Critical Metals Research From Primary And Secondary Sources at KIEM

Dr. Corby G. ANDERSON

Kroll Institute for Extractive Metallurgy
 The George S. Ansell Department of Metallurgical and Materials Engineering
 Colorado School of Mines
 Golden, Colorado USA 80401
E-mail : cganders@mines.edu

Globally, Critical Metals have become a focus in many countries and jurisdictions. While the primary production of Rare Earths has been highlighted, other less known but even more Critical Metals from primary and secondary sources have also been studied. At the Kroll Institute for Extractive Metallurgy, KIEM, much of the research effort is currently focused upon either the primary or secondary production of Critical Metals. In addition, the key underlying aspect of Criticality is also being addressed in the form of the development of desperately needed technically skilled personnel and technologies which are increasingly in demand. This paper will outline aspects of these topics.

Keywords : Critical, Metals, Materials, Rare Earths, Bastnaesite, Xenotime, Monazite, Eudialyte, Ancylyte, Germanium, Gallium, Zinc, Electronic Scrap, Galvanized Steel.

1 INTRODUCTION

Critical Metals have come to the forefront of global discussion in the past ten years. Most recently, the US DOI USGS has published a comprehensive study of Minerals currently deemed Critical to the United States⁽¹⁾. This book presents resource and geologic information on the following 23 mineral commodities currently among those viewed as important to the national economy and national security of the United States: antimony (Sb), barite (barium, Ba), beryllium (Be), cobalt (Co), fluorite or fluorspar (fluorine, F), gallium (Ga), germanium (Ge), graphite (carbon, C), hafnium (Hf), indium (In), lithium (Li), manganese (Mn), niobium (Nb), platinum-group elements (PGE), rare-earth elements (REE), rhenium (Re), selenium (Se), tantalum (Ta), tellurium (Te), tin (Sn), titanium (Ti), vanadium (V), and zirconium (Zr). For a number of these commodities—for example, graphite, manganese, niobium, and tantalum—the United States is currently wholly dependent on imports to meet its needs. Of these the Rare Earths have globally received the vast amount of attention. Unfortunately, Criticality is considered both a subjective and localized phenomenon. The US DOE CMI program has further delineated those Critical Materials as a subset that are specifically crucial for Energy and that are largely produced as by products^(2,3). Hence, different jurisdictions and countries have varying needs for and applications of various metals. That said, the defining aspect of Criticality is a demand situation coupled with limited availability of supply. Limited availability may be due to many factors and most often is based upon either resource scarcity or control of supply by a singular entity. More importantly, a critical lack of skilled talent or technology is clearly the current and long-term root of this issue^(4,5).

2 THE KROLL INSTITUTE FOR EXTRACTIVE METALLURGY

The Kroll Institute for Extractive Metallurgy, KIEM, was established in 1974 at the Colorado School of Mines in accordance with a bequest from William J. Kroll, world renowned extractive metallurgist best known for his inventions of processes for the production of titanium and zirconium. The financial resources of Dr. Kroll's bequest were intended to provide for the establishment of a Center for Excellence in Extractive Metallurgy at the Colorado School of Mines. Since its inception, the Kroll Institute has provided financial support to both undergraduate and graduate students at CSM, many of whom, subsequently, have made important contributions, nationally and internationally, to the fields of mining, minerals, metals and advanced materials.

Today, the mission of the Kroll Institute is to support the minerals, metals and materials industries through the following activities:

- Maintain expertise and research capabilities important to the minerals, metals and materials industries
- Perform cutting edge research
- Train process engineers for industry
- Develop short courses
- Develop specialty conferences

The academic environment creates a unique opportunity to

build scientific directions that accumulate expertise and can produce results of importance to the industry. Research at KIEM in electronic scrap processing is a good example. With one technological “foot” placed firmly in the mining-related area of metallurgy, KIEM stands astride the field of metallurgy, focusing on the process of Extractive Metallurgy regardless of application. Specific areas include:

- Processing of waste materials and the development of clean technologies
- Process development research focusing on improved commercial operations
- Production of new minerals-based by-products
- Chemical processing of materials, including materials synthesis
- Corrosion and reactive metals processing

As such KIEM is playing a key role in addressing the key aspect of Critical Materials availability by creating both desperately needed functional technical talent and technologies.

3 RARE EARTHS

Rare Earths, sometimes called the vitamins of modern materials, captured public attention when their prices increased more than ten-fold in 2010 and 2011^(6,7). As prices fell between 2011 and 2016, rare earths receded from public view—but less visibly they became a major focus of innovative activity in companies, government laboratories and universities. Geoscientists worked to better understand the resource base and improve our knowledge about mineral deposits that will be mines in the future. Process engineers carried out research that is making primary production and recycling more efficient. Materials scientists and engineers searched for substitutes that will require fewer or no rare earths while providing properties comparable or superior to those of existing materials. As a result, even though global supply chains are not significantly different now than they were before the market disruption, the innovative activity motivated by the disruption likely will have far-reaching, if unpredictable, consequences for supply chains of rare earths in the future.

At KIEM, extensive studies have been undertaken in the beneficiation of Rare Earth ores with a focus on separation and concentration by flotation as well as hydrometallurgical separations^(8,9,10,11). Much of this research has been undertaken through the DOE Critical Materials Institute hub. The Critical Materials Institute (CMI) focuses on technologies that make better use of materials and eliminate the need for materials that are subject to supply disruptions. These critical materials are essential for American competitiveness in clean energy. Many materials deemed critical by the U.S. Department of Energy are used in modern clean energy technologies, including wind turbines, solar panels, electric vehicles, and energy-efficient lighting.

3.1 Bastnaesite Beneficiation

Bastnaesite beneficiation by gravity and flotation have been studied at KIEM^(10,12,13,14,15). Flotation separation of bastnaesite from carbonate gangue has proved to be an exceedingly difficult task. Yet it remains the dominant unit operation for beneficiation of rare earth element-bearing minerals. The high specific gravity of

these minerals (bastnaesite and monazite) in relation to the gangue (calcite) suggests the opportunity for beneficiation through gravity separation. The purpose of this investigation was to determine the applicability of centrifugal concentrators to the beneficiation of a bastnaesite ore from Southern California containing large amounts of calcite gangue. Heavy Media Separation, MLA Analysis, and a Falcon Concentrator were used to show the amenability of this ore to gravity separation. From a feed averaging 12% calcium, 6.7% barium, and 3.4% rare earth elements (lanthanum, cerium, praseodymium, samarium, and neodymium), an optimum product of 14.5% calcium, 13.13% barium, and 7.8% rare earth elements was generated using the longest grinding time, lowest feed rate, and lowest G-force.

Many fundamental studies have been done using hydroxamates, fatty acids, and phosphoric acids as collectors to selectively float Bastnaesite. The focus of some KIEM current research is to find an economically viable collector that provides selectivity of Bastnaesite over its gangue minerals such as calcite. The fundamental studies included mineralogical characterization, adsorption density, zeta potential, micro flotation, and bench flotation. Recently, a suite of novel flotation collectors has been delineated with micro flotation and subsequent verification by bench and pilot scale testing to greatly enhance the rougher flotation of bastnaesite in terms of concentrate grade and recovery while separating away over 90% of the deleterious calcite gangue^(12,13,14,15).

3.2 Xenotime Beneficiation

In Xenotime flotation has been studied at KIEM. In one study⁽¹⁶⁾, a pre-concentrated xenotime sample and four selected gangue minerals, ilmenite, zircon, schorl and staurolite were used in this project. Using octano-hydroxamic acid as a collector, the surface chemistry was investigated through surface area measurements, zeta potential tests and adsorption density determinations. The results of adsorption studies were then correlated with microflotation tests conducted at room temperature in a Partridge-Smith cell. In this study, the surface chemistry and microflotation behaviors were discussed based on both lab observations and a literature review.

Because of their selective depressing power, sodium silicate and lignosulfonate have been widely used as depressants in rare-earth mineral flotation to separate minerals from specific types of gangue minerals. In this project⁽¹⁷⁾, the flotation of a xenotime pre-concentrate and pure samples of the gangue minerals ilmenite, zircon, schorl and staurolite using octano-hydroxamic acid and sodium oleate as collectors was conducted in a Partridge-Smith microflotation cell. The flotation of the mixed samples (weight ratio = 1:1) of xenotime and each one of its gangue minerals was also investigated at room temperature and 80°C, using sodium silicate and ammonium lignosulfonate in the presence of octano-hydroxamic acid and sodium oleate respectively. The flotation results are described and compared with those observed by previous researchers. The effects of sodium silicate and ammonium lignosulfonate on weight recoveries and grade of xenotime are also discussed and compared.

3.3 Monazite Beneficiation

Monazite flotation has been studied at KIEM⁽¹⁸⁾. Global

increase in rare earth demand and consumption has led to a further understanding of their beneficiation and recovery. Monazite is the second most important rare earth mineral that can be further exploited. In this study, the surface chemistry of monazite in terms of zeta potential, adsorption density, and flotation response by microflotation using octanohydroxamic acid is determined. Apatite, ilmenite, quartz, rutile, and zircon are minerals that frequently occur with monazite among other minerals, hence were chosen as gangue minerals in this study. The Iso Electric Point (IEP) of monazite, apatite, ilmenite, quartz, rutile, and zircon are 5.3, 8.7, 3.8, 3.4, 6.3, and 50.1 respectively. The thermodynamic parameters of adsorption were also evaluated. Ilmenite has highest driving force for adsorption. Adsorption density shows that hydroxamate adsorbs on to monazite and its gangue minerals. This observation was further confirmed by microflotation experiments. Increasing temperature to 80°C raises the adsorption and floatability of monazite and gangue minerals, which does not allow for separation. Appropriate use of depressants is recommended in order to achieve separation of monazite from its gangue

3.4 Ancylyte Beneficiation

The Bear Lodge Project is an important rare earth deposit in the United States^(19,20,21). KIEM has investigated recovery of Rare Earths from this deposit. Ancylyte, a strontianite rare earth carbonate, is a significant source of rare earth bearing minerals at Bear Lodge. In this research, essential aspects of the magnetic separation and flotation processes are presented. Based on an optimization of the variables and flotation simulation, a flowsheet was proposed. Furthermore, the economic feasibility for obtained processing conditions was analyzed. While extensive testing has settled on a crushing, screening, gravity and magnetic separation process, this study sets out to investigate an alternative flowsheet based on flotation and wet high intensity magnetic separation (WHIMS) to effectively beneficiate the rare earth oxide (REO) content of the Bear Lodge ore. Mineral characterization found ancylite was the dominant rare earth mineral, associated mainly with calcite and strontianite. Zeta potential studies indicated that the isoelectric points (I.E.P) of the material was around 5.27. The Sr^{2+} and CO_3^{2-} ions in solution significantly affected the surface change of the material. Hydroxamic acid, used as the collector, was chemically adsorbed onto the surface of the material, which was confirmed by both zeta potential and adsorption tests. WHIMS was employed to remove the iron content to reduce the interference of iron in following flotation process and consumption of hydroxamic acid. After cleaner flotation a REO grade of 11.2% at 72.7% recovery from a feed material of 4.5% REO was obtained. Overall REO grade of 11.2% at 61.2% recovery was achieved compared to previous grade of 6.64% at 86.4% recovery from similar feed grade material.

3.5 Eudialyte Processing

The beneficiation and hydrometallurgical treatment of eudialyte from Norra Karr has been researched at KIEM.^(22,23) The Norra Karr project in Sweden was undertaken by Tasman Metals Ltd., in consultation with ANZAPLAN, with the intention on determining the most suitable beneficiation route for the Norra Karr mineralized material. Different techniques were investigated, such as spiral concentration, electrostatic separation, high-G separation, magnetic separation and froth flotation. Results showed that aegirine could be selectively floated, but co-flotation of non-liberated particles

concluded that a direct flotation of eudialyte would be unsuccessful. recovery values were recorded for eudialyte via WHIMS, but with no significant upgrade in the rare earth concentration.

The literature survey regarding eudialyte beneficiation experiments indicate that at least a multiple step process is necessary for separation of the eudialyte mineral from its gangue components. At present, at KIEM, physical rejection of iron followed by sulfuric acid leaching appears to be a tangible approach allowing enhanced Rare Earth and Zirconium recoveries while minimizing the process impacts of iron gangue.

4 RECYCLING OF CRITICAL METALS

The production of Critical Materials from Recycling is a growing global industry⁽²⁴⁾. At KIEM, primarily through membership in the Center for Resource Recovery and Recycling (CR³), recycling research is active. The CR³ is a multi-university, member-driven collaborative. Four of the world's leading universities in materials engineering steer CR³, ensuring that it is making a difference globally.

4.1 Recycled Electronic Scrap Processing

The amount of e-scrap is growing globally. These highly engineered, complex materials are now being recycled to an ever higher degree. As such, enhanced separations as found in hydrometallurgy may play a key role in their processing. For example, 41.8 million tonnes of e-scrap was generated in 2014, and it is expected that the amount of e-scrap will reach to 49.8 million tonnes in 2018 with annual growth of 4% to 5%. E-scrap contains plastic and various metals, including precious and base metals. There are two primary reasons for recycling e-scrap: Economic potential of recycling precious and base metals Facilitate environmental and human health risks.

At KIEM recovery of Critical Metals from e scrap is also being studied. This study has provided an up-to-date review on the recycling of printed circuit boards (PCBs), specifically with hydrometallurgical treatment⁽²⁵⁾. Waste printed circuit boards, which are rich in base and precious metals, are the essential component of end-of-life electrical and electronic equipment. From the economic and environmental perspectives, the efficient recycling of PCBs is of importance. For the extraction of metals from PCBs, a large amount of work has been done to establish an environmentally friendly and economic way to recover metals from PCBs based on physical, pyrometallurgical and hydrometallurgical processes. Among those processes, hydrometallurgy is a promising treatment due to its low capital cost, high selectivity and less environmental impact. This review emphasizes the recycling of PCBs by physical and hydrometallurgical treatments.

4.2 Dezincing of Recycled Galvanized Steel

Globally, zinc supplies have recently been depleted while demand is increasing. AT KIEM a CR³ research project has developed a novel process for the dezincing of galvanized steel⁽²⁶⁾. This process is a pre-treatment step that removes the zinc coating from the steel, leaving a steel product with low zinc and sulfur residue that can be used as a feed in foundries. Galvanized steel is not presently used in foundries as they generally aren't set up to deal with zinc fuming from the coating.

The dezincing process involves leaching the zinc coating

from the galvanized scrap in sulfuric acid. This research has established there is an electro kinetic effect from steel surfaces on the dezincing reaction. Adjacent steel surfaces to the zinc increase the reaction rate by acting as a site for hydrogen reduction, the rate limiting step in the dezincing reaction. Acid concentration and temperature also greatly affect the dezincing reaction rate. When all these parameters are optimized the dezincing rate, and therefore plant throughput, of a dezincing operation can greatly increase.

In an effort to make the dezincing process a zero-discharge process, diffusion dialysis acid recovery technology was successfully coupled with the leach process, allowing for a large recirculating load of acid to be recycled between these two-unit operations. This minimizes acid use while maintaining optimum leach conditions.

It was determined that the low acid high zinc sulfate solution produced by the leaching and acid recovery is ideal for the generation of a value-added zinc fertilizer product through spray drying, a conventional route for zinc fertilizer production.

If the feed material and leach conditions are controlled to minimize dissolution of impurities, the need for a bleed is made redundant as the minimal amount of impurities can report to the final salable zinc fertilizer product. This can truly make this a zero-discharge process as the only outlets need be the dezincing scrap and the zinc product. Keeping the scrap in the leaching solution for as short a time as possible is key to accomplishing this. A method of monitoring the progression of the leach through monitoring a bulk corrosion potential of the scrap was tested and found to be successful at indicating completion of the dezincing reaction.

This work incorporates an economic analysis of the zinc fertilizer and decoated scrap markets. A dezincing process design with mass and energy balance was generated and used to cost a 20,000 tonne/yr dezincing operation for two flowsheet configurations. This culminates in indications for under which market conditions this process could be economically viable.

4.3 By Product Gallium and Germanium Recycling

In the production of zinc, both by product gallium and germanium may be produced. The use of tannins in this application has been researched at KIEM^(27,28). This study provided an up to date review of tannins, specifically quebracho, in mineral processing and metallurgical processes. Quebracho is a highly useful reagent in many flotation applications, acting as both a depressant and a dispersant. Three different types of quebracho are mentioned in this study; quebracho 'S' or Tupasol ATO, quebracho 'O' or Tupafin ATO, and quebracho 'A' or Silvafloc. It should be noted that literature often refers simply to "quebracho" without distinguishing a specific type. Quebracho is most commonly used in industry as a method to separate fluorite from calcite, which is traditionally quite challenging as both minerals share a common ion—calcium. Other applications for quebracho in flotation with calcite minerals as the main gangue source include barite and scheelite. In sulfide systems, quebracho is a key reagent in differential flotation of copper, lead, zinc circuits. The use of quebracho in the precipitation of germanium from zinc ores and for the recovery of ultrafine gold is also detailed in this work. As well, the industrial recovery of both gallium and germanium at the pilot

scale has been accomplished⁽²⁹⁾.

5 SUMMARY

This paper outlines the key aspects of Critical Metals being researched and developed at KIEM. It also addresses the Critical need for technical personnel and development that KIEM still continues to provide.

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