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[1.] Denisa VONICA, [2.] Mircea HRITAC,
[3.] Florentina NICULESCU, [4.] Nicolae CONSTANTIN

A REVIEW OF THE STATE-OF-ART FOR THE COPPER INDUSTRY

[1-4.] University "Politehnica" Bucharest, ROMANIA

Abstract: Copper has outstanding electrical and thermal conductivity, brought about in both cases by electron transfer. The recycling of copper is, for example, in Europe, well-functioning with established business for collection, treatment and processing of highgrade scrap. Copper is a versatile metal with a variety of industrial and residential applications, such as in electronic products, construction, industrial machinery, transportation and as alloying element inbrass and bronze. This is shown in the rather large proportion of the copper produced originating from secondary sources. Various secondary sources and wastes containing copper-based alloys are generated in industries such as brass scrap, waste residue of electric arc furnace, automobile shredder scrap, rayon industry sludge, and the alkaline batteries. Materials form the fabric of our present society and are everywhere in our lives. Many gold producers are today processing gold ores containing significant amount of cyanide soluble copper. There are many studies about the separating and recovering or hydrometallurgical process.
Keywords: resources, scrap, copper, recycling

INTRODUCTION

It can be assumed that there will continue to be a demand for copper also for future generations, as it has properties that are difficult to compete with in certain applications. The recycling rates for copper are good, some challenges can be foreseen, such as a scarcity of pure and high-grade scrap and an increased amount of products containing a mixture of materials and with low copper concentrations, which means that the processing industry must deal with more impurities.[1]

In recent years, there is a gaining considerable interest to recover metals, such as zinc, copper, iron etc., from the secondary sources and wastes. Separating and recovery of these metals is important and necessary both from view of economic point and the increased requirement of environmental protection.[2] Copper has outstanding electrical and thermal conductivity, brought about in both cases by electron transfer; many of its alloys have a very useful level of corrosion resistance.

In the galvanic series, their corrosion resistance is below that of noble metals, graphite, titanium, silver, passive stainless steel, and certain nickel alloys, but above that of active nickel, stainless steels, tin, lead, cast irons, carbon steels, and aluminum, zinc, and magnesium systems.[3]

The challenge of sustainability is rooted in the way that we now process resources to make materials and products, which are often discarded at the end of life. This linear economy is now running into its limits given the large demand for materials and resources of an increasing (and increasingly affluent) global population. Industrial society has become extremely dependent on resources, as it produces more, builds an increasingly complex society and accumulates an incredible volume of resources. Mankind now dominates the global flows of many elements of the periodic table (Howard and Klee, 2004).

The materials are drawn from natural resources. However, the Earth's resources are not infinite, but until recently, they have seemed to be: the demands made on them by manufacturing throughout the industrialization of society appeared infinitesimal, the rate of new discoveries outpacing the rate of consumption. Increasingly we realize that our society may be approaching certain fundamental limits. This has made access to materials an issue of national security of many nations, especially also to ensure that emerging new "sustainable" technologies can be supplied with metals and materials. [4]

THE STUDY OF THE ISSUE

Many different approaches have been taken to quantify the rates at which metals are recycled. Inevitably, recycling rates have been defined in different ways, and this has made it difficult to determine how effectively recycling is occurring. [5]

Copper is an essential trace element found in all organs and cells. The redox chemistry of this element makes copper highly suitable as a catalytic co factor in oxidative enzymes. The absorption is dependent on the amount ingested, its chemical form, and the composition of other dietary components such as zinc. [6] Typically, cyanide destruction is used to prevent the discharge of copper cyanide into tailings storage facilities. This imposes a significant financial cost to producers from the additional cyanide used to solubilise the copper and the cost of cyanide destruction reagents. This includes enabling the treatment of gold ores with even higher soluble copper. Over the *years, a variety of processes have been developed or proposed to recover the copper and/or cyanide including acidification based technologies such as AVR and SART, direct electrowinning, activated carbon, ion exchange resins, solvent extraction, polychelating polymers, and membrane technologies.*

In the paper, „A review of copper cyanide recovery technologies for the cyanidation of copper containing gold ores", these processes are critically reviewed and compared, with particular focus on the advantages and limitations, and the separation of copper from cyanide. Ultimately, there is no universal process solution and the choice is highly dependent on the nature of the stream to be treated and integration with the whole processing plant Due to the dwindling resources of simple cyanide extractable gold deposits, a large proportion of the gold processed in the 21st century will be recovered from complex gold ores, many of which will contain soluble copper mineralsVarious processes have been developed or proposed which all require a clarified feed solution.[7]

„A review of the genesis, geochronology, and geological significance ofhydrothermal copper and associated metals deposits in the great xing'an range", provides informations about the Great Xing'an Range, which is situated NE China, and hosts many hydrothermal Cu and other base and precious metal mineral deposits and mineralization. Is an important part of the giant Central Asian metallogenic belt, and has been the focus of many recent studies (Chen et al., 2011; Liu et al., 2004; Liu et al., 2012; Rui et al., 1994; Zeng et al., 2009, 2010, 2011; Zhao et al., 1997). Mineral exploration in this area resulted in the discovery of numerous large-,middle-, and small-sized Pb–Zn, Cu, andMo deposits, including the Errentaolegai and Jiawula Pb–Zn deposits, the Duobaoshan and Wunugetushan Cu–Mo deposits, the Lianhuashan and Naoniushan Cu–Ag deposits, and the Maodeng and Aonaodaba Cu–Sn deposits, and recent studies have increased our understanding of the processes that formed these deposits (Chen et al., 2011; Chu et al., 2012; Li et al., 2007; Liu et al., 2012). The hydrothermal copper and associated metals deposits in this area can be divided into three genetic types based on their geology and geochronology: porphyry Cu–Mo, high-sulfidation Cu–Ag and Cu–Sn epithermal, and Cu–Fe skarn.

All of these mineral deposits, barring the Cu–Sm epithermal deposits, are closely related to high-K calc-alkaline I-type graniticmagmatism. The geodynamic setting of the region during these mineralizing events is consistent with Early Paleozoic collision between the Xing'an Massif and the Songnen Terrane, Late Permian collision between the North China Craton (NCC) and the Heilongjiang Plate, Middle Jurassic collision between the Siberian Plate and the NCC epicontinental aggradational belt, and crustal extension and thinning during an Early Cretaceous collisional orogenic event. This indicates that the mineral deposits formed in an intracontinental transitional orogenic or post-orogenic extensional tectonic setting. [8] The work, "A critical review of the thermodynamics of hydrogen cyanide and copper-cyanide complexes in aqueous solution", brings the available thermodynamic data for the hydrogen/ cyanide and copper/cyanide systems in aqueous solution with special emphasis on measurements made at elevated ionic strengths and as a function of temperature.

The copper/cyanide system is of particular importance in gold hydrometallurgy as gold is often associated with copper sulfide minerals such as chalcopyrite, chalcocite, covellite and bornite, all of which except chalcopyrite are reasonably soluble in cyanide solutions due to the formation of copper/cyanide complexes. It has been found that,while reliable data are available at 25°C and very low ionic strengths, the data for higher ionic strengths and temperatures are limited. An attempt has been made to rationalize the available data, and to point out areas where further careful measurements are desirable. At low cyanide concentrations, Cu will be mostly present as the sparingly soluble white cuprous cyanide solid, CuCN(s). The solubility product for CuCN(s) at 25°C and infinite dilution was determined after an extensive study by Vladimirova and Kakovskii (1950).

In aqueous HCN solutions, the solubility of CuCN(s) varies with the square root of the HCN concentration. When copper minerals are present in gold cyanidation systems, especially those where remnant gold is recovered from copper sulfide flotation tailings, the cyanide-soluble copper is generally present in much higher concentrations than the gold, and can therefore compete with the gold for both available cyanide and for adsorption sites on activated carbon. This can cause significant processing problems both from excessive cyanide consumption and reduced gold adsorption into carbon, thereby increasing overall treatment costs and reducing recoveries. The equilibria between Cu and CN, in aqueous solutions are thus of critical importance in the study and modelling of real copper–gold–cyanide processes. The formation constants for Cu–CN– complexes, except for the difficult-to-detect CuCN0(aq), are well documented at 25 °C and at low ionic strengths. However, there is limited systematic knowledge on how these formation constants vary with ionic strength, solution composition and temperature. Further careful measurements of these effects are highly desirable because such constants are essential for modelling a variety of observed effects under actual hydrometallurgical conditions. A similar case can be made with regard to the corresponding enthalpies and entropies of reaction. [9]

ANALYSIS AND DISCUSSION

An important realization regarding metal recycling is that it is a sequence of steps. If any one step is done poorly, the efficiency of the entire sequence suffers. Attention needs to be paid to each of the steps, because one step may be the most inefficient for some types of products, other steps for others. The key questions, of course, are whether overall recycling efficiencies can be improved and, if so, by how much. That is, can materials cycles be transformed from open (without comprehensive recycling) to closed (completely reusable and reused), or at least to less open than they are at present.

These are issues that turn out to be quite complex, to involve everything from product designers to policies for pickup of discarded *electronics.[10] The use and degradation of refractory linings in copper furnaces are discussed, thereby describing the main steps taken at the research, developmentand industrial level to minimize refractory wear. Which combination of chemical, thermal and mechanical degradation mechanisms is dominantdepends on many factors such as the furnace type, the lining design, including the selection of the refractory type, and the process conditions.*

Magnesia-chrome bricks are widely used to line copper furnaces, despite the potential risk for the formation of hexavalent Cr under specificconditions, typically in the presence of alkali or alkaline earth oxides. This review concludes with refractory selection and use on the industrial level, including the waste and recycling management of spent refractories.The pyrometallurgical processing of copper from ores or recycled scrap, may comprise either batch, semi-continuous, or fully continuous processes, thereby involving smelting, converting and/or refining furnaces. The reliable and profitable operation of these furnaces strongly depends on the integrity of the vessel, which is often subjected to turbu-lent and aggressive process conditions.

It is however not the only driving force for the refrac-tory companies to develop new bricks and procedures. Although the most appropriate material to line the furnaces of the copper industry so far is considered to be the magnesia-chrome type due to its high resistance against slags with different basic, the possible formation of Cr6+, above all when working with calcium ferrite slags in converting processes or sodium carbonate/hydroxide slags in refining processes, has increased the interest in magnesia and alumina bricks as alternatives. To the best of our knowledge, the use of the latter brick types is still mainly in the research and development phase, and their future evolution will depend amongst others on how the use of Cr containing bricks in the steel industry will evolve.

Finally, with respect to the recent evolutions in the copper production, two trends that will affect further brick development should be mentioned. Firstly, the input material of the primary copper production is changing as concentrates with low levels of impurity elements are becoming more scarce. These increased level of impurity elements can change the refractory degradation behavior, either directly or through a change in operation conditions. Secondly,secondary copper production is gaining importance, there by introducing new flow sheets, operating conditions and input material compared to the primary production processes. Prior to this work, multiple interesting review papers on refractory for use in the copper production can be found. Schlesinger provides an overview of the copper production units and their factors influencing the refractory behavior, the history of refractory material types, the use of magnesia-chrome refractories for copper production and the prospects for chrome-free refractories. For a summary of the main chemical, thermal and mechanical degradation mechanisms, the work by Barthel, Taschler and Rigby can be recommended. The paper by Barthel describes the factors influencing the refractory lining in copper smelting furnaces and how chrome-magnesia and magnesia-chrome bricks behave under these conditions. Besides the wear mechanisms, the review work by Taschler, for refractory use in the copper and lead industry, describes the main slag properties, the evolution in brick development and the quality requirements.

The paper by Köffel and Taschler, has similar content as the review paper by Taschler. The review paper by Rigby is in particular interesting for the refractory linings of converters and anode furnaces in the copper industry. The main wear mechanisms, the operational factors influencing there fractory life-span and the effect of lining installation practice and brick quality for these furnaces are summarized.[11] The pyrometallurgical recovery of copper-based alloys with zinc from secondary resources had been studied under different conditions. The equipment used in the pyrometallurgical process always includes blast furnace, reverberatory furnace, and converter et al. Zinc existed in scrap copper-based alloys is widely distributed in various parts of the process, which not only result in some trouble in recovery of zinc but also reduces the recovery rate of other metals. For example, when copper-based alloys with zinc are smelted in the blast furnace, 12% w 15% by weight of zinc exists in black copper, 45% w 55% volatilizes into smelter flue dusts in the form of ZnO, and 30% w 35% remains in slag, which causes the melting point of slag to rise and viscosity to magnify, thus, copper is prone to be mixed in slag, which reduces the recovery rate of copper.

In the hydrometallurgical process, different leaching agents, including sulfuric acid, hydrochloric acid, acetic acid, cyanide and ammonia, were used, which were studied or developed by many authors. However, the hydrometallurgical methods have draw backs such as complex process flows, high consumption of chemical reagents, high cost in operation and secondary environmental pollution. Therefore, it is necessary to research a progressive process for the recycling scrap copper-based alloy containing zinc for a complex system in the form of piece or block. Treatment of zinc based on conventional pyrometallurgical process Separation and recovery process of zinc from scrap copper-based alloy was carried out under vacuum condition in a sublimation reactor. [12]

In the study, „Effect of accumulative roll bonding process on the electrochemical behavior of pure copper" the effect of accumulative roll bonding (ARB) process on the electrochemical behavior of pure copper in 0.01 M borax solution has been investigated. The microhardness tests showed that by implementing the ARB process the values of microhardness improve with increasing the number of ARB cycles. Copper are extensively used in industrial applications, corrosion prevention, power generation, and heat exchanger tubes. So, there is an interest in studying the corrosion and electrochemical behavior of this metal in different conditions, particularly in alkaline environments.

The passivation behavior of copper in the alkaline solutions is very important because of the scientific importance of this phenomenon. Indeed, the passive film provides an efficient barrier against the metal dissolution. This behavior has been studied in correlation to the *protective nature and the electrochemical behavior of the copper passive film. [13] The authors Graham Llong ,Yongjun Peng, Dee Bradshaw, in their work, related that the arsenic is a toxic and volatile element that has little commercial use. This is causing some concern to copper smelters as they are obliged to dispose of arsenic materials produced as a by-product to the smelting process in accordance with ever tightening environmental guidelines. The onus is to move back to concentrate producers to remove toxic elements, such as arsenic, earlier in the concentrate supply chain.*

The common copper–arsenic bearing minerals in copper ores, enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$), contain significant amounts of copper; 48.4% and 51.6% respectively. Removal of these minerals from the concentrate removes valuable metal, hence income. There is a dearth of literature concerning the selective removal of enargite and tennantite from sulphide ores, but there are reports on some success using either chemical oxidation or potential control. These methodologies have been applied to ores from mines as they deepen where arsenic levels in concentrate are becoming prohibitive. In copper ores, arsenic is often contained within tennantite ($Cu_{12}As_4S_{13}$) or enargite (Cu_3AsS_4). These copper–arsenic minerals contain 51.6% and 48.4% copper respectively, so they tend to float similarly to other copper sulphide minerals, reporting to the concentrate.

With smelters having to dispose of arsenic products in accordance with environmental regulations, they are becoming more selective in the concentrates they buy, and imposing financial penalties for excessive arsenic levels on concentrates when appropriate.[14]

CONCLUSIONS

Materials will play a key role in the transition of our society toward sustainability. Today, China produces half of all the cement, steel and other commodities in the world. Recyclable wastes are often collected by cities and municipalities, selling them into a market of traders and secondary processors who reprocess the materials to eventually sell them to manufacturers. In the recycling market, prices fluctuate according to the balance of supply and demand, the prices of materials made from primary resources, as well as the behavior and organization of markets and its stakeholders (the role of increased market power concentration, and speculation of silver and copper). This couples the price of the recycled material to that of the primary or virgin material. The markets are also affected by economic or policy interventions.[15] There are few studies of exposure levels in the work environment of copper-producing plants or plants using copper in their production in the scientific literature. Even fewer reported studies have used sampling techniques that take into account health-related aerosol fractions by sampling particles according to size. [16] Therefore, the recovery of copper as a valuable by-product and the recycle of cyanide to the leach circuit have the potential for significant economic and environmental benefits. It has been estimated that about 20% of all gold deposits have significant copper mineralization commonly associated with chalcopyrite, tetrahedrite, tennantite, as well as bornite and chalcocite in certain ores (Muir et al., 1989). It has also been found that the majority of copper minerals including copper oxides, carbonates, sulfides (with the exception of chalcopyrite) and native copper are highly soluble in cyanide solutions (Marsden and House, 2006). [17] There is limited systematic knowledge on how these formation constants vary with ionic strength, solution composition and temperature.

Further careful measurements of these effects are highly desirable because such constants are essential for modelling a variety of observed effects under actual hydrometallurgical conditions. A similar case can be made with regard to the corresponding enthalpies and entropies of reaction.[18] The factors affecting the evaporation ratio of copper-based alloy and the separation efficiency of zinc, such as heating temperature, residual gas pressure, vacuum evaporation time and the amount of scrap copper-based alloy were separately investigated. The experimental results revealed that zinc was successfully separated from the scrap copper-based alloy, where the evaporation ratio of copper-based alloy reached 18.43%.

Namely, 96.09% by weight of zinc could be removed under the condition: residual gas pressure of 50 Pa, heating temperature of 1323 K and vacuum evaporation time of 90 min. If corresponding to the residual gas pressure 500 Pa, the evaporation ratio reached 18.17%, and 94.73% by weight of zinc could be removed under the following experimental conditions: temperature 1323 K, vacuum evaporation time 180 min. Meanwhile, the thermodynamics of vacuum sublimation and refining to recover zinc was analyzed and calculated.[19] Copper are extensively used in industrial applications, corrosion prevention, power generation, and heat exchanger tubes. So, there is an interest in studying the corrosion and electrochemical behavior of this metal in different conditions, particularly in alkaline environments.

The passivation behavior of copper in the alkaline solutions is very important because of the scientific importance of this phenomenon. Indeed, the passive film provides an efficient barrier against the metal dissolution. This behavior has been studied in correlation to the protective nature and the electrochemical behavior of the copper passive film.[20] The authors Graham Llong, Yongjun Peng, Dee Bradshaw, in their work, related that the development of an economical method of removing arsenic bearing minerals earlier in the beneficiation stream is becoming increasingly more important. Magnetic separation of copper and copper–arsenic sulphides present a low chance of separation, so little work to progress this treatment option appears to have been conducted. Roasting was also used to reduce the arsenic content of copper concentrates at the El Indio mine, Chile.

A high arsenic–copper flotation concentrate was produced that contained 10.5% arsenic, contained within enargite and tennantite. Kappes et al. (2007) investigated an unnamed gold–copper deposit that contained elevated levels of tennantite. Product specifications required a copper concentrate below 2000 ppm arsenic.[21]

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