Gold cyanidation

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Gold cyanidation (also known as the **cyanide process** or the **MacArthur-Forrest process**) is a <u>metallurgical</u> technique for extracting <u>gold</u> from low-grade <u>ore</u> by converting the gold to a water soluble <u>coordination complex</u>. It is the most commonly used process for <u>gold extraction</u>. Production of reagents for mineral processing to recover gold, copper, zinc and silver represents approximately 13% of cyanide consumption globally, with the remaining 87% of cyanide used in other industrial processes such as plastics, adhesives, and pesticides. Due to the highly <u>poisonous</u> nature of cyanide, the process is controversial and its usage is banned in a number of countries and territories.

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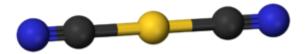
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[edit] History

In 1783 <u>Carl Wilhelm Scheele</u> discovered that gold dissolved in aqueous solutions of cyanide. He had earlier discovered cyanide salts. <u>[citation needed]</u> Through the work of <u>Bagration</u> (1844), Elsner (1846), and <u>Faraday</u> (1847), it was determined that each atom of gold requires two cyanide, i.e. the <u>stoichiometry</u> of the soluble compound. Cyanide was not applied to extraction of gold ores until 1887, when the MacArthur-Forrest Process was developed in <u>Glasgow</u>, <u>Scotland</u> by <u>John Stewart MacArthur</u>, funded by the brothers Dr Robert and Dr William Forrest. In 1896 Bodländer confirmed that oxygen was necessary, something that was doubted by MacArthur, and discovered that <u>hydrogen peroxide</u> was formed as an intermediate. [3]

[edit] Chemical reaction



Ball-and-stick model of the aurocyanide or dicyanoaurate(I) complex anion, [Au(CN)₂]^{-[4]}

The <u>chemical reaction</u> for the dissolution of gold, the "Elsner Equation", follows:

$$4 \text{ Au} + 8 \text{ NaCN} + \text{O}_2 + 2 \text{ H}_2\text{O} \rightarrow 4 \text{ Na[Au(CN)}_2] + 4 \text{ NaOH}$$

In this redox process, oxygen removes four electrons from the gold simultaneous with the transfer of protons (H⁺) from water.

[edit] Application

The <u>ore</u> is <u>comminuted</u> using grinding machinery and is sometimes further concentrated by <u>froth flotation</u> or by centrifugal (gravity) concentration, depending on the ore. The alkaline ore slurry can be combined with a solution of <u>sodium cyanide</u> or <u>potassium cyanide</u>, however many operations utilize calcium cyanide, which is more cost effective. The extracting solution is maintained at an alkaline <u>pH</u> to prevent release of toxic <u>hydrogen cyanide</u>. <u>Lead nitrate</u> can improve gold <u>leaching</u> speed and quantity recovered, particularly in processing partially oxidized ores.

[edit] Effect of dissolved oxygen

Oxygen is one of the <u>reagents</u> consumed during cyanidation, and a deficiency in <u>dissolved oxygen</u> slows leaching rate. Air or pure oxygen gas can be purged through the pulp to maximize the dissolved oxygen concentration. Intimate oxygen-pulp contactors are used to increase the partial pressure of the oxygen in contact with the solution, thus raising the dissolved oxygen concentration much higher than the saturation level at <u>atmospheric pressure</u>. Oxygen can also be added by dosing the pulp with hydrogen peroxide solution.

[edit] Pre-aeration and ore washing

In some ores, particularly those that are partially sulfidized, <u>aeration</u> (prior to the introduction of cyanide) of the ore in water at high pH can render elements such as iron and sulfur less reactive to cyanide, and therefore the gold cyanidation process more efficient. Specifically, the oxidation of iron to <u>iron (III) oxide</u> and subsequent <u>precipitation</u> as <u>iron hydroxide</u> minimizes loss of cyanide from the formation of ferrous cyanide complexes. The oxidation of <u>sulfur</u> compounds to sulfate ions avoids the consumption of cyanide to thiocyanate (SCN) byproduct.

[edit] Recovery of gold from cyanide solutions

In order of decreasing economic efficiency, the common processes for recovery of the solubilized gold from solution are (certain processes may be precluded from use by technical factors):

- Carbon in pulp
- Merrill-Crowe process
- Electrowinning
- Resin in pulp

[edit] Effects on the environment



Sodium cyanide drum at the abandoned Chemung Mine in Masonic, California

Despite being used in 90% of gold production, [5] gold cyanidation is <u>controversial</u> due to the toxic nature of cyanide. Although aqueous solutions of cyanide degrades rapidly in sunlight, the less-toxic products, such as cyanates and thiocyanates, may persist for some years. The famous disasters have killed few people — humans can be warned not to drink or go near polluted water — but cyanide spills can have a devastating effect on rivers, sometimes killing everything for several miles downstream. However, the cyanide is soon washed out of river systems and, as long as organisms can migrate from unpolluted areas upstream, affected areas can soon be repopulated. In the <u>Somes</u> river below <u>Baia Mare</u>, the plankton returned to 60% of normal within 16 days of the spill. [6] Famous cyanide spills include:

Year	Mine	Country	Incident
1985-91	Summitville	USA	Leakage from leach pad
1980s- present	Ok Tedi	Papua New Guinea	Unrestrained waste discharge
1995	Omai	Guyana	Collapse of tailings dam
1998	<u>Kumtor</u>	Kyrgyzstan	Truck drove over bridge
2000	Baia Mare	Romania	Collapse of tailings dam (see <u>2000 Baia</u> <u>Mare cyanide spill</u>)
2000	Tolukuma	Papua New Guinea	Helicopter dropped crate into rainforest ^[7]

Such spills have prompted fierce protests at new mines that involve use of cyanide, such as <u>Roşia Montană</u> in Romania, <u>Lake Cowal</u> in Australia, <u>Pascua Lama</u> in Chile, and Bukit Koman in Malaysia.

[edit] Cyanide remediation processes

The various species of cyanide that remain in tails streams from gold plants are potentially toxic, and on some operations the waste streams are processed through a detoxification process prior to tails deposition. This reduces the concentrations of these cyanide compounds, but does not completely eliminate them from the stream. The two major processes utilised are the INCO licenced process or the Caro's acid process. Both processes utilise oxidants to oxidise cyanide to cyanate, which is not as toxic as the cyanide ion, and which can then react to form carbonates and ammonia. The Inco process can typically reduce cyanide concentrations to below 50 mg/L, while the Caro's acid process can reduce cyanide levels to between 10 and 50 mg/L, with the lower concentrations achievable in solution streams rather than slurries. Hydrogen peroxide and alkaline chlorination can also be used, although these are typically less common.

One of the alternative oxidants for the degradation of cyanides that has been attracting industrial interest is Caro's acid – peroxomonosulphuric acid (H₂SO₅). Caro's acid converts cyanide to cyanate. Cyanate then hydrolyses in the water to ammonium and carbonate ions. The Caro's acid process is able to achieve discharge levels of WAD below 50 mg/L, which is generally suitable for discharge to tailings. Generally, the best application of this process is with tailings slurries containing low to moderate initial levels of cyanide and when treated cyanide levels of less than about 10 to 50 mg/L are required.

Over 90 mines worldwide now use an Inco SO₂/air detoxification circuit to convert cyanide to the much less toxic cyanate before waste is discharged to a tailings pond. Typically, this process blows compressed air through the tailings while adding sodium metabisulfite which releases SO₂, lime to maintain the pH at around 8.5, and copper sulfate as a catalyst if there is insufficient copper in the ore extract. This procedure can reduce concentrations of "Weak Acid Dissociable" (WAD) cyanide to below the 10 ppm mandated by the EU's Mining Waste Directive. This level compares to the 66-81 ppm free cyanide and 500-1000 ppm total cyanide in the pond at Baia Mare. Remaining free cyanide degrades in the pond, while cyanate ions hydrolyse to ammonium. Recent studies show that residual cyanide trapped in the gold-mine tailings causes persistent release of toxic metals (e.g. mercury) into the groundwater and surface water systems. [8][9]

[edit] Legislation

The US states of Montana, [10] Wisconsin, [11] the Argentine state of Río Negro, [12] the Czech Republic, [13] Hungary, [14] and other countries have banned cyanide mining. However, the European Commission rejected a proposal for such a ban, noting that

existing regulations (see below) provide adequate environmental and health protection. [15]

In the EU, industrial use of hazardous chemicals is controlled by the so-called Seveso II Directive (Directive 96/82/EC, [16] which replaced the original Seveso Directive (82/501/EEC brought in after the 1976 dioxin disaster. "Free cyanide and any compound capable of releasing free cyanide in solution" are further controlled by being on List I of the Groundwater Directive (Directive 80/68/EEC which bans any discharge of a size which might cause deterioration in the quality of the groundwater at the time or in the future. The Groundwater Directive was largely replaced in 2000 by the Water Framework Directive (2000/60/EC). [19]

In response to the 2000 Baia Mare cyanide spill, the European Parliament and the Council adopted Directive 2006/21/EC on the management of waste from extractive industries. [20] Article 13(6) requires "the concentration of weak acid dissociable cyanide in the pond is reduced to the lowest possible level using best available techniques", and at most all mines started after 1 May 2008 may not discharge waste containing over 10ppm WAD cyanide, mines built or permitted before that date are allowed no more than 50ppm initially, dropping to 25ppm in 2013 and 10ppm by 2018.

Under Article 14, companies must also put in place financial guarantees to ensure cleanup after the mine has finished. This in particular may affect smaller companies wanting to build gold mines in the EU, as they are less likely to have the financial strength to give these kinds of guarantees.

The industry has come up with a voluntary Cyanide Code that aims to reduce environmental impacts with third party audits of a company's cyanide management.

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- 9. <u>^ Effects of acid-sulfate weathering and cyanide-containing gold tailings on the transport and fate of mercury and other metals in Gossan Creek: Murray Brook mine, New Brunswick, Canada</u>
- 10. ^ The Citizens Initiative banning of cyanide mining in the State of Montana, USA

- 11. ^ 2001 Senate Bill 160 regarding the use of cyanide in mining.
- 12. ^ Río Negro passes bill banning cyanide use, Argentina
- 13. ^ "Czech Senate bans use of cyanide in gold mining"
- 14. A Zöld siker: törvényi tilalom a cianidos bányászatra!
- 15. <u>^</u> International Mining <u>European Commission rejects proposed ban on using cyanide</u> in extractive industry, July, 2010
- 16. <u>^ Council Directive 96/82/EC of 9 December 1996 on the control of major-accident hazards involving dangerous substances.</u> For the modifications see the consolidated version.
- 17. <u>^ Council Directive 82/501/EEC of 24 June 1982 on the major-accident hazards of certain industrial activities.</u> Not in force.
- 18. <u>^ Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater</u> against pollution caused by certain dangerous substances. Not in force.
- 19. <u>^ Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (the Water Framework Directive)</u>. For the modifications see the consolidated version.
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