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Occurrence and recovery potential of rare earth elements in Finnish peat
and biomass combustion fly ash

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Abstract

Rare earth elements (REEs) are highly important in the modern society as a result of their wide use in various fields of industry. Their high supply risk and increase in demand has led to classification as critical materials, and consequently, new resources for REEs are being prospected widely. Coal fly ash has been suggested as a possible secondary resource for REEs, but very little information is available regarding REE occurrence in biomass or peat derived fly ash.

In this paper, fly ash samples from commercial power plants using peat and biomass as fuel were studied for REEs. The average concentration of REEs was 530 ppm, with up to 920 ppm in one fly ash. Five out of seven fly ashes were identified promising for profitable REE recovery according to outlook coefficients of >0.7 and critical REE content of $>30\%$. Four fly ashes were found to exhibit medium REE enriched distributions, whereas three fly ashes displayed light REE enriched distributions. These enriched distribution patterns, as well as the observed Gd, Ce, Eu, La, and Y anomalies in the patterns, are proposed to originate mainly from the granitic bedrock at the fuel source. Additionally, positive correlation between REEs and iron was found, indicating REE association with iron minerals.

Keywords: rare earth element; fly ash; peat; biomass; occurrence; recovery

1 Introduction

REEs are a group of chemically similar elements including lanthanoids, i.e. elements from lanthanum to lutetium, and commonly also yttrium and scandium. They can be classified into following groups: light rare earth elements (LREE: La, Ce, Pr, Nd and Sm), medium (MREE: Eu, Gd, Tb, Dy and Y) and heavy (HREE: Ho, Er, Tm, Yb and Lu) [1]. REEs are present in the earth's crust in moderate concentrations varying from 0.2 ppm of Tm to 70 ppm of Ce [2], with their total concentration ranging from 100 to 220 ppm [3]. Due to their unique chemical and physical properties, REEs are essential in permanent magnets, lamp phosphors, catalysts, rechargeable batteries, and in numerous other high technology applications [4–6].

REEs have recently become increasingly critical due to the vast number of applications, uncertain market availability and low recycling rates [4–7]. While China was producing 81 % of the world's REEs in 2017 [8], the supply risk has been high for many years especially in western countries. Moreover, most currently mined REE deposits have high concentrations of the abundant REEs and low concentrations of the less abundant REEs, leading to oversupply of the abundant REEs, most prominently Ce. Hence, the European Union has classified REEs among critical materials in their reports [7,9,10] and the U.S. Department of Energy has included Nd, Eu, Tb, Dy and Y in their Critical Materials Strategy in 2011 [11]. Due to these concerns, new deposits and secondary sources of REEs are being prospected widely [12].

REE recovery from coal fly ash has been a subject of interest for more than 20 years, since coal beds with REE contents of 0.2-0.3 wt% in ash were found in Russian Far East [12]. Coal fly ash is the most widely produced fly ash in the world at 750 million tons annually [13], with an average REE concentration of 404 ppm [12]. REEs and their recovery potential in coal fly ash have consequently been studied extensively [1,14-26]. However, EU's 20 %

target of renewable energy by 2020 [27] favors the use of biomass as a CO₂ emission neutral fuel alternative to coal [28]. In spite of the significant production of biomass fly ash, estimated at 480 million tons annually [28], only few studies have focused on biomass fly ash as a potential REE resource. This is likely caused by the previously reported low concentrations: typically between 10-100 ppm in biomass based ashes [29,30]. The same applies to peat and peat ash, with REE concentrations in Russian Siberian peat ashes ranging from 35 to 340 ppm (incl. La, Ce, Sm, Eu, Tb, Yb and Lu) [31]. However, high concentrations of REEs in peat ashes from mires at rapakivi granite areas in Finland have been reported, with an average REE concentration of 1 300 ppm (incl. Y, La, Ce, Pr, Nd, and Sm) and individual REE concentrations as high as 3 500 ppm for Y [32].

The total concentration of REEs in fly ash can be used to evaluate their potential for economic recovery. A cut-off grade for profitable utilization in coal ash has been suggested by Seredin [33] at ≥ 1000 ppm of rare earth oxides (REO), and $\geq 800-900$ ppm in coal seams with thickness of >5 m. However, the total amount of REO in fly ash should not be the only consideration, as there are significant differences in the use and availability of individual REEs. For evaluation of REE deposit quality, REEs can be divided into critical (Nd, Eu, Tb, Dy, Er, Y), uncritical (La, Pr, Sm, Gd) and excessive (Ce, Ho, Tm, Yb, Lu) according to their production and consumption quantities, as introduced by Seredin and Dai [12]. The ratio of critical REEs to excessive REEs is called the outlook coefficient ($C_{outl.}$), which can be calculated as:

$$C_{outl.} = \frac{Nd+Eu+Tb+Dy+Er+Y}{Ce+Ho+Tm+Yb+Lu} \quad (1)$$

Promising fly ashes have high outlook coefficients (>0.7), since they contain high concentrations of critical REEs and low concentrations of excessive REEs.

In order to gain knowledge about REE enrichment in fly ashes, it is useful to normalize REE concentrations to some relevant frame of reference, for example to the upper continental crust (UCC) [34]. From these appropriately normalized distribution patterns, REE rich fly ashes may be observed to be enriched with either light (L-type), medium (M-type) or heavy (H-type) REEs [12], of which the latter two are most suitable for recovery of REEs, by containing more of the least abundant REEs. Anomalous behavior is occasionally observed for Ce, Eu, La, Gd, and Y in the otherwise fairly smooth UCC normalized REE distributions patterns of coals and coal fly ashes [34]. This is due to Ce and Eu being redox-sensitive elements, differentiating from the other REEs by occurring at oxidation states +4 and +2, respectively. Anomalous behavior of La, Gd, and Y, on the other hand, is based on the slight differences in the stabilities of REE complexes [34]. In a negative anomaly, the studied material is depleted with respect to a certain element when compared to the other REEs, and vice versa in a positive anomaly. REE anomalies develop under specific conditions, and the observation of these anomalies can give insights into the geochemical history and sediment-source region where the fuel originates.

This is the first paper to investigate REE concentrations and distribution patterns in peat and biomass fly ash from commercial power plants in Finland. REE content in fly ashes is evaluated using outlook coefficients, content of critical REEs, and enrichment compared to the UCC. REE distribution patterns and anomalies are assessed for information about the geochemistry of the region where the fuel originates. Correlation of REEs with other elements as well as fly ash mineralogy is studied to gain knowledge about REE associations with certain minerals. Ashes being produced from energy production in Finland alone during 2012 were 1.0 million tons [35], presenting a potentially important secondary resource for REEs.

2 Materials and methods

2.1 Samples and reagents

Seven fly ash samples were obtained from two combined heat and power (CHP) plants located in central Finland. Power plant 1 utilizes fluidized bed combustion (FBC) and power plant 2 circulating fluidized bed (CFB) technology. The samples were collected from the first rows of electrostatic precipitators. The CHP plants used a mixture of peat and biomass as a fuel, of which composition is presented in Table 1. Standard reference material (SRM) 1633c coal fly ash from the National Institute of Standards and Technology (NIST) was used to verify sample treatment and analytical procedure. Coal fly ash SRM was considered to be a suitable alternative in monitoring the sample treatment and analytical procedure, since no peat and biomass fly ash SRM was available. High-purity water was used throughout the work, with resistivity of 18.5 M Ω ·cm, produced with a Purelab Ultra water purification system supplied by Elga (Buckinghamshire, U.K.).

Table 1

Fly ash samples' collection dates, fuel compositions and power plants (1: FBC, 2: CFB)

| Sample ID | Date collected (month/year) | Fuel composition (peat:bio %) | Power plant |
|-----------|-----------------------------|-------------------------------|-------------|
| A | 5/2010 | 30:70 | 1 |
| B | 3/2010 | 50:50 | 1 |
| C | 2/2012 | 50:50 | 2 |
| D | 1/2010 | 65:35 | 1 |
| E | 2/2010 | 70:30 | 1 |
| F | 3/2012 | 80:20 | 1 |
| G | 5/2010 | 100:0 | 2 |

2.2 Microwave digestion

A dried subsample of 250 mg was weighed into a Teflon microwave vessel, into which 7.0 ml of nitric acid (Sigma-Aldrich, puriss p.a., 65-68 wt%), 1.0 ml of hydrochloric acid (Sigma-Aldrich, puriss p.a., 37-39 wt%), and 1.5 ml of hydrofluoric acid (Merck, EMSURE ISO, 40 wt%) was added. The sample was mixed with the acids by swirling the vessel. The sample vessel was closed and placed in a microwave oven Mars 6 iWave, supplied by CEM (North Carolina, U.S.A.). The temperature was ramped with microwave power of 290-1800 W during 20 minutes to 200 °C, in which the temperature was held for 15 minutes.

After cooling, the vessel was opened and 10 ml of 5 % (m/v) boric acid (Sigma-Aldrich, purity >99.99%) water solution was added. The vessel was closed and placed in the microwave oven. The temperature was ramped with microwave power of 290-1800 W to 170 °C during 20 minutes, in which it was held for 15 minutes. After cooling, the vessel was opened and the sample was filtered (Whatman no. 42 filter paper) into a plastic 50 ml volumetric flask. The microwave vessel was rinsed three times with 5-10 ml of ultrapure water, which was poured onto the filter paper. The sample was finally diluted to 50 ml volume with ultrapure water.

2.3 Elemental analysis

The digested samples were analyzed for REEs using an ICP-MS (inductively coupled plasma –mass spectrometer) NexIon 350D, supplied by PerkinElmer, (Massachusetts, U.S.A.) equipped with prepFAST 4DX autosampler, supplied by Elemental Scientific (Nebraska, U.S.A.). The digested fly ash samples were diluted hundredfold with prepFAST for the analysis. PerkinElmer PurePlus multi-element standard containing 10 ppm of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Y, Yb was used for the calibration of

the instrument, after dilutions to concentration range of 0.01-100 ppb. The samples and calibration standards were adjusted to contain 1 % (v/v) of nitric acid (Analytica, ANALPURE ULTRA, >67 wt%). More detailed information about the analytical procedure is presented in the SI.

Major and minor elements were analyzed from digested fly ash samples using an ICP-OES (inductively coupled plasma –optical emission spectrometer) Avio 500 equipped with an AS10 autosampler, both supplied by PerkinElmer (Massachusetts, U.S.A.). The samples were diluted 10-100 fold prior to measurements. PerkinElmer PurePlus multi-element standards with concentration of 10 ppm were used in calibration of the instrument after dilution to concentration range of 0.1-10 ppm. The standards contained the elements: Al, Ag, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn in one solution, and B, Ge, Mo, Nb, P, Re, S, Si, Ta, Tl, W, and Zr in one solution. Samples and calibration standards were adjusted to contain 5.0 % (v/v) nitric acid (Sigma-Aldrich, puriss p.a., 65-68 wt%), and 0.3 % (v/v) hydrofluoric acid (Merck, EMSURE ISO, 40 wt%). More detailed information about the analytical procedure is presented in the SI.

2.4 *Quality control*

Quality control was performed by digestion and analysis of method blanks and SRM 1633c along with the samples. The method blanks resulted in concentrations below 5% of the sample concentrations, and analysis of the SRM in recoveries of 91 to 101 % for reference values (La, Eu, Tb, Dy, and Lu), and 96 to 113 % for informational values (Ce, Nd, Sm, and Yb). Recoveries of major and minor elements were between 90-109%, and 83% for Ti. Relative standard deviation in replicate samples was <5%.

2.5 XRD analysis

X-ray powder diffraction (XRD) analyses were conducted on a PANalytical X'Pert Pro alpha 1 Bragg-Brentano diffractometer using a fixed-anode Cu tube operating at 45 kV and 40 mA with a Johansson monochromator installed ($\text{CuK}_{\alpha 1}$ $\lambda = 1.5406 \text{ \AA}$). All samples were gently mortar ground before measurements. Data were collected in ambient conditions from spinning samples prepared in a stainless steel disc cavity of 16 mm diameter with an X'Celerator detector over a 2Θ -range of $3 - 100^\circ$ with 0.017° and 90 s step size and counting time, respectively. Diffraction data were analyzed using PANalytical HighScore Plus program (v. 4.7) with PDF4+ reference database installed.

2.6 Calculations

REE concentrations were normalized to the UCC using data published by Taylor and McLennan [36]. REE distribution types were then determined from the following UCC normalized ratios: L-type distribution: $\text{La}_N/\text{Lu}_N > 1$, M-type distribution: $\text{La}_N/\text{Sm}_N < 1$ and $\text{Gd}_N/\text{Lu}_N > 1$, and H-type distribution: $\text{La}_N/\text{Lu}_N < 1$ [12]. REE anomalies were decoupled from the other REEs using the following formulae [34]:

$$\text{Ce}_N/\text{Ce}_N^* = \text{Ce}_N / (0.5\text{La}_N + 0.5\text{Pr}_N) \quad (2)$$

$$\text{Eu}_N/\text{Eu}_N^* = \text{Eu}_N / (0.67\text{Sm}_N + 0.33\text{Tb}_N) \quad (3)$$

$$\text{La}_N/\text{La}_N^* = \text{La}_N / (3\text{Pr}_N - 2\text{Nd}_N) \quad (4)$$

$$\text{Gd}_N/\text{Gd}_N^* = \text{Gd}_N / (0.33\text{Sm}_N + 0.67\text{Tb}_N) \quad (5)$$

$$\text{Y}_N/\text{Y}_N^* = \text{Y}_N/\text{Ho}_N \quad (6)$$

Ratios of 0.95-1.05 were treated as no anomalies to account for normal analytical uncertainty in the concentrations. Ratios of <0.95 were identified as a negative anomalies, and ratios of >1.05 as positive anomalies.

3 Results and discussion

3.1 Concentrations and recovery potential

REE and REO concentrations, as well as division into critical, uncritical and excessive REEs, along with outlook coefficients are presented in Table 2. Total REE concentrations are within 259-920 ppm range, with an average concentration of 531 ppm. The highest REO content is observed for fly ash F at 1102 ppm. REE concentrations observed here are significantly higher than reported previously: biomass fly ash from a commercial plant in California has been reported to contain REEs at 81.8 ppm, other wood ashes 9.5-91.2 ppm [29], and horticulture waste 101 ppm [30]. Moreover, the REE concentrations are more comparable to coal fly ash, which have an average concentration of 404 ppm [12].

Calculation of outlook coefficients results in values higher than 0.7 for all but one fly ash, with $C_{outl.}$ up to 0.86, observed for fly ash C. This indicates that the fly ashes can be considered promising for economical REE recovery. The content of critical REEs in the samples ranges from 28 to 32 %, with five fly ashes containing more than 30% of critical REEs, also suggesting recovery possibilities. The contents of critical REEs are similar to those found previously in coal fly ashes, which have been reported to contain 29-39% of critical REEs [19]. According to these results, five of the studied peat and biomass fly ashes (A, C, D, E, and G) can be considered promising for recovery of REEs, based on the outlook coefficients and content of critical REEs. However, only one of these five, fly ash E, contains REO in concentration exceeding 800 ppm, which has been suggested as the cut-off grade.

Table 2

REE concentrations (ppm), total REE and REO concentrations (ppm), critical, uncritical and excessive REEs (ppm), outlook coefficients and content of critical REEs of total REEs (%) in fly ashes A-G

| | Fly ash samples | | | | | | |
|--------------|-----------------|------|-------|------|-------|-------|------|
| | A | B | C | D | E | F | G |
| La | 41.5 | 102 | 90.8 | 88.5 | 136 | 187 | 74.3 |
| Ce | 86.5 | 201 | 178 | 164 | 271 | 378 | 151 |
| Pr | 10.2 | 23.4 | 21.3 | 20.8 | 30.7 | 40.4 | 18.1 |
| Nd | 38.2 | 86.1 | 83.5 | 78.5 | 119.4 | 150.4 | 68.2 |
| Sm | 6.73 | 13.9 | 14.7 | 13.2 | 21.2 | 24.1 | 11.3 |
| Eu | 1.37 | 2.50 | 2.73 | 2.29 | 3.75 | 3.59 | 2.1 |
| Gd | 6.1 | 12.7 | 13.3 | 11.9 | 19.5 | 20.4 | 10.6 |
| Tb | 0.86 | 1.73 | 1.87 | 1.59 | 2.72 | 2.57 | 1.5 |
| Dy | 4.76 | 9.41 | 10.24 | 8.57 | 14.8 | 13.9 | 8.3 |
| Ho | 0.97 | 1.88 | 2.10 | 1.69 | 2.88 | 2.70 | 1.6 |
| Er | 2.81 | 5.29 | 6.06 | 4.67 | 8.20 | 7.71 | 4.6 |
| Tm | 0.40 | 0.73 | 0.84 | 0.65 | 1.11 | 1.06 | 0.6 |
| Yb | 2.61 | 4.74 | 5.60 | 4.04 | 7.22 | 6.94 | 4.0 |
| Lu | 0.38 | 0.73 | 0.85 | 0.61 | 1.09 | 1.09 | 0.6 |
| Y | 25.9 | 47.5 | 57.5 | 44.0 | 83.5 | 78.6 | 40.8 |
| Σ REE | 229 | 514 | 489 | 445 | 723 | 918 | 398 |
| Σ REO | 275 | 616 | 587 | 533 | 868 | 1102 | 478 |
| Critical | 73.9 | 153 | 162 | 140 | 232 | 257 | 126 |
| Uncritical | 64.6 | 152 | 140 | 134 | 207 | 271 | 114 |
| Excessive | 90.9 | 209 | 187 | 171 | 283 | 389 | 158 |
| $C_{outl.}$ | 0.81 | 0.73 | 0.86 | 0.82 | 0.82 | 0.66 | 0.79 |
| Critical (%) | 32.2 | 29.7 | 33.1 | 31.4 | 32.1 | 28.0 | 31.5 |

3.2 Distribution patterns and anomalies

UCC normalized REE distribution patterns are presented in Fig. 1 and UCC normalized La_N/Lu_N , La_N/Sm_N , Gd_N/Lu_N –ratios in Table 3. Most REEs are enriched in fly ashes at least twofold compared to the UCC, and even up to sixfold in fly ash F, whereas fly ash A shows very little enrichment. Fly ashes B, D, and F present L-type distributions, i.e. are enriched in light REEs, and fly ashes A, C, E, and G show M-type distributions, i.e. are enriched in

medium REEs. In coal fly ashes, L-type distribution indicates terrigenous or tuffaceous origin of REEs at the peat bog stage, and M-type distribution is typical for coal basins with acidic circulating water [12]. Also, higher sorption of MREEs by humic matter compared to other REEs is a possible reason for an M-type distribution pattern in coal fly ashes [12].

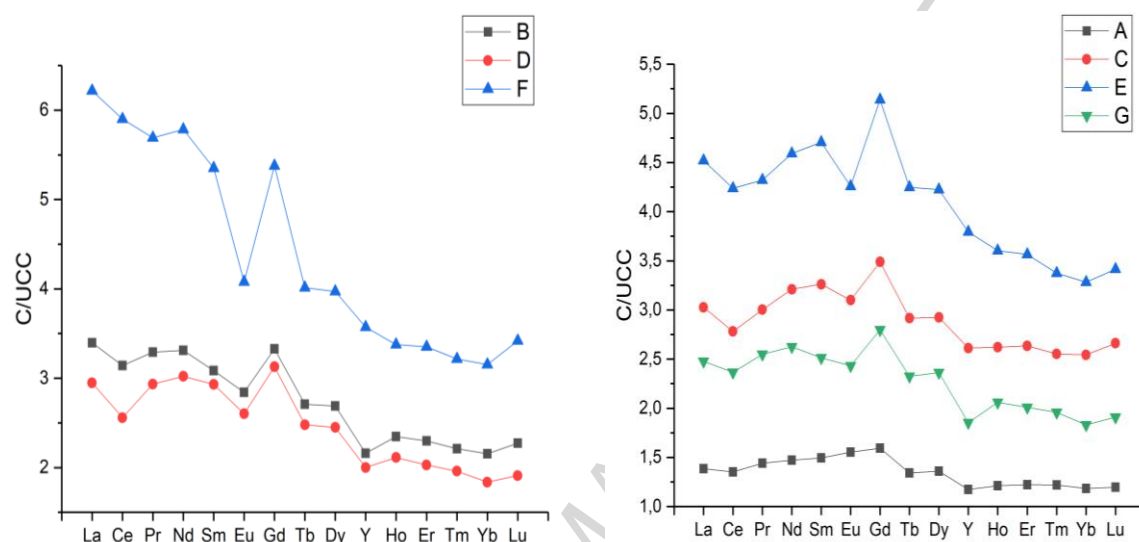


Fig. 1. REE distribution in L-type fly ash samples (left) and M-type fly ash samples (right), where REE concentrations are normalized to concentrations in the upper continental crust (C/UCC) [12].

REE anomalies in the UCC normalized REE distribution patterns can be observed from Fig. 1, and are also presented as RE_N/RE_N^* -ratios in Table 3. All the fly ashes show clear positive Gd anomalies, with Gd_N/Gd_N^* -ratios of 1.14-1.21. These anomalies are usually controlled by the rocks in the sedimentary rock region, as well as the influence of seawater, hydrothermal fluids and other waters, causing positive Gd anomalies in coal [34]. M-type REE spectra combined with a Gd maximum is typical for acidic waters [34], which can be the cause for M-type distributions and positive Gd anomalies observed for fly ashes A, C, E, and G. Positive La anomalies are present for fly ashes C, D, E, and F with La_N/La_N^* ratios of

1.07-1.20. Similar positive La anomalies have previously been observed in coals from high-Ti mafic basalts, or coals which have been subjected to acidic waters [34].

Table 3

UCC normalized REE ratios, distribution types, and Ce, Eu, La, Gd, and Y anomalies

| | Fly ash samples | | | | | | |
|-------------------|-----------------|---------|---------|---------|---------|---------|---------|
| | A | B | C | D | E | F | G |
| La_N/Lu_N | 1.16 | 1.49 | 1.14 | 1.54 | 1.32 | 1.82 | 1.30 |
| La_N/Sm_N | 0.93 | 1.10 | 0.93 | 1.01 | 0.96 | 1.16 | 0.99 |
| Gd_N/Lu_N | 1.33 | 1.46 | 1.31 | 1.64 | 1.50 | 1.57 | 1.46 |
| Distribution type | M | L | M | L | M | L | M |
| Ce_N/Ce_N^* | 0.96 | 0.94(-) | 0.92(-) | 0.87(-) | 0.96 | 0.99 | 0.94(-) |
| Eu_N/Eu_N^* | 1.08(+) | 0.96 | 0.98 | 0.94(-) | 0.93(-) | 0.83(-) | 0.99 |
| La_N/La_N^* | 1.00 | 1.04 | 1.17(+) | 1.07(+) | 1.20(+) | 1.13(+) | 1.03 |
| Gd_N/Gd_N^* | 1.14(+) | 1.18(+) | 1.15(+) | 1.19(+) | 1.17(+) | 1.21(+) | 1.17(+) |
| Y_N/Y_N^* | 0.97 | 0.92(-) | 1.00 | 0.95 | 1.05 | 1.06 | 0.90(-) |

(+) Positive anomaly with ratio >1.05

(-) Negative anomaly with ratio <0.95

Negative anomalies for Ce, Eu, and Y are present in some of the studied fly ashes, and have previously been reported in coals originating from sediment-source regions dominated by felsic rocks [34]. Fly ash A also shows a weak positive Eu anomaly, which can be caused by isomorphous replacement of Ca^{2+} with Eu^{2+} , present in high Ca minerals such as plagioclase feldspars [37]. Coals with mafic basalts origin have also been characterized with strong positive Eu anomalies [34]. Plagioclase was observed in the XRD analysis of all fly ash samples (see section 3.3.), and isomorphous replacement is a possible cause for the observed positive Eu anomaly.

The studied fly ashes originate from combustion of Finnish peat and biomass, where the distribution patterns and anomalies can indicate local geological conditions, as well as REE accumulation in plants. Weathering of the bedrock and sedimentary source region are

sources of REEs, and in Finland where the fuel originates, 53 % of the bedrock consists of granitic rocks and 22% of migmatites [38]. Some ferns have been found to accumulate REEs, and the roots usually have higher concentrations of REEs compared to other parts of the plants [39]. Finland also has REE rich areas, in which REE appear for example in apatite (CaPO_4) with monazite inclusions $[(\text{Ce},\text{La},\text{Nd},\text{Th})\text{PO}_4]$, allanite $[(\text{Ce},\text{Ca},\text{Y})_2(\text{Al},\text{Fe})_3(\text{SiO}_4)_3(\text{OH})]$, and fergusonite $[(\text{Y},\text{Er},\text{Ce},\text{Fe})(\text{Nb},\text{Ta},\text{Ti})\text{O}_4]$ [40]. REE content in some of these deposits are as high as 4.2 wt% [41]. Weathering of minerals and accumulation in the peat bog due to sorption by humic matter are possible explanations for the observed REE distributions in fly ashes.

3.3 Associations with other elements and minerals

Major and minor element concentrations from the elemental analysis are presented as oxides in Table 4. Silica is the major component in all but one fly ash, with concentration range of 30-53 wt%. This is consistent with the XRD analysis of fly ash samples, with quartz (SiO_2) identified as the main component from the diffraction patterns, presented in Fig. 2. Silica in fly ash originates not only from the fuel, but also from the bed sand used in fluidized bed combustion. The fly ashes also contain high concentrations of oxides of calcium, aluminum, and iron in the range of 6-23 wt%, 10-14 wt%, and 4-10 wt%, respectively. Oxides of K, Na, Mg, and P are present in all fly ashes with concentrations of 1-3 wt%. In XRD analysis, plagioclase ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$), anhydrite (CaSO_4), orthoclase (KAlSi_3O_8), and calcite (CaCO_3) were identified in most of the fly ash samples. Additionally, berlinite (AlPO_4) was identified in fly ash F and G, enstatite (MgSiO_3) in fly ash B, and maghemite (Fe_2O_3) in fly ash F. Minor element oxides are present in the fly ashes in ppm levels, and were not identified in XRD analysis. Major and minor elemental concentrations in the studied fly ashes are similar to those found in coal fly ashes [13] as well as wood and

woody biomass ashes [29], although biomass ashes have significant variations in elemental composition due to different biomass types. Interpretation of XRD diffraction patterns of fly ash samples presented some challenges due to peak overlap and low sample crystallinity, and some peaks (especially the ones overlapping with quartz main peak at theta value 26.5°) could not be unambiguously identified.

Table 4

Major and minor element concentrations (wt%) expressed as oxides in fly ashes A-G.

| Component | Fly ash samples | | | | | | |
|--------------------------------|-----------------|------|------|------|------|------|------|
| | A | B | C | D | E | F | G |
| SiO ₂ | 30.7 | 33.7 | 47.6 | 46.5 | 53.3 | 43.8 | 30.4 |
| Al ₂ O ₃ | 11.9 | 12.5 | 12.4 | 13.0 | 14.1 | 12.5 | 9.9 |
| Fe ₂ O ₃ | 4.0 | 6.9 | 9.3 | 6.2 | 9.0 | 9.9 | 7.7 |
| CaO | 6.4 | 14.2 | 15.2 | 6.7 | 8.6 | 7.1 | 23.3 |
| K ₂ O | 3.0 | 3.1 | 3.3 | 2.5 | 2.3 | 2.2 | 1.4 |
| P ₂ O ₅ | 0.93 | 2.7 | 2.8 | 1.1 | 2.0 | 1.4 | 1.1 |
| Na ₂ O | 2.3 | 1.6 | 1.6 | 2.0 | 1.6 | 1.7 | 1.3 |
| MgO | 1.3 | 2.4 | 2.4 | 1.2 | 1.6 | 1.4 | 2.2 |
| SO ₃ | 0.31 | 1.7 | 3.5 | 0.17 | 0.25 | 0.40 | 3.1 |
| MnO | 0.22 | 0.64 | 0.47 | 0.19 | 0.24 | 0.19 | 0.09 |
| TiO ₂ | 0.36 | 0.35 | 0.35 | 0.33 | 0.37 | 0.37 | 0.27 |
| BaO | 0.13 | 0.18 | 0.16 | 0.10 | 0.11 | 0.10 | 0.08 |
| SrO | 0.05 | 0.09 | 0.08 | 0.05 | 0.06 | 0.05 | 0.05 |
| ZnO | 0.04 | 0.10 | 0.07 | 0.03 | 0.03 | 0.03 | 0.01 |

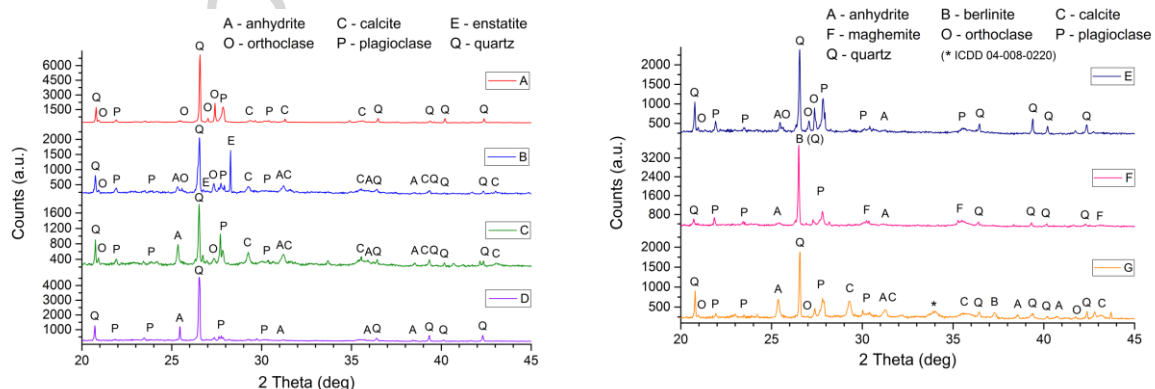


Fig. 2. XRD analysis diffraction patterns with identified sample constituent peaks.

Correlation of REEs with major and minor elements, as well as peat content of the fuel, was studied by calculation of squared Pearson's correlation coefficients (R^2), which are presented in Fig. 3 for components with $R^2 > 0.3$. Fig. 4 shows La and Lu, representing light and heavy REEs, concentrations plotted against Fe_2O_3 , SiO_2 , Al_2O_3 content in fly ash and peat content of the fuel. REE concentrations correlate positively with Fe content in the samples, with R^2 values 0.63-0.83, indicating association of REEs with iron minerals. A single iron mineral (maghemite) was observed in XRD analysis of one fly ash sample, but other Fe containing minerals were most likely present as well. It is likely that samples consisted of several species in such low individual quantities that they could not be identified in XRD analysis.

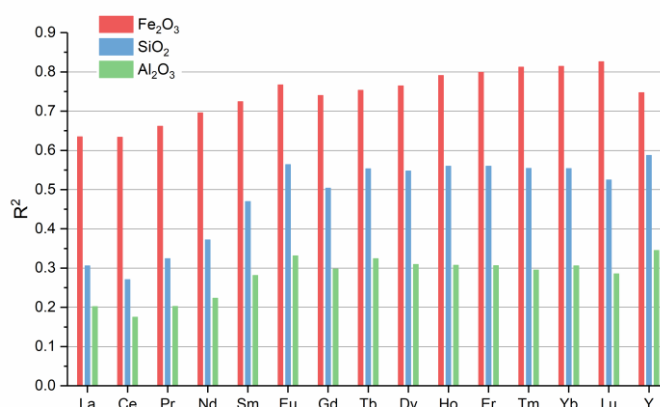


Fig. 3. Squared Pearson's correlation coefficients between REEs and Fe_2O_3 , SiO_2 , and Al_2O_3 concentrations in fly ashes.

The heavier REEs were also found to correlate positively with silica and aluminum oxide to some extent, with R^2 values up to 0.59 and 0.35, respectively. This could indicate heavier REE associations with aluminosilicates in fly ashes. Aluminosilicates plagioclase and

orthoclase were observed in XRD analysis of most of the fly ash samples. Franus *et al.* [42] have reported REE in coal fly ash to correlate with oxides of Al and Si, similar to Vassilev *et al.* [43], who studied biomass ash and found REE to correlate with S, Ti, and phosphates in addition to oxides of Si and Al.

For other major and minor elements, as well as for the peat content of the fuel, the R^2 values were lower than 0.3, and associations with REEs could not be concluded. Correlation of REEs with peat content of the fuel had R^2 values up to 0.2, which is not statistically significant. However, visual evaluation of data in Fig. 4 indicates that there might be some positive correlation between REE concentrations and peat content of the fuel. The low correlation coefficient is due to fly ash G with 100 % peat content, which deviates from the otherwise observed rather linear trend. Peat used as a fuel during the collection of the fly ash samples can originate from different batches and locations in Finland, which makes assessment of correlation between REEs and peat content difficult.

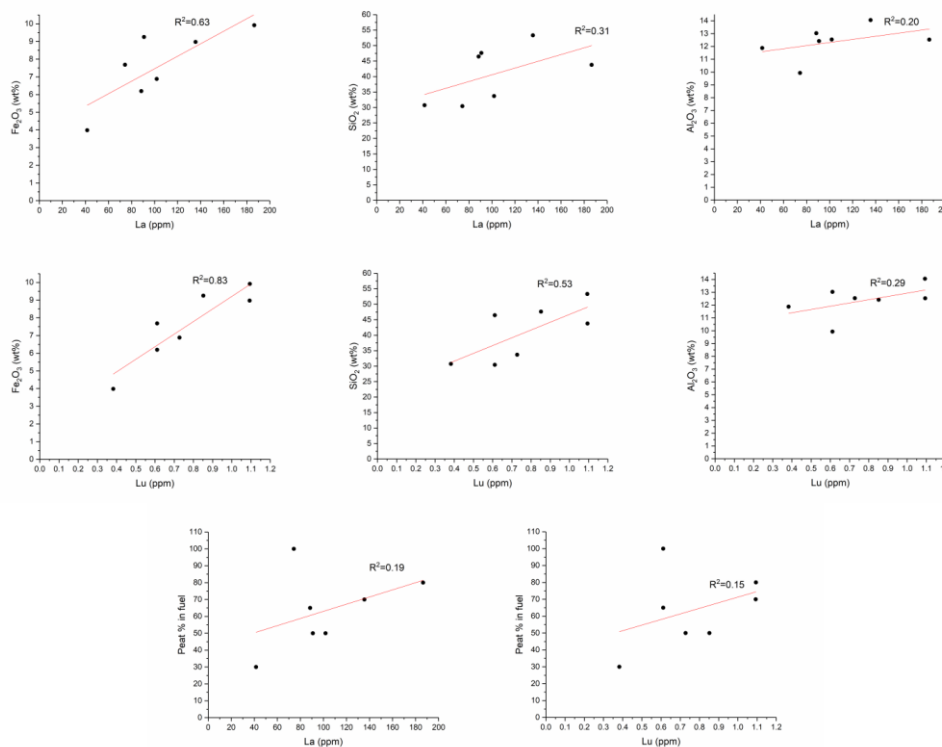


Fig. 4. Content of Fe_2O_3 , SiO_2 , and Al_2O_3 (wt%) and peat percentage of fuel as functions of La and Lu concentrations (ppm) in fly ashes.

4 Conclusions

This paper is the first to present REE concentrations in fly ashes from commercial CHP plants using peat and biomass as fuel, and to produce new information about REE occurrence in bio-based fly ashes. The observed REE concentrations at an average of 530 ppm were significantly higher than previously reported for biomass fly ash, and were similar to those of coal fly ash. Five of the seven fly ashes were classified promising for economic recovery of REEs according to the outlook coefficients and the concentration of critical REEs. The studied fly ashes were enriched with medium or light REEs and had concentrations up to 6 times higher compared to the UCC. Positive Gd anomalies, and some Ce, Eu, La, and Y anomalies, were present in the UCC normalized REE distributions, most likely originating from Finnish bedrock of granitic rock and migmatites. REEs we found to be associated with iron, and to some extent with silicon and aluminum, suggesting REE associations with iron minerals and possibly with aluminosilicates in biomass and peat fly ash.

Declaration of interest

One of the funders of this work, Jyväskylä Energy Group has a patent (Patent no. FI123432B) where two of the authors, S.P. and A.V., are included as inventors. The patent is based on previous research collaboration related to the topic of this paper.

Role of the funding source

The fly ash samples and information about the fuel composition and combustion process were received from Jyväskylä Energy Group. The funders had no role in research design or in

the collection, analysis and interpretation of the data or in the writing of the paper. Nor did they have any role in the decision to submit the paper for publication.

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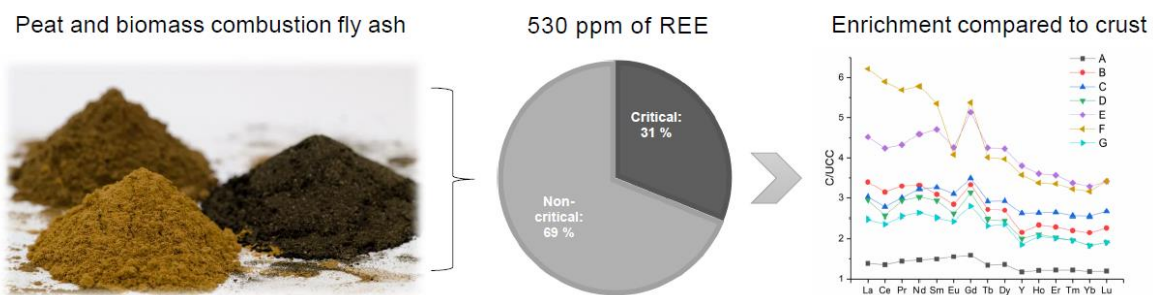
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Graphical abstract



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Highlights:

- Average REE concentration of 530 ppm, up to 920 ppm in one fly ash
- Five out of seven fly ashes found promising for profitable REE recovery
- REE distributions exhibit enrichment for medium or light REE
- Correlation found between REE and Fe indicating REE associations with iron minerals
- Ce, Eu, La, Gd, and Y anomalies present in fly ashes

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