Distribution of trace elements in coal and coal fly ash and their recovery with mineral processing practices: A review

I. Kursun Unver* and M. Terzi

Department of Mining Engineeering, Faculty of Engineering, Istanbul University, Istanbul, Turkey

Abstract

Today coal is among the most important energy sources. In order to meet the world's energy demands, low-calorie lignite with a high ash content is generally used in the large capacity coal-fired thermal power plants. As a result of coal firing, wastes such as fly ash, slag, and flue gas are also produced. Subsequently, toxic trace elements within coal are transferred to wastes such as slag, fly ash, and flue gases. Large amounts of these, which are usually stored in collection ponds or stockpiles, are problematic in terms of environment. Although coal fly ash (CFA) has been utilized in construction and several other industries for decades, its current ratio of utilization is still quite limited. As an important fact, CFA also contains many valuable metals including germanium (Ge), gallium (Ga), vanadium (V), titanium (Ti), and aluminum (Al). In addtion, coal and CFA can be regarded as alternative sources of radioactive elements. Therefore, they also have a great potential in terms of the precious metals and trace elements they contain. In this study, the present literature on the distribution of trace elements in coal and coal ash during firing and ore preparation processes and their recovery possibilities with mineral processing practices are reviewed. While many research works on the subject clearly indicate that the large amounts of the ashes produced from firing of coal could be problematic in terms of environment, many studies and practices also show that coal combustion products also have a great potential in terms of the precious metals and trace elements.

Keywords: *Coal, Trace Elements, Fly Ash, Utilization.*

1. Introduction to trace elements in coal

In primary energy consumption, coal takes the second place with approximately 29% share after oil, which takes the first place with approximately 33% share as of 2015 [1]. As a result of coal firing, wastes such as fly ash, slag, and flue gas are also produced. Coal fly ash (CFA) is a finely divided residue, which is mainly composed of spherical glassy particles and has resulted from the combustion of pulverized coal. After its occurrence in the boiler, CFA is then transported by flue gases from the combustion zone to the particle removal system [2-3]. Thermal power plants generate large amounts of fly ashes [4]. Globally, China is the largest producer of fly ash, followed by Russia and USA [5]. On the other hand, an average of about 45 million tons of coal are burned and 20 million tons of fly ash are produced in Turkey annually [6]. Inorganic matters in coal are the main source of fly ash [7]. Ninety-five percent of the mineral matters in coal are clay minerals, carbonate minerals, sulfides/disulfides, silica, and sulfates [8]. Silica minerals such as quartz, feldspar, and clay minerals detritically enter the environment due to decrease in the water flow rate in the marsh environment. Minerals such as kaolinite and pyrite are mostly syngenetic with diagenetic processes during the burial and charring processes. The third type of minerals that can be observed in coals are the minerals such as calcite and pyrite that are epigenetically formed in fractures and cracks after carbonization [9-11]. The inorganic matters in coal include trace elements, and they are not uniformly distributed.

The coal–mineral and mineral–mineral associations play an important role in the formation of fine particles and in the subsequent condensation of trace elements in various phases [12].

Elements such as Fe, Mg, As, Zn, Cu, F, Th, and V whose contents in coal are generally less than 1000 ppm are generally considered as the trace elements in coal [13]. As expected for a natural substance with a long and diverse history, coal contains most of the elements in the periodic classification, and there is data for 73 trace elements [14-15]. The major trace elements present in coals are given in Figure 1.

The group I elements are known to be hazardous in some circumstances but their concentrations in most coals are low. However, care should be taken to check for possible untoward effects,

especially with As and Se. Group IIA includes B, Mn, and Mo, which should be taken into consideration in leachates from wastes and for reclamation after mining. Relatively high concentrations of U and Th should be avoided in order to minimize radioactivity from fly ash [16]. Problems with the other group IIB elements are unlikely, although high-Cl coals may cause some corrosion and add to acidity in the atmosphere. The concentrations of trace elements in group III coals are not expected to give troublesome effects. Toxicity of elements per se is a trap to be avoided, especially because many elements may be essential or hazardous [16]. The associations of some trace elements with inorganic mineral phases and organic phases found in coal are given in Table 1.

Figure 1. Major trace elements present in coals (Adapted from [15]).

Table 1. Distribution and association of some trace elements in coal [17, 13].

Inorganic	
Minerals	**Associated elements**
Clay Minerals, Kaolinite, Montmorillonite, Feldspars	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y, and rare earths.
Iron Sulphides, Pyrite, Sphalerite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W, Zn.
Calcite, Dolomite, Ankerite	C, Ca, Co, and Mn.
Sulphates	Ba, Ca, Fe, and S.
Heavy Minerals, Turmaline	B.
Others	Co and W (carbonates and sulfides), Ni, Cu, Pb (clay minerals and sulfides), S (sulfides, sulfates and organic matters), C (carbonates and organic matters).
Organic	
Minerals	**Associated elements**
-	C, N, S, Be, B, Ge, V, W, V, Zr

1.1. Toxic trace elements and heavy metals

In general terms, metals may be found in the lower-left side of the diagonal of semi-metals or metalloids (from boron to polonium) in the periodic table, which may act as both metals and non-metals. Metals are distinguished from non-metals by their capacity to lose electrons, forming positively charged ions or Lewis acids, and by their speciation-dependent affinity for abiotic and biological interactions. Several metals such as iron, cobalt, copper, manganese, molybdenum, and zinc are required at certain concentration levels by the human body, while others are toxic above the not-observed adverse effect concentration level such as lead, cadmium, mercury, and arsenic, which have no beneficial influences on the human health [18]. Heavy metals are usually defined as metals with a density greater than 4-5 g/cm^3. Heavy metals such as arsenic (As), chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) are of great concern due to their potentially adverse health effects to humans. While certain amounts of exposure to Cu and Zn are not harmful, exposure to elevated concentrations or excessive intake of these elements are also damaging [19-20]. Similar to Cu and Zn, while Fe is an essential element for the growth, high contents of tissue Fe has been found to be associated with cell injury and several pathological conditions including liver and heart disease and cancer [21-22]. Owing to their chemical characteristics, metals remain in the environment, in many cases only changing from one chemical state to another and eventually accumulating in the food chain. Antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc are defined as heavy metals, which among 35 metals are considered dangerous for the human health. However, most important heavy metals whose exposures possess danger to the human health are lead, cadmium, mercury, and arsenic, which are metalloids and are usually defined as heavy metals [23-24].

As stated earlier, coal is a material that contains relatively high concentrations of trace elements when compared with other geological materials [25]. Significant amounts of heavy metals are also present in coal [26-27]. Furthermore, coal combustion products are enriched 4 to 10 times in terms of some trace elements. If this fact is considered together with the high fly ash production rate of the power stations (a 1000 MW power plant produces about 1,000,000 tons of wastes per year), some ideas of the environmental importance of heavy metals in fly ash may be obtained. Therefore, an important variety and quantity of some potentially toxic trace elements including Cd, Co, Cu, Ni, Pb, Sb, and Zn are mobilized during the energy production in coal-fired power plants. In this respect, the fly ash constitutes an important source of pollutants for groundwater contamination and biological uptake [25].

1.2. Toxicity of trace elements

The effects of some toxic elements in coal on human health is given in Table 2.

Table 2. Effects of some toxic elements in coal on human health [28].

Element	Possible adverse effects on human health
As	Anemia, nausea, renal signs, ulcer, skin and lung cancer, defective births.
Be	Respiratory and lymph, lung, spleen and kidney disorders, carcinogen effects.
Cd	Pulmonary emphysema and fibrosis, kidney disease, cardiovascular effects, carcinogenic effects
Hg	Neural and kidney damage, cardiovascular effects, birth problems.
Mn	Respiratory effects.
Ni	Skin and intestinal disorders, carcinogen effects.
Pb	Anemia, neural and cardiovascular problems, growth retardation, stomach and intestinal problems, carcinogenic effects, birth problems.
Se	Stomach and intestinal disorders, lung and spleen destruction, anemia, cancer, teratogenic effects.
V	Acute and chronic pulmonary dysfunctions.

1.3. Radioactive elements

Like many other materials found in nature, coal contains traces of ^{238}U, ^{232}Th, and ^{40}K with decay products. The average natural radionuclide activity concentrations in coal are given as 20 Bq kg^{-1} for ^{238}U, ^{232}Th and decay products, and 50 Bq kg^{-1} for ^{40}K. In general, the content of natural radionuclide activity in coal is smaller than the average concentrations in the Earth's crust. However, low-quality coal such as lignite (especially young lignite) has been observed to have a high uranium content [29]. Uranium in

coal is mainly associated with the organic matters, and to a lesser extent occurs in minerals [30]. During the first half of the 20th century, U-bearing coals were utilized as an alternative source of U. Currently, U-bearing coals are considered to be a potential source of radioactive contamination [31]. In contrast to coals, the natural radionuclide activity concentrations of the coal combustion products are much higher than the average concentrations in the Earth's crust. The average natural radionuclide activity concentrations for ^{40}K, ^{238}U, ^{226}Ra, ^{210}Pb, ^{210}Po, ^{232}Th, ^{228Th}, and ^{228}Ra are 265, 200, 240, 930, 1700, 70, 110, and 130 Bq kg^{-1}, respectively. In this direction, coal-based thermal power plants are considered as the most important source of technologically enriched natural radioactivity [32].

In a power plant, concentrations of natural radionuclide activity discharged to the atmosphere per unit electric power generation depending on the factors such as concentration of natural radionuclide activity in coal, coal to ash ratio, combustion temperature, fly ash and bottom ash ratio, and efficiency of the filter system. Therefore, the difference between natural radionuclide activities that are gererated per unit energy in different plants should be expected [29]. Concentration of ^{226}Ra in the atmosphere has increased by 100 factors in the last 80 years, and this increase is mainly assocaitaed with coal-based thermal power plants [28]. In Greece, it was calculated that the 1.6×10^{12} Bq for ^{226}Ra, which constitutes more than 80% of the ^{226}Ra content in a lignite coal burning plant, is released by gas or fly ash [33].

As a known fact, the origin of lignites is plants. Although plants do not contain uranium, humic acid extracted from lignite shows a greater adsorption capacity to uranium than lignites itself. Several hypotheses have been raised on how and where uranium in lignite coal and other carbonaceous materials came from. According to the most held hypothesis on the accumulation of uranium in the lignites today:

a) Granites that are the primary source of uranium are subject to chemical degradation;

b) Uranium is dissolved in sea water through the solution in the form of alkaline uranyl carbonate;

c) These compounds are adsorbed on the lagoon basins or in the marshes by the humic substances resulting from the decay of organic substances under water.

Along with carbonization, uranium is bound to the organic body via strong bonds by the humic acid

contents of the bioliths [34]. The connection mechanism of uranium to coal is shown in Figure 2.
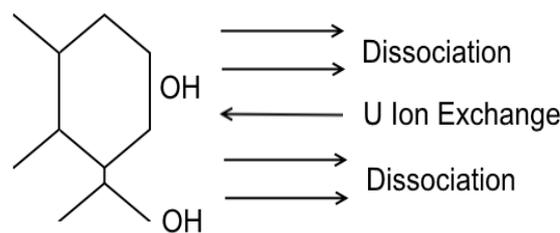
Figure 2. Connection mechanism of uranium to coal (Adapted from [34]).

Abruzov et al. (2011) have investigated the geochemistry of radioactive elements in more than 5000 coal and peat samples of Northern Asia by quantitative methods. They have found that the average U content in the coals of deposits and basins of the region ranges from 0.6 to 32.8 ppm, and for Th, from 0.8 to 9.2 ppm. The authors have stated that the distribution of U and Th in the investigated coal basins is irregular due to the influence of a combination of several factors such as heterogeneity of rock composition of folded boundaries of the basins, difference of the facies conditions of the coal accumulation, influence of volcanism, climatic conditions, and degree of coal metamorphism. They have also pointed out that the high concentrations of U and Th in coal-bearing deposits are related to the blocks of rocks enriched with U and Th at the peripheries of the basins or connected with the occurrence of a volcanism in the period of the coal accumulation. In a majority of USA coals covering approximately 2000 coal samples from the West United States and 300 coals from the Illinois Basin, the U concentration falls within the range of slightly below 1 to 4 ppm. Coals containing U in excess of 20 ppm are rare in the United States. Th concentrations in USA coals fall within a similar 1-4 ppm range compared to an average crustal abundance of approximately 10 ppm. Coals containing more than 20 ppm of Th are extremely rare in the United States [31, 35-37]. Also the coal from the Kangal basin, Turkey, disposes a high U concentration ranging between 5.5 and 131 ppm but the coal from the Sorgun basin disposes a higher Th (1.4–69 ppm) compared to the U concentration (<0.7–11 ppm). The highest possible concentration of U in Turkish coals (140 ppm) was detected in the deposit within the Aegean Region [37-40].

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2. Transfering behaviors of trace elements
2.1. Coal firing processes

During combustion, the boiler flame temperature can exceed 1600 °C in thermal power plants. A number of complex physico-chemical changes take place within the particles under the high temperature conditions of the boiler flame. The particles can be transformed into spherical forms very quickly by the effect of surface tension forces. In addition, the molten material in the gas stream is partially or completely converted into spherical ash particles [41].

During the combustion of pulverized coal in thermal power plants, the carbon, nitrogen, and sulfur in the coal are oxidized into carbon oxide (CO_X), nitrogen oxide (NO_X), and sulfur oxide (SO_X), respectively. During this conversion, some water vapor is also produced. While the slag is collected under the combustion boilers, the fly ash is kept in the electro-filters, and some of it is carried by the flue gas. Studies have shown that trace elements are mostly concentrated on fly ash [42]. A simplified mechanism of CFA formation from pulverised fuel combustion is given Figure 3.

On combustion, the trace elements in coal are transferred to slag, fly ash or gases, and are discharged to the environment. Annually, the total quantities of trace elements produced in coal combustion are comparable to the quantities mobilized by weathering of crustal rocks [44]. The distribution of some trace elements after combustion is shown in Figure 4.
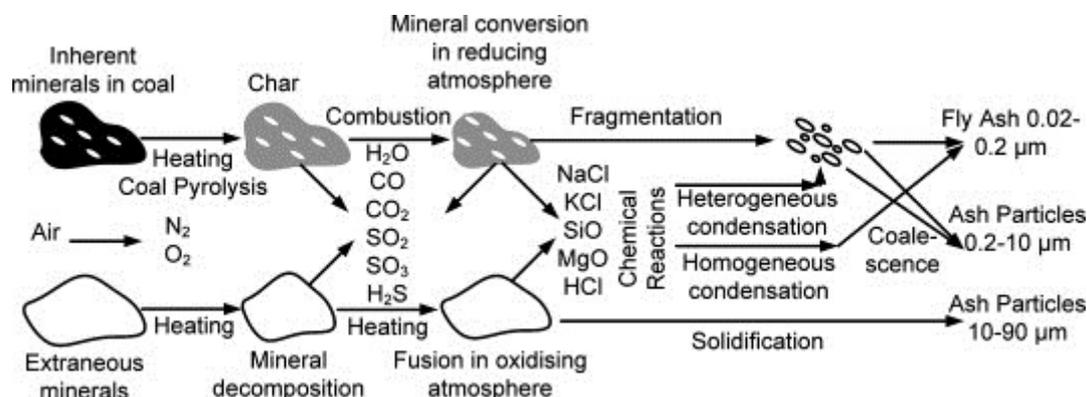

Figure 3. Simplified mechanism of CFA formation from pulverised fuel combustion [43].
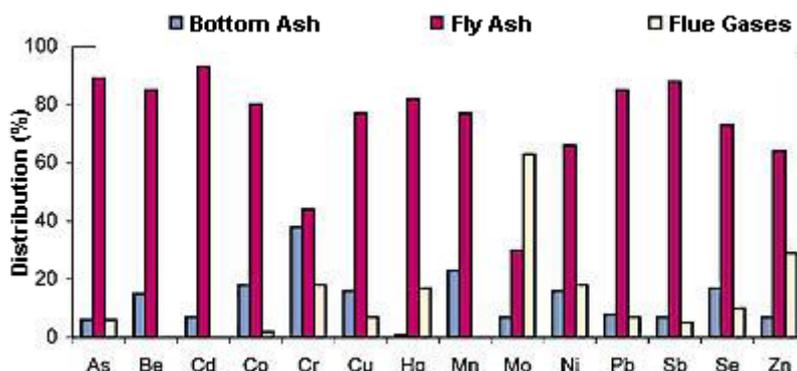

Figure 4. Distribution of some trace elements after combustion [15].

The distribution of trace elements during coal combustion is affected by several physical processes such as the turbulence, pollution control mechanism, and temperature in the boiler. As stated earlier, most of the TE contents are removed by solid residues, especially by fly ash. However, some parts of trace elements are released as aerosols or as vaporized elements in the gas phase [12]. In terms of the pollution control mechanisms, Meij (1994) has suggested that the gaseous inorganic trace elements are not removed by ESP. Lopez-Anton et al. (2011) have suggested that the performance of the mills may also siginicantly affect the trace element composition of CFA [45-46].

According to Helble and Sarofim (1993), several other factors such as feed coal particle size and coal type also affect trace element behavior during coal combustion. They have found that the enrichment in fly ashes is typically lowest for the sub-bituminous coal among the three different coal types investigated, namely bituminous coal,

sub-bituminous coal, and lignite coal. As and V have been found to be most volatile in the bituminous coal. On the other hand, Cr was found to be the most volatile in lignite. They have suggested that the differences in the predominant forms of the element in the parent coals greatly affects their behavior during combustion [47].

Hg, As, Se, Ni, Pb, Ce, and Zn are predominantly associated with sulfide minerals and organic matters. The formation of coal minerals or trace elements in organic matters can significantly affect the evaporation limit and thus the rate of flue gas being discharged. Trace elements detected in flue gases are mainly related to sulfite minerals [15]. According to a study conducted in a coal-fired thermal power plant in India, the Ni, Cr, and Pb concentrations have been found to be high in the analysis of fly ash that cannot be captured by the power plant panel electro filters [48]. According to Kaakinen et al. (1994), the Cu, Zn, As, Mo, Sb, Pb, [210]Po, and Se concentrations are generally the highest in fly ashes among coal combustion products due to vaporization of these elements in the furnace. Subsequently, they condense or absorb onto fly ash, which have large specific surface areas [49]. Tang et al. (2013) have investigated the distribution of trace element coal combustion products from two different power plants operating at Huainan, Anhui, China. They have reported that As, B, Sn, and Zn tend to increase toward smaller particle sizes [50].

Generally, less volatile elements such as Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn, and oxidized Hg can be found together with finely-grained materials such as fly ash and bottom ash. As and Se represent medium volatility, and spread widely through the atmosphere. Many research works on heavy metals such as Pb, Cd, Cr, As, and Hg have been carried out in the field of enrichment according to different grain sizes, and removal and reaction with absorption or adsorption. However, the actual behavior of these elements can not be predicted in laboratories because it is conditioned by highly complex processes such as combustion of burning coal, combustion temperature, halogen sample concentration, redox conditions, and interaction between different samples [13]. A diagram showing the behavior of trace elements in coal during and after combustion is shown in Figure 5.
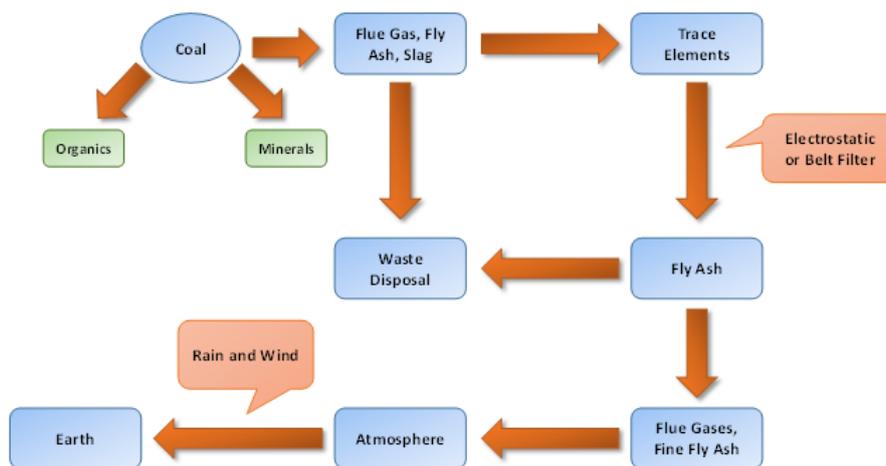

Figure 5. Behavior of trace elements in coal during and after combustion (Adapted from [13]).

In an examplary study, the behavior of heavy metals has been investigated during a mixture of straw and paper mud fired in fluidized bed fuels. It was found that most of the elements escaped from the fluidized bed but were obtained as fly ash fractions. It was observed that the emission of Hg, Pb, Cd, Cr, Cu, Ni, Mn, and Zn was generally below the emission limits during combined burning of sewage sludge and coal in a fluidized bed combustor [13].

Coal-to-ash enrichment rates of the radionuclides are characterized by the enrichment factor (EF) (Equation 1) [29].

$$EF = \frac{(X)_{sample} / \left(^{40}K\right)_{sample}}{(X)_{coal} / \left(^{40}K\right)_{coal}} \tag{1}$$

Since ^{40}K activity is stable in almost all ash types, ^{40}K is used as the reference radionuclide to determine the enrichment factor. When the enrichment rate of radionuclides from the coal is examined, it is seen that the enrichment at ^{210}Po and ^{210}Pb is the highest, followed by ^{238}U, ^{226}Ra, ^{228}Ra, and ^{232}Th. Enrichment of natural radionuclides in ashes from various types of thermal power plants has been found to vary

greatly with the particle size. High enrichment rates were observed in particles with a diameter of 2.4 μm and the EF values for [226]Ra, [238]U, and ^{210}Pb were determined to be 1.9, 2.8, and 5.0, respectively. As a rule of thumb, EF increases with the combustion temperature of the coal and decreases with the particle size (if greater than 1 μm) [29]. EFs in terms of the particle size variation in fly ashes are given in Table 3.

Table 3. EFs in terms of particle size variation in fly ashes [29].

Particle size (μm)	EF			
	[238]U	[228]Th	[226]Ra	[210]Pb
0-2.5	2.8	1.9	1.2	4.9
2.5-5	2.2	1.6	1.1	4.1
5-10	1.6	1.4	1.1	2.9
>10	1.3	1.0	1.0	1.5

During burning, the [40]K and [232]Th isotopes dissolve with aluminum silicate minerals and settle as bottom ash, while the uranium isotopes act according to their chemical or mineralogical forms in the coal. If uranium is mineralized as coffinite in coal, it remains in the bottom ash but if it is dispersed as uraninite, it can be volatile in the UO_3 form and moves by concentrating on fly ash particles. Radium, a decaying product of uranium, behaves in a similar way. However, [228]Ra, a decaying product of [232]Th, remains in the matrix of fly ash particles. The enrichment of [226]Ra is higher than that of [228]Ra in the volatile form due to the main elements of both isotopes found in different froms in the coal matrix. The [210]Po and ^{210}Pb radionuclides are highly volatile, and therefore, they evaporate during combustion and concentrate on fine fly ash particles with large surface area ratios [29].

Two radiation-based techniques have been used for determining the distribution and relative abundance of radionuclides in fly ash and bottom ash samples from a Kentucky power plant. The results obtained indicate that radium isotopes are not significantly (within l0-15%) fractionated from parent [238]U and [232]Th during coal combustion. In contrast, ^{210}Pb appears to be preferentially enriched in some samples of fly ash, and deplete in the bottom ash relative to [238]U and [226]Ra [36].

Coles et al. (1978) have investigated the behavior of the naturally occurring radionuclides [40]K, ^{210}Pb, [226]Ra, [228]Th, [228]Ra, [235]U, and [238]U in coal-fired power plants. They have stated that the varying degrees of enrichments for all the nuclides studied are observed in the fly ash particles. These values range from 5.0 for ^{210}Pb to 1.2 for [228]Th. The [235]U and [238]U EF values are both 2.8. The [226]Ra and [228]Ra EF values are 1.9 and 1.6, respectively. The thorium nuclides and [40]K show little fractionation in the fly ash and the bottom ash when compared to the original coal. [210]Pb shows a definite depletion in the bottom ash and the fly ash. They have also stated that uranium also shows a tendency for depletion in both ash types. An explanation for the behaviors of U and nuclides derived from the [235]U decay chain includes a bimodal residence for this element in the coal [51].

In summary, the coal-to-ash natural radionuclide EF varies depending on the mineralogy of the coal, type of burning, combustion temperature, and particle size. From the radiological viewpoint, [40]K, [232]Th, and the decay products remaining in the bottom as well as [238]U, [226]Ra, ^{210}Pb, and [210]Po that concentrate on fly ash particles are very important. [238]U, [226]Ra, ^{210}Pb, and [210]Po, which have different physico-chemical properties, exhibit different behaviors and are enriched at different ratios during the burning of the carcass, leading to radioactive imbalance in the ash, rather than coal. In addition to the uranium series, this radioactive imbalance is also favored by the products in the thorium series, and causes different radiological characteristics of the bottom ash and fly ash [28].

2.2. Coal preperation processes

There are several studies conducted in the literature regarding the behavior of trace elements in coal preparation processes. Lutrell et al. (2000) have evaluated the capabilities of coal preparation technologies for the pre-combustion removal of hazardous air pollutant precursors (HAPPs) from coals. They have carried out the washability characterization of three different coal samples and pilot-scale evaluations of a variety of coal-cleaning processes. The results of this study show that HAPPs tend to be concentrated in the mineral matters of coal. On the other hand, it has also been indicated that the substantial reductions in trace element content can be achieved via coal

preparation. The trace element removal rate for the total plant varied from 46.7% for mercury to 80.0% for lead with a combustible recovery of aprroximately 90% [52].

The pilot-scale test work indicated that elements such as arsenic, cadmium, and mercury were rejected at approximately the same level as pyritic sulfur 50%, while elements such as chromium, cobalt, lead, and manganese were rejected at levels approximately equal to that achieved for ash 70%. The rejections of lead and nickel were higher than expected in the light of the characterization data, showing that these elements tend to associate more intimately with pyrite than other ash-forming minerals. Float–sink data indicates that trace element rejections can be theoretically improved by reducing the coal topsize to liberate mineral matters [52].

Valissev et al. (2001) have investigated the behavior of elements and minerals during preparation of coal from Pernik, Bulgaria. In this context, they have used several fractions such as feed coal (FC); low-grade coal (LGC), which was obtained after coal sieving 30 mm; high-grade coal (HGC), which was obtained after coal sieving and dense media separation; and waste products, namely coal slime (CS) and host rock (HR) of Pernik CPP. They have found that HGC shows a relative enrichment of Fe, Ca, S, Mg, Ti, P, Sr, Mn, Co, Ni, Zn, Pb, Cl, Br, illite, chlorite, gypsum, calcite, siderite, and pyrite; and reduction of Si, Al, K, Li, Rb, Cu, ash yield, quartz, kaolinite, and feldspars in comparison with FC. LGC reveals a relative enrichment of Si, Al, K, Na, Rb, Mn, Pb, quartz, illite, calcite, and siderite; and reduction of Fe, S, Mg, P, Sr, Cr, Ni, Cu, Zn, kaolinite, chlorite, feldspars, gypsum, and pyrite in comparison with FC. HGC is abundant in authigenic minerals and the organic matters and elements associated with them. The authors have stated that such constituents are commonly disseminated intimately with each other in coal, and their physical isolation-separation by screening and dense media is limited during coal cleaning. In contrast, LGC, CS, and, in particular, HR, are normally enriched in physically separable detrital and authigenic-quartz, illite, mica, chlorite, calcite, and siderite. Coal minerals, and especially in rock fragments-sandstones, sandy clays, sandy limestones, and argillites from intra-seam layers, roof, and floor strata fallen in the FC during coal mining [53].

Demir (2009) has investigated the behavior of trace elements in some major Turkish coals during coal preparation operations. As a result of this study, it was found that some trace elements envisaged to be enriched in the sinking coal are actually enriched in floating coal at a high rate. It was suggested that these results were due to the dependence of such elements on the components in the organic structure. The behaviors of the trace element contents of the coal studied for the coal preparation processes are as what follow.

Th in the Zonguldak-Kozlu coal was found to be 4.76 ppm in feed coal and 16.20 ppm in sinking coal. Furthermore, when the ash after burning of these fractions were examined, Th in ash of the sinking fraction and original coal were found to be 26.20 ppm and 20.00 ppm, respectively. These results clearly show that Th is located in the sinking fraction after the coal preparation, and it is also further enriched in the fly ash after the firing. In the same way, the U content was found to be 1.78 ppm and 4.90 ppm in the original coal the sinking fraction. When viewed from the aspect of ashes, it was seen that the ash of coal feed had a U content of 7.20 ppm, and U was enriched in the sinking coal ash with a rate of 8.70 ppm. As, Be, Co, Hg, Se, Pb, and Ni, as air pollutant elements, were also enriched in sinking fractions and their ashes [15].

In the Muğla-Yatağan coal, Th was 11.46 ppm in the original coal and 33.10 ppm in the sinking fraction. Additionally, when the ashes of these coals were examined, it was found that the Th contents of the original coal ash and sinking fraction were 50.60 ppm and 70.00 ppm, respectively. These results clearly show that Th is concentrated in the sinking fraction after the coal preparation, and it is further enriched in the ash. In the same way, U was found to be 5.88 ppm in the orginal coal and 16.70 ppm in the sinking fraction after the sink-float process. On the other hand, it was seen that the Th contents in the ash of the original coal and the sinking fraction were enriched to 20.90 ppm and 36.20 ppm, respectively. As for the air pollutant elements, As, Ni, and Se concentrated in the floating fractions and in their ashes; in contrast, Be, Cd, Co, Sb, and Pb concentrated in the sinking fractions and their ashes [15].

3. Leaching properties of trace elements in fly ashes

The formation properties of trace elements in coal have an important role in the formation of trace elements in fly ash and the distribution of these elements in ash particles. Although the elements enriched in the core of fly ash particles are not directly exposed to the leaching, the

surface-associated elements are more susceptible to leaching in an aqueous environment. Thus the formation properties of elements in coal greatly control whether an element is mobile and easily released into the environment or not [54].

Be, Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Re, Si, Sn, Th, Ti, U, and Zn show minimum solubilities at pH 7-10. These elements are characterized as insiginificant under alkaline volatile climatic conditions (for example, from moderate acid to alkaline pH). Their leachability is low and not related to their concentration in bulk but depends on pH. Thus the high content of any of these metals in the fly ash due to their high concentration of a coal should not be considered as a limiting factor for various applications. However, this definition does not apply to acidic ashes as the mobility of the above given elements decreases with pH [54].

Conversely, oxyanionic constituents such as As, B, Mo, Sb, Se, V, and W show maximum solubilities at pH 7-10. Therefore, a particular attention should be paid to the disposal of alkaline ashes containing these elements. As, B, Cr, Mo, and Se are especially important in terms of being potentially harmful to both plants and animals, highly soluble in water, and therefore, highly active in surface and ground waters. The leachability of As and V can be reduced due to the formation of solubility limiting phases in the presence of Ca. Ettringite possesses a great potential for metaloid removal due to its high affinity for capturing the elements As, B, Cr, Sb, Se, and V into the lattice structure [54].

4. Recovery of trace elements from coal and fly ashes

Valuable metal recovery is one of the many application areas of CFA. Besides certain heavy elements, CFA also contains valuable metals including germanium (Ge), gallium (Ga), vanadium (V), titanium (Ti), and aluminum (Al), which are extractable if an acceptable process can be developed [55].

4.1. Aluminum, Titanium, and Iron recovery from coal fly ash

CFA contains between 25 and 30% Al_2O_3, making it a potential alternative source of alumina for aluminum production after bauxite, which contains about 50% Al_2O_3. This relative abundance of Al_2O_3 in the ash is significant enough to justify an attempt to exploit it commercially [56]. There are a number of methods that have been developed for the

recovery of major elements from CFA [57]. The recovery of alumina from CFA was pioneered by Grzymek in Poland in the 1950s, and was developed mainly due to the bauxite embargo during the Cold War. The recovery process was based upon the auto-disintegration of sinter containing calcium aluminates and dicalcium silicate. The sinter was mixed with sodium carbonate and underwent a series of complicated chemical treatments including carbonization and water scrubbing to produce alumina and Portland cement. In 1953, a demonstration plant for recovering 10 thousand tons of alumina and producing 100 thousand tons of Portland cement was established in Poland. Recently, a number of processes have been reported for recovering alumina from CFA, which can be grouped into three types: the sinter process, the acid leach process, and the HiChlor process [58].

One of the proposed methods for recovering aluminum from fly ashes is the lime-sinter and lime-soda-sinter processes. $CaCO_3$ is added as a limestone in the calcination process and reacts with the silicon in ash at 1380 °C to form calcium orthosilicate ($2CaOSiO_2$). In the lime-soda-sinter process, Na_2CO_3 is added to system in addition to the limestone. Soluble metals are recovered by crystallization and separation followed by organic dissolution and ion exchange [13].

Toraman (1995) has investigated the recovery of metal oxides such as Al, Fe, and Ti by leaching methods from Afşin-Elbistan fly ash. In this context, direct acid leaching experiments were carried out for recovery of Al, Fe, and Ti from fly ash. The best results are an acid concentration of 300 g/L, a temperature of 90 $^{\circ}$C, a mixing rate of 1500 rpm, a solid/liquid rate of 5% solids at a extraction time of 6 h for Al and Ti, 8 h for Fe. Using these conditions, 97% Al, 95% Fe, and 98% Ti extraction recoveries were obtained [59]. Matjie et al. (2005) have investigated the extraction of alumina and titanium from CFA of a South African Coal containing 29.2% Al_2O_3, 2.53% Fe_2O_3, and 1.49% TiO_2. Direct leaching results have indicated that alumina in the mullite phase is not readily dissoluble in mineral acids. Therefore, mullite-containing fly ash was mixed with calcium oxide and calcined. Subsequently, the calcined ash was leached at 80 °C for 4 h with a 6.12 mol/dm^3 sulfuric acid solution. The precipitation, solvent extraction, and crystallization methods were evaluated to selectively separate Al and Ti. The final products contained approximately 99.4% alumina and 97%

titanium oxide, obtained with the solvent extraction method [60].

4.2. Recovery of Germanium, Gallium, and Vanadium from coal fly ash

In one of the previous studies on the extraction of gallium from CFA by acid leaching, the major elements in fly ashes such as aluminum, iron, silicon, and calcium were also succesfully recovered [61]. CFA is also a potenital source of germanium, and many studies have focused on the recovery of germanium from CFA by several methods. The first step of most of these processes is leaching of fly ash, followed by a process to separate germanium from other elements contained in leachates such as arsenic, molybdenum, nickel, antimony, vanadium or zinc. Conventional processes are precipitation with tannin, distillation of $GeCl_4$, and solvent extraction (SX). SX appears to be the most attractive procedure due to the easy scale-up and operation control. In an examplary study, a simple hydrometallurgical method for the selective recovery of germanium from fly ash (FA) generated in an integrated gasification with combined cycle (IGCC) process was presented. The method consisted of leaching FA with water and the subsequent concentration and selective separation of germanium by a solvent method. As a result, a high-purity germanium solution was obtained with germanium extraction yields higher than 90% [62].

There were also several studies on the recovery of vanadium from coal and CFA. In their exemplary study, Chen et al. (2010) have investigated the extraction of vanadium from stone coals by the sulfuric acid leaching method. The extraction rate of vanadium was found to be 95.86% after leaching for 5 h at 90 °C using 6 mol/dm^3 H_2SO_4 [63].

4.3. Recovery of rare earth elements from coal fly ash

There are a number of studies available on rare earth elements (REE) extraction and separation from CFA. The efficiencies obtained in these studies varied in the range of 50–90% due to several factors including concentration and mode of occurrence of different elements in the fly ash [64].

For example, Hower et al. (2013) have suggested that the distribution of Ce throughout the fly ash has implications for its recovery in processing in this regard. According to the authors, recovery of Ce requires leaching of the entire cenosphere

particles. They have also stated that the surface area properties of the particles are important; however, due to the void spaces in glass cenospheres, large particles can have a greater effective surface area as long as acids or other leaching agents can make contact with all or most surfaces [65].

Kashiwakura et al. (2013) have investigated the dissolution behavior of the REE content of CFA in a dilute H_2SO_4 solution. They have stated that REEs in CFA dissolve gradually in H_2SO_4 over time, and this finding implies two types of occurrences of the REEs in the studied CFA samples. For the two different CFA samples investigated, dissolution rates varying in the range of 30-50% were obtained under the leaching conditions of 2 h leaching time, 80 °C leaching temperature, and 10% (w/w) H_2SO_4 [66].

4.4. Recovery of U and Th from coal fly ash

Various studies have been conducted using several types of acids for the 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 using 10% H_2SO_4 with concentrations of 0.05-0.15 mol/dm^3. The results obtained indicated that 80% of uranium dissolution efficiency was obtained through the use of 180 kg H_2SO_4 per ton of ash [67]. In another study, where solvent extraction of uranium in the leach solution with trioctilamine was used, the 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 [68].

In another examplary study conducted for the acquisition of uranium from fly ash, again, the H_2SO_4 leaching method was used. In this context, 500 g fly ash was first added to the sample by adding acid in a concentration of 750 kg H_2SO_4/ton fly ash. Water was added slowly to provide 40% solid ratio, and then fly ash was dissolved using 16 kg of H_2O_2/t oxidant at 60 °C for 18 h with stirring. The pulp obtained was filtered with the aid of a vacuum pump, and a dark green-colored solution with a dense structure was obtained. The residue with S/L = 2/3 was washed for 30 min using a 5% H_2SO_4 solution.After the pulp was filtered, a clear green clear washing solution was obtained. The concentration of uranium in the solution was determined spectroscopically with Arsenazo-III, a specific and sensitive reagent for uranium. After the leaching process, re-washing of the residue was

carried out to obtain a part of the remaining uranium. The total uranium recovered after washing was also determined by analyzing the uranium remaining in the washing residue by the standard addition method using the uranium analyzer. As a result, the total uranium gain was obtained to be 86.4% [13].

Kursun et al. [69-71] have investigated the dissolution characteristics of uranium and thorium from the fly ash samples taken from the Soma and Yatagan thermal power plants in Turkey under different leaching conditions, where H_2SO_4, HCl, and CH_3COOH were used as the leaching reagents, and the best results were obtained using H_2SO_4. According to the analyses of thin section samples of the Soma fly ashes, uranium was mineralized on the glass phase as a uraninite (UO_2) form, and thorium was mineralized on the glass phase as a thorite ($Th(SiO_4)$) form. On the other hand, uranium was mineralized on the glass phase as a uraninite (UO_2) form, and thorium was

mineralized on the glass phase as the monazite ($(Ce, La, Nd, Th)[PO_4]$) and thorite ($Th(SiO_4)$) forms in Yatagan fly ashes. Radioactive minerals were distributed on the glass phase in both fly ashes.

Leaching tests were carried out with sulfuric acid using various solid rates, dissolution periods, amounts of acid, and leaching temperatures. The results of the experiments for the effect of the amount H_2SO_4 per ton ash on U and Th dissolution efficiency is given in Figure 6.

As it could be seen in Figure 6, the U and Th dissolution efficiencies for both Yatagan and Soma fly ash samples increased to 120 g/per ton ash H_2SO_4 amount, and reached a plateau at this point. Therefore, it was concluded that the optimum amount of H_2SO_4 was 120 g/per ton ash. On the other hand, the results of the experiments for the effect of pulp temperature on the U and Th dissolution efficiency is given in Table 4.
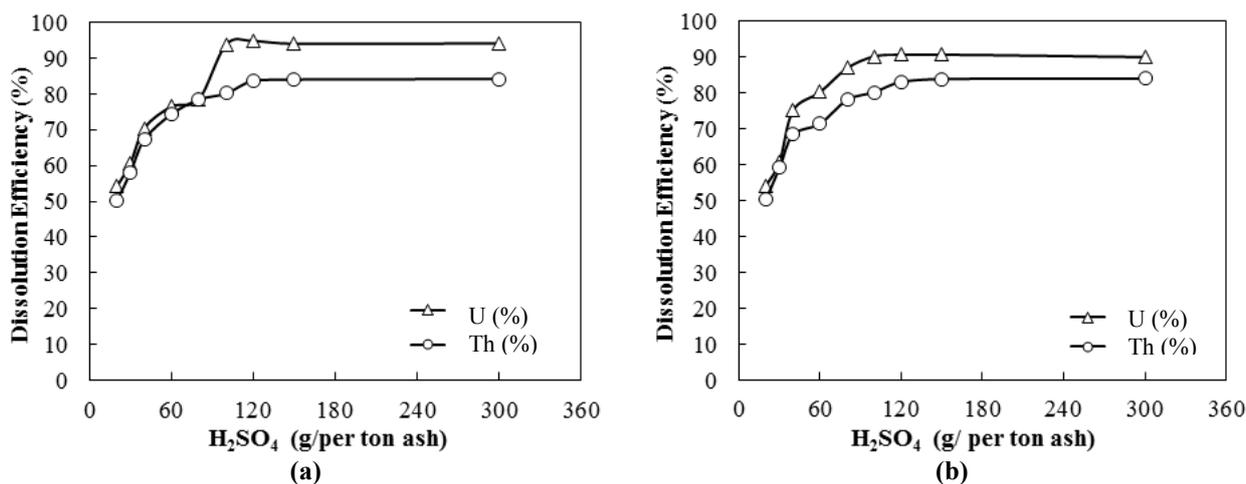

Figure 6. Effect of amount of H_2SO_4 per ton ash on U and Th dissolution efficiency of Yatagan (a) and Soma (b) fly ashes (solid ratio: 30%; leaching time, 240 min, pulp temperature, 20 ºC).

Table 4. Effect of pulp temperature on U and Th dissolution efficiency of Yatagan and Soma fly ashes (solid ratio, 30%; leaching time, 240 min; amount of H_2SO_4, 120 g/per ton ash).

Pulp temperature (ºC)	Yatagan CFA		Soma CFA	
	U dissolution (%)	Th dissolution (%)	U dissolution (%)	Th dissolution (%)
20	94.12	83.79	90.22	83.48
40	97.03	89.11	94.18	91.78
60	97.12	91.21	94.71	93.21

As it can be seen in Table 4, the pulp temperature has a positive effect on the dissolution efficiencies of U and Th in both fly ashes. On the other hand, the results clearly showed that the pulp temperature had a more prominent effect on the Th dissolution as it ineased the Th dissoluiton efficiencies for the Yatagan and Soma fly ashes with rates of 7.42% and 9.73%, respectively.

The best results were obtained at 30% solids, 120 g/ton H_2SO_4, 240 min leaching period, and 60 °C leaching temperature. Under these conditions, 94.71% uranium dissolution efficiency and 93.21% thorium dissolution efficiency for Soma fly ash and 97.12% uranium dissolution efficiency and 91.21% thorium dissolution efficiency for Yatagan fly ash were obtained. The results

obtained from the study showed that H_2SO_4 leaching of the uranium and thorium contents from the fly ashes could be successfully used for dissolution of both elements.

5. Conclusions

Coal is among the most important energy sources. In primary energy consumption, coal has taken the second place with approximately 29% share after oil, which has taken the first place with approximately 33% share in 2015. In order to meet the world's energy demands, low-calorie lignite with a high ash content has been generally used in the large capacity coal-fired thermal power plants. As a result of coal firing, wastes such as fly ash, slag, and flue gas are also produced due to the fact that the coal contains relatively high concentrations of trace elements when compared with other geological materials. Subsequently, toxic trace elements such as As, Cd, Ga, Ge, Pb, Sb, Se, Sn, Mo, Ti, and Zn, among the potential contaminants to environment within coal, are transferred to wastes such as slag, fly ash, and flue gases.

Total quantities of the trace elements involved in coal combustion are large, being roughly comparable with the quantities annually mobilized by the natural process of weathering of crustal rocks. Generally, less volatile elements such as Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Zn, and oxidized Hg can be found together with finely grained materials such as fly ash and bottom ash. As and Se represent medium volatility, and spread widely through the atmosphere. Many research works on heavy metals such as Pb, Cd, Cr, As, and Hg have been carried out in the field of enrichment according to different grain sizes, removal, and reaction with absorption or adsorption. On the other hand, coal-to-ash enrichment rates of the radionuclides are characterized by the enrichment factor. The enrichment of natural radionuclides in ashes from various types of thermal power plants has been found to vary greatly with particle size. In summary, the coal-to-ash natural radionuclide enrichment factor varies depending on the mineralogy of the coal, type of burning, combustion temperature, and the particle size. From the radiological viewpoint, ^{40}K, ^{232}Th, and decay products remaining in the bottom as well as ^{238}U, ^{226}Ra, ^{210}Pb, and ^{210}Po that concentrate on fly ash particles are very important.

Generally, the characterization data obtained in the studies regarding the behavior of trace elements in coal indicate that trace elements tend to be concentrated in the mineral matters of coal.

Pilot-scale and lab-scale testing of traditional dense medium and froth flotation processes showed that substantial reductions in the trace element content could be achieved via coal preparation. When viewed from the aspect of fractions obtained from coal processing and ashes of these fractions, elements such as U and Th as radioactive elements and As, Be, Co, Hg, Se, Pb, and Ni, as air pollutant elements, were enriched in certain processing fractions and their ashes. Therefore, valuable metal recovery is one of the many application areas of CFA, and a considerable atteniton has been given to this in the recent studies.

Besides certain heavy elements, CFA also contains valuable metals including germanium (Ge), gallium (Ga), vanadium (V), titanium (Ti), and aluminum (Al), which are extractable if an acceptable process can be developed. In addtion, coal and CFA can be regarded as alternative sources of U and Th. The U and Th extraction from coal and CFA have been an active research area from the beginning of nuclear era to the recent studies.

In conclusion, large amounts of the ashes produced from firing of coal, which are usually stored in collection ponds or stockpiles, could be problematic in terms of environment if necessary precautions were not taken. On the other hand, coals have high trace element contents, and their waste products also have a great potential in terms of precious metals and trace elements they contain. Therefore, the future studies in this area should be supported in order to fully emphasize the true potential of these alternative sources.

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بررسی توزیع عناصر نادر در زغال‌سنگ و دوده زغال‌سنگ و بازیابی آن‌ها با روش‌های فرآوری مواد معدنی

I. Kursun Unver* and M. Terzi

Department of Mining Engineeering, Faculty of Engineering, Istanbul University, Istanbul, Turkey

* نویسنده مسئول مکاتبات: ilginkur@istanbul.edu.tr

چکیده:

امروزه زغال‌سنگ یکی از مهم‌ترین منابع انرژی است. عموماً به منظور رفع نیازهای انرژی در جهان، از لیگنیت با انرژی حرارتی کم که همراه خاکستر بـالایی اسـت در نیروگاه‌های حرارتی با ظرفیت بالا استفاده می‌شود. در نتیجه سوختن زغال‌سنگ، باطله‌هایی مانند دوده، سرباره و دود تولیـد مـی‌شـود. در نتیجـه عناصـر نـادر سمی همراه در زغال‌سنگ به باطله‌های ذکر شده انتقال می‌یابند. مقدار زیادی از این عناصر نادر سمی که معمولاً در مخازن و کپه‌ها ذخیـره‌سـازی مـی‌شـوند، بـه عنوان یک مشکل محیط‌زیستی مطرح می‌شوند. اگرچه دوده زغال‌سنگ در دهه‌های گذشته در ساخت‌وسازها و چندین صنایع دیگر مورد استفاده قـرار مـی‌گرفتـه است اما میزان استفاده فعلی آن بسیار محدود شده است. همچنین دوده زغال‌سنگ دارای بسیاری از فلزات با ارزش از جمله ژرمانیوم، گـالیم، وانـادیوم، تیتـانیوم و آلومینیوم است. علاوه بر این، زغال‌سنگ و دوده زغال‌سنگ را می‌توان به عنوان منابع جایگزین عناصر رادیواکتیو در نظـر گرفـت؛ بنـابراین، آن‌هـا همچنـین دارای پتانسیل زیادی از نظر فلزات گران‌بها و عناصر نادر است. در این پـژوهش، سـابقه‌ی علمـی موضـوع، در مـورد بررسـی توزیـع عناصـر نـادر در زغال‌سـنگ و دوده زغال‌سنگ در طی سوختن و بازیابی آن‌ها با روش‌های فرآوری مواد معدنی مورد بررسی قرار گرفته است. در حالی که تحقیقات در مورد ایـن موضـوع انجـام شـده است به وضوح نشان می‌دهند که مقادیر زیاد خاکستر تولیدی از سوختن زغال‌سنگ می‌تواند مشکلات زیست‌محیطی ایجاد کند، همچنـین بسـیاری از مطالعـات و اقدامات نشان می‌دهد که محصولات ناشی از احتراق زغال‌سنگ به طور بالقوه دارای فلزات گران‌بها و عناصر نادر هستند.

کلمات کلیدی: زغال‌سنگ، عناصر نادر، خاکستر بادی، بهره‌برداری.