RECENT ADVANCES IN THE TREATMENT OF REFRACTORY GOLD ORES

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ABSTRACT

After a century of overwhelming dominance in the extractive metallurgy of gold, the cyanid process is coming under pressure. Increasing importance of refractory gold ores, together with the growing concern about the environmental impact of cyanid-containing discharges, have given renewed impetus to research and development into alternative leaching methods of gold ores. A wide variety of methods are under investigation, with some already being in industrial use. This paper reviews the current situation and describes, inter alia, recent progress made in the use of thiourea, in the application of pressure leaching techniques and in the use of bacteria for the preoxidation of gold ores. Experimental results on the application of some of these new methods to different types of gold ores depleted from Royal School of Mines. Extensive ore collection are described.

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Recent advances in the treatment of refractory gold ores

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1. INTRODUCTION

The past decade has seen a renascence in research and development into new gold extraction processes. This has been brought about primarily by the increase in the price of gold since the abolition of the gold standard at the beginning of the nineteen seventies. The consequent rise in the price of metal was sustained throughout the decade and peaked at over $800 per ounce in 1980. In recent years, the price has dropped back to the $300-400 range, but gold mining remains a financially attractive proposition, especially in comparison with most other metals, where producers are barely able to survive at present price levels.

Much of the development activity in gold extraction has been directed towards reducing the capital investment required in the application of the standard cyanide process to free-milling gold ores. The development of carbon-in-pulp processing has had a major impact on costs in agitation leach plants by eliminating the expensive liquid-solid separation requirements of the traditional Merrill-Crowe zinc precipitation process. The introduction of heap leaching into gold metallurgy is a major innovation which has lowered economic cut-off ore grades to 1 g Au/T or less in some cases.

However it is the treatment of refractory gold ores that the greatest diversity of new developments is evident. Because of the overwhelming dominance of the cyanide process for gold extraction over the past 100 years, the term "refractory" applied to a gold ore simply means that a high gold recovery is not attainable by cyanide leaching. There are various causes of refractoriness in gold ores, which include: inclusions of submicron gold in sulphide minerals, in particular pyrite and arsenopyrite; the presence of iron, copper or lead minerals which consume cyanide by the formation of metal-cyanide complex ions; the presence of arsenic and antimony minerals which act as oxygen scavengers; the presence of tellurium which alloys with gold and silver; and the presence of either carbonaceous materials of organic origin, or clays, capable of reabsorbing gold cyanide complex ions from the leach solution (the American term is "preg-robblng").

A comprehensive review of methods which had been tried over the years to treat these various types of difficult gold ores was published twenty years ago by workers at the National Institute for Metallurgy in South Africa (1). This remained virtually the only authoritative account of work on refractory gold ores until 1980. Since then several other review articles have been published (2-5), the last of these appearing in 1983. The pace of developments in this area is increasing and it is the purpose of this paper to bring up to date the situation as it pertains in late 1986. Various different technologies are reviewed, namely: pressure oxidation, pressure cyanidation,
biooxidation, thiourea leaching and some quite recent work on nitric acid leaching. Several of these have moved from the development stage into commercial use in the past few years.

2. PRESSURE OXIDATION

An excellent detailed historical account of the development of pressure oxidation as a pretreatment method for refractory gold ores has been published by Berezowsky and Weir (6). According to them, the first patent on the use of pressure leaching for preoxidation of arsenical gold ores was granted to the Chemical Construction Company (Chemico) in 1955 (7). Two years later, the parent company, American Cyanamid, was granted a second patent (8) which taught that pressure oxidation could be successfully applied to a range of refractory gold ores, including pyritic, antimonial and carbonaceous materials, in addition to arsenical ores.

In 1956 Sherritt Gordon Mines Ltd. purchased the rights to the Chemico patents and "know-how" in the metallurgical field. This purchase was primarily motivated by Sherritt's requirement to use Chemico technology for pressure hydrogen reduction to produce nickel and cobalt metal powders from pentlandite concentrates, a process which was put into operation at a new refinery in Fort Saskatchewan. Sherritt subsequently continued development of pressure oxidation for refractory gold ores in the late fifties but, although the metallurgical results were very good, the low price of gold at that time precluded commercial development on economic grounds. Interest in the application of pressure hydrometallurgy to gold ores then died out and has only revived in the last few years, when the increase in the price of gold has made capital intensive recovery methods economically interesting.

Perhaps not surprisingly, in view of their current dominating position in the technology of pressure hydrometallurgy, Sherritt Gordon have carried out much of the recent pressure oxidation work on refractory gold ores. They claim to have tested nearly one hundred ores and concentrates since starting work in this area in 1980 (9). In batch pressure oxidation tests, the standard conditions used by Sherritt are temperatures in the range of 170 to 190°C at total pressures of 1500 to 2000 kPa and reaction times of 2 hours (10). Under these conditions, sulphide sulphur in the feed material is totally oxidised to sulphate and much of the iron and arsenic is precipitated as hematite, jarosites and arsenates. The total disruption of the sulphide crystal lattice caused by this drastic attack virtually ensures that any occluded or locked gold is released and reports in the leach residue in a form which is easily amenable to subsequent cyanide leaching. Sherritt report results obtained from nearly 70 different gold ores and concentrates and show gold recoveries by cyanidation improving from the range 5 to 75% before pressure oxidation to 85 to 98% after oxidation.

Although pressure oxidation is very effective for liberating gold associated with sulphides, extraction of silver is usually adversely affected and cyanidation gives lower recoveries after oxidation than before. This behaviour is generally attributed to the incorporation of silver in argentochlorsite in the leach residue, which is refractory to cyanide leaching. Sherritt have developed a post-treatment which is said to liberate the silver.
This involves atmospheric conditioning of the oxidised leach residue in a slurry of lime at an elevated temperature (9). In a recent paper, Tourre et al (11) showed that silver losses could be prevented either by oxidising at 190°C or higher, where jarosites become unstable and hematite is formed, or alternatively by leaching under under high acid conditions or adding excess potassium, to form preferentially potassium jarosite instead of silver jarosite. Of these methods, the first, i.e. increasing the reaction temperature, was considered to be the most economically feasible.

2.1 Commercial Developments

The first commercial pressure preoxidation plant to be put into operation is at Homestake Mining Company’s McLaughlin mine in northern California (12,13). The McLaughlin ore body, which was discovered in 1980, is estimated to contain about 18M T of ore with an average grade of 5.2g Au/T (0.152 oz/st). The total development costs of the project were $280 million, to build the mine with a production of 2700 T/d of ore and a treatment plant involving pressure preoxidation with an annual gold production capacity of about 5.5 T Au. The first bar of dore metal at McLaughlin was poured on March 4th, 1985.

The McLaughlin ore is sulphidic, the major mineral being pyrite, with smaller amounts of chalcopyrite, sphalerite and cinnabar. The gold occurs typically as a fine-grained electrum (18-26% Ag, approx.20μm), associated primarily with silver-antimony sulphosalts, such as miargyrite (AgSbS₂) and pyrargyrite (Ag₃SbS₃). The ore also contains some clays and carbonaceous matter which reabsorb dissolved gold. The ore body is quite heterogeneous and 12 different ore types are identified. Gold recoveries from these various ore types by direct cyanidation vary from 5 to 80%.

During process development and selection, various pretreatment methods were investigated, with a number of different laboratories being involved at that stage. This work led to the conclusion that pressure preoxidation was the preferred route and consequently Sherritt Gordon were contracted to run a continuous pilot plant simulation of the whole process.

The flowsheet of the commercial plant is shown in Figure 1. Crushing and grinding of the ore is carried out at the open pit mine site to produce a feed material sized at 80% -200 mesh. This is transported as a slurry by a 5 mile pipeline to the metallurgical plant. There the ore pulp enters the preoxidation tanks where it is mixed with recycled acidic leach liquor from the autoclaves. Acid-soluble material in the ore, e.g. carbonates, help to partially neutralise this liquor, which is then sent for complete neutralisation with lime, to remove dissolved metals, prior to recycle within the process. Thickened pulp is first pre-heated in heat exchangers, using steam from the flash tanks, and is pumped into one of the three continuous, horizontal, oxidation autoclaves, which operate in parallel. The autoclaves are 4.2m in diameter and 16m long, each with four, independently agitated compartments, and are constructed of mild steel, lined with lead and acid-proof brick. Ore slurry enters the autoclaves at 90 - 120°C and pH 1.8 to 1.9 at a pressure of 320 psi (2.2 MPa). The residence time of the ore in the autoclaves is 60 minutes and oxygen is supplied at the rate of 40-50kg O₂/T ore. Due to the exothermic nature of the oxidation of the sulphide
minerals to metal sulphates and sulphuric acid, the temperature and acidity rise along the autoclave and, at the exit, the pulp contains 10 - 20g/L free acid and the temperature is 170 - 180°C. This is discharged to atmospheric pressure in flash tanks, the steam being recycled to heat incoming feed, and is then thickened and washed in a 2-stage counter-current decantation circuit. Lime is added to the thickened pulp to raise the pH to 10.8 prior to cyanide leaching, which is carried out in two 540 m³ agitated tanks. This is followed by gold extraction by carbon-in-pulp absorption in a series of eight similar-sized tanks. Activated coconut-shell carbon is added at 20 g/L and is loaded to about 3000g Au/T before passing to a hot elution and thermal regeneration circuit. Gold is recovered from the pregnant eluate by electrowinning on steel wool cathodes. The loaded cathodes are first heated in retorts to recover mercury and are then smelted to dore bullion. Gold recovery at McLaughlin is reported at 92% in early 1986, with a throughput of 2900T ore/day, which exceeds the design capacity. Operating costs are quoted at $322/oz Au [13]

3. PRESSURE CYANIDATION

A pressure technique with considerably older origins than pressure oxidation is pressure cyanidation. In a paper entitled, "Some studies in the gold-dissolution rate in cyanide solutions" published in 1939, Fahrenwald and Newton (14) investigated the effect of oxygen pressure on cyanide leaching, reasoning that according to the Elsner equation,

\[ 4Au + 8CN^- + 2H_2O + O_2 = 4Au(CN)_2^- + 4OH^- \]

the dissolution rate should be a function of both oxygen pressure and cyanide concentration. Their apparatus consisted of a pressure-tight steel cylinder, lined with paraffin, agitated by being slowly rotated on rollers. Partial pressures of oxygen of up to 120psi (827kPa) were investigated. Initially dissolution of specimens of gold foil was studied by measuring the weight loss after various times of leaching. It was shown that, in the presence of excess cyanide, the rate of dissolution of gold was directly proportional to the partial pressure of oxygen. Tests were then carried out in the same apparatus using samples of a free-milling siliceous gold ore. The leach solution was a 0.5 g/L KCN solution and the liquid to solid ratio was 7. It was shown that the rate of leaching of gold from the ore could be increased by up to about seven times by increasing the oxygen partial pressure from 3 psi (i.e. atmospheric air) to 30 - 40 psi. At higher oxygen pressures the dissolution rate started to decrease.

Perhaps due to the imminent second World War, this work, together with Soviet work on the same subject, published a little earlier (15), lapsed into obscurity and it was over 40 years before the concept of pressure cyanidation was revived and re-examined. In 1983 a paper from Lurgi in Germany (16) reported results obtained with a free-milling gold ore containing 17.6 g Au/T and 1.5 wt% Fe, mostly as pyrite. Leaching with 0.5kg NaCN/T ore at pH 11.5 with air at atmospheric pressure resulted in a gold extraction of about 95% in 24 hours. Using pressurised oxygen at 20 bar, however, it was found possible to extract the same amount of gold in only 30 minutes. In addition to increasing pressure the effects of increasing temperature were also
examined. The stability of cyanide towards decomposition by hydrolysis or oxidation was first examined and was shown to be adequate up to about 75°C. At higher temperatures, decomposition occurred rapidly. It was found that the rate of gold dissolution was slightly increased by temperatures up to 70°C, but it was considered that the advantage was not sufficient to warrant the more elaborate and expensive equipment that would be required for elevated temperature operation.

One of Lurgi's motives for carrying out this work was to investigate new applications for the VAW tube digester, or pipe reactor, which had been the subject of an earlier agreement between Lurgi and Vereinigte Aluminium Werke (VAW), who originally developed and applied tube digester technology for bauxite leaching. Following the laboratory work outlined above, a continuous test in a pilot-scale tube reactor was carried out. In this 10T of ground ore assaying 10.2g Au/T were slurried with water at a solid-liquid ratio of 1 and the pH was adjusted to 11.5. Sodium cyanide at 1 kg/T ore was added and the slurry was pumped through the tube reactor at a flow rate of 2.5m³/hr. The pressure in the tube was 25 bar (2.6MPa) and the flow velocity of the slurry was 2.5 m/s. Oxygen was added at the rate of 6kg O₂/T ore. The pilot-scale tube reactor used for the test was 1200m long which gave a residence time of only 8 minutes. However the discharged solids were found to have a residual gold content of only 0.2g Au/T, indicating that 98% extraction of gold had been achieved.

3.1 Commercial Developments

Pressure cyanidation in a tube reactor is in commercial use for treating an auriferous stibnite concentrate at the Consolidated Murchison mine near Gravelotte in South Africa. The experimental work which led to this development is described in a paper by Muir, Hendriks and Gussman (15). Three arsenical and one stibnite concentrate were tested. Batch cyanide leaching experiments were carried out in a 5L stirred autoclave at various temperatures and pressures. "Low-alkalinity" conditions, i.e. terminal pH's of 10 or less, were used, since alkali attack on the sulphide minerals and consequently cyanide consumption was greatly reduced at these pH values. It was shown that the stibnite concentrate responded very well to pressure cyanidation with gold recoveries of about 90% being achieved. With the arsenical materials, lower recoveries, in the 60 - 70% range, were obtained. Optimum leaching conditions were found to be 1 to 2 hours residence at 20°C with 50 to 80 bar (5.3-8.4MPa) oxygen overpressure and cyanide additions of 10 to 20kg/T ore, although cyanide consumptions were considerably lower. Following the laboratory work, a full-scale continuous leaching test was carried out in a 4 km long, 100 mm diameter, Lurgi tube reactor which was available at one of JCI's uranium mines. The test was carried out on a 250 T sample of arsenical flotation middlings. A residence time of two hours in the tube with an inlet pressure of 48 bar (5MPa) and a cyanide addition of 10kg NaCN/T ore gave a gold extraction of 90%. This extraction value was a marked improvement over that obtained for the same material in the laboratory-scale stirred autoclave, where less than 70% extraction had been achieved. The superior performance of the tube reactor compared with the stirred autoclave, which had also been found by Lurgi in their pilot-scale work, noted above, was confirmed in the production plant built as a result of these test results for the treatment of stibnite concentrates at the Consolidated Murchison mine. The heart of this plant is
a 1.5 km length of 50 mm steam pipe, through which a slurry of stibnite concentrate is pumped at 80 bar (8.4 MPa) pressure. With a retention time of only 15 minutes, up to 85% gold extraction is achieved, compared with only about 65% obtained in autoclave tests.

4. BACTERIAL OXIDATION

The use of the sulphide-oxidising bacterium, *Thiobacillus ferrooxidans*, has been actively exploited in the leaching of sulphide minerals for at least a quarter of a century. It has also been known for a similar length of time that *T. ferrooxidans* is capable of oxidising arsenical minerals such as arsenopyrite (17, 18). However the practical application of this knowledge to the problem of oxidation of refractory gold ores is of more recent origin.

One of the first published investigations into the bacterial oxidation of a gold ore was by Pinches in 1975 (19), who investigated the action of *T. ferrooxidans* on an auriferous pyrite/arsenopyrite concentrate. He showed that, in common with the bacterial oxidation of other sulphide minerals, attack on the pyrite/arsenopyrite concentrate could be initiated only within the pH range 1.8 to 4.0, with the optimum temperature being 32-35°C. The rate of leaching could be increased by increasing the available mineral surface area, either by reducing particle size or increasing the leach pulp density, up to a certain point, above which the rate became independent of surface area. This was thought to be due to some unidentified growth-limiting factor and was taken as an indication that long reaction times would be required to achieve extensive oxidation. The effects of bacterial oxidation on gold extraction from the ore were not reported by Pinches.

Following this work, little was published on the subject until 1983, when several papers appeared. Lawrence and Bruynesteyn (20) described work on refractory gold ores that had been carried out at B.C. Research in Vancouver, Canada, an institution where much pioneering work on bacterial leaching of sulphides has been undertaken over the years. The results of the bacterial oxidation of three refractory pyritic gold concentrates were reported. One of the concentrates came from Porgera in Papua New Guinea, the other two from the Cinola property in British Columbia. Experiments were carried out in batch stirred tanks at 20% pulp density, held at 35°C and sparged with CO₂ enriched (1%) air. With the Porgera concentrate, biooxidation improved gold recovery by cyanidation from 24% with the untreated ore to 81% in ore where 84% of the sulphur had been oxidised. Using a continuous leach liquor replacement technique to prevent excessive levels of acid and dissolved iron from accumulating, they were able to achieve this level of sulphur oxidation in 400 hours (17 days). Iron concentrations of 13-15 g/L and a pH of about 1 were maintained. For this concentrate it was found that the amount of gold extracted by cyanide was directly proportional to the extent of sulphur oxidation in the mineral. The Cinola concentrates were found to be more amenable to bacterial attack, with over 80% sulphur oxidation occurring in 6 days. Gold and silver recoveries increased to over 90% and 98%, respectively, compared with 60-78% and 80-86% before biooxidation. The Porgera ore has a very complex mineralogy and is particularly refractory. This is well illustrated in
a paper by Robinson, also published in 1983 (5), which compared the results obtained with many different gold recovery processes and clearly showed that only extensive disruption of the sulphide minerals by either biooxidation or pressure oxidation resulted in high gold recoveries.

South African experience with bioleaching is described in a paper from GENCOR (21) in which a financial comparison is made between biooxidation and roasting for the treatment of an arsenopyrite/pyrite gold ore. Two bioleaching schemes were investigated. In one, the run-of-mine ore was treated directly; in the other, flotation was first used to produce a concentrate which was subjected to biooxidation. An economic comparison was made of the three options, each sized to treat 450T ore per day. It was found that the gold recovery and hence revenue was higher for both bacterial leaches than for roasting, but that the capital and operating costs of the bacterial treatment of r.o.m. ore were too high to be compensated by the higher gold recovery. These high costs were largely due to the high volume throughput requirements of the r.o.m. treatment method. Prior flotation concentration reduced the weight of material to be treated, by either bioleaching or roasting, by twenty times. Under these circumstances, it was found that the bioleaching operating costs were still higher than for roasting the concentrate, but the capital costs were about 13% less. It was concluded that flotation and bioleaching of the concentrate was potentially a viable process and it was stated that a pilot plant was to be built to test the process at a larger scale.

Bioleaching pilot plants have been run by other companies and several have published their results recently. In the United Kingdom, Davy McKee have carried out engineering studies based on bioleaching work done at University College, Cardiff (22) and in Canada, two consulting companies, both based in Vancouver, have both carried out pilot plant work. P.M. Mineral Leaching Technologies have described their proprietary "Biotankleach" process (23,24) and Coastech Research have described the bioleaching pilot plant at Equity Silver Mines in British Columbia (25,26).

The Biotankleach process is carried out in agitated, air-sparged tanks, operated in series in continuous mode, with total residence times of 1 to 5 days, depending on the sulphide content of the feed. The pH is maintained at not less than 1, by partial neutralisation of the leach liquor if necessary. Dissolved arsenic and antimony levels are also controlled, but the bulk of these metals are fully oxidised and precipitated during leaching as ferric arsenates and antimonates. The leach residues, which contain all the precious metals, are washed, neutralised and subjected to standard cyanide leaching. Estimated capital and operating costs of the Biotankleach process are given for various plant capacities (24). These range from a capital cost of US$233/annual T for a 50 T/d plant, with a corresponding operating cost of $60.50/T feed, to $148/annual T and $40.50/T feed, respectively, for a 200 T/d plant.

The pilot plant operated at Equity Silver Mines has been described by Marchant (25,26). The flowsheet of this pilot plant is shown in Figure 2. The feed to the plant was an arsenical bulk sulphide concentrate scavenged from flotation tailings. Direct cyanidation of this concentrate resulted in an extraction of about 10% for both gold and silver. The biooxidation pilot plant was sized to treat 2T of concentrate per day. Bioleaching was carried out in a series of 5m$^3$ air-sparged agitated tanks. The concentrate was ground to 80% -70µm and was biooxidised at 13% w/w pulp density with a residence
time of 40 hours in the leaching system. The temperature in the leaching tanks was maintained at 30°C and air was added at 0.05 L/min/L pulp. Nutrients were added to maintain biological activity at steady state at the rate 0.6 kg [(NH₄)₂SO₄]/T and 0.12 kg KH₂PO₄/T concentrate and the pH and Eh in the leach tanks were 1.2 and 520mV, respectively. Following bioleaching, the leach residue was filtered, neutralised and then leached with cyanide to recover the precious metals. Recoveries of 70-75% for gold and 30-35% for silver were obtained. It was concluded from this work that the biohydrometallurgical and subsequent cyanidation response would be insensitive to the effects of scale-up, but that careful engineering design would be required to ensure adequate aeration, agitation and heat removal from large bioleaching tanks. A summary of the estimated capital and operating are given for a full-scale plant to treat 800 T/d of Equity concentrate containing 5.5 g Au/T and 90 g Ag/T.

Recent Soviet experience with bioleaching of gold ores is described in a paper by Polkin et al. (27) in which details of a pilot plant treating an arsenical gold flotation concentrate are given. The concentrate contained 8.4% As, 24.1% Fe and 26.6% S. The pyrite to arsenopyrite ratio in the concentrate was 2 to 1 and the gold was predominantly contained in the arsenopyrite. The bioleaching pilot plant consisted of nine pachuca tanks, made of acid-proof steel, used in two banks. The pachuca tanks were constructed with external casings through which hot water was circulated to maintain the required temperature in the tanks. The first stage of leaching was carried out in four pachuca used in series to give a residence time of 48 hours with 78% oxidation of arsenopyrite occurring. A further 60 hours of residence time in the remaining five pachuca increased the oxidation of arsenopyrite to 86%. Following solid liquid separation, the leach residue was sent to cyanidation while the leach solution was neutralised with lime suspension to precipitate iron, arsenic and sulphur. Raising the pH to 2.9-3.3 precipitated at least 90% of the dissolved arsenic. After removal of the precipitate and reacidification to pH 2.0 to 2.2, the liquor was returned to the head of the bioleaching circuit. It was found that gold recovery from the oxidised leach residue was 88-92% compared with only 7-10% from the untreated concentrate.

5. NITRIC ACID-BASED PROCESSES

Nitric acid reacts rapidly with arsenopyrite to form either soluble iron salts,

\[ 3\text{FeAsS} + 17\text{HNO}_3 = \text{Fe}_2(\text{SO}_4)_3 + \text{Fe(NO}_3)_3 + 3\text{H}_3\text{AsO}_4 + 4\text{H}_2\text{O} + 14\text{NO} \]

or insoluble ferric arsenate,

\[ 3\text{FeAsS} + 14\text{HNO}_3 + 2\text{H}_2\text{O} = 3\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}_\text{s} + 3\text{H}_2\text{SO}_4 + 14\text{NO} \]

The nitric oxide, NO, can be regenerated to nitric acid by reaction with oxygen and water,

\[ 4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_3 \]
Oxidation of NO by oxygen to NO\textsubscript{2} is very fast, but the exothermic absorption of NO\textsubscript{2} in water to give HNO\textsubscript{3} is much slower. In nitric acid plants, many stages of adsorption are used with interstage cooling of gases and liquids. However two recent refractory gold ore treatment processes have shown that it is possible to carry out the above leaching reactions under conditions where the readesorption of NO\textsubscript{2} into the leach slurry is very rapid, so that the nitric acid is continuously regenerated and effectively acts as an oxidation catalyst, with the primary oxidant being oxygen.

In the Arseno process (28-31), nitric acid attack on the sulphide minerals is carried out at 80-100°C under an oxygen overpressure of 50-100 psi (345-690kPa). Under these conditions, the reactions are extremely fast, with complete decomposition of the sulphides occurring within 15 minutes for batch reactions. On a continuous basis, two stages of leaching with residence times of 15 minutes each are sufficient (32). One of the main design problems in this process is the short time over which the exothermic heat of the decomposition reactions is released. In order to prevent excessive temperature excursions, the leaching autoclaves have to be fitted with extremely efficient cooling systems. Following leaching, the slurry is thickened and filtered to give a gold-bearing leach residue for cyanidation and a leach liquor which contains dissolved iron, sulphur and arsenic. This is sent to a precipitation circuit where it is heated to 100°C and limestone is added to precipitate sulphate as gypsum and to raise the pH to cause the precipitation of ferric arsenate:

\[
2\text{Fe(NO}_3\text{)}_3 + 4\text{H}_2\text{AsO}_4^- + \text{Fe}_2\text{(SO}_4\text{)}_3 + \text{H}_2\text{SO}_4 + 7\text{CaCO}_3(s) = 2\text{FeAsO}_4(s) + \text{Fe}_2\text{O}_3(s) + 4\text{CaSO}_4(s) + 7\text{CO}_2(g) + 3\text{Ca(NO}_3\text{)}_2 + 4\text{H}_2\text{O}
\]

Solid-liquid separation of the slurry from precipitation gives a nitrate solution which is recycled to the head of the leach circuit to conserve the nitrate catalyst, and a precipitate for disposal. For pyrite feeds to the process, the precipitate consists of anhydrite and hematite which can be disposed of with the tailings from cyanidation. With arsenical concentrates it is said that the ferric arsenate precipitates as crystalline scorodite, Fe\textsubscript{3}As\textsubscript{4}.2H\textsubscript{2}O. Normally there is excess iron in solution which coprecipitates as hematite and it is claimed that scorodite in the presence of excess hematite is suitable for dumping without hazard to the environment. The capital and operating costs of an Arseno process plant with a capacity of 250 T/d of concentrate have been estimated at CAN$ 25M for the process plant, with an operating cost of CAN$ 41.5 /T concentrate (32).

The primary oxidant in the Arseno process is pure oxygen and thus a tonnage oxygen plant is a necessary part of the overall investment. In the capital costing quoted above, the turnkey oxygen plant accounted for nearly 30% of the cost of the whole plant. A recently announced, nitric acid-based process which avoids the use, not only of pure oxygen, but also of pressure, is the Nitrox process, developed by Prochem Ltd in Canada (33). A flowsheet of this process, which is designed to treat arsenical and pyritic concentrates, is shown in Figure 3. In principle the process is very similar to the Arseno process, the essential differences being the conditions under which the oxidising leach is carried out.

Concentrate is slurred to 40-50 wt% solids with recycled calcium nitrate solution. The pH of the slurry is then adjusted from about 5 to less
than 1 by recycling about two thirds of the oxidised slurry leaving the Nitrox reactor. Sulphate in the oxidised slurry reacts with the calcium and gypsum is precipitated in the pH adjustment tank, the recycled slurry particles acting as nuclei for precipitation. This helps to prevent unwanted gypsum precipitation on vessel walls and pipelines. The slurry then enters the Nitrox reactor where it is mixed with air in a specially designed agitation system. Oxidation of the pyrite and arsenopyrite occurs in the presence of the nitrate catalyst and the temperature of the slurry rises until there is a thermal balance between the exothermic sulphide oxidation and nitric acid regeneration reactions and the endothermic evaporation of water. The equilibrium temperature is about 85°C. The oxidation reactions occur rapidly, usually within minutes. Off-gases from the oxidation reactor contain approximately 5% NOx, which are scrubbed out with lime slurry before the gases are discharged to atmosphere. The remainder of the process is then similar to the Arseno process, consisting of the addition of limestone to cause precipitation of ferric arsenate, hydrated iron oxides and gypsum. The mixture of leach residue and precipitate is then filtered off and washed, the pH is adjusted with lime and then the solids are cyanided to recover gold. The filtrate which is essentially calcium nitrate solution at pH 5 is recycled to be mixed with incoming feed in the slurry make-up tank. The overall recovery of nitrate is claimed to be better than 99% per pass through the process.

6. THIOUREA

It has been claimed (34,35) that the use of thiourea as a leachant for gold was first reported by Russian workers in 1941. In fact the potential of thiourea for gold dissolution was recognised much earlier by Moir, who in 1906, read a paper to the Chemical, Metallurgical and Mining Society of South Africa entitled, "Thiocarbamide - a new solvent for gold." (36). Moir describes experiments in which he dissolved pieces of gold leaf in thiocarbamide (thiourea) solutions. These experiments enabled him to establish the essential features of the reactions between gold and thiourea. Thus he showed that acid conditions were necessary and that the reaction was very rapid in the presence of suitable oxidants, reporting that dissolution times could be reduced from a few hours in the absence of an oxidant to a few seconds with the addition of ferric chloride, chromic acid or hydrogen peroxide. He recognised that, in contrast to the negatively charged gold cyanide complex ion, the gold thiourea complex was positively charged. He showed that gold metal could be precipitated from thiourea solutions by cementation with zinc or iron metal. Moir also carried out experiments on the recovery of gold from ores, concentrates and tailings with thiourea solutions. He obtained extractions of up to 66% and remarked that the reagent was promising for use in the retreatment of residue dumps. Its main drawback for technical use at the time was cost, which was reported to be 25 shillings per lb. In thanking Dr. Moir for presenting his paper, the President of the Society is quoted in the Proceedings as saying "... we cannot tell what value this new solvent may have, ten, twelve, or perhaps a lesser number of years hence, and the paper may be of the greatest interest apart from its scientific value." History has shown that the President's words were premature. The use of cyanide, which by the time of Moir's experiments was well established as an industrial process for gold extraction, increased its dominating position and became virtually the only
reagent used for gold leaching for at least the next half century. In the Western world, thiourea remained in obscurity until the 1970's when interest was revived in this reagent, culminating in 1982 in Australia when the first commercial gold leaching plant to use thiourea was commissioned (37). In the Eastern block, interest in thiourea began earlier, with laboratory test work being carried out in the 1960's and, it is believed, industrial use beginning in the 1970's.

6.1. Chemistry of thiourea

Unlike cyanide, which is thermodynamically stable over wide ranges of Eh and pH, thiourea has to be used under relatively restricted conditions. It is fairly stable in acid and neutral solutions, but decomposes rapidly in basic solutions. In strong acid solutions, however, thiourea hydrolyses to form urea and hydrogen sulphide:

$$H_2N \cdot CS \cdot NH_2 + H_2O = H_2N \cdot CO \cdot NH_2 + H_2S$$

Gold ore leaching with thiourea is normally carried out in the pH range 1 - 2. In the presence of oxidising agents, thiourea oxidises first to formamidine disulphide. An example of a suitable oxidant is ferric iron:

$$2CS[NH_2]_2 + 2Fe^{3+} = NH_2[NH]CSSCNH_2 + 2H^+ + 2Fe^{2+}$$

The standard reduction potential of the thiourea/formamidine disulphide half-cell is 0.42 volts (38). Formamidine disulphide can then act as an oxidant for gold:

$$2Au^0 + 2CS[NH_2] + NH_2[NH]CSSCNH_2 + 2H^+ = 2Au[CS(NH_2)_2]^+$$

Thus the formation of formamidine disulphide is a necessary precursor for successful gold leaching, but at the same time it provides another route for reagent decomposition, since it is less stable than thiourea and can decompose to cyanide, elemental sulphur and thiourea:

$$NH_2 \quad NH_2$$
$$C \quad S \quad S \quad C$$
$$NH \quad NH_2$$

$$NH_2 \quad NH$$
$$C \quad S^6 \quad C = S$$
$$NH \quad NH_2$$

Among the advantages claimed for thiourea over cyanide in gold leaching are the following (39):

- dissolution rates are ten to twelve times faster than cyanide;
- thiourea is non-toxic;
- consumption of thiourea by base metals is far less than that of cyanide;
- a variety of oxidants can be used to oxidise thiourea to formamidine disulphide including: $Fe^{3+}$, $H_2O_2$, $O_2$, $O_3$, $KMnO_4$ and $NaOCl$. 

Table 1. Details of some recent investigations into thiourea leaching.

<table>
<thead>
<tr>
<th>ORE TYPE</th>
<th>REAGENT LEACHING CONDITIONS</th>
<th>CONSUMPTIONS (kg/T ore)</th>
<th>EXTRATIONS</th>
<th>EXTRACTIONS</th>
<th>ORE TYPE</th>
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<th>CONSUMPTIONS (kg/T ore)</th>
<th>EXTRATIONS</th>
<th>EXTRACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxydeasy clayey gold ore concentrate</td>
<td>Bulk flotation concentrate</td>
<td>11.5 tu 2665 CN 5.8 tu 268 CN 50 tu 8.5 tu</td>
<td>Au %, Ag %</td>
<td>Time(h)</td>
<td>93.5 tu 93.5 %</td>
<td>?</td>
<td>?</td>
<td>1.5-2 tu 70.5% HSO4</td>
<td>95.2 tu 2 0.5M HCN, pH 10</td>
</tr>
<tr>
<td>Auto clave leach residue</td>
<td>Pyrite concentrate</td>
<td>50 tu 6.1 tu 6.1 tu</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>94 tu 40</td>
<td>75 tu 85.4</td>
<td>24</td>
<td>6</td>
</tr>
<tr>
<td>Gossan gold ore</td>
<td>Oxidised Pb/Zn/Fe ore</td>
<td>10.6 tu 315 CN 11 tu 14 ?</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>93 tu 95.2</td>
<td>2 0.5M HCN, pH 1, EMF 200-290 mV</td>
<td>95.2 tu 2 0.5M HCN, pH 1, EMF 200-290 mV</td>
<td>93</td>
</tr>
</tbody>
</table>
Successful use of thiourea requires careful optimisation and control of pH, redox potential, thiourea concentration and leaching time. Details of recent experimental investigations into thiourea leaching, including ore types, leaching conditions, gold extractions and reagent consumptions, are collected in Table 1. Also shown, where available, are gold extractions obtained by conventional cyanide leaching. It is evident that gold extractions with thiourea at least match, and in some cases exceed, those achievable with cyanide.

As indicated in Table 1, Schulze (45,46) has used SO2 in combination with thiourea. It is claimed that addition of SO2 during thiourea leaching avoids passivation of the precious metals and prevents chemical degradation of the reagent, resulting in low consumptions of thiourea. It is further claimed that maximum leaching rates are obtained when half the initial thiourea is converted to formamidine disulphide, although little evidence is presented to substantiate this assertion (45). The use of SO2 has been re-examined recently (47) in a detailed study into the application of thiourea leaching to a typical South African gold/uranium ore from the Witwatersrand. It was found that under optimised conditions, gold extractions approaching those obtained by cyanide leaching in 18 hours could be obtained with thiourea in 6 hours, with thiourea consumptions in the region of 1 kg/T ore. Control of solution redox potential was found to be important to prevent excessive degradation of thiourea, the optimum region being 200 - 250 mV (vs SCE). It was further found that addition of sulphur dioxide did not give any savings in thiourea consumption and gold extraction was not improved. An interesting part of this investigation was a simulated heap leach of gold ore with thiourea, where it was shown that its performance in terms of gold extraction over 25 days was similar to that achieved by heap leaching with cyanide.

6.2. Commercial Developments.

The first gold leaching plant to use thiourea in the Western world is located at the New England Antimony Mines (NEAM) in northern New South Wales, Australia (37). The gold-bearing mineralisation consists primarily of stibnite (Sb2S3) with associated pyrite/pyrrhotite and arsenopyrite. The current ore grade averages 4.5% Sb and 9 g Au/T. This is put through a gravity circuit to recover free gold, followed by flotation to give a stibnite concentrate grading 68% Sb and 30 - 40 g Au/T. This concentrate is treated for gold recovery in a thiourea leach plant which was commissioned in March, 1982. A flowsheet of the plant is shown in Figure 4. The plant is run as a batch operation with a capacity of about 8T concentrate per 8 hour shift. Leaching time is less than fifteen minutes and the critical operating parameters are pH, redox potential and thiourea concentration. Dissolved gold is recovered from the leach solution by adsorption on activated carbon. Desorption is not practiced; instead a carbon concentrate is sold, containing 6 - 8 kg/T Au. Following gold adsorption, the barren thiourea solution is recycled after Eh adjustment with hydrogen peroxide. Overall gold recoveries range between 50 and 80%, depending on the gold liberation in the antimony concentrate.

The second commercial thiourea plant is likely to be at the Jamestown
mine in northern California (48). This mine, which has reserves of 30M T with an average grade of 2.1g Au/T, is due to start production in the first quarter of 1987. Initial production will be 6000 T ore per day. Gold will be recovered into a flotation concentrate which will contain about 55g Au/T and 40g Ag/T. The concentrate will be leached with thiourea and a gold extraction of 87% is expected. Recovery of gold from solution will be by cementation with aluminium dust. The reason for using thiourea rather than cyanide at Jamestown is primarily environmental, since the ore responds at least as well to cyanide leaching. California's strict environmental laws make the obtaining of permits for cyanide leaching so time consuming and expensive that the balance is swung in favour of thiourea, in spite of the anticipated slightly higher operating costs. However, before final decisions are made it is intended that a thiourea pilot plant will be operated using fresh concentrate from the mine. The projected cost of the mine and mill at Jamestown, including the thiourea leaching system is $45.6M, with an operating cost of $184/oz gold. The leach plant itself will cost about $2M.

7. DISCUSSION

The various processes discussed above can be classified in two groups; (i) those involving extensive oxidation of sulphide minerals, namely, biooxidation, pressure oxidation and the nitric acid processes; and (ii) those where there is little or no attack of the sulphides, i.e. pressure cyanidation and thiourea leaching. For either of the latter two processes to be successful, gold in the refractory ore must be physically accessible to the leaching solutions. This implies that the refractoriness of the ore is likely to be due to the presence of either oxygen-scavenging elements, such as arsenic or antimony, or cyanides, such as copper or lead minerals.

Pressure cyanidation increases the solubility of oxygen in cyanide solutions and thus is likely to be most successful with oxygen-consuming ores. Fine grinding is often necessary to achieve access to the gold. Fast rates of reaction can be achieved with suitable ores and in order to prevent cyanide diffusion becoming rate limiting, higher cyanide concentrations may be required, compared with conventional cyanide leaching. In spite of the higher concentrations, cyanide consumptions can be kept at low levels by leaching at ambient temperature and minimising reaction times, since loss of cyanide by hydrolysis and oxidation is relatively slow.

Thiourea should also be a suitable leachant for ores with high oxygen consumptions, since condensed phase oxidants can be used for gold dissolution, which can be supplied in much greater concentrations than dissolved oxygen. However since thiourea itself is susceptible to decomposition by oxidation, careful control of Eh, pH and concentration is required to prevent excessive losses. With many ores, providing the gold is accessible, gold extractions at least as good as with cyanide can be achieved, with the advantages that thiourea is non-toxic and its rates of leaching are very much faster than cyanide. Thiourea also shows to advantage over cyanide for ores containing copper and lead, since its complexes with these metals are weaker than cyanide and hence its gold leaching capability is less affected. The main disadvantages of thiourea are that its chemistry is less straightforward than cyanide and, to date, there is very little available experience in its use on an industrial scale.

With many sulphidic refractory gold ores, however, an oxidative
pretreatment to disrupt the sulphide crystal lattice and to release the gold is a necessary precursor for successful gold leaching. The Sherritt Gordon approach to this problem, namely pressure oxidation using high temperatures, high oxygen overpressures and relatively long residence times of one hour or more, is the most drastic solution. These conditions assure total oxidation of any sulphidic or arsenical components in the ore, and Sherritt Gordon have shown that the method is applicable to many different types of ores and concentrates, with very high gold extractions achieved in most cases by cyanide leaching of the oxidised residues. The price to be paid for this success is the capital and operating costs of the pressurised process plant which is comprised of large acid resistant autoclaves and associated support equipment such as heat exchangers, flash tanks and pressure pumps.

In the Arseno process, total oxidation of the ore is achieved at lower reaction temperatures and total pressures by the use of nitric acid as a catalyst to improve the effective reactivity of oxygen. Very fast reaction rates can be obtained, 15 minutes or less on a batch basis, and the nitric acid is recycled within the process as a nitrate salt. Low losses of nitrate are claimed, although some production of inert nitrous oxide $\text{N}_2\text{O}$ is highly likely. The very fast reaction rates lead to low reactor volume requirements, but on the other hand, the large heat flux caused by the rapid exothermic reactions mean that very effective cooling systems are necessary for the autoclaves in order to control the process.

The primary oxidant in both the Sherritt Gordon and the Arseno process is pure oxygen. Thus the capital investment required for either process includes the cost of a tonnage oxygen plant. This is a major item of expenditure which can account for more than half the total investment cost. In the cost estimates made for the application of pressure oxidation to the Porgera deposit in Papua New Guinea, the oxygen plant accounted for two thirds of the capital cost of the leaching plant and for 80% of the operating costs of the process (5). The traditional method of treating sulphidic and arsenical ores is by roasting, which of course utilise the cheapest oxidant available, namely air. Two of the processes discussed in this paper are also designed to use air, while avoiding the atmospheric pollution problems associated with roasting processes.

The Nitrox process is very similar in principle to the Arseno process with the important difference that air at atmospheric pressure is used as the primary oxidant. This is achieved by the use of a highly efficient proprietary gas-liquid-solid mixing system. The process, which involves recycle of up to two thirds of the oxidised slurry back into the oxidation reactor to control gypsum precipitation will require larger reactors than the Arseno process for a given throughput, but the compensating factor is that the Nitrox reactors are not pressurised. Temperature control is also much easier as heat generated by the oxidation reactions is balanced by evaporation of water during oxidation. This evaporation also aids the water balance in the process circuit. Reported results (33) indicate that the process works very well, but as yet it has only been run at laboratory or small pilot scale. The key question is whether the proprietary mixing system can be successfully scaled-up to industrial scale. If this can be achieved, the Nitrox process should be a technically attractive method for treatment of suitable refractory gold ores.
Biooxidation also uses air as the primary oxidant for sulphidic gold ores. The catalytic effect of the bacteria is, however, very much slower than that of nitric acid. Residence times of days and low pulp densities are required and thus large reaction tanks are necessary. Power consumption for agitation and air dispersion will be significant. A recently published cost study comparing pressure oxidation with biooxidation for sulphidic concentrates indicated that the capital costs of the two processes would be quite similar, but that the operating costs of biooxidation would be significantly lower (49).

8. REFERENCES

38. Preisler, P.W. and Bergler, L. Oxidation-reduction potentia
Figure 1. The McLaughlin pressure oxidation process
Figure 2  Bioleaching pilot plant at Equity Silver Mines.
_solution to gold recovery

**Figure 3** The Nitrox Process
Figure 4. New England Antimony Mines thiourea process.