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RECOVERY OF TRACE ELEMENTS WITH URANIUM AND THORIUM FROM YATAGAN THERMAL POWER PLANT FLY ASHES BY LEACHING

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Abstract: In this paper, characterization of fly ashes obtained from the Yatagan Thermal Power plant, Mugla, Turkey was performed in order to determine their radioactive element contents, especially uranium and thorium. The representative fly ash samples were subjected to hydrochloric acid (HCl) leaching considering solid concentration, acid dosage, leaching time and temperature in order to reach certain uranium and thorium recoveries. The obtained results showed that the optimum conditions for leaching tests were: 30% solid concentration, 2.36 mmol/dm³ HCl addition, 240 min leaching time and 40 °C temperature. Dissolution efficiencies for uranium and thorium from the Yatagan Thermal Power Plant fly ashes were calculated as 90.12 and 81.18%, respectively.

Keywords: *uranium, thorium, leaching, fly ash*

Introduction

Fired coal wastes consist of significant part of all fossil fuel firing products generated throughout the world. Fly ashes are the main combustion by-products in coal fired power plants, and they contain primarily of silica, alumina, iron and calcium oxides within their structure. In Turkey, approximately 15 teragrams (Tg) of fly ashes occur during electricity generation in coal fired thermal power plants. The mineral substances in a coal structure do not burn in thermal power plant, therefore they are released into pipes as fly ashes. Generally, electrofilters situated at reactor outlet can filter 99.4% of dust particles inside these ashes. The fly ashes are diffused in air through plumes and deposited inside pipes within certain distances depending on their weights and atmospheric events. It is reported that only 20% of such fly ashes can be recovered, while the remaining part is used for landfill purposes or deposited in

surface impoundments (Ozdemir and Celik, 2002; Arora and Kumar, 2006; Ahmaruzzaman, 2010).

Fly ashes are particularly utilized in construction, agriculture and chemical industries. The segment among such industries provides the most economical conditions and offers technical benefits mostly for cement and concrete industry (Siddique, 2004; Felekoglu, 2006). Upon commencement of coal firing process in thermal power plants, some toxic trace elements available with coal such as As, Cd, Ga, Ge, Pb, Sb, Se, Sn, Mo, Ti, and Zn are accumulated and they have potential of contamination transfer to wastes (as slags, ashes, and gases). Coals and asphaltites generally contain high amount of radioactive and rare metals with Mo, Ni, V and etc., and they are also combined with mineral substances containing such radioactive metals as U and Th within the fly ashes.

In general sense, content of natural radionuclide activity is less than average concentrations in the earth crust. On the other hand, it is observed that the uranium content of such low quality coals as lignite (particularly young age lignites) is high (Yukse, 2006). There is a very limited information available regarding to type of uranium connection with coal. It is possible to identify whether uranium minerals are available or not through autoradiography. According to Davidson and Ponsford (1954), uranium occurrence in coal should be accepted as linked to sandstones in coal beds, which belong to the Trias age. It is possible to encounter with uranium and vanadium on sandstones located in England at the Trias age. It is another possibility that uranium penetrated into coal through sand layers together with underground waters (Davidson and Ponsford, 1954; Schwandorf, 2001).

Various studies have been conducted with the use of several types of acids for purpose of uranium recovery from fly ashes through chemical dissolution. Within a previous study, the best results were obtained from the bulk leaching tests performed with the use of 10% H₂SO₄ with concentrations 0.05-0.15 mol/dm³. The results indicated that 80% of uranium dissolution efficiency was obtained through the use of 180 kg H₂SO₄ per Mg of ash (Cioroianu et al., 2005). According to Enkhtaivan (2013), the dissolution characteristics of uranium and thorium from the fly ash samples taken from the thermal power plants in Turkey using H₂SO₄, HCl and CH₃COOH were performed under different leaching conditions, and the best results were obtained by using H₂SO₄ (Enkhtaivan, 2013; Kursun et al., 2014).

In one of the previous studies on extraction of gallium from coal fly ashes by acid leaching, the major elements in fly ashes such as aluminum, iron, silicon, and calcium were also successfully recovered (Fang and Gesser, 1996). In another study, where solvent extraction of uranium in the leach solution with trioctylamine was used, effects of the diluting agent, phase rate, solvent percentage, aqueous phase pH, mixing period, and stage numbers out of the parameters affecting uranium extraction were examined (Turkmenoglu, 2010). The dissolution of uranium and thorium contents from various uranium and thorium resources using HCl have also been reported in some studies (Phillips et al., 1982; Mudd, 1998; Yusoff, 2002; Morimoto, 2003; Fouad, 2010).

Materials and methods

Materials

Fly ash samples used in this study were obtained from the Mugla Yatagan Thermal Power Plant (TPP), Turkey. The particle size distribution of the representative sample was determined by wet screening and it was found that all samples were under 500 μm . The d_{80} , d_{50} , and d_{10} values of the fly ash sample were also determined as 270, 130 and 30 μm , respectively. The results of the moisture analyses showed that the moisture content of the sample was 4.21%. Densities of the fly ash samples were obtained with a pycnometer which had a 50 cm^3 . Distilled water was used in the study. The average density of the sample was determined as 2.17 g/cm^3 . The chemical analysis of the sample was performed using the ICP-ES method, and the results are presented in Table 1. According to the results of the chemical analyses presented in Table 1.

Table 1. Chemical analysis of the fly ash sample. Basic oxides and trace elements shown separately

Content (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	Cr ₂ O ₃	Total/C	Total/S	LOI*
	45.94	19.28	7.14	4.43	17.28	0.57	1.93	0.78	0.24	0.06	0.047	0.87	0.43	3.00

Content	Assay Value (ppm)	Content	Assay Value (ppm)	Content	Assay Value (ppm)
Ni	117.00	Tb	2.18	Ta	1.20
Sc	19.00	Dy	13.35	Th	210.00
Ba	533.00	Ho	2.76	U	160.00
Be	4.00	Er	8.14	V	159.00
Co	21.20	Tm	1.26	W	5.50
Cs	9.40	Yb	7.64	Zr	152.70
Tl	0.30	Lu	1.14	Pb	9.40
Se	2.00	Mo	9.80	Zn	58.00
La	66.00	Cu	37.10	As	34.00
Y	87.30	Hg	0.07	Cd	0.68
Ce	134.10	Hf	5.00	Sb	1.50
Pr	15.49	Ga	20.10	Bi	0.20
Nd	61.60	Nb	18.80	Ag	<0.0001
Sm	12.95	Rb	104.50	Au	<0.0005
Eu	2.37	Sn	4.00		
Gd	13.20	Sr	406.40		

LOI: Loss on ignition

The mineralogical properties of the samples were also analysed with the X-ray diffraction method (XRD), where Graphite Monochromator was used in the device, which had a Cu-sourced (A4 1L-Cu / 60 kV, 2.0 kw) X ray tube with a water cooler

controlling for temperature changes that ensures the acquisition of monochromatized X-ray. The XRD patterns indicated that the fly ash samples contained high amount of quartz SiO_2 and slightly lower amount of albite- $\text{Na}(\text{AlSi}_3\text{O}_8)$, and calcite CaCO_3 minerals (Figure 1).

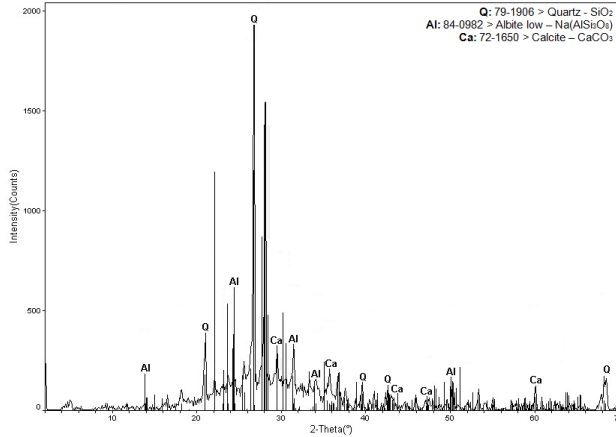


Fig. 1. XRD diffraction pattern of the fly ash sample

Additionally, the microscopic photographs and scanned electron microscope (SEM) images of the fly ash sample were investigated for the purpose of more detailed determination of its by-products (Figure 2).

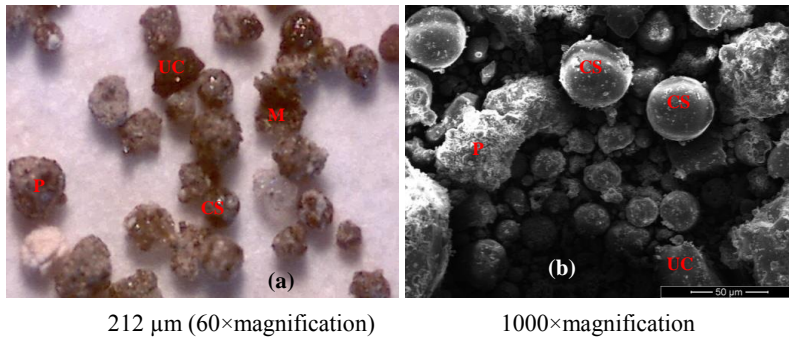


Fig. 2. Optical microscope and SEM photographs of fly ashes samples
 UC: unburned carbon, P: pozzolan, CS: cenosphere, M: magnetite

As a result of the examinations under the optical microscope and SEM images, the fly ash sample predominantly contained silicate minerals as an amorphous and vitreous structure. This structure can be explained in such a way that the sample was processed under high temperature values as an incineration product, and hence the crystal structure of the mineral contents changed.

Based on these results, it is seen that uranium and thorium are found as uraninite (UO_2) and monazite ($\text{Ce, La, Nd, Th}[\text{PO}_4]$). Thorite (ThSiO_4) also forms in the sample. The radioactive minerals were distributed in glass phase, and their particles sizes range from 5 to 80 μm . The results also show that the angular particles available in the ashes are clay particles. Some of the angular particles are thought to be unburned carbons. On the other hand, the source of the semi-round particles may be due to cooling down of these particles under the melting temperature after the fraction of round structures and burning of clay minerals. Meanwhile, the fly ash sample also showed a non-homogenous particle distribution. Quartz and orthoclase minerals in the sample are coal-induced, and they were included with the fly ash without burning due to their stable crystal lattices. No agglomeration was encountered within the fly ash particles.

Methods

The leaching tests were performed using diluted hydrochloric acid (HCl) as a dissolution reagent for investigation of uranium and thorium contents. The effect of parameters such as the solid concentration, HCl dosage, leaching time and temperature on dissolution of uranium and thorium was investigated. The leaching experiments were carried out in a shaking water bath, where the temperature and mixing speed were adjusted according to the desired parameters. The mixing speed was kept constant as 250 rpm. During the leaching experiments, pH value of the pulp was controlled every 1 hour. After leaching, the solutions were subjected to solid/liquid separation by a suitable filter paper with a pore size of 4 μm . Finally, the filter cakes from each experiment were washed with 500 cm^3 of 1% HCl concentration. Dissolution efficiency (% *D.E.*) was calculated according to the following equation:

$$\% D.E. = \frac{\text{U,Th content of feed} - \text{U,Th content of leach cake}}{\text{U,Th content of the feed} \cdot 100}$$

Results and discussion

The results of leaching of uranium and thorium from the fly ash samples as a function of solid concentration are shown in Figure 3. It shows that the dissolution efficiency of uranium from the fly ash showed an increase up to a certain point respect to the solid concentration. The highest dissolution efficiency of uranium of 70.78% was obtained at 30% of the solid concentration under the constant conditions, and then the efficiency started to decrease after that point. Moreover, the 63.41% dissolution efficiency of thorium was obtained at 30% solids concentration. The decrease in the dissolution efficiency after 30% solid concentration indicated that the amount of HCl was not enough to efficiently dissolve these elements. In addition to this, the high solid concentration also caused the difficulties in suspension mixing. Based on the results obtained from this experiment, the optimum pulp solid concentration was determined to be 30% of HCl for the subsequent leaching tests.

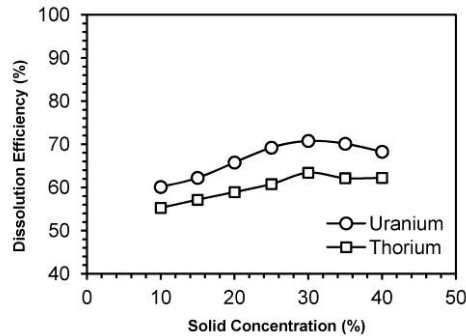


Fig. 3. Effect of solid concentration on dissolution efficiency of uranium and thorium from the fly ash sample (1.18 mmol/dm³ HCl, 240 min leaching time at 20 °C, pH~2.79)

Leaching time is an important parameter because it ensures the dissolution reagent to contact with the substance for a longer period of time, and provides opportunity for the completion of long term reactions. The results of leaching of uranium and thorium from the fly ash sample as a function of leaching time is shown in Figure 4. It can be seen that the dissolution efficiencies of the both elements were increased up to 240 min of leaching time with the dissolution efficiencies of 63.55% and 69.99% for uranium and thorium, respectively and no significant change was observed after that point. Therefore, these results clearly indicated that the dissolution reactions of both uranium and thorium were completed after about 240 min of leaching time under the constant experimental conditions. Based on the results obtained, the optimum leaching time was determined as 240 min.

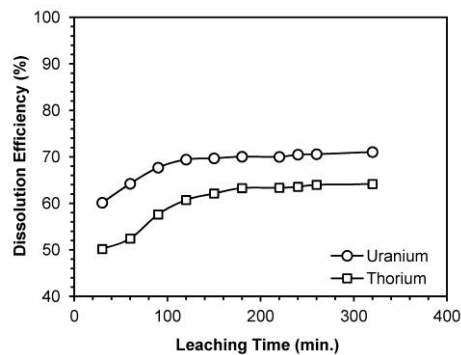


Fig. 4. Effect of leaching time on the dissolution efficiency of uranium and thorium from the fly ash sample (1.18 mmol/dm³ HCl, 30% solid concentration, temperature 20 °C, pH~2.81)

The results for the leaching of uranium and thorium from the fly ash sample as a function of reagent dosage is shown in Figure 5. Figure 5 shows that the dissolution

efficiency of uranium from the fly ash showed an increase up to a certain point respect to the HCl dosage. The highest uranium dissolution efficiency of 86.95% was obtained by addition of 2.36 mmol/dm³ HCl under the constant conditions, and no significant change was observed after that point. Moreover, the thorium dissolution efficiency of 74.16% was also obtained by using the same acid dosage. The dissolution efficiencies of both elements showed a linear relationship with respect to the dosage of HCl, which seems to reached a plateau at this point. Although the dissolution efficiency of thorium showed a slight increase, the usage of high acid concentrations showed negative effects in terms of environment and economy. Based on the evaluation of findings obtained from this experiment, the optimum reagent dosage was determined as 2.36 mmol/dm³ of HCl for the leaching tests.

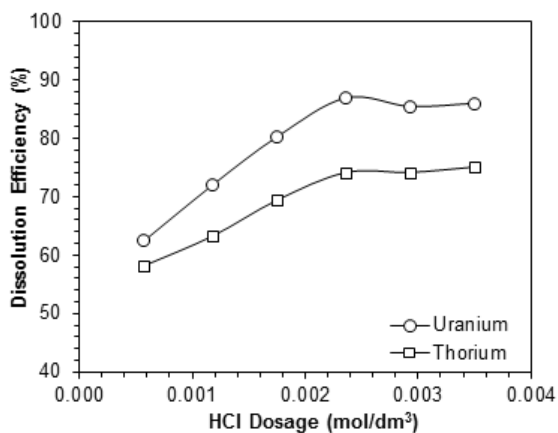


Fig. 5. Effect of reagent dosage on dissolution efficiency of uranium and thorium from the fly ash sample (30% solid concentration, 240 min leaching time, temperature 20 °C)

The results of leaching of uranium and thorium from the fly ash sample as a function of leaching temperature is shown in Figure 6. The dissolution efficiency of uranium from the fly ash showed an increase up to a certain point in respect to the leaching temperature. The highest dissolution efficiency of uranium of 90.12% was obtained at 40 °C under the constant conditions, and no significant change was observed after that point. Moreover, the dissolution efficiency of thorium of 82.77% was obtained at 60 °C. Although the dissolution of thorium increased with temperature, it only showed a slight increase after 40 °C. More importantly, the dissolution of uranium decreased, and aluminum silicates started to dissolve after 40 °C. Based on the evaluation of the findings obtained from this experiment, the optimum leaching temperature was determined as 40 °C.

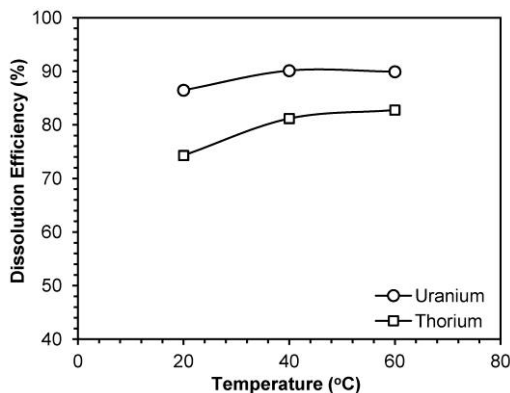


Fig. 6. Effect of temperature on dissolution efficiency of uranium and thorium from the fly ash sample (2.36 mmol/dm³ HCl, 30% solid concentration, 240 min leaching time, pH~2.77)

Conclusions

In this study, the dissolution behaviour of uranium and thorium elements from the fly ash sample obtained from the Yatagan Thermal Power Plant, Turkey was investigated in details. For this purpose, the optimum process conditions were obtained by studying the effect of several leaching parameters such as solid concentration, dosage of HCl, leaching time and temperature. The results of leaching tests showed that uranium and thorium from the fly ash sample can be recovered with 90.12% and 81.18% dissolution efficiencies, respectively, under the optimum conditions of 30% solid concentration, 2.36 mmol/dm³ HCl dosage, 240 min leaching time at temperature of 40 °C. The obtained results clearly indicate that acid (HCl) leaching can be one of the effective alternatives for recovery of uranium and thorium elements from the fly ashes obtained from thermal power plants with higher dissolution efficiencies under the optimum conditions.

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