Hydrophobic-Hydrophilic Separation Process for the Recovery of Ultrafine Particles

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Academic Abstract

The demands for copper and rare earth elements (REEs) in the U.S. will keep rising due to their applications in green energy technologies. Meanwhile, copper production in the U.S. has been declining over the past five years due to the depletion of high-grade ore deposits. The situation for REEs is worse; there is no domestic supply chain of REEs in the U.S. since the demise of Molycorp, Inc. in 2016. Studies have shown that the rejected materials from copper and coal processing plants contain significant amounts of valuable metals. As such, this rejected material can be considered as potential secondary sources for extracting copper and REEs, which may help combat future supply risks for the supply of copper and REEs in the U.S. However, the valuable mineral particles in these resources are ultrafine in size, which poses considerable challenges to the most widely used fine particle beneficiation technique, i.e., froth flotation. A novel technology called the Hydrophobic-Hydrophilic Separation (HHS) process, developed at Virginia Tech, has been successfully applied to recover fine coal in previous research. The results of research into the HHS process showed that the process has no lower particle size limit, similar to solvent extraction. Therefore, the primary objective of this research is to explore the feasibility of using the new process to recover ultrafine particles of coal, copper minerals, and rare earth minerals (REMs) associated with coal byproducts.

In the present work, a series of laboratory-scale oil agglomeration and HHS tests have been carried out on coal with the objectives of assisting the HHS tests in pilot-scale, and the scale-up of the process. The knowledge gained from this study was successfully applied to solving the problems encountered in the pilot-scale tests. Additionally, a new and more efficient equipment known as the Morganizer has been designed and constructed to break up the agglomerates in oil phase as a means to remove entrained gangue minerals and water. The effectiveness of the new Morganizers has been demonstrated in laboratory-scale HHS tests, which may potentially result in the reduction of capital costs in commercializing the HHS process. Furthermore, the prospect of using the HHS process for processing high-sulfur coals has been explored. The results of this study showed that the HHS process can be used to increase the production of cleaner coal from waste streams.

Application of the HHS process was further extended to recover the micron-sized REMs from a thickener underflow sample from the LW coal preparation plant, Kentucky. The results showed that the HHS process was far superior to the forced-air flotation process. In one test conducted during the earlier stages of the present study, a concentrate assaying 17,590 ppm total REEs was obtained from a 300 ppm feed. In this test, the Morganizer was not used to upgrade the rougher concentrate due to the lack of proper understanding of the fundamental mechanisms involved in converting oil-in-water (o/w) Pickering emulsions to water-in-oil (w/o) Pickering emulsions. Many of the studies has, therefore, been focused on the studies of phase inversion mechanisms. The results showed that phase inversion requires that i) the oil contact angles (θ_0) of the particles be increased above 90°, ii) the phase volume of oil (ϕ_0) be increased, and iii) the o/w emulsion be subjected to a high-shear agitation. It has been found that the first criterion can be readily met by using a hydrophobicity-enhancing agent. These findings were applied to produce high-grade REM concentrates from an artificial mixture of micron-sized monazite and silica.

Based on the improved understanding of phase inversion, a modified HHS process has been developed to recover ultrafine particles of copper minerals. After successfully demonstrating the efficacy and effectiveness of this process on a series of artificial copper ore samples, the modified HHS process was used to produce high-grade copper concentrates from a series of cleaner scavenger tails obtained from operating plants.

Hydrophobic-Hydrophilic Separation Process for the Recovery of Ultrafine Particles

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General Audience Abstract

Recovery and dewatering of ultrafine particles have been the major challenges in the minerals and coal industries. Based on the thermodynamic advantage that oil droplets form contact angles about twice as large as those obtainable with air bubbles, a novel separation technology called the hydrophobic-hydrophilic separation (HHS) process was developed at Virginia Tech to address this issues. The research into the HHS process previously was only conducted on the recovery of ultrafine coal particles; also, the fundamental aspects of the HHS process were not fully understood, particularly the mechanisms of phase inversion of oil-in-water emulsions to water-in-oil emulsions. As a follow-up to the previous studies, emulsification tests have been conducted using ultrafine silica and chalcopyrite particles as emulsifiers, and the results showed that phase inversion requires high contact angles, high phase volumes, and high-shear agitation. These findings were applied to improve the HHS process for the recovery of ultrafine particles of coal, copper minerals, and rare earth minerals (REMs). The results obtained in the present work show that the HHS process can be used to efficiently recover and dewater fine particles without no lower particle size limits.

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Chapter 1 Introduction and Literature Review

1.1 Introduction

Coal and minerals, which are well known as non-renewable resources, are essential to human society because they and their extracts are exploited in an almost infinite array of products and services to fulfill the diverse needs of human beings, e.g., heat, chemicals, electronics, transportation, housing, cosmetics, weapons, etc. However, as a result of sustained growth in both global population and economy, the global market will face an impending shortage of seven primary metals (including copper) in the next few years (Elshkaki et al., 2018) owing to the facts that metallic ores grades are declining, and the high-quality mineral deposits are depleting globally (Calvo et al., 2016).

To alleviate the potential supply crisis of mineral resources, there is no doubt that the mineral processing activities will be progressively moved on those poorer-quality mineral resources, and also the tailings discarded in the historic impoundments. It has been reported that the tailing wastes contain significant amounts of valuable minerals and may even be of higher metal contents than some primary ore deposits currently being exploited (Falagán et al., 2017; Gordon, 2002). When the supply crisis of mineral resources comes, the mineral processing industry will have to deal with the challenges of recovering ultrafine minerals from these two sources. The problem of ultrafine particles associated with the former source comes from the essential fine comminution for liberation. For example, in order to have a good liberation of minerals for flotation, the zinc-lead ore at Mt Isa Mine (Australia) was forced to be ground to d₈₀ = 7-12 μ m (Pease et al., 2005). While the tailings sitting in the impoundments are already of ultrafine sizes because they have mainly consisted of particles, which previously had been lost in the flotation circuits and were rejected purposely using deslime cyclones.

Of the mineral resources, rare earth elements (REEs), which are a group of 17 elements consisting of 15 lanthanides plus yttrium and scandium, play irreplaceable roles in developing renewable energy resources, securing national security, and promoting advanced manufacturing (Dutta et al., 2016). With the closure of the Molycorp Inc. in 2016, the U.S. now relies on 100% of its supply of REEs to foreign sources (Ober, 2017), over 80% of which were imported from China from 2014 to 2017 (USGS, 2018). Recently, the increasing trade tensions between the U.S. and China have sparked concerns about the supply of REEs in the U.S. (Snow, 2019). Given the strategic importance of REEs to the defense interests and modern economy of the U.S., it is urgent and imperative to develop a reliable domestic REE supply chain. A recent study initiated by the National Energy Technology Laboratory (NETL) showed that the U.S. coals contain significant amounts of REEs, suggesting the possibility that rare earth minerals (REMs) and/or REEs can be extracted from coal preparation refuse as byproducts (Ekmann, 2012). A large body of evidence has shown that REEs-enriched authigenic mineral grains exist in coal, most of which are characterized as monazite (Lin et al., 2017; Hower et al., 1999; Seredin, 1996; Zhang et al., 2017). In principle, REMs associated with coal should be recoverable using flotation technique, which has been widely used for the concentration of conventional REMs. However, it is worth mentioning that REMs associated with coal are of ultrafine sizes that exceed the limits of flotation separation. According to Honaker et al. (2014) and Zhang et al. (2017), the sizes of monazite grains identified in the Fire Clay coal seam in eastern Kentucky are mostly of less than 5 µm.

In current fine particle processing practice, froth flotation is the most widely used beneficiation technique. However, as the particle size falls within the ultrafine and colloidal ranges, the efficiency of the froth flotation process substantially decreases, which is interpreted as the decline of recovery and flotation rate, and the increase of gangue entrainment (Wills and Finch, 2016). The difficulty in the flotation recovery of ultrafine particles is due to the small mass, high specific surface area, and high surface energy of the ultrafine particles (Fuerstenau, 1980). More details on this topic can be found in Sivamohan's (1990) summarization.

Generally, it is necessary to dewater a flotation concentrate before subjecting it to further processing or shipping out because moisture is a contaminant as significant as the associated gangue. Reducing the water content in a concentrate not only can decrease the transportation cost, but also reduce the requirements for energy consumption when a mineral concentrate is smelted or coal is combusted. According to Luttrell (2010), a 1% moisture increase in coal could lead to approximately 150 Btu/lb energy loss, roughly equivalent to the energy loss resulting from the increase of 1% ash content. The dewatering of a flotation concentrate can be achieved by thermal drying or mechanical filtration. However, the former is not commonly used due to the high operating cost. Currently, the dewatering of flotation concentrates is mainly achieved by mechanical methods with the formation of a filter cake consisting of capillaries of various radii, which are determined by the particle size distribution. According to the Laplace equation, the smaller the capillary, the larger the capillary pressure, which in turn leads to an increase of the applied pressure drop in the dewatering process (Yoon, 2002). As a result, the mechanical dewatering process of ultrafine particles is extremely difficult, costly, and cannot produce a product with a low moisture content that can be obtained on coarse particles. Therefore, an ideal technique for the beneficiation of fine and ultrafine particles should also solve the dewatering problem.

Numerous froth flotation processes have been developed to solve the problems associated with the recovery of fine and ultrafine particles. This has been accomplished by various mechanisms, such as reducing air bubble size, enlarging apparent separation size of target particles, and employing hydrophobic carrier and new collectors. Additionally, processes using oil droplets rather than air bubbles to collect particles, namely, oil agglomeration and two-liquid flotation, are applied extensively in the recovery of ultrafine particles. Furthermore, a novel separation process known as the Hydrophobic-Hydrophilic Separation (HHS) can both recover ultrafine particles and simultaneously dewater the particles has been developed at Virginia Tech. Some of these technologies and their applications will be briefly introduced in the following section.

1.2 Ultrafine Particle Recovering Technologies

1.2.1 Advances in Flotation Process

<u>1.2.1.1 Aggregation Before Flotation</u>

The poor flotation performance of ultrafine particles is primarily due to the low collision probability between particles and air bubbles, as ultrafine particles are more intended to follow the fluid streamlines around air bubbles rather than to collide with them (Laskowski, 1974; Yoon and Luttrell, 1989). It has been shown in different particle-bubble collision models that collision efficiency increases with increasing particle size (Trahar and Warren, 1976). Thus, in the past four decades, a large range of modified flotation processes were developed using this mechanism to improve the recovery of ultrafine particles.

<u>Selective Flocculation-Flotation</u> The selective flocculation-flotation (SFF) is a flotation process conducted after the target fine particles have been selectively flocculated. The flocculation of the target fine particles is achieved by preferentially absorbing them with a long-chain organic polymer (flocculant), by which aggerates or flocs of a suitable size range for effective flotation are induced through the bridging mechanism of the flocculant (Mathur et al., 2000). Polyacrylamide and its modified products are the most commonly used flocculants. It is also reported that microorganisms can be used as flocculants for the selective flocculation of fine and ultrafine particles (Patra and Natarajan, 2003; Raichur et al., 1996).

The SFF process has been effectively applied to recover ultrafine particles of diverse resources, such as iron ore (Frommer and Colombo, 1966; Houot, 1983; Ng, et al., 2015), uranium ore (Woolery, 1964), coal (Attia et al., 1988; Ding and Laskowski, 2007; Liang et al., 2019; Poulos and Hightower, 1977; Raichur et al., 1996), sylvinite ore (Brogoitti and Howald. 1972), and sericite (Tian et al., 2017). However, the major issue associated with the SFF process is its low selectivity, which has inhibited its commercial application.

The low selectivity of the SFF process is largely due to the physical entrapment of gangue within the aggregates (Mathur et al., 2000; Ng et al., 2015). This problem may be remediated by the employment of multiple-stage cleaning (Rubio and Marabini, 1987). Additionally, since the typical flocculants used in SFF also contain hydrophilic components, the adsorption of the polymers on the surface of some undesired ultrafine particles is unavoidable (Forbes, 2011). Some ideas have been proposed to overcome the selectivity problem occurring in the SFF process; however, no effective methods have been found (Rubio et al., 2007).



Fig. 1.1 A schematic representation of the hydrophobic flocculation flotation (HFF) process (Song and Lopez-Valdivieso, 1998).

Hydrophobic Flocculation Flotation Fig 1.1 shows the schematic representation of the hydrophobic flocculation flotation (HFF) process (Song and Lopez-Valdivieso, 1998). The HFF process is very similar to the SFF process, but what distinguishes them from each other is that nonpolar oils rather than flocculants are used in the former to aggregate the fine particles. Depending on the oil dosage and addition regimes, the HFF process has also been termed as agglomerate flotation (Sadowski and Polowczyk, 2004) and emulsified oil extender flotation (Rubio et al., 2007).

Song et al. (2012) compared the results of the HFF process with the conventional flotation process using an ultrafine molybdenite single mineral sample ($d_{71} = 10 \ \mu m$). They showed that the HFF process gave 90% weight recovery of molybdenite, which was 55% higher than that obtained by the conventional flotation process. Applications of the HFF process have also been reported on other artificial ultrafine mineral particles, including rhodochrosite (Song et al., 1999), galena and sphalerite (Song et al., 2001). The effectiveness of the HFF process is not limited to the artificial samples; it has also been successfully applied to selectively recover real samples, which included ultrafine coal, gold ore, and ilmenite ore (Song and Trass, 1997; Song and Lopez-Valdivieso, 1998).

However, the HFF process suffers from the same drawback that appeared in the SFF process; that is, it is required to perform a multi-stage cleaner with washing water in order to achieve high concentrate grades. Besides, the hydrophobic flocculation, which is the core of the HFF process, is impacted by numerous factors (Song and Lopez-Valdivieso, 2002), so that the control of flocculation is very complex, making the HFF process impracticable for industrial application.

<u>Carrier Flotation</u> Technically speaking, there is no essential difference between carrier flotation and HFF (Sivamohan, 1990). Instead of using nonpolar oils to aggregate ultrafines, coarse hydrophobic particles are used in carrier flotation to fulfill the aggregation purpose. The particles being used as carriers can either be of the same material as the ultrafine particles to be recovered or of a different type (Eckert et al., 2019). During conditioning, the target ultrafine particles adhere to the surfaces of carriers due to hydrophobic interaction, by which the apparent separation size of valuable particles increases. Consequently, the probabilities of collision and attachment between particles and air bubbles increase, which in turn will significantly enhance the flotation recovery of ultrafine particles (Zhang et al., 2017).

Abdel-Khalek et al. (1998) used limestone particles as a carrier for the flotation removal of anatase from a kaolin pre-concentrate with $d_{80} = 2 \ \mu m$. The results showed that the whiteness of kaolin product attained by carrier flotation was 12% higher than that obtained by the conventional flotation. A comparative study conducted by Fuersteanau et al. (1988), in which three flotation techniques (conventional, hydrophobic flocculation, and carrier flotation) were used to separate ultrafine hematite (< 10 \ \mum) from quartz, found that the carrier flotation assisted with coarser hematite particles gave the highest recovery, as well as the highest grade. The efficacy of carrier flotation was also demonstrated on a difficult-to-float low-rank coal by Ateşok et al. (2001), in which a coarser hydrophobic high-rank coal played the role of the carrier. Non-mineral particle polypropylene, which has been hydrophobized with a fatty acid, was even used as a carrier to recover ultrafine sulfides, oxides, and salt-type minerals (Rubio and Hoberg, 1992).

It appears that carrier flotation is a promising technique for the recovery of ultrafine particles; however, some issues associated with this process have hampered its further application. First of all, if the carrier is not naturally hydrophobic, additional reagent cost resulting from rendering the carrier hydrophobic will be inevitable. Moreover, if the carrier is not the same type as that of the valuable particles to be floated, the recycling process of the carrier will be necessary. Furthermore, if the coarser carrier particles are of the same mineral type as the ultrafine particles to be floated, they may get lost as a result of slime coating by the ultrafine gangue particles (Yu et al., 2017).

1.2.1.2 Size Reduction of Air Bubble

The reason why the flotation recovery would decline with the decrease of particle size has been clearly revealed by different bubble-particle collision models (Reay and Ratcliff, 1973; Weber and Paddock, 1982; Yoon and Luttrell, 1989), from which it also can be seen that reducing bubble size is a solution to the problem in recovering fine and ultrafine particles. As such, numerous methods dedicated to reducing air bubble size have been developed, and several generalized review articles of these methods can be found elsewhere (Agarwal et al., 2011; Miettinen et al., 2010).

There is a large body of experimental evidence showing that the use of smaller air bubbles improves the flotation performance in terms of recovery of fine and ultrafine particles. Yoon et al. (1991) developed a microbubble flotation process and successfully applied it to remove anatase and mineral matter from ultrafine clay ($< 2 \mu m$) and coals ($< 5-25 \mu m$). In this process, air bubbles of diameters ranging from 50 to 400 μm were generated using static inline mixers. Santana et al. (2008, 2012) investigated the flotation performance of a phosphate ore ($d_{50} = 17 \mu m$) using both the conventional column flotation and the dissolved air flotation (DAF) techniques. They found that DAF, where most of the bubbles are of a size smaller than 100 μm , gave a higher recovery of ultrafine apatite at a higher grade.

Most recently, it was found that nano-scale bubbles of a diameter smaller than 1 µm could be generated jointly with microbubbles utilizing hydrodynamic cavitation, which was described in detail by Etchepare et al. (2017). As a consequence, a number of studies regarding using nanobubbles to facilitate the flotation recovery of ultrafine particles, e.g., coal (Fan et al., 2010; Sobhy and Tao, 2013), phosphate (Fan et al., 2010), muscovite (Zhou et al., 2019), quartz (Calgaroto et al., 2015), chalcopyrite (Rahman et al., 2014) etc., have been conducted. The results all showed that the use of nanobubbles significantly improved the recovery of ultrafine particles, and the following reasons may account for the improved separation. One is that nanobubbles nucleated on the surfaces of ultrafines act similarly as collectors, and therefore enhance the hydrophobicity of the target ultrafines (Calgaroto et al., 2015; Fan et al., 2010; Zhou et al., 2019), which, in turn, results in increases in the probability of bubble-particle attachment and also the stability of bubble-particle aggregates (Calgaroto et al., 2015). Another is that nanobubbles nucleated on the surfaces of ultrafines can serve as a bridge to promote the aggregation of ultrafines, and then attach the aggerates consisting of ultrafines to microbubbles (Zhou et al., 2019), which is a more favorable case for particle collection due to the increase of the apparent separation size of ultrafines.

The discussion presented in this section showed that reducing air bubble size is an effective approach for improving the recovery of ultrafine particles; however, the use of fine bubbles has also brought some negative influences. One disadvantage is that the required residence time in flotation circuits will be increased because the rising velocity of rather small bubbles attached with particles is low. Another disadvantage is that the gangue entrainment will become more significant and thereby lead to the low selectivity of the flotation process because the water recovery in froth increases with decreasing bubble size (Miettien et al., 2010). Particularly in the case of nanobubble

flotation, the energy consumption for nanobubble generation is relatively high, and it is still too challenging to control the size distributions of microbubbles and nanobubbles in a more practical way (Etchepare et al., 2017).

1.2.1.3 Nanoparticle Flotation Collector

Surface hydrophobicity of particles is another critical factor that influences the flotation performance, as it determines the attachment of particles to the bubble surfaces. Typical collectors used to render the target particles hydrophobic are hydrocarbon oils and chemicals comprised of hydrocarbon tails. In 2011, an investigation conducted by Yang et al. (2011) revealed that hydrophobic nanoparticles could also function as a collector for fine hydrophilic silica beads. Since then, numerous studies have been carried out to evaluate the effectiveness of nanoparticle collectors in the flotation recovery of fine particles.

Yang and Pelton (2011) successfully recovered hydrophilic glass beads (30-50 μ m) using nano-sized latex particles with a suitable hydrophobicity as a collector. They found that a nanoparticle collector is more effective than those conventional collectors because the water did not thoroughly wet the specific areas on the glass surfaces where hydrophobic nanoparticles had been deposited. In a recent study conducted by Lai et al. (2018), the flotation recovery of fine coal (< 74 μ m) was investigated using hydrophobic nano-silica particles as a collector. They pointed out that the enhanced fine coal recovery by the nanoparticle collector may also be attributed to the increase of coal surface roughness, which has positive impacts to flotation, according to Li et al. (2019) and Hassas et al. (2016). Application of nanoparticle collectors has also been reported in the flotation of a synthetic nickel sulfide ore containing ultrafine pentlandite particles with a 12 μ m mean particle size. The results showed that the flotation grade versus recovery curve obtained

with St-VI-MAPTAC-158 nanoparticle collector was superior to that obtained with xanthate, which is a conventional molecular collector.

Problems associated with applying nanoparticle collector in the flotation of fine particles have been reported in the literature. First, the hydrophobic aggregation of the nano-scale collector particles is hard to prevent, making the consumption of nanoparticle collectors unexpectedly high, as reported by Yang et al. (2013). Second, according to the researchers (Yang et al., 2012), the hydrophobizing process by a nanoparticle collector requires a long conditioning time, which has an adverse influence on the flotation throughput. In addition, the process of depositing nanoparticles onto the target particles is primarily driven by electrostatic attraction (Hajati et al., 2019), which could be readily interfered by the ions that were dissolved from their associated mineral ores or presented in the recycled processing water in a real flotation plant.

1.2.2 Oil Agglomeration

The oil agglomeration process is another separation technique pertaining to recovering finely dispersed target particles that are naturally hydrophobic or rendered hydrophobic with a collector in liquid suspension by enlarging the apparent size of the fine particles. This is accomplished by agitating the suspension in the presence of small amounts of oil which is capable of preferentially wetting the target particles and acting as a bridging liquid between oil-wetted particles. By adding adequate amounts of oil and providing sufficient mechanical agitation, the oil-wetted particles are bonded together to form discrete agglomerates in the course of collision because of the small interfacial tension of the oil and the capillary attraction of oil bridges between particles (Mehrotra et al., 1983). At the same time, the non-wetted undesired particles remain finely dispersed in the aqueous phase. This substantial difference in size between the agglomerates consisting of the target particles and the undesired particles makes it feasible to separate the former

from the latter by means of conventional separation techniques, of which screening is the most common method.

The Trent process, which was developed in 1920 for the recovery of coal fines, was the first application of the oil agglomeration technique. Since then, a considerable amount of attention has been given to the beneficiation of fine and ultrafine coal by oil agglomeration, which led to the development of a number of coal processing techniques based on the concept of oil agglomeration, some of which have been successfully demonstrated in pilot-scale and commercial-scale (Mehrotra et al., 1983; Özer et al., 2017). The oil agglomeration process is capable of selectively recovering fine and ultrafine coal, and this has been confirmed in numerous studies (Aktaş, 2002; Kelly and Burry, 1990; Shen and Wheelock, 2001; Trass and Bajor, 1988; Wang et al., 2018). One advantage of this process is that its separation efficiency is unaffected by a reduction in particle size (Steedman and Krishnan, 1987). Another advantage of the oil agglomeration process, as shown in the work of Capes and Darcovich (1984), is that the dewatering of the fine coal particles that have been recovered in the form of hydrophobic agglomerates is much easier compared to the dewatering of a flotation froth product.

Despite these advantages, all the pilot- and commercial-scale coal agglomeration plants, which had been successfully operated for a short time, were closed due to the high operating cost resulting from oil loss. There has been no further attempt to propel the commercialization of the oil agglomeration process on coal since 1994. To minimize oil consumption, recently, a high internal phase (HIP) water-in-oil emulsion binder was used as the agglomerant for oil agglomeration of low-ash fine coal (10%) by Netten et al. (2015, 2017). The results showed that at the same high level of coal recovery, the oil consumed in the oil agglomeration test using an emulsion binder as the agglomerant was only 16-20% of that was consumed in the test using the

pure oil as the agglomerant. However, the decrease in oil consumption was achieved at the expense of an irrecoverable consumption of the emulsifier. Furthermore, some shortfalls of using the new oil-saving agglomerant versus a pure oil agglomerant were clearly shown in a later work published by Netten and Galvin (2018), in which a fine coal tailing assayed 42% ash was agglomerated by the former. One disadvantage is that the new agglomerant deteriorated the selectivity of the process, as evidenced by the fact that the performance of flotation was superior. This was most probably due to the more severe gangue entrainment in oil agglomeration since the emulsion binder was consisted of 80-90% of water by volume. It is noted that the degree of entrainment was related to the feed ash since the low selectivity issue that occurred on a high-ash coal feed was not reported in other studies of theirs, which were conducted on a low-ash feed (Netten et al., 2015, 2017). Another disadvantage of using this new agglomerant lies in the course of dewatering the agglomerates. They found that coal agglomerates obtained using the emulsion blinder were too stable, and thereby, a high-shear agitation had to be applied to break them up before they could be dewatered (Netten and Galvin, 2018).

In addition to its widespread use for coal beneficiation, the oil agglomeration process has also been applied for the recovery of a large variety of fine and ultrafine minerals in lab-scale, which include chalcopyrite (Cadzow et al., 1984; House and Veal, 1989), celestite (Cebeci and Sönmez, 2004), barite (Sadowski, 1993; Sönmez and Cebeci, 2003), nickel ore (Polowczyk et al., 2008), wolframite (Kelsall and Pitt, 1987; Wei et al., 1986), pyrite (Drzymala et al., 1986), iron ore (Puddington, 1966; Spark and Sirianni, 1974; Uwadiale, 1990;), celestite (Cebeci et al., 2000), ilmenite (Sparks and Wong, 1973), graphite (Farnand et al., 1961; Puddington, 1966), and tin ore (Cadzow et al., 1984; Farnand et al., 1964). These examples demonstrated that the oil agglomeration process is capable of producing mineral concentrates with high recoveries as well as high grades. However, aside from the drawback of oil loss, some particular problems associated with oil agglomeration of mineral particles that have inhibited its commercial development are worthy of attention.

One of the problems lies in the reagent cost. Unlike coal, most of the minerals are naturally hydrophilic, such that the employment of a collector is necessary prior to performing oil agglomeration. Previous work conducted by Kavouridis et al. (1981) showed that it is necessary to make oil contact angles of particles above 90° in order to form agglomerates. In some cases, oil agglomeration may require an even larger oil contact angle. For example, Kelsall and Pitt (1987) investigated the oil agglomeration of wolframite fines and found that mineral agglomerates would not form unless the oil contact angle approached 180°. In this regard, the collector consumption is expected to be high in oil agglomeration of mineral particles, especially for mineral particles with ultrafine sizes. According to Sparks and Wong (1973), in order to achieve the success of oil agglomeration, the amount of collector required is generally 10-100 times as much as that used in flotation.

Another problem encountered in the beneficiation of minerals is that the efficacy and efficiency of the oil agglomeration process are very sensitive to the feed ore grade. Cadzow et al. (1984) investigated the feasibility of separating ultrafine chalcopyrite and cassiterite particles from quartz by oil agglomeration. They found that when the mineral concentration in the artificial feed was low (0.5% and 2% for chalcopyrite and cassiterite, respectively), no sizable agglomerates could be formed regardless of the increasing use of oil. However, high agglomeration recoveries would be achieved on both samples once the population of valuable particles in the feed slurries was increased to a certain extent. It is also noted that all the studies regarding the oil agglomeration of minerals were carried out either on pure minerals or samples of high grades and no previous oil

agglomeration work using real ore samples with low grades has been reported. It appears that there may be a lower limit of the ore grade for implementing the oil agglomeration process.

1.2.3 Two-Liquid Flotation

Two-liquid flotation (TLF), which is also referred to as oil flotation or liquid-liquid extraction, is very similar to the oil agglomeration process. The major difference between these two processes is that the amount of oil used in TLF is far larger than that used in oil agglomeration, such that a separate oil phase is visible at the end of the TLF separation (Stratton-Crawley and Park, 1979). In principle, the oil droplet-particle interactions occurring in the pulp phase of a mixing tank in oil agglomeration and TLF can be considered as a second-order process in that its rate should depend on the concentrations of both particles (N₁) and oil droplets (N₂). Thus, the particle recovery rate can be represented by the following expression:

$$\frac{dN_1}{dt} = -kN_1N_2 \tag{1.1}$$

where t is time, and k is the rate constant. It clearly shows in Eq. (1.1) that the recovery rate increases with increasing the populations of both particles and oil droplets. When the feed ore is given, increasing the oil dosage can improve the recovery rate, indicating that the TLF process should not have the problem of handling low-grade ores that the oil agglomeration process has.

TLF is a separation process based on the stabilization of emulsions between oil and water phases by particles. If a particle can be partially wetted by oil and water phases constituting an emulsion, the particle will be stably held at the oil-water interface, as shown in Fig. 1.2. The distribution of particles between oil and water phases is governed by the relative values of the solid/water (γ_{sw}), solid/oil (γ_{so}), and oil/water (γ_{ow}) interfacial tensions. According to Reinders (1913), the following three situations are likely to occur in an oil-water-solid system:

(a) If $\gamma_{so} > \gamma_{sw} + \gamma_{ow}$, the solid particle tends to disperse within the water phase;



Fig. 1.2 Interfacial tensions on a solid particle sitting at oil-water interface.

(b) If $\gamma_{sw} > \gamma_{so} + \gamma_{ow}$, the solid particle tends to disperse into the oil phase;

(c) If $\gamma_{wo} > \gamma_{so} + \gamma_{sw}$, or if none of the three interfacial tensions is greater than the sum of the remaining two, the solid particle will be concentrated at the oil-water interface.

For hydrophilic particles, condition (a) is the case, while for hydrophobic particles, condition (b) or (c) is the case. If the three interfacial tensions associated with the particles of interest are adjusted by the use of suitable chemicals such that condition (b) or (c) is accomplished, meanwhile maintaining the condition (a) for other particles accompanied with the target particles, it should be possible to separate this target mineral from others selectively. This concept was well demonstrated in work conducted by Otsuki et al. (2007), where a two-stage TLF process was applied to separate three fluorescent powers of different colors from each other by selectively hydrophobizing the fluorescent powders in sequence.

TLF has been regarded as a promising method for the separation of fine and ultrafine particles. This conclusion was based on a large body of evidence in the literature. Shergold and Mellgren (1966, 1970) concentrated fine quartz particles (-44 μ m) at the iso-octane/water interface using dodecylamine as the collector. They found that there was a good correlation between the recovery and oil contact angle. Their findings were supported by the work of Raghaven and

Fuerstenau (1975), who showed that the TLF recovery of 0.2 µm hematite particles increased with the contact angle of heptane droplet. They also compared the separation performance of TLF and air flotation conducted on an artificial submicron hematite-quartz mixture and concluded that TLF is the more effective method in that an oil droplet gives a much larger contact angle on a given mineral surface than an air bubble can. Other good examples concerning applications of the TLF process for the separation of ultrafine particles can be found in literature reported by Lai and Fuerstenau (1968), Stratton-Crawley and Shergold (1981), Marinakis and Kelsall (1984), Hui and Wei (1993), Kusaka et al. (1992, 1993,1994, 1998, 1999), Kocabag and Guler (2007), Machunsky et al. (2009), and Ozkan and Duzyol (2014). The TLF studies cited here all demonstrated that oil and other organic liquids are better immiscible fluid than air for collecting hydrophobic particles in water, particularly for ultrafine particles. It appears that there is no lower particle size limit, which is not surprising in that the process is similar to solvent extraction.

Although it is rare, the potential of TLF on the recovery of ultrafine particles has also been demonstrated using real ores. Coleman et al. (1967) successfully applied the TLF process for the removal of calcite from a naturally occurring shale that has been ground to below $37 \,\mu\text{m}$. However, it was also pointed out by them that the high oil consumption may hamper this technique. In work conducted by Zambrana et al. (1974), a continuous TLF process has been developed to concentrate cassiterite ore (< 10 μ m) obtained from the Itos concentrator of an operating processing plant. In this process, gasoline and Aerosol 22 were used as the oil phase and collector, respectively. The results showed that 80% of cassiterite fines could be recovered in the rougher concentrate, but the Sn grade was only slightly increased from 1.5% to 6.5%. By conducting a two-stage water washing cleaner, the Sn grade was improved to 14% but at the cost of 20% reduction in recovery. Nevertheless, the Sn grade in the cleaner concentrate was still too low as compared to the Sn grade

of pure cassiterite, which is 78.7%, suggesting that water washing could not be an efficient cleaning method for further upgrading the concentrate product. The TLF process has also been applied for fine coal beneficiation (Pires and Solari, 1988). In addition to a low-ash concentrate consisting of coal particles that have been extracted into the oil phase, the TLF process also produced a high-ash concentrate, which represented the stable emulsions well-stabilized by coal particles.

From the above, it appears that the main disadvantage associated with the TLF process is the formation of stable emulsions, which in turn leads to the issues related to the separation selectivity and oil consumption (Sivamohan, 1990). To tackle this issue, it is necessary to liberate the hydrophobic particles from the emulsion droplets; however, no prior work on this topic has been reported.



Fig. 1.3 Conceptual representation of the hydrophobic-hydrophilic separation (HHS) process; a) a hydrophobic particle with $\theta > 0$ is transferred from water to oil/water interface and subsequently to oil phase with corresponding changes in interfacial tensions, b) w/o emulsions are broken mechanically to liberate the entrapped water droplets along with the hydrophilic particles dispersed in them (Yoon et al., 2016).

<u>1.2.4.1 Principle of The HHS Process</u>

4

Recognizing the limitations of TLF, Virginia Tech has developed the hydrophobichydrophilic separation (HHS) process (Yoon, 2016), which is essentially a continuation of the TLF process. What distinguishes the two is that in the HHS process, the oil-in-water emulsions formed during the recovery step are converted to water-in-oil emulsions so that they can be dispersed in oil by means of mechanical force in a specially designed device called a Morganizer, which can remove the entrained impurities and water.

Fig. 1.3 is a conceptual representation of the HHS process (Yoon et al., 2016). Consider a single hydrophobic particle suspended in an aqueous phase, which is located below a hydrocarbon liquid (e.g., pentane, heptane) phase. The particle will adsorb to the oil/water interface if the contact angle (θ) measured through water is greater than zero as shown in Fig. 1.3a and Fig. 1.4 (Yoon et al., 2016). It can be readily shown that for a hydrophobic particle of radius r,

$$\Delta G_a^w = -\pi r^2 \gamma_{ow} (1 - \cos \theta)^2 \tag{1.2}$$



Fig. 1.4 Contact angle of an oil droplet on a hydrophobic surface in water; γ_{so} , γ_{sw} , and γ_{ow} are the interfacial tensions at the solid/oil, solid/water, and oil/water interfaces, respectively (Yoon et al., 2016).

where ΔG_a^w is the Gibbs free energy of adsorption from the water phase and γ_{ow} is the oil/water interfacial tension. Eq. (1.2) can be derived in the same manner as the equation for the adsorption of the hydrophobic particle to air bubble (Yoon and Mao, 1996).

Fig. 1.3b represents the case of agitating an aqueous slurry of fine coal in the presence of oil, as in the Otisca T-process (selective agglomeration, Kelly and Burry, 1990) and TLF process. A high-shear agitation is necessary to disperse the oil in water as small droplets and hence increase the probability of oil droplet-particle collision. Some of the more hydrophobic particles will enter the organic phase as individual particles, while others will form Pickering emulsions. Eq. (1.2) should give the free energy change associated with the emulsification. The w/o emulsions (or agglomerates) will become smaller at higher shear rates. This mechanism may be responsible for the "massive water globules" in coal agglomerates as observed by Keller and Burry (1987).

Thermodynamically, hydrophobic particles forming Pickering emulsions in water are equivalent to those adsorbed to the oil/water interface from bulk oil phase, with its free energy change (ΔG_a^o) being given as,

$$\Delta G_a^o = -\pi r^2 \gamma_{OW} (1 + \cos\theta)^2 \tag{1.3}$$

which can be derived in the same manner as Eq. (1.2). According to Eq. (1.3), hydrophobic particles adsorb to the oil/water interface at $90^{\circ} < \theta < 180^{\circ}$ and thereby stabilize the w/o emulsions.

In the HHS process, Pickering emulsions are destabilized to liberate the water globules from the particle-stabilized emulsions and/or agglomerates by various means. One is to use mechanical energy to break the emulsions and liberate water droplets, and another is to use sonic energy to do the same (Smith, 2012). Eq. (1.3) may be used to determine the energy required to liberate coal particles, as $-\Delta G_a^o = \Delta G_d^o$ in which the latter is the energy of detaching coal particles from the oil/water interface to the oil phase. Fig. 1.5 shows the relationship between particle radius
and energy of detachment at the pentane-water interface, suggesting that less energy is required to detach particles of smaller size (r) and higher contact angles (θ) from the interface to the oil phase. The liberated water droplets fall by gravity along with the hydrophobic particles dispersed in them, and enter the aqueous phase below, while the coal particles, which are relatively free of moisture and mineral matter, exit the reactor along with the oil in which they are dispersed. The reactor, shown in Fig. 1.3b, is equipped with a set of vibrating screens to mechanically destabilize the w/o emulsions. It is called a Morganizer in honor Mr. E. Morgan Massey, who funded the development of the HHS process.



Fig. 1.5 The effects of contact angle and particle size on the free energy required for detaching a particle from the pentane/water interface to the pentane phase.

In effect, hydrophobic particles are transported to a hydrophobic liquid phase from an aqueous phase. The free energy of transfer (ΔG_t) may be given as

$$\Delta G_t = \gamma_{SO} - \gamma_{SW} \tag{1.4}$$

Where γ_{so} and γ_{sw} represent the solid/oil and solid/water interfacial tensions, respectively. Combining with Young's equation, Eq. (1.4) becomes

$$\Delta G_t = \gamma_{OW} \cos \theta \tag{1.5}$$

This suggests that the transfer process is spontaneous if $\theta > 90^{\circ}$. This finding also suggests that the coal-in-oil dispersion is stable, allowing it to be discharged from the top of a Morganizer as a clean coal product with low ash and moisture contents. Spent oil is recovered from clean coal by solid-liquid separation and recycled.

In the HHS process, oil droplets rather than air bubbles are used to collect hydrophobic particles from the aqueous phase. The type of oils used in this process exhibited $\theta > 90^{\circ}$, a condition that can be realized if $\gamma_{sw} > \gamma_{so}$ (see Fig. 1.4). This inequality can be realized with low-boiling oils of short-chain *n*-alkanes and explained using the acid-base theory (Van Oss, 2006),

$$\gamma_{sw} = \gamma_s + \gamma_w - 2\sqrt{\gamma_s^{LV}\gamma_w^{LV}} - 2\sqrt{\gamma_s^+\gamma_w^-} - 2\sqrt{\gamma_s^-\gamma_w^+}$$
(1.6)

$$\gamma_{so} = \gamma_s + \gamma_o - 2\sqrt{\gamma_s^{LV}\gamma_o^{LV}} - 2\sqrt{\gamma_s^+\gamma_o^-} - 2\sqrt{\gamma_s^-\gamma_o^+}$$
(1.7)

in which the superscripts Lv, +, and - represent the Lifshitz-van der Waals, acidic, and basic components of the surface tensions, respectively. For the case of using pentane (C₅H₁₂) as an oil phase, $\gamma_0 = 16.05 \text{ mJ/m}^2$ and $\gamma_w = 72.8 \text{ mJ/m}^2$ at 20 °C. The large difference between these two surface tensions immediately supports that $\gamma_{sw} > \gamma_{so}$. If a solid is sufficiently hydrophobic, both γ_s^+ and γ_s^- are negligibly small in addition to the γ_0^+ and γ_0^- of Eq. (1.7) being close to zero, as a result of which the last two terms may be ignored. Also, the *LV* terms of the two equations are approximately equal to each other, as $\gamma_w^{LV} \cong \gamma_o^{LV}$ for the short-chain hydrocarbon oils. Thus, the magnitudes of γ_{sw} and γ_{so} are mainly determined by the first two terms. Eqs. (1.6) and (1.7) also show that the inequality becomes greater with decreasing γ_o , suggesting that a shorter-chain hydrocarbon oil may be a better collector for hydrophobic particles.

Fig. 1.6 shows the contact angles of *n*-alkane oils with n = 4-10 placed on a U.S. bituminous coal in water (Yoon et al., 2016). As shown, θ increases with decreasing *n* due to a corresponding decrease in γ_0 . The surface tensions of a C8 alkane is 23.8 mJ/m², while that of C5 alkane is 16.1 mJ/m², for example (Van Oss, 2006). Note also that all of the contact angles are in the range of 94°-110° due to the inequality of interfacial tensions discussed above, which gives negative wetting tensions. These contact angles are substantially larger than those with air bubbles (using the captive bubble technique) on a variety of U.S. coals; the most hydrophobic bituminous coal shows $\theta \approx 65^{\circ}$ only (Gutierrez-Rodriguez and Aplan, 1984). These findings provide a thermodynamic justification of using short-chain *n*-alkane to collect hydrophobic particles from water. As it is well known, the higher the contact angle, the higher the recovery, regardless of using air bubbles or oils as a collector for hydrophobic particles.



Fig. 1.6 The contact angles (θ) of n-alkane oils measured on a U.S. bituminous coal in water. The angles were measured through the aqueous phase as shown in Fig. 1.4 (Yoon et al., 2016).

<u>1.2.4.2 Previous Work on the HHS Process</u>

The development of the HHS can be dated back to 1995, when a dewatering process named dewatering-by-displacement (DbD) was patented by Yoon and Luttrell (1995). The DbD process was developed based on the thermodynamic reasoning that the interaction energy between hydrophobic liquid and hydrophobic coal is more significant than that between the coal and water (see Fig. 1.7, Yoon et al., 2016). A demonstration example illustrated in the patent showed that the DbD process conducted using butane as the hydrophobic liquid was able to produce a dry coal product assaying 3.6% moisture from a coal slurry containing only 5% solids.

Encouraged by this initially obtained excellent result, Yoon et al. (1997) continued the study of the DbD process on fine coal dewatering, in which the effects of butane-to-coal mass ratio, % solids in the feed, and settling time for phase separation on the product moisture were investigated. According to this report, under optimal operating conditions, a Microcel column flotation clean coal product can be dewatered to be of moisture content as low as 1%, which would never be achieved by any conventional mechanical dewatering methods. Since the boiling point of butane is only 30.2 °F, the butane used in the DbD process is readily recovered, and thereby the loss of butane due to dissolution in water is negligible. However, the process was required to be operated under a pressured environment due to this property of butane, which may increase the operating cost. Additionally, the capability of using the DbD process for the separation of hydrophobic particles was not explored.

Recognizing the abovementioned questions pertaining to the DbD process, Smith (2008) explored the feasibility of simultaneously removing both mineral matter and surface moisture from fine coal slurry by the DbD process, in which pentane, a liquid form hydrophobic oil at room temperature, was used as the substitute for butane. In this project, the DbD tests were performed

using a two-step testing protocol, in which the coal concentrates recovered by agglomeration were subjected to dewatering using five different methods including handshaking, screening, air classification, centrifugation, and filtration. By comparing the separation results obtained using different dewatering methods, Smith (2008) found that the adapted DbD process of cleaning with spherical oil agglomeration in conjunction with dewatering by centrifugation performed the best. Dry clean coal products assayed 7-9% ash contents, and 7-10% moistures were produced by centrifuging the agglomerates at 3280 RPM within 1 minute, while the combustible recoveries varied from 71% to 98%. The work conducted by Smith was of significant importance to the development of the HHS process, as it was the first time that the recovery of fine coal, in addition to dewatering, was also given attention to the DbD process.



Fig. 1.7 Conceptual illustration of the dewatering-bydisplacement (DbD) process (Yoon et al., 2016). Color code: water-blue; coal-black; white-air, and oil-orange.

The major problem associated with using the centrifugation in the DbD process resulted from pentane evaporation, which caused difficulties in sealing the centrifuge and recovering the spent oil. Therefore, research on developing new methods for dewatering coal agglomerates was continued at Virginia Tech. In the work of Smith (2012), two new methods were developed to dewater the coal agglomerates: one is based on employing ultrasonic energy, and another is based on using mechanical energy. In both methods, the dewatering of agglomerates was achieved by breaking them in an oil phase for the first time, which is a milestone in the development history of the HHS process. Smith (2012) reported that, using these new methods, the DbD process was capable of producing clean coal products containing low-ash and low-moisture contents at high combustible recoveries, and the separation efficiency of this newly adapted DbD process was substantially higher than that of the froth flotation. More importantly, with this improved DbD process, the spent oil was recovered at a low energy cost. In this work, Smith demonstrated the DbD process for simultaneously recovering and dewatering fine coal on a semi-continuous labscale testing unit.

Encouraged by the promising results obtained by Smith (2012), the research work on the DbD process was continued by Gupta (2014) with the objectives of developing and demonstrating

	Feed	HHS Produ	ct	%Organic
Feed Source	Ash (%)	Moisture, %	Ash, %	Recovery
Eastern Kentucky	67.5	6.8	3.8	91.6
Southern WV	53.0	8.5	3.4	89.5
Western Pennsylvania	40.4	3.9	4.3	95.5
Southern WV	53.6	3.5	3.9	95.4
Northern WV	13.7	4.9	5.0	97.7
SW Virginia	7.0	3.8	2.1	97.6
Southern WV	10.7	3.8	3.1	98.6

Tab. 1.1 Results of the Proof-of-Concept scale HHS tests conducted on various U.S. coal feedstocks (Gupta, 2014).

this novel fine coal beneficiation technique on a Proof-of-Concept (POC) pilot-scale. During the course of this development, a brand-new trade name, Hydrophobic-Hydrophilic Separation (HHS), was given to this groundbreaking process with the patent application filed in 2013 (Yoon, 2016). Fig. 1.8 shows the schematic representation of the flowsheet of the HHS POC-pilot plant (Gupta, 2014), which has the capacity of processing 100 lbs/hr dry feed solids. In this project, the deagglomeration device (Morganizer) was designed using vibrating screens rather than using ultrasonic energy, and the HHS demonstration work was performed both on low-ash and high-ash fine coal feedstocks. Excellent HHS tests results, as shown in Tab. 1.1, which were comparable to those obtained from bench-scale tests, demonstrated that the HHS process can be operated continuously with excellent separation performance, and it is feasible to apply it on pilot scale or even commercial scale.



Fig. 1.8 A schematic representation of the flowsheet of the HHS POC-pilot plant (Gupta, 2014).

Process	Description	Application	Drawback	Merit
Selective flocculation flotation	Increase apparent separation size by selectively aggreating the target ultrafine particles using flocculants	Coal, iron ore, uranium ore, sylvinite ore, sericite, etc.	Low selectivity	ı
Hydrophobic flocculation flotation	Increase apparent separation size by selectively aggreating the target ultrafine particles using nonpolar oils	Coal, molybdenite, gold ore, ilmenite ore, etc.	Low selectivity, high oil consumption, high-shearing engergy input	ı
Carrier flotation	Coarse hydrophobic particles used as carrier for ultrafine particles	Anatase, coal, quartz, hematite, sulfides, oxides, salt type minerals, etc.	Require additional recovery process for the carriers, risks for lossing valuable coarse carriers	ı
Nanobuble flotation	Increase the collision probabilities between bubble and particle by decreasing the air bubles to nano-sizes	Coal, phosphate ore, chalcopyrite or, etc.	Long flotation residence time, high energy consumption, low selectivity	ı
Flotation with nanoparticle collector	Use hydrophobic nano-sized particles as collector	Glass bead, coal, nickel sulfide ore, etc.	High consumption of collector, long hydrophobization treatment time	ı
Oil agglomeration	Bridging oil-coated particles to form agglomerates that can be separated from gangue particles	Coal, chalcopyrite, calcite, dolomite, hematite, etc.	High consumption of oil, require large population of hydrophobic particles	High selectivity
Two-liquid flotation	Use oil droplets to collect particles with the formation of emulsions	Coal, quartz, monazite, hematite, cassiterite, etc.	Low selectivity, high oil consumption, high moisture	No lower limits of particle size
Hydrophobic-hydrophilic separation	Break water-in-oil emulsions that stabilized by hydrophobic particles in the presence of oil	Coal	ı	No lower limits of particle size, low moisture product, high selectivity

Tab. 1.2 Comparison of various ultrafine particle recovering technologies

Encouraged by the excellent results obtained at the POC-scale, a pilot plant was constructed at an operating coal preparation plant in the Appalachian coalfield with a design capacity of 2.8 ton/hr dry feed solids. Overall, the pilot plant testing was very successful after solving some issues encountered at the early testing stage. A related report can be found in the reference (Yoon et al., 2016). So far, the HHS process has only been studied for the separation of fine coal. It will be of great interest to explore the application of the HHS process on the recovery of fine particles other than coal.

A summarization of the ultrafine particle recovering technologies discussed in the foregoing sections is given in Tab.1.2.

<u>1.2.4.3 Pickering Emulsions</u>

It is well recognized that solid particles of nano-scale and micro-scale sizes possessing suitable wettability can function the same as the chemical emulsifiers to stabilize emulsions involving oil and water, the so-called Pickering emulsion (Pickering, 1907). Depending on the wettability of the particles, which is characterized using the oil contact angle (θ_o) of particles measured through the water phase, either an oil-in-water (o/w) emulsion or a water-in-oil (w/o)



Fig. 1.9 Effect of contact angles on the emulsification (Aveyard et al., 2003).

emulsion can be stabilized by particles. As illustrated in Fig. 1.9, for particles of $\theta_o < 90^\circ$, solidstabilized o/w emulsions may form, while for particles of $\theta_o > 90^\circ$, solid-stabilized w/o emulsions may form (Aveyard et al., 2003). As stated earlier, in order to successfully implement the HHS process, it is necessary to form a w/o emulsion, which can then be broken up in the presence of a large amount of oil in a Morganizer. Typically, it is not difficult to form w/o emulsions using coal particles as an emulsifier since most of the coals are naturally hydrophobic with $\theta_o > 90^\circ$ as shown in Fig. 1.6. However, the HHS process may face the challenge of forming w/o emulsions in the cases of mineral particles that usually are hydrophilic and not fully liberated. In light of this, the methods of converting an o/w emulsion to a w/o emulsion are reviewed as follows.

As seen in Fig. 1.9, the simplest way for achieving a phase inversion from o/w emulsions to w/o emulsions is to increase the hydrophobicity of the particles. The results obtained from



Fig. 1.10 Effect of Conductivity of water-toluene emulsions stabilized by hydrophobic H30 silica particles as a function of the volume fraction of water (Binks and Lumsdon, 2000a).

emulsification tests using fumed silica particles as the stabilizer showed that the phase conversion of o/w emulsions to w/o emulsions took place when the silanol content on the fumed silica surface decreased to less than 50% (Binks and Rodrigues, 2003; Ding et al., 2005). As for mineral particles, their hydrophobicity may be enhanced with the assistance of collectors. Schulman and Leja (1954) investigated the stabilization of emulsions by barium sulfate particles, which were rendered hydrophobic using alkyl sulfates of different carbon chain lengths. The results revealed the mineral powders only stabilized o/w emulsions when they were hydrophobized by a collector of chain length less than C10, and w/o emulsions could be stabilized by the mineral powders that had been treated with a collector of chain length greater than C12. The former case may be often encountered during the hydrophobization treatment of real mineral particles due both to the complex surface chemistry and the poor liberation of the particles.



Fig. 1.11 Conductivity of water-toluene emulsions stabilized by silica particles of varying hydrophobicity as a function of the volume fraction of water. The hydrophobicity of silica particles is measured by %SiOH on silica particles' surface. The higher the %SiOH, the less hydrophobic the silica particles are. (Aveyard et al., 2003).

Another approach to achieve the conversion of o/w emulsions to w/o emulsions is to increase the oil phase volume (ϕ_o); this type of conversion is known as catastrophic inversion (Binks and Lumsdon, 2000a). Fig. 1.10 gives an example of how the water phase volume (ϕ_w) affects the emulsion formation, in which hydrophobic H30 silica particles were used as the emulsifier (Binks and Lumsdon, 2000a). In Fig. 1.10, a small conductivity represents oil was the continuous phase and emulsions were in the form of w/o while a large conductivity manifests water was the continuous phase and emulsions were in the form of o/w. As shown, o/w emulsions were stabilized at $\phi_w > 0.6$, while w/o emulsions were stabilized as the ϕ_w decreased to < 0.5. Another example regarding the effect of ϕ_w on the phase inversion is shown in Fig. 1.11, which plotted the results obtained using silica particles of various hydrophobicity as the emulsifiers (Binks and Lumsdon, 2000b). The results show that the minimum ϕ_o required for inducing a phase inversion is related to particles' hydrophobicity and the more hydrophobic the smaller ϕ_o is. For example, when the emulsions were stabilized by the most hydrophilic particles (100%SiOH), phase



Fig. 1.12 Conductivity of water-toluene emulsions ($\phi_w = 0.5$) containing 2 wt.% N20 (hydrophilic) in water (fixed) as a function of added H30 (hydrophobic) in toluene. (Binks and Lumsdon, 2000c).

inversion occurred at $\phi_o > 0.65$; when they were stabilized by the most hydrophobic particles (20 %SiOH), phase inversion occurred at $\phi_o > 0.35$. These findings suggest that oil usage in the HHS process can be reduced by making the target particles more hydrophobic.

Another alternative for making o/w emulsions phase-inversed to w/o emulsions is to add hydrophobic particles. Binks and Lumsdon (2000c) investigated the phase inversion of emulsions stabilized by hydrophobic (H30) and hydrophilic (N20) silica particle mixtures. They found that by adding H30 particles to the system, the initial o/w emulsions stabilized by N20 particles were able to be converted to w/o emulsions as the weight percentage of H30 particles in oil phase increased to > 0.4% as shown in Fig. 1.12. This phase inversion is attributed to the decline of the hydrophile-lipophile balance (HLB) of the system resulting from increasing the proportion of hydrophobic particles in the particle mixtures. Likewise, the w/o emulsions can also be inverted to o/w emulsions by adding hydrophilic particles, which is shown in Fig. 1.13 (Binks and Lumsdon,



Fig. 1.13 Conductivity of water-toluene emulsions ($\phi_w = 0.5$) containing 2 wt% H30 (hydrophobic) in water (fixed) as a function of added N20 (hydrophilic) in toluene. (Binks and Lumsdon, 2000c).

2000c). In a real feed to the HHS process, undesirable hydrophilic gangue particles are inevitably co-existing with target particles. The gangue particles, generally, will consist of the vast majority of the feed mass. As such, it may be difficult to form w/o emulsions directly in a real mineral ore system without removing most of the gangue particles.

1.3 Recovery of Rare Earth Elements from Coal and Coal Byproduct

1.3.1 Rare Earth Elements and Its Supply Risk in the U.S.

Rare earth elements (REEs) are a group of 17 elements comprising of 15 lanthanides plus yttrium and scandium, any of which can be categorized either into the heavy REEs group (Eu, Gd, Tb, Dy, Ho, Er, Tm Yb, Lu, Y) or the light REEs group (La, Ce, Pr, Nd, Sm, Sc) based on the differences in their atomic numbers (Zhang et al., 2015). REEs are not rare, but they do not naturally occur in concentrated forms that are readily extractable. The nature occurrences of REEs are in the form of mineral species rather than pure metals. According to Kanazawa and Kamitani



Fig. 1.14 Utilizations of REEs (Dutta et al., 2016).

(2006), over 200 distinct minerals containing REEs have been identified, of which bastnaesite, monazite, and xenotime are the most common commercial rare earth minerals (REMs).

REEs play essential roles in the development of the global economy due to their widespread applications in high-tech products, pollution control, medical devices, oil refining, electronics, aerospace and so on (Fig. 1.14, Dutta et al., 2016). Due to their strategic importance to national defense and sustainable energy applications, by assessing their potential supply risk, the U.S. Department of Energy identified 5 REEs as critical materials: neodymium, terbium, yttrium, dysprosium, and europium (Chu, 2011). However, the global REE supply has been dominated by China since the early 1990s. China has produced about 85% of the world production of REE raw material and oxides since then (Dai and Finkelman, 2018). In 2017, the U.S. consumed 11,000 tonnes of REEs measured as rare earth oxides (REOs), 100% of which were imported due to the demise of Molycorp Inc. in 2016. Furthermore, 78% of the imported REEs were purchased from China (Mineral Commodity Summary, 2018). Such a high dependence of REE supply on China is exceptionally detrimental because even small changes in China's REE export policy can lead to immeasurable loss to the U.S., which is very likely to happen due to the increasing trade tensions between the U.S. and China.

1.3.2 Rare Earth Elements in the U.S. Coal

In 2012, the National Energy Technology Laboratory (NETL) assessed the amounts of REEs in four U.S. coal basins using the USGS Coal Quality Database and other selected data obtained from state geologic surveys. The analysis showed that the REEs contained in the identified coal basins may exceed 2 million tons, over 25% of which are heavy REEs (Ekmann, 2012). According to the report, the coal-based REEs were unintentionally mined with coal mining activities, and the yearly production of mined REEs exceeded 40,000 tonnages in 2010, which is

equal to 4 times the U.S. REEs consumption in 2018. These results suggest that U.S. coals are a promising alternative resource for the recovery of REEs.

It has been known for a long time that coal contains trace amounts of REEs (Goldschmidt, 1935). Since then, numerous investigations have been carried out to study their occurrences and mineralogy in coal. Good summarization of these studies can be found in review articles by Dai and Finkelman (2018), Seredin and Dai (2012), and Zhang et al. (2015). It has been identified that REEs associated with inorganic matter occur in various mineral forms, such as monazite, xenotime, apatite, rhabdophane, zircon, florencite, clinochlore, allanite, goyazite, boehmite, and authigenic kaolinite while organic REE compounds are mainly associated with low-ash and low-rank coals in which heavy REEs are more enriched than light REEs. As to the U.S. coal, especially for the studied subject in this work – Fire Clay coal seam in eastern Kentucky–most of the REEs-enriched mineral grains are characterized to be monazite and xenotime (Hower et al., 1999; Zhang et al., 2017). In principle, it should be possible to recover REMs from coal by physical separation methods based on the knowledge and technologies established on the recovery of conventional REMs.

1.3.3 Recovery of Coal-based REEs by Physical Separation Techniques

Physical separation methods, including gravity separation, magnetic separation, electrostatic separation, and froth flotation, are sophisticated techniques that have been exploited in the beneficiation of conventional REMs (Jordens et al., 2012). However, there has been relatively little research on using these techniques to recover REEs from coal and coal byproducts. Blissett et al. (2014) investigated the feasibility of concentrating REEs in a coal fly ash by employing a complicated processing scheme, which was comprised of flotation, magnetic separation, and hydrocyclone classification. Even though this process involved three different

physical beneficiation methods, there was only a 26% enrichment of REEs in the product possessing the highest REEs concentration. Moreover, it was found that it was the size reduction by classification that has led to the enrichment. In another work performed by Soundarrajan et al. (2015), float-sink, magnetic, and electrostatic separation techniques were employed to enrich REEs from Pit cleanings and refuse samples. The results showed that the efficiency of each method was different from each other and dependent on the feedstock. Overall, there was no significant increase in REEs concentration using any of these methods.

Most recently, Honaker et al. (2014) investigated the effectiveness of density-based separation, froth flotation, and magnetic separation on the recovery of REEs from three coal samples. Comparison of the separation results suggested that flotation was the most promising method for REEs recovery and enrichment. As a result, a further investigation was carried out to compare the flotation performance between the flotation cell and column on a Fireclay coal sample (Zhang et al., 2017). This study showed that column flotation was more effective than conventional flotation for the concentration of REMs from coal, and the highest REEs grade that was obtained by column flotation was 4,700 ppm on an ash basis, which equated to an enrichment ratio of 10:1. However, it is noted that the REEs recovery was only 4%, so it is hard to justify flotation as an effective separation technique for the recovery of REEs from coal and coal byproducts.

In all, none of the four abovementioned physical methods is capable of effectively separating REMs from coal and coal byproducts. This may be most likely due to the very small sizes of REMs associated with coal and coal byproducts. It has been identified that most of the monazite particles in coal are of a size smaller than 5 μ m (Honaker et al., 2014). As such, one of the objectives of this work is to develop an advanced method for recovering ultrafine REMs in coal and coal byproducts.

1.4 Copper Statistics and Copper Ore Recovery by Mineral Processing

1.4.1 Copper Statistics

Copper is a material featured with malleability, high ductility, and thermal/electrical conductivity. As one of the first metals ever employed in civilization, copper, which is also call the "metal with a Ph.D. in economics", continues to make important contributions to sustaining and improving our society today, due to its wide applications for building construction, power generation and transmission, electronic product manufacturing, and the production of industrial machinery (Doebrich and Masonic, 2009). According to the USGS (2019), the total global production of copper was approximately 21 million metric tons in 2018, of which the U.S. produced 1.2 million metric tons of copper that made up around 5.7% of the worldwide production. The USGS (2019) also points out that U.S mine production of copper has been decreasing since 2016 and the U.S. copper market has been partially relying on import since 2014, which is mainly attributed to the decrease in copper ore grade. The declining of copper ore grade is not unique in the U.S., but very common worldwide. At present, the average Cu grade of ores mined globally is about 0.62% and will decrease to about 0.2% in 2050 (Elshkaki et al., 2016), which makes it very difficult to increase the copper production in the future. Meanwhile, the global copper demand has kept growing rapidly due to the rising electric vehicle production, the expanding power industry, and a positive global economic growth (Fitch Solution, 2019). Many studies have projected that the global Cu supply will be deficient over the next few years (Elshkaki et al., 2016; Northey et al., 2014).

1.4.2 Recovery of Copper Sulfide Mineral Particles

According to Norgate and Jahanshahi (2010), approximately 80% of the world's copper is extracted from copper sulfide ores at which chalcopyrite is the most common copper source. In

the mineral processing industry, copper sulfide mineral particles are mainly recovered by froth flotation after the mined ores have been subjected to a series of crushing and grinding to improve liberation. However, froth flotation is ineffective in recovering copper mineral particles that are smaller than 30 µm (Monkosa et al., 2016). As stated earlier, the global copper ore grade is continuously decreasing; thus, the amounts of ultrafine particles fed to the flotation circuit will inevitably increase as a result of the required much finer grinding for achieving sufficient liberation of copper minerals. Obviously, this will further deteriorate the recovery of copper minerals by flotation. According to Greene (2017), about 90.67 million tons of copper will be lost due to the loss of ultrafine particles during the flotation process. In this projection, only the 18 largest copper porphyry deposits in the world was considered. The tons of copper lost in flotation would be much larger if all of the active copper mines in the world had been included in the projection. It appears that one of the possible solutions to the future copper undersupply risk is to improve the recovery of ultrafine copper mineral particles.

In light of the abovementioned issue, a new flotation technique, known as emulsified oil extender flotation, was developed by Rubio et al. (2007) and the size-by-size flotation results showed that both the flotation kinetics and recoveries of fines (37-5 μ m) and ultrafines (< 5 μ m) were improved significantly in comparison with the standardized flotation. The flotation recovery of ultrafine chalcopyrite particles (d₈₀ =12 μ m) was also studied using microbubbles by Tussupbayev et al. (2015). Comparison of the column flotation results obtained with and without the microbubbles showed a 50% increase in Cu recovery was obtained in the presence of microbubbles in the amount of 50 L per 1 kg of chalcopyrite. It appears that these two approaches are promising; however, it is noted that the increase in Cu recoveries was achieved at the cost of decreasing Cu grades. In the former, Cu grade in the concentrate was dropped from 12.5% to

11.5%. In the latter, that was decreased from 18.0% to 14.7%. These studies indicate that the problem in recovering fine and ultrafine copper mineral particles cannot be solved by a modified flotation process. In addition to modified flotation processes, the oil agglomeration process has also been utilized to improve the recovery of ultrafine copper mineral particles. House and Veal (1989), and Cadzow et al. (1985) explored the feasibility of using the oil agglomeration process to recover ultrafine chalcopyrite particles on artificial copper ores. Their results showed that oil agglomeration is capable of producing high-grade copper concentrates at high recoveries. One problem associated with this process identified by Cadzow et al. (1985) is that the agglomeration of hydrophobic copper mineral particles requires a certain level of particle population, which can barely be met on real copper ore samples due to their low grades. Another problem is that the spent oil cannot be recovered economically. It is also noted that no prior work on oil agglomeration conducted using a real copper ore sample has been reported; therefore, it is still questionable whether it can be applied for recovering real ultrafine copper mineral particles.

1.5 Objectives and Dissertation Outline

1.5.1 Objectives

Despite the fact that the HHS process has been successfully applied in the recovery of fine coal, the importance of phase conversion of o/w emulsions to w/o emulsions was not realized until the HHS process was employed for minerals beneficiation. Thus, the principal objective of the current study was to understand the fundamental aspects affecting the phase inversion, which would provide critical information for implementing the HHS process to recover ultrafine coals, copper minerals, and REMs associated with coal.

1.5.2 Dissertation Outline

Chapter 1 gave a brief introduction of the background information and comprehensive review of the beneficiation techniques for the recovery of fine and ultrafine particles and the current status of recovering REEs from coal and coal byproducts by physical separation processes. Chapter 2 identified both the agglomeration problems that occurred in the HHS pilot plant at the early testing stage and the potential challenges of scaling up the vibrating mixer type Morganizer in the commercial employment of the HHS process. The former could be solved by increasing either particles' oil contact angle or agglomeration energy dissipation rate. Three new Morganizers were developed as alternatives to address the latter and they were successfully demonstrated in bench-scale HHS tests. The benefit of the application of the HHS process to the recovery of Illinois high-sulfur coal was also discussed based on a case study. Chapter 3 expanded the application of the HHS process to recover REEs from coal byproduct. The effects of different experimental conditions on the HHS separation performance were evaluated and discussed. Also, comparison of the results of the HHS and flotation tests was made. Chapter 4 studied the role of ultrafine particles in forming o/w and w/o emulsion and improved the understanding of phase transition of o/w to w/o emulsions. The effects of oil phase volume and particle hydrophobicity on phase inversion and the stability of emulsions were investigated. The knowledge base gained from these fundamental studies was applied successfully in the HHS demonstration tests on model samples. Chapter 5 studied the effects of different experimental variables on oil agglomeration of a model copper ore. The effect of hydrophobicity-enhancing agent PX-1 on the agglomeration kinetics was also studied. Chapter 6 explored the feasibility of the HHS process in the recovery of ultrafine copper ores in a semi-continuous lab-scale HHS testing unit where a special Morganizer for heavy minerals recovery was developed. The effects of various operating parameters in the Morganizer,

mixing methods, gangue minerals, and process modification to the HHS performance were examined and discussed to provide critical information for the design of a mineral-based HHS demonstration unit. Chapter 7 provided a summary of the present work and gave some suggestions for future work.

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Chapter 2 Application and Development of the HHS Process for Coal Recovery

Abstract

Encouraged by the consistently excellent results obtained both on bench- and proof-ofconcept-scale testing, the hydrophobic-hydrophilic separation (HHS) process, which is a unique non-thermal process that can remove nearly all of the surface moisture and mineral matter from fine and ultrafine coal streams that are being discarded in the impoundments, was scaled up to pilot-scale testing at LM coal preparation plant (VA, USA). However, the HHS pilot plant had faced difficulties in forming spherical agglomerates and obtaining high recoveries at the early testing stage due to the imperfect engineering design on agglomeration energy input and the quality change of the feed coal by time variation. As such, a series of lab-scale agglomeration tests was carried out to address these issues. The results show that the solution could be either to increase the oil contact angle (θ_o) of coal with sorbitan monooleate or to apply high-shearing mixing in agglomeration. The latter was actually implemented at the pilot plant and successfully tackled the agglomeration issues. During the course of pilot-scale HHS testing, it was realized that the vibrating mixer type Morganizer might be difficult to scale up because of mechanical challenges. To cope with this potential problem, new Morganizers, including Rushton mixer-screen basket type, pulsating type, and Wemco Morganizers, were developed and successfully demonstrated in lab-scale HHS tests. The HHS tests involving using the new Morganizers consistently produced clean coal products containing single-digit levels of ash and moisture, which were comparable to those obtained on a vibrating mixer type Morganizer. Lastly, a new application of the HHS process regarding upgrading Illinois high sulfur coal was also discussed.

2.1 Introduction

Froth flotation is regarded as the best available technology for the recovery of fine coal. However, the coal fines below 30-50 μ m are challenging to recover by flotation. Furthermore, the clean coal products are difficult to dewater. Therefore, many coal producers in the U.S. remove the < 44 μ m (325 mesh) fraction using deslime cyclones prior to flotation (Bethell et al., 2005), with the froth products being dewatered using screenbowl centrifuges. However, approximately 50% of the < 35 μ m fraction is lost as screenbowl effluents (Schultz et al., 2009). According to a recent National Research Council (NRC) report, 70-90 million tons of coal fines are lost in this manner annually, creating environmental concerns (Orr, 2002). The report also shows that more than 2 billion tons of fine coal have been discarded over the years, of which 500-800 million tons are in active impoundments. These numbers must be substantially larger now than when the report was written. This is unfortunate since studies indicate that the fine and ultrafine particles contained in the waste streams are very well liberated and, as such, possess the potential to be upgraded into high-value products if a suitable method is available for the recovering and dewatering fine organic matter contained in these waste streams.

In order to tackle the fine coal processing problem, a research program was initiated between the Center for Advanced Separation Technologies (CAST) and the Minerals Refining Company (MRC). This joint effort resulted in the engineering development and commercial deployment of an entirely new concept for turning fine coal wastes into a high-quality saleable product. This new technology, which is called the HHS process (Yoon, 2016), uses organic liquid droplets rather than air bubbles to collect ultrafine particles while at the same time displacing the surface moisture to obtain practically dry products. The organic liquids are used with low boiling point and low heat of vaporization, which can be recycled easily. The process was successfully
demonstrated using batch and semi-continuous laboratory equipment and a continuous proof-ofconcept (POC) test facility (Gupta, 2014). The test results obtained using deslime cyclone overflows and screenbowl effluents showed that the HHS process consistently produced a clean coal product containing single-digit levels of ash and moisture for a wide variety of different coal feed sources. In light of these encouraging results, a larger 2.8 ton/hr (dry feed solids) pilot plant was constructed, installed, and commissioned at an industrial coal preparation plant site (Gupta et al., 2016). The results obtained from this continuous demonstration unit further demonstrated the unique capabilities of the HHS process to produce low-ash and low-moisture (practically dry) products in a single operation (Yoon et al., 2016).

Overall, the demonstration of the HHS process for recovering and dewatering ultrafine coal at a pilot-scale was successful, but spherical agglomerates, which are necessary for conducting the HHS process, were difficult to form at the early testing stage. This might be due to both the designing deficiencies in energy consumption for agglomeration and the change of feed coal quality by time variation. Therefore, in the present work, solutions to this issue were found and discussed. In the HHS process, coal agglomerates are dispersed by a Morganizer, which is very crucial to the process since the dispersion dewaters the hydrophobic coal particles by releasing water droplets trapped in the agglomerates along with the ash dispersed in the droplets. Currently, a vibrating mixer type Morganizer as described by Gupta (2014), which typically is a screensmounted shaft that is connected to a reciprocating motor, is employed in the HHS process. In principle, the production capacity of this Morganizer should depend on the surface area of the screens. Therefore, the number or size of screens employed in the Morganizer of a commercial HHS process plant may be considerable, making the future commercializing development of the HHS process very challenging. As such, in this work, several new Morganizers with the potential to be easily scaled up were developed and demonstrated in lab-scale HHS tests. At last, the application of the HHS process was expanded to the recovery of an Illinois high sulfur fine coal, and the benefit of the HHS process on increasing the throughput of the coal preparation plant was discussed and analyzed in a case study.

2.2 Experimental

2.2.1 Materials

A sample of 6-inch deslime cyclone overflow (100% minus 44 μ m) was procured from the LM coal preparation plant (VA, USA), where the pilot-scale HHS plant was constructed and tested. As such, this sample was employed for studies on improving the agglomeration efficiency and developing new Morganizers. During the study, a fresh sample was taken biweekly from the plant to avoid the effect of oxidation, so that the feed ash and solids content varied in the range of 54-60% and 4-6%, respectively. However, the feed sample exploited in a specific set of HHS tests was kept the same. Another deslime cyclone overflow sample, which assayed 79.7% ash and 1.91% sulfur on a dry basis, was obtained from a coal preparation plant operating in southern Illinois Basin. The feed slurry consisted of 100% of particles of < 44 μ m at a 3.7% solids content.

Sorbitan monooleate (SMO) was purchased from Sigma Aldrich and used for improving the agglomeration efficiency. HPLC grade n-heptane (99.3% purity) obtained from Fisher Scientific was used for studying the agglomeration kinetics. HPLC grade n-pentane (99% purity) purchased from Fisher Scientific was used in all HHS tests. Tap water was utilized for all the experiments.

2.2.2 Oil Agglomeration Test

Agglomeration tests were carried out in a cylindrical stainless vessel (5.5 inches in diameter) with four baffles of 0.25 inches in width. The agitation for coal agglomeration was

provided using an overhead mixer with the capability of displaying the values of RPM (revolutions per minute) and torque (N.cm) while operating, which was equipped with a pitched blade impeller (3 blades, 2 inches in diameter). In each test, 650 ml representative LM deslime cyclone overflow slurry sample with solids content at 5% was agglomerated with the addition of 6 ml heptane. A series of agglomeration tests was performed to study the effect of the energy input to the recovery by varying both the conditioning time and agitation speed. The energy input of agglomeration was calculated using the following formula:

Energy Consumption (kW·hr/m³) =
$$\frac{RPM X Torque (N.cm, corrected)}{954880 \times 650 \text{ ml}} X Time (hr)$$

After agglomeration, the suspension was transferred to an 800 ml beaker and allowed to stand for 2 minutes prior to skimming out all the floated agglomerates using a screen sheet with an aperture of 1.5 mm. The products obtained were assayed for ash.

Another set of agglomeration tests was also conducted on coal samples that had been pretreated with a hydrophobicity-enhancing agent – SMO. The SMO dosage was kept at 3 lbs/t by weight of dry feed in all tests. The SMO was used in the form of emulsions, which was prepared in a blender by high-shearing a mixture consisting of 2 ml SMO, 20 ml heptane, and 100 ml water. The energy consumption in this set of tests was the sum of the energy spent on SMO conditioning and agglomeration.

2.2.3 HHS Test

In a given laboratory test, a volume of coal slurry was agitated in a kitchen blender (Oster®) equipped with a 6-Cup glass jar at high rotational speed for 40 to 60 seconds in the presence of a sufficient amount of pentane. The coal agglomerates formed under this condition were mostly small. By agitating the slurry further at a lower speed for 2 to 5 minutes, the agglomerates became large enough to be separated from the tailing by sieving using a screen with an aperture of 106 μ m.

The coal agglomerates were then transferred to the oil phase in a Morganizer, which was initially filled with water and a sufficient volume of pentane. A mechanical force was applied to break the agglomerates and subsequently disperse the hydrophobic coal particles in pentane. The mechanical forces were created by means of vibrating screen mesh, dynamic mixer, and a pulsating jig. As hydrophobic agglomerates were broken, entrapped water droplets were liberated from coal and settled to the bottom of the device along with the hydrophilic mineral matter dispersed in the water droplets. The coal-in-pentane dispersion was allowed to overflow into a beaker, while the water and mineral matter settled to the bottom. The coal-in-pentane dispersion recovered in the beaker was subjected to solid-liquid separation, and the coal was subsequently analyzed for moisture and ash contents. The samples collected from the HHS tests on the Illinois coal were also subjected to sulfur content analysis, which was performed by the Precision Testing Laboratory (Beckley, WV).

2.3 Results and Discussion

2.3.1 Solutions to Agglomeration Problems Previously Occurred in the Pilot-scale Practice

2.3.1.1 Increase the Oil Contact Angle of Coal Using SMO

Fig. 2.1 shows the effect of using SMO on the organic recovery of oil agglomeration as measured by the energy consumption criterion. If the coal slurry was pre-conditioned with 3 lbs/t SMO prior to the agglomeration, the energy consumption would be substantially shortened. For example, in order to achieve a 90% organic recovery, the energy required for an untreated feed was in the range of 0.1 to 0.2 kW·hr/m³; while for the case with SMO pretreatment, that was in the range of 0.01 to 0.02 kW·hr/m³. These results show that SMO is an efficient reagent for promoting the coal oil agglomeration process at high recoveries under low energy input levels, and therefore, it is a potential solution to the agglomeration problem occurred in the pilot-scale HHS plant of the



Fig. 2.1 Comparison of the HHS test results obtained without SMO and with 3 lbs/t SMO: effect of energy consumption on the organic recovery.

original engineering design. The advantage of using SMO to address the agglomeration issue is that the engineering modification of the current processing plant can be minimized.

Fig. 2.2 compares oil contact angles (θ_o) obtained on a polished coal plate that had been treated with and without SMO. The coal plate was cut from a chunky clean coal sample procured from the dense medium cyclone overflow at the LM plant. The results of θ_o presented in Fig. 2.2 clearly show that SMO is an efficient agent for increasing the θ_o . As can be seen, the θ_o was increased from 71° (Fig. 2.2A) to 112° (Fig. 2.2B) after the coal plate was preconditioned in the presence of 10⁻⁴ M SMO, and the θ_o measured on the same SMO-treated coal plate was further increased to 163.8° (Fig. 2.2C) when the heptane drop was contaminated with 10⁻⁴ M SMO. The θ_o is given by Young's equation:

$$\cos\theta_o = \frac{\gamma_{so} - \gamma_{sw}}{\gamma_{ow}}$$

in which γ_{so} is the interfacial tension at the solid/oil interface, γ_{sw} is the interfacial tension at the solid/water interface, and γ_{ow} is the interfacial tension at the water/oil interface. According to the Young's equation, the θ_o value is determined synergistically by values of γ_{so} - γ_{sw} , and γ_{ow} . And the $\theta_o > 90^\circ$ can only be achieved by making $\gamma_{so} - \gamma_{sw}$ negative, at which $\cos \theta_o < 0$. The transition of θ_o from < 90° to > 90°, as shown in Fig. 2.2B, it was partly due to the increase in hydrophobicity of coal resulting from the adsorption of SMO, the work conducted by Song et al. (2018) supported this inference. Moreover, when the θ_o is increased to > 90°, the value of $\cos\theta_o$ becomes more negative with decreasing the value of γ_{ow} , and therefore the larger value of θ_o . It appears that the increase in θ_o in the latter case (the heptane oil drop was contaminated with SMO, Fig. 2.2C), was mainly ascribed to the decrease in γ_{ow} . It was observed in the agglomeration tests that coal agglomerates formed in the presence of SMO were compact and of spherical uniform sizes, while those obtained without SMO were foamy and of small sizes. This evidence in conjunction with the contact angle measurement results suggest that the improvement of agglomeration on the aspect of energy consumption might be the result of the increase in θ_o of coal particles. In general, the larger the θ_o , the smaller energy barrier that needs to be overcome to bring the oil-coated coal particles together.



Fig. 2.2 Comparison of the contact angle of a heptane droplet measured on a polished coal plate after different SMO-treatment schematic: A: coal conditioned with Heptane, B: coal conditioned with SMO as o/w emulsion, C: coal conditioned with SMO, contact angles measured with heptane in which SMO is dissolved. The SMO concentration was 10⁻⁴ M.

During the agglomeration process, part of the agitation energy is used to break the added bulk oil into small droplets so that the oil-particle collision becomes more efficient. SMO is a wellknown water/oil emulsifier, small heptane droplets can be easily formed in the presence of SMO because of the decrease in γ_{ow} . This effect could partially explain why the energy consumption required for achieving high recoveries was decreased after using SMO.

It is noteworthy that the advantage of using SMO to aid agglomeration is also manifested in reducing the capital cost of the agglomeration process. As compared to the results obtained without SMO, high recoveries can be achieved at a shorter agglomeration time, as well as a lower agitation speed in the presence of SMO. This will lead to a size reduction of the agglomeration tank and agitator, resulting in the potential reduction in both the equipment investments and maintenance costs.

Based on the laboratory results, a test using SMO was conducted at the HHS pilot plant. The results showed that good agglomerates were easily formed and a high-ash tail sample was produced. However, without optimizing the reagent dosage, it was found that coal agglomerates formed in the presence of SMO were too sticky and therefore caused issues for transportation of agglomerates in the circuit. In addition, the consumed SMO reagent was not recyclable. As such, another solution to the agglomeration issue, which occurred in the pilot plant, was explored and the HHS results were presented in the following section.

2.3.1.2 Increase Agglomeration Energy Dissipation Rate

The results of three agglomeration tests conducted without using SMO were extracted out from Fig. 2.1 and presented in Tab. 2.1. As shown, the highest total energy input for agglomeration did not guarantee the highest recovery. This was consistent with the results obtained in the pilot

-	Agglomeration	Total	Organic	
Test No	Dissipation Rate	Time	Energy	Recovery
	kw∙m⁻³	S	kw•h/m ³	%
1	1.9	300	0.16	88.7
2	2.7	180	0.14	92.3
3	8.0	60	0.13	90.4

Tab. 2.1 Coal agglomeration test results obtained on the LM deslime cyclone overflow sample without SMO.

Feed ash = 58%

plant, where it was found that coal recovery was not improved to a desirable extent by increasing agglomeration resident time despite the substantial increase in the total energy input.

It has also been noted in Tab. 2.1 that when agglomeration tests were carried out at highshear rate, coal recoveries were relatively higher despite the total energy consumptions which were lower. In this regard, another solution of the agglomeration problem previously existed in the HHS pilot plant is to use a high-shear mixer to replace the initially designed mixer, which has no capability of increasing its agitation speed over 1500 RPM. This thought was verified by



Fig. 2.3 L5M-A lab-scale Silverson mixer used in coal agglomeration tests.

Test	High-shearing		Low-shearing	%Organic
No.	RPM	Time/s	RPM	Recovery
1	6000	10	400	91.9
2	6000	20	400	95.4
3	7000	10	400	95.2
4	7000	20	400	96.9
5	9000	10	400	97.8
6	9000	20	400	97.8

Tab. 2.2 Results of agglomeration tests conducted on the LM deslime cyclone overflow sample using a Silverson mixer for high-shearing.

Feed ash = 58%

conducting a series of lab-scale agglomeration tests using a L5M-A laboratory Silverson mixer (Fig. 2.3) in the absence of SMO. The mixer workhead was installed with a square hole high-shear screen with a diameter of 3 inches.

In this set of agglomeration tests, the mixture of coal slurry and heptane was subjected to a two-stages of agitation, which included 10-20 seconds high-shearing in a Silverson mixer and 30 seconds low-shearing in an overhead mixer. The results are presented in Tab. 2.2. As shown, as the agglomeration shear rate varied in the range of 6000-9000 RPM, the oil agglomeration tests all produced > 90% organic recoveries within less than 1 minute. The improvement in both recoveries and agglomeration kinetics could be attributed to the reduction of the oil droplet sizes at a high-shearing rate (Bensley et al.,1977). Based on these promising lab-scale results, a commercial Silverson mixer was installed in the HHS pilot plant and successfully solved the agglomeration issue.

2.3.2 HHS Tests Conducted Using New Morganizers

2.3.2.1 Rushton Mixer-Screen Basket Morganizer

Fig. 2.4 shows the schematic representation of a Rushton mixer-screen basket (RM-SB) Morganizer, which is two Rushton impellers installed in a cylindrical tank with the impellers



Fig. 2.4 Schematic representation of the Rushton Mixer-Screen Basket type Morganizer.

RPM -	HHS Product		Reject	%Organic
	Moisture%	Ash%	Ash%	Recovery
360	7.0	3.9	89.0	94.0
450	1.9	4.0	88.9	93.8
540	3.3	3.8	89.2	94.4
650	4.5	3.8	90.2	96.1
720	6.6	3.9	89.6	95.1

Tab. 2.3 Results of the HHS tests conducted on LM deslime cyclone overflow using a Rushton Mixer-Screen Basket type Morganizer.

Feed ash = 55.9%

surrounded by a screen basket. During the de-agglomeration, the turbulence created by the impellers breaks coal agglomerates, leaving the hydrophobic coal particles dispersing in the pentane, while at the same time releasing the small droplets of water that have been trapped in between the hydrophobic particles constituting the agglomerates. The small water droplets coalesce to form larger droplets on the screen basket surface and eventually fall to the aqueous phase at the bottom by gravity.

Tab. 2.3 shows the results of the HHS tests carried out using the RM-SB type Morganizer to disperse the coal agglomerates obtained on a LM deslime cyclone overflow sample. The diameter of the Rushton impeller and the cylindrical tank were 2 inches and 3 inches, respectively. As shown, from a feed containing 55.9% ash, the HHS tests produced clean coal products with low-ash, low-moisture, and high-organic recovery. These results are comparable with those obtained using a vibrating mixer type Morganizer, which were not shown here, demonstrating the efficacy of the RM-SB type Morganizer.

As can be seen in Tab. 2.3, the clean coal products obtained at 360 and 720 RPM were of relatively higher moisture contents than those obtained at 450-650 RPM, indicating that the clean coal product moisture was dependent on the impeller rotation speed. It is most likely that at 360 RPM the energy input was not that sufficient so that some of the w/o emulsions were not sufficiently destabilized, causing the relatively high product moisture. At 720 RPM, some water droplets were pumped up to the oil phase from the water phase, evidenced by visual observation.



Fig. 2.5 Schematic representation of the Jig Morganizer.

Thus, the comparably higher moisture may be attributed to the fact that some of those water droplets were overflowed along with the dispersed coal particles under sufficient rising force.

2.3.2.2 Jig Morganizer

In a vibrating mixer type Morganizer, the agglomerates are broken up by the mechanical forces provided from the up-down motion of the screen. This is very similar to the pulsating motion performed in a Jig separator (Schuchard, 1912), which has been commercially employed in coal preparation. Thus, a new Morganizer was developed based on the Jigging mechanism with the schematic representation exhibited in Fig. 2.5. As shown, hydrophilic quartz particles (ragging) are packed atop a screen mesh disposed in the interior of a cylindrical vessel, which is initially filled with liquid pentane and water. The aperture of the screen mesh is smaller than the size of the particles such that the quartz particles are unable to pass through the screen mesh and remain dispersed in the hydrophobic oil phase while de-entrained water and mineral matter coalesce on the surface of the quartz particles forming droplets. When droplet size becomes sufficiently large, the coalesced water and mineral matter fall off the surface of the quartz particles and pass through



Fig. 2.6 Lab-scale Jig Morganizer.

the screen mesh and oil-water interface, where they are separated as underflow from the water phase. In operation, a modified diaphragm pump provides the pulsion and suction (Jigging) cycles that force the agglomerates through the tortuous path between the packed quartz particles, liberating the entrained water and mineral matter, while the de-agglomerated hydrophobic coal particles in suspension are recycled in the overflow. Fig. 2.6 shows the Jig Morganizer constructed for the lab-scale HHS tests using a glass column with a diameter of 1.5 inches.

Tab. 2.4 shows the HHS test results obtained using a Jig Morganizer. In each test, 25 g irregular quartz particles of a size fraction between 3.35 mm and 6.3 mm were placed on the screen mesh with an aperture of 1 mm. The characteristics of pulsation motion, which impacts the de-agglomeration, was controlled by adjusting the frequency and loaded stroke of the diaphragm pump. The operating frequency and loaded stroke were ranged from 3 to 6 Hz and 60 to 100%, respectively.

Stroke	Frequency	HHS Produ	Reject	%Organic	
%	Hz	Moisture% Ash%		Ash %	Recovery
	3	1.8	3.0	91.1	97.3
60	4	1.5	3.2	90.9	96.9
00	5	1.8	3.7	91.2	97.4
	6	1.8	3.5	90.8	96.7
80	3	1.8	3.2	91.1	97.3
	4	1.5	3.6	91.2	97.5
	5	1.3	3.8	90.9	96.9
	6	1.5	4.0	90.8	96.7
	3	1.3	3.3	91.0	97.0
100	4	1.3	3.5	91.2	97.5
100	5	1.5	3.8	90.8	96.7
	6	2.4	3.9	91.4	97.8

Tab. 2.4 Results of the HHS tests conducted on LM deslime cyclone overflow using a Jig Morganizer.

Feed ash = 58.3%

As shown in Tab. 2.4, the ash and moisture contents of clean coal products obtained at different operating conditions were less than 4.0% and 2.4%, respectively. While the organic recoveries were all greater than 96%. These excellent results indicate that Jigging is a very efficient means for de-agglomeration in the HHS process.

2.3.2.3 Wemco Morganizer

Fig. 2.7 shows the schematic representation of the Wemco Morganizer, which is a baffledcylindrical vessel centrally equipped with two impellers. The impeller has the same shape as that of the Wemco®-type flotation cell marketed by FLSmidth and is coupled to a rotating shaft that rotates the impeller to create turbulence in the middle of the vessel rather than near the vessel wall. Fig. 2.8 shows the lab-scale Wemco Morganizer in which coal agglomerates were fed to a cylindrical vessel with a diameter of 3 inches. The vessel was equipped with four identical baffle plates (W x L: 0.25 x 2.5-inch) located 1 inch above the floor of the vessel. The vessel was filled



Fig. 2.7 Schematic representation of the Wemco Morganizer.



Fig. 2.8 Lab-scale Wemco Morganizer.

with water and pentane and allowed to form a distinct oil/water interface at 0.5 inches from the vessel floor. The Wemco-type impellers with a diameter of 2 inches were driven by an overhead mixer. Two sets of dispersion tests with varying the agitation speed were conducted at d = 55 mm and 35 mm, where d is the distance from the bottom of the impeller to the o/w interface.

Tab. 2.5 shows the results obtained using a Wemco Morganizer when the d is equal to 55 mm. As can be seen, the clean coal products obtained at different RPM were all of the low moisture and ash contents, which were varied in the range of 1.4-2.9% and 2.7-3.1%, respectively.

RPM -	HHS Product		Reject	%Organic
	Moisture%	Ash%	Ash%	Recovery
450	1.9	2.8	90.2	96.3
550	1.4	2.7	90.4	96.6
650	1.9	3.0	90.4	96.7
750	2.9	3.1	90.1	96.2
850	2.8	3.1	90.2	96.4

Tab. 2.5 Results of the HHS tests conducted on LM deslime cyclone overflow using a Wemco Morganizer: d = 55 mm.

Feed ash = 54.2%

	HHS Product		Reject	%Organic
	Moisture%	Ash%	Ash%	Recovery
450	13.3	3.5	90.4	96.7
550	18.4	4.0	90.5	96.8
650	19.2	4.2	90.4	96.7

Tab. 2.6 Results of the HHS tests conducted on LM deslime cyclone overflow using a Wemco Morganizer: d = 35 mm.

Feed ash = 55.9%

Additionally, the organic matter recoveries were consistently > 96% for all tests. These results suggest that agitation at 450-850 rpm was sufficient to destabilize the hydrophobic coal agglomerates and to disperse the de-agglomerated particles in suspension.

Tab. 2.6 presents another set of results obtained from the HHS tests conducted using a Wemco Morganizer at d = 35 mm. As shown, the clean coal product ash and moisture were increased with increasing the impeller agitation speed, with the ash and moisture contents varied in the range of 13.3-19.2% and 3.5-4.2%, respectively. It is noted that the ash and moisture contents of clean coal products obtained at d = 35 mm were much higher than those obtained at d = 55 mm. Also, the moisture contents achieved in this set of tests even exceeded the general quality requirement (10%). One reasonable explanation for the deteriorated performance at d = 35 mm is that the distance between the bottom of the impeller and the o/w interface was too small so that some ash contaminated water droplets were elevated up from the water phase by the Wemco impeller because it creates upward flows, and eventually overflowed with the dispersed coal particles. These results suggest that it may be necessary to conduct the computational fluid dynamics (CFD) simulation when designing a commercial Wemco Morganizer.

2.3.3 Application of the HHS Process for Recovering a Fine Illinois Basin Coal

Reports by Rubiera et al. (1997), Chafin et al. (2012), and Bratton et al. (2014, 2015) indicate that the classifying cyclone circuits currently used in modern coal processing plants

typically deplete the overflow stream of high-density particles containing pyrite. As such, the overflow streams are typically very low in pyritic sulfur. Therefore, if the subsequent removal of moisture and ash-bearing minerals (such as clay) from these well-liberated feeds will be viable, the produced clean coal products would have much lower lb SO₂/MM Btu levels than can be obtained from other processing circuits within the preparation plant.

Tab. 2.7 shows the results of four laboratory HHS tests conducted on a sample of deslime cyclone overflow obtained from a preparation plant operating in the Illinois Basin. The feed sample assayed 79.7% ash and 1.91% sulfur on a dry basis. The HHS tests were carried out using SMO as a hydrophobicity-enhancing agent as the as-received feed sample did not respond to agglomeration. As shown, the HHS process generated clean coal products containing 1.4-1.6% sulfur and 2.9-4% ash (dry) with organic recoveries ranging from 81-84%. These results were far superior to the overall clean coal product from this plant, which averages 2.8% sulfur and 8.7% ash (dry). The moisture content of the HHS product was 6.9-8.1%, which was within the range of the average moisture of 8% typically shipped from this coal plant. Noted here that the average sulfur content of the clean coal products was 0.7% lower than that of the feed, showing that the HHS process also has the capability of desulfurizing. This most likely resulted from the settling of the hydrophobic pyrite particles in the vibrating mixer type Morganizer because it was not designed to recover fine particles of densities higher than that of coal.

Tab. 2.7 Lab-scale HHS test results obtained on an Illinois basin coal sample

SMO	HHS Product			Reject (%)		Organic	Clean Coal	
1h /+	Sulfur	Moisture	Ash	Btu/lb	Sulfur	Ash	Recovery	lb SO ₂ /MM BTU
ID/L	(%, dry)	(%, a.r.)	(%, dry)	(a.r.)	(dry)	(dry)	(%wt.)	
2.79	1.54	6.9	3.8	12,714	2.02	89.1	81.4	2.26
2.91	1.55	7.2	4.0	12,651	1.92	89.4	83.7	2.27
3.58	1.49	6.8	3.4	12,864	1.96	89.2	82.1	2.16
4.87	1.45	8.1	2.9	12,761	1.97	89.1	81.4	2.09

Feed sample: 3.7% solids, 79.7% ash (dry), 1.91% sulfur (dry)

Average clean coal from existing preparation plant: 8% moisture (AR), 8.7% ash (dry), 2.78% sulfur (dry)

Tab. 2.7 shows that the SO₂ emission specifications of HHS clean coals were in the range of 2.0-2.3%, which is only about half of the plant's clean coal product. Therefore, it was thought that by adding high-quality HHS product to the plant's clean coal product, high-sulfur middlings that may previously have been discarded in the coarse circuits can be recovered without exceeding the SO₂ emission specification at the plant, which was estimated to be 4.3 lb SO₂/MM Btu.

Fig. 2.9 shows simulation results of the additional dry tons of middlings that could be added to the plant product for each dry ton of HHS "sweetener" product generated. The calculations assumed that the HHS product would contain 1.49% sulfur and 3.4% ash (dry). The moisture of the total plant product, HHS product and added middlings were all assumed to be at the contract specification of 8% moisture (as received). As shown, the middlings tonnage gain is a function of



Fig. 2.9 Gain in middlings tons for each ton of HHS product (Assumes HHS product with 3.4% ash (dry), 1.49% sulfur (dry), middling and HHS product with 8% moisture (AR). Shipped product from preparation plant limited to 4.3 lb SO₂/MM Btu).

the middlings ash content (which established the coal heating value) and the middlings sulfur content (which established the SO₂ emulsion level). According to this plot, a plant constrained to 4.3 lb SO₂/MM Btu can add about 1 additional ton of 24% ash middlings containing 3.5% sulfur (dry) for each ton of low-sulfur HHS product generated. The amount added increases to 1.8 tons for 3% sulfur middlings and decreases to 0.43 tons for 5% sulfur middlings. These calculations show coal preparation plants processing the Illinois high sulfur coals can use this low sulfur "sweetener" produced by the HHS process to either (i) reduce the total sulfur content in their product or (ii) increase the recovery of saleable coal from coarse circuits that are otherwise forced to discard high-sulfur middlings because of a sulfur emission constraint.

2.4 Conclusion

The HHS pilot plant has faced the challenge of not forming spherical coal agglomerates in the early testing stage. To address this issue, in the present work, two feasible solutions, including using SMO and increasing agglomeration energy input with high energy dissipation rate, were proposed and successfully demonstrated in a series of lab-scale agglomeration tests. Finally, the problem that occurred in the pilot plant was solved by installing a Silverson high-shear mixer.

A Morganizer plays a vital role in the HHS process, which is to liberate the hydrophobic particles from the water droplets so that coal particles are recovered and dewatered simultaneously. Given the limitation of the initially designed vibrating mixer type Morganizer to commercialize the HHS process, three new Morganizers (Rushton mixer-screen basket type, Jig type, and Wemco Morganizers) were developed based on mechanical means that can be or have been commercialized. Lab-scale HHS tests performed with the employment of these new Morganizers all showed excellent results that were comparable to those obtained on a vibrating mixer type Morganizer. Further investigations on these new Morganizers in pilot-scale testing is needed to accurately assess their efficacies and capabilities for commercial utilization.

The HHS process also has been tested on an Illinois deslime cyclone overflow coal sample containing a large amount of pyritic sulfur. The lab-scale tests show that the HHS is capable of producing low-ash, low-moisture, and low-sulfur clean coal products, which are ideal for back-blending with other readily available sources of coal, such as plant middlings, that would otherwise be lost due to their low quality. Estimates for one case study indicate that 1 to 1.8 tons of additional middlings may be recoverable from coarse coal cleaning operations that are constrained by ash and sulfur limits. This added benefit is particularly important for coal processing operations in the Midwestern coalfields, which are often forced to discard high-sulfur middlings from coarse coal circuits to meet contract limitations involving SO_2 emissions.

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Chapter 3 Concentration of REEs Associated with Coal Byproduct by the HHS Process without Using Morganizer

Abstract

Rare earth elements (REEs) are critical for the development of renewable energy resources, national security, and advanced manufacturing. However, the domestic supply of REEs in the U.S. was terminated after the closure of Molycorp Inc. in 2016, and the U.S. now relies entirely on foreign imports, mainly from China. The concern about the potential supply risk of REEs in the U.S. has sparked great interest in recovering REEs from unconventional resources. Most recently, coal has been identified as an abundant and promising source for extracting and recovering REEs. Previous characterization studies showed REE-enriched monazite grains of size $< 5 \mu m$ occurred in coals, which are too small in size to be effectively recovered by froth flotation. It is, therefore, the objective of this work to explore the feasibility of using the HHS process to recover rare earth minerals (REMs) associated with coal byproduct. The coal sample employed in this study was a thickener underflow obtained from the LW coal preparation plant at Kentucky, USA. A series of HHS tests was conducted to study the effects of the collector, decarbonization, liberation, depressant, sorbitan monooleate, and sample aging. Comparison of the results of the HHS and forced air flotation processes shows that the HHS process is far superior to air flotation even though a Morganizer step was not used in these HHS tests. The best HHS product assayed 17,590 ppm total REEs (TREEs) on an ash basis, which represented a 50 times REE enrichment from a feed assaying ~ 350 ppm TREEs.

3.1 Introduction

REEs are a group of 17 elements comprising of 15 lanthanides plus yttrium and scandium, which are critical elements for developing renewable energy resources, securing national security,

and promoting advanced manufacturing. According to the United States Geological Survey (USGS), in 2017, the U.S. consumed 11,000 tons of REEs measured as rare earth oxides (REOs) (Mineral Commodity Summary, 2018), 100% of which were imported due to the demise of Molycorp Inc. in 2016. Since the early 1990s, China has gradually dominated the global supply of REEs and now controls about 85% of world production of rare earth raw material and oxides (Dai and Finkelman, 2018). Given the strategic importance of REEs to defense interests and the modern economy of the U.S. and potential trade fluctuations due to the tight export quota policies by China (Long et al., 2012), it has become an urgent matter to develop a reliable domestic REEs supply chain in the U.S. A recent study initiated by the National Energy Technology Laboratory (NETL) showed that U.S. coals contain significant amounts of REEs, suggesting the possibility that they can be extracted from coal preparation refuse as byproducts (Ekmann, 2012).

According to Seredin (1996) and Lin et al. (2017), REEs in coal either occur as authigenic mineral grains or exist as adsorbed forms in organic matter and clay particles. Mineral grains of monazite and xenotime are often found in coal, particularly in the Fire Clay coal seam in the eastern Kentucky in the U.S. (Hower et al., 1999; Zhang et al., 2017). In principle, there is no essential difference between the REMs in coal and the conventional REMs. The latter has been commercially recovered by physical separation techniques. As such, Honaker et al. (2016) investigated the feasibility of using physical concentration technologies, including density-based separations, froth flotation, and magnetic separation, to recover REMs from three coal samples. The main finding of this work is that flotation was the most promising method for REEs recovery and enrichment. In light of this, Zhang et al. (2017) conducted another investigation to compare the performance of conventional flotation and column flotation on the recovery of REEs from a coal byproduct. The results showed that column flotation was more effective than conventional

flotation. However, the highest grade achieved in this investigation was only 4,700 ppm TREEs on an ash basis, which was still far away from their targeted concentration (20,000 ppm), owing to the fact that froth flotation was ineffective in handling ultrafine monazite particles, which are on average, less than 5 μ m particle sizes (Honaker et al.,2014), presented in the coal sample.

To overcome the deficiency of air flotation, the concept of two-liquid flotation (TLF) was developed during the 1960-70s. In this process, oil droplets rather than air bubbles were used to collect hydrophobic particles from the aqueous phase. Many investigators found that oil drops were more efficient than air bubbles for the recovery of ultrafine particles. Sennett and Olivier (1969) patented a process in which anatase (TiO₂) and iron oxides (Fe₂O₃) were removed from kaolin clay (5 μ m top-size) using emulsified oil droplets. Lai and Fuerstenau (1968) recovered 0.1 μ m alumina (Al₂O₃) particles using an emulsified oil (isooctane), while Shergold et al. (1981a, b) used various organic liquids, such as cyclohexane, toluene, and benzene, to recover 0.18 μ m rutile (TiO₂). More relatively, Kusaka et al. (1992) investigated the applicability of TLF for recovering ultrafine monazite particles of a specific surface area of 3.8 m²/g in the presence of various amounts of collectors. They found that there was a characteristic correlation between the work of adhesion and monazite recovery, and over 95% recovery was obtained using dodecylbenzene sulfonate as the collector at a suitable dosage.

The TLF tests results discussed here indicate that oil and other organic liquids are better immiscible fluid than air to collect hydrophobic particles in water, particularly for the ultrafine particles. It appears that there is no lower particle size limit for the TLF separation, which is not surprising in that the process is similar to solvent extraction.

Based on the concept of TLF, a similar process known as Hydrophobic-Hydrophilic Separation (HHS) was developed at Virginia Tech, and has been successfully demonstrated on the selective recovery of ultrafine coal and chalcopyrite particles (Yoon et al., 2016; Gupta et al., 2016). Given the advancement of the HHS process in processing ultrafine particles, it will be of interest to expand its application for recovering the ultrafine REMs associated with coal and coal byproducts. As such, the objective of the present work was to examine the technical feasibility of the HHS process for the concentration of REEs from a thickener underflow sample collected from the LW coal preparation plant at Kentucky, USA. The effects of collector dosage, decarbonization, particle size, depressant dosage, hydrophobicity-enhancing reagent dosage, and sample aging on the HHS recovery of REEs were investigated. The results obtained using the HHS process were compared with those obtained using conventional flotation and column flotation.

3.2 Experimental

3.2.1 Materials

The representative thickener underflow coal sample used in this study was collected from the LW coal preparation plant (Kentucky, USA), which processes coal from the Fire Clay coal seam. The original sample assayed ~ 56% ash; therefore, all the samples were first decarbonized by column flotation prior to conducting grinding and separation tests. The carbon removal work was performed at the University of Kentucky, and the detailed procedure was described by Honaker et al. (2014). After decarbonization, the column flotation tailing sample of particle size 50% finer than (d_{50}) 35 µm and ash content of 91% contained a TREEs content about 350 ppm on a dry, ash basis.

Octanohydroxamic acid (OHA) of > 95% purity (TCI American) and reagent grade sodium metasilicate nonahydrate (Sigma Aldrich) were utilized as collector and depressant for recovering REMs, respectively. Sorbitan monooleate, namely the hydrophobicity-enhancing reagent, was purchased from Sigma Aldrich and used as 1:2 mixture with kerosene. HPLC grade n-heptane



Fig. 3.1 Homemade attrition mill.



Fig. 3.2 Low shear mixer.

(99.3% purity) was obtained from Fisher Scientific. The pH values of the slurry samples were regulated using hydrochloric acid and potassium hydroxide solutions. Tap water was used for all the experiments.

3.2.2 Attrition Mill Grinding Tests

Grinding tests were carried out using a homemade attrition mill with a volume of 2 L, as shown in Fig. 3.1. The detailed information of the mill construction has been given by Mankosa et al. (1986). In each test, approximately 350 g of decarbonized sample was pulverized in the presence of 3.2 kg stainless steel balls of diameter ¹/₄-inch. The pulp density was held at 30%. The 80% passing size (d_{80}) of the mill products produced after grinding for 45 minutes and 180 minutes were 8 µm and 3.9 µm, respectively. Most of the HHS tests were conducted on the milled samples. *3.2.3 Hydrophobic Hydrophilic Separation Tests*

In a given HHS test, approximately 1.4 L of decarbonized slurry (10-25% solids) was conditioned with sodium metasilicate nonahydrate (SMSN) for 15 minutes at a natural pH in a

low-shear mixer (Fig. 3.2) at 250 RPM and subsequently conditioned with OHA at pH 9.5 for 5 minutes in a 0.5 Gallons Waring commercial blender (Fig. 3.3). In some tests, the OHA-treated slurry was further conditioned with sorbitan monooleate (SMO) for an additional 3 minutes in the blender. The OHA and SMO used in this initial step known as rougher served as a primary and secondary hydrophobicity-enhancing agent for REE-bearing particles, respectively, while the SMSN served as a dispersant (or depressant) for gangue minerals. The conditioned slurry, which became warm during conditioning, was cooled first and then mixed with 400 ml heptane. The mixture was subjected to a low-shear mixing for 5 minutes to allow for the collision between small droplets of oil and mineral particles in suspension. The oil droplets formed during agitation selectively collected hydrophobized REE-bearing particles and formed an oil-in-water (o/w) emulsion, while the hydrophilic gangue minerals were left in the aqueous phase. After the agitation, the mixture was transferred to a 3 L separatory funnel and allowed to stand for 10 minutes for phase separation, as shown in Fig. 3.4. The aqueous phase at the bottom was drained and subjected



Fig. 3.3 High shear blender.



Fig. 3.4 Separatory funnel.

to a scavenger, in which the tailings slurry was conditioned again with OHA and/or SMSN in the same manner as described for the rougher to recover additional REE-bearing particles.

During rougher, oil droplets collect hydrophobic REE-bearing particles and form an o/w emulsion, as noted above. During phase separation, the oil drops rise and coalesce with each other to form an oil-water-oil (o/w/o) multiple emulsion. This process is akin to flotation, in which the air bubbles loaded with hydrophobic particles form an air-water-air (a/w/a) multiple emulsion, otherwise known as froth on top of the aqueous pulp phase. In both the o/w/o and a/w/a emulsions, water constitutes the continuous phase. Therefore, both are miscible with water, which makes it possible to remove the entrained hydrophilic gangue minerals using wash water as in column flotation. In a batch HHS process, however, it is difficult to use the wash water. Therefore, a volume of fresh water together with a certain amount of SMSN was added to the o/w/o emulsion left in a separatory funnel and was agitated by handshaking. The mixture was then left to stand so that the additional water drained out by gravity along with the entrained gangue minerals. This step, known as cleaner, was repeated several times until the amount of the hydrophilic gangue minerals being drained became minimal. Thus, the HHS process described here is similar to the process of froth flotation, except that oil drops rather than air bubbles are used to collect hydrophobic particles. In some tests, the rougher and scavenger concentrates were cleaned separately. In other tests, the cleaning was performed after mixing the rougher and scavenger concentrates. The experimental details can be found in corresponding figures showing the processing flowsheets.

3.2.4 REE Content Determination

All of the products produced from the HHS tests were dried and shipped to the University of Kentucky for REE content analyses using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). The sample preparation protocol was followed elsewhere (Zhang et al., 2018). The content of TREEs, which include Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, was used to calculate the REEs' recoveries.

3.3 Results and Discussion

3.3.1 Effect of Collector Octanohydroxamic Acid

Previous mineralogical studies showed that mineral form REEs presented in the LW thickener underflow (TUF) were mainly monazite (Zhang et al., 2017). Therefore, OHA, which is recognized as the best collector for the flotation of monazite in the industry, was used as the primary hydrophobizing agent in the present work.

A set of HHS tests was conducted on the LWTUF sample micronized to an 80% passing size (d_{80}) of 8 µm using OHA as the collector in the range of 1 to 1.5 kg/t. In this set of tests, the scavenger concentrates and the rougher concentrates were combined and then subjected to a series



Fig. 3.5 Flowsheet of the HHS tests conducted on the micronized ($d_{80} = 8 \mu m$) LWTUF using various amounts of OHA.

of cleaner tests using washing water containing 0.1 kg/t SMSN at each stage. The detailed procedures and reagent dosages used in these tests are given in Fig. 3.5.



Fig. 3.6 Effect of OHA on the recovery of REEs from a micronized ($d_{80} = 8 \mu m$) LWTUF sample.

Fig.3.6a shows the results of HHS tests conducted at varying amounts of OHA. As the collector dosage was increased from 1 kg/t to 1.5 kg/t, the REEs recovery increased from 16.7% to 33.4%, while the ash-based REEs grade was decreased. The highest REEs grade (8,586.1 ppm) was obtained at 1 kg/t OHA. Studies showed that REMs and REEs are closely associated with the clay minerals that are finely disseminated in the coal organic matrix (Zhang et al., 2018; Zhang, 2017); therefore, the declining of REE content in concentrate at a higher collector dosage was most likely due to the dilution effect caused by the increased recovery of low REE content clay particles. The relationship between the OHA dosage and concentrate ash content shown in Fig. 3.6b supports this explanation.

3.3.2 Effect of Removing Coal Prior to REMs Recovery

In order to improve the liberation of REMs, the as-received decarbonized LWTUF sample has been subjected to grinding prior to the HHS test. This should have also liberated a certain



Fig. 3.7 Comparison of the HHS tests conducted on a micronized ($d_{80} = 8 \mu m$) LWTUF sample with and without decarbonization.

amount of hydrophobic carbonaceous materials, and the recovery of these particles will dilute the concentrates grades. In this regard, the effect of removing additional coal from a ground sample on the HHS recovery of REMs was studied. Fig. 3.7 compares the HHS results obtained with and without a decarbonization step. The decarbonization was achieved by flotation. Fig. 3.8 shows the detailed procedures and reagent dosages used in these two tests.

As shown in Fig. 3.7, the employment of a decarbonization step prior to the HHS test has led to an increase in REEs concentration of the HHS concentrate product both on coal basis and ash basis, as well as in REEs recovery. The coal-based grade was increased from 3,158.3 ppm to



Fig. 3.8 Flowsheet of the HHS tests conducted on the micronized ($d_{80} = 8 \ \mu m$) LWTUF: (a) with decarbonization; and (b) without decarbonization.

4,615.6 ppm, the ash-based grade was increased from 7,316.0 ppm to 8,087.6 ppm, and the REEs recovery was increased from 22.2% to 23.1%.

Note that the HHS test involving a decarbonization step (see Fig. 3.8a) produced a concentrate assayed 57.1% ash, which is 14 percentage points higher than that obtained without a decarbonization step, indicating that the improvement in REEs enrichment by a decarbonization step was due to the mitigation of carbon dilution effect.

3.3.3 Effect of Grinding

Fig. 3.9 shows the results of HHS tests conducted on the LWTUF sample of different particle sizes. The experimental procedures and conditions for these tests were kept the same, and the details are presented in Fig. 3.10.



Fig. 3.9 Effect of particle size on the recovery of REEs from a LWTUF sample.



Fig. 3.10 Flowsheet of the HHS tests conducted on the LWTUF sample with various particle size distributions.

As shown in Fig. 3.9, the grade versus recovery curve is shifted upward and to the right as the particle size decreases, which clearly shows the benefits of micronizing the LWTUF. Without liberation, the HHS process produced a concentrate assayed 3,526 ppm REEs on an ash basis with only 8.1% recovery. When the sample was ground to $d_{80} = 3.9 \,\mu$ m, the HHS produced a concentrate assayed 8,813 ppm REEs on ash basis at a 37.1% recovery. That is to say, the improved liberation of REMs increased the grade by 2.5 times and recovery by 4.6 times. This finding suggests that REMs are finely associated with clay minerals.

In order to compare the results, the collector dosage was kept constant in this set of HHS tests. However, theoretically, a higher dosage of collector is required to render the small particles as much hydrophobic as the large particles. This is because the total surface area of the former is much larger than the latter. Thus, a better separation would be expected at higher dosages of OHA for the micronized sample.

Previous mineralogical studies using SEM-EDX revealed that ultrafine REMs presented in the Fire Clay coal were associated with parent particles, which were aluminosilicates (Zhang et al., 2018; Zhang et al., 2017). If REM particles are not fully liberated, the contact angle of the composite particles will be low, resulting in poor recovery and grade. The contact angle of a composite particle may be estimated by the Cassie-Baxter equation (Cassie, 1948),

$$\cos \theta_c = f_r \cos \theta_r + f_q \cos \theta_q \tag{3.1}$$

where θ_c is the composite contact angle, θ_r and θ_g are the contact angles of REM and gangue minerals, respectively; f_r and f_g are the respective surface area fractions. If $\theta_g = 0$ and f_g is large, for example, θ_c will be low, resulting in poor separation efficiency.

According to Eq. (3.1), the composite contact angles of REMs of three different grain sizes associated with a 30 μ m x 30 μ m parent gangue particle were calculated. In the calculation, the values of θ_r and θ_g were given as be 75° and 5°, respectively. Based on the contact angle measurements conducted on chalcopyrite surface in Chapter 4, here, it was assumed that the contact angle measured with oil on the composite particle was equal to two times of that measured with an air bubble. As shown in Fig. 3.11, the oil contact angle of the composite grain gradually



Fig. 3.11 Effect of liberation on the hydrophobicity of REMs.

increases with the reduction of grinding size. That is to say, the hydrophobicity of the REM associated composite particle increases with improving liberation. For example, if a 30 μ m x 30 μ m composite particle comprising of a 5 μ m x 5 μ m REM grain is ground to 8 μ m, its oil contact angle will be increased from 14° to 65°, and hence its chance of being collected by an oil droplet can be significantly increased. Apparently, this simulation results of the oil contact angles corresponded with the HHS results presented in Fig. 3.9.

The simulation results shown in Fig. 3.11 also suggest that when the REM grain size is finer than 1 μ m, in order to selectively recover this REM constituted composite particle by oil droplets, the sample needs to be ground to at least 2 μ m. Therefore, it will be a considerable challenge for efficiently recovering the submicron-sized REMs as the cost of grinding is very high.



Fig. 3.12 Effect of SMSN on the recovery of REEs from a micronized $(d_{80} = 8 \ \mu m)$ LWTUF sample.
3.3.4 Effect of SMSN

Fig. 3.12 shows the results of HHS tests conducted on the micronized ($d_{80} = 8 \mu m$) LWTUF sample with the SMSN dosage in the rougher varied from 0 to 15 kg/t. The detailed reagent dosages and procedures are shown in Fig. 3.13. As shown, as the SMSN dosage was increased from 0 to 5 kg/t, the REE recovery was substantially increased from 22.7% to 36.8%. However, as the SMSN dosage was further increased to10 kg/t and 15 kg/t, the grade versus recovery curves were gradually shifted downward and to the left to be below the curve obtained without using SMSN. Obviously, the amount of SMSN used was excessive, as both recovery and grade deteriorated above 5 kg/t SMSN.

A systematic mineralogy study on the Fire Clay coal and coal refuse conducted previously by Zhang et al. (2018) showed that the LWTUF contains significant amounts of calcite and dolomite. These gangue minerals can consume collectors and starve REMs during the HHS process and also deteriorate the REE grade once they are reported to the concentrate. The improved separation obtained at 5 kg/t SMSN may be attributed to the preferential depression of those carbonaceous gangue minerals at this suitable dosage. Note, however, that an excessive SMSN



Fig. 3.13 Flowsheet of the HHS tests conducted on the LWTUF sample using various amounts of SMSN in the rougher.

dosage caused both the REE grade and recovery to decrease, which may be attributed to the likelihood that the reagent caused the hydrophobicity of the collector-coated REMs to decrease.

In the mineral processing industry, SMSN is considered to work as a dispersant for ultrafine particles such as clay. Essentially, it acts as a polyelectrolyte that can make mineral surfaces more negatively charged, so that they can be dispersed in an aqueous phase away from the surface of minerals to be recovered. If clay particles adsorb to a hydrophobic surface, it renders the surface less hydrophobic. Therefore, another possible reason for the improvement shown using 5 kg/t SMSN may be that in the presence of SMSN, hydrophilic gangue minerals such as clay and fine silica were detached from the REMs hydrophobized by OHA, which in turn caused an increase in surface net hydrophobicity and hence the REE recovery. This explanation is reasonable and in line with the results obtained using SMSN in the cleaner. For example, in the test using 5 kg/t SMSN (see Fig. 3.12), the TREE content in the concentrate was increased to 7,525.7 ppm from 815.2 ppm after it had been subjected to a series of cleaners in the presence of 0.1 kg/t SMSN.

3.3.5 Effect of a Hydrophobicity-enhancing Agent Sorbitan Monooleate

It has been shown previously that the use of a non-ionic surfactant in addition to a primary collector can substantially increase the hydrophobicity of a mineral and hence improve flotation recovery (Yoon, 2005). The reagents may be any non-ionic surfactants of HLB numbers less than 15. In this regard, SMO, which has an HLB value of 4.3, was used to enhance the hydrophobicity of the OHA-coated REMs in this study.

Fig. 3.14 shows the results of a series of HHS tests conducted on two micronized ($d_{80} = 8$ µm and 3.9µm) LWTUF samples, in which the results obtained without using SMO were compared with those obtained using 0.9 kg/t SMO as a hydrophobicity-enhancing agent. It was thought that the REMs or the composites thereof recovered in the rougher and scavenger

operations could be different and that the two different materials could heterocoagulate with each other during cleaning. In principle, heterocoagulation can be stronger than homocoagulation, which can create problems in breaking coagula and obtaining high-grade concentrates. Therefore, an experimental protocol different from that used in the abovementioned sections was employed



Fig. 3.14 Effect of SMO on the recovery of REEs from a micronized LWTUF sample: (a) $d_{80} = 8 \ \mu m$, (b) $d_{80} = 3.9 \ \mu m$.

in these two sets of HHS tests, which was that the rougher and scavenger concentrates were separately cleaned. Fig. 3.15 shows the details of the new experimental protocol and reagent dosages.

The results presented in Fig. 3.14 clearly show that the use of a hydrophobicity-enhancing agent significantly improves both the recoveries and grades of the REE concentrates. As shown in Fig. 3.14a, at 0 kg/t SMO, the HHS test produced a concentrate assayed 8,279.1 ppm on an ash



Fig. 3.15 Flowsheet of the HHS tests conducted on the LWTUF sample using various amounts of SMO in the rougher: (a) $d_{80} = 8 \ \mu m$, (b) $d_{80} = 3.9 \ \mu m$.

basis at a 2.1% recovery; when the HHS test was conducted using 0.9 kg/t SMO as a secondary hydrophobizing agent, the grade and recovery of the concentrate were increased to 17,590 ppm and 7.3%, respectively. Thus, the use of SMO increased the grade by 2.1 times and recovery by 3.5 times. The benefits of using SMO are also clearly shown in Fig. 3.14b on the sample of $d_{80} = 3.9\mu$ m, the final cleaner concentrate obtained at 0.9 kg/t SMO assayed 12,393.9 ppm TREEs with a recovery of 15%, which were significantly higher than those of the final concentrate obtained without SMO (4,225.5 ppm TREEs and 5.5% recovery).

Comparison of Fig. 3.14a and Fig. 3.14b reveals that micronizing the LWTUF from $d_{80} = 8 \ \mu m$ to $d_{80} = 3.9 \ \mu m$ greatly improved the recovery of REEs. This was achieved in conjunction with a judicious use of SMO as a hydrophobicity-enhancing agent. These findings suggest that both improving mineral liberation and particle hydrophobicity are critically important for the recovery of REEs from coal and coal byproducts.

The data used to draw the curves in Fig. 3.14 are given in Tab. 3.1 to Tab. 3.4. What is interesting to note in these tables is that both the final grade and recovery of the scavenger-cleaner products were higher than those of the rougher-cleaner products, which was contrary to the flotation of typical minerals, such as chalcopyrite and other minerals. For example, as shown in Tab. 3.4, the final scavenger-cleaner concentrate assayed 12,393.9 ppm TREEs on an ash basis with a recovery of 15%, while the final rougher-cleaner concentrate assayed 9,230 ppm TREEs with a recovery of 4%. In addition, it was observed during the operation of the HHS tests that the color of the rougher concentrates was always much darker than that of the scavenger concentrates. These findings suggest that REE-bearing particles recovered in the rougher step were different from those recovered in the scavenger step, and other types of REE-bearing particles rather than monazite minerals might also be recovered by the HHS process.

			Weight				REE (I	(udd			Distributio	n (%wt)	
Produc	cts	ł	%		Ash (0% wrt)	Ash Ba	asis	Coal B	asis	Individ	dual	Fee	p
	<u> </u>	ac	Stages	Feed	(1 % 0/)	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.
	Conc.	0.6	40.9	0.3	28.6	5,435.8	5,435.8	1,553.5	1,553.5	69.2	69.2	1.6	1.6
Rghr/Clm-2	Tail	0.9	59.1	0.4	77.1	620.4	1,604.0	478.2	918.1	30.8	100.0	0.7	2.3
	(Feed)	1.5	100.0	0.7	57.2	1,604.0	I	918.1	I	100.0	I	2.3	I
	(Conc.)	1.5	31.8	0.7	57.2	1,604.0	1,604.0	918.1	918.1	53.1	53.1	2.3	I
Rghr/Clnr-1	Tail	3.3	68.2	1.6	91.3	414.7	683.9	378.7	550.3	46.9	100.0	2.0	4.4
	(Feed)	4.8	100.0	2.3	80.5	683.9	I	550.3	I	100.0	I	4.4	1
	Conc.	0.6	28.7	0.3	28.2	8,279.1	8,279.1	2,330.6	2,330.6	50.8	50.8	2.1	6.5
Scvgr/Clnr-2	Tail	1.4	71.3	0.7	78.9	1,150.9	2,046.7	908.0	1,316.6	49.2	100.0	2.1	8.6
	(Feed)	2.0	100.0	0.9	64.3	2,046.7	I	1,316.6	I	100.0	I	4.2	1
	(Conc.)	2.0	16.5	0.9	64.3	2,046.7	2,046.7	1,316.6	1,316.6	42.4	42.4	4.2	1
Scvgr/Clm-1	Tail	9.8	83.5	4.7	92.5	383.0	584.5	354.3	513.5	57.6	100.0	5.7	14.3
	(Feed)	11.8	100.0	5.7	87.9	584.5	1	513.5	I	100.0	I	9.9	I
	(Conc.)	11.8	5.8	5.7	87.9	584.5	584.5	513.5	513.5	10.4	10.4	9.9	1
Scvgr	Tail	190.7	94.2	91.7	92.8	294.9	310.9	273.6	287.5	89.6	100.0	85.3	9.66
	(Feed)	202.5	100.0	97.4	92.5	310.9	1	287.5	1	100.0	1	95.3	I
	(Conc.)	4.8	2.3	2.3	80.5	683.9	683.9	550.3	550.3	4.4	4.4	4.4	I
Rghr	(Tail)	202.5	7.79	97.4	92.5	310.9	318.5	287.5	293.7	95.6	100.0	95.3	1
	Feed	207.3	100.0	99.7	92.2	318.5	-	293.7	1	100.0	-	9.66	1
	Conc.	0.5	0.3	0.3	42.8	1,050.7	1,050.7	450.2	450.2	0.4	0.4	0.4	100.0
Coal Float.	(Tail)	207.3	99.7	99.7	92.2	318.5	319.4	293.7	294.1	99.6	100.0	9.66	1
	Feed	207.8	100.0	100.0	92.1	319.4	I	294.1	I	100.0	I	100.0	1

Tab. 3.1 Results of the HHS tests conducted on LWTUF of $d_{80} = 8 \ \mu m$: SMO = 0 kg/t (See Fig. 3.14a).

			Weight		•		REE (p	(mdc			Distributio	n (%wt)	
Produc	cts	,	%	ف	Ash (%/)	Ash B	asis	Coal E	3asis	Indivi	idual	Fee	p
		00	Stages	Feed	(100 J	.bnd.	Cum.	.bnd.	Cum.	.pul	Cum.	Ind.	Cum
	Conc.	6.0	28.6	0.4	15.2	10,284.8	10,284.8	1,559.5	1,559.5	282	28.2	2.2	2.2
Rghr/Clm-2	Tail	2.1	71.4	1.0	66.0	2,409.6	3,073.3	1,591.5	1,582.3	71.8	100.0	5.6	7.7
	(Feed)	3.0	100.0	1.4	51.5	3,073.3	1	1,582.3	'	100.0	'	7.7	'
	(Conc.)	3.0	56.6	1.4	51.5	3,073.3	3,073.3	1,582.3	1,582.3	81.7	81.7	7.7	'
Rghr/Clm-1	Tail	2.3	43.4	1.1	89.9	515.3	1,608.6	463.0	1,096.2	18.3	100.0	1.7	9.5
	(Feed)	5.3	100.0	2.5	68.1	1,608.6	1	1,096.2	1	100.0	'	9.5	'
	Conc.	6.0	20.6	0.4	29.8	17,590.0	17,590.0	5,241.3	5,241.3	55.6	55.6	7.3	16.8
Scvgr-1/Cltrr-2	Tail	3.3	79.4	1.6	67.7	1,604.5	3,240.6	1,086.6	1,941.7	44.4	100.0	5.9	22.7
	(Feed)	4.1	100.0	2.0	59.9	3,240.6	'	1,941.7	'	100.0	'	13.2	'
	(Conc.)	4.1	29.2	2.0	59.9	3,240.6	3,240.6	1,941.7	1,941.7	69.2	69.2	13.2	'
Scvgr-1/Clnr-1	Tail	10.0	70.8	4.8	93.3	382.2	981.6	356.5	819.8	30.8	100.0	5.9	28.6
	(Feed)	14.1	100.0	6.8	83.5	981.6	•	819.8	'	100.0	'	19.1	'
	Conc.	1.8	25.7	0.9	76.4	5,507.5	5,507.5	4,209.6	4,209.6	73.5	73.5	12.3	40.8
Scvgr-2/Clnr-2	Tail	5.1	74.3	2.5	82.2	638.7	1,823.1	524.9	1,471.5	26.5	100.0	4.4	45.2
	(Feed)	6.9	100.0	3.3	80.7	1,823.1	1	1,471.5	'	100.0	'	16.7	'
	(Conc.)	6.9	22.0	3.3	80.7	1,823.1	1,823.1	1,471.5	1,471.5	64.2	64.2	16.7	
Scvgr-2/Clnr-1	Tail	24.4	78.0	11.8	94.5	244.8	551.4	231.4	504.5	35.8	100.0	9.3	54.5
	Feed	31.3	100.0	15.2	91.5	551.4	'	504.5	'	100.0	'	26.0	'
	(Conc.)	31.3	16.8	15.2	91.5	551.4	551.4	504.5	504.5	36.6	36.6	26.0	'
Scvgr-2	Tail	155.1	83.2	75.1	93.3	188.5	248.4	175.9	231.1	63.4	100.0	44.9	99.5
	Feed	186.4	100.0	90.3	93.0	248.4	-	231.1	-	100.0	-	70.9	
	(Conc.)	14.1	7.0	6.8	83.5	981.6	981.6	819.8	819.8	212	21.2	19.1	'
Scvgr-1	(Tail)	186.4	93.0	90.3	93.0	248.4	295.1	231.1	272.5	78.8	100.0	70.9	'
	Feed	200.6	100.0	97.1	92.3	295.1		272.5	'	100.0	'	0.06	'
	(Conc.)	5.3	2.6	2.5	68.1	1,608.6	1,608.6	1,096.2	1,096.2	9.5	9.5	9.5	
Rghr	(Tail)	200.6	97.4	97.1	92.3	295.1	320.0	272.5	293.5	5.06	100.0	90.06	'
	(Feed)	205.8	100.0	99.7	91.7	320.0	-	293.5	'	100.0	-	5.99.5	'
	Conc.	0.7	0.3	0.3	43.4	1,083.8	1,083.8	469.8	469.8	2.0	0.5	0.5	100.0
Coal Float.	(Tail)	205.8	99.7	99.7	91.7	320.0	321.2	293.5	294.1	5.66	100.0	5.99	'
	Feed	206.5	100.0	100.0	91.6	321.2	1	294.1	1	100 0	'	100.0	'

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			Weight				REE (F	(udd			Distributio	n (%wt)	
Produc	ts		%		Ash	Ash B	asis	Coal I	Basis	Individ	dual	Fee	p
	1	50	Stages	Feed	(1 M 0/)	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.
	Conc.	1.0	31.6	0.7	17.8	2,110.3	2,110.3	375.0	375.0	16.6	16.6	0.9	0.9
Rghr/Clnr-2	Tail	2.1	68.4	1.5	71.4	1,221.5	1,313.2	872.2	715.1	83.4	100.0	4.3	5.1
	(Feed)	3.1	100.0	2.1	54.5	1,313.2	I	715.1	I	100.0	I	5.1	1
	(Conc.)	3.1	43.7	2.1	54.5	1,313.2	1,313.2	715.1	715.1	60.6	60.6	5.1	I
Rghr/Clnr-1	Tail	4.0	56.3	2.8	90.3	399.5	690.4	360.8	515.5	39.4	100.0	3.3	8.5
	(Feed)	7.1	100.0	4.9	74.7	690.4	I	515.5	I	100.0	I	8.5	I
	Conc.	1.2	17.5	0.8	45.6	4,225.5	4,225.5	1,928.5	1,928.5	30.4	30.4	5.5	13.9
Scvgr/Clnr-2	Tail	5.8	82.5	4.0	84.8	1,101.9	1,421.5	934.3	1,108.0	69.6	100.0	12.5	26.4
	(Feed)	7.0	100.0	4.8	<i>9.77</i>	1,421.5	I	1,108.0	I	100.0	1	17.9	I
	(Conc.)	7.0	44.6	4.8	<i>9.17</i> .	1,421.5	1,421.5	1,108.0	1,108.0	72.8	72.8	17.9	I
Scvgr/Clnr-1	Tail	8.7	55.4	6.0	90.9	366.3	797.3	332.9	678.6	27.2	100.0	6.7	33.1
	(Feed)	15.7	100.0	10.8	85.1	797.3	-	678.6	I	100.0	-	24.6	I
	(Conc.)	15.7	11.4	10.8	85.1	797.3	797.3	678.6	678.6	26.9	26.9	24.6	I
Scvgr	Tail	121.9	88.6	84.3	93.9	252.1	308.9	236.6	286.9	73.1	100.0	6.99	100.0
	(Feed)	137.6	100.0	95.1	92.9	308.9	1	286.9	I	100.0	I	91.5	
	(Conc.)	7.1	4.9	4.9	74.7	690.4	690.4	515.5	515.5	8.5	8.5	8.5	
Rghr	(Tail)	137.6	95.1	95.1	92.9	308.9	324.1	286.9	298.1	91.5	100.0	91.5	I
	Feed	144.7	100.0	100.0	92.0	324.1	I	298.1	I	100.0	ı	100.0	'

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			Weight				REE (I	(udc			Distributic	on (% wt)	
Produc	ts		%		Ash	Ash B	asis	Coal E	asis	Indivi	dual	Fee	pç
		aa	Stages	Feed	(70 W L)	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.
	Conc.	0.8	28.4	0.6	22.6	9,230.0	9,230.0	2,085.1	2,085.1	57.5	57.5	4.0	4.0
Rghr/Clnr-2	Tail	2.1	71.6	1.5	78.5	777.2	1,642.8	609.7	1,028.4	42.5	100.0	3.0	7.0
	(Feed)	3.0	100.0	2.0	62.6	1,642.8	1	1,028.4	1	100.0	1	7.0	I
	(Conc.)	3.0	35.1	2.0	62.6	1,642.8	1,642.8	1,028.4	1,028.4	48.6	48.6	7.0	I
Rghr/Clm-1	Tail	5.5	64.9	3.8	91.1	645.4	915.5	587.7	742.3	51.4	100.0	7.4	14.3
	(Feed)	8.4	100.0	5.8	81.1	915.5	I	742.3	1	100.0	1	14.3	I
	Conc.	1.2	22.8	0.9	42.6	12,393.9	12,393.9	5,282.3	5,282.3	66.4	66.4	15.0	29.3
Scvgr/Clnr-2	Tail	4.2	77.2	2.9	81.6	965.2	2,488.9	787.6	1,810.2	33.6	100.0	7.6	36.9
	(Feed)	5.5	100.0	3.7	72.7	2,488.9	-	1,810.2	1	100.0	1	22.6	I
	(Conc.)	5.5	27.1	3.7	72.7	2,488.9	2,488.9	1,810.2	1,810.2	63.5	63.5	22.6	I
Scvgr/Clnr-1	Tail	14.7	72.9	10.0	91.2	423.9	896.3	386.6	772.6	36.5	100.0	13.0	49.9
	(Feed)	20.1	100.0	13.8	86.2	896.3	1	772.6	1	100.0	1	35.5	I
	(Conc.)	20.1	14.6	13.8	86.2	896.3	896.3	772.6	772.6	41.5	41.5	35.5	I
Scugr	Tail	117.3	85.4	80.4	93.1	200.9	296.1	187.0	272.6	58.5	100.0	50.1	100.0
	(Feed)	137.4	100.0	94.2	92.1	296.1	1	272.6	1	100.0	1	85.7	I
	(Conc.)	8.4	5.8	5.8	81.1	915.5	915.5	742.3	742.3	14.3	14.3	14.3	I
Rghr	(Tail)	137.4	94.2	94.2	92.1	296.1	327.9	272.6	299.8	85.7	100.0	85.7	T
	Feed	145.8	100.0	100.0	91.4	327.9	I	299.8	I	100.0	I	100.0	I



Fig. 3.16 REE concentration on both ash basis (a) and whole mass basis (b) as a function of ash content, data adapted from Tab. 3.1 to Tab.3.4.

Fig. 3.16 plots the relationships of REE concentration on both ash basis and whole mass basis as a function of ash content based on the data given in Tab. 3.1 to Tab. 3.4. In general, there is a strong linear correlation between REE concentrations on a whole mass basis and ash content, since carbonaceous matter is normally a dilutant to REEs. However, the results presented in Fig. 3.16b show that the high TREE grades were obtained in the low-to-middle ash products. This may be because that most of the REEs recovered by the HHS process are associated with organic rather than mineral matter in coal. It may also be a result of the fact that ultrafine (micron- or submicronsized) REMs are finely disseminated in organic matrix. These speculations need to be verified by advanced mineral characterization technologies. Note also that the high TREE grades were obtained under the condition that SMO was employed, indicating that it was the SMO rather than the OHA that had played a more important role in recovering those low-to-middle ash particles containing high concentrations of REEs. Fig. 3.16b also shows that the HHS products assayed ~ 20% ash have somewhat lower REE contents. This is probably because some low REE coal is also being recovered in these products (i.e., the decarbonization was incomplete). This also explains why the "scavenger" leg in the HHS process produced the highest REE concentrations.

3.3.6 Effect of Aging

Fig. 3.17 shows the results of two sets of HHS tests conducted on the pulverized samples that have been stored in an open-air environment without special intention for different periods of time. The HHS tests were all conducted without using SMO. The results presented in Fig. 3.17a and Fig. 3.17b were obtained on a sample with an 80% passing size (d_{80}) of 8 µm and 3.9 µm, respectively. In a given HHS test, 1.2 kg/t OHA was employed in the rougher stage. One exception is that a higher dosage of OHA (1.5 kg/t) was used for hydrophobizing a sample that were aged for the longest time period in each set of tests.

As shown in Fig 3.17, the grade versus recovery curves are shifted to the left with the increase of aging, indicating that the performance of the HHS process would deteriorate on a more aged sample. Note also in Fig. 3.17a that the final concentrate obtained on the 3-months aged sample has a much higher REE concentration (15,027.9 ppm, ash basis) than that obtained from the 1-month aged sample. What made this difference is that in the former case a second-stage water

washing cleaning was carried out at much higher SMSN dosages. Therefore, had the reagent been used for cleaning on the fresher sample, the final REE concentration would have been greatly improved.



Fig. 3.17 Comparison of the results obtained on aged and fresh samples of different sizes: (a) $d_{80} = 8 \ \mu m$, and (b) $d_{80} = 3.9 \ \mu m$.

Size	Aging Time	Ash	REE Concentration
$d_{80,}\mu m$	month	%	ppm, ash basis
	1	57.1	8,087.6
8	3	31.9	15,027.9
	5	28.2	8,279.1
	1	53.3	8,812.7
3.9	5	35.6	8,131.5
	8	45.6	4,225.5

Tab. 3.5 Ash values of final concentrates presented in Fig. 3.18.

As shown in Tab. 3.5, the ash contents of final cleaner concentrates (indicated in Fig. 3.17) are in the range of 28.2% to 57.1%, which are much lower than the feed ash, indicating that some of REEs reporting to the final concentrates were associated with organic matter. Therefore, the deteriorated effect of aging on the recovery of REEs may be attributed to the oxidation of this organic matter.

In addition to monazite, other REE-bearing minerals (e.g., apatite) have also been identified in coal samples (Montross et al., 2018). A study by Guimaraes and Peres (1999) showed that apatite recovery decreased significantly with an increase in the concentration of interfering ions. Previous researchers reported that the Fire Clay coal sample contains calcite and dolomite (Honaker et al., 2018; Zhang et al., 2018). Thus, it is highly possible that metal ions dissolved out from these gangue minerals during the aging of the ground slurry and precipitated at the surface of REE-bearing minerals (e.g., apatite) in the form of hydroxy-complexes under alkaline condition, and therefore made them less hydrophobic to be recovered. This may be another possible explanation for the decrease of the recovery of REEs with aging.

The negative influences of aging on the recovery of REEs from coal may also be ascribed to the water leaching of REEs from the solids. It is evidently shown in Tab. 3.6 that the REEs concentration in feed decreases with increasing aging time.

Size	Aging Time	Feed REE Concentration	on (ppm)
$d_{80,}\mu m$	month	coal basis	ash basis
	1	341.5	304.3
8	3	326.2	300.7
	5	319.4	294.1
	1	358.7	324.6
3.9	5	301.2	277.0
	8	324.7	298.1

Tab. 3.6 REE concentrations in feed as a function of aging time.

3.3.7 Comparison of Flotation and HHS

Fig. 3.18a compares the results of flotation and HHS tests obtained on a micronized sample with $d_{50} = 2.76 \,\mu m \,(d_{80} = 8 \,\mu m)$. The conventional and column flotation tests were conducted with multiple stages of cleaning using 1.5 kg/t sodium oleate as the collector (Zhang et al., 2017), while the HHS test was conducted using 1.5 kg/t OHA as the collector.

As shown, column flotation is more efficient than the conventional flotation assessed from observation of the position of REE grade versus recovery curve. The plots also show that the HHS process is far superior to any type of flotation. The performance of column flotation started to outperform the conventional flotation when the REE recovery fell below 20%, while the performance of HHS already surpassed the flotation at a recovery of 45%. The HHS final concentrate assayed 17,590 ppm on an ash basis, which equates to 3.8 times that of column flotation (4,593.3 ppm) and 7.9 times that of conventional flotation (2,230 ppm). The significant improvement in separation performance seen by the HHS process can be ascribed to the much higher contact angles achieved by oil than air and more efficient control of hydraulic entrainment in the HHS test due to the employment of SMSN in cleaners.



Fig. 3.18 Comparisons of the REE recovery tests results obtained from flotation and HHS: (a) cumulative REE recovery as a function of REE content on an ash basis, and (b) HREE/LREE Ratio as a function of REE content on an ash basis. Flotation tests data adapted from Zhang et al. (2017).

Fig. 3.18b shows the HREE/LREE ratio as a function of ash-based REE concentration using the data extracted from the tests shown in Fig. 3.18a. As shown, there is an almost linear

relationship between the ratio of HREE/LREE and the ash-based REE content in a flotation product: the HREE/LREE ratio decreases with increasing REE concentration, indicating that REMs, which are more enriched with LREEs, might have been efficiently recovered by flotation. In contrast, the HREE/LREE ratios in the HHS products do not differ significantly after the ash-based REE content in an HHS product reached above 1000 ppm. Additionally, the ratio of HREE/LREE in the HHS final concentrate is higher than those in the flotation concentrates (which are 0.23 and 0.16, respectively). These results suggest that the HHS test might have recovered both REMs and other minerals that contain significant amounts of HREEs, such as the REE ion-adsorption clay. In all, the HHS process is advanced over flotation.

3.4 Conclusion

The feasibility of recovering REEs associated with coal byproduct was explored using the HHS technology on a representative TUF sample collected from the LW coal preparation plant at Kentucky, USA. The results obtained from a systematical study show that the control of hydrophobicity (or contact angle) is the key to achieve success in recovering REMs or REEs from coal byproduct. The hydrophobicity of particles can be affected by the collector, mineral liberation, depressant, hydrophobicity-enhancing agent (SMO), and aging. The highest TREEs grade obtained in this work was 17,590 ppm on an ash basis, which equates to an REE enrichment of 5,026% compared to ~350 ppm in the feed. Comparison of air flotation and the HHS process indicates that the HHS process is far superior to flotation. In comparison to many other physical separation technologies that have been explored for the recovery of REEs from coal and coal byproducts (Lin et al., 2017; Zhang et al., 2017; Zhang et al., 2015; Lanzerstorfer, 2018), the HHS process is the most promising physical separation technologie. It is worth mentioning that all of the HHS results shown in this work were obtained without the use of a Morganizer, which is essential

to the HHS process and intended to further upgrade the concentrates. Therefore, HHS products containing TREE concentrations higher than 17,590 ppm will be easily produced once the Morganizer can be used in the HHS process.

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Chapter 4 Fundamental Studies on Phase inversion

Abstract

In order to use a Morganizer, it is necessary to form water-in-oil (w/o) emulsions. However, the work presented in Chapter 3 showed that when mineral particles were used as emulsifiers, the formation of w/o emulsions was not as easy as with coal particles. Therefore, the objective of this work is to understand the fundamental aspects affecting the phase inversion of oil-in-water (o/w) emulsions to w/o emulsions.

The emulsification results obtained on silvlated silica particles show that the emulsions conversion from o/w to w/o can be achieved by increasing the oil contact angle (θ_o) above 90° or increasing the oil phase volume (ϕ_{a}). It is also noted that the conversion of o/w emulsions stabilized by particles with $\theta_o < 90^\circ$ to w/o emulsions by increasing ϕ_o only can be achieved at a high-shearing mixing condition. Moreover, a series of emulsification tests was also carried out at $\phi_o = 0.5$ using ultrafine chalcopyrite particles with $\theta_o < 90^\circ$ as emulsifiers to study the effects of hydrophobicityenhancing agents. The results show that the use of Span[®] group emulsifiers at suitable dosages makes possible the formation of w/o emulsions on particles with $\theta_o < 90^\circ$. Based on these findings, a series of HHS demonstration tests was successfully conducted on the recovery of ultrafine silvlated silica particles using sorbitan monooleate (SMO). The results reveal that $\theta_o > 90^\circ$ is a thermodynamic requirement for implementing the HHS process. The adsorption behaviors of SMO at different concentrations were discussed in relation to the liberation of particles from water drops. Lastly, a SMO-assisted HHS test was performed to separate ultrafine monazite particles from a model ore sample. The results imply that the HHS work conducted in Chapter 3 on the recovery of ultrafine disseminated rare earth minerals (REMs) associated with coal byproduct would have been greatly improved with a better knowledge of phase inversion at that time.

4.1 Introduction

Since the discovery by Pickering (1907) that solid particles with suitable wettability can function as an emulsifier to stabilize oil-water emulsions, the science of Pickering emulsion has been extensively studied in terms of its application in a variety of fields including food (Xiao et al., 2016), pharmaceutical (Khan et al., 2011), cosmetic (Lam et al., 2014), oil recovery (Alvarado et al., 2011), polymerization (Chen et al., 2007), and catalyst recycling (Tang et al., 2015). Although Pickering emulsion has been prepared for recovering ultrafine mineral particles in the two-liquid flotation (TLF) process long ago (Lai and Fuestenau,1968; Shergold and Stratton-Crawley, 1981), little attention has been paid to exploring the science of Pickering emulsion in regards to mineral processing.

Raghavan and Fuerstenau (1975) showed that the TLF process is superior to froth flotation because oil droplets can form substantially larger contact angles than air bubbles in water on the same flat mineral surface. However, the inadequate selectivity resulted from entrainment, and the high operating cost resulted from oil loss are the major problems associated with this process (Zambrana et al., 1974). Recognizing the pros and cons of the TLF, Yoon (2016) invented the hydrophobic-hydrophilic separation (HHS) process based on the amelioration of the TLF process. The results obtained on fine and ultrafine coal particles from various feedstocks showed that the HHS process should have the capability of recovering any particles that can be rendered hydrophobic (Gupta et al., 2016; Yoon et al., 2016).

The work presented in Chapter 3 of this dissertation, however, showed that it was difficult to use the Morganizer in the HHS tests regarding recovering ultrafine REMs associated with a thickener underflow sample procured from a coal preparation plant. As a result, all the HHS tests were performed without using a Morganizer so that water rather than oil was used to clean the rougher concentrates, leading to the unsatisfactory separation results despite the employment of a complicated processing flowsheet. By contrasting the HHS process on coal, it was found that w/o emulsions stabilized by oil-coated coal particles were readily formed in the presence of large amounts of oil, whilst that of REMs were not, revealing that a phase conversion from o/w Pickering emulsions to w/o Pickering emulsions is critical to the success of the HHS process. In this regard, the main objective of this work is to study how to achieve a phase inversion when particles of low hydrophobicity are present as emulsifiers so that the application of the HHS process can be expanded for the recovery of other ultrafine particles other than coal, such as copper minerals, and REMs associated with coal and coal byproducts.

In general, an o/w emulsion can be converted to a w/o emulsion either by increasing the oil phase volume or by increasing the hydrophobicity of particles (Binks and Rodrigues, 2003; Binks et al., 2010). Therefore, in this work, a series of emulsification tests using silylated silica particles as an emulsifier was conducted to investigate the effects of oil phase volume and hydrophobicity on phase inversion. Noted that a phase inversion induced by changing oil phase volume requires a high energy input, therefore, from the view of the practical application of the HHS process, the phase inversion was further investigated with focus on the aspect of increasing hydrophobicity. As a result, a series of emulsification tests was carried out using ultrafine chalcopyrite particles with $\theta_o < 90^\circ$ and different hydrophobicity-enhancing agents as emulsifiers in the presence of equal volumes of heptane and water. In these tests, the effects of various hydrophobic polymers and non-ionic surfactants on the phase inversion and the stability of w/o emulsions (if phase inversion occurs) were discussed and evaluated. At last, on the basis of the knowledgeable information attained from the study on achieving phase inversion, a series of HHS

tests was conducted on both silvlated silica and artificial REMs sample (monazite) with the aid of a hydrophobicity-enhancing agent.

4.2 Experimental

4.2.1 Materials

The glass microspheres (EMB-10) with a mean size of 5 μ m were purchased from Potters Industries LLC. They were cleaned in a piranha solution – a mixture of sulfuric acid and hydrogen peroxide – to remove organic matter, rinsed with deionized water, and then dried. The glass beads cleaned in this manner were hydrophobized by immersion in an octadecyltrichlorosilane (OTS)in-toluene solution. The hydrophobicity of the glass beads was controlled by varying the OTS concentration and immersion time. The glass beads were silylated together with a quartz plate in the same OTS solution, making it possible to measure the contact angles using the sessile drop technique.

Chunky samples of chalcopyrite were purchased from Ward's Science. They were crushed by means of a handheld hammer to < 0.6 mm and subsequently wet-ground in a motor-driven mortar and pestle. The samples obtained in this manner assayed 32.8 %Cu as determined by using the ICP-MS analyzer.

Monazite pre-concentrate of > 95% purity originating from Hebei, China was obtained from the University of Kentucky. The samples assayed 54.85% TREEs as determined by using an ICP-MS analyzer (Zhang and Honaker, 2017). The as-received 300 x 150 μ m monazite sample was wet-ground in a motor-driven mortar and pestle to ultrafine sizes.

Potassium amyl xanthate (KAX) of > 95% purity from TCI America was used to hydrophobize the chalcopyrite sample. The reagent was purified twice before use by dissolving in acetone (HPLC grade, FisherSci.) and re-crystallizing in diethyl ether (99.9%, Sigma-Aldrich). A

KAX solution was prepared freshly just before use. Octanohydroxamic acid (OHA) of minimum 95% purity purchased from Fisher Scientific was used to hydrophobize the monazite sample. An HPLC grade heptane (99%, Fisher) was used in all tests. Non-ionic surfactants, which included Pluronic L101, Pluronic L81, and Genapol PF-20, are freely provided by Clariant Chemicals. Other chemicals, which included Span 65 (sorbitan tristearate), Span 80 (sorbitan monooleate, SMO), Span 83 (sorbitan sesquioleate), Span 85 (sorbitan trioleate), polyethylene-block-poly(ethylene glycol), polymethylhydrosiloxane (PMHS), polybutadiene (dicarboxy terminated), poly(methyl methacrylate), and poly(ethyl vinyl ether), KCl, and NaOH were obtained from Sigma-Aldrich. Deionized water with a resistivity of 18.2 MΩ cm at 25 °C was exploited for the preparation of reagent solutions and emulsions.

4.2.2 Preparation of Pickering Emulsions

Hydrophobic Silica as Emulsifier In the tests on studying the effect of oil contact angle (θ_o) , 0.5 g silica particles were placed in a 50 ml beaker containing 20 ml water or heptane. The mixture was agitated using an overhead mixer, which has an impeller with 3-twisted blades of 1inch diameter at 800 RPM for 5 minutes to disperse the particles. If $\theta_o < 90^\circ$, the silica particles were first conditioned in water. Otherwise, they were first conditioned in heptane. Upon the completion of dispersion, 20 ml heptane or water was added to the beaker, and the mixture was mixed at 800 RPM for another 5 minutes to allow emulsions to form. The mixture was then transferred to a vial with a screwcap and allowed to settle.

Another set of emulsification tests was conducted using silica particles of $\theta_o = 79^\circ$ as an emulsifier to study the effect of oil phase volume on phase inversion. In each test, 2 g silica particles were initially placed in a blender cup (Magic Bullet Multifunction Blender, 250 Watts) containing 40 ml water. The mixture was then agitated for 2 minutes to disperse the silica particles

in water. After that, a desired volume of oil (heptane) was then added to the dispersion, and the mixture was sheared for another 2 minutes to form emulsions. The prepared emulsions were poured into 250 ml beakers and allowed to settle.

Hydrophobic Chalcopyrite as Emulsifier In emulsification tests conducted using KAX alone as a hydrophobizing agent, 1 g solid was added to a 150 ml cylindrical separatory funnel containing 40 ml of a KAX solution of known concentration and the mixture was hand-shaken for 5 minutes to allow chalcopyrite particles to be hydrophobized by xanthate adsorption. The pH was 9.5. After the particles had been hydrophobized, a volume (40 ml) of heptane was added to the separatory funnel. The mixture was then agitated by hand for another 5 minutes. During this time, the oil was broken into small droplets, which then collected the hydrophobic chalcopyrite particles and formed emulsions droplets. Thereafter, the cylindrical separatory funnel was allowed to stand to achieve a phase separation, with the aqueous phase at the bottom and oil phase at the top. The weights of the particles collected from the aqueous and oil phases were recorded to calculate the recovery of chalcopyrite particles.

In emulsification tests conducted using both primary and secondary hydrophobizing agents, a 20 ml chalcopyrite suspension (5 % solids) was conditioned in the presence of 2.5 x 10⁻⁵ M KAX at pH 9.5 in a 50 ml beaker for 5 minutes at 800 RPM. After this first hydrophobization step, a hydrophobicity-enhancing agent (hydrophobic polymer or low HLB non-ionic surfactant) was added to the beaker before agitating the mixture for another 5 minutes at the same RPM. After this second hydrophobization step, a volume (20 ml) of heptane was added to the beaker, followed by agitation of the mixture for another 5 minutes at 1050 RPM. The emulsions formed in this manner was then transferred to a glass vial with a screw cap and allowed to stand.

All of the emulsification tests were conducted at room temperature. Sideview photographs of the vials were taken after allowing the emulsions to stand for overnight. The emulsion type was inferred by observing in which phase the emulsion droplets were located after standing. For o/w emulsions, which contained mainly light oil, and therefore, they would float and sit in the oil phase. Conversely, the w/o emulsions would droop or sink into the water phase. This method was confirmed using the emulsion droplet dispersion method described by Binks et al. (2006).

4.2.3 HHS Tests on the Recovery of Hydrophobic Silica

In each test, 1 g OTS-coated silica powers with $d_{80} = 5 \,\mu$ m was added to 50 ml of tap water in a 150 ml separatory funnel and mixed for 5 minutes by handshaking. A small amount of sorbitan monooleate (SMO) was then added to the mixture to further increase the hydrophobicity of the silica particles. The reagent SMO was added in the form of a heptane-in-water emulsion stabilized by SMO. The SMO dosages were varied in the range of 0 to 4×10^{-4} M SMO in water. After the SMO addition, the mixture was agitated for 5 minutes to allow for the reagent to adsorb on the surface of the OTS-coated silica and increase the contact angles of the particles. A volume of heptane (50 ml) was subsequently added to the aqueous slurry of silica particles. The mixture was agitated for 5 minutes and allowed to stand for a phase separation before removing the aqueous phase at the bottom. The organic phase left in the separatory funnel was then agitated by handshaking to break the w/o emulsion by a gentle mechanical force. The amount of silica particles fully dispersed into the oil (heptane) phase was recorded as recovery. If the contact angle of the OTS-coated silica particles was greater than 90°, the particles were dispersed in the oil phase directly.

4.3 Results and Discussion

4.3.1 Hydrophobic Silica Particles as Emulsifier

4.3.1.1 Effect of Contact Angle

Fig. 4.1 shows the results of the TLF tests conducted on the 5 µm silica particles suspended in water using heptane as a collector. As shown, the results varied with the θ_o of the particles. At $\theta_o = 5^\circ$, most of the particles stayed in the water phase at the bottom, resulting in a low recovery. As θ_o was increased to 54° and 79°, the silica recovery was increased substantially as can be visually seen in the second and third vials.

The particles collected under these conditions, i.e., $\theta_o < 90^\circ$, o/w emulsions were formed. Thermodynamically, this phenomenon is rather similar to the recovery of hydrophobic particles by air bubbles in flotation. In effect, the bubble-particle aggregates formed during flotation may be considered as air/water (a/w) emulsions. In both the TLF and the conventional air bubble flotation, hydrophobic particles stabilize the oil droplets and air bubbles, respectively, so that the

two hydrophobic collectors, i.e., oil droplets and air bubbles, acquire certain degrees of kinetic stabilities in the aqueous phase.

When the θ_o of the silica spheres was further increased to > 90°, the situation changed drastically. As shown in the fourth vial, the silica particles of



Fig. 4.1 Recovery of silica particles with θ_o ranging from 5° to 145° using the two-liquid flotation method. At $\theta_o < 90^\circ$, the particles were recovered in the form of o/w emulsions. At $\theta_o > 90^\circ$, they were recovered as w/o emulsions. At $\theta_o = 95^\circ$, a substantial amount of water was entrained in the form of w/o emulsions. The entrained water decreased at higher contact angles.

 $\theta_o = 95^\circ$ formed w/o emulsions rather than the o/w emulsions observed at $\theta_o < 90^\circ$. This phenomenon is referred to as phase inversion in emulsion science. A conversion of an o/w emulsion to a w/o immersion can be readily induced by using a low-HLB surfactant, e.g., sorbitan monooleate. In the present, the same conversion of phase inversion was observed when the contact angle of silica particles was increased above 90°.

Note here that the w/o emulsions formed with silica spheres of $\theta_o > 90^\circ$ are located in aqueous phase below the oil/water phase boundary. The reason for this is that hydrophobic particles can cross the oil/water interface and enter the oil phase if the contact angle is greater than 90° as shown below,

$$\Delta G = \gamma_{OW} \cos \theta_O \tag{4.1}$$

where ΔG is the free energy of transfer, and γ_{ow} is the oil/water interfacial tension. If θ_o is slightly above 90°, the silica particles may stabilize the entrained micro-water droplets effectively, forming w/o emulsions inside an oil droplet, which may be considered as multiple emulsion. If θ_o is substantially larger than 90°, no such emulsions will form. The results obtained at $\theta_o = 95^\circ$, 120°, and 145° support this thermodynamic analysis. As shown in Fig. 4.1, drooping of oil droplets diminished with increasing contact angle, indicating that water entrainment becomes less significant at higher contact angles.



Fig. 4.2 Effect of contact angle on the recovery of fine particles by twoliquid flotation.

Based on the results shown in Fig. 4.1, the effect of contact angles on the TLF flotation recovery is illustrated in Fig. 4.2. At $\theta_o < 90^\circ$, hydrophobic particles were collected on the surface of oil droplets in the same manner as with air bubbles in flotation. At θ_o slightly above 90°, some particles adsorbed water droplets went inside the oil droplet, forming a w/o/w multiple emulsion. At $\theta_o >> 90^\circ$, the particles were fully submersed into the oil droplet. In practice, particles will have distributed contact angles, allowing all three cases to be possible.

4.3.1.2 Effect of Phase Volume of Oil

The results presented in the foregoing paragraphs showed that one can readily form w/o emulsions by increasing θ_o above 90°. It would be of interest to explore the possibility of achieving phase inversion at $\theta_o < 90^\circ$. According to Binks and Lumsdon (2000), this could be achieved by controlling the volume fraction of oil (or phase volume, ϕ_o). Therefore, a series of emulsification tests was conducted by varying ϕ_o in the range of 0.1 to 0.8 in the presence of silica spheres with $\theta_o = 79^\circ$.

As shown in Fig. 4.3, the emulsions stabilized by silica particles were gradually converted from o/w emulsions to w/o emulsions with the increase of ϕ_o . At $\phi_o = 0.1$ -0.4, silica particles were recovered as o/w emulsions. At $\phi_o = 0.5$, some silica particles were recovered as w/o emulsions as



Fig. 4.3 Effect of phase volume (ϕ_o) of oil on the recovery of silica particles with $\theta_o = 79^\circ$. At $\phi_o = 0.1$ -0.4, the particles were recovered as agglomerates (or o/w emulsions). At $\phi_o > 0.5$, the silica particles were recovered as w/o emulsions. At $\phi_o = 0.8$, the phase inversion was complete.

evidenced by the occurrence of emulsions droplets drooping into the aqueous phase. At $\phi_o = 0.8$, the phase inversion was complete with all silica particles recovered as w/o emulsions.

Thus, the results presented in Fig. 4.3 show that it is possible to achieve a phase inversion with particles of $\theta_o < 90^\circ$. However, it is interesting to note that the phase inversion at $\theta_o = 79^\circ$ was achieved by using a high-shear agitation in a blender, while phase inversion did not occur in emulsification tests performed using a low-shear mixer at 1050 RPM, of which phase inversion was induced with particles of $\theta_o > 90^\circ$ as shown in Fig. 4.1. This finding suggests that certain energy is also needed to induce phase inversion with particles of $\theta_o < 90^\circ$, although the ϕ_o is large.

Another set of emulsification tests with particles of $\theta_o = 54^\circ$ at $\phi_o > 0.5$ was also conducted using the high-shear agitation (the results were not shown), however, it was not possible to induce phase inversion at any ϕ_o level. It indicates that a higher energy input would be necessary in order



Fig. 4.4 The effects of contact angle and particle size on the energy required for the removal of a particle sitting at the interface into the heptane phase.

to achieve a phase inversion with less hydrophobic particles. On the other hand, the converted w/o emulsions are required to be broken to disperse the particles sitting at the oil-water interfaces in the Morganizer step of the HHS process. The energy E for a particle on the oil-water interface detaching to the bulk oil phase can be obtained using the following Eq. (4.2) (Binks and Lumsdon, 2000),

$$\mathbf{E} = \pi R^2 \gamma_{ow} \left(1 + \cos\theta\right)^2 \tag{4.2}$$

Fig. 4.4 shows the simulation results of detachment energy as a function of the contact angle at different particle sizes. As shown, at a given particle size, the detachment energy decreases with increasing contact angle, implying that the breakage of emulsions in a Morganizer would be more efficient if particles are of strong hydrophobicity. Recognizing the importance of increasing hydrophobicity to both phase inversion and breaking-up emulsions for the sake of energy-saving, the following work on how to make phase inversion using chalcopyrite particles as emulsifiers was carried out with emphasis on increasing the hydrophobicity of particles.

4.3.2 Hydrophobic Chalcopyrite Particles as Emulsifier

4.3.2.1 Effect of Using KAX Alone as Primary Hydrophobizing Agent

A series of TLF tests was conducted using pure chalcopyrite samples wet-ground to $d_{80} = 29$ and 15 µm. The samples were hydrophobized with KAX at different concentrations and subjected to the tests using a cylindrical separatory funnel, with the results presented as images shown in Fig. 4.5. The mineral sample with $d_{80} = 29 \,\mu\text{m}$ was recovered as o/w emulsions at KAX concentrations below 10^{-4} M, while the same was recovered as w/o emulsions at higher concentrations. The $d_{80} = 15 \,\mu\text{m}$ sample behaved likewise. The changeover from the o/w to w/o emulsions represented a phase inversion due to contact angle change.



Fig. 4.5 Results of the two-liquid flotation tests conducted on the pure chalcopyrite samples with a) $d_{80} = 29 \ \mu m$ and b) $d_{80} = 15 \ \mu m$. The samples were hydrophobized at different KAX concentrations (M), pH 9.5, and $\phi_o = 0.5$.

After recording the images shown in Fig. 4.5, the mixture was allowed to settle for 5 minutes before removing the aqueous along with the particles left in it. The weight of the particles in the aqueous phase was determined after filtration and drying. The particles left in the separatory funnel were separated from the water and heptane and weighed after appropriate solid-liquid separation and drying. From the weights, the chalcopyrite recoveries were determined and plotted as functions of KAX concentrations (Fig. 4.6). As shown in Fig. 4,6, the chalcopyrite recovery increased with the increase in KAX concentration due to the increase of hydrophobicity. This was further confirmed by the contact measurement results presented in Tab. 4.1. Fig. 4.6 also shows



Fig. 4.6 Effect of KAX concentration on the two-liquid flotation recoveries of chalcopyrite particles with $d_{80} = 29$ and 15 μ m.

Tab. 4.1 Effect of KAX on the air bubble and heptane drop contact angles on chalcopyrite surfaces.

KAX	Contact Angl	$e(\theta^o)$
М	Air	Heptane
1 x 10 ⁻³	91.0	145.6
1 x 10 ⁻⁴	87.7	136.1
5 x 10 ⁻⁵	71.6	125.6
1 x 10 ⁻⁵	64.5	98.9
1 x 10 ⁻⁶	44.7	76.7
0	27.7	52.1

that the TLF performed much better on the finer particles in terms of recovery, suggesting that oil is an efficient collector for ultrafine particles.

To better understand the mechanisms of phase inversion shown in Fig. 4.5, contact angle measurements were conducted on polished chalcopyrite surfaces after KAX treatment. The measurements were conducted using two different methods: one using deionized water drops and the other using pure heptane drops. The results obtained with the former are equivalent to those measured with air bubbles. The results presented in Tab. 4.1 show that the contact angles measured

using heptane drops were substantially larger than those measured with air bubbles, which is a thermodynamic rationale to use oil drops rather than air bubbles to recover fine particles. The data also shows that θ_o became larger than 90° at 10⁻⁵ M KAX, according to which phase inversion should occur at this concentration, while the images of Fig. 4.5 show that it actually occurred at higher concentrations. This discrepancy may be attributed to the likelihood that the KAX concentration decreased considerably during experiments due to adsorption on the surface of fine chalcopyrite particles. Placing a flat mineral surface in a xanthate solution for contact angle measurement would not significantly change the xanthate concentration due to the small surface area.

The emulsification results procured on the artificial chalcopyrite sample show that phase inversion can be easily induced even though the particles were solely hydrophobized by a primary hydrophobizing agent. However, emulsification tests performed on copper samples obtained from processing plants showed that it was difficult to achieve phase inversion with a primary hydrophobizing agent alone. This may be due to the facts that copper mineral particles presented in real samples may occur as Janus particles and the adsorption of a primary hydrophobizing agent seldom gives close-packed hydrocarbon coating on the surface. Moreover, it was noted (see Fig. 4.5) that the required primary hydrophobizing agent dosage for inducing a phase inversion in the TLF of chalcopyrite was much higher than that of the air flotation (10^{-6} - 10^{-7} M). As such, a series of emulsification tests was conducted by increasing the contact angles of chalcopyrite samples using a secondary hydrophobizing agent. The chalcopyrite particles ($d_{80} = 10 \mu m$) were subjected to a two-step hydrophobization process using KAX as a primary hydrophobizing agent, and various hydrophobic polymers and non-ionic surfactants as a secondary hydrophobizing agent. The results were presented in the following section.



Fig. 4.7 Effect of using polybutadiene (dicarboxy terminated) to increase the hydrophobicity of chalcopyrite particles; dosages in kg/t.

4.3.2.2 Effect of Using Hydrophobic Polymers as Hydrophobicity-Enhancing Agent

<u>Polybutadiene(dicarboxy-terminated)</u> Fig. 4.7 shows the emulsification tests conducted using KAX (2.5 x 10⁻⁵ M) in the first step and 0 to 2.8 kg/t polybutadiene(dicarboxy-terminated) in the second step. All tests were conducted at $\phi_o = 0.5$, i.e., 20 ml water and 20 ml heptane.

With KAX alone, i.e., at 0 kg/t polymer, most of the mineral particles were recovered in the oil phase most probably as an o/w emulsion. It appears that $\theta_o < 90^\circ$. Under this condition, hydrophobic particles were collected on the surface of oil drops, as shown in Fig. 4.2a.

At 0.11 kg/t polymer, a large volume of the particles settled at the bottom of the vial, possibly as a w/o emulsion (Fig. 4.2b). The emulsion may consist of oil drops loaded with small droplets of water stabilized by hydrophobic chalcopyrite particles. In view of the large SG (= 4.2) of the copper mineral, the emulsion drops could not stay in the oil phase. At 0.56 kg/t polymer, the amount of chalcopyrite particles with $\theta_o > 90^\circ$ would be increased, causing more o/w emulsions to be inversed to w/o emulsions, and therefore a relatively larger volume of emulsion settled at the bottom in the third vial than that in the second vial (refer Fig. 4.7). When the polymer dosage was increased to 2.8 kg/t, the phase inversion became complete with all the particles recovered in water phase in the form of w/o emulsions as evidenced by the occurrence of a clear oil phase in the fourth



Fig. 4.8 Effect of using poly (methyl methacrylate) to increase the hydrophobicity of chalcopyrite particles; dosages in kg/t.

vial in Fig. 4.7. The results presented in Fig. 4.7 show that the polybutadiene(dicarboxy-terminated) is an efficient hydrophobicity-enhancing agent that can be used to increase the oil contact angles of chalcopyrite particle above 90°.

<u>Poly(methyl methacrylate)</u> Fig. 4.8 shows the results obtained with chalcopyrite particles using varying amounts of poly(methyl methacrylate) (PMMA) as a hydrophobicity-enhancing agent. As shown, the chalcopyrite particles were recovered as o/w emulsions regardless of the variation of PMMA dosage in the range from 0 to 4 kg/t, indicating that the use of this polymer failed to increase the contact angles above 90°. A possible explanation could be the inefficient hydrophobizing conditioning employed during the emulsification tests. According to Liu and Su (2006), and Moulay (2010), the surface modification by grafting of PMMA onto particles normally takes a few hours at elevated temperatures. In this set of tests, however, the hydrophobization conditioning was carried out at room temperature for 5 minutes.

<u>Polymethylhydrosiloxane</u> Fig. 4.9 shows the results obtained using different dosages of polymethylhydrosiloxane (PMHS) – a water-soluble polymer – as a hydrophobicity-enhancing agent. Comparison of the appearance of emulsions in the first and third vials (left to right) shows clearly that some emulsion drops became too heavy to stay in the oil phase and hence drooped into


Fig. 4.9 Effect of using polymethylhydrosiloxane (PMHS) to increase the hydrophobicity of chalcopyrite particles; dosages in kg/t.

the water phase at 0.5 kg/t PMHS. This observation suggests that some of the chalcopyrite particles have been rendered hydrophobic enough to stabilize w/o emulsions. At 2 kg/t PMHS, some of the emulsion drops became so heavily loaded with particles that they fell to the bottom of the vial. As the PMHS dosage was further increased to 10 kg/t, o/w emulsions were still observed and there was no significant difference in the volume of the emulsion drops protruding from the oil/water interface as compared with those of 0.5 kg/t and 2 kg/t, indicating that the hydrophobicity of chalcopyrite particles did not change much with the PHMS dosage varied from 0.5 to 10 kg/t.



Fig. 4.10 Effect of using poly (ethyl vinyl ether) to increase the hydrophobicity of chalcopyrite particles; dosages in kg/t.

Poly(ethyl vinyl ether) Fig. 4.10 shows the effects of using poly(ethyl vinyl ether) as a hydrophobicity-enhancing agent for the KAX treated chalcopyrite particles. The results obtained in the range of 0 to 4 kg/t showed practically no difference, suggesting that the reagent did not work well as a hydrophobicity-enhancing agent. Under this condition, the chalcopyrite particles were recovered as an o/w emulsion.

The results presented in this section show that w/o emulsions could be stabilized by chalcopyrite particles that have been subjected to a second hydrophobizing treatment with polybutadiene(dicarboxy-terminated) and PMHS, but not with PMMA and poly(ethyl vinyl ether). This may be attributed to the difference in the content of hydrophilic functional groups in the molecular structure of the hydrophobic polymers. As shown in Fig. 4.11, both the PMMA and poly(ethyl vinyl ether) do not contain any hydrophilic functional groups. Thus, the adsorption of these very hydrophobic polymers to the relatively hydrophilic chalcopyrite particles becomes very difficult under the treatment conditions employed in this work. Although polybutadiene(dicarboxy-terminated) and PMHS both can be useful for the formation of w/o



Fig. 4.11 Molecular structure of hydrophobic polymers: a) polybutadiene (dicarboxy terminated), b) poly (methyl methacrylate) (PMMA), c) polymethylhydrosiloxane (PMHS), d) poly (ethyl vinyl ether).

emulsions, PMHS is less efficient than polybutadiene(dicarboxy-terminated) in terms of inducing phase inversion because a complete phase inversion did not occur in the tested PMHS dosage range. Wu et al. (2014) found that the chemical grafting of PMHS onto particle surfaces, by which the hydrophobicity of particles would increase, happens under alkaline conditions and a phase inversion from o/w to w/o could be induced at pH above 11. Given the pH was kept at 9.5 in this study, the poorer performance of PMHS was probably due to use of a non-optimal pH condition in the emulsification tests.

Converting an o/w emulsion to a w/o emulsion is a prerequisite for conducting the HHS process. Additionally, the converted w/o emulsion is expected to be readily broken up in oil in order to recover the hydrophobic particles. It is clearly shown in Fig. 4.7 that the w/o emulsions stabilized by chalcopyrite particles that had been treated with polybutadiene(dicarboxy-terminated) were flocculated into one paste-like lump. Moreover, particles did not disperse in the oil phase after gently hand-shaking the vial. As such, it was not surprising to find that these w/o emulsions did not break in the presence of a large amount of oil in a later test. In this regard, polybutadiene(dicarboxy-terminated) was not considered as an excellent hydrophobicity-enhancing agent for the HHS process.

Sela et al. (1994) compared the stability of emulsions stabilized both by polymeric surfactants and non-ionic surfactants. They found that because of the formation of thick rigid films at the o/w interfaces in the presence of polymeric surfactants, the emulsion drops were surprisingly stable as compared to those stabilized by non-ionic surfactants. Polybutadiene(dicarboxy-terminated), an oil-soluble polymer, has viscosity over six orders of magnitude relative to that of heptane. As such, the w/o emulsions formed in the tests using polybutadiene(dicarboxy-terminated)

as a hydrophobicity-enhancing agent were highly stable to break primarily due to the same reason indicated by Sela et al. (1994).

4.3.2.3 Effect of Using Non-ionic Surfactants as Hydrophobicity-Enhancing Agent

The foregoing section displayed that the HHS process will encounter problems in the emulsion breakage step if the phase inversed w/o emulsions were induced by the use of a hydrophobic polymer. It is, thereby, of importance and interest to identify other types of hydrophobicity-enhancing agent, which can promote phase inversion with the formation of w/o emulsions that are readily to be broken up. Previous studies on emulsions by Binks et al. (2007) and Tshilumbu et al. (2014) both showed that particles became increasingly hydrophobic upon the addition of a non-ionic surfactant. Moreover, non-ionic surfactants with low hydrophile-lipophile balance (HLB) are well known as emulsifiers to prepare w/o emulsions (Griffin, 1954). As such, several non-ionic surfactants with HLB numbers in the range of 1.0 to 4.3 were chosen as hydrophobicity-enhancing agents to study the phase inversion of o/w emulsions stabilized by KAX-treated chalcopyrite particles.

<u>*Pluronic L101*</u> Pluronic L101 is a difunctional block copolymers of propylene and ethylene oxide with HLB = 1.0. Fig. 4.12 shows the results obtained with KAX-pretreated chalcopyrite



Fig. 4.12 Effect of Pluronic L101 on emulsification using KAX-treated chalcopyrite particles as solid surfactant; dosages in kg/t.

particles using Pluronic L101 as a potential hydrophobicity-enhancing agent. It seems that the chalcopyrite particles were recovered as o/w emulsions rather than w/o emulsions, indicating that Pluronic L101 failed to increase the θ_o of the chalcopyrite particles above 90°. At 10.6 kg/t L101, the surface of the vial located in the oil phase was free of particles, indicating that the lamella films of the o/w foam collapsed in the presence of a non-ionic surfactant with an HLB number of 1.

<u>Span 85</u> A series of emulsification tests was conducted using Span 85 (sorbitan trioleate) with HLB = 1.8. The tests were conducted using KAX-treated chalcopyrite particles as a solid surfactant. As shown in Fig. 4.13, the test conducted at 5.5 x 10⁻⁵ M Span 85 showed drooping of emulsion drops to the aqueous phase, which became more evident at 8.2 x 10⁻⁵ M Span 85. At 1.4 x 10⁻⁴ M Span 85 and higher, the o/w emulsions, which were clearly seen in the oil phase at Span 85 < 5.5 x 10⁻⁵ M, were entirely disappeared. Under this condition, chalcopyrite particles were either recovered as w/o emulsions that fell into the aqueous phase, or recovered into the oil phase as evidenced by the observation that the oil phases were murky and green upon the completion of emulsification. These findings indicate that the reagent caused $\theta_o > 90^\circ$. It appears, therefore, that Span 85 is an excellent hydrophobicity-enhancing agent.



Fig. 4.13 Effect of Span 85 (M) on emulsification using KAX-treated chalcopyrite particles as solid surfactant.

<u>*Pluronic L81*</u> This reagent is another kind of difunctional block copolymer with HLB = 2.0. The results obtained with this reagent are given in Fig. 4.14. At 0.09 kg/t, some emulsion

drops were drooping into the water phase. The amount of the drooping emulsion drops became less at higher concentrations, suggesting that the reagent adsorbs on the KAX-treated chalcopyrite surface with an inverse orientation. At > 0.36 kg/t, there was no evidence for drooping indicating that the contact angles of the particles were less than 90°. It appears, therefore, that Pluronic L181 is not a good hydrophobicity-enhancing agent.



Fig. 4.14 Effect of Pluronic L81 on emulsification using KAX-treated chalcopyrite particles as solid surfactant; dosages in kg/t.

Span 65 Fig. 4.15 shows the results obtained with KAX-treated chalcopyrite particles in the presence of Span 65 (sorbitan tristearate, HLB = 2.1). With this reagent, much of the emulsion drops fell into the water phase at 5.2 x 10⁻⁵ M Span 65 and higher, indicating that the reagent is an efficient hydrophobicity-enhancing agent that can increase the θ_o above 90°.



Fig. 4.15 Effect of Span 65 (M) on emulsification using KAX-treated chalcopyrite particles as solid surfactant.



Fig. 4.16 Effect of Span 83 (M) on emulsification using KAX-treated chalcopyrite particles as solid surfactant.

Span 83 Fig. 4.16 shows the emulsification tests conducted with KAX-treated chalcopyrite particles in the presence of Span 83 (sorbitan sequioleate, HLB = 3.0). The results varied substantially with Span 83 concentration. At 7.4 x 10⁻⁶ M, most of the chalcopyrite particles were recovered into the heptane phase, possibly in the form of o/w emulsions. At 1.5×10^{-5} M, it is evident that about 40% volume of the water phase was occupied by drooping emulsion drops, indicating that phase inversion has occurred as the θ_o of some particles became larger than 90°. When the concentration was further increased to 2.2×10^{-5} M, the phase inversion became complete with all the particles recovered in water phase in the form of w/o emulsion, which is the most desirable form of minerals recovery for the HHS process. At a higher Span 83 concentration, some particles became dispersed in the oil phase as their θ_o were increased near 180°, which could not be directly visualized in the photographs as they were taken after allowing particles to settle for overnight. However, it is clearly indicated by the appearance of emulsions in the fifth vial (left to right) of Fig. 4.16 (7.4 x 10^{-5} M) where the color of emulsions sitting nearby the o/w interface is much greener as those dispersed particles were accumulated into the oil channels among the w/o emulsions after allowing to settle for overnight.

<u>Genapol PF-20 and Polyethylene-block-poly(ethylene glycol)</u> Both Genapol PF-20 and polyethylene-block-poly(ethylene glycol) were surfactants with HLB = 4.0. Fig. 4.17 and Fig. 4.18 show the emulsification tests results obtained with Genapol PF-20 and polyethylene-block-poly(ethylene glycol), respectively. As shown, chalcopyrite particles were recovered as o/w emulsions rather than w/o emulsions with varying reagent dosages. Apparently, the contact angles of the chalcopyrite particles have not been increased sufficiently in the presence of Genapol PF-20 (Clariant Chemicals) or polyethylene-block-poly(ethylene glycol).



Fig. 4.17 Effect of of Genapol PF-20 on emulsification using KAX-treated chalcopyrite particles as solid surfactant; dosages in kg/t.



Fig. 4.18 Effect of polyethylene-block-poly (ethylene glycol) (M) on emulsification using KAX-treated chalcopyrite as solid surfactant.

<u>Span 80</u> This reagent (sorbitan monooleate, HLB = 4.3) is widely used for the formation of w/o emulsions, and its usefulness in facilitating the phase inversion of o/w emulsions to w/o emulsions using hydrophobic silica as a solid surfactant was shown in work conducted by Tshilumbu and Masalova (2015). As such, Span 80 was used in emulsification tests where KAXtreated chalcopyrite particles were used as a solid surfactant, with the results presented in Fig. 4.19. As shown, phase inversion began to occur at 4.7 x 10⁻⁵ M Span 80. As the concentration was increased to > 7 x 10⁻⁵ M, practically all of the mineral particles were recovered as w/o emulsions in the water phase.

The results obtained with various non-ionic surfactants presented in the foregoing paragraphs show that the HLB number is a useful guide for choosing an appropriate hydrophobicity-enhancing agent. However, it is not an absolute guide for predicting phase inversion. Of the various low-HLB surfactants tested in the present work, Span[®] group emulsifiers, obviously, are suitable for inducing the phase inversion.

It is worth mentioning that when the Span[®] concentration was increased to a certain level at which phase inversion was complete, chalcopyrite particles were seen dispersing into the oil phases with the case of Span 65 as an exception. This indicates that the w/o emulsions formed with



Fig. 4.19 Effect of Span 80 (M) on emulsification using KAXtreated chalcopyrite particles as solid surfactant.

Span 65 were more stable to break as compared to those formed with the other three Span[®] emulsifiers.

Emulsion stability is well correlated to the emulsion drop size, the higher instability of emulsion droplets, the easier for them to coalesce and therefore forming larger emulsion droplets. Emulsification tests using hydroxyapatite particles and Span 80 as emulsifiers performed by Song et al. (2018) showed that with increasing Span 80 concentration, the droplet diameter of the w/o emulsion increased while the emulsion stability decreased. It is noted in Fig. 4.15 that the apparent size of the w/o emulsion droplets obtained at different Span 65 concentrations were fine and did not change significantly. While those obtained with Span 85, Span 83, and Span 80, presented in Fig. 4.13, Fig. 4.16, and Fig. 4.19, respectively, were gradually increased with the increase of Span[®] concentration. These pieces of evidence also indicated the w/o emulsions stabilized by Span 65 were more stable than those obtained with the other three Span[®] emulsifiers. Since the HHS process would favor a w/o emulsion with weak stability, it can be concluded that when the surfactant concentration is in the range that was used in this work, Span 80, Span 83, and Span 85 are better hydrophobicity-enhancing agents than Span 65.



Fig. 4.20 Effect of SMO on the air and oil (heptane) contact angles.

As has been mentioned in this section, it is easy to transform an o/w Pickering emulsion to w/o Pickering emulsion by using a small amount of Span[®] emulsifiers with low HLB values. To obtain a better understanding of the mechanism, a series of contact angle measurements were conducted on a hydrophobic quartz plate that has been further hydrophobized with various amount of SMO (Span 80). When the plate was silvlated with octadecyltrichlorosilane (OTS), the contact angles measured with an air bubble and an oil (n-heptane) drop were 52° and 84°, respectively. When the plate was treated in SMO-in-heptane solutions of different concentrations, the air and oil contact angles changed, as shown in Fig. 4.20. As shown, the oil contact angles were substantially larger than the air contact angles, which is a rationale to use oil droplets rather than air bubbles to recover fine particles. At 1.4 x 10⁻⁴ M SMO, the oil contact angle became larger than 90° , which is a thermodynamic requirement for phase inversion. After treating the plate in a 5.7 x 10⁻³ M SMO-in-pentane solution, the oil contact angle became as large as 170°, while air contact angle decreased to 45°. The results presented in Fig. 4.20 shows that SMO is an excellent 'tool' to induce phase inversion, which is essential to use the Morganizer in the HHS process and hence produce high-grade concentrates.

The reasons for the large differences between the air (52°) and oil (84°) contact angles can be explained by means of Young's equation. For air contact angle (θ_A), one can write the following relation:

$$\cos\theta_A = \frac{\gamma_S - \gamma_{SW}}{\gamma_W} \tag{4.3}$$

For oil contact angle (θ_0), one can write:

$$\cos\theta_0 = \frac{\gamma_{SO} - \gamma_{SW}}{\gamma_{WO}} \tag{4.4}$$

in which γ_{SO} is the interfacial tension at the solid/oil interface, and γ_{WO} is the interfacial tension at the water/oil interface.

One can determine the γ_{SW} and γ_{SO} using the acid-base theory (Van Oss, 2006) as follows,

$$\gamma_{SW} = \gamma_S + \gamma_W - 2\sqrt{\gamma_S^{LW}\gamma_W^{LW}} - 2\sqrt{\gamma_S^+\gamma_W^-} - 2\sqrt{\gamma_S^-\gamma_W^+}$$
(4.5)

$$\gamma_{SO} = \gamma_S + \gamma_O - 2\sqrt{\gamma_S^{LW}\gamma_O^{LW}} - 2\sqrt{\gamma_S^+\gamma_O^-} - 2\sqrt{\gamma_S^-\gamma_O^+}$$
(4.6)

in which γ_0 is the surface tension of oil, γ^{LW} is the surface tension component due to the Lifshitzvan der Waals interactions (apolar), and γ^+ and γ^- are the surface tension component due to the acid-base interaction (polar). If the oil is *n*-heptane, then the polar parts of oil (γ_0^+ and γ_0^-) will become zero, because *n*-heptane is a completely apolar liquid. Eq. (4.6) can then be simplified as

$$\gamma_{SO} = \gamma_S + \gamma_O - 2\sqrt{\gamma_S^{LW} \gamma_O^{LW}} \tag{4.7}$$

In general, $(\gamma_0 - 2\sqrt{\gamma_s^{LW}\gamma_0^{LW}}) < 0$,

Therefore,

$$\gamma_{SO} < \gamma_S \tag{4.8}$$

and, hence,

$$\gamma_{SO} - \gamma_{SW} < \gamma_S - \gamma_{SW} \tag{4.9}$$

From Eqs. (4.9), (4.3), and (4.4), one obtains that $\theta_0 > \theta_A$, which is consistent with the measurements.

SMO is a non-ionic surfactant, which has a polar (hydrophilic) group at one end and an apolar group (hydrocarbon chain) at the other end. If a moderately hydrophobic solid surface with θ_A in the range of 55-65° is treated with a small amount of SMO, γ_S will decrease due to the surfactant adsorption with its polar group in touch with the hydrophilic part of the surface *via* an acid-base interaction, which will lead to a lower γ_{SO} . This will, in turn, cause the numerator ($\gamma_{SO} - \gamma_{SW}$) of Eq. (4.4) to decrease and hence increase θ_O . The SMO adsorption should also increase γ_{SW} by decreasing γ_S^+ and γ_S^- and hence cause the last two terms of Eq. (4.5) to be more negative, while

at the same time causing γ_{SO} to decrease as has been noted above. If SMO adsorption continues, the numerator of Eq. (4.4) will become negative and cause θ_O to be larger than 90°. The SMO should also adsorb to the oil/water interface, in which case γ_{WO} will decrease, which should in turn increase θ_O approaching 180° as shown in Fig. 4.20.

According to the acid-base theory, the interfacial tension at the water/oil interface (γ_{WO}) can be written as follows,

$$\gamma_{WO} = \gamma_W + \gamma_O - 2\sqrt{\gamma_W^{LW}\gamma_O^{LW}} - 2\sqrt{\gamma_W^+\gamma_O^-} - 2\sqrt{\gamma_W^-\gamma_O^+}$$
(4.10)

In the absence of surfactant, the last two terms of Eq. (4.10) drop out as both γ_0^+ and γ_0^- are zero. In the presence of SMO, however, they will have finite positive values, causing the interfacial tension to decrease.

As for θ_A , the numerator of Eq. (4.3) can become negative if the wetting tension, i.e., $\gamma_S - \gamma_{SW}$, becomes negative, which should increase the air contact angle above 90°. However, the denominator of Eq. (4.3), *i.e.*, γ_W , is much larger than γ_{OW} . It is, therefore, difficult to increase θ_A close to θ_O , which is a distinct advantage of the HHS process over flotation.

4.3.3 Application of Phase Inversion to Recover Ultrafine Particles

Previous phase inversion studies show that a phase inversion can be achieved by increasing particle hydrophobicity, which can be achieved by virtue of hydrophobicity-enhancing agents. It will be of interest to see how this kind of phase inversion affects the HHS process. As such, a series of HHS tests was conducted on single OTS-coated silica mineral sample, and also an artificial monazite ore sample, in which SMO (Span 80) was chosen as the hydrophobicity-enhancing agent.



Fig. 4.21 Effect of oil contact angle (θ_o) on the recovery of OTScoated silica particles using the HHS process (red). Phase inversion from o/w to w/o emulsions occurs at $\theta_o > 90^\circ$, which is necessary for the liberation of hydrophobic particles from water drops in oil phase (green). Liberation increases with increasing θ_o .

4.3.3.1 Silica Sample

Effect of Oil Contact Angle The red curve of Fig. 4.21 shows the results obtained using the OTS-coated silica particles of varying oil contact angle (θ_o). As shown, the silica particles with θ_o < 90° were recovered as o/w emulsion drops, while those with $\theta_o > 90°$ were recovered as w/o emulsion drops. The results show also that the recovery increased with increasing contact angle, reaching a 100% recovery at $\theta_o = 95°$. A small decrease in recovery observed at higher contact angles was due to the falling of some w/o emulsion drops that were heavily loaded with particles into the water phase.

The green curve in Fig. 4.21 represents the percentages of silica particles constituting w/o emulsions broken away from the small droplets of water by gentle agitation by handshaking. As shown, amounts of particles broken away (or liberated) from water in this manner increased with



Fig. 4.22 Effect of SMO on the recovery of OTS-coated silica particles with $\theta_o = 79^\circ$ (red). SMO increased the recovery of hydrophobic particles and induced phase inversion at $\theta_o > 90^\circ$, which made it possible to liberate hydrophobic particles from water drops (green). Liberation increased with SMO dosage.

increasing contact angle (θ_o). The reason may be given as follows: the higher the contact angle of a particle, the smaller volume of the particle is immersed into a water drop, which should make it easier to detach the particle from a water droplet. The results presented in Fig. 4.21 show how critical contact angle is in the HHS process.

<u>Effect of SMO</u> Fig 4.22 shows the results obtained with silica particles whose oil contact angle was only 79°. The test conducted without using SMO as a secondary hydrophobizing agent showed a 74.2% recovery. When small amounts of SMO were added in the amounts of 0.5- and 1.0 x 10⁻⁴ M to increase $\theta_o > 79^\circ$ but still below 90°, the recoveries were increased to 100% as shown by the red curve. Under these conditions, the silica particles were recovered as o/w emulsion drops. When the SMO dosage was further increased to 2 x 10⁻⁴ M and higher, θ_o became larger than 90°, which in turn caused o/w emulsion drops to be converted to w/o emulsions drops. Under this condition, the w/o emulsion drops could be broken more readily by the mechanical force



Fig. 4.23 Effect of SMO on the recovery of OTS-coated silica particles with $\theta_o = 120^\circ$ (red). Mineral liberation is much higher than observed with the OTS silica particles of lower contact angles (green).

created by handshaking. The silica particles liberated from emulsion drops stayed in the organic phase as a dispersion. The water droplets free of hydrophobic silica particles fell to the aqueous phase below. The green curve represents the percentages of the silica particles liberated from w/o emulsion drops.

Fig. 4.23 shows the results obtained with silica particles with $\theta_o = 120^\circ$. Since it was difficult to disperse the particles with such a high contact angle in water, they were dispersed in heptane first and treated with SMO before adding 50 ml of water. The recoveries were 89.0% in the absence of SMO. In the presence of SMO, the recovery was further increased (red curve). Note also that the percentages of silica particles liberated from water droplets were substantially higher than obtained with particles with lower contact angles (see Fig. 4.22 and Fig. 4.23). As noted above, the higher the contact angle, the easier it is to liberate the particles from water drops.

Mechanism of Pickering Emulsions Stabilized by OTS-coated Silica Particles with

Different Concentrations of SMO Comparison of Fig. 4.21 and Fig. 4.22 clearly shows that SMO increased the hydrophobicity of the less hydrophobic OTS-coated silica particles. However, it is also evidently shown in Fig. 4.22 and Fig. 4.23 (green curves) that the liberation of hydrophobic particles from water drops was deteriorated at a relatively high concentration of SMO. Therefore, it will be meaningful to discuss the adsorption mechanisms of SMO at different concentrations.

Nesterenko et al. (2014) investigated the effect of SMO on the paraffin oil/water interfacial tension, which was measured with and without the presence of silica particles in the system. The data showed that when no particles were added, the oil/water interfacial tension decreased with increasing the SMO concentration. When silica particles were added to the system, however, the oil/water interfacial tension did not decrease unless the SMO concentration reached > 0.01% (w/w). They attributed this to the interactions between SMO and silica particles were much stronger than that of the oil/water interface at lower concentrations. This was supported further by the work of Raman and Aichele (2018), where the depletion of SMO from the o/w interface was due to the presence of partially hydrophobic silica particles in the oil-water mixture. In this regard, it is reasonable to infer that when the SMO concentration used in Fig. 4.22 was less than 3 x 10⁻⁴ M, SMO primarily acted as a hydrophobicity-enhancing agent such that all of the SMO molecules adsorbed preferably onto the OTS-coated silica particles to increase their hydrophobicity to above 90° for phase inversion. Once the silica particles are saturated with SMO molecules, the excess SMO molecules would start to concentrate at the o/w interfaces. Due to the reduction of oil/water interfacial tension, the θ_o of particles was further increased and facilitated the liberation of hydrophobic particles from water drops to the oil phase, as evidenced in Fig. 4.22 (green curve).

On the other hand, as shown in Fig. 4.22, when the SMO concentration was increased to no less than 4 x 10^{-4} M, the recovery of liberated particles reduced. This could be related to the presence of additional free SMO molecules in the system at this SMO concentration level, such that w/o emulsions could be stabilized by SMO alone without involving particles. These emulsions were of much finer drop sizes as compared to the Pickering emulsions. The flocculation and aggregation of these fine drops allowed the creation of barriers to prevent the coalescence of large Pickering emulsion drops and thereby deteriorated the liberation of particles from w/o emulsions (Nesterenko et al., 2014).

4.3.3.2 Monazite Sample

<u>TLF Method</u> Fig. 4.24 shows the results of TLF tests conducted on a single monazite sample ($d_{80} = 7.4 \mu m$) using OHA in a range of 0 to 5.8 x 10⁻⁴ M as a collector. In a given TLF test, 1 g sample together with 80 mL OHA solution was put into a 250 mL separatory funnel. After adjusting the solution to pH = 9.5, the separator funnel was hand-shaken for 10 minutes to render



Fig. 4.24 Effect of OHA on the weight recovery of ultrafine monazite particles by two-liquid flotation.

monazite particles hydrophobic. After that, a volume (40 mL) of heptane was added to the slurry. The mixture was again hand-shaken for 5 minutes to stabilize Pickering emulsions such that the hydrophobic particles can be recovered. After the emulsion forming operation, the mixture was allowed to stand for 5 minutes in order to separate the emulsion phase (top) from the water phase (bottom). The dried solids in these two phases were weighed to determine the weight recovery of ultrafine monazite particles.

As shown, an increase in the collector concentration has led to an increase in weight recovery, and the maximum weight recovery was 96% at 5.8 x 10^{-4} M OHA. Note here that the monazite particles were initially recovered as o/w emulsions in the tested OHA concentration ranges, which suggests that the θ_o of monazite particles did not reach above 90° using a primary hydrophobizing agent alone. On the other hand, w/o emulsions could be formed by means of hand-shaking after removing the aqueous phase at the bottom of the separator funnel. However, these w/o emulsions that were induced by increasing the oil phase volume would not break in oil. These findings are consistent with the results obtained on OTS-coated silica particles (see Fig. 4.3), all indicating that $\theta_o > 90^\circ$ is a necessary thermodynamic requirement for dispersing the particles from w/o emulsions into the oil. Only under such condition, the HHS process can be implemented.

<u>HHS Method</u> The HHS test results attained from OTS-coated silica particles showed that it is feasible to perform the HHS test on particles of $\theta_o < 79^\circ$ after the employment of SMO. Therefore, a SMO-assisted HHS test was also conducted on an artificial rare earth ore sample. The sample was prepared by mixing 2 g monazite with 50 g silica with d₈₀ = 3 and 9 µm. The grade of the artificial ore was 2.11% REE.

In the HHS test, a feed sample was first dispersed in a 250 ml separatory funnel containing 80 ml water via 10 minutes hand-shaking. After fully dispersing the particles, the suspension pH

was adjusted to 9.5 prior to the addition of 1 kg/t OHA to the separatory funnel. The separatory funnel was then hand-shaken for another 5 minutes to selectively render monazite particles hydrophobic. Thereafter, a volume (80 ml) of heptane was added to the separatory funnel before hand-shaking the mixture for another 5 minutes. During this step, hydrophobic monazite particles were recovered as o/w emulsions. The mixture was then stood for 2 minutes to allow for a phase separatory funnel, 2 x 10^{-4} M SMO carried in heptane was added to the remaining emulsion phase. The mixture was then subjected to agitation to further increase particles hydrophobicity such that all the o/w emulsions were converted to w/o emulsions. The w/o emulsions formed were subsequently broken by a gentle mechanical force that resulted the hydrophobic monazite particles to get dispersed into the oil phase. The particles recovered as a particle-in-oil dispersion were considered as the monazite concentrate.

It is noted that in this monazite HHS test SMO was added after rejecting most of the gangue silica particles, which differed from that of the OTS-coated silica HHS test. This is because, in the feed of the former, there existed a large amount of hydrophilic gangue particles. According to Binks and Olusanya (2018), the type of Pickering emulsion stabilized by particles is dependent on the composite wettability of all particles presented in the system rather than the wettability of one specific type particle in the particles mixture. By increasing the weight fraction of hydrophilic particles, transitional phase inversion of emulsions from w/o to o/w would be favored. In other words, the formation of w/o emulsions stabilized by hydrophobic target particles may be prohibited if the majority of the particles in the system are hydrophilic. This is very true in the synthetic monazite ore system. From this viewpoint, it is of significant importance to eliminate the majority of silica particles in this Monazite HHS test.

Products	Weight	REE (%	REE (%)	
	%	Grade	Recovery	
Conc.	3.1	62.57	93.1	
Tail	96.9	0.15	6.9	
Feed*	100.0	2.11	100.0	

Tab. 4.2 Results of the HHS test conducted on an artificial monazite ore sample.

Feed: 2 g monazite ($d_{80} = 3 \mu m$) mixed with 50 g silica ($d_{80} = 9 \mu m$)

As shown in Table 4.2, the results were excellent. A high-grade monazite concentrate assaying 62.57 %REE was obtained at a recovery of 93.1%. This result shows that it is highly possible to further improve the work that will be discussed in the Chapter 6 on the recovery of ultrafine disseminated rare earth mineral particles from coal by using this new HHS approach.

4.4 Conclusion

Previous studies indicated that phase inversion of o/w emulsions to w/o emulsions was an essential prerequisite for applying the HHS process; therefore, the fundamental aspects affecting phase inversion were studied in the present work. The emulsification tests using OTS-coated silica particles as emulsifiers show that emulsion transformation from o/w to w/o can be achieved either by increasing the oil phase volume or by increasing particles' hydrophobicity. However, it is worth noting that when the particles were of $\theta_o < 90^\circ$, the phase conversion induced by increasing oil phase volume also relied on energy input. In general, the less hydrophobic the particles, the higher the energy input required.

The emulsification study to achieve phase inversion was also carried out using ultrafine chalcopyrite particles as emulsifiers at $\phi_o = 0.5$, in which the phase inversion was induced by increasing particles' hydrophobicity by virtue of various hydrophobicity-enhancing agents. The results show that o/w emulsions stabilized by less hydrophobic chalcopyrite particles could be

converted to w/o emulsions when the particles were further treated using suitable amounts of polybutadiene(dicarboxy-terminated) and Span[®] group non-ionic surfactants. The results also show that the HLB number is not an absolute guide for predicting phase inversion.

In the HHS process, the prepared w/o emulsions were broken up using a Morganizer, which liberated the hydrophobic particles from the surface of water drops into the oil phase. This Morganizing process is more efficient if the formed w/o emulsions are less stable. In this regard, of the effective hydrophobicity-enhancing agents capable of promoting the phase inversion of o/w emulsions stabilized by chalcopyrite particles of $\theta_o < 90^\circ$ to w/o emulsions, Span[®] group non-ionic surfactants are better than polybutadiene(dicarboxy-terminated).

Based on this improved understanding of phase inversion, a series of HHS tests was carried out on OTS-coated silica particles of various θ_o , in which SMO (Span 80) was used as a hydrophobicity-enhancing agent for OTS-coated silica particles. The HHS results show that $\theta_o >$ 90° is a thermodynamic requirement both for converting o/w emulsions to w/o emulsions and liberating particles from water drops to oil, which can be achieved by SMO. In light of the role of SMO, ultrafine monazite particles were selectively recovered from an artificial sample using the SMO-assisted HHS process. The information collected from the HHS test on a model monazite ore may be readily applicable to address the problem discussed in the Chapter 3, in which the HHS process was exploited to recover ultrafine REMs from coal byproduct.

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Chapter 5 Fundamental Aspects of Oil Agglomeration of Chalcopyrite Particles

Abstract

Studies in previous chapters show that oil agglomeration is an essential step in the HHS process for the recovery of coal fines. However, no work has been reported in the past regarding the oil agglomeration of chalcopyrite using a recyclable oil. As such, the fundamental aspects affecting the oil agglomeration of chalcopyrite using heptane as the agglomerant was investigated in order to guide the application of the HHS process for copper minerals. In this study, oil agglomeration tests were first conducted on an artificial mixture consisting of chalcopyrite and silica particles using KAX alone, in which the effects of agitation time, oil dosage, and stirring speed were studied. The results show that high Cu grades and recoveries were achieved, albeit at slow agglomeration kinetics. Recognizing this problem, oil agglomeration of chalcopyrite was further investigated by hydrophobizing particles with two-step hydrophobization, in which KAX and hydrophobic polymer (PX-1) were used as primary and secondary hydrophobizing agents, respectively. Comparison of the agglomeration results obtained with and without PX-1 shows that the use of PX-1 had significant effects on the kinetics of oil agglomeration. When 250 g/t of PX-1 was employed, the agglomeration time was reduced substantially to 10 minutes from 50-70 minutes in achieving a similar high Cu recovery. Furthermore, oil contact angle measurements carried out on a polished chalcopyrite plate treated with PX-1 showed that adsorption of PX-1 on chalcopyrite particles' surface significantly increased its hydrophobicity.

5.1 Introduction

The number of fine and ultrafine particles in the flotation feed will be increased due to the popularization of mechanized mining methods and the demand of finer grinding for suitable

liberation of target minerals, owing to the declining of raw ore grades on a world scale (Calvo et al., 2016). High volume of fine fraction could bring considerable challenges to the air flotation technique because of its limitations in recovering fine particles (Miettinen et al., 2010). In search of a solution to this problem, numerous studies with emphasis on either reducing the bubble size or enlarging the apparent size of target particles have been performed on fine coal and mineral flotation.

With respect to bubble size, lab-scale flotation investigations showed that the recovery of particles beyond the optimum size range can be enhanced by using nanobubbles (Tao et al., 2008, Ahmadi et al., 2014, Calgaroto et al., 2015); however, the very slow rising velocity of nanobubbles and relatively high energy consumption required to generate nanobubbles limited its practical application at the industry-scale. In addition, the selectivity in the flotation process using nanobubbles is not extensively explored because most of the related research was conducted on single mineral systems. An investigation regarding the fine coal flotation with nanobubbles conducted by Sobhy and Tao (2013) showed that under most testing conditions, the clean coal obtained in the presence of nanobubbles had higher ash contents than those obtained without nanobubbles.

Based on the concept of increasing apparent separation size, shear flocculation flotation, carrier flotation, and agglomeration flotation techniques were developed to recover fine and ultrafine particles with many successes being reported in the literature (Fu et al., 2012; Pascoe and Doherty, 1997; Rubio and Hoberg, 1993; Song et al., 2001; Subrahmanyam and Forssberg, 1990; Valderrama and Rubio, 1998). Unfortunately, these methods were more or less problematic due to inevitably unselective adsorption of flocculants on the gangue particles in shear flocculation flotation, slime coating occurred on coarser valuable particles which function as carriers in carrier

flotation, and the enhanced destabilizing effect of oil and oil/particle agglomerates to froth zone in agglomeration flotation (Attia and Deason, 1989; Capponi et al., 2003; Leistner et al., 2016).

According to the above discussion, it can be inferred that flotation may not be a viable technique for the selective recovery of fine and ultrafine particles. Therefore, many researchers explored alternative methods. One of them is the oil agglomeration, which is a process that depends on the preferential wetting of the suspended hydrophobic particles by the bridging liquid. Under an appropriate mixing condition, the oil-coated particles collide with each other, and liquid bridges form among particles and thereby cause agglomeration. The oil agglomeration process has been demonstrated in the recovery of fine and ultrafine particles, including coal (Armstrong, 1979; Capes and Darcovich, 1984; Meherotra, 1983), barite (Sadowski, 1994; Sönmez and Cebeci, 2003), celestite (Cebeci and Sönmez, 2003), ilmenite (Sparks and Wong, 1973), wolframite (Kelsall and Pitt, 1987; Wei et al., 1985), pyrite (Drzymala et al., 1990), molybdenite (Yang et al, 2014), nickel ore (Polowczyk et al., 2008), and chalcopyrite (Cadzow et al., 1984; House and Veal, 1988). Mehrotra et al. (1983) have concluded that the oil agglomeration process is the most promising method for the recovery of fine and ultrafine particles.

Chalcopyrite is the most abundant copper-bearing mineral that consists of approximately 70% of the world's known copper reserves (Wang, 2005). Mankosa et al. (2016) reported that it is difficult for flotation to selectively recover the chalcopyrite particles of a size smaller than 30 μ m. In addition, oil agglomeration of chalcopyrite has only been studied using heavy oils, such as kerosene, that are not able to be recovered at a low heating temperature (Cadzow, 1985; House and Veal, 1989). As such, in this work the oil agglomeration of chalcopyrite fines (< 30 μ m) was further explored using heptane, which is recyclable, as an agglomerant. Experimental parameters investigated were collector dosage, agglomeration time, stirring speed, condition time, oil dosage,

and hydrophobicity-enhancing agent dosage. The effect of hydrophobicity-enhancing agent PX-1 on the agglomeration kinetics was discussed in conjunction with the contact angle measurements.

5.2 Experimental

5.2.1 Materials

A sample of specimen-grade chalcopyrite was purchased from Ward's Science. The chunky chalcopyrite, received as 1 x 1" to 1 x 2", was crushed by means of a handheld hammer to < 1.18 mm prior to wet-grinding in a laboratory ball mill. Chalcopyrite samples with $d_{80} = 29.3 \mu m$ ($d_{50} = 12.5 \mu m$) and 12.3 μm ($d_{50} = 5.8 \mu m$) obtained after 7 minutes and 25 minutes grinding, respectively, were used in this work. The samples obtained in this manner assayed 26.6 %Cu as determined by using the ICP-MS analyzer. Silica powder sample with $d_{80} = 35 \mu m$ was used as a diluent to prepare the artificial copper feed sample. Potassium amyl xanthate (KAX) of > 95% purity obtained from TCI America was used as the collector for chalcopyrite without further purification. Hydrophobic polymer poly (2-ethyl hexyl) methacrylate (PX-1) blended with kerosene at a weight ratio of 1:2 was obtained from Nalco Company and used as the secondary hydrophobizing agent for chalcopyrite fines. HPLC grade n-heptane (99.9% purity) was obtained from Fisher Scientific. Hydrochloric acid and sodium hydroxide of analytical grade were used as pH modifiers. All tests were carried out using tap water.

5.2.2 Agglomeration

The agglomeration tests were carried out in a 6-Cup glass jar with the 7-speed Oster® kitchen blender. In each test, a mixture of 5 g chalcopyrite particles and 95 g silica particles was placed in the glass jar containing 750 ml water. After agitating the suspension using an overhead mixer with a 2-inch diameter impeller with 3-twisted blades for 10 minutes at 750 RPM, the slurry pH was adjusted to 9.5 and further conditioned for 5 minutes with the addition of a known amount

of KAX. After the hydrophobizing treatment with KAX, a volume of heptane varying in the range of 2.1-6.2 % weight of feed was added to the slurry before high-shearing the slurry using the kitchen blender for 90 seconds. Thereafter, the slurry was agitated again using the overhead mixer at a low-shear speed at which agglomerates formed and grew up. The details of the experimental conditions are given in related figures. On completion of the agglomeration test, the slurry was poured over a 106 µm test sieve to recover the agglomerated material. Agglomerates were filtered and oven-dried overnight prior to sending out for Cu elemental analysis by ICP-MS analyzer.

In this work, the effect of hydrophobic polymer PX-1 on the agglomeration of chalcopyrite particles was also studied. The test procedure was about the same as described above, except that another 2 minutes conditioning with PX-1 was conducted right after the hydrophobization step with KAX.

5.2.3 Contact Angle Measurement

A chalcopyrite plate with a dimension of 1" x 0.5" x 0.2" cut from a piece of chunky chalcopyrite specimen was used in all measurements. Before conducting the contact angle measurement test, the chalcopyrite surface was polished wet using a set of silicon carbide papers and then with 0.25 μ m diamond paste. The polished chalcopyrite plate was rinsed with deionized water and dried by blowing ultra-pure nitrogen prior to the hydrophobizing treatment.

In each test, the chalcopyrite plate was first conditioned in 30 ml of 10⁻⁶ M KEX solution at a natural pH for 10 minutes and then transferred to a beaker containing a known amount of PXlin the form of emulsions and agitated by means of a magnetic stirrer for 10 or 20 minutes. After this two-step hydrophobizing treatment, the chalcopyrite plate was taken out of the solution, dried with nitrogen, and placed in deionized water. A pentane drop was then brought to the polished surface from underneath the surface for contact angle measurement using a Ramé-Hart goniometer.

5.3 Results and Discussion

5.3.1 Oil Agglomeration without Hydrophobic Polymer PX-1

A series of agglomeration tests was conducted on chalcopyrite particles with a size of d_{80} = 29.3 µm. All the tests were performed using 1 kg/t KAX as the collector and without using hydrophobic polymer PX-1 as a secondary hydrophobizing reagent.

5.3.1.1 Agitation Time

The effect of agitation time on the oil agglomeration of chalcopyrite is given in Fig. 5.1. The agitation time varied in the range of 30 to 90 minutes. This set of tests was conducted using 4.8% wt. of heptane as an agglomerant at 1300 RPM. As shown, the variation of agitation time in the chosen range did not cause significant changes in the Cu grade, which varied only slightly, around 28%. Meanwhile, the Cu recovery increased with increasing agitation time. However, the agglomeration rate was too slow as it took at least 70 minutes to achieve a > 90% Cu recovery. The highest Cu recovery was obtained at 90 minutes agitation time, which was 95.78%.



Fig. 5.1 Effect of agitation time on the agglomeration of chalcopyrite. Oil agglomeration was conducted without the addition of PX-1.

According to Bemer and Zuiderweg (1980), four growth regimes occur during the course of spherical agglomeration. The low recovery at 30 minutes agitation time might be because the growth of agglomerates was still in the zero-growth regime; thereby most of the oil-coated particles were present in the form of loose flocs and micro-agglomerates that had dimensions smaller than the screen opening. Increasing the agitation time to 50 minutes brought the agglomeration to the fast growth regime, in which most of the flocs and micro-agglomerates consolidated and formed compact agglomerates with a considerable size, resulting in a rapid increase in Cu recovery to 85.73%. With further increase in agitation time to 70 minutes and 90 minutes, the growth of the agglomerates fell to the equilibrium regime and consequently slowed down the increase rate of recovery. It was observed that the average size of agglomerates did increase with the increase of agitation time. Apparently, the Cu recovery correlates with the size of agglomerates.



Fig. 5.2 Effect of oil dosage on oil agglomeration of chalcopyrite. Oil agglomeration was conducted without the addition of PX-1.

5.3.1.2 Oil Dosage

Fig. 5.2 shows the oil agglomeration results obtained at various amounts of heptane. Agglomerant dosage was based on the mass ratio of heptane to feed. In this set of tests, chalcopyrite particles were agglomerated for 70 minutes at 1300 RPM. As can be seen, the Cu recovery increased with the increase of the heptane dosage and reached its maximum value (91.75%) at 4.8 % wt. of heptane; after that, it decreased to 82.52% at 6.2 % wt. of heptane.

At 2.1 %wt. of heptane, the oil agglomeration test gave the lowest recovery. This was attributed to insufficient liquid bridges formed among the chalcopyrite particles so that some of them were agglomerated at the pendular state. As a result, they were easily broken down by agitating and were lost during the screening separation (Sparks and Wong, 1973). As the amount of heptane increased to 3.4 and 4.8 %wt., the voids among particles progressively filled up with oil and the hydrophobic particles were drawn closer by capillary forces, which led to the formation of the compact spherical agglomerates that are of stronger physical strength as compared to the pendular state agglomerates. Therefore, the recovery was increased. At 6.2 %wt. of heptane dosage, a thin green oil film, in which ultrafine hydrophobic chalcopyrite particles were dispersed, was seen floating over the top of the slurry phase after stopping the agitation. Thus, the decrease in Cu recovery at this oil dosage was most probably due to the loss of the oil film during screening. According to Cebeci et al. (2002), the same problem was observed in the agglomeration of a bituminous coal sample.

It is also shown in Fig. 5.2 that the Cu grade was increased from 27.8% to 30.7% as the heptane dosage was increased from 4.8% to 6.2 %wt. This may be a result of the enhanced replacement by oil of the water droplets containing silica particles from the voids inside the agglomerates.

5.3.1.3 Stirring Speed

According to classical DLVO theory, hydrophobic agglomeration of particles will not occur unless the particles are endowed with enough kinetic energy to overcome the potential energy barrier. The energy input is mainly determined by the stirring speed in terms of a defined experimental system. Therefore, the effect of kinetic energy on the oil agglomeration of chalcopyrite was carried out by varying the stirring speed. Fig 5.3 shows the results of agglomeration tests performed at two different oil dosages with the stirring speed varied from 700 to 1500 RPM. The agitation time was 70 minutes. As shown, the Cu recovery increased with increasing stirring speed and reached the maximum at 900 RPM. However, a further increase in the stirring speed to 1500 RPM would lead to a significant decline of the Cu recovery. It is also noted in Fig. 5.3 that oil agglomeration tests conducted at 3.4 %wt. of heptane all produced higher Cu recoveries than those conducted at 2.1 %wt. of heptane, which is in line with the results presented in Fig. 5.2.



Fig. 5.3 Effect of stirring speed on oil agglomeration of chalcopyrite. Oil agglomeration was conducted without the addition of PX-1.

Hydrophobic agglomeration is a dynamic process of agglomerate formation and disruption (Lu et al., 1998). At 700 RPM, the kinetic energy input was not enough, resulting in the small collision probability between oil-coated particles in the suspension, consequently causing the low recovery. At 900 RPM, it is highly possible that the formation and disruption of agglomerates reached equilibrium, resulting in maximum Cu recovery. When the stirring speed was increased above 900 RPM, the breakage rate of agglomerates became faster than the formation rate of agglomerates so that the recovery gradually decreased. A similar agglomeration behavior at varying stirring speeds was observed by Cebeci and Sönmez (2004).

As noted in Fig. 5.3, the Cu grades obtained at various conditions were consistently high with the exception of the test conducted at 1500 RPM in the presence of 2.1 % wt. of heptane. The apparent drop of Cu grade in this test was largely due to the vast decrease of Cu recovery.

5.3.2 Oil Agglomeration with Hydrophobic Polymer PX-1

The results achieved in the above-mentioned section demonstrated that the oil agglomeration technique could effectively recover fine mineral particles with high separation efficiency. However, the kinetics of oil agglomeration of chalcopyrite was fairly slow as evidenced by the fact that it took 70 minutes to achieve > 90% Cu recoveries at 4.8 % wt. of heptane (see Fig. 5.1). Thus, exploring the possibility of improving the agglomeration kinetics would be of interest. Duzyol and Ozkan (2014) studied the influence of contact angle on the oil agglomeration of celestite mineral fines and found that the recovery of celestite significantly improved by increasing the contact angle. The foregoing agglomeration tests were carried out using KAX as the sole collector, which might have a limited ability to increase the hydrophobicity of chalcopyrite particles. Zhang et al. (2012) employed a two-step hydrophobization process to hydrophobize small diamonds, and the flotation results showed that near 100% recoveries were obtained using



Fig. 5.4 Effect of hydrophobic polymer PX-1 on oil agglomeration of chalcopyrite. Oil agglomeration was conducted on two different sizes(d_{80}): 12.3 µm and 29.3 µm.

PX-1 as a secondary hydrophobizing agent. In light of this, a series of oil agglomeration tests was performed with the aid of hydrophobic polymer PX-1. In order to differentiate the effect of PX-1, the optimum conditions identified in previous tests were not adopted in the following tests.

5.3.2.1 Hydrophobic Polymer PX-1

Fig. 5.4 shows the results of agglomeration tests conducted at varying PX-1 dosages on artificial samples comprising of chalcopyrite particles at two sizes: $d_{80} = 29.3$ and 12.3 µm. Prior to employing the hydrophobicity-enhancing agent PX-1, the samples were conditioned at 2 kg/t KAX. The tests were carried out at 2.1 % wt. heptane, 900 RPM, and 30 minutes agitation time. As shown, the Cu recovery increased with increasing the dosage of PX-1, and high recoveries (> 90%) were produced on feeds containing chalcopyrite particles of $d_{80} = 29.3$ and 12.3 µm, indicating that there is no size limitation for the oil agglomeration process as long as the particles are rendered sufficiently hydrophobic. Fig. 5.4 also shows when the PX-1 was at 250 and 375 g/t, the Cu recoveries obtained on chalcopyrite particles of $d_{80} = 12.3$ µm were lower than those


Fig. 5.5 The contact angle of a pentane drop on a 10⁻⁶ M KEX-treated chalcopyrite plate measured in water as a function of PX-1 concentration at nature pH. PX-1 treatment time: a) 10 minutes;
b) 20 minutes.

obtained on chalcopyrite particles of $d_{80} = 29.3 \ \mu\text{m}$. This can be attributed to the lack of the amounts of KAX and PX-1 used in the former as the total particles' surface areas had been increased substantially as a result of size reduction.

A series of contact angle measurements was conducted to reveal the beneficial role PX-1 played in the oil agglomeration of the fine and ultrafine chalcopyrite particles, with the results presented in Fig. 5.5. As shown, the oil contact angle increased with the increase of both PX-1 concentration and conditioning time. At a suitable dosage of PX-1, it could easily be increased to > 90°, of which the agglomeration of chalcopyrite particles was favored. This finding showed that PX-1 could further enhance the hydrophobicity of a slightly hydrophobic surface. It is also noted that the untreated chalcopyrite surface has a non-zero oil contact angle, which was due to oxidation during drying.

5.3.2.2 KAX

The results given in Fig. 5.4 were obtained at a high collector dosage of 2 kg/t of KAX. Meanwhile, Fig. 5.5 shows that PX-1 can also function as a collector. As such, another set of agglomeration tests was conducted in the presence of 250 g/t of PX-1 to explore the possibility of reducing the consumption of the primary hydrophobizing agent KAX, with the results presented in Fig. 5.6. When the agglomeration was performed without KAX, almost no agglomerates were collected on the screen; therefore, the Cu grade and recovery were 4.28% and 7.72%, respectively. This finding suggests that the hydrophobicity-enhancing agent would not absorb on a very hydrophilic surface. As the dosage of KAX was increased, the Cu recovery was increased significantly and rapidly reached the maximum (94.63%) at 0.5 kg/t KAX. This was because the chalcopyrite particles were rendered sufficiently hydrophobic by a small amount of KAX so that PX-1 could absorb on them, which then caused the further increase of their hydrophobicity. This result confirms the statement made by Duzyol and Ozkan (2010) that agglomerates will start to form only after the fine particles have been rendered sufficiently hydrophobic.



Fig. 5.6 Effect of KAX on oil agglomeration of chalcopyrite. Oil agglomeration was conducted with 250 g/t PX-1.

It is also shown in Fig. 5.6 that the Cu recovery was slightly reduced to 93.23% at 2 kg/t of KAX, which may be attributed to the dispersion of some very hydrophobic particles into oil or the enlargement of the repulsion forces between highly charged hydrophobic particles. Thus, the optimum KAX dosage was determined as 0.5 kg/t. These results showed the advantage of using a hydrophobicity-enhancing agent in the oil agglomeration process, particularly in reducing the consumption of a primary hydrophobizing agent without deteriorating the recovery.

5.3.2.3 Stirring Speed

Fig. 5.7 shows the effect of stirring speed on the recovery of chalcopyrite by oil agglomeration. The tests were conducted using 250 g/t PX-1 as a secondary hydrophobizing agent with the stirring speed varied in the range of 900 to 1700 RPM. As shown, the Cu recoveries were all greater than 90% regardless of the stirring speed. Comparison of Fig. 5.3 and Fig. 5.7 shows that the Cu recovery became less sensitive to the changes of stirring speed when PX-1 was utilized. As shown in Fig. 5.7, the Cu recovery would not decrease until the stirring speed reached above



Fig. 5.7 Effect of stirring speed on oil agglomeration of chalcopyrite. Oil agglomeration was conducted with 250 g/t PX-1.

1500 RPM. In contrast, the Cu recovery obtained from the agglomeration tests conducted without using PX-1 already started decreasing as the stirring speed was increased to above 900 RPM, as shown in Fig. 5.3. These results indicate that the mechanical strength of agglomerates formed with the assistance of PX-1 was much stronger than those obtained without PX-1. This may be due to the high viscosity characteristics of PX-1. As a result, the agglomerates comprised of chalcopyrite particles that were further hydrophobized by PX-1 were able to resist breaking up at high stirring speeds.

5.3.2.4 Agglomeration Time

The preceding paragraphs in section 5.3.2 show that the oil agglomeration of chalcopyrite with the aid of PX-1 was capable of producing > 90% Cu recoveries at 30 minutes agitation time, which showed a significant improvement in the agglomeration kinetics in comparison with the agglomeration conducted without using PX-1. However, the shorter the residence time in mineral processing, the higher the throughput. As such, a series of agglomeration tests was carried out at



Fig. 5.8 Effect of agitation time on oil agglomeration of chalcopyrite. Oil agglomeration was conducted with 250 g/t PX-1.

250 g/t PX-1 to explore the possibility of further decreasing the agitation time. Fig. 5.8 shows the agglomeration results obtained with the agitation time varying from 10 to 40 minutes. As shown, the Cu recovery decreased with lowering the agitation time, but the recovery obtained at 10 minutes, 88.52%, was still fairly high. These findings show that the use of PX-1 would significantly improve the agglomeration kinetics, and therefore it is promising to further reduce the agglomeration time by optimizing the PX-1 dosage.

5.3.3 Effect of PX-1 on Cu Grade

The results in sections 5.3.1 and 5.3.2 showed high copper concentrate grades irrespective of agglomeration conditions, demonstrating that oil agglomeration is selective for recovering fine particles. However, it is noted that the use of PX-1 would slightly deteriorate the selectivity of oil agglomeration due to the fact that in the tests without using PX-1, the concentrate grades varied from 20.6% to 30.7%, with an average grade of 27.9%; in contrast, in the tests with PX-1, the concentrate grades varied from 15.2% to 29.6%, with an average grade of 25.2%. The reasons for this may be explained as follows.

Since the agglomeration tests were conducted at pH = 9.5, it is highly possible that some copper ions, which dissolved from the chalcopyrite minerals, formed Cu^{II} hydrolysis products and precipitated at the silica surfaces (Kent and Ralston, 1985). Xanthate ions could then absorb on these sites at the silica surfaces and render them slightly hydrophobic but not enough to be agglomerated. When PX-1 was employed in the tests, silica particles that have been activated in this manner were able to be absorbed by the hydrophobic polymer PX-1 and hence were recovered into the chalcopyrite agglomerates, leading to the lowering of Cu grade. The decrease in Cu grade might also be a result of the enhanced gangue entrainment, owing to the increased mechanical strength of agglomerates in the presence of PX-1.

5.4 Conclusion

Recognizing the limitation of conventional flotation technique on the recovery of fine and ultrafine mineral particles, the oil agglomeration process using a recyclable oil has been applied to selectively recover chalcopyrite fines from an artificial mixture consisting of chalcopyrite and silica particles. A series of oil agglomeration tests using KAX alone was carried out to study the effects of agglomeration time, oil dosage, and stirring speed. The results showed that the kinetics of oil agglomeration were fairly slow. In order to address this issue, oil agglomeration of chalcopyrite was also investigated after the hydrophobicity of the KAX-pretreated chalcopyrite particles had been further enhanced with a hydrophobicity-enhancing agent: hydrophobic polymer PX-1. Comparison of the results obtained with and without PX-1 showed that the use of PX-1 in oil agglomeration substantially increased the agglomeration kinetics as the required agitation time was reduced from 50-70 minutes to 10 minutes for achieving about 90% Cu recovery. The results also show that the consumption of a primary hydrophobizing agent and oil may be reduced due to the use of PX-1.

A series of oil contact angle measurement tests was conducted on a polished chalcopyrite plate. The results show that PX-1 is capable of further increasing the hydrophobicity of mineral particles, which may explain why the agglomeration kinetics was improved. It has been noted that Cu concentrates produced from the tests conducted with using PX-1 had a slightly lower average grade as compared to those obtained without using PX-1, indicating that the selectivity of oil agglomeration was slightly decreased by PX-1; however, it was still acceptable. Further investigation will be necessary to address this problem, and the use of dispersant may be a solution.

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Chapter 6 Development of an HHS Process for the Recovery of Ultrafine Copper Mineral Particles

Abstract

The inevitable finer liberation of copper ores resulted from the decline in grades and the increase of complex ores brings huge challenges to the copper mining industry as the widely-used froth flotation technique is inefficient in processing fine and ultrafine particles. In this regard, the feasibility of using the HHS process to recover ultrafine chalcopyrite particles was explored in this work. The HHS test work was conducted on a semi-continuous scale with the employment of a new Morganizer specially designed for heavy mineral particles. The effects of various operating parameters in the Morganizer, mixing methods, gangue minerals, and process modification to the HHS performance were examined and discussed. The results demonstrated that the HHS process is capable of producing high-grade copper concentrates with low moistures from an ultrafine artificial sample. On the basis of the success achieved with the artificial samples, the HHS process was further demonstrated on ultrafine-ground real plant copper samples. The HHS tests produced concentrates with 34-36 %Cu grades on a Plant F run-of-mine (ROM) copper ore sample, which outperformed the flotation. In addition, the HHS process was capable of producing a concentrate assaying 20 %Cu on the Plant K cleaner scavenger tail sample that is currently discarded as waste of the processing plant. These findings imply that the persistent undersupply problems faced by the U.S. and global copper market may be addressed by employing the HHS technique to recover copper minerals from those discarded copper tailings.

6.1 Introduction

The importance of copper in sustaining and improving our society has been seen in many ways, such as building construction, power generation and transmission, electronic product manufacturing, and the production of industrial machinery. According to the investigation conducted by Norgate and Jahanshahi (2010), approximately 80% of the world's copper is extracted from copper sulfide ores, of which chalcopyrite is the most common copper source. These copper minerals are mainly recovered by the froth flotation technique. In a typical copper flotation circuit, grinding is an essential step to improve the liberation of copper minerals from gangue minerals associated with them. As the progressive depletion of easy-float and high-grade copper ores, the impending exploited copper ores are of more complex mineralogy characteristics, and their grades are falling globally (Norgate and Jahanshahi, 2010). To process the low-grade copper ores, much finer grinding will be necessary to guarantee the sufficient liberation of copper minerals. However, this will definitely deteriorate the recovery of copper minerals by flotation as ultrafine copper mineral particles (< 30 µm) cannot be efficiently recovered by flotation (Monkosa et al., 2016). According to the projection by Greene (2017), the future loss of copper values due to the loss of ultrafine copper mineral particles in flotation from the 18 largest copper porphyry deposits in the world will equal 90.67 million tons. The ineffectiveness in flotation of fine and ultrafine particles, in fact, has caused the continuous decline of copper production in the U.S. in recent years (Flanagan, 2018).

On the other hand, the global demand for copper has grown rapidly as the results of the rising electric vehicle production, the expanding power industry and a positive global economic growth (Fitch Solution, 2019). It is projected that the global copper supply will be deficient over the next few years, which has raised concern regarding the future availability of copper. Obviously, one solution to this problem would be to increase the productivity by developing a separation method that can selectively recover ultrafine copper mineral particles that are being lost in tailing streams.

In light of the abovementioned issue, a great deal of work has been done to improve the flotation recovery of fine and ultrafine copper mineral particles. Rubio et al. (2007) proposed a new flotation technique called emulsified oil extender flotation and the size-by-size flotation results showed that the flotation kinetics and recoveries of fines (37-5 μ m) and ultrafines (< 5 μ m) were greatly improved as compared to the standardized flotation. Tussupbayev et al. (2015) used microbubbles to recover chalcopyrite particles of d₈₀ =12 μ m. Comparison of the column flotation results obtained with and without the microbubbles showed the addition of microbubbles in the amount of 50 L per 1 kg of chalcopyrite has resulted in a 50% increase in copper recovery. It seems like these two approaches are promising; however, it is noted that the copper recoveries were increased at the cost of decreasing copper grades in these two examples. In the former, the copper grade was dropped from 12.5% to 11.5%. In the latter, it was decreased from 18.0% to 14.7%. It appears that a modified flotation process cannot selectively recover fine and ultrafine copper mineral particles.

Many other physical beneficiation methods have also been developed to recover ultrafine particles. Of them, oil agglomeration has been considered as a promising method for a long time. House and Veal (1989), and Cadzow et al. (1985) explored the feasibility of using the oil agglomeration process to recover ultrafine chalcopyrite particles on artificial copper ores. Their results showed that oil agglomeration is capable of producing high-grade copper concentrates at high recoveries. The main problem associated with this process is that the spent oil could not be recovered economically. It is also noted that there is no report on the application of the oil agglomeration process on a real copper sample in the past 30 years; therefore, it is still questionable whether the oil agglomeration technique is capable of efficiently recovering real ultrafine copper mineral particles.

The HHS process, which incorporates the oil agglomeration technique and is capable of recovering and recycling the spent oil, has been developed to recover and dewater fine and ultrafine particles simultaneously at Virginia Tech. It is believed that there is no lower particle size limitation for the HHS process (Yoon, 2016). This new technique has been demonstrated successfully on various coals in lab-scale and pilot-scale, but not on copper minerals or other metallic ores (Yoon et al., 2016; Gupta et al., 2016). As such, the objective of this study is to explore the applicability of the HHS process on the recovery of ultrafine copper minerals. Given that the density of the typical copper mineral-chalcopyrite is 3.2 times higher than that of coal, a vibrating mixer type Morganizer previously employed in the HHS process for coal recovery would have problems on lifting heavier copper minerals. Thus, a new Morganizer was developed to satisfy the purpose of using the HHS process to recover copper minerals. In this study, the HHS tests were first carried out on artificial copper ores, in which the effects of air bubbles, various operating parameters in the Morganizer, mixing methods, gangue minerals, and process modification to the HHS performance were examined and discussed. The experience and knowledge base gained on artificial samples were then applied for testing the HHS process on real copper samples.

6.2 Experimental

6.2.1 Materials

Artificial Copper Ore Samples Specimen-grade chalcopyrite samples, received as 1 x 1" to 1 x 2", were purchased from Ward's Science. Lumps of the chalcopyrite samples were crushed by means of a handheld hammer to < 0.5 mm and subsequently wet-ground in a lab ball mill for 45 minutes. After vacuum filtering and air drying in a lab fume hood, the ground chalcopyrite particles were homogenized and evenly split into small sample bags, and then stored in a refrigerator to

prevent further oxidization. The particle size of the ground chalcopyrite sample was determined by an LA-960 laser particle size analyzer (Horiba Scientific), and the result showed that 80% of the chalcopyrite particles were smaller than 10 μ m. Mono-size silica particles with a 5 μ m mean particle size (Potter Industry, Inc.), which were mixed with chalcopyrite particles to prepare the artificial copper feed sample, was used directly without any purification. Most of the HHS tests were performed using an artificial mixture of chalcopyrite and silica particles. One set of tests was also conducted on an artificial mixture of chalcopyrite and kaolin clay particles. The clay sample with ~2 μ m top size was mined at east Georgia and provided by the Thiele Kaolin Company.

<u>Plant Copper Samples</u> In this study, the HHS process was also demonstrated on the actual copper ore samples taken from the two largest copper producers in the U.S. The sample procured from Plant K assaying 0.55%Cu was a cleaner scavenger tail, in which 67 %wt. of particles were smaller than 45 μ m. This sample was received as a wet filter cake of ~32% moisture. All the HHS tests on this sample were carried out after grinding it for 1 h to d₈₀ = 3 μ m in a lab-scale attrition mill. The run-of-mine (ROM) ore sample (-10 mesh) obtained from Plant F assaying 0.24 %Cu was wet ground in a ball mill to reduce the particle size to 80% passing (d₈₀) 5.8 μ m before conducting separation tests.

Tab. 6.1 Chemicals used in the experiments.

Reagent	Supplier
Potassium amyl xanthate, > 95%	TCI America
Poly(methylhydrosiloxane)	Sigma Aldrich
Polybutadiene, dicarboxy terminated	Sigma Aldrich
Sodium dithionite	Sigma Aldrich
Sodium cyanide	Sigma Aldrich
n-Heptane, HPLC grade, 99.9% purity	Sigma Aldrich
4-Methyl-2-pentanol, 98%	Sigma Aldrich
Potassium hydroxide	Sigma Aldrich
Hydrocloride acid	Fisher Scientific

<u>Chemicals</u> Tab. 6.1 lists the chemicals employed in this study. Potassium amyl xanthate (KAX) of > 95% purity was used as the collector for chalcopyrite without further purification. Poly(methylhydrosiloxane) (PMHS), polybutadiene (PBD), sodium dithionite (Na₂S₂O₄), and sodium cyanide (NaCN) were used as modifiers in the batch HHS tests conducted on the Plant K cleaner scavenger tail sample. Heptane was used for collecting hydrophobized chalcopyrite particles. Hydrochloric acid and potassium hydroxide of analytical grade were used to adjust solution pH. 4-Methyl-2-pentanol (MIBC) was used as a frother in the flotation test on the Plant F ROM ore sample. All tests were carried out using tap water.

6.2.2 Development of a New Morganizer

The vibrating mixer type Morganizer, which has two mesh screens centrally mounted on a shaft that is connected with an up-down motion shaker, has been successfully applied for breaking water-in-oil (w/o) emulsions to recover fine coal particles (Gupta, 2014; Yoon et al., 2016).



Fig. 6.1 Bench-scale semi-continuous testing unit for the HHS process.

However, initial exploratory HHS experiments with chalcopyrite using this vibrating mixer type Morganizer showed that both the emulsions stabilized by chalcopyrite particles and the dispersed chalcopyrite particles would sink at the bottom of the Morganizer due to the much higher density of chalcopyrite as compared to coal. To address this issue, as shown in Fig. 6.1, a new Morganizer (or extraction column) was designed and constructed to recover heavier chalcopyrite or other metallic mineral particles by introducing the upward flows of hydrophobic hydrocarbon and air bubbles from the bottom of the Morganizer, which was originated from the idea of using the packed column for liquids separation in the chemical industry (Jiao et al., 2015).

Fig. 6.1 shows the bench-scale semi-continuous HHS apparatus, which consists of a mixer, three pumps, and a Morganizer (or extraction column). The Morganizer was made of 1-inch diameter glass tubing and was constructed from a series of 4-inch long glass tubes connected via easy-to-dismantle glass O-ring joints. As shown in Fig. 6.1, the Morganizer consists of three feed ports (feed, oil, and air), two packing zones which are separated by the feed port, and two outlet ports (concentrate and tail).

6.2.3 Semi-Continuous HHS Tests

In each HHS test, a volume (3 L) of a copper ore slurry was conditioned with a known amount of KAX at pH 9.5 in a 5 L rectangular mixing tank for 10 minutes at 650 RPM. A measured volume of hydrocarbon oil (400 mL heptane) was then added to the conditioned copper ore slurry to selectively collect the mineral particles rendered hydrophobic. After mixing for 5 minutes in the presence of heptane, the hydrophobic particles collected on the surface of oil droplets acted as solid surfactants (or emulsifiers) and form a stable Pickering emulsion. The oil-in-water (o/w) emulsions formed in this manner were fed directly to the Morganizer by means of a peristaltic pump, while a volume of oil (heptane) was added to the bottom section of the column. The additional oil addition at the bottom section of the column served two purposes. One was to convert the o/w emulsion to w/o emulsion. The phase inversion occurs when oil becomes the major component of the two-phase mixture (Binks and Lumsdon, 2000). The other purpose was to create an upward flow of fluid in the column so that the copper mineral particles detached from the water droplets would not fall to the bottom section of the column. When the converted w/o emulsions passed through the top packing zone of the glass column, the water droplets coated with hydrophobic particles liberated the hydrophobic particles from the interface due to the turbulence created in the packed zone. The water droplets freed of hydrophobic particles were then coalesced with each other, making themselves become bulkier and fell to the bottom. The hydrophobic mineral particles stayed dispersed in the organic phase were collected in the overflow as the concentrate, while the water droplets that fell were collected at the bottom as tail along with the hydrophilic gangue minerals particles dispersed in them. The concentrate product was de-oiled using a lab pressure filter to recover the spent heptane, leaving a dry copper concentrate. Moisture measurements of the copper concentrate were conducted right after the filtration. The dried products were sent for digestion by means of a microwave digestor and then subjected to ICP analysis of copper content.

6.2.4 Batch HHS Tests

In a given test, 100 mL of a copper ore slurry at a solid content of 12% was conditioned with a hydrophobizing agent, potassium amyl xanthate (KAX), at pH 9.5 in a 250 ml separatory funnel for 5 minutes by hand-shaking. After the mineral particles had been sufficiently hydrophobized, a volume (40 ml) of heptane was added to the separatory funnel, and the mixture was hand-shaken again for another 5 minutes. The mixture was then allowed to settle to form an o/w emulsion on the top and the aqueous slurry at the bottom. After removing the latter from the

separatory funnel, fresh tap water was added to the o/w emulsions left in the funnel, hand-shaken, allowed to settle, and the aqueous slurry was removed from the bottom section of the funnel. This step was designed to remove the entrained gangue minerals from the o/w emulsion phase. After repeating this step once more, additional oil (heptane) was added to increase the volume of oil > 76%, so that the o/w emulsion was converted to a w/o emulsion. The latter was then gently agitated by hand-shaking to detach the hydrophobic particles from the water droplets constituting the w/o emulsions. The water droplets freed of hydrophobic particles became larger in size by coalescence, while the hydrophobic particles were dispersed in the oil phase. Both the hydrophobic mineral concentrate and hydrophilic tail were analyzed for copper to determine the Cu recovery in each test.

6.3 Results and Discussion

6.3.1 Semi-Continuous HHS Tests Conducted without Air Using Artificial Samples

Fig. 6.2 shows the effect of varying KAX dosages on the semi-continuous HHS tests conducted in the absence of air. The artificial copper ore was a mixture consisting of 10 g chalcopyrite and 190 g silica. The dosage rates were varied in the range of 0.3 to 0.8 kg/t. As shown, the copper grades were increased from 1.05 %Cu in the feeds to 27.7-28.5 %Cu in the concentrates in a single-stage operation, indicating that the HHS process was capable of producing high-grade copper concentrates despite the fact that the sizes of particles were well below the effective particle size range for flotation. Typically, multiple stages of rougher, scavenger, and cleaner are necessary to produce > 20 %Cu concentrates in flotation. In this regard, the HHS process is far superior to flotation.

It is also noted that the copper recovery decreased at higher dosages of the primary hydrophobizing agent. As the dosage was increased from 0.3 to 0.4 kg/t, the recovery was reduced

from 88.8% to 87.3%. As the dosage was further doubled to 0.8 kg/t, the copper recovery was decreased dramatically to 49.5%. In general, the higher the reagent dosage, the higher the contact angle (θ_o) and hence the recovery in flotation. In the HHS process, the oil contact angle of hydrophobic particles can be easily increased to > 90° as it is in general twice as large as an air contact angle. According to Lai and Fuerstenau (1968), hydrophobic particles with $\theta_o > 90^\circ$ can readily enter into an oil drop rather than adsorbing on the surface. Therefore, the reason for the reduction in recovery at 0.8 kg/t of KAX was probably because too many particles entered the o/w emulsion drops, making them too heavy to be lifted in the Morganizer.



Fig. 6.2 Results of the HHS tests conducted on artificial copper ore samples in the absence of air: effect of KAX. Packing: copper wool; feed flow rate: 790 ml/min; oil flow rate: 300 ml/min.

6.3.2 Semi-Continuous HHS Tests Conducted with Air Using Artificial Samples

It is shown in the foregoing section that the HHS process performed well for the recovery of chalcopyrite particles with sizes that flotation cannot handle. During the operation of the Morganizer, however, it was noted that the kinetics of emulsions breakage, which was justified based on the waiting time needed for one to observe the occurrence of particles dispersing in the oil phase, was too slow. The driving forces for breaking up a w/o emulsion are created by the pressure drop across the packing as the upward oil flow passes through it. However, the oil flow rate has been limited due to the constraint of column height in the lab-scale tests. Additionally, increasing the oil flow rate would result in a high cost. It was, therefore, decided to rely on a bubbly air flow instead, which greatly reduced the amount of oil used in each experiment. The air bubbles were introduced from the bottom of the Morganizer (Fig. 6.1) through a fritted glass dispersion tube. In a test, air bubbles were injected along with oil droplets.

6.3.2.1 Effect of Packing

The addition of packing in the Morganizer serves two purposes. One is to create turbulence through the pressure drop, by which the hydrophobic particles can be dropped off a w/o emulsion. Another is to provide a hydrophilic surface for quickening the coalescence of water droplets released from the w/o emulsions. Fig. 6.3 shows the three different types of packing materials employed in this study, which are perforated saddles made of stainless steel, copper wool, and corrugated stainless steel plate.



Fig. 6.3 Different packing used in the extraction column Morganizer: a) no packing, b) stainless saddles, c) copper wool and d) corrugated plate.



Fig. 6.4 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of packing. Feed: mixture of 15 g chalcopyrite and 190 g silica; 0.6 kg/t KAX at pH = 9.5 & 6.8 % solids; feed flow rate: 790 ml/min; oil flow rate: 210 ml/min; air flow rate: 92 ml/min.

Fig. 6.4 shows the results obtained using different packing materials on an artificial copper ore assaying 2.29 %Cu, which was prepared by blending 15 g chalcopyrite with $d_{80} = 10 \ \mu m$ and 190 g silica with $d_{50} = 5 \ \mu m$. In all tests, concentrate grades were > 32 %Cu, which was very close to the theoretical maximum of 34.62 %Cu in pure chalcopyrite. The copper recoveries were in the range of 77 to 81%, which would have been higher if the test conditions were optimized, and better packing material was used.

Comparison of the results presented in Fig. 6.2 and Fig. 6.4 shows that the HHS tests conducted using air bubbles produced higher copper grades than the tests performed without using air bubbles, since the average copper grade of concentrates in Fig. 6.2 and Fig. 6.4 were 28.22% and 32.82%, respectively. Also noted that the oil flow rate used in Fig. 6.4 was much slower than that used in Fig. 6.2. These results suggest that the bubbly air flow was more efficient than the oil flow for the breakage of w/o emulsions in the Morganizer. Another advantage of the use of air

bubbles is that it can substantially improve the emulsion breakage kinetics, which was evidenced by the observation during testing that hydrophobic chalcopyrite particles were instantly dispersed into oil phase as soon as emulsions were introduced to the Morganizer.

Fig. 6.4 also shows that the Morganizer packed with copper wool produced a copper concentrate assayed only 0.4% moisture. The reason for this is that the local pressure drop produced among the copper wool type packing may be much larger than those obtained with other types of packings due to the smallest gaps among the copper wool, as shown in Fig. 6.3. In addition, it seems like the copper wool packing may give the highest surface area, this will be beneficial for promoting the coalescence process of water drops freed of hydrophobic particles, by which small water drops become larger water drops that are more readily to be separated from the copper mineral particles. The next best packing may be the corrugated stainless plate, which had 2.7% moisture, followed by stainless saddle packing. The results obtained without packing gave 33.3% moisture, suggesting that packing was useful to obtain low-moisture products. Based on these results, the copper wool and corrugated stainless plate were determined as suitable packing materials, and thereby the following semi-continuous HHS tests were conducted using a Morganizer packed with one of these two.

6.3.2.2 Effect of Oil Flow Rate

Oil addition in the bottom of the Morganizer column serves two purposes as noted above. One is to induce phase inversion, and the other is to create an upward flow of fluids to prevent high-density chalcopyrite minerals falling to the bottom. If the amount of oil employed in the Morganizer is too large, it will increase the cost occurring in the oil-particle separation after the HHS separation. Therefore, a set of HHS tests was carried out to study the effect of oil flow rate at a fixed air flow rate of 92 ml/min. Fig. 6.5 shows the results obtained at two different oil flow



Fig. 6.5 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of oil flow rate in Morganizer. Feed: mixture of 15 g chalcopyrite and 190 g silica; packing: corrugated stainless plate; 0.6 kg/t KAX at pH = 9.5 & 6.8 % solids; feed flow rate: 790 ml/min; air flow rate: 92 ml/min.

rates, 75 and 210 ml/min. As shown, the results did not differ significantly, indicating that the performance of the Morganizer is independent of the oil flow rate in the presence of air bubbles. That is to say, the results obtained at 75 ml/min oil flow rate were as good as that obtained at 210 ml/min oil flow rate, but the oil consumption in the former was only 0.36 times of that in the latter, suggesting that the addition of air bubbles would greatly reduce the use of oil in the HHS process.

6.3.2.3 Effect of KAX

Fig. 6.6 shows the effects of varying KAX dosages on the semi-continuous HHS tests conducted using the Morganizer packed with copper wool. The KAX dosage rates were varied in the range of 0.3 to 0.6 kg/t. As the dosage was increased from 0.3 to 0.6 kg/t, the copper recovery was first increased slightly from 76.4% to 78.1% and then slightly decreased to 77.2%. Meanwhile, all the HHS tests produced high concentrate grades at 32.4-33.3 %Cu and low moistures in the



Fig. 6.6 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of KAX. Feed: mixture of 15 g chalcopyrite and 190 g silica; packing: copper wool; KAX at pH = 9.5 & 6.8 % solids; feed flow rate: 790 ml/min; oil flow rate: 210 ml/min; air flow rate: 92 ml/min.

range of 0.4-3.1%. Therefore, the optimum KAX dosage was determined to be 0.4 kg/t. In comparison to the results presented in Fig. 6.2, the impact of KAX dosage on Cu recovery was less significant in Fig. 6.6, indicating that the air bubbles in the Morganizer indeed help pick up those falling emulsion drops overloaded by particles with $\theta_o > 90^\circ$.

6.3.2.4 Effect of Air Flow Rate

Fig. 6.7 shows the results of HHS tests conducted using bubbly air flow to prevent highdensity minerals from being lost at an oil flow rate of 210 ml/min. As the air flow rates increased from 55 to 167 ml/min, the copper concentrate grades remained high and in the range of 32.45-33.12%, while the copper recovery increased slightly from 77.9% to 78.3%, and then decreased to 75.3%. When the air flow rate was too large in the Morganizer, the flow turned churn-turbulent and increased the disturbance to the emulsion drop-bubble contact, which in turn caused the



Fig. 6.7 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of air flow rate in Morganizer. Feed: mixture of 15 g chalcopyrite and 190 g silica; packing: copper wool; 0.4 kg/t KAX at pH = 9.5 & 6.8 % solids; feed flow rate: 790 ml/min; oil flow rate: 210 ml/min.

emulsions stabilized with hydrophobic minerals to fall. Additionally, an increase in air flow rate caused the increase of the air bubble size, and hence, the decrease of the air bubble surface area flux, which affected the bubbles' carrying capacity to the drop-back oil droplets filled with hydrophobic particles. These both could have led to the decrease in Cu recovery at an air flow rate of 167 ml/min. Similar findings have been reported by Haryono et al. (2017). It appears that the air flow rate required to prevent high-density minerals falling is low.

6.3.2.5 Effect of Feed Flow Rate

Fig. 6.8 compares the results of two HHS tests conducted at 720 and 790 ml/min of slurry feed rates to the Morganizer. In these tests, the Morganizer was packed with copper wool. As shown, at 720 mL/min, the HHS tests produced a copper concentrate with a recovery of 80.1%, which was higher than the 75.3 %Cu recovery achieved at 790 ml/min. This may be attributed to



Fig. 6.8 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of feed flow rate in Morganizer. Feed: mixture of 15 g chalcopyrite and 190 g silica; packing: copper wool; 0.4 kg/t KAX at pH = 9.5 & 6.8 % solids; air flow rate: 167 ml/min; oil flow rate: 210 ml/min.

the decrease of both residence time for emulsion breakage and water coalescence at a faster feed flow rate.

6.3.2.6 Dynamic Mixing vs. Static Mixing

In a typical HHS test, oil is added to a feed slurry tank and broken into small drops by mixing to promote collision between hydrophobic particles and oil drops. In this study, the oil droplet-particle interactions also were achieved using an inline mixer installed on the high-pressure side of a centrifugal pump (Fig. 6.9). Fig. 6.10 compares the HHS results obtained using these two different mixing techniques.



Fig. 6.9 In-line mixer and dynamic mixer.



Fig. 6.10 Comparison of HHS tests conducted using different emulsification methods: dynamic mixer and inline mixer.

As shown, the average recovery of the HHS tests conducted using the inline mixer was 85.2%, while that of using the dynamic mixer was 77.4%. Obviously, the inline mixer was substantially more efficient than the dynamic mixer. It is also noted that the residence time required for the HHS using different mixers were different despite the dynamic mixer and the centrifugal pump were equipped with 0.2 HP motors. With the dynamic mixer, 5 minutes of mixing time was employed. When using the inline mixer, the residence time was less than 2-3 seconds.

6.3.2.7 Process Modification

The HHS results presented in the prior paragraphs in this section were achieved using the testing protocol described in Fig. 6.11a, in which the o/w emulsions were directly fed to the Morganizer and the phase inversion was therefore conducted in the Morganizer. However, the lack of phase separation in this testing protocol brings concerns over the processing capacity of the Morganizer, since the particles fed into the column mostly were gangue minerals. In this regard, the HHS process has been evolved to a procedure shown in Fig. 6.11b, in which phase separation

and phase inversion steps are added. These changes greatly increased both the recovery and grade for copper minerals, as shown in Fig. 6.12. As a result of the modifications, copper recovery was increased by 10-15%, and the best copper grade approached the theoretical maximum of 34.6%.



Fig. 6.11 The schematic representation of HHS tests: a) without phase separation; b) with phase separation.



Fig. 6.12 Effect of process modification (see Fig. 6.11) on the recovery of chalcopyrite by the HHS process.

6.3.2.8 Effect of Gangue Mineral

Silica, quartz, and clay were the major gangue minerals associated with copper ores. The abovementioned study was carried out on an artificial copper ore sample, which was a mixture consisting of chalcopyrite and silica particles. According to Farrokhpay and Bulelwa (2013), the presence of clay minerals in the flotation of chalcopyrite has deleterious effects on the copper grade and recovery. Hence, it will be of practical significance to test the viability of the HHS process on an artificial copper ore sample containing clay particles as the gangue mineral.

Fig. 6.13 compares the results of HHS tests conducted on two different artificial copper ore samples: one was prepared by blending chalcopyrite particles with silica particles, and another was a mixture comprising of chalcopyrite particles and clay particles. The weight percentage of chalcopyrite particles in these two samples were kept the same. As shown, the HHS process was successfully applied for separating chalcopyrite from clay. However, evidently, the copper recovery obtained on the artificial feed containing clay as the gangue mineral was 66.5%, approximately 23% less than that obtained using silica as the gangue mineral. This result indicated



Fig. 6.13 Results of the HHS tests conducted on artificial chalcopyrite ore samples: effect of gangue mineral. HHS test with phase separation; packing: copper wool; 0.6 kg/t KAX at pH = 9.5 & 6.8 % solids; feed flow rate: 790 ml/min; air flow rate: 167 ml/min; oil flow rate: 210 ml/min.

that the HHS process was more efficient in removing silica than clay from the copper minerals. The lower recovery obtained using clay as the gangue mineral may be attributed to the slime coating associated with submicronic clay particles (Jeldres et al., 2019). Therefore, further studies on how to improve the performance of HHS process on an artificial copper ore sample containing clay particles would be necessary for implementing the HHS process on real copper ores. The use of electrolytes may be a possible solution to mitigate clay coating on copper minerals (Zhao and Peng, 2014).

6.3.3 Semi-Continuous HHS Tests Conducted Using Plant Copper Samples

So far, the HHS process has been demonstrated on an artificial copper ore sample. On the basis of experimental knowledge gained through testing the artificial samples, semi-continuous HHS tests were also conducted using ultrafine copper ore samples procured from different copper processing plants operating in the U.S. The experimental procedure was identical to the one shown in Fig. 6.11a that included air bubble addition at the Morganizer stage. Copper wool was used as the packing material. The Morganizer was operated at 790 ml/min of feed flow rate, 167 ml/min of air flow rate, and 300 ml/min of oil flow rate.

Products	Wt.%		Cu Grade (%)		Cu Recovery (%Wt.)	
	Ind.	Cum.	Ind.	Cum.	Ind.	Cum.
Cleaner Conc.	1.2	1.2	16.78	16.78	79.9	79.9
Cleaner Tail	5.5	6.7	0.57	3.44	12.6	92.5
Rougher Conc.	6.7	-	3.44	-	92.5	-
Rougher Tail	93.3	100.0	0.02	0.248	7.5	100.0
Feed	100.0	-	0.248	-	100.0	-

Tab. 6.2 Results of the flotation test conducted on a flotation feed ground to $d_{80} = 5.8 \ \mu m.$

0.1 kg/t KAX, pH = 9.5, 2 minutes float

6.3.3.1 Plant F ROM sample

Tab. 6.2 shows the results obtained from a flotation test conducted on the -10 mesh ROM ore sample. The test was conducted after wet grinding it in a ball mill to reduce the particle size to 80% passing (d_{80}) 5.8 µm. The mill product was conditioned with 0.1 kg/t potassium amyl xanthate (KAX) at pH 9.5 and floated for 2 minutes. A shown, the rougher concentrate assayed 3.44 %Cu at a recovery of 92.5%. After a single-stage cleaning, the grade was improved to 16.78 %Cu with an overall recovery of 79.9%. These results were inferior to those obtained at coarser grinds, not shown in this study, due to the smaller particle sizes.

Tab. 6.3 shows the results obtained using the HHS process on the same mill product that was used for the flotation test. The mill product was conditioned with KAX at 0.1 and 0.3 kg/t. As shown, single-stage HHS tests produced a 34.23 %Cu concentrates at a recovery of 83.4% recovery at 0.1 kg/t KAX, and a 36.24 %Cu concentrate at an 87.6% recovery at 0.3 kg/t KAX. These results were far superior to those obtained using flotation both in terms of recovery and grade. Note here that the moisture contents of the copper concentrates were 4.1 and 2.8 %wt. It is interesting to note also that concentrate grades were very close to the theoretical maximum for chalcopyrite (34.6 %Cu), indicating that the HHS process is very selective and/or that the ore contains significant amounts of covellite (CuS) and/or chalcocite (Cu₂S).

KAX (kg/t)	Products	Cu Grade (%)	Cu Distribution (%Wt.)	Concentrate Moisture (%Wt.)
	Conc.	34.23	83.4	
0.1	Tail	0.04	16.6	4.1
	Feed	0.24	100.0	
0.3	Conc.	36.24	87.6	
	Tail	0.03	12.4	2.8
	Feed	0.24	100.0	

Tab. 6.3 Results of the HHS tests conducted on a ground Plant F copper flotation sample.

Feed size: $d_{80} = 5.8 \ \mu m$, pH = 9.5, semi-continuous tests



Fig. 6.14 Comparison of flotation and HHS tests conducted on the Plant F copper flotation sample.

The results shown in Tab. 6.2 and Tab. 6.3 were plotted in Fig. 6.14. As can be seen, the copper recoveries obtained from the flotation and HHS tests were about the same; however, the concentrate grades obtained from the HHS tests were ~2 times higher than that obtained from the flotation, showing a clear advantage in favor of the HHS process.

6.3.3.2 Plant K Cleaner Scavenger Tail

Elshkaki et al. (2016) projected that the cumulative global demand for copper will exceed its reserves by 2050. Thus, it is becoming unarguably urgent and important to look for other potential copper sources. The work by Gordon (2002) showed that the historic copper tailings had the grade ranges from 0.09% to 0.75%. This data indicates that some of the tailing streams in a copper flotation plant may have copper grades close or even higher than the current world average feed copper grade of 0.62% (Calvo, 2016). Also, an industrial study showed that the energy consumed in recovering copper from a tailing sample is normally about one-sixth of the energy

spent on a raw ore (Kennecott Utah Copper, 2004). In these regards, the cleaner scavenger tail sample that typically contains more than 50 %wt. of < 10 μ m particles, may be a promising secondary copper sources to cope with the future copper supply crisis. As such, the HHS process has also been tested on a Plant K cleaner scavenger tail sample in this study.

Preliminary experiments using both flotation and HHS techniques were conducted on the as-received Plant K cleaner scavenger tail sample. However, neither methods produced high-grade copper concentrates. It was thought that the sample was superficially oxidized or not sufficiently liberated. Therefore, the sample was wet-ground in a ball mill to $d_{80} = 3 \mu m$, and the mill product was used for the semi-continuous HHS test, with the results being presented in Tab. 6.4.

As shown, the HHS test conducted at 690 g/t KAX produced a 10.71%Cu concentrate from a 0.55 %Cu feed with a 43.1% recovery. The low copper grade was possibly due to the insufficient hydrophobicity of copper minerals, and the unselectively recovery of pyrite. In light of these issues, further investigations were continued to improve Cu grade in concentrates. Compared to semicontinuous testing, batch testing can determine the best experimental conditions and check the validity of testing in a timely manner. As such, a series of batch HHS tests aiming to improve the concentrate grade was conducted. The results were exhibited in the following section 6.3.4.

KAX (kg/t)	Products	Cu Grade (%)	Cu Distribution (%Wt.)	Concentrate Moisture (%Wt.)
	Conc.	10.71	43.1	
0.69	Tail	0.32	56.9	3.5
	Feed	0.55	100.0	

Tab. 6.4 Results of the HHS tests conducted on a ground Plant K copper cleaner scavenger tail sample.

Feed size: $d_{80} = 3 \mu m$, pH = 9.5, semi-continuous tests

6.3.4 Batch HHS Tests Conducted on Plant K Cleaner Scavenger Tail Sample

6.3.4.1 Effect of Secondary Hydrophobizing Agent

It is possible that the low Cu grade achieved in previous tests was because the hydrophobizing treatment with KAX alone did not render the copper minerals sufficiently hydrophobic. Thus, the KAX-treated chalcopyrite particles were further hydrophobized by a secondary hydrophobizing agent that can increase particles water contact angles beyond what can be achieved using a primary hydrophobizing agent such as xanthates alone. Two hydrophobic polymers, i.e. Polymethylhydrosiloxane (PMHS) and polybutadiene (dicarboxy terminated) (PBD), were studied in this work. In a given test, a secondary hydrophobizing agent was added to the slurry right after the primary hydrophobizing treatment with KAX. Thereafter, the slurry was conditioned for another 5 minutes before adding oil.

<u>Polymethylhydrosiloxane</u> PMHS is a water-soluble hydrophobic polymer, and its effectiveness in improving the separation of copper minerals has been demonstrated in flotation



Fig. 6.15 HHS tests conducted on a ground Plant K copper cleaner scavenger tail sample ($d_{80} = 3 \mu m$) at varying PMHS dosages.

(Yoon, 2005). Fig. 6.15 shows the results of HHS tests conducted on a ground Plant K cleaner scavenger tail copper sample using PMHS as a secondary hydrophobizing agent at 250 g/t KAX. As shown, both Cu grade and recovery were increased with increasing PMHS dosage from 0 to 800 g/t. The highest copper grade, which was 12.01 %Cu, was obtained at 800 g/t of PMHS, which equates 1.33 times the Cu grade obtained from a test without using PMHS. These results suggest that PMHS is an efficient agent for increasing Cu grade.

<u>Polybutadiene (dicarboxy terminated)</u> Fig. 6.16 shows the HHS tests results obtained on copper samples that were hydrophobized using 250 g/t KAX in the first step and 0 to 800 g/t polybutadiene (dicarboxy terminated) (PBD) in the second step. As shown, initially, the concentrate grade increased with increasing PBD dosage. However, after reaching the peak, the concentrate Cu grade decreased with a further increase in PBD dosage. Meanwhile, within the tested dosage range, the Cu recovery decreased with the increase of PBD dosage. The highest Cu



Fig. 6.16 HHS tests conducted on a ground Plant K copper cleaner scavenger tail sample ($d_{80} = 3 \mu m$) at varying PBD dosages.

grade achieved in this set of tests was 10.61 %Cu at 400 g/t PBD. Apparently, PBD was not that effective on increasing Cu concentrate grade compared with PMHS.

6.3.4.2 Effect of Depressant

The abovementioned HHS results showed that using secondary hydrophobizing agents can increase concentrates' grades. However, the achieved highest copper grade was still undesirable. A previous study has shown that there is a significant amount of pyrite associated with the Plant K copper ore (Reddick et al., 2009). The insignificant improvement in Cu grade by a secondary hydrophobizing agent was most likely due to the recovery of pyrite to the concentrate. As a result, the HHS testing work was continued with the use of depressants. In a given test, a 10 minutes conditioning with a depressant was carried out prior to the hydrophobization conditioning at 1.3 kg/t KAX. All tests were performed in the absence of a secondary hydrophobizing agent.

<u>Sodium Dithionite</u> One possible way to depress the flotation of pyrite is to control the pulp potential (Mu et al., 2016). Kydros et al. (1993) showed that sodium dithionite (Na₂S₂O₄) could depress the flotation of arsenopyrite by reducing the pulp potential. Drzymala and Wheelock (1992) also showed that Na₂S₂O₄ reduced the oil agglomeration of pyrite from a mixture containing coal and pyrite particles. Based on this, a series of HHS tests was conducted on the Plant K copper sample using Na₂S₂O₄ as a depressant. The Na₂S₂O₄ dosage was varied in the range of 0 to 32 g/t.

As can be seen in Fig. 6.17, the Cu recovery decreases with the increase of $Na_2S_2O_4$ dosage. At 32 g/t of $Na_2S_2O_4$, the recovery was decreased to 48.15% from 66.78%. Fig. 6.17 also shows that the Cu grade was first increased and then decreased with increasing the $Na_2S_2O_4$ dosage. The best concentrate assaying 16.07 %Cu was obtained at 16 g/t $Na_2S_2O_4$, which had a 4% higher Cu grade than the best result obtained using a secondary hydrophobizing agent. These results showed that $Na_2S_2O_4$ is an effective agent for depressing pyrite.


Fig. 6.17 HHS tests conducted on a ground Plant K copper cleaner scavenger tail sample ($d_{80} = 3 \ \mu m$) at varying Na₂S₂O₄ dosages.

<u>Sodium Cyanide</u> Fig. 6.18 shows the HHS results obtained using sodium cyanide (NaCN) as a pyrite depressant, which has been regarded as the most effective depressant for iron sulfide minerals. As shown, an increase of NaCN dosage would increase the copper concentrate grade and decrease the copper recovery. At 32 g/t NaCN, the HHS test produced a concentrate with the highest Cu grade, which was 20.0%, while the Cu recovery was 44.4% under this condition.

Comparison of the results of HHS tests conducted using secondary hydrophobizing agents and depressants reveals that the use of a depressant was more efficient than the secondary hydrophobizing agents in terms of increasing Cu grade, implying that the unselective recovery of pyrite might be the main reason accounting for the fairly low Cu grade obtained from HHS tests performed using KAX alone. The highest Cu grade obtained on the Plant K cleaner scavenger tail sample was 20.0%, which represented a 36.4 times enrichment from the feed assaying 0.55 %Cu.



Fig. 6.18 HHS tests conducted on a ground Plant K copper cleaner scavenger tail sample ($d_{80} = 3 \mu m$) at varying NaCN dosages.

6.4 Conclusion

In this study, a novel Morganizer has been specially developed to demonstrate the feasibility of using the HHS process for recovering ultrafine high-density minerals. An intensive study was conducted on an artificial copper sample to identify the factors that would affect the separation efficiency of the HHS process. The results show that introducing air bubbles to the Morganizer would increase the kinetics of emulsions breakage, cut down oil usage, and increase Cu grade in concentrates. The results also show that copper wool and corrugated plate are suitable packings for the Morganizer in order to achieve a low moisture concentrate product. It is noted that the Cu recovery can be increased by using an efficient mixing method, and by conducting phase separation and phase inversion prior to using a Morganizer.

The capability of the HHS process for the selective recovery of ultrafine particles was also successfully demonstrated on real copper samples on semi-continuous scale. On a Plant F ROM ore, the HHS process produced nearly pure chalcopyrite concentrates with high recoveries. On the Plant K cleaner scavenger tail, the HHS process produced a concentrate assayed 10.71 %Cu. After depressing the recovery of pyrite, the Cu concentrate grade was improved to 20.0% at 32 g/t of NaCN, of which the Cu concentrate can be salable. These results suggest that, potentially, the HHS process makes it feasible to recover copper from those tailing impoundments, which consist of a significant amount of lost ultrafine copper minerals that cannot be recovered by conventional flotation techniques.

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Chapter 7 Conclusions

The HHS process has been successfully demonstrated in previous work for its effectiveness in the recovery of ultrafine coal particles. However, the fundamental aspects of the HHS process were not fully understood, particularly the mechanisms of phase inversion. Also, the process had been tested on coal only, and its application for the beneficiation of ultrafine minerals remained to be explored.

The major findings of the present research may be summarized below:

The fundamental reason why oil-assisted processes such as oil agglomeration, twoliquid flotation, and HHS, are superior to flotation may be that oil droplets form contact angles about twice as large as those with air bubbles in water on a given hydrophobic surface. The reason is mainly due to the fact that the interfacial tension (γ_{so}) at the solid/oil interface is lower than the interfacial tension (γ_{sa}) at the solid/air interface.

• It has been found that the use of a hydrophobicity-enhancing reagent greatly improves the agglomeration of hydrophobic particles and hence increase the recoveries. Another way to improve the agglomeration kinetics is to increase the energy dispersion rate, which should increase collision efficiencies.

• New Morganizers have been developed by improving the breakage of agglomerates in an oil phase as a means to disperse hydrophobic particles in an oil phase and thereby remove entrained water and hydrophilic impurities. The new Morganizers are designed to destabilize agglomerates under conditions of turbulent mixing using a combination of Rushton mixer-screen basket, Jig, and a Wemco blade. These new designs performed better that the vibrating screens that were used initially.

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• Since the HHS process is capable of producing low-ash, low-moisture, and lowsulfur clean coal products from an Illinois fine coal waste, an improved flowsheet that can improve sulfur rejection can be readily developed. The new flowsheet can back-blend the HHS clean coal product with the discarded plant middlings while meeting the contract requirements. A case study showed that one ton of HHS product can be blended with 1 to 1.8 tons of middlings to increase the production of compliance coal.

The HHS process has been used for the recovery of micron-size rare earth minerals associated with a Leatherwood thickener underflow (LWTUF) sample. Comparison of the results of the HHS and forced air flotation processes showed that the HHS process performed much better than air flotation even though a Morganizer step was not used in these HHS tests. The best HHS product assayed 17,590 ppm TREEs on ash basis, which represented a 50 times REE enrichment from a feed assaying ~350 ppm REEs. The effects of different experimental parameters were studied to show that increasing the hydrophobicity (or oil contact angle) of the rare earth minerals is the key to effectively recover them from coal byproducts. It has been shown that the hydrophobicity of rare earth minerals increased by using appropriate collectors, depressant, hydrophobicity-enhancing agent, and sample aging. From this work, for the first time, it was found that phase inversion from o/w to w/o Pickering emulsions is necessary for improving the selectivity of the HHS process.

• Emulsification studies using ultrafine OTS-coated silica particles and chalcopyrite particles as solid surfactants (or emulsifiers) greatly improved the understanding of the role of ultrafine particles in forming Pickering emulsions and controlling the phase inversion. A model has been proposed to show the phase inversion improved with particle contact angles as measured with oil. The emulsification results revealed that making the oil contact angles of particles above

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90° is a thermodynamic requirement to achieve a phase inversion from an o/w to a w/o emulsion, which allows the Morganizer to remove entrained gangue minerals more efficiently and obtain higher grade concentrates. The phase inversion studies showed further that the Span[®] group non-ionic surfactants with low HLB values are effective hydrophobicity-enhancing agents for the phase inversion.

 \circ It has been shown that Sorbitan monooleate (SMO or Span 80) can greatly improve coal agglomeration, phase inversion, and hence the efficiency of the HHS process. The reasons for these benefits were that SMO can enhance particles hydrophobicity and also decrease the oil/water interfacial tension, which was confirmed by both contact angle measurements and thermodynamic analysis based on the acid-base theory. With the aid of SMO, the oil contact angle on a moderately hydrophobic surface can be increased to ~170°. By analyzing the HHS results obtained on a model silica sample, the adsorption mechanism of SMO on particles at different concentrations during the HHS process has been proposed.

• To explore the feasibility of expanding its application to recovering metallic minerals, the HHS process has been tested on artificial copper ore samples consisting of fine particles of 'pure' chalcopyrite and silica particles. The test conducted on the sample using KAX alone as a hydrophobizing agent required a long retention time. The problem has been amended by using a hydrophobic polymer (PX-1) as a hydrophobicity-enhancing agent. When using 250 g/t PX-1 in addition to KAX, the kinetics was greatly improved with the agglomeration time reduced from 50-70 minutes to 10 minutes to a ~90% recovery.

• A series of HHS tests was conducted on the cleaner scavenger tails samples taken from operating plants, which represented the slowest-floating particles. Encouraging results were obtained when the samples were ground further to improve mineral liberation. It was possible to

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produce copper concentrates assaying >20 %Cu from feeds assaying 0.25 to 0.5% Cu. The HHS tests conducted on a cleaner scavenger tail sample obtained from a large copper plant (Plant F) produced a 20 %Cu concentrate with a 44.4% recovery

• An HHS test conducted on a cleaner scavenger tail from Plant K produced a copper concentrate assaying 20 %Cu at recovery of 44.4% after a single stage operation. The HHS tests conducted on a flotation feed taken from Plant K produced 34-36 %Cu concentrates at recoveries in the range of 83-88%. These results demonstrated that the new process can be used to recover scavenger cleaner tails without creating a circulating load.

• The artificial copper ore samples were also used to conduct a series of continuous tests using an extraction column filled with packings. The packings provided a degree of turbulence and sites at which water droplets liberated from the w/o emulsions can coagulate and fall out from the oil phase. The column was operated using a flow of air in the form of small air bubbles, which helped create turbulence and prevent the chalcopyrite particles from falling by gravity.