Supercritical solvent extraction of lignite combustion products by water and HNO$_3$ – Rare Earth Elements recovery study

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Abstract. Coal Combustion Products (CCPs) are anthropogenic materials generated during coal burning in coal-fired power plants and in case of lignite majority of these materials is disposed on land. CCPs contain various metals including Rare Earth Elements (REE). The purpose of this study was to assess if supercritical solvent extraction of CCPs, i.e. fly ash and bottom slag is effective to recover Rare Earth Elements. For that purpose two methods were compared: atmospheric and supercritical solvent extraction with the use of water and 10% HNO$_3$. Result show that extraction of REE is unjustified when considering efficiency of solvent extraction process and obtained REE concentrations.

1. Introduction
Coal Combustion Products (CCPs) are anthropogenic materials generated during coal burning in coal-fired power plants. These materials are categorized in the following groups: a) fly ash, b) bottom slag, c) bottom slag/fly ash mixtures, d) gypsum, e) fly ash and dry desulphurization product mixtures [1,2]. Since World’s energy generation is based mostly on fossil fuels where lignite and hard coal play a dominant role (according to International Energy Agency over 40% of secondary energy is produced from coal where 3.0% from lignite [3,4]) CCPs should be considered as a resource rather than a waste. For the case of Poland over 80% of hard coal CCPs is utilized for, e.g.: concrete or cement production, road foundation construction [5]. In contrary, 65% of lignite CCPs in Poland are considered as a waste and are mostly disposed on land. This is due to the relatively high carbon content of CCPs as a result of incomplete combustion. Hence, there is a limited use of those products in construction industry [7]. Large volumes of disposed CCPs from lignite have an adverse impact on the environment. Land where CCPs are disposed is degraded by the wet form of fly ash storage that prevents dust emission. Another problem is related to the fact that CCPs contain heavy metals such as Cr, As or Pb (that can be leached and migrate to groundwater) and, at low concentrations, Rare Earth Elements (REE) [8].

There were several attempts to use solvent extraction for recovery of metals from lignite fly ash. Authors focused on the use of solvents such as, e.g.: citric acid [9], sulfuric acid [10] or mixture of HCl and NaOH [11]. Since the share of lignite in overall electricity production is relatively low available information related to solvent extraction of lignite fly ash is scarce. Nevertheless, sulfuric acid was already used for extraction of lignite fly ash [12,13].
The purpose of this study was to assess if supercritical solvent extraction of CCPs, i.e. fly ash and bottom slag is effective to recover Rare Earth Elements. For that purpose two methods were compared atmospheric and supercritical solvent extraction with the use of neutral or “eco” solvents – water and 10% HNO₃. This approach is sustainable and in accordance with the rules of circular economy where every useful product can be recovered and reused.

2. Materials
For the purpose of the study commercially available lignite Coal Combustion Products were used i.e.: fly ash and bottom slag from one of the polish lignite power plants. Table 1 presents chemical composition of materials used in the study. In Figure 1 SEM images presenting surface morphology of materials are shown.

Table 1. Chemical composition of materials used in the study.

| Parameter/Compound, (m/m) | fly ash | bottom slag |
|--------------------------|---------|-------------|
| LOI, 5.47                |         | 48.74       |
| B₂O₃, 1.32               |         | 0.99        |
| F, 0.20                  |         | 0.09        |
| Na₂O, 0.108              |         | 0.097       |
| MgO, 0.95                |         | 0.84        |
| Al₂O₃, 24.00             |         | 23.80       |
| SiO₂, 33.40              |         | 47.20       |
| P₂O₅, 0.148              |         | 0.100       |
| SO₃, 3.43                |         | 1.33        |
| Cl, 0.01                 |         | 0.01        |
| K₂O, 0.16                |         | 0.22        |
| CaO, 25.30               |         | 12.60       |
| TiO₂, 0.97               |         | 1.32        |
| V₂O₅, 0.06               |         | 0.04        |
| Cr₂O₃, 0.03              |         | 0.03        |
| MnO, 0.075               |         | 0.031       |
| Fe₂O₃, 8.11              |         | 5.77        |
| Co₂O₃, 0.00              |         | 0.00        |
| NiO, 0.01                |         | 0.01        |
| CuO, 0.01                |         | 0.01        |
| ZnO, 0.02                |         | 0.01        |
| Ga₂O₃, 0.00              |         | 0.00        |
| As₂O₃, 0.01              |         | 0.00        |
| SeO₂, 0.01               |         | 0.00        |
| Br, 0.00                 |         | 0.00        |
| Rb₂O, 0.00               |         | 0.00        |
| SrO, 0.07                |         | 0.05        |
| Y₂O₃, 0.01               |         | 0.01        |
| ZrO₂, 0.04               |         | 0.03        |
| Nb₂O₃, 0.00              |         | 0.00        |
| BaO, 0.09                |         | 0.06        |
| HgO, 0.00                |         | 0.00        |
Figure 1. Surface morphology of a) fly ash, b) bottom slag

3. Methods
Supercritical solvent extraction and atmospheric extraction was carried out for both samples: fly ash and bottom slag. For each test the solid to solvent ratio was 1:2 (w/w). Minimum purity of solvents used in the experiments was 99.9%. In Figure 2 block diagram of experimental procedure is presented.

Figure 2. Block diagram of experimental procedure.

In the case of extraction under atmospheric pressure, experiments were carried out in a round bottom flask equipped with a reflux condenser at the temperature of 400°C for 5 hours. Supercritical solvent extraction of CCPs was carried out in interconnected Haas autoclaves presented in Figure 3 [14]. Connection between autoclaves partially eliminated the need for further filtration and as a consequence, lowered the loss of extracts and solid residue. Temperature of the process was kept constant at 400°C with pressure of 20-22 MPa. Duration of the experiments was the same as atmospheric extraction - 5 hours. Obtained extract were subjected for further analysis of metal content using ICP-OES method.
Figure 3. High pressure autoclaves used for the supercritical solvent extraction.

4. Results and Discussion
In Table 2 and 3 mass balance of lignite CCPs solvent extraction processes carried out in the study are presented. Extract yield ($Y$) was calculated with the following formula:

$$Y = \frac{m_{\text{extract}} - m_{\text{H2O}}}{m_{\text{fly ash}}} \times 100\%$$

Where $m$ indicates masses of feed and products in grams.

Table 2. Mass balance of solvent extraction processes under atmospheric pressure of fly ash and bottom slag.

| FEED     | YIELDS          |          |          |          | Y (%) |
|----------|-----------------|----------|----------|----------|-------|
| Fly ash  | – 10 g          | Solid residue | – 9,4 g  | Extract  | – 20,5 g | Y = 3% |
| H2O      | – 20 g          | Loss     | – 0,3 g  |          |        |       |
| Fly ash  | – 10 g          | Solid residue | – 9,1 g  | Extract  | – 20,6 g | Y = 6% |
| 10% HNO3 | – 20 g          | Loss     | – 0,3 g  |          |        |       |
| Fly ash  | – 10 g          | Solid residue | – 8,4 g  | Extract  | – 21,1 g | Y = 11% |
| H2O      | – 20 g          | Loss     | – 0,5 g  |          |        |       |
| Fly ash  | – 10 g          | Solid residue | – 7,1 g  | Extract  | – 22,6 g | Y = 26% |
| 10% HNO3 | – 20 g          | Loss     | – 0,3 g  |          |        |       |

Table 3. Mass balance of supercritical solvent extraction of fly ash and bottom slag.

| FEED     | YIELDS          |          |          |          | Y (%) |
|----------|-----------------|----------|----------|----------|-------|
| Fly ash  | – 10 g          | Solid residue | – 6,1 g  | Extract  | – 22,4 g | Y = 24% |
| 10% HNO3 | – 20 g          | Loss     | – 0,3 g  |          |        |       |
| Bottom slag | – 10 g          | Solid residue | – 4,7 g  | Extract  | – 23,7 g | Y = 37% |
| 10% HNO3 | – 20 g          | Loss     | – 0,2 g  |          |        |       |
Results show that a more efficient extraction was with 10% HNO₃ as a solvent for both materials – maximum yield was 37% (m/m). As expected better results were obtained for supercritical extraction under elevated pressure and temperature. Extracts were consequently subjected for further analyses of metal content using ICP-MS technique (see Fig. 4).

**Table 4. Metal content of extracts.**

|       | APE, H₂O FA | APE, H₂O BS | ATM, HNO₃ FA | ATM, HNO₃ BS | CSE, HNO₃ FA | CSE, HNO₃ BS |
|-------|-------------|-------------|--------------|--------------|--------------|--------------|
| Ag    | 0,0063      | 0,0067      | 0,0070       | 0,0074       | 0,0078       | 0,0081       |
| Al    | 13,6653     | 14,6396     | 15,6140      | 16,5883      | 17,5627      | 18,5371      |
| As    | 0,0733      | 0,0701      | 0,0670       | 0,0638       | 0,0607       | 0,0575       |
| B     | 4,3727      | 4,4097      | 4,4467       | 4,4836       | 4,5206       | 4,5576       |
| Ba    | 0,0037      | 0,0037      | 0,0037       | 0,0037       | 0,0037       | 0,0037       |
| Bi    | 0,0310      | 0,0347      | 0,0384       | 0,0421       | 0,0458       | 0,0495       |
| Cd    | 0,0012      | 0,0012      | 0,0012       | 0,0011       | 0,0011       | 0,0010       |
| Co    | 0,0011      | 0,0017      | 0,0024       | 0,0030       | 0,0036       | 0,0043       |
| Cr    | 0,0112      | 0,0146      | 0,0181       | 0,0215       | 0,0249       | 0,0283       |
| Cu    | 0,0652      | 0,0977      | 0,1303       | 0,1629       | 0,1954       | 0,2280       |
| Eu    | 0,4414      | 0,4736      | 0,5057       | 0,5378       | 0,5700       | 0,6021       |
| Fe    | 1,2641      | 1,3296      | 1,3950       | 1,4605       | 1,5260       | 1,5914       |
| Ga    | 0,1370      | 0,1373      | 0,1377       | 0,1381       | 0,1384       | 0,1388       |
| In    | 0,0077      | 0,0078      | 0,0079       | 0,0080       | 0,0081       | 0,0082       |
| Ir    | 0,0019      | 0,0022      | 0,0026       | 0,0029       | 0,0033       | 0,0037       |
| La    | 0,0519      | 0,0556      | 0,0593       | 0,0629       | 0,0666       | 0,0703       |
| Li    | 1,1955      | 1,1991      | 1,2027       | 1,2063       | 1,2099       | 1,2136       |
| Mg    | 7,0900      | 7,4114      | 7,7328       | 8,0542       | 8,3756       | 8,6970       |
| Mn    | 0,0767      | 0,1004      | 0,1240       | 0,1477       | 0,1713       | 0,1950       |
| Mo    | 0,0901      | 0,0938      | 0,0975       | 0,1012       | 0,1049       | 0,1085       |
| Na    | 12,4947     | 12,9659     | 13,4371      | 13,9083      | 14,3795      | 14,8507      |
| Nb    | 0,0096      | 0,0127      | 0,0159       | 0,0190       | 0,0221       | 0,0253       |
| Ni    | 0,0328      | 0,0374      | 0,0420       | 0,0466       | 0,0511       | 0,0557       |
| P     | 0,1777      | 0,1777      | 0,1778       | 0,1778       | 0,1778       | 0,1779       |
| Pb    | 0,0375      | 0,0378      | 0,0381       | 0,0385       | 0,0388       | 0,0391       |
| Rh    | 0,0198      | 0,0202      | 0,0206       | 0,0209       | 0,0213       | 0,0216       |
| Si    | 16,6547     | 17,2025     | 17,7504      | 18,2983      | 18,8462      | 19,3941      |
| Sm    | 0,0071      | 0,1052      | 0,2033       | 0,3014       | 0,3995       | 0,4976       |
| Sr    | 0,5372      | 0,5436      | 0,5500       | 0,5564       | 0,5628       | 0,5692       |
| Th    | 0,0484      | 0,0854      | 0,1224       | 0,1594       | 0,1964       | 0,2333       |
| Ti    | 0,0107      | 0,0117      | 0,0127       | 0,0136       | 0,0146       | 0,0156       |
| Tl    | 0,0059      | 0,0058      | 0,0057       | 0,0057       | 0,0056       | 0,0055       |
| Tm    | 0,0005      | 0,0005      | 0,0005       | 0,0006       | 0,0006       | 0,0006       |
| V     | 0,0250      | 0,0285      | 0,0320       | 0,0355       | 0,0390       | 0,0425       |
| W     | 0,0281      | 0,0318      | 0,0355       | 0,0391       | 0,0428       | 0,0465       |
| Yb    | 0,0011      | 0,0014      | 0,0018       | 0,0022       | 0,0025       | 0,0029       |
| Zn    | 0,2710      | 0,2823      | 0,2935       | 0,3048       | 0,3161       | 0,3273       |
| Zr    | 0,0222      | 0,0259      | 0,0295       | 0,0332       | 0,0369       | 0,0405       |

APE – atmospheric pressure extraction, CSE – critical solvent extraction, FA – fly ash, BS – bottom slag

Extracts have a form of a pulp with various metal content including Rare Earth Metals and alkaline metals. Calcium content is not included in the table since the concentration exceeded calibration curve.
This could be explained by the affinity of calcium toward solvents used and high content of calcium in the raw material. Higher yields were obtained in case of bottom slag which can be attributed to the grain morphology (large, porous grains). Content of Rare Earth Elements increases in case of supercritical solvent extraction, eg. Europium (Eu) concentration increased by 36.4%.

5. Conclusions
Results of this study show that recovery of REE is unjustified when considering efficiency of solvent extraction process and REE concentrations. Both fly ash and bottom slag do contain REE such as Samarium or Europium at very low concentrations and it might be difficult to upscale a complex process of solvent extraction to industrial scale. Cost of such process will most probably be higher than the income.

Other potential solutions would be using other solvents such as citric acid or sulfuric acid yet the environmental footprint of such process would be significant.

High LOI indicates high carbon content. Therefore, an alternative is to first separate unburned coal (UC) which is less prone to solvent extraction (it adsorbs solvent) by gravity separation or flotation and later use upgraded material for extraction process.

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