TREATMENT OF SECONDARY RAW MATERIALS
BY INNOVATIVE PROCESSES

Stefano Ubaldini a*, Daniela Guglietta a, Francesca Trapasso a,
Serena Carloni b, Daniele Passeri a, Adalgisa Scotti c

aInstitute of Environmental Geology and Geoengineering, Italian National Research Council,
Km 29.300, Via Salaria str., Monterotondo Stazione 00015, Italy
bResearch Institute on Terrestrial Ecosystems, Italian National Research Council,
Km 29.300, Via Salaria str., Monterotondo Stazione 00015, Italy
cFaculty of Exact and Natural Sciences, University of Cuyo, National Atomic Energy Commission,
International Center of Earth Sciences, 1300, Padre Jorge Contreras str., Mendoza 5502 JMA, Argentina
*e-mail: stefano.ubaldini@igag.cnr.it; phone: (+39 06) 906 72 748; fax: (+39 06) 906 72 733

Abstract. This paper presents an overview of the various innovative methodologies used in the
recovery of valuable metals and critical raw materials (CRMs) from secondary sources. Valuable metals
are interesting due to their vast industrial applications, high market prices and extensively used precious
metal. The sanctuary value attributed to valuable metals such as gold during international political and
economical crises and the limited resource of this metal, may explain the recent increasing gold share
value. This article provides an overview of past achievements and presents scenario of studies carried
out on the use of some promising methods which could serve as an economical means for recovering
valuable metals and CRMs. The review also highlights the used varieties of application on large scale in
real situations and hopes to provide insights into valorization of spent sources.

Keywords: critical raw material, precious metal, circular economy, bio-hydrometallurgy, electrowinning.

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List of abbreviations:

RMs raw materials
CRMs critical raw materials
WEEE wastes from electrical and
electronic equipment
PMs precious metals
PGMs platinum group metals
ISL in-situ leaching
HL heap leaching
HBL heap bio-leaching
CIP carbon in pulp
CIL carbon in leach

Introduction
This paper has reviewed the most promising techniques for recovery of valuable
metals and CRMs from secondary raw materials (RMs), which is an important subject not only
from the point of monetary and high demand but also from waste treatment management. Although
considerable research has been undertaken at a laboratory scale, most, if not all, of the
technologies have proven to have limitation that hinders their widespread adoption in the valuable
metals and CRMs recovery from secondary sources [1,2].

As a traditional technology, pyrometallurgy has been used for recovery of metals from spent
materials. However, it has encountered some challenges from environmental considerations
[3-5]. Consequently, state of the art smelters are highly dependent on investments. Today,
the attention is directed towards the hydrometallurgical processes that are already
widely used for treatments from primary sources; in fact, most of the metals extracted from the
mines are recovered by hydrometallurgical techniques [6-8].

For example, cyanide leaching of gold has been used by the mining industries for more than
100 years. However, a series of environmental accidents at various gold recoveries around the
world has precipitated widespread concern over the use of cyanide [9-11]. Based on a critical
comparison of various leaching methods from the economic points of view, feasibility and
environmental impact, it is concluded that leaching of gold by thiourea and other potential
leachants may be the most realistic substitute. These leachants should be taken into

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consideration due to a rapid reaction with gold, as well as less environmental impact compared with cyanide [12-18].

Bio-hydro-technology has been one of the most capable technologies in precious metals metallurgical processing [10,17,19-21]. Bio-oxidation has been used for recovery of gold from spent materials [19,22-24]. However, limited researches were carried out on the bioleaching of precious metals and CRMs from secondary sources. Research in biosorption of metals from leaching solutions has received a great deal of attention in the recent years using various potential biosorbents [22,25,26]. Compared to conventional methods of recovery, a biosorption based process offers a number of advantages including eco-friendly, easy operation, low costs and minimization of chemical or biological sludge [20,22,23,26]. It was reported that living or dead biomass including bacteria, fungi, yeast, and algae has been used for recovery of metals from wastewater. It should be pointed out here that biomass of all groups has been immobilized by encapsulation or cross-linking to improve the stability and other physical/chemical properties [26]. Additional research would be needed in searching and modifying a biomass to have a high uptake capacity and good biosorption characteristics to recover valuable metals from secondary sources.

This paper presents an overview of the various innovative methodologies used in the recovery of valuable metals and critical raw materials (CRMs) from secondary sources. In particular, CRMs are interesting due to their vast industrial applications, high market prices and extensively used CRMs, the sanctuary value attributed to CRMs during international political and economical crises, and the limited resource of these metals may explain the recent increasing CRMs share value.

**Background**

**Classification of the secondary RMs**

Secondary RMs can be classified in scraps and by-products of industrial and mining processes such as new scraps (in process scraps), residues deriving from industrial processing (scrap, powders achieved during the production, refining and metalworking operations) (Figure 1), tailings from mining operations with interesting metallic contents (Figure 2) and wastes as old scraps (post consumer scraps), scraps of metals from the collection of end-of-life products (Figure 3), wastes from electrical and electronic equipment (WEEE) (Figure 4) [8,27-30].

![Figure 1. Residues from industrial processing (Central Europe) [31].](image1)

![Figure 2. Tailings from mining operations (Bolivia, South America) [32].](image2)
Why treat the secondary RMs

Why treat the secondary RMs? Mainly to preserve the environment from technological waste and avoiding the release of pollutants components (toxic plastics and metals) (Figure 5), that belong to the fastest growing category of waste in the world: from 33.8 million tons in 2010 to 41.8 million tons in 2014 with a forecast of 50 million tons in 2018 [1,2].

Other important objective is the transformation of the wastes in resources. In particular, WEEE are very interesting for the recycling of metal components because they have concentrations of precious metals (Figure 6) even typically higher than those of primary resources (minerals) and don’t require extraction and pretreatment being available after collection in urban centers (urban mining) with significant economic and environmental benefits. WEEE are not only generically rich in metals, but are rich in metals called critical [2,27,28].

The metals present in secondary RMs can be divided into five main categories [5,25,27,28,30,33]:
1. base metals: Cu, Al, Ni, Sn, Zn, Fe;
2. precious metals (PMs): Ag and Au;
3. platinum group metals (PGMs): Pd, Pt, Rh, Ir, Ru;
4. hazardous metals: Hg, Be, Pb, Cd, As, Sb;
5. critical metals: rare earth elements (top five: Nd, Dy, Eu, Y, Tb), Te, Ga, Se, Ta, In, Ge.

The recovery of base metals is not a target of the innovative treatments, which vice versa point to precious metals, PGMs and critical metals, for their high market value, low availability, high demand, importance in emerging technologies, the relatively high content in secondary RMs to primary sources [5,9,19,25,33].

The availability of RMs is fundamental for the economy of the European countries and essential for maintaining and improving the standard of living of citizens. Ensuring access to certain RMs is becoming a growing concern in the EU and around the world. To tackle this problem, the European Commission has created a list of RMs that defined CRMs (Figure 7) [2]. CRMs are characterized by a high economic importance for the EU and a high risk associated with their supply. Examples include rare earths (Sc, Y and lanthanoids), Co, Nb. Why are CRMs so important? For industrial activities, the application of modern technologies and the environment [1,2,33].

China is the largest producer of the 27 CRMs. Other countries are predominant for
specific CRMs (U.S.A. for Be and Brazil for Nb), as shown in Figure 8 [2].

At this point, it is very interesting to introduce the concept of \textit{circular economy}. The \textit{circular economy} is an approach that aims to maximize the productivity of resources and reduce waste and by-products that become RMs entering in other processes marking the transition from a linear production scheme (extraction of natural resources, use, disposal of waste) to a circular production scheme, shown in Figure 9 [1,2].
Secondary RMs: current situation

The research topics to be addressed in the framework of the valorization of secondary RMs can be manifold; some examples can be made \[8,11,13,22,27,34-39\]:
- metals recovery (Cu, Ni) from the electronic wastes;
- recovery of Zn and Mn from spent batteries;
- recovery of Y and Zn by phosphorus coming from the treatment of cathode ray tubes abandoned;
- exploitation of secondary copper deposits;
- recovery of precious metals from refractory ores;
- enhancement of agro-industrial wastes;
- to prevent pollution by removal of heavy metals and metalloids from water basins and aquifers.

During the year 2014, about 41.8 million tons were produced worldwide, mainly located in the U.S.A. and in the EU \[2\]. Of these, only 15-20% have been recycled directly in the nations that have produced them. About 80% of e-waste from the U.S.A. and the EU are exported to China.
(from the U.S.A.), Eastern Europe and Africa (from EU) [2]. About 50% of e-waste produced in EU follow unofficial collection schemes [2]. Apart from the negative environmental effects, these illegal flows prevent the recovery of basic RMs for the EU countries that are completely dependent on the supply from non-EU countries.

In the EU, the European Community directive establishes targets for the recovery of WEEE but requires to the member states to choose the processes to obtain these targets (in the directive and in the national laws there are no technical details on how to carry out the recovery processes) [1,2]. In the current situation, pyrometallurgical processes are widely used for the recovery of metals from secondary RMs, mainly those already used in traditional mining routes [3,5,8,11,28].

**Secondary RMs: current situation and possibility of exploitation**

The pyrometallurgical route for the treatment of secondary RMs seems to be the simplest way, not necessarily the best [5,17]. Pyrometallurgical processes can only be operated on a large scale to be economically viable; moreover, they are not able to recover non-metallic components (plastics) and some metals, they are highly energy-consuming and are associated with the production of harmful gaseous emissions [5,17].

The research work for the development of innovative processes is fundamental [10,11,17].

In this panorama, the complexity and heterogeneity of the secondary RMs such as the WEEE type, plays a fundamental role, and can be addressed mainly according to the following strategy:

“... application of physical pretreatments capable of generating homogeneous fractions, automating the initial dismantling, and development of flexible and environmentally friendly treatment routes able to recover all the fractions of the waste (hydrometallurgical processes)...”

[11,19,21,25,28,36].

Figure 10 shows deposits of mining wastes, Figure 11 preliminary physical operations in progress, while Figure 12 the first products obtained from preliminary treatments of WEEE by physical way.

(a)  
Figure 10. Deposits of mining wastes (a) and (b) (Peru, South America, 2017) [32].

(b)  
Figure 11. Deposits of mining wastes: preliminary physical operations in progress (a) and (b) (Peru, South America, 2017) [32].
Disadvantages of the treatment of the secondary RMs by pyrometallurgical processes

The application of the pyrometallurgical processes to the treatment of the secondary RMs, presents the following main disadvantages [9,11,13,17]:

- Unsustainable management and treatment from the economic and environmental points of view.
- Production of polluting gases (halogenated compounds) that require large investments for monitoring and abatement.
- Organic materials are not recycled.
- Failure to recover metals such as Fe and Al, which end up in the slag as oxides.
- Dust generation in exhaust fumes containing metals Zn, Pb, Sn, Cd, and Hg.
- Partial separation of the precious metals, such as Au and Ag, which requires the use of hydro and electrometallurgical methods.

Treatment of the secondary RMs by hydrometallurgical processes

Hydrometallurgy consists in the extraction of metals through aqueous solutions. Hydrometallurgical processes are generally characterized by the following main phases [6,7,41]:

- Leaching with appropriate chemical agent: the metals are extracted from the solid phase and transferred in the aqueous phase in the form of soluble ionic species.
- Separation of the solid phase from the liquid phase through filtration, decantation or centrifugation.
- Purification, concentration, recovery: removal of interfering species and/or concentration of the target metal by precipitation, cementation, solvent extraction, adsorption on activated carbon, ion exchange on resins, electrolysis.

Hydrometallurgy is a new technology compared with pyrometallurgy, but offers interesting perspectives, linked to the exhaustion of primary resources and the use of RMs [19,37,40].

Advantages of the treatment of the secondary RMs by hydrometallurgical processes

The application of hydrometallurgical processes to the treatment of the secondary RMs, presents the following main advantages [36,39,42-44]:

- Materials that have low metal content to be treated with pyro processes can be treated sustainably with hydrometallurgical processes.
- Hydrometallurgical methods are treatments at low temperatures that require little energy expenditure in comparison with the pyrometallurgical processes.
- Hydrometallurgical processes can handle a wide range of incoming solids through the same operations, optimizing operating conditions (flexible systems).
- Pyrometallurgical processes become sustainable only for very large scales that require large initial investments and security over the supply of large quantities of minerals for a long time; vice versa, hydrometallurgical processes are sustainable even on medium-small scales, requiring lower initial investment costs and lower operating costs.
- The reagents used in the hydrometallurgical processes can be regenerated and recirculated into the circuit of treatment.
- The hydrometallurgical processes allow obtaining high purity metals that do not require further refining.
In the hydrometallurgical processes there are limited corrosion problems compared to those of the pyro processes that require refractory linings. The hydrometallurgical processes constitute the future of metallurgical treatments as they allow treating, by flexible and sustainable circuit, secondary resources, of different mineral and technological origin, for metals recovery.

**Hydrometallurgical processes: main methods**

The possible applicable methods are many. The choice depends on various factors, as the type of material to be treated and the concentration of useful metals [6,7,19].

**In-situ leaching (ISL)** is used on exposed minerals or on deep deposits characterized by low metal content, which does not justify excavation and transport costs (Figure 13) [5-8]. The deposit is cracked, the solvent is left to percolate and then the leached solution containing the extracted metal sent to the plant is pumped.

To apply the **heap leaching (HL)**, the grinded mineral is piled up into hills (heap) 10-15 meters high by truck or stacker. The hills are sprayed with solvent; the leached solution is collected through a channeling system and sent to the recovery plant (Figure 14). In addition, HL is advisable when the metal content is low [5-8].

The same technology of HL can be used by exploiting the oxidizing action of iron-and sulfur-oxidizing bacteria that catalyze the leaching of sulfides (Figure 15(a)). In this case, the method takes the name of **heap bio-leaching (HBL)** [19-21,45]. HBL is a commercial technology used in the U.S.A. (25% of extracted Cu), Australia and Finland. The grinded mineral is aggregated and accumulated in hills 400 meters wide and 1200 meters long, sprayed with the solution by a recirculation system (Figure 15(b)) [7,20,21].

When the **percolation** method is used, the mineral of 6-10 mm in dimensions is placed in large packaged reactors inside and the solvent is recirculated (Figure 16) [6-8]. The particles must be large enough to allow the liquid to pass easily through the empty spaces between one particle and another. On the bottom, there are grids to facilitate the recovery of the solvent and wash water. This system improves the transfer of matter between the liquid phase and the solid phase (with respect to HL) by increasing the extraction kinetics (days instead of months or years), while recovery yields improve by recirculating the leaching solution several times, producing more concentrated solution [6-8].

**Leaching under stirring** (Figure 17), is used for suspensions of particles smaller than 0.4 mm that are stirred by mechanical agitation systems with blades or pneumatic systems (reactors pachucas) by blowing air or steam at high pressure (which simultaneously heats) from the bottom in this case conical (like fluid bed) [6-8].
Figure 14. Heap leaching method. Schematic representation of the process used in China and U.S.A. for gold, copper and uranium extraction (a) and example of practical application in U.S.A. for gold extraction (b) [5-8].

Figure 15. Heap bio-leaching method. Example of iron-and sulfur-oxidizing bacteria Acidithiobacillus ferrooxidans that catalyzes the leaching of sulfides (research laboratory of the Slovak Academy of Science, 2016) (a) and an example of practical application in the U.S.A. for gold and copper extraction (b) [7,20,21].

Leaching under pressure (Figure 18) is carried out in autoclaves at high pressures that allow working in water at temperatures above 100°C, with kinetic advantages on the reaction (hours) [6,7].

Hydrometallurgical processes: main methods of metal purification and concentration after solid/liquid separation

After dissolution by leaching and subsequent solid/liquid separation, various methods of metal purification and concentration can been applied [41,46-49]; the main have been reported as follows:
- ion-exchange resins;
- adsorption on activated carbons: in the column, carbon in pulp (CIP), carbon in leach (CIL);
- solvent extraction;
- precipitation;
- electrometallurgical processes.

Electrometallurgy includes metallurgical techniques that use electricity to recover metals such as Cu and Zn by reducing from the purified and concentrated leached solution (electrodeposition or electrowinning), to refine metals from pyrometallurgical processes (electrorefining of Cu and Pb) and to recover metals from high purity oxides that are melted and reduced (Al, Mg, Na and Ca by electrolysis of molten salts) [16,46].

Schematic exemplification of innovative processes

Schematic exemplification of innovative circuit of the integrated processes have been reported [16,17,21,35,36,38,50]; in particular, Figure 19 shows the flow chart of the integrated processes developed in the pilot plant, while Figure 20 the flow chart of integrated physico-hydro-bio-metallurgical processes.
Figure 16. Percolation: schematic representation (a) and practical application (b) on industrial scale for gold extraction in South America [6-8].

Figure 17. Leaching under stirring: schematic representation (a) and practical application (b) on industrial scale in North American plant [6,7].

Figure 18. Leaching under pressure: schematic representation (a) and practical application (b) on industrial scale in North American plant [6,7].
Figure 19. Flow chart of the integrated processes developed for pilot plant applications by the research laboratory of the Institute of Environmental Geology and Geoengineering, Italian National Research Council (IGAG-CNR), year 2017.

Figure 20. Flow chart of the physico-hydro-bio-metallurgical processes, realized by the research laboratory IGAG-CNR, year 2018.
Conclusions

After having underlined the strategic importance of the valuable and critical raw materials (CRMs) and introduced the concept of circular economy, the innovative technologies that can be adopted for the treatment of secondary RMs have been reported and synthetically described.

The processes described are economically and environmentally friendly. These processes could be integrated with physical treatments and procedures followed by bio-hydrometallurgical applications, reducing pollution and at the same time recovering useful metals (Au, Ag, Cu, Ni, Zn, etc.). Valuable metals and CRMs can be recovered with the dual aim, to achieve high extraction efficiency and metals of high degree of purity.

The benefit to the environment will result in the reduction of toxic effects on living organisms.

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**Short biography of the corresponding author**

Dr. Stefano Ubaldini is a senior research scientist, Member of the Board of the Institute of Environmental Geology and Geoengineering of the Italian National Research Council and head of the Hydrometallurgy and Electrochemical Laboratories of the Institute.

He has been appointed to take part of the Governance of the European Innovation Partnership on Raw Materials (EIP on RM), as a Sherpa member for Science Europe at the European Commission, in the framework of the High Level Steering Group/Sherpa Group of the EIP on RM.

Dr. Ubaldini’s main area of expertise is in hydrometallurgy and bio-hydrometallurgy. His activity has been carried out mainly in the framework of the primary and secondary raw materials (mineral and materials industry) for over 25 years, including fundamental research, hydrometallurgy and biometallurgy of low-grade ores, metal extraction from solutions, precious metals recovery with novel leachants, treatment of waste materials, process development and design.
Dr. Ubaldini is the author of more than 150 publications on national and international journals and proceedings of international congresses. He has participated, as a member of the scientific committees, chairman or invited speaker, in numerous national and international conferences.

Its current research interests are primary and secondary raw materials, with particular reference versus the hydrometallurgy and biometallurgy of low-grade georesources, with the main aim to recover base and precious metals and to develop sustainable and innovative technologies for processing of industrial wastes (spent catalysts, industrial tailings, batteries, WEEE, etc.) and mining residues, coming also from abandoned sites, and treatment of waste waters.

Dr. Stefano UBALDINI
Institute of Environmental Geology and Geoengineering, Italian National Research Council,
Km 29.300, Via Salaria str., Monterotondo Stazione 00015, Italy
Website: https://www.igag.cnr.it/index.php/12-elenco-personale/37-stefano-ubaldini
Phone: (+39 06) 906 72 748
Fax: (+39 06) 906 72 733
E-mail: stefano.ubaldini@igag.cnr.it