



Functional speciation and leachability of titanium group from industrial fly ash



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HIGHLIGHTS

- Functional speciation of titanium group in ash and their mobility were investigated.
- The sequential extraction and ICP–OES methods were used.
- New parameters were defined: accumulation and parameter of leaching metal from ash.
- Proposed parameters used for evaluation of leachability of titanium group from ashes.

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ABSTRACT

Functional speciation and leachability of titanium group from industrial fly ash were investigated by using sequential extraction. Fractions: soluble in water and exchangeable, soluble in acids (pH 5), oxide, pseudosulfide and residual were characterized. Results of the fractions analyses were compared with the total content of metals in ash: Ti – 0.48%, Zr – 85.8 mg kg⁻¹, Hf – DL. Two parameters were defined for the evaluation of leachability of metals from ashes: the accumulation of metal in the soluble fraction (a = mass of soluble fraction metal/mass of the soluble fraction of ash) and the parameter of metal leaching from ash (w = mobility of metal (%) / solubility of ash (%)). Accumulation of titanium group (mg kg⁻¹) was found in fractions: oxide (43.4 Ti), pseudosulfide (5.3 Ti; 4.3 Zr), residual (2378 Ti; 22.8 Zr) and not-digested residue (8862 Ti, 167.6 Zr). The oxide fraction was characterized by low parameter of leachability (0.01 Ti, 0.05 Zr), while the residual was high parameter of leachability (0.50 Ti, 0.25 Zr). It is possible to apply new defined parameters for the evaluation of leachability of metals from ashes in relation to the mass solubility of ash.

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1. Introduction

Coal fly ashes are the main waste material of the power industry, their production was estimated to be 780 Mt per annum [1]. The source of mobile metals, which pollute environment can be the landfill of wastes. The emission of metals from ashes to environment can occur through direct environmental impact on landfill or secondarily by their the economic application.

Titanium group can modify the composition of the surface layer of the soil, because of their presence in ashes. So far, leaching of titanium group and their functional speciation in ashes, despite they were studied for many years, are undescribed unequivocally, mainly because of their low mobility to neutral solutions [2–4] and methodical problems of determination of titanium group in various fractions of ash [4]. Up to now, mainly contents of titanium

in coal fly ashes were investigated, the contents of zirconium and hafnium were studied seldom [5]. The Ti was found in ashes on percentage levels: 0.13–0.56% (China) [6,7], 0.30–1.13% (Czech) [8,9], 0.41–0.75% (Brazil) [10,11], 0.48% (Canada) [12], 0.54–1.08% (Netherlands) [13], 0.60–0.96% (USA) [14,15], 0.70% (Italy) [16], 0.77% (South Africa) [17], 0.17–2.11% (Japan) [18–20], 0.82% (Israel) [21], 0.84% (Spain) [22], 1.26% (India) [15]. Coal ashes contains zirconium in amounts appropriately: 72.6 mg kg⁻¹ (Turkey) [23], 215 mg kg⁻¹ (South Brazil) [10], 262–630 mg kg⁻¹ (USA) [14,24], 762 mg kg⁻¹ (China) [25]. Several works shown, that there is little presence of hafnium in industrial ashes: 1.61 mg kg⁻¹ (Northern Greece) [26], 10.2 mg kg⁻¹ (South Brazil) [10], 23.3 mg kg⁻¹ (China) [25].

The review of the methods used today in the analysis of metals speciation in ash was included in the review papers [1,4,27–30]. An analysis of metals functional speciation in ash by means of sequence extraction provide information mainly on their fractions released into solutions by means of different mechanisms

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including: the mechanism of a simple solubility in water, ionic exchange, dissolution and desorption, oxidation and reduction, complexation and digestion that is through the mechanisms characteristic to environmental conditions. The analysis is made on the basis of procedures of a multi-stage sequential extraction (up to 6 stages). Extractants are most often used in the following order: (i) unbuffered solutions of salts (MgCl_2 , CaCl_2 , KNO_3 , NH_4NO_3 , BaCl_2) [30,31]; (ii) buffer solutions or solutions of weak acids ($\text{CH}_3\text{COONH}_4/\text{CH}_3\text{COOH}$, $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) [30,31]; (iii) reducing extractants and/or oxidizing extractants ($\text{NH}_2\text{OH}\cdot\text{HCl}$, H_2O_2 pH2) [30,31]; (iv) strong acids and their mixtures ($\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$, $\text{HNO}_3/\text{HF}/\text{HCl}$) [30,31]. Sequential extraction schemes differ from each other both by means of conditions of their making and by extractants used. The Tessier method and its modifications [4,29,32–34], as well as BCR [4,29,30,35], TCLP (Toxicity Characteristic Leaching Procedure) [29,36], Kersten and Forstner's [29], Salomons and Fortsner's [35] are universal procedures of the sequential extraction and analysis of a functional speciation of metals in ash.

The few works were performed, especially significant from a point of view of the evaluation of the influence of ashes on the natural environment, concerning leachates of titanium and zirconium from industrial ash. Among others, in conditions simulating washing of ash with the rain, contents of Ti (method ICP–OES) in eluates of ash (India) were analysed. It was found, that Ti was not present in solutions [2]. A method for determination of Ti in coal fly ash samples using ultrasound assisted digestion followed by inductively coupled plasma optical emission spectrometry (ICP–OES) was proposed in [37]. The lower detection limit for Ti was characterized at 4.0 mg kg^{-1} for this method. It was also shown, that leaching Ti and Zr from ashes by tetraoxosulfuric(VI) acid solutions was not very effective, and in this conditions (pH 1) metals remain practically in ash [3], or recovery of Ti is 35% (pH ~ 1), Ti total -8.2 g kg^{-1} [21]. Using the mixture of hydrochloric acid and nitric acid in ash extraction do not causes the total recovery of titanium (Ti < 80%) [4]. Evaluation of functional speciation of titanium group in environmental conditions was so far impossible, due to the lack of data about leaching them from industrial ash.

The aim of this study was investigation the functional speciation of titanium group in industrial coal fly ash and mass balance of fractions, study of mass solubility of ash and evaluation of the leachability of titanium group with using the new defined parameters: accumulation of metal in soluble fraction of ash and parameter of leaching metal from ash.

2. Material and methods

2.1. Ash preparation and conditions of research

The fly ash particles generated during the fluidised bed combustion of the coal in the Rzeszow Power Plant were collected in the dedusting device and then, stored on the storage heap. The samples used in leaching tests were collected according to BN-81/0623-01 norm (by Polish Standards). All of them were collected at a depth of about 10 cm. The subsamples weighing 0.5 kg were prepared from the 5 kg sample. The obtained material was homogenized by shaking and placed in the dark. Then, the ash samples were kept in polyethylene containers until extraction.

The sample of fly ash which was used in experiments was first brought to air-dried condition (in laboratory the ash was air-dried at ambient – temperature for two weeks), then ground to a grain diameter of $\phi_{\text{ash}} \leq 0.3 \text{ mm}$.

Preliminary research shown, that fly ash had the following properties: bulk density 540 kg m^{-3} , content of combustible part 10.1%, moisture content 0.47% [32]. The content of some metals

oxide was found in ash as follow: 47% SiO_2 , 24% Al_2O_3 , 14% Fe_2O_3 , 3% MgO , 2.5% CaO , 0.8% Na_2O , 0.2% K_2O [32].

2.2. Sequential extraction

Leaching of ash was conducted according to 5 – steps Tessier's procedure [33] including preliminary leaching of ash with distilled water and digesting of ash in $\text{HNO}_3/\text{HClO}_4$ mixture after 4 step of the extraction [34]. Research was performed on four ($n = 4$) parallel samples. Scheme of investigation, composition of extraction solvent and extraction conditions were presented on Fig. 1.

Stage 0. Samples of ash (10.0 g every) were placed in Erlenmeyer flasks, to all samples the 50 cm^3 of distilled water was added and they were shaken through the one hour. Eluates from remains of ash were separated by centrifugation, and then filtration. Eluates were interconnected, acidified, led to the constant volumes (250 cm^3) and titanium group were determined. Ash remains G(0) were applied in the next stage of sequential extraction.

Stage 1. To every ash remains G(0) the 50 cm^3 of 0.5 M MgCl_2 was added, samples were shaken through the one hour, than centrifuged and filtered. Eluates were interconnected, acidified, led to the constant volumes (250 cm^3) and titanium group were determined. Ash remains G(1) were applied in the next stage of sequential extraction.

Stage 2. To every ash remains G(1) the 50 cm^3 of acetate buffer ($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) pH 5 was added, samples were shaken through the five hours, than centrifuged and filtered. Eluates were interconnected, acidified, led to the constant volumes (250 cm^3) and titanium group were determined. Ash remains G(2) were applied in the next stage of sequential extraction.

Stage 3. To every ash remains G(2) the 50 cm^3 of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ was added. Solutions were heated for the six hours on the heating plate ($96 \text{ }^\circ\text{C}$) using periodic mixing. After cooling the solutions were centrifuged and filtered. Eluates were interconnected, acidified, led to the constant volumes (250 cm^3) and titanium group were determined. Ash remains G(3) were applied in the next stage of sequential extraction.

Stage 4. To every ash remains G(3) the 50 cm^3 of 30% solution of H_2O_2 (acidification by HNO_3 , pH 2) was added. Solutions were heated for the six hours on the heating plate ($85 \text{ }^\circ\text{C}$), after cooling the samples were centrifuged and filtered, in that method eluate F4a was obtained. To ash remains the 50 cm^3 of 3.2 M ammonium acetate in 20% HNO_3 solution was added and shaken for one hour. Eluates F4b from ashes remains G(4) were separated by centrifugation and filtration. After acidified and led to the constant volumes (250 cm^3) in eluates F4a and F4b the titanium group were determined. Ash remains G(3) were applied in the next stage of sequential extraction.

Stage 5. To every ash remains G(4) the 20 cm^3 of concentrated HNO_3 and 10 cm^3 HClO_4 were added. That prepared solutions were heated for the one hour on the heating plate ($90 \text{ }^\circ\text{C}$). Subsequently, the flask content was evaporated to dryness. Fifteen milliliters of HCl solution (1:1) were added to the cooled dry residual, which was then placed on a heating plate and heated as before. The hot content of flask was filtered by a medium quantitative filter paper, decanted sediment traces with the help of the hot 1% HCl solution. Eluates were interconnected and in volumetric flask (250 cm^3) by distilled water were complete.

2.3. Single stage mineralization of ash

2.3.1. Total coal fly ash digestion

Fly ash samples ($n = 3$) were digested in open platinum crucibles. 1.00 g of ash was digested with a mixture of 8 cm^3 65% HNO_3 , 4 cm^3 40% HF, 2 cm^3 37% HCl and 10 cm^3 H_2O . After

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