Literature Review on Critical Elements in Coal

Kane Maxwell[a,*], Yuhao Long[b], Evan Ginting[b]

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[b]

Abstract

This paper summarises the literature on critical elements contained in coal. Specifically the paper adresses the following questions:

1) What are critical elements, what are they used for and what is their projected demand?
2) What types of critical elements are found in coal, and in what concentrations?
3) What concentrations of critical elements would be considered economic to extract?
4) Are there any existing coal mines, or coal basins that are extracting critical elements from coal, or coal tailings?
5) What analytical and processing methods can be used to extract critical elements from coal?

Keywords: Coal, Critical Elements, Rare Earth Elements

1. Critical elements overview

Answer the following question:

1. What are critical elements (also referred to as critical minerals including rare earth elements)? What are they used for and what is their projected demand?

As the burgeoning ideology of environmental sustainability and geopolitical tension, The concept of critical elements received paramount attentions in the contemporary global landscape. Critical elements, or also referred as critical minerals, is vital metallic or non-metallic element that underpin the functionality and advancement of core technologies, economic frameworks, and national security but may be susceptible for exogenous risk in supply chain.

According to Critical Minerals Strategy 2023–2030 issued by Geoscience Australia (2023),There has total 15 elements are listed as top vulnerability for the future (Table 1, Coyne and Campbell (2023) & Skirrow et al. (2013)):

Table 1: summary of crtical element in Australia

CRITICAL ELEMENT	PRODUCTION(KT)	% of Global production	ORE RESERVE(KT)	USAGE
Aluminum & derivative(Al)	20	14%	1,160	Aerospace sector and coating in Li-ion batteries

*Corresponding author

Email addresses: kane.maxwell@matrixgeoscience.com (Kane Maxwell), ylon0012@student.monash.edu (Yuhao Long), egin0003@student.monash.edu (Evan Ginting)

Cobalt(Co)	5.9	3%	613	Li-ion battery cathodes,superalloys, steel, and magnets
Gallium(Ga)	-	-	-	ICs, GaN laser diodes and photovoltaics films
Germanium(Ge)	-	-	-	Fiber/infared optics,Polymerization Catalysts and semiconductors
Lithium(Li)	61	47%	4,563	Li-ion batteries and Lithium carbonate and lithium oxide in glass or ceramics
Magnesium(Mg)	2.6	10%	Not available	Pyrotechnics, medicine and nanocomposites in automotive/aerospace
Manganese(Mn)	3.3	17%	120,000	Steel,Agricultral fertiliser and dry cell batteries
Nickel(Ni)	150	4.5%	20.4[1]	Non-ferrous alloys,magnets and electroplating
Rare-earth elements(REE)[2]	18	6%	3,121	Catalyst,magnets and polishing
Silicon(Si)	0.05	1%	-	Silicon wafer in electronic & photovoltaic cells and synthetic polymers
Tantalum(Ta)	0.057	3%	49.8	Micro-capacitors and medical technology
Titanium(Ti)	0.85	8.4%	82,100	Aerospace and marine application or pigment through Titanium dioxide
Tungsten(W)	-	-	213	Lightning and chemical compunds
Vanadium(V)	-	-	2,948	Steel alloys
Zirconium(Zr)	0.5	36%	29,200	Cladding fuel rods in nuclear reactors

[1] data collected in 2012.
[2] 17 elements, including lanthanoid,Scandium(Sc) and Yttrium(Y).
Source: Skirrow et al., 2013 & Coyne and Campbell, 2023

Rare-earth elements,a significant branch in critical element, comprise of 15 element in lanthanoid family and 2 extra elements with similar chemical properties–Scandium(Sc) and Yttrium(Y). Unlike name implication, albeit their overall natural abundance(NA) in earth crust is not extremely rare (average 180-200 ppm) their distribution in earth is quite scattered and strong propensity to coexist in pairs or group within ore deposits in terms of geochemical properties. Therefore, only few REE can be concentrated to a degree that permits for commercial mining. The largest segment of global consumption is catalyst(24%) in automotive or petrochemical industry, as well as equally high demand(23%) in magnet(NdFeB, SmCo etc.) Zhou et al. (2017).

With the exuberant demand shock from EVs and clean energy exploration, the consumption of critical minerals is foreseeable to be thrived: Geoscience Australia estimates that by 2040, critical elements related to lithium batteries (such as Li, Co, and Ni) will see an exponential surge of 20 to 40 times, while REEs (rare earth elements) will see a 7-fold increase during the same period.

2. Critical elements in coal

Answer the following question:

2. What types of critical elements are found in coal, and in what concentrations? In an ideal state, any chemical elements can be detected in coal deposit, which may originate from syn-genetic plant decays or epigenetic source after . Its concentration will be determined on coalified compaction and the heat & pressure environment.

In Hodgkinson and Grigorescu (2020) element mapping project on Bowen basin,the largest coal reserves in Australia, the concentration of element composition is subjective to sample's lithology rather than the depth grading:

1). In coal and derivative, albeit majority of element concentrations is inferior of the benchmark against earth crust average, local samples exhibit enrichment in HREE and Scandium in respect to McLennan (2011) Post-Archaean Australian Shales (PAAS) standard , while abnormal 4-6 times higher than crustal average in moderate critical element, Bismuth(Bi) .

2). Siltstone and mudstone has a lackluster finding to classify enrichment for majority of elements concentration,except for the concentration of Cobalt compound barely meet crustal average, whose ubiquitous economic value may warrant further examination.

3). As the sediment from volcanic ash, tuffaceous rock is rich in pumice and lithic fragments. The sample display a series of elevated concentrations of strategic elements including REE, Ga and Bi. Besides, a potential Lithium-rich borehole is found, with approximate 5 times higher than crustal average.

Below is the summary result (Table 2) from the distribution of critical element :

Table 2: summary of crtical element in Australia

CRITICAL ELEMENT	Crust[1]	AVERAGE CONCENTRATION(PPM)	HIGEST CONCENTRATION(PPM)	% of above crustal average
Coal& associate				
Lithium	21.0	13.70	25.0	22.22%
REE	184.0	115.80	205.0	11.11%
Cobalt	17.0	16.90	30.0	44.44%
Nickel	47.0	11.20	40.0	0.00%
Tantalum	1.0	0.33	1.0	33.33%
Vanadium	97.0	85.60	140.0	22.22%
Zirconium	193.0	102.10	160.0	0.00%
Gallium	17.0	12.30	25.0	44.44%
Bismuth	0.2	**0.59**	1.0	66.67%
Siltstone & mudstone				
Lithium	21.0	17.20	28.0	33.33%
REE	184.0	138.80	189.0	16.67%
Cobalt	17.0	**39.30**	134.0	66.67%
Nickel	47.0	25.80	73.0	33.33%
Tantalum	1.0	0.20	1.0	16.67%
Vanadium	97.0	**102.00**	225.0	33.33%
Zirconium	193.0	116.80	243.0	16.67%
Gallium	17.0	15.00	22.0	33.33%
Bismuth	0.2	0.18	0.4	66.67%
Tuffaceous rocks				
Lithium	21.0	**21.50**	105.0	12.50%
REE	184.0	**244.00**	441.0	87.50%
Cobalt	17.0	9.25	19.0	12.50%

Nickel	47.0	3.75	30.0	0.00%
Tantalum	1.0	**1.10**	2.0	100.00%
Vanadium	97.0	27.90	70.0	0.00%
Zirconium	193.0	153.75	282.0	25.00%
Gallium	17.0	**32.25**	37.0	100.00%
Bismuth	0.2	**0.71**	1.2	100.00%

[1] McLennan 2011 Post-Archean Australian Shale standard
Source: Hodginkson et al., 2020

3. Economic concentrations

Answer the following question:

3. What concentrations of critical elements (including rare earth elements) would be considered economic to extract from coal?

The booming demand for critical element, has not merely driven interest in alternative sources beyond traditional mining but also stimulate the exploration of operational feasibility from an economic value perspective. Economic assessment is hinged with the priority concern on concentrations, as well as demand-supply dynamic and operational cost United States Department of Energy (2017).

In general, Seredin and Dai (2012) study for the coal mining in Far east region, Russia manifest the cut-off criterion for REE extraction will range from 800-1000 ppm, subject to seam thickness of the coal. However, the primitive cut-off grading does not correct reflect market trend on each individual composition. The new outlook coefficient(Table 3) is introduced to lever the economic degree of rarity for REY oxide(REO). Elements with plentiful deposits or relatively narrow application markets will be graded as ‘Excessive’, vice versa to be graded as ‘Vital’. The ratio formula can be written as:

$$C_{Outlook} = \frac{\sum C_{Vital}}{\sum C_{Excessive}} \tag{1}$$

$$C_{\text{Critical percent}} = \frac{\sum C_{Vital}}{\sum C_{REE}} \tag{2}$$

Table 3: summary of crtical element in Australia

REE	Category[1]	SIGNIFICANCE
Scandium(Sc)	-	-[2]
Yttrium(Y)	M	Vital
Lanthanum (La)	L	Moderate
Cerium (Ce)	L	Excessive
Praseodymium (Pr)	L	Moderate
Neodymium (Nd)	L	Vital
Promethium (Pm)	-	-[2]
Samarium (Sm)	L	Moderate
Europium (Eu)	M	Vital
Gadolinium (Gd)	M	Moderate
Terbium (Tb)	M	Vital
Dysprosium (Dy)	M	Vital
Holmium (Ho)	H	Excessive
Erbium (Er)	H	Vital
Thulium (Tm)	H	Excessive
Ytterbium (Yb)	H	Excessive
Lutetium (Lu)	H	Excessive

[1] L- Light; M- Middle; H- Heavy
[2] Not included due to heterogeneous and radioactive reason.
Source: Seredin et al., 2012

Ketris and Yudovich (2009) research measured average trace REE concentration globally at 403.5 ppm, with an approximately 1 outlook coefficient and 35% $C_{\text{Critical percent}}$. Continual research by Choudhary et al. (2022) analyzed approximately 288 coal,fly ash samples, reporting 11 of 13 nations has been detected above-average case, especially notably enrichment in China, Russia and Central Asia.

Furthermore, Dai and Finkelman (2018) also compiled the cut-off grade(Table 4) for key elements in coal.

Table 4: summary of crtical element in Australia

ELEMENT	CUT-OFF GRADE
Uranium(U)	1000
Germanium(Ge)*	300
Vanadium(V)*	1000
Scandium(Sc)*	100
Selenium(Se)	500-800
Niobium(Nb)	300
Zirconium(Zr)*	2000
Molybdenum(Mo)	1000
Rhenium(Re)	1
Tungsten(W)*[1]	1000
Antimony(Sb)	100
Beryllium(Be)	300

[1] High-demand critical element
Source: Dai et al., 2018

4. Existing economic deposits

Answer the following question:

4. Are there any existing coal mines, or coal basins that are extracting critical elements from coal, or coal tailings?

The extraction of critical elements from coal mines is still in the observation and exploration stage. Industrial-grade REE and lithium deposits have been respectively probed in the Jungar basin in Inner Mongolia and the Ningwu basin in Shanxi Province, China. Sun et al. (2010) study on the Antaibao surface coalfield(Ningwu basin) found Lithium enrichment with 10 times higher than China WAV in roof rock, floor rock and coal seams. Another independent anlysis Dai et al. (2012) of mineralogical and geochemical compositions in Daqingshan coalfield(Jungar basin) exhibits L-type or H-type of REY ,Ga and Al_2O_3 abnormalities in coal bench, widely distributed in chlorite,kaolinite and goyazite.

5. Extraction of critical elements

Answer the following question:

5. What analytical and processing methods can be used to extract critical elements from coal?

The analytic methods in critical element mapping and quantification can be summarized as Eterigho-Ikelegbe et al. (2021):

1). **Proximate analysis**: As the standard practice of ASTM D3172, it incorporates the composition breakdown through the learning of moisture,volatile matter, ash and carbon content attribute.

2). **X-Ray Fluorescence (XRF) analysis**: As the standard practice of ASTM D4326-13, it incorporate spectrometric identification and quantification of the concentration of the critical element.

3). **Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)**:As the standard practice of ASTM D 6357–19,it is particularly utilized to determine the occurrence and concentration for trace elements e.g. arsenic, cadmium, mercury, lead, and other potentially hazardous or valuable elements.

4). **Laser-induced breakdown spectroscopy (LIBS)**:A short pulse laser is focused on the sample surface to form a plasma, and then the plasma emission spectrum is analyzed to determine the material composition and content of the sample.

5). **Transmission Electron Microscopy(TEM)**: It is a is an advanced diagnostic technique used to observe material structures at the nanometer scale. With transmitting a beam of electrons through an ultra-thin specimen, it can return an image that reveals its internal structure and pattern.

6). **Intelligent Scanning Electron Microscopy (SEM)**: Similar to TEM, SEM is a computer-controlled scanning for coal and ores's surface morphology and topography that reveal the texture, grain structure, and other attribute in the sample.

7). **Chemical fractionation**: It refers to the process of seperating mixture of mineral matters into different phrase, which can help to target isolating elements or compounds.

The traditional techniques of element extraction primarily focus on

1). **acid-alkine** reagent to dissolve impurities in compound mineral matters. Although this approach can achieve 70%-80% recover rate, recently it has been controversial due to the excessive waste of acid and alkaline solvents and the production of hazardous pollutants.

2). **Biological leaching** is another relatively environment-beneficial approach that allow extraction under mild reacting conditions and high operating safety.However, it encountered the bottleneck of strain cultivation and microbial control, incurring the scale-up challenge to industrial-level production.

Recently, **water-leaching** is a prevailing approach since it mitigate the flaw from traditional techniques. Water leaching can be considered as less environmentally detrimental compared to strong acid/alkaline leaching, as well as cost effective for solvent selection. The crucial stages on this preparation workflow are **low temperature activation** and **water leaching**. During the stage of low temperature activation, the chemical reaction within coal fly ash(CFA) will be facilitated by complexation agents(ammonium salts or weak acids) in covered alumina crucibles, which help liberate critical elements from the matrix of the CFA. After the activation and cool down to ambient temperature, the tablets are placed in water for the leaching and dissolve process. Water acts as the leaching solvent, extracting these soluble elements into the leachate.The configuration in temperature and mass ratio of solvent will be the vital determinant for optimized recovery. Take Lithium example, it can achieve a stable leaching efficiency of 90% through ammonium fluoride leaching at 150°C with a SiO_2/NH_4F mass ratio of 1:1.35 Xu et al. (2021).

Another innovation is Hydrophobic-Hydrophilic Separation (HHS), designed to leverages the disparity of affinity(water-repellent &water-friendly) properties of substances to achieve separation.It can treat as a complemetary application for small particle delamination without size limit, providing flexible and extensible purpose in the segregation of ultrafine coal Hodgkinson and Grigorescu (2021).

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