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Research article

Yttrium partitioning and associations in coal-combustion ashes prior to and after their leaching in HCl

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ABSTRACT

Yttrium associations and partitioning within fluidised-bed coal combustion ashes were studied in particle-size fractions prior to and after their leaching in cold dilute HCl. In original ash fractions (not leached in HCl), the dominant association of Y to P_2O_5 and TiO_2 was revealed while after the leaching, the strength of relationship to P_2O_5 decreased considerably and TiO_2 exhibited the only significant correlation. Overall HCl-extraction percentage of Y from these ashes was ca. 50% with TiO_2-associated Y predominantly contributing to insoluble fraction. Yttrium percentage dissolved in HCl can be attributed to its affinity to soluble phosphates (e.g., fluor/hydroxy apatites) or its potential occurrence in the form of Y_2O_3 or YCl_3.

1. Introduction

According to list of Critical Raw Materials (newly revised by The European Commission in May 2014) [1], rare earth elements (REE) are for the first time split into two separate categories: light and heavy rare earths. The criticality assessment of the light and heavy REE in terms of economic importance and the supply risk showed that heavy rare earths were much more critical than the light ones [1].

Despite the low atomic number of Y (39), it is traditionally included in the heavy REE group due to similarity of its chemical and physical properties. Typical utilization of Y are phosphors, ceramics, glass additives etc. [2,3] and even if Y is relatively abundant in the Earth's crust, it belongs to the most critical elements because economically mineable deposits are very scarce [3,4]. For this reason, there is a growing need to expand the production to some new sources, optimally some waste materials, whose vast amount is produced annually throughout the world (e.g., coal combustion ashes).

In general, the concentrations of minor and trace elements in coals and ashes have been investigated intensively and numerous studies have been published so far [5–9]. However, as dominant driving force behind this effort was environmental protection and abatement of toxic emissions, the attention has been paid preferentially to behaviour of toxic volatile elements, such as Hg, S, As, Cl, some heavy metals etc. [10–14].

Therefore, in case of ashes, detailed studies focused preferentially to Y (and/or REE) are quite scarce [15–19]; more often, there are studies where Y was studied within a large suite of the studied elements [20–23]. Unlike the ashes, more information can be found for Y modes of occurrence in coal [24–26]. Such results are undoubtedly important because it is known for long that the elemental associations in coal strongly influence their behaviour during the combustion [27]. As the ashes contain typically much higher concentrations of Y (related to coal) and due to an advantage of possible utilization of these wastes, according to Seredin and Dai [28], coal ashes should be considered as possible sources of these metals in case of comparable REE content as in traditional ores.

It is generally accepted that elemental mobility and distribution within the coal combustion ashes depend on numerous factors (Y concentration, combustion temperature, desulphurization additives etc. [29,30]); therefore, more studies are needed to better understand the individual effects. For example, Klyucharev et al. [31] concluded that extraction of REE from slag varies significantly with combustion temperature – the extracted fractions at 1300 °C, 900 °C and 650–700 °C were 7%, 60% and 75% with optimal range between 700 and 900 °C. This observation is important and practical indicating (i.a.) that fluidised-bed coal combustion ashes are advantageous in terms of potential Y and/or REE extraction due to low combustion temperature (850 °C).

Due to the reasons reviewed above, herein, fluidised-bed coal-combustion bottom ash and three fly ashes (from 3 sections of ESP) were studied for Y associations and partitioning within particle-size fractions of these ashes and their HCl-leached counterparts.

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2. Materials and methods

Lignite, bottom ash and three fly ash samples (from three sections of the same electrostatic precipitator) were collected at atmospheric circulating fluidised-bed power station where lignite was combusted with limestone at combustion temperature of 850 °C.

During the combustion test at the power station, partial samples of bottom ash and fly ash were collected at regular time intervals. After mixing, composite samples were prepared, from which representative average samples were set apart (by quartering) for further preparation and analyses in the laboratory.

Size fractionation of bulk bottom ash was carried out by dry mechanical sieving using 2, 1, 0.6, 0.5, 0.4, 0.2, 0.1, 0.071, 0.053 and 0.045 mm sieves and for the fly ashes fractionation 0.125, 0.100, 0.090, 0.080, 0.071, 0.063, 0.056, 0.053, 0.050, 0.040, 0.036 and 0.032 mm sieves were used.

The three bulk fly ash samples as well as their particle-size fractions were also leached by cold dilute HCl (HCl: water = 2:1 vol./vol.) and washed by two portions of demineralised water (supernatant solution was removed by centrifugation at 3000 rpm) and dried at 105 °C. These leached ashes were used for the determination of the studied elements and the unburned carbon.

In these residues, unburned carbon levels were determined on Leco CS-244 and recalculated to its content in the original ash sample. Leaching the samples in dilute HCl removed carbonates, which could otherwise increase the concentration of unburned carbon in ash [32].

Determination of elemental contents in the original and leached ash samples was carried out by means of X-Ray fluorescence spectrometry with wavelength-dispersive X-ray fluorescence spectrometer ARL PERFORM'X (Switzerland) and polarized beam X-ray spectrometer SPECTRO XEPOS (Germany).

Ash content of the samples was determined gravimetrically in a muffle furnace at 815 °C.

The statistical analysis of the measured data was performed by means of QC Expert statistical-analysis software (TriloByte) including advanced statistical methods specified by various international standards and regulations, such as ISO 9000, ISO 14000 or QS 9000 etc.

3. Results and discussion

3.1. Original ash samples (prior to leaching)

3.1.1. Chemical analysis

Lignite, bulk BA, bulk FAs from 3 sections of ESP (FA S1, FA S2 and FA S3) and particle-size fractions of BA and FAs were subjected to chemical analysis. Unburned carbon content (UC) and the concentrations of target elements in BA fractions (and the lignite) are given in Table 1 and the same for the FAs from sections 1–3 are presented in Table 2.

The lignite contains 4.4 ppm of Y, which is comparable (slightly lower) than the world coal average of 8.93 ppm reported by Bouška and Pešek [33]. The concentrations of Y in the bulk BA and FA S1-S3 are 31.3, 34.1, 46.3 and 53.5 ppm, which roughly corresponds with the average for the brown-coal ashes (44 ppm) according to Ketris and Yudovich [34]. The values also approximately corresponds with Y concentrations in fly ashes from other European power stations – for Polish fly ashes Y levels of 6.2–29.0 ppm [35] and 44.0–53.8 ppm [19] were reported and UK fly ashes contained 37.3–60.7 ppm [19]. Higher Y concentrations were reported for U.S. power station ashes [18,36] – 180–260 ppm, which can be a result of quite high Y content in the pulverized coal (180 ppm).

It is interesting to note in this context that the concentration of Y increases in the order: lignite < bulk BA < bulk FA S1 < bulk FA S2 < bulk FA S3, which could be attributed to the volatilization/condensation mechanism as well as it can be brought about by the different distribution of the particle size with different Y concentrations. It is worth further discussion – so it will be discussed in the next section along with particle-size distribution and the effect of the unburned carbon. The similar (increasing) trend was observed by Mardon and Hower [36] for PCC power station where the concentrations of Y in the coal, bottom ash, economizer, mechanical hopper and ESP were 180, 184, 203, 199–212 and 238–259 ppm.

3.1.2. Distribution within particle-size fractions and the effect of unburned carbon

The distribution of Y within the particle size fractions of BA is straightforward (Table 1, Fig. 1) – Y concentration increases with increasing particle size (from 8.8 ppm in < 0.045 mm fraction up to 37.1 ppm in > 2.0 mm fraction). The considerable depletion of Y in the finer fractions can be attributed to huge amount of limestone that was combusted with the coal. For the efficient desulphurization, limestone is finely ground (to enhance its specific surface area for the interaction); so its unreacted residues and its main desulphurization product (anhydrite) tend to be significantly enriched in the finest fractions (concentrations of CaO and S decrease from 55.76% CaO and 31.11% S in the finest fraction to 1.33% CaO and 0.57% S in the coarsest fraction). Therefore, most of other major elements are enriched in the coarser fractions. Except for Fe_2O_3 and MnO (that are enriched in the fractions of medium size), the coarsest fractions of BA was composed namely of Al, Si, K and Ti - compounds.

Unlike BA with quite clear trend, the distribution of Y within the FA fractions is rather variable showing no explicit partitioning trend (Table 2, Fig. 1). In the first section (FA S1), Y is depleted in the medium-size fractions unlike FA S2 and FA S3 where the medium-sized ashes are enriched in Y. In any case, the clear trend showing enrichment of Y in the coarsest fractions (similarly as in BA) was not observed. Moreover, the volatilization/condensation mechanism usually results in the enrichment of the studied element in the fine-grained ash fractions.

Table 1
Chemical composition of particle-size fractions of bottom ash (BA).

		% fraction	UC (%)	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	P_2O5 (%)	SO_3 (%)	K_2O (%)	CaO (%)	TiO_2 (%)	MnO (%)	Fe_2O_3 (%)	Y (ppm)
	Lignite	–	–	0.035	3.57	9.23	0.069	3.75	0.27	0.31	0.234	0.010	2.06	4.4
Bottom ash	< 0.045	1.10	–	3.683	1.36	1.50	0.012	31.11	0.13	55.76	0.309	0.025	0.44	8.8
	0.045–0.053	1.03	–	4.100	1.45	1.66	0.012	32.05	0.13	54.42	0.344	0.025	0.60	9.6
	0.053–0.071	1.47	–	3.554	1.40	1.61	0.011	30.29	0.12	54.47	0.330	0.031	0.70	9.3
	0.071–0.100	1.54	–	3.479	1.39	1.66	0.011	27.35	0.12	54.91	0.307	0.038	0.99	10.7
	0.1–0.2	3.90	–	2.455	6.57	14.42	0.051	18.13	0.90	31.13	0.817	0.123	8.69	28.0
	0.2–0.4	20.07	–	1.806	12.78	32.86	0.132	7.18	2.25	13.49	0.891	0.135	9.99	33.2
	0.4–0.5	5.88	–	1.719	16.94	45.33	0.174	3.05	3.23	6.80	0.995	0.135	10.28	30.6
	0.5–0.6	9.56	–	1.521	16.85	45.14	0.147	2.07	3.35	5.04	0.958	0.125	9.90	31.9
	0.6–1.0	21.03	–	1.544	17.06	46.75	0.115	1.66	3.55	3.60	0.935	0.119	9.81	28.8
	1.0–2.0	19.34	–	1.516	17.57	49.55	0.105	0.89	3.79	1.89	0.926	0.094	7.68	28.5
	> 2.0	15.08	–	1.545	17.80	51.09	0.085	0.57	3.86	1.33	0.909	0.087	5.63	37.1
	Bulk BA	100	0.38	1.650	15.32	42.65	0.151	5.09	3.21	9.30	0.930	0.118	8.53	31.3