

The brief review on Coal origin and distribution of rare earth elements in various Coal Ash Samples

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Abstract

Rare earth elements together with Y and Sc (REEs) are essential in the development of technology for clean and efficient use of energy. In recent years coal deposits have much attention and attracted as a promising alternative raw sources for rare earth elements, not only because the REEs concentrations in many coals or coal ashes are equal to or higher than those found in conventional types of REEs ores but also because of the world wide demand for REEs in recent years has been greater than supply. In the coal ashes, REEs are mainly associated with carbonates, silicates and aluminosilicates in ashes at 800 and 1100°C. These elements are known to be powerful environmental tracers in natural biogeochemical compartments. In this study, to reviewed the REEs originating and distribution patterns in coal ash samples from the bedrock and/or soil weathering that were entrapped by lichens and mosses was investigated. The REEs patterns of different organisms species allowed minor influence of the species to be highlighted compared to the regional lithology.

Key words : Coal origin, Rare earth elements, Mechanism of REEs formation.

Introduction:

Rare earth elements have been widely used for many years as geochemical indicators [1] of the sedimentary environment and post-depositional history of coal deposits because of their coherent behavior during different geochemical processes and their predictable patterns of fractionation [2,3]. REEs play an important role in the development of alternative power and energy efficient technologies and its main source are coal deposits [3]. Generally, in coals, REEs are associated with clay-like minerals, silicates, feldspars, oxyhydroxides, phosphates, sulphates, sulphides and carbonate minerals [4]. Moore and Esmaeili [5] concluded that REEs in coals can be

associated with kaolinite, hornblende, biotite and muscovite. Associations of REEs with organic matter were also reported [6].

Coal is still one of the most important primary energy resources in the world, The coal combustion produces significant quantities of ashes, which may be also used as a source of REEs, thus achieving further exploitation of these materials. In addition, coal fly ashes can be a REEs source, since these elements are concentrated in ashes. The knowledge of the composition of REEs in ashes is important to evaluate the recovery potential of these elements for their uses in energy-efficient technologies [7]. Thus, there exist several studies that evaluate the REEs content of coal fly ashes [8,9]. Blisset et al. [8] studied fly ashes of one anthracite and two bituminous coals from the United Kingdom and three bituminous coals from Poland. The REEs distribu-

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tion in fly ashes was similar in the studied coals, although the highest concentrations (commercially viable) were found for the fly ash of a coal from the UK [8]. Dai et al. [6] studied how the concentrations of REEs vary from the coarsest to the finest fractions of the fly ashes produced from a high volatile bituminous coal from China in a 200-MW power plant. They found that there is an enrichment of all REEs in the finer fly ash [6]. They also observed that La, Ce, Pr and Nd occur in minerals within some glassy phases in the fly ash [6].

Coal fly ashes (CFAs) have been estimated to contain 445 ppm REEs on an average global basis [21]. There have been many reports of CFAs with REEs contents that far exceed the world average (0.1-1.0 wt%) as elevated REEs levels have been reported in the Russian coal deposits [10,11], Jungar coalfield in Inner Mongolia [12] and the southern China coalfields [13]; the Songzo coalfield, southwestern China, eastern Yunnan, China and the Fire Clay coal bed in Eastern Kentucky, United States. For a review of coal deposits as a potential source of REEs readers are referred to the work of Seredin and Dai [3].

Rare earth elements global demand has grown due to their wide applications as metal catalysts, phosphors, light emitting diodes, permanent magnets, various components for renewable green energy equip-

ment, and batteries [14]. The importance of REEs has been universally recognized in the last ten years due to relative changes in supply and demand [15].

The main objective of this study is to provide a brief review on the formation of coal ash and origin of REEs with distribution in coal ash and the current state of knowledge on anomalous REEs concentrations within coal basins and also the detailed studies include the mechanisms of REEs incorporation into coal-forming biomass and how REEs become mobilized during and after the coalification process and its mechanisms are discussed.

I. Formation of Coal and Global demand.

Despite growing importance of renewable energy sources (i.e., geothermal, wind and solar) [16], coal's share of the global energy mix continues to rise and by 2017 will come close to surpassing oil as the world's biggest energy source. Energy demand was increases globally and coal is the main source and many countries are increasing its consumption [17]. Consequently, the global coal ash production increases as shown in Fig. 1 [18], and there is a pressing need of its recycling and utilization. Coal fly ash have number of applications and averagely 25 % was utilized, and remaining consider as a pollutant and disposed of as waste [19]. In coal combustion process represent a large-scale naturally

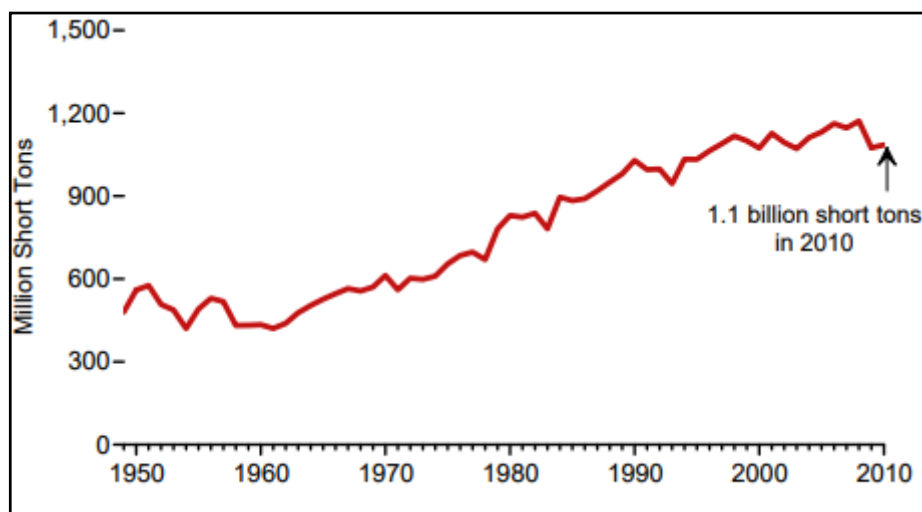


Fig. 1. Annually Coal Ash production worldwide.

occurring elements are mobilized in a magnitude that is comparable to the rates of mobilization and transport that occur as part of natural geochemical cycling of elements [20].

In 2016, approximately 85% of world REEs mine production was in China; following closure of the only U.S. mine source in late 2015, there was no domestic U.S. REEs production in 2016 [21]. As market conditions for alternative REEs sources have become more favorable, recent papers showing the distribution of REEs in coal and coal ash, and considering the prospects for recovery of REEs from these sources have attracted considerable attention [22]. Pending shortages of REEs in the U.S. and elsewhere have drawn renewed consideration to coal and coal ash as possible REEs sources, leading to new research opportunities supported in part by a U.S. Department of Energy effort to develop domestic production of REEs from coal and coal ash [23].

Kertis and Yudowich [24] estimated that coal fly ash contain 445 ppm of rare earth elements (REEs) on an average global basis and as Seredin and Dai [3] noted in coal ash samples average REEs content, based on these results on numerous samples, the wastes of coal combustion should be considered as possible source for REEs. The average concentrations of REEs for world low-rank and hard coals, as

well as those for Chinese and US coals, are presented in Table 1. The average sum of REEs in US coals (62 $\mu\text{g/g}$) is close to the average for world coals (68 $\mu\text{g/g}$). However, the estimated average sum of REEs in Chinese coals is around twice that for world and US coals because more coal samples of Late Permian age from southwestern China, which contain higher REEs concentrations, than those from northern China and northwestern China [25,26].

Coal originated from the plants are physically and chemically accumulate and alteration that settle in swampy areas to form peat as known as peatification and which thickens until heat and pressure transform it into the coal is known as coalification, the following steps are followed in Fig. 2. Coal ash samples as a sedimentary rocks and it has combustible property and it composed from carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulphur (S), and various trace elements (it has a carbonaceous content of more than 50 % by weight and more than 70 % by volume). In South African has much amount approximately 70 % of the estimated coal reserve is located in the Waterberg, Witbank, and Highveld coalfields, as well as lesser amounts in the Ermelo, Free State and Springbok Flats coalfields [27]. South Africa is the third largest coal producer in the world, and coal accounts for 64 % of South Africa's

Table 1. Average concentration ($\mu\text{g/g}$) of rare earth elements and yttrium for Chinese coals, US coals and World coals [24]

Coal	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sum
World hard coal	11	23	3.4	12	2.2	0.43	2.7	0.31	2.1	8.4	0.57	1	0.3	1	0.2	69
World low-rank coal	10	22	3.5	11	1.9	0.5	2.6	0.32	2	8.6	0.5	0.85	0.31	1	0.19	65
World coal	11	23	3.5	12	2	0.47	2.7	0.32	2.1	8.4	0.54	0.93	0.31	1	0.2	68
US coal	12	21	2.4	9.5	1.7	0.4	1.8	0.3	1.9	8.5	0.35	1	0.15	0.95	0.14	62
China	26	49	5.5	22	4.3	0.9	3.7	0.7	3.1	18	0.7	1.9	0.27	2.1	0.3	138
World coal ash	69	130	20	67	13	2.5	16	2.1	14	51	4	5.5	2	6.2	1.2	404

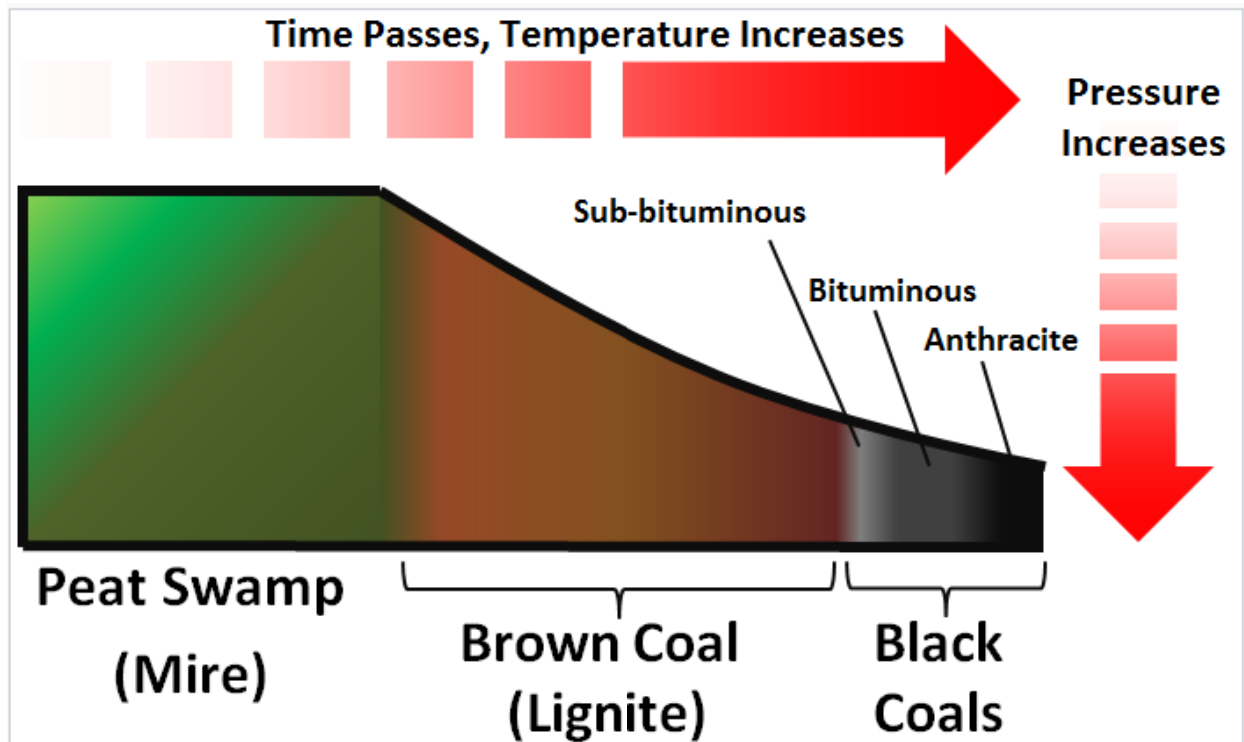


Fig 2. Coal formation by peatification and coalification process [76].

primary energy supply [28]. Electricity generation accounts for 61 % of the total coal consumption in South Africa and more than 90 % of the country's electricity requirements are provided for by coal-fired power plants [28]. Generally low levels of phosphorus, nitrogen and sulphur contents are present in South African coals and in the case of the first two the contents are dependent on maceral composition and rank [29].

II. Classification of REEs

There are several classifications for REEs [3,30]. REEs can be divided into critical (Nd, Eu, Tb, Dy, Y, and Er), uncritical (La, Pr, Sm, and Gd), and excessive (Ce, Ho, Tm, Yb, and Lu) groups according to the demand-and-supply relationship of individual REEs [3]. Also, according to the atomic number difference, the REEs can be divided into the cerium group or light REEs (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd) and the yttrium group or heavy REEs (Y, Tb, Dy, Ho, Er, Tm, Yb, Lu) [31]. Sui et al. [30]

classified REEs based on the solubility of rare earth salt: the insoluble cerium group or light REEs (Sc, La, Ce, Pr, Nd, and Sm), slightly soluble terbium group or middle REEs (Eu, Gd, Tb, Dy), and soluble yttrium group or heavy REEs (Ho, Er, Tm, Yb, Lu, Y).

III. Rare Earth Elements accumulations in coal deposits:

Rare Earth Elements (REEs) are rich in coals are formed under various geological conditions at different stages in the evolution of coal basins and by various ore-forming processes [32]. Four genetic types of REEs accumulation in coal can be identified. a) Terrigenous type, with REEs input in ionic and colloidal forms from surface waters, b) Tuffaceous type, connected with the fall of felsic and alkaline volcanic ash enriched in REEs, c) Infiltration or meteoric ground water driven type and d) Exfiltration type, connected with ascending flows of thermal and cold gas-saturated mineral waters and

deep fluids of various origins.

The first two types of REEs mineralization in coal basins are formed at the sedimentary stage, the infiltration type is mainly epigenetic, and the ex-filtration type may be formed at any stage of coal basin development. In some cases, both the high REEs coals and REEs mineralization in adjacent geological units may have a polygenetic and multistage origin [33]. For example, some REEs tuffaceous layers in coal basins from southwestern China and the Russian Far East were subjected to hydrothermal alteration, and as a result of the process, these pyroclastic rocks were transformed into kaolinite clays, the initial magmatic REEs bearing minerals were destroyed, and the REEs were re-distributed either as secondary mineral phases or as ionic species adsorbed onto the clay matrix [3]. Therefore, such mineralization may be attributed to a mixed tuffaceous hydrothermal type [3].

Several studies [34] have addressed the origin of rare earth elements in coal. Eskenazy discussed the complications of REEs enrichment in coals. Eskenazy [35] was observed the organic associations as a evident in the bituminous coals was studied. The REEs are loosely attached with clays because with acidic waters releases the heavy REEs from the coal ash samples and these REEs are increases in the solution would lead to enrichment in HREEs bound to organics. As a supplemental or alternative source, the high organic-bound HREEs could have resulted from high HREEs in the waters feeding the swamp. Heavy REEs are generally have stronger affinity with organic compare than light REEs and these HREEs complexes with organics are more stable than LREEs complexes. Aide and Aide [36] confirmed that heavy REEs organic complexes are more stable than light REEs organic complexes. Decreases in pH cause a decrease in the stability of the REEs-organic complexes.

It is generally accepted that REEs were mobilized and fractionated during intense weathering of the granite under warm and humid conditions. REEs division and mobilization mechanisms responsible

for the during weathering conditions like solubility of REEs and complexation and the differential stability of the aqueous complexes [37]. Most of the REEs in granitoids tend to be concentrated in LREEs-rich mineral phases such as apatite, monazite-(Ce) and fluorcarbonate minerals. Dissolution of these minerals would result in LREEs enrichment. The formation of aqueous complex ions can also fractionate REEs during weathering. HREEs form stronger complexes with fluoride and carbonate relative to LREEs at ambient temperature, thereby increasing the concentration of the HREEs in solution and making them available for adsorption.

In coal burning for power generation, REEs are strongly retained in the solid residue (ash) remaining after coal combustion [38] and to a large extent, do not enter the gas phase, as is the case for more volatile elements. This solid fraction, consisting predominantly of fly ash and bottom ash, is derived from non-combustible mineral matter originally present in the coal. In commercial coals, the ash fraction is relatively small compared to the overall mass of the coal; therefore, during the combustion process, REEs are preferentially retained in a much smaller mass fraction. For example, relative to REEs concentrations in coal, enrichment by factors of approximately 5 to 10 might be expected for coals having mineral matter contents of 20 to 10%, respectively, assuming total REEs retention.

IV. Mechanisms for Introducing REEs into Coal Basins:

When considering possible mechanisms on how REEs material can be introduced into coal and coal bearing basins, recent studies by Andersen et al., [39] suggest three plausible means. These include, i) Introduction of REEs via widespread volcanic ash falls (or tuff), ii) Introduction of REEs from igneous intrusions (diapirs, dikes, sill, and pipes), and iii) Introduction of REEs with the fluvial-detrital transport of resistate heavy black sands. In Fig. 3, shows the expected influence and distribution of REEs in a

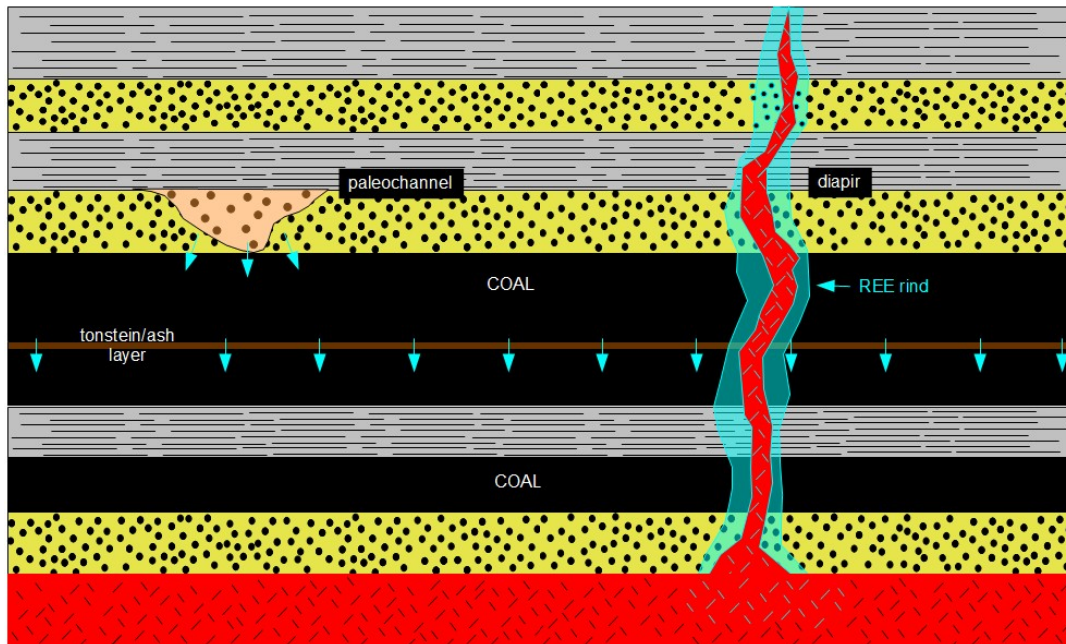


Fig. 3. Mechanisms for introducing REEs into Coal Basins [40].

basin using these three mechanisms.

Based on the known geology history and character of the Raton basin, the influence of kaolinitic-rich volcanic ash/tuff deposits or ton steins layers plus local igneous activity during the middle Tertiary resulted in the formation of igneous dikes and sills associated with the development of the Spanish Peaks are likely sources for the observed REEs content in both the coals and coaly shales. Many of these igneous features “coked” coal in place in portions of the basin. If they contained REEs then their influence on the observed REEs in sediments may be substantial.

REEs do not readily fit into early-formed minerals because their ionic radii are generally incompatible. Because of this incompatibility, they are progressively enriched into the “leftover” igneous magma. So as the magma continues to cool and minerals are formed, the remaining melt becomes progressively enriched in these elements until they are forced into very late-stage minerals and/or form their own assemblages. Hence, late-formed igneous rock commonly contains minerals with greater REEs contents. As a result, REEs end up in very late-stage minerals or in

volcanic glass at the end of the magmatic process. If these materials are introduced into the coal basin by volcanic tephra (fragmental material of various sizes produced by a volcanic eruption), considerable amounts of REEs can accumulate in the coal. Further, when chemical or mechanical weathering of the ash occurs, further REEs enrichment will occur. Introduction by erosional and detrital processes of heavy resistant minerals (black sands) also introduces REEs into a coal basin.

Although coal swamps are generally low-energy environments not prone to heavy detrital input, periodic geologic transgression/regression cycles (cyclical increases/decreases in sea level relative to land) can introduce detrital material into the basin between coal layers. Finally, diapiric emplacement (upward movement of igneous material through the rock underlying the basin) can introduce REEs material into an area of the basin where associated hydrothermal fluids can mobilize the REEs until they find a suitable receptor material such as kaolinite. Coals evaluated in this report from both the eastern and western United States show episodic volcanic ash falls, diapiric activity, and metamor-

phic/igneous complexes either within or adjacent to the basins that contain late-stage REE-rich minerals.

V. Conclusions

Coal is a valuable resource not only for its energy content but also for the metals enriched within it. Many have realized the potential value of REEs in coal, and the increasing demand for REEs continues to drive the exploration of REE recovery from coal. Currently several REEs recovery technologies are developed and recovered from various sources of coal. The distribution and abundance of REEs in coal display regional characteristics. For example, REEs in coal sources in China are nearly twice that of the world average level. The occurrence of REEs in coals has a variety of forms, both organic and inorganic. For inorganic forms, REEs can occur as accessory minerals, resistate minerals, clay minerals, and authigenic minerals, and the latter is normally dominant for high-REE coals. So coal formation and distribution of REEs is necessary to investigate for recovery of REEs. In this review to investigate the coal origin and REEs distribution in coal ash samples and possible mechanisms for accumulation of REEs in coal ash samples are discussed. Based on this review, the recovery of REEs from secondary sources such as coal and coal by-products is crucial considering their increasing demand and limited economic reserves.

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