Green gold production from primary and secondary resources

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ABSTRACT

The excellent chemical resistance of gold is an important property of the precious metal, but it becomes a disadvantage when it comes to gold extraction. Many metallurgical processes are based on highly aggressive or toxic reagents. Especially artisanal and small-scale gold mining activities are heavily criticized, as their environmental impact can hardly be controlled. Ecological concerns are forcing society and industry to find a solution for efficient gold recovery by the use of alternative methods to replace the mercury or cyanide process. In the last decades, many alternative leaching reagents have been investigated extensively. Researchers showed promising results in terms of technical and environmental characteristics. Furthermore, different demonstration and pilot-scale application tests were conducted around the world to generate information for a potential industrial application. Nevertheless, to this day there is just one reported industrial-scale application using the cyanide alternative thiosulfate. Besides chlorination or aqua regia in refineries and the recycling of specific waste streams, there is no notable industrial application of cyanide alternatives. Especially gold recycling from secondary resources would have a high ecological impact, as mining activities would be reduced. For example, electronic waste is a resource growing in volume and importance for gold recovery but lacking an efficient decentralized process.

In this work, the potential of cyanide alternative reagents for industrial application in gold production and recycling is discussed, along with various reasons that explain the restrained acceptance of gold producers.

Keywords: Gold, Cyanide Alternatives, Green Gold, Recycling.

1. Introduction

Since its inception in the late 1800s, cyanidation has been the dominant process for the recovery of gold and silver from ores, due to its simplicity and cost efficiency. The main disadvantage of cyanide is related to environmental issues, which may occur due to improper storage and transport or failed tailings management and storage. Industrial gold producers barely face critical, or deadly accidents, but these problems especially occur for unregulated, small-scale operations in the informal sector. The informal sector, which includes small-scale miners, accounts for approximately 20% of the world’s primary gold production. Especially the application of mercury for gold recovery has detrimental effects on the environment and human health, including contaminated water sources, soil degradation, and toxic exposure (Marsden 2006; Springer et al. 2020). With rising ecological awareness, public pressure on gold extraction is rising continuously. There are many alternative reagents to cyanide that have been intensively investigated and tested up to pilot scale in the last decades, including thiosulfate, thiourea, and halides. Despite their general capability for gold extraction and much lower environmental hazards, alternative reagents have barely been adopted in the gold mining industry (Aylmore 2016). At the same time, consumers' demand for “green gold” rises, and progressively more companies are abandoning gold from primary production (e.g., smartphone producers and jewelry).

Recycling helps to supplement the global gold supply by providing a significant source of secondary gold. According to the World Gold Council, approximately one-third of the world’s annual gold supply comes from recycled gold. The main resources for gold recycling arise from such as jewelry, coins, electronic waste (e-waste), and industrial by-products (Fritz et al. 2020).
2. State of the Art Gold Production

2.1. Cyanidation

Since its inception in the late 1800s, replacing the early chlorination process (Plattner process), cyanidation has been the primary process for the extraction of gold and silver from ores due to its technical and economic merits (Hilson und Monhemius 2006; Marsden 2006):

- Highly efficient and stable process (simple and well-established chemistry);
- Alkaline, non-corrosive process (low-cost construction material);
- Low reagent consumption for most ore types;
- Established, effective downstream gold recovery process;
- Availability of efficient industrial processes for detoxification of effluents.

The main drawback to cyanide leaching is environmental issues associated with the use, storage, and transport of cyanide due to its high toxicity to humans and many living organisms even at very low concentrations (Gökelma et al. 2016). With increasing public pressure and increasingly tightening regulations, the gold industry could even face a widespread ban on the use of cyanide. Consequently, an increasing number of feasible gold mine projects could not be realized, or their development was stopped in an early stage due to social opposition. Besides environmental concerns, cyanide shows some technical limitations. The industrial gold recovery becomes more difficult, easy-to-process deposits are depleted and gold producers are forced to use complex, refractory, and carbonaceous preg-robbing ores (Marsden 2006).

2.2. Informal Gold Sector

The informal sector accounts for approximately 20% of the global primary gold production, mainly from deposits that are located in remote areas or forests and therefore cannot be exploited by large industries. Gold is recovered via underground mining, processing of secondary deposits with sluice boxes or from riverbeds (Springer et al. 2020; Kahhat et al. 2019). While this sector can provide a source of income for many individuals and small communities, it often includes illegal practices, including the use of harmful chemicals like mercury or cyanide. These practices can have detrimental effects on the environment and human health, including contaminated water sources, soil degradation, and toxic exposure. Many efforts have been made to improve transparency, formalize the sector, and promote sustainable mining practices, without success. It is frequently neglected that the informal sector wants to maintain its independence, which could be at risk if other mining techniques are used. Legal regulations are not effective, as the informal mining takes place in very abundant areas (Springer et al. 2020; Wotruba et al. 1998).

The environmental damage of amalgamation is particularly devastating in Indonesia. Although the Indonesian government banned mercury in small-scale gold mining in 2018, its application could not be curbed, since informal mercury production was established supplying the miners. The black-market was that prosperous, that Indonesia became a major global supplier of mercury in 2018 (report final 2022). A major problem is the lacking awareness of miners and local communities for the health and environmental hazards of mercury. Throughout the country, gold miners work with mercury without fear to be punished. The police are even accused of actively contributing to the distribution of the mercury process, while also governmental employees participate on the revenue. It is estimated that this mining practice has poisoned approximately 500,000 people in the last decades (Paddock 2019; Satriastanti 2015). A similar situation prevails in Brazilian Amazonas. Just approximately 10% of artisanal miners work legally, because claiming mining rights is very bureaucratic and expensive. Gold mining is organized by individuals who own the required equipment, open camps, and hire miners, who are paid with a share of the recovered gold. In the absence of the government, these structures have strengthened, and miners understand their activities to be illegal since they are not prosecuted (Springer et al. 2020; Kolen et al. 2018, 2015).

2.3. Gold Recycling

Gold recycling is an essential component of the global gold supply chain, due to the depletion of easy-to-access gold deposits. Recycling gold not only helps to meet this demand but also helps to reduce the environmental impact of gold mining, as it requires much less energy and shows significant economic benefits. Comparing the global warming potential of gold recovery processes, one can see the importance of recycling: 16 t CO₂-Eq. for mining, 1 t CO₂-Eq. for electronic waste recycling, and just 53 kg CO₂-Eq. for high-value gold scrap (Fritz et al. 2020).

According to the World Gold Council, the total global recycled gold accounted for approximately 11.44 t in 2021, which is around 24% of the global supply. The main applications of gold are jewelry, which has an average life span of 50 years, and the investment sector, which are barely available for recycling (Fernandez und Klimas 2019). Gold from electronics, medical or other applications is often not recycled due to insufficient collection (Birich 2020). These circumstances explain why the global gold demand cannot be satisfied just by gold recycling. In 2018, 23% of the gold supply was recycled from high-grade waste such as jewelry and coins followed by e-waste with 3% (Fritz et al. 2020). Nevertheless, E-waste is considered an important resource, because of its wide application and fast-growing production.

Chlorination and aqua regia are industrially used worldwide for refining of gold but also for the recycling, for jewelry, coins, medical or industrial residues, while e-waste is mainly recycled in the pyrometallurgical copper route. Although there are many studies on gold recovery from e-waste by using cyanide alternative reagents, there is no commercialized, environmentally sound process (Birich 2020; Latacz et al. 2020). Nevertheless, there are many informal businesses around the world that use aqua regia to recover gold under harsh environmental and safety conditions. In China, for example, e-waste is mostly recycled in the informal sector, where a huge number of trash recyclers are engaged to use crude and polluting recycling technologies to quickly separate gold and other precious metals (Chi et al. 2011). Similar, India is facing an expanding dilemma with the growth of the informal recycling sector, which releases hazardous organic pollutants, aggressive effluents and other toxicants (Chakraborty et al. 2018).

Own research proved the applicability and advantages of cyanide alternative leaching reagents, as displayed in Figure 1. Especially Cu is a critical contaminant in e-waste for gold leaching, as it is dissolved by most reagents causing a chemical consumption and other negative side effects. Nonetheless, especially thiourea and thiosulfate were capable to achieve a good gold recovery. Just when the initial Cu concentration of the input material is strongly reduced, also cyanide achieves a reasonable gold recovery but anyway being less selective to copper (Birich et al. 2023).

The leaching experiments were validated on different waste streams from electronic equipment reaching robust gold recovery of more than 95%, for PCB reproducibly more than 98% (Figure 2). A nearly complete gold recovery can be achieved in less than 4 hours, which is also a benefit of cyanide alternative reagents (Birich et al. 2018; Birich et al. 2019; Birich et al. 2023).

3. Industrial Application of Cyanide Alternative Reagents in Primary Gold Production

Environmental issues appear to be the major stimulus for the search and development of alternative leaching systems for gold and silver extraction. To overcome the drawbacks of cyanide, many alternative reagents were intensively investigated for their capability as a suitable...
A. Birich et al.

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3.1. Thiosulfate

Thiosulfate has received particular attention as an alternative to cyanide in recent years, although its use dates to the mid-19th century. Thiosulfate leaching was first used in the “Von Patera Process” in 1858. In this process, silver was extracted using sodium thiosulfate solutions after chlorination roasting of the ore (Molleman und Dreisinger 2002). Newmont Gold Co. operated a pilot plant for the extraction of gold using ammonium thiosulfate solutions from a refractory ore (preg-robbed) by heap/column leaching in 1996 - 1999. In the pilot plant, gold cementation with Cu/Zn powders was applied (Wan und LeVier 2003). In 1998, Placer Dome Co. applied gold extraction from preg-robbing type refractory ores using a Cu(II)-ammonia-thiosulfate system in pilot scale (West-Sells und Hackl 2005). The process had two different applications: Mill Ammonium Thiosulfate for tank leaching and Heap Ammonium Thiosulfate. Ammonium sulfide ((NH$_4$)$_2$S) was used for gold recovery from PLS. Neither the Newmont nor the Placer Dome processes were commercialized. More recently, a demonstration plant for the application of a thiosulfate leaching process for small gold deposits has been built in Australia. The operation seems to involve vat leaching of gravity tails followed by gold recovery from PLS by ion exchange (Breuer 2017; Heselev 2017). After 20 years of R&D studies, Barrick Gold Co. developed a technically and economically viable thiosulfate leaching process. In 2015, a commercial thiosulfate leaching facility at the Goldstrike mine (Nevada/USA) started processing a double refractory ore (see Figure 3). Cyanide gold recovery of this ore type was just 30 % (Aylmore 2016; Choi 2016). The process is a non-ammoniacal process that uses Cu(II) and calcium thiosulfate (CaS$_2$O$_3$) and operates at pH 8. Before leaching, pressure oxidation (225°C, 7 bar p$_{O_2}$, 1 h) and neutralization to pH 8 - 8.5 is applied. Gold is recovered from PLS by a resin-in-leach (RIL) process. Thiosulfate regeneration is accomplished in contact with sulfites and elemental sulfur derived from partial oxidation of sulfide ores during pressure leaching at 150 °C (Evans et al. 2017; Choi und Chefai; Choi et al. 2013).

Despite several environmental and technical advantages of thiosulfate, there are some technical and economic constraints, especially in the solution purification and gold recovery stage (Xia 2008; Zhang und Dreisinger 2004). In addition, reagent consumption may be high under certain conditions, owing to the need for higher thiosulfate addition. Therefore, the reagent concentration is often significantly higher than in cyanide leaching i.e., 11-22 g/L thiosulfate vs. 0.25 - 1 g/L cyanide (Xie et al. 2021; Marsden 2006). These are the main reasons for the unique application of the thiosulfate process by Barrick Gold.

Fig. 1. Leaching of pyrolyzed and crushed RAM PCB after foregoing base metal leaching (left: initial Cu-concentration 16.8 wt.%; right: initial Cu-concentration 1.3 wt.%) (Birich et al. 2023)

Fig. 2. Gold dissolution from pyrolyzed and pre-leached and comminuted RAM PCBs via thiourea TU and thiosulfate TS over time (Birich et al. 2023)
3.2. Thiourea

The dissolution of gold by acidic thiourea is much faster than by cyanidation. Compared with cyanide, thiourea has a lower sensitivity to base metals (Pb, Cu, Zn, As) and residual sulfur in calcines. It allows high gold recovery from pyrite and chalcopyrite concentrates, and satisfactory recovery of gold from carbonaceous (refractory) ores (Tremblay et al. 1996; Deng et al. 2001; Hilson and Monhemius 2006). Pilot and in situ leaching tests were reported by several researchers. In comparative studies, gold recovery in thiourea leaching was often a similar to cyanide leaching, but thiourea consumption (9 – 10 kg/t) was much higher than cyanide consumption (2.5 - 3 kg/t). (Kavanagh et al.; van Staden und Laxen 1989; Tremblay et al. 1996).

The high consumption of thiourea appears to be the most serious drawback. Other disadvantages include its complexity of leaching reactions, corrosive solution, low selectivity, complicated reagent regeneration, and difficult gold recovery from PLS. The overall operating cost incurred by high thiourea consumption is estimated to be at least twice the cost of cyanide leaching for the same ore. (Aylmore 2016).

3.3. Halides

Halide leaching involves leaching with chloride/chlorine, bromide/bromine and iodide/iodine lixiviants systems (Konyratbekova et al., 2015). The history of halide leaching of gold dates to the early 19th century. Chlorination was a common process used for extraction of gold from ores before cyanide leaching and is currently industrially used worldwide for refining of gold and platinum group metals (PGM).

The Platsol process was successfully demonstrated for the extraction of gold from Cu/Ni/PGM and copper-gold concentrates with gold extraction of >90% for non-preg-robbing refractory gold concentrates. After leaching and S/L separation, gold/PGM can be recovered from pregnant leach solutions by precipitation with NaHS. A feasibility study concluded that the process has "potential to generate positive economic returns" (Dreisinger et al., 2018; ; Ferron et al., 2003; (Zachary J. Black et al. 2018). Kell process involves two-stages: first Cu/Ni/Co sulfides are oxidized in autoclaves (200-225°C, 3000 kPa, 20-45 min.) using sulphate solutions (Adams et al., 2015), second roasting at 900 °C to generate soluble sulphate salts. A 3.5 M HCl solution was used with chlorine at 80 °C for gold extraction. The process was demonstrated at pilot scale and a full-scale plant is considered (Adams et al., 2015; Chadwick, 2017). Similar leach conditions are employed in Intec and N-Chlo processes, which use mixed chloride/bromide solutions with cupric ions (Cu++) as oxidant for pyritic/arsenopyritic gold concentrates (Abe et al., 2008; Moyes et al., 2005). Gold is recovered from PLS by activated carbon or ion exchange with the latter being more selective. Intec process was tested at pilot scale while a demonstration plant for N-Chlo process was established and operated in Perth (Australia).

DST (formerly Nichromet) process is also a mixed chloride/bromide leaching process similar to Intec and N-chlo but differs from these processes by using Cl2/Br2 as the oxidant at low temperatures (35 - 45 °C) (Aylmore, 2016). In addition, the process includes roasting as a pre-treatment stage to remove sulfides prior to gold leaching. Hypochlorite (OCl-) and hypobromite (OBr-) used as a source of Cl and Br, respectively, are generated by electrolysis. The process was tested at pilot and demonstration scale (Chadwick, 2017; DST, 2018). Outotec's mixed chloride/bromide based leaching process is performed at 80 – 90 °C under atmospheric conditions in the presence of cupric ions. Gold recovery from PLS is carried out by solvent extraction using an own developed organic reagent (Lundström et al., 2015). The process is tested at pilot scale and still under development (Aylmore, 2016).

Fast leaching kinetics and suitability for treatment of refractory sulfide ores are the most important features of halide leaching processes. However, there is no commercial application of halide leaching for gold extraction, due to important shortcomings: high OPEX, high reagent consumption, not suitable for preg-robbing ores, highly corrosive nature and need for closed systems and high reagent cost, particularly for bromine and iodine. Therefore, to date, there is no commercial application of halides for gold extraction from ores/concentrates.

3.4. Further Reagent Alternatives

Further reagents like bisulfides, thiocyanate, ammonia, organic nitriles, or glycine were extensively tested at laboratory scale, with partially promising results in gold recovery. There are several further gold solvents on the market declared as environmentally sound cyanide alternatives, but their composition is not clearly described, or they contain thiocyanates or other compounds, which may form cyanide complexes during leaching. The major limitations of these reagents are, inter alia, high reagent price, low selectivity, high OPEX, environmental and health concerns or a lower gold recovery at similar conditions compared to cyanide. Because of these drawbacks, no further reagents were tested successfully on a pilot or demonstration scale (Sun et al. 2020; Kholov et al. 2021).

4. Conclusion

Despite decades of research and extensive efforts on industrial application tests, there is still no cost-effective universal replacement for the cyanide process. The search for alternative lixiviants systems is
essentially driven by the environmental impact of using cyanide and the inefficiency of cyanide for certain types of refractory ores (e.g., preg- 
robbing and copper-rich ores). Thiosulfate, thiourea and chloride can be 
identified as the most promising alternatives to cyanide. One of 
the significant challenges for the exploitation of non-cyanide lixiviant 
systems is the availability or development of suitable downstream 
processes for the recovery of gold from pregnant leach solutions. 
Thiosulfate is the only alternative reagent developed into commercial 
application in the Barrick Goldstrike process. Nonetheless, the 
increasing need for processing more complex gold ores will force an 
increasing application of cyanide alternatives in the future. On the other 
side, for the informal or small-scale gold mining sector, no effective 
approach was found to regulate the hazardous practices, especially 
the application and utilization of the mercury. The approaches of banning mercury or 
implementing a formal registration system for mining activities were 
not successful, as mining operations take place in abundant places in 
the absence of authorities. Consequently, the risk of environmental 
pollution due to amalgamation or improper use of cyanide will continue.

Recycling gold is very energy-efficient and avoids the environmental 
damage caused by mining and metallurgical operations. While in 
industrial recycling, gold is dissolved by aqua regia for further refining 
under safe conditions, including proper effluent treatment, the same 
technique is applied by informal recyclers in a very hazardous way. 
Especially electronic waste becomes more and more important for 
recycling because it is the fastest growing waste stream. Due to a lack 
of collection systems or improper disposal of electronic equipment, 
nowadays only half of the gold is recycled from this waste stream. Also, 
the gold recovery technique may be optimized in terms of being less 
hazardous, more selective, and faster than state-of-the-art recycling 
processes, e.g., by the application of thiosulfate. Published work from 
different researchers and own research work proved the capability of 
thiosulfate and thiourea for gold recovery from e-waste and similar 
metal waste streams. Besides safer working conditions, these reagents showed 
a much faster dissolution rate and were much more selective than cyanide. 
Thus, the application of cyanide alternative reagents in gold recycling 
from different secondary resources constitutes a very promising approach, 
not just for small scale informal recyclers.

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