The potency of rare earth elements and yttrium in Konawe coal ashes, Indonesia

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Abstract: Fly ash and bottom ash (FABA), which not utilized is considered waste, has been regarded as the promising source of rare earth elements and yttrium (REY). REY has been recognized as critical raw materials to several modern high-technology applications. This research aims to identify the potential resource of REY in FABA, by investigating FABA samples from two different coal-fired power plant (KNW-1 and KNW-2) in Konawe, Southeast Sulawesi Province, Indonesia. The geochemical compositions of coal and FABA include major elements and REY determined by ICP-MS and ICP-AES. The major elements in coal and FABA samples showed the highest concentration in SiO₂, Al₂O₃, Fe₂O₃, CaO, and MgO. The individual REY contents in FABA from KNW-1 are about 17-21 times higher than in coal samples while FABA from KNW-2 are about 57-73 times higher than in coal. The total REY concentration in FABA KNW-1 ranged from 227.34-276.41 ppm while the concentration in FABA KNW-2 ranged from 278.49-356.45 ppm. The total REO content of KNW-1 FABA samples ranged from 274.08-333.45 ppm. These values are lower than the REO content of the KNW-2 FABA (335.67-429.80 ppm). The percentage critical REY (30% ≤ REY ≤ 51%) and coefficient outlook (0.7 ≤ Cout ≤ 1.9%), showed all FABA samples are potential for promising raw material REY.

1. Introduction
Rare Earth Elements and Yttrium (REY) are resources that are often utilized in the fields of metallurgy, medical industry, fluid catalysts, high technology to defense and military systems [1]. As a result of this utilization globally, the demand for REY increased by 5.3% per year in the world [2]. According to the US Geological Survey [3], China already controls about 85% of the world's REY production [4]. The limitation of REY supply by China causes Indonesia to look for other alternative sources to play a role in meeting the world's REY needs. This causes research on alternative sources of new REY deposits to become important for further studies.

One of the alternative sources of REY's new deposits is coal and ash from coal combustion [4–13]. Indonesian coal deposits located in Banko coalfield and Muara Tiga Besar Utara coalfield has been confirmed as potential source for REY with heavy REY enrichment type [11–13]. Ash from coal combustion or better known as FABA (Fly Ash and Bottom Ash). According to Hower [14], FABA is the ash from burning coal in a power plant that is composed of organic and inorganic components. Fly Ash (FA) is ash particles resulting from coal combustion which are fine and light in size, while Bottom Ash (BA) is ash particles resulting from combustion which are coarse in size [15]. The enrichment and potential extraction of rare earth elements from FABA and other coal combustion products has attracted
attention in recent years [7,8,16–23]. Previous research about FABA compositions and REY enrichment only conducted in FABA samples from power plant in Java [18,24]. This study will provide comprehensive information about the potency of FABA from Konawe as the potential source for REY. FABA samples used in this study were taken from two different coal-fired power plant (KNW-1 and KNW-2), Konawe, Southeast Sulawesi (Figure 1).

Figure 1. Location of KNW-1 and KNW-2 coal-fired power plant.

2. Materials and Methods
In this study, there are 6 samples consisting of coal, fly ash, and bottom ash from KNW-1 and KNW-2 coal-fired power plant, Konawe, Southeast Sulawesi (Table 1).

Table 1. Types of samples from KNW-1 and KNW-2 coal-fired power plant.

| No | Code       | Coal-fired Power Plant | Sample types |
|----|------------|------------------------|--------------|
| 1  | KNW-1-01   | KNW-1                  | Coal         |
| 2  | KNW-1-02   | KNW-1                  | FA           |
| 3  | KNW-1-03   | KNW-1                  | BA           |
| 4  | KNW-1-01   | KNW-2                  | Coal         |
| 5  | KNW-1-02   | KNW-2                  | FA           |
| 6  | KNW-1-03   | KNW-2                  | BA           |

The research method used is laboratory analysis. This stage is an advanced stage for making observations on predetermined samples. The sample was then prepared according to standards prior to further analysis. Laboratory analysis used ICP AES / MS geochemical analysis.

2.1. Geochemical analysis
This analysis aims to determine the content of major and trace elements. This analysis uses several tools, namely: inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine major elements, and inductively coupled plasma - mass spectrometry (ICP-MS) to determine REY content.
3. Results and Discussion

Based on laboratory analysis and data normalization calculations, some major oxide and REY data were obtained. The analyses of major elements in coal and FABA of all samples showed highest concentration in SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, and MgO (Table 2).

| Sample | KNW-1-01 | KNW-1-02 | KNW-1-03 | KNW-2-01 | KNW-2-02 | KNW-2-03 |
|--------|----------|----------|----------|----------|----------|----------|
| SiO$_2$ | 44.37    | 40.59    | 52.38    | 38.20    | 48.28    | 57.39    |
| Al$_2$O$_3$ | 11.64    | 21.92    | 16.91    | 4.08     | 26.96    | 23.70    |
| Fe$_2$O$_3$ | 17.17    | 19.67    | 16.14    | 21.59    | 13.84    | 13.06    |
| CaO     | 13.02    | 9.28     | 5.89     | 12.23    | 3.95     | 1.46     |
| MgO     | 10.37    | 5.51     | 6.42     | 18.12    | 3.68     | 2.07     |
| Na$_2$O | 1.04     | 0.44     | 0.31     | 3.47     | 0.74     | 0.19     |
| K$_2$O  | 0.81     | 0.60     | 0.28     | 0.60     | 0.31     | 0.19     |
| Cr$_2$O$_3$ | 0.31     | 0.05     | 0.19     | 0.50     | 0.04     | 0.07     |
| TiO$_2$ | 0.58     | 1.14     | 0.92     | 0.15     | 1.61     | 1.37     |
| MnO     | 0.35     | 0.31     | 0.30     | 0.30     | 0.22     | 0.23     |
| P$_2$O$_5$ | 0.12     | 0.24     | 0.13     | 0.45     | 0.24     | 0.16     |
| SrO     | 0.12     | 0.12     | 0.07     | 0.15     | 0.07     | 0.04     |
| BaO     | 0.12     | 0.13     | 0.06     | 0.15     | 0.08     | 0.05     |
| Ce      | 4.1      | 84.6     | 73       | 1.3      | 112.5    | 87.6     |
| Dy      | 0.42     | 9.2      | 7.26     | 0.12     | 11.85    | 9.04     |
| Er      | 0.28     | 5.84     | 4.3      | 0.14     | 7.27     | 4.81     |
| Eu      | 0.11     | 1.89     | 1.53     | 0.04     | 2.57     | 2.09     |
| Gd      | 0.42     | 9.48     | 7.03     | 0.19     | 12       | 9.14     |
| Ho      | 0.08     | 1.93     | 1.5      | 0.04     | 2.4      | 1.75     |
| La      | 2.1      | 40       | 34.8     | 0.7      | 52.6     | 42.4     |
| Lu      | 0.04     | 0.8      | 0.59     | 0.02     | 0.95     | 0.77     |
| Nd      | 1.8      | 40.3     | 34       | 0.8      | 52.6     | 42.5     |
| Pr      | 0.47     | 10.05    | 8.61     | 0.2      | 12.95    | 10.35    |
| Sm      | 0.32     | 8.4      | 6.86     | 0.17     | 10.95    | 8.78     |
| Tb      | 0.06     | 1.47     | 1.18     | 0.02     | 1.81     | 1.35     |
| Tm      | 0.04     | 0.74     | 0.6      | 0.03     | 1.04     | 0.79     |
| Y       | 2.8      | 56.5     | 42.1     | 1        | 68.6     | 52.1     |
| Yb      | 0.25     | 5.21     | 3.98     | 0.11     | 6.36     | 5.02     |
| Sum REY | 13.29    | 276.41   | 227.34   | 4.88     | 356.45   | 278.49   |
| Sum REO | 22.48    | 468.22   | 381.68   | 5.874    | 429.8    | 335.67   |
| LREY    | 8.79     | 183.35   | 157.27   | 3.17     | 241.60   | 191.63   |
| HREY    | 4.50     | 93.06    | 70.07    | 1.71     | 114.85   | 86.86    |
| Critical| 5.47     | 115.20   | 90.37    | 2.12     | 144.70   | 111.89   |
| Uncritical| 3.31    | 67.93    | 57.30    | 1.26     | 88.50    | 70.67    |
| Excessive| 4.51    | 93.28    | 79.67    | 1.50     | 123.25   | 95.93    |
| % Critical| 41.16   | 41.68    | 39.75    | 43.44    | 40.59    | 40.18    |
| Coutl   | 1.21     | 1.23     | 1.13     | 1.41     | 1.17     | 1.17     |

Table 2. Major oxide and REY contents (ppm) in sample.
Market or industrial classification of REY is created based on the Dudley Kingsnorth (IMCOA) forecast of the relationship between demand and supply of individual REY in recent years [10]. The classification is divided into three classifications, i.e., critical group (Nd, Eu, Tb, Dy, Y, and Er), uncritical group (La, Pr, Sm, and Gd), and excessive group (Ce, Ho, Tm, Yb, and Lu). Estimation of the prospect of REY in FABA generally used some parameters include (1) cut-off grade represented by rare earth elements oxide (REO) content, (2) ore quality represented by an index called outlook coefficient (Coutl), (3) the percentage of critical elements in total REY (REY\text{def,rel}), and (4) concentration coefficient (CC) [4], and also the individual composition of REY. In this study, it was found that the total REY concentration of KNW-1’s coal sample is 13.29 ppm while KNW-2’s coal sample is 4.88 ppm, lower than the average concentration of coal in US of about 62.1 ppm and China in the average of 139.9 ppm [10]. The total REY concentration in FABA from KNW-1 ranged from 227.34-276.41 ppm while the total REY concentration in FABA from KNW-2 ranged from 278.49-356.45 ppm. Individual REY contents in FABA from KNW-1 power plant are about 17 - 21 times higher than that in coal samples while FABA from KNW-2 power plant are about 57 - 73 times (Figure 2).

![Figure 2. Comparison of individual REY contents in coal and FABA samples (normalized to UCC).](image)

The total REO content of KNW-1 FABA samples ranged from 274.08-333.45 ppm. These values are lower than the REO content of the KNW-2 FABA samples that abundances range from 335.67-429.80 ppm. All of this value is close to the cut-off grade of REO contents that determined by [8] but significantly lower than the cut-off grade of REO contents determined by Seredin and Dai [10] (Figure 3). The minimum value for the cut-off grade of REO contents ≥ 500 ppm applied by [8]. REO content ≥ 1000 ppm was considered as the cut-off grade for beneficial recovery REY. This cut-off grade could be lowered to 800-900 ppm for coal seams more than 5 meters in thickness [10].
All of the FABA samples had the percentage of total critical REY contents greater than 30% and outlook coefficient ($C_{outl}$) greater than 0.7 (Figure 4). The value of $C_{outl}$ and percentage of critical REY in FA and BA are significantly higher than the result of those parameters in samples from Inner Mongolia (C-18) and Guizhou (C-21) [10] and also higher than FA from Polandia (P1-P3) and UK (UK-1 – UK-3) [8] (Figure 4).

**Figure 3.** Comparison of total REO concentrations in this study with published data.

**Figure 4.** Comparison of percentage of critical REY concentrations and $C_{outl}$ in this study with published data.
Evaluation of individual REY contents in terms to know the potential industrial value performed by plotted the percentage of critical REY in total REY (REY_{def,rel}) and C_{outl} in a REY_{def,rel} – C_{outl} graph [10]. All of FABA samples plotted on this graphic and grouped in to the second cluster (Figure 5). The second cluster characterized by 30% ≤ REY_{def} ≤ 51%, 0.7 ≤ C_{outl}, generally various in REY distribution type, and regarded as promising REY raw materials for economic interest [10].

Figure 5. Comparison of percentage of critical REY concentrations and C_{outl} in this study with published data.

4. Conclusions
The data discussed in this paper have demonstrated that it is possible to find high REY contents in ash, that are comparable with those of conventional in many coal deposits worldwide. FABA from KNW-1 and KNW-2 power plant are potential for promising raw material REY based on the value of the percentage critical REY (30% ≤ REY_{def} ≤ 51%) and coefficient outlook (0.7 ≤ C_{outl} ≤ 1.9%). Besides that, there is also occur individual REY enrichment in FABA samples ranged from 17-73 times higher than the coal samples. The estimation and exploitation of the resources and the recovery of the REY as a by-product from coal ash may thus be considered as a promising way for obtaining these critical metals for the present world industry.

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