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Investigation of Solubility of Radioactive Elements Contained in Ashes of Yatagan Thermal Power Plant in Acetic Acid

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Coal combustion residuals consist of 90 % of all fossil fuel combustion residuals generated across the world. Million tons of fly ashes are generated on a yearly basis. For now, only 20 % of such fly ashes can be utilized and the remaining amount is used for land filling purposes or deposited in surface impoundments. The most important waste material in modern thermal power plants is very fine ash particles generated through the combustion of powder coals and spread by flue gases. About 110 g ashes release as a waste material in the generation of 1 kWh energy by a thermal power plant. Approximately 650.000 tons of fly ashes and bottom ashes are obtained from a power plant with the capacity of 1000 MW. Such toxic trace elements as arsenic, cadmium, lead, antimony, selenium, tin, molybdenum and zinc are transferred to wastes upon the combustion of lignite coals. Toxic trace elements contained in fly ashes can sweep even into surface and underground waters as a result of the contact of ash with water under suitable atmospheric conditions due to improper storage of the ashes. Furthermore, there are many studies conducted in terms of the recovery of precious metals and radioactive minerals in fly ashes. Such studies are important both for economical purposes and environmental pollution. Within the scope of this study, a series of characterization studies then leaching tests were carried out on the samples of fly ashes taken from a thermal power plant operated in Turkey. In order the ashes to be evaluated, the leaching of the samples and the optimum leach parameters were investigated with the use of acetic acid. Finally, opportunities for the recovery of uranium and thorium from the ashes were addressed.

Keywords: Fly ash, Leaching, Uranium, Thorium.

INTRODUCTION

Coal combustion residuals consist of 90 % of all fossil fuel combustion residuals generated across the world. Million tons of fly ashes are generated on a yearly basis. For now, only 20 % of such fly ashes can be utilized and the remaining amount is used for land filling purposes or deposited in surface impoundments[1-3]. The dissolution of potentially toxic substances into soil and underground waters leads to a decrease in plantation and plant growth and a change in the element compositions of the vegetables grown in ashes due to the particular negative chemical effects of the ash[1]. The annual amount of fly ashes obtained as a result of the combustion of coal in high incineration plants is approximately over 413.7 million tons across the world. 160 million tons of such fly ashes were generated in China whereas 89.5 million tons, 76.5 million tons and 30 million tons of it were respectively generated in India, USA and South Africa[4].

As a result of the combustion of coal in thermal power plants, toxic trace elements such as As, Cd, Ga, Ge, Pb, Sb, Se, Sn, Mo, Ti and Zn which present in contents of coal and potentially cause pollution are transferred into wastes (slag, ash and gas). Fly ashes and sub-incinerator ashes which containing various toxic elements are deposited in storage reservoirs or in bulk. However, only a fraction of such wastes are used[5]. Being combustion residuals, these ashes are generally stored in large volume of reservoirs or regular storage areas. The distribution of the elements within the ash structure is different than the coal. Some of them present in aluminosilicate matrix (Ti, Na, K, Mg, Hf, Th and Fe) or concentrated on the surface (As, Se, Mo, Zn, Cd, W, V, U) and consist of in acid soluble phase (Ca, Sr, La, rare earth elements and possibly Ni). Mn, Be, Cr, Cu, Co, Ga, Ba and Pb are distributed between matrix and non-matrix materials. Coals and asphaltites generally contain high amounts of radioactive and rare metals in Turkey. Fly ashes are combined with mineral substance containing such rare metals as Mo, Ni, V and radioactive metals as U, Th in their structure and they are also rich hydrocarbon resources. Rare metals are essentially germanium, molybdenum, vanadium, thorium, uranium and nickel[6]. Fly ashes spread in the air trough flue gas and deposit on the ground at certain distances depending on their weight and atmospheric conditions[7].

Fly ashes generated as residuals and sub-incinerator ashes lead to different environmental problems. Therefore, the use and evaluation of fly ashes in various areas is highly important. Fly ashes are known to have such usage areas as the removal of heavy metals from waste waters and applied as cement and asphalt additive[8].

Fly ashes chemically consist of amorphous alumino-silicates. Significant compounds are SiO_2, Al_2O_3, CaO and Fe_2O_3. Being main compounds of fly ashes, silicon, aluminium, iron and calcium oxides constitute about 80-95 % of the total composition. Such minor compounds as magnesium, titanium, sodium, potassium, sulphur and phosphor, on the other hand, constitute about 0.5-10 % of the total composition. Fly ashes contain 20 or 50 elements such as Sb, Ar, Ag, Ba, Be, B, Cu, F, Pb, Mn, Mg, Mo, Ni, Se, Te, Tl, Sn, Ti, U, V and Zn at trace concentrations[9-11].

Constituting the subject of this study, Yatagan thermal power plant situated within the boundaries of Mugla and it was included in the investment program in 1975 for the purpose of the evaluation of low calorie coals in the lignite basin of Mugla-Yatagan and the satisfaction of the energy need of the national system. The 1st, 2nd and 3rd units were, respectively commissioned in 1982, 1983 and 1984[12]. The first zoning plan of Yatagan was made in 1966. Electricity energy was initially provided to this location in 1967 through a generator and then in 1971 from Kemer hydroelectric power plant. The economy of the district is generally dependent on agriculture, industry and forestry. The number of the farmer houses in the district is 8930 and this figure stands for 79 % of the total number of houses in the region. The majority of the community deals with the production of tobacco, grain, olive and some other agricultural products. The mines extracted in and around Yatagan are particularly lignite and then marble and emery stone[6]. Mugla territory is one of the most important coal basins of Turkey and General Directorate of Turkish Coal and General Directorate of Mineral Research and Exploitation express the existence of 800 million tons of usable coal. As the lower thermal value of the lignite coal in the territory is 1750-2100 kcal/kg, it is not suitable for use in any other industry than thermal power plants[13].

The ashes and slugs arising as a result of the incineration of coal in boilers at the power plant are transferred to the ash disposal area through conveyors. In order for the thermal power plant wastes of Yatagan to be discharged without damaging the territory, such wastes as ashes and slugs are stored at about 2 km south west of the power plant. Ash wastes are mixed with water in order to prevent the stored wastes from spreading around. The ashes are prevented from flying due to wind by using this procedure as they are depositing at the bottom of the water and creating a firm ground layer. 32.000.000 m^3 wastes are stored in the waste reservoir. However, as the wastes are mixed with water and create a firm ground layer, waters are accumulated at this area and have turned into a 15.000.000 m^3 of waste water dam[12].

EXPERIMENTAL

The samples used within the scope of this study are fly ash samples obtained from the MuglaYatagan thermal power plant. The samples were taken and deposited for a month from each shift of the electro-filtration department of the power plant. For the preparation of ash samples for characterization studies and leach tests, Denver branded laboratory type ball mill was used. Before and after the comminution process with the ball mill, some samples were subjected to chemical analysis and their contamination statuses were checked. Total moisture analyses (*i.e.* the moisture content of the sample when it was brought to the laboratory) were also performed on the sample in accordance with TS 690 ISO 598 (Method-C) standards. Memmert ULM500 branded drying oven was used in the context of moisture analyses. Wet sieving method was used for the particle size analyses of the fly ash sample and the analyses were performed in accordance with TS ISO 2395 standard. Retsch branded sieve series were used in sieving analyses. Density analyses were also carried by using a 50 mL pycnometer in order to determine the density values of the fly ash samples. Distilled water was used in the context of all density tests. XRD analyses, on the other hand, were conducted by using Rigaku D/Max-2200/PC XRD device in Advanced Analyses Laboratory of Istanbul University.

The device in question has a power capacity of 200 Vac 3q 20 A/50 Hz and both standard and high temperature stove units were used. As a result of the comparison of X-ray diffraction pattern data with about 120.000 substances having PDF card numbers included in Jade 6.5 software program, mineral analysis was performed.

The device has a high temperature unit which ensures measurement at high temperature values. Phase diagrams of various substances undergoing thermal changes and the modifications in the crystal structure can be observed with the help of the unit. SEM analyses of the samples were made with Quanta FEG 450 branded scanning electron microscope (SEM). An image is obtained in the scanned electron microscope (SEM) through the focus of the high voltage accelerated electrons on the sample, the collection of the effects arising as a result of various attempts between electron and atoms of the sample during the scanning of this electron beam through suitable detectors and transfer of it to the monitor of cathode beam tube after being subjected to signal amplifiers. In leach experiments, a Wise Bath branded mixing water bath was used. Following the leach process, the solutions were subjected to a solid-liquid separation process. Within the scope of the solid-liqud separation, Whatman branded grade 1 filter paper with pore size of 4 μm was used.

RESULTS AND DISCUSSION

Physical characteristics: As a result of the moisture analyses performed, it was determined that the fly ash sample of Yatagan thermal power plant contain a total of 4.21 % moisture.

The ashes taken from thermal power plants were subjected to particle size analyses with their original sizes. Wet sieving method was applied in the particle size analyses of the ash samples. It was found through the particle size distribution graph which is given in Fig. 1, d_{50} and d_{80} sizes of the sample were determined as 0.13 and 0.27 mm, respectively.

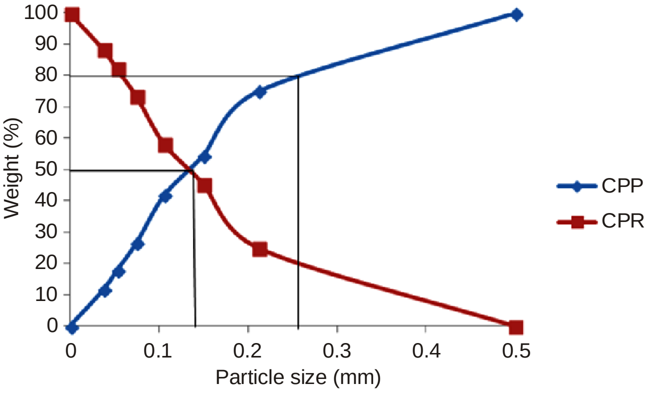

Fig. 1. Cumulative undersize and oversize graph of the fly ash samples obtained from Yatagan thermal power plant

For the purpose of determining the densities of the fly ash samples taken within the scope of the study, density analyses were performed with the help of a pycnometer. The tests were repeated three times for each sample in order to minimize the margin of error during the measurements and their average values were taken into consideration. According to the results of the performed tests, average density of the ashes taken from Yatagan thermal power plant was determined as 2.17 g/cm^3.

Mineralogical characteristics: In order to obtain information on the mineralogical structure of the fly ashes of Yatagan thermal power plant, XRD (X-ray diffraction) analyses were performed on the fly ash samples of Yatagan thermal power plant in Advanced Analyses Laboratory of Istanbul University. As a result of the XRD measurement, it was determined that the fly ash sample taken from Yatagan thermal power plant contain high amount of quartz-SiO_2 and albite-$Na(AlSi_3O_8)$, calcite $CaCO_3$ minerals at slightly less amounts. It was not possible to monitor rare earth and radioactive minerals with XRD; however, they were able to be identified in ICP-MS and SEM analyses. XRD diffraction pattern of the ash sample taken from Yatagan thermal power plant is presented in Fig. 2.

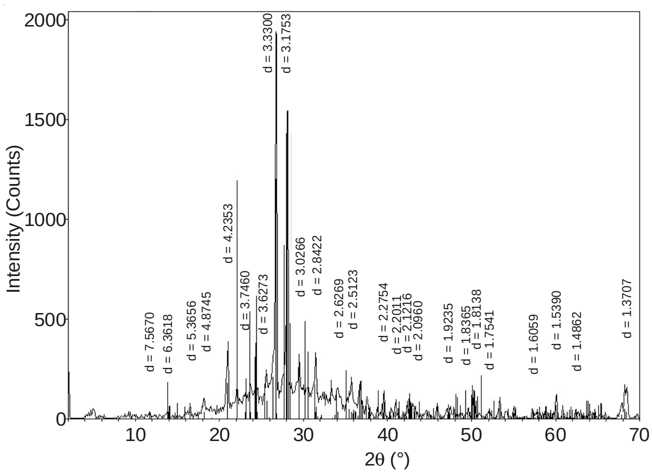

Fig. 2. XRD diffraction pattern of the ashes of Yatagan thermal power plant

The fractions obtained as a result of the sieve analysis were examined under optic microscope and photographed for the determination of mineral compositions. As a result of the examinations, it was observed that the fly ash samples predominantly contain amorphous and vitreous silicate minerals. This, in turn, can be explained as the change of the crystal structures of the mineral contents due to the fact that the samples were processed at high temperatures as an incineration product. Fig. 3 shows microscopic photographs of the fly ashes of Yatagan thermal power plant. According to the thin section analyses of Yatagan fly ashes, it is considered that uranium and thorium are, respectively presented in the ashes of Yatagan thermal power plant in the form of uraninite (UO_2) and of monazite [(Ce, La, Nd, Th)(PO_4)] and thorite [Th(SiO_4)]. Radioactive minerals show a distribution on the glass phase. The particle sizes vary between 80-5 μm for uranium and thorium bearing minerals in the fly ashes of Yatagan thermal power plant.

The images obtained within the scope of SEM analyses were performed in order to identify the morphologies of the fly ashes of Yatagan thermal power plant are given in Fig. 4. The quartz and orthoclase minerals in the fly ashes were coal based and they mixed with the ashes without combustion due to their stable structures. Agglomeration was observed in the fly ash particles. The unburned carbons (char) in the ash sample were observed to be of slightly block structure and predominantly of plexal and pellet structure.

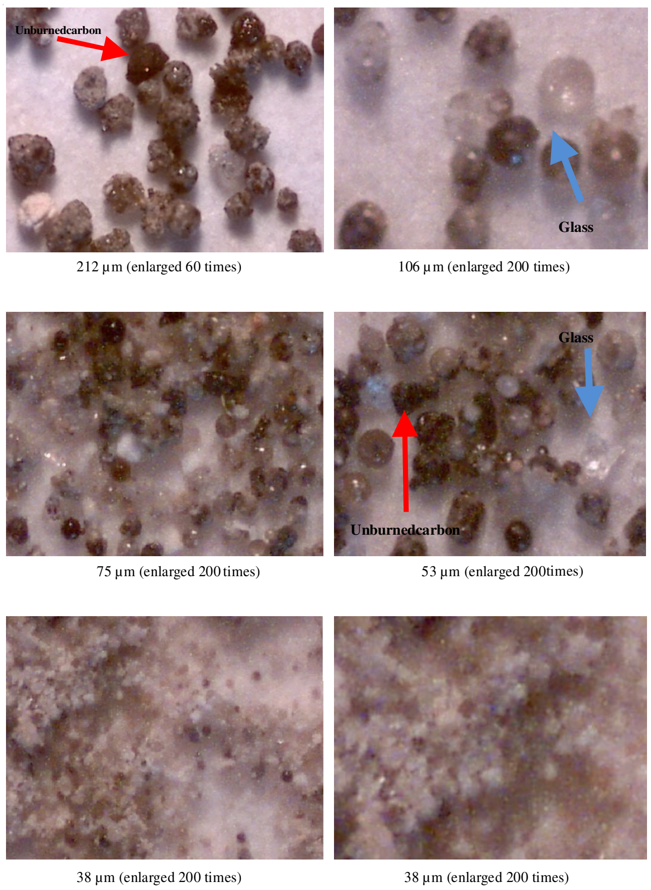

Fig. 3. Optic microscope images of the sieve fractions of Yatagan ashes

Chemical analyses: The contents of principal oxides, base metals and trace elements of the fly ashes taken from Yatagan thermal power plant which were determined as a result of chemical analysis are given in Table-1. As can be seen from the table, V, Zr, Sr, U, Th and Ba contents of the sample are particularly high.

TABLE-1
COMPLETE CHEMICAL ANALYSIS PERFORMED ON ASHES TAKEN FROM YATAGAN THERMAL POWER PLANT

Content	Assay value	Content	Assay value	Content	Assay value
SiO_2 (%)	45.94	Y (ppm)	87.30	Ga (ppm)	20.10
Al_2O_3 (%)	19.28	La (ppm)	66.00	Hf (ppm)	5.00
Fe_2O_3 (%)	7.14	Ce (ppm)	134.10	Nb (ppm)	18.80
MgO (%)	4.43	Pr (ppm)	15.49	Rb (ppm)	104.50
CaO (%)	17.28	Nd (ppm)	61.60	Sn (ppm)	4.00
Na_2O (%)	0.57	Sm (ppm)	12.95	Sr (ppm)	406.40
K_2O (%)	1.93	Eu (ppm)	2.37	Ta (ppm)	1.20
TiO_2 (%)	0.78	Gd (ppm)	13.20	Th (ppm)	210.00
P_2O_5 (%)	0.24	Tb (ppm)	2.18	U (ppm)	160.00
MnO (%)	0.06	Dy (ppm)	13.35	V(ppm)	159.00
Cr_2O_3 (%)	0.047	Ho (ppm)	2.76	W (ppm)	5.50
Ni (ppm)	117.00	Er (ppm)	8.14	Zr (ppm)	152.70
Sc (ppm)	19.00	Tm (ppm)	1.26	Pb (ppm)	9.40
LOI (%)	3.00	Yb (ppm)	7.64	Zn (ppm)	58.00
Total (%)	99.74	Lu (ppm)	1.14	As (ppm)	34.00
Ba (ppm)	533.00	Total/C (%)	0.87	Cd (ppm)	0.68
Be (ppm)	4.00	Total/S (%)	0.43	Sb (ppm)	1.50
Co (ppm)	21.20	Mo (ppm)	9.80	Bi (ppm)	0.20
Cs (ppm)	9.40	Cu (ppm)	37.10	Ag (ppm)	< 0.10
Tl (ppm)	0.30	Hg (ppm)	0.07	Au (ppb)	< 0.50
Se (ppm)	2.000	-	-	-	-

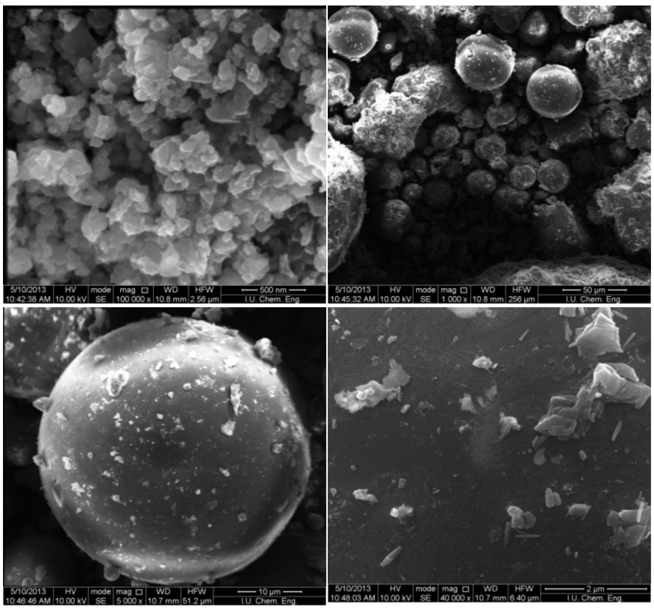

Fig. 4. Scanned electron microscope (SEM) images of Yatagan thermal power plant fly ashes

Leach tests: Uranium and thorium contents were aimed to be recovered in acetic acid with high grade and efficiency in the leach tests performed on the fly ash samples that representatively taken from Yatagan thermal power plant. Acetic acid is a weak acid and uranium and thorium mix with the solution, respectively as uranium acetate and thorium acetate as a result of their reaction with acetic acid.

Within the scope of the leach tests, the effects of different leach parameters were investigated in order to determinate the optimum dissolution conditions both for uranium and thorium. The particle size was -75 µm within the leach tests. Leach tests were performed with the help of the leach unit of Wise Bath branded mixing water bath. Mixing speed and mixing temperature were continuously measured during the leach test. pH measurement was also carried out in all leach tests periodically. Obtained solutions were subjected to solid-liquid separation with the use of Whatman grade 1 filter papers. The solid part is dried and made ready for relevant analysis whereas both solid and liquid phase was sent to chemical analysis. Leach efficiencies were calculated according to the following equation:

$$\text{Efficiency (\%)} = \frac{\text{U, Th in the ash} - \text{U, Th in the residuals}}{\text{U, Th in the ash}} \times 100$$

Variation of uranium and thorium dissolution efficiency according to percentage of solids in the leach of Yatagan thermal power plant fly ashes with acetic acid: The graph of the variation of uranium and thorium dissolution efficiency according to percentage of solids in the leach of Yatagan thermal power plant fly ashes with acetic acid is given in Fig. 5.

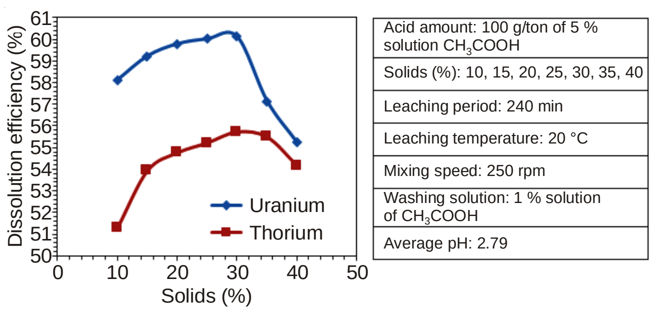

Fig. 5. Graph of the variation of uranium and thorium dissolution efficiency according to percentage of solids in the leach of Yatagan thermal power plant fly ashes with acetic acid

According to the graphically presented results, uranium dissolution efficiencies in Yatagan thermal power plant fly ashes reached to the highest level under 30 % solids conditions. Following such rate where 60.11 % uranium dissolution efficiencies were obtained for Yatagan thermal power plant fly ashes, the efficiency showed a decrease tendency in an inversely proportional way to percentage of solids increase. When the dissolution efficiencies of thorium are observed, it exhibited a similar behaviour to the dissolution efficiency of uranium presented in Yatagan thermal power plant fly ashes and reached to the highest level under 30 % solids conditions with the rate of 55.72 % and a decrease was observed after this point. When both uranium and thorium dissolution efficiencies are taken into consideration for the fly ash samples of Yatagan and the difficulties arising from the mixing of pulp as percentage of solids increases are considered, it was decided to take optimum as 30 % solids in subsequent tests.

Variation of uranium and thorium dissolution efficiency according to the leaching period within the scope of the leach of Yatagan thermal power plant ashes with acetic acid: The graph of variation in the uranium and thorium dissolution efficiency according to leaching period within the scope of the leach process of Yatagan thermal power plant fly ashes in acetic acid that plotted with the use of the obtained test results is presented in Fig. 6.

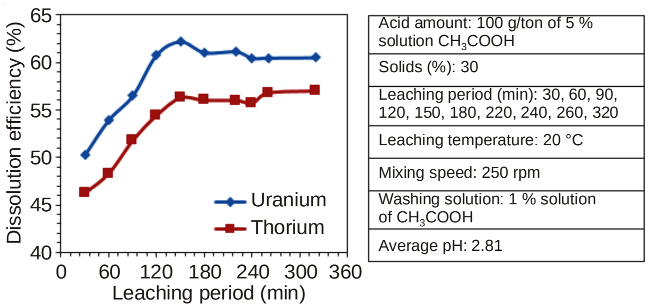

Fig. 6. Graph of the variation of uranium and thorium dissolution efficiency according to leaching period in the leach of Yatagan thermal power plant fly ashes with acetic acid

According to the graphic results, it can be seen that uranium dissolution efficiency in the fly ash increase to a certain point depending on the time and decrease after such point and undergo a slightly fixation tendency. Uranium dissolution efficiency for Yatagan thermal power plant fly ashes linearly increased until 150 min. and decreased averagely 1 % after this point and did not show a significant variation. Accordingly, it can be said that optimum leaching period is 150 min. where highest uranium dissolution efficiencies were obtained with the rate of 62.18 % for Yatagan thermal power plant fly ashes. Thorium dissolution efficiencies, on the other hand, generally increased with the increase of the leaching period. The best thorium dissolution efficiencies for Yatagan thermal power plant fly ashes were obtained as a result of the leach tests performed respectively with the values of 57.01 % and for 320 min. In the light of these results, optimum leaching period was taken as 240 min in subsequent leach tests performed with acetic acid.

Variation of uranium and thorium dissolution efficiency according to the acid amount within the scope of the leach of Yatagan thermal power plant fly ashes with acetic acid: The variation of uranium and thorium dissolution efficiencies of Yatagan thermal power plant fly ashes with acetic acid according to the acid amount is given in Fig. 7.

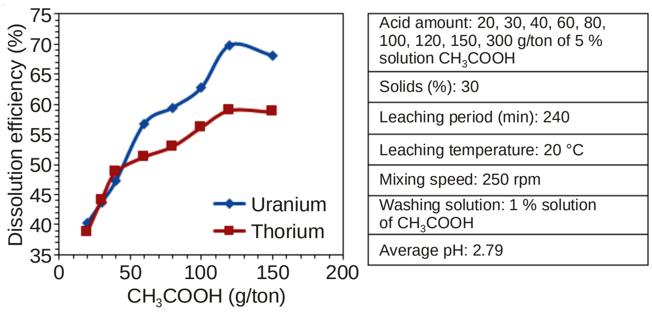

Fig. 7. Graph of the variation of uranium and thorium dissolution efficiency according to acid amount in the leach of Yatagan thermal power plant fly ashes with acetic acid

According to the experimental results, it can be seen that uranium dissolution efficiency increase up to a certain point in the thermal power plant fly ashes depending on the amount of acetic acid and decrease after such points. Uranium dissolution efficiency for Yatagan thermal power plant fly ashes increased up to 120 g/ton acid amount and decreased at the rate of 1.76 % after this point with the efficiency of 69.77 %. Accordingly, optimum acid amount was observed to be 120 g/ton where the highest dissolution efficiency was obtained. Thorium dissolution efficiency, on the other hand, increased up to the acid amount of 120 g/ton for Yatagan thermal power plant ashes and decreased at the rate of 0.28 % at 150 g/ton acid amount after this point where the value of 58.99 % was obtained. Accordingly, optimum acid amount in terms of thorium dissolution efficiency was observed to be 120 g/ton where the highest dissolution efficiency was obtained. In the light of these results, it was determined that optimum amount of acetic acid was 120 g/ton for uranium and thorium dissolution efficiencies for Yatagan thermal power plant ashes.

Conclusion

A significant part of the electricity generation in Turkey is provided from coal fired thermal power plants. Large volumes of fly ash residuals arise during the electricity generation process from by thermal power plants. Few amount of annual fly ash residuals are evaluated in such industries as cement and brick and the remaining amount directly constitutes waste areas. Such wastes are deposited in fly ash storage reservoirs or in bulk as for now.

The aim of this study is the characterization and classification of fly ashes in an environmental sense and investigation of the degradability of environmental effects of heavy metal, trace element and radioactive element contents that contained in these ashes as well as the recovery of the contents which can constitute an economical value. Fly ash samples were taken from Yatagan thermal power plant on this regard and these samples were subjected to characterization as well as mineral processing and ore dressing tests. As part of the characterization studies, such analyses as particle size analysis, moisture analysis, density determination, chemical analyses, mineralogical analyses were performed. Within the scope of mineral processing and ore dressing studies, on the other hand, laboratory scale leaching tests were carried out.

During the leach tests performed with the use of acetic acid, such parameters as 10-15-20-25-30-35 % solids; 30-60-90-120-150-180-220-240-260-320 min. leaching periods and

20-30-40-60-80-100-120-150 g/ton acetic acid amounts were used and the best results were obtained for the fly ash samples taken from Yatagan thermal power plant at 30 % solids, 150 g/ton CH_3COOH amount, 240 min. of leaching period and 20 °C leach temperate conditions. As a result of the tests performed under the above mentioned conditions, 97.12 % uranium dissolution efficiency and 91.21 % thorium dissolution efficiency were obtained for the ash samples of Yatagan thermal power plant.

It is true that nuclear energy will have an important role in the energy generation activities of Turkey. Within this context, the raw materials of uranium and thorium which stand for the fuel of particularly nuclear energy driven thermal power plants as well as the recovery of such raw materials from alternative resources are strategically important.

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REFERENCES

1. S. Gurkan, M.Sc. Thesis, The Removal of Mineral Matter from Çayirhan lignites by Caustic Wash Method, Institute of Science and Technology of Gazi University, Turkey (1992).
2. H.Y. Aruntas, *J. Eng. Architec. Fac. Gazi Univ*., **21**, 193 (2006).
3. I. Demir, M.Sc. Thesis, Investigation of Evaluation possibilities of Turkish Coals in terms of the Trace Element Contents by Use of Coal Preparation Methods, Science and Technology Institute of Istanbul University, Istanbul, Turkey (2009).
4. M. Ozturk, Trace Elements in Coal and Environmental Pollution, Environment '89 5. Scientific and Technical Environment Congress Book, pp. 857-868 (2012).
5. G. Aycik, Removal of Radioactive Isotopes from Coal Ashes and Biomass Ashes, Publication of Ankara University, Faculty of Engineering (2008).
6. K. Haktanir and S. Sozudogru, Creating of a Pollution Database for the Agriculture and Forest Lands Under the Effect of the Emissions from Mugla Yatagan Thermal Power Plants, Scientific Research Projects of Ankara University, Ankara University, Ankara, Turkey (2007).
7. V. Arora and S. Kumar, Journal of The Institution of Engineers (India), **3**, 361 (2006).
8. I. Gunindi, M.Sc. Thesis, Investigation of Compressive, Flexural and Abrasion Resistance of Concrete Containing Flyash from Yumur Talik Sugozu, Science and Technology Institute of Cukurova University Cukurova, Turkey (2005).
9. W. Douglas, Effects of Coal Fly-Ash Disposal on Water Chemistry an Intradunal Wetland, Indiana Dunes, State University of New York (1988).
10. Z.I. Asar, M.Sc. Thesis, Investigations on Concentrations of Some High Technology Elements (Ga-Ge-Se-Te) at Some Coal Deposits in Turkey, Science and Technology Institute of Ankara University, Ankara, Turkey (2009).
11. O. Kirdim, M.Sc. Thesis, Mineralogy and Petrography of Feed Coals and Combustion Residues from the Seyitomer (Kutahya, Turkey) Thermal Power Plant, Science and Technology Institute of Hacettepe University, Turkey (2006).
12. A. Baba, Use of the Fly Ashes Obtained from Can Thermal Power Plant in Ceramic Glazes, III. Internationally Participated Ceramic, Glass, Enamel Glaze and Paint Seminar, 17-19 October 2005, Eskisehir, pp. 591-598 (2005).
13. YEAS, http://www.yeas.gov.tr (2008).