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The Potential Utilizing of Critical Element from Coal and Combustion Residues

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Abstract: Strategically critical elements are becoming significant for the rising demand of emerging energy-efficient technologies and high-tech applications. These critical elements are mostly geologically dispersed, and mainly recovered from recycled materials. Coal with high concentrations of critical elements is supposed to stable alternative sources. The abundances of critical elements in coal varies widely among different deposits and regions. The high concentrations of critical elements are found in many Chinese and Russian coal ores. The global mining potential ratio (MPR) is applied and suggests scandium, hafnium, cesium, yttrium, germanium, gallium, thallium, strontium and rare-earth elements could be potential recovery from coal. A number of benefits are expected with the extraction of critical elements during coal utilization.

Keywords: critical element; abundance; utilization potential; coal

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1. Introduction

Rare metals, known as lithium (Li), gallium (Ga), Germanium (Ge), rare-earth elements (REE), and platinum group elements (PGE) are regarded as strategic mineral resources, which are indispensable substances of emerging energy-efficient technologies or high-tech applications for their unique electrical, magnetic, catalytic, metallurgical, nuclear and luminescent characteristics [1–7]. The production of critical elements increased significantly in the past few decades. Gallium and lithium production in 2017 was 310 t and 107,322 t, which rose by 59.8% and 30.1% from 2016 to 2017, respectively [8]. Meanwhile, the prices of these elements rose remarkably. Due to their extreme significance for economic development and national security, these metals are intensively valued (Table 1). China listed 24 minerals as strategic minerals in the *National Plan for Mineral Resources (2016–2020)* in 2016. The European Union listed 27 substances in the *EU Critical Raw Material List of 2017* to prompt future utilization of these critical raw materials. The Japanese government released a report, and 31 minerals were presented in 2018. In addition, 35 minerals were identified as critical materials by the United States in 2018 and published in the *Final List of Critical Minerals 2018*. Australia announced *Australia's Critical Minerals Strategy in 2019* and 24 critical metals were identified. Due to the incremental demand and exhaustive conventional ores of these critical elements, the necessity to develop alternative resources has become an irresistible trend [9–13]. Moreover, many critical elements (including Ga, Sc, Ge) are rare dispersed elements and mainly recovered from recycled materials [14]. Therefore, a stable, reliable, and sustainable supply of these critical elements is of extremely urgent.

Table 1. Detailed list of critical elements.

Critical Element	USA	Australia	EU	Japan	China
Aluminum (Al)	X			X	X
Antimony (Sb)	X	X	X	X	X
Arsenic (As)	X				
Beryllium (Be)	X	X	X		
Bismuth (Bi)	X	X	X		
Cesium (Cs)	X				
Chromium (Cr)	X	X		X	X
Cobalt (Co)	X	X	X	X	X
Copper (Cu)				X	X
Gallium (Ga)	X	X	X	X	
Germanium (Ge)	X	X	X	X	
Hafnium (Hf)	X	X	X		
Nickel (Ni)				X	X
Indium (In)	X	X	X	X	
Iron (Fe)				X	X
Lead (Pb)				X	
Lithium (Li)	X	X		X	X
Magnesium (Mg)	X	X	X	X	
Manganese (Mn)	X	X		X	
Molybdenum (Mo)				X	X
Niobium (Nb)	X	X	X	X	
Potassium (K)	X				X
Rhenium (Re)	X	X		X	
Rubidium (Rb)	X				
Scandium (Sc)	X	X	X	X	
Silicon (Si)			X	X	
Strontium (Sr)	X				
Tantalum (Ta)	X	X	X	X	
Tellurium (Te)	X				
Tin (Sn)	X			X	X
Titanium (Ti)	X	X		X	
Tungsten (W)	X	X	X	X	X
Uranium (U)	X				
Vanadium (V)	X	X	X	X	
Zinc (Zn)				X	
Zircon	X	X		X	X
REE	X	X	X	X	X
PGE	X	X	X	X	X

PGE: platinum-group elements; REE: rare-earth elements.

Coal resources occupy a significant place in the world's energy consumption and supply the largest share of global power generation at 38% [15]. Coal production was approximately8012.8 Mt in 2018 and accounted for 27.2% of global primary energy [15]. With the growing primary energy consumption, coal is and will continue to be a crucial energy source in the foreseeable future for its available abundance and cost-effectiveness [16]. Coal not only supplies calorific value, but also contains high concentrations of potential critical elements during complex geological evolution [17,18]. The enrichment characteristics of critical elements (Li, Ga, Ge, U, etc.) have been widely reported [19–22]. Coal with high concentrations of critical elements (10 times higher than world coal average) is regarded as metalliferous coal [23]. The concentrations of critical elements in metalliferous coal may be equal to (or even higher than) conventional ores, particularly enriched in coal combustion products with the decomposition of organic matter during high-temperature oxidation [16,17]. Therefore, the critical elements extraction from coal (ash) may be positive and stable substitutions to these nonrenewable resources. It is worth noting that coal mining and combustion activities have already resulted in serious environmental impacts, and the traditional pathways to decrease the negative effects are inefficient [24–26]. Therefore, recovering critical elements from coal (ash) may not only relieve the environmental implications associated with coal mining activities and reduce conventional ore deposits operation expenses, but also greatly benefit socioeconomic and resource conservation.

The concentrations, associations, enrichment genetic and extraction technologies of critical elements (Ga, Ge, Li, U, REE, PGE) in metalliferous coals have received fairly intensive study [17,20,21,23,27]. Seredin and Finkelman reviewed the genetic types, geochemical processes and modes of occurrence of critical elements in coal deposits (2008). Dai and Finkelman evaluated the potential utilizations of critical elements from coal and discussed the challenges (2018). However, a systematic global-level analysis related to the potential utilization of critical elements in coal is limited [28]. Consequently, the quantitatively investigation of potential significance of coal as an alternative critical element resource is necessary.

2. Methods

The mining potential ratio (MPR) described by Chen and Graedel (2015) was carried out to investigate the potential utilization of coal for the global supply of critical element. The MPR is a dimensionless ratio, defined as the quantity of elemental production from coal to the conventional production of element. According to Chen and Graedel (2015), the quantity of elemental production from phosphate rock was obtained by multiplying the median concentrations of element in global phosphate rock and the global production of phosphate rock. The ranges of elemental concentrations widely differ among different regions and geological environments. The national concentrations of elements in coal and the national coal production are applied in this study to minimize uncertainty. The modified MPR could be calculated be the following formulas:

$$\mathrm{MPR_i} = \frac{\mathrm{MQ_{ij}}}{\mathrm{GP_i}} \tag{1}$$

$$\mathrm{MQ_{ij}} = \sum \mathrm{P}_j \times \overline{\mathrm{C_j}} \tag{2}$$

where MPR represents the mining potential ratio of element i; MQ_{ij} represents the summation of quantity of element i (Tg) accompanying coal production of country j; GPi is the global conventional production of element i (Tg); P_j is the coal production of country j (Tg); $\overline{C_j}$ is the elemental abundance in coal from country j (ppm).

3. Coal Production and Consumption across the World

The share of coal in the global primary energy consumption has steadily reduced and was 27.2% in 2018 [15]. However, coal production and consumption increased gradually due to the high requirement for it in Asia region, particularly in China and India. According to the national production and consumption of coal reported by the BP Statistical Review of World Energy (Figures 1 and 2a), 12 countries (China, India, USA, Indonesia, Australia, Russia, South Africa, Germany, Poland, Kazakhstan, Colombia, and Turkey) are the main producers and consumers that contribute approximately 90% of the global production and 85% of the world coal consumption, respectively [15]. This is attributed to the energy reserve, consumer structure and socioeconomic aspects of the countries. The coal reserve of the 12 countries accounts for approximately 90% of the world's coal reserve (Figure 2b). Among them, China is the largest coal producer and consumer in the world, and accounts for 46% of the global coal production and 51.7% of the world coal consumption in 2018, respectively. In addition, coal plays a significant role in each national primary energy structure, especially for Asia regions. The share of coal accounts for 58.2%, 55.9%, 33.2%, 30.7% and 25.9% of the national primary consumption in China, India, Indonesia, Australia, and Japan, respectively. Therefore, coal is and always will be the major primary energy source.

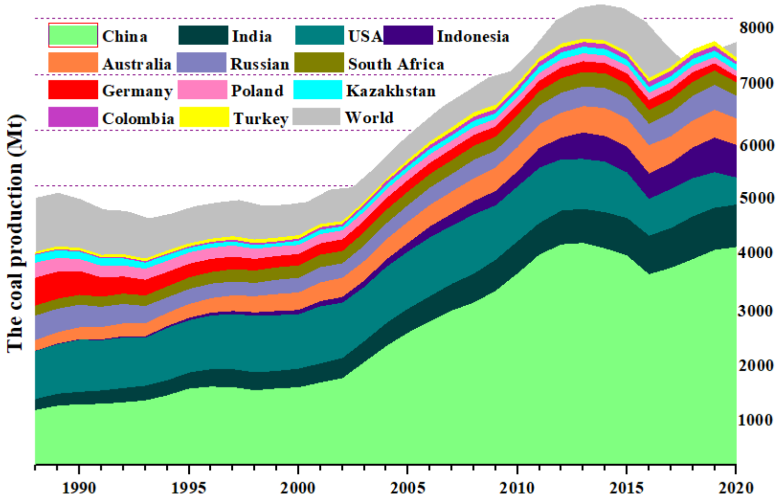

Figure 1. The distributions of the world's coal production from 1989–2020.

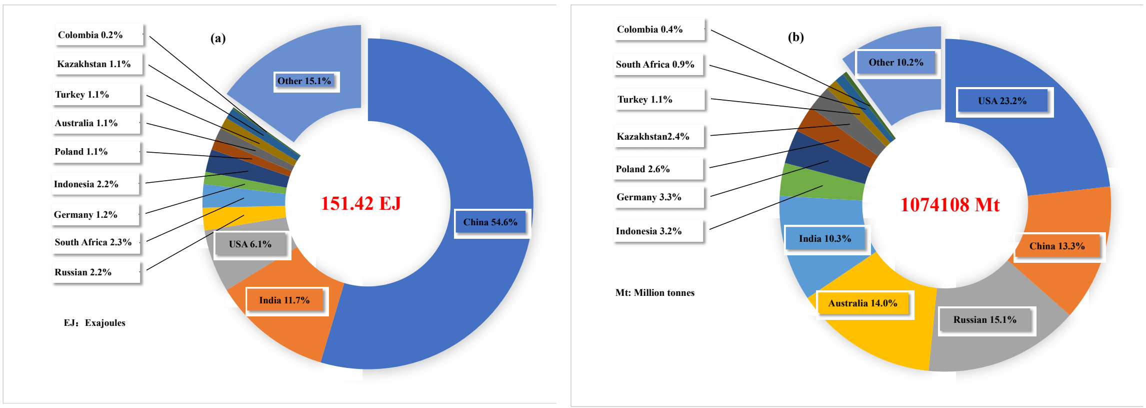

Figure 2. The distributions of the world's coal consumption (**a**) and reserve (**b**) in 2020.

Coal is widely employed in power generation, metallurgical, coal chemistry, gasification, building industrial and activated carbon extraction. Among them, power generation is the main use of coal, accounting for 62.7% of global coal production [15]. According to the *China Energy Statistical Yearbook 2017*, coal used for power generation accounted for approximately 49.3% of total coal consumption in China. However, the ratio of coal consumption for power generation in developed countries is mostly higher than 80%, such as 91% and 82.7% for the USA and Organization for Economic Cooperation and Development (OECD), respectively. The combustion of coal can not only provide calorific value, but also discharge coal ash. The global production of coal ash is about 750 Mt per year [29]. Although the global utilization of coal ash increased gradually with the growing application of new technologies (building materials, road construction, soil amendment, adsorbent), a large amount is disposed of or landfilled [30]. The improper disposal of coal ash has resulted in potential environmental problems [30]. Therefore, further multi-component utilization of coal ash should be prompted.

4. The Abundance of Trace Element in Coal and Coal Ash

Coal is an organic resource formatted by long-term biological and geological processes. Elements are almost found in coal except for a small amount of extremely rare elements such as actinium (Ac), astatine (At), francium (Fr), polonium (Po), and protactinium (Pa) [31]. The concentrations of the elements in coal varies among different regions, geological ages, coal rank and coal seam [32,33]. These variations may be attributed to the different plant communities, source material, depositional environment, detrital influx, diagenetic processes, and epigenetic processes [23,34]. The average elemental abundances in coal and coal ash (Table S1) reported by Ketris and Yudovich (2009) were modified intothe periodic table as shown in Figure 3.

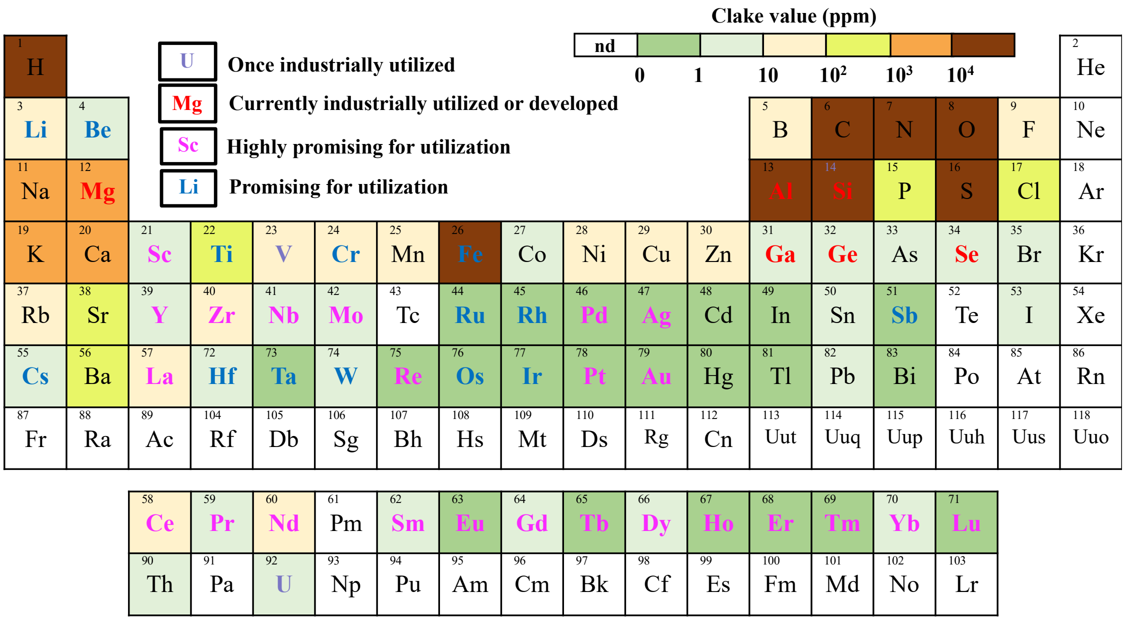

Figure 3. The Clake values of major elements and trace elements in the world coal. The element in different colors mean the current situation of utilization.

The concentrations of elements range from 10^{-12} ppm to more than 50 wt%. As typical hydrocarbons, C, O, H, N and S are the most common elements in coal, which can totally reach to more than 90 wt%. Si, Al, Fe, Ca, Mg, Na, and K are the most common components of inorganic minerals in coal, with median abundance higher than 10^3 ppm. The base metals (V, Cr, Ni, Cu and Zn), Li, Rb, Zr, and some light REE (La, Ce and Nd) generally range from 10 to 100 ppm in coal. The other rare, dispersed elements are mostly less than 10 ppm. The correlation between the median elemental abundances in coal (ash) and continental crust (Table S1) [35] is presented in Figure 4. It could be found that most of the critical elements are depleted in coal when compared with continental crust. The enhanced PGEs (Ag and Au) are found in coal.

Significantly, the natural elemental abundances in coal ash are obviously higher than that of continental crust, indicating the potential utilization of critical elements from coal ash.

According to the description of Swaine (2000), 26 trace elements (Table 2) in coal are supposed to be of environmental concern and could lead to potential environmental impacts during discharge with effective interventions [36]. It could be found that some environmentally sensitivity elements (As, B, Cd, Hg, Mo, Se and Sb) are found to be relatively abundant in coal (Figure 4), which suggests potential environmental impacts during coal utilization. In addition, the concentrations of all the environmentally-sensitive elements in coal ash are much higher than that of continental crust. These metal elements are accumulated and transferred among the ecosystem without degradation. The long-term and excess discharges of these elements during coal activities undoubtedly lead to adverse environmental effects. Nevertheless, these environmentally-sensitive elements are important substances for industrial development. The negative environmental impacts and the element supply shortages could be relived once these elements recovery from coal and coal ash. Therefore, for global development and environmental protection, the potential utilization of elements from coal will be worthy.

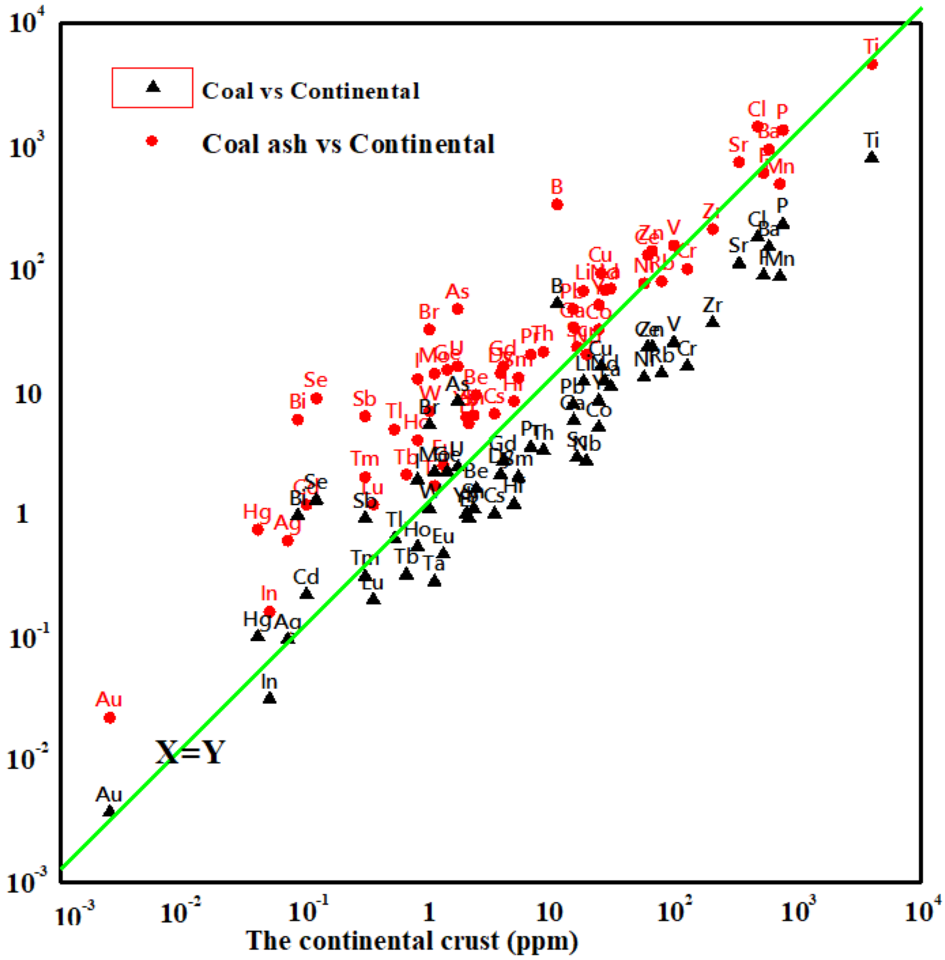

Figure 4. The correlation between the median elemental abundances in coal (ash) and continental crust.

Table 2. Trace elements considered to be of environmental concern in coal (Swaine, 2000).

Grade	Elements
Extremely high concern	As, Cd, Cr, Hg, Pb, Se
High concern	B, Cl, F, Mn, Mo, Ni, Be, Cu, P, Th, U, V, Zn
Moderate concern	Ba, Co, I, Ra, Sb, Sn, Tl

5. The Potential Utilization of Critical Element from Coal

Twelve countries (China, India, USA, Indonesia, Australia, Russia, South Africa, Germany, Poland, Kazakhstan, Colombia, and Turkey) contributed90% of the global coal production. Therefore, the MQ was obtained by the summation of the 12 countries to ensure feasibility. The elemental concentrations in coal (Table S2) and coal production (Table S3) of the 12 countries could be found in the Supplementary Material.

The MPRs of the critical elements are calculated and presented in Figure 5 and Table S4. Meanwhile, the enhanced MPRs are listed in Table 3. The MPRs of scandium (Sc),hafnium (Hf),cesium (Cs),yttrium (Y),germanium (Ge),gallium (Ga), Thallium(Tl), strontium (Sr), REE, selenium (Se),vanadium (V),lithium (Li)and beryllium (Be) are higher than 2, suggesting potential utilization.

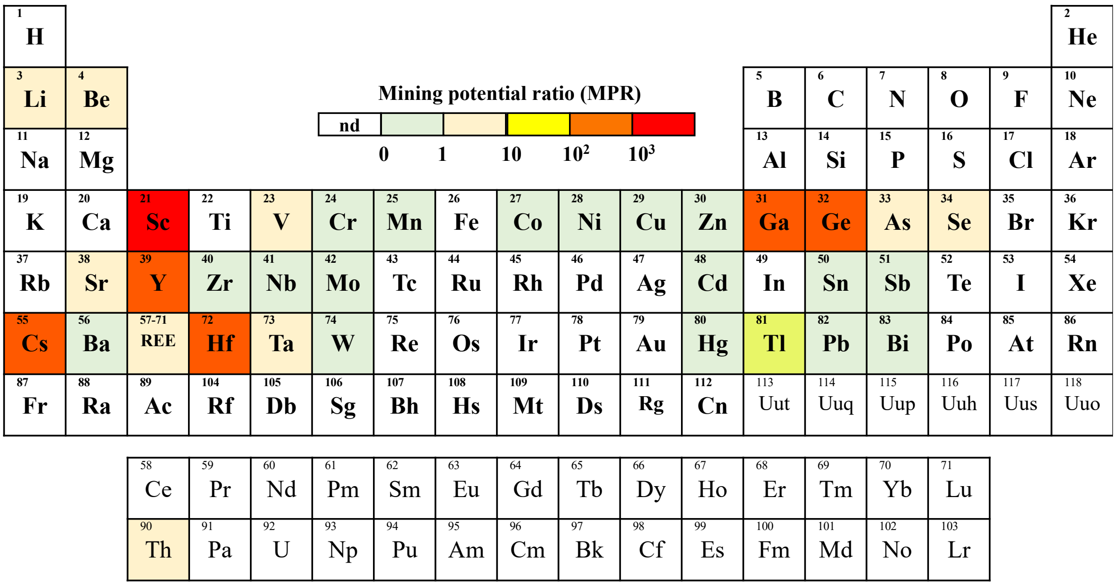

Figure 5. Mining potential ratios for critical elements in coal. The actual values are listed in Supplementary Information.

Table 3. The MPRs of some trace elements in coal.

Element	Sc	Hf	Cs	Y	Ge	Ga	Tl
MPR	0.6	370.6	351.9	280.6	234.3	152.7	93.9
Element	Sr	REE	Se	V	Li	Be	
MPR	6.31	5.06	4.11	3.06	2.48	2.33	

Sc is the element with highest MPR. The potentially recoverable Sc amount from coal is approximately 29.5 Gg, which is much more than the traditional productions (500 kg) [8]. Sc is generally recovered from the by-products of W, Ti, U and other metals, with the concentration of 80–100 ppm [23]. The low production of Sc is attributed to the low demand and the unfixed sources. The occurrence of Sc in the conventional sources varies widely and is difficult to extract for the existence of thorium [37]. Although the natural abundances of Sc in coal (2.9 ppm) and coal ash (23 ppm) are lower than the suggested cut-off grade (100 ppm) [21,38], the high concentration of Sc (Table S5) is mainly found in Russian and Chinese coal deposits such as Yakhlinsk, Nizhen-Bikinsk, Rettikhovsk, Minusa, and Xinde [23,39–42]. The highest concentration of Sc was found in the low-ash coal of the Yakhlinsk deposit with 1320 ppm in the ash [41]. Meanwhile, the high concentration of Sc (560 ppm in the ash) was also found in the Amos coal bed in Western Kentucky [43]. Consequently, Sc recovered from coal ash deserves further investigation.

Hf is used in electronics, nuclear industry, chemistry, and alloy material for its excellent performance. Hf is naturally paragenesis with Zr, and mainly recovered from the waste of Zr extraction with the production of 0.05 Gg in 2017 [8]. The MPR and potential extraction of Hf from coal are 370.6 and 18.5 Gg, respectively. The average concentrations of Hf are 1.2 ppm and 8.3 ppm in coal and coal ash, respectively [38]. Nevertheless, the natural abundance of Hfis 11.6 ppm and 9.54 ppm in Chinese coal [27] and Indian coal [44], respectively. Meanwhile, the high concentration of Hf (Table S5) is explored in Chinese coal mines including Adaohai [45], Datanhao [46], Huayingshan [47], Xinde [42], Fushui [48] and Hailiushu [49]. The extraction of Hf from coal ash is regarded as feasible in Asia regions.

Cs is the softest element with the average concentration of 3.4 ppm in the continental crust [35]. Cs is mostly used in the extractive oil industry as drilling fluids. Meanwhile, commercial uses of Cs including application in electricity, electronics, chemistry, and nuclear applications. Cs is mainly associated with and refined from the pollucite ore with the annual production of 20 t [8]. The MPR and potential recovery amount of Cs from coal are 351.9 and 7 Gg.The elevated concentration of Cs (Table S5) is found in the Spetsugli, Lincang and Fushui coal [48,50,51]. The average Cs concentration in Spetsugli coal is 30.3 ppm with maximal content of 50.7 ppm [50]. The accumulation of Cs is related to the circulation of volcanogenic thermal solutions [23]. It is noteworthy that Cs is mainly enriched in Ge-bearing coals in the form of host sedimentary rocks and underlying granites [23]. Therefore, the recovery of Cs with Ge from coal can reduce the mining expense effectively.

Y is usually grouped with REE for similar physicochemical properties and tends to be paragenetic in geological processes [52]. REE and Y are widely incorporated in various emerging power and energy-efficient technologies including catalysts, fuel cells, super-power permanent magnets applied in energy conversion, hybrid and electrical vehicles, and superconducting electrics [22,23]. The natural continental crust and annual production are 168.3 ppm [35] and 167.1 Gg [8], respectively. The REE and Y are mainly recovered from carbonatites (bastnaesite and monazite) and weathered crust elution-deposited ores, both of which are predominantly produced in China (>80%) [52]. With the long-term and excess exploitation, the resources of conventional ores are being exhausted and cannot provide growing demand in the foreseeable future. The natural median abundances of REE+Y in coal and coal ash are 68.5 ppm and 404 ppm, respectively [38], which are lower than the suggested cut-off grade (1000 ppm) [21]. Nevertheless, the coal deposits with high REE+Y have received fairly intensive study [21,47,53–58]. TheREE oxides concentration in coal deposits including Guanbanwusu [59], Daqingshan [45], Huayingshan [47], Moxinpo [58], Guxu [57], Eastern Kentucky [53], Vanchinsk [21] are more than 0.1% (Table S5), suggesting recovery potential. In addition, potential recovery amount of REE and Y from coal is 843.2 Gg and 112.2 Gg, respectively, which are greatly higher than the annual production of 166.7 Gg and 0.4 Gg [8]. Therefore, the recovery of REE and Y from coal may be an alternative with the traditional ores exhausted and growing demand of emerging cleaning energy technologies.

Ge is regarded as a technology-critical element for its wide application in electronics, polymerization catalyst, and organometallic chemistry. The annual production of Ge was 98 t in 2017 [8], of which more than 50% was recovered from coal [22]. However, the average concentration of Ge in world coal and coal ash are 2.2 ppm and 15 ppm, respectively [38]. The high concentration of Ge (Table S5) is found in many Chinese and Russian coal ores (including Lincang, Wulangtuga, Spetzugli and Novikovsk coals) with the total reserves more than 10 Gg [23]. It has been reported that the designed capacities for Ge production inLincang, Wulangtuga and Spetzugli coal ores are 150–170 t/a [60], which can satisfy industrial requirements completely. Therefore, the recovery of Ge from coal is and continues to be the main source.

Semiconductor applications (integrated circuits, optoelectronics, and satellites) account for 98% of the commercial production of Ga. Meanwhile, the application of Ga in hydrogen storage is growing gradually with the development of emerging power technologies. The annual production of Ga was 310 t, which was rose 496.2% since 2000 [8]. It is foreseeable that the production of Ga will continuously increase with the growing requirement. More than 90% of Ga is extracted from the bauxite processing, and 10% of Ga is recovered from the residues of Zn-ores. The concentration of Ga in the residues of bauxite and Zn ores ranged from 30 to 80 ppm with the median value of approximately 50 ppm [23]. The natural abundances of Ga in world coal and coal ash are 5.8 ppm and 33 ppm, respectively [38], which meets the suggested cut-off grade (30 ppm). In addition, elevated Ga concentration (Table S5) and large reserves are detected in many coal deposits [45,54,56,58,59]. The concentration and reserve of Ga are 92 ppm in coal ash and 49 Gg in Jungar Coalfield, respectively. The utilization potential is proven by the MPR of Ga (152.71) [20]. Therefore, coal could be considered as new deposits for Ga.

The traditional production of Tl is mainly recovered from the by-products of Cu, Pb and Zn processing with annual amounts of 30 t [8]. More than 60% of Tl is used in the electronics industry, and the remainder is utilized in the pharmaceutical industry and glass manufacturing. The high MPR and potential recovery amount suggest that the mining potential of Tl from coal may increase the production of Tl effectively. Sr is an alkaline earth metal that is highly chemically reactive. The consumption of Sr is decreasing with the substitution of cathode ray tubes in color televisions. Nevertheless, the large annual production of Sr (137 Gg) suggests the mining potential from coal [8]. The MPRs of Se, V, Li and Be range from 2 to 5, thus, the utilization potential should not be ignored. According to Table S5, the elevated concentrations of Se, V, Li and Be are found in many coal ores [20,21,23,40,56,58,61]. Among then, the recovery of Se from coal was commercialization [20]. The recovery cost and efficiency of these elements from coal may be equal to or even lower than conventional productions.

6. Future Prospects

Most of the aforementioned critical elements are produced from the by-products of base metals (Cu, Pb, Ni and Zn) without steady production capacity. The recovery of these critical elements from coal with high concentrations may be expected for the many mineral resources, and economic and environmental benefits (Figure 6).

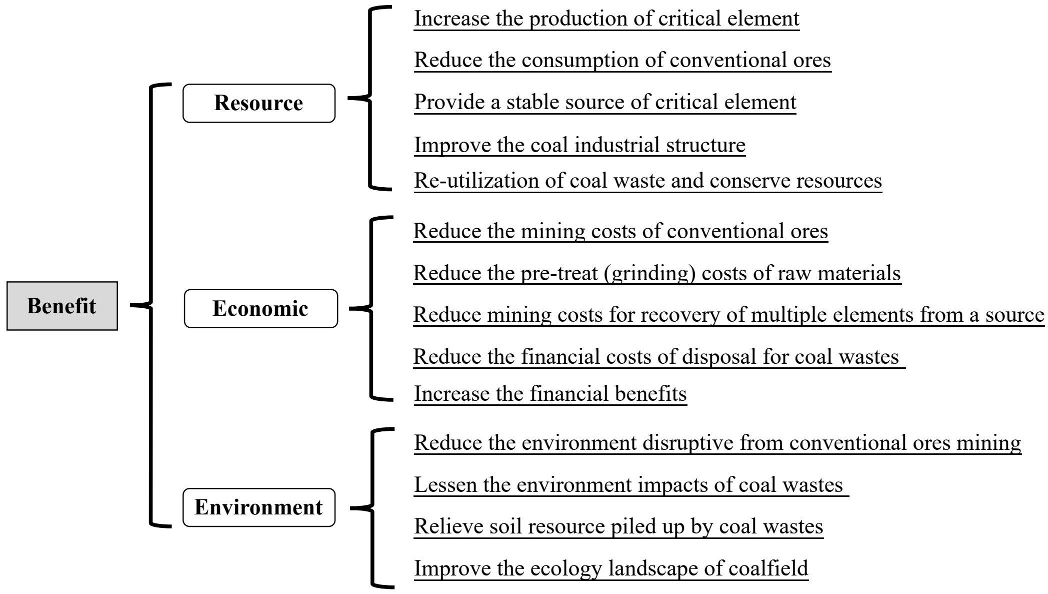

Figure 6. The benefits for recovery of critical elements from coal.

Nevertheless, the commercial extraction of critical elements from coal and coal ash suffers from different theoretical, technological, economic and environmental difficulties.

(1) Many theoretical issues need to be studied. The high-efficiency and cost effective recovery of critical elements from coal is greatly determined by their concentrations and associations in coal. The concentration and reserve of critical elements in coal is of extreme significance for the mining potential. The modes of occurrence of critical elements in coal can provide important information for the design of recovery methods. The enrichment mechanisms and modes of occurrence of critical elements should be solved.

(2) Various technological difficulties including exploration, joint-mining, and co-extraction methods should be developed. The concentrations of critical elements varied among different coal-forming period, coal rank, coal seam and even in the different location of the same coal seam. In addition, many critical elements are enriched in the coal seam. For example, V, Se, Mo, REE, Y and Ga are usually co-enriched in the high-Ga coal ores. To minimize mining costs and maximize extracting multiple elements, high precision exploration methods, joint mining and extraction technologies should be developed.

(3) The recovery cost and market price of critical elements should be considered. The recovery cost is a very important factor in critical element recovery. Much effort has been expanded in studying the recovery of critical elements from coal. Solvent extraction

is regarded as a promising method for the extraction of critical elements. However, the extraction costs of solvent recovery are unfavorable economics for the high prices of regents. Meanwhile, the market prices of the critical elements also influence the commercial mining potential of critical elements.

(4) Emerging environmental issues should also be of concern. Some toxic elements (As, Hg, Cd) may be co-enriched with critical elements in coal ores during the complex geological processes. These toxic elements may be released and enter intothe environment during recovery of critical elements, resulting in potential environmental and health risks. Therefore, the countermeasures for control of toxic elements during recovery should be adopted.

7. Conclusions

Coal contains high concentrations of potential critical elements during complex geological evolution. The abundances of critical elements in coal varied widely among different deposits and regions. The high concentrations of critical elements are found in many Chinese and Russian coal ores. The potential utilization of elements from coal will be worthy for global development and environmental protection. The concentrations of critical elements in the global coal ash are higher than that of continental crust. According to the mining potential analysis and enrichment characterizations of critical elements, the coal hosted ore deposits are regarded as highly alternative sources for Sc, Hf, Cs, Y, Ge, Ga Tl, Sr and REE. The industrial extraction of critical elements from coal can obtain both economic and environmental benefits. Nevertheless, the commercial recovery of critical elements from coal still suffers from many theoretical, technical, environmental, and economical difficulties.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14154710/s1, Table S1: The natural abundances of trace elements in continental crust, world coal and coal ash (ppm), Table S2: The abundances of trace elements in different countries coal (mg/kg), Table S3: The coal productions of the selected countries (million tons). Table S4: The Mining potential ratios (MPR) for trace elements in coal when compared to the global production in 2017. Table S5: Distribution of high concentrations of critical resources in coal (ppm).

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