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Urban Mining: the way out for recycling non-renewable metal values

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Urban Mining: the way out for recycling non-renewable metal values

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RESUMO

Devido ao crescente avanço tecnológico, os equipamentos eletrônicos tornam-se obsoletos mais rapidamente, aumentando, progressivamente, a geração de sucata eletrônica. O número total de elementos químicos encontrados em resíduos de equipamentos elétricos e eletrônicos podem chegar a um número significativo de 60 elementos diferentes, com diferentes características físico-químicas, variando de metais de base aos metais preciosos, elementos do grupo das terras raras e recalcitrantes, como, por exemplo, o cádmio, o chumbo, o selênio etc. Diante deste cenário, é de fundamental importância que as atividades de pesquisa e desenvolvimento, com foco na reciclagem de metais, sejam realizadas. Esses metais advêm de recursos não renováveis que já foram extraídos do meio ambiente que, atualmente, estão disponíveis na superfície, na grande maioria dos casos, ainda mais concentrado em relação ao minério nativo de onde são originários. Em considerando, por exemplo, que para cada quilograma de metal reciclado com êxito evita-se a necessidade de prospecção para um quilograma de metal a partir do minério nativo, que, aliás, significa exploração de dezenas de toneladas de minério, considerando os baixos teores desses metais nas ocorrências atuais. Essa afirmação mostra que o resíduo eletrônico existente no planeta deve ser considerado como uma mina urbana à espera de ser processada. O objetivo da presente contribuição técnica é apresentar uma revisão da literatura sobre a extração de metais provenientes de fontes secundárias, com abordagens químicas e físicas, e acenar para rotas tecnológicas que podem ser utilizadas para a extração desses metais, a saber: rota pirometalúrgica, processos oxidativos, processos químicos convencionais, processos eletrolíticos e processos biotecnológicos.

Palavras chaves: reciclagem de sucata metálica, resíduos metálicos, separação de ligas, processos de recuperação, regulamentação ambiental.

ABSTRACT

Due to the increasing technological advancement, the electronic equipment are often replaced in an ever shorter period of time increasing gradually the generation of electronic scrap. The total number of chemical elements found in electronic waste may reach a significant number of 60 different elements, with different physico-chemical characteristics, ranging from base and precious metals, rare earth elements and recalcitrant ones, such as cadmium, lead, selenium etc. Facing these facts, it is of paramount importance that research and development activities focused on the recycling of these metals are carried out. They are non-renewable resources that have already been extracted from the environment, which are currently available on the surface, in the vast majority of cases even more concentrated when compared to the native ore. Bearing in mind, for instance, that for every kilogram of successfully recycled metal avoids the need of prospecting for a kilogram of metal from native ore, which, in fact, means exploring for dozens of tons of that ore, considering, nowadays, their low metal contents. This statement shows that the existing electronic residue on the planet should be considered as an urban mine, waiting to be processed. The objective of this technical contribution is to present a literature review on metals extraction from secondary sources, with physical and chemical approaches, waving to technological routes that may be used for extracting metals, namely: Pyrometallurgical processes, Oxidative Chemical Processes, Electrolytic and Biotechnological Processes.

Keywords: scrap metal recycling, metals waste streams, alloy separation, recovery processes, environmental regulation.

1 | INTRODUÇÃO

Metals play an important part in modern societies and have historically been linked with industrial development and improved living standards. Society can draw on metal resources from Earth's crust as well as from metal discarded after use in the economy. Inefficient recovery of metals from the economy increases reliance on primary resources and can impact nature by increasing the dispersion of metals in ecosystems. Though, the practice of recovering metals for their value dates back to ancient civilizations (WILSON, 1994). Today, the protection of Earth's resource endowments and ecosystems adds to the incentive for recovering metals after use.

Industrial society values metals for their many useful properties. Their strength makes them the preferred material to provide structure, as girders for buildings, rails for trains, chassis for automobiles, and containers for liquids. Metals are also uniquely suited to conduct heat (heat exchangers) and electricity (wires), functions that are indispensable to industrial economies.

Finally, metals and their compounds are used for their chemical properties as catalysts for chemical reactions, additives to glass, electrodes in batteries, and many other applications. The basic and unique properties of metals, including the ability to work them into complex shapes (*i.e.*, ductility), insure that long term demand for metals will certainly grow. Opinions on long-term metals demand range from predictions that grow in demand will pace the global economy (WILLIAMSON, 1997) to the position that the ascent of knowledge-based industries as economic drivers, competition from other materials, greater

consumption of lighter more sophisticated metal products, and more efficient use in the economy will slow the rate of future growth (TILTON, 1990; WILLIAMS, LARSON & ROSS, 1987).

Metals can be recycled nearly indefinitely. Unlike polymer plastics, the properties of metals can be fully restored, though not always easily, regardless of their chemical or physical form. Nevertheless, the ability to recover metals economically after use is largely a function of how they are used initially in the economy and their chemical reactivity. The success of secondary metals markets depends on the cost of retrieving and processing metals embedded in abandoned structures, discarded products, and other waste streams and its relation to primary metal prices.

Demand for scrap metals depends on industry structure and the availability of production technologies that accommodate scrap feeds to yield value added products. This complex market relies on the decisions of many independent actors including scrap dealers, brokers, dismantlers, and smelters. The model of industrial ecology emphasizes the containment and reuse of wastes generated by society as an overarching guideline for improving environmental quality. To realize this model, industry and society should work together to recover metals by recirculating them from all secondary sources and losing a minimum amount of material from the industrial/social system (ALLENBY, 1992; TIBBS, 1992).

The commercial success of scrap markets in the United States is evidenced by the fact that recovered metals comprise more than half of the metals input to producers. In the early 1990, net U.S. exports of scrap metal averaged 8-10 million metric tons (MMT) and net export earnings totaled from \$1.5-3 billion

annually (SIBLEY, BUTTERMAN & STAFF, 1995). International trade in scrap metal neared 40 MMT in 1995, rising more than 65% from a low level in the early 1980 (WULFF, 1997). Global commercial interest in secondary metals supports daily published price reports for secondary metals (AMERICAN METALS MARKET), industry standards for metal scrap (INSTITUTE OF SCRAP RECYCLING INDUSTRIES, 2012), and comprehensive global industry surveys of primary and secondary production for individual metals.

Governments have historically been interested in the available supply of scrap metals particularly during wartime. In the United States, the U.S. Bureau of Mines traditionally collected information on secondary metals production and conducted research on secondary metals processing for industry. Beginning in the 1980s, the Bureau began analyzing secondary and primary metals trends in the context of other material classes, such as plastics and forest products (U.S. BUREAU OF MINES, 1990; ROGICH & STAFF, 1993). Since the closing of the Bureau in 1995, this function has been assumed by the U.S. Geological Survey (USGS) Minerals Information team, which continues to collect and analyze data on secondary metals (BIVIANO, SULLIVAN & WAGNER, 1997).

In the interest of containing metals once they have entered the industrial/social system, barriers are identified to this goal by describing the primary and secondary metal resources available to society, current and past levels of metals recovery, processes for isolating and processing metals from secondary sources, and the major environmental regulations affecting secondary metals processors. We refer almost exclusively to data and examples from the United States, while emphasizing the underlying science and technology, which is universal.

One hundred percent recovery to satisfy demand represents more of a goal than an attainable reality, even for precious metals where the incentive to recover value is highest. Thus, even if demand for metals were to stay level in the future, new metal would always be sought. Nonetheless, this exercise provides an incentive and a framework for examining alternatives to dispersive metals use, improving conditions for the efficient operation of secondary metals markets, identifying design changes for industrial and consumer products to provide for greater recovery, and stimulating research on industrial processes for recovering metals.

2 | METALS EXTRACTION FROM PRIMARY AND SECONDARY RESOURCES

Metal production begins with either primary or secondary resources. Primary resources, or ores, contain relatively high concentrations of metals and are generally found at depths up to 1 kilometer beneath the surface. Secondary sources include all metals that have entered but no longer serve a purpose in the economy. For metal producers, the choice of whether to use primary or secondary sources is determined primarily by the type and capacity of existing capital equipment, quality of the feed, metal prices, and relative supply.

Metals exist in nature mostly in combination with oxygen (oxides) or sulphur (sulphides). Ore deposits are of three types. The first class, high grade "alluvial" (such as the metal mined in the "gold rush") and "massive" deposits can be subjected directly to pyrometallurgical (smelting) or hydrometallurgical (leaching) processes to produce metal. The second class consists of metal compounds mixed with relatively valueless "gangue" minerals, like silica (SiO_2) and calcium carbonate (CaCO_3), that after liberation by crushing and grinding can be removed by physical separation methods (e.g., gravity or magnetic separation and flotation) to produce high-grade concentrates for metallurgical processing. The third class includes finely dispersed minerals that cannot be separated physically from the gangue minerals and must be smelted or leached directly despite their low metal contents. To process complex metal ores that contain several metals in varying concentrations, metals producers have developed sophisticated methods to separate and refine individual metals starting from complex mineral hosts.

i) Thermodynamics and Kinetics Aspects for Extracting Metals out of Secondary Sources

Extracting metals from primary or secondary resources generally requires chemical processing to isolate the metal in the desired chemical form. Thermodynamic principles establish the feasibility of a chemical reaction under certain operating conditions while kinetics (chemical rate, mass and heat transfer) determine the overall rate at which the reaction will proceed. For metal concentrations, recovering metal generally requires stripping metal atoms of oxygen or sulphur atoms. Recovery of metal from scrap on the other hand generally requires removal of alloying elements or the attainment of a given alloy composition. The melting point needed to be reached for re-melting and refining scrap metal is also determined by the chemical composition of the scrap, which depends on the presence of alloying elements and other metals.

Determining whether the reaction will proceed depends on the available free energy of the particular reaction and the latter is a function of temperature. For example, the Ellingham diagram for oxidation-reduction reactions, plots the available free energy in kJ/mol of oxygen reacted against temperature for all known oxidation reactions including that of C, CO, and H₂ and shows graphically the relative reducibility of any particular oxide. Considering the most commonly used metal, iron, which is found naturally as an oxide and is reduced by carbon or hydrogen to form metallic iron and CO, CO₂, or H₂O. Figure 1 shows that at 1200K, carbon will reduce FeO but not Cr₂O₃, which requires a higher temperature (EVANS & JONGHE, 1991). Figure 1 also shows that higher temperatures generally decrease the free energy of the reduction reaction and explain

the dominance of pyrometallurgy in primary metal production and recycling. Similar diagrams exist for other metallic compounds such as chlorides and also for metals in aqueous solutions.

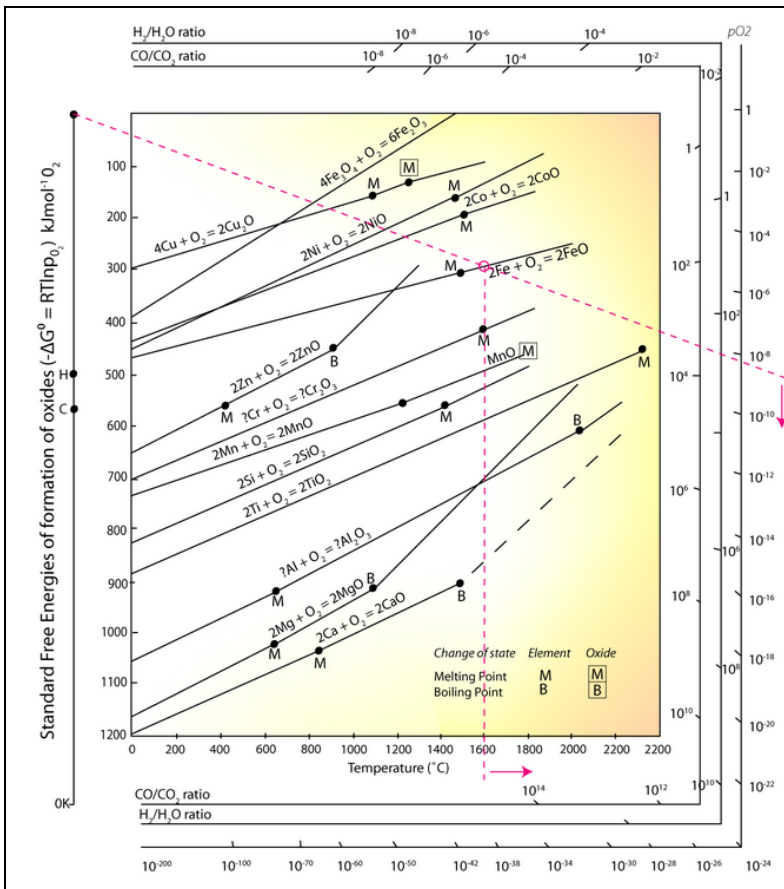


Figure 1. Ellingham Diagram for Oxides.

Source: http://www.doitpoms.ac.uk/tlplib/ellingham_diagrams/printall.php

Ellingham diagrams also illustrate the available options for restoring value to secondary metals sources. For example, the Ellingham diagram for chloride formation shows that it is possible to remove magnesium from aluminum alloys by exposing the molten alloy to chlorine gas. The same diagram shows that this method is only useful for magnesium, sodium, and calcium, and that other refining methods must be used to remove other alloying elements (BUTTERWICK & SMITH, 1986).

ii) Mineral Reserves and related economic aspects

Deciding whether to mine and process a given ore body relies on the current and projected prices of the contained metals and their relation to the production costs. The discovery of new deposits increases the global supply. Technological advances in the excavation and processing of minerals that reduce production costs can render previously neglected ore bodies economically recoverable. As a result, the quantity of ores considered as reserves changes dynamically with technological innovation as well as fluctuations in global metal prices. The reserve base (including resources currently uneconomic to mine) appears adequate for the near term even if humanity relies exclusively on primary resources. However, fully exploiting the reserve base would entail high environmental costs through significant emissions of carbon (FORREST & SZEKELY, 1991; THEMELIS & WERNICK 1997) and sulphur oxides and landscape disturbance for mineral exploration and development.

Secondary metal supplies fall into two general classes, new and old scraps. The former refers to metal discards generated within an industrial setting, either at metals producers or from metals

fabricators. As new scrap stays within the mill or factory, the quality (*i.e.*, chemical composition) is generally well known and homogeneous. As a result, this metal readily returns to the production loop. Old, or obsolete, scrap refers to metal collected after use in the economy in the form of discarded infrastructure, industrial equipment, or consumer goods. This scrap is more heterogeneous and often contains a mix of metals, alloys, and non-metals. Moreover, the buildup of residual elements makes refining difficult, reducing the market value of recycled metal with each cycle of recovery. The ability to determine precise scrap's metal contents constrain old scrap utilization. For example, erroneous estimates of bulk content made by extrapolating surface composition or through sampling can serve to disrupt optimal production schedules.

iii) Metal Prospection and Related Environmental Impacts

One of the most striking environmental benefits of secondary metals production is the reduction in energy needed to produce a ton of metal. The primary reason for this phenomenon is that melting metal requires less energy than that needed for reducing naturally occurring oxides and sulphides. Steel produced from primary ore uses three and one half times more energy than steel from melted scrap. Copper from ore requires five to seven times more energy than that required for processing recycled metal as this ratio rises with decreasing ore grade. Aluminium from ore uses approximately twenty times more energy than from recycled metal (CHAPMAN & ROBERTS, 1983).

In addition to conserving energy resources, metals recycling also reduces mining and beneficiation activities that disturb ecosystems. Though land used for the extraction of primary

metals represents under 0.1% of Earth's terrestrial surface (BARNEY, 1980), exploration and mining activity can affect surrounding ecosystems due to necessary infrastructure and by dispersing metal compounds into the environment, either as air borne particles or as ions in aqueous solutions. Developing newly discovered resource deposits can also damage sensitive ecosystems, especially in less developed regions where the need for foreign exchange from mineral rents overshadows domestic environmental concerns (HODGES, 1995).

Secondary metals sources include other liquid and solid waste streams that are not considered traditional scrap but contain significant metal contents. Examples include metal slags, dross, and dusts from metals producers and sludges generated from metal using industries. Unlike traditional scrap recovery, the main objective here is to reduce disposal costs and avoid regulatory liability by removing metals from voluminous wastes. For these sources, the value of the recovered metal at prevailing metal prices generally provides insufficient economic incentive to individual operators. Nonetheless, recovery from these sources amounts to substantial quantities at the national scale.

2.1 | Extracting Metals Out of Waste Streams

Due to the increasing technological advancement, the electronic equipments are often replaced in a period of time increasingly short causing the gradual increase in the generation of electronic scraps (SILVA *et al.*, 2007). The total number of chemical elements found in electronic waste may reach a significant number of 60 different elements, with different physico-chemical characteristics, ranging from base

kilogram of metal from native mineral resources, which, in fact, means exploring dozens of tons of ores, bearing in mind, nowadays, their low metal contents. This statement shows that the existing electronic waste on the planet should be considered as an urban mine, waiting to be processed.

2.1.1 | Physical separation

The first stage in the recycling of metal is its separation from other materials. The difficulty of separation increases with lower metal contents in the source. Pieces of an individual metal (e.g., copper wires in cables) are the easiest to recycle, while metals thinly distributed in products (e.g., copper in printed circuit boards) require additional processing steps for recovery. The largest single source of scrap metal from obsolete products comes from discarded automobiles. At the first stage, valuable components are removed from the car hulk, whose value as parts far exceeds that of the contained material. After parts are stripped, the hulk is shredded to yield a ferrous and nonferrous metal fraction as well as Automotive Shredder Residue (ASR) comprised of plastic, rubber, glass, carpet etc. The auto scrap industry is highly efficient, recycling 90-95% of the roughly 10 million automobiles discarded annually in the U.S. and producing about 11 MMT of iron and steel scrap in a typical year (JOM, 1995), as well as over 0.7 MMT of other metal scrap.

Separating the iron and steel from shredded automobiles takes direct advantage of their magnetic properties to isolate them from nonferrous metals and non-metallics. Advances in materials science have led to the introduction of rare earth alloy permanent magnets with high field strength (e.g., neodymium-boron-iron magnets that generate fields up 35 million gauss)

that require no power to operate and have sufficiently high fields to allow for the recovery of even weakly magnetic stainless steels (VEASEY, 1997).

To recover non-ferrous metals from mixed feeds, scrap processors exploit differences in physical characteristics, such as density and electromagnetic properties, for isolating metals from other materials and from one another. Immersing mixed scrap feeds in high density liquids produces a “sink” and “float” fractions that separate lighter metals such as aluminium and magnesium from heavier ones like copper and zinc. Hydrocyclones afford greater control in stratifying waste streams containing different metals and alloys by creating a density gradient proportional to applied centrifugal forces. Air classifiers separate metals from non-metallics, such as paper and plastic packaging, by allowing these lighter materials to be carried away by a jet of air that is too weak to carry the heavier metal components of the waste (WAKESBERG, 1994).

Both surface and bulk electromagnetic properties of metals can also be exploited to isolate metal waste streams. For instance, differences in surface electrostatic properties allow scrap handlers to remove plastic sheathing from copper and aluminium wire (BORSECNİK, 1995). The eddy current separator produces an oscillating magnetic field that induces currents in conductors (*i.e.*, metals) that generate a repulsive force to separate them from non-conductors (NORRGRAN & WERNHAM, 1991). After removal of the ferrous fraction, conventional eddy current separators isolate nonferrous metals from non-metallic. Advanced models can sort among various nonferrous metals as well. Though primarily used for scrap recovery from shredded automobiles and MSW (municipal solid

waste), these devices have been tested successfully for recovering fine metal fragments from industrial wastes like ground slag and foundry sand.

Scrap processors use several techniques to separate metal alloys. To achieve gross separation, scrap handlers examine clean pieces of metal (e.g., drill cuttings that have not been allowed to oxidize) to distinguish between copper (red) and zinc (yellow) alloys for instance. More precise characterization is achieved by testing the alloy's reactivity when exposed to various acids. Chemical spot testing, for instance, indicates the presence of the major alloying elements in 2000 series (high copper), 5000 series (high magnesium), and 7000 series (high zinc) aluminium alloys. Scrap handlers can also examine the spectroscopic signature of metal samples thus determining alloy composition for any given sample. In 1990, spectroscopic analysis using lasers was introduced in automobile shredding operations (SATEER, 1995). On the basis of rapid spectroscopic analysis of laser light reflected from a piece of metal, the mixed metal scrap is automatically sorted into streams containing aluminum, zinc, and copper alloys, as well as stainless steel and lead destined for different conveyor belts. The use of automated systems that rely on these various methods for alloy separation should increase scrap throughput as well as scrap quality and thus help society process more of the metal currently discarded.

2.1.2 | Chemical separation

Several technologies dominate the industrial processes used to remove or recover metals from industrial waste streams, including contaminated soils (SMITH, MEANS & BARTH, 1995). The efficiency of metals recovery in these cases depends on

the metal concentration in the solution, properties of the host solvent (e.g., pH, viscosity), and the other metals and chemicals also present in the solution. Standard hydrometallurgical as well as pyrometallurgical processes are used to remove metals from some industrial wastes. Depending on the waste stream, other recovery methods may be appropriate. Chemical precipitation removes metal ions from aqueous solutions by transforming them into insoluble compounds, which are then removed by physical methods. Ion exchange techniques remove metal ions from solution by exchanging them with weakly bound ions in a resin or organic liquid. Membrane technologies rely on differences in the permeability of metals and the host solution.

Another relatively obscure source of secondary metal is found in the metals flows associated with Acid rock Drainage (ARD). While contemporary mining regulations require mine owners to seal mines after their useful life, mines abandoned decades and centuries ago were simply left exposing elements. With time, the acidity levels in these mines rises as sulphurous material lay exposed to water, air and indigenous microorganisms. The high acidity levels serve to mobilize metal atoms that would otherwise remain bound in the geologic matrix. Streams and rivers in old mining regions, such as south-western Pennsylvania, in the U.S, and the ancient Lavrion silver mines in Greece, typically carry thousands of tons of metals values annually (KONTOPOULOS *et al.*, 1996), without mentioning the pyrite bearing coal residues out of the coal mining. These streams impact the environment by introducing abnormally high metals to surrounding and also distant ecosystems. Most technical work done to address ARD problems has the explicit objective of remediating past pollution. However, recent attempts in the U.S. and Europe have quantified the metal

values available from recovering these high concentration metals streams using chemical, biological, and electrochemical technologies (CONCURRENT TECHNOLOGIES CORPORATION, 1996). For a review of the ARD treatment methods for remediation and recovery, see Gazea, Adam & Kontopoulos (1996).

2.1.3 | Chemical Catalysts

The value of minor metals used as chemical catalysts (e.g., molybdenum, vanadium, and cobalt) has stimulated industry to develop new methods for recovery (INOUE & ZHANG, 1995; GABALLAH *et al.*, 1995). Typically, these methods employ hydrometallurgical techniques to leach waste materials in strong acid solutions and which are then subjected to solvent extraction or ion exchange treatment to bind metal ions with an organic agent that is later "stripped" to yield concentrated solutions of individual metals. The individual metals can, then, be obtained from the solutions by electrowinning or as precipitated salts of a particular metal.

Petroleum refineries use metal catalysts to remove sulphur compounds from crude oil, for "cracking" it to smaller molecules, as well as other unit operations. Several hydrometallurgical processes have been developed for recovering molybdenum, vanadium, cobalt, and nickel from petroleum catalysts (LLANOS & DEERING, 1995). A typical spent catalyst contains 5-16% sulphur, 1-8% molybdenum, 1-13% vanadium, 1-3% nickel, 10-30% carbon and 20-30% aluminium in the form of alumina (Al_2O_3). These materials are recycled by four principal processors globally. All together, they handle about 65 kMT metric tons of catalysts annually (CASE, GARRETSON & WIEWIOROWSK, 1995).

Automobile emissions control in most developed countries is achieved with the help of catalytic converters that use the platinum group metals (PGM), platinum, palladium and rhodium. In 1992, the global use of these metals in automobile catalysts amounted to 1.5 million troy ounces of platinum (34% of total global), 0.5 million ounces of palladium (13%) and 0.3 million ounces of rhodium (87%). Catalytic converters consist of a stainless steel canister containing platinum group metals deposited on alumina with high surface area, which lies on a substrate of synthetic cordierite ($(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$ a silicate mineral), a ceramic material. Depending on the size of the automobile, the weight of the packed canister ranges from about 2 to 11 kg and typically contains about 1 kg of metal catalyst per metric ton of packing. Recovering PGMs is accomplished by dissolving the contained metals in a copper melt followed by conventional electrorefining of the copper, or leaching in sulphuric acid solutions followed by electrowinning. Other processes in various stages of development have been reviewed by Hoffman (1988), Mishra (1993) and Kuczynski, Atkinson & Dolinar (1995).

2.2 | Metal Extraction From Secondary Sources

Over the twentieth century, US metals consumption grew consistently until the mid 1970, when several factors combined to reduce domestic demand. Though the capacity and output of secondary production plants in the U.S. grew significantly during World War II, when national metal demand for armaments rose sharply and the war severely restricted world metal exploration and trade. From 1939 to 1943, secondary copper production rose almost 120% and secondary aluminium

production shot up over 300% (U.S. BUREAU OF THE CENSUS, 1975). Recovery rates for secondary aluminium are only now beginning to approach World War II levels. Following the energy shocks of the 1970s, metals demand failed to resume its upward trajectory due to several factors including saturated markets, other materials substituting for metals, and a shift to lighter metals, most notably aluminium (WERNICK, 1996). Since 1960, when data on secondary metals were first systematically collected, secondary metals production rose in fits and started with an average annual increase of about 4.9%. Primary metal production grew at less than 0.5% annually over the same period.

Steel dominates the metal tonnage handled by the secondary metal industry, but not the value. In 1993, iron and steel comprised 90% of the weight of the old scrap recycled in the U.S. while it represented only 42% of the metal value. In value terms, aluminium follows with 26%, copper at 15%, and gold with 10% of old scrap value (SIBLEY, BUTTERMAN & STAFF, 1995).

Several metals that are commonly alloyed with commodity steels to improve properties (*e.g.*, strength and machinability) follow steel through the recycling loop. For example, 75% of molybdenum (1996 US consumption 14.5 kMT) went to iron and steel producers in 1996. Depending on the fate of the steel, some of this metal will recycle in the general ferrous scrap stream. Similarly, vanadium (4.7 kMT) finds its primary use as an alloying agent for iron and steel and most recovered vanadium recycles in ferrous scrap. As a final example, though the recovery of manganese (716 kMT) as an individual metal is negligible, a considerable amount is recycled annually during recovery of ferrous scrap and iron and steel slag.

The recovery of several toxic metals depends on how they are used in products. Nickel-cadmium batteries now account for almost two thirds of the market for cadmium metal (KUCZYNSKI, ATKINSON & DOLINAR, 1995) and expanded recovery systems are now developing. On the other hand, over 90% of the arsenic consumed in the U.S. is used for wood preservation.

The recycling of toxic metals may not be as important to the environment as ensuring that these metals do not become biologically available during or after use in the economy. Humans and animals require trace amounts of certain metals (e.g., iron, aluminium, zinc) as part of their diet, but can experience both chronic and acute adverse health effects at levels too high. Metals like arsenic, cadmium, and lead; however, are toxic in even small amounts and have no known nutritional value. For metals in solution, the ability to cause harm depends on their solubility, and their ability to leach through soils and wastes relies on the acidity and composition of the medium. Efforts to reduce human exposure, through efficient recovery or by sequestration in products, landfills, or some vitrified form, need to primarily consider the environmental transport mechanisms.

2.2.1 | Extraction Processes

i) Iron and Steel

As noted earlier, iron and steel constitute over 90% of all metal production and a similar fraction of the scrap metals market. Steel mills consume about three quarters of the scrap, and iron and steel foundries consume the remainder to produce ferrous castings.

The ability of steel plants to accept scrap inputs has been influenced by technology changes. For a good review of developments in pneumatic steelmaking in this century until the 1980, see Pehlke (1980). From the beginning of the century until the 1950, the open hearth furnace dominated steelmaking technology. It used primarily pig iron, but could accommodate more than 50% scrap in its mix due to the use of an external heat source. The succeeding technology, the Basic Oxygen Furnace (BOF) process was introduced by Voest Alpine in Austria in 1952 as the Linz-Donawitz (LD) converter, and has undergone further developments with innovations such as the Q-BOP (bottom-injected) oxygen converter. Today BOF processes account for about 60% of US steel production. The primary feed of the BOF is molten pig iron from the blast furnace. The BOF also accepts from 10% to 30% scrap in the metal charge to the furnace. The US average is about 25% (KIRK-OTHMER, 1996). It should be noted, though, that most scrap used in BOF comes from the mill itself. Old scrap comprises at most half of the scrap in the charge (FOSTER, 1994).

The Electric Arc Furnace (EAF), introduced commercially for the melting of iron and steel scrap in the mid 1960s, accounts for the other 40% of US steel production. Electric arc furnaces use electricity conveyed by graphite electrodes (arcing) to melt scrap and can accommodate 100% scrap in the feed. EAF production is sensitive to the presence of residual elements like zinc, copper, chromium, and molybdenum, which can cause defects in the finished steel at levels measured in tens of parts per million. Metals with low boiling points like zinc and cadmium volatilize when the charge is smelted and collect in dust filters used to treat emissions. Other residuals are more difficult to

refine out, though some novel methods for removing residual elements using flotation processes to recover aluminium, magnesium, and plastics from ferrous scrap and micro-alloying methods that make positive use of residual elements (MCMANUS, 1997).

The Institute for Scrap Recycling Industries classifies more than one hundred standard grades or codes for ferrous scrap (INSTITUTE OF SCRAP RECYCLING INDUSTRIES, 2012). The grades specify gross physical characteristics such as acceptable dimensions for individual pieces and densities for baled scrap. The presence of coated metal as well as threshold levels of residual alloying elements are also specified. The different grades of scrap distinguish between sources such as factory stampings, shredded auto bodies, and obsolete railroad equipment. The grading system has helped the industry grow through standardization and its extent indicates the heterogeneity of ferrous scrap available on the market. New scrap supplies with known chemical composition can be introduced in a controlled manner into the EAF. However, the supply of new scrap is inelastic and tied to current production levels. Furthermore, innovations such as continuous casting and other efficiency improvements have reduced the amount of clean home scrap generated in mills and factories. Therefore, expanding EAF capacity must rely on old scrap whose supply may be essentially unlimited but whose quality ranges widely. EAF plants still use almost 95% scrap in their furnaces. However, as EAF mills seek to improve the quality and value of their products, they have come to rely on augmenting the scrap charge with primary iron products such as Direct Reduced Iron (DRI) and pig iron to dilute the residual elements present in the scrap charge (KISER, 1994).

ii) Aluminium

Like other metals, aluminium is used either in pure form (e.g., aluminium foil) or alloyed with other metals. The ASTM specifications for the most common aluminium alloy, Al6061, include copper (0.15-.6%), magnesium (0.8-1.2%), silicon (0.4-0.8%), zinc (<0.25%) and iron (<0.7%) (ASME/ASTM, 1992). This alloy, used widely for aerospace, automotive, railroad and other industrial applications, offers light weight, good corrosion resistance, and excellent formability. As indicated by the above specifications, alloying contents above a certain level have a detrimental effect on the desirable properties. This makes the sorting of aluminium scrap, prior to melting, essential to avoiding difficult and costly refining procedures. Van der Donk *et al.*, (1995) report that aluminium scrap from Dutch household waste contained 0.06% copper, 0.03% zinc, 0.10% silicon, 0.50% manganese and 2.6% iron. A comparison with the ASTM specification for alloy Al6061 shows that only the iron content of the recycled household scrap is above specification.

Aluminium scrap is usually processed in a reverberatory furnace. The name "reverberatory" derives from the consideration that heat "reverberates" ("radiates" is more technically correct) from the roof and walls of the furnace onto the molten metal bath. Then, superheated metal is pumped through the charge well in which metal scrap and fluxing materials are charged continuously. Existing furnaces can process up to 5-6 tons per hour (t/h) of scrap. Wells *et al.*, (1995) investigated the effects of various operating parameters on the efficiency and metal recovery of an aluminium reverberatory furnace. The formed dross material (aluminium and other oxides) is skimmed periodically from the surface of the bath and can contain 20-80% aluminium. The incentives to

process this by-product material are tempered by concern over the treatment of the generated wastes. New processes are under development to recover metal value from aluminium dross and generate benign waste products (KEMENY, SOSINSKY & SCHMITT, 1992).

iii) Copper

Copper is used primarily in electrical and plumbing systems and in heat exchangers. It enters the economy either as pure metal, copper alloys, or in combination with tin and zinc in bronze and brass. Recycled pure metal can be simply re-melted and combined with primary electrorefined copper. Copper alloyed or physically mixed with other metals is melted either at secondary or primary smelters and cast into anodes along with the virgin metal prior to electrorefining (GOCKMANN, 1992). Segregated copper alloys can also be used as raw material in bronze and brass foundries. Secondary copper smelters feed low grade copper scrap with coke into a blast furnace to produce "black" copper that contains lead, zinc, and other impurities. Volatile elements like zinc and lead oxides are then driven off by partial oxidation to produce "blister" copper. Hanusch & Bussmann (1995) report on the refining of copper scrap to remove associated metals. Prado and Prado (1995) discuss the treatment of copper dusts rich in lead and zinc.

The KALDO reactor of the Boliden corporation in Sweden uses another process for smelting low-grade copper scrap. In the Boliden process, metal scrap containing on average 40% copper, 10% zinc, and 15% iron is charged to an inclined rotating vessel. Coke is added as required and oxygen-enriched air is injected through a lance. The heat of oxidation of the iron, zinc, and lead drives off the volatile metal oxides and produces

impure copper and an iron-rich slag that can be reduced to less than 0.5% copper and zinc. The copper smelter at Porto Marghera, Italy uses this process and has annual capacity of 25 kMT per year of secondary copper (HENDLUND, 1995). Much copper, as well as other metals, is discarded annually in millions of computers and other pieces of electronic equipment that end up in landfills. Discarded electronic scrap contains roughly 40% metals (e.g., copper, iron, aluminium, nickel, tin, lead) with the remainder accounted for by plastics and refractory oxides (HOFFMANN, 1992). Precious metals recovery gives the primary incentive for recovering metal from electronic scrap with typical contents (circa late 1980s) of 770 grams/ton (g/t) for gold, 1500 g/t for silver, and 40 g/t for palladium. Copper, silver, gold, palladium, platinum and other noble metals are generally integrally distributed in circuit elements and can be recovered pyrometallurgically by smelting into liquid copper and then recovered by conventional electrorefining. To optimize value recovery, processors remove steel and aluminium structural components that would anyway be discarded in the by-product slag of the pyrometallurgical process.

The Noranda process reactor at Noranda, Quebec, recycles about 100 kMT of used electronics per year in addition to 6-700 kMT of primary copper concentrates (VELDHUIZEN & SIPPEL, 1994). Even when used electronics are collected, as of the early 1990s, the market price in the U.S. was only 50-60\$ per ton. Initial design for easy disassembly and downstream "manufacturing" technologies can reduce the cost of recovery and allow for more economic recovery of metals. This is especially important as future electronic scrap waste streams

may contain even smaller volumes of precious metals as industry becomes more efficient at depositing thinner layers of precious metals on electronic components.

iv) Lead

The largest use of lead (~80%) in the U.S. total goes to automotive and industrial lead acid batteries. About 95% of the used batteries in the U.S. and other developed nations undergo recycling. Lead batteries consist of a polypropylene case, lead lugs, electrodes (typically screens), plastic spacers between the electrodes, lead oxide paste (PbO_2 and PbSO_4) and sulphuric acid.

A typical lead battery weighs about 11 kg and contains 7 kg of lead and 3 kg of sulphuric acid. At a typical recycling plant, batteries are crushed or sliced and separated into three streams: lead materials (about 60% lead, 15% PbO_2 and 12% PbSO_4) (CHAVEZ *et al.*,1995), polypropylene scrap, and sulphuric acid. The lead-containing materials are smelted (*i.e.*, heated to produce a molten bath) to produce lead bullion and a molten silicate solution containing all of the lead oxides. This slag by-product is smelted and reduced with carbonaceous material and fluxing agents in a lead blast furnace, similar to those used in the primary smelting of lead oxides. The low-lead slag produced in such furnaces is environmentally inert and is disposed in industrial landfills.

In another lead recycling process, used extensively in Europe, lead components are smelted at 1000°C with coke breeze and sodium carbonate flux and iron filings, used to fix sulphur by forming an iron sulphide matte, in a short fuel-fired rotary furnace. It is reported that use of bulk oxygen and other innovations can increase the production capacity of such

furnaces by 40% (SUTTIE, 1995). The ISASMELT furnace process, used in Australia and South Korea, introduces lead materials with lump coal into a vertical reactor containing a slag bath (WRIGHT, JAHANSHAHI & ERRINGTON, 1994). Air and oxygen are injected in this reactor that is similar to the top blown BOF furnace used for steelmaking. During smelting, metallic lead containing less than 0.01% antimony settles in the bottom and is periodically tapped out of the furnace. When the upper slag layer in the reactor reaches a certain depth, the slag is reduced from 40-60% lead and 5-6% antimony, to 2-4% lead and less than 1% antimony by continuous injection in the presence of coal. Most of the treated slag is then tapped out of the reactor and the cycle repeats (BREW, FOUNTAIN & PRITCHARD, 1991). Thus, the two-reactor process used in the U.S. (reverberatory and blast furnace) is replaced by a two-stage process in a single reactor.

v) Zinc

The foremost use of zinc today (55% of total US consumption) is as a corrosion-inhibiting coating on steel products (*i.e.*, galvanizing) (DIAZ, MARTIN & LOMBERA, 1995). Therefore, much of the recycled zinc originates in the re-melting of steel scrap in the EAF and the waste materials of the zinc coating process (ash and dross). Other uses of zinc include brass and bronze alloys (~20%), zinc alloys (13%) and chemicals (10%).

The high temperature of the EAF process results in the volatilization of zinc and some iron, and the production of a very fine EAF dust that may contain anywhere from a few percent up to thirty percent zinc, depending on the feed to the furnace. Typically, the EAF operation produces 10-15 kg of dust per ton of steel produced that also contains 20-40% iron, 1-4% lead,

0.5%-3% chlorine and 0.1-0.5% fluorine (ZUNKEL, 1995). The predominant process used for smelting high zinc recycled materials is the Waelz rotary kiln in which zinc is reduced, volatilized and recovered in the form of impure zinc oxide containing 50-60% zinc. The iron residue from the kiln can be used along with iron scrap to produce steel in an EAF. The zinc oxide dust can be sent for further processing to a zinc-lead blast furnace (Imperial Smelting Process) or to a primary zinc plant where it is dissolved in sulphuric acid along with the primary zinc oxides.

A number of other pyrometallurgical processes have been developed for the treatment of EAF dusts, including the Flame Reactor process of Horse head Resources (BOUNDS & PUSATERI, 1990; WU & THEMELIS, 1992). The University of British Columbia and Chaparral Steel have developed a hydrometallurgical process that recovers pure zinc hydroxide-zinc carbonate materials as well as lead, copper and cadmium from EAF dust (DREISINGER, PETERS & MORGAN, 1990). Other emerging hydrometallurgical processes such as the Ezinex (OLPER, 1995), and the Zincex (DIAZ, MARTIN & LOMBERA, 1995), processes leach the EAF dust and separate the metal ions by cementation (*i.e.*, displacing one metal in solution by another), solvent extraction, and electrowinning. By the mid 1990, US capacity for EAF dust recovery of zinc exceeded 95 kMT (SIBLEY, BUTTERMAN & STAFF, 1995).

2.2.2 | Extraction Metals from Electronic Scraps

There are several technological ways of processing electronic scraps for extracting base and precious metals, and each one of those has its own particularity.

i) Pyrometallurgical process

The pyrometallurgical technological route is commonly used for extracting metals out of electro-electronic scraps, from which we can produce pure metals, alloys or chemicals. In this process, the electronic scrap, that contains high copper content, is sent to a blast furnace, where the majority of the volatile impurities are oxidized. Then, a copper bullion is generated, which contains almost all the precious metals. That copper bullion is further electro-refined to produce electrolytic copper and an anode slime, which is further treated for extracting its precious metals.

ii) Oxidative Chemical Process

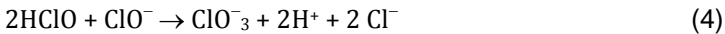
In this process the electronic scrap, properly fragmented, is mechanically suspended in hydrochloric acid solution in an optimized concentration, with the addition either of hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaClO), generating chlorine gas (Cl_2) in the bulk, as shown in the equations 1 and 2 below:



The reaction of chlorine gas with the acid aqueous medium generates hypochlorous acid in solution, as shown in equation (3):



The oxidative chemical process goes on a dismutation reaction that takes place between hypochlorite ions (ClO^-) generating chlorate ions (ClO_3^-), as shown in reaction 4, thus, increasing the oxidative power of the reaction medium, causing more intense dissolution of base and precious metals (Au, Ag, Pt and Pd).



iii) Electrolytic Process

In electro-leaching of electronic scraps, the material to be treated is mechanically suspended, in sodium chloride solution, and the metals in solution are electrowon and the metallic deposit at the cathode surface, is further electro-refined, in another electrolytic system, which produces the electrolytic copper (999.9/1000) and an anodic slime, as a result of anodic dissolution of impure copper, which contains, in its majority, precious metals (Au, Ag, Pd and Pt). What characterizes this process is the generation of strong oxidizing agents in the reaction system, through the electrolytic oxidation of chloride ions in solution. The Figure 3 depicts the reaction system where the electro-leaching process takes place. The reaction 5 shows the oxidation of chloride ions into chlorine gas, which in contact with the aqueous phase, produces the strong oxidizing species, as above mentioned in reactions 3 and 4.



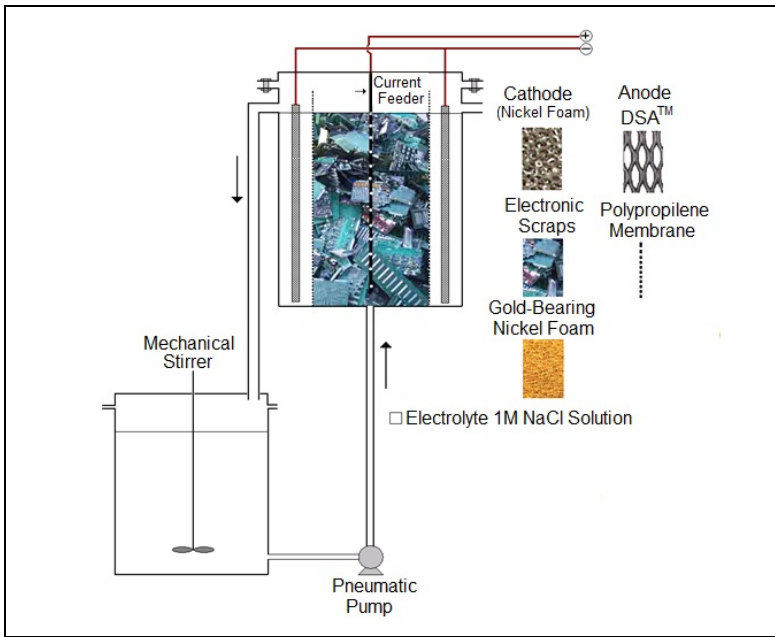


Figure 3. Electro-leaching reaction system.

iv) Biotechnological Process

More recently, a few studies were conducted on bioleaching metals from electronic scraps (XIANG, 2010; LIANG, 2011; YAMANE 2010, LEE, 2012). For example, acidophilic strains of chemolithotrophic and heterotrophic bacteria were cultivated together to extract metals from PCBs (LEE, 2012). In addition, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were mixed culture to bioleach metals from printed wire boards (PWBs) (WANG, 2009). Moreover, factors influencing copper recovery from PCBs by *A. ferrooxidans* were studied (YAMANE, 2010). Undoubtedly, using microorganisms to bioleach metals

from electronic scraps will be a promising alternative in comparison to traditional methods. As it is known, ultimate goal for metals bioleaching from PCBs by microorganism is to maximize its addition amounts and metals recovery, which was closely related to bacterial growth.

This process is a promising alternative, because it does not require high energy consumption and has low implementing and operating costs, as the microorganisms are responsible for the generation of oxidizing agent in the reaction system (Fe^{3+}) out of the Fe^{2+} oxidation that can be added to that system either as in the soluble form ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or insoluble one (FeS_2). The Figure 4 depicts how the bioleaching process takes place.

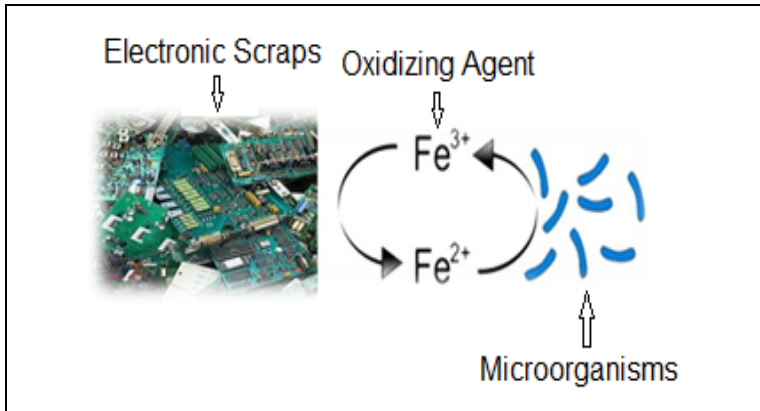


Figure 4. Bio-extraction of metals out of electronic scraps.

Brandl *et al.*, (2001), Choi *et al.*, (2004), Ilyas *et al.*, (2007), Wang *et al.*, (2009) and Yang *et al.*, (2009) demonstrated, in studies in which employees were acidophilous mesophilic and thermophilic micro-organisms, which metals can be recovered from printed circuit boards by microbial leaching. The

mechanism for dissolving the metals contained in electronic scrap is very similar to the mechanism of sulphide minerals dissolution, the example is the copper oxidation (equation 5) in which the Fe^{3+} produced biologically oxidizes metallic copper to Cu^{2+} , as shown in the equation 6.



The role of the micro-organism, in this case, is to re-oxidize Fe^{2+} to produce Fe^{3+} thus establishing a reaction cycle.

The Figure 5 shows the flow of operation and process units for extracting base metals from electronic scraps we are considering in our bio-extraction of metals out of electronic scraps at CETEM.

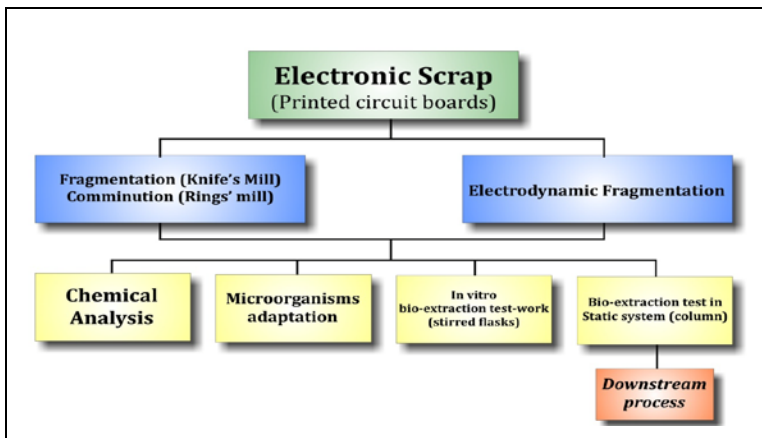


Figure 5. Operation and process units for Bio-extracting metals out of electronic scraps being used in lab-scale at CETEM.

The micro-organisms able to promote the oxidation of Fe^{2+} are acidophilous, quimiothrophics (obtains energy from the oxidation of inorganic compounds), autotrophic organisms (running the biosynthesis of all cellular constituents using the carbon dioxide (CO_2) as the only source of carbon) and are classified according to the temperature in which they develop, distinguishing themselves in: mesophiles (up to $\sim 40^\circ\text{C}$), moderate thermophiles ($\sim 40 - \sim 55^\circ\text{C}$) and extreme thermophiles ($\sim 55 - \sim 80^\circ\text{C}$) (SOBRAL, OLIVEIRA & SOUZA, 2011)

2.3 | Environmental Regulation

Federal, state, and local environmental regulations affect the secondary metals industry like any other. Government regulates the air emissions coming from secondary smelters and storm water runoff emissions from open scrap yards. Regulatory waste classifications also determine the transport, handling, treatment and disposal options available for metals loaded wastes (FOSTER, 1994).

The Clean Air Act (CAA) mandates the use of Best Available Technology for secondary smelters to control for criteria air pollutants. The 1990 amendments to CAA require Maximum Achievable Control Technologies to reduce hazardous emissions and directly affect operations at EAF mills, integrated steel mills, and secondary smelters of aluminium and lead. The Clean Water Act (CWA) controls for environmental discharges of toxic pollutants including the metals copper, lead, zinc, and their compounds, as well as organic materials commonly found in scrap, such as machining oils and polychlorinated biphenyls (PCBs).

The most comprehensive solid waste regulation, the Resource Conservation and Recovery Act (RCRA), regulates the generators and transporters of wastes with rigid requirements for treatment and disposal. The Hazardous and Solid Waste Amendments to RCRA define e-Solid Waste to include recyclable materials thus placing the full regulatory burden of waste disposal on scrap handlers. Many metals-loaded wastes exhibit one of USEPA's conditions (*i.e.*, ignitability, corrosivity, reactivity, or toxicity) for being considered hazardous waste. Due to its indiscriminacy, this regulatory designation impedes the collection, transport and recovery of metal wastes without improving environmental protection. Responding to outside criticism, the USEPA initiated efforts in the early 1990's to reform RCRA and to facilitate greater national metal (and other material) recovery (EPA, 1995). For instance, the economic recovery of metal from discarded consumer products like nickel-cadmium batteries and mercury thermostats require central processing facilities and must thus contend with regulations on inter-state waste transport. In the mid 1990, USEPA issued the Universal Waste Rule (ELECTRONIC CODE OF FEDERAL REGULATIONS, 1995), to reduce regulatory requirements for metals waste such as these and stimulate investment in recovery facilities. The economic success of facilities that have begun to introduce these wastes into their process stream will be essential to greater closure of the metal system.

2.3.1 | The Comprehensive Environmental Response, Compensation, and Liability Act

CERCLA/"Superfund" affects the secondary metals industry by holding liable Potentially Responsible Parties that generate, transport, or treat metal wastes associated with a Superfund

site. The Basel convention agreement designed to limit the unchecked flow of hazardous waste from rich to poor countries also has the effect of subjecting international scrap trade to a new regulatory regime. While regulations have been effective in controlling air and water emissions from point sources, much remains to be done to promulgate legal definitions in sweeping regulatory packages such as these that serve to protect the environment, as well as encourage the optimal metals recovery (FROSCH, 1996).

3 | CONCLUSIONS

The preceding analysis offers some perspective on the economic, technical, and regulatory factors affecting secondary metals recovery worldwide. Estimates of the quantity of metal dissipated from the industrial system need to consider the nature of the products that incorporate the metal, production losses, and losses from corrosion and wear over time. Despite the difficulty, many excellent studies have been carried out for individual metals (THOMAS & SPIRO, 1994; FROSCHE, 1996), though much room remains for systematic analysis.

The metal incorporated into infrastructure and products can be considered as valuable inventory and is prevented from returning to the production stream. Much potentially recoverable metal also lies in obsolete scrap heaps for which market forces have been so far insufficient to enable economic recovery. For instance, the accumulation of discarded ferrous scrap alone in the U.S. was estimated to be nearly 700 MMT by the late 1980 (FROSCHE & GALLOPOULOS, 1989).

Secondary sources include recycled metal scrap that remains within industry and metal contained in consumer products. Metals producers have returned process scrap to the production stream since antiquity. In the past decades, however, this recovery has become more efficient and has included clean scrap generated within downstream industries. Metals recovery systems have also developed for some consumer products (e.g., discarded lead-acid batteries, autos bodies) with recovery rates approaching one hundred percent. Metal recovery from products benefit from increased industry adoption of design for recyclability (e.g., reducing the number of alloys used, alloy compatibility, easy disassembly) guidelines by manufacturers.

Improved instrumentation and sorting systems enable scrap processors to reduce the degradation of properties and increase the throughput of scrap. Secondary smelters contribute by developing blending technologies that minimize the loss of metal to metallurgical by-products like slag, and the loss of value in metal alloys.

More dilute metals waste streams remain largely unexploited. Over 60% of the metal discarded in MSW (municipal solid waste) and the metals values in many industrial waste streams go unrecovered. Metals used in small amounts for specialized applications not requiring bulk are not easily retrieved from products or individual waste streams. However, in several instances, industry has found it profitable to capture opportunities to collect metal wastes from disparate sources to profitably recover metal values. These initiatives typically involve large capital investments in centralized facilities and must take advantage of economies of scale to collect and process metal waste streams. The profitability of such facilities depends on market forces, which are shaped by the regulatory environment, collection infrastructure, and capital costs.

Reducing human exposure to highly toxic metals depends on continued diligence in controlling emissions from metals producers and from their use in non-dissipative products. Major dispersive uses of toxic metal in applications such as herbicides and gasoline additives have been phased out in the U.S. over the last several decades by legislative decree. In other instances, research has enabled substitutes to replace toxic metals in consumer and industrial applications. Recovery of the toxic metals bound in products relies on regulatory incentives, the development of a suitable collection infrastructure, and available process technologies. These factors combine to

determine the economics of secondary metals recovery from disparate sources. Alternatively, the potential environmental impact of toxic metals can be reduced by their disposition in an inert form.

Metals will remain an integral part of future industrial society due to their unique and valuable properties. Decades of increased productivity and more efficient technologies for metals production and use has diminished the share claimed by the primary and secondary metals industries in world's economy. Nonetheless, metals appear in every rung in the ladder of value addition in the manufacturing base and are ubiquitous in the everyday activities and industrial backbone that supports modern economies. Because of the centrality of metals in industrial and consumer artefacts, improving resource efficiency and reducing losses in the metals sector cannot help but influence positive environmental change throughout the fabric of industrial society.

Finally, this technical contribution aimed at bringing about a technological discussion on the recycling metal values from non-renewable sources as an attempt to save money, energy and time while searching for metals out of ores bearing in mind that they are available in elemental form in a real "Urban Mine".

REFERENCES

- ALLENBY B.R., Industrial Ecology: The Materials Scientist in an Environmentally Constrained World. *Materials Research Bulletin*, vol. 17(3), p46-51, 1992.
- AMERICAN METALS MARKET. Available in < <http://www.amm.com>>.
- ASME/ASTM Boiler and Pressure Vessel Code, Section II, Part B: Non-ferrous Materials, ASME, NY, SB308/308M, 1992.
- BIVIANO M, SULLIVAN D & WAGNER L. Materials Flow Studies, Total Materials Consumption ñ An Estimation Methodology and Example Using Lead. US Geological Survey, Minerals Information Office, Presented at the 8th International Symposium on Raw Materials, Federal Institute for Geosciences and Natural Resources, Hannover, Germany, 1997.
- BORSECNIK J. Carpcó Resolving Separation Anxiety. *Scrap Processing and Recycling*, January/February 1995, pp. 108-113, 1995.
- BOUNDS C.O & PUSATERI J.F. EAF Dust Processing in the Flame Reactor Process. pp. 511-528 in *Lead-Zinc '90*. Mackey TS, Prensaman RD (eds.) TMS, Warrendale, PA, 1990.
- BRANDL, H. BOSSHARD, R., WEGMANN, M., Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. *Hydrometallurgy*, vol. 59, p.319-326, 2001.
- BREW R.B.M., FOUNTAIN C.R. & PRITCHARD J. ISASMELT for Secondary Lead Smelting. pp. 170-181 in *Lead '90*, Lead Development Association, London, 1991.
- BUTTERWICK L, SMITH GDW. Aluminum Recovery From Consumer Waste, Part I Technology Review. *Conservation and Recycling* 9(3):281-292, 1986.
- CASE A, GARRETSON G & WIEWIOROWSKI E. Ten Years of Catalyst Recycling. *Ibid*. pp. 449-468, 1995.

- CHAPMAN P.F. & ROBERTS F. Metal Resources and Energy, p. 138. Butterworths. Boston, MA, 1983.
- CHAVEZ F, MORALES RD, ROMERO A & GUERRERO A. Optimizing Rotary Furnace Smelting of Battery Residue. pp. 337-347 in Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials. Queneau PB and Peterson RD eds. Available from TMS, Warrendale, PA. 1995.
- CHOI, M-S., CHO, K-S. & KIM, D-J. Microbial recovery of copper from printed circuit boards of waste computer by Acidithiobacillus ferrooxidans. J. Environ. Sci. Health, Part A, Environ. Sci. Toxic. Hazard, vol. A39, n^o 11, p. 1-10, 2004..
- CONCURRENT TECHNOLOGIES CORPORATION. Recovering Metal Values From Acid Mine Drainage: Market and Technology Analyses. Prepared for the Southern Alleghenies Conservancy, Bedford, PA. Available on web at <<http://ctcnet.net/sac/ctc001.htm>>50, 1996.
- DIAZ G, MARTIN D, LOMBERA C. Zinc Recycling by the Modified Zincex Process. pp. 623-638 in Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials. Queneau PB and Peterson RD eds. Available from TMS, Warrendale, PA. 1995.
- DREISINGER DB, PETERS E, MORGAN G. The Hydrometallurgical Treatment of Carbon Steel EAF Dusts by the UBC-Chapparral Process. Hydrometallurgy 25(2):137-152. 1990.
- ELECTRONIC CODE OF FEDERAL REGULATIONS (CFR) 40 part 273, 1995.
- EVANS J.W, DE JONGHE L.C. The Production of Inorganic Materials. p. 58. Macmillan Publishing. New York, NY. 1991.
- FORREST D & SZEKELY J. Global Warming and the Primary Metals Industry. JOM 43(12):23-30. 1991.

- FOSTER R.J. Recycling in the Major Metal Industries: Trends, Developments, and Regulatory Impacts. U.S. Bureau of Mines Information Circular/1994, Report no. PB94-203585, U.S. Department of Interior. 1994.
- FOSTER, R.J., Recycling in the Major Metal Industries: Trends, Developments, and Regulatory Impacts. U.S. Bureau of Mines Information Circular/1994, Report no. PB94-203585, U.S. Department of Interior. 1994.
- FROSCHE R.A, Toward the End of Waste: Reflections on a New Ecology for Industry, *Daedalus* 125(3):199-212. 1996.
- FROSCHE R.A & GALLOPOULOS NE. Strategies for Manufacturing: Waste from one industrial process can serve as the raw materials for another, thereby reducing the impact of industry on the environment. *Scientific American*, September 1989, pp. 144-152. 1989.
- GABALLAH I, DJONA M, MUGICA JC & SOLOZABAL R. Low Temperature Selective Chlorination of Used catalysts for the Recovery of Transition and/or Refractory Metals. *Ibid*, pp. 405-424. 1995.
- GAZEA B, ADAM K & KONTOPOULOS A. A review of passive systems for the treatment of acid mine drainage. *Minerals Engineering* 9(1): 23-42. 1996.
- GOCKMANN K. Recycling of Copper. *CIM Bulletin* 85:150-6.54.1992.
- HANUSCH K & BUSSMANN H. Behavior and Removal of Associated Metals in the Secondary Metallurgy of Copper. pp. 171-188 in *Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials*. Queneau PB and Peterson RD eds. Available from TMS, Warrendale, PA. 1995.
- HENDLUND L. Flexible Recycling with Boliden Technology. *Ibid* pp. 155-162. 1995.

- HOFFMAN J.E. Recovering Platinum-Group Metals from Auto-Catalysts. JOM 40(6):40-44. 1988.
- HOFFMANN J.E. Recovering Precious Metals From Electronic Scrap. JOM 44:43-8. 1992.
- ILYAS, S., ANWAR, M. A., NIAZI, S. B., GHOURI, M. A. Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. Hydrometallurgy, vol. 88, n^o 1-4, p. 180-188, 2007.
- INOUE K & ZHANG P. Separation and Recovery of Rare Metals From Spent Hydrodesulfurization Catalysts by Solvent Extraction. pp. 393-404 in Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials. Queneau PB and Peterson RD eds. Available from The Minerals, Metals, and Materials Society, Warrendale, PA. 1995.
- INSTITUTE OF SCRAP RECYCLING INDUSTRIES. Annual. Scrap Specifications Circular: Guidelines for Nonferrous Scrap, Ferrous Scrap, Glass Cullet, Paper Stock, Plastic Scrap, Electronics Scrap, Tire Scrap, Washington, DC., 2012.
- JOM - Journal of the Minerals, Metals and Materials Society, 47(5):4, 1995.
- KEMENY FL, SOSINSKY DJ & SCHMITT RJ. Development of a dc Plasma-Arc Furnace for Processing Aluminum Dross. pp. 1147-1153 in Light Metals 1992 Proceedings of the 121st TMS Annual Meeting Mar 1-5 1992 San Diego, CA. The Minerals, Metals & Materials Society (TMS) Warrendale, PA.53, 1992.
- KIRK-OTHMER Encyclopedia of Chemical Technology, Fourth edition. Vol. 20, p. 1097.52, 1996.
- KISER K. 1994. Ferrous Scrap Substitutes: A Growing Piece of the Mill Mix. Scrap Processing and Recycling 51(6):40-48.
- KOEHN S., Urban Mining: Recycling as a Key to Ensure Raw Material Supply, Business Journal of the German Chamber of Commerce in China, 2012.

- KONTOPOULOS A., XENIDIS A, KOMNITSAS A & PAPASSIOPI N. 1996. Environmental Characterization and Monitoring of the Wastes in Lavrion. Fourth International Symposium on Environmental Issues and Waste Management in Energy and Minerals Production, Cagliari, Italy, Oct. 7-11, 1996.
- KUCZYNSKI RJ, ATKINSON GB & DOLINAR WJ. Recovery of Platinum Group Metals From Automobile Catalysts-Pilot Plant Operation. pp. 527-544 in Proceedings of the Third 51 International Symposium on the Recycling of Metals and Engineered Materials. Queneau PB and Peterson RD eds. Available from The Minerals, Metals, and Materials Society, Warrendale, PA. 1995.
- LEE J. & PANDEY B.D., Bio-processing of solid wastes and secondary resources for metal extraction – A review, Waste Management 32, p. 3–18, 2012.
- LIANG G., MOB Y. & ZHOU Q., Novel strategies of bioleaching metals from printed circuit boards (PCBs) in mixed cultivation of two acidophiles, Enzyme and Microbial Technology 47, p 322–326, 2010.
- LLANOS Z.R, DEERING W.G. Processes for the Recovery of Metals from Spent Hydroprocessing Catalysts. Ibid, pp. 425-448. 1995.
- MCMANUS GJ. Getting the Full Value Out of Scrap. Iron and Steel Engineer 74(10):58-9. 1997.
- MISHRA RK. Review of Platinum Group Metals Recovery from Automobile Catalytic Converters. p. 449-474 in Proceedings of the International Precious Metals Institute: Precious Metals 893. ed. RK Mishra Proceedings of the International Precious Metals Institute, Newport RI. 1993.
- NORRGRAN D.A & WERNHAM J.A. Recycling and Secondary Recovery Applications Using An-Eddy-Current Separator, Minerals & Metallurgical Processing 8(4):184-187. 1991.
- OLPER M. Zinc Extraction from EAF Dust with Ezinex Process. pp. 563-578. 1995.

- PEHLKE R.D. Steelmaking-The Jet Age. Metallurgical Transactions B 11B: 539-562. 1980.
- PRADO F & PRADO F.L. Secondary Copper Smelter Dusts: An Economical and Environmentally Friendly Reclamation. Ibid. pp. 831-840. 1995.
- ROGICH D.G, &STAFF. Materials Use, Economic Growth, and the Environment, Presented at the International Recycling Congress and REC'93 Trade Fair, U.S. Bureau of Mines, Washington, DC. 1993.
- SATEER H.P. The Laser Scrap Sorting Technique: New Developments and First Operational Experience. pp. 57-64 in Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials. Queneau PB and Peterson RD eds. Available from The Minerals, Metals, and Materials Society, Warrendale, PA. 1995.
- SIBLEY S.F, BUTTERMAN W.C & STAFF. Metals Recycling in the United States. Resources, Conservation, and Recycling 15: 259-267. 1995.
- SIBLEY SF, BUTTERMAN WC & STAFF. Metals Recycling in the United States, Resources, Conservation, and Recycling, 15: 259-267. 1995.
- SILVA, B. D.; MARTINS, D. L. & OLIVEIRA, F. C. Resíduos eletrônicos no Brasil. Santo André, 2007. Revisão em Abril de 2008 – Felipe Fonseca. Disponível em:< <http://www.lixoeletronico.org/>> Acesso em: 14/05/2012.
- SMITH LA, MEANS J & BARTH E. Recycling and Reuse of Industrial Wastes. Battelle Memorial Institute, Battelle, Columbus, OH. 1995.
- SOBRAL L. G. S., OLIVEIRA D. M.& SOUZA C. E. G. (Ed.), Biohydrometallurgical processes: a practical approach, Rio de Janeiro: CETEM/MCT, 2010.

- SUTTIE AB. Lead Recycling via Rotary Furnaces. *Ibid.* pp. 329-336. 1995.
- THEMELIS NJ, WERNICK IK.. Metal Production and Greenhouse Gases. pp. 595-610 in the Proceedings of The Julian Szekely Memorial Symposium on Materials Processing, Cambridge, MA October 6-8, 1997. Available from The Minerals, Metals, and Materials Society (TMS), Warrendale, PA. 1997.
- THOMAS V & SPIRO T. Emissions and Exposure to Metals: Cadmium and Lead, pp. 297-318 in *Industrial Ecology and Global Change*. Socolow R, Andrews C, Berkhout F, and Thomas V, eds. Cambridge University Press, New York, NY. 1994.
- TIBBS H. *Industrial Ecology: An Environmental Agenda for Industry*, *Whole Earth Review*, Winter 1992. Pp. 4-19. 1992.
- TILTON JE. (ed.). *World Metal Demand: Trends and Prospects, Resources for the Future*, Washington, DC. 1990.
- U.S. BUREAU OF MINES. *The New Materials Society: Volume I-III*. U.S. Government Printing Office, Washington, DC. 1990.
- U.S. BUREAU OF THE CENSUS, *Historical Statistics of the United States, Colonial Times to 1970*, U.S. Government Printing Office, Washington, DC. 1975.
- U.S. GEOLOGICAL SURVEY. 1997. *Mineral Commodity Summaries*. U.S. Government Printing Office. Washington, DC.
- UNITED STATES ENVIRONMENTAL PROTECTION AGENCY Office of Solid Waste and Emergency Response. *Summary of OSW's RCRA regulatory reform analysis: preliminary results*. U.S. Environmental Protection Agency. Washington, DC. 1995.
- VAN DER DONK HM, NIJHOF GH & CASTELIJNS CAM. The Removal of Iron from Molten Aluminum. pp. 651-661 in *Proceedings of the Third International Symposium on the Recycling of Metals and Engineered Materials*. Queneau PB and Peterson RD eds. Available from TMS Warrendale, PA. 1995.

- VEASEY TJ. Overview Of Metals Recycling By Physical Separation Methods, Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering 211(E1):61-45, 1997.
- VELDHUIZEN H & SIPPEL R. Mining Discarded Electronics. UNEP Industry and Environment July-September 1994, pp. 8-11. 1994.
- WAKESBERG S. The Air Knife: What Is It and What It Means To Can Recycling. Scrap Processing and Recycling July/August 1994, pp. 97-99. 1994.
- WANG J., BAI J., XU J. & LIANG, B. Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture, Journal of Hazardous Materials 172, 1100–1105, 2009.
- WERNICK IK. Consuming Materials: The American Way. Technological Forecasting and Social Change 53(1): 111-122. 1996.
- WILLIAMS RH, LARSON, ED & ROSS MH. Materials, Affluence and Industrial Energy Use Annual Review of Energy and Environment (12):99-144. 1987.
- WILLIAMSON D. Into the Next Millennium: The Long Bull Market in Metals and Minerals. Paper presented at the Society for Mining, Metallurgy, and Exploration Annual Meeting, Denver, Colorado, February 24-27, 1997.
- WILSON AJ, The Living Rock: The Story of Metals Since Earliest Times and Their Impact on Developing Civilization, Woodhead Publishing Ltd., Cambridge, UK. 1994.
- WRIGHT S, JAHANSHAHI S & ERRINGTON WJ. Reduction of Battery Paste Slags with Graphite. pp. 11 in Processing for Treatment and Minimization of Wastes, ed. Hager et al. Available from TMS, Warrendale, PA. 1994.

- WU L, THEMELIS NJ. The Flash Reduction of Electric Arc Furnace Dusts. JOM44(4):35-39. 1992.
- WULFF SW. Scrap Supply for Steelmakers: Observations from the USA Experience. Paper presented at the Third ASM International Conference on the Recycling of Metals, Barcelona Spain, June 11-13, 1997.
- XIANG Y., WUA P., N., ZHANGA Z., LIUD W. &WUA J., LI P., Bioleaching of copper from waste printed circuit boards by bacterial consortium enriched from acid mine drainage, Journal of Hazardous Materials, 184, p.812–818, 2010.
- YAMANE L. H., ESPINOSA D.C.R. & TENÓRIO J.A.S., Biolixiviação de cobre de sucata eletrônica REM: R. Esc. Minas, Ouro Preto, 64(3), 327-333, 2011
- YANG, T., XU, Z., WEN, J. & YANG, L. Factors influencing bioleaching copper from waste printed circuit boards by *Acidithiobacillus ferrooxidans*. Hydrometallurgy, vol. 97, nº 1-2, p. 29-32, 2009
- ZUNKEL AD. EAF Dust as an Electrolytic Zinc Resource. Ibid pp. 579-588. 1995.

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