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Methods for recovering precious metals from industrial waste

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Abstract. The accelerated rate of industrialization increases the demand for precious metals, while high quality natural resources are diminished quantitatively, with significant operating costs. Precious metals recovery can be successfully made from waste, considered to be secondary sources of raw material. In recent years, concerns and interest of researchers for more increasing efficient methods to recover these metals, taking into account the more severe environmental protection legislation.

Precious metals are used in a wide range of applications, both in electronic and communications equipment, spacecraft and jet aircraft engines and for mobile phones or catalytic converters. The most commonly recovered precious metals are: gold from jewellery and electronics, silver from X- ray films and photographic emulsions, industrial applications (catalysts, batteries, glass/mirrors), jewellery; platinum group metals from catalytic converters, catalysts for the refining of crude oil, industrial catalysts, nitric acid manufacturing plant, the carbon-based catalyst, e-waste.

An important aspect is the economic viability of recycling processes related to complex waste flows. Hydrometallurgical and pyrometallurgical routes are the most important ways of processing electrical and electronic equipment waste. The necessity of recovering precious metals has opened new opportunities for future research.

1. Introduction

Exponential growth of world's population and limited natural resources are causing new challenges. Pollution prevention, waste minimization, recycling and products at end of life (ELP) have become topics of interest. Sustainable development involves creating materials and products that can be more easily recycled through proper management. In terms of sustainability, recycling activities mean maximizing re-use, minimizing energy consumption, reducing costs and waste.

Increased pace of industrialization increases the demand for precious metals, while the high quality natural resources are disappearing (reducing the amount) with high operating costs. Alternative solutions lead to a need of increasing education regarding recovery of these metals. As a consequence of industrialization, solid and liquid waste generated from various technological processes or various consumer goods is increasingly high. These wastes may be organic or inorganic. Organic substances are, in general, biodegradable and environmentally friendly. Inorganic wastes contain toxic metallic and non-metallic elements with many serious negative consequences on ecosystems. Some of these non-ferrous metals have a mid deteriorating grade that lasts for a long time, having a cumulative toxic effect. Also, many of them are carcinogenic. The most significant solid waste materials contain non-ferrous metals such as gold, silver, nickel, molybdenum, copper, zinc, chromium and others, as potential heavy metals. Therefore, these residues would be considered secondary resources or artificial resources. Precious metals mainly originate from electric and electronic equipment, medical activities, spent catalysts, used batteries and ashes.

Non-ferrous metals, including aluminum, copper, lead, nickel, tin, zinc and others, are among the few materials that do not degrade and do not lose their chemical or physical properties during the recycling process. Consequently, nonferrous metals, and therefore precious metals, have the capacity to be recycled for an infinite number of times.

2. Overall view on the study

Currently, precious metals are used in a wide range of applications, not only for electronic and communications equipment, spacecraft and jet aircraft engines, but also for mobile phones or catalytic converters. The most commonly recovered precious metals are: gold from jewellery and electronics; silver from electronics, radiography, films and photographic emulsions, industrial applications (catalysts, batteries, glass/ mirror), jewellery; platinum group metals from catalytic converters, catalysts for refining crude oil, industrial catalysts, nitric acid manufacturing plants, carbon-based catalysts, e-waste. Technological progress must be seen in relationship with the protection of human health, ecosystems, having clean technologies at both levels: production and recycling, improvements of environmental legislation and improved methods in waste recycling as a source of secondary raw materials, avoiding emissions and contamination of water, air and soil. Another important aspect is the economic viability of recycling processes related to complex waste streams. In some situations the mixture of metals or the amount too small of these metals in mixtures makes them difficult to separate from waste. New technologies, such as spectroscopic analysis, facilitate and accelerate technical developments in this area.

Quality control waste and also establishing their chemical composition in terms of quality and quantity is critical in order to harness the most appropriate techniques for each type of waste. A proper diagnosis determines the profitability of the entire recycling process. This analysis can be made through spectroscopy which involves:

- chemical analysis of ferrous and non-ferrous materials by optical emission spectrometry and X-ray spectrometry;
- qualitative and quantitative analysis in various stages by X-ray diffraction.

X-rays can be used in analytical chemistry for the qualitative, quantitative and structure analysis. In the first category of methods, the analysis is based on X-rays emitted by the atoms of the sample. By determining the wavelength of the emitted radiation can be made a qualitative analysis and by determining their intensity, a quantitative analysis. This type of devices provides essential advantages over other traditional testing methods. Analysis can be done in seconds, and significantly reduces cost analysis, obtaining an accurate value of the precious metal concentration. Gathering concrete data is crucial for the recovery process. Traditional testing techniques take hours or even days.

Advantages of spectrometric analysis:

- The analysis is non-destructive
- No hazardous waste issued
- The results appear in seconds
- Sample preparation is not difficult [1].

Because of the relative rarity and of the high value per unit, precious metals continue to be recycled at a high recovery rate. US Geological Survey estimated that 240 tons of gold residues (new and old) were recycled in 2012 in the United States, which is more than the total domestic consumption of gold that was reported. In addition, Census Bureau data indicate that about 14,000 tons of remnants precious metals were exported in 2012 worth US $ 5.5 billion [2].

For an effective recycling on industrial scale several conditions must be met:

- waste involved in the recycling process to be accessible;
- an economic viability needs to exist;
- gathering mechanisms need to ensure availability of the product for recycling;
- the entry of the product into recycling chain has to ensure a safe storage of secondary waste;

- configuration of the recycling chain has to be optimized technical and organizational;
- enough capacity along the entire chain so that recycling to be complete [3].

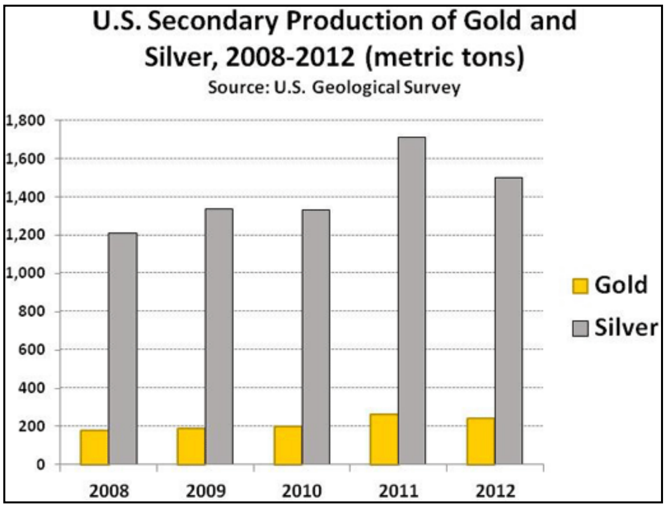

Figure 1. Secondary production of gold and silver between the years 2008-2012

In the last decade, many countries have issued regulatory laws regarding waste management. Underground storage or burning in incinerators is not allowed anymore without isolation of hazardous materials. Moreover, export of waste in underdeveloped countries is illegal according to international regulations [4].

The underground storage, the combustion with the flue gas released into the air endanger the environment, drinking water and lead to release of toxic gases into the atmosphere. Therefore, the recovery of precious metals is essential from the point of view of minimizing environmental pollution and of resource management. The incineration and mechanical biological treatment is by far the most important alternative of treatment.

By the year of 2020 it must be achieved the preparation for reuse and the recycling at least of paper, metal, plastic and glass from household waste and possibly originated from other sources, as far as these streams are similar to waste from the waste to a minimum of 50% from their total weight. The ways of treatment have to be designed to reduce the organic carbon content so as to meet the criteria of final disposal. Unlike simple storing, the new processing methods allow recover materials contained in solid waste containing precious metals. The production of such metals from primary resources is limited and the process is characterized through high energy consumption. Therefore, recycling can greatly contribute to an energy saving and reducing carbon dioxide emissions [5].

Precious metals play an important role in modern society, being inextricably linked to developments in technology and everyday life. Figure 2 presents the four pillars for environmental and energy by Tanaka [6]. Fractions of precious metals separated from waste during pre-processing can be further processed using hydrometallurgy, pyrometallurgy, electrometallurgy, biometallurgy and combinations of them [7].

Hydrometallurgical and pyrometallurgical processes are the most important ways of processing waste from electrical and electronic equipment. These routes can be followed by electrometric processes/electrochemical (eg electrowinning or electrolysis) for separation and recovery of a particular metal. Currently, studies on processing electronic waste through bio metallurgical ways are not confined to a simple lab work, an example may be the bioleaching of metals from e-waste. Pre-processing for electrical and electronic waste is not always necessary in pyrometallurgy. For example, complex electronic equipment such as mobile phones and MP3 players can be treated directly during the melting process [8].

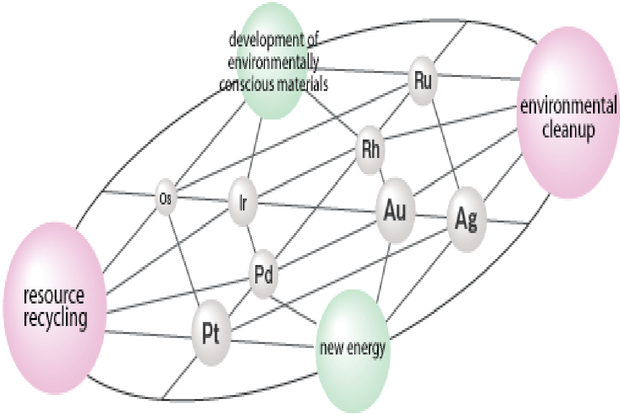

Figure 2. Tanaka Precious Metals Group's four pillars for its environmental and energy-related businesses [6]

However, for hydrometallurgical processes, pre-processing is required to separate fractions of metal from other fractions. This will increase the efficiency of each phase associated with hydrometallurgical processes. Each route has advantages and disadvantages that must be taken into account in selecting a suitable recycling process. Hydrometallurgical processes involve lower power consumption and lower cost compared to pyrometallurgical treatment, being also applicable in plants with relatively small capacities. The main problem of hydrometallurgical processes is the high consumption of water and/or chemicals that need further treatment. Lately hybrid methods were applied, which integrates chemical approach (more efficient) biological strategies (more eco compatible), thereby applying the benefits of both solubilization, chemical and biological.

3. Analyzes. Discussions

3.1. Gold recovery

The interest in gold recovery is due to its vast industrial applications, high market prices, but also for the value attributable during international political and economic crisis, as a limited resource. Experts believe that from the beginning of gold exploitation were extracted 160,000 tonnes [9]. Due to previous ineffective methods for gold recovery (an efficiency of only about 1 g of gold per 1 ton ore) the result was approximately 160 billion tons of tailings heavily contaminated, especially from the early 20th century, when for gold production the cyanide leaching process was the main method [10]. Gold is widely used in computer components. Motherboards and computer pins contain precious metals. Although computers and laptops contain a bigger amount of gold, precious metals are found in many other technological devices, from coffee makers to cars. Obvious deposits of gold from technological and household items can be fragmented. However, gold is too finely layered to be easily removed. For example, the amount of gold in a motherboard is one order of magnitude higher than the ore from which it is usually extracted. Given the growing demand for technological equipment in industrialized countries and in developing countries, is a priority and a real need the recycling of metals rather than extracting them from ores [11].

Gold leaching method with „aqua regia”, a mixture of 3:1 between the hydrochloric acid and nitric acid, is a conventional one. The reaction mechanism is the following:

$$2HNO_3 + 6\ HCl \rightarrow 2\ NO + 4H_2O + 3Cl_2 \quad (1)$$

$$2Au + 11\ HCl + 3\ HNO_3 \rightarrow 2\ HAuCl_4 + 3NOCl + 6H_2O \quad (2)$$

Solubilization using chlorides is more difficult to apply because of its high corrosion level of solutions involved and because of its high toxicity. Leaching with thiosulphate is widely used in photography and pharmaceutical industry. Gold form a stable anion complex with thiosulfate [12]:

$$4\ Au + O_2 + 8\ S_2O_3^{2-} + 2\ H_2O \rightarrow 4\ Au(S_2O_3)_2^{\ 3-} + 4\ OH^- \quad (3)$$

Gold is being dissolved slowly in thiosulfate, but good rates of leaching can be obtained if ammonia and copper are present. The problem is the large amount of reagent needed.

Another method is the gold recovery through leaching with thiourea:

$$Au + 2\ CS(NH_2)_2 \rightarrow Au(CS(NH_2)_2)^{2+} + e^- \quad (4)$$

Gold recovery from various solutions can be made by cementation, adsorption, solvent extraction or ion exchange [13]. The high cost and high degree of environmental pollution, due to secondary waste generated in this process, open the path of research in the recovery of gold by enzymatic methods with various bio-adsorbents, such as bacteria, yeasts, fungi, actinomycetes, algae, biopolymers [14].

3.2. Platinum group metals recovery

The platinum group metals include platinum, palladium, rhodium, ruthenium, iridium and osmium. Secondary resources such as spent catalysts from motor vehicles and waste of electrical and electronic components, also represent important sources of recovery of these metals. They are also present in the anode sludge and can be separated from gold and silver through a variety of hydrometallurgical processes.

The main steps in the recovery of metals from the platinum group are:

• raw material pre-treatment, sampling and analysis;

• concentration and separation using pyrometallurgical and hydrometallurgical techniques such as chemical precipitation, chemical dissolution, extraction liquid/ liquid, osmium distillation, ion exchange and electrolytic processes;

• pyrolysis or reduction of chloro-metallic compounds to form the pure metallic sponge [15].

Some specific methods have been developed for the carbon-based catalyst, using incineration, prior the leaching step. „Aqua regia" is used on the commercial scale to recover Pt, Pd and Rh from spent catalysts and electronic scrap. However, the process suffers from an environmental viewpoint as it generates NOx, chlorine and acid fumes during leaching, due to the presence of HNO_3 in the leaching agent. Although platinum leaching rate by this method is high, the economy of the process needs further improvement [16].

Among solvent extraction techniques that have been referred to, a relevant example is that with 8-hydroxyquinoline or tri-butyl phosphate. The solvent for extraction requires substantial investment in factories, moreover solvents can be toxic. Electrochemical recovery of platinum group metals is feasible, but the recovery of thin coated metal deposits out of electrodes may limit application of it on an industrial scale [17].

Recovery becomes increasingly necessary both economically and environmentally. The recycling process helps to protect natural resources, also to set a limit for increasing prices caused by the growing demand in the automotive industry. A considerable yearly volume of scrapped auto catalytic converters makes the recovery of metals from the platinum group very profitable. The catalytic converter is a device used to reduce the toxicity of emissions from internal combustion engines. A catalytic converter provides an environment for a chemical reaction of combustion and the products are converted to less toxic substances [18].

The catalyst itself contains platinum group metals. Platinum is the most active catalyst and is widely used. It is not suitable for all applications because of unwanted additional reactions and/ or costs. Palladium and rhodium are two other precious metals used. Platinum and rhodium are used as a reduction catalyst, while platinum and palladium are used as oxidation catalyst. Cerium, iron, manganese and nickel are also used, although each has its own limitations. For example, nickel is not legal to be used in the European Union (due to its reaction with carbon monoxide), while copper can be used, but its use is illegal in North America due to the formation of dioxin [19].

Since 1981 3-way catalytic converters were used in vehicle emissions control systems in North America, Europe and Asia. 3-way catalytic converter has three simultaneous tasks:

1. The reduction of the nitrogen oxides which are converted to nitrogen and oxygen:

$$2NOx \rightarrow xO_2 + N_2 \quad (5)$$

2. The oxidation of the carbon monoxide which is converted to carbon dioxide:

$$2CO + O_2 \rightarrow 2CO_2 \quad (6)$$

3. The oxidation of unburned hydrocarbons (unburned or partially unburned fuel) which is converted to carbon dioxide and water [20]:

$$2C_xH_{2x} + 3xO_2 \rightarrow 3xCO_2 + 3xH_2O \quad (7)$$

The exact amount of platinum varies depending on the formula used. Catalytic converters for gasoline vehicles contain on average about 5 grams of platinum, while those for diesel vehicles can contain more than 15 g for high power machines. Researches in terms of optimization of methods for platinum group metals recovery have aroused a growing interest, as shown in Figure 3 [21].

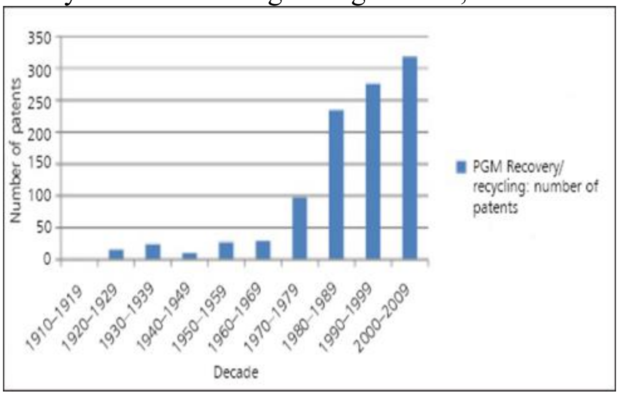

Figure 3. Number of patents for the platinum group metal recovery

3.3. Silver recovery

Recovery of silver from waste as solutions, such as those produced by conventional medical processing and industrial processing of X-ray films, photographic films and images has been practiced for over 100 years. However, the economic viability of the process has dramatically changed over the past decade. Silver is being used in infinite ways, from eye drops to lubricants for jet engines. It is used by each hospital, medical clinic, dentist, as well as by photographic processing departments, printers and by anyone performs photographic processing using a wet mixture. In Figure 4 is presented the forecast for global silver extraction.

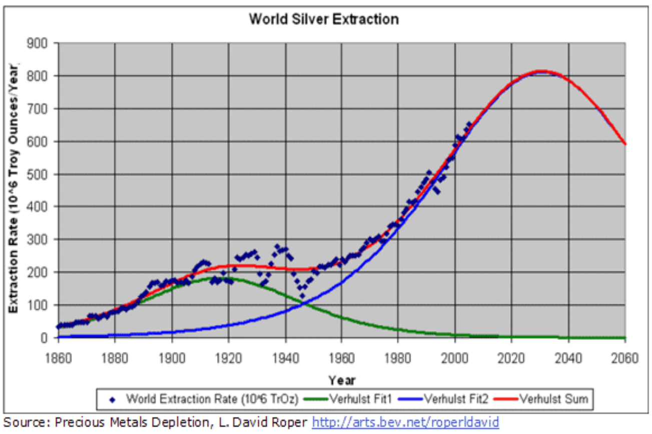

Figure 4. Forecasts for global silver extraction

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Radiographic film is a polyester sheet coated on both sides with radioactive material, photosensitive. Every year around the world there are performed an estimated 2 billion radiographies, CT scans etc. Silver world production is currently not enough to meet the demand that is increasingly growing, respectively ~ 2-2.5% per year [22]. Traditionally, 94-98% of X-ray films are being used in healthcare services. Radiographies may contain 5-15 grams of silver per 1 kg of film, representing a significant secondary source of silver.

4. Approaches. Interpretations

Over the time, studies regarding the recovery of silver from radiographic films waste have shown two typical methods: through pyrometallurgical processes and through hydrometallurgical processes, more exactly by acid leaching. Pyrometallurgical processes for silver recovery require temperatures higher than 950° C (higher than 1742° F), with the destruction of the polymer substrate. Hydrometallurgical methods used for silver recycling were initially based on incorporating the silver in solution, in ionic form, and then through electrolysis in silver metal [23]. The silver recovery process depends on the leaching temperature of radiographic films in oxalic acid, in nitric acid or in sodium hydroxide solutions at boiling point, in order to separate the inorganic component out of the polymer substrate. For example, dissolution of silver in ammoniacal copper-thiosulphate system takes place according to the following reaction [24]:

$$Ag^0+5S_2O_3{}^{2-}{}_{(aq)}+Cu(NH_3)_4{}^{2+}{}_{(aq)} \rightarrow Ag\,(S_2O_3)_2{}^{3-}{}_{(aq)}+4NH_{3(aq)}+Cu\,(S_2O_3)_3{}^{5-}{}_{(aq)} \quad (8)$$

In the next steps, metals are concentrated and purified through precipitation, cementing, extraction using solvents and ion exchange, with the purpose to be recovered after that in pure form using electrolytic methods and precipitation.

The method of electrolysis, in which a continuous electric current is applied between two electrodes, is capable of producing silver with purity higher than 98%. However, this method is used only for silver-rich effluents, because is unable to reduce silver concentration under 100 mg/ l, which is higher than the limit allowed for the environment of 5 mg Ag/ l [25].

Metallic replacement, also called cementation process, is based on the use of metals such as iron, zinc and copper, which are more active than silver to effectively recover of the effluent. Ions that belong to the more active metal are released into solution, while atoms that belong to the less active metals replace them in a solid state [6]. Impurities from active metals, such as Fe^{2+}, Zn^{2+} and Cu^{2+}, effluent and silver sludge require an expensive process for remediation. The process, generally, consists of two reactions: reduction of the metallic ion more active and oxidation of the less active metal. For an optimum performance of the process, it had been recommended a pH 5 to 7.6. Abdel-Aal and Farghaly have reported silver recovery of 98% at 90°C (at 194° F) over a period of 50 minutes retention time, using Zn metal powder 6% concentration of nitric acid. With a careful control, silver can be easily recovered through chemical precipitation. As precipitating agents were used: sodium sulfide, sodium dithionite, potassium boro hydride and 2, 4, 6-tri mercapto-s-triazine. It has been investigated the effect of ethylene glycol as a stabilizer to hydrogen peroxide in the process of silver recovering. Utilizing hydrogen peroxide with ethylene glycol leads to reducing the consumption of acid to less than 25%, resulting in an improvement of efficiency in recovery to 18.7%. The pH has also an influence on potassium boro hydride in silver recovery from radiographies and effluents. Increasing of the pH led to a reduced amount of potassium boro hydride required in order to achieve the desired purity and recovery [26].

Silver recovery from radiographies represents a long term solution, with a high potential in the future. Based on multiple studies and researches in this field, it seems that precious metals recovery is a promising solution in order to minimize the impact of industrial waste toward the environment. Scientists will conduct more thorough research on silver recovery from radiographies using leaching based on several types of acids and will analyze the relationship between the efficiency of result solutions according to various parameters: the leaching time, pH, the temperature and density of the paste. An example of technological flow for silver recovery from radiographic films is presented in Figure 5.

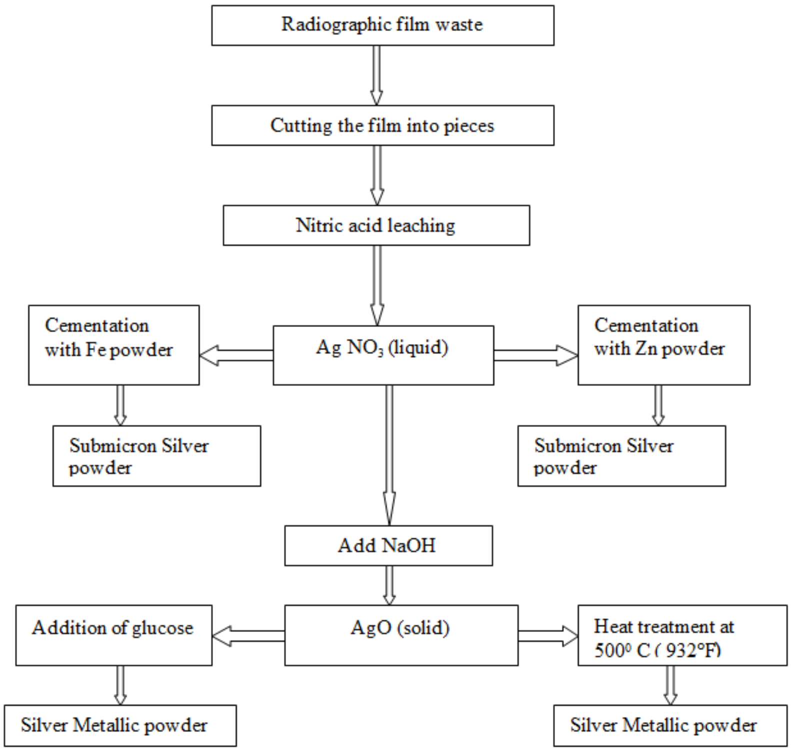

Figure 5.Technological flow in processing radiographic films and silver recovery [27]

5. Conclusions

Precious metals are not affected by the economic destabilization triggered by the financial crisis and this fact is confirmed by price-performance ratio achieved by the companies involved in the extraction of metals as a raw material. Sustainable development and increasingly severe legislation regarding the environment are making from the precious metals recovers, a possible approach in conserving natural resources and reducing waste without high costs. Optimizing recovery solutions opens up new paths in research field, considering growing demand, resources depletion and global need of development.

Precious metals resulted after the recovery processes have the same properties, even after multiple life cycles, therefore recycling allows:

- recovery of the valuable material without quality loss;
- energy saving in comparison with primary production;
- reducing resulted emissions and reducing greenhouse gas emissions;
- reduction of mining activities;
- reducing waste.

Industrialized countries have switched to a positive environmental policy, aimed at reducing technological risks, showing a great power of adjustment, through a culture of change and adopting long-term strategies. Finding new precious metal recovery technologies can balance the economic pressure with the need of preserving natural ecosystems and can have a positive global impact.

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