one of the Steam Power Plants in Japan, containing 420 mg/kg which is equivalent to REE in monasites or basnasites (CeFCO\(_3\))[6]. Detailed analysis of REE in coal combustion product from the Kentucky power plant, the United States has contains of rare earth elements ranging from 1,213.6 to 1,667.6 mg/kg of total rare earth elements (TREE) contained in fly ash and 1,202.5 mg/kg of TREE contained in bottom ash. Coal combustion product in the form of...
bottom ash and fly ash can be seen as a source of strategic elements towards advanced technology. Thus, the potential for utilizing coal combustion products as a source for strategic elements becomes very clear [7].

In Indonesia, the use of coal as an energy source has increased in recent years. The biggest use of coal in the country is as fuel at the power plant. The increasing standard of living of the people, the need for electricity also continues to increase. This can be seen with the continued construction of new power plants that use coal, including the 35,000 MW program launched by the government. The use of coal in the power plant serves as a fuel for boilers. The boiler will produce steam which is used as a turbine to generate electricity. In the combustion of coal will be removed the remaining combustion in the form of coal ash in the form of fly ash, bottom ash, boiler slag, economizer ash and gypsum.

The rare earth oxide content in coal combustion product can reach the order of percent (%) as identified in coal ash originating from Russia, the amount is more than 1% [8]. Given the fact that coal is still widely burned throughout the world, besides having a negative impact on the environment and climate, coal combustion product can also be seen as an important source of LTJ [9]. Fly ash from a coal fired power plant is around 74% of the total coal combustion product [10]. Coal combustion product (fly ash) material can be used in various ways, including in the manufacture of concrete, cement raw material, former mining fill material, highway construction materials, adsorber (used in synthetic zeolites) as well as plant media [11][12]. Other uses are used in overburden encapsulation which is potentially acid forming (PAF) to prevent the formation of acidic mine drainage (AMD) at the Lati site of PT. Berau Coal [13], waste rock layering for the prevention of AMD [14][15], AMD treatment from pH 2.5 to 6.5 within 30 minutes because it has a 10-12% CaO content [16], mixing with Musselwhite gold mine tailings to increase the pH of leachate water [17].

This research is important to find out the potential of rare earth elements from coal combustion waste (fly ash and bottom ash) at the Banjarsari Mine Mouth-Power Plant, increasing the volume of waste will be even greater and so far has not been utilized optimally still being stockpiled as PAF rock layerings. In addition, rare earth elements is an advanced material that is very potential to be extracted. Inventory of REE resources as future resources and reserves is very important. Coal ash as a residual combustion mine mouth-power plant has the potential of REE content so it must be utilized properly so that in the future it can be removed from hazardous and toxic waste groups.

2. Methods
The research began with coal combustion product (CCP) sampling from the Banjarsari power plant, both fly ash (FA) and bottom ash (BA). Banjarsari power plant is a mine mouth coal-fired power plant because it is located near the mining site and is in the area of PT. Bukit Asam Tbk Muara Enim Regency, South Sumatra. Samples were prepared, including sampling material to obtain representative samples or grinding to refine the material. Sampling is done by quoning & quartering methods combined with a splitter box so that samples are ready for testing. Physical properties testing includes the distribution of grain size and grain morphology. The mineral content is detected by X-Ray Diffraction (XRD) while the oxide content is detected by X-Ray Fluorescence (XRF). The content of REE was tested using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) so that it can be identified potential REE for extraction.

3. Result and Discussion
Fly ash (FA) and bottom ash (BA) samples were analyzed for grain size using the dry and wet sieving method. Sifting with two methods to obtain the actual grain size of CCP. Dry sieves tend not to reflect actual grain size because the sample is easy to absorb or hygroscopic. Fly ash with dry sieve is only 66.84% which passes 200 mesh sieve whereas the wet sieve that passes 76.15%. Based on USCS, fly ash is a fine-grained material (clay and silt) because more than 50% passes 200 mesh
sieve (Figure 1). Bottom ash has a fraction of the size of sand as much as 99% and only 1% of its fine fraction, so it is categorized as coarse grained material [18].

![Grain size distribution of samples](image)

**Figure 1.** Grain size distribution of samples

Banjarsari power plant uses BUKIT ASAM-45 brand coal with a Circulating Fluidized Bed (CFB) combustion system. The size of the coal input is larger so it produces ash with a large grain size, especially bottom ash. The coal ash waste is very much determined by the coal input that becomes the fuel and the combustion system at each power plant. When compared to other power plants whose Pulverized Coal Boiler (PCB) combustion systems, the bottom ash grain size is very small. Morphology of CCP from the Banjarsari power plant waste based on observations with a microscope is shown in Figure 2. Observation with a microscope to determine the morphology of fly ash and bottom ash samples including observing whether the coal burned completely or not during the combustion process.

![Grain morphology of fly ash (FA) and bottom ash (BA)](image)

**Figure 2.** The grain morphology of fly ash (FA) and bottom ash (BA)

Fly ash material is relatively smaller in size compared to bottom ash and has a sub-rounded shape showing the combustion results at high temperatures with a fast time. There is still visible coal that has not been completely burned. Black grains are remnants of coal that has not been completely burned. Observation of grain morphology confirms the grain size of the sieve test results, that fly ash has a finer grain size compared to bottom ash.

Results of XRD, fly ash contains mineral quartz, muscovite, kaolinite, periclase, magnetite and lime. Bottom ash contains the minerals quartz, siderite, aragonite and hematite (Table 1). The dominant content for both samples is quartz minerals. In addition, it contains mineral mica (muscovite) and clay mineral (kaolinite) as minor minerals. Other minor minerals iron metal carriers such as hematite, magnetite and siderite as well as lime and aragonite minerals as metal carriers Ca. Test results with
XRD have not shown the mineral content that carries REE. Minerals that carry REE, contents are low compared to dominant minerals.

**Table 1. Result of XRD**

| Samples | Minerals Content                                      |
|---------|------------------------------------------------------|
| FA      | Quartz (SiO₂), Muscovite ([K₂Na₆] Al₂(Si₆Al₂O₁₈), Kaolinite (Al₃Si₄O₁₀(OH)₄), Periclase (MgO), Magnetite (Fe₃O₄) and Lime (CaO) |
| BA      | Quartz (SiO₂), Siderite (FeCO₃), Aragonite (CaCO₃) and Hematite (Fe₂O₃) |

The XRF test results confirm the XRD test results, which are found oxides which are also readable in the XRF test, such as SiO₂, CaO and Fe₂O₃. The XRF test results of SiO₂ oxide content above 50% for both samples. In addition, other dominant oxides are Al₂O₃, Fe₂O₃ and CaO. The other oxide contained less than 3% for both samples. These XRF results have not shown oxides that carry REE because they contain less than 0.01% (the minimum limit to be detected on XRF). The XRF test results are the basis for the grouping of coal ash according to ASTM-C-618, where the fly ash and bottom ash of the Banjarsari power plant are included in class F. The content of SiO₂ + Al₂O₃ + Fe₂O₃ is at least 70% while the FA and BA contain 90.37% and 93.25%. The maximum SO₃ content is 5% (class F) while FA and BA are only 2.17% and 1.2%. The water content of the FA sample was 2.53% and BA was only 0.17% while that for Class F was a maximum of 3% so that it was still eligible.

**Table 2. Result of XRF**

| Component | Mass (%) | Component | Mass (%) |
|-----------|----------|-----------|----------|
|           | BA       | FA        | BA       | FA       |
| Na₂O      | 0.22     | 0.53      | -        | -        |
| MgO       | 0.39     | 1.72      | MnO      | 0.09     | 0.07     |
| Al₂O₃     | 7.50     | 27.60     | Fe₂O₃    | 4.62     | 5.35     |
| SiO₂      | 81.13    | 57.40     | CoO      | 0.09     | -        |
| P₂O₅      | 0.05     | 0.28      | CuO      | 0.02     | -        |
| SO₃       | 0.12     | 2.17      | ZnO      | 0.20     | 0.02     |
| Cl        | 0.01     | -         | Rb₂O     | -        | -        |
| K₂O       | 0.38     | 0.59      | SrO      | 0.07     | 0.08     |
| CaO       | 3.08     | 3.27      | ZrO₂     | 0.06     | 0.06     |
| TiO₂      | 0.49     | 0.90      | WO₃      | 1.96     | -        |
| **Total Content** | **100** | **100** |           |          |

Testing of REE content is effectively carried out by the ICP-MS method because the detection limit is up to part per billion (ppb) units. The results of testing with the ICP-MS method showed that there were 16 elements detected. The total REE content for both samples, FA and BA were 264.97 ppm and 49.22 ppm, respectively. The REE content of fly ash samples is higher than bottom ash because some REE elements will be evaporated at high temperatures when burning coal, then condensed again after joining solid particles in the fly ash and caught on the electrostatic precipitator. The detected metals include scandium (Sc), lanthanum (La), yttrium (Y), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), gadolinium (Gd), dysprosium (Dy), terbium (Tb), erbium (Er), tuliump (Tm), iterbium (Yb), lutetium (Lu), europium (Eu) and holmium (Ho), only prometium (Pm) is not detected. Complete ICP-MS test results in Table 3.

**Table 3. Result of ICP-MS**

| Samples | REE Content (ppm) |
|---------|-------------------|
|         | Sc | Y | Ce | Pr | Nd | Sm | Gd | Dy | Tb | Er | Tm | Yb | Lu | Eu | La | Ho |
| FA      | 21.2 | 41.8 | 80.5 | 10.1 | 42.9 | 9 | 6.6 | 6.2 | 1.2 | 4.1 | 0.7 | 5.5 | 0.9 | 1.47 | 31.4 | 1.4 | 264.97 |
| BA      | 3.5 | 67 | 17.1 | 2 | 7.7 | 1.6 | 1 | 0.9 | 0.2 | 0.6 | <0.1 | 0.8 | 0.1 | 0.22 | 6.5 | 0.2 | 49.22 |
The dominant contents are cerium, neodymium, yttrium and lanthanum. Cerium metal content reaches 80.5 ppm in fly ash samples. If in 1000 kg of fly ash with 100% recovery (ideal conditions) 80.5 grams of cerium metal (Ce) will be obtained, 42.9 grams of neodymium, 41.8 grams of yttrium and 31.4 grams of lanthanum. The rare earth metal in the bottom ash sample is only cerium which contains 17.1 ppm while others contain very small content. Rare earth metals are classified into light rare earth elements (LREE) and heavy rare earth elements (HREE). LREE consists of Sc, Y, La, Ce, Pr, Nd, Pm, Sm and Eu while the rest includes HREE. LREE is a rare earth metal which has an atomic number of 63 and below while HREE is a rare earth metal which has an atomic number of 64-71[19]. The rare earth metal which is dominant in both coal ash is mild LTJ. The LREE and HREE ratio in the FA sample is 9:1 whereas in the BA sample it is 12:1. Coal ash containing LREE is more dominant than HREE. This is in line with the results of research conducted by Suganal et al. (2018) at the Ombilin power plant[20].

The REE content in coal ash is strongly influenced by coal input at the power plant. Coal is used in the combustion process in boilers. Coal combustion can be likened to the enrichment process of several metal elements in ash including REE. The Banjarsari power plant uses coal from the Muara Tiga Besar (MTB) site and the Tambang Air Layai (TAL) site with a specific depositional environment. The coal deposits are included in the Muara Enim formation in the Tanjung Enim region. Location of deposition of this formation is in the environment of shallow sea, delta land, and non-marine. This formation has the characteristics of rocks such as sandstone, siltstone, claystone and coal. This formation occurs in the syn-rift phase where the deposition process occurs during the formation of active rift in the Eocene-Oligocene (Paleogen) period. The fluviatyl-lacustrine deposit is the association for most of the coal deposited in this phase. Coal in this phase has a high calorific value (up to 7000 kcal/g) with low sulfur content (<1%), varying ash content and relatively limited lateral distribution [21]. Depositional environmental conditions and the pembatubaraan process makes the accumulation of coal-forming materials along with rare earth metals.

4. Conclusions
The conclusions of this study are as follows:
1. CCP of Banjarsari power plant waste combustion contains 16 elements of REE, namely scandium (Sc), lanthanum (La), yttrium (Y), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), gadolinium (Sm) Gd), dysprosium (Dy), terbium (Tb), erbium (Er), tildium (Tm), itterbium (Yb), lutetium (Lu), europium (Eu) and holmium (Ho), the dominant metal content is cerium and the lowest content is tildium.
2. Banjarsari fly ash has a total REE content 264.97 ppm while the bottom ash is only 49.22 ppm.
3. REE content of fly ash samples that are potential to be extracted, namely cerium (80.5 ppm), neodymium (42.9 ppm), yttrium (41.8 ppm) and lanthanum (31.4 ppm) while the bottom sample is not potential.
4. The research can be continued with coal ash from the combustion of the mine-mouth power plant or other power plant to be a resource and reserve of REE in the future and to see the metal that is potential to be processed.

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