



Full Length Article

Coal and sewage sludge ashes as sources of rare earth elements



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HIGHLIGHTS

- REY distributions in ashes of a bituminous coal and three sewage sludges were studied.
- REY concentrations in sludge ashes are lower than in coal ashes, excepting for La.
- Correlations and associations between major and minor elements and REY were obtained.

ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form 1 December 2016

Accepted 7 December 2016

Available online 18 December 2016

Keywords:

Rare earth elements

Bituminous coal

Sewage sludge

Ashes

ABSTRACT

Rare earth elements together with Y and Sc (REY) are essential in the development of technology for clean and efficient use of energy. Apart from the potential of coal and sewage sludge as energy resources, the enrichment of REY in their ashes may provide a feasible source of them. The concentrations of REY in ashes obtained at 800 and 1100 °C of a bituminous coal and three types of sewage sludge were determined. Also, their relationships with major and minor elements and minerals were studied. The concentrations of REY, excepting for La, are higher in the coal ashes than those of the sludge ashes. In both types of materials, REY are associated with the inorganic matter, although the associations are different for the coal than for the sludges. In the coal ashes, La, Ce, Pr and Nd are mainly associated with silicates and aluminosilicates in ashes at 800 and 1100 °C. The rest of REY (excepting Sm and Yb) are associated with carbonates in ashes at 800 °C and with sulphates in ashes at 1100 °C. In the sludge ashes, Y is associated with carbonates, while other REY are mainly associated with phosphates, silicates and aluminosilicates.

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1. Introduction

Scandium (Sc) and yttrium (Y), together with rare earth elements (REE), which include 15 lanthanides, were incorporated to a list of raw materials defined by the European Union as critical materials due to their risks of supply shortage and impact on the economy [1]. Although promethium (Pm (61)) is also a rare earth element, it is not usually included in the studies about REE because it is not found naturally on earth. According to the nomenclature used by Blissett et al. [1], the following elements, whose atomic numbers are indicated in brackets, can be named by the acronym (REY): Sc (21), Y (39), La (57), Ce (58), Pr (59), Nd (60), Sm (62), Eu (63), Gd (64), Tb (65), Dy (66), Ho (67), Er (68), Tm (69), Yb (70), Lu (71). Sc (21) and Y (39) plus the light REE (LREE), with lower atomic numbers, from La (57) to Sm (62), are more abundant than those with higher atomic numbers (HREE) from Eu (63) to Lu (71).

REY play an important role in the development of alternative power and energy efficient technologies. Y is a basic component of superconducting electric power lines, whilst Nd, Pr, Sm, Dy and Tb are important components for super-power permanent magnets [2,3]. They are needed in industrial generators, since they can transform renewable energies into electricity effectively [2,3]. Moreover, REY are commonly used in hybrid and electric vehicles, while phosphors of Y, Eu, and Tb are components of compact fluorescent lights and light-emitting diodes [2,3]. These elements were therefore considered critical by the European Commission in 2010, since their use is increasing rapidly in several clean technologies, which include alternative power and energy saving applications [1].

The main sources of REY are carbonatites and weathered crust elution-deposited ores [2]. On the one hand, some carbonatite deposits have high REY contents and large reserves, but usually only of LREE [2]. Weathered crust elution-deposited ores, on the other hand, are characterised by low REY content, providing scarce reserves of these elements, although their exploitation is easy [2,4]. Other REY sources are coal deposits [2,3]. Generally, in coals, REY

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are associated with clay-like minerals, silicates, feldspars, oxyhydroxides, phosphates, sulphates, sulphides and carbonate minerals [5–7]. Moore and Esmaeili [8] concluded that REY in coals can be associated with kaolinite, hornblende, biotite and muscovite. Associations of REY with organic matter were also reported [7,9–11].

In addition, coal fly ashes can be a REY source, since these elements are concentrated in ashes. The knowledge of the composition of REY in ashes is important to evaluate the recovery potential of these elements for their uses in energy-efficient technologies [2–4]. Thus, there exist several studies that evaluate the REY content of coal fly ashes [1,5,7,11–13]. Blisset et al. [1] studied fly ashes of one anthracite and two bituminous coals from the United Kingdom and three bituminous coals from Poland. The REY distribution in fly ashes was similar in the studied coals, although the highest concentrations (commercially viable) were found for the fly ash of a coal from the UK [1]. Dai et al. [11] studied how the concentrations of REY vary from the coarsest to the finest fractions of the fly ashes produced from a high volatile bituminous coal from China in a 200-MW power plant. They found that there is an enrichment of all REY in the finer fly ash [11]. They also observed that La, Ce, Pr and Nd occur in minerals within some glassy phases in the fly ash [11]. Investigating the fly ashes resulting from the combustion of bituminous coal and lignite, Franus et al. [5] observed the existence of relationships between REY and aluminium and silicon oxide contents. Similarly, Querol et al. [12] found that REY occurred in glassy aluminosilicates areas of fly ashes and slags. REY were also found associated with minerals, such as carbonates and phosphates, in fly ashes from coals. Thus, Dai et al. [11] identified REY-bearing calcite in fly ashes, and, in ashes from a coal-fired plant in Poland, Smolka-Danielowska [14] found cerium monazite (Ce,La,Nd,Sm,Th,U)(PO₄). Vassilev and Menendez's studies [13] revealed that Ce, Gd and Tb can be recovered from coal fly ashes produced in Spanish thermo-electric power stations, in an environmentally safe way, if they are previously divided into fractions rather than using the highly heterogeneous bulk fly ashes.

Not only ashes from coals but also ashes from biomass and wastes can be a source of REY. Allegrini et al. [15] found that REY concentrations in the ashes from municipal solid waste (MSW) incineration were two or three orders of magnitude lower than typical ore concentrations. Vassilev and Braekman-Danheux [16] found that refuse-derived char and ashes from MSW may be a potential source for the recovery of REY among other valuable elements. Therefore, for recovering REY from this type of ashes, only wastes with an adequate REY content should be incinerated. This would require a better knowledge of the waste streams, as well as the sampling enhancement, preparation and analysis of heterogeneous waste streams, which was proposed by Morf et al. [17] as a way to make REY recovery from wastes feasible. Regarding sewage sludge, Kawasaki et al. [18] have shown that this type of sludge can be contaminated with REY, since their concentration is higher than the crust-normalized pattern of REY. As the combustion of the sludge concentrates REY, sludge ashes may be a source of these elements. However, from the study of the sludge ashes of 26 incineration facilities for sewage sludge in Germany, Krüger et al. [19] found that the sum of REY was between 36.6 and 729 ppm with a mean of 136 ppm, which is within the range reported for the earth's crust (160–242 ppm) and soils (131–322 ppm).

As some published studies [19,20] have reported, REY concentrations in incinerator and coal ashes are low, which means that the recovery of these elements is unlikely to be very profitable unless this recovery were part of a comprehensive, zero-waste, "product-centred" valorisation scheme. Thus, the knowledge of the concentrations of REY in ashes from different sources is vital in order to design an adequate process and to determine the

mixture of wastes that would make this recovery feasible and profitable.

Coal is still one of the most important primary energy resources in the world, whereas sewage sludge may come to be an alternative by means of its combustion or its co-combustion with coal. Coal and sludge combustion produces significant quantities of ashes, which may be also used as a source of REY, thus achieving further exploitation of these materials. Accordingly, the main objective of this study is to find out if coal and sludge ashes may be a suitable source of REY. Thus, three samples of a bituminous coal with high carbonate content and three types of sewage sludge with different sludge treatments were chosen. The coal comes from a coal mine sited in Asturias (Spain). REY concentrations of ashes obtained at 800 and 1100 °C of the samples were determined and compared to the Clarke values for hard coal ashes and other concentrations reported in the literature. Moreover, the associations of REY with major and minor elements and minerals in ashes were also studied in order to find out which types of inorganic and mineral matter of coal may be related to higher concentrations of REY and if sludge treatment may influence the above concentrations in any way.

2. Experimental

2.1. Materials

Three different samples of a bituminous coal and samples of three types of sewage sludge were used. The bituminous coal (coal C) comes from a coal mine in the NW of Spain (Asturias). The three sewage sludges (L, V and F) come from three wastewater treatment plants that are also in the NW of Spain. Sludges V and F come from Asturias and sludge L comes from León. During the stabilisation and chemical conditioning treatments carried out in the urban wastewater treatment plants, sludge F was treated with Ca(OH)₂ and FeCl₃ and sludge V with FeCl₃ and organic polyelectrolyte. Sludge L, however, underwent anaerobic digestion and was treated with lime.

2.2. Ashes obtained at different temperatures (800 and 1100 °C) and analysis methods

To study REY in the ashes of coal C and the sludges (L, F and V), their combustion was conducted in an electric laboratory furnace under an atmosphere of dynamic air at the temperatures 800 and 1100 °C. Samples of 3 g (ground at <200 μm) were spread out in a layer about 0.5 cm thick at the bottom of ceramic crucibles (8 cm diameter and 2 cm height) and, then gradually heated at a rate of 10 °C/min up to 800 or 1100 °C, maintaining the final temperature for one hour.

Major and minor elements of ashes obtained at the above temperatures were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) after a LiBO₂ fusion.

REY in the ashes and unburnt samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) and ICP-atomic emission spectrometry (ICP-AES).

The crystalline minerals of the ashes obtained at 800 and 1100 °C were identified by X-ray diffraction (XRD). The diffractograms were obtained using a Philips X'Pert PRO powder diffractometer. Diffraction intensities were recorded in the 2θ range of 5–65°.

3. Results and discussion

3.1. Ash characterisation and REY concentrations

The data obtained from ash characterisation are seen in Table 1, which shows the major and minor elements of ashes obtained at

Table 1

Major and minor elements of ashes at 800 °C expressed as oxides (mean ± standard deviation, 3 measurements) and ash yields at 800 °C and 1100 °C.

	Coal C ₁ (wt%)	Coal C ₂ (wt%)	Coal C ₃ (wt%)	Sludge L (wt%)	Sludge V (wt%)	Sludge F (wt%)
SiO ₂	6.00 ± 0.17	10.5 ± 0.9	7.79 ± 0.08	40.3 ± 0.3	44.4 ± 0.3	23.7 ± 0.2
Al ₂ O ₃	5.5 ± 0.2	9.4 ± 0.7	6.82 ± 0.10	15.06 ± 0.10	11.94 ± 0.01	8.6 ± 0.4
Fe ₂ O ₃	13.2 ± 0.5	17.3 ± 1.5	14.50 ± 0.11	6.87 ± 0.01	15.47 ± 0.09	21.59 ± 0.10
MgO	4.54 ± 0.17	6.2 ± 0.5	6.51 ± 0.05	2.18 ± 0.01	2.17 ± 0.01	2.02 ± 0.01
CaO	44.1 ± 1.5	38 ± 3	45.4 ± 0.2	12.73 ± 0.04	7.1 ± 0.2	34.03 ± 0.14
Na ₂ O	0.06 ± 0.01	0.10 ± 0.02	0.09 ± 0.01	0.43 ± 0.02	0.22 ± 0.04	0.17 ± 0.04
K ₂ O	0.28 ± 0.04	0.50 ± 0.05	0.40 ± 0.05	2.26 ± 0.02	3.06 ± 0.01	0.78 ± 0.03
TiO ₂	0.10 ± 0.00	0.19 ± 0.02	0.15 ± 0.01	0.86 ± 0.01	0.70 ± 0.01	0.42 ± 0.00
P ₂ O ₅	0.04 ± 0.00	0.17 ± 0.01	0.11 ± 0.02	16.74 ± 0.11	12.7 ± 0.3	4.64 ± 0.01
MnO	0.26 ± 0.01	0.26 ± 0.02	0.27 ± 0.00	0.06 ± 0.00	0.05 ± 0.00	0.33 ± 0.00
Cr ₂ O ₃	0.007 ± 0.001	0.010 ± 0.000	0.009 ± 0.003	0.180 ± 0.002	0.028 ± 0.001	0.061 ± 0.001
CO ₂	7.9 ± 0.3	1.82 ± 0.02	1.06 ± 0.03	0.26 ± 0.01	0.15 ± 0.04	0.42 ± 0.04
SO ₃	18.1 ± 0.9	15.3 ± 1.3	16.9 ± 0.2	2.06 ± 0.03	1.95 ± 0.02	3.24 ± 0.03
Ash ^a	6.48	5.89	6.44	27.40	34.57	47.58
Ash ^b	6.26	5.81	6.39	26.76	33.80	45.57

^a Ash yield (dry basis) obtained at 800 °C.^b Ash yield (dry basis) obtained at 1100 °C.**Table 2**

REE contents (mean ± standard deviation, 3 measurements) in the ashes at 800 °C of the coal and the sludges together with the Clarke values for hard coal ashes.

REE	Bituminous coal ashes (ppm)			Sludge ashes (ppm)			Clarke's for hard coal ashes [21]
	C ₁	C ₂	C ₃	L	V	F	
Sc	40.0 ± 1.4	24.4 ± 1.4	13.6 ± 0.7	9.1 ± 0.2	6.2 ± 0.5	5.5 ± 0.4	23
Y	126 ± 4	105 ± 8	95 ± 5	13 ± 3	11 ± 4	14.2 ± 1.5	51
La	21.0 ± 0.1	42 ± 3	33 ± 2	34.0 ± 0.2	31 ± 3	23 ± 3	69
Ce	64.7 ± 1.0	113 ± 7	90 ± 6	64 ± 3	63 ± 6	45.4 ± 0.3	130
Pr	9.9 ± 0.1	15.3 ± 0.6	12.0 ± 0.9	6.6 ± 0.1	6.1 ± 0.6	4.7 ± 0.2	20
Nd	58.3 ± 1.4	80 ± 6	67 ± 5	25.4 ± 1.0	26 ± 2	21.5 ± 0.8	67
Sm	21.2 ± 0.6	22.9 ± 1.5	19.9 ± 1.6	5 ± 0.2	4.8 ± 0.4	4.0 ± 0.1	13
Eu	6.3 ± 0.1	5.9 ± 0.3	4.9 ± 0.4	1.0 ± 0.0	0.7 ± 0.1	0.6 ± 0.1	2.5
Gd	30.7 ± 0.8	27.0 ± 1.7	23.6 ± 1.4	3.3 ± 0.3	3.4 ± 0.4	3.3 ± 0.2	16
Tb	4.7 ± 0.1	3.7 ± 0.2	3.4 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	2.1
Dy	25.1 ± 0.6	19.4 ± 0.9	16.4 ± 1.3	2.3 ± 0.6	2.1 ± 0.5	2.2 ± 0.1	14
Ho	4.5 ± 0.1	3.3 ± 0.2	2.8 ± 0.2	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	4.0
Er	11.4 ± 0.4	8.1 ± 0.7	7.6 ± 0.4	1.1 ± 0.4	1.1 ± 0.3	1.3 ± 0.2	5.5
Tm	1.5 ± 0.1	1 ± 0.1	0.8 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.0	2.0
Yb	8.3 ± 0.5	6.6 ± 0.3	5.5 ± 0.7	1.1 ± 0.4	1.2 ± 0.2	1.3 ± 0.3	6.2
Lu	1.2 ± 0.1	0.8 ± 0.1	0.7 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	1.2

800 °C and ash yields at 800 and 1100 °C. As can be seen in Table 1, there are significant differences in the compositions of the ashes at 800 °C.

The ashes of coal C show higher CaO contents than sludge samples, which is due to the high calcium carbonate content of this coal. For sludge ashes, the SiO₂ content is higher than in the coal ashes, being very high in V ash (44.4 wt%) and L ash (40.3 wt%). Moreover, the sludge ashes have a much higher P₂O₅ content (ranging from 4.64 to 16.74 wt%) than the coal ashes (0.04–0.17 wt%). Due to the addition of FeCl₃ to sludges V and F, their ashes have high concentrations of Fe₂O₃ (15.5 and 21.6 wt%, respectively).

Table 2 shows the concentrations of REY in the ashes obtained at 800 °C of the coal samples (C₁, C₂ and C₃) and the sludges L, V and F. Clarke REY concentrations for hard coal ashes [21] are also included in Table 2. In Fig. 1, the distribution of REY concentrations in coal ashes at 800 °C is shown. The REY concentrations in ashes obtained at 1100 °C are higher than in those obtained at 800 °C.

The bituminous coal ashes have the highest concentrations of Y, Ce and Nd (between 58 and 126 ppm) and the lowest ones of Eu, Tb, Ho, Tm and Lu (between 0.7 and 6.3 ppm). As can be seen in Table 2, the concentrations of Y in the three samples of coal ashes are approximately double the Clarke values for hard coal ashes. Also, the Sm, Eu, Gd, Dy and Er concentrations are higher than the Clarke values. According to Seredin and Dai [3] and taking into account the likely supply and demand forecast of REY over the next

few years, Y, Eu, Dy, Er and Tb, together with Nd, are critical elements. Vassilev and Menendez [13] studied the potential to recover various trace elements from the fly ashes produced in four large Spanish thermo-electric power plants, including Ce, Gd, Tb and Sc. The mean concentrations of these elements were around 120, 7, 0.5 and 50 ppm, respectively, the concentrations of Gd and Tb being significantly lower than those of the bituminous coal of this work. They proposed various procedures of separation and concentration, which were useful for Ce, Gd and Tb, but not for Sc. Thus, Ce was enriched in the ceramic cenosphere concentrate and in the improved fly ash residue, Gd in the heavy concentrate and in the improved fly ash residue and Tb in the char concentrate.

The sludge ashes obtained at 800 °C and 1100 °C have lower concentrations of REY than the coal ashes. Also, other researchers [16] found that the high temperature ashes of refuse-derived char from MSW have lower Y, Pr, Sm and Ho concentrations than the Clarke values for coal ashes. The distributions of REY concentrations in the sludge ashes obtained at 800 °C are shown in Fig. 2. As can be seen, these distributions are similar in the three sludge ashes, although slightly different to those of the coal ashes. Thus, La concentration is much lower than that of Y and Ce in the coal samples, but it is intermediate between Y and Ce in sludges L, V and F. Moreover, Ce concentrations are higher than any of the other REY in the sludge ashes (around 63 ppm for sludges L and V, and 45 ppm for sludge F), although these levels of Ce are lower than those observed in coal ashes C₂ and C₃. Kawasaki et al. [18],

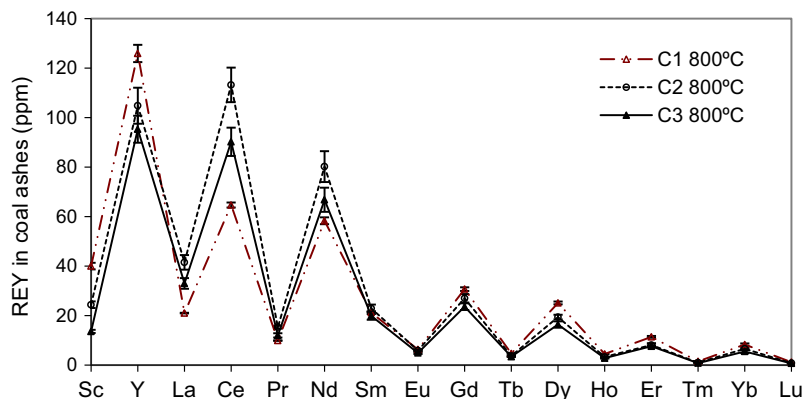


Fig. 1. REY distribution in the bituminous coal ashes obtained at 800 °C (error bars correspond to the standard deviation of three measurements).

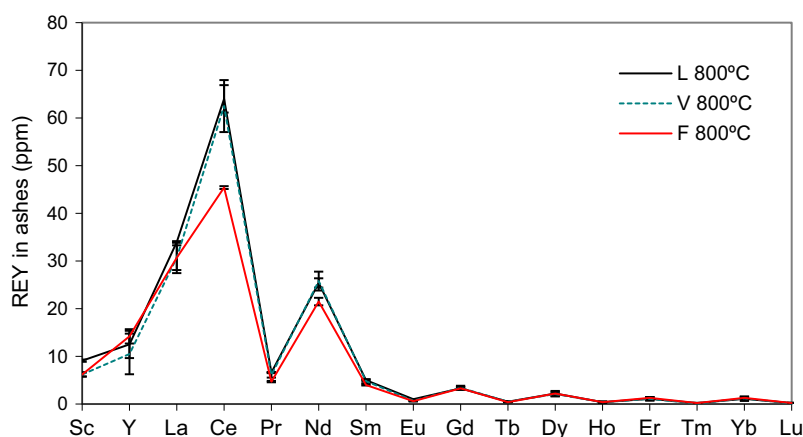


Fig. 2. REY distribution in the ashes obtained at 800 °C from sludges L, V and F (error bars correspond to the standard deviation of three measurements).

analysed 14 samples of sewage sludge and obtained a mean concentration of Ce of 14.1 ppm, the maximum being 37.9 ppm. La and Nd concentrations in the sludge ashes are relatively high, ranging from 23 to 34 ppm and from 22 to 26 ppm, respectively. Again, these concentrations are higher than those obtained by Kawasaki et al. [18], whose mean and maximum values were, respectively, 6.7 and 13.6 for La and 6.0 and 13.4 for Nd. For the rest of REY, their concentrations in the sludge ashes are lower than 15 ppm.

As was previously mentioned, Y, Sm, Eu, Gd, Dy and Er concentrations in the coal ashes are higher than the respective Clarke values, the majority of these elements being critical in the development of clean technologies.

3.2. Minerals detected by XRD in ashes

Some authors [10,14,22] found REY in association with minerals in ashes, so it was important to know what minerals are present in the ashes investigated in this study. In Figs. 3 and 4, the XRD diffractograms of the coal and sludge ashes can be seen.

In coal ashes at 800 °C, the following minerals were detected: lime (CaO), anhydrite (CaSO₄), portlandite (Ca(OH)₂), periclase (MgO), iron oxides (Fe₂O₃ and Fe₃O₄), srebrodolskite (2CaO·Fe₂O₃), larnite (2CaO·2SiO₂) and gehlenite (2CaO·SiO₂·Al₂O₃) (Fig. 3). The presence of these minerals indicates that during combustion CaO reacted with Fe₂O₃ and SiO₂ to form ferrites and silicates. Moreover, C₁ ashes at 800 °C contain a large quantity of carbon, much more than C₂ and C₃ ashes (Table 1), which is related to the presence of non-decomposed carbonates (calcite).

During heating to 1100 °C, the reactions between CaO and Fe₂O₃ or SiO₂ continue, which explains the higher quantities of 2CaO·Fe₂O₃, 2CaO·2SiO₂ and 2CaO·SiO₂·Al₂O₃ in C ashes at 1100 °C compared to those seen in the ashes at 800 °C. As C₁ has the highest molar (CaO/Fe₂O₃) ratio, iron oxides (Fe₂O₃ and Fe₃O₄) react completely with CaO, which is why iron oxides are not detected in C₁ ashes at 1100 °C.

In the ashes of the sewage sludges at 800 °C, there are quartz (SiO₂), aluminosilicates and phosphates (Fig. 4). The aluminosilicates detected in L ash were anorthite (CaO·Al₂O₃·2SiO₂) and dehydroxylated muscovite (KAl₃Si₃O₁₁), while triiron dialuminium tris (silicate) (Fe₃Al₂(SiO₄)₃) was detected in V ash and gehlenite (2CaO·Al₂O₃·SiO₂) in F ash. Apart from these minerals, there is anhydrite (CaSO₄) in L and V ashes and larnite (2CaO·SiO₂) in F ash. Also, there is iron oxide (Fe₂O₃) in V and F ashes.

In the ashes of the sewage sludges at 1100 °C, quartz (SiO₂), aluminosilicates and phosphates were also found (Fig. 4). Moreover, due to the heating up to 1100 °C, anhydrite of L and V ashes undergoes desulphation.

3.3. REY associations in both the bituminous coal ashes and the sludge ashes

REY concentrations in the unburnt samples and in the ashes at 800 and 1100 °C show that there was no volatilisation of these elements in any of the samples (bituminous coal and sludges) during the combustion process. This lack of volatilisation occurs even in sludges F and V, in spite of the fact that they have high chlorine

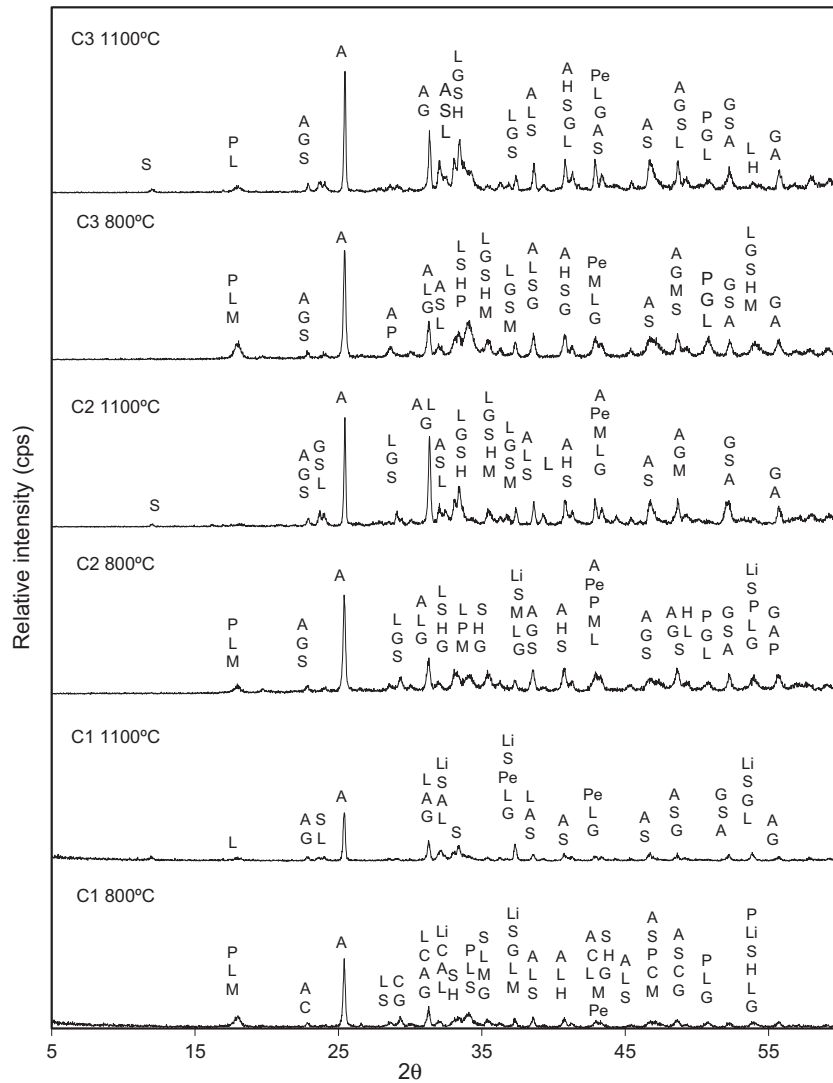


Fig. 3. Minerals detected by XRD in the coal ashes (C₁, C₂ and C₃) obtained at 800 and 1100 °C. Minerals: A, anhydrite; C, calcite; G, gehlenite; H, hematite; L, larnite; Li, lime; M, magnetite; P, portlandite; Pe, Periclase; S, srebrodolskite.

contents, 1.49 and 0.67 wt% (db) respectively, due to their treatment with FeCl₃ in the wastewater treatment plants. Chlorine can form volatile chlorides with certain trace elements, such as Ag, Cd, Cs, Cu, Li, Pb, Rb and Tl [23]. Thus, REY concentrations in the unburnt samples and in the ashes at 1100 °C can be easily calculated from those of ashes at 800 °C taking into account the ash yield at 800 and 1100 °C. In contrast to this, Dai et al. [11] found some volatilisation of REY after coal combustion in a power plant, which was indicated by the enrichment of some REY in the finer sized fractions. As elements associated with organic matter and sulphides tend to vaporize and then be adsorbed on fine particles when flue gas temperature decreases, they attributed this volatility to REY organic-bound modes of occurrence. Also, Vassilev and Vassileva [7] asserted that some REY, such as Y, La and Sc, may be released into the atmosphere due to coal combustion in thermo-electric power plants. Their study indicates that the modes of occurrence of the trace elements have a significant influence on their migration. Therefore, the lack of REY volatility in the samples studied in this work may be due to the fact that they are mainly associated with the inorganic matter. However, there are other factors that influence on trace element volatilisation, such as fuel preparation, burning process, size of minerals and phases containing trace elements and their physico-chemical properties [7].

3.3.1. REY associations in the bituminous coal ashes

In this section, the relationships between major and minor element concentrations and those of the REY in coal ashes are studied. Thus, Figs. 5–7 show some relationships found as well as the correlation coefficient ranges.

3.3.1.1. Scandium (Sc), yttrium (Y) and HREE (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). For these elements, the concentrations in C₁ ashes at 800 °C are higher than those in C₂ and C₃ ashes. Moreover, carbon concentration (expressed as CO₂) in C₁ ash at 800 °C is much higher than in C₂ or C₃, which indicates that there are higher quantities of carbonates in C₁ than in the C₂ and C₃ samples. Thus, the higher Sc, Y and HREE concentrations in C₁ ashes may be related to the presence of these carbonates. By XRD, calcite was detected in C₁, but not in C₂ or C₃ ashes. There exist positive linear relationships between these REY concentration and CO₂ concentration in C ashes at 800 °C (R² ranges from 0.7 to 0.9, excepting for Eu with a R² value equal to 0.4). Fig. 5 shows the relationships for Y, Tb and Dy. This indicates that C ashes at 800 °C contain REY-bearing carbonates. Dai et al. [11] detected Y in REY-bearing calcite and CaCO₃ in the fly ashes from a Chinese coal. Seredin and Dai [3] reported that, in some coal basins, the concentrations of those REY that play a key role in clean energy development (Nd, Eu, Dy, Tb, Y) are high,

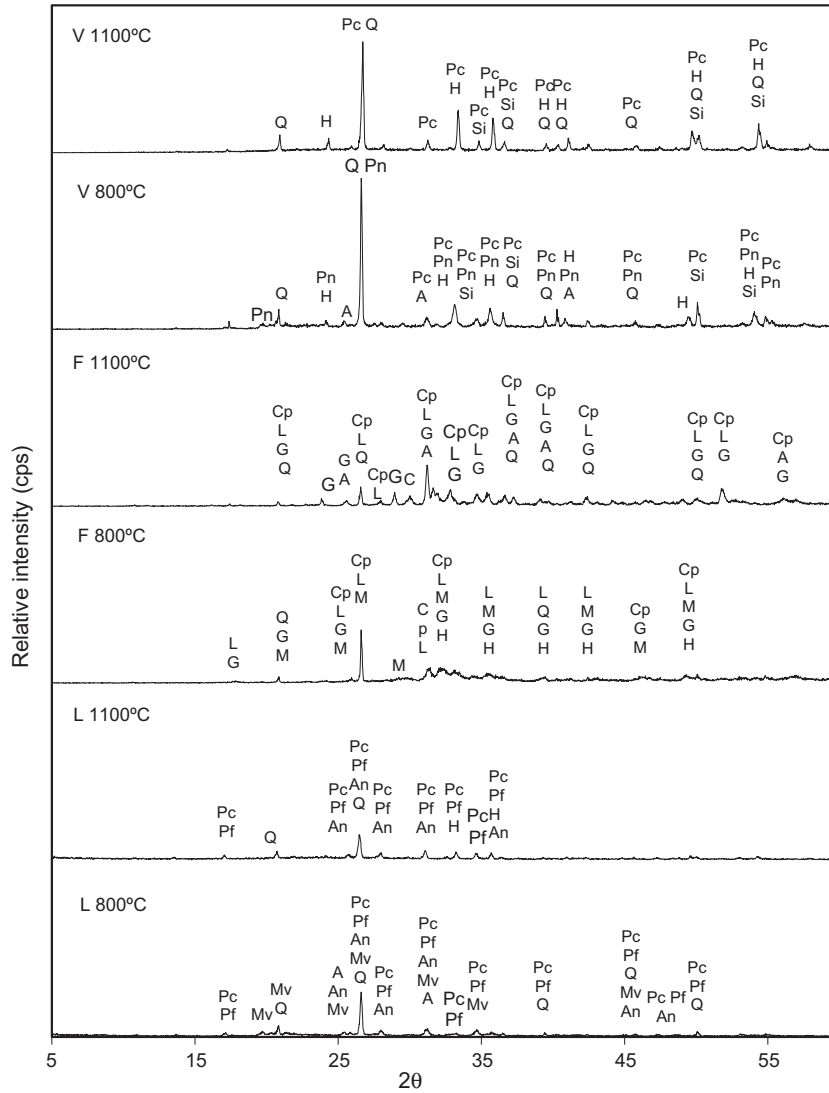
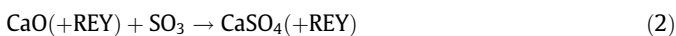


Fig. 4. Minerals detected by XRD the sludge ashes (V, F and L) obtained at 800 and 1100 °C. Minerals: A, anhydrite; An, anorthite; Cp, chlorapatite; G, gehlenite; H, hematite, L, larnite; M, magnetite; Mv, dehydroxylated muscovite; Pc, calcium magnesium phosphate; Pf, noncalcium iron phosphate; Pn, sodium iron phosphate; Q, quartz; Si, triiron dialuminium tris(silicate).

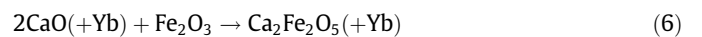
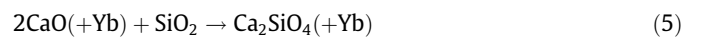
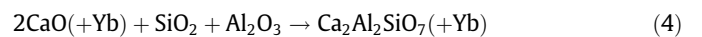
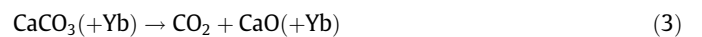
even higher than those of conventional REY ores. These coals usually contain authigenic minerals such as hydrous phosphates, Al phosphates, carbonates and fluorocarbonates.

Unlike ashes at 800 °C, for C ashes at 1100 °C, there exist positive linear relationships between these REY concentrations, excepting Eu and Yb, and SO₃ concentrations (the correlation coefficients range from 0.6 to 0.8) (Fig. 5). Anhydrite was detected in the ashes in the three C ash samples obtained at 1100 °C. The variation in these REY associations between ashes at 800 °C and at 1100 °C may be due to the fact that REY bearing – alkali and alkaline earth oxides released from carbonate decomposition react with SO₂ and O₂ to form sulphates. Sulphation of CaO released from calcite, ankerite and dolomite is reported to take place over the range of temperatures 500–1000 °C [24]. That is why REY are associated with the sulphates in the ashes at 1100 °C, since the reactions (1) and (2) occur:



For Yb, in C ashes at 1100 °C, there are positive linear relationships between Yb and SiO₂, Al₂O₃, Fe₂O₃, Na₂O, K₂O and TiO₂ and

the correlation coefficients range from 0.6 to 0.8. Fig. 6 shows these relationships. The variation in associations between the ashes at 800 and 1100 °C may be due to the following: on the one hand, in coal C, Yb is mainly associated with carbonates (CaCO₃) and the majority of these carbonates did not decompose on the heating up to 800 °C. Therefore, there is a good correlation between Yb and CO₂ at 800 °C. On the other hand, in the ashes obtained at 1100 °C, carbonates decomposed and Yb-bearing CaO reacted with SiO₂ and Al₂O₃ to form calcium aluminosilicates and with Fe₂O₃ to form calcium ferrite. This would explain why at 1100 °C there exist good correlations with SiO₂, Al₂O₃ and Fe₂O₃ and not with CaO because it is present in other minerals (Fig. 3). According to this, the following reactions (3)–(6) would be produced during heating:



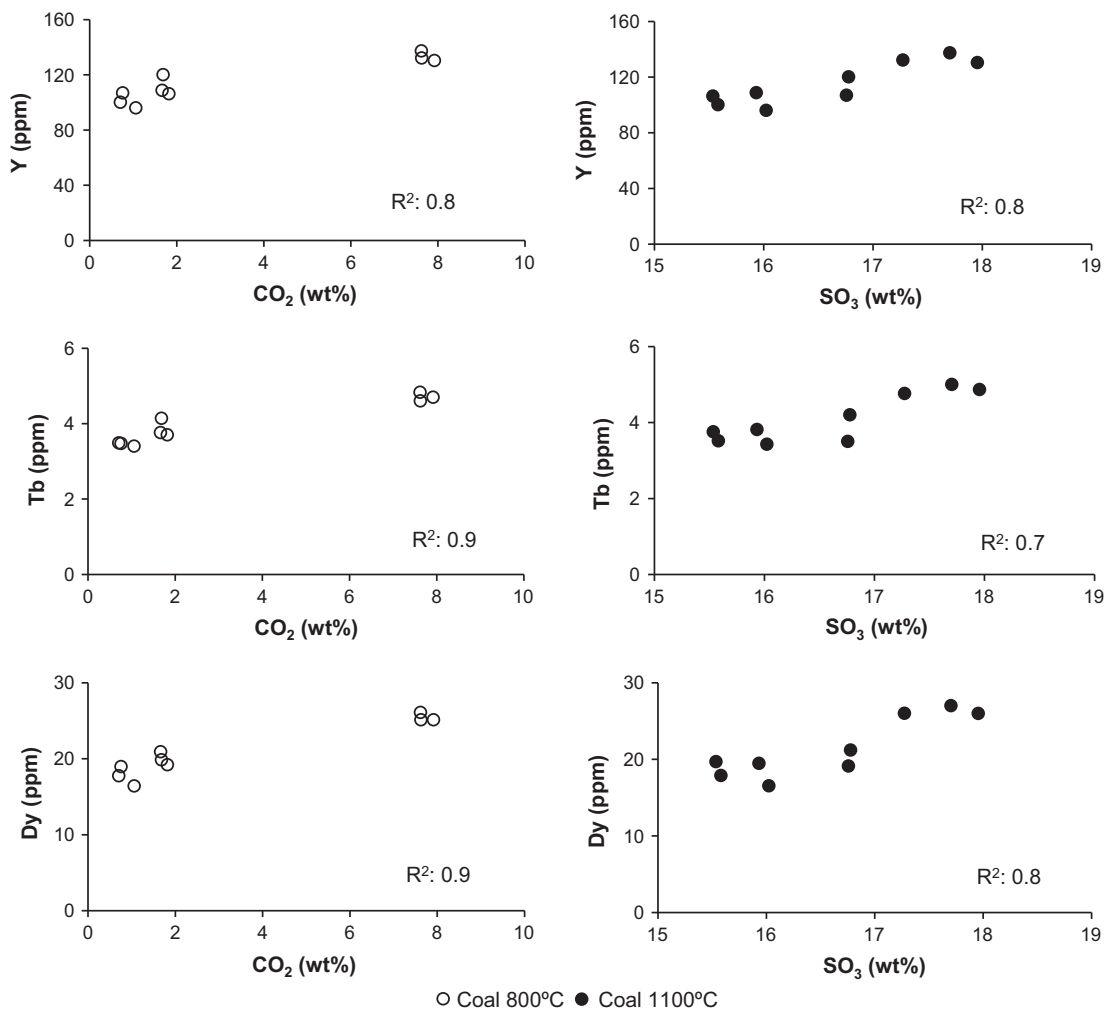


Fig. 5. Y, Tb and Dy versus CO₂ for coal ashes at 800 °C, and versus SO₃ for coal ashes at 1100 °C.

Minerals with Na₂O, K₂O, TiO₂ and P₂O₅ were not detected in C ashes. This may be due to the presence of amorphous compounds. Thus, there may be REY-glass association in these amorphous compounds. Hower et al. [25] reported REY-glass associations in coal fly ashes. Vassilev and Vassileva [7] studied several Bulgarian coals (from lignitic to anthracitic ones) that are burnt in thermoelectric power stations, as well as their ashes. They found that, in fly ashes, trace elements are commonly present as impurities in the glass phases and in the crystalline components. They also indicated that REE may be present in the crystal structure of zircon, apatite and feldspars, while Y in those of zircon and apatite [7].

3.3.1.2. LREE (La, Ce, Pr, Nd and Sm). For C ashes, apart from Sc and Y, the elements La, Ce, Nd and Sm have the highest concentrations together with Gd and Dy. Franus et al. [5] reported that LREE are dominant in coal fly ashes.

For the bituminous coal ashes at 800 °C and 1100 °C, there are positive linear relationships between La, Ce, Pr and Nd concentrations and those of SiO₂, Al₂O₃, Fe₂O₃, Na₂O, K₂O, TiO₂ and P₂O₅. Moreover, for La, also linear correlations with MgO were obtained, but their coefficients were lower, 0.7 in both cases. Fig. 7 shows the relationships for La. Also, for ashes at 800 °C, linear relationships were found between La, Ce, Pr, Nd and Cr₂O₃. For Sm, no correlations were found. In contrast to the relationships obtained, Dai et al. [11] detected La, Ce, Pr and Nd in REE-bearing calcite in fly ashes from a Chinese coal. However, Franus et al. [5] observed

the existence of relationships between REE and aluminium and silicon oxides contents. Thus, these elements may be mainly associated to silicates, aluminosilicates and ferrites. These types of minerals were detected by XRD in ashes at both 800 and 1100 °C (Fig. 3). The association of the above elements with Cr₂O₃ at 800 °C and not at 1100 °C may be explained by reaction (7), with the formation of CrCl₃, whose melting point is in the range 631–947 °C [24] and whose boiling point is below 1550 °C.



3.3.2. REY associations in the sludge ashes

As was previously seen, in the bituminous coal ashes, excepting Sm, the REY can be classified into two large groups according to their associations. However, in general, the associations in the sludge ashes are different from those in the coal ashes and it is not possible to establish two clear groups. Thus, with regard to the association of REY with major and/or minor elements, in the sludge ashes there are much more scattering. Figs. 8 and 9 show the relationships between Sm and Sc and major and minor element concentrations for the sludge ashes at 800 and 1100 °C as well as the correlation coefficient ranges.

3.3.2.1. LREE (La, Ce, Pr, Nd and Sm). For the sludge ashes at 800 and 1100 °C, there exist positive linear relationships between the LREE concentrations and those of SiO₂, Al₂O₃, MgO, Na₂O, K₂O, TiO₂ and

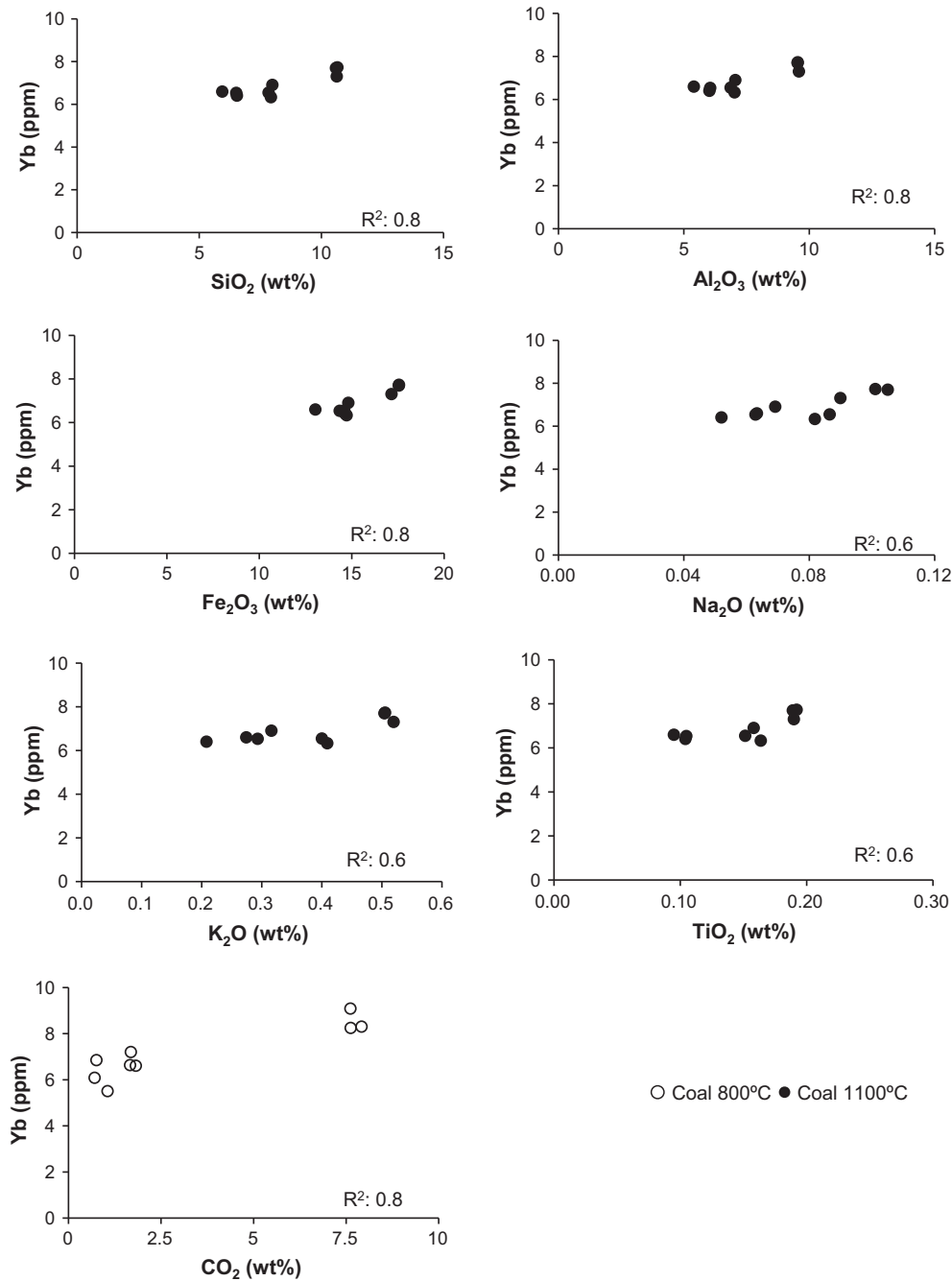


Fig. 6. Yb versus major and minor elements for coal ashes obtained at 800 and 1100 °C.

P₂O₅. Fig. 8 shows the relationships for Sm. Thus, in sludge ashes, La, Ce, Pr and Nd are associated with the same major and minor elements as in C ashes, except for Fe₂O₃ and, in the case of Nd, for Na₂O. There are no positive linear relationships for Fe₂O₃ due to the fact that an iron fraction comes from the addition of FeCl₃ to the sludges V and F. The correlation coefficients range from 0.6 to 0.9. Thus, these LREE may be associated with aluminosilicates and phosphates in the sludge ashes. Both types of minerals were detected by XRD.

For the ashes of eight samples of biomass including herbaceous, agricultural residues and algae obtained at 500 °C, Vassilev et al. [26] found positive relationships for La with phosphates and Ti, for Ce with Al and Ti, for Pr and Nd with Ti, Al and phosphates and for Sm with Si. The concentrations of LREE in the sludge ashes

are much higher than those of the biomass ashes analysed by Vassilev et al. [26]. In fact, for La, Ce, Pr and Nd, in the sludge ashes, the concentrations are around seventeen times higher than in the biomass ashes and, for Sm, five times higher.

3.3.2.2. Scandium (Sc) and Europium (Eu). In the sewage sludge ashes obtained at 800 and 1100 °C, there are good fits between Sc and Eu concentrations and those of Al₂O₃, Na₂O, TiO₂, P₂O₅ and Cr₂O₃, with correlation coefficients that range from 0.7 to 0.9. Fig. 9 shows the relationships for Sc. Probably, these elements are associated with phosphates and certain types of aluminosilicates, both detected in the sludge ashes by XRD (Fig. 4). A certain percentage of the phosphates in wastewater come from detergents, which are obtained from phosphate rock that contains Sc and Eu.

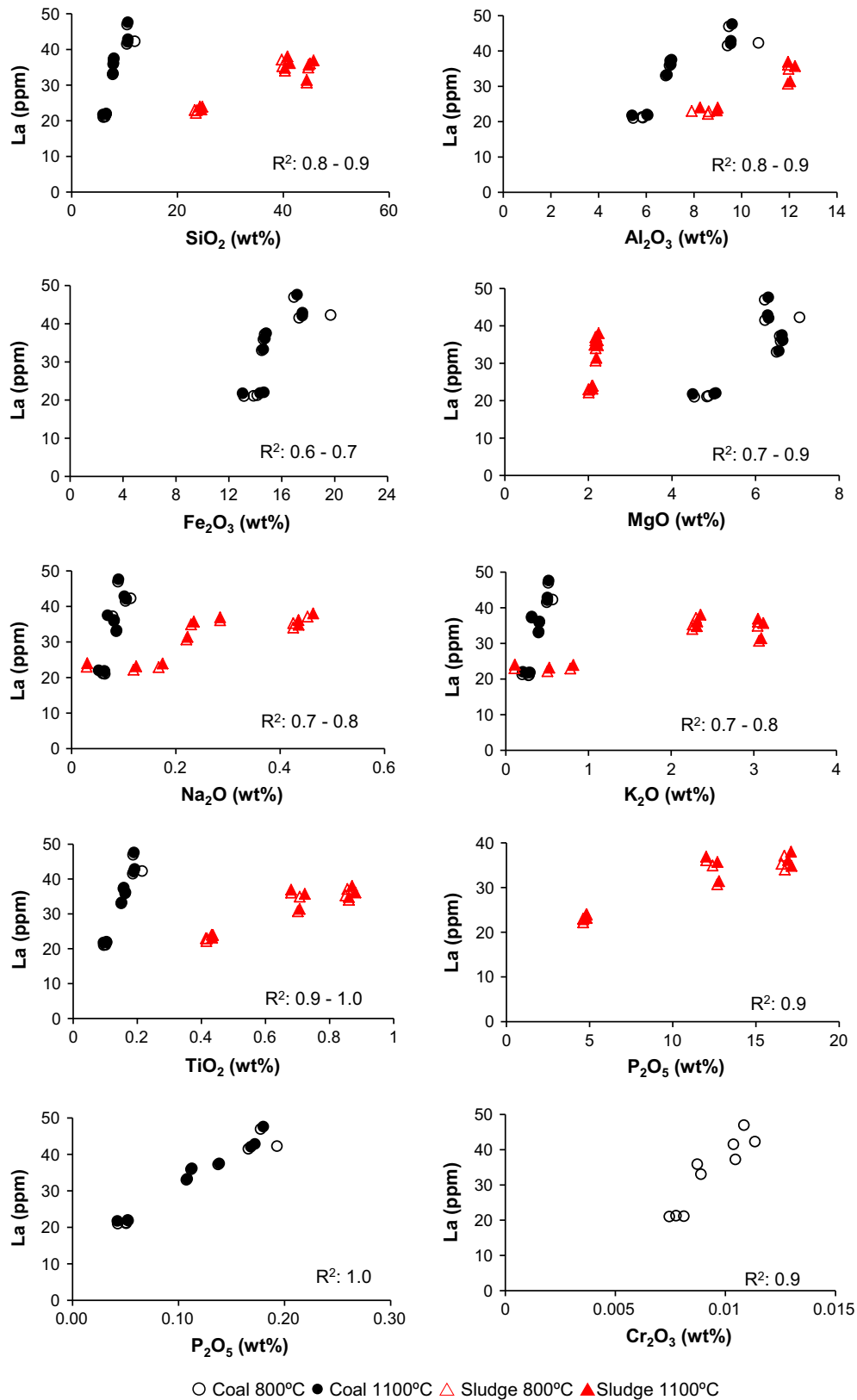


Fig. 7. La versus major and minor elements for coal and sludge ashes obtained at 800 and 1100 °C.

Sedimentary phosphate rocks contain high concentrations of heavy elements, such as U, Th and REE and environment polluting elements (Cd, As, Sb, V, Cr, Zn, Cu, Ni, etc.) [27,28]. Moreover, sludges usually contain clays and phyllosilicates that have associated REY.

After heating, these minerals undergo dehydration, REY-bearing silicoaluminates being produced (reaction (8)). For biomass ashes, Vassilev et al. [26] found strong positive relationships for silicates and Si with Sc and Eu.

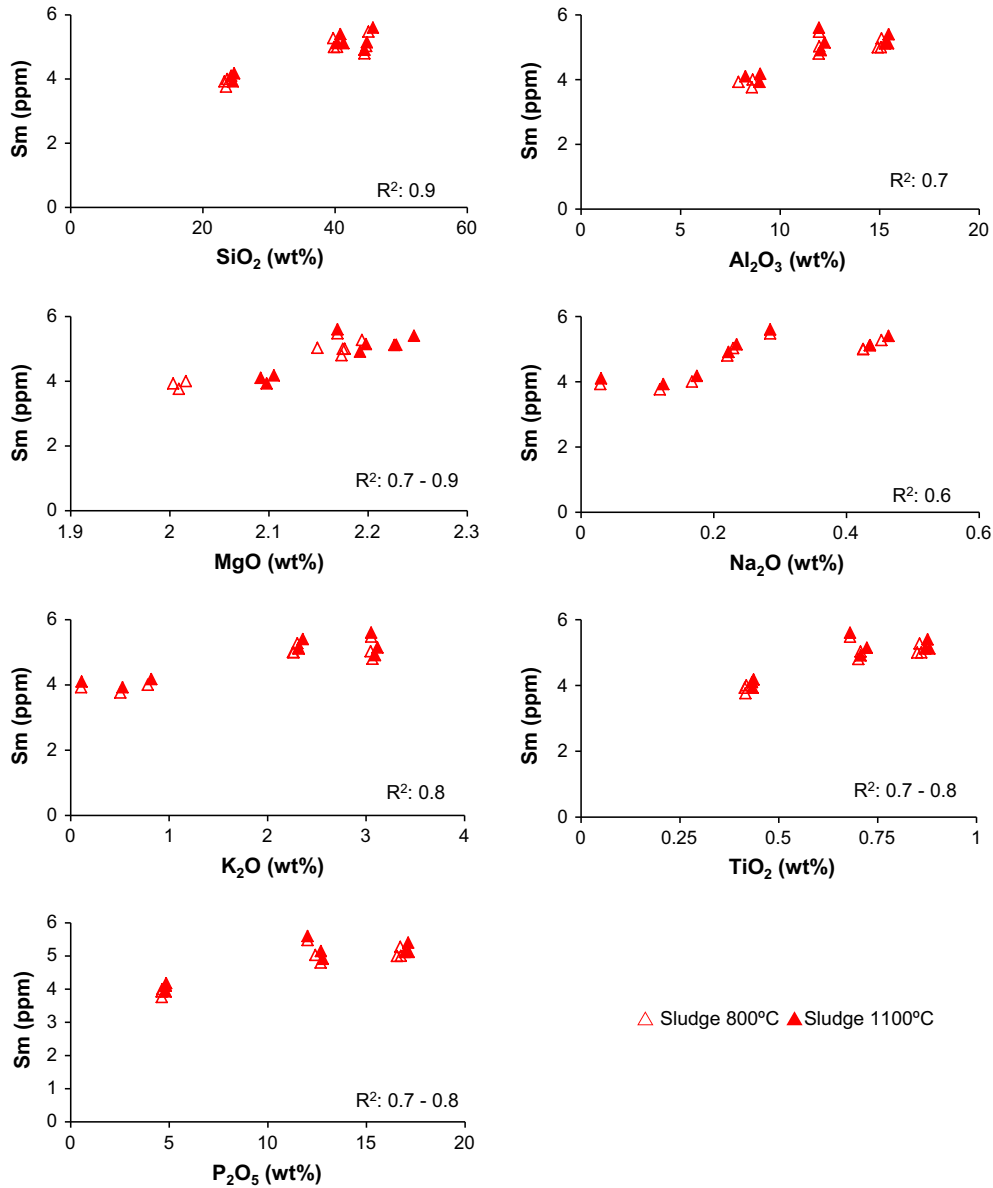
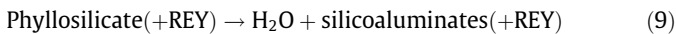
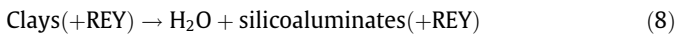


Fig. 8. Sm versus major and minor elements for sludge ashes obtained at 800 and 1100 °C.



3.3.2.3. *Yttrium (Y)*. For sludge ashes at 800 and 1100 °C, there are positive linear relationships between Y concentration and carbon concentration (expressed as CO₂), the correlation coefficients being 0.9 and 0.7, respectively. Therefore, similarly to C coal, this element is associated with carbonates in the sludges. However, it should be remembered that carbonates were not detected by XRD in sludge ashes at 800 and 1100 °C.

Vassilev et al. [26] found strong positive relationships for carbonates, oxides and hydroxides with Y for biomass ashes.

3.3.2.4. *Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu)*. The concentrations of these elements in the sludge ashes are low and approximately equal for the three types of sludges, independently of their type of treatment in the wastewater

treatment plant. Thus, the values are 3.3 ± 0.1 , 0.5 ± 0.1 , 2.2 ± 0.1 , 0.4 , 1.2 ± 0.1 , 0.2 ± 0.1 , 1.2 ± 0.1 and 0.2 ± 0.1 , respectively.

Vassilev et al. [26] found positive associations for silicates and Si with Gd and for Si with Lu in biomass ashes.

4. Conclusions

From the study of REY concentrations in the ashes of a bituminous coal with a high carbonate content and three sewage sludge ashes, from sludges that had undergone different waste water treatments, the following conclusions can be drawn.

The concentrations of the critical elements Y, Eu, Dy, Er and Tb are especially high in the bituminous coal studied (higher than the Clarke values for hard coal ashes) due to its high content of carbonates. The REY concentrations in sludge ashes are lower than those in coal ashes, excepting La. Moreover, the concentrations of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu in sludge ashes at 800 °C are very low, lower than 4 ppm and approximately equal for the three types of sludge. The distributions of REY concentrations are similar in the

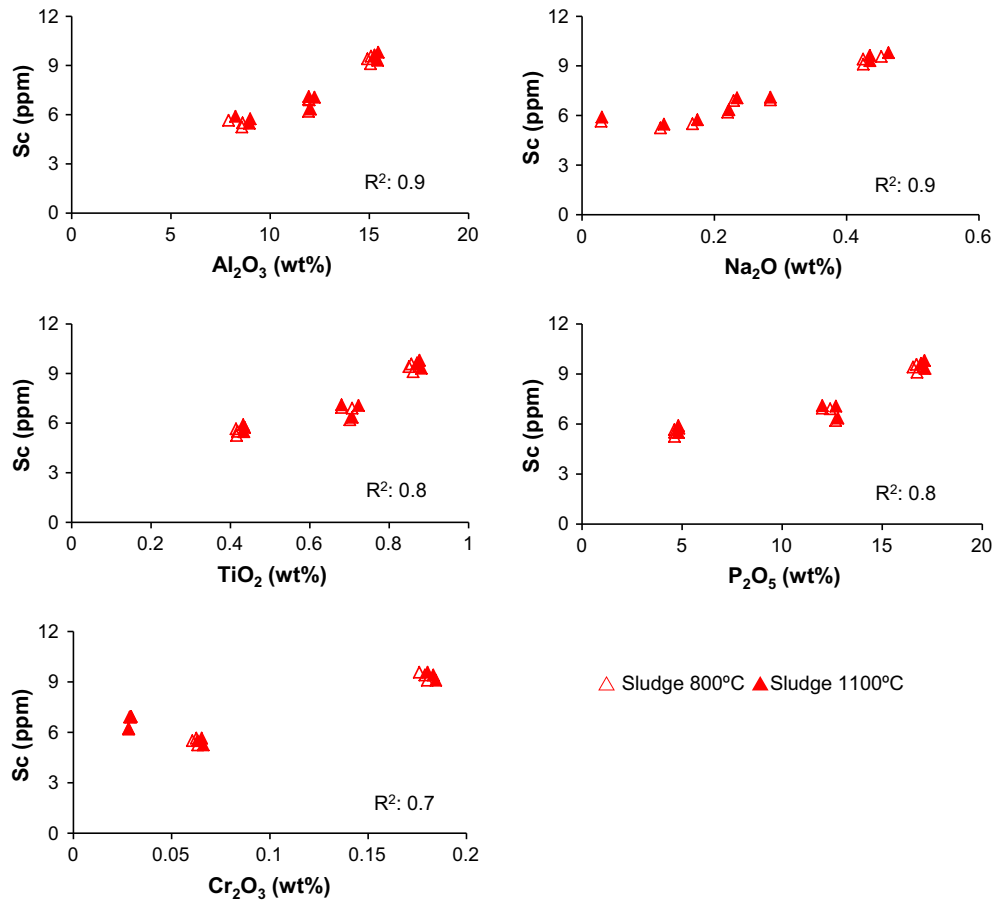


Fig. 9. Sc versus major and minor elements for sludge ashes obtained at 800 and 1100 °C.

three types of sludge ashes, but they differ from those of coal ashes in the cases of Y, La and Ce.

Not only the concentrations and distribution of REY in the sludge ashes but also their associations and behaviour are significantly different from those of the coal ashes. In the bituminous coal ashes obtained at 800 °C, the following 11 elements Sc, Y, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, show positive linear relationships with carbon (expressed as CO_2), these elements being associated with the carbonates such as calcite (CaCO_3). In coal ashes at 1100 °C, due to carbonate decomposition, there are positive relationships between Sc, Y, Gd, Tb, Dy, Ho, Er and Tm and SO_3 , while for Yb there exist positive relationships with SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , K_2O and TiO_2 . The behaviour of the first group of elements may be due to the fact that REY-bearing alkali and alkaline earth oxides released by carbonate decomposition react with SO_3 to form sulphates, such as anhydrite (CaSO_4). On the other hand, Yb-bearing CaO reacts with SiO_2 , Al_2O_3 , Fe_2O_3 to form ferrites, silicates and aluminosilicates, which explains Yb associations with SiO_2 , Al_2O_3 and Fe_2O_3 in ashes at 1100 °C. There are also positive relationships between La, Ce, Pr and Nd concentrations in ashes at 800 and 1100 °C and several oxides including SiO_2 , Al_2O_3 and Fe_2O_3 , which indicates that they are associated with larnite (Ca_2SiO_4) and gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and to calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) in the ashes.

For sludge ashes, unlike coal ashes, only Y maintains a good correlation with CO_2 in the sludge ashes at 800 °C, which indicates that it is associated with carbonates. Moreover, there exist positive linear correlations between La, Ce, Pr, Nd and Sm concentrations and several oxides including SiO_2 , Al_2O_3 and P_2O_5 , such correlations also being found for Sc and Eu with Al_2O_3 and P_2O_5 . Thus, these

elements are probably associated with phosphates and certain types of aluminosilicates.

As this study shows, ashes from coals with a high content of carbonates may be a suitable source for the critical elements Y, Eu, Dy, Er and Tb, especially yttrium. However, further studies are needed in order to find more conclusive results.

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