# WASHABILITY AND ENRICHMENT OF CRITICAL METALS ANALYSIS ON PALUDA COAL USING DENSE MEDIUM SEPARATION, BARRU REGENCY, SOUTH SULAWESI PROVINCE

ANALISIS KETERCUCIAN DAN PENGAYAAN LOGAM KRITIS PADA BATUBARA PALUDA MENGGUNAKAN METODE *DENSE MEDIUM SEPARATION*, KABUPATEN BARRU, PROVINSI SULAWESI SELATAN



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# THESIS

## WASHABILITY AND ENRICHMENT OF CRITICAL METALS ANALYSIS ON PALUDA COAL USING DENSE MEDIUM SEPARATION, BARRU REGENCY, SOUTH SULAWESI PROVINCE

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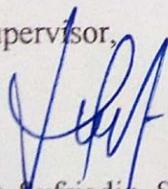
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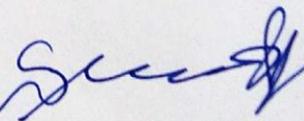
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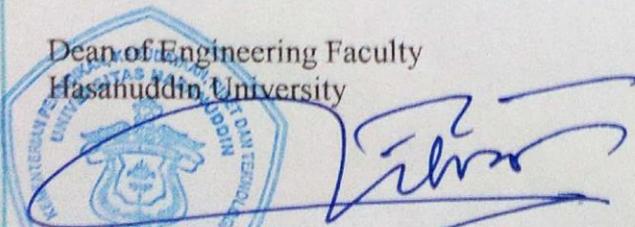
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# ABSTRACT

Paluda coal is known to have high ash and sulfur content, hence it requires beneficiation to improve the economical value of the coal. This aims to characterize the quality, mineral and chemical composition, to determine the washability degree of Paluda Coal, and to determine the enrichment of critical metals content in coal density series. The sink-float test was applied by using a mixture of perchloroethylene and wash benzene to make density series. Results of the raw coal analysis show that Paluda Coal can be classified as Sub-Bituminous Coal A with a medium ash content of 8.17% and a high sulfur content of 3.07%. The minerals contained in Paluda Coal consist of illite, kaolinite, quartz, and pyrite. The results of chemical analysis for the major elements show that $SiO_2$ is the most dominating, followed by $Fe_2O_3$ and $Al_2O_3$, trace elements that have high content include As, Cr, Hg, Mo, Ni, and V. The rare earth elements that have a high content in coal are Gd, Y, Er, and Yb. The coal washing results show that the studied coal is easy to wash with coal yield up to 94% with relative density of 1.45 $g/cm^3$. The majority of trace elements from coal washing results show a strong positive correlation with coal ash content, except for Sc and Sr which have positive correlation with coal matter. Meanwhile, REY tends to have positive correlation with coal matter, presumably because REY is likely bound to organometallic compound. The highest critical metals enrichment was found in the density fraction 1.3-1.4 $g/cm^3$ with the Tm having the highest enrichment level up to 120%, followed by Er, Lu, Yb and Dy with 110%, 107%, 100%, and 99%, respectively.

**Keywords:** Paluda Coal; mineral; washability; enrichment; critical metals.

# ABSTRAK

Batubara Paluda diketahui memiliki kandungan abu dan belerang yang tinggi, sehingga perlu dilakukan benefisiasi untuk meningkatkan nilai ekonomis batubara tersebut. Penelitian ini bertujuan untuk mengkarakterisasi kualitas, komposisi mineral dan kimia, menentukan derajat ketercucian Batubara Paluda, dan menentukan pengayaan kandungan logam kritis dalam seri densitas batubara. Uji endap-apung diaplikasikan dengan menggunakan campuran perkloroetilen dan wash-bensin untuk membuat seri densitas. Hasil analisis sampel batubara menunjukkan bahwa Batubara Paluda dapat digolongkan sebagai Batubara Sub-Bituminous A dengan kadar abu sedang 8,17% dan kadar belerang tinggi 3,07%. Mineral yang terkandung dalam Batubara Paluda terdiri dari ilit, kaolinit, kuarsa, dan pirit. Hasil analisis kimia untuk unsur-unsur utama menunjukkan bahwa $SiO_2$ paling mendominasi, diikuti oleh $Fe_2O_3$ dan $Al_2O_3$, unsur-unsur jejak yang memiliki kandungan tinggi antara lain As, Cr, Hg, Mo, Ni, dan V. Unsur-unsur tanah jarang yang memiliki kandungan yang tinggi adalah Gd, Y, Er, dan Yb. Hasil pencucian batubara menunjukkan bahwa batubara yang diteliti mudah dicuci dengan perolehan batubara bersih hingga 94% dengan densitas relatif 1,45 $g/cm^3$. Sebagian besar unsur hasil pencucian batubara menunjukkan korelasi positif yang kuat dengan kadar abu batubara, kecuali Sc dan Sr yang berkorelasi positif dengan material batubara. Sementara itu, REY cenderung berkorelasi positif dengan material batubara, diduga karena REY cenderung terikat pada senyawa organometalik. Pengayaan logam kritis tertinggi terdapat pada fraksi densitas 1,3-1,4 $g/cm^3$ dengan Tm memiliki tingkat pengayaan tertinggi hingga 120%, disusul oleh Er, Lu, Yb, dan Dy masing-masing sebesar 110%, 107%, 100%, dan 99%.

**Kata Kunci:** Batubara Paluda; mineral; ketercucian; pengayaan; logam kritis.

# ACKNOWLEDGMENTS

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# GLOSSARY

| Terms | Definition |
|---|---|
| Ash Yield | Percentage of ash content from coal beneficiation product. |
| CFA | Coal Fly Ash. Powdery particulate material that is carried off in the flue gas and usually collected from the flue gas by means of electrostatic precipitators, baghouses, or mechanical collection devices such as cyclones. |
| Clark Value | Average content of an element in coal (hard and brown) and black shales around the world. |
| Coal Yield | Weight percentage of coal beneficiation product. |
| Critical Metals | Groups of metals identified as having rarity based on its supply, demand, imports, and market factors. |
| Dense Medium Separation | Gravity separation method that uses a heavy solution as a medium to separate materials based on their density. |
| Enrichment Factor | A widely used metric for determining how much the presence of an element in a sampling media has increased relative to average natural abundance because of human activity. |
| FABA | Fly Ash-Bottom Ash. By products from coal combustion. |

| Terms | Definition |
| --- | --- |
| Framboidal | Micromorphological feature common to certain sedimentary minerals, particularly pyrite ($FeS_2$) |
| ICP-AES | Inductively Coupled Plasma Atomic Emission Spectroscopy. An analytical technique based on the principles of atomic spectroscopy for the determination of more than 70 elements with detection limits in the parts per billion to parts per million range. |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry. An elemental analysis technology capable of detecting most of the periodic table of elements at milligram to nanogram levels per liter. |
| Organometallic | Any member of a class of substances containing at least one metal-to-carbon bond in which the carbon is part of an organic group. |
| Perchloroetylene | Colorless liquid widely used for dry cleaning of fabrics, hence it is sometimes called "dry-cleaning fluid" |
| REE | Rare Earth Element. Group of 15 elements referred to as the lanthanide series in the periodic table of elements. |
| REY | Rare Earths and Yttrium. Group of lanthanides plus yttrium. Yttrium is added because it had similar chemical characteristic with the lanthanides. |

| Terms | Definition |
|---|---|
| Washability | The ease with which washing will remove impurities from the sample. |
| Wash Benzene | Cleaning fluid that dries very quickly and is generally used in the garment and automotive industries. Sometimes also known as thinner washing. |
| XRD | X-Ray Diffraction. A widely used technique to assess the crystallinity and structure of solid samples. |
| XRF | X-Ray Fluorescence. A non-destructive analytical technique used to determine the elemental composition of materials. |

# CHAPTER I

# INTRODUCTION

## 1.1    Background

Coal plays an important role in power generation around the world. Coal-fired power plants currently account for 38% of global electricity and, in some countries, coal uses a higher percentage of electricity. British Petroleum (2020) released statistical data on production, reserves and energy use in the world. Indonesia itself is a contributor to 9.4% of the world's total coal production, reaching a total production of approximately 15 million tons by 2019. Coal production in Indonesia is dominated by sub-bituminous and bituminous coal mining. The use of coal in Indonesia is currently widely used as fuel for Steam Power Plants (PLTU) and as fuel in cement processing plants (ESDM, 2020).

The use of coal as fuel for Steam Power Plants produces by-products in the form of fly ash and bottom ash. Even though according to Government Regulation of the Republic of Indonesia Number 22 of 2021 concerning the Implementation of Environmental Protection and Management, fly ash and bottom ash (FABA) are no longer classified as toxic (B3) waste, still FABA cannot be left alone without direct use to prevent pollution that can cause harm. Currently, the use of FABA from steam power plants in Indonesia is still limited because it is only used as a planting medium or as a mixture for asphalt concrete (Kurniawan, et al., 2014).

According to ESDM data (2020), South Sulawesi contributes about 231.12 million tons of coal resources or about 0.14% of the total coal resources in Indonesia. The quality of South Sulawesi's coal is still relatively low so that its utilization is still limited, such as for additional fuel in cement factories or for some local industries. Due to its high as content, the potential for FABA formation when used is quite large and increases the potential for critical metal content to be extracted as by-products. South Sulawesi coal is spread in several regencies, one of which is Barru Regency. One of the locations for coal deposits in Barru Regency is in the

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Paluda Region, Pujananting District. The quality of Paluda coal ranges between lignite and sub-bituminous with an ash content of up to 37.81% and a sulfur content of up to 5.37% (Brotowati, et al., 2019; Priyono, et al., 2014; Widodo, et al., 2017;).

To increase the economic value of low grade coal, special treatment in the form of beneficiation is required before the coal is used. Various beneficiation methods have been developed, including physical methods (dense medium separation, shaking table, and jigging), chemical leaching, physico-chemical (flotation and agglomeration), and using organic materials as reagents (bio-beneficiation). These methods are suitable for coal which has a high ash and sulfur content.

Dense Medium Separation (DMS) is a method of separating coal and its impurities based on its specific gravity, known as the sink and float process. Dense Medium Separation (DMS) is used on coal with the condition that the coal material should not be too fine-sized, because when the material combines with liquid, it will form a suspension that is more viscous. The washing process produces two products, namely sinks which are heavy coal products (unwanted), and floats which are light coal products (desired) (Wardhany, et al., 2018). The application of the DMS method can also be used as an effort to enrich the precious metals contained in coal.

Current technology also makes coal an alternative resource for strategic metals, such as Li, Ge, Ga, U, V, Se, rare earth elements (REE), Y, Sc, Nb, Au, Ag, and Re, as well as light metals such as Al and Mg. Extraction and utilization of these essential elements from coal can produce a number of benefits, which will make this source an economically and environmentally attractive option especially for China, the US, Russia, India and other countries that will remain the main users of coal for the foreseeable future (Dai & Finkelman, 2018). Critical metals correlate with coal ash-forming impurity minerals such as clay minerals (eg. kaolinite and illite) (Wang, et al., 2019; Qin, et al., 2015; He, et al., 2020).

Therefore, research on reducing ash content can be carried out through a coal washing process using the Dense Medium Separation method. Based on the explanation above, it is necessary to conduct research on Paluda Coal including coal characterization, coal beneficiation, and analysis of coal beneficiation products.

## 1.2 Problem Statements

There are several problems that underlie this study plan such as the high ash content of Paluda Coal so that it cannot be utilized properly, limited utilization of coal ash as a mixed material for building and road materials or planting media, and the gravity separation is possible to separate clean coal and impurities.

## 1.3 Objectives of Research

Based on the previous explanation, the objectives to be achieved from this study plan are as follows:

1. To analyse the quality of Paluda Coal;
2. To analyse the mineralogical and chemical composition of Paluda Coal;
3. To analyse the washability characteristics of Paluda Coal using the Sink-Float test;
4. To analyse the mineral and chemical distribution at different density fraction;
5. To analyse the enrichment of critical metal in different density fraction.

## 1.4 Benefits of Research

The expected benefits of this research are:

1. Benefits to industry: this research is useful as a reference in making innovations to find alternative sources of other critical metals.
2. Benefits to academics: this research can be used as a basis for developing coal utilization methods as well as other critical metal enrichment methods.

## 1.5 Previous Studies

1. Widodo et al. (2017) conducted a proximate analysis to determine the coal quality of Paludda, Barru Regency. The results of the analysis show that the moisture content ranges from 1.59 to 1.99%, the ash content is 13.89 to 36.63%, the volatile matter content is 24.54 to 35.74%, and the total sulfur content is 4.52 to 5.37%.
2. Malaidji, et al., (2018) conducted a proximate analysis to determine the coal quality in Patappa Village, Barru Regency. The analysis results showed an

average water content of 7.98%, ash content of 16.95%, volatile matter content of 45.63%, total sulfur content of 0.56%, and calorific value of 4460.89 cal/gr.

3. Wei, et al., (2018) investigated the washability of coal and the distribution of trace elements in high-sulfur coal, SW Guizhou, China. The washability of the coal obtained is difficult to separate from impurities in the form of sulfur. The clean coal obtained is 75.50%, ash yield is 11.33% and sulfur is 2.5%. The trace elements contained almost all have inorganic affiliations except for Sn, Co, Re, U, Mo, V, Cr, Ni, and Be.

4. Adinugraha, et al., (2018) conducted a study on washability of Kendilo Coal to improve its quality. The results obtained for the Bindu Block coal are in the fraction size of -12.5+5.6 mm with a density of 1.36 g/cc and 50% clean coal. As for the Betitit Block, net coal recovery is found in the same fraction size of 50.82% and density of 1.39 g/cc.

5. Dai, et al., (2021) has conducted a research on the occurrence of 73 elements and rare gases that occur in coal an coal ashes. Elements occurrence modes in coal and coal ash are key aspects for developing the method and technology for recovering critical metals from coal or coal ash. Inorganic, organic, and intimate organic linkages are the three types of associations found in coal. Various modalities of occurrence for each element in different coals are dependent on the geological conditions of coal formation and do not always indicate inconsistency in the reported results.

# CHAPTER II

# LITERATURE REVIEW

## 2.1    Coal Beneficiation Method

Coal beneficiation or coal preparation refers to the process by which inorganic impurities are separated from the mined raw coal, thereby providing better combustion characteristics for the resulting fuel. The separation process used is primarily based on exploiting the physical differences between organic (ie, coal) and inorganic (ie, ash) components. Given the low unit value of coal, this separation process must be efficient and cost-effective. The most commonly used processes are jig washing, density separation, sizing, and froth flotation (Groppo, 2017).

Coal beneficiation is the most effective method for removing minerals (such as clay and pyrite) before coal combustion. In general, the beneficiation process for low-rank coal is more difficult to achieve than bituminous and/or anthracite coal. However, almost 50% of the worlds total coal deposits are low-rank coal. It is urgently needed to develop an effective beneficiation technology for low-rank coal (Xia, et al., 2015).

In the last decade, technological improvements have been developed. The development of drying and dewatering for low-rank coal is summarized by Rao, et al., (2015). It is well known that beneficiation is also a very important aspect in the process of improving the quality of low-rank coal. Therefore, it is necessary to summarize the latest developments in beneficiation technology for low-rank coal.

To highlight the recent advances in beneficiation technology for low-rank coal, it is necessary to classify the beneficiation technology. The classification of beneficiation technology for low-rank coal is shown in Fig. 2.1. The beneficiation technology includes physics, chemistry, physico-chemistry, and bio-beneficiation technology. The physical methods are gravitational separation and magnetic separation. The chemical method is chemical washing with acid or alkali while the Physico-chemical method is oil flotation and agglomeration. Finally, the bio-benefit technology is achieved by certain bacteria. Sometimes a combination of two or

three beneficiation technologies is required to achieve an effective beneficiation process for low-rank coal (Xia et al, 2015).
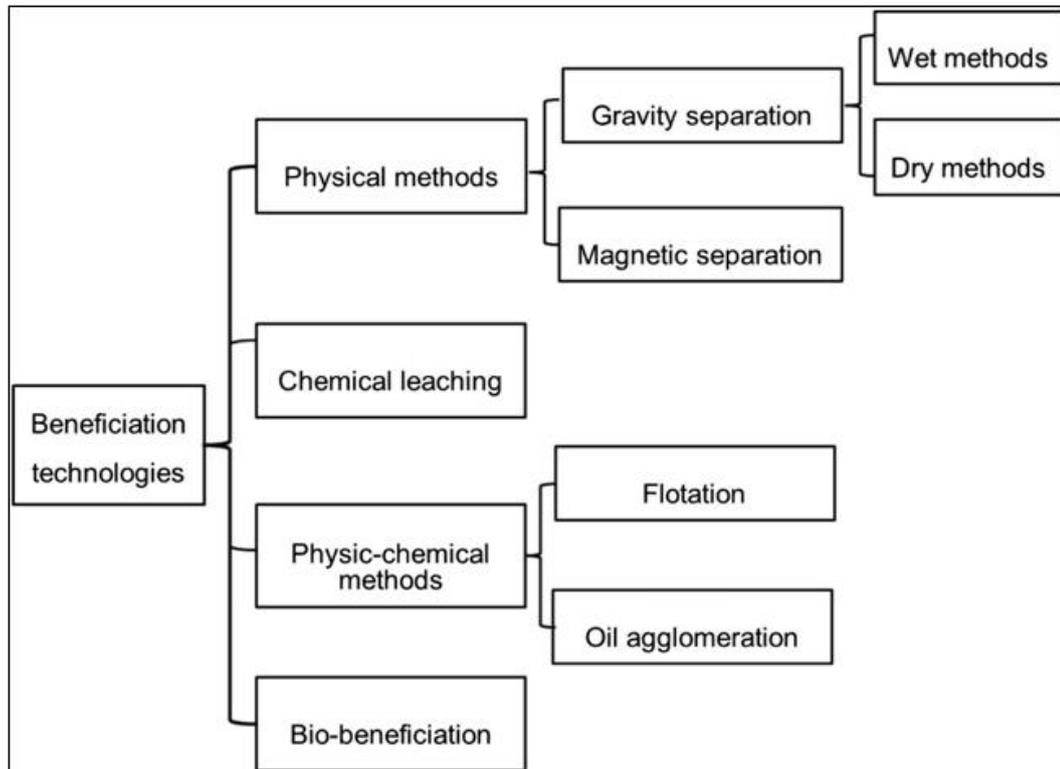


**Figure 2.1** Classification for beneficiation method of low-rank coal (Xia et al, 2015).

## 2.2    Gravity Concentration

When allowed to settle in a fluid media, gravity concentration is a method of separating mineral particles depending on their specific gravity. The velocity of a particle in a fluid is affected by its size as well as its specific gravity; the larger the particle, the more influential it is relative to smaller particles. The effectiveness of gravity concentration performance is controlled by particle size, with smaller particles resulting in less efficient performance than bigger particle sizes. This is due to the fact that surface friction dominates the mobility of smaller particles. The goal of feed size management is to ensure that particles flow in accordance with their specific gravity (Rao, 2016). Coal washing based on the specific gravity method consists of 3, namely Heavy/Dense Medium Separation, Jigging, dan Tabling.

2.2.1 Heavy/Dense Medium Separation

Heavy medium separation or dense medium separation is the process of separating coal using heavy media. This process aims to separate the valuable minerals which are heavier from the impurities consisting of light minerals by using a separating medium with a density greater than that of water. The products of this concentration process are sink and float deposits. Sand, shale, barite, magnetite, ferrosilicon, galena, and some types of clay are the types of solids used in heavy media.

2.2.2 Jigging

The jig (Fig 2.2) is a coal separation instrument that operates mechanically by leveraging differences in the penetrating ability of the grains to be separated. The particles are only allowed to settle for a short time in jigging and never reach their terminal velocity. This indicates that the separation will be determined by the particle's initial deposition rate. During the acceleration period, the particles settle, and the initial depositional velocity is very low, thus there is no frictional influence on the drag force.
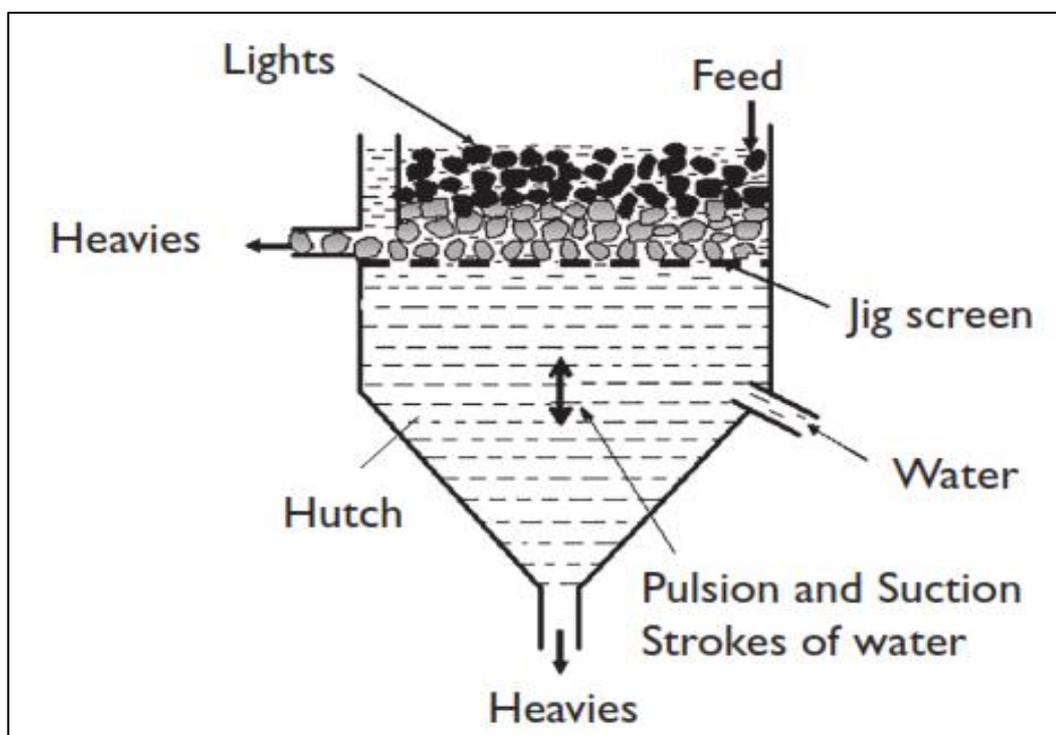


**Figure 2.2** Basic construction of a Hydraulic jig (Rao & Gouricharan, 2016).

2.2.3 Tabling

Tabling is the process of separating materials by flowing a narrow fluid stream on a vibrating table (Fig 2.3) via a thin water flow medium (flowing film concentration). The principle of tabling is based on the weight and particle size difference versus the frictional force caused by thin water flow. Particles of the same dimension will have the same force, but if their specific gravity differs, the frictional force on heavy particles will be greater than on light particles.

The table applies a longitudinal force to the particles by slowly moving ahead and quickly moving backward. Additionally, the particles are subjected to a perpendicular force by the moving water layer. Particles travel diagonally and in a direction parallel to the vibration of the shaking table under the effect of these two forces. Particle stratification takes place inside the secure compartments behind the guns. Therefore, the coarse light particles are washed away by the flowing water film and report into the tailing launder, while the fine heavy grained particles go the furthest and report in the concentrate launder (Jyothi and Kumar, 2021).



**Figure 2.3** Willey shaking table (Jyothi and Kumar, 2021)

**2.3      Dense Medium Separation**

Dense Medium Separation (DMS), or sink-float test, is a method of separating minerals and coal using its specific gravity which produces sinks and floats. DMS is a washing process between floating and sinking material on the condition that there should be no fine material because if the material combines with the solution, it will form a high and thick suspension. This process produces two separation results, namely sink which is heavy coal, while float is light or desired coal. Sink-float experiments should not only consume a lot of manpower and resources but

also take a long time. In addition, further understanding is needed about the leaching nature of coal to evaluate, predict, and optimize the results of the separation process carried out (Zhang, et al., 2011). The stages of the sink-float test are illustrated in Figure 2.4.

Dense medium separation is one of gravity concentration method. This method using heavy liquid as the medium in which the separation process takes place. Gravity concentration used water as its medium, while dense medium separation used other liquid that has a higher density than water and between the densities of minerals to be separated. This medium can be dissolved salt in water, or suspension of fine-grained high-density particles such as fine magnetite, ferrosilicon (FeSi), or a mixture of the two, depending on the density demanded (Kelly and Spottiswood, 1982).
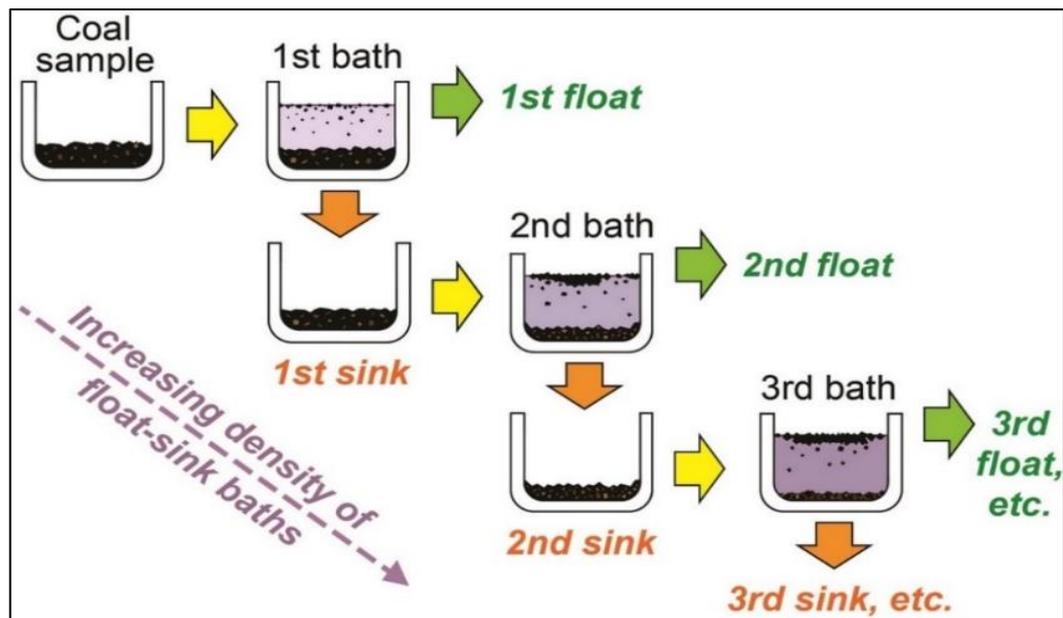


**Figure 2.4** Illustration of coal sink-float test (Survey, 2020).

Density separation takes advantage of the density difference between the organic and inorganic components found in mined coal. As is well known, coal usually consists of a collection of maceral and inorganic materials. Macerals containing mainly organic matter generally have a density of <1.4 g/cm$^3$, and as the amount of ash associated with maceral increases, the particle density also increases, because the main component of ash associated with coal is a weathering product of

quartz (density 2.65 g/cm$^3$). So particles in the density range of 1.6 – 1.8 g/cm$^3$ have higher ash content. Pyrite (FeS$_2$), another commonly associated mineral, has a much higher density of 5.0 g/cm$^3$. Given the density difference between the desired material (coal) and the unwanted material (ash and pyrite), density separation can be an efficient approach for producing coal with low ash content, provided that particles with high ash content are freed from particles with low ash content (Groppo, 2017).

Some of the heavy liquids that are commonly used in dense medium separation are listed in Table 2.1 below. If a density value that is different from the solution used is required, mixing it with a lighter or heavier solution is required. Simple laboratory equipment, such as a beaker, test tube, or separatory flask, is sufficient for the separation process. Sometimes centrifuges are also needed to accelerate the separation of the finer grains. Laboratory float and sink test is performed on coal to know the washability characteristics of coal thereby to determine the economic separating density. Suitability of heavy medium separation can also be assessed from this test (Kelly and Spottiswood, 1982).

**Table 2.1** Dense liquids (Kelly and Spottiswood, 1982)

| Compound | Formula | Specific Gravity (g/cm$^3$) |
|---|---|---|
| Clerici Solution | $(TlCOHOH)_2C/TlCOOH$ | 5.00 |
| Methylene iodide | $CH_2I_2$ | 3.31 |
| Acetylene tetrabromide | $CHBr_2$-$CHBr_2$ | 2.95 |
| Bromoform | $CHBr_3$ | 2.89 |
| Tribromo-fluor-methane | $CBr_3F$ | 2.75 |
| Methylene bromide | $CH_2Br_2$ | 2.48 |
| Methylene chlorobromide | $CH_2BrCl$ | 1.92 |
| Pentachloroetylene | $CCl_3$-$CHCl_2$ | 1.67 |
| Perchloroetylene | $CCl_2$-$CCl_2$ | 1.61 |
| Carbon tetrachloride | $CCl_4$ | 1.59 |
| Trichloroetylene | $CCl_2$-$CHCl$ | 1.46 |
| Methyl chloroform | $CCl_3$-$CH_3$ | 1.33 |
| Ethylene dichloride | $CH_2Cl$-$CH_2Cl$ | 1.25 |

Organic solutions are commonly used in the application of heavy solutions. The use of organic solutions as a separating medium to replace inorganic solutions in the float-sink test is due to the fact that organic solutions are volatile, drying the

sample is simple, and the process is quick. It's simple to distinguish between floating and sinking coal washing outcomes. The organic solution has a low viscosity (Singh, et al., 2015).

## 2.4    Impurities in Coal

The term mineral refers to the inorganic constituents of coal and does not correspond to all the organic elements of coal (carbon, hydrogen, nitrogen, oxygen, and sulfur). Minerals are the main source of the elements that form ash when coal is burned in air or oxygen.

Minerals in general make up a significant proportion of the composition of coal, and the amount of minerals in coal varies from seam to seam, even along the same seam. Coals containing up to 32% by weight of mineral have been identified, and although the fair value of the average mineral content is much lower, care should be taken in using the average. Averages are often unrelated to reality, where the range can vary from significantly below average to significantly above average. Coal efficiency on a moderate basis is acceptable, but the use of coal with a high mineral content can cause significant problems in a power plant. As a general rule, minerals in coal (regardless of their content) are considered undesirable and harmful to coal utilization, and the presence of minerals affects almost every aspect from mining, preparation, transportation, and utilization.

The preparation of coal is aimed at reducing the amount of mineral matter, and the effectiveness of using the selected methods depends on its concentration and composition. However, no matter how effective the coal preparation technique is, there is always a substantial amount of mineral content present. This residual material is of considerable importance in coal use.

Minerals in coal are the geochemical indicators of coal. Minerals and other inorganic materials in coal are important factors for evaluating the quality of coal in mining, preparation, storage, coking, gasification, liquefaction, and other applications. Environmental problems caused by minerals are increasingly concerned. Certain mineral-rich coals are notable sources of metals and non-metals. During the combustion of coal in the burner, the mineral material undergoes

significant changes leading to problems with clinker formation, fly ash, slag, and corrosion of the boiler tubes. The efficiency of a combustion unit is related to the amount of ash produced, as it is a diluent. On the positive side, ash has been used as a building material and can be a source of refractory materials, cement additives, or adsorbents for gas cleaning processes. However, the composition of the ash must be known before it can be used in this way.

One of the major obstacles to coal mineralization studies is the difficulty in obtaining statistically valid (representative) samples of mineral phases that do not contain organic matter. At first glance, it may seem that separating minerals from coal using density separation would be very simple. Coal, the organic fraction, has a low density (between 1.2 and 1.4), while the minerals present in coal have a density of 2 to 5 and more. However, the finely dispersed nature of the minerals in coal prevents their complete separation. Incomplete separation based on specific gravity, which is the basis of many carbon cleaning or washing processes, is effective in separating samples into relatively mineral-rich fractions and other relatively pure carbon-containing fractions. Specific gravity can be used to determine the occurrence patterns of chemical elements and minerals in coal, which makes the procedure important, but it is not capable of providing a representative sample of mineral in coal (Speight, 2005).

2.4.1   Types of Mineral Formation in Coal

Minerals in coal are often classified as inherent or all-purpose minerals. The mineral is inherently inorganic which is too tightly bound to the coal-containing substance to be easily separated from it by existing methods. The adventitious mineral is an inorganic substance that is less closely bound to coal and can be dissociated. It has also been suggested that the minerals transported and deposited in the peat bogs by wind and water are called allogeneic or detrital and that the remaining minerals are all formed in situ (authigenic) are broken down into minerals that form at the same time with the formation of coal (syngenetic) and those whose formation follows an early stage of coalification (epigenetics) (Speight, 2005).

Detrital minerals are substances that are transported to a swamp or marsh by air or water. A wide variety of minerals can be found in coal, they are generally primarily quartz, carbonate, iron, and clay minerals with a range of minor minerals that may be unique to the local source rock.

The minerals in the water are transported through the coal basin along the channels through the organic debris that accumulates there. When such channels are flooded, debris settles on organic matter, such events are often preserved as mineral-rich parting in coal. The mineral-rich materials present in the floor of peat basin can be incorporated into the organic layer by various compaction within the marsh and by biological disturbance action. Windborne minerals is important, as it can contribute significantly to the mineral content of coal due to its low accumulation rate in peat basin. Coal marsh areas near active volcanic regions can receive large amounts of mineral matter. Coal-related lithologies such as igneous clays and asbestos are indicative of volcanic mineral deposition and, if short-lived but widespread volcanic events, are extremely useful as horizons mark stratigraphy in the coal sequences.

Authigenic minerals are those that are introduced into peat during or after deposition, or into coal during coalification. Precipitated minerals can be disseminated through peat or present as agglomerates, while mineral-rich liquids in the later stages of coalification tend to precipitate minerals at cracks and gaps in coal. Common products of mineralization are calcium and ferric minerals such as calcite, ankerite, siderite, and pyrite, with silica in the form of quartz. Elemental sulfur is present in most coals, it is usually in the organic part of the coal, but inorganic or mineral sulfur is in the pyrite form. Pyrite can occur as a primary detrital mineral or as secondary pyrite by desulfurization from seawater, so it is now considered that there is a strong correlation between high sulfur coal and The environment deposited in the sea.

2.4.2   Common Minerals in Coal

Although lists of minerals in coal may contain a huge number of minerals, the majority of them fit into one of five groups: (1) aluminosilicate minerals (clay minerals), (2) sulfide and sulfate minerals, (3) carbonate minerals, (4) silicate

minerals (principally quartz), and (5) other minerals, which may occur in trace amounts or be unique to single coal due to localized deposition and maturation circumstances.

   a. Clay Minerals (Aluminosilicates)

   The most prevalent inorganic elements of coal and the strata associated with coal seams are clay minerals. Many distinct clay minerals have been found within and associated with coals, but kaolinite and mixed-layer illite–montmorillonite are the most prevalent. In most coal basins around the world, kaolinite-rich clay is found within and associated with coal. Tonstein or kaolin-tonstein are the common names for these minerals.

   b. Sulfide Minerals

   The major sulfide minerals in coal are the dimorphs pyrite ($FeS_2$) and marcasite ($FeS_2$), with pyrite being the more abundant. The crystal morphologies of pyrite and marcasite are distinct; pyrite is isometric, while marcasite is orthorhombic. These two minerals are easily visible and, to some extent, easily removed, as well as being especially fascinating since they contribute significantly to the total sulfur content of coal, which causes boiler tube fouling, corrosion, and pollution through sulfur dioxide emissions.

   c. Sulfate Minerals

   In fresh, un-oxidized coal samples, the sulfate minerals found do not usually make up a significant fraction of the mineral composition. After the coal is mined, the iron disulfides oxidize quickly, and a variety of hydrated sulfates ($FeSO_4xH_2O$) have been found in weathered coals and coal waste piles. Fresh coal contains the sulfates gypsum ($CaSO_4 \cdot 2H_2O$) and barite ($Ba_2SO_4$). The majority of sulfates formed during pyrite weathering (oxidation) are various hydrated forms of ferrous and ferric sulfate.

   d. Carbonate Minerals

   Calcium, magnesium, and iron are the most common cations found in carbonate minerals in coals. In some coals, the relatively pure end

component calcite ($CaCO_3$) dominates, while siderite ($FeCO_3$) dominates in others. Some coals are rich in calcite and ankerite (a mixed crystal comprised of Ca, Mg, and Fe carbonates).

e. Silicate Minerals

Quartz is the most common form of silica found in coals, and it is abundantly present. There is a distinction to be made between clastic quartz grains carried by the wind or water and authigenic quartz deposited by solutions. Quartz is also a significant component of detrital clay and siltstone partings in coal.

f. Other Minerals

In addition to the minerals above mentioned, coal has been claimed to include a significant number of other minerals. Not all of them have been positively identified, and it's sometimes impossible to tell from the accounts whether the mineral was closely linked with the coal or if it was found in the rock units that make up the roof, floor, or a seam parting. The majority of these additional minerals are of minor importance in coal usage, but a few stand out. Apatite [calcium fluorochlorohydroxyphosphate, $Ca_5(PO_4)_3FClOH$] has been discovered in coal mining in a variety of locations across the world (Speight, 2005).

2.4.3 Mode of Occurrence

According to Finkelman, et al. (2018), total of 42 elements have been analyzed from 20 types of coal samples spread from several countries to determine the mode of presence of these elements in coal. Table 2.2 shows the presence of elements in low-rank coal.

**Table 2.2** Modes of occurrence of elements in low-rank coal (Finkelman, et al., 2018).

| Elements | Modes of Occurence |
|---|---|
| Aluminium | **65% silicate**, 35% organic association |
| Antimony | 50% silicate, 20% sulfide, 10% monosulfide, 20% organic association, other |
| Arsenic | **40% pyrite**, 30% organic, 15% silicate, 15% monosulfide, carbonates |
| Barium | 75% carbonate, 10% silicate, *15% organic association, sulfate, phosphate* |

| Elements | Modes of Occurence |
|---|---|
| Beryllium | **30% silicate**, *60% organic, oxyhydroxide, or clay* |
| Bromine | 80% organic, 10% silicate, 10% unknown |
| Calcium | *60% carbonate, 35% organic association, 5% silicate* |
| Cadmium | 80% monosulfides (sphalerite), 10% pyrite, 10% silicate |
| Cesium | **80% silicate**, *20% organic association* |
| Chromium | *75% silicate, 10% sulfide, 10% organic, 5% oxide* |
| Cobalt | *30% organic, 25% monosulfide, 25% clays, 15% pyrite* |
| Copper | 30% pyrite, 30% chalcopyrite, 20% clays, 20% organic association |
| Hafnium | 70% zircon, 25% clay, 5% other phase |
| Iron | 60% carbonate & other, 20% sulfide, 15% silicate, 5% organic association |
| Lead | 50% monosulfides (galena), 10% pyrite, 25% silicates, 15% other phase |
| Lithium | **70% silicate,** 30% organic association; insoluble phase |
| Magnesium | 60% organic association, 30% calcite, 10% silicate |
| Manganese | 75% calcite, 10% silicate, 5% siderite, 10% organic association |
| Mercury | **75% sulfide (primarily pyrite),** *25% organic association and other phase* |
| Molybdenum | 65% silicate, 15% sulfide, *20% organic association, etc* |
| Nickel | *30% organic association, 30% monosulfides, sulfates, carbonates,* 20% clays, 20% sulfides |
| Phosporus | **85% phosphates**, *15% organic association* |
| Potassium | **75% silicates,** *50% organic association, salts* |
| Light Rare Elements | 60% clays, 20% phosphates, 20% carbonates, organic association |
| Heavy Rare Elements | 50% clays, *25% phosphates, 25% organic association, carbonates* |
| Rubidium | **85% silicate,** *15% other phase* |
| Scandium | 95% silicate, 5% organic association |
| Selenium | *75% organic, 20% sulphides and selenides, 5% silicates* |
| Sodium | *65% organic association, 35% clay, salts, pore water* |
| Strontium | 50% organic association, 50% phosphates, carbonates |
| Tantalum | 60% oxides, 40% silicates |
| Titanium | 70% clays, 15% Ti-oxides, 15% organic association |
| Tungsten | 60% silicate, 20% sulfide, 20% organic association, other phase |
| Uranium | 55% organic association, 35% silicates, 5% phosphates, 5% insoluble phase such as zircon |
| Vanadium | 50% silicates, 50% organic association, other phase |
| Zinc | 55% sphalerite, 15% pyrite, 15% silicates, 15% organic association |
| Zirconium | 70% zircon, 25% clay, 5% other, organic association |

**Bold= High degree of confidence;** non-bold= moderate degree of confidence, *italics= low degree of confidence.* The numbers indate the estimation of the proportion of that element occurring in that phase

## 2.5    Critical Metals in Coal

Critical metals are raw materials whose demand increases in line with technological advances, but still have little reserves or there is no suitable technology to extract these metals economically. Technologically, critical metals are critical to many cutting-edge technologies, but their supply is potentially unstable. This condition requires strategic planning based on long-term demand and supply expectations of these metals and their implications. Commodity prices have risen sharply in recent years. Many metals that play a central role in high-tech products are rare. Scarcity is not only defined by geologically, but also in a socioeconomic context. Recent studies point to emerging limitations for technical innovation (Schmidt, 2012; Graedel, et al., 2014; Watari, et al., 2020).

Primary ores of critical metals still play a major role as the main source of each metal. However, technological developments have also made it possible to extract critical metals as by-products from primary ores or from recycling products. The dramatic increase in the prices of strategic minerals and rare earth elements is due to a lack of global supply and increasing demand. Critical metals is an integral component of advanced technology, such as cell phones, wind turbines, permanent magnets and semiconductors. The scarcity of these valuable elements has prompted many companies to seek new mineral sources (Mayfield & Lewis, 2013).

2.5.1 Classification of Critical Metals

The limited of metal resources that are not proportional to the amount of demand causes these metals to be categorized as critical metals. Primary sources of some metals are few so they are still obtained as a by-product of other metal's mining operation. In some situations, certain metals which are normally mined as by-products can also be mined by themselves if the concentration and availability allows. For example, cobalt is generally a by-product of copper mining, however, it can be mined on its own. Similarly, PGM is generally a by-product of nickel

mining but most of its production comes from PGM's specialty mines in South Africa.

The United States is the first in an experiment to classify metals that belong into the critical category. The US National Research Council proposes that criticality depends on two parameters, one parameter is supply risk and the other is the impact on supply disruption. A total of 23 types of minerals or commodity groups are classified in the group, including antimony, barite, beryllium, cobalt, fluorite, gallium, germanium, graphite, hafnium, indium, lithium, manganese, niobium, platinum group elements (PGE), rare earth elements (REE), rhenium, selenium, tantalum, tellurium, tin, titanium, vanadium, and zirconium have been listed as critical and (or) strategy in one or more recent studies based on the assessed risk to supply and (or) potential impact to supply offering (Schulz, et al., 2017).
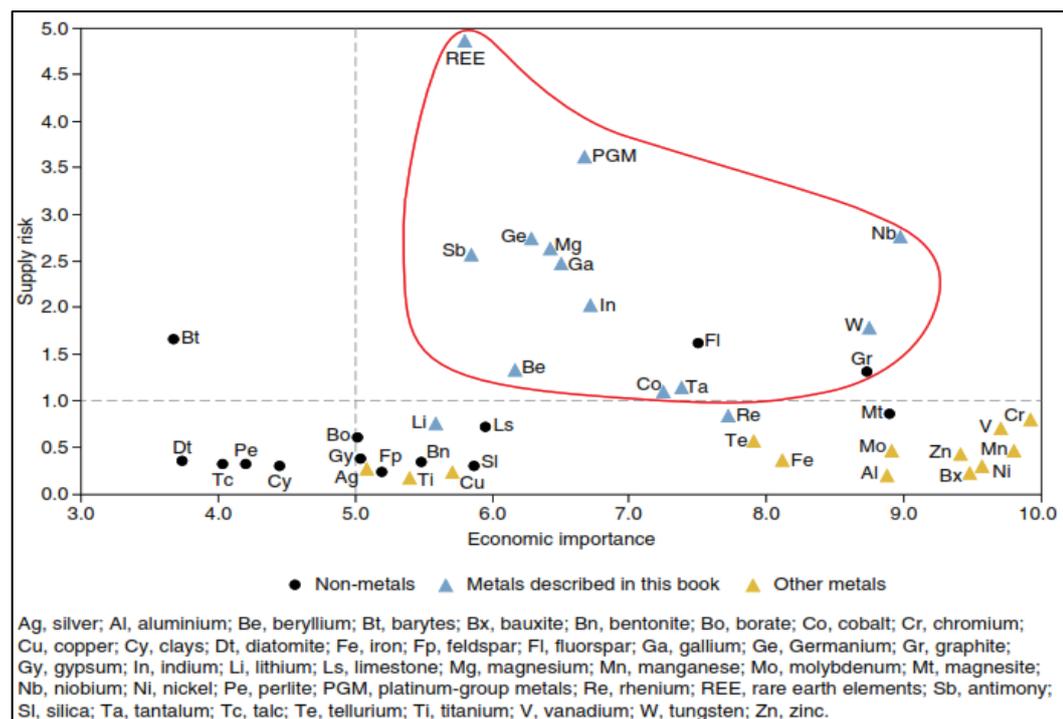


**Figure 2.5** Critical metal grouping based on the results of an assessment by the European Commission (EC) (Graedel, et al, 2014).

In 2009, the European Commission (EC) released the results of an assessment of the level of metal rarity. The EC performs this assessment based on the level of risk from the offer and the potential economic impact it will have on the local

industry. A total of forty-one metals and minerals were assessed and several of them were declared in critical status. Among them are antimony, beryllium, cobalt, gallium, germanium, indium, magnesium, niobium, tantalum, and tungsten as well as two groups of metals, namely rare earth elements (REE) and platinum group elements (PGE). The results of the assessment are illustrated in Figure 2.5 (Graedel, et al, 2014).

2.5.2 Critical Metal in Coal

    a.  Gallium

        Gallium is a soft, silvery metallic element with the chemical symbol Ga and an atomic number of 31. Gallium is used in a wide range of devices that include either gallium arsenide (GaAs) or gallium nitride (GaN) as microelectronic components. Gallium arsenide is applied in the fabrication of optoelectronic devices (laser diodes, light-emitting diodes [LEDs], photodetectors, and solar cells), which are crucial for aerospace and telecommunications applications as well as industrial and medical equipment. Gallium arsenide is also utilized to make highly specialized integrated circuits, semiconductors, and transistors, which are required for defense and high-performance computing applications. Gallium nitride is primarily utilized in the production of LEDs and laser diodes, as well as in power and radio-frequency circuits. GaN power transistors operate at greater voltages and have a higher power density than GaAs devices, so future applications for sophisticated GaN-based products are projected to grow.

        Gallium can be found in small amounts in a variety of minerals and rocks, where it is used to replace elements with similar size and charge, such as aluminum and zinc. Gallium, for example, can be found in moderate concentrations (approximately 50 parts per million) in aluminum-bearing minerals like diaspore-boehmite and gibbsite, which are found in bauxite deposits, and in the zinc-sulfide mineral sphalerite, which can be found in various mineral deposits (Foley, et al., 2017).

To assess the extraction efficiency of gallium, a comparison of open wet digestion and microwave-assisted digestion was given. Both procedures use HF to extract gallium. According to the findings of the microwave-assisted digesting approach, adding HCl, which preferentially combines with Ga, can improve gallium recovery. Furthermore, utilizing open wet digestion, 93% of gallium was extracted under ideal conditions (5 mL $HNO_3$, 3 mL HF, 3 h, and 120°C). Under ideal conditions (5 mL $HNO_3$, 1 mL HF, 5 mL HCl, 1400 W, 45 minutes, and 180°C), 97 percent of gallium was leached by microwave-assisted digestion (Huang, et al., 2020).

b.  Rare Earth Elements (REE)

The development of technology is currently advancing with the increasing need for modern equipment that uses raw materials from rare earth metals (REE) such as permanent magnets for missiles and aircraft, as well as amplification for radar and sonar detection (Joshi, 2013). Due to their unique magnetic and chemical properties, REEs play an important role in the manufacture of materials and products (from household use to defense) that provide modern standards of living. These include cell phones; computers; PDP (Plasma Display Panel) and LCD (Liquid Crystal Display); microwaves; video and photo cameras; air conditioner; electric vehicles; magnets; power plants; nuclear reactor; laser; and rockets. REEs are irreplaceable in electronics and optics, oil extraction, oil refining, automotive industry, information and nanotechnology, medicine, and environmental protection. The metal is also widely used in the manufacture of special alloys, industrial ceramics, catalysts, superconductors, high-quality glass, optical fibers, and storage batteries (Seredin & Dai, 2012).

Serendin and Dai (2012) have divided REE into three groups based on their geochemical properties, including the light rare earth elements (LREE) including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), and samarium (Sm); the medium rare earth elements (MREE) group includes europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), and yttrium (Y); the third group is the heavy rare earth elements (HREE)

group which includes holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu).

REEs are generally obtained as a by-product of metallurgical processing of carbonatite, uranium, bauxite, and placer deposits (Castor and Hedrick, 2006; Wang et al., 2011). Until 2009, China was the largest producer of rare earth metals supplying about 95% of the world's demand for REE, but its production rate decreased by 19% in 2010, making some elements in the REE class declared as critical raw materials (Zhang, et al., 2015).

There have been many studies discussing REE resources from electronic wastes, such as fluorescent lamps, monitors, etc. (Michelis, et al., 2011; Jakobsson, et al., 2016). Another alternative source of REE is coal and coal ash. With so many studies that have covered the emergence and abundance of REE in coal and coal ash from various regions of the world, it can be said that coal has the potential to be an alternative source of REE and can be compared with conventional ores (Serendin and Dai, 2012).

The beneficiation of coal fly ash (CFA) as a source of REE shows several advantages compared to the use of ore containing REE. First, CFA is the residue available from steam power plants, some of which are still stored in landfills. Second, CFA is a fine-sized material that makes it ideal for processing by leaching, saving the energy required for ore comminution (Lanzerstorfer, 2018).

Several coal processing methods such as gravity separation, magnetic separation, and flotation have been applied to increase The REE content in coal ash before being extracted using existing methods. The result of this beneficiation is very significant to increase the recovery rate when the extraction is carried out (Zhang, et al., 2020).

c. Vanadium

Vanadium (V) is a strategic metal that is primarily utilized in the manufacture of metal alloys, such as high-strength steel and aerospace alloys. Catalysts for the chemical industry, as well as ceramics, glassware, and pigments, are secondary uses. Vanadium is a hard, silvery gray, ductile,

and malleable transition metal in its natural condition. Steel production trends have a big influence on vanadium use.

Vanadium is plentiful in mafic igneous rocks (about 250 ppm), less abundant in ultramafic and intermediate composition rocks (about 50 ppm), and only little in felsic rocks (about 50 ppm) (about 20 ppm). Vanadium is abundant in titaniferous magmatic magnetite deposits; vanadium values in these deposits typically vary from 1,000 to 5,000 ppm. Organic-rich sediments are also linked to vanadium. Vanadium concentrations in shale range from 130 to 205 parts per million, but some carbonaceous shales can have as much as 5,000 parts per million. Reduction, adsorption, and complexation all contribute to the presence of vanadium in organic carbon-rich sedimenter (Kelley, et al., 2017).

The influence of the influential factors of direct acid leaching on the vanadium leaching ratio was investigated using orthogonal experiments and single factor experiments. Under the best process parameters of $CaF_2$ dosage 5 mass percent, $H_2SO_4$ dosage 40 mass percent, leaching temperature 95 °C, and leaching time 10h, the vanadium leaching ratio attained a maximum value of 89.22 percent. The reaction mechanisms of the major impacting factors were also investigated. Finally, a two-stage counter-current leaching technique was used to reduce sulfuric acid and neutralizer consumption, with the results showing that sulfuric acid consumption was reduced by 12.50 percent and neutralizer consumption was reduced by 35.80 percent (Zhang, et al., 2017).

d. Zirconium

The majority of zirconium is used in the form of zircon ($ZrSiO_4$), zirconium oxide, or other zirconium compounds. With a melting point of 2,550 degrees Celsius (°C) or above, zircon is a highly refractive material. Zircon is used for facings on foundry molds, and milled or powdered zircon is utilized to coat the surfaces of molds in refractory paints. For confining molten metals, zircon bricks and blocks are employed in furnaces and hearths, whereas glass tank furnaces use fused-cast and bonded alumina-zirconia-silica-based

refractory metal. Zircon is also used as a gemstone in small quantities, and it can be processed to make cubic zirconia, a synthetic gemstone and diamond simulant.

Zircon is the most abundant ore material ($ZrSiO_4$). Baddeleyite ($ZrO_2$) is a zirconium-rich mineral that is less frequent yet commercially valuable. In igneous rocks, zircon and baddeleyite occur as accessory minerals and are normally found in moderate abundances. They can also be found in a variety of rock types and geologic settings. The world's most important ore deposits are heavy-mineral sands formed by the weathering and erosion of preexisting rocks, as well as the concentration of zircon in sedimentary systems, particularly in coastal environments (Jones, et al., 2017).