

ADVANCEMENT OF THE HYDROPHOBIC-HYDROPHILIC SEPARATION PROCESS

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ACADEMIC ABSTRACT

Froth flotation has long been regarded as the best available technology for ultrafine particles separation. However, froth flotation has extreme deficiencies for recovering ultrafine particles that are less than 30-50 μm in size for coal and 10-20 μm for minerals. Furthermore, dewatering of flotation products is difficult and costly using currently available technologies. Due to these problems, coal and mineral fines are either lost to tailings streams inadvertently or discarded purposely prior to flotation. In light of this, researchers at Virginia Tech have developed a process called hydrophobic-hydrophilic separation (HHS), which is based originally on a concept known as dewatering by displacement (DbD). The process uses non-polar solvents (usually short-chain alkanes) to selectively displace water from particle surfaces and to agglomerate fine coal particles. The resulting agglomerates are subsequently broken (or destabilized) mechanically in the next stage of the process, whereby hydrophobic particles are dispersed in the oil phase and water droplets entrapped within the agglomerates coalesce and exit by gravity along with the hydrophilic particles dispersed in them. In the present work, further laboratory-scale tests have been conducted on various coal samples with the objective of commercial deployment of the HHS process. Test work has also been conducted to explore the possibility of using this process for the recovery of ultrafine minerals such as copper and rare earth minerals. Ultrafine streams produced less than 10% ash and moisture consistently, while coarse coal feed had no observable degradation to the HHS process. Middling coal samples were upgraded to high-value coal products when micronized by grinding. All coal samples performed better with the HHS process than with flotation in terms of separation efficiency. High-grade rare earth mineral concentrates were produced with the HHS process ranging from 600-2100 ppm of total rare earth elements, depending on the method and reagent. Additionally, the HHS process produced copper concentrates assaying greater than 30% Cu for both artificial and real feed samples, as well as, between 10-20% Cu for waste samples, which all performed better than flotation.

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GENERAL AUDIENCE ABSTRACT

Froth flotation has long been regarded as the best available technology for separating fine particles. Due to limitations in particle size with froth flotation, and high downstream dewatering costs, a new process has been developed called the hydrophobic-hydrophilic separation (HHS) process. This process was originally based on a concept known as dewatering by displacement (DbD) which was developed by researchers at Virginia Tech in 1995. The process uses hydrocarbon oils, like pentane or heptane, to selectively collect hydrophobic particles, such as coal, for which it was originally developed. In coal preparation plants, a common practice is to purposefully discard the ultrafine stream that flotation cannot recover and has an increased dewatering cost. The HHS process can effectively recovery this waste stream and produce high-grade salable product, with significantly reduced cost of dewatering. In the work presented, laboratory-scale tests have been conducted on various coal samples with the objective of commercial deployment of the HHS process. In this respect, several varying plant streams have been tested apart from the traditional discard stream. Additionally, test work has expanded into mineral commodities such as copper and rare earth minerals. In this work, salable high-value coal products were achievable with the HHS process. Ultrafine streams consistently produced less than 10% ash and moisture. Coarse coal feeds had no observable degradation to the HHS process and were able to produce single digit ash and moisture values. Middling coal samples were upgraded to high-value coal products when micronized by grinding. All coal samples performed better with the HHS process than with flotation in terms of separation efficiency. High-grade rare earth mineral concentrates were produced with the HHS process ranging from 600- 2100 ppm of total rare earth elements depending on the method and reagent. Additionally, the HHS process produced copper concentrates assaying greater than 30% Cu for an artificial and feed samples, as well as, between 10-20% Cu for waste samples, which all performed better than flotation.

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CHAPTER 1. GENERAL INTRODUCTION

1.1 Preamble

Froth flotation has long been regarded as the best available technology for the separation of ultrafine mineral particles and is used in the separation of many different minerals due to its high adaptability to different mineralogy. Flotation, however, is ultimately limited to a narrow size range and ultrafine particles less than 30-50 μm are not recovered efficiently. Furthermore, the required dewatering cost of ultrafine particles is very high and requires an enormous amount of energy. Because of these inefficiencies ultrafine particles are either lost in flotation tails or removed altogether before flotation, and because these particles are well liberated based on their fine size, impoundments across the United States are filled with valuable material. Moreover, these impoundments create potential environmental issues specifically concerning acid mine drainage and damage to surrounding ecosystems. In light of these issues, a novel separation process known as Hydrophobic-Hydrophilic Separation (HHS) has been developed to simultaneously clean and dewater ultrafine particles.

Extensive studies on the HHS process have been done to classify its efficiency in regards to recovering ultrafine coal from plant tailings. The HHS process can remove unwanted impurities or gangue minerals, such as clay, from an ultrafine waste stream and remove surface moisture of the coal by using a hydrophobic liquid to displace it. As high-quality coal reserves continue to deplete, the industry continues to look for alternative solutions to increase recovery of carbon material. Furthermore, recent market shifts and the continued use of low-cost natural gas have made it crucial for the HHS process to be evaluated for varying carbon-based feedstocks and alternative carbon uses, creating new markets for coal. One such solution has come on the heels of research into rare earth elements and their association with coal and coal by-products.

Rare earth elements are increasingly important in modern day society. They are vital to many industries in various sectors of the world economy. Their use in many high-tech applications makes them a high-value target for recovery. Rare earth elements are currently used in the production of motors, disc drives, microphones and speakers including cellular devices, metallurgical alloys, fluorescent lighting, lasers, x-ray imaging, fertilizers, camera lenses,

magnets, and much more (British Geologic Survey, 2011). Currently, China dominates the production of rare earth minerals, and has essentially, a monopoly on the industry, while the United States is presently solely reliant on imports, with no domestic production due to environmental concerns shutting down one of the larger rare earth mines in the world that was located in California.

In light of the market shifts with coal, it is increasingly crucial that HHS be evaluated for efficiency in recovering minerals with similar problems to that of coal. Copper is one such mineral that usually forms in sulfide minerals such as chalcopyrite. Copper is used across several industries and is being mined at increasingly high rates. Demand for copper continues to rise, but due to decreasing ore grades, producers are looking for new ways to increase production to match demand. Sulfide copper minerals are most often treated with flotation, which means that most ultrafine copper is lost during beneficiation and reports to the tails. Furthermore, increased grinding is needed to improve liberation in low-grade ores, which causes a more substantial fraction of ultrafine copper to report to tailings. In many cases, the tailings copper grade is equal to or even higher than the feed copper grade (Calvo et al., 2016). This presents a tremendous economic opportunity for recovering this fraction of ultrafine copper from plant tails in a large copper industry.

1.2 Research Objectives

The goal of this research is to evaluate the application of the HHS process for recovery of various carbon-based feedstocks, rare earth minerals, and metallic ore (specifically copper). The following objectives were developed to fulfill this goal:

- To demonstrate the effectiveness of the HHS process for ultrafine coal recovery and decarbonization, showing the degree of upgrading that can be expected for various plant streams. This objective involves:
 - Comprehensive laboratory-scale batch tests using traditional HHS procedures, consisting of pentane-based oil-agglomeration and mechanical breaking of the formed agglomerates, from various feedstocks.

- Production of clean coal products with low moisture and low ash, less than 10%, while simultaneously producing a free rare earth feedstock.
- To demonstrate the capability of the HHS process to economically concentrate non-coal minerals, including rare earth elements (REEs) from coal and coal by-products and copper.

This objective involves:

- Laboratory-scale batch tests using a modified version of HHS simulating two liquid flotation using heptane-based oil-in-water emulsion formation, phase inversion to water-in-oil emulsion formation, and breaking of emulsions to disperse rare earth minerals and copper minerals.
- Development of a semi-continuous laboratory unit to test the process on a larger scale and over an increased period of time to provide proper scale-up criteria for the construction of a mineral recovery based HHS pilot plant.
- Production of high-grade mineral concentrates that allows for the HHS process to expand its capabilities beyond that of traditional coal recovery.

1.3 Thesis Organization

This thesis consists of seven chapters. The first chapter is a general introduction to the topic of the HHS process and its need/benefit in recovering ultrafine mineral particles. In addition, a detailed account of the objectives of this research is provided in this chapter. The second chapter is a literature review of prior work and background information intended to help the reader better understand the process and methodologies behind the research work. This chapter provides an overview of the HHS process and the mechanisms that govern its separation process, a comprehensive summary of rare earth minerals importance and their relation to coal and coal-byproducts, a review of common, rare earth mineral and copper recovery processes, and prior work completed in relation to these topics.

The third chapter focuses on the experimental results from laboratory-scale batch tests on various carbon-based feedstocks. This chapter walks through the experimental procedures and apparatus used for this test work and provide a discussion of the results obtained. In short, this chapter discusses oil-agglomeration, use of the laboratory morganizer, methods used to improve coal recovery, and separation results.

The fourth chapter focuses on the experimental results for laboratory-scale batch tests for recovering rare earth minerals from coal tailings. This chapter explains the methods used for this test work and evaluate the performance of HHS on rare earth recovery. In short, this chapter discusses emulsion formation with heptane, phase inversion study, separation results, and feasibility.

The fifth chapter focuses on the experimental results for laboratory-scale batch and semi-continuous tests for recovering copper minerals from plant tailings. This chapter discusses the results obtained from these tests and comment on the feasibility of HHS for mineral recovery. A detailed discussion of the experimental methods and apparatus is given as well as an analysis of the development of the semi-continuous unit and scale up criteria.

The sixth and seventh chapters provides a summary of the work completed in this thesis and the results obtained, as well as, recommendations for future work in this area respectively. These chapters seek to tie in chapters three, four and five, comment on HHS' performance, and relate them to items discussed in chapters one and two regarding the shortcomings of ultrafine mineral processing and the need for new technology.

CHAPTER 2. LITERATURE REVIEW

2.1 Background

Work on the Hydrophobic-Hydrophilic Separation (HHS) process has been ongoing for several years. It began as a concept of dewatering-by-displacement (DbD) in 1995 when Drs. Yoon and Luttrell at Virginia Tech patented a novel method for dewatering fine coal particles (Yoon and Luttrell, 1995). Work on DbD was fueled by the concept of the Otisca T-Process, which was patented in 1984 by Douglas V. Keller, Jr. and developed by Otisca Industries. The process involved agglomeration of micronized coal using chloro-flouro carbon. The resulting agglomerates are separated from dispersed mineral mater by gravity in a chloro-flouro carbon medium bath. The organic liquid was of low boiling point and could quickly be recovered by low-temperature heating to be used again at the head of the process (Keller, 1982).

In 1984, Keller decided to start using short chain hydrocarbon oils (i.e., pentane) instead of the chloro-flouro carbon to induce agglomeration. This switch was made due to the high cost of the recovery process and potential environmental hazards (Seaman, 1992). With this switch, the process could produce a similar final product of low ash coal from fine coal plant streams (< 1 or 2% ash) with nearly 100% recovery, however, the moisture content of the final product was very high around 40% (Keller, 1985). Because of this problem, the process would only survive a few years in practice and lost prominence around 1990. Thankfully, the initial success of the Otisca T-Process inspired research from Drs. Yoon and Luttrell at Virginia Tech, which led to advancements in oil agglomeration technology that could be used to produce low ash and low moisture coal product from fine coal waste streams. The resulting advancements produced what is known as the HHS process which simultaneously cleans and dewater fine coal.

As previously stated, DbD was disclosed in 1995 when Drs. Yoon and Luttrell patented the method for dewatering fine coal and was directly inspired by the Otisca T-Process. This novel concept provided the basis for which HHS was built on. In DbD, a hydrophobic liquid is allowed to displace surface moisture of fine coal particles, effectively producing similar moisture contents to that of thermal drying. This would come at a much lower energy cost due to the fact that only the bottom-most layer of moisture is removed in DbD, whereas in thermal drying each layer of

moisture must be stripped at high temperature. Because this process is thermodynamically spontaneous, there is virtually no energy cost other than the required energy to recover the hydrophobic liquid for recycle use (Yoon and Luttrell, 1995). Figure 2-1 shows a visual representation of the thermodynamically spontaneous DbD process in comparison to conventional thermal drying technology.

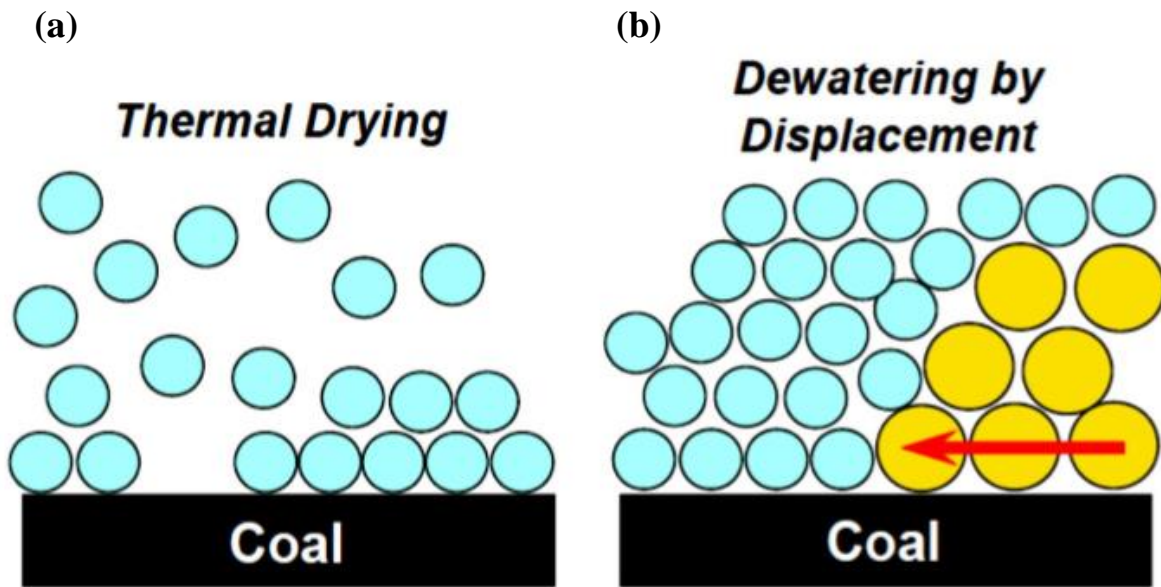


Figure 2-1: a) Thermal drying where a large amount of energy is required to heat beyond the point of evaporation in order to strip all the water molecules layer by layer. b) dewatering by displacement method where a hydrophobic liquid spontaneously displaces the bottom-most layer of surface moisture, requiring no energy (Gupta, 2014; Yoon and Luttrell, 1995)

Dewatering-by-displacement utilizes the principle of hydrophobic displacement. The DbD process can simultaneously clean and dewater naturally hydrophobic coal particles due to the higher affinity that hydrocarbons have to gravitate towards the coal surface, whereas hydrophilic mineral matter will not be collected by the hydrocarbon and remain in the aqueous phase. Figure 2-2 shows a conceptual representation of hydrophobic displacement as a thermodynamically spontaneous process. In this representation, a single hydrophobic particle must move through an aqueous phase and into a non-polar hydrophobic liquid phase. From the schematic in Figure 2-2, the particle will advance to the oil-water interface so long as the contact angle measured through

the water phase is greater than zero. For the particle to spontaneously move to a hydrophobic liquid phase the change in Gibbs free energy (G) concerning the particle surface area (A) must be less than zero. As shown in Equation 1, this change is equal to the difference between the surface free energy at the solid/oil (γ_{so}) interface and solid/water interface (γ_{sw}) (Yoon et al., 2016).

$$\frac{\Delta G}{dA} = \gamma_{so} - \gamma_{sw} < 0 \quad [1]$$

From the three-phase equilibrium shown in Figure 2-2, a relationship between the surface free energy at the oil/water interface (γ_{ow}) and the surface free energy at both the solid/oil (γ_{so}) and the solid/water (γ_{sw}) interfaces can be drawn. This relationship is shown in Equation 2.

$$\gamma_{so} - \gamma_{sw} = \gamma_{ow} \cos \theta \quad [2]$$

In Equation 2, θ is the contact angle between the solid surface and a hydrophobic liquid droplet on that solid surface measured through the water phase. Combining Equations 1 and 2, it can be seen that if the contact angle θ is greater than 90° , a hydrophobic liquid can spontaneously displace surface moisture of a hydrophobic solid surface (Yoon et al., 2016).

$$\frac{\Delta G}{dA} = \gamma_{ow} \cos \theta \quad [3]$$

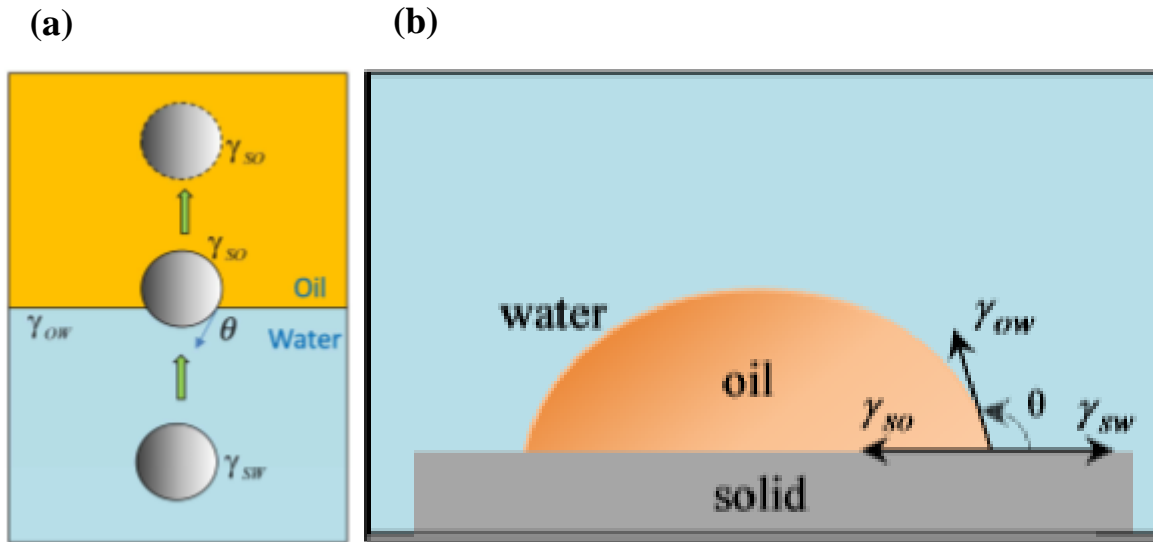


Figure 2-2: a) Representation of displacement of a hydrophobic solid from a water phase to an oil phase and b) representation of three-phase equilibrium with contact angle θ (Yoon et al., 2016).

2.2 Coal-Based Rare Earth Elements

This section covers general information about rare earth elements, their production, uses and a unique new potential source for extraction. Coal-based rare earth elements provide a significant opportunity for the United States as a source of new rare earth production, in a global race. This section serves to bring the reader up to date on current rare earth element extraction, and understand the need for HHS in this process.

2.2.1 Importance of Rare Earth Elements

Fifteen total elements in the periodic table make up what is commonly known as the rare earth elements (REEs). Those fifteen elements span from atomic number 57 to 71, excluding promethium (atomic number 61), and including Yttrium (atomic number 39) as shown in Figure 2-3. The lanthanides, as they are officially called, are usually characterized in two distinct groups, light and heavy. The light series consists of Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Europium, and Gadolinium. The heavy series consists of Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium, Lutetium, and Yttrium. The name of rare earth is typically misleading as they usually are quite abundant in the earth’s crust. Cerium, in fact, is more abundant than copper or lead (USGS Minerals Resources Program, 2014).

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt										
Lanthanides																		
La			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides																		
Ac			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Figure 2-3: REEs on the periodic table (King, 2018)

The REEs are used in a variety of products including magnets, glass, phosphors, batteries, and much more. In glass manufacturing, REEs are used for the production of camera lenses (Lanthanum), as well as coloring compounds and X-ray imaging. Rare earth magnets are very commonly used in the automotive industry for speakers, power steering/seats, and electric windows. These magnets are also used for various disk drives, MP3 players and earphones. REEs used for phosphors are applicable in many fluorescent lighting applications, as well as lasers and LCDs (British Geological Survey, 2011). Figure 2-4 shows several other significant uses of REEs, which because of their unique properties are used in numerous applications. As shown, REEs are vital to many modern technologies due to their diversity in application and as such economic and consistent recovery of REEs via traditional reserves or alternative solutions is of paramount importance to the United States. As discussed in later sections China currently dominates the production of REEs globally, and this only further escalates the need for increased U.S production via alternative REE sources as it is currently reliant on imports.



Figure 2-4: REE applications (British Geological Survey, 2011)

2.2.2 Production Statistics for Rare Earth Elements

Originally mined from granite pegmatite's, Brazil and India controlled most of the world's production of REEs up to the 1940s. In the mid-1940s Australia became a major player with the discovery of placer deposits that contained a high population of REE-bearing monazite. During the 60s, 70s, and 80s the United States dominated the global rare earth production thanks in large part to the Mountain Pass bastnasite mine, which was operated until the early 2000s before it closed due to environmental issues. The Mountain Pass mine produced around 2000 tons of REE concentrate per year following closure by using stockpiled material, up until late in 2015 when it was put on the care-and-maintenance status and ceased production. Today the market is almost solely dominated by China, and the United States is heavily reliant on imports (British Geological Survey, 2011). According to USGS China produced more than 80% of the world's REE supply in 2016 and 2017, without accounting for undocumented production which could make the production greater than 90%, in addition, they account for nearly 40% of the world's total reserves. The United States imports almost 80% of all its REEs from China (U.S. Geological Survey, 2018). In 2010, China accounted for as high as 97% of total world production. Figure 2-5 shows the production trend of REEs for the world and China between 1992 and 2010.

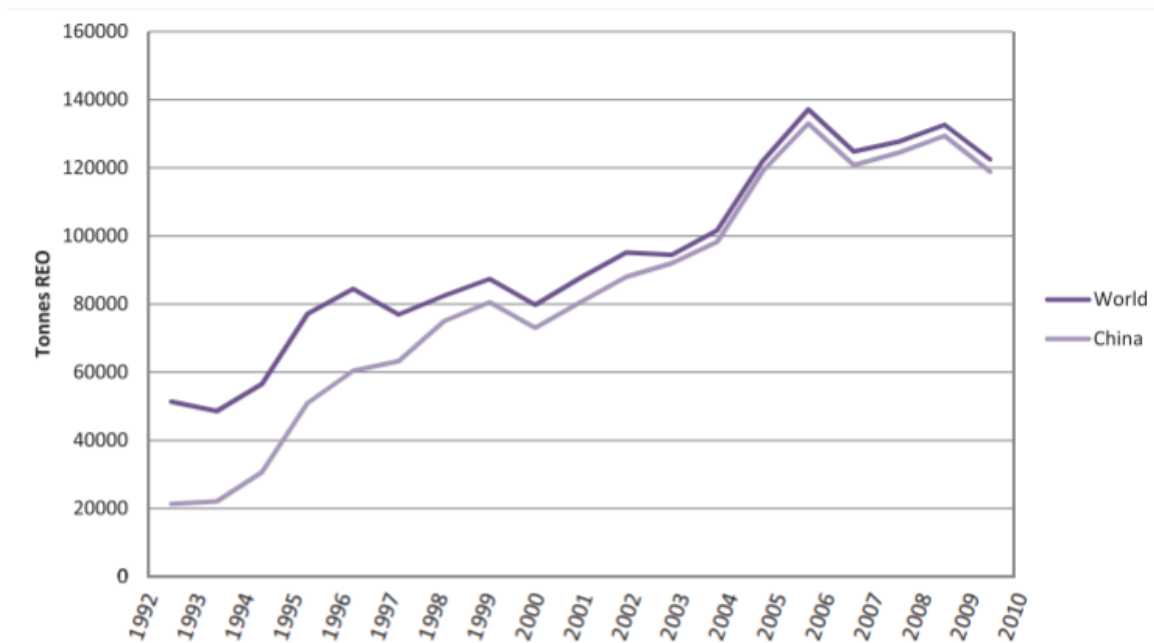


Figure 2-5: Global REE production vs. China REE production (British Geological Survey, 2011)

China currently produces the bulk of its REEs as a by-product of iron ore from Bayan Obo. The more significant issue at hand is that with the growing concern of shortage of adequate supply of REEs and increased domestic need, China has imposed strict quotas limiting their exports. China also includes 25% tariff rate on Neodymium, Yttrium, Europium, Dysprosium, Terbium, and Scandium, as well as, 15% on all others. Looking at Figures 2-6 through 2-8, which show world import/export data as well as Chinese quotas, it is easy to see that there is an increasing need to produce REE's domestically in the United States, and alternative solutions like coal-based REEs may be the solution (British Geological Survey, 2011).

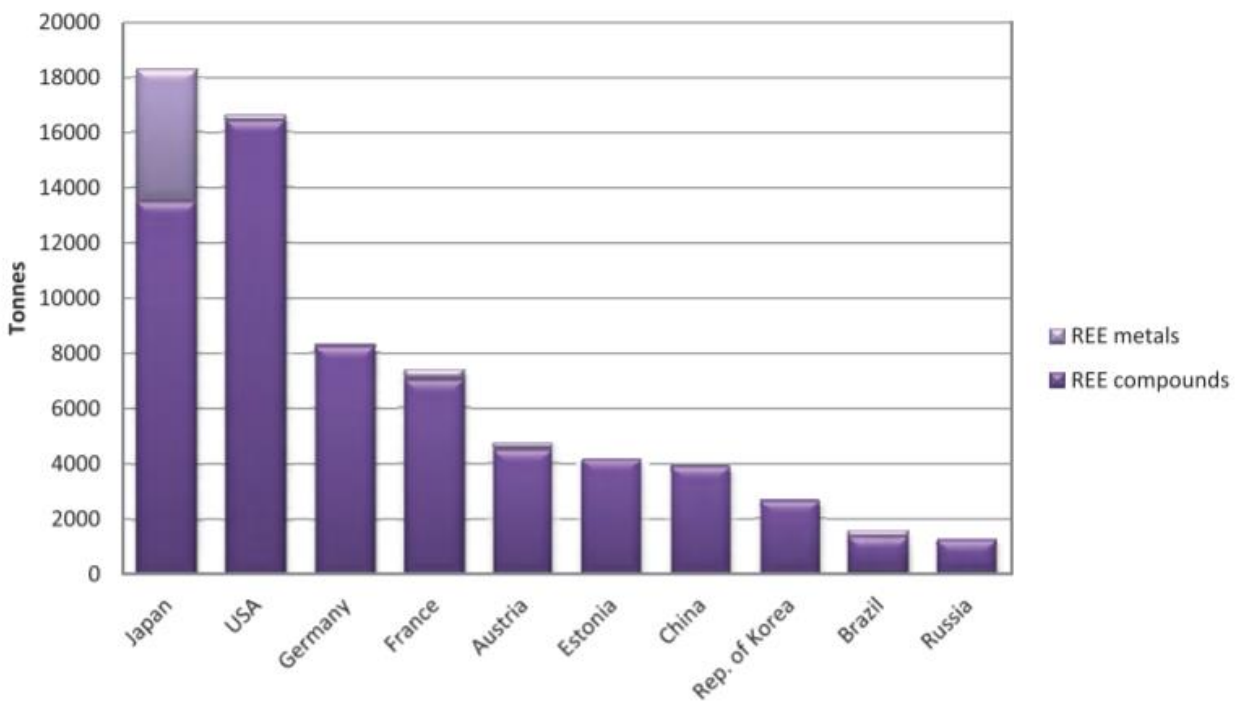


Figure 2-6: Global imports of REEs (British Geological Survey, 2011)

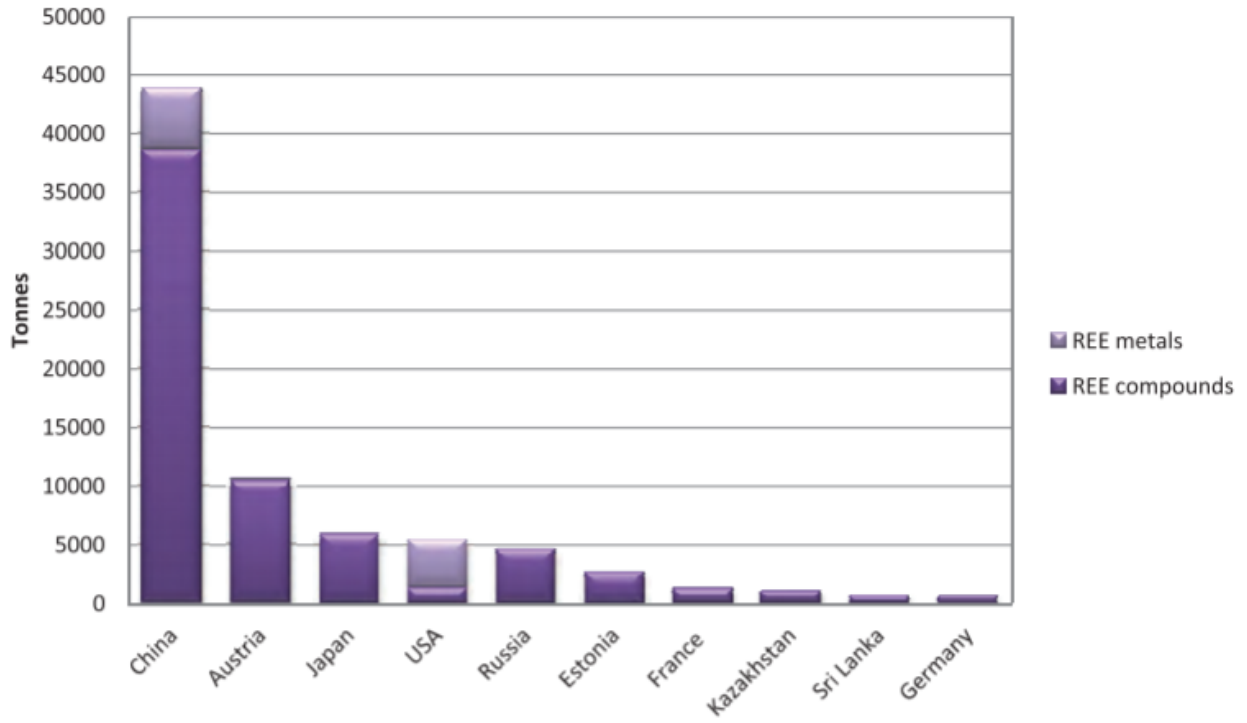


Figure 2-7: Global exports of REEs (British Geological Survey, 2011)

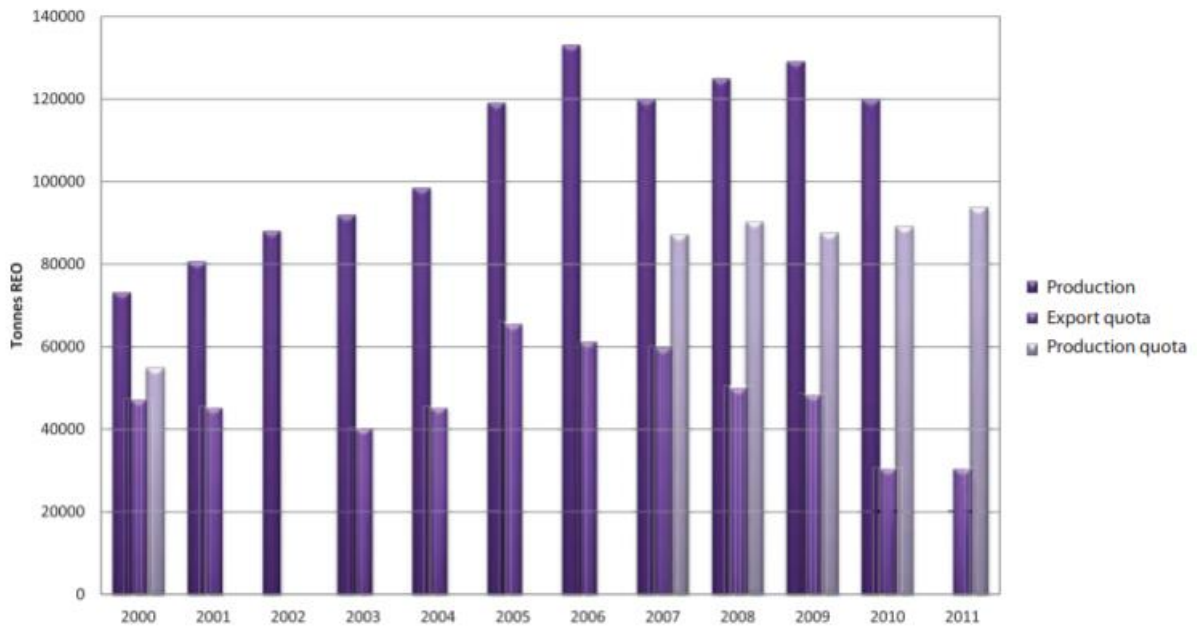


Figure 2-8: Global REE production vs. China REE production and exports (British Geological Survey, 2011)

2.2.3 Rare Earth Elements in Coal

Researchers at the University of Kentucky and Virginia Tech have identified a promising new alternative source of rare earth production domestically in the United States. As earlier stated, China currently dominates the production of REEs in the world and REEs present in coal and coal by-products could be the answer for the United States to combat this, for all intents and purposes, monopoly. Coal and coal by-products contain an enriched amount of REEs. In total, they account for nearly 50% of world reserves. In the United States, the Fire Clay coal bed contains REEs content of 500-4000 ppm of total rare earth elements. Zhang et al. (2015) found that on average coal ash can be enriched with REEs, but the coal REE content is roughly 62 ppm. However, the distribution of the REEs appears to be regional and seams in Northern and Central Appalachia, as well as, the Black Warrior basin have been found to have >1000 ppm REEs content (Zhang et al., 2015). Figure 2-9 shows the abundance of REEs from coal seams in the United States. In Figure 2-9 black dots indicate where the samples are located.

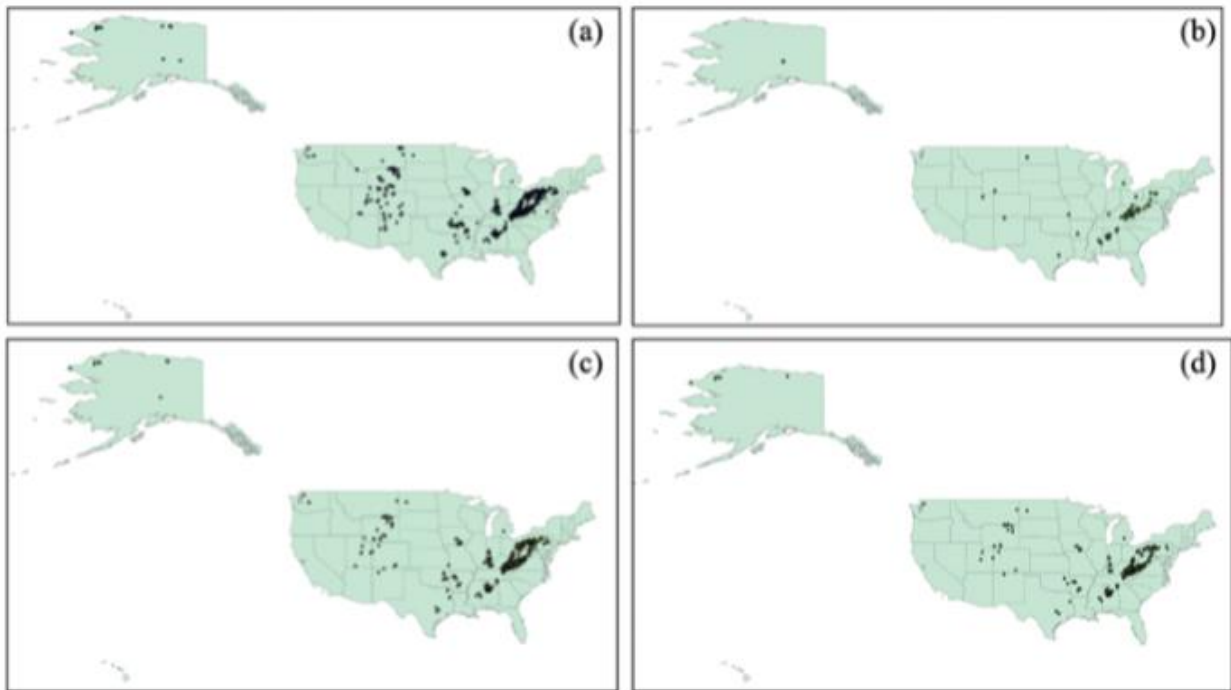


Figure 2-9: Abundance of REEs in coal and coal by-products (a) >700 ppm REEs (b) >700 ppm REE and >400 ppm heavy REE (c) >850 ppm REE (d) >1000 ppm REE (Zhang et al., 2015)

The high concentrations of REEs in these coal basins are typically associated with inorganic mineral matter associated with the coal. Hu et al. (2006), Birk and White (2000), and Karayigit et al. (1991), all discovered a strong correlation between REE's (both light and heavy) and coal ash yield in DPR Korea, Sydney Basin, and Turkish coal respectively. Zhang et al. reported that REEs are typically associated with auxiliary minerals such as monazite or clay minerals like kaolinite. Hower et al. (1999) discovered that the REEs in these high concentration seams shown above (Central Appalachia/Eastern Kentucky) are primarily in the form of monazite. These small monazite particles, <2 μm , are found in small bands inside cracks in the underlying clays associated with the coal seams (Zhang et al., 2015). For practical purposes, these REEs can be recovered from coal waste streams due to their affinity for inorganic material, and this process is crucial for the United States as it is heavily reliant on imports, and there are limited reserves available.

2.2.4 Extraction Processes for Rare Earth Elements

REEs are typically found in several types of deposits. Carbonatites are the largest source of REE deposits and have a high affinity for light REEs. These are igneous rocks formed from magma that is rich in carbonate. Presently, the Mountain Pass mine in California and the Bayan Obo mine in China are the two largest open-pit, hard-rock, REE producing mines in the world and both are carbonatite deposits. The former of which is currently closed due to environmental concerns. Alkaline igneous rocks represent the second largest group for hard-rock mining of REEs. These are formed from cooling of magmas that have silica deficiencies and are usually rich in carbon dioxide. A relatively new abundant source of REEs is ion-adsorption clay deposits found in China. REEs are leached by groundwater and become weakly fixed onto clays in the soil. They form from common igneous rocks such as granite and can be economically recovered using weak acids. This discovery has become a significant producer of heavy REEs. Additionally, REEs can be mined from placer deposits, pegmatite's, iron-oxide deposits, and marine phosphates. Although REEs occur in as many as 200 minerals, 95% occur in bastnasite, monazite, and xenotime. Bastnasite is observed in hard rock deposits (Mountain Pass) only, while monazite and xenotime can occur in placer deposits as well (Krishnamurthy and Gupta, 2016). These REEs are commonly found in trace amounts, and therefore the extraction process can be difficult and often costly.

Hard-rock deposits exist more predominately than placer mines as 93% of rare earths are mined in open-pit or underground hard-rock mines. The open pit mines like Mountain Pass and Bayan Obo employ traditional drill-blast-load-haul methods. Underground mines operate standard room and pillar mining. From a processing standpoint, gravity concentration, magnetic separation, electrostatic separation, and froth flotation are all applied in the recovery of REEs. However, flotation is the most often used method of beneficiation because it is the best available technology for fine particle separation and can be adapted to specific mineralogy of deposits. Froth flotation is applied at both Mountain Pass and Bayan Obo (Krishnamurthy and Gupta, 2016).

Flotation employed for hard-rock REEs deposit, typically use collectors such as hydroxamates, fatty acids, dicarboxylic acids, and organic phosphoric acids. Of these collectors, hydroxamates and fatty acids have been found to have the best success, with hydroxamates being more selective. During flotation, various depressants are added to suppress gangue minerals. These depressants are usually either sodium silicate, sodium hexafluorosilicate, lignin sulfonate, or sodium carbonate. The type of depressant is dependent on the gangue material. Following flotation, traditional hydrometallurgical processes are used to refine the REEs. Acid or alkaline leaching is commonly used for chemical beneficiation due to the chemical properties of rare earths that make them agreeable to dissolution and precipitation (Krishnamurthy and Gupta, 2016).

Two good examples of common beneficiation for REEs are the two largest REEs mines, Mountain Pass and Bayan Obo. The simplified process flow diagram for Mountain Pass is shown in Figure 2-10. Run of mine ore, after blasting from the pit and haulage to the plant, is crushed and blended to have plant feed of 7% REEs grade. This material is sent to a ball mill for grinding to a d_{80} of 150 μm . The ground material is sent through a series of hot flotation. Before flotation six conditioning stages are employed, using soda ash, sodium fluosilicate, steam, ammonium lignin sulfonate, and steam-distilled tall oil. After conditioning, the slurry is fed to a rougher flotation followed by a 4-stage cleaner circuit to increase the final concentrate grade. Scavenging is employed off the first cleaner and concentrate sent to a regrind to be added back to the rougher flotation in order to increase recovery. The final concentrate off the cleaner circuit assays 60% REEs with 70% recovery. This concentrate can be sold or processed further by leaching to further increase product grade (Krishnamurthy and Gupta, 2016).

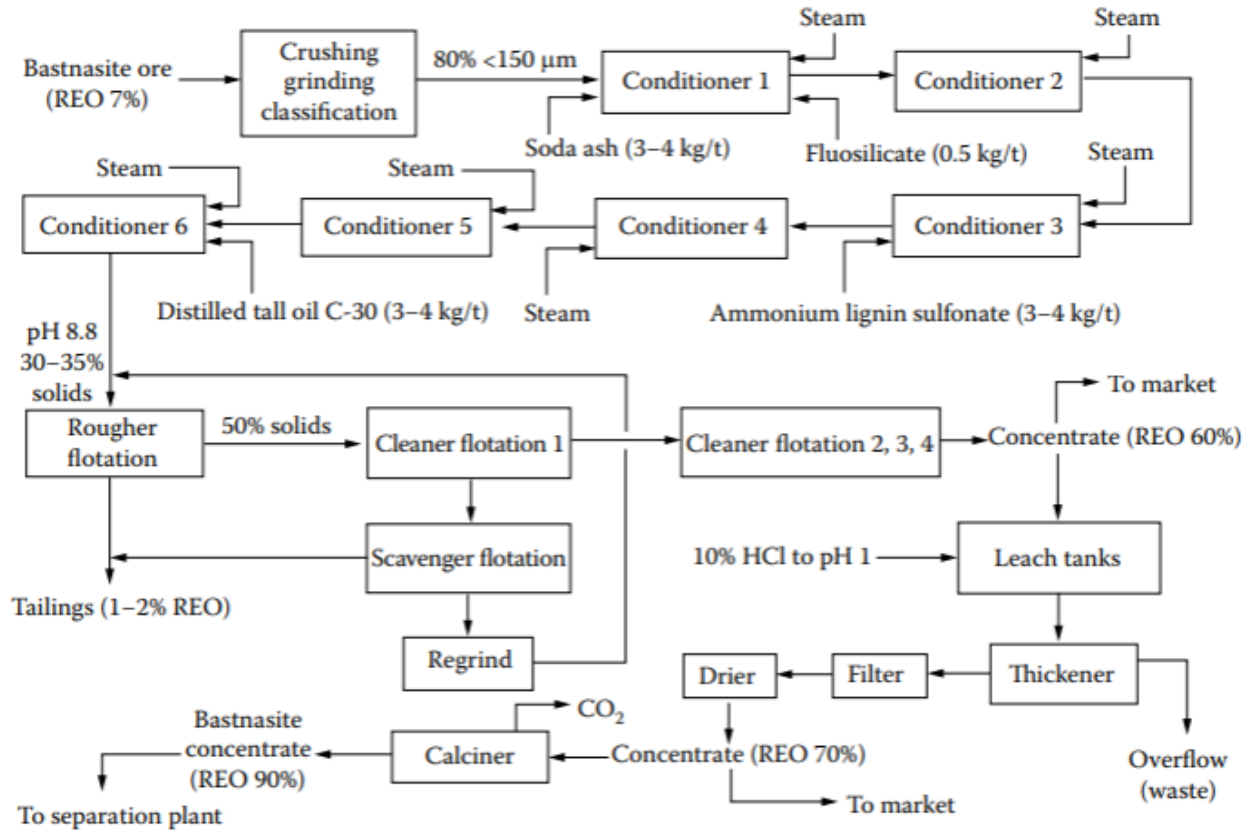


Figure 2-10: Process flow diagram for Mountain Pass (Krishnamurthy and Gupta, 2016)

Figure 2-11 shows the process flow diagram for the Bayan Obo mine. Run of mine ore is brought in to the plant and ground to a d_{90} of 74 μm . Afterwards, a bulk flotation is carried out to separate out iron minerals and silicates which remain with the tails. This flotation uses paraffin soap as a collector which is less selective. The goal in the bulk flotation is to produce iron minerals and silicates in the tails to be taken for iron beneficiation and niobium recovery, as Bayan Obo is an iron ore mine that produces REEs as a by-product. After the bulk flotation, slurry is processed through a 3 stage cleaner circuit using the more selective hydroxamic acid as a collector. After cleaning, gravity separation via shaking tables are used to produce a monazite concentrate assaying 47% REEs and a bastnasite concentrate assaying 68% REEs. Though fairly similar in beneficiation processes, the major difference lies in the amount of conditioning needed at Mountain Pass (Krishnamurthy and Gupta, 2016).

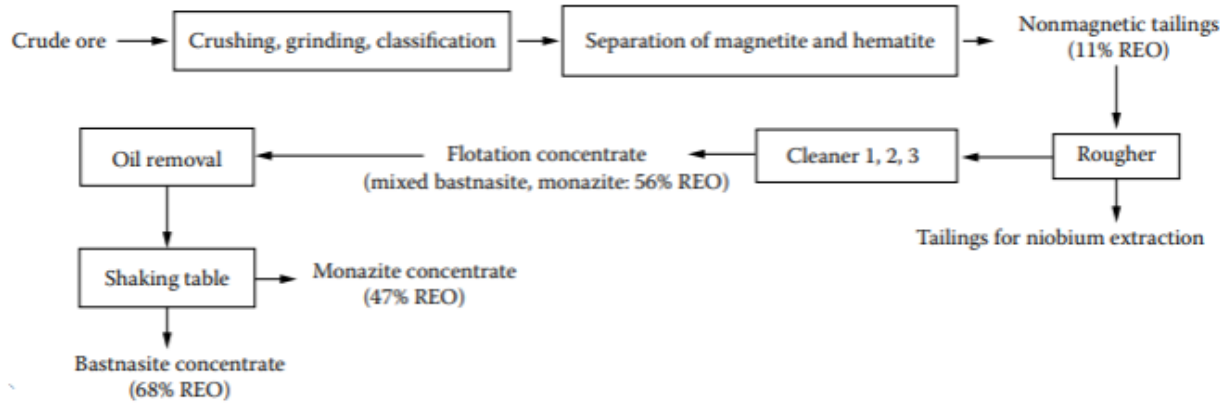


Figure 2-11: Process flow diagram for Bayan Obo (Krishnamurthy and Gupta, 2016)

As previously discussed, ion-adsorption clay deposits are a relatively new abundant source of REEs. They are unique to China, and little is understood about their formation. As such, they have unique beneficiation in that there isn't any real beneficiation needed. They occur at a substantially lower grade than their hard-rock counterparts but come at a much cheaper extraction and processing cost. Typical methods like magnetic separation, electrostatic separation, gravity separation, and flotation have been ineffective in treating this type of ore body. Figure 2-12 shows a characteristic process flow diagram for ion-adsorption clay deposits. They are mined by open pit method and REE's are recovered by leaching which exchanges and desorbs the REEs (Krishnamurthy and Gupta, 2016).

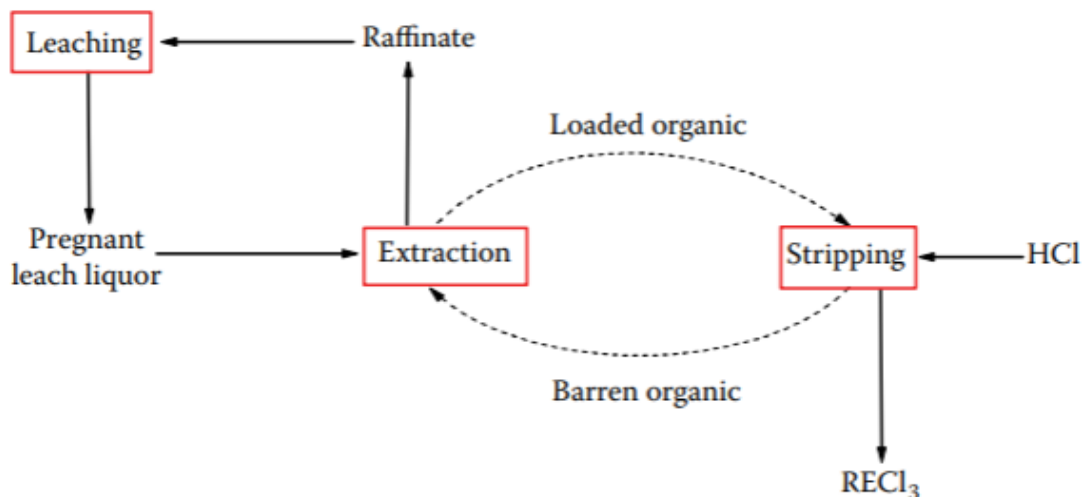


Figure 2-12: Process flow diagram for ion-adsorption clay (Krishnamurthy and Gupta, 2016)

2.3 Metallic Ore

This section delivers a brief overview of the existing state of the metals mining industry. Production statistics are provided to bring the reader up to date on current global metal mining. In later sections, preference is given to copper-bearing ore as the test work done in this thesis has been completed with copper. A brief synopsis of copper mining, processing, and issues are also discussed here.

2.3.1 Metallic Ore Production Statistics

Metallic ore production has been a global staple for hundreds of years, and their importance in everyday life is well known. Today, the demand for metals continues to increase, and countries are mining at increased rates to meet demand. Some of the top metals mined in 2017 include aluminum, copper, gold, lead, zinc, and nickel. These metals are vital to everyday life and continued plant improvements in recovery of ultrafine particles is crucial with decreasing ore grades. Figure 2-13 shows the total world production for each of the metals listed. For aluminum, copper, gold, lead, zinc, and nickel global production was 60 million, 19.7 million, 3,150, 4.7 million, 13.2 million, and 2.1 million metric tons respectively (U.S. Geological Survey, 2018).

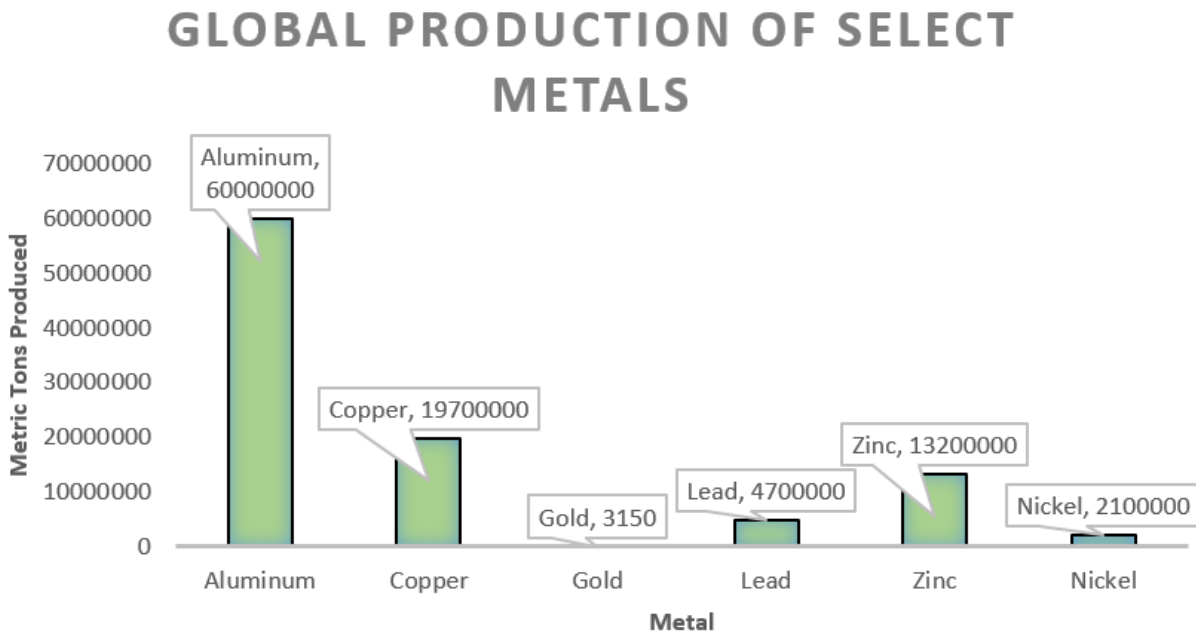


Figure 2-13: Global production of select metals in metric tons (U.S. Geological Survey, 2018)

Of all metallic ore bodies in the earth, aluminum is the second most abundant, and only iron is produced at a higher rate. Aluminum is used in the transportation industry, packaging industry, construction industry, consumer durables industry, basic machinery and more. In 2017 global production was approximately 60 million metric tons. Of these 60 million metric tons, China produced 32.6 million metric tons, Russia produced 3.6 million metric tons, Canada produced 3.21 million metric tons, and India produced 3.2 million metric tons. China is the dominant producer of aluminum, and for comparison, the United States produced 740,000 metric tons in 2017, which is down 12% from that in 2016. Aluminum price increased throughout 2017 starting at \$0.90 per pound and ending at \$1.06 per pound (U.S. Geological Survey, 2018).

Copper is usually mined via copper sulfide minerals such as chalcopyrite. It is one of the oldest metals used in civilization and is crucial in many sectors of the global economy due to its high ductility, malleability, and thermal/electrical conductivity. In 2017, worldwide production was approximately 19.7 million metric tons. Of these 19.7 million metric tons, Chile, Peru, China, and the United States make up around 55% of the global production, with Chile leading the way at 5.33 million metric tons. Peru, China, and the United States each produced 2.39, 1.86, and 1.27 million metric tons respectively. Global copper production dipped by roughly 400,000 metric tons from 2016 likely due to decreasing ore grade in many major mines. Copper price fluctuated between \$2.55 per pound and \$3.10 per pound for most of the year (U.S. Geological Survey, 2018).

Gold has been mined for centuries and has had several uses throughout history. Today, most of the gold mined is used in the manufacturing of jewelry, with some used as an industrial metal due to its chemical and physical properties specifically electrical conductivity. Total global production of gold was estimated at 3,150 metric tons in 2017. China led the way in the production of gold with 440 metric tons, followed by Australia and Peru with 300 and 255 metric tons respectively. The United States produced 245 metric tons of gold in 2017 (U.S. Geological Survey, 2018). Lead is corrosion-resistant and malleable metal that has been used traditionally for building materials, pigments, and piping. However, today most lead is used in the production of lead-acid storage batteries. Total lead production in 2017 was 4.7 million metric tons, with China producing 51% or 2.4 million of those tons. No other country came close to that production with the next highest production coming from Australia at 450,000 metric tons. The United States produced 313,000 metric tons in 2017 (U.S. Geological Survey, 2018).

Zinc is very prominent in the earth's crust. It is 4th most mined metal in the world today. Zinc is typically used as a coating product to protect against corrosion. The United States produced 730,000 metric tons in 2017. 13.2 million tons of zinc were produced globally in the same year, and as seen with some previous metals discussed China leads global production with 5.1 million metric tons produced. Peru, India, and Australia all produced 1.52, 1.4, and 1 million metric tons respectively (U.S. Geological Survey, 2018). Nickel is primarily produced in the manufacturing of austenitic stainless steel or superalloys. Nickel production exceeded 2 million metric tons in 2017, and the United States produced 23,000 metric tons. The world production of nickel did not change from 2016 to 2017. Indonesia was the top producer of nickel at 400,000 metric tons (U.S. Geological Survey, 2018).

2.3.2 Copper Need and Usage

As earlier stated, global copper production in 2017 was 19.7 million metric tons. However, global consumption of copper was estimated to be 24 million metric tons, which is slightly higher than the total produced. Copper production has declined likely due to decreasing ore grade and lack of new mines to be excavated. In the United States, copper production dropped an estimated 11% in 2017 but was valued at \$8 billion, which is an increase of 13% from the prior year. Copper prices have continued to increase over the past several years and growing production via recovery of waste streams can lead to a tremendous profit for copper producers (U.S. Geological Survey, 2018). Figure 2-14 shows the annual copper consumption in millions of tons for the United States, China, India, and the rest of the world from 1980 to 2008. This graph shows the dramatic increase in copper consumption over the last 30+ years. With relatively new larger developing countries like China entering the global market, the demand for commodities like copper has doubled since 1980 (USGS Mineral Resources Program, 2009).

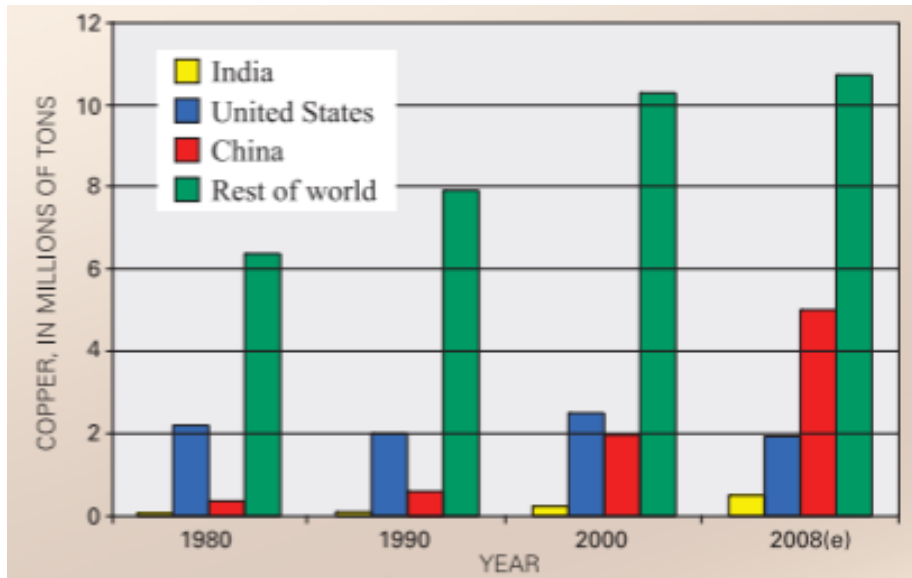


Figure 2-14: Copper consumption 1980-2008 (USGS Mineral Resources Program, 2009)

Copper was initially used in coins during early civilization, and later as tools when moving out of the stone age. Copper is corrosion resistant and has very efficient thermal/electrical conductivity. Today copper is used in a variety of industries including construction, power generation, electronics, transportation, and industrial machinery. Copper is essential for plumbing and wiring. Telecommunication is an increasingly important part of everyday society in the growing connected world, and copper wiring is an integral part of that process. In the transportation industry, it is used for the manufacturing of wiring, radiators, connectors, brakes, and bearings. In fact, on average vehicles use 1.5 kilometers of copper wire, and hybrid cars, which is a quickly growing industry, employ around 100 pounds of copper per vehicle. Copper is often combined with zinc, tin, or nickel for specialized use (e.g., copper-nickel alloy applied to the hull of a ship to prevent corrosion). The uses of copper are vast, and it has become a go-to metal for several industrial and high-tech applications, and as such global demand will continue to increase, providing increased pressure on copper companies and countries to keep up (USGS Mineral Resources Program, 2009).

2.3.3 Current Copper Processing Techniques

The vast majority of copper-bearing ore comes in the form of sulfide minerals (i.e., Cu-Fe-S minerals), most commonly chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), and chalcocite (Cu_2S). Copper is mined in massive deposits typically by open pit method or deep underground mines.

Essentially, there are two main processing routes for copper ore depending on whether it is originating from a sulfide mineral or an oxide mineral. Run-of-mine ore, for sulfide minerals, is typically sent through a series of crushing and grinding to reduce the particle size and improve liberation, followed by physical separation by flotation to concentrate Cu product with around 30% grade. Figure 2-15 shows a typical plant flowsheet for concentrating sulfide-copper ore via flotation, after which it will be sent for smelting and refining. This is known as a pyrometallurgical process. In the case of oxide ore bodies, a heap leaching process is used to concentrate the copper followed by solvent extraction and electrowinning. This is known as a hydrometallurgical process. However, since the work presented concerns only sulfide ores, which are the vast majority, this review will focus on that process (Davenport et al., 2002).

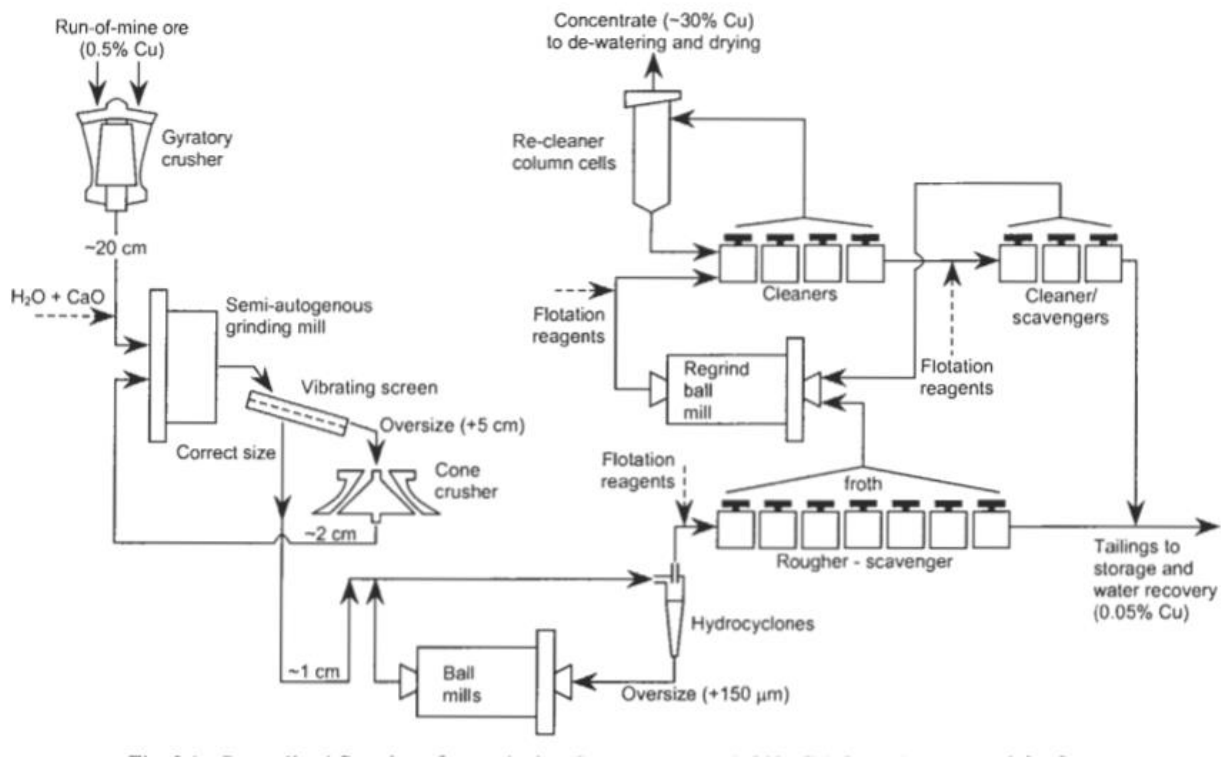


Figure 2-15: Typical copper flowsheet (Davenport et al., 2002)

A crushing and grinding circuit is placed at the head of the plant to receive run-of-mine ore which needs to be liberated to be concentrated from 0.5% Cu to 30% Cu, which can then be sent for smelting and refining. Ore will be fed through a cone crusher, followed by a semi-autogenous grinding mill, another cone crusher, and finally, a ball mill to ensure proper liberation for flotation (-150 μm). After crushing and grinding to this size, the slurry is fed to a bulk rougher+scavenger

conventional flotation which produces two concentrates and a main plant tails which goes to a storage facility. The rougher+scavenger concentrate will process through a regrind before being passed to a cleaner circuit. In the cleaner circuit slurry from the regrind stage is sent into another conventional flotation bank and the concentrate is passed to column flotation, while a cleaner+scavenger conventional bank processes tails. The tails from the cleaner+scavenger bank are sent to the main tailings and out to the storage facility with the rougher+scavenger tails. The concentrate from the cleaner+scavenger circuit is sent back to the regrind. The column flotation will produce a copper concentrate of 30%, and tails are forwarded to the head of the cleaner circuit (Davenport et al., 2002).

Flotation is used to selectively concentrate copper in the plant. The process entails conditioning of the copper minerals with common collectors such as xanthate, and frother such as MIBC. Figure 2-16 shows a cut view a typical conventional flotation cell. In the cell, air is introduced through a rotating agitator at the bottom of the cell. The agitator will shear air bubbles into finer sizes to promote the probability of attachment to a particle. Conditioned copper mineral particles will attach to the air bubbles in the system, while gangue minerals remain in the aqueous phase. The bubbles will rise through the pulp and create a semi-stable froth which overflows the cell carrying the copper particles (Davenport et al., 2002).

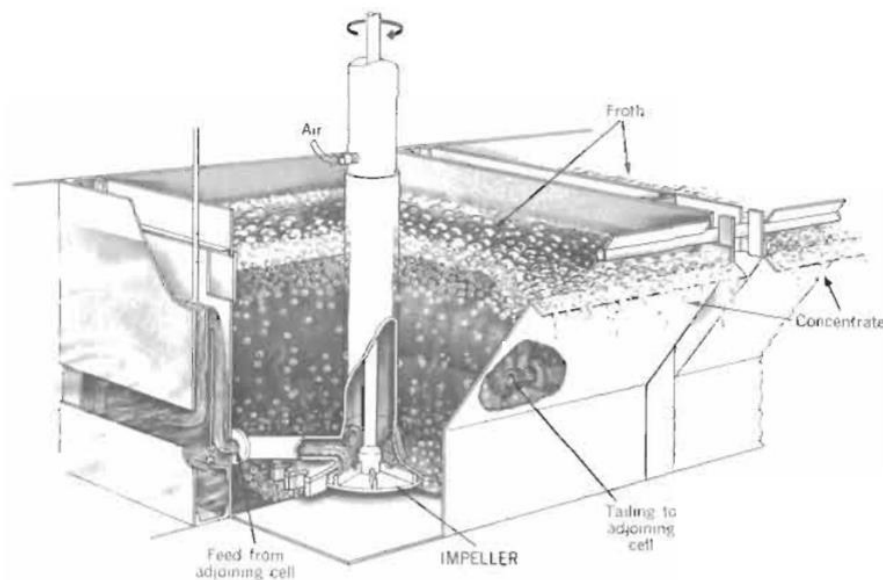


Figure 2-16: Conventional flotation cell (Davenport et al., 2002)

Once flotation is completed and a final copper concentrate assaying roughly 30% Cu is achieved the concentrate is passed on for smelting and refining. The full process is shown in Figure 2-17, but in general matte smelting is done to oxidize Fe and S from the concentrate which can be removed from the matte to produce 99% molten copper. Finally, electro-refining purifies the copper to less than 20ppm impurities (Davenport et al., 2002).

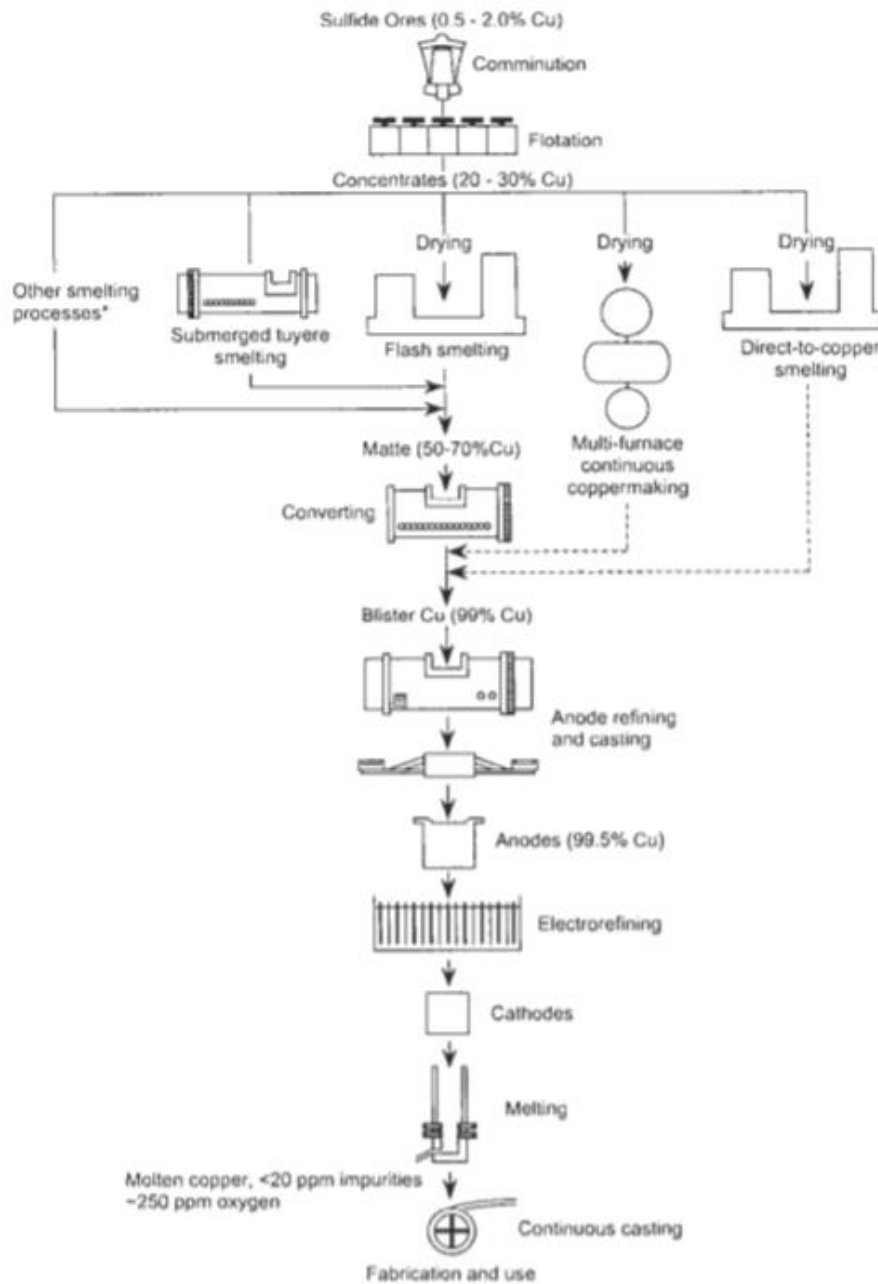


Figure 2-17: Processing of sulfide-copper ore (Davenport et al., 2002)

2.3.4 Challenges for Copper Flotation and Processing

The copper process described in the previous section is a general case but is used commonly throughout the industry, especially given the abundance of sulfide copper minerals. However, this process is not a perfect separation, and ultimately there are some challenges that the copper industry faces today with regards to declining ore grade and waste streams. As shown previously, copper production dipped by roughly 400,000 metric tons in 2017 and fell short of consumer demand by approximately 4 million metric tons. This is presently attributed to declining ore grades and lack of new deposits, causing decreased tonnage. The world average copper feed grade is currently 0.62%, and that number will continue to drop as more and more excavation of copper deposits continue. This decrease in ore grade is seeing an increased concern for copper companies to increased production in order to meet demand. However, additional recovery of waste stream copper lost from flotation cells could be the answer (Calvo et al., 2016).

Flotation tailings currently make up 90-95% of total plant tailings in sulfide-copper ore processing plants. Flotation, though the best available technology for fine particle separation, is very limited to a narrow size range where it is efficient; typically, this range for copper is between 30 and 150 μm . The coarse size fraction can be taken care of with the use of crushing and grinding equipment prior to flotation, but the fine fraction is a significant problem for flotation cells. In principle, lower recovery of ultrafine particles can be attributed to the reduced probability of bubble-particle attachment with the particle size reduction compared to the intermediate size range. Often the solution of decreasing the bubble size can be offset due to increase retention time needed in the cell. Figure 2-18 illustrates the decreased recovery when operating outside the size range mentioned above. In addition, it shows copper deportment in tailings data, which was collected from operating plants. As seen here there is immense contained value in the tailings stream from flotation cells in copper plants (Mankosa, 2016). Additionally, the tailings include metal sulfides which can be a particular problem with regards to the formation of acid mine drainage. This can lead to metal contamination in the environment specifically water sources, and can significantly deteriorate the water quality. (Calvo et al., 2016).

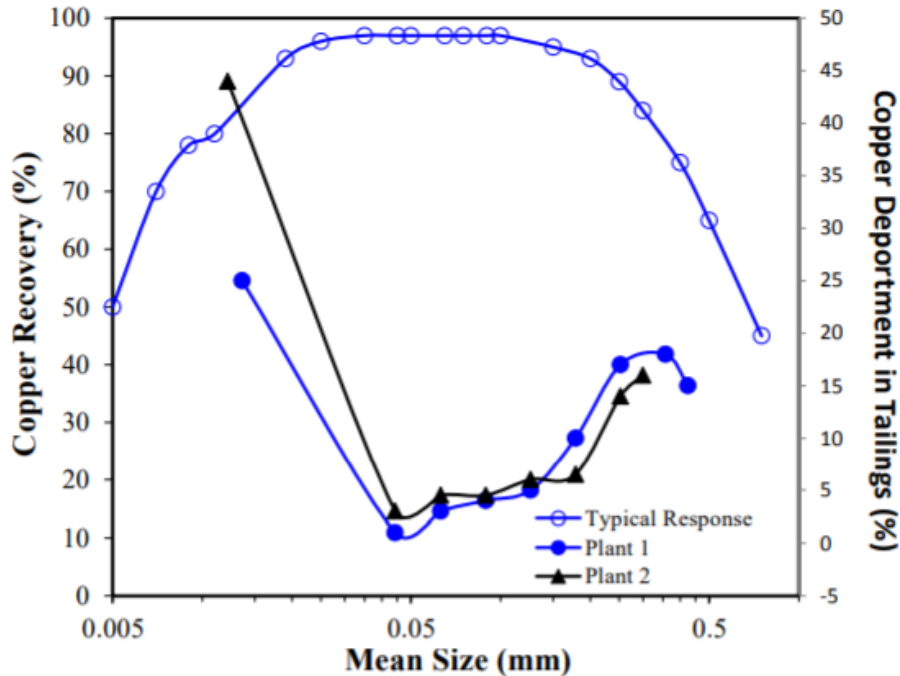


Figure 2-18: Copper recovery and department with respect to particle size (Mankosa, 2016)

2.4 Hydrophobic-Hydrophilic Separation Process

This section covers the general principles governing the HHS process. In detail, it lays the groundwork for the topics covered in this thesis. This section serves to educate the reader on the overall process as well as, design and operating variables. It concludes with a discussion of prior work done in the area of HHS.

2.4.1 Overview

As discussed in section 2.1 background, the HHS process began as the concept of dewatering-by-displacement (DbD), which was founded on principles of hydrophobic displacement and the Otisca T-Process. The process was developed for ultrafine coal recovery, that being the $-44 \mu\text{m}$ size fraction, which is currently discarded as waste in most coal preparation plants. The HHS process is a solution to ultrafine coal recovery, which can recover that size fraction, which is generally the most well liberated and pure, carbon material.

Conventional fine coal cleaning (reducing ash and moisture content) is achieved by froth flotation, the current leading technology in the field of fine particle separation, and the only commercially applied method in the United States. Flotation treats coal particles below 100 mesh or 150 μm , and of this stream, the minus 325 mesh or 44 μm particles are first removed using a classifying cyclone because flotation becomes inefficient when treating ultrafines. Flotation is a surface-based process that is based on differential wettability of particles. It can easily distinguish between hydrophobic and hydrophilic particles. In other words, it separates coal from mineral matter based on the particles' surface chemistry. Air bubbles selectively collect hydrophobic coal particles and form a froth at the top of the cell. When the concentrate is collected, it is significantly reduced in mineral matter but has very high moisture. Therefore, the resulting flotation concentrate must be dewatered before it can be sold to market. This dewatering process is usually done with either screenbowl centrifugation, vacuum filtration or thermal drying (Gupta, 2014). However, these methods are also limited with regards to particle size as cost and moisture both increase with decreasing particle size, as shown in Figures 2-19 and 2-20.

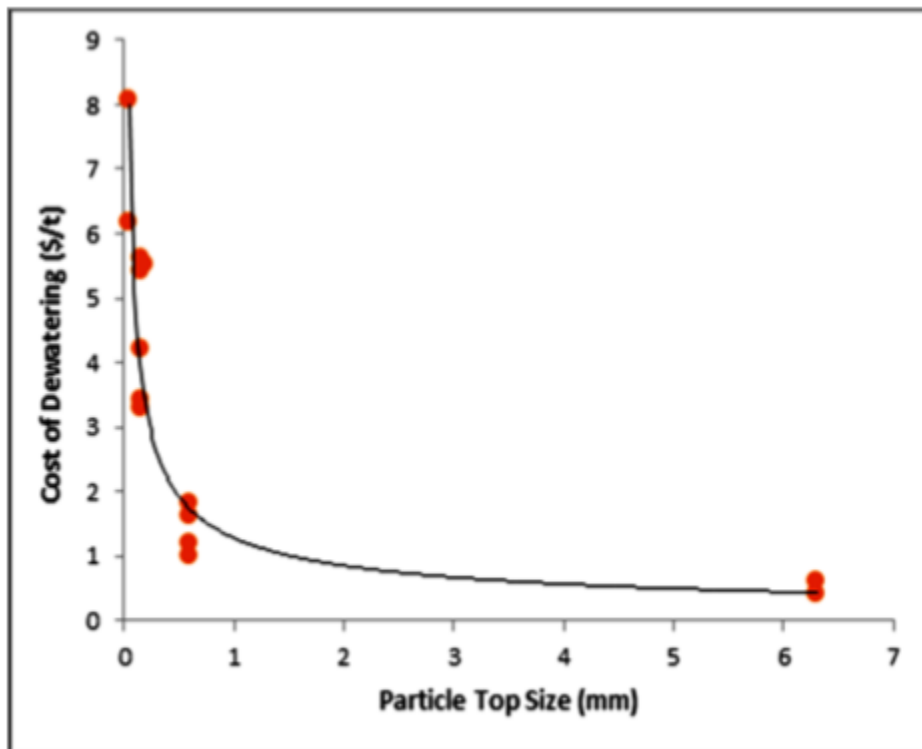


Figure 2-19: Dewatering cost in \$/ton with respect to particle size (Gupta, 2014)

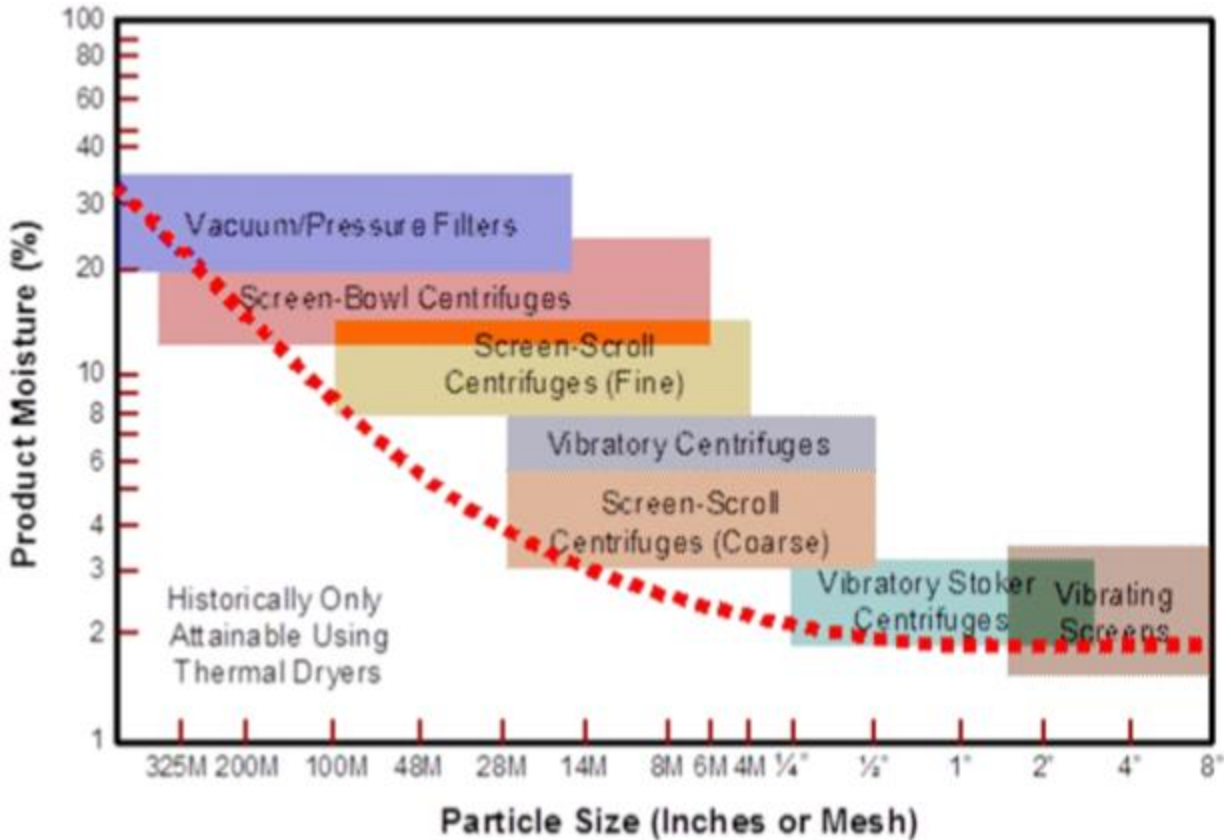


Figure 2-20: Product moisture with respect to particle size for various dewatering methods (Gupta, 2014)

The high cost of dewatering is the main issue plaguing fine coal cleaning. Advancements made in flotation technology such as the microcell column flotation, have led to the ability to clean ultrafine coal particles but dewatering cost increases significantly. Because dewatering cost is so high for minus 325 mesh particles, operators discard this fraction all together leading to enormous waste impoundments. These impoundments hold an estimated 500-800 million tons of fine coal product according to a 2002 study (Orr, 2002). These impoundments, in addition to maintaining a massive economic value, pose existing environmental threats.

The HHS process is a novel solution to the problems listed above. It uses principles of DbD to reduce the cost of dewatering significantly, eliminating the need for thermal drying of moisture. It selectively cleans the minus 325 mesh screen currently being discarded as waste using a process similar to flotation called oil-agglomeration. The result is ultrafine clean coal product (low ash/low moisture) that can be directly sold to market or blended with coarser streams.

2.4.2 Process Description

The HHS process was developed as an ultrafine coal separation process in which minus 44 μm coal particles could be simultaneously cleaned and dewatered. In the HHS process, coal slurry is fed to the system from the de-slime cyclone used to remove fines prior to flotation in the existing coal preparation plant. The slurry is subjected to oil agglomeration under high shear conditions to disperse fine oil droplets and promote the probability of attachment to coal particles. After high shear mixing the agglomerates are subjected to low shear mixing to allow them to grow. The large agglomerates are separated from the aqueous phase containing the bulk of mineral matter via conventional flotation cells as a means of phase separation. The phase separated agglomerates are fed to a unit coined the morganizer, where the agglomerates are broken in the presence of a large volume of oil, allowing entrained water (which contains mineral matter) to coalesce and fall to the tails, while the overflow includes dispersed ultrafine coal particles in oil. Finally, the oil is stripped from the coal via gentle heating and recovered to be used again in the process. Figure 2-21 shows a conceptual representation of this process.

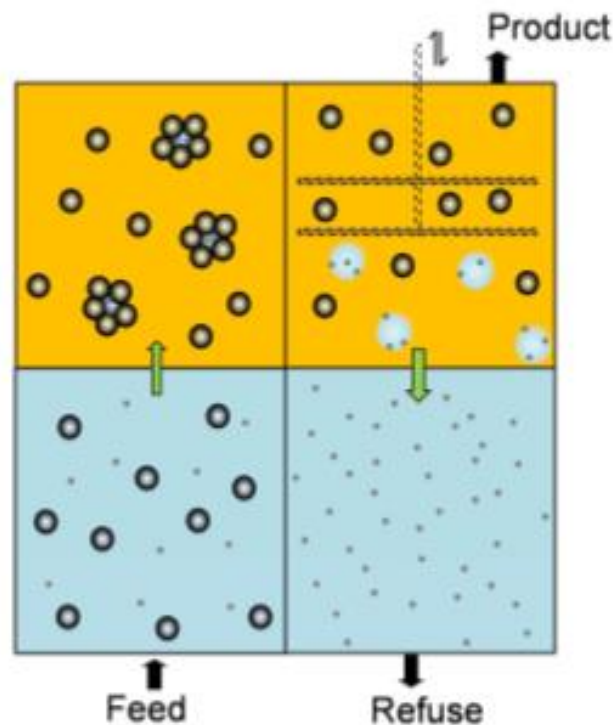


Figure 2-21: Conceptual representation of the HHS process (Yoon et al., 2016)

Figure 2-21 shows the case for coal agglomeration and breaking of agglomerates by the morganizer. In the bottom left block coal in an aqueous slurry enters the system and a small amount of oil is used to agglomerate the coal under high shear conditions. The resulting agglomerates, which are oil-in-water emulsions stabilized by coal particles, are transferred to a large volume of oil and phase inverse. Under phase inversion conditions, shown in the top left block, the agglomerates become water-in-oil emulsions stabilized by coal particles. The agglomerates are fed into the morganizer shown in the top right block. Here the emulsions/agglomerates are destabilized by a set of vibrating mesh screens in a bulk oil phase. This process liberates entrained water droplets, which are able to coalesce and separate by gravity into the bottom right block. The liberated water droplets carry with them hydrophilic particles and exit via the tailing stream. The dispersed coal in oil, which is free of moisture and mineral matter, exit the system and the oil is recovered (Yoon et al., 2016).

2.4.3 Design and Operating Variables

The HHS process is a complex process which builds upon many concepts like DbD, hydrophobic displacement, and oil agglomeration, and therefore many different factors govern its performance. A sufficient understanding of these processes is crucial to developing a working system that plants across the United States can use. With this realization, several key indicators have been identified as variables that affect the performance of the HHS process. Oil agglomeration is a critical step in the HHS process, and proper formation controls the efficiency of the operation. Capes and Darcovich in 1984 identified three key variables that affect oil agglomeration: i) free energy relationship between water, solid, and hydrophobic liquid, ii) hydrophobic liquid dosage, and iii) mixing intensity (Capes and Darcovich, 1984).

Agglomeration is dependent on the free energy relationship between water, solid and the hydrophobic liquid. Because free energy must be negative for agglomeration to occur, it is dependent on the interfacial tensions between the three phases. Thus, the solid hydrophobicity and type of hydrophobic liquid used are two major governing aspects of the process. Research has shown that an increase in the density and viscosity of oil (decrease in interfacial tension between water and oil), deteriorates the efficiency of oil agglomeration. Short-chain hydrocarbons have been found to be the most effective in this regard (Keller and Burry, 1990). Furthermore, the selection of an appropriate hydrocarbon oil is vital to the potential contact angle from a solid

surface to the oil droplet measured through the water phase. Figure 2-22 shows the contact angle achieved with various carbon number. As shown contact angle increases with decreasing carbon number due to a decrease in the oil surface tension (Yoon et al., 2016).

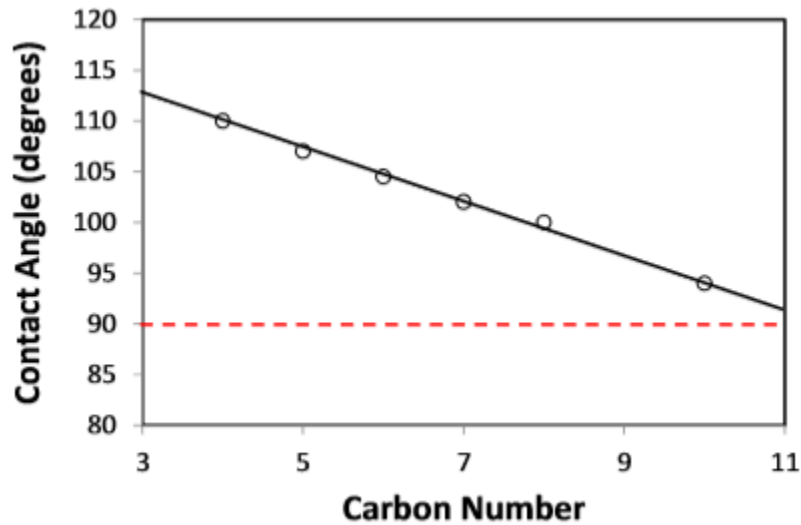


Figure 2-22: Contact angle of hydrocarbons with varying carbon number (Yoon et al., 2016)

Oil dosage is a critical variable in the oil agglomeration process. Lower dosages of oil allow more entrainment of water and therefore mineral matter, while higher dosages form lower ash agglomerates. However, in both cases, moisture is still high. This is due to the massive water globules that are trapped inside the structure of the agglomerates. Keller and Burry estimated that 7-30% of the moisture is due to surface moisture on the agglomerates and the rest is due to the massive water globules (Keller and Burry, 1990). For this purpose, the HHS process makes use of a mechanical force to break the agglomerates and liberate these large water droplets. In this case, lower dosages can be used to still achieve low ash, low moisture product (Capes and Darcovich, 1984).

Mixing intensity is an essential variable in the agglomeration process. High shear mixers are often used to improve the kinetics of oil agglomeration by creating smaller oil droplets leading to efficient dispersion and increased probability of attachment to the hydrophobic particle. Furthermore, higher mixing intensity can reduce the residence time needed to produce agglomerates. For example, in the Trent process, one of the earliest instances of oil agglomeration,

a residence time of up to 15 minutes was needed to produce agglomerates using a low shear mixing tank. In addition to the increased residence time, the Trent process required a large amount of oil, up to 30% by weight of coal, significantly increasing solvent cost. In high shear applications, residence time can be as little as 30 seconds and use as little as 2% oil by weight of coal (Capes and Darcovich, 1984).

The final major parameter governing the HHS process is a particle's energy of detachment. Equation 4 shows the calculation for the energy of detachment where r is the particle radius and γ_{ow} is the tension at the oil-water interface.

$$E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2 \quad [4]$$

The equation uses a positive sign for removal into an oil phase and negative for removal into a water phase. This realization is crucial to the HHS process as agglomerates need to be destabilized in order to liberate entrapped water globules and mineral matter in the morganizer. From the equation, particles are easier to destabilize when the contact angle moves further away from 90 degrees. Furthermore, particles with smaller size exhibit lower energy of detachment, as shown in Figure 2-23. The conclusion is that smaller particle size and increasing contact angle is very beneficial to the HHS process and should be considered a vital parameter (Binks, 2002).

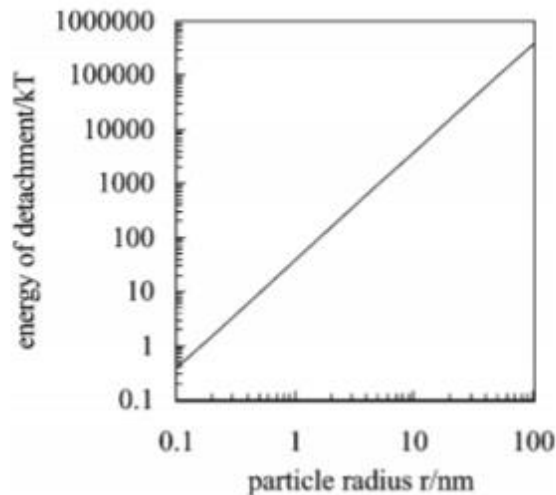


Figure 2-23: Energy of detachment as a function of particle size (Smith, 2012)

2.4.4 Prior Work

Work on HHS has been ongoing at Virginia Tech, since 1995 when the concept of DbD was first disclosed by Drs. Yoon and Luttrell. Some of the earliest test work into DbD, which would become modern-day HHS, was done with bituminous coal and butane as the hydrophobic liquid. Sohn et al. in 1997, reported that gently agitated coal with butane would form dry powder but only with a large volume of oil. The best results achieved with this method were with a butane to coal ratio of 2.0 with respect to mass and a low percent solids at 5% (Sohn et al., 1997).

In 2008, Kara Smith completed work on laboratory-scale research into hydrophobic displacement. The heart of her study was innovating dewatering methods for oil-agglomerated coal, which was found to have moisture contents as high as 40%, due to massive water globules trapped in the agglomerates. For all tests pentane was used as the preferred hydrophobic liquid. Smith tested various methods that included shaking, screening, air classification, centrifugation, filtering, and displacement. In the shaking tests, Smith concluded that the technique of hand shaking had a high inherent error, which led to large variations in product moisture, yield, and recovery. The lowest average moisture that was obtained was 16.2% at a pentane to coal mass ratio of 0.32 and a solids concentration of 6.3% and reported greater than 90% recovery regardless of the oil dosage. However, moisture varied greatly. She found increasing the solids concentration to 14.8%, also increased moisture by roughly 14%. She also concluded that a slurry sample that had been left for several months drastically impacted the final moisture with increases of 137%. (Smith, 2008)

After abandoning the hand shaking method, Smith began to test an innovative screen technique first popularized by Kerem Eraydin at Virginia Tech. The technique would screen out dry coal product and allow the trapped water droplets to coalesce on the screen. This method proved useful for producing single digit moistures, but ultimately Smith concluded that recoveries were also single digit and therefore the method would not be practical for plant use. In the air classification tests, Smith was unable to produce quantitative results (Smith, 2008).

In the filtering tests vacuum filtration was used in an attempt to improve the moisture content. Smith reported that this method resulted in moisture anywhere between 20 and 32%, and lower moisture products were observed when ultrafine material was not present. The displacement

method offered similar results with reported moisture values between 22-28%. The tests were run using pentane poured on top of the coal slurry during filtration. In principle, the oil should have displaced moisture in the slurry. However, Smith reported that in practice this did not happen. Smith concluded that this was likely due to pentane filtering around the water droplets following the path of least resistance, rather than displacing them (Smith, 2008).

Smith ultimately concluded that the most promising method of dewatering after oil-agglomeration was by centrifugation. Smith was able to achieve low moisture product (7.5%) and high recovery (>90%) when centrifuging for 1 minute at 3280 RPM. Smith concluded that lower moisture product was due to an increase in g-force by centrifugation. However, Smith also identified several critical problems with this method: i) the need for a sealed centrifuge as small amounts of pentane can leak under high pressure, or evaporate during addition to the system, and ii) there is great difficulty in producing an even cake as the agglomerates tend to form a wide wedge (Smith, 2008).

In 2012, Smith continued work on HHS with research into methods of improving oil-agglomeration. In general, Smith researched three methods for breaking agglomerates with the HHS process. The three methods tested were screening, ultrasonic energy, and vibrating mesh. For the screening tests, Smith concluded that single digit moistures could be achieved. However, the process was inefficient with an average separation efficiency of 66.3%. This is due to very low recoveries with losses of coal due to blinding. Smith attempted multi-stage screening, but the results showed no improvement to moisture or recovery (Smith, 2012).

Smith's next set of tests involved setting up a cylindrical column cell that was filled with water and pentane. An ultrasonic energy source was applied to break agglomerates and disperse coal in the pentane phase. The agglomerates were formed using a kitchen blender as a high shear reactor. The ultrasonic probe was set at a high frequency (20 KHz). The process was successful in dispersing coal in the pentane phase and achieving good recoveries. Finally, Smith tested using a vibrating mesh to break agglomerates. Ultimately, she concluded this process to be very effective, achieving similar moisture and recoveries to that of the ultrasonic energy, but with several advantages such as decreased operating cost, lower operating temperatures, and higher throughput (Smith, 2012). The work done was instrumental in the design of the current HHS process.

In 2014, Nikhil Gupta developed the initial Proof-of-Concept pilot plant for the HHS process. The process flow diagram for the plant is shown in Figure 2-23. The plant would operate at 100 lbs/hr feed. The process has undergone a few changes since this work, but the overall principles are still present. The plant used pentane as the preferred hydrophobic liquid at 25% oil by weight of carbon content for the initial oil-agglomeration process. Agglomerates were passed through a sieve to separate the agglomerates from the process tails containing mineral matter. Next, they entered the reactor known as the vibrating mixer/phase separator. This was the fundamental unit in the plant and the inspiration for the traditional morganizer used in the HHS process today. The vibrating mixer employed a mechanical force to break the agglomerates with vibrating mesh screens. The overflow would be gently heated to recover pentane to be recycled (Gupta, 2014).

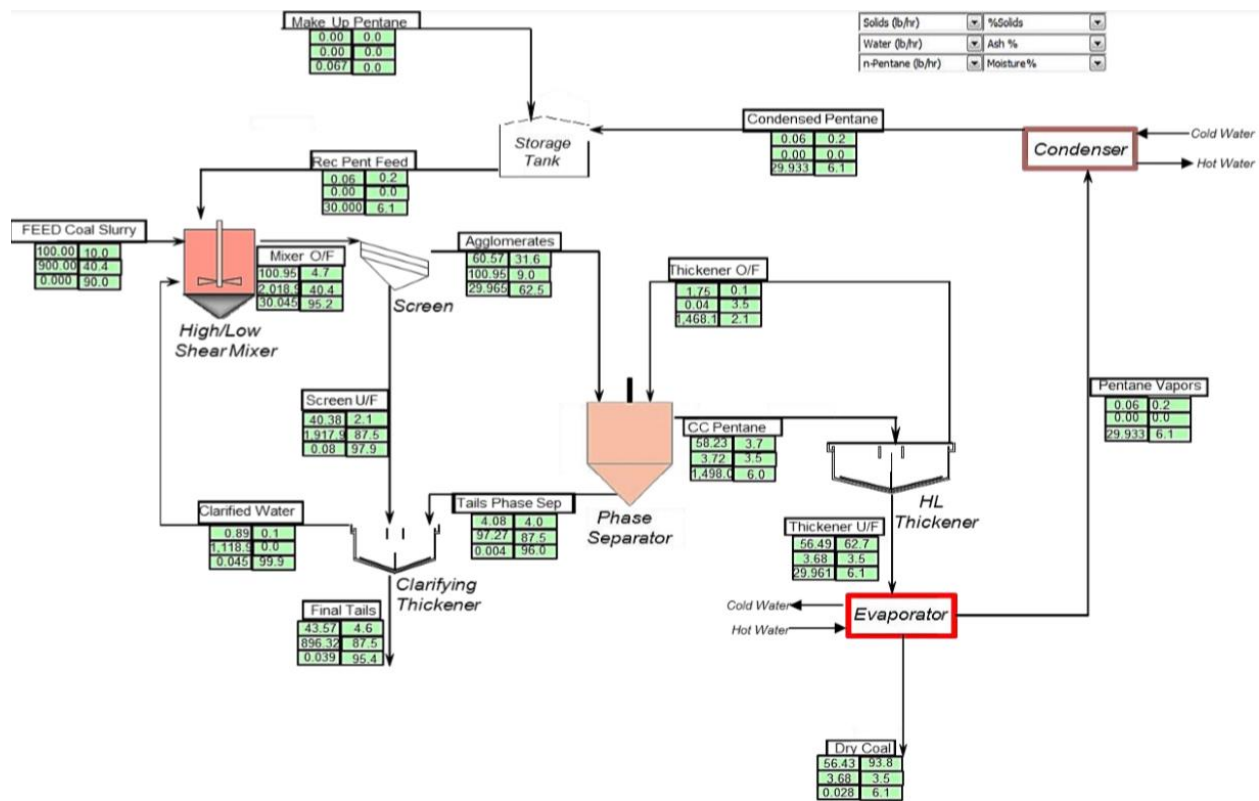


Figure 2-23: Process flow diagram for proof-of-concept unit (Gupta, 2014)

The primary goal for Gupta's work was to demonstrate the HHS on a larger scale than previous laboratory-scale testing. The unit was very successful in this regard after some initial operating issues. The unit tested four different types of coals from several prominent processing plants and consistently achieved low ash and low moisture products. Ash values were typically

less than 5%, and moisture values were consistently below 10%. Recoveries were as high as 97% with this unit. Overall, this was a major step forward for the HHS process as for the first time it was demonstrated on a large scale for continuous operation (Gupta, 2014).

CHAPTER 3. DECARBONIZATION AND COAL RECOVERY

3.1 Introduction

With froth flotation currently residing as the prominent technology for ultrafine coal separation, and with knowledge of its ultrafine deficiencies, the Hydrophobic-Hydrophilic Separation (HHS) process was developed to help recover ultrafine coal from plant waste streams. Furthermore, estimates state that active impoundments hold anywhere between 500 and 800 million tons of ultrafine coal product, which presents not only a large economic opportunity with valuable, well-liberated coal waiting to be recovered, but also a growing environmental concern (Orr, 2002). Additionally, HHS was born from a concept of dewatering-by-displacement (DbD), which sought to combat challenges presented in ultrafine coal dewatering that is needed due to the water-based separation employed by flotation. Moisture is often considered as an addition impurity to coal, and conventional techniques cannot produce single digit moistures, and as such thermal strippers are often still needed, but are expensive and increasingly difficult to permit. Thus, much of the highly liberated, and therefore high value, ultrafine coal is impossible to economically recovery.

Several years of test work has been completed in the areas of DbD, hydrophobic displacement, and HHS for various coal applications. This test work has helped to refine the process to what we see today. However, not much work has been completed on plant streams outside of de-slime overflow, flotation feed, and screenbowl effluent. In order for HHS to be competitive as a new technology and effectively recover a sizable proportion of waste material in coal preparation plants, extensive studies need to be completed on various carbon-based feedstocks. In this chapter, comprehensive laboratory-scale batch testing of various plant streams and impoundment coal in the United States and India are discussed.

3.2 Experimental Procedure

This section discusses the experimental equipment and testing methods used to complete the batch-scale tests that have been completed to characterize the effectiveness of the HHS process on various carbon-based feedstocks. The experimental procedures are used to liberate coal samples and separate mineral matter from fine coal samples. Various materials such as reagents and

hydrophobic liquid used are discussed in this section. In general, two methods were used to produce low ash and low moisture products: oil-agglomeration, and phase inversion/breakage of agglomerates.

3.2.1 Decarbonization and Coal Recovery Samples

Samples were collected from various plants in the Appalachian region of the United States, as well as, from prominent operations in India to test the effectiveness of the HHS process on various carbon feedstocks. Samples were generally fine coal samples from various plant streams. However, some coarse coal and middling streams were tested to characterize the adaptability of the HHS process. In addition, a few impoundment coal samples were tested as this is a major source of economic opportunity and environmental concern that can be combatted with the HHS process. For confidentiality of the various companies and plants tested during this research, company names are listed as company A, B, C, etc., while the specific preparation plants are listed by the state they are located in (i.e., WV Coal A, B, C, etc.).

3.2.1.1 Coal Company A

Samples were collected from various plants in the Appalachian region of the United States. Coal Company A generously provided several samples from three preparation plants in West Virginia: [1] WV Coal A preparation plant, [2] WV Coal B preparation plan, and [3] WV Coal C preparation, as well as, an impoundment coal sample from their VA Coal A impoundment. Three initial samples were taken at the WV Coal A plant from the flotation tailings (88% minus 325 mesh, 4.4% solids, 87.1% ash), raw coal cyclone overflow (79% minus 325 mesh, 7.4% solids, 67.6% ash), and decanter main drain to thickener (86% minus 325 mesh, 3.2% solids, 38.6% ash). Later new samples were collected from the same plant for both a metallurgical and steam run. Samples collected were metallurgical screenbowl effluent (97% minus 325 mesh, 2.7% solids, 31.1% ash), metallurgical deslime cyclone overflow (94% minus 325 mesh, 4.5% solids, 61.7% ash), steam screenbowl effluent (98% minus 325 mesh, 3.5% solids, 45.5 % ash), and steam deslime cyclone overflow (91% minus 325 mesh, 8.4% solids, 63.2% ash). Samples were consumed quickly to avoid any oxidation issues and to maintain a representative trial that would closely resemble an HHS process connected to each individual stream.

Three samples were also collected at the WV Coal B preparation plant from the scrubber to thickener (78% minus 325 mesh, 12.1% solids, 10.1% ash), thickener feed (76% minus 325 mesh, 3.5% solids, 55.1% ash), and spiral refuse underflow (9% minus 325 mesh). Because of a size complication with the spiral refuse underflow samples (63% plus 100 mesh), HHS was not a viable solution to recovering this stream and testing was not completed. Two samples were taken at the WV Coal C preparation plant from flotation cell tails (93% minus 325 mesh, 5.3% solids, 78.2% ash), and Jameson cell tails (96% minus 325 mesh, 1.4% solids, 56.9% ash). An additional middling samples was collected from the WV Coal C preparation plan and contained minus 4 mm size material which would be crushed and ground to various sizes for testing. The sample contained an average 29% ash after grinding. Coal Company A provided one last sample from their VA Coal A impoundment. The sample was relatively coarse with a large percentage of plus 100 mesh material, nearly 50%. The sample would be ground to a d_{80} size of 75 μm for testing with a feed ash of 34.9%. All samples were consumed quickly and those that were not were sealed to prevent oxidation.

3.2.1.2 Coal Company B

Coal Company B generously provided several samples for this research. Initially, a single middling sample was collected from their WV Coal D preparation plant. This sample was very coarse and would need to be crushed and ground to various sizes for comprehensive HHS testing, the feed ash for these tests were between 22% and 25%. Later two samples were collected from the same plant. The first of which was a low ash middling sample (roughly 30% ash) that would again be crushed and ground to various sizes for testing. The second was a coarse refuse sample from which a middling sample was produced and separated by size and density with feed ash values ranging from 49 to 95%. Samples were sealed when not in use to prevent oxidation. The coarse refuse characterization is shown in Figure 3-1. Streams that were collected for HHS testing are highlighted.

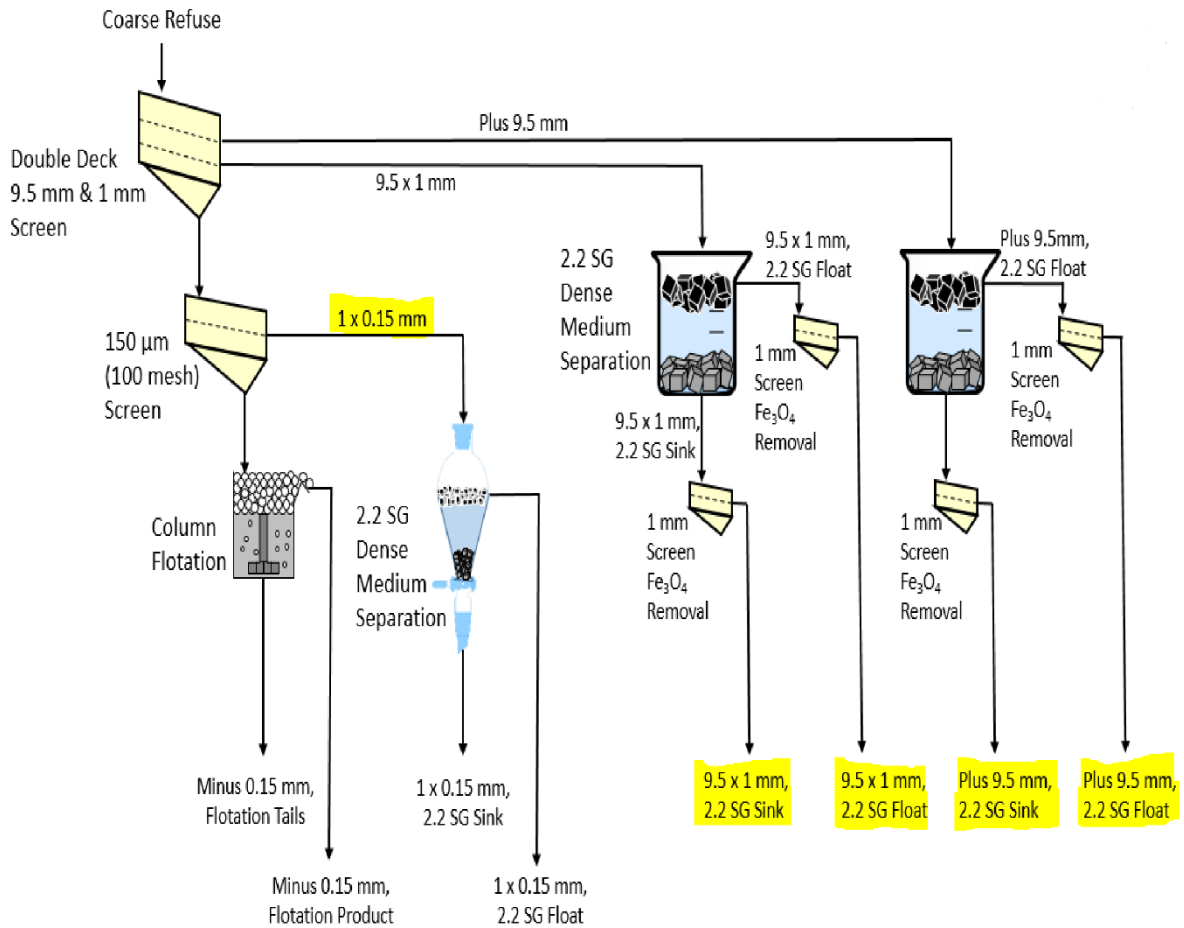


Figure 3-1: WV Coal D high ash middling coarse refuse characterization

3.2.1.3 Coal Company C

Three samples were procured from Coal Company C’s WV Coal E preparation plant for this research. Samples were collected from the thickener underflow (22.4% solids, 66.5% ash), underflow mud pump (32.3% solids, 60.1% ash), and screenbowl effluent (1.4% solids, 74.1% ash). Unfortunately, the samples appeared to be oxidized when received and did not respond well to HHS or flotation at first. In these tests, reagents would be used to help hydrophobized the coal. Samples were consumed immediately after hydrophobizing small batches for test work to prevent further degradation of the samples.

3.2.1.4 Coal Company D

Several fine and coarse coal samples were collected for HHS testing from Coal Company D’s KY Coal A preparation plant. The samples were collected from both a low-ash and mid-ash

product runs. Initially eight samples were collected from the ultrafine circuit including flotation feed mid-ash run (81% minus 325 mesh, 3.4% solids, 57.7% ash), flotation feed low-ash run (70% minus 325 mesh, 2.1% solids, 42.4% ash), flotation product mid-ash run (87% minus 325 mesh, 9.1% solids, 13.4% ash), flotation product low-ash (69% minus 325 mesh, 17.9% solids, 14.5% ash), flotation tailings mid-ash (81% minus 325 mesh, 2.9% solids, 56.9% ash), flotation tailings low-ash (70% minus 325 mesh, 2.4% solids, 43.0% ash), screenbowl effluent mid-ash (96% minus 325 mesh), and screenbowl effluent low-ash (99% minus 325 mesh). With less than 1% solids in the screenbowl effluent samples, only sizing data was completed. As with previous samples, sealed buckets were used to prevent sample oxidation. Some tests were run several months after they had been received with little noticeable degradation in the sample response to HHS. In addition to the eight fine coal samples, two coarse coal samples were collected from the plant spiral circuit for a low-ash and mid-ash run. The samples would be screened into two size classes (plus 0.25 mm and minus 0.25 mm) and then ground to various sizes to characterize the HHS process.

3.2.1.5 Coal Company E

Coal Company E's process works on impoundment coal from Kentucky (KY Coal B). The process seeks to use impoundment coal to be converted into liquid fuel, by stripping hydrocarbon from mineral matter. These tests were completed to identify potential alternative coal uses and test the effectiveness of the HHS process for these applications. A sample from their Kentucky project impoundment was collected. Tests were completed after grinding to various sizes and with the use of several reagents in order to produce ultra-clean coal product assaying 1% ash, a specification for the process.

3.2.1.6 Coal Company F

India continues to have a fast-growing coal industry, and as such samples have been collected for testing the validity of HHS on coal feedstocks from an entirely different region than has been tested previously. In light of this Coal Company F generously provided several key samples to help determine to what degree HHS is effective on Indian coal samples. The samples were collected from West Bokaro at their India Coal A washery and are as follows: flotation feed (minus 0.5 mm, 20.1% ash), flotation feed (minus 0.25 mm, 21.4% ash), froth (49% minus 0.15 mm, 17% ash), tailings (35% minus 0.15 mm, 50% ash), combined tailings set 1 ($d_{80} = 0.6$ mm, 41.4% ash), and combined tailings set 2 ($d_{80} = 0.55$ mm, 36.7% ash). Many of the samples were

very coarse as is typical for India processing circuits, and therefore prescreening was often employed as a cheap solution to reducing particle size and test natural fines. All samples were shipped from India as dry coal in small sacks, and as such were slurried in small batches for HHS testing.

3.2.1.7 Coal Company G

Four samples were collected from three different washeries of Coal Company G. Firstly, a fine coal slurry sample (minus 0.5 mm) and a raw coal sample (minus 80 mm) were collected from their India Coal B washery. The coal feed in this plant is a low-volatile medium coking coal. Secondly, a raw coal sample (minus 80 mm) was collected from their India Coal C washery and is also a low-volatile medium coking coal. Lastly, a raw coal sample (minus 80 mm) was collected from their India Coal D washery. This is low-volatile poor coking coal. All coarse material would have to be crushed and ground to sizes that are workable for the HHS process. This testing was completed to show the effectiveness of HHS for plant feed coal that has been untreated.

3.2.2 Experimental Apparatus

Several pieces of equipment were used throughout this research to prepare as-received samples effectively and produce HHS clean coal product. This equipment included sample preparation equipment to allow for basic size reduction of coarse samples, mixing vessels to effectively subject the fine coal slurry to oil-agglomeration, a novel phase inversion, and agglomerate breakage device known as the morganizer, and a thermal evaporator to gently heat the resultant oil and coal slurry, in order to recovery spent hydrocarbon. Additionally, moisture and ash determination equipment was used to achieve the results shown in section 3.3.

3.2.2.1 Sample Preparation

Several samples were too coarse to use directly with the HHS process, and therefore a series of crushing and grinding was undertaken. This would also be used to liberate coal from mineral matter in an attempt to help reduce ash content for some middling samples. A variety of crushing machinery was used to perform the initial size reduction, typically achieving samples of minus 1 mm so that grinding could be used to further reduce the size. To achieve this size a laboratory jaw and cone crusher was used. After running two passes through the jaw and cone crushers, a laboratory coffee grinder was used to further reduce the size to roughly 80 mesh. At

least three passes were needed to achieve this size for most coal samples that required this stage of sample preparation. This size could be used for the HHS process or be ground again in a laboratory ball or attrition mill. The laboratory cone crusher and coffee grinder are shown in Figure 3-2. Preliminary crushing was completed at the plantation road laboratory which is operated by the mining and minerals engineering department at Virginia Tech.



Figure 3-2: (Left) laboratory cone crusher, (Right) laboratory coffee grinder

After initial size reduction by crushing, or if the sample was already at an acceptable size, HHS test could be performed on minus 80 mesh material or ground using a laboratory ball and attrition mill. Wet grinding was used for all samples in both types of mills. For the laboratory ball mill, a solids concentration of approximately 50% by weight was used, as opposed to roughly 30% by weight for the attrition mill. The grinding media used were steel balls ranging from 6 to 26 mm with a relatively even distribution for the laboratory ball mill. Samples were ground for various lengths of time depending on the size reduction that was necessary. Attrition mill grinding media ranged from 3 to 6 mm in size (steel media) and was only used for grinding samples to ultrafine sizes, typically minus 10 μm , where theoretically the best liberation could occur.

3.2.2.2 Oil-Agglomeration

The first step in the HHS process is subjecting coal slurry to oil-agglomeration. In later chapters, this is adapted to oil-in-water emulsion formation. For oil-agglomeration, a laboratory Denver flotation cell was used as the mixing vessel. Air was not introduced in the cell during agglomeration. For the vast majority of tests, a two-liter cell was used and filled with coal slurry. High shear agitation was firstly used to form micro-agglomerates as the high shear agitation helps to disperse oil droplets and promote the probability of attachment to coal particles. During high shear agitation, roughly 50 ml of pentane oil was used as the hydrophobic liquid. Once micro-agglomerates had formed, low-shear agitation was used to help grow the resulting agglomerates and ensure ease of screening. Agglomerates could be screened off easily using a standard 100 mesh screen. In cases where higher shear agitation was required than could be provided by a Denver flotation cell, a standard kitchen blender was used with a much smaller slurry volume. This was often the case for difficult to agglomerate coals (less hydrophobic), some middling samples, or oxidized samples.

3.2.2.3 Phase Inversion and Agglomerate Breakage

A critical component of the HHS process and test work completed for this research is in the novel separation equipment known as the morganizer. In this vessel coal agglomerates are de-agglomerated into individual particles and dispersed into a bulk pentane phase, while entrained water droplets are liberated and allowed to coalesce, becoming heavy and falling to the tailings stream. A custom glass column was developed at Virginia Tech with a 1.5-inch inner diameter. The column had three ports. The topmost port was used for overflow of pentane and coal mixture. The bottommost port was a discharge port. And lastly, the middle port was used to maintain the oil-water interface. In the vessel, a thin shaft was fixed with two mesh screens and connected to an electro-dynamic shaker. The screens would operate at a frequency of roughly 3 Hz for all tests and varying amplitude. The amplitude was visually set in order to reduce the overall pumping effect which could lift unwanted moisture. The screens served to provide a mechanical force for breaking the agglomerates. A peristaltic pump was used in order to feed pentane into the system for continuous overflow.

3.2.2.4 Solvent Evaporation

After the pentane and coal mixture was collected from the laboratory morganizer, spent solvent (pentane) was recovered by way of evaporation and condensing. The evaporator was in the form of a glass jar sealed with vapor ports on the lid. The glass jar was placed in a liquid water bath which was mounted on a hot plate and set to a constant temperature of approximately 70°C. Boiled pentane was captured using a two-stage condenser unit and transported back to a holding container to be used again for future testing.

3.2.2.5 Moisture and Ash Determination

Samples were evaluated on the basis of ash and moisture percentage in the final product. A laboratory moisture analysis machine was used to quickly determine the moisture content of the various products produced from HHS, based on mass loss. After moisture determination samples were burned in a TGA analyzer for ash determination again based on mass loss. After burning away, the carbon material in the TGA machine what is left is mineral matter and is typically discarded.

3.2.3 Methods and Materials

For most testing done on the aforementioned coal samples, a standard HHS procedure was used. Where a procedure would differ from the following, it was discussed in a later section that was specific to that sample. In accordance with this procedure, it is often necessary for the use of various reagents to aid in the oil-agglomeration process. Some test work was also completed using flotation for comparison which also requires the use of frother and collector.

3.2.3.1 Experimental Method

In general, for the test work completed, samples were first looked at on a size basis, and a determination was made as to whether any sample preparation was needed prior to initiating HHS testing on the sample. Crushing and grinding would be used to reduce the particle size of samples to a workable top size or d_{80} for use with the HHS process. Often this size would vary based on testing requirements or specifications. After size reduction, the slurry sample would be subjected to oil-agglomeration and the resulting agglomerates would be separated from the aqueous phase containing the bulk of mineral matter using a standard 100 mesh screen. The agglomerates would

be fed to the laboratory morganizer unit in small quantities and two vibrating mesh screens would provide a mechanical force to de-agglomerate the coal, and thereby liberating entrained water droplets and mineral matter. The overflow from this unit would be collected in a beaker and transferred into the solvent evaporator to apply a gentle heating and recover the pentane hydrocarbon. As such, what is left is dry coal with low-ash and low-moisture.

3.2.3.2 Reagents

Pentane (C_5H_{12}) was the only hydrophobic liquid used for testing during this phase of the research. Pentane has been used in previous work done on HHS because of its low boiling point at 98°F, making it easy to recover in the system. Pentane is a short chain hydrocarbon that is naturally hydrophobic and therefore an excellent candidate for HHS. For all experiments HPLC Grade 99+% n-pentane was used, which is obtained from Alfa Aesar. Table 3-1 shows the various relative properties of pentane. In several tests, oil-agglomeration proved difficult with pentane alone. In such cases, small amounts of Sorbitan Monooleate (SMO), were used as a hydrophobizing agent. Other notable chemicals used during testing were the use of Sodium Silicate as a dispersing agent, diesel as a collector for flotation, and an alcohol/glycol blend based frother for flotation.

Table 3-1: Relevant Properties of Pentane

Chemical or Physical Property	Value
Molecular Weight (g/mol)	72.15
Density (g/cm^3)	0.626
Boiling Point ($^{\circ}C/^{\circ}F$)	36 / 98
Viscosity (N-sec/ m^2)	0.0003
Surface Tension (N/m)	0.016
Vapor SG	2.5
Solubility with Water (mg/L)	0.04

3.3 Results and Analysis

The following section presents the results obtained during this phase of the research project. It focuses on highlighting the various experiments/procedures used to obtain the results as

well as any variations from the previously reported experimental method. This section also serves to provide results from various testing conditions, across a broad range of size classes, and from varying regions. The results presented in this section help to characterize the HHS's effectiveness on various carbon-based feedstocks and determine the validity of its use in creating new coal markets.

3.3.1 Coal Company A Batch Testing

In total, 48 tests were conducted on samples received from four different sites operated by Coal Company A during this phase of the research project. Three different West Virginia preparation plants were tested during this phase, along with a Virginia impoundment. The samples tested included a variety of plant streams and a mix of coarse and fine-sized material. The feed ash across all samples tested ranged between 28% and 87% indicating high variability in the quality of the feed coal across these samples. The first West Virginia preparation plant (WV Coal A), provided samples from three different streams for initial HHS testing. These samples were obtained from the flotation cell to thickener, raw coal cyclone overflow, and decanter main drain to thickener. Sizing data was collected on each sample by wet screening, to determine the validity of each sample as an acceptable stream for HHS testing and determine the need, or lack thereof, for sample preparation via grinding. In each case, a 30, 100, and 325 mesh sieves were all used to wet screen a representative sample from the 5-gallon bucket of sample that was collected for each stream. The pass material through the 30 mesh sieve would be passed through the 100 mesh sieve to determine the percentage retained in that size class. The process would be repeated with the 325 mesh sieve. In total, all three samples were very fine with >80% of the material being less 325 mesh. The full sizing data can be found in Appendix A.

Due to the relatively fine size nature of the initial WV Coal A samples, no sample preparation was deemed necessary. Samples were all subjected to standard HHS procedure described in the previous section. The results from the HHS testing for the initial WV Coal A samples, which are summarized in Table 3-2, indicate that the HHS process can effectively clean and dewater these fine coal samples. The process was able to produce consistently high-value material which was low ash and low moisture. With the exception of the flotation cell to thickener sample, combustible recoveries were above 80%. The flotation cell to thickener sample is a tailings sample from the flotation cells at the preparation plant which is rejected into the thickener as waste

and has a feed ash of 87.1%. This sample, by nature, has a relatively low percentage of coal and a high percentage of mineral mater, and as such, a single test was conducted on this sample as the relative yield for this stream was low at only 6.3% by weight. The sample did not respond well to oil agglomeration due to the low percentage of solids (4%) and high feed ash resulting in a very low population of coal within the sample. As such, micro-agglomerates were formed but could not grow to form large agglomerates that could be fed to the morganizer. Along with some small micro-agglomerates, a coal-oil foam was formed, rather than completely agglomerating to form spherical agglomerates. This resulted in difficulties in the morganizer and low recovery of coal material. Combustible recovery and separation efficiency were thus low at 45.9% and 46.1% respectively. The latter two samples both performed very well with the HHS process. They resulted in single digit ash and moisture product values as well as combustible recoveries and separation efficiencies above 80%. The yield was relatively low at 27% for the raw coal cyclone overflow despite a high percent solids (7.4%). This was due to the high feed ash of 67.6% with a low population of coal material. As anticipated, the HHS process was able to effectively recover coal from the WV Coal A sample streams and upgrade the product to a high-value coal product. A full separation efficiency plot is shown in Appendix B with all coal samples tested.

Table 3-2: WV Coal A Preparation Plant Initial HHS Testing Results

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	%Solid	Ash	Moisture				
Flotation								
Cell to	87.1	4.4	4.8	1.9	92.6	6.3	45.9	46.1
Thickener								
Raw Coal			3.8	1.6	92.1	27.7	82.5	80.7
Cyclone	67.6	7.4	3.9	1.0	92.3	27.9	82.9	81.2
Overflow			3.8	2.4	92.2	27.8	82.8	81.0
Decanter								
Main			3.2	4.3	88.5	58.5	92.2	87.4
Drain to	38.6	3.2	3.1	3.0	89.2	58.8	92.8	88.0
Thickener			3.1	5.0	87.7	58.0	91.6	87.0

Later in the testing period, four additional samples were procured from Coal Company A's WV Coal A preparation plant. The samples were both screenbowl main effluent and deslime cyclone overflow for a metallurgical and steam operation run. Testing was performed to evaluate the HHS process under traditional waste stream conditions but with varying coal quality for two different coal markets. Several past researchers have evaluated coal recovery with the HHS process for these streams, and therefore the project team was confident in the ability of the process for these samples. A common practice in coal preparation plants is to remove ultrafine coal prior to fine coal processing by froth flotation with classifying cyclones deemed deslime cyclones, due to the flotation inefficiencies and high downstream dewatering costs associated with this size fraction. The cyclone overflow, which will contain all minus 325 mesh material removed from the flotation feed, is typically rejected to the plant thickener. Screenbowl centrifuges are commonly used in coal preparation plants as dewatering circuits for concentrate products from the froth flotation circuit but often lose ultrafine material in the main effluent.

Each sample was first investigated on a size basis with individual and cumulative size and ash values. Sizing data was collected by wet screening the samples with a 100, 200, and 325 mesh sieve according to the same procedure described earlier. For the screenbowl effluent samples, regardless of whether it was the steam or metallurgical run, the sample was extremely fine with 97% of the material being minus 325 mesh. For the deslime cyclone samples, roughly 90% of the material was minus 325 mesh. It is for this reason during the testing of the metallurgical deslime cyclone overflow sample that testing was done on the as-received sample, as well as, the sample prescreened at 200 and 325 mesh. The full size analysis for these samples are found in Appendix A. Overall the metallurgical samples performed extremely well and are presented in Tables 3-3 and 3-4. Combustible recovery values were 93% and 78-85% for the screenbowl effluent and deslime cyclone sample respectively. Single digit ash and moisture values were recorded across both samples. The screenbowl effluent sample proved difficult during oil agglomeration due to the very low percent solids concentration at 2.7%. Similarly, to the aforementioned flotation cell to thickener sample, only micro-agglomerates were formed, however, the sample performed well in the morganizer, and overall yield was acceptable. Separation efficiency values were consistently high for the metallurgical operation samples at above 80%.

The results for the testing of the steam operation samples, which are reported in Tables 3-5 and 3-6, are slightly poorer than their metallurgical counterparts. Combustible recovery values ranged between 55% and 74%, with the higher recovery values observed with the deslime cyclone overflow sample. While the HHS process consistently produced single-digit ash values, moisture was higher across the samples ranging between 7.1% and 14.3%. The high end of which is above the target value of 10% moisture. In terms of separation efficiency, the samples again performed poorer than the metallurgical runs boasting separation efficiency values of 55-72%.

Table 3-3: WV Coal A Preparation Plant Screenbowl Effluent Results (Met)

Feed (%wt.)		HHS Product (%wt.)		Refuse Ash	Mass Yield	Combustible Recovery	Separation Efficiency
Ash	%Solids	Ash	Moisture	(%wt.)	(%wt.)	(%wt.)	(%)
31.1	2.7	3.4	4.2	87.1	66.9	93.8	86.5
		3.3	2.2	86.9	66.7	93.7	86.7

Table 3-4: WV Coal A Preparation Plant Deslime Cyclone Overflow Results (Met)

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse Ash	Mass Yield	Combustible Recovery	Separation Efficiency
	Ash	%Solids	Ash	Moisture	(%wt.)	(%wt.)	(%wt.)	(%wt.)
As-Rec	61.7	4.5	3.6	1.0	91.4	33.8	85.2	83.1
			4.1	1.0	91.8	34.3	85.9	83.6
-200 mesh	62.5	n/a	3.4	0.9	91.7	33.1	85.2	83.4
			3.7	2.3	91.5	33.0	84.8	82.8
-325 mesh	66.6	n/a	3.5	1.3	90.2	27.2	78.6	77.2
			4.0	1.2	90.6	27.7	79.7	78.0

Table 3-5: WV Coal A Preparation Plant Screenbowl Effluent Results (Steam)

Feed (%wt.)		HHS Product (%wt.)		Refuse Ash	Mass Yield	Combustible Recovery	Separation Efficiency
Ash	%Solids	Ash	Moisture	(%wt.)	(%wt.)	(%wt.)	(%)
45.5	3.5	2.9	8.6	71.5	37.9	67.5	65.1
		3.3	14.3	71.1	37.7	67.0	64.2
		2.8	9.9	65.8	32.2	57.5	55.5
		2.9	12.1	65.1	31.4	55.9	54.1

Table 3-6: WV Coal A Preparation Plant Deslime Cyclone Results (Steam)

Feed (%wt.)		HHS Product (%wt.)		Refuse Ash	Mass Yield	Combustible Recovery	Separation Efficiency
Ash	%Solids	Ash	Moisture	(%wt.)	(%wt.)	(%wt.)	(%)
63.2	8.4	3.5	8.6	85.7	27.4	71.9	70.3
		3.2	7.1	85.6	27.1	71.4	70.0
		4.0	11.0	86.1	27.9	72.8	71.0
		4.1	10.4	86.9	28.6	74.5	72.7

Samples were procured from Coal Company A’s WV Coal B preparation plant in order to test different waste streams that appeared promising for HHS testing. Three different samples were tested from this plant. The scrubber to thickener, thickener feed, and spiral refuse underflow samples were all tested. For the case of the spiral refuse underflow, at the time of testing it was determined that there was too high of a percentage of coarse particles (>0.25mm), and therefore only sizing data was collected on this sample. In later testing sections, coarse particle samples were tested with the HHS process but at this time the sample was not deemed a priority. The scrubber to thickener and thickener feed samples both had a high percentage of minus 325 mesh material at 77% and 75% respectively and were assumed to be good candidates for HHS testing as both streams are rejected to the plant thickener. Size analysis of these samples can be found in Appendix A.

Both samples performed well under HHS testing procedure. Specifically, the scrubber to thickener sample performed exceptionally well, with a combustible recovery of 98% and a separation efficiency of 77%. The sample produced extremely low ash values around 2% with less than 1% moisture. The process produced consistently low ash and low moisture products for the thickener feed sample, similarly to the scrubber sample, with slightly less combustible recovery at 72-82%. However, the separation was higher when compared to the scrubber to thickener sample at around 80%. Full results for these samples are shown in Table 3-7 and indicate that the HHS process is well suited to recover these streams.

Table 3-7: WV Coal B Preparation Plant HHS Testing Results

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse	Mass	Combustible	Separation
	Ash	%Solid	Ash	Moisture	Ash (%wt.)	Yield (%wt.)	Recovery (%wt.)	Efficiency (%)
Scrubber			2.9	0.9	85.7	91.3	98.5	72.4
to	10.1	12.1						
Thickener			2.3	1.0	86.9	90.8	98.7	77.8
Thickener			3.2	3.6	87.2	38.2	82.3	80.2
Feed	55.1	3.5	3.1	1.3	81.4	33.6	72.6	70.6
			3.6	1.7	86.9	38.2	82.0	79.5

Three samples were collected from Coal Company A’s WV Coal C preparation plant. Two initial samples of both their conventional flotation cell tailings and Jameson cell tailings were tested. Later in the testing period, the plant sent a third middling sample to be tested. This is a non-traditional feedstock for HHS testing which represents a large tonnage of recoverable material if proven to be upgradable via the HHS process. Size analysis showed that both the conventional flotation tailings and the Jameson tailings contained greater than 90% material minus 325 mesh, making them suitable candidates for HHS testing. Full sizing results are shown in Appendix A. Both samples, the results of which are shown in Table 3-8, responded very well to HHS testing, and relatively similar to other Coal Company A samples discussed, despite relatively low percent solid material and high ash material, albeit with a low mass yield between 15% and 36%. These samples vastly out-performed the flotation tailing sample tested from the WV Coal A plant.

Regarding recovery, the samples ranged between 69% and 82%, which was far superior to the 45.9% recovery seen at the WV Coal A plant. The process succeeded in producing single digit ash and moisture values indicating its viability for recovering these specific plant streams.

Table 3-8: WV Coal C Preparation Plant Initial HHS Testing Results

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	%Solids	Ash	Moisture				
	Flotation Tails	78.2	5.3	4.5	2.6	92.6	16.4	71.7
			4.5	0.8	92.0	15.9	69.3	68.6
			4.6	1.5	92.0	15.8	69.4	68.2
Jameson Tails	56.9	1.4	3.7	5.4	87.3	36.4	81.3	78.9
			3.4	5.5	87.8	36.7	82.1	79.9
			3.3	2.8	87.7	36.5	82.0	79.8

Later in the testing period, during this phase of the research project, the WV Coal C preparation plant sent a middling sample to be tested for the degree of upgrading that the HHS process could provide. This is a very different sample from those previously presented in this thesis, as well as, those presented in previous works on the subject of HHS. Traditional market targets for the HHS process have been in ultrafine waste streams, specifically deslime cyclones, screenbowl main effluent, and flotation feed. Flotation feed has been a more recent development for the process due to the fact that while the HHS process was developed for ultrafine coal waste recovery, the scope of the process is not limited and the goal would be to replace existing fine coal circuitry in existing plants with the HHS process. Because of this several flotation feed samples have been previously tested by other researchers, and this research project continued some of that work with several flotation feed samples being discussed in upcoming sections. In this same light, middling samples provide an enormous opportunity for the HHS process to upgrade low-value coal product into salable high-value carbon material. In this respect, the scope of the HHS process can be expanded to include coarse material and handle a much larger role in existing and future coal preparation facilities.

The WV Coal C middling sample that was to be tested with the HHS process was coarse coal sample with a feed ash of roughly 29%. This material was very coarse with some material greater than a few inches in size. The sample underwent several series of crushing and grinding to test the material at four different size fractions. The size fractions tested were 100 mesh x 0, 300 μm x 0, 40 μm x 0, and 9 μm x 0. These fractions allow for the determination of the best liberation point for this material at the cheapest crushing and grinding stage. In order to prepare the samples, the whole sample was crushed using a jaw crusher and roll crusher to minus 1 mm in size. A laboratory Jones riffler was used to split the sample into smaller quantities for grinding while maintaining representative splits. The first of the four samples was pre-screened at the 100 mesh size class to test natural fines from the crushing circuit, while the remaining three samples were wet ground in a laboratory ball mill or attrition mill according to the sample preparation guidelines outlined in the previous section.

Overall the middling sample tested well. The results of the HHS testing, broken down by size class, are shown in Table 3-9. Combustible recoveries were consistently exceptional, ranging between 91% and 95%. Moisture values were all single digit across the four size classes, once again demonstrating the HHS process' ability as superior dewatering technology. Single digit ash values were never achieved during this testing period; however, at the weakest improvement, the ash content was upgraded from 28.7% to 17.7%, an 11% improvement. The best liberation was achieved at the finest size fraction which almost achieves the project goal of single-digit ash values, with roughly 12% ash in the HHS coal concentrate. However, there was essentially no change in the quality of the HHS product between 100 mesh and 40 μm , indicating liberation only occurred at the finest of size fractions. It would, therefore, be recommended to grind the material as fine as economically possible to achieve the highest value coal product from the HHS process, but only if economically viable to grind to minus 10 μm . As expected with high product ash values, ash rejection was low, and therefore separation efficiency was less than optimal ranging between 42% and 64%.

Table 3-9: WV Coal C Preparation Plant Middling Sample HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
		- 100 Mesh					
Pre-Screened	28.7	15.7	3.5	78.1	79.2	93.6	50.2
		15.5	3.2	78.2	79.0	93.6	50.8
d_{80} 300 μm	28.8	16.1	1.1	80.6	80.3	94.6	49.8
		15.0	1.2	78.9	78.4	93.6	52.8
d_{80} 40 μm	29.5	15.6	5.4	77.9	77.7	93.1	51.9
		15.5	8.8	77.9	77.6	93.0	52.2
d_{80} 9 μm	29.7	11.9	6.6	86.1	76.0	95.2	64.8
		12.1	9.7	85.8	76.1	95.2	64.2

A major project goal for this phase of the research project was to demonstrate the effectiveness of the HHS process in recovering coal from existing plant impoundments. As discussed previously, impoundment coal provides a large economic and environmental opportunity. Estimates state that active impoundments hold anywhere between 500 and 800 million tons of ultrafine coal product (Orr, 2002). The economic value in this virtually untapped resource is plain to see, but the environmental impact is also a major concern, and the HHS process could help to clean existing impoundment pounds while producing salable coal product. As such, Coal Company A provided a sample from their VA Coal A impoundment for HHS testing.

The sample was investigated for size analysis, which showed that 83% of the material was less than 0.35 mm in size with 53% of the material being less than 0.15 mm in size. Full results of the size-by-size analysis can be found in Appendix A. With a large percentage of coarse material present in the sample, the sample was wet ground in a laboratory ball mill to a d_{80} of 75 μm , using the standard sample preparation procedure. Feed ash for the sample was 35%. The results of the HHS testing on this sample are shown in Table 3-10. Combustible recoveries were adequate ranging from 64% to 70%. The HHS process was successful in demonstrating that single digit moisture and ash value product could be obtained from coal waste sitting in an active

impoundment. These results are encouraging, as they demonstrate that the HHS process can be used to recover coal from active impoundments at existing preparation facilities, which provide a large economic reserve.

Table 3-10: VA Coal A Impoundment HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
34.9	4.0	2.3	62.4	47.2	69.5	64.0
	3.5	3.9	62.8	47.1	69.9	65.0
	3.1	4.7	62.3	46.4	69.0	64.7
	3.3	4.2	61.9	46.1	68.4	64.1
	3.2	4.3	58.8	43.1	64.0	60.0

3.3.2 Coal Company B Batch Testing

In total 46 tests were completed on three different samples procured from Coal Company B's WV Coal D preparation plant. Initially, a true middling sample was sent for testing with the HHS process. Similarly, to the WV Coal C preparation plant middling sample, this was a non-traditional stream for the HHS process that would open the scope of the technology. The investigation of these middling samples was undertaken to determine the degree of upgrading that could be expected using the HHS process. The initial WV Coal D middling sample was a coarse coal sample. Per the testing procedure, the sample was crushed using a jaw crusher to a d_{80} size of 4 mm. It would then be wet ground in a ball or attrition mill according to the experimental sample preparation described in the previous section to the following size classes: [1] d_{80} of 100 μm , [2] d_{80} of 42 μm , and [3] d_{80} of 8 μm . Lastly, the sample was pre-screened at 100 μm to test natural fines after crushing.

The sample was tested with the standard HHS process, and the results of this testing are shown in Table 3-11. Feed ash across the various size classes ranged from 22% to 25%. Combustible recoveries were exceptionally high for these tests ranging from 96% to 98%, with corresponding coal yield values of 86% to 89%. The HHS process consistently produced single-

digit moisture values. Additionally, with the exception of two tests moisture values were less than 5% and three tests recorded less than 1% moisture. As with the aforementioned WV Coal C sample, single-digit product ash values were not achievable in this testing. Single digit ash values are a major project goal as they greatly increase the value of the coal product. The best liberation was seen at finest size class with product ash values ranging from 11% to 13%, however as with the WV Coal C middling sample, the two larger size classes showed no decrease in product ash values. As expected, due to high ash products, ash rejection was low and therefore separation efficiency was less than optimal. The best separation occurred at the best liberation with a separation efficiency ranging from 50% to 58%.

Table 3-11: WV Coal D Preparation Plant Middling HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
d_{80} 100 μm	25.7	17.1	0.8	78.9	86.0	96.0	38.9
		16.4	0.8	82.1	85.8	96.6	41.9
d_{80} 42 μm	25.5	16.9	2.3	81.5	86.9	96.7	38.8
		16.7	1.2	80.8	86.3	96.5	39.9
		16.6	4.7	80.8	86.2	96.4	40.2
d_{80} 8 μm	24.3	13.0	4.8	89.7	85.3	98.0	52.3
		13.5	5.2	89.7	85.8	98.1	50.5
		12.8	5.8	82.3	83.5	96.1	52.1
		11.3	1.8	84.1	82.1	96.2	58.1
-100 μm Pre-Screened	22.7	16.2	0.5	76.2	89.2	96.7	33.0
		15.7	2.9	76.2	88.4	96.5	35.3

During the testing period for this phase of the research project, two additional samples were collected from Coal Company B's WV Coal D preparation plant. The first of which was a low ash middling sample (LAM), collected from a secondary dense media cyclone circuit with roughly 30% feed ash. The second was a coarse reject sample (HAM) from which several samples were

produced by size and density separation, with feed ash values ranging from 49% to 95%. The sample characterization of the HAM sample is shown in the previous section. Per the testing procedure each sample was to be tested for viability with the HHS process at three different size classes: [1] 80 mesh x 0, [2] 325 mesh x 0, and [3] 10 μm x 0. Additionally, each sample would undergo a conventional flotation test for comparison with the HHS process. Each sample was prepared using the standard procedure, undergoing crushing and grinding techniques to produce the size classes required for testing. Per the HAM characterization, HHS and flotation tests were to be conducted on the plus 9.5 mm SG 2.2 float and sink material. However, both of these samples contained extremely high feed ash (>95%), and therefore it was determined that there was too little recoverable carbon material to warrant HHS or flotation testing.

For convenience, the testing summary is shown in Table 3-12. In general, all samples had some difficulty during HHS testing. Firstly, problems occurred during oil agglomeration and morganizer treatment for the coarsest size fraction (80 mesh x 0) for nearly all samples. Oil agglomeration was slow to occur, and in some cases, only a coal-oil foam was formed rather than spherical agglomerates. This was attributed to poorly liberated sample at the 80 mesh x 0 size range in which oil droplets did not attach to partially hydrophobic particles. Additionally, low population of coal material in some higher ash samples caused difficulty for oil-agglomeration, forming only micro-agglomerates after considerable retention time in the reactor. In the case of the 9.5 x 1 mm SG 2.2 sink HAM sample, a kitchen blender was required rather than the conventional Denver flotation cell for oil-agglomeration of the 80 mesh x 0 size fraction in order to increase the energy input for oil-agglomeration. Secondly, the coarser size range (80 mesh x 0) incurred consider losses due to coal settling in the morganizer during early testing. This problem was eventually overcome with increased pentane flow rate through the morganizer providing a higher rise velocity to carry coarser particles.

Table 3-12: LAM/HAM HHS and Flotation Testing Summary

Sample	Size (mm)	SG	HHS Product			Flotation Product		
			Ash (%) / Yield (%)			Ash (%) / Yield (%)		
			-80 M	-325 M	-10 µm	-80 M	-325 M	-10 µm
HAM	+9.5	Flt 2.2	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash
	+9.5	Snk 2.2	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash	High Feed Ash
	9.5x1	Flt 2.2	20.9/50.7	18.2/53.1	15.0/51.4	44.3/88.3	38.3/78.2	26.2/57.6
	9.5x1	Snk 2.2	10.6/2.0	15.7/2.8	11.8/2.9	75.9/20.3	76.7/19.0	78.7/12.7
	1x0.15	--	19.2/6.7	13.8/9.2	11.2/9.5	62.0/41.7	61.4/39.4	59.2/32.5
LAM	50x12.5	1.4x1.7	20.9/75.3	16.5/77.2	7.2/66.3	22.1/81.0	27.7/92.2	22.6/77.1

The detailed results for the samples tested are shown in Tables 3-13 through 3-20. In general, the best results are seen at the highest degree of liberation, the 10 µm size fraction. The LAM sample performed very well in this size fraction producing product ash values as low as 7%, with corresponding mass yields between 66% and 67%. Combustible recovery ranged from 85% to 98%. For the HAM samples micronizing the samples again yielded the best results. The 9.5 x 1 mm float sample was unable to produce single digit ash values but effectively reduced the ash content from 48.9% to 15% at the finest size, with a corresponding mass yield of 52%. Combustible recovery ranged from 78% to 86% across the various sizes. The 9.5 x 1 mm sink sample was nearly able to produce single digit ash values at the coarsest size range tested. This was likely due to the fact that coarse material was lost during the morganizer step and only ultrafine highly liberated coal was recovered. This would also make sense as it corresponds to the lowest mass yield, and the product collected was less than the remaining tests. Combustible recoveries were very low for this sample as well as the corresponding mass yields. Recovery values were all less than 25%, and mass yield values were less than 3%. The 1 x 0.15 mm sample had feed ash of roughly 80%. The product ash reduced across all three size classes but never produced single-digit ash values. Combustible recoveries were low ranging from 26% to 46%. All samples were able to produce single digit moisture values, once again proving the HHS as a superior dewatering technology. Flotation test results were poor across all size fraction for the samples tested. No

product ash values below 20% were achieved. The data clearly indicates that HHS is superior to flotation. Additionally, Figure 3-3 shows the separation efficiency plot for the HHS products vs. flotation products. Full separation efficiency data can be found in Appendix B across all samples.

Table 3-13: LAM HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	31.4	20.9	1.1	58.2	75.3	85.2	32.6
-325 M	32.2	16.5	1.1	85.5	77.2	95.1	55.6
		19.5	4.0	85.7	80.8	95.9	47.0
-10 µm	30.1	7.2	2.7	79.0	66.3	89.7	76.5
		8.3	3.4	78.6	67.1	89.7	73.9
		8.2	3.8	79.6	67.5	90.3	74.6

Table 3-14: LAM Flotation Testing Results

Feed Conditions	Feed Ash (%wt.)	Flotation Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	31.4	22.1	--	71.1	81.0	92.	35.0
-325 M	32.2	27.7	--	85.1	92.2	98.3	18.9
-10 µm	30.1	22.6	--	55.4	77.1	85.4	27.5

Table 3-15: HAM 9.5 x 1 mm Float Sample HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	48.9	30.7	1.2	77.2	60.9	82.5	44.3
		20.9	1.3	77.7	50.7	78.5	56.8
-325 M	48.8	18.2	2.3	83.5	53.1	84.9	65.1
		22.9	1.9	83.7	57.4	86.4	59.5
-10 µm	48.3	15.0	2.4	84.4	52.0	85.5	69.4
		16.0	5.6	84.7	52.3	85.0	68.6

Table 3-16: HAM 9.5 x 1 mm Float Sample Flotation Testing Results

Feed Conditions	Feed Ash (%wt.)	Flotation Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	48.9	44.3	--	83.7	88.3	96.3	16.3
-325 M	48.8	38.3	--	86.5	78.2	94.3	32.9
-10 µm	48.3	26.3	--	78.2	57.6	82.1	50.8

Table 3-17: HAM 9.5 x 1 mm Sink Sample HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	88.5	10.6	4.0	85.1	2.0	15.7	9.8
-325 M	89.5	15.7	2.8	91.6	2.8	22.2	22.0
		17.7	4.3	91.8	3.1	24.3	23.7
-10 µm	89.7	11.8	3.7	92.0	2.9	24.6	24.4
		12.4	4.1	91.5	2.3	19.4	19.2

Table 3-18: HAM 9.5 x 1 mm Sink Sample Flotation Testing Results

Feed Conditions	Feed Ash (%wt.)	Flotation Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	88.5	75.9	--	91.7	20.3	42.4	25.1
-325 M	89.5	76.7	--	92.5	19.0	42.1	25.9
-10 µm	89.7	78.7	--	91.3	12.7	26.3	15.1

Table 3-19: HAM 1 x 0.15 mm HHS Testing Results

Feed Conditions	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	79.6	20.1	1.4	87.6	11.8	46.4	43.3
		19.2	1.6	83.9	6.7	26.3	24.9
-325 M	79.7	18.3	1.7	88.7	12.8	51.5	48.6
		13.8	1.2	86.4	9.2	39.2	37.5
-10 µm	81.0	11.2	3.9	88.3	9.5	44.3	43.1
		11.4	6.8	88.5	9.7	45.4	43.9

Table 3-20: HAM 1 x 0.15 mm Flotation Testing Results

Feed Conditions	Feed Ash (%wt.)	Flotation Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
-80 M	79.6	62.0	--	92.2	41.7	77.7	45.2
-325 M	79.7	61.4	--	91.6	39.4	74.9	44.6
-10 µm	81.0	59.2	--	91.5	32.5	69.8	46.0

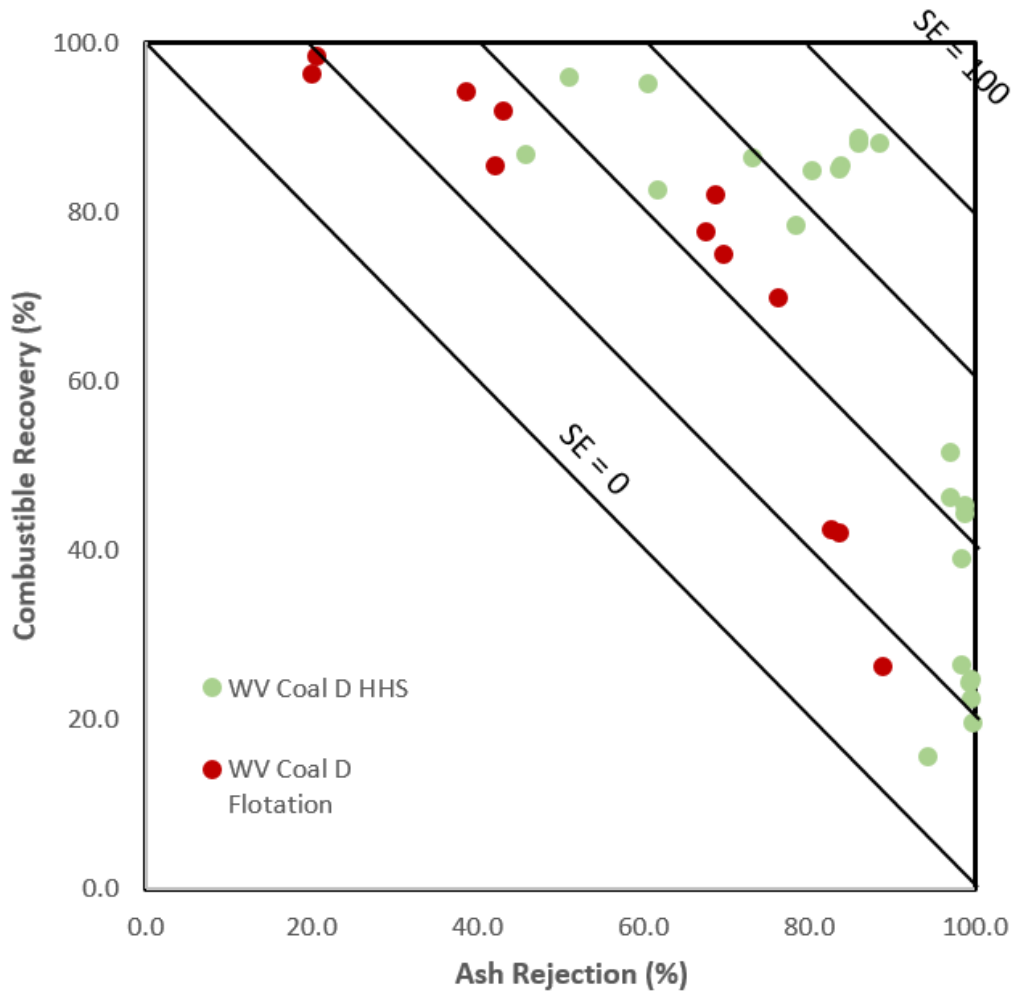


Figure 3-3: WV Coal D middling separation efficiency HHS vs. flotation

3.3.3 Coal Company C Batch Testing

In total seven tests were run on three samples received from Coal Company C’s WV Coal E preparation plant. The samples were more traditional coal waste streams from screenbowl effluent, thickener underflow, and underflow mud pump. Feed ash for these samples ranged from 60% to 74%. Unfortunately, the screenbowl effluent sample was unable to be tested with the HHS process due to the high feed ash of 74% and a very low solids concentration at only 1%, leading to the determination that the sample had no recoverable coal for practical purposes.

Table 3-21 summarizes the test results of the underflow mud pump and thickener underflow samples using the HHS process. Both samples appeared oxidized when they were

received and did not respond to conventional flotation. As such an attempt was made to add a dispersing agent and a hydrophobizing agent to induce oil-agglomeration and make the HHS process possible for these oxidized samples. Sodium silicate, a common dispersing agent, was added to the slurry in the Denver flotation cell and allowed to condition for several minutes. The sodium silicate helps to reduce slime build up depress ash. Sorbitan Monooleate was also added as a hydrophobizing agent, and allowed to condition the sample for several minutes in order to increase the hydrophobicity of the coal sample. With increased hydrophobicity provided by the Sorbitan Monooleate, small oil droplets were able to attach to coal particles and form micro-agglomerates. The thickener underflow sample had a feed ash of 66%. Single digit moisture and ash values were easily achieved with the HHS process. However, combustible recovery and mass yield were low, ranging between 20% and 32%, and 7% and 11% respectively. The underflow mud pump performed almost identically to the thickener underflow sample. Feed ash for this sample was 60%. Combustible recovery ranged from 22% to 35%, but single digit moisture and ash values were achievable. Overall, the samples were difficult due to the oxidation problem incurred but gave valuable insight into the HHS performance with oxidized samples. The HHS process was superior to flotation which had no response and achieved project goals of single-digit ash and moisture values. However, substantial reagent use was needed in order to promote oil-agglomeration.

Table 3-21: WV Coal E HHS Testing Results

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	%Solid	Ash	Moisture				
Thickener U/F			2.6	3.1	74.5	11.1	32.4	31.9
	66.5	22.4	2.5	2.4	71.2	6.8	19.9	19.6
			3.4	1.2	74.6	11.4	30.8	32.3
U/F Mud Pump	60.0	32.3	2.0	1.5	65.9	9.2	22.6	22.3
			2.0	1.8	66.1	9.5	23.3	23.0
			1.8	2.3	69.9	14.5	35.7	35.2
			1.6	3.2	65.8	9.0	22.2	21.9

3.3.4 Coal Company D Batch Testing

In total, 67 tests were conducted across ten samples from Coal Company D' KY Coal A preparation plant in Kentucky. Two of these samples were spiral concentrate samples from a low ash run and a mid-ash run. The remaining eight samples were a flotation feed, flotation concentrate, flotation tails, and screenbowl effluent samples, both for a 1% ash run, and a 3% ash run. Testing was completed on an as received basis and grinding basis to determine the efficiency and degree of upgrading of the hydrophobic-hydrophilic separation process in producing salable clean coal product. Sizing data, as well as, ash and recovery results were produced from each of these tests in accordance with typical testing procedures. For the flotation feed, flotation concentrate, flotation tails, and screenbowl effluent tests, as received samples were used to obtain the following results. Hence, no sample preparation was required. For convenience, the best results obtained with each test are shown in the test matrix, Table 3-22, below with detailed results to follow. In general, the best results are seen in the flotation product samples with very low ash, high yield, and high recovery.

Table 3-22: Test Matrix of KY Coal A Flotation Circuit and Screenbowl Effluent

Sample	Run	% Passing 100 Mesh	% Solids	HHS Product Ash (%) / Yield (%)
Flotation Feed	3%	97	3.4	2.1 / 35.3
	1%	97	2.1	1.3 / 50.2
Flotation Product	3%	99	9.1	1.9 / 85.9
	1%	98	17.9	1.2 / 83.3
Flotation Tailings	3%	97	2.9	2.2 / 35.6
	1%	95	2.4	1.4 / 49.1
Screenbowl Effluent	3%	98	0.9	N/A
	1%	99	1.0	N/A

The flotation circuit results are shown in Table 3-23, with all sizing data shown in Appendix A. For the 3% ash run of the flotation feed sample, sizing data indicated a large percentage of material below 100 mesh (approximately 97%), which is ideal for the hydrophobic-hydrophilic separation process. It also contained a relatively high feed ash of approximately 57%. The sample responded very well to the hydrophobic-hydrophilic separation process, producing single digit ash and moisture results around 2%, with combustible recoveries in 80% range.

However, yield was relatively low at only 35%, and a small amount of Sorbitan Monooleate (SMO) span 80 was added to improve the kinetics of oil agglomeration as a hydrophobizing agent similarly to what was done for the Coal Company C samples. The flotation feed sample was the only sample tested where this addition was required; all other samples performed very well as received. The flotation feed sample that was sent also contained a 1% ash run the results of which are shown below in Table 3-23. The sample responded very well to the HHS process. Oil-agglomeration was quick with just a small dosage of pentane and required no SMO addition. Additionally, the sample dispersed well in the morganizer. Size analysis yielded similar results to the 3% ash run, with approximately 97% of the material falling below 100 mesh. Feed ash on this run was lower, as expected, at 42% ash. The product reached the target ash of 1.5%, and moistures were low at 2% and 3%. The sample tested also recorded high combustible recoveries at 86%. For this test, with respect to the 3% ash run, yield was much better up to 50%, indicating that the HHS process is capable of recovering this stream.

The flotation product sample, 3% ash run, for KY Coal A also responded very well to the hydrophobic-hydrophilic separation process. This concentrate product coming from the flotation circuit has approximately 99% of its material passing 100 mesh. This is extremely advantageous for hydrophobic-hydrophilic separation, and as such the sample performed very well with oil agglomeration and the morganizer. Feed ash for this sample was very low at 13% and was reduced to around 2% ash in the hydrophobic-hydrophilic separation product, which met the target ash of -3%. Yield and combustible recovery were also very good around 86% and 97% respectively. This is a high-quality feed for the HHS process but less desirable on practical purpose to that of the flotation feed sample. Along with the 3% ash run, a 1% ash run for the flotation product at KY Coal A's preparation plant was tested, the results of which are also shown in Table 3-23 below. Again the sample responded very well to oil agglomeration and recovery from the morganizer which was encouraging. Approximately 98% of the material coming off the flotation circuit for this run passed 100 mesh. Ash reduction was very good for this sample, reducing from a feed ash of 14.5% to product ashes of 1.2% and 1.5%, which met the target of 1.5% ash. The yield was again very high at 84%, and the corresponding combustible recovery was exceptional at 94% to 96%, indicating good performance of the HHS process.

The flotation tailings samples were concerning as they appeared to very closely resemble the flotation feed samples we received. On a feed ash basis, they were nearly identical, and on a sizing basis, there was essentially no difference besides a minor change in coarse material ash content. This is indicative of a poor flotation circuit. However hydrophobic-hydrophilic separation results were encouraging, as well as, the performance of oil agglomeration without the need for any surfactant. The results for the 3% ash run indicate approximately 98% of the material fell below 100 mesh with feed ash of about 57%. The hydrophobic-hydrophilic separation process was able to successfully reduce the ash content down to 2.2% which meets the target ash. The process also achieved combustible recovery of 80%, and as seen with the flotation feed samples yield was relatively low at only 35%. The 1% run for the tailings of the flotation circuit performed similarly to the 3% run. Again there was a very close resemblance to the flotation feed sample. However, the kinetics for oil agglomeration were far better. Size analysis was similar, with 95% of the material falling below 100 mesh. This sample also reached a target product ash at 1.5% with product ash of 1.4%. Combustible recoveries were high at 85% to 86%, but again a low yield result of just 50% was observed. This yield is better than previous tests with similar feed characteristics but still relatively low compared to previous hydrophobic-hydrophilic results for other coals.

Both screenbowl effluent samples were extremely low in percent solids with only 0.9% and 1% for the 3% and 1% ash run samples respectively. Due to this low concentration of solids, hydrophobic-hydrophilic separation tests could not be run and only sizing data was recorded. The results of both size analyses are shown in Appendix A. Both samples appear to be appropriate for hydrophobic-hydrophilic separation on a size basis with 98% and 99% of material falling below 100 mesh in both cases. In fact, most of the material falls below 325 mesh which is typical for screenbowl effluent samples. Overall for these flotation circuit samples, the flotation product stream performed the best under hydrophobic-hydrophilic separation, however, all samples besides the screenbowl effluent reach their target ash values with very good recoveries. This circuit and corresponding coal seams can produce low moisture and low ash clean coal salable product. This is a major source of encouragement for the HHS process as the ultimate goal would be to replace existing flotation circuitry in preparation plants with the superior HHS process. This work serves to show that the HHS process is suitable for the purpose of handling flotation circuit feed and upgrading the material to high-value low ash and low moisture product while providing a cheaper dewatering technology.

Table 3-23: KY Coal A Preparation Plant Flotation Circuit HHS Testing Results

Sample	Feed (%wt.)		HHS Product (%wt.)		Refuse	Mass	Combustible	Separation
	Ash	%Solid	Ash	Moisture	Ash	Yield	Recovery	Efficiency
			(%wt.)	(%wt.)	(%wt.)	(%wt.)	(%wt.)	(%)
Flotation	57.7	3.4	2.1	2.1	87.8	35.1	81.2	80.0
Feed 3%			2.1	2.7	88.0	35.3	81.6	80.4
Flotation	42.4	2.1	1.4	2.6	84.0	50.3	86.2	84.6
Feed 1%			1.3	3.4	83.8	50.2	86.0	84.4
Flotation	13.4	9.1	1.9	4.5	83.1	85.9	97.2	84.7
Product			2.1	2.9	82.7	86.0	97.2	83.6
3%			2.2	7.3	83.0	86.1	97.3	83.3
Flotation	14.5	17.9	1.2	1.9	74.4	83.3	95.1	81.9
Product			1.2	5.5	73.6	83.2	94.9	81.4
1%			1.5	3.6	78.7	84.6	96.2	81.0
Flotation	56.9	2.9	2.2	2.5	87.0	35.4	80.5	79.1
Tailings			2.2	2.9	87.2	35.6	80.9	79.5
3%								
Flotation	43.0	2.4	1.5	1.8	83.5	49.4	85.3	83.6
Tailings			1.4	1.6	83.1	49.1	84.9	83.3
1%			1.6	1.2	84.4	50.0	86.3	84.5

The remaining two samples received from Coal Company D’s KY Coal A preparation plant were a low ash and mid ash run from their spiral circuit. This is coarser material by definition and not wholly suitable for hydrophobic-hydrophilic separation. Therefore, some sample preparation was required. A flowchart was developed to determine the proper testing procedure to take place. This flowchart is shown in Figure 3-4. Two tasks were determined as essential, task 1 feed characterization and task 2 laboratory testing to determine the degree of upgrading expected in the clean coal product. For the laboratory testing, the samples would be screen at 0.25mm. The undersize would be pre-concentrated using conventional froth flotation and the run through the hydrophobic-hydrophilic separation process as is, after grinding to 150 mesh, and after grinding

to 500 mesh. The oversize would be split to save a portion for Float-Sink analysis and then tested at three different sizes (60 mesh, 150 mesh, and 500 mesh). For all laboratory test, a target ash of -1.5% was considered. Ground samples were achieved using a laboratory ball mill for wet grinding, using approximately 300 grams of sample. For the grinding media, iron balls were used ranging from 6 to 26 mm in diameter with a relatively even distribution. Float-Sink data, unfortunately, has not yet been received at the time of this report.

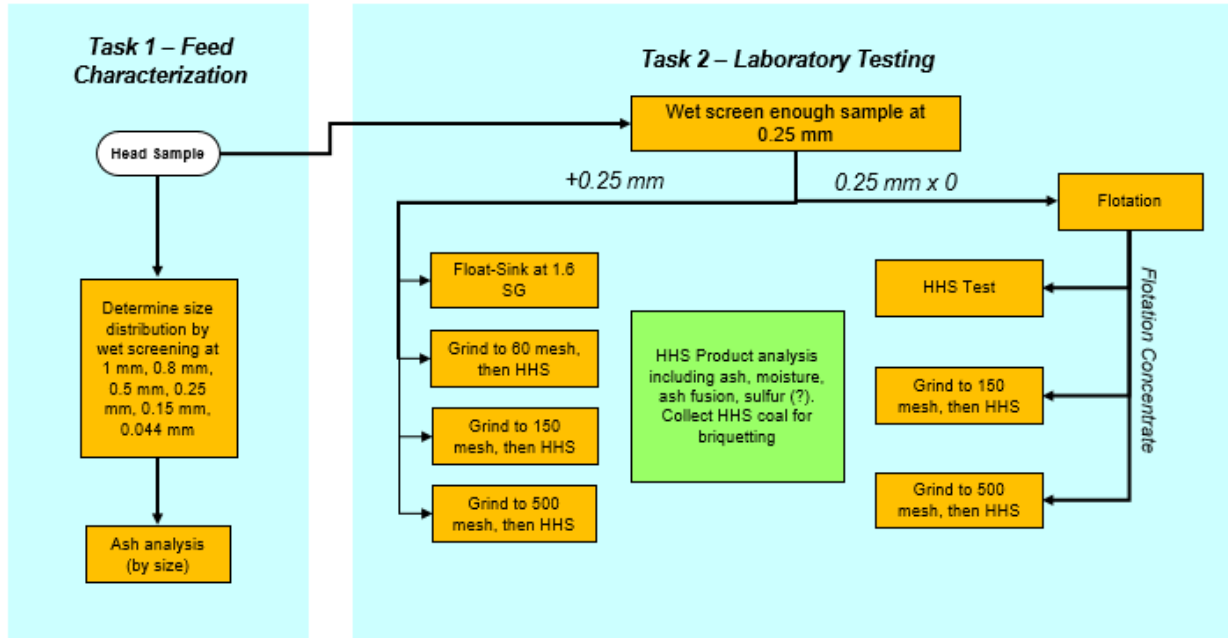


Figure 3-4: Procedure for KY Coal A preparation plant spiral concentrate HHS testing

The low ash run sample was tested first. The detailed results from these tests are shown in Table 3-24 for the undersize material and Table 3-25 for the oversize. Size analysis of the sample with individual and cumulative weight and ash are shown in Appendix A. A large portion of the as-received material (55%) was held in the $-0.84+0.25$ mm size fraction with a relatively low ash of just 3.1%. The difficulty with this sample seems to be with the fine fraction ($-0.15+0.045$ mm and -0.045 mm) which accounts for a very high ash at 26.8% and 63.2% respectively. This is typically the size fraction targeted for hydrophobic-hydrophilic separation, which is why there was more difficulty in producing the target ash of 1.5% for the undersize material than the oversize material. Several results were obtained for the -0.25 mm pre-concentrated run. The tests highlighted were run using a dispersant during the agglomeration stage in an attempt to improve the ash reduction of the sample by depressing fine clay material. Without dispersant, the results achieved

low ash but not at the target of 1.5%. Product ash values were between 1.5% and 1.7% with high yield and recovery. However, using a small amount of sodium metaphosphate dispersant, the process was able to achieve 1.1% and 1.2% ash values. This is likely due to the presence of fine clay in the slurry feed. Recoveries for this series of test were around 97%, and yield was around 80%. Once the undersize material was ground to 80% passing 95 microns, there was still a need to use a dispersant to achieve the target ash. Ash values of the product ranged from 0.9 to 1.1 after use of dispersant. The undersize was also ground all the way to 80% passing 24 microns, and the results were similar. Dispersant helped to achieve target ash values between 1.3 and 1.5. This all indicates that for this sample there is no significant advantage to grinding as increased liberation does not equate to lower ash products. However, the addition of dispersant can help achieve extremely low ash values, with low moisture and high recovery.

In the oversize material for this sample, the process observed the opposite phenomenon. Grinding still made very little difference to the product ash results, yields, or recoveries, however, the addition of dispersant (tests shown in highlighted cells) did not help achieve any lower ash values. This supports the theory that there is a large portion of fine clay material in the undersize fraction, which would not be present in the oversize. Interestingly, all tests on the oversize material, even at the coarsest size, met the target ash value. When ground to 80% passing 270 microns, ash values were around 1%. When ground to 80% passing 80 microns, ash values were between 1% and 1.1%. When ground to 80% passing 35 microns, ash values were also around 1%. For all sizes yield values were extremely high around 97% and recovery values were around 99% for both combustible and organic recovery. All moisture values were low, typically less than 5%.

Table 3-24: KY Coal A Low Ash Spiral Concentrate Undersize 0.25 mm x 0 HHS Test Results

Feed State	Head Feed Ash (%wt.)	HHS Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)	
			Ash	Moisture					
-0.25 mm	18.1	10.0	1.5	1.9	75.6	77.7	93.5	86.6	
			1.5	1.7	73.0	76.6	92.1	86.5	
			1.7	2.9	79.4	78.7	94.5	87.9	
		9.7	1.2	1.4	82.2	80.7	96.9	85.0	
			1.2	3.3	82.4	80.8	97.0	84.9	
d_{80} 95 μm	18.1	8.8	1.6	2.5	71.6	77.0	92.5	83.5	
			1.5	5.4	71.4	76.9	92.5	83.6	
		8.8	0.9	5.3	74.7	77.8	94.1	85.8	
			1.1	4.5	75.5	78.0	94.2	86.0	
			1.1	3.1	69.2	75.7	91.4	84.3	
			1.0	5.0	77.0	78.3	94.6	87.0	
d_{80} 24 μm	18.1	9.5	1.4	5.5	76.7	78.5	94.5	85.6	
			1.4	7.0	76.5	78.5	94.5	85.4	
		9.5	1.4	4.5	78.0	78.9	94.9	85.9	
			1.5	6.2	78.8	79.1	95.0	86.1	
			9.1	1.3	4.3	79.6	78.9	94.6	87.9
				1.3	4.2	79.7	78.9	94.6	88.0

Table 3-25: KY Coal A Low Ash Spiral Concentrate Oversize +0.25 mm HHS Test Results

Feed Size	Ground Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
d_{80} 270 μm	2.6	1.1	3.2	58.2	97.3	98.8	59.2
		1.1	2.2	59.0	97.4	98.9	57.9
	2.6	1.1	2.7	59.5	97.4	98.9	58.4
		1.1	2.2	59.1	97.4	98.9	58.0
		1.1	5.4	74.4	98.0	99.4	54.7
d_{80} 80 μm	2.7	1.0	2.6	74.5	98.0	99.5	54.9
		1.2	3.3	73.7	97.9	99.4	56.7
	2.7	1.1	4.3	73.9	97.8	99.4	59.6
		1.1	2.6	74.8	97.9	99.5	57.7
		1.1	4.2	69.1	97.8	99.3	57.8
d_{80} 35 μm	2.6	1.0	3.7	69.0	97.7	99.3	60.3

The mid ash sample was the last to be tested. Similar to the low ash spiral sample a large portion of material (50%) was held in the -0.84+0.25 mm size fraction with a relatively low ash of just 3.6%. Again the -0.15+0.045mm and -0.045mm sizes contained high ash values at 33.8% and 79.3% respectively. After testing the low ash sample and determining that a dispersant would help achieve the target ash value of 1.5%, it was decided to run tests with dispersant on this sample as well. The detailed results of these tests for the mid ash sample, with dispersant tests highlighted, are shown in Table 3-26 for the undersize material and Table 3-27 for the oversize. Interestingly enough, it was determined for these samples that not only did increase grinding not help reduce ash values significantly by improvement in liberation but neither did the addition of a dispersant. For the undersize material product, ash values remained around 1.7% regardless of grinding conditions, which is a little higher than the target ash of 1.5% but still a significant reduction from the feed ash of 27.1%. Yield and recovery for these tests were around 70% and 90% respectively across all grinding tests. For the oversize material, there was a slight reduction in ash from 1.5%

to 1.3% when moving from 80% passing 230 microns to 80% passing 28 microns. The oversize, like the low ash sample, performed much better overall hitting the target ash and achieving high yield and recovery. In general, for these two samples, the oversize material with slight grinding can be a very good feed stream for the hydrophobic-hydrophilic separation process, while the undersize material will require the use of dispersant to be effective.

Table 3-26: KY Coal A Mid Ash Spiral Concentrate Undersize 25 mm x 0 HHS Test Results

Feed State	Head Feed Ash (%wt.)	HHS Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
			Ash	Moisture				
-0.25 mm	27.1	10.2	1.6	6.0	76.3	65.9	88.9	85.0
			1.6	3.5	76.6	66.0	89.1	85.2
		10.2	1.5	2.1	77.4	66.3	89.6	85.8
			1.6	2.7	76.9	66.1	89.3	85.4
d_{80} 75 μm	27.1	10.2	1.8	3.1	85.5	69.7	94.0	89.5
			2.0	3.6	84.9	69.7	93.7	88.6
		10.2	1.7	3.4	79.9	67.5	91.0	86.8
			1.8	4.1	80.0	67.6	91.1	86.7
d_{80} 30 μm	27.1	10.4	1.9	5.0	80.8	68.1	91.6	86.8
			2.1	6.7	80.7	68.2	91.6	86.3
		10.4	1.7	4.0	79.3	67.3	90.7	86.4
			1.8	4.9	79.6	67.5	90.9	86.4

Table 3-27: KY Coal A Mid Ash Spiral Concentrate Oversize +0.25 mm HHS Test Results

Feed Size	Ground Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
		d_{80} 230 μm	3.2				
		1.6	2.5	44.5	96.3	97.9	49.3
	3.2	1.5	2.7	50.9	96.5	98.2	53.9
		1.6	5.0	48.7	96.7	98.3	48.5
d_{80} 75 μm	3.3	1.4	3.1	45.5	95.6	97.5	58.1
		1.4	2.6	45.4	95.7	97.6	56.7
	3.3	1.4	2.6	42.6	95.4	97.3	56.7
		1.5	2.9	43.1	95.6	97.4	54.8
d_{80} 28 μm	3.2	1.3	8.2	60.0	96.7	98.6	60.5
		1.3	7.5	59.8	96.7	98.6	60.3
	3.2	1.4	5.4	57.3	96.2	98.3	66.0
		1.4	9.2	58.0	96.6	98.5	60.0

Altogether, of the tested samples, the flotation circuit streams (particularly the flotation product stream), tested very well for the hydrophobic-hydrophilic separation process. All tests done on these samples achieved low ash, low moisture product that met the set project specifications. The oversize material from both the low ash and mid ash spiral concentrate samples also performed extremely well. The degree of upgrading is phenomenal in these samples as it is with the flotation circuit. Extremely low ash high-value product can be produced from these streams with little grinding necessary. The undersize material looks promising as well, and capable of extremely low ash product. However, it will require the addition of some dispersant to aid in the agglomeration process. Therefore, the HHS process is ideally suited to recover these process streams, adding value to the technology as a whole and increasing the scope of the HHS process to include coarse streams for upgrading the value of the product, as well as, handling typical flotation circuitry feed.

3.3.5 Coal Company E Batch Testing

Coal Company E located in Kentucky mines abandoned impoundment coal to produce a high-value coal-oil fuel. A pond fines sample (KY Coal B) was received from their operation for HHS testing. In this series of testing, it was investigated the effect of dispersant, grinding, and subsequent re-cleaning methods in order to produce an extremely low ash coal product (less than 1% ash). The HHS has proven to be a superior technology for recovering ultrafine coal waste and upgrading low-value coal products. Therefore this would be another market for the HHS project to expand its scope if proven able to produce the specified ash values. In total, 30 tests were completed on this sample under several different operating conditions. Initially, to establish a baseline for testing, a few tests were run on the as-received sample to determine the degree of upgrading and recoverability the HHS process can provide without any sample preparation or reagent addition. In these tests, the results of which are shown in Table 3-28, product ash values were low ranging between 3.4% and 3.9% but failed to reach less than 1% ash. Combustible recoveries ranged between 80% and 84%, with corresponding yield values between 44% and 47%.

Table 3-28: KY Coal B Pond Fines As-Received HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
46.5	3.9	1.6	84.1	46.9	84.2	80.3
	3.9	2.2	84.3	47.0	84.4	80.5
	3.4	1.8	80.9	44.3	80.2	76.9
	3.9	5.6	84.0	46.8	84.1	80.2

After failing to achieve the target product ash on an as-received basis, it was decided to attempt to improve liberation by grinding the sample in a laboratory ball mill to a d_{80} size of 12 microns. For these tests, steel media was used in the ball mill with media size ranging from 6 to 26 mm. This grinding did little to improve the ash reduction with product ashes between 3.2% and 4.9%. However, in the last test, there was a slight improvement to 2.6% ash. Combustible recovery values were high averaging around 89%, and single digit moisture values were consistently

achieved. This was achieved by subjecting the ground feed to oil-agglomeration (traditional HHS), and then screening off the agglomerates and re-agglomerating to remove more entrained ash. It is well known, that the agglomerate structure traps large water globules which are crucial to its stability and that mineral matter is typically associated with these globules. It is for this reason that subsequent re-cleaning of the agglomerates may improve ash reduction following the morganizer step of the HHS process. The results of the tests are shown in Table 3-29.

Table 3-29: KY Coal B Pond Fines Ground Feed d_{80} 12 μm HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
46.5	3.9	4.6	84.1	46.9	84.2	80.3
	3.8	5.4	84.3	47.0	84.4	80.6
	4.9	3.5	89.9	51.1	90.8	85.4
	3.2	5.5	89.5	49.9	90.2	86.7
	3.9	2.5	88.6	49.7	89.2	85.1
	2.6	1.9	88.4	49.0	89.0	86.2

After seeing marginal improvement in ash reduction with re-cleaning of the agglomerates, the sample was ground to a d_{80} of 8 microns and subjected to various re-cleaning stages. Again this was done in a laboratory ball mill with steel media. One to four stages of re-cleaning were tested to see if any improvement could be made. Product ash values ranged between 1.9% and 2.9% for these tests which again missed the target of <1%. Single digit moistures were achieved regardless, along with combustible recovery values in the mid-80% range. However, with more re-cleaning stages employed, the greater the ash was reduced, and this progress is encouraging for the HHS process. The best results obtained in these test came with three or four stages of re-cleaning. The results for these tests are shown in Table 3-30. Figure 3-5 shows a graphical representation of the product ash reduction as a function of the number of re-cleaning stages.

Table 3-30: KY Coal B Pond Fines d_{80} $8 \mu\text{m}$ Re-Cleaning HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
46.3	2.9 ¹	2.8	83.3	45.8	83.1	80.3
	2.5 ²	4.7	84.2	46.1	84.0	81.7
	2.3 ³	2.2	84.2	46.0	84.0	81.9
	2.0 ⁴	1.7	84.0	46.0	83.9	81.9
	2.1 ⁴	1.1	83.8	45.9	83.7	81.6
	1.9 ³	1.5	86.2	47.3	86.5	84.5
	1.9 ³	2.3	80.0	43.1	78.8	77.1

¹ One-stage re-cleaning of agglomerates prior to the Morganizer; ² Two-stage re-cleaning; ³ Three-stage re-cleaning; ⁴ Four-stage re-cleaning.

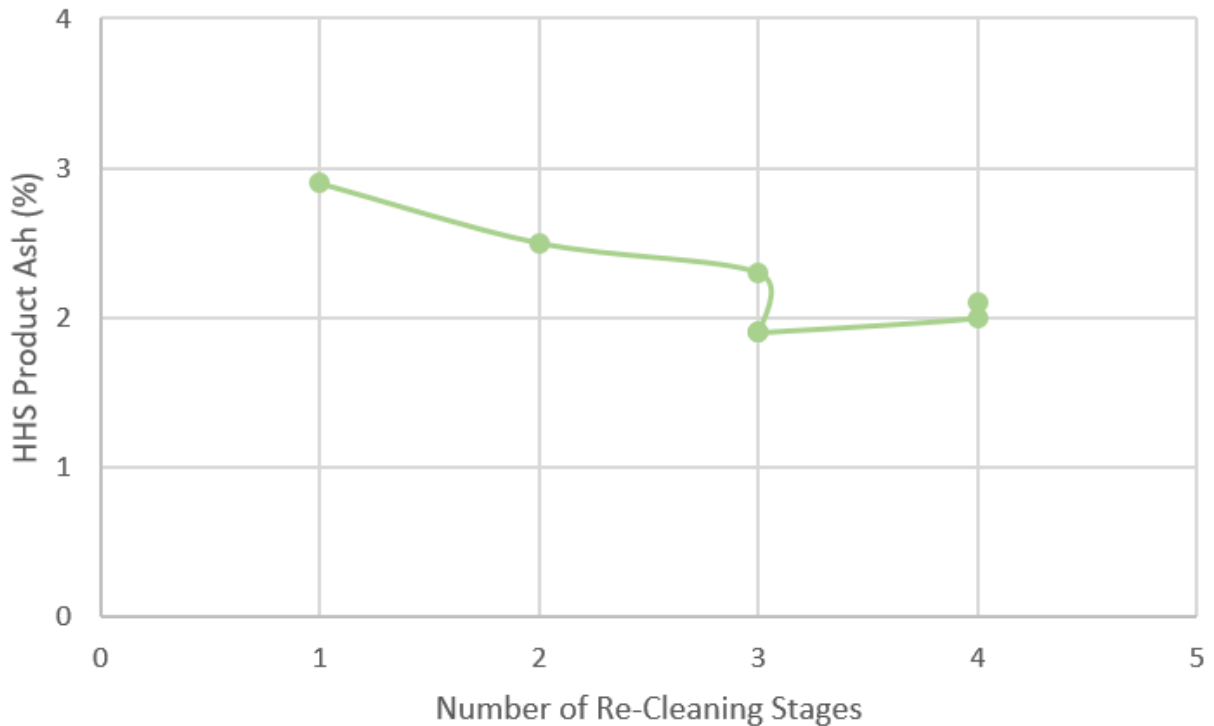


Figure 3-5: KY Coal B pond fines graphical representation effect of re-cleaning stages

After seeing the effect of subsequent re-cleaning stages, it was determined to try to improve the ash reduction by attrition mill grinding rather than ball mill grinding and to use sodium silicate during the oil-agglomeration step as a dispersant to help reduce ash content in the agglomerates. The results did not differ much from previous tests. The use of sodium silicate had no effect in reducing the product ash, and it was actually observed that in the tests with sodium silicate, product ash values were higher than without. The feed was ground in an attrition mill to a d_{80} of 5 microns using steel media. Product ash values ranged from 2.4% to 3% for these tests, the results of which are shown in Table 3-31.

It was then decided to try attrition mill grinding the agglomerates down to a d_{80} of 4 microns. It was also decided to switch from using steel media, as in the previous tests, and use ceramic media to reduce the possibility of grinding the media/mill and increasing the ash content. For these tests, product ash values were between 1% and 1.2%, with corresponding combustible recoveries ranging between 83% and 86%. This was very close to the target of <1% ash. In fact, one test produced a 0.96% ash product after two-stages of agglomerate re-cleaning. It would appear that this approach of regrinding oil-agglomeration product is the most effective way to produce very low ash product with the HHS process. The results of the tests for grinding agglomerates are shown in Table 3-32. Figure 3-6 shows the performance plot of grinding prior to agglomeration and grinding after agglomeration. For achieving super clean coal of less than 1% ash, grinding the agglomerates followed by conventional HHS is the superior method, however, it comes with the cost of a slight decrease in combustible recovery, and therefore separation efficiency is slightly lower for these tests as well. Furthermore, the use of ceramic media appeared to aid in reducing the effect of chipping media in the attrition mill, which likely attributed to the low ash values seen in the agglomerate grinding tests.

Table 3-31: KY Coal B Pond Fines Attrition Mill Grinding HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
52.2	3.0	3.1	91.9	44.7	90.7	88.1
	2.7 ¹	2.9	91.8	44.2	89.9	88.2
	2.7 ²	1.7	91.6	44.4	90.2	87.9
	2.6 ³	1.9	91.5	44.3	90.1	87.9
	2.5 ¹	2.3	92.2	44.6	91.0	88.8
	2.5 ²	3.7	91.9	44.4	90.6	88.5
	2.4 ³	1.8	91.6	44.3	90.3	88.2

¹ One-stage re-cleaning of agglomerates prior to the Morganizer; ² Two-stage re-cleaning; ³ Three-stage re-cleaning. For the first 4 tests, sodium silicate was used as dispersant during agglomeration, For the last three, no dispersant was used.

Table 3-32: KY Coal B Pond Fines Attrition Mill Grinding Agglomerates HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
46.5	1.21	0.8	86.3	46.8	86.4	85.2
	1.03	1.3	86.3	46.6	86.2	85.3
	0.96	0.9	86.1	46.5	86.1	85.1
	1.14	2.1	85.7	46.4	85.7	84.5
	1.07	2.3	85.7	46.3	85.7	84.6
	1.02	1.7	85.6	46.3	85.6	84.5

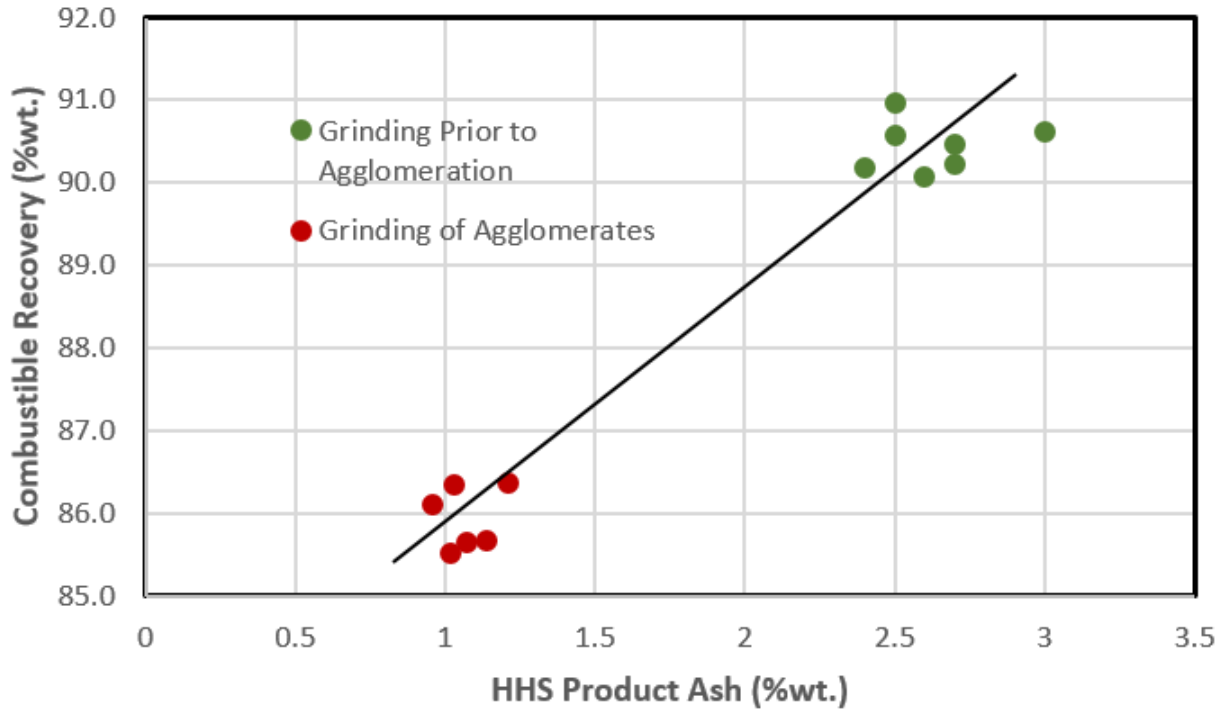


Figure 3-6: Performance plot KY Coal B pond fines grinding prior to agglomeration vs. grinding after agglomeration HHS testing

3.3.6 Coal Company F Batch Testing

In total, 25 tests were conducted across six samples received from Coal Company F’s India Coal A washery in West Bokaro. The site operates a heavy media washery for producing coking coal. The washery provided the following samples for testing: [1] Flotation Feed (minus 0.5 mm), [2] Flotation Feed (minus 0.25 mm), [3] Froth Product, [4] Tailings, [5] Combined Tailings Set 1, and [6] Combined Tailings Set 2. Size by size analysis was completed on each sample and is presented in Appendix A. These tests were conducted in order to validate the HHS process’ performance on coal from a region other than the Appalachian region of the United States. India presents a large opportunity as their coal industry continues to expand.

In the first testing group, the minus 0.5 mm flotation feed sample was investigated. As earlier discussed the scope of the HHS process is not limited and flotation feed is a primary target of HHS testing, in the attempt to change existing coal preparation plants by replacing the flotation

circuit with the HHS process. Size analysis indicated a large percentage of coarse material with 41.6% of the material above 0.15 mm, and 22.2% of the material above 0.3 mm. The d_{80} size of this sample was 0.325 mm. Because testing was conducted on an as-received basis with no sample preparation the coarse nature of the sample presented some problems for the morganizer. Initially, significant losses were observed during the morganizer stage of the HHS process with coarse material settling in the column. Similarly, to other coarse samples tested, the upward flow velocity of pentane oil through the morganizer had to be increased to combat this settling velocity. After some initial trial and error, four successful tests were conducted. The feed ash for these tests was 20%. Single digit moisture and ash values were achieved, with average values of 3.1% and 6.2% respectively. Combustible recovery was high for these tests ranging between 89% and 91%. The full test results are shown in Table 3-33. Additionally, a flotation release analysis was conducted, which gives the theoretical best performance that can be achieved with flotation. A performance plot was developed to compare the results of the release analysis with the results of the HHS process, and is shown in Figure 3-11. As shown in this plot the HHS process is far superior to flotation and is well suited to recover this stream.

Table 3-33: India Coal A Flotation Feed (-0.5mm) HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
20.1	7.5	1.7	66.9	78.9	91.3	61.6
	6.9	4.1	66.5	77.9	90.7	63.9
	5.0	3.1	64.6	74.8	88.9	69.9
	5.3	3.4	66.4	75.8	89.8	69.8

The flotation feed (minus 0.25 mm) sample performed extremely well with the HHS process, and the results are shown below in Table 3-34. There was significantly less coarse material in this sample with a large percentage of material less than 0.15 mm. The d_{80} size of the feed was 0.125 mm. Single digit moisture and ash values were again achievable by HHS indicating that the process is a very efficient cleaning and dewatering technology. Product ash values ranged between 6% and 7%, with corresponding combustible recoveries ranging between 93% and 94%.

Additionally, a flotation release analysis was also run to compare with HHS results, which is shown in Figure 3-7. The results of this analysis again show that HHS is superior to flotation and can be used to recover this stream.

Table 3-34: India Coal A Flotation Feed (-0.25mm) HHS Testing Results

Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
	Ash	Moisture				
21.4	7.6	3.2	76.7	80.0	94.1	65.7
	7.9	3.0	74.2	79.6	93.3	64.0
	6.4	3.7	75.3	78.2	93.1	69.8
	6.9	3.6	75.9	78.9	93.5	68.3

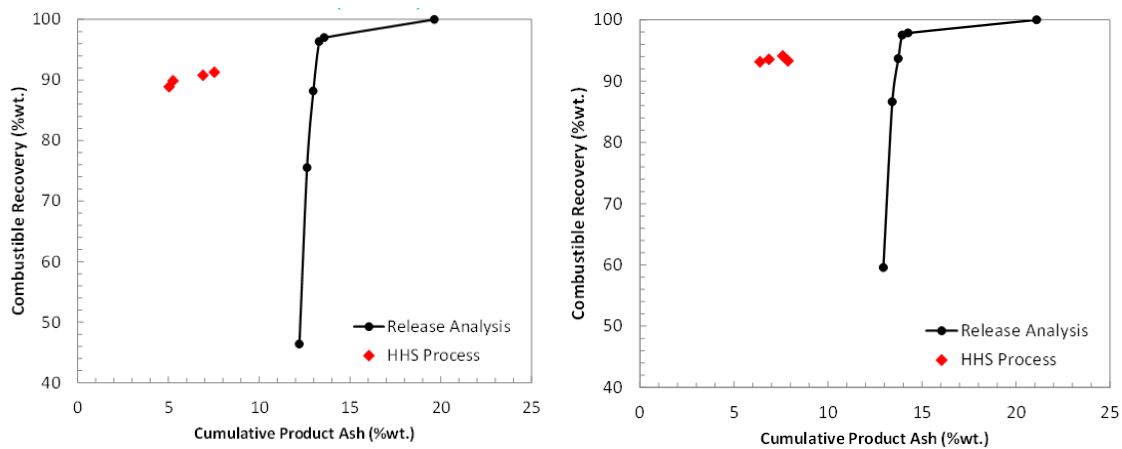


Figure 3-7: India Coal A flotation feed (Left) -0.5 mm HHS vs. flotation release (Right) -0.25 mm HHS vs. flotation release

The froth product sample had a d_{80} size of 0.425 mm, with a significant amount of coarse material. The sample responded well to the HHS process but had some difficulties with coarse material much like the minus 0.5 mm flotation feed sample. As such two tests were run with the feed prescreened at 0.425 mm, and this size fraction performed much better increasing ash rejection and combustibility recovery. For the as received feed ash and moisture values were low, averaging 4.2% and 2.1% respectively. Combustible recovery was roughly 81% with a yield around 70%. The prescreened sample increased combustibility recovery to between 93% and 95%

with a mass yield as high as 80%. The full results of these tests are shown in Table 3-35. The last result in the table represents the final product characterization if the +0.425 mm size fraction was blended back in with the HHS process.

Table 3-35: India Coal A Froth Product HHS Testing Results

Feed Size	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
		As Received	17.2				
Pre-Screened 0.425 mm	18.6	4.1	2.3	48.4	70.5	81.6	64.7
		5.5	3.1	72.3	80.4	93.3	69.5
		5.0	2.8	71.9	79.7	93.0	71.5
Blended Product	17.2	6.9	--	72.3	84.3	94.7	60.8

Three separate tailings samples were collected from Coal Company F's India Coal A washery. The results for the tests on these samples are shown in Tables 3-36, 3-37, and 3-38. Size analysis indicated that these samples had a large percentage of coarse material having d_{80} sizes of 0.675 mm, 0.6 mm, and 0.55 mm for the tailings, combined tailings set 1, and combined tailings set 2 samples respectively. Feed ash values varied for these samples ranging from 36% to 50%. Because of the large percentage of coarse material, the last two tests of each sample were run after pre-screening the material. The true tailings sample did not respond well to HHS. Coarse material (+0.425 mm) presented a major problem combining for 59% of the mass and assaying 49.7% ash. Single digit moisture and ash values were achieved, however, combustible recovery and mass yield were low resulting in 46% and 24% respectively at their highest. The combined tailings sets tested better with the HHS process. Combustible recoveries ranged from 61% to 74% across these samples with single digit ash and moisture values. Overall the HHS process performed well on coarser Indian coal samples and has the ability to recover these sample streams. Coal preparation

facilities in India are lacking this type of technology and the implementation of HHS in these plants could provide a major upgrade to coal preparation in India.

Table 3-36: India Coal A Tailings HHS Testing Results

Feed Size	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
As Received	49.9	4.6	6.2	61.0	19.8	37.6	35.7
		4.8	3.4	60.5	19.0	36.3	34.3
Pre-Screened 0.425 mm	50.2	4.1	2.9	64.9	24.2	46.6	44.6
		4.5	2.4	64.4	23.7	45.5	43.3

Table 3-37: India Coal A Combined Tailings Set 1 HHS Testing Results

Feed Size	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
As Received	41.4	5.1	3.5	63.8	38.2	61.8	57.1
		4.5	1.5	64.8	38.7	63.1	59.0
Pre-Screened 0.5 mm	46.0	5.4	1.8	74.1	40.9	71.7	66.9
		5.2	2.6	74.8	41.4	72.7	68.0

Tale 3-38: India Coal A Combined Tailings Set 2 HHS Testing Results

Feed Size	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
		As Received	36.7				
Pre-Screened 0.425 mm	39.9	4.4	2.2	61.1	43.0	65.0	59.8
		6.6	1.6	70.3	47.8	74.2	66.3
		6.3	7.4	70.0	47.3	73.7	66.2

3.3.7 Coal Company G Batch Testing

Coal Company G sent four samples from three different washery operations in India. These samples were examined on a size-by-size basis and tested for effectiveness with the HHS process. These tests serve to demonstrate the ability of the HHS process to process raw coal, if economically viable, expanding the scope of the technology. Additionally, these tests, along with the India Coal A tests serve to prove the viability of the HHS process on India coals. In total, 34 tests were conducted on the following samples: [1] India Coal B Washery Fine Coal, [2] India Coal B Washery Raw Coal, [3] India Coal C Washery Raw Coal, and [4] India Coal D Washery Raw Coal. Size analysis was completed on each sample and can be found in Appendix A. For the India Coal B fine sample size analysis was completed on an as received basis, while for the raw coal samples size analysis was completed on each grind size that was tested.

For the India Coal B fine coal sample, both HHS testing and flotation testing was conducted for comparison of performance. The sample, though labeled a fine coal, had a fairly significant portion of coarse particles (> 0.3mm). Therefore, testing was completed on an as-received basis as well as pre-screened to 300 µm, 150 µm, and 75 µm. The fine coal sample, the results of which are shown in Tables 3-39 and 3-40, performed well under HHS testing producing single digit ash and moisture values across all sizes. Combustible recovery averaged 76%, with increasing

recovery as the particle size decreased. Flotation results, which are shown in Table 3-40, were poor compared to HHS results, which is encouraging when noting that the HHS process would eventually replace this circuit. Flotation product ash was substantially higher, as high as 18.2% in one test, with low combustible recoveries ranging from 38% to 78%. From the data, it is clear to see that the HHS process is far superior to flotation in producing low moisture clean coal product at a lower cost than conventional fine coal dewatering methods. Furthermore, this superiority is represented in Figure 3-8, which show a performance plot (ash vs. recovery) and separation efficiency for HHS vs. flotation. Overall, these results indicate that the HHS process is well suited to recover this fine coal stream which is a major source of opportunity in India.

Table 3-39: India Coal B Fine Coal HHS Testing Results

Sample	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
As Received	33.3	4.0	5.8	56.3	43.9	63.2	58.0
		3.5	2.8	55.9	43.1	62.4	57.9
Pre Screened 300 µm	36.5	4.2	8.0	72.6	52.8	79.6	73.5
		4.0	6.3	73.2	53.0	80.1	74.4
Pre Screened 150 µm	40.4	5.1	9.3	78.5	51.8	82.6	76.1
		5.0	2.5	77.8	51.4	81.9	75.5
Pre Screened 75 µm	46.4	5.0	1.9	78.8	44.0	77.9	73.1
		5.0	4.7	78.6	43.8	77.6	72.8

Table 3-40: India Coal B Fine Coal Flotation Testing Results

Sample	Flotation Time (min)	Feed Ash (%wt.)	Product Ash (%wt.)	Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
As Received	0.5	33.7	15.0	44.7	36.9	47.4	31.0
	1.0		16.9	59.5	60.6	75.9	45.5
Pre Screened 300 μm	0.5	35.9	13.1	51.5	40.8	55.2	40.2
	1.0		15.5	65.6	59.4	78.2	52.5
Pre Screened 150 μm	0.5	39.9	12.6	49.7	26.5	38.5	30.1
	1.0		15.3	59.4	44.2	62.3	45.4
Pre Screened 75 μm	0.5	46.0	14.1	58.0	27.3	43.4	35.1
	1.0		18.2	66.3	42.3	64.0	47.2

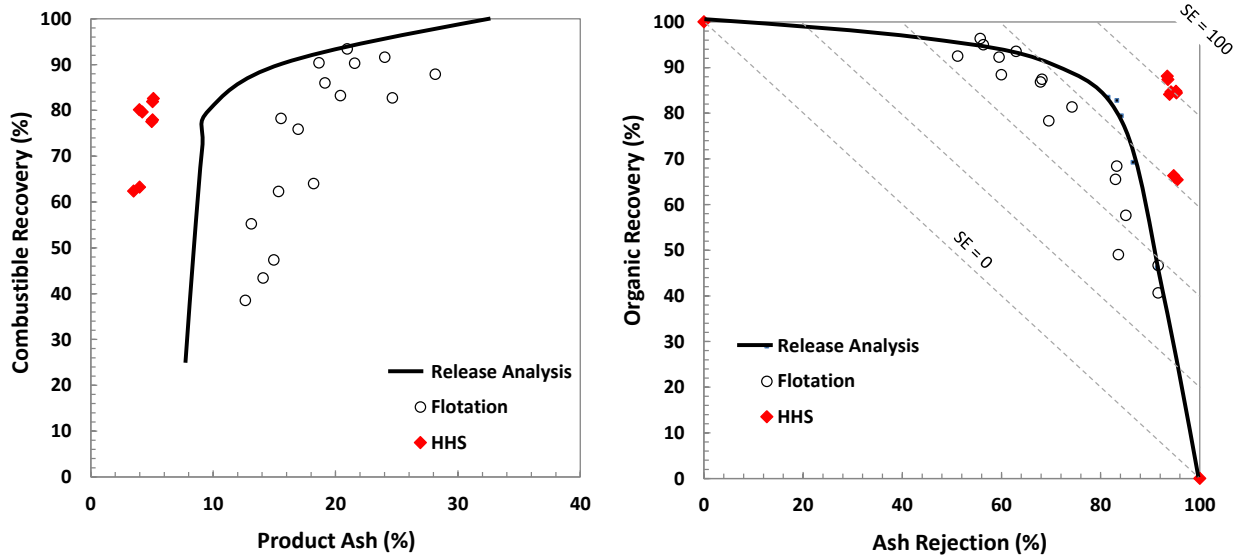


Figure 3-8: India Coal B fine coal (Left) performance plot flotation vs. HHS (Right) separation efficiency flotation vs. HHS

The raw coal samples all performed well under HHS testing producing low ash and low moisture products with high combustible recoveries. The process as a whole responded well to upgrading raw coal feeds. The limiting factor in these tests is the level of sample preparation required to work the samples down to reasonable sizes for HHS testing. Crushing and grinding is necessary to reduce the particle size of these samples for HHS testing. In light of this issue, three different degrees of grinding were tested on each sample to identify at what level of grinding the best results are achieved, and whether suitable results can be obtained at the cheapest level of grinding. Ideally, HHS would be adapted to replace the flotation circuitry in these plants and not handle raw feed. However, the results for the tests on raw feed are encouraging and indicative of good performance. The results of the raw coal tests are shown in Tables 3-41, 3-42, and 3-43 for India Coal B, India Coal C, and India Coal D respectively.

The India Coal B washery circuit treats 80 mm x 0 raw coal and has a plant capacity of 3 million metric tons/year. The current circuit evolves a heavy media bath for treating 80 x 13 mm, heavy media cyclone for treating 13 x 0.5 mm, and flotation for treating 0.5 x 0 mm. However, the flotation circuit is currently not operated by the washery. This is a substantial opportunity for the HHS process, especially on the fine circuit. The fine coal stream is a major target for the HHS product due to the fact that, as shown above, the HHS process can efficiently upgrade the quality of that coal and produce high recovery product. For the raw coal feed, sample preparation was required, and the standard procedure used. Three different grind sizes were tested: [1] 220 μm , [2] 160 μm , and [3] 65 μm . Combustible recoveries were as high as 92% in these tests and single digit ash, and moisture values were recorded. Product ash values were higher compared to the as-received fine coal sample that was tested, likely due to the presence of a high amount of middlings in the raw coal coarse fraction which were crushed and ground. There was no significant ash reduction when grinding finer in these tests which is encouraging as single digit ash and moisture can be achieved at the cheapest grinding stage tested.

The India Coal C washery circuit treats 80 mm x 0 raw coal and has a plant capacity of 2.6 million metric tons/year. The circuit treats 80 x 13 mm feed with a Batac gig, while the 13 x 0.5 mm feed is treated with a fine coal jig. As was the case for the India Coal B washery, the circuit employs flotation to handle the 0.5 x 0 mm feed. However, the washery is not operating this circuit, leading to revenue loss due to poor upgrading of the fine coal, a major issue that could be solved

with the HHS process. The sample did not achieve the same success as the India Coal B raw coal, failing to consistently produce single digit ash products (9.5% was the lowest achieved). However, combustible recovery was consistently above 90% with above 70% mass yield. All moisture values with the exception of one tests were 3% or less. Again, as seen with the India Coal B raw coal, there was no significant advantage to grinding to a finer size as the cheapest level of size reduction produced only slightly higher ash values.

The India Coal D washery operates the same circuit as the India Coal C washery using a combination of Batac jigging and fine coal jigging, with non-operational flotation circuitry that would handle the fine coal feed. The sample responded well to the HHS process with ash values and moisture values ranging between 5% and 8%, and 2% to 5% respectively. Combustible recovery dipped slightly compared to the previous two raw coal samples tested ranging between 77% and 82%. The effect of grinding, in this case, is uncertain as the sample produced the lowest ash content at the intermediate size tested, and were relatively similar for the other two sizes. Further grinding studies may be employed to understand the nature of this sample. Overall the HHS process is well suited to handle these Indian coal streams, especially on the fine circuitry. The HHS process would be poised in these cases to replace the non-operational flotation circuitry and provide a high degree of upgrading for the fine coal feed at these washeries.

Table 3-41: India Coal B Raw Coal HHS Testing Results

Sample	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
Ground	28.5	8.4	1.7	74.7	69.7	89.3	68.7
Feed d_{80} 220 μm		8.6	1.9	74.3	69.8	89.2	68.0
Ground	28.4	7.2	3.8	76.4	69.3	89.9	72.4
Feed d_{80} 160 μm		6.8	2.7	76.5	69.0	89.8	73.3
Ground	28.8	9.3	3.0	79.4	72.2	91.9	68.6
Feed d_{80} 65 μm		9.9	2.7	79.2	72.7	92.1	67.1

Table 3-42: India Coal C Raw Coal HHS Testing Results

Sample	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
Ground	30.5	12.8	2.0	75.7	71.8	90.1	60.1
Feed d_{80} 240 μm		13.0	1.8	75.4	71.9	90.0	59.5
Ground	29.7	11.1	3.0	80.1	73.1	92.4	65.0
Feed d_{80} 140 μm		9.5	3.2	79.9	71.4	91.8	68.9
Ground	30.4	9.6	3.6	79.6	70.2	91.3	69.2
Feed d_{80} 55 μm		11.0	5.2	80.0	71.8	91.9	66.0

Table 3-43: India Coal D Raw Coal HHS Testing Results

Sample	Feed Ash (%wt.)	HHS Product (%wt.)		Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Separation Efficiency (%)
		Ash	Moisture				
Ground		7.4	3.8	75.2	47.4	77.1	68.9
Feed d_{80} 400 μm	43.1	7.1	2.2	75.4	47.4	77.3	69.4
Ground		5.2	3.4	77.4	47.3	79.1	73.4
Feed d_{80} 150 μm	43.2	5.6	5.6	77.1	47.4	78.9	72.7
Ground		8.2	3.8	81.7	48.8	82.7	74.0
Feed d_{80} 80 μm	45.8	7.8	2.4	81.1	48.2	82.0	73.7

3.4 Discussion and Conclusions

The cumulative results obtained from HHS testing on various coal feedstocks throughout the Appalachian region of the United States, and India, have successfully demonstrated the capability of the hydrophobic-hydrophilic separation process to clean and dewater alternative coal feed sources. Previous test work has indicated several target streams for the HHS process, namely screenbowl main effluent, deslime cyclone overflow, and flotation feed. Priority has generally been given to the testing of these samples, however, as past research has demonstrated the effectiveness of the HHS process to recover these streams, the scope of the technology has thusly expanded to include alternative waste streams, impoundment coal, and middling products. Successful testing completed during this research has demonstrated the versatility of the process.

In terms of an ultrafine waste coal recovery system, the HHS process thrives. Consistently, the process has proven itself as a superior separation process to that of flotation, which is well established as the best available ultrafine separation equipment. Results from this period of testing

confirm this claim. Consistent single digit ash and moisture values were achieved across several different fine coal samples received from the WV Coal A preparation plant, WV Coal B preparation plant, WV Coal C preparation plant, WV Coal E preparation plant and KY Coal A preparation plant, as well as ultrafine waste samples from Coal Company F and Coal Company G in India. Additionally, in the vast majority of ultrafine tests the average ash and moisture values fell below 5%, as shown in Figure 3-9. This was well under the target of 10%, which is a precursor for high-value product. Only two ultrafine tests averaged greater than 5% moisture. These tests were the only steam coal samples tested, indicating less hydrophobic coal produces higher moisture product, although one of these two samples did come under the target of 10%. Furthermore, combustible recovery values were generally high across all tested samples. The major advantage of the HHS process is in the evaluation of its performance as a dewatering technology. The ability to consistently produce single digit moisture is typically only achievable through thermal drying which is a costly process and has become increasingly difficult to permit. The performance of the HHS process for these ultrafine waste samples is evaluated primarily in terms of separation efficiency compared to flotation results on the same samples. In Appendix B, a composite separation efficiency plot was developed showing the performance of all samples tested and compared to the performance of flotation. From the plot, it is clear to see that the HHS process is far superior to flotation in terms of separation efficiency, which is a performance indicator that is defined as the recovery of valuable material minus the recovery of undesirable material. This method can account for variation in the feed of samples, and provide a key performance indicator.

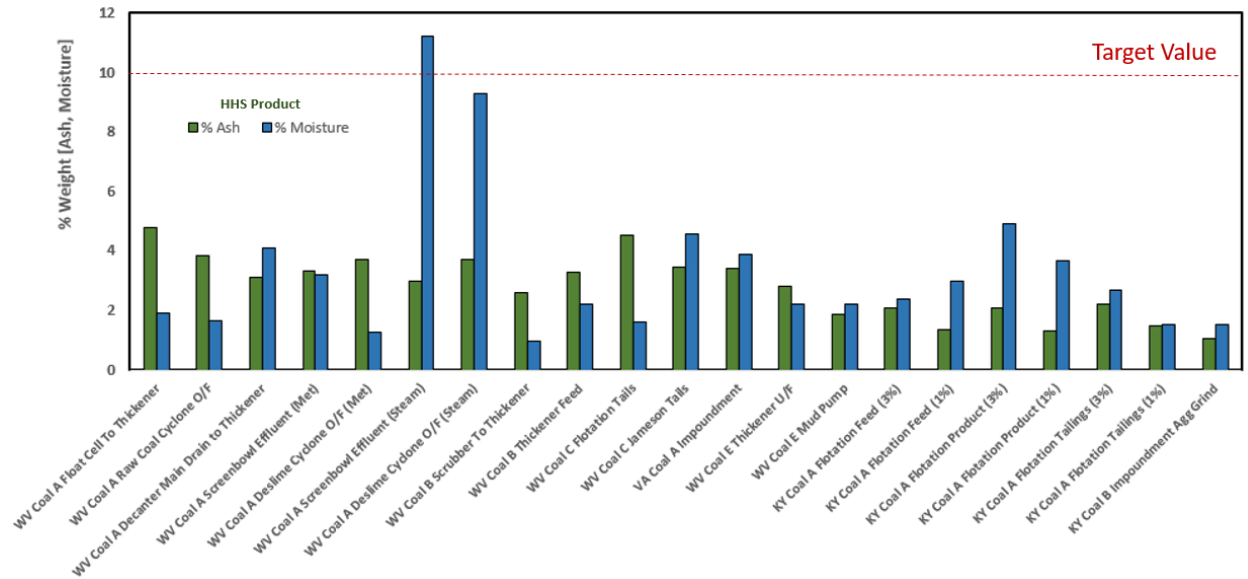


Figure 3-9: Ultrafine coal HHS testing average ash and moisture

The strong performance of the HHS process in terms of recovering ultrafine coal from plant waste streams comes as no surprise with knowledge of previous work completed on the subject. Where this research expands the reach of the HHS process is in testing non-traditional target HHS feedstocks. In this research, three different middling samples were tested, WV Coal C, LAM, and HAM. The results of these tests are also shown in Appendix B in terms of separation efficiency which again outperformed flotation. The middling sample presented new and significant challenges for the HHS process. In the vast majority of tests single digit ash values were not achievable, in fact only one series of tests on micronized LAM sample produced single-digit ash values, and although the tests all produced superior results to that of flotation in terms of recovery and ash, they did not meet project specifications on <10% ash and moisture. Primarily these tests were conducted to determine the degree of upgrading that could be achieved and the impact of grinding on these samples. In the vast majority of testing, grinding had little effect on product ash and recovery until the samples were micronized to achieve the highest degree of liberation. In any given case a determination would need to be made as to the product ash needs of the plant, which would dictate the level of liberation needed for HHS testing. In terms of upgrading the middling products to salable coal, the tests all recorded significant ash reduction from the feed, even though they were unable to produce single digit ash. Future liberation studies should be continued on

middling samples to determine the best practical method for increasing liberation and coal recovery in these samples.

Two spiral concentrate samples were procured during this phase of the research project. These samples both responded well to HHS testing. In general, all tests produced single-digit ash and moisture values, though a target ash of less than 1.5% was specified for these tests based on plant specifications. In these tests grinding was found to have virtually no effect on ash reduction in the product indicating a well-liberated sample. The spiral concentrate feed was screened at 0.2 mm and in terms of the undersize material it is noted that sodium silicate provided an increase in ash reduction, while in the oversize material the opposite held true. In theory, it is believed that this is attributed to a large amount of clay fines in the sample, which are not present in the oversize. Sodium silicate helped to reduce the effect of fine clay on HHS performance, and as such further testing with sodium silicate should be undertaken to replicate these results and begin to adapt the process as such. Two different impoundment coals were tested during this research. Both samples responded extremely well to the HHS process. This was another breakthrough for the HHS process and a major project goal. Active and abandoned impoundments represent a large tonnage of material that can sustain the HHS process as an ultrafine particle separation. In terms of the KY Coal B process impoundment, site-specific product conditions were taken into consideration. The results of the testing showed that regrinding agglomerates may be required to achieve a product ash of less than 1%. The data is clearly positive for recovery of coal from impoundments.

India samples provided several unique challenges, raw coal samples could not be tested as received and therefore needed significant sample preparation. It may be recommended to obtain more analysis of these samples in order to determine the best method of handling the coarse size fraction. In addition, natural fines should be tested on these samples to simulate a more typical HHS feed. All tests were compared to release analysis and flotation results, with separation efficiency shown in Appendix B. In the separation efficiency plot three distinct curves form. The first showing flotation results as poor based on separation efficiency and far inferior to that of HHS. The middle curve represents the case for middling products which do not perform as well as ultrafine coal with the HHS process but still have a significant advantage to flotation. The final curve represents the ultrafine testing. In this series of testing greater than 80% separation efficiency is achievable with some tests showing greater than 90% separation efficiency. This is very

uncommon, and shows the high performance of this technology. In general, the HHS process is well suited to clean and dewater ultrafine coal particles. In most current preparation plants these streams are discarded as waste due to inefficiencies in flotation providing a major opportunity for the HHS process due to the lost revenue of these waste streams and the well-liberated coal material held within them. Studies conducted showed exceptional recovery for ultrafine streams and superior performance to flotation. Liberation will continue to be an issue for middling samples and should be investigated further. The process is well equipped to handle coarser streams such as spiral concentrate and raw coal feed provided that the economics of grinding are in workable ranges. However, grinding in these samples proved to have little effect on the performance of the HHS process, and therefore the cheapest level of liberation can be used. Additionally, as seen in Figure 3-10, moisture content of the HHS product is exceptional regardless of particle size. Figure 3-10 shows the average product moisture of all HHS tests with respect to particle size. 82% of the tests achieved moisture values averaging less than 5% regardless of the size. Conventional dewatering methods cannot achieve this same level of success. The HHS process is a phenomenal cleaning and dewatering method for coal recovery, and the data presented serves to increase the scope of the technology beyond ultrafine waste streams.

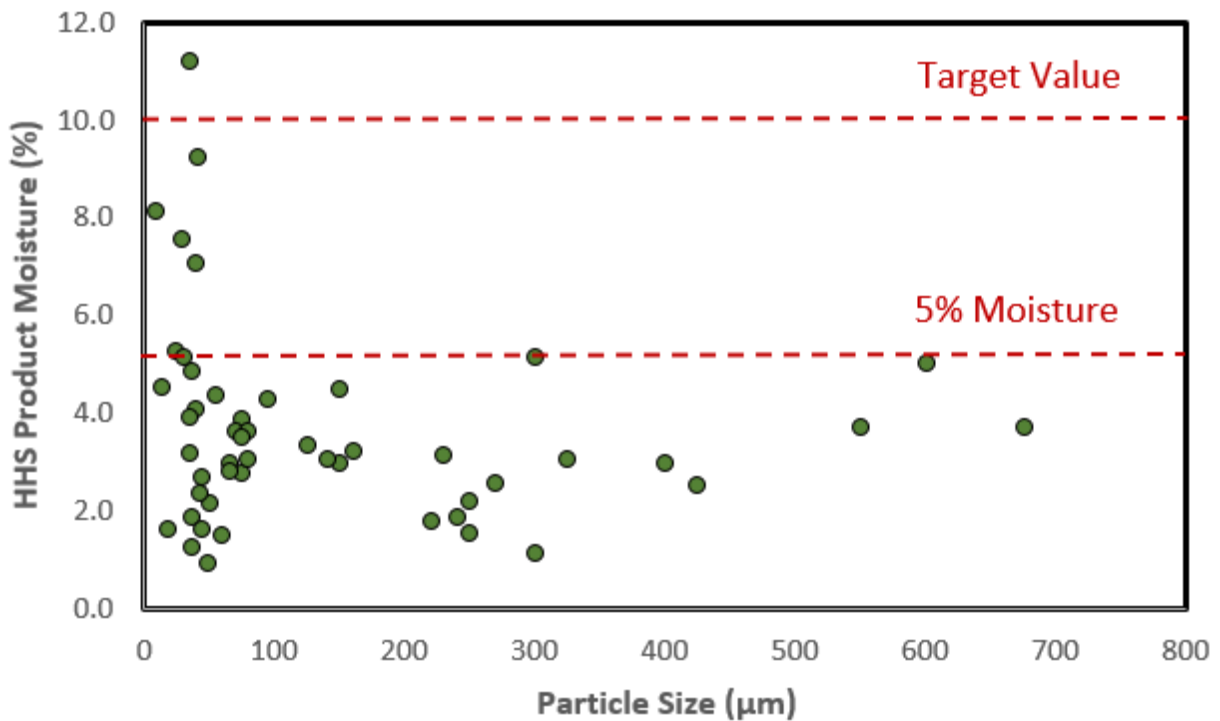


Figure 3-10: HHS product moisture vs. particle size

CHAPTER 4. RARE EARTH ELEMENT CONCENTRATION

4.1 Introduction

In order to successfully advance the hydrophobic-hydrophilic separation (HHS) process, and integrate it as a premier ultrafine separation process, actions must be taken to explore its viability in recovering mineral commodities outside of the coal sector. One such mineral commodities are the rare earth elements (REEs). As discussed in chapter 2, REEs are vital to many modern-day technologies. In addition, China currently dominates the world market for REEs production with estimates showing >90% of production originating in China (U.S. Geological Survey, 2018), making domestic economic production of REEs crucial to the United States. Furthermore, REEs are often found in small amounts with a small particle size, making them a perfect candidate for recovery with the HHS process.

Researchers at Virginia Tech and the University of Kentucky have identified an elevated concentration of REEs in coal seams throughout the Appalachian region. This alternative source of REEs production can be a solution to the global production issues for the United States. Zhang et al. (2015), found that nearly 50% of world REEs reserves and accounted for in coal and coal by-products. While reserves in the Northern and Central Appalachia regions along with the Black Warrior basin have been found to have >1000 ppm REEs content (Zhang et al., 2015), economically recovering these minerals has proven difficult due to their small population and particle size. The high concentrations of REEs in these coal basins are typically associated with inorganic mineral matter associated with the coal. Due to this fact, ultrafine coal can be recovered from active mine waste streams, as well as, active or abandoned impoundments and simultaneously produce a free REEs feedstock. This feedstock can be processed nearly identically to the coal using the HHS process, modified for REEs.

4.2 Experimental Procedure

This section describes the experimental procedure, as well as, equipment and materials, used to determine the viability and effectiveness of the HHS process in producing REEs concentrate from coal waste. Various experimental procedures are used to decarbonize coal tailings and liberate trapped REE's to be recovered. Several reagents were needed both during the

decarbonization step and recovery step for hydrophobizing the REEs. This section describes all procedures and materials used in each process step when producing REEs concentrate by the HHS process.

4.2.1 Rare Earth Samples

Samples were collected from several coal preparation plants in the Appalachian region of the United States to demonstrate the ability of the HHS process to upgrade the coal waste product, producing low ash and low moisture coal, while simultaneously producing a free REEs feedstock. These samples were then tested for response to HHS with regards to recovery of REEs. Samples were mainly fine coal samples that are currently discarded as waste. In addition, some middling samples were tested as they were found to be enriched in REEs. For confidentiality, names of the various companies and plants from which samples were taken are changed and listed as Coal Company A, B, C, etc.

Coal Company B's WV Coal D preparation plant was kind enough to provide several samples for testing during this phase of the research. As discussed in the previous chapter two samples were collected from the WV Coal D plant for decarbonization studies. These same samples were examined for viability with HHS for REEs recovery. The first of these samples was a low ash middling sample, henceforth referred to as WV Coal D low ash middling (LAM), of roughly 30% ash. This was a coarse sample that would need various methods of sample preparation (crushing and grinding) to produce acceptable size fractions for HHS REEs testing. For the LAM sample, plant audit data reports high REEs content for the 25-45% ash range. This middling product is currently produced from a secondary dense media cyclone circuit. The second sample was a coarse refuse sample, henceforth referred to as WV Coal D high ash middling (HAM), in which a middling sample was produced and separated by size and density. Similarly, to the LAM sample, plant audit data shows that ash rejects in the range of 50-90% ash is also elevated in REEs content. This sample contains feed ash values in the range of 49-95%. Per the testing procedure, the characterization of the coarse refuse sample is shown in Figure 4-1.

4.2.2 Experimental Apparatus

During this phase of the research project, several pieces of equipment were used in order to produce the results as shown in the next section 4.3. The equipment ranged from tanks and mixers to handle and condition slurry, to crushing and grinding machinery for appropriate size reduction and liberation of samples, and to separatory equipment for emulsion breakage and recovery. This section attempts to identify the major equipment used during this phase of research as well as, give a brief introduction to their use in the HHS process. Further detailed analysis of specific tests and samples are provided in the results section of this chapter.

4.2.2.1 Oil Agglomeration and Decarbonization

Initially, carbon material must be recovered from the various coal waste streams that are being tested as the REE's have been found to be associated with the inorganic mineral matter in these streams. Additionally, the HHS process for recovery of REEs can be considered a two-step process with the first step being HHS recovery of low ash and low moisture coal followed by the second step of REEs recovery. Initial decarbonization of these samples is achieved by oil-agglomeration in the same fashion as discussed in Chapter 3. The coal product that is removed by oil-agglomeration can then be processed by HHS to produce low ash and low moisture product, as shown in Chapter 3. For oil-agglomeration and decarbonization, a laboratory Denver flotation cell was used as the mixing vessel, and no air was introduced into the system. A two or four-liter cell was used for each test. The cell is filled with coal slurry and subjected to high shear agitation in the presence of oil in order to promote the probability of attachment of oil droplets to coal particles. Pentane is used as the hydrophobic liquid oil for coal oil-agglomeration, and roughly 50 ml is used for each batch run. The micro-agglomerates that are formed in this first phase are subjected to low-shear agitation in order to grow the agglomerates for recovery. The coal agglomerates are then screened off using a standard 100 mesh screen, leaving a tailings product and coal product that could both be processed using HHS to produce a dry coal product and a REEs concentrate.

4.2.2.2 Sample Preparation

Some variation of sample preparation was required for all samples used during the REEs testing phase of this research. For the WV Coal D samples, both LAM and HAM, they were too coarse to apply directly with the HHS process for coal and therefore a series of crushing and

grinding was needed to produce a few acceptable size classes. As discussed in the results section, the samples would be ground to three different size classes: minus 80 mesh, minus 325 mesh, and minus 10 microns for coal testing. This same level of size reduction is needed prior to sample decarbonization for HHS REEs processing. A series of jaw and cone crushers were used to reduce the size to less than 1 mm, while a laboratory coffee grinder was used to further reduce the size to roughly 80 mesh. While only a single pass was required through the jaw and cone crushers, at least three passes were needed to achieve the 80 mesh top size from the coffee grinder. 80 mesh was considered an appropriate size class for decarbonization prior to HHS REEs testing. The laboratory crushers used for this sample preparation are shown in Figure 4-2.



Figure 4-2: (Left) laboratory cone crusher, (Right) laboratory coffee grinder

For the remaining thickener underflow samples that were tested from the WV Coal F, KY Coal D, and KY Coal C sites, the particle size was appropriate for decarbonization and therefore could be used as received when subjected to oil-agglomeration. After oil-agglomeration, all samples would need further sample preparation to be subjected to HHS REEs. Grinding would be required to reduce the particle size to less than 10 μm successfully. This sample preparation was needed to help liberation of REEs from mineral matter. Wet grinding was used with a laboratory

ball mill and attrition mill. For the laboratory ball mill, 50% solids by weight was used, while 30% solids by weight was used for the attrition mill. The grinding media used ranged from 6 to 26 mm with a relatively even distribution in the laboratory ball mill. Attrition mill grinding media ranged from 3 to 6 mm in size.

4.2.2.3 Conditioning and Emulsion Formation

After successful decarbonization and sample preparation, the sample would need some conditioning before emulsions could be formed for the HHS process. Conditioning is the first step of the HHS process for REEs and is achieved by adequately dispersing the REEs in slurry using a standard agitator and impeller set up with a 5L Plexiglas cell and the addition of a dispersing agent, or blunging the material prior to emulsion formation in a small tank a high shear agitation. These dispersing agents primarily act as a depressant to prohibit the recovery of gangue minerals. After proper conditioning with a depressant, a collector could be added (Hydroxamate or Fatty Acid), to help the hydrophobicity of the REEs. For the HHS coal process oil agglomeration is used, whereas in the case of HHS REEs emulsion formation is used to collect the REEs. Firstly, oil-in-water emulsions are formed by adding a more substantial amount of oil (roughly 300 ml oil to 2 liters' slurry), than seen in oil agglomeration. This creates large oil droplets that are stabilized by hydrophobized particles in an aqueous phase, very similar to oil-agglomeration. The large volume of oil is needed due to the low population of REEs in the feed slurry as opposed to the high population for coal making oil agglomeration possible. In this stage of the process, heptane oil is used as the hydrophobic liquid for emulsion formation.

4.2.2.4 Phase Separation and Phase Inversion

After successfully forming oil-in-water emulsions, the most critical step in the HHS REEs process is undergoing phase separation and inversion. The emulsions are separated from the slurry by a separatory funnel. Here the water is drained from the mixture removing the mineral matter tailings and can be considered the rougher tailings for the test. In some cases, the rougher concentrate, which is the oil phase and emulsions left in the separatory funnel, is reprocessed for a cleaner run, or the tails are reprocessed for a scavenger run. After successful phase separation, a large amount of oil is added to the separatory funnel to produce a slurry that is greater than 76% oil. This condition is necessary to successfully phase inverse the emulsions from oil-in-water to water-in-oil. The phase inversion is necessary to destabilize the emulsions and release particles to

the oil phase and entrained mineral matter to the water phase. The oil phase can then be collected and recovered to be used again in the process while leaving a REEs concentrate.

4.2.2.5 Solvent Recovery

Solvent recovery is a major step for the HHS process. Spent solvent, heptane, in the case of HHS REEs, must be recovered to be recycled back to the head of the circuit. This is done to keep solvent cost low which is a driving economic factor for the process. In the case of HHS for coal, pentane was recovered by way of evaporation and condensing. This is plausible because pentane is a low boiling point hydrocarbon. In the case of HHS REEs, heptane is the preferred hydrocarbon used, and due to its higher boiling point this is not as plausible an option. For solvent recovery, a laboratory pressure filter was used.

4.2.3 Methods and Materials

For the HHS REEs testing completed during this research, a general approach was taken to develop a standard testing procedure. In general, an attempt was made to keep the procedure as close to that of the HHS process for coal as discussed in Chapter 3. Often, due to the experimental nature of the work presented, this procedure was adapted to fit specific needs and attempt to find the optimal condition in which REEs could be recovered using HHS. Per the testing procedure, it is often necessary for the use of specific reagents to aid in the emulsion formation process. This section discusses the general experimental method used to complete the testing of viability for the HHS REEs process, as well as, the reagents used to aid the process.

4.2.3.1 Experimental Method

For the HHS REEs testing samples were first examined on a size basis and determined if sample preparation was required. If sample preparation is required, crushing and grinding techniques were employed as described earlier to reduce the size to a workable range for the HHS process. Once complete the samples were decarbonized to remove coal from the samples prior to HHS testing using oil agglomeration with pentane as the hydrophobic liquid. This will properly simulate the process for coal recovery with these samples, as a major component of the research is to successfully recover coal from waste streams while producing a free REEs feedstock for recovery. Decarbonization is necessary as research has shown that REEs are associated with the inorganic mineral matter in these streams. Further size reduction is required after decarbonization

to liberate REEs particles. Samples would be ground using a laboratory ball or attrition mill to a d_{80} of less than 10 μm . After size reduction, the sample would be conditioned under low shear agitation with the addition of a depressant such as sodium silicate. Depressant is needed to prohibit the recovery of gangue minerals. This is because in typical coal waste streams there is a small population of REEs and a large amount of gangue mineral which contain little to no REEs. After low shear agitation with a depressant, high shear agitation with a collector is used to render the REEs bearing minerals hydrophobic, in which case they can then be recovered by the HHS process. After the conditioning process is completed oil-in-water emulsions could be formed and subsequently separated from the bulk slurry using a separatory funnel. Additional oil would be added to the system to induce phase inversion. Particles could then be released to the oil phase of the system and recovered by collecting the oil phase. The REEs concentrate could be recovered using a pressure filter and the oil recycled to the head of the process.

4.2.3.2 Reagents

Heptane (C_7H_{16}) was the hydrophobic liquid used during HHS REEs testing for this phase of the research. Pentane was also used during the decarbonization step and was discussed in Chapter 3 of this work. For all experiments HPLC Grade 99+% n-heptane was used, which was obtained from Alfa Aesar. Table 4-1 shows the relative properties of heptane for this work. In all tests, a depressant would be added to help prohibit the recovery of gangue material during the HHS process. In the REEs industry, sodium silicate and phosphate are typically used to accomplish this goal. For the HHS REEs tests completed in this phase of the research both sodium silicate and sodium hexametaphosphate were used. In accordance with the testing procedure, collector addition is necessary to aid in the recovery of REEs bearing minerals. In the case of this research, two primary collectors were examined. The first being hydroxamate and the second being sodium oleate (C-18 fatty acid).

Table 4-1: Relevant Properties of Heptane

Chemical or Physical Property	Value
Molecular Weight (g/mol)	100.21
Density (g/cm ³)	0.684
Boiling Point (°C/°F)	98.4 / 209.2
Viscosity (N-sec/m ²)	0.00037
Surface Tension (N/m)	0.0197
Vapor SG	3.45
Solubility with Water (mg/L)	3.4

4.3 Results and Analysis

The following section serves to present the results of testing the HHS process for REEs concentration. Testing was completed to investigate the extent that HHS coal tailings could concentrate REE's and produce a 'free' REEs feedstock, and to investigate whether the HHS process could be modified to recover REEs from the HHS coal tailings. Where testing differs from the aforementioned experimental method, it will be discussed here. The following results are the preliminary testing results for expanding the HHS process to encompass mineral recovery. REEs were selected due to previous research showing elevated concentration in US coalfields, and the HHS processes success with coal recovery. This allows for the recovery of ultrafine waste coal while simultaneously producing a "free" REEs feedstock.

4.3.1 WV Coal D REE Testing

During this phase of the research project, two main samples were procured from Coal Company B's WV Coal D preparation plant for decarbonization and coal recovery studies utilizing the HHS process to determine the degree of upgrading that the HHS process could provide for middling coal product, converting low value-waste and middlings into high-value salable coal. The first of these samples was a low ash middling sample (LAM) that was produced from a secondary dense media cyclone circuit, which would be sold into the low-value steam market when applicable. The second sample was a high ash coarse reject sample from which a middling product

was extracted (HAM), which is currently a waste product. After successfully conducting thorough HHS coal testing on these samples, it was determined from plant audit data that these samples had elevated concentrations of REEs. Therefore, per the project goals, it was firstly investigated if any of these samples could produce a concentrated REEs feedstock in the form of HHS coal tailings while upgrading the coal middling product.

HHS coal tests on the WV Coal D preparation samples were presented in the previous chapter. The samples were tested at three different sizes: [1] 80 mesh x 0, [2] 325 mesh x 0, and [3] 10 μm x 0. Because few tests provided good upgrading of the coal product, few samples were available for REE's analysis that satisfied the initial project condition of converting low-value coal to salable high-value coal. One such sample that did successfully upgrade the coal product during HHS coal testing was the LAM sample. After micronizing the sample (10 μm x 0), the HHS coal process produced a 7.2% ash product with 89.7% combustible recovery. Therefore, the analysis was conducted on this test's product streams to determine the REE's content and distribution.

The results of the REE's are shown in Figure 4-3, which includes the total rare earth element (TREE) concentration of each product stream, calculated as parts-per-million of a whole-sample basis (ppm_w) and on an ash basis (ppm_a), as well as, the distribution to tails. The tailings stream resulted in a TREE whole of 335 ppm with a contained value of \$75/ton and a TREE ash of 426 ppm with a contained value of \$95/ton. The Coal product, in contrast, resulted in a TREE whole of 89.8 ppm with a contained value of \$26/ton, and a TREE ash of 1123 ppm with a contained value of \$336/ton. The full distribution is shown below. However, the sample seems to have some peaks, those being Ho, Lu, and Eu (Holmium, Lutetium, and Europium) all reaching around 80%. La, Ce, Pr, Nd, Sm, and Tm (Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, and Thulium) all reported around 70%, closely behind. As shown, the HHS process was very successful in concentrating REE's in the process tailings stream. The TREE content was upgraded from 194 ppm on a whole sample basis in the feed to 335 ppm on a whole sample basis in the tailings stream. The data clearly indicates that the HHS process can produce an REE's feedstock from upgraded low-value coal feed.

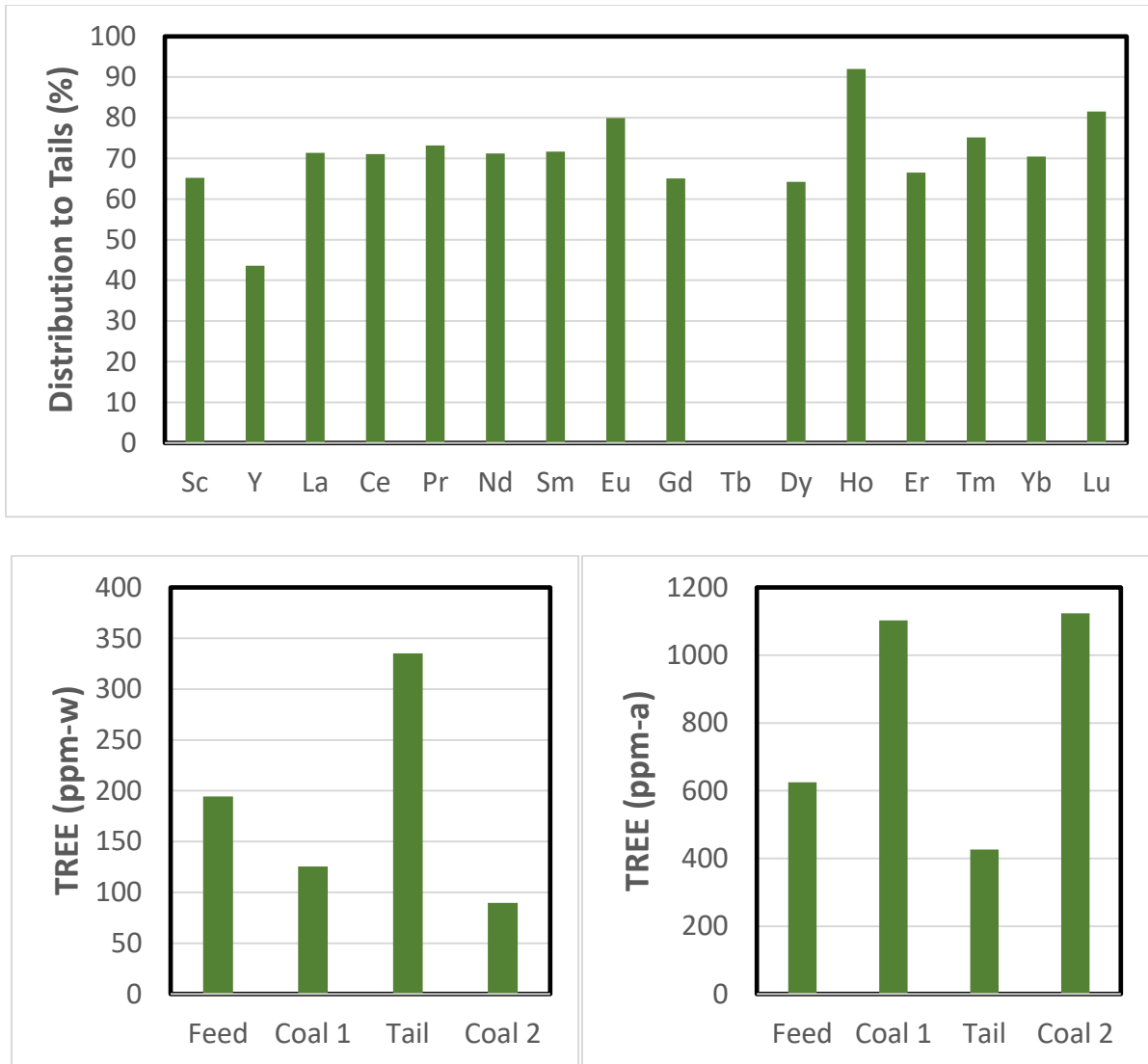


Figure 4-3: LAM HHS coal (10 μm x 0) TREE analysis

After determining that the HHS process could successfully upgrade low-value coal middlings or waste into high-value salable coal product and simultaneously produce a REEs feedstock from the HHS tailings, a secondary project goal was developed of determining if the HHS process could be modified to successfully recover REEs-bearing minerals from the coal concentrated coal tailings. In order to investigate this project goal, the HHS process was tested for REEs recovery on the HAM sample. This sample was successfully tested in the previous chapter for the degree of upgrading in the coal product. The sample was separated based on size and density for the coal testing. One sample proved superior, in terms of coal upgrading, compared to the other samples. Producing near single digit ash values and needing the smallest degree of size reduction

(i.e., the cheapest degree of grinding), the HAM 1x 0.15 mm sample was tested for REEs recovery using the HHS process. Specifically, the 10 μm x 0 ground feed of this sample was tested.

The HHS process was modified to emulate two-liquid flotation rather than oil-agglomeration that is typically employed for HHS coal testing. In this process, a large amount of oil is added after conditioning to form oil-in-water emulsions rather than agglomerates. This is done due to the small population of REEs-bearing minerals in the feed. In this test, the decarbonized slurry (produced by the HHS coal process), was conditioned for 15 minutes using 2kg/ton sodium silicate, a common depressant used in the REE industry to prohibit the hydrophobizing of non-REE bearing gangue minerals. After conditioning with sodium silicate, the slurry was conditioned for an additional 15 minutes using 1kg/ton Sodium Oleate (C-18 fatty acid) as a collector. After conditioning, a large volume of heptane oil was added (approximately 15% by volume of slurry) and mixed under high shear conditions to form emulsions. The emulsions were transferred to a separatory funnel, and the tailings were removed. The oil phase was collected and the solvent recovered leaving a rougher concentrate product. The rougher tailings were re-processed as a scavenger circuit using the same process. This produced a scavenger concentrate and tailings products.

The results of the testing are shown below in Table 4-2 and graphically represented in Figures 4-4 and 4-5. TREE content of the rougher concentrate was 306 ppm and 384 ppm on a whole sample and ash basis respectively. The TREE content of the scavenger concentrate was 352 ppm and 400 ppm on a whole sample and ash basis respectively. This was a corresponding increase from the feed grade of 306 ppm on a whole sample basis. The coal product contained a high TREE content on an ash basis at 726 ppm. The testing indicated a slight improvement in REEs concentration in the concentrate samples provided by the HHS process, and a cleaning stage could be employed to attempt to improve the REEs concentration.

Table 4-2: HAM 1 x 0.15 mm Ground Sample (10 μm) HHS REEs Testing Results

Product	Ash (%wt.)	REE (ppm)	
		Ash Basis	Whole Basis
Feed	79.8	383.9	306.1
Rougher Concentrate	67.5	477.6	322.6
Scavenger Concentrate	88.0	400.0	351.9
Scavenger Tails	92.5	371.6	343.5
Coal Product	18.3	726.3	133.1

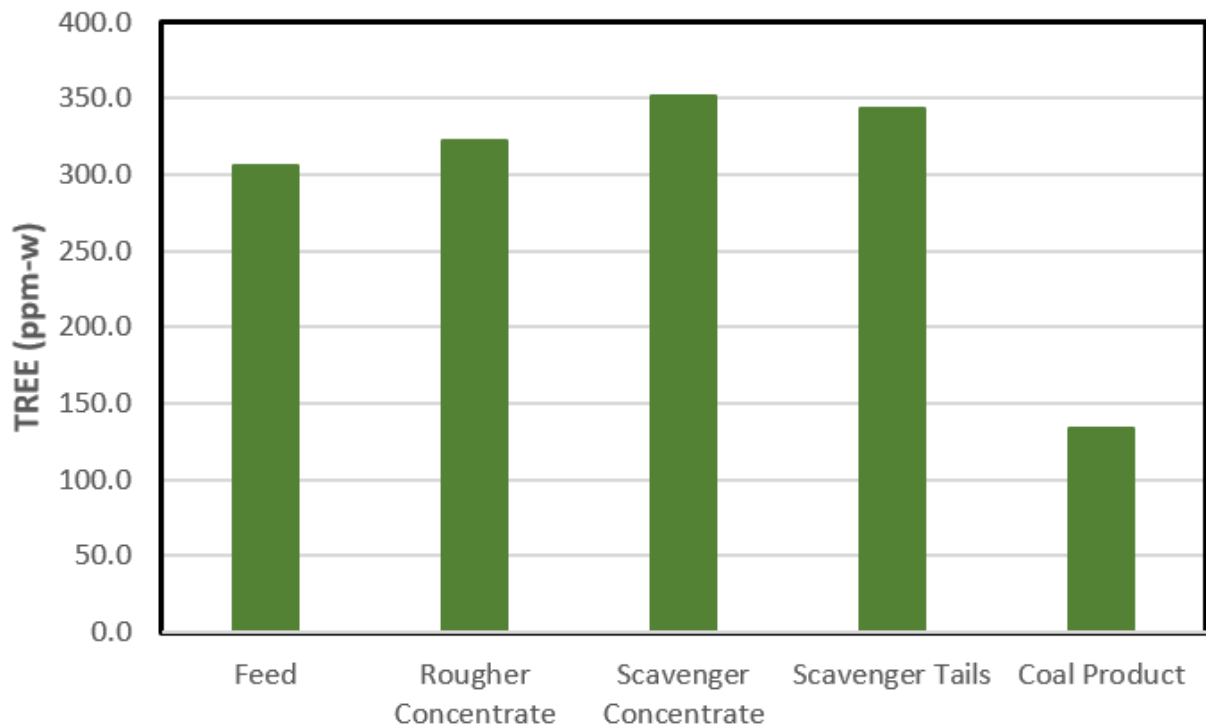


Figure 4-4: TREE whole sample basis HAM HHS REEs testing results

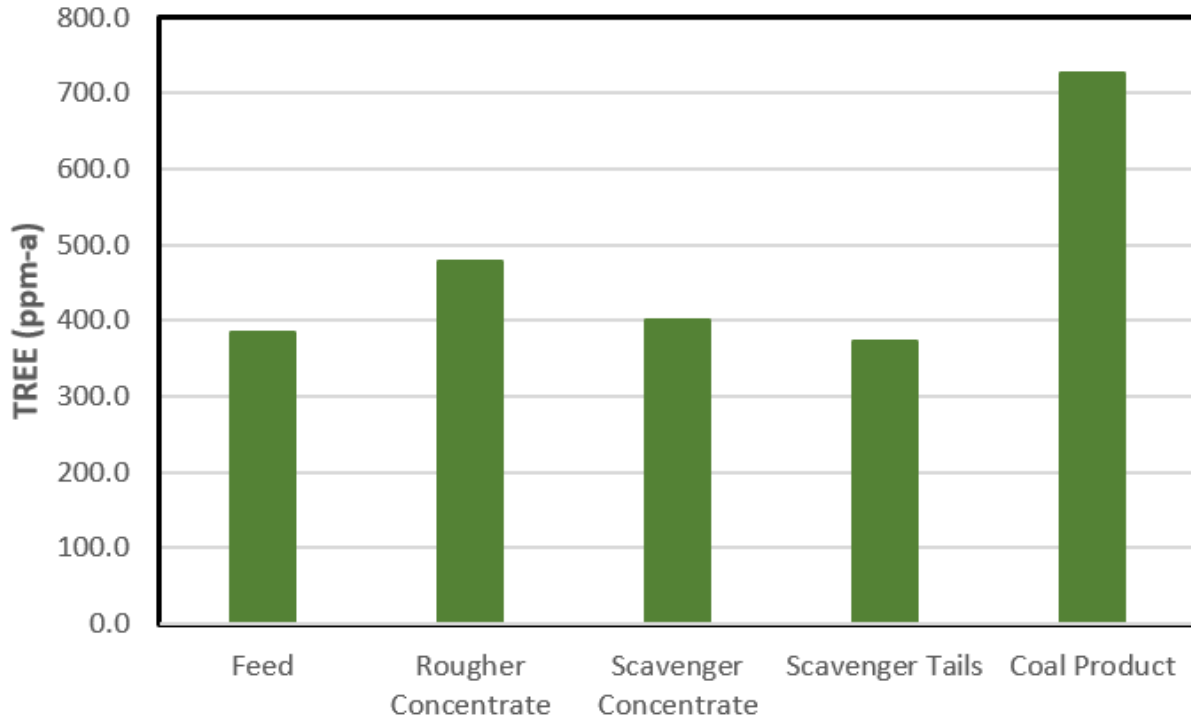


Figure 4-5: TREE ash basis HAM HHS REEs testing results

In addition to TREE analysis on the various product streams, splits were taken from each stream and sent for SEM-EDX analysis, which was performed by Lexi Russell, an undergraduate research assistant in the department. After 6.5 hours of scanning, 0 REE particles, 53 pyrite particles, 8 Zr particles, and a few Fe particles were found in the scavenger tails. For the scavenger concentrate, 1 REE particle, 60 pyrite particles, 19 Zr particles, and 1 Cu-Fe-S mineral particle was found. For the Rougher Concentrate, 2 REE particles, 24 pyrite particles, 3 Zr particles and one each of Fe, Zn-S, and Cu-Fe-S mineral particles were found. Finally, for the coal sample, 1 REE particle was found, along with 77 pyrite particles, 3 iron particles, and one Cu-Fe-S mineral particle. The results of the SEM-EDX analysis is shown in Figures 4-6 through 4-10. All visible REE grains had a phosphate peak. Overall, the sample contains a lot of pyrite, and very few distinct REE particles are visible. In terms of REE of interest, the rougher concentrate contained a mean value of 1.94% Lanthanum, 3.93% Cerium, and 0.04% Thorium. The scavenger concentrate contained a mean value of 6.62% Cerium and 2.67% Lanthanum. The coal product contained a mean value of 7.76% Cerium and 3.64% Lanthanum. Additionally, SEM/EDX analysis indicated a strong correlation between Lanthanum and Cerium, as well as, a correlation between both Lanthanum and Cerium and Phosphorous. These relationships are shown in Figure 4-11.

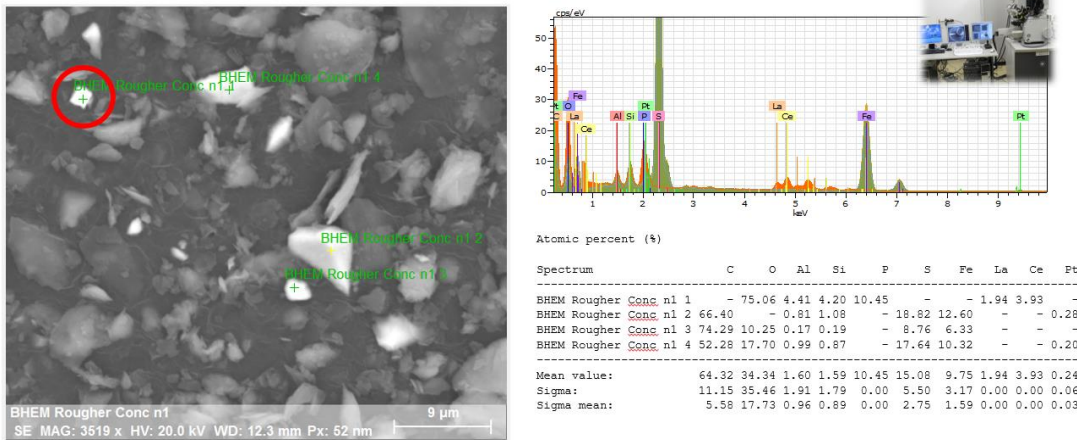


Figure 4-6: SEM-EDX analysis rougher concentrate (run 1)

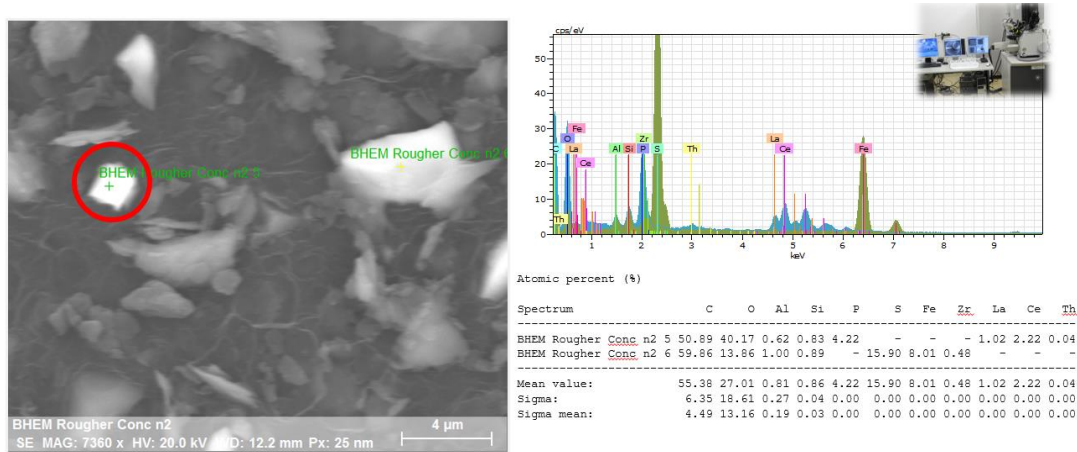


Figure 4-7: SEM-EDX analysis rougher concentrate (run 2)

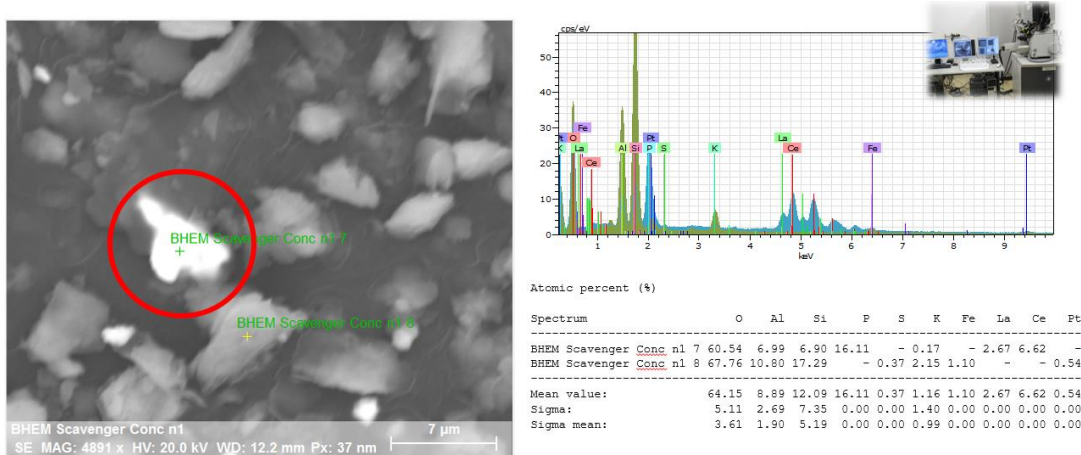


Figure 4-8: SEM-EDX analysis scavenger concentrate

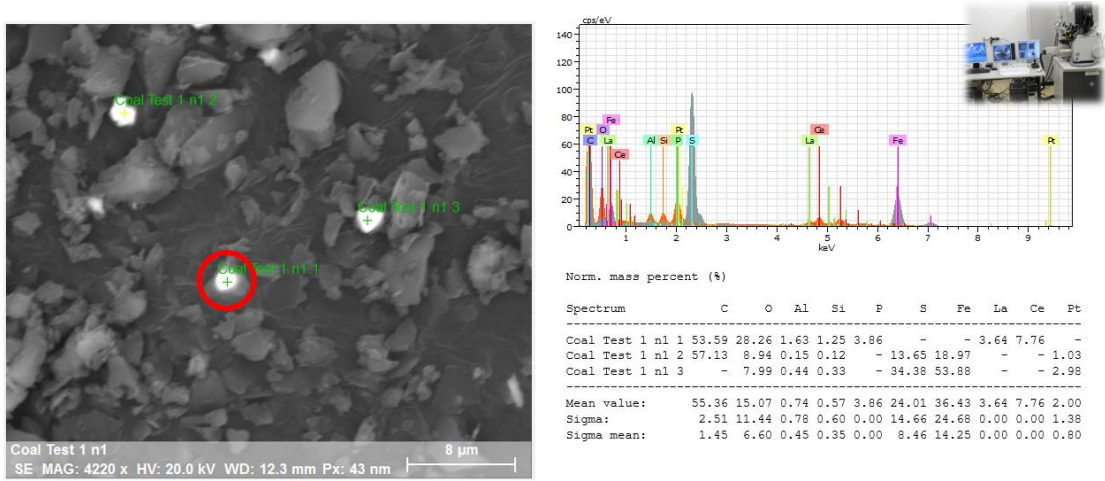


Figure 4-9: SEM-EDX analysis coal product (run 1)

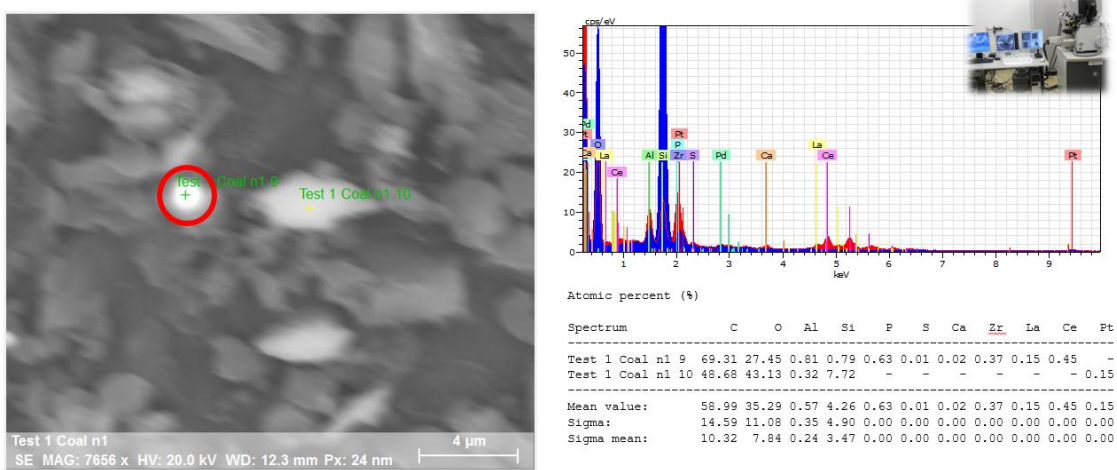


Figure 4-10: SEM-EDX analysis coal product (run 2)

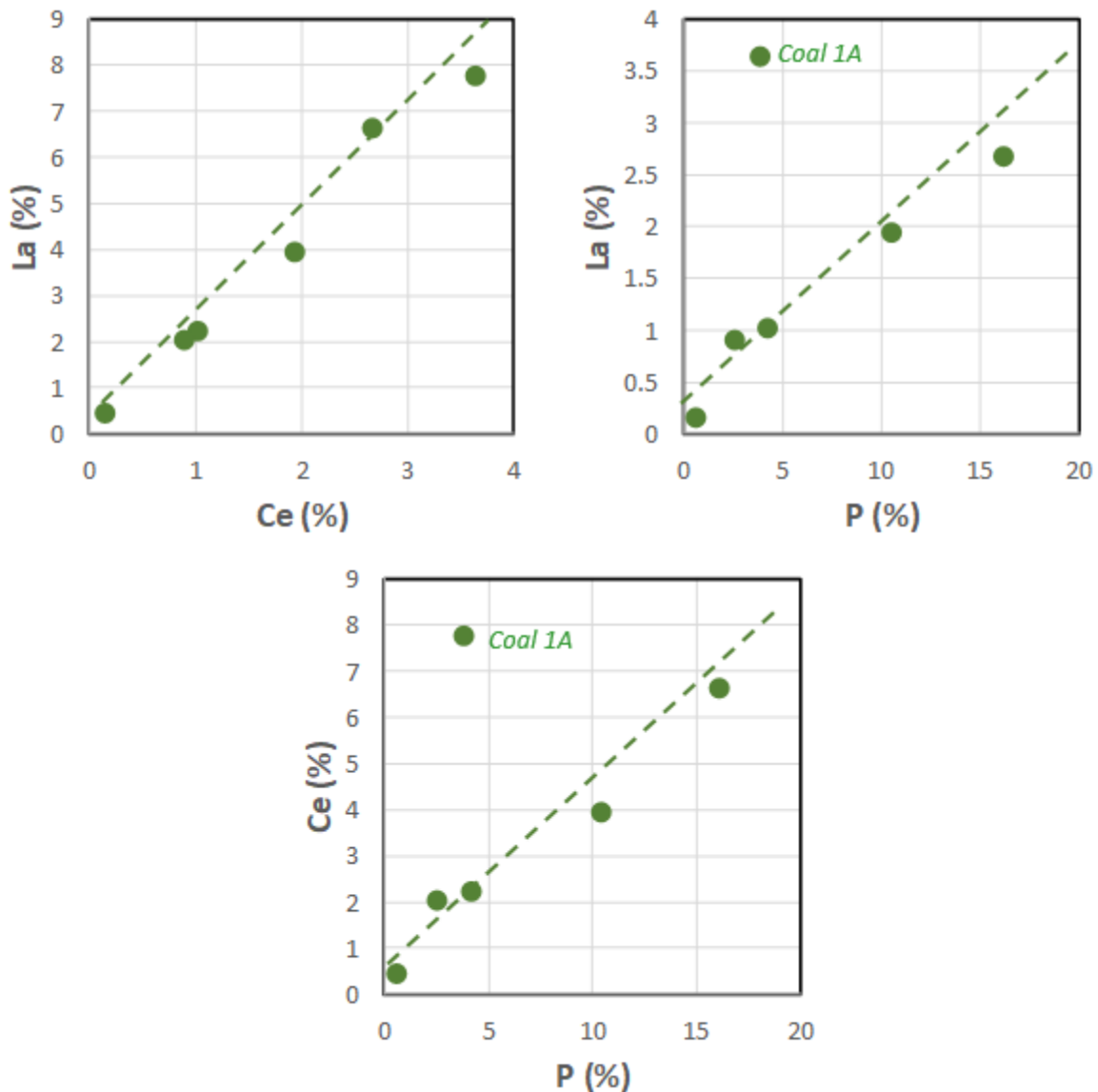


Figure 4-11: SEM-EDX HAM correlation between La, Ce, and P

4.3.2 KY Coal C REE Testing

During this phase of the research, another sample was tested for concentration of REE's in decarbonized coal tailings from the HHS process. Coal Company H provided a sample of thickener underflow from their KY Coal C operation for analysis of HHS coal upgrading and REE concentration. As previously discussed, this was a major project goal as it provides an additional product for the HHS process, and expands the technology into the minerals sector. For the HHS coal process thickener underflow is an ideal sample to test as it is a fine coal waste stream for most typical preparation plants. The waste material can be upgraded to high-value salable coal by the

HHS process. As such, the as-received thickener underflow sample from KY Coal C was tested for coal decarbonization and upgrading and analyzed for TREE content.

The sample was decarbonized using the HHS coal process by oil-agglomeration with pentane oil as the hydrophobic liquid. A two-liter Denver flotation cell was filled with a representative sample of thickener underflow slurry. The sample was mixed under high shear conditions to form micro agglomerates and then under low shear conditions to grow the agglomerates and recover all the carbon material. In order to remove the highest amount of carbon material, the tails from the initial oil-agglomeration were re-agglomerated to remove any remaining coal product. The agglomerates in both cases were screened off using a standard 100 mesh sieve and combined to create a single coal product for analysis. The process resulted in a coal product ash of 11.3% with a high combustible recovery of 80.3%. Tail ash for this sample was high at 91.3%. Moisture was also very high (approximately 40%) due to the fact that the coal-agglomerates were not processed using the morganizer, which is the key dewatering step of the HHS process and has the added benefit of further ash reduction. Based on the previous testing, it is likely the process would have produced single-digit ash and moisture coal values if processed using the morganizer.

Table 4-3: TREE KY Coal C Decarbonization Results

Product	Ash (%wt.)	Mass Yield (%wt.)	TREE (ppm)		REE
			Ash Basis	Whole Basis	Recovery (%wt.)
Coal	11.3	28.7	909.9	102.5	11.6
Tails	91.2	71.3	344.5	314.3	88.4
Feed	68.3	100.0	371.2	253.5	100.0

Due to the positive coal results for decarbonization, each product stream was sent for TREE analysis the results of which are shown in Table 4-3 and graphically represented in Figure 4-12. In addition, distribution to the tails data is provided in Figure 4-13. TREE for the thickener underflow feed was 253 ppm on a whole sample basis and 371 ppm on an ash basis. The HHS tails were able to concentrate this feed to 314 ppm on a whole sample basis, with a resulting REE

recovery of 88.4%. The data clearly indicates that the HHS process can be used to concentrate REEs in coal tailings while simultaneously producing salable clean coal product. The HHS coal tailings had several peaks in terms of distribution to the tails, with a high amount of Scandium, Lutetium, and Praseodymium recovery, all close to 90%.

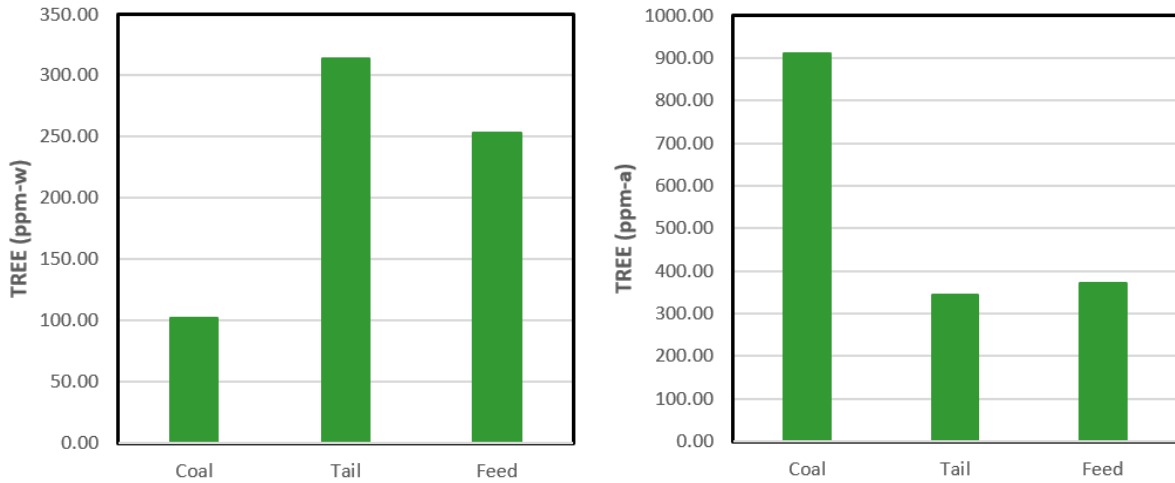


Figure 4-12: TREE analysis KY Coal C decarbonization

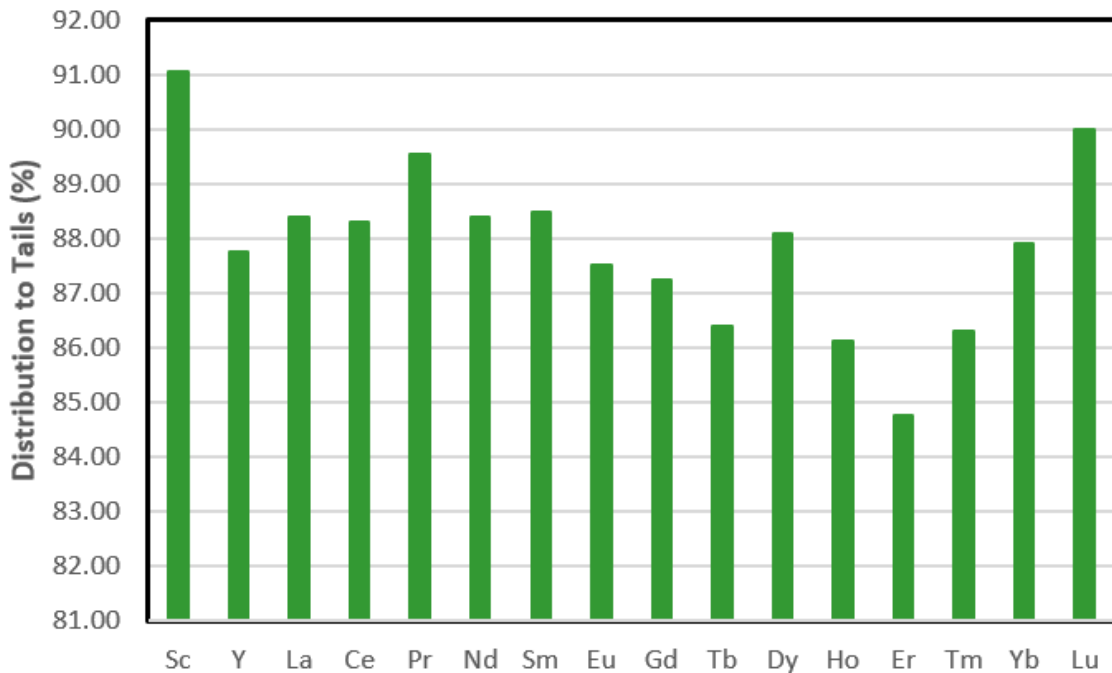


Figure 4-13: Distribution to tails KY Coal C decarbonization

4.3.3 WV Coal F REE Testing

Coal Company B, in addition to providing middling samples from their WV Coal D preparation plant, provided a thickener underflow sample from their WV Coal F operation for studies with the HHS process. Based on prior characterization and test work the thickener underflow sample appeared to be a good candidate for recovery of REEs from HHS coal tailings. Four tests were conducted on this sample, and all product streams were sent for TREE concentration analysis. In accordance with previous test work, these tests were conducted using several stages of cleaning stages in an attempt to improve REE recovery and find the optimum testing conditions for the HHS REE modified process.

In the first test, the experimental procedure for which is outlined below in Figure 4-14, feed, which was decarbonized using oil-agglomeration, was conditioned with 1.2 kg/ton hydroxamate and 1.2 kg/ton of sodium silicate. Hydroxamate was the collector used across all WV Coal F tests, and sodium silicate was used as a depressant across all tests. Approximately 15%, by volume of slurry, heptane oil was added after conditioning and mixed under high shear conditions to form oil-in-water emulsions. The slurry was transferred to a separatory funnel, and the water phase (tailings) was separated from the oil phase (concentrate). The tailings were reprocessed using 0.6 kg/ton of hydroxamates and 1.2 kg/ton of sodium silicate. Two-stages of cleaning were employed on both the rougher and scavenger concentrates, to produce two final concentrate products.

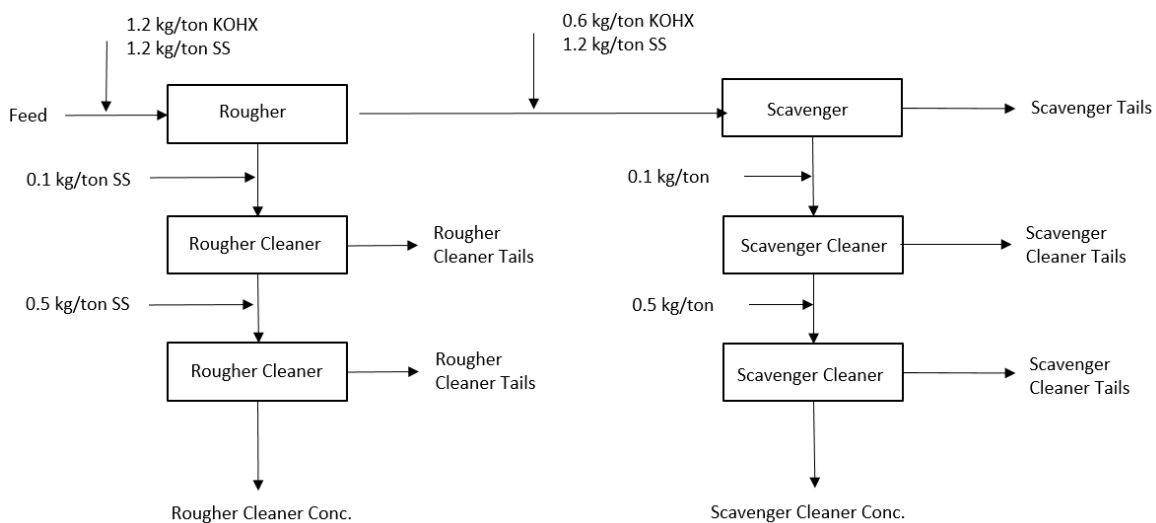


Figure 4-14: WV Coal F HHS REE test 1 experimental procedure

In tests 2 and 3, the same experimental procedure was repeated. Test 2 was a replica test of test one to check for reproducibility of the results obtained. In test 3, the same procedure was used. However, Sorbitan Monooleate (SMO) was used to aid in the hydrophobicity of REE-bearing minerals in an attempt to increase recovery. In this test, 1.1 kg/ton of SMO was added during the rougher and scavenger stages of the HHS process. The experimental procedures for these two tests are shown in Figures 4-15 and 4-16.

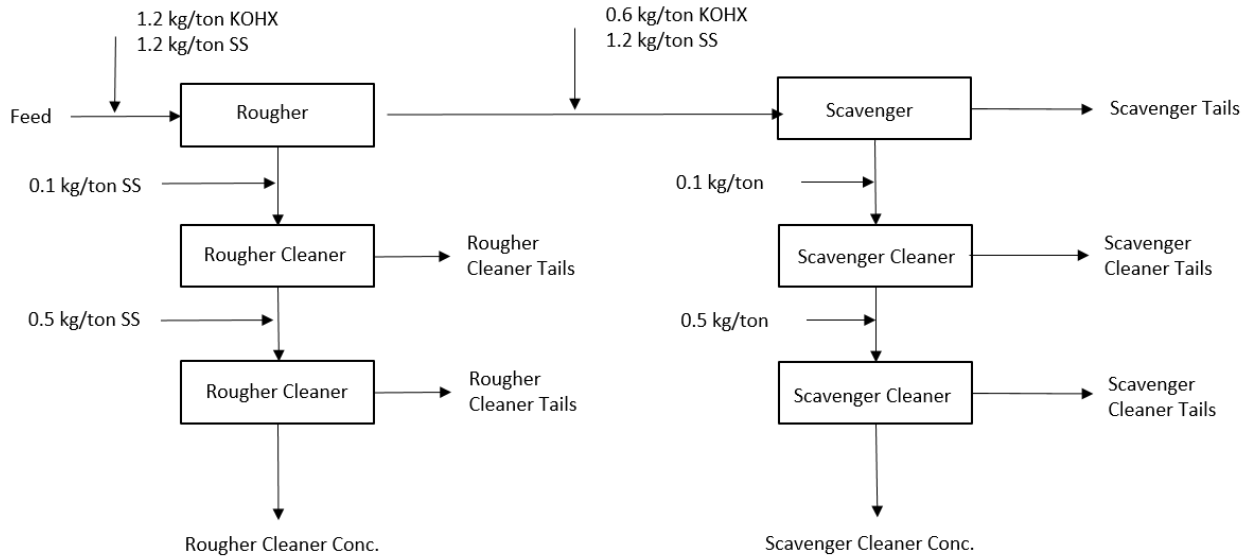


Figure 4-15: WV Coal F HHS REE test 2 experimental procedure

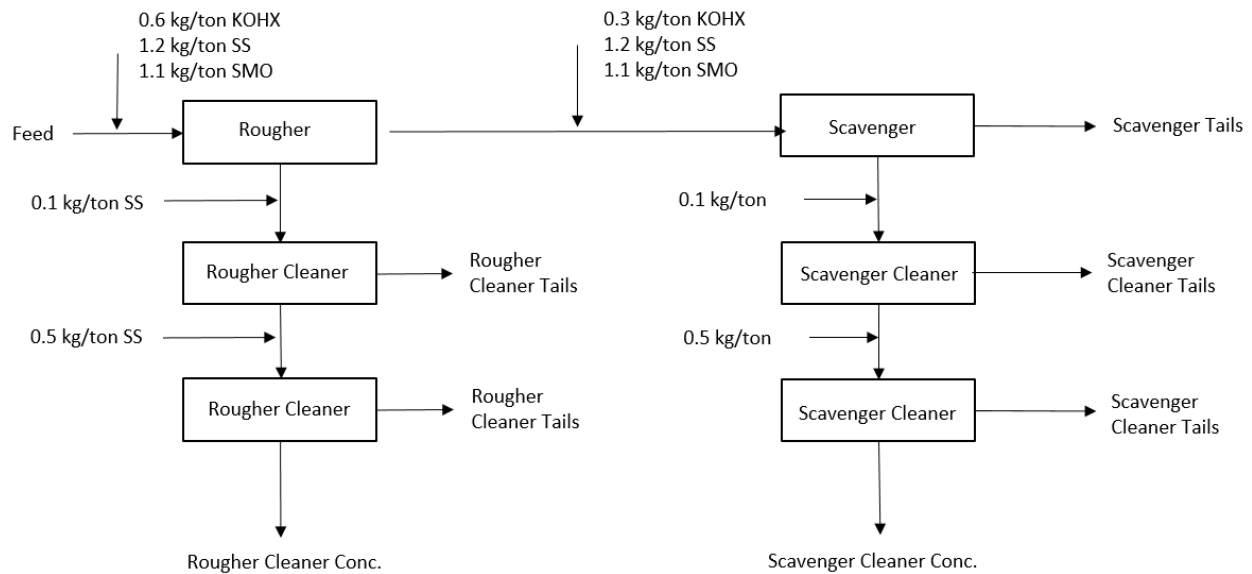


Figure 4-16: WV Coal F HHS REE test 3 experimental procedure

In the final test conducted on this sample, it was decided to attempt, in addition to adding SMO to improve hydrophobicity, attrition mill grinding on the rougher and scavenger concentrates. This would theoretically improve liberation of the REE-bearing minerals and help to prohibit gangue recovery in the concentrate streams. One hour of grinding in the laboratory attrition mill was used. Furthermore, increased dosage of hydroxamate collector was used to see the impact on REE recovery. In this test, 2 kg/ton of hydroxamate was added during the rougher stage, and 1 kg/ton was added in the scavenger circuit. After attrition mill grinding, more hydroxamate was added to further improve hydrophobicity. The procedure used during this test is outlined in Figure 4-17.

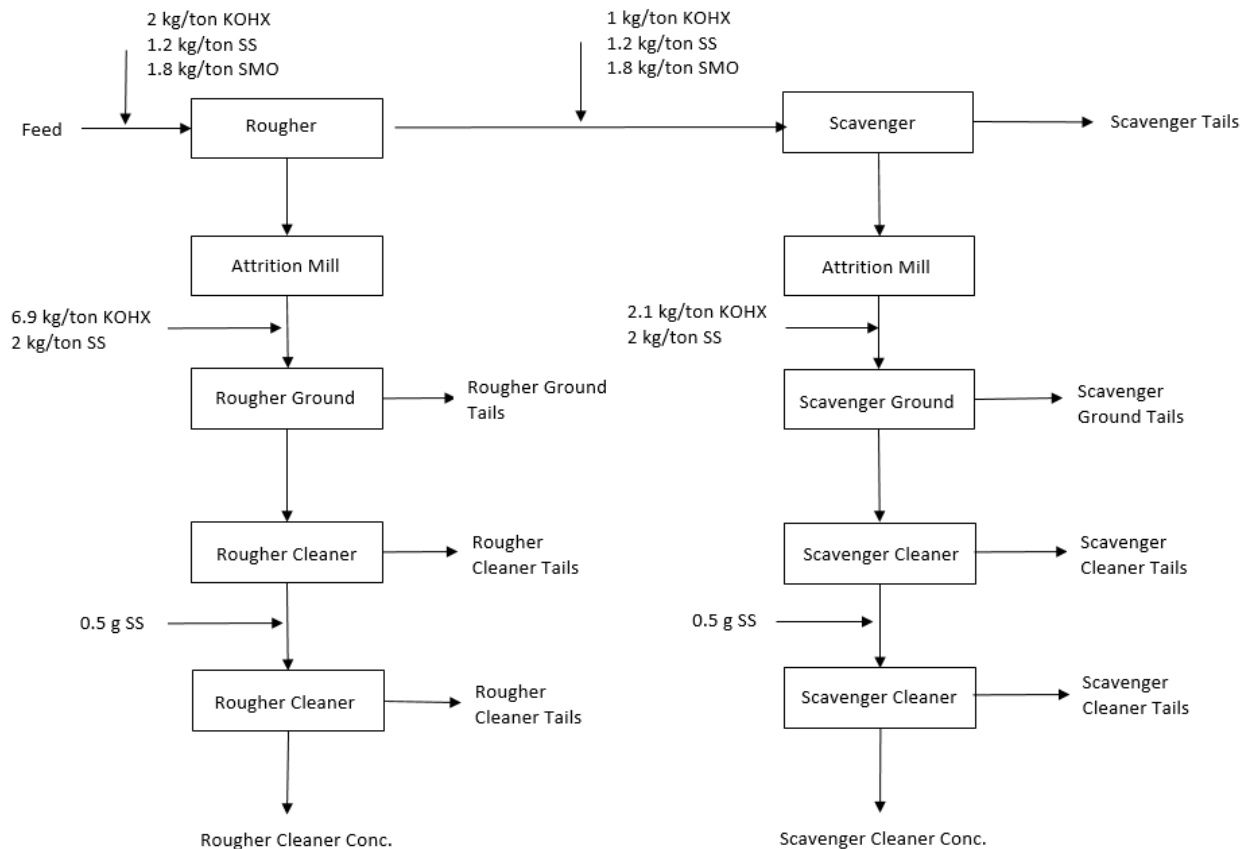


Figure 4-17: WV Coal F HHS REE test 4 experimental procedure

The results of the four tests indicate good performance by the HHS process in concentrating REEs. In test one, the results of which are shown in Table 4-4, the rougher cleaner concentrate and scavenger cleaner concentrate produced TREE concentrates above 800 ppm on a whole basis and above 1000 ppm on an ash basis. This is an increase of over 516 ppm on a whole basis and over

706 ppm on an ash basis. Recovery values for these two streams were low, however, at 1.7% and 0.6% respectively. When repeating the test for test 2, the results of which are shown in Table 4-5, the results were much improved. The rougher cleaner concentrate produced similar TREE values. However, the scavenger cleaner concentrate sample produced 2,118 ppm whole basis, and 2,657 ppm ash basis. This corresponds to an increased recovery of 7.1%. In test 3 where SMO was added, the results of which are shown in Table 4-6, recovery dropped to only 3.7% for the scavenger cleaner concentrate though the TREE concentration increased on both a whole sample and ash basis. The rougher cleaner concentrate produced similar results to the previous two tests. It appears that SMO did not have any added benefit to increasing REE recovery in this sample. Test 4, the results of which are shown in Table 4-7, shows the effect of grinding the rougher and scavenger concentrates prior to the cleaning circuit. In this case, recovery was much higher for the scavenger cleaner concentrate at 11%, with 1,389 ppm whole basis and 1,796 ppm ash basis TREE content. The data clearly shows that the HHS process can concentrate REEs-bearing minerals from HHS coal tailings. Additionally, it appears that liberation plays a major role in the performance of the HHS process, due to the micronized size of REE particles. Furthermore, additional cleaning stages assist in producing higher grade products. It is also observed that initial recovery in the rougher leg of the circuit is poor, likely due to the collector hydrophobizing non-REE bearing gangue minerals. Composite performance plots of the 4 tests are shown in Figures 4-18 and 4-19. These plots show REE recovery as a function of TREE concentration.

Table 4-4: WV Coal F HHS REE Test 1 Results

Products	Weight		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Rougher Cleaner 2 Conc.	1.2	0.6	70.2	1,234.3	866.6	1.7
Scavenger Cleaner 2 Conc.	0.4	0.2	78.8	1,025.2	807.9	0.6
Rougher Cleaner 2 Tail	4.2	2.0	93.6	721.7	675.6	4.7
Rougher Cleaner 1 Tail	3.0	1.4	90.7	598.3	542.6	2.6
Scavenger Cleaner 2 Tail	6.4	3.0	92.7	447.1	414.7	4.3
Scavenger Cleaner 1 Tail	15.5	7.4	93.5	307.9	287.9	7.3
Scavenger Tail	178.5	85.4	91.5	294.2	269.2	78.8
Feed	209.2	100	91.6	318.4	291.5	100

Table 4-5: WV Coal F HHS REE Test 2 Results

Products	Weight		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Scavenger Cleaner 2 Conc.	1.8	1.0	79.7	2,657.4	2,117.8	7.1
Rougher Cleaner 2 Conc.	0.7	0.4	82.0	970.3	796.0	1.0
Scavenger Cleaner 2 Tail	5.6	3.0	89.1	933.0	831.3	8.8
Rougher Cleaner 2 Tail	7.6	4.1	94.5	413.4	390.7	5.6
Rougher Cleaner 1 Tail	9.7	5.2	91.6	344.9	316.0	5.8
Scavenger Cleaner 1 Tail	40.7	22.0	93.8	324.5	304.5	23.4
Scavenger Tail	118.9	64.3	91.6	235.0	215.2	48.3
Feed	185.0	100.0	92.0	311.6	286.6	100.0

Table 4-6: WV Coal F HHS REE Test 3 Results

Products	Weight		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Scavenger Cleaner 2 Conc.	1.6	0.5	69.9	3,122.4	2,181.3	3.7
Rougher Cleaner 2 Conc.	1.9	0.6	63.5	1,090.2	691.8	1.4
Scavenger Cleaner 2 Tail	8.5	2.8	86.6	991.0	858.4	7.5
Rougher Cleaner 2 Tail	5.6	1.8	86.9	864.3	751.0	4.3
Rougher Cleaner 1 Tail	19.1	6.2	91.3	583.0	532.5	10.5
Scavenger Cleaner 1 Tail	51.8	16.8	92.7	401.1	371.9	19.8
Scavenger Tail	219.0	71.2	92.0	254.9	234.6	52.9
Feed	307.6	100.0	91.6	345.2	316.1	100.0

Table 4-7: WV Coal F HHS REE Test 4 Results

Products	Weight		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Scavenger Cleaner 2 Conc.	4.4	2.3	77.4	1,795.7	1,389.0	11.0
Rougher Cleaner 2 Conc.	1.4	0.7	71.8	1,476.9	1,060.8	2.8
Rougher Cleaner 2 Tail	2.0	1.1	83.5	661.7	552.7	2.0
Rougher Cleaner 1 Tail	7.8	4.1	88.5	607.6	537.5	7.6
Rougher Ground Tail	4.0	2.1	90.6	559.1	506.3	3.7
Scavenger Cleaner 2 Tail	5.5	2.9	82.9	433.6	359.4	3.6
Scavenger Ground Tail	49.9	25.9	90.3	286.2	258.3	23.2
Scavenger Cleaner 1 Tail	27.3	14.2	93.7	240.1	225.0	11.1
Scavenger Tail	89.9	46.8	90.5	239.1	216.3	35.1
Feed	192.3	100.0	90.1	320.3	288.4	100.0

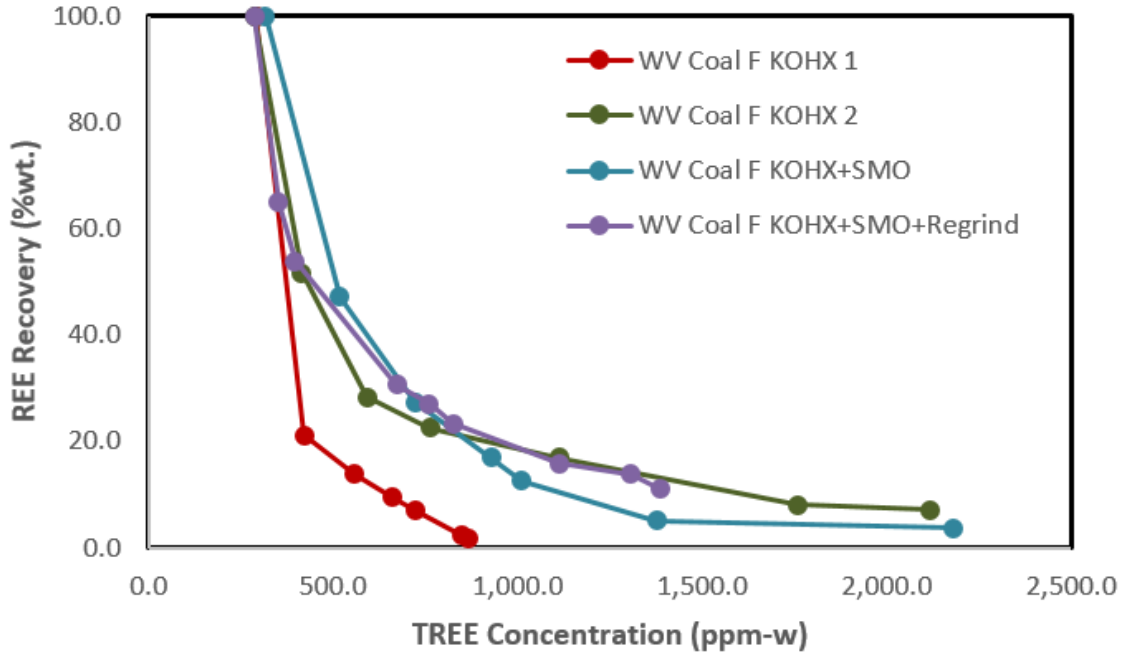


Figure 4-18: Performance plot summary for WV Coal F HHS REE testing REE recovery vs. TREE concentration whole sample basis

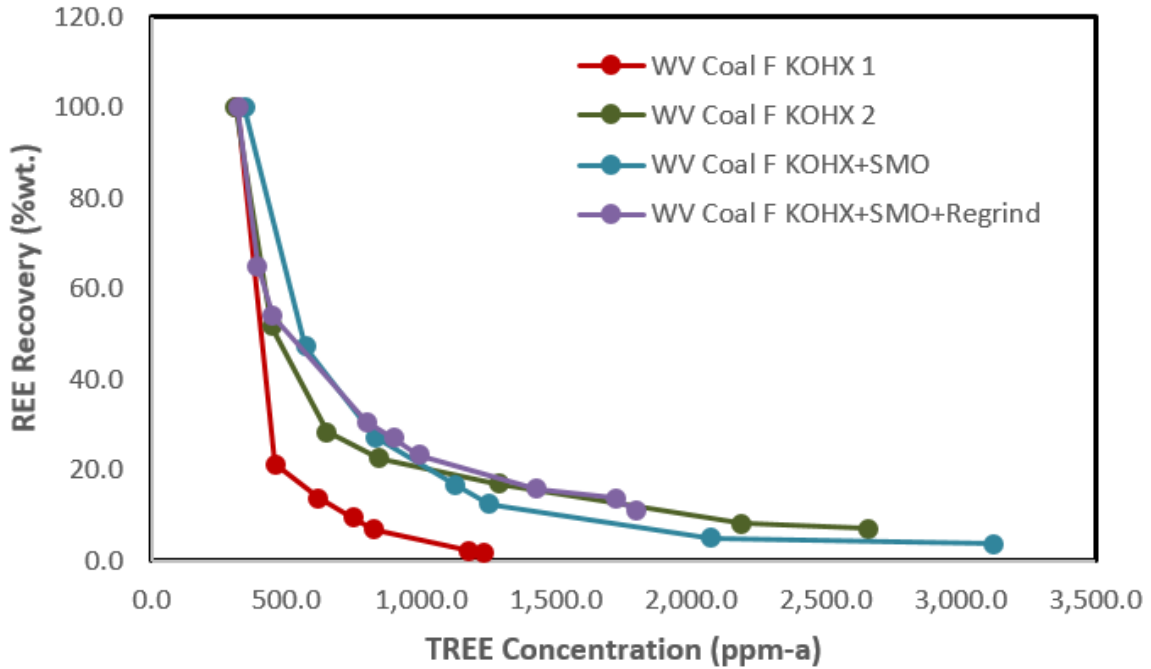


Figure 4-19: Performance plot summary for WV Coal F HHS REE testing REE recovery vs. TREE concentration ash basis

4.3.4 KY Coal D REE Testing

Coal Company I provided samples of their thickener underflow at their KY Coal D preparation plant for HHS REE testing during this phase of the research project. This series of testing was done to continue evaluation of the HHS process for REEs recovery. Specifically, in these tests different collectors were investigated, as well as, methods to achieve liberation at a cheaper cost than grinding and methods to increase the population of hydrophobic particles in the feed slurry.

For the KY Coal D thickener underflow sample, four tests have been completed and analyzed for rare earth element (REE) recovery, using Sodium Oleate and Hydroxamate as collectors. These tests were completed to see the effect of Sodium Oleate versus Hydroxamate. REE recovery is reported on an ash basis and a coal basis. Each test produced a rougher concentrate, scavenger concentrate, and tailings. The HHS process adapted for rare earth recovery was used to produce the rare earth concentrates. Per the testing procedure, the sample was decarbonized using oil-agglomeration and then ground to a d_{80} of 6 microns. The sample was then conditioned under low shear mixing with sodium silicate and then high shear mixing with Sodium Oleate for test 1 and 3, and Hydroxamate for tests 2 and 4. Standard HHS procedure followed after the condition step where oil in water emulsions (o/w) were formed and then cleaned and dewatered to produce a rougher and scavenger product. The procedure for each test is shown in Figures 4-20 through 4-23. In general, the tests with Sodium Oleate performed better than those with Hydroxamate, producing rougher and scavenger concentrates of 1439-1690 and 660-684 ppm respectively on an ash basis and 1063-1153 and 609-626 ppm respectively on a coal basis. While Hydroxamate produced rougher and scavenger concentrates of 924-1248 and 648-1118 ppm respectively on an ash basis and 782-961 and 605-1005 ppm respectively on a coal basis. The results are shown in Tables 4-8 through 4-11, and clearly indicate the HHS process is well suited to recover REEs from this stream and that Sodium Oleate may be the better collector moving forward. In addition to rare earth recovery, one test was performed on the decarbonized coal agglomerates to determine the efficiency of HHS for coal at this site. HHS performed very well for this coal reducing ash from feed of 24.8% to 3.9% with combustible recovery of 94%. This result is shown in Table 4-12.

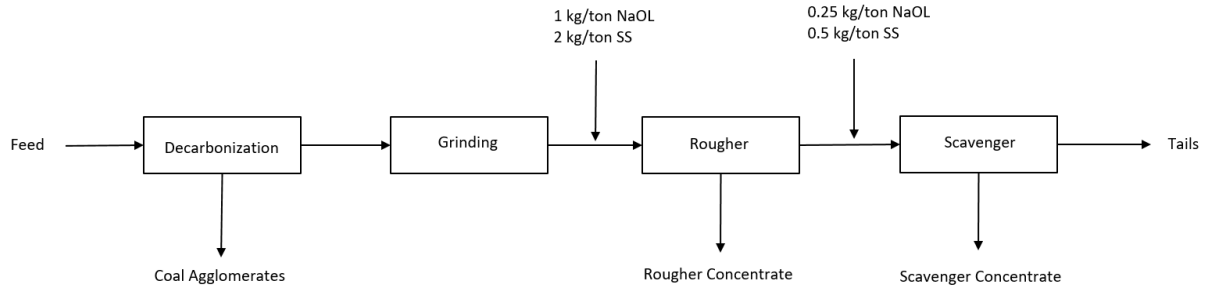


Figure 4-20: KY Coal D HHS REE test 1 experimental procedure

Table 4-8: KY Coal D HHS REE Test 1 NaOL Results

Products	Mass		Ash (% wt.)	REE (ppm)		Recovery (% wt.)
	Grams	% wt.		Ash Basis	Whole Basis	
Coal	125.8	50.0	36.9	462.7	170.7	33.0
Rougher Concentrate	2.5	1.0	68.2	1,690.5	1,153.6	4.5
Scavenger Concentrate	7.8	3.1	91.5	684.6	626.4	7.5
Tail	115.5	45.9	94.1	329.3	309.8	55.0
Feed	251.7	100.0	65.2	396.9	258.6	100.0

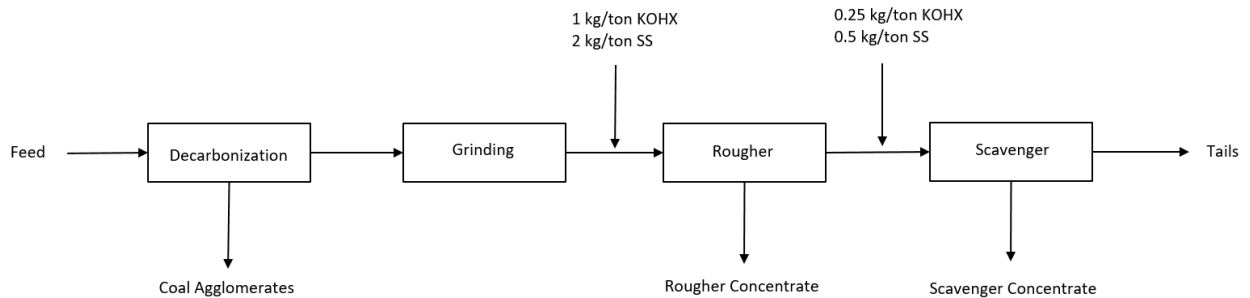


Figure 4-21: KY Coal D HHS REE test 2 experimental procedure

Table 4-9: KY Coal D HHS REE Test 2 KOHX Results

Products	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Coal	123.5	50.0	36.9	462.7	170.7	32.5
Rougher Concentrate	6.8	2.8	84.6	924.1	782.2	8.2
Scavenger Concentrate	9.8	4.0	93.3	648.5	605.1	9.2
Tail	107.0	43.3	93.8	324.2	304.2	50.1
Feed	247.2	100.0	65.1	403.4	262.6	100.0

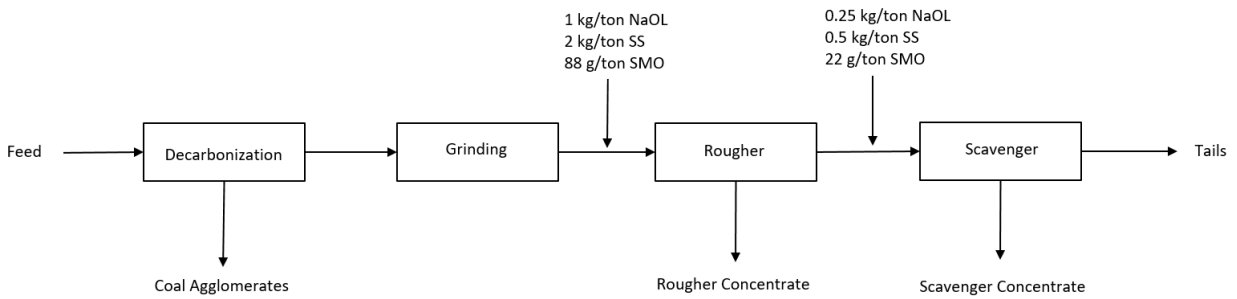


Figure 4-22: KY Coal D HHS REE test 3 experimental procedure

Table 4-10: KY Coal D HHS REE Test 3 NaOL Results

Products	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Coal	111.1	43.8	29.6	507.1	150.3	25.2
Rougher Concentrate	4.6	1.8	73.9	1,439.5	1,063.5	7.4
Scavenger Concentrate	11.4	4.5	92.3	660.1	609.2	10.5
Tail	126.6	49.9	94.1	317.0	298.3	57.0
Feed	253.7	100.0	65.4	399.5	261.4	100.0

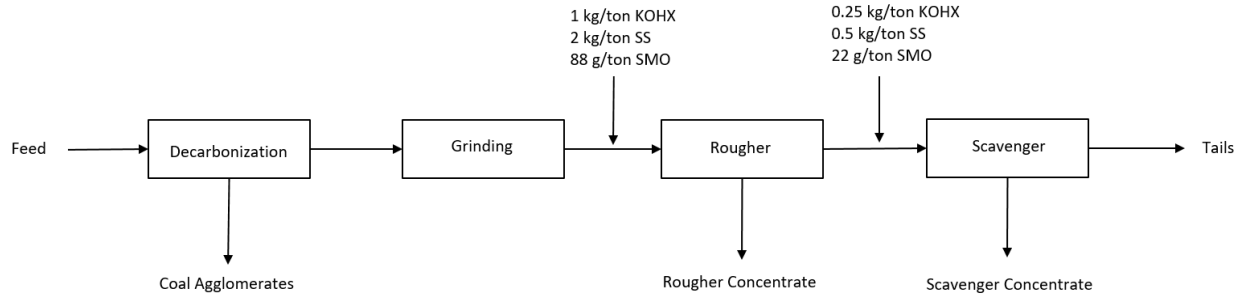


Figure 4-23: KY Coal D HHS REE test 4 experimental procedure

Table 4-11: KY Coal D HHS REE Test 4 KOHX Results

Products	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Coal	111.0	43.8	29.6	507.1	150.3	25.1
Rougher Concentrate	4.2	1.7	77.0	1,248.7	961.9	6.1
Scavenger Concentrate	6.2	2.5	89.9	1,118.8	1,005.5	9.4
Tail	131.9	52.1	93.8	319.7	299.8	59.4
Feed	253.4	100.0	65.3	402.3	262.7	100.0

Table 4-12: KY Coal D Decarbonization Results

Feed Ash (%wt.)	Product Ash (%wt.)	Refuse Ash (%wt.)	Mass Yield (%wt.)	Combustible Recovery (%wt.)	Ash Rejection (%wt.)
24.8	3.9	93.2	73.7	94.1	88.5

During this phase of the research, after completion of initial HHS REE testing, testing was completed on the KY Coal D thickener underflow sample in an attempt to improve the performance of the HHS process for REEs. From previous test work done on the sample, it has been determined that the REE population (i.e., hydrophobic particle population), and liberation are the main issues hindering the HHS process. In this series of test work, steps were taken to address these issues via increasing the hydrophobic particle population and attempting a new method for liberating REEs bearing minerals.

The first issue addressed in this series of tests was the issue of liberation. Blunging is a common technique employed in the clay industry for dispersing ultrafine clay. In the case of the KY Coal D thickener underflow sample, SEM-EDX data has previously indicated that monazite particles bearing REEs have a particle size ranging from 1 μm to 10 μm , and they appear to be already well liberated in the thickener underflow sample. Therefore, in the following test, blunging was introduced as a method of dispersing and removing fine clay particles that could create a slime effect and reduce REE recovery by the HHS process. In this test an octagonal vessel was used with a blunging impeller, as shown in Figure 4-24, to achieve the high shear agitation needed to disperse ultrafine clay particles. Roughly 500 grams of decarbonized KY Coal D thickener underflow sample in slurry at 50% solids was mixed in the vessel at 1000 rpm, with the addition of 10lb/ton of sodium silicate dispersant. The mixture was allowed to condition with the sodium silicate for 30 minutes before being transferred to a settling cylinder. Settling distance was determined using 8 μm monazite settling velocity. After a predetermined settling time and distance the overflow was collected for standard HHS testing.



Figure 4-24: (Left) blunging impeller, (Right) blunging mixing vessel

The test was completed and analyzed for rare earth element recovery after blunging with the HHS process. The results of this test are shown in Table 4-13. 100 grams of sample after blunging was mixed with 350 ml of water at roughly 400 rpm. The slurry was allowed to condition

with 2kg/ton of sodium silicate for 15 minutes. This was to help with the remaining clay in the sample and depress non-rare earth bearing minerals preventing collector adsorption. After 15 minutes 1.2kg/ton of hydroxamate collector was added to hydrophobize the REE-bearing minerals and conditioned for an additional 15 minutes. 200 ml of heptane oil, which is the preferred hydrophobic liquid for HHS REE testing, was added and mixed under high shear conditions to form oil-in-water emulsions. The sample would then be poured into a separatory funnel phase separated to remove tailings. Hand shaking was then employed with the addition of more oil in an attempt to induce phase inversion and release hydrophobic REE minerals to the oil phase. A rougher, scavenger and cleaner circuit was used to clean the sample further and attempt to increase REE recovery. The testing procedure used is shown in Figure 4-25. Both cleaner circuits required no additional reagent consumption; only water washing was used to break and reform emulsions releasing entrained tailings.

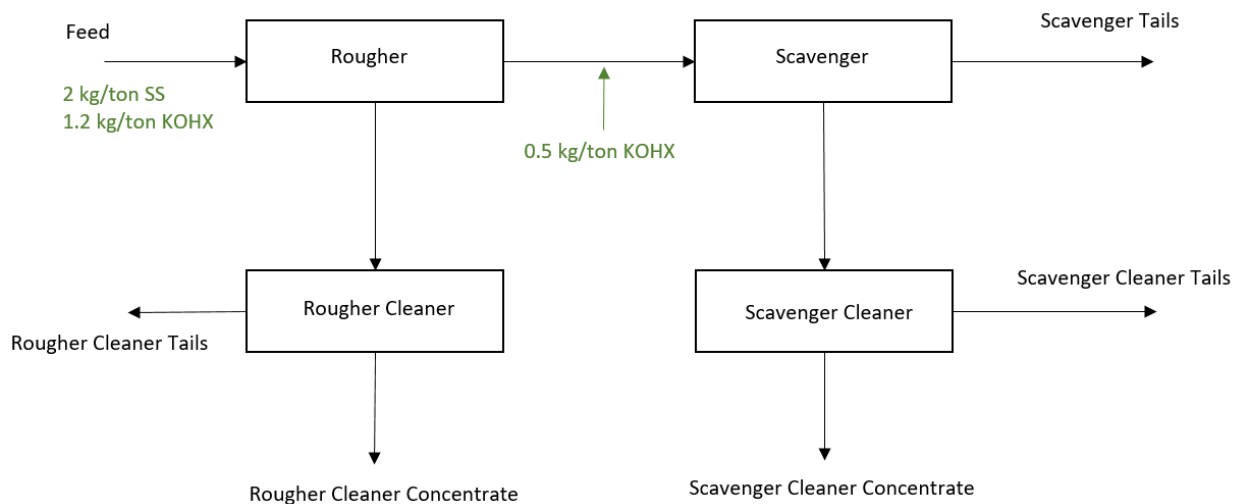


Figure 4-25: Blunging HHS REE testing procedure

The test results for blunging of the KY Coal D thickener underflow sample HHS testing, which are shown in Table 4-13, do not indicate an improvement to conventional HHS testing results presented in previous testing periods. On a whole ash basis, there is little separation seen, with REE ppm values reaching only 326 ppm in the rougher cleaner concentrate product and 288 ppm in the scavenger cleaner concentrate product. This is increased only slightly from the feed grade of 295 ppm for the rougher cleaner concentrate and decreased in the scavenger cleaner concentrate. On an ash basis, the recovery is slightly better with 622 ppm in the rougher cleaner concentrate, 538 ppm in the scavenger cleaner concentrate and 318 ppm in the feed. Additionally,

only 0.1 grams were recovered in the rougher cleaner concentrate, and 5.1 in the scavenger cleaner concentrate, out of 104 grams feed material. Recovery was low for the two concentrate products at 0.1% and 4.8% for rougher and scavenger respectively. This separation is poor compared to the separation seen with traditional grinding of the sample and HHS testing. A graphical representation of the results is shown in Figures 4-26 and 4-27.

Table 4-13: KY Coal D Thickener Underflow Blunging HHS REE Testing Results

Product	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Feed	104.1	100.0	92.9	318.0	295.3	100.0
Rougher Cleaner Conc.	0.1	0.1	52.4	622.5	326.0	0.1
Rougher Cleaner Tail	1.2	1.1	92.2	287.4	265.0	1.0
Scavenger Cleaner Conc.	5.1	4.9	53.6	538.4	288.8	4.8
Scavenger Cleaner Tail	2.7	2.6	92.0	197.1	181.3	1.6
Scavenger Tail	95.0	91.3	93.0	316.9	294.6	91.1

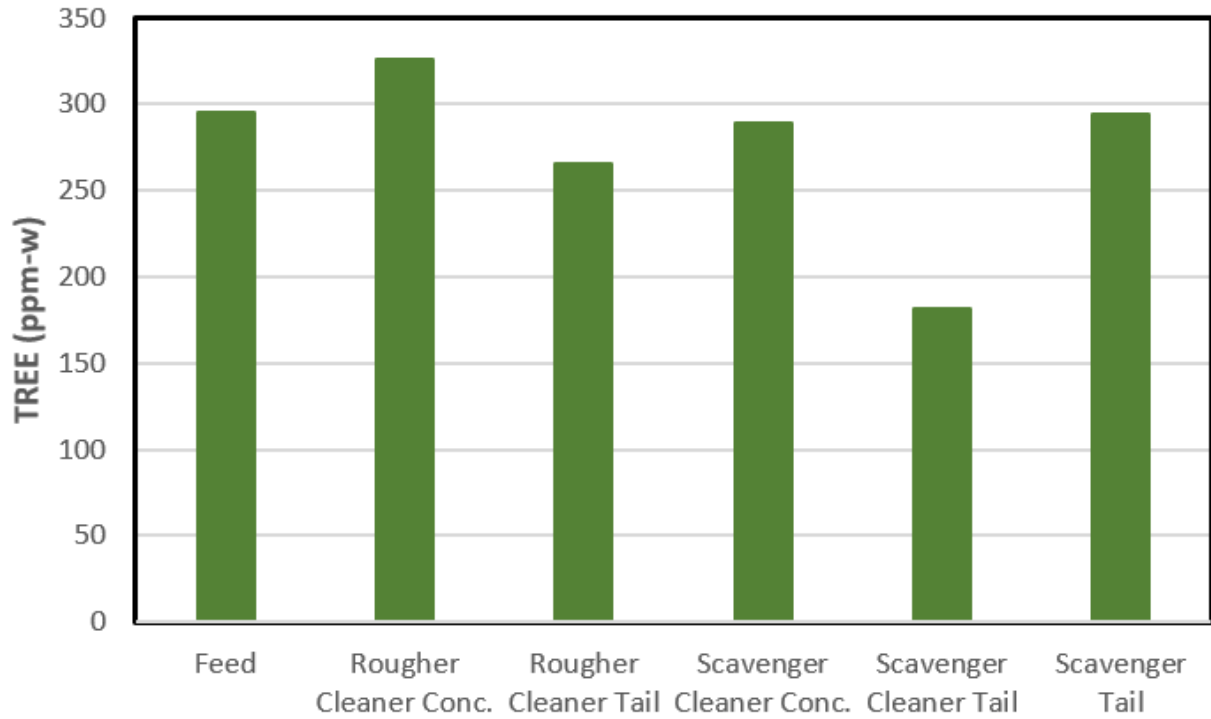


Figure 4-26: TREE whole sample basis KY Coal D thickener underflow blunging HHS testing results

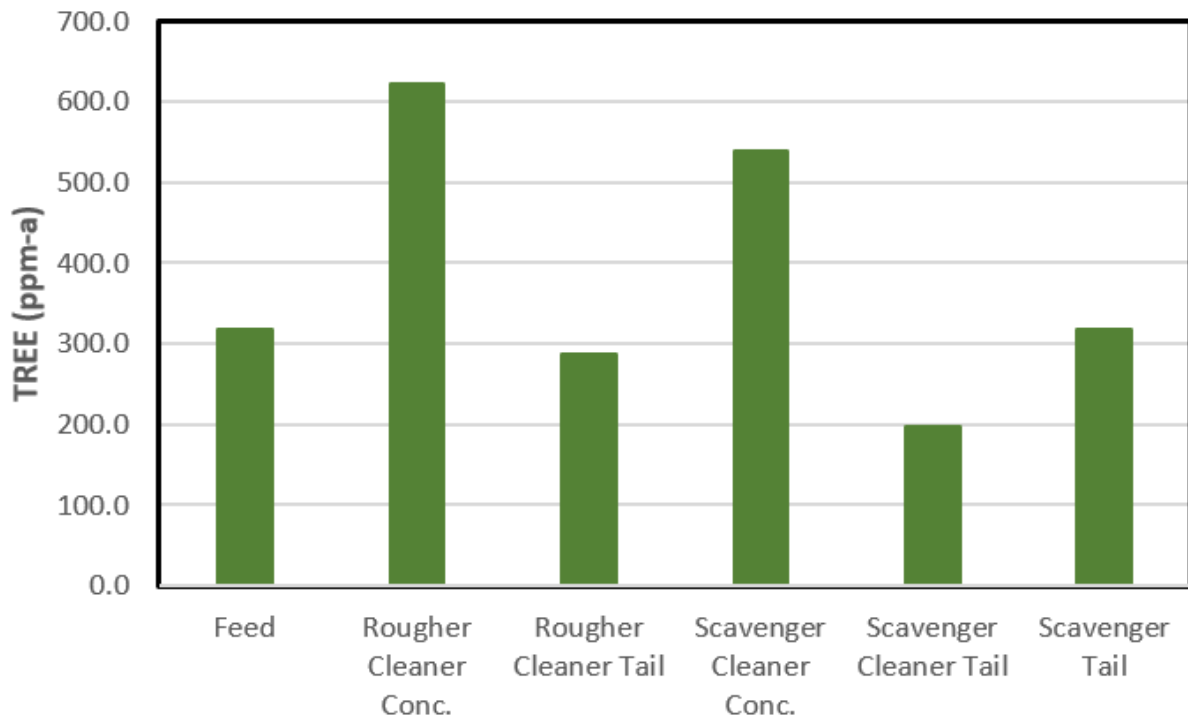


Figure 4-27: TREE ash basis KY Coal D thickener underflow blunging HHS testing results

The second parameter that was investigated during this testing period was increasing the population of hydrophobic particles in order to improve emulsion formation and collection of REEs bearing minerals into the oil phase. In order to accomplish this goal, a sample of KY Coal D thickener underflow was decarbonized using oil-agglomeration, and the coal agglomerates were saved. The tailings from oil-agglomeration were vacuum filtered and then wet ground in a laboratory attrition mill for 1 hour to a d_{80} size of 4 μm . Three total tests were then run on this sample, two with coal added back to the reactor and one as a traditional HHS REE test for comparison.

In the first test, the results of which are shown in Table 4-14 and Figures 4-28 and 4-29, 6 grams of coal was added to the mixing tank with approximately 72 grams of dry solids thickener underflow which was slurried. The mixture was conditioned with 1 kg/ton of hydroxamate for 30 minutes, after which a small amount of heptane oil was added and mixed under high shear conditions in an attempt to form agglomerates rather than traditional emulsions. After 30 minutes of high shear mixing small micro-agglomerates were formed and screened off from the tails. The agglomerates were transferred to the laboratory morganizer used during decarbonization studies for HHS coal testing. The laboratory morganizer is a glass column with two vibrating mesh screens. The column is separated into a water phase and an oil phase. The vibrating screens provide a mechanical force to de-stabilize and de-agglomerate the agglomerates in the oil phase. This releases entrained gangue minerals and water droplets which are allowed to coalesce and fall to the water phase. The free hydrophobic particles move into the oil phase and out through the overflow port. Feed grade for this sample was 290 ppm. It appears that this sample had an extremely good separation with a concentrate grade of 1789 ppm and a corresponding recovery of 16.2%. However, the original sample was lost during analysis due to over-pressure and had to be re-run with the little sample that remained, causing a high degree of possible error. It is possible this high recovery is also due to a nugget effect skewing the results. Neither of the other two tests runs on this thickener underflow sample performed nearly as well. Therefore this test should be repeated in order to determine if oil-agglomeration with coal addition actually improves the concentration of REEs by HHS.

Table 4-14: KY Coal D Thickener Underflow Coal Addition HHS REE Test 1 Results

Product	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Feed	77.9	100.0	94.2	308.1	290.3	100.0
Concentrate	2.1	2.6	4.0	44,282.2	1,789.0	16.2
Agglomerates	2.8	3.5	6.8	1,463.3	99.8	1.2
Morganizer Tails	0.7	0.9	19.0	773.4	146.6	0.5
Tails	75.2	96.5	92.2	283.2	261.1	86.8

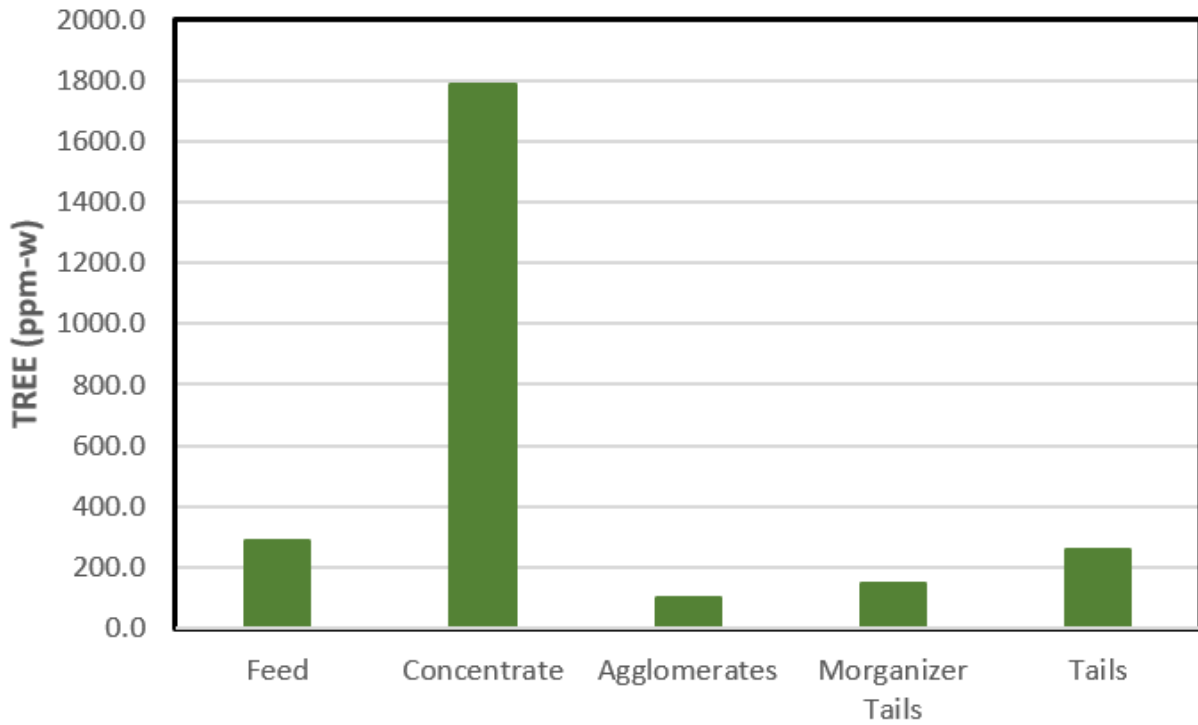


Figure 4-28: TREE whole sample basis KY Coal D thickener underflow coal addition test 1

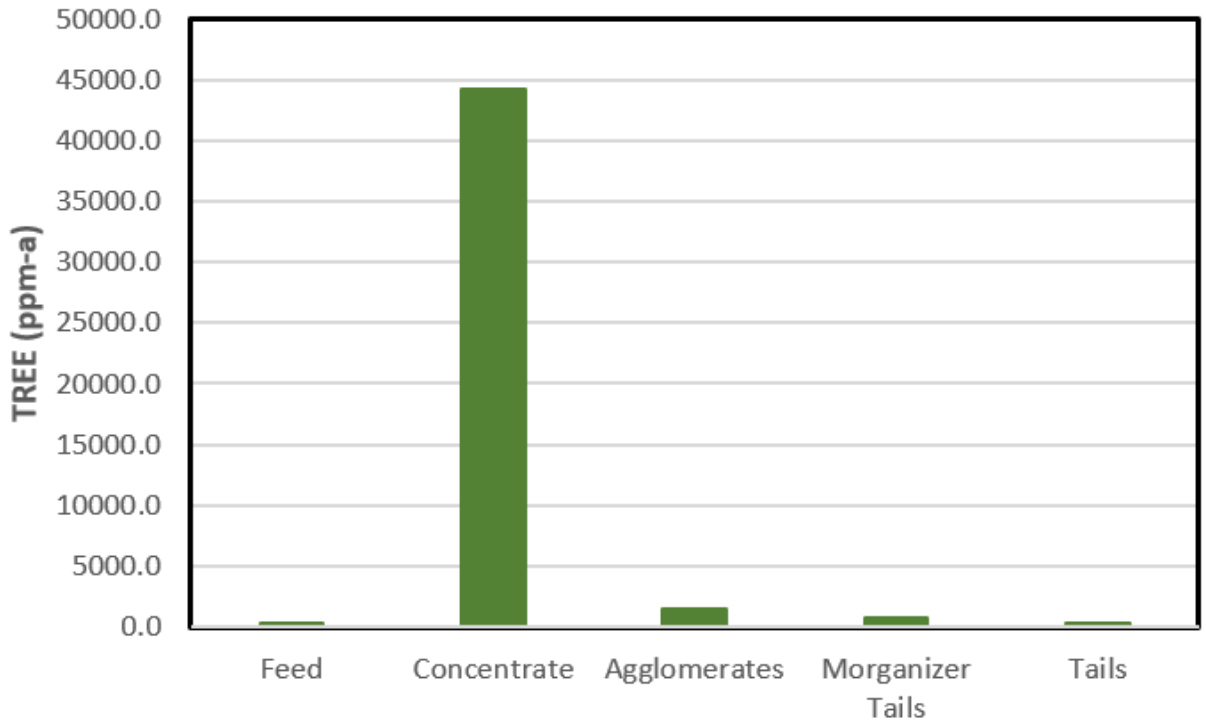


Figure 4-29: TREE ash basis KY Coal D thickener underflow coal addition test 1

In the second test, the results of which are shown in Table 4-15 and Figures 4-30 and 4-31, the procedure used in test one was modified by using the more traditional two-liquid flotation method of HHS testing with coal addition. For this test oil-in-water emulsions were formed and separated in a separatory funnel. 1 kg/ton of hydroxamate was used to condition the slurry, and 6 grams of coal were added at this time. A larger amount of heptane oil was added to form emulsion after 15 minutes of conditioning, and the emulsions were transferred to a separatory funnel. After removing the water phase, which held gangue minerals, additional oil was added to the system and hand shook to break the emulsions releasing hydrophobic particles to the oil phase and entrapped gangue to the water phase. The oil phase was collected as a concentrate sample while the remaining emulsions that did not break were collected as a middling product. This test was unsuccessful in increasing REE concentration by increasing the hydrophobic particle population. There was essentially no separation as both the concentrates and middling products produced grades of 101 ppm and 121ppm respectively compared to a feed grade of 290 ppm. In essence, only coal was recovered during this test.

Table 4-15: KY Coal D Thickener Underflow Coal Addition HHS REE Test 2 Results

Product	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Feed	91.6	100.0	94.2	308.1	290.3	100.0
Concentrate	2.9	3.1	3.1	1,228.0	101.3	1.1
Tails	87.5	95.5	95.5	324.4	303.0	99.7
Middling	1.3	1.4	1.4	1,298.5	121.0	0.6

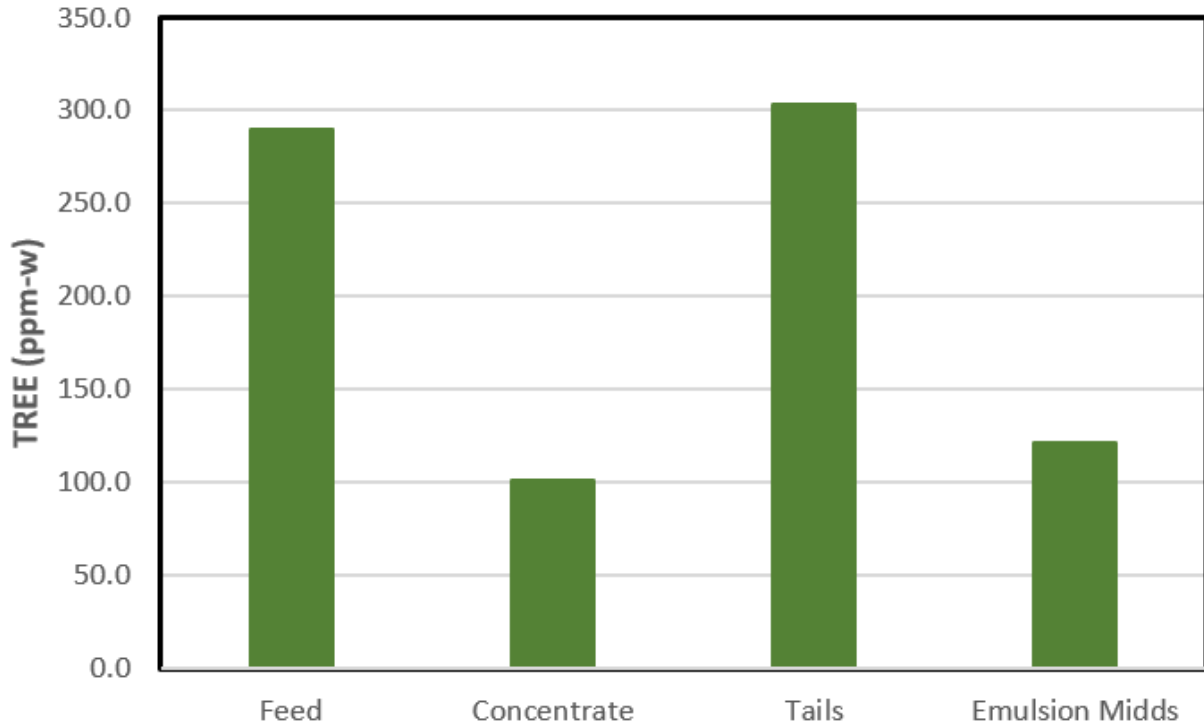


Figure 4-30: TREE whole sample basis KY Coal D thickener underflow coal addition test 2

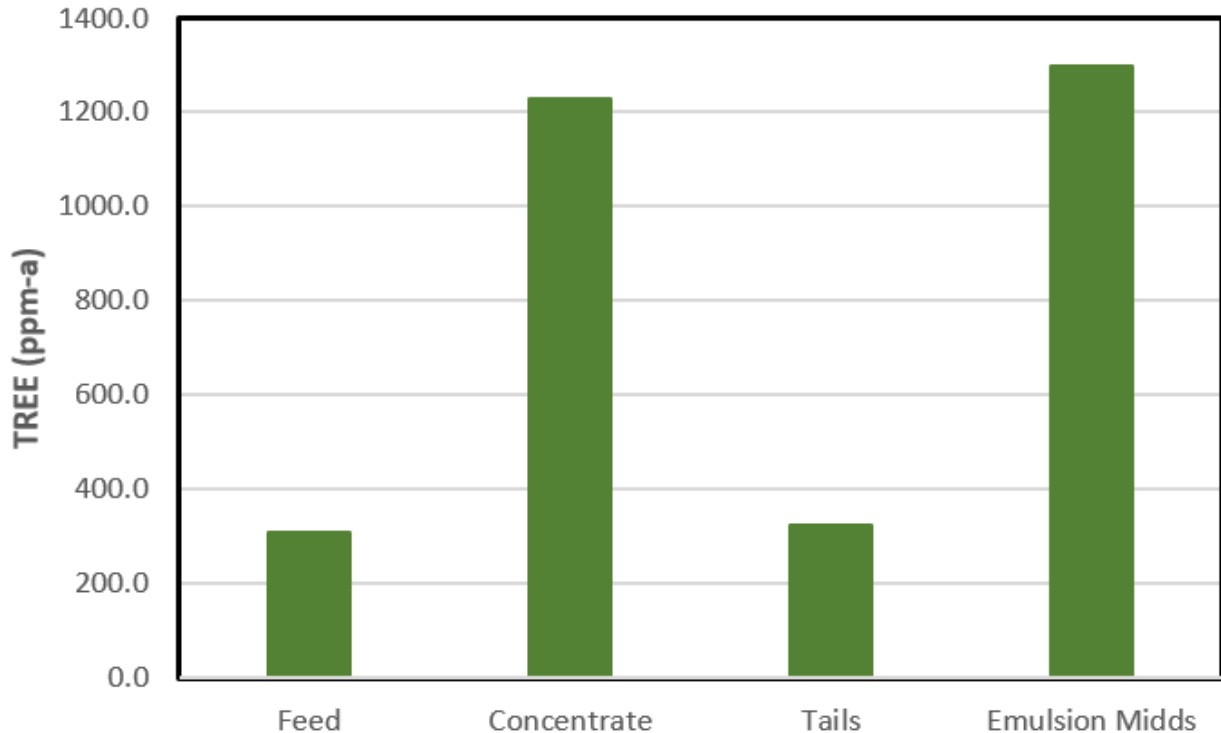


Figure 4-31: TREE ash basis KY Coal D thickener underflow coal addition test 2

The final test, the results of which are shown in Table 4-16 and Figures 4-32 and 4-33, was a control test without any addition of coal for comparison purposes to indicate the impact if any that coal addition had of REE concentration. The test was performed in the same way as test 2 but without the addition of coal. Additionally, two stages of water washing were employed in an attempt to remove further entrapped gangue minerals and induce phase inversion to allow for emulsion breakage and release of particles to the oil phase. This test performed much better than the previous two tests, assuming test 1 is in error. The cleaner concentrate product had a grade of 583 ppm whole basis and 1,197 ppm ash basis, compared to 290 ppm whole and 308 ppm ash observed in the feed. Interestingly, the middling sample recorded the highest grade product at 641 ppm whole basis. Unfortunately, recovery values were low at 1.8% and 0.9% for the cleaner concentrate and middling products respectively. Overall coal addition does not appear to improve the HHS REE process in terms of improving REE concentration based on the few tests run. It appears in most cases the HHS process preferentially recovers coal in these cases without collecting REE minerals, as coal is naturally hydrophobic and well suited for HHS. Additional tests should be undertaken to validate or invalidate the results of test 1, and further investigate solutions to liberation and population which still appear to hinder the HHS process.

Table 4-16: KY Coal D Thickener Underflow Coal Addition HHS REE Test 3 Results

Product	Mass		Ash (%wt.)	REE (ppm)		Recovery (%wt.)
	Grams	%wt.		Ash Basis	Whole Basis	
Feed	83.1	100.0	94.2	308.1	290.3	100.0
Cleaner Concentrate	0.7	0.9	48.8	1,197.2	583.6	1.8
First Cleaner Tails	1.4	1.7	92.2	286.0	263.6	1.5
Final Cleaner Tails	1.7	2.0	94.0	327.9	308.1	2.1
Middling	0.3	0.4	90.4	710.0	641.9	0.9
Rougher Tails	79.0	95.0	94.3	286.8	270.5	88.6

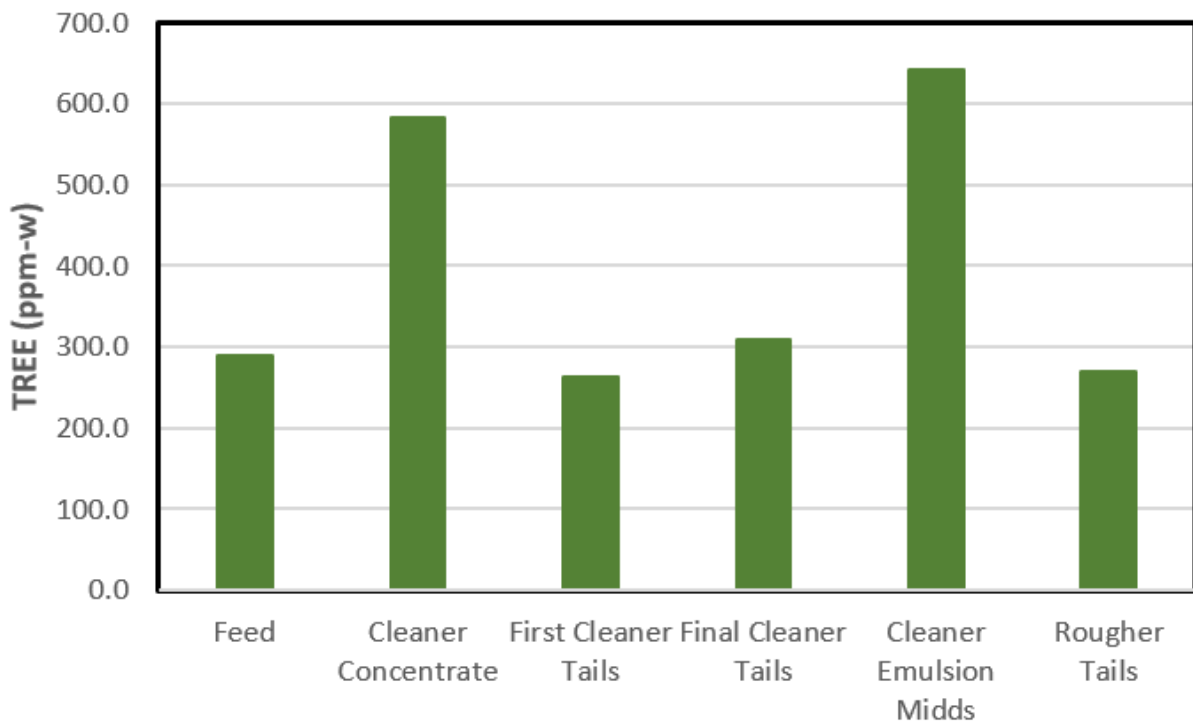


Figure 4-32: TREE whole sample basis KY Coal D thickener underflow coal addition test 3

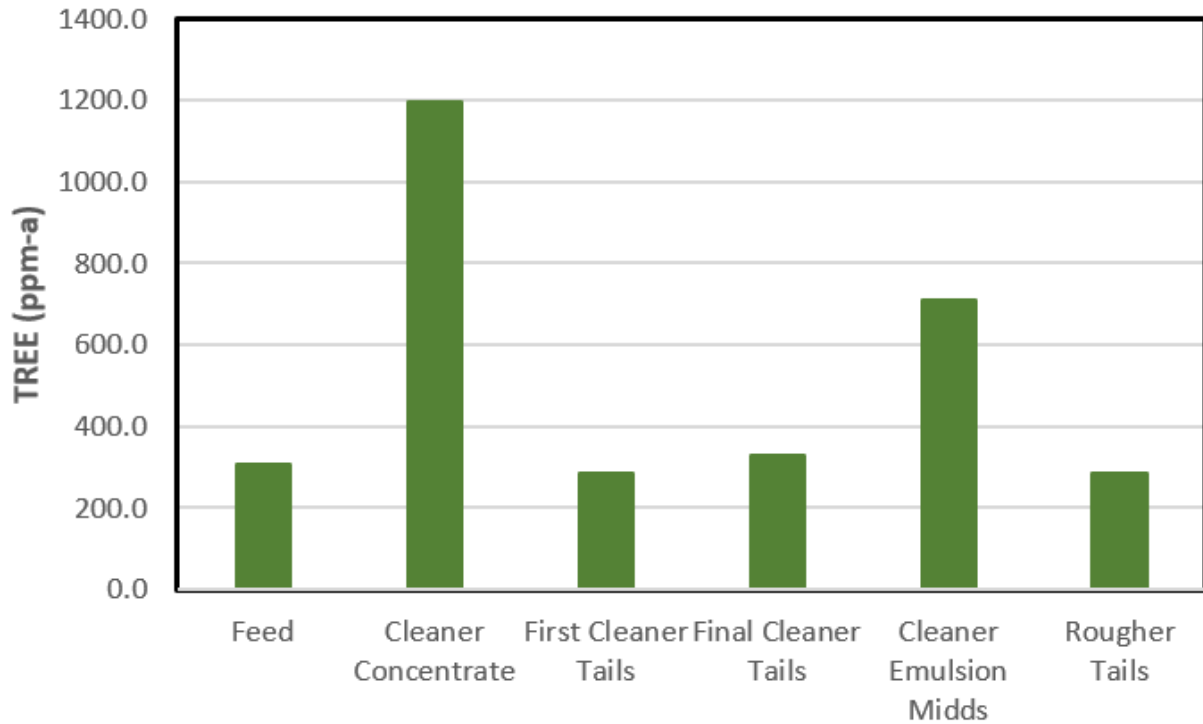


Figure 4-33: TREE ash basis KY Coal D thickener underflow coal addition test 3

4.4 Discussion and Conclusions

The HHS process for REE recovery proved successful on a few samples tested. Firstly, the results of this research clearly indicate that the HHS process is well equipped to decarbonize REE-rich coal streams and upgrade the coal product into a salable coal product while simultaneously producing a “free” REE feedstock. Decarbonization analysis was performed on both the WV Coal D Low Ash Middling sample and KY Coal C thickener underflow sample. In both cases, the HHS tailings were enriched in REEs with high recovery from the feed coal. TREE content was increased in the tailings of these samples.

While concentrating REE in coal tailings was successful, and characterization of these samples showed elevated concentrations. REE recovery by the HHS process was varied. Two main samples were tested for REE recovery, those being KY Coal D thickener underflow and WV Coal F thickener underflow. The results of these tests indicated that the HHS process could produce concentrate products of concentrated REEs. However, recovery was often low. Liberation and low population of hydrophobic minerals were determined as the main deterring factors for the HHS

process. REE-bearing minerals were determined to be as small as 1 micron in some SEM-EDX data, with the possibility of sub-micron particles. In light of this, liberation is extremely important to free REE-bearing minerals from gangue to allow for a collector to properly act as a hydrophobizing agent. The low population also plays an important role in REE recovery. With a low population of hydrophobized particles the probability of attachment to oil droplets is low, and therefore recovery during emulsion formation is very difficult. This was often observed to be the case.

Tests on the effect of Hydroxamate vs. Sodium Oleate indicated that Sodium Oleate (C-18 Fatty Acid) was superior in producing a high-grade product with high recovery. Although tests were positive in terms of grade and recovery, most batch tests resulted in the collection of emulsion product for analysis rather than collection of the oil phase of the separatory funnel which should be dispersed with REE minerals. Phase inversion is a key step in the process allowing for the destabilization of emulsions and release of entrapped water and gangue minerals. Coal addition and blunging failed to aid in the recovery of REEs and in these cases no phase inversion was observed. Grinding is clearly the superior method for liberation of decarbonized samples.

Overall, the testing met the project goals, demonstrating that the HHS process can successfully decarbonize ultrafine coal waste samples, producing a low ash/low moisture salable coal product, and simultaneously produce a “free” REE feedstock from the HHS tailings. TREE analysis indicated elevated concentrations in the samples. REE recovery results were mixed, but some test work was extremely encouraging, producing high-grade REE concentrate with a moderate recovery. In future testing liberation and population should continue to be investigated for their specific effect on the HHS process.

CHAPTER 5. METALLIC ORE RECOVERY

5.1 Introduction

Realizing the need to continue the progression of the hydrophobic-hydrophilic separation (HHS) process, and having successfully demonstrated its ability to recover rare earth elements (REEs), research shifted to focus on metallic ore, specifically copper. Originally, test work was completed to develop a semi-continuous HHS testing unit for the recovery of ultrafine rare earth minerals (REM). As shown in the previous chapter batch scale tests were completed without the use of a laboratory morganizer. A new morganizer unit was developed for the purpose of improving the quality of REM concentrates achieved with the HHS process. Because monazite, a common REM, is radioactive copper was chosen as an appropriate substitute for the development, testing, and optimization of this unit. The testing provided a positive outlook of REM recovery, while simultaneously proving the HHS process as a capable method for producing high-grade copper concentrates. As discussed in chapter 2, metallic ore is a major staple of the mining industry, and demand for many essential metals has continued to increase dramatically, leading companies to mine at higher rates to meet the demand. With decreasing ore grades and lack of new reserves being developed, plant improvements with regards to ultrafine processing and waste recovery are essential to the global market. While several candidates for HHS research were considered (Aluminum, Copper, Gold, Lead, Zinc, Nickel, etc.), copper was eventually chosen to show the viability of the HHS process for metallic ore.

The importance of copper is well established in modern day society. Production has decreased recently due to declining ore grade and lack of new mines, while global consumption has continued to increase. (USGS Mineral Resources Program, 2009). With these challenges identified, the industry should look to increased plant recovery in terms of ultrafine particles from waste. Flotation tailings make up 90-95% of total plant tailings, and because of its limited size range fine particles often leave in the tailings stream. Furthermore, the coarse limit of flotation cells is typically ground and reground to help increase flotation recovery. Therefore, the vast majority of recoverable copper particles in plant tailings streams are less than 30 μm in size (Mankosa et al., 2016). The HHS process can overcome the challenges faced by the copper industry by recovering

this ultrafine waste fraction. In this chapter, the development of the HHS process for copper is discussed, and results from three major copper producers are presented.

5.2 Experimental Procedure

The following section describes the experimental procedure, materials, and equipment used during this phase of the research to successfully demonstrate the HHS process' ability to recover ultrafine copper particles from plant tailings. This section explores the processes used to liberate chalcopyrite particles from gangue minerals and recover those particles using the HHS process, as well as, the development of a new morganizer for copper and metallic ore recovery.

5.2.1 Copper Samples

Initial exploration into metallic ore testing began with artificial copper samples obtained from Wards Science. These samples were student specimen samples that were approximately 2 inches in size and would therefore require significant sample preparation for HHS testing. Samples were described as having good grade, and being brass-yellow copper ore. Samples were purchased in bulk from Wards Science at 10 samples per pack. These samples provided a cheap, easily accessible alternative to testing true plant ore. The samples allowed for exploratory HHS copper testing, which was necessary due to the experimental nature of the work. Because new equipment and methods had to be developed for the copper modified HHS process, the artificial samples provided an effective source to carry out more trial and error type of work. The samples varied in feed grade across all tests. Samples were prepared in whole when received at the laboratory and stored in bags within a refrigerator to prevent oxidation. Later in the testing period, samples were procured from three operating U.S. processing plants. For confidentiality, names of the various companies and plants from which samples were taken are changed and listed as Mineral Company A, B, C, etc.

Mineral Company A, located in Arizona, provided two samples for testing with the HHS process during this phase of the research project. The first of which was a plant feed sample assaying 0.24% Cu. This sample would require some sample preparation for HHS testing but was the only feed copper tested during this phase of the research. The second sample provided by Mineral Company A was a fine copper waste product that was received as a filter cake for HHS testing. This sample was a scavenger-cleaner tails sample collected from the flotation circuit after

the regrind circuit in the processing plant and assayed 0.15% Cu. These samples would serve to test the HHS process on real copper ore, and determine the effectiveness of the new morganizer in recovering and upgrade waste copper ore.

The UT Copper A mine provided a scavenger-cleaner tailing sample for HHS testing during this phase of the research project. This is a tailings sample that is currently discarded as waste from the column flotation circuit in the plant. The sample was received as a filter cake sample and has a feed grade assaying 0.55% Cu which is higher than the plant feed grade, but due to poor efficiency in the flotation circuit for recovery the fine fraction it is regrettably discarded. This provides a huge opportunity for the HHS process to recovery high-value copper from currently discarded waste, which is the primary objective of the HHS process.

Lastly, a sample was procured from Mineral Company C's AZ Copper C Mine in Arizona. This was again a scavenger-cleaner tailings sample, as the HHS process attempts to recovery waste stream product that is not recoverable with conventional methods. The sample assayed roughly 0.39% Cu, and was received as a dry powder for HHS testing.

5.2.2 Experimental Apparatus

This section serves to present the various pieces of equipment that were used during testing for copper recovery with the HHS process. Specifically, it highlights the sample preparation equipment and methods to work samples into acceptable product for HHS testing, the emulsion formation, and phase inversion equipment, and the solvent recovery system. Any equipment not described in this section, but used in specific testing, is described in the results section.

5.2.2.1 Sample Preparation

Sample preparation is a major requirement across all samples tested with the HHS process during this research. In many cases sample preparation is required due to inadequate particle size, as if the material is too coarse it does not work effectively with the HHS process, though the process has effectively no bottom size constraint. In other cases, sample preparation is required to help with liberation of the target mineral, as was the case with several coal and REE samples previously discussed. In the case of copper, this is no different. Virtually all samples required some form of sample preparation to be viable with the HHS process modified for copper.

In the case of the artificial copper sample, samples arrived as coarse rocks with an average size of about 2 inches. This sample would need significant crushing and grinding to work the sample into an acceptable size range. Typically, samples would be first crushed using a laboratory jaw and cone crusher and then ground in a laboratory ball or attrition mill to an acceptable size class. However, for the artificial copper sample, this method was modified due to significant amounts of coal dust in the crushing units at Virginia Tech, and the need to prevent sample contamination. There for samples were hand crushed to minus 0.5 mm using a standard hammer and 0.5 mm sieve and collection pan. After achieving minus 0.5 mm the sample was wet ground in a laboratory ball mill, as shown in Figure 5-1, to a d_{80} size of 10 μm . After grinding, the sample was stored in bags and held in a refrigerator until consumed.



Figure 5-1: Laboratory ball mill

For the remaining samples, liberation is a major concern in most copper processing operations and as such, samples undergo extensive grinding prior to the flotation circuit in these plants. Accordingly, samples were investigated on an as-received basis to determine if additional grinding was needed. In many cases liberation still proved to be an issue in these samples and as such sample preparation was required. Samples would be ground in a laboratory ball or attrition mill to improve the liberation of chalcopyrite particles.

5.2.2.2 Conditioning and Emulsion Formation

Once samples were evaluated on an as received basis and sample preparation was completed if required, samples could be tested using the HHS process modified for copper recovery. The first step in this process is similar to the process for REE recovery. Copper samples would need to be conditioned using a standard collector as a hydrophobizing agent. This would be handled in one of two ways. Firstly, the slurry would be conditioned in a 5 L Plexiglas mixing tank with an agitator, and secondly, conditioning and emulsion formation would be done in a separatory funnel by hand shaking. For sulfide copper ores, xanthate collectors are well established as effective collectors and are widely used in processing plants. Therefore, for the copper HHS tests completed in this research, potassium amyl xanthate (KAX) was used to condition the copper slurry prior to emulsion formation. After condition for a certain amount of time (time varied between tests), a small amount of hydrocarbon oil (heptane) was added to the mixing vessel. This would be done to collect hydrophobic chalcopyrite particles as oil-in-water emulsions. This process of forming oil-in-water emulsions is identical to the emulsion formation process described for REEs, where oil droplets are stabilized by hydrophobized particles in an aqueous phase. The Plexiglas mixing vessel and separatory funnel used for hand shaking are shown in Figure 5-2.



Figure 5-2: (Left) separatory funnel for hand shaking tests (Right) Plexiglas tank for conditioning and emulsion formation

5.2.2.3 Phase Separation and Phase Inversion

After successful formation of oil-in-water emulsions, the slurry was processed by two different methods. The first method was to phase separate the slurry removing the bulk tailings and pump the slurry into the new laboratory morganizer. The morganizer development and use is in the next subsection. The second method was similar to the REE process where the slurry would be transferred to a separatory funnel and phase separated by removing the bulk tails using the bottom valve on the funnel. Once the bulk tails were removed in the separatory funnel, additional oil would be introduced to the system and the funnel would be hand shook to induce phase inversion. Phase inversion is necessary in order to release entrapped water droplets which also carry a certain amount of gangue minerals. Gentle shaking would provide enough energy to break the emulsions and release entrapped water and gangue if phase inversion occurs. This process of phase inversion and breaking of emulsions also allows high grade hydrophobic chalcopyrite particles to be released from the emulsions and travel to the oil phase which can be collected as concentrate.

5.2.2.4 Solvent Recovery

Solvent recovery is a major step for the HHS process and a driving economic factor in the commercialization of the process, which is the ultimate goal, as the solvent cost is a large expenditure. The spent solvent must be recovered and recycled back to be used again in the process. In the case of coal, pentane oil is used, and so gentle heating is sufficient to recover the solvent. However, for the copper process, heptane oil is used and must be filtered for recovery. In this case, a laboratory pressure filter operating at a pressure of 1-2 bar is used to remove solvent from the concentrate stream and recycle the solvent back to the head of the process. The laboratory pressure filter is shown in Figure 5-3.



Figure 5-3: Laboratory pressure filter

5.2.3 Development of a New Morganizer

Previous testing had been completed in an attempt to break mineral emulsions in the laboratory morganizer used for the HHS coal process. This morganizer is a glass column with a set of vibrating mesh screens that serve to provide a mechanical force for breaking coal agglomerates. However, coal has a much lower SG than the minerals tested and as such researchers observed that the emulsions would sink in the morganizer as the upward flow of hydrophobic liquid was not sufficient and very little product was able to disperse in the oil phase. This would be the case of copper which has a specific gravity ranging between 4.1 and 4.3. In light of these problems, an attempt was made to develop a new morganizer that would be designed to handle metallic ore feed. It was firstly determined that the new morganizer would be a larger throughput unit so that the development of a semi-continuous unit could eventually be undertaken. The chemical industry often uses packed bed columns, which are hollow columns filled with either a random or structured packing, for liquid-liquid separation, as the column promotes contact with a

collector liquid in these cases. In principle, this idea of a stationary packed column could provide proper breakage of emulsions, similar to the vibrating mesh morganizer while having an economic advantage

The initial column was a 1.25-inch inner diameter, that was 48 inches long. The column had two feed ports (bottom and middle of the column), and two outlet ports (overflow and tailings). The column utilized a structured copper mesh packing that was installed above and below the emulsion feed port. The active packing section was 36 inches. The column was fed with emulsions during operation through the middle port, and heptane oil through the bottom port. This creates a countercurrent flow of heptane and water in the column. Emulsions and oil are fed using a peristaltic pump. The column allows for a much higher oil velocity to provide a carrying velocity to pick up released chalcopyrite particles, which prevents the major issue of particle settling seen in the old morganizer. The packing sections provide a restriction for which emulsions can pass through resulting in enough energy to break the emulsions and release entrapped water and gangue. Alternatively, the packing also provided a surface for water droplets to coalesce on and become heavy and fall to the tails. Based on experimental work, roughly 2-3 ft/min heptane flow was needed to carry chalcopyrite particles. The new morganizer is shown in Figure 5-4, with a detailed drawing that is found in Appendix C.

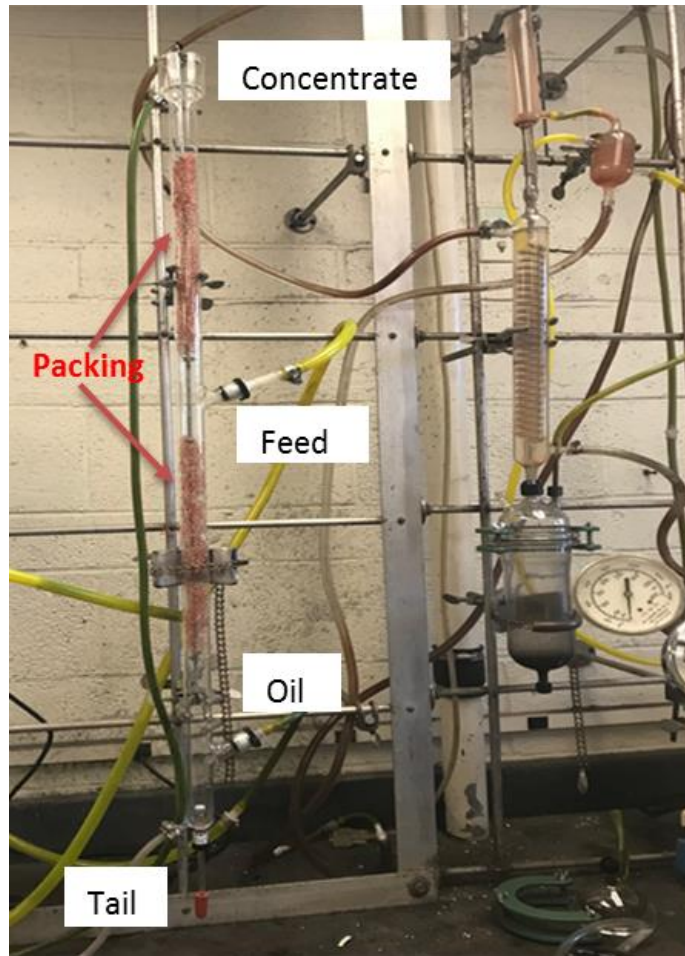


Figure 5-4: New laboratory morganizer

5.2.4 Methods and Materials

The HHS process was again modified to include testing for metallic ore. In this phase of the research, copper was chosen for HHS initial progression into metallic ore. An attempt was made to keep the process as similar to the coal process as possible, but some changes were inevitably made, namely the addition of a conditioning stage and the new morganizer, as well as, emulsion formation or two-liquid flotation rather than oil-agglomeration. Per the testing procedure, different reagents were often used to aid in the recovery process. This section serves to present the general method used to complete HHS testing on copper ore and to discuss the various reagents used during testing.

5.2.4.1 Experimental Method

For the HHS copper testing, samples were firstly examined on a size basis and determined if sample preparation was required. After which, samples were slurried in a mixing vessel and prepared for HHS testing. In a given HHS test, approximately 3L of slurry was conditioned with potassium amyl xanthate (KAX) at a pH of 9.5. Low-shear mixing was employed at approximately 400 RPM for the conditioning step. After conditioning for a set period of time, typically 15 minutes though varied throughout the tests, approximately 400 ml of heptane oil was added to the tank to induce emulsion formation. Under high-shear conditions (600 RPM), oil-in-water emulsions were formed, which in general were oil droplets coated with hydrophobized chalcopyrite. After 5 minutes, the slurry was pumped into the new morganizer (packed bed extraction column) using a peristaltic pump, and additional heptane was pumped into the bottom of the column by means of a peristaltic pump to create an upward flow that would carry chalcopyrite particles released from the breakage of emulsions. A mechanical force is needed to break agglomerates or emulsions by overcoming the weak intermolecular forces that hold them together, which has traditionally been provided by a vibrating mesh screen. This force is applied in the extraction column by passing the emulsions through the structured packing section. In the extraction column, the packing also serves to allow a surface for the coalescing of water droplets, which become heavy and fall to the tails. Tails are collected from the bottom of the column, and a heptane-chalcopyrite mixture is collected from the overflow port. The dispersed chalcopyrite in heptane is poured into a pressure filter to recover the spent oil and recycle for further use, leaving a dry chalcopyrite concentrate. This has proven to be a very effective process for recovering chalcopyrite from plant waste streams.

5.2.4.2 Reagents

Heptane (C_7H_{16}) was the hydrophobic liquid used during HHS copper testing in this phase of the research project. No other hydrophobic liquid was used. HPLC Grade 99+% n-heptane from Alfa Aesar, was obtained for used during this testing. Table 4-1 in chapter 4 shows the relative properties of heptane for the work completed. In all tests a single collector was used as the primary hydrophobizing agent which was potassium amyl xanthate (KAX) obtained from Tokyo Chemical. Xanthate is a common collector used in the processing of metal sulfides. In some cases, Sorbitan Monooleate was used to aid in the hydrophobicity of chalcopyrite. In some tests, there was a need

to depress pyrite activation by the formation of dixanthogen. In these cases, lime and sodium cyanide were used, as they are common industry used pyrite depressants.

5.3 Results and Analysis

Phase 3 of this research was originally developed to test ultrafine copper as a substitute for ultrafine rare earth minerals (REM) like monazite. Monazite is radioactive and therefore difficult to work with. Because of this, copper was chosen as a substitute monazite with similar properties. Previous results, such as those seen in chapter 4 of this work, show that in batch tests the HHS process is able to produce relatively high-grade concentrates with lower recoveries. However, these tests were conducted without the use of a laboratory morganizer unit. A new morganizer was developed for this series of testing to attempt to increase grade and recovery of REMs. This series of testing had the added benefit of proving the HHS process as capable of producing high grade copper concentrates, to go along with, the promising outlook on recovery of REMs with the new laboratory morganizer. This section serves to present the results of the HHS testing on copper waste samples. Where experimental procedure differs from the aforementioned procedure, it is discussed in this section. Additionally, analyses are given on the results presented as it pertains to the performance of the HHS process. Samples from the three distinct processing sites are discussed as well as, the results obtained from testing on the artificial sample.

5.3.1 Artificial Copper Testing

During this phase of the research project, artificial samples were procured from Wards Science for exploratory testing using the modified HHS process for copper and to test the new morganizer design. The testing presented on the artificial copper samples represent the first expansion of the HHS process into the metals industry. As described above the artificial samples were hand crushed and then wet ground to a d_{80} size of 10 μm for HHS testing, as typically particle sizes less than 15-20 μm are discarded as waste. Four initial testes were run to determine the viability of the new morganizer for breaking copper emulsions and producing a high-grade concentrate product.

In the first series of HHS testing, 3L of artificial slurry at 6.8% solids was conditioned with KAX at a pH of 9.5 for 10 minutes. The slurry consisted of 15 grams of pure chalcopyrite assaying

23.54 %Cu and 190 grams of pure silica assaying 0 %Cu. After conditioning 400 ml heptane was added to the mixing vessel and oil-in-water emulsions were formed. The entire feed was then pumped into the morganizer with a peristaltic pump, along with additional oil fed from the bottom of the column at approximately 2 ft/min. Table 5-1 shows the results of the initial HHS testing, obtained with artificial copper samples. Two different KAX dosages were used for these tests at 0.3 kg/ton and 0.4 kg/ton. The results of the initial testing were very positive, indicating that the HHS process is well capable of producing high-grade copper concentrates from the ultrafine copper feed which would be finer than the effective flotation size range. Copper grades ranged between 14.6% and 29.4%, which is quite high on the top end, for the concentrate product. These grades corresponded to recovery values ranging between 86% and 93%. Often times multiple stages of cleaning are required in processing plants to achieve as high copper grades as seen with a single HHS run, indicating that the HHS process is likely superior to flotation with regards to fine copper.

Table 5-1: Artificial Copper Initial HHS Testing

Test #	KAX (kg/ton)	Products	Grade (%Cu)	Recovery (%wt.)
1	0.3	Concentrate	14.6	93.0
		Tail	0.1	7.1
		Feed	1.6	100.0
2	0.3	Concentrate	25.8	91.3
		Tail	0.1	8.7
		Feed	1.5	100.0
3	0.3	Concentrate	25.9	91.9
		Tail	0.1	8.1
		Feed	1.6	100.0
4	0.45	Concentrate	29.4	86.8
		Tail	0.2	13.2
		Feed	1.5	100.0

It is also worth noting that the recovery of copper to the concentrate stream dropped for the last test in which the KAX dosage was increased to 0.45 kg/ton, reducing from as high as 93% to

only 86%. This may be attributed to an overdose of KAX causing a much higher contact angle, resulting in particles moving into the oil drops rather than sitting on the surface, and then not being lifted by the oil but falling to tails. However, this test did result in the highest grade across the initial tests.

Further tests were conducted for reproducibility with the artificial sample. During these tests it was observed that there was a high degree of variability in the performance of the new morganizer. Nearly half of all tests produced no quantitative results. Having achieved significant progress and success with the initial tests, this was a major concern. The main issue plaguing the performance of the morganizer was inefficient breaking of emulsions leading to no product in the overflow. Several different packing materials were tested to attempt to improve the breaking of emulsion but to no avail. A breakthrough occurred when a small amount air addition to the bottom of the column was introduced, roughly 0.9 cfm. This created additional turbulence in the column which promoted the breaking of emulsions. The air addition also serves to occupy some volume in the column which in turn increases the oil flow velocity. The increased turbulence provided by the air addition resulted in consistent performance in the new morganizer, as well as, higher-grade products.

The tests for artificial copper, with the addition of air, are shown in Table 5-2. The procedure was identical to that of the initial tests with the exception of a constant KAX dosage of 0.45 kg/ton, and the addition of air in the column. The results of this testing clearly indicate that the HHS process is well equipped to recover fine copper. Consistent high-grade concentrate products were achieved with all grades reporting higher than 30 %Cu, with a single pass through the HHS process (i.e., no need for additional cleaning steps). Recovery was also high throughout the tests, ranging between 76% and 85%. Clearly, from the data, the addition of air made a huge difference in consistency of testing results, and achievable high-grade concentrates.

Table 5-2: Artificial Copper (Air Addition) HHS Testing Results

Test #	KAX (kg/ton)	Products	Grade (%Cu)	Recovery (%wt.)
1	0.45	Concentrate	33.1	76.2
		Tail	0.5	23.8
		Feed	2.0	100.0
2	0.45	Concentrate	33.2	77.4
		Tail	0.5	22.6
		Feed	2.1	100.0
3	0.45	Concentrate	32.1	85.0
		Tail	0.3	15.0
		Feed	1.9	100.0
4	0.45	Concentrate	33.1	76.2
		Tail	0.5	23.8
		Feed	2.0	100.0
5	0.45	Concentrate	31.0	80.0
		Tail	0.4	20.0
		Feed	1.9	100.0
6	0.45	Concentrate	32.7	76.2
		Tail	0.5	23.8
		Feed	2.0	100.0
7	0.45	Concentrate	32.0	85.0
		Tail	0.3	15.0
		Feed	1.9	100.0
8	0.45	Concentrate	32.5	85.8
		Tail	0.3	14.2
		Feed	2.0	100.0
9	0.45	Concentrate	33.1	81.0
		Tail	0.4	19.0
		Feed	2.0	100.0

A major concern with the process as it had been developed, was the lack of phase separation prior to feeding the morganizer. The concern stemmed from visual observation of the column performance during testing. Toward the end of operation significant plugging of the packing material was often observed due to a high amount of solids flowing through the column. It was decided to perform a phase separation prior to feeding the morganizer to reduce the amount of gangue material entering the column. This is already implemented in the HHS coal process and the HHS REE process and therefore makes sense to implement for the copper process.

Table 5-3 presents the results for the HHS process on artificial copper with phase separation. Phase separation was achieved by draining the mixing tank after conditioning and

emulsion formation, leaving the oil phase and a small portion of tailings remaining in the tank. Because this process left very little slurry to be fed to the morganizer additional oil was added to the mixing tank (approximately 1.6 L) to allow for increased operation of the column. In light of this, the process can be described as undergoing phase inversion prior to the morganizer rather than in the morganizer. Because of the large amount of oil added in the mixing tank only a small amount of oil was introduced in the morganizer to carry emulsions that tend to sink. The tests were performed using the same experimental procedure as the previous tests, with the addition of the phase separation process, and 0.6 kg/ton KAX. Phase separation testing resulted in concentrate grades of 34% and 33%, with corresponding recoveries of 89%. These results are very encouraging in terms of the increase in copper recovery. Clearly, phase separation is superior to no phase separation and should be employed. Figure 5-5.

Table 5-3: Artificial Copper HHS Testing Results Comparison of Performance With and Without Phase Separation

Test	Products	Grade (%Cu)	Recovery (%wt.)
With Phase Separation	Concentrate	34.0	89.3
	Tails	0.25	10.7
	Feed	2.2	100.0
With Phase Separation	Concentrate	33.6	89.8
	Tails	0.2	10.2
	Feed	2.1	100
Without Phase Separation	Concentrate	33.1	74.5
	Tails	0.5	25.5
	Feed	2.0	100.0
Without Phase Separation	Concentrate	33.2	78.1
	Tails	0.5	21.9
	Feed	2.0	100.0

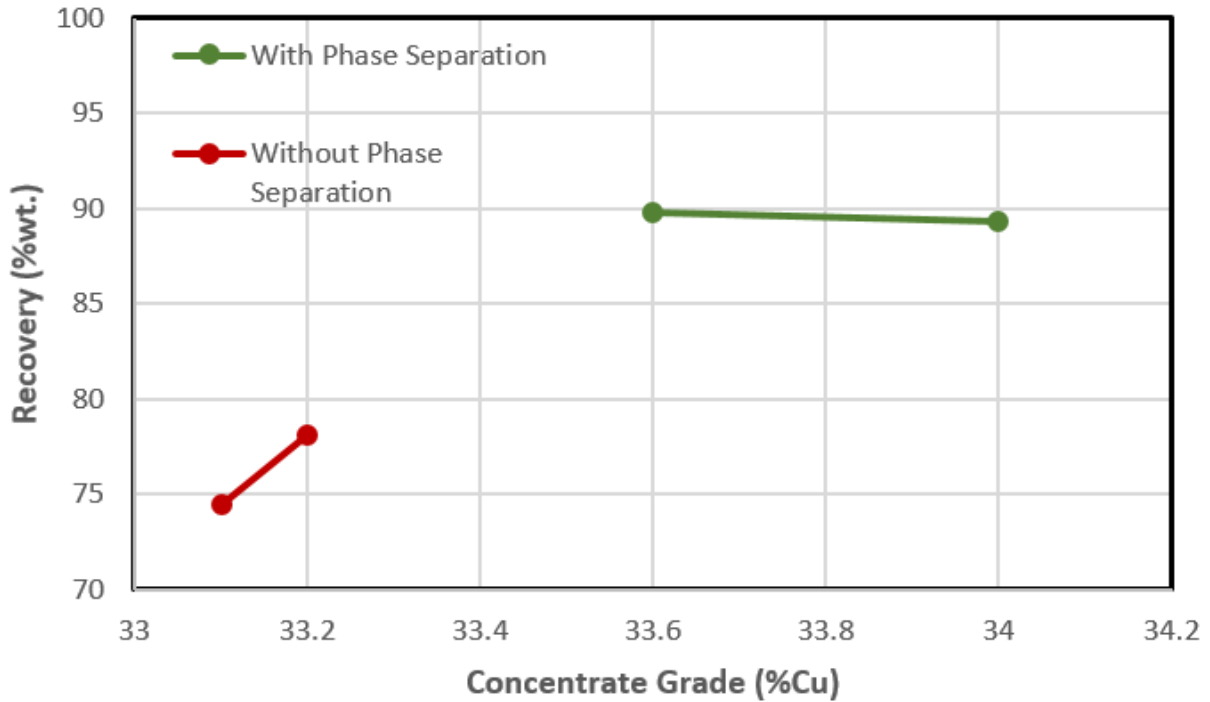


Figure 5-5: Comparison of HHS copper results with phase separation on artificial copper

5.3.2 Mineral Company A Copper Testing

Two samples were procured from Mineral Company A during this testing phase. The first sample was a plant feed sample assaying 0.24% Cu. The second sample was a scavenger-cleaner tailings sample from their flotation circuit which is currently discarded as waste, assaying 0.15 %Cu. The testing presented along with other actual ore samples was an attempt to move away from artificial testing and prove the HHS technology on actual ore so that it could be well marketed to copper producers as a superior technology to flotation circuits.

The plant feed sample was tested for HHS performance on a real or sample rather than artificial. The result of this test is shown in Table 5-4. The feed sample was ground to a d_{80} of 5.8 μm using a laboratory ball mill to improve liberation in the sample and effectively test the feed as a fine copper sample. Testing procedure was to use the emulsion formation process in the mixing tank, conditioning with 100 g/ton of KAX. The slurry was then phase separated and pumped to the morganizer. The feed sample responded well to HHS testing producing a concentrate grade of

34%, with a corresponding recovery of 85%. Based on the data, the HHS process can produce high-grade copper concentrate at high recovery, which is not achievable by flotation at this fine size.

Table 5-4: AZ Copper A Feed Sample HHS Testing

Test	Products	Grade (%Cu)	Recovery (%wt.)
HHS Test	Concentrate	34.2	85.1
	Tail	0.04	14.9
	Feed	0.24	100.0

Mineral Company A also provided a scavenger-cleaner tailings sample for HHS testing. These tests were completed on a batch scale using a separatory funnel and hand shaking to evaluate the process prior to attempting a test with the new morganizer. The sample was relatively coarse as received with a large portion of +325 mesh material. Because copper producers already employ significant grinding in the existing processing plants, the need for regrinding the fine material is not always an attractive option. As such, the sample was pre-screened at 325 mesh to test the natural fines from this stream. In these tests, approximately 100 ml of slurry was added to the separatory funnel and conditioned by hand shaking for 15 minutes with three different KAX dosages of 0.15 kg/ton, 0.5 kg/ton and 1 kg/ton. After conditioning 100 ml of heptane oil was added to form emulsions. Once emulsions had formed the tails were drained, and additional oil was added to induce phase inversion. Unfortunately, the phase inverted emulsions did not easily break under hand shaking, and a small amount of SMO (0.3 kg/ton) was added in the oil phase to help break the emulsions. Very few distinct particles were observed to disperse in the oil phase during these tests and as such concentrate results, which are shown in Table 5-5, were poor. The highest achievable concentrate grade was 3.2% with a recovery of only 24%. From the data, liberation is likely a key prohibiting factor for this sample. Additionally, from visual inspection, the +325 mesh sized material appeared to have an elevated chalcopyrite concentration, and as such it is likely that there is a very low population of copper particles in the sample tested leading to poor performance.

Table 5-5: Batch Testing AZ Copper B Scavenger-Cleaner Tailings Sample

KAX (kg/ton)	Products	Grade (%Cu)	Recovery (%wt.)
0.15	Concentrate	1.9	17.6
	Tails	0.13	82.4
	Feed	0.15	100.0
0.5	Concentrate	3.2	24.5
	Tails	0.12	75.5
	Feed	0.15	100.0
1.0	Concentrate	1.9	21.3
	Tails	0.12	78.7
	Feed	0.15	100.0

5.3.3 Mineral Company B Copper Testing

Mineral Company B’s Utah Copper A mine, like Mineral Company A, provided a sample of their scavenger-cleaner tailings stream, which is currently discarded as waste from their column flotation circuit. Batch testing was initially conducted prior to testing the morganizer in order to determine the best sample conditions and validity of testing quickly. The batch and morganizer results were also compared to flotation to determine the degree of upgrading HHS can provide. Batch testing was completed using a separatory funnel in the same manner as described with the AZ Copper B scavenger-cleaner tails. The sample was firstly determined to have an unusually large amount of coarse material, +325 mesh, and therefore was wet ground in a laboratory ball mill to a d_{80} of 3 μm . Additionally, the sample appeared to have some surface oxidation due being dried in an oven after filtration to be sent to the Virginia Tech lab, and grinding would effectively help to create a fresh surface. Approximately, 100 ml of slurry was added to the separatory funnel and conditioned with various dosages of KAX that were 250 g/ton, 500 g/ton, and 1 kg/ton. 100 ml of heptane was then added to form oil-in-water emulsions, and then phase separated. Additional oil was added to induce phase inversion. The dispersed chalcopyrite oil phase was collected for analysis. The results of the batch and morganizer testing as well as the flotation test are shown in Table 5-6. The morganizer test was conducted using phase separation and the standard HHS procedure as previously described. From the data, the HHS process is far superior to flotation and

can be used to recover this waste stream. Concentrate grades for the HHS process ranged from 7% to 10%, upgrading from a feed assaying 0.55%Cu. Recovery values were average across all tests ranging from 43% to 62%. The data indicates that there are significant losses to the tails in the morgанизер tests which may require a higher dosage of KAX, or higher oil flow rate in the morgанизер to carry particles.

Table 5-6: Flotation vs. HHS Results UT Copper A Scavenger Cleaner Tails

Test	KAX	Products	Grade (%Cu)	Recovery (%wt.)
Flotation	120 g/ton	Concentrate	2.05	59.8
		Tails	0.28	40.2
		Feed	0.57	100.0
HHS Batch Test 1	250 g/ton	Concentrate	9.06	58.3
		Tails	0.24	41.7
		Feed	0.55	100.0
HHS Batch Test 2	500 g/ton	Concentrate	10.45	59.4
		Tails	0.23	40.6
		Feed	0.55	100.0
HHS Batch Test 3	1 kg/ton	Concentrate	9.93	62.5
		Tails	0.21	37.5
		Feed	0.55	100.0
HHS Batch Test 4	200 g/ton	Concentrate	7.83	60.0
		Tails	0.23	40.0
		Feed	0.55	100.0
HHS Morgанизер Test	500 g/ton	Concentrate	10.71	43.1
		Tails	0.32	56.9
		Feed	0.55	100.0

Additionally, six more batch tests were conducted to attempt to improve concentrate grade and recovery by using two different hydrophobic polymers to aid in the breakage of emulsions in the separatory funnel, and aid the recovery of released particles to the oil phase. The two polymers tested were Polymethylhydrosiloxan (PMHS) and Polybutadiene, dicarboxy terminated (PBTD).

In terms of experimental procedure, the same batch testing methods were used with varying KAX dosages. With respect to performance, the PBTD hydrophobic polymer had no observable effect on concentrate grade or recovery. However, PMHS was able to produce a concentrate product assaying 12.01%Cu, with a corresponding recovery of 59%. The full results are shown below in Table 5-7, which indicate that performance is improved with PMHS.

Table 5-7: Effect of Polymer Addition on HHS Performance

Test	KAX/Polymer	Products	Grade (%Cu)	Recovery (%wt.)
PMHS Test 1	250 g/ton / 200 g/ton	Concentrate	7.83	60.0
		Tails	0.23	40.0
		Feed	0.55	100.0
PMHS Test 2	250 g/ton / 400 g/ton	Concentrate	9.34	58.1
		Tails	0.24	41.9
		Feed	0.55	100.0
PMHS Test 3	1 kg/ton / 800 g/ton	Concentrate	12.01	59.2
		Tails	0.23	40.8
		Feed	0.55	100.0
PBTD Test 1	250 g/ton / 200 g/ton	Concentrate	7.40	58.0
		Tails	0.24	42.0
		Feed	0.55	100.0
PBTD Test 2	250 g/ton / 400 g/ton	Concentrate	10.61	57.2
		Tails	0.24	42.8
		Feed	0.55	100.0
PBTD Test 3	1 kg/ton / 800 g/ton	Concentrate	9.36	48.8
		Tails	0.29	51.2
		Feed	0.55	100.0

5.3.4 Mineral Company C Copper Testing

Mineral Company C provided a scavenger cleaner sample from their AZ Copper C Mine in Arizona assaying 0.39%Cu. Testing was completed to evaluate the performance of the modified

HHS process for copper recovery from plant waste. This provides a large economic opportunity as previously mentioned, and an opportunity to expand the reach of the HHS process. The technology is not limited to ultrafine coal recovery and should be viewed as superior ultrafine particle separation and dewatering process rather than an ultrafine coal recovery process. The scavenger-cleaner tailings sample provided by Mineral Company C was ground firstly, to achieve better liberation as previous samples have proven is necessary. The sample was ground to 4 µm in size and then tested under batch conditions for HHS copper recovery. The results of these tests are shown in Table 5-8.

Table 5-8: AZ Copper C Batch Testing Results

Test	KAX/NaHS	Products	Grade (%Cu)	Recovery (%wt.)
Flotation	0.45 kg/ton / --	Cleaner Conc.	14.31	48.7
		Cleaner Tail	0.99	13.7
		Rougher Tail	0.15	37.6
		Feed	0.38	100.0
HHS Batch Test 1	0.45 kg/ton / --	Concentrate	16.29	37.8
		Tails	0.24	62.2
		Feed	0.39	100.0
HHS Batch Test 2	1 kg/ton / --	Concentrate	17.08	37.3
		Tails	0.24	62.7
		Feed	0.39	100.0
HHS Batch Test 3	0.6 kg/ton / 100 g/ton	Concentrate	30.64	39.8
		Tails	0.23	60.2
		Feed	0.39	100.0
HHS Batch Test 4	0.6 kg/ton / 310 g/ton	Concentrate	26.57	28.9
		Tails	0.28	71.1
		Feed	0.39	100.0

The results of these test show that the HHS process can effectively produce a high-grade copper product, with concentrate grades ranging between 16% and 30%. However, recovery for these tests was low with no recovery above 40%. Varying dosages of KAX were used during the

testing and sodium hydrosulfide was used in test 3 and 4 to help clean the surface of the chalcopyrite. The data clearly shows that NaHS has an effect on the effectiveness of the HHS process for this sample, increasing the concentrate grade by a minimum of 9%. NaHS was added during the conditioning step prior to adding KAX. Batch testing methods were replicated from previous tests.

5.4 Discussion and Conclusions

The comprehensive results obtained during this phase of the research for batch testing and semi continuous testing of the HHS process for copper demonstrated its effectiveness in producing high grade copper concentrate from discarded waste copper. Due to inefficiencies in flotation circuits, they are limited to a narrow size range. As such the ultrafine copper particles, which are abundant, are discarded as flotation tailings. During this research, a new morganizer was developed as a packed bed extraction column, in light of shortcomings observed in the vibrating mesh morganizer used for coal recovery, namely particle settling. The results of this research clearly indicate that the new morganizer is well suited to break phase inversed emulsions and provides a sufficient upward flow velocity to carry particles to the overflow. Tests conducted with this morganizer produced high-grade copper concentrate and was superior to flotation results obtained on the same samples.

Several key operating parameters were developed or modified during testing to the new laboratory morganizer. The first realization was the addition of a small amount of air to the bottom of the column, which was attempted after several poor tests with the new morganizer. The main issue plaguing the performance of the morganizer was inefficient emulsion breakage, which in theory should be less difficult to handle due to phase inversion that occurs in the column. The addition of air caused increased turbulence in the column and displaced some volume, which increased oil velocity. The results obtained with air on artificial copper were very encouraging all producing high-grade concentrates above 30% Cu. The addition of air has proven to be a major contributor to the performance of the morganizer.

The second large parameter tested during this research was the phase separation prior to the morganizer. In essence, the phase separation was introduced to reduce the risk of plugging in the column due to the high population of gangue minerals. The phase separation results were

excellent and again serve to remind that the HHS process is a fine particle separation process, rather than just a coal recovery process. HHS performed well with phase separation rather than without. In all tests with the new morgанизер, the data was compared to flotation on the same samples, and it is encouraging to note that the HHS process vastly outperformed flotation. Much like the REE samples liberation is a major issue as well as, surface oxidation for these samples. Grinding results vastly outperformed those tests in which natural fines were tested. Grinding also provided a means of creating a fresh surface for HHS testing. Both the UT Copper A sample and AZ Copper C samples appeared to have some level of surface oxidation due to being dried in ovens before being sent. The effect of sodium hydrosulfide was well documented in this series of tests drastically increasing the concentrate grade of the AZ Copper C samples tested.

The development of the new morgанизер will also help to advance the HHS process for rare earths. The new process, developed for copper, can now be tested with rare earth feedstocks like thickener underflow samples to produce high-grade REM concentrates. The lack of a morgанизер unit in phase 2 of this research, presented in chapter 4, likely caused some of the poorer results seen. The morgанизер unit helps to improve the grade of mineral products by removing entrapped water and hydrophilic gangue, which coalesce on the packing structure and fall by gravity to the tailings stream. Additionally, the use of air will help to disperse hydrophobic REMs in the oil phase for recovery, reducing the need for excessive cleaning stages. Furthermore, the use of phase separation prior to the morgанизер has shown to increase recovery of copper, and can provide the same upgrading for REMs.

Overall, the HHS process has proven to be a superior method of recovering ultrafine copper waste when compared to flotation, as shown in Figure 5-6, in which a composite performance plot of concentrate grade vs. recovery is given. HHS testing conducted on the AZ Copper A feed resulted in a concentrate assaying 34.3% Cu with 85.1% recovery and 4.1% moisture, again proving the HHS process a premier dewatering technology. The HHS process is more selective than flotation and hence can produce high-grade copper concentrates at high recoveries. Reagents can be used during the conditioning step to handle surface oxidation, and likewise, grinding can be used to achieve the same effect with the added benefit of increased liberation. As seen in Figure 5-6, the scavenger cleaner tailings samples proved better than flotation in terms of concentrate grade, but not necessarily recovery. The morgанизер assists in producing high-grade concentrates,

while recovery appears to be a hydrophobization issue, likely due to some oxidation or reduced liberation. The process as a whole is well suited to recover metallic ore, which presents a huge benefit to the HHS process as it expands its reach into the mineral sector. Copper provides an excellent opportunity, having a high degree of losses, as with case of UT Copper A where the tailings grade is higher than the feed grade. In light of this testing should continue to determine the optimal operation of the new laboratory morganizer as well as, determining proper auxiliary equipment to create a small-scale continuous process. The extraction column is well documented in the chemical industry and scale up data is readily available for this process. In general, velocity and column diameter will dictate the design of the column and packing material that should be used. Additionally, other types of packing should be investigated such as bulk random packing which provides a cheap and easily replaceable option, as well as, other structure packing such as corrugated plates.

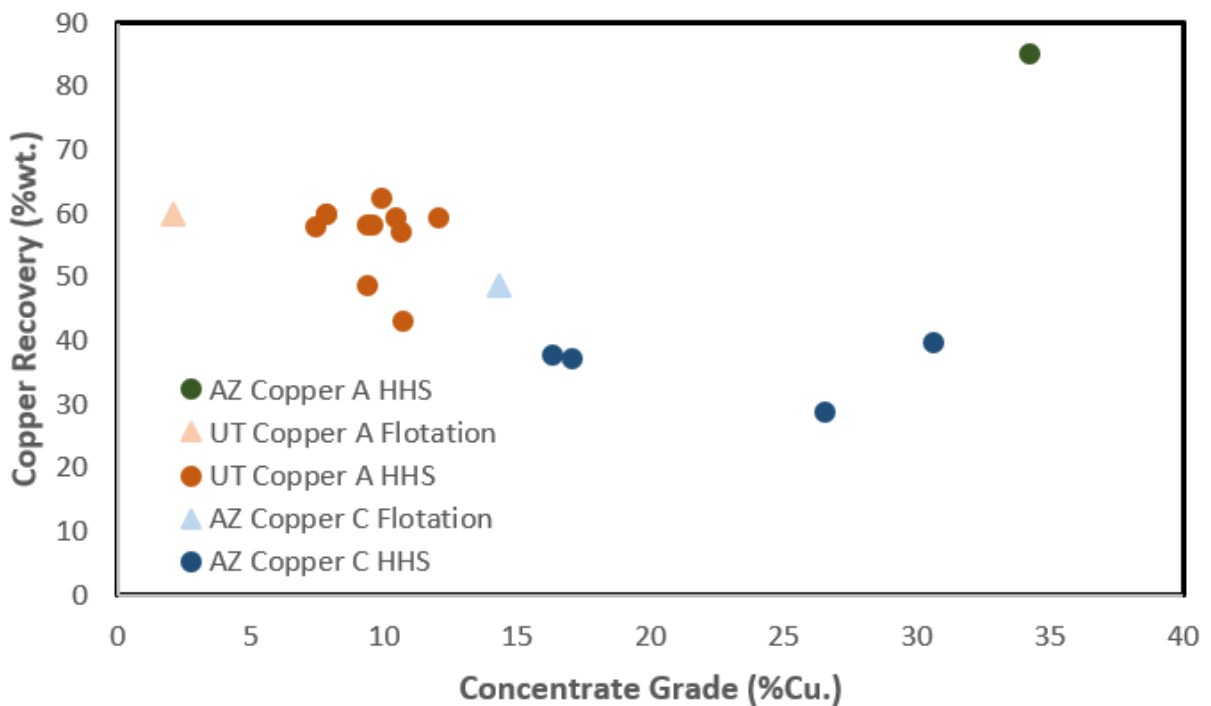


Figure 5-6: Composite grade vs. recovery for copper ore

CHAPTER 6. GENERAL SUMMARY

The hydrophobic-hydrophilic separation process is a novel fine particle cleaning and dewatering process that has been extensively tested, in past research, for effectiveness in recovering ultrafine coal from plant waste streams. While the HHS process works extremely well in this operation, the time has come to advance the process beyond its small niche, and test on alternative coal preparation plant streams that require upgrading of low-value coal to high-valuable salable product, as well as, expanding into the minerals sector. The HHS process' scope is undefined and does not have to remain a true coal preparation technology. The process is extremely versatile and can be used across a variety of ores. To complete this research three different research phases were developed for testing. The first phase of the research was completed to test the effectiveness of the HHS process for recovering coal from a variety of carbon-based feedstocks across different regions. The second phase of the research was completed to expand the HHS process into the minerals sector moving away from coal. These tests were completed to determine three key items: [1] Can low-value coal and coal by-products be upgraded to high-value salable coal product? [2] Can recovery and upgrading of coal by the HHS process simultaneously produce a "free" REEs feedstock? [3] Can HHS coal tailings be processed by a modified version of the HHS process to concentrate REEs? The last phase of the research project was developed to expand the reach of the HHS process into the metals industry. Testing in this phase was conducted to determine if a modified HHS process for copper can recover high-grade concentrate from a low-grade waste product.

In the first phase of this research, project samples were collected from Coal Company A, Coal Company B, Coal Company C, Coal Company D, Coal Company E, Coal Company F, and Coal Company G. These tests varied across a wide range of size class in which screenbowl effluent 99% minus 325 mesh was tested, as well as, 80 mm x 0 raw coal feed. The tests had a very different feed ash values and characteristics. The HHS process was demonstrated to be highly effective for when testing ultrafine waste coals that were procured, consistently producing single digit ash and moisture values. Testing on middling samples required a high degree of grinding to improve liberation enough to produce some respectable results. In general testing on the middling samples never reached single digit ash values, but produced 11% and 12% ash values when ground to minus

10 microns. Additionally, the WV Coal D preparation plant middling sample was able to produce a 7% ash at the highest degree of liberation. Spiral concentrate samples tested well producing single digit ash and moisture values. Finally, impoundment coal presents a major opportunity for recovering a very large source of ultrafine waste coal. In these tests, single-digit ash and moisture values were easily achievable. Overall this phase of the research was able to demonstrate that the HHS process can consistently recover ultrafine waste coal, as well as, impoundment coal, and some coarse streams.

In the second phase of the research project, samples were collected from Coal Company B, Coal Company I, and Coal Company H. This phase of the research was able to demonstrate that the HHS process could effectively upgrade low-value coal into a high-value salable product. In these tests, it was easily identifiable that liberation and population of hydrophobized particles played a major role in the effectiveness of the HHS process. Two collectors were discussed during the phase of the research, Hydroxamate, and Sodium Oleate. Sodium Oleate appeared to be the superior collector for aiding in the hydrophobicity of the REE sample. High-grade (ppm) REEs concentrates were produced across the testing samples. The HHS process is very well positioned to expand testing on these samples.

In the final phase of the research, several samples were collected from Mineral Company A, Mineral Company B Copper, Mineral Company C, and Wards Science. The samples from Wards Science were artificial samples. In order to proceed with testing a new morganizer was developed, in order to combat settling velocity which was the main source of problems for the vibrating mixer morganizer. During the artificial testing, two key parameters were identified. The first of which was air addition to the bottom of the morganizer, in order to create more turbulence aiding in the breakage of emulsions. Air addition proved to increase concentrate grade above 30% and provide consistency across tests. The second parameter was the need for phase separation to prevent plugging in the morganizer and provided phase inversion prior to the morganizer. Results were compared to flotation results and determined that the HHS process was vastly superior to flotation in terms of grade and recovery. Testing on actual ore was positive, after determining the need for grinding to remove surface oxidation and increase liberation. Overall, this research has proven the HHS process viable for sectors outside of the traditional coal markets the process has targeted.

CHAPTER 7. RECOMMENDATIONS FOR FUTURE WORK

This research has proven the ability of the HHS process to recover various coal and mineral based feedstocks. However, additional work may be needed in order to continue the advancement of the process. The author of this thesis recommends the following additional research be completed to help evaluate the process:

1. Further assessment of various carbon-based feedstocks, specifically coal middling product. Investigation into improved liberation could lead to lower ash products converting low-value coal into a high-value salable product. Additionally, plant audit data often shows middling products to be elevated in REEs, therefore improving coal recovery from middling product can lead to increase feed for the REE process
2. Further testing into concentrating REEs using the HHS process. Studies should focus on liberation and low population of hydrophobic particles as they are the main deterrents for successful operation.
3. Development of a small scale process using the new morganizer design. Further testing should firstly be focused on real ore samples and determining optimal operating conditions.
4. Lastly modifications to the new morganizer to allow for the ability of handling coarse material. A single test has been conducted using a laboratory jig. The jig serves as the morganizer in these tests and was able to effectively produce low ash/low moisture product.

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APPENDIX A: SIZING DATA

The following appendix contains the results from size-by-size analysis of select samples where sizing data was collected.

Table A – 1: WV Coal A Flotation Tailings Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0.6	0.6
-30 + 100	1.8	2.4
-100 + 325	9.6	12.0
-325	88.0	100.0

Table A – 2: WV Coal A Raw Coal Cyclone Overflow Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0	0
-30 + 100	1.8	1.8
-100 + 325	19.2	21.0
-325	79.0	100.0

Table A – 3: WV Coal A Decanter Main Drain to Thickener Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0	0
-30 + 100	2.8	2.8
-100 + 325	10.8	13.6
-325	86.4	100.0

Table A – 4: WV Coal B Scrubber to Thickener Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0	0
-30 + 100	1.57	1.57
-100 + 325	20.54	22.11
-325	77.89	100.0

Table A – 5: WV Coal B Thickener Feed Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0.47	0.47
-30 + 100	11.20	11.67
-100 + 325	12.59	24.26
-325	75.74	100.0

Table A – 6: WV Coal B Spiral Refuse Underflow Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	6.1	6.1
-30 + 100	63.0	69.1
-100 + 325	21.5	90.6
-325	9.4	100.0

Table A – 7: WV Coal C Flotation Tails Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0	0
-30 + 100	4.44	4.44
-100 + 325	2.93	7.37
-325	92.63	100.0

Table A – 8: WV Coal C Jameson Tails Size Analysis

Size (Mesh)	Weight (%)	
	Individual	Cumulative
+30	0	0
-30 + 100	2.37	2.37
-100 + 325	1.77	4.14
-325	95.86	100.0

Table A – 9: WV Coal A Screenbowl Effluent (Met) Size Analysis

Size Mesh	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+100	0.4	15.6	0.4	15.6
-100 + 200	0.6	5.0	1.0	9.2
-200 + 325	1.7	3.2	2.7	5.4
-325	97.3	30.8	100.0	30.1

Table A – 10: WV Coal A Deslime Cyclone (Met) Size Analysis

Size Mesh	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+100	0.3	8.0	0.3	8.0
-100 + 200	1.9	4.0	2.2	4.5
-200 + 325	3.9	7.6	6.1	6.5
-325	93.9	66.3	100.0	62.6

Table A – 11: WV Coal A Screenbowl Effluent (Steam) Size Analysis

Size Mesh	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+100	0.76	28.6	0.76	28.6
-100 + 325	1.26	28.6	2.02	28.6
-325	97.98	45.9	100.0	45.5

Table A – 12: WV Coal A Deslime Cyclone (Steam) Size Analysis

Size Mesh	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+100	1.0	3.3	1.0	3.3
-100 + 325	8.1	7.7	9.1	7.2
-325	90.9	68.8	100.0	63.2

Table A – 13: KY Coal A Flotation Feed (3%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.2	8.1	0.2	8.1
-35 + 70	1.4	8.1	1.6	8.1
-70 + 100	1.0	2.8	2.6	6.0
-100 + 325	16.3	13.1	18.9	12.1
-325	81.1	67.2	100.0	56.8

Table A – 14: KY Coal A Flotation Feed (1%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.2	5.5	0.2	5.5
-35 + 70	1.8	1.5	2.0	1.9
-70 + 100	1.5	1.8	3.5	1.9
-100 + 325	26.1	14.5	29.6	13.0
-325	70.4	56.3	100.0	43.5

Table A – 15: KY Coal A Flotation Product (3%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.2	24.1	0.2	24.1
-35 + 70	0.1	24.1	0.3	24.1
-70 + 100	0.6	24.1	0.9	24.1
-100 + 325	12.0	2.0	12.9	3.5
-325	87.1	13.1	100.0	11.9

Table A – 16: KY Coal A Flotation Product (1%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.1	6.9	0.1	6.9
-35 + 70	1.0	1.6	1.1	2.1
-70 + 100	1.2	1.4	2.3	1.7
-100 + 325	28.2	2.3	30.5	2.2
-325	69.5	20.0	100.0	14.6

Table A – 17: KY Coal A Flotation Tailings (3%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.2	2.2	0.2	2.2
-35 + 70	0.7	2.2	0.9	2.2
-70 + 100	2.1	2.2	3.0	2.2
-100 + 325	15.8	6.3	18.8	5.6
-325	81.2	68.6	100.0	56.8

Table A – 18: KY Coal A Flotation Tailings (1%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0.36	1.8	0.36	1.8
-35 + 70	2.38	1.8	2.74	1.8
-70 + 100	2.77	1.3	5.5	1.6
-100 + 325	24.8	6.4	30.3	5.5
-325	69.7	57.7	100.0	41.9

Table A – 19: KY Coal A Screenbowl Effluent (3%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	1.0	74.2	1.0	74.2
-35 + 70	0.3	8.3	1.3	59.0
-70 + 100	0.6	8.3	1.9	43.0
-100 + 325	1.8	8.3	3.7	26.1
-325	96.3	51.6	100.0	50.7

Table A – 20: KY Coal A Screenbowl Effluent (1%) Size Analysis

Size (Mesh)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+35	0	0	0	0
-35 + 70	0.21	13.0	0.81	13.0
-70 + 100	0.34	13.0	1.15	13.0
-100 + 325	0.25	13.0	1.8	13.0
-325	99.2	39.3	100.0	39.1

Table A – 21: KY Coal A Low Ash Spiral Concentrate Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+1.18	6.1	7.4	6.1	7.4
-1.18 + 0.84	9.7	2.9	15.7	4.6
-0.84 + 0.50	22.5	2.0	38.2	3.1
-0.50 + 0.25	33.5	2.2	71.8	2.7
-0.25 + 0.15	15.1	4.2	86.9	2.9
-0.15 + 0.045	10.5	26.8	97.4	5.5
-0.045	2.6	63.2	100.0	7.0

Table A – 22: KY Coal A Mid Ash Spiral Concentrate Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+1.18	5.1	5.1	5.1	5.1
-1.18 + 0.84	15.7	3.3	20.8	3.7
-0.84 + 0.50	20.1	3.2	40.9	3.4
-0.50 + 0.25	30.0	3.7	70.9	3.6
-0.25 + 0.15	13.5	6.0	84.4	3.9
-0.15 + 0.045	11.6	33.8	96.0	7.6
-0.045	4.0	79.3	100.0	10.4

Table A – 23: VA Coal A Impoundment Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.84	5.8	49.9	5.8	49.9
-0.84 + 0.50	5.7	49.4	11.5	49.6
-0.50 + 0.35	5.5	35.5	17.0	45.0
-0.35 + 0.15	29.6	27.1	46.6	33.7
-0.15 + 0.075	22.6	29.7	69.2	32.4
-0.075	30.8	46.2	100.0	36.6

Table A – 24: India Coal A Flotation Feed (-0.5 mm) Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.50	7.4	20.1	7.4	20.1
-0.50 + 0.30	14.8	20.4	22.2	20.3
-0.30 + 0.15	19.4	17.1	41.6	18.8
-0.15 + 0.075	15.2	16.3	56.8	18.2
-0.075 + 0.045	10.7	16.8	67.5	17.9
-0.045	32.5	24.8	100.0	20.2

Table A – 25: India Coal A Flotation Feed (-0.25 mm) Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.30	0.4	12.2	0.4	12.2
-0.30 + 0.21	4.2	14.2	4.6	14.0
-0.21 + 0.15	5.7	14.2	10.3	14.2
-0.15 + 0.106	12.1	15.9	22.4	15.1
-0.106 + 0.075	11.1	17.4	33.5	15.9
-0.075	66.5	25.2	100.0	22.1

Table A – 26: India Coal A Froth Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.85	1.6	9.5	1.6	9.5
-0.85 + 0.50	13.3	12.0	14.9	11.7
-0.50 + 0.30	17.8	14.3	32.7	13.1
-0.30 + 0.15	18.5	16.1	51.2	14.2
-0.15 + 0.045	21.7	15.6	72.9	14.6
-0.045	27.1	23.7	100.0	17.1

Table A – 27: India Coal A Tailings Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.85	7.9	40.7	7.9	40.7
-0.85 + 0.50	26.6	50.6	34.5	48.3
-0.50 + 0.30	18.1	54.1	52.6	50.3
-0.30 + 0.15	12.6	53.2	65.2	50.9
-0.15 + 0.075	7.8	52.3	73.0	51.0
-0.075	27.0	45.8	100.0	49.6

Table A – 28: India Coal A Combined Tailings Set 1 Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.85	7.4	32.2	7.4	32.2
-0.85 + 0.50	19.3	32.6	26.6	32.5
-0.50 + 0.30	21.2	32.8	47.8	32.6
-0.30 + 0.15	18.9	37.9	66.7	34.1
-0.15 + 0.075	8.6	45.4	75.3	35.4
-0.075	24.7	57.9	100.0	41.0

Table A – 29: India Coal A Combined Tailings Set 2 Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.85	5.1	25.6	5.1	25.6
-0.85 + 0.50	18.7	29.3	23.8	28.5
-0.50 + 0.30	18.1	30.4	41.9	29.3
-0.30 + 0.15	18.0	35.7	59.9	31.2
-0.15 + 0.075	10.5	39.0	70.4	32.4
-0.075	29.6	49.3	100.0	37.4

Table A – 30: India Coal B Fine Coal Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+0.50	5.8	8.5	5.8	8.5
-0.50 + 0.30	6.4	12.3	12.2	10.5
-0.30 + 0.15	16.1	19.0	28.3	15.3
-0.15 + 0.075	15.6	19.2	43.9	16.7
-0.075 + 0.045	13.4	28.2	57.3	19.4
-0.045	42.7	52.1	100.0	33.3

Table A – 31: India Coal B Raw Coal d_{80} 220 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	7.3	25.3	7.3	25.3
-0.30 + 0.15	24.6	26.2	31.9	26.0
-0.15 + 0.075	20.7	26.9	52.6	26.4
-0.075 + 0.045	12.3	29.3	64.9	26.9
-0.045	35.1	31.7	100.0	28.6

Table A – 32: India Coal B Raw Coal d_{80} 160 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	2.4	28.4	2.4	28.4
-0.30 + 0.15	21.8	25.7	24.2	26.0
-0.15 + 0.075	26.4	28.5	50.6	27.3
-0.075 + 0.045	13.2	26.5	63.8	27.2
-0.045	36.2	31.4	100.0	28.7

Table A – 33: India Coal B Raw Coal d_{80} 65 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.15	1.1	27.1	1.1	27.1
-0.15 + 0.075	11.5	25.9	12.6	26.0
-0.075 + 0.045	19.5	25.5	32.1	25.7
-0.045	67.9	30.3	100.0	28.8

Table A – 34: India Coal C Raw Coal d_{80} 240 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	2.8	24.1	2.8	24.1
-0.30 + 0.15	40.5	27.2	43.3	27.0
-0.15 + 0.045	26.3	30.0	69.6	28.1
-0.045	30.4	32.1	100.0	29.3

Table A – 35: India Coal C Raw Coal d_{80} 140 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	0.2	28.7	0.2	28.7
-0.30 + 0.15	18.1	28.0	18.3	28.0
-0.15 + 0.045	39.7	27.5	58.0	27.6
-0.045	42.0	32.3	100.0	29.6

Table A – 36: India Coal C Raw Coal d_{80} 55 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.15	2.5	26.5	2.5	26.5
-0.15 + 0.075	10.1	26.6	12.6	26.6
-0.075 + 0.045	12.7	27.0	25.3	26.8
-0.045	74.7	31.7	100.0	30.4

Table A – 37: India Coal D Raw Coal d_{80} 400 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	27.4	53.0	27.4	53.0
-0.30 + 0.15	17.3	43.2	44.7	49.2
-0.15 + 0.075	17.2	38.3	62.0	46.2
-0.075 + 0.045	9.9	41.4	71.9	45.5
-0.045	28.1	51.6	100.0	47.2

Table A – 38: India Coal D Raw Coal d_{80} 150 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	6.6	34.3	6.6	34.3
-0.30 + 0.15	13.6	34.0	20.2	34.1
-0.15 + 0.075	22.7	38.1	42.9	36.2
-0.075 + 0.045	14.1	41.1	57.0	37.4
-0.045	43.0	53.3	100.0	44.3

Table A – 39: India Coal D Raw Coal d_{80} 80 μ m Size Analysis

Size (mm)	Individual (%)		Cumulative (%)	
	Weight	Ash	Weight	Ash
+ 0.30	2.1	51.4	2.1	51.4
-0.30 + 0.15	5.7	30.6	7.8	36.1
-0.15 + 0.075	15.3	32.3	23.1	33.6
-0.075 + 0.045	17.9	40.7	41.0	36.7
-0.045	59.0	52.6	100.0	46.1

APPENDIX B: SEPARATION EFFICIENCY

The following appendix serves to present the combined separation efficiency plot for the decarbonization and coal recovery results for comparison. The plot shown distinguishes between flotation results and HHS results, by denoting flotation results with a “Δ”. Additionally, three curves were developed to show the performance of flotation, HHS middlings, and HHS ultrafine results.

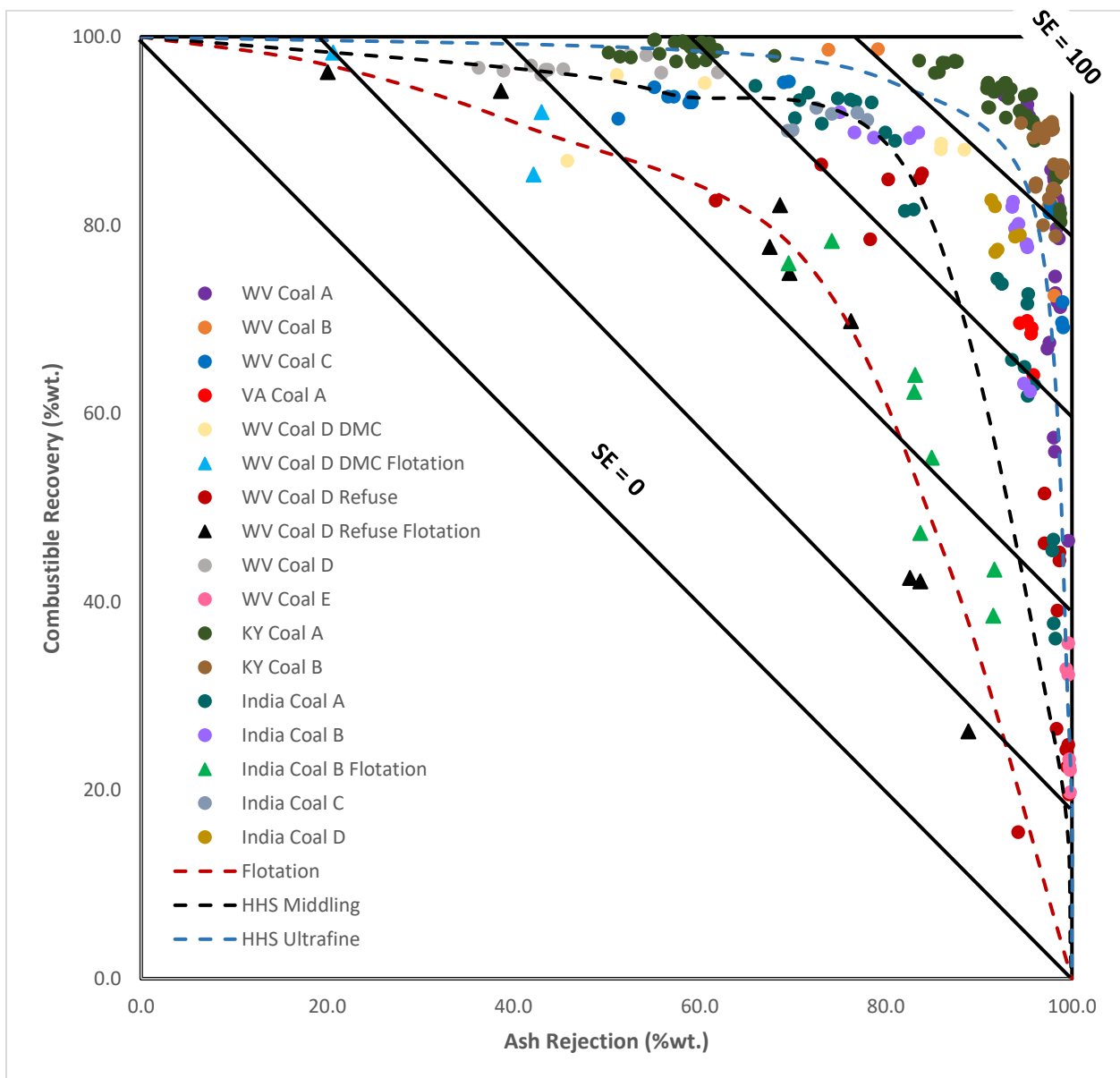


Figure B-1: Combined separation efficiency performance plot

APPENDIX C: NEW MORGANIZER DRAWING

The following appendix depicts a simplified schematic of the new morganizer design for the copper recovery process.

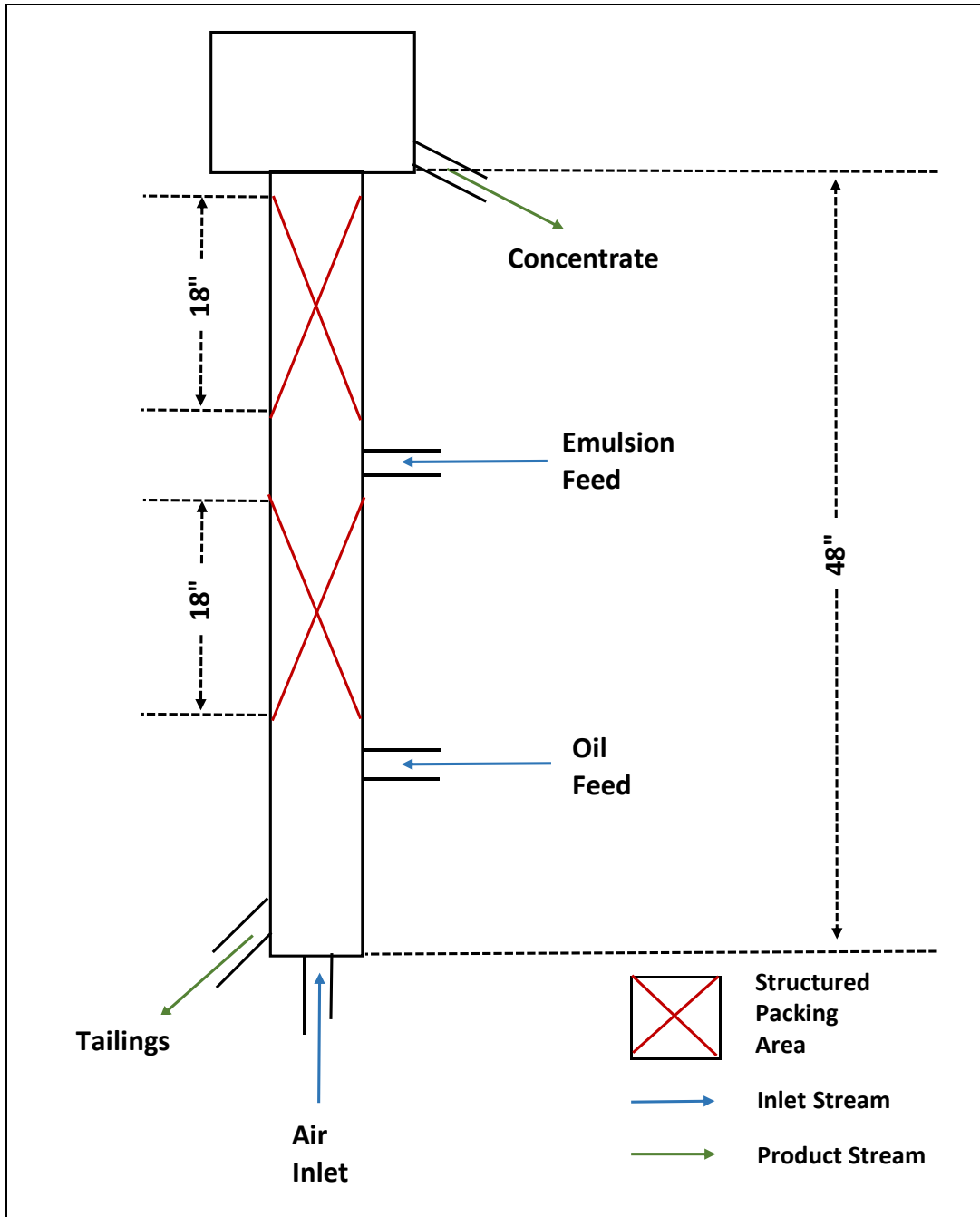


Figure C-1: New morganizer drawing