Abstract

Distribution of rare earth metals (REMs) and rare valuable metals (RVMs) contents in coal ashes (fly ash, bottom ash, and pond ash) and leachate from 11 coal-fired power plants in Korea were investigated. Coal ashes and leachates were found to contain important REMs and RVMs such as Yttrium (Y) and Neodymium (Nd), which was in the range of 23–75 mg/kg. However, it still requires developing effective recovery and separation methods in order to utilize REMs and RVMs in ash and leachate. Recovery of valuable elements (Y and Nd) from various and extensive ash sources (8.21 million tons/year in 2013) can provide the existing power plants with additional profit; therefore, it can significantly improve economics of the power plants.

Keywords: Rare Earth Metals, Rare Valuable Metals, Coal Ash, Coal-fired Power Plant, Urban mine

I. INTRODUCTION

Coal has been used as main fuel for power plants around the world due to its abundant reserves, relatively low price, stable supply and etc. As of December 2014, coal-fired power plants using anthracite and bituminous coal have taken about 46% (203,765,391 MWh) of the gross generation (442,914,458 MWh) of Korea Electric Power Corporation (KEPCO)'s subsidiary companies [1]. In Korea, it's expected new coal-fired power plants (10,500 MW) will be constructed by 2027 based on the 5th (1999~2015) and the 6th (2013~2027) basic plan for electricity supply and demand, and the importance of coal-fired power generation has been growing. Accordingly, the annual amount of coal ashes is likely to increase (8.21 million tons/y in 2013 to 16.6 million tons/y in 2020).

At present, the ash ponds of coal-fired power plants in Korea are filled with about 57.08 million tons of coal ashes and most of them are high carbon ashes which contain more than 5% of LOI (loss on ignition). Coal ashes have been mainly recycled as admixture for cement mortar and concrete, but the recycling rate (end-of-life) is expected to drop to less than 50% by 2020 because of increasing amount of coal ashes and low growth rate of the cement industry. On the other hand, the ministry of environment in Korea is going to enforce the levy system on waste landfill from 2017 to reduce the landfill rate to 3% of the amount of waste by 2020. When considering the trend of national policy on waste landfill and the situation of ash ponds, it is shown burdens and pressure to recycle coal ashes will grow heavier. Therefore, it is desperately needed to develop various high value-added technologies on recycling of coal ashes.

Numerous studies on the contents of REMs and RVMs in coal ashes have been reported. Rare earth elements (REEs) are a collection of chemical materials in the periodic table of which atomic numbers are 21, 39 and 57~71 and they can be classified as light REEs (LREEs), medium REEs (MREEs) and heavy REEs (HREEs) by their own mineral characteristics, namely scandium (Sc), yttrium (Y) and the 15 lanthanides such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), ruthenium (Ru) [2]. The price of REEs have rapidly risen and the competition for securing resources are severely proceeding because of the limitation of supply and the drastic increase of demand in new industries. Especially, some of REEs are classified as strategic materials due to lack of deposits and the Department of Energy (DOE) of United States is carrying out various research projects about Y, Eu, Nd, Tb and Dy. The market and demand for REEs are expected to continuously grow and it has been reported the predicted market size of Y and Nd, which are mainly used as light emitting displays and permanent magnet, is about 46.7 billion USD and 294 billion USD by 2025, respectively [3].

Therefore, the contents distribution of REMs and RVMs in coal ashes of coal-fired power plants in Korea and the economic valuation as urban mines were investigated in this study.

A. Content distribution of REMs and RVMs in coal ashes

Since large amounts of coal slurry have been leaked into nearby tributaries at Tennessee Valley Authority's Kingston Plant of U.S. in 2008, the Environmental Protection Agency (EPA) of U.S. has strengthen monitoring on coal ashes and established related legislation on safe usage of coal ashes. In this process, it was shown that coal ashes contained various kinds of REEs including strategic materials as well as heavy metals. Therefore, DOE and EPA of U.S. established the recycling standard through monitoring 'Trace Elements', which include heavy metals and REEs, in coal ashes from coal-fired power plants in the U.S. by 2015 and they are supporting to develop extraction technologies. Table 1 shows the major elements’ contents of strategic materials in coal and coal ashes (between 2011 and 2012) in about 10 coal-fired power plants of the U.S. As Table 1, the content of Ga was ranged from 212 to 299 mg/kg, Ce was 405 - 565 mg/kg, Y was 191–259 mg/kg, Eu was 3.90–5.90 mg/kg, and Nd was 183–256 mg/kg [4].
Table 1. Mean and range of contents of strategic REEs and some rare metals in coal and coal ashes of U.S. (Unit: mg/kg)

| Element | Raw Coal | Coal ash | Coal Fly Ash |
|---------|----------|----------|--------------|
| Ce      | 20.9 (0.79 – 790) | 468.78 (151 – 1,784) | 405 (0 – 565) |
| Dy      | 2.09 (0.11 – 28) | 61.84 (18 – 527) | 32.1 (0 – 50.3) |
| Eu      | 0.28 (0.025 – 5.8) | 7.64 (2.00 – 31) | 3.9 (0 – 5.9) |
| La      | 9.09 (0.07 – 230) | 259.85 (60 – 838) | 206 (0 – 286) |
| Nd      | 8.48 (0.47 – 230) | 236.02 (70 – 957) | 183 (0 – 256) |
| Pr      | 1.81 (0.17 – 63) | 59.92 (17 – 239) | 59.0 (0 – 68.4) |
| Tb      | 0.34 (0.001 – 21) | 10.29 (1.00 – 840) | 4.9 (0 – 7.3) |
| Y       | 8.18 (0.10 – 100) | 408.34 (97 – 3,540) | 191 (0 – 259) |
| Total REE 54.9 (0.20 – 1,031) | 1,723 (721 – 8,426) | 1,213.6 – 1,667.6 |
| Ga      | 5.24 (0.044 – 41) | N.A. | 212 (0 – 299) |
| Ge      | 4.23 (0.007 – 220) | N.A. | 10 (0 – 1,841) |
| Lu      | 0.71 (0.025 – 25) | N.A. | N.A. |
| Te      | 1.82 (8.8 – 510) | N.A. | 0.14 (0 – 2.7) |

*N.A.: not analyzed, ‘-’ means no average value.

In the previous reports, Wojciech et al. [5], Blissett et al. [6] and Querol et al. [7] have reported REEs’ contents in bituminous coal were ranged from 28.8 to 359.1 mg/kg. On the other hand, Zhang et al. [8-10] measured the contents of REEs in incineration ashes of food waste, animal husbandry waste, horticulture waste, sewage sludge and incinerators' bottom ash and it was shown the contents of 11 REEs such as Y, La, Ce and etc. were ranged from 53.7 to 130 mg/kg and other metals such as Li, Ga, Ru and Zr were in the range of 5–300 mg/kg.

In Korea, Korea Western Power Co., Ltd. and Kunsan National University have examined the recovery of Li in coal ashes and they found the content of Li in ash pond was 2–3 mg/kg (average Li content of seawater : 0.17 mg/L). It was limited to the certain metal (Li), so it is regarded there is no study on monitoring REMs or RVMs in coal ashes from coal-fired power plants in Korea. Lee et al. [2] collected fly ash and bottom ash of Korea South-East Power Co. and tried to measure existence of REEs indirectly by examining chemical composition by X-ray fluorescence spectrometry (XRF), but they failed due to limitation of analytical instrument.

B. Global trend on REMs and RVMs

There is yet no international organization to appropriately evaluate and determine the prices of REMs and RVMs and the prices are being set by supply and demand. In the past, REMs were supplied at controlled prices by a few major producers. However, China became a major producer of REEs and took over about 90% of REMs market in 2000s because of low labor and mining costs in China. Australia and U.S. have been mining their own iron ore for REMs from the beginning of 2010s, but the prices of REEs were still under the control of China’s policy on environmental problems and the domestic demands [11].

U.S. has prepared several short-term countermeasure and policy on matters of REMs supply and demand, but alternative technologies and recycling plans in the US have been prepared for the long-term. European Union (EU) implemented the 'Raw Material Initiative' in 2008 and classified 14 metals such as Sb, Be, Co, Ga, Ge, In, Ta, and W, termed as major management objects. In addition, B, coking coal and phosphate rock were included on May 2014. On the other hand, Japan has been carried out research projects to substitute each REE and save resources and put efforts into reducing risks of discontinuance of supply, but the balance of demand and supply is deteriorating in case of some REEs [3][12].

II. ANALYTICAL METHOD

In this study, the content distributions of REMs and RVMs in coal ashes (fly, bottom, and pond ashes) and leachate of 11 coal-fired power plants was investigated. The fly ash samples were collected soon after produced and samples of bottom and pond ashes were collected at the points of ash pond which are not under the influence of seawater. Supernatant water was collected as leachate samples.

Pre-treatment of coal ash was performed because coal ash is produced at high temperature. First of all, about 0.2 g of coal ash sample was put into Teflon bottle and 3 mL of sulfuric acid (H2SO4, 95–98%) and 2 mL of hydrofluoric acid (HF, 47–51%) were subsequently added. Sample drying was conducted in two-step drying process; i.e. coal ash on aluminum heating block was initially dried at 110°C and then temperature was increased to 160°C for second step of drying. After cooling the sample bottle, 1 mL of nitric acid (HNO3, 68.5–71%) and 19 mL of 1% nitric acid solution (HNO3, 1%) were added. Then, sample bottle cover with lid was heated at 100°C for 30 min.
Table 2. Content of rare earth metals in coal ashes and leachate from coal-fired power plants

| Ashes   | Y    | Nd   | Eu   | Tb   | Dy   | Ce   | La   | Nb   | Te   | Th   | Tl   | Ag   | Au   | Ba   | Bi   | Co   | Ga   | Li   | Ni   | V    | Zr   |
|---------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| F-avg   | 48.6 | 40.6 | 1.9  | 1.5  | 8.2  | 101.5| 54.6 | 31.4 | <20.0| <20.0| <10.0| <0.1 | <0.1 | <1.164| <10.0| 33.3 | 67.9 | 99.0 | 55.8 | 146.7| 365.4|
| B-avg   | 47.0 | 44.9 | 1.9  | 1.5  | 8.1  | 97.9 | 54.2 | 50.2 | <20.0| <20.0| <10.0| <0.1 | <0.1 | 1.019 | <10.0| 53.4 | 71.8 | 117.6| 167.1| 117.7| 583.5|
| F-max   | 46.7 | 42.9 | 1.8  | 1.5  | 8.1  | 104.5| 53.2 | 31.6 | <20.0| <20.0| <10.0| <0.1 | <0.1 | 872   | <10.0| 46.0 | 72.3 | 117.2| 58.9 | 120.4| 367.4|
| B-max   | 47.0 | 44.9 | 1.8  | 1.5  | 8.1  | 104.5| 53.2 | 31.6 | <20.0| <20.0| <10.0| <0.1 | <0.1 | 872   | <10.0| 46.0 | 72.3 | 117.2| 58.9 | 120.4| 367.4|

* F: fly ash, B: bottom ash, P: pond ash, L: leachate

Samples fused through this process were used to measure the contents of REMs and RVMs by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The amount of samples, kinds and amount of acid solutions depend on the characteristic of coal ash samples. The target metals were 11 REMs (Y, Nd, Eu, Tb, Dy, Ce, La, Nb, Te, Th and Tl) and 10 RVMs (Ag, Au, Ba, Bi, Co, Ga, Li, Ni, V and Zr).

III. RESULT AND DISCUSSION

Table 2 summarizes the contents of REEs in coal ashes and leachate samples. Y was ranged from 30 to 71 mg/kg in fly ash, 21 to 68 mg/kg in bottom ash, 26 to 75 mg/kg in pond ash and the mean values of all three ash samples were higher than 40 mg/kg. In particular, Y content in fly ash and bottom ash of C1 power plant and pond ash of E1 power plant were the highest. In case of Nd, the content was ranged from 23 to 56 mg/kg in fly ash, 19 to 86 mg/kg in bottom ash, 19 to 67 mg/kg in pond ash and C1 power plant, E3 power plant and E1 power plant had the highest value in fly ash, bottom ash and pond ash, respectively. The content of Ce was ranged from 33 to 178 mg/kg (38.5 to 166.0 mg/kg in fly ash, 33.0 to 138.0 mg/kg in bottom ash and 61.2 to 178.0 mg/kg in pond ash) and La was ranged from 17.3 to 98.8 mg/kg (21.0 to 84.0 mg/kg in fly ash, 17.3 to 98.8 mg/kg in bottom ash and 24.9 to 90.9 mg/kg in pond ash) and Nb was ranged from 12.0 to 89.4 mg/kg (19.0 to 46.5 mg/kg in fly ash, 14.4 to 89.4 mg/kg in bottom ash and 12.0 to 53.3 mg/kg in pond ash). The content of Th was ranged from 20.0 to 60.8 mg/kg (20.0 to 63.5 mg/kg in fly ash, 20.0 to 60.8 mg/kg in bottom ash and less than 20.0 mg/kg in pond ash), but the contents of Te and Tl were less than 20 mg/kg. In case of leachate samples, the contents of all REMs and RVMs were less than 20 mg/kg and it was regarded leachate samples weren’t under the influence of seawater.

Also, the contents of Ag and Au were less than 0.1 mg/kg and Ba was ranged from 354 to 2,120 mg/kg (462 to 2,120 mg/kg in fly ash, 354 to 2,090 mg/kg in bottom ash and 447 to 1,590 mg/kg in pond ash). The content of Bi was less than 10 mg/kg and Co was ranged from 13.1 to 77.0 mg/kg (13.1 to 77.0 mg/kg in fly ash, 33.2 to 77.0 mg/kg in bottom ash and 27.6 to 62.7 mg/kg in pond ash). The content of Ga was ranged from 38.9 to 110 mg/kg (53.4 to 88.9 mg/kg in fly ash, 38.9 to 110.0 mg/kg in bottom ash and 45.6 to 93.9 mg/kg in pond ash) and Ni was ranged from 25.0 to 97.5 mg/kg (31.0 to 77.9 mg/kg in fly ash, 34.1 to 97.5 mg/kg in bottom ash and 25.0 to 86.3 mg/kg in pond ash). The content of V was ranged from 72.0 to 191 mg/kg (109 to 191 mg/kg in fly ash, 72.6 to 169 mg/kg in bottom ash and 82.2 to 171 mg/kg in pond ash) and Zr was ranged from 129 to 584 mg/kg (140 to 584 mg/kg in fly ash, 129 to 551 mg/kg in bottom ash and 166 to 489 mg/kg in pond ash). The content of Li in leachate samples was ranged from 0.1 to 0.9 mg/L, but it was shown other REMs and RVMs were not dissolved in leachate.

The amounts of REMs and RVMs in fly ash of coal-fired power plants in Korea based on the amount of coal ashes in 2013 are shown in Table 3. The amount of fly ash was about 6.95 million tons/y and the amount of REMs and RVMs was 15,823 tons/y. In particular, the annual amount of Y was 338 tons, Nd was 282 tons and La was 379 tons. And it was shown 688 tons of Li, 388 tons of Ni, 1,019 tons of V and 2,538 tons of Zr were generated annually.

In case of bottom ash, the annual amount was 1.26 million tons/y and the amount of REMs and RVMs was 2,899 tons. Especially, the annual amount of Y was 59 tons, Nd was 57 tons and La was 69 tons. And it was shown 149 tons of Li, 211 tons of Ni, 149 tons of V and 485 tons of Zr were generated annually.

On the other hand, about 640 million tons of pond ash, which was filled from 1983 to 2015, is in ash pond of coal-fired power plants and the amount of REMs and RVMs contained in it was 128,357 tons. The amount of Y was 2,985 tons, Nd was 2,742 tons and category of Te was 3,836 tons. Also, 7,492 tons of Li, 3,765 tons of Ni, 8,080 tons of V and 23,487 tons of Zr were contained in pond ash. The contents of ultra-expensive metals such as Dy, Te, Ga and etc were quite high.

The economic value of REMs and RVMs contained in the annual amount of fly ash and bottom ash (based on 2013) and total pond ash in ash pond in coal-fired power plants in Korea by using international trade price (based on Jan. 2015) from Metal-pages (http://metal-pages.com), MineralPrices.com (http://www.mineralprices.com) and Korea Resources Corporation (http://www.kores.or.kr) were shown in Table 4.

As a result, the economic values of REMs and RVMs in A power co. were estimated to be approximately 532.9 billion KRW. Among the three different sources of ashes, the pond ash of A1 power plant was found to be the highest (339.7 billion KRW). On the other hand, the economic values of REMs and RVMs in B power co. were estimated to be approximately 541.5 billion KRW, which was the highest value among five KEPCO's subsidiary companies. Consequently, the economic values of REMs and RVMs in coal-fired power plants in Korea was...
estimated to reach about 1,670 KRW, which is worth to develop recovery technologies for REMs and RVMs.

3) The economic values of REMs and RVMs contained in coal ashes (fly ash, bottom ash and pond ash) of coal-fired power plants in Korea were currently estimated to reach about 1,670 billion KRW. In particular, B power co. had the highest value of about 541.5 billion KRW and A power co. had the value of 1,699 billion KRW. In conclusion, effective recovery technology for REMs and RVMs from coal ashes should be developed to improve the overall economics of coal power plants facilities.

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Table 4. Estimate value of rare earth metals and rare valuable metals from coal-fired power plants (Unit: 0.1 billion-KRW)

| coal-fired power plants | Estimated value of rare earth metals | Estimated value of valuable metals | Sum |
|------------------------|--------------------------------------|----------------------------------|------|
|                        | Y         | Nd       | Dy       | La         | Pr         | Ce         | Nb         | Te/Th/Ti   | Co         | Ga         | Li         | Ni         | V          | Zr         |                  |
| A                      |          |          |          |            |            |            |            |            |            |            |            |            |            |            |                  |
| F                      | 7.45      | 6.99     | 7.76     | 1.09       | 305.94     | 2.04       | 2.62       | 97.12      |            |            |            |            |            |            |                  |
| B                      | 1.27      | 1.34     | 1.55     | 0.19       | 46.03      | 0.33       | 0.74       | 16.93      |            |            |            |            |            |            |                  |
| A1-P                   | 39.12     | 61.34    | 62.56    | 8.75       | 1,893.99   | 17.18      | 21.73      | 799.23     |            |            |            |            |            |            |                  |
| A2-P                   | 20.16     | 20.96    | 21.02    | 2.98       | 645.99     | 5.86       | 7.41       | 272.65     |            |            |            |            |            |            |                  |
| A3-P                   | 3.56      | 3.73     | 3.62     | 0.53       | 115.14     | 1.05       | 1.34       | 49.01      |            |            |            |            |            |            |                  |
| SUM                    | 91.56     | 94.36    | 96.68    | 13.53      | 3,007.09   | 26.44      | 33.84      | 1,234.93   |            |            |            |            |            |            |                  |
| B                      | 6.01      | 5.65     | 6.20     | 0.88       | 247.71     | 1.64       | 2.12       | 78.41      |            |            |            |            |            |            |                  |
| B1-P                   | 57.34     | 59.53    | 60.49    | 8.48       | 1,836.05   | 16.67      | 21.08      | 775.17     |            |            |            |            |            |            |                  |
| B2-P                   | 28.97     | 30.05    | 30.50    | 4.29       | 928.55     | 8.43       | 10.68      | 392.04     |            |            |            |            |            |            |                  |
| SUM                    | 93.25     | 96.27    | 98.23    | 11.79      | 3,048.47   | 26.99      | 34.43      | 1,258.98   |            |            |            |            |            |            |                  |
| C                      | 4.49      | 4.21     | 4.65     | 0.65       | 183.10     | 1.21       | 1.57       | 57.92      |            |            |            |            |            |            |                  |
| B1-P                   | 0.51      | 0.57     | 0.52     | 0.08       | 20.33      | 0.14       | 0.32       | 7.13       |            |            |            |            |            |            |                  |
| SUM                    | 7.28      | 7.29     | 7.27     | 1.14       | 294.76     | 2.18       | 2.95       | 103.36     |            |            |            |            |            |            |                  |
| D                      | 4.57      | 4.31     | 4.65     | 0.66       | 186.29     | 1.23       | 1.61       | 58.81      |            |            |            |            |            |            |                  |
| B                      | 0.76      | 0.86     | 1.03     | 0.12       | 28.75      | 0.21       | 0.46       | 10.69      |            |            |            |            |            |            |                  |
| D1-P                   | 30.32     | 31.49    | 32.05    | 4.48       | 970.23     | 8.80       | 11.14      | 409.86     |            |            |            |            |            |            |                  |
| SUM                    | 35.66     | 36.65    | 37.74    | 5.26       | 1,185.27   | 10.24      | 13.21      | 479.36     |            |            |            |            |            |            |                  |
| E                      | 5.84      | 5.55     | 6.20     | 0.86       | 241.61     | 1.60       | 2.07       | 76.63      |            |            |            |            |            |            |                  |
| B1-P                   | 1.52      | 1.63     | 1.55     | 0.22       | 56.05      | 0.41       | 0.87       | 20.49      |            |            |            |            |            |            |                  |
| SUM                    | 78.20     | 79.66    | 80.42    | 1.02       | 2,446.61   | 1.60       | 2.07       | 76.63      |            |            |            |            |            |            |                  |
| Total                  | 286.20    | 294.66   | 302.45   | 42.27      | 9,449.76   | 82.52      | 105.93     | 3,856.25   | 120.03     | 1,442.63   | 55.11      | 73.76      | 548.41     | 42.39      | 16,702.38 |

* F: fly ash, B: bottom ash, P: pond ash

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