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CHALLENGES AND OPPORTUNTIES IN THE TREATMENT OF REFRACTORY GOLD ORES

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ABSTRACT

The introduction of pressure and biological oxidation as well as some innovations to roasting starting in the mid 1980's has revolutionized the way that refractory gold ores are treated. These technologies allowed previously uneconomical gold deposits to be processed. This paper provides a high level overview of the flowsheets and chemistry used in each of the technologies. A breakdown of where and who are currently using the different technologies is also provided. Finally some discussion is presented on what the future may hold in respect of challenges and opportunities.

INTRODUCTION

ALTA 2012 Free Paper There are numerous classifications and definitions of gold ores to be found in the literature. Unfortunately there are many factors that influence the recovery of gold and therefore a universal and simple classification based on ore characteristics has been difficult⁽¹⁾. A classification that has won wide acceptance is one propose by La Brooy⁽²⁾ In this classification 'free milling' gold ore is defined as yielding over 90% recovery under conventional cyanide leaching conditions. For those ores that give acceptable economic gold recovery only with the use of significantly higher chemical additions (e.g. cyanide, oxygen, carbon) are defined as 'complex ores'. Refractory ores are thus defined, by exception, as those that still give inadequate gold recovery⁽¹⁾⁽²⁾. It is implicit in this definition that additional recovery requires some degree of pre-treatment prior to cyanidation⁽¹⁾. The major focus in refractory gold processing has been on gold-bearing iron sulfides, such as pyrite, arsenopyrite, arsenian pyrite as well as the telluride and the stibnite family.

> The economics of refractory gold treatment dictate a higher gold content in the feed or higher gold price or both compared to the 'break even' economics for free gold treatment. This is a result of the higher capital and operating cost associated with refractory gold processing. Another driver from an operating perspective is the cost and availability of utilities (electricity and water) as refractory gold treatment has a greater demand for both. Reagent consumptions and unit costs for acid neutralization and cyanide consumption play a major part of operating costs as do maintenance costs given the extreme operating conditions. Downtime for major equipment repairs is also an important consideration

> Prior to 1986 most refractory gold ores were treated by the roasting technology⁽³⁾. The introduction of pressure and biological oxidation processes for the pretreatment of refractory gold ores commenced in 1986 and since that time there has been a tremendous increase in the application of these technologies⁽⁴⁾. Conversely there has been a considerable decrease in the use of roasting technology to treat refractory gold ores. This has mainly been due to more stringent air pollution regulations worldwide. Not to say that water quality for the biooxidation and pressure oxidation processes is less stringent however it is easier to manage

> The gold price trend for the last 30 years is provided in Figure 1 and it shows the rapid increase in the gold price since 2007. Unfortunately the operating costs have escalated along similar lines as seen in Table 1. Escalation has been more dramatic in the last couple of years and has outpaced the gold price on a percentage basis. Notwithstanding this there has been an 11% (extra 322 tonnes of gold) increase in the world gold production since 2004 as shown in Table 2. The main contributors to this increase are China (91 tonnes), Russia (43 tonnes), Mexico (43 tonnes) incremental small tonnages from the rest of the world (172 tonnes). In terms of gold resources in China, the present refractory gold mineral resource accounts for about two-thirds of the gold reserves⁽⁵⁾⁽⁶⁾. The treatment of refractory ore in Russian and related countries has also increased in the last ten years.

> In China there are more than 1200 gold mines and about 700 of them have a capacity of only 50t/d or less⁽⁵⁾⁽⁶⁾. Most small mines produce a concentrate only and this is sold or toll treated. The preferred technology for the treatment of concentrates is biooxidation followed by cyanide leaching and then zinc cementation $^{(5)(6)}$.

MINERALOGY-GOLD DEPORTMENT FOR REFRACTORY GOLD ORES

Most of the very refractory gold ores contain what is sometimes referred to as 'invisible gold' that is either present as extremely fine particles (less than 5 µm) or it is actually incorporated into the structure of minerals such as arsenopyrite, arsenian pyrite and pyrite⁽⁷⁾⁽⁸⁾. The reason is that the gold is in the form of a solid-solution or at a colloidal size. Solid-solution gold refers to gold that is atomically distributed in the crystal structure of sulfide minerals.

Other refractory ores contain naturally occurring 'active' carbon. The gold in the ore may be adequately exposed to the cyanide leach solution and dissolution proceeds to completion however adsorption of the gold onto the carbon leads to low overall gold recovery. This phenomenon is generally known as 'preg-robbing⁽⁷⁾⁽⁹⁾.



Figure 1: Gold Price 1973 to 2012

Table 1: Gold Production Costs (weighted average US\$/oz.)

	1985		1996		2001		2005		2011	
Country	Cash	Total								
Australia	195	240	294	358	179	226	264	326	742	913
South Africa	147	189	293	334	196	214	354	395	904	1085
Canada	218	271	222	282	176	235	196	275	572*	746*
United States	219	302	237	300	189	257	250	314	572*	746
Other	NA	NA	216	296	153	219	198	263	530	624
Total	NA	NA	262	317	176	228	252	323	643	809

(* combined production for Canada and USA)

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Table 2: World Gold Production by Country (metric tons of gold)

	YEAR									
Country	1996	2000	2004	2005	2006	2007	2008	2009	2010	2011
China	159	172	217	224	247	281	292	324	351	371
Australia	290	296	258	263	247	247	215	224	261	258
United States	329	355	260	262	222	238	234	221	230	233
Russia	133	154	182	176	173	169	189	205	203	212
South Africa	495	428	343	296	296	270	234	220	203	198
Peru	65	133	173	218	214	184	196	201	185	188
Indonesia	93	140	114	167	114	150	96	161	140	111
Canada	165	155	129	119	104	102	95	96	104	108
Ghana	50	74	58	63	70	77	80	90	92	91
Mexico	25	26	22	31	39	44	51	62	79	87
Uzbekstan	78	88	84	79	74	73	72	71	71	71
Brazil	64	53	43	45	49	58	59	64	68	68
Papua New Guinea	54	76	75	69	62	62	70	71	70	62
Argentina	1	26	28	28	43	43	40	49	64	59
Tanzania	6	17	48	49	45	40	36	41	45	50
Mali	7	30	40	47	57	52	47	49	45	46
Chile	56	50	40	40	40	42	39	41	38	45
Philipines	32	35	32	32	36	39	36	37	41	37
Columbia	23	21	24	25	26	26	26	27	34	37
Kazahstan	4	22	15	19	22	23	22	23	30	37
Rest of the world	249	239	288	271	316	279	301	335	388	451
Total	2375	2591	2470	2519	2495	2497	2429	2611	2741	2818

There are at least twenty gold compounds found in nature in which the gold is combined with tellurium, antimony, bismuth, copper, selenium, or lead and ores with these compounds can be refractory⁽⁷⁾. These compounds are not very common, although tellurides are a problem in some deposits.

Ores from some important gold producing areas around the world are 'double-refractory', meaning that more than one mechanism is at work to reduce gold extraction. The most common reason for the double-refractory problem is the occurrence of most the gold in solid-solution associated with arsenian pyrite, arsenopyrite and pyrite or all of these and also the presence of a preg-robbing carbonaceous material in the same ore⁽¹⁾⁽³⁾⁽⁷⁾.

Gangue mineralization, especially clays and carbonate minerals, is also an important consideration when dealing with refractory gold ores. The type and quantity of clay minerals (e.g. montmorillonite, kaolinite, pyrophillite, illite) are extremely important as the presence of these minerals will impact slurry viscosity leading to lower oxygen transfer during the oxidation of the sulphide minerals. Flotation performance is as a rule impacted by the presence of clay minerals resulting in lower concentrate grades. This implies more feed to the oxidation process and hence more refractory treatment volume.

It is vitally important that the occurrence and deportment of gold be fully understood for a new refractory gold deposit⁽¹⁾. Following this the quantity and type(s) of sulfide mineralization are important as is the presence of preg-robbing carbon. The efficiency of concentrating the gold bearing minerals into a flotation concentrate is the next step in the evaluation⁽¹⁾. Biooxidation plants all incorporate flotation to reduce the volume of material being oxidized. Similarly for high arsenic bearing ores flotation is employed to produce the feed to a 2-stage roasting process. Should flotation performance be poor then a number of treatment options can be eliminated. Another important parameter is the gold to sulfur ratio, if this is too low then the economics of treating the material by pressure leaching is questionable. On a similar note if the iron (in sulfides) to arsenic ratio is too low then the formation of stable ferric arsenate in the treatment process will be a problem

REFRACTORY GOLD TREATMENT PROCESSES

The treatment of refractory gold ores requires the oxidation of the sulphide minerals that contain the gold. For the roasting process the removal of the sulfur as sulfur dioxide generates a porous matrix in the residual solid thereby exposing the gold and allowing access to cyanide solution for gold leaching the gold. During pressure leaching and biooxidation the sulfide minerals are oxidised and solubilized in an aqueous acidic medium. In essence the process dissolves the matrix that encapsulates the gold and exposes/liberates the gold prior to the cyanide leaching step. Roasting can also destroy preg-robbing carbon especially in an oxygen-enriched environment⁽¹⁾⁽³⁾⁽⁹⁾.

Roasting Process

Roasting as a pretreatment process for refractory gold flotation concentrates has been practiced for more than a 100 years⁽³⁾. Up until 25 years ago, roasting was the standard process option for pretreating a refractory gold flotation concentrate. As environmental restrictions increased and alternative processes became available its application has decreased significantly. However, new roasting technologies, and several new whole ore roasting installations, developed in the 1990s have improved the flexibility of roasting to treat some refractory gold ores⁽³⁾⁽¹⁰⁾⁽¹¹⁾⁽¹²⁾⁽¹³⁾⁽¹⁴⁾. A list of operating roasters is shown in Table 3. Presently there are 9 known operations worldwide using roasting. Total plant capacity is around 22,000t/d and whole ore roasting accounts for 91% of this capacity.

The early days of gold roasting were characterized by the use of bubbling fluidized bed (BFD) roasters treating flotation concentrate. A major disadvantage of this type of roaster is the temperature differential between roaster bottom and top^{(10).} This was finally eliminated with the introduction of circulating fluidized bed (CFD) technology in the 1990s. Gold ores are rather sensitive to temperature and for maximum gold recovery, roasting must be carried out over a small temperature range. For high throughputs the CFB has a big advantage compared to BFB in controlling the roasting temperature. The first CFB roaster for refractory gold treatment was the Gidgi roaster, Kalgoorlie, Western Australia and this roaster was commissioned in 1991⁽¹⁵⁾. Operating temperature for roasters are performed in the range of 450-700°C

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0124	< ⁰	Та	ble 3: Gold Ro	asting Plants Are	ound the World		
ALAL	Company	Country	Owner	Roaster Type*	Feed Material	Total Capacity (mt/d)	Start-up Date
Ÿ	Gidji/W.A. KCGI	Australia	Barrick/Ne wmont	1 x CFB	Concentrate (Te)	1,150	1987
	Kanowna Belle	Australia	Barrick/Ne wmont	2 x CFB	Concentrate (As)		1994
	Carlin	USA	Newmont	2 x CFB	Whole Ore	7,680	1994
	Tongling	China		BFB	Concentrate	150	1997
	Goldstrike	USA	Barrick/Ne wmont	2 x CFB	Whole Ore	11,600	2000
	Dongfang	China	Dongfang smelting	BFB	Concentrate (As)	200	2004
	Syama	Mali	Resolute Gold	1 x CFB	Concentrate	590	200
	Tanjiansha	China	Eldorado Gold	BFB	Concentrate (As)		2008
	Tongguan	China	Tongguan	BFB	Concentrate (As)	200	2010

Table 3: Gold Roasting Plants Around the World

ubbling fluidized bed; CFB=circulating fluidized bed)

When treating a flotation concentrate with a high content of arsenic the preferred roasting option is a two-stage BFD roaster⁽³⁾⁽⁴⁾⁽¹⁰⁾. In the first roaster (stage 1) the conditions are 'reducing' to optimize the removal of 90-99% of the contained arsenic. This is sometimes referred as a 'partial roast' as only a portion of the contained sulfides is oxidized. During the second stage all the remaining sulfides are oxidized.

The chemical and mineralogical changes affecting common sulfide minerals during the roasting process are well understood. Pyrite progressively loses sulfur to form pyrrhotite and then magnetite and finally a porous hematite (referred to as calcine). Sulfur associated with the pyrite and pyrrhotite is oxidized to sulfur dioxide.

The sulfur dioxide exiting from the roaster can be release to atmosphere⁽¹⁵⁾, converted to sulfuric acid⁽¹⁶⁾ or treated with an alkali to generate calcium sulphate⁽³⁾. Sulfuric acid production may be practical for flotation concentrates and for whole ore roasting using oxygen enrichment. In some ores containing natural or added limestone or dolomite, sulfur dioxide will react with these minerals forming a stable compound that be incorporated in the calcine. Scrubbing the roaster off-gases with alkaline solutions or slurries is practiced by some companies⁽³⁾.

Under oxidizing conditions arsenic in arsenopyrite is oxidized to arsenic pentoxide which is not volatile⁽³⁾⁽⁴⁾. Arsenic pentoxide combines with iron oxide to give iron arsenites and arsenates. These present problems because they give low porosity calcines and produce arsenic that is soluble in the cyanide circuit. Under reducing conditions arsenic from arsenopyrite is oxidized to volatile arsenic trioxide which leaves the roaster in the off-gas (stage 1) thus eliminating arsenic as a problem in the gold recovery step. However the reducing conditions are not conducive to the total elimination of the sulfides and another step of oxidation (stage 2) is required to do this. This chemistry led to the two stage roasting process for treating flotation concentrates having large amounts of arsenopyrite. The arsenic trioxide can be condensed by cooling the gas and collecting the solid product in a baghouse or electrostatic precipitator. The main issue is the disposal of the arsenic product as in today's world it cannot be sold. The best solution is to convert it to a stable ferric arsenate before disposal to the final tailings facility or storage elsewhere (underground).

Roasting can eliminate natural occurring preg-robbing carbon present in the roaster feed by oxidizing (burning) it. However there are instances where roasting has been known to 'active' what was otherwise inactive carbon. For instance when coal is added to increase the roaster temperature

Roaster off-gasses will contain suspended solids, the products of combustion and oxidation, and any volatile species present in the roaster feed. Solids can be removed using hot cyclones, scrubbers, and electrostatic precipitators⁽³⁾⁽⁴⁾⁽¹⁰⁾. Removal of noxious components (carbon dioxide and nitrous oxide) requires a separate gas cleaning train⁽³⁾.

Any mercury in the feed to a roaster will be volatilized and report to the roaster off-gas. This can be adsorbed onto sulfur impregnated activated carbon. Another technique available is the Outotec sulfidizing process which uses concentrated sulfuric acid as a gas scrubbing medium for both mercury and selenium removal⁽³⁾⁽⁴⁾.

Freeport McMoRan developed a two-stage 'whole' ore roasting process using oxygen as a fluidizing gas⁽¹³⁾. The first whole ore roaster using oxygen injection was built in 1989 at Jerritt Canyon, USA. The process has significant advantages⁽³⁾⁽¹³⁾. The use of oxygen dramatically reduces the heat losses present in the exit gases. Also expensive to maintain 'intensive' heat and recovery systems were not required⁽¹³⁾. The use of pure oxygen provides for good sulfur and preg-robbing carbon oxidisation at very low temperatures that are not realized in traditional roasting with air only. Another improvement to the whole-ore roasting process is the use of dry grinding of the feed⁽³⁾ to minimize the heat loss associated with water removal as steam. This also allows lower sulfide sulfur ores to be treated by roasting.

Pressure Oxidation Process

The purpose of the pressure oxidation (POX) process is to oxidise, with pure oxygen, the gold bearing sulfides at relatively high temperatures and pressures. The first commercial POX plant for refractory gold treatment was built at the McLaughlin Gold Mine, USA in 1986⁽¹⁷⁾. Presently there are 8 gold treatment plants that use pressure oxidation to treat refractory gold ores. The location and treatment capacity for each of these operations is shown in Table 4. The total daily treatment capacity is around 35,000t/d.

Plant	Company	Location	Feed	Capacity (t/d)	Temperatur	Start-up
Goldstrike	Barrick	USA	Ore	15,000	225	1990
Campbell	Placer Dome	Canada	Concentrate	71	190	1990
Porgera	Barrick	PNG	Concentrate	1,350	190	1991
Lihir	Newcrest	PNG	Ore/Concentrate	9,000	210	1994
Twin Creeks	Newmont	USA	Ore	7,260	225	1996
Macraes	OceanaGold	New Zealand	Concentrate	20	225	1999
Killita	Agnico-Eagle	Finland	Concentrate		190	2008
Amursk	Polymel	Russia	Concentrate		190	2010?

Table 4: Gold Pressure Leach Plants Around the World

In a typical pressure oxidation plant, ore or flotation concentrate is continuously processed through an autoclave at temperatures that range from 180 to 225° C and pressures between 1600 to 3000 kPa⁽⁴⁾. Residence time is commonly in the range of 45 to 200 minutes⁽⁴⁾.

The pressure vessel commonly used for pressure oxidation is the horizontal multi-component autoclave⁽⁴⁾⁽¹⁷⁾. Vessels are usually lined with lead (not a preferred option today), organic membranes and brick to protect the steel shell from corrosion and erosion. The most difficult areas to protect are the nozzles which allow the agitators and various pipes to enter the vessel

Pressure oxidation is generally conducted under acidic conditions. It is therefore essential to ensure that the first compartment of the autoclave is acidic. For some ores or flotation concentrates this is not a problem, however some ores and concentrates contain appreciable amounts of carbonate minerals (calcite or dolomite). In such cases acid addition to the feed will ensure appropriate autoclave performance. Another problem with carbonate minerals is the generation of carbon dioxide in the autoclave. This accumulates in the autoclave vapour space thereby reducing the oxygen partial pressure in the vessel. Controlled venting of the accumulation inert gases is a normal practice in autoclave operation. However the frequency increases when carbonate dioxide is generated removing oxygen which reduces oxygen utilisation.

Ores containing more than 5% sulfide sulfur can usually be processed autothermally in the autoclave⁽⁴⁾⁽¹⁸⁾. If the ore contains less than 4% sulfide it is usually economical to preheat the feed using steam flashed off during the release of pressure from the autoclave discharge or generating extra steam. Regardless of sulfur levels the discharge from the autoclave is eventually 'flashed/let down' to atmospheric pressure and at a temperature below a 100°C. There are occasions where preferential oxidation of particular sulfides in the feed (arsenian pyrite, arsenopyrite), rather than oxidizing all the sulphide minerals, will lead to high gold recover in the gold leaching circuit⁽¹⁹⁾. This approach was employed to treat gold ores at the Lone Tree mine in Nevada, USA. The autoclave was designed to operate at a low temperature (180°C) and pressure (1600 kPa)⁽²⁰⁾.

capital and operating costs saving were realised from this circuit configuration.

ALTA 2012 Free Paper Autoclave discharge contains excess acid and iron sulfates in solution. If acid recycle is practiced much of these species are recycled to the acidification circuit ahead of the autoclave to neutralize the incoming carbonates⁽²¹⁾. In other plants a neutralising agent is required to neutralize the stream before pumping it to the cyanide leach circuit.

> The chemistry of the elevated temperature acidic oxidation of pyrite and arsenopyrite in aqueous medium involves the oxidation of the divalent iron and trivalent arsenic to their respective ferric and arsenate states⁽²²⁾. The major reaction however is the conversion of sulfidic sulphur to sulphate. Under mildly oxidizing conditions (100-160°C) and in the presence of relatively large amounts of sulfuric acid and ferric sulphate, elemental sulfur may form as the preferred or as an intermediate product of the oxidation of arsenopyrite. The formation of elemental sulfur is undesirable for a number of reasons including occlusion of unreactive sulfides, hindering or preventing complete oxidation, occlusion of gold particles, hindering or preventing extraction during cyanidation, increased cyanide and air/oxygen consumption during the cyanide process

> Sufficient oxygen must be added to the autoclaves for oxidation of the contained sulfides. If too little oxygen is added, oxidation kinetics are slowed and oxidation is incomplete, resulting in reduced gold recovery⁽⁴⁾⁽¹⁸⁾. If too much oxygen is added, heat is lost from the autoclaves through venting of excess oxygen and steam, and through cooling by excess cold oxygen entering the autoclave. Oxygen is a high cost consumable and every effort is made to maximize utilization of oxygen by operating as close to the stoichiometric limit without impacting on the sulfide oxidation kinetics. Oxidation is therefore conducted at temperatures in excess of 160°C to promote complete oxidation of the sulfides to sulfate. Under the appropriate oxidation conditions a significant portion of the iron and arsenic is precipitated as ferric arsenate⁽²²⁾. Some of the ferric sulfate can be hydrolysed and precipitated as hematite, as a basic ferric sulfate or as a hydronium jarosite. In the presence of potassium and sodium ions released by the dissolution of gangue minerals, hydrolysis of at least a portion of the ferric sulfate to the corresponding jarosite occurs. A number of other metals such as silver, mercury and lead are also precipitated as jarosites either through substitution of the potassium, sodium or hydronium ions or through formation of solid solutions in the jarosite that is precipitated⁽²²⁾.

Bacterial Oxidation Process

Bacterial oxidation has been at work for many centuries and has very efficiently converted millions of tons of refractory ore to a form that requires cyanide leaching only to recover the gold. The oxide caps overlying the many refractory ores have all been created by bacterial action. The biooxidation process for the treatment of refractory gold ores and concentrates was commercialized in 1986 with the successful application of the biooxidation technology (BIOX[®]) at the Fairview Gold Mine in South Africa⁽²³⁾⁽²⁴⁾. The biooxidation process has been shown to be robust and currently there are 19 plants in operations around the world as shown in Table 5. Total concentrate treatment capacity for these plants is around 7500t/d.

The biooxidation process utilises a mixed population of bacteria to oxidise the sulfide mineral matrix at temperatures around 40-50°C. A typical biological oxidation plant for flotation concentrate treatment consists of agitated tank reactors, air delivery into the reactors, cooling of the reactor solution, counter current decantation washing and effluent neutralization⁽²⁸⁾.

The basic chemistry of the biooxidation process is similar to that for pressure oxidation however there are a number of important differences⁽⁴⁾. The bacteria both catalyze and directly take part in the oxidation reactions. Bacteria being a living organism then both a stable temperature and appropriate food source (carbon and nutrients including phosphate, nitrogen, potassium trace elements) are important for the growth and survival of the bacteria. The operating temperature depends on the bacterial culture being employed⁽⁵⁾⁽²⁵⁾⁽²⁶⁾⁽²⁷⁾. An important factor in reactor design is to allow for the bacterial population to double in the first stage, thus preventing bacterial washout.

For arsenical flotation concentrates the iron, sulfur and arsenic are solubilized during biological oxidation to ferric sulfate, sulfuric acid and arsenic acid. The acidic solution exiting the bacterial reactors flows to a CCD circuit and the overflow solution is then sent to neutralization. In general the acidic arsenic liquors arising from bioxidation have high ferric iron to arsenic ratios. Two stage neutralization (around pH 4 and then to around pH 8⁽⁴⁾⁽²⁸⁾) results in the formation of a stable precipitates of ferric arsenate

A large quantity of air must be introduced into the biological reactor to ensure satisfactory oxidation rates⁽²⁸⁾. Many oxidation plants grind the flotation concentrate to enhance leach kinetics. The heat released during the oxidation process is significant. So it is important that this be dispersed efficiently since the bacteria do not function effectively outside their operating temperature range. The heat is collected by internal cooling coils inserted in the biooxidation reactors and the heat is then dispersed to the atmosphere through cooling towers⁽⁴⁾⁽²⁸⁾.

The key areas that have the most significant impact on capital costs are throughput, biooxidation residence time, air delivery system (blower), agitators for the dispersion of air and suspension of solids and, reactor design (materials of construction). The residence time for concentrate treatment is typically four to six days, with the longer residence time caused by high sulfide content, coarse particle size of the concentrate or bacterial inhibitors in the ore or liquor^{(4) (28)}.

Mine	Owner	Technology	Location	Capacity(t/d)	tal Reactor (m	Sart-up
Fairview	Pan African R	BIOX®	South Africa	55	1260	1986
Wiluna	una Apex Minerals		Australia	158	4230	1993
Ashanti	AngloAshani	BIOX®	Ghana	960	21,600	1994
			Yantai,			
Yantai Gold		CCGRI	Shandong	50+80	5000	2000
Beaconsfield	BCD Resourc	BACOX	Australia	70	2241	2000
Laizhou	Tarzan BioGo	BACOX	China	200	8100	2001
Olympiada	Polyus	BIONORD®	Russia	1000	33000	2001
			Fengcheng,			
Tianli		CCGRI	Liaoning	100	3800	2003
			Yining,			
Axi		JLMRI	Xinjiang	50+80	5600	2004
Fosterville	Crocodile Gol	BIOX®	Australia	211		2005
	South					
	Verhoyansk					
	Mining					
Suzdal	Company	BIOX®	Kazakhstan	520		2005
Sanhe		CCGRI	Dexing, Jiangxi	70	2400	2006
Bogoso	Star Resource	BIOX®	Ghana	820	21,000	2007
Jinfeng	Elderado Golo	BIOX®	China	790	16,000	2007
Innovation		CCGRI	China	150	3800	2007
			Zhaoyuan,			
Jinchiling		CCGRI	Shandong	100	4200	2007
	Novi Mining					
	and					
	Metallurgical					
Kokpatas	Combinat	BIOX®	Uzbekistan	1069+1069	43,200	2009
Agnes	Galaxy Gold	BIOX®	South Africa	20		2010

Table 5: Biooxidation Plants Around the World

Pulp density has a major impact on tankage requirements, with a 40% increase in volume between the typical densities of 15% and 20% w/w solids proposed by the technology providers. An important consideration in the design of the biooxidation reactors is the impact on oxygen transfer efficiency at higher pulp densities, although at 20% solids, high efficiencies are still obtained⁽²⁸⁾.

BIOX® Process

The biooxidation process for the treatment of refractory gold ores was pioneered by Gencor and the technology known as BIOX® is now marketed by Gold Fields Ltd⁽²⁵⁾⁽²⁹⁾. The first biooxidation process for the treatment of refractory gold flotation concentrates was commercialized in 1986 with the successful application of the technology at the Fairview Gold Mine in South Africa⁽²³⁾⁽²⁴⁾. The BIOX® biooxidation process has been proven to be robust and has since grown to 9 of the 19 currently operating biooxidation plants.

The BIOX process has undergone significant improvement over the last 25 years⁽³⁰⁾⁽³¹⁾ that has led to improvements in flowsheet design and lower operating cost. Agitator design has been improved to lower power demand. Increasing washing capacity (CCD circuit) ahead of neutralization and decreasing the amount of sulphur/polysulphides (oxidizing these to sulfate) ahead of cyanidation has led to significantly reductions in cyanide consumption⁽³⁰⁾. By implementing these and some other changes it is claimed that a 10% reduction in operating cost can be realized⁽³⁰⁾.

BACOX Process

The first operation to use the BACOX process commercially was the Youanmi mine in Western Australia in 1994⁽²⁶⁾⁽³²⁾. BACOX technology was then incorporated into the sulphide treatment plant at the Beaconsfield Gold Mine in Tasmania in 1998⁽³³⁾. The bacterial oxidation circuit installed at Beaconsfield uses the Mintek-Bactech technology. The bacteria are a combination of mesophilic iron and sulfur oxidizing cultures.

The Laizhou Gol Metallurgy Plant (renamed to 'Tarzan Bigold') of Shandong Province, China, also uses the BACOX technology⁽³⁴⁾. Interestingly the primary focus was to operate the plant as a toll treatment facility. Commissioned occurred in 2001⁽⁵⁾⁽³⁴⁾.

REBgold Corp, a Canadian gold mining development company now markets the BAXOX technology.

Changchun Gold Research Institute (CCGRI) Process

Changchun Gold Research Institute (CCGRI) provides the process technology support for many biooxidation plants in China⁽⁵⁰⁾. The microorganism cultures used by CCGRI were originally isolated from hot water springs and mines in south China. After years of culture development in special environments, there are cultures that now form a series of products including ones suitable for high arsenic or high organic carbon in flotation concentrates. All of the CCGRI cultures are termed moderate thermophiles. Archaea Ferro plasma acidophilus is the key member in the cultures. The members of bacteria are quite different for the different applications⁽⁵⁾.

BIONORD® Process

The Olympiada Mining Combine, Russian Federation, developed and uses the BIONORD® technology⁽²⁷⁾. The process was developed to accommodate the harsh extremely cold climatic conditions found at the Olympiada mine in the Krasnoyarsk Region of Russia.

COUNTER CURRENT WASHING, NEUTRALISATION AND CARBON-IN-PULP

Counter Current Decantation Washing Circuit

For both pressure oxidation and biooxidation plants that process flotation concentrate the treatment of the oxidised product (oxidized solids, acid and metals in solution) exiting the circuit are similar⁽⁴⁾. As a first step the acid and soluble metals generated during the oxidation process need to be separated from the solids. This is achieved in a counter current decantation (CCD) wash circuit. The CCD circuit also cools the oxidized slurry ahead of CIL treatment. The number of wash stages is usually of the order of three, however the important point is to remove as much of the ferric/ferrous iron from the solids as possible to minimise cyanide consumption in the gold leaching circuit⁽⁴⁾⁽²⁸⁾. For whole ore pressure oxidation there is no wash step and the autoclave tailings go directly to neutralization.

Neutralisation Circuit

The wash solution from the CCD circuit is neutralised and again the neutralization circuits used in biological and pressure oxidation plants are similar⁽⁴⁾. The basic criteria is for a total residence time of 4-6 hours in 4 to 6 stages. Whilst only 3-4 stages are necessary, this circuit can have a significant maintenance requirement due to gypsum scaling and so additional tanks are appropriate.

The major cost of the neutralisation circuit is associated with both the large quantity and cost of neutralising agent, nominally limestone⁽⁴⁾⁽²⁸⁾. The cost of limestone including delivery on site has driven many operators and potential users to investigate alternative and novel sources of calcium carbonate, such as seashells and calcrete⁽²⁸⁾. On site production of lime is also an option if a suitable deposit can be found close to the mine⁽²⁸⁾. Over the last 10 years many operations are

ALTA 2012 Free Paper using flotation tailings high in carbonate in the neutralization circuit to minimize the amount of lime added to this circuit.

Carbon-in-Leach (CIL)

Comparison of cyanide consumption between pressure oxidation and biological oxidation shows that in some instances, this differential can be as high as 15 kg/t NaCN. This can significantly impact the process economics due to the additional costs associated with high cyanide demand and cyanide destruction contained in water discharged to the environment⁽¹⁾⁽²⁸⁾. Typical cyanide consumption is for biooxidation is 7-15 kg/t and for pressure oxidation it is usually less or around 1kg/t. The main cause of high cyanide consumption in the biooxidation process is due to the formation of thiocyanate from polysulfides⁽²⁶⁾ and sulphur that then report to the gold leaching circuit. Reducing the quantity of polysulfides and sulfur in the biooxidation circuit is not an easy task; however reasonable strides have been made in this direction by a combination of longer biooxidation leaching time with different bacterial cultures that convert sulfur to sulfate. Another downside of thiocyanate is that it is fairly expensive to destroy. Lastly there is more and more pressure on plants to fully close their water circuits, so there is a need to destroy the free cyanide and other contained cyanide complexes (e.g. WAD cyanide and thiocyanate).

The biooxidation process generates organic compounds and these will impact the activity of activated carbon in the gold adsorption circuit⁽²⁸⁾. This has flow on effects on the gold loading capacity of the carbon⁽²⁸⁾. Whilst relatively high carbon loadings have been achieved in practice, a careful balance with residence time, activity and carbon inventories is still required⁽²⁸⁾.

Foaming in the cyanide leach section of a biooxidation plant is a problem that has impacted all plants to some degree⁽²⁶⁾⁽²⁸⁾. This has led to the prevalence of CIL circuits using draft tube agitators. In addition anti-foaming agents and froth breaking agitators are commonly used.

Cyanide Detoxification

The CCD overflow ahead of the neutralization circuit contains significant quantities of ferrous and ferric ions in an acid environment making it ideal for complexing cyanide species. A number of operations therefore add a portion of this stream to the CIL tailing to aid in the detoxification process⁽¹⁸⁾ (21)

The presence of reasonable levels of thiocyanate in the cyanide tailings is problematic as it is not easily broken down and consequently there will be a steady build-up in the recycle water circuit. As mentioned previously thiocyanate is toxic to bacteria and is also known to reduce the activity of activated carbon in the CIL circuit. Fortunately this only occurs at high thiocyanate concentrations. Destruction of thiocyanate is expensive as a strong oxidant such as Caros Acid is required.

UTILITIES IN REFRACTORY GOLD TREATMENT

Roasting, pressure oxidation and biooxidation processes are energy intensive plus they all require a reasonable quality of water. Electrical power is becoming more expensive and good quality water is a scarce commodity in remote locations.

Water Quantity and Quality

As a general rule biooxidation consumes more water than pressure leaching and roasting. From a quality standpoint local groundwater available for gold processing is usually saline. The problems with saline water in biological oxidation processes are relatively minor compared with those for pressure oxidation, which required a chloride level of <150mg/L. For this reason a number of pressure oxidation plants have chloride wash system ahead of the autoclave. Furthermore the presence of chlorides in pressure oxidation treatment has been shown to result in the formation of a gold chloride complex under certain operating conditions. This complex will be reduced to metallic gold on preg-robbing carbon that cannot be leached in cyanide solution. Roasting also requires a low level of chloride as gold chloride (gaseous) can be generated in the roaster leading to gold losses. Again some roasters wash the roaster feed to remove chlorides.

The biooxidation process is extremely sensitive to cyanide and thiocyanate. At levels above 5ppm it becomes extremely toxic to the bacteria. For this reason process streams need to be separate to ensure thiocyanate does find its way back into the biooxidation feed stream.

The c The power costs for oxidation processes are proportional to the amount of sulphur that needs to be oxidized⁽⁴⁾. For pressure leaching the oxidant is pure oxygen and the cost of production is directly proportion to the cost of electricity. Bioxidation and roasting generally use air to oxidise the sulfides. In both cases large blowers are required to provide the required quantity of air for the oxidation of the sulphides. Air is also required for fluidizing the solids in a roaster.

TREATMENT OF PREG-ROBBING GOLD ORES

For some gold ores, gold recovery by cyanidation is limited by the presence of naturally occurring organic carbonaceous material, which adsorbs gold from alkaline cyanide solution unless steps are taken to prevent this adsorption reaction from occurring. Such ores are most often referred to as preg-robbing ores^{(7) (9) (35)}.

Options for Treating Preg-Robbing Ores

Certain chemical reagents passivate the carbonaceous matter by what seems to be selective adsorption or wetting of the carbon surface. Earlier studies regarding blinding of preg-robbing carbonaceous materials indicated that both flotation reagents (xanthates, pine oil) and non-polar hydrocarbons such as diesel, light oil, fuel oil and kerosene can be used⁽⁹⁾⁽³⁵⁾⁽³⁶⁾⁽³⁷⁾.

The use of large quantities of activated carbon in a full CIL circuit to preferential adsorb soluble gold onto this carbon in preference to adsorption onto the preg-robbing ore has and is still practiced. While relatively effective this method has disadvantages, in that the circuit requires high carbon inventories and a large elution and regeneration treatment capacity⁽¹⁾⁽³⁷⁾.

In the late 1960's the U. S. Bureau of Mines recognized that aqueous chlorination could be used to destroy carbonaceous material^{(12) (38)}. Gaseous chlorine and sodium or calcium hypochlorite have been used as a chlorine source. A number of gold operations in Nevada, USA used chlorination/flash chlorination to treat preg-robbing oxidized gold ores during the1980's to the late 1990's. In general, the chlorine consumption ranged from 30 to 50 kg/t of ore depending on the mineral constitution. The process was abandoned when the deeper mined ores encountered sulfide minerals that drove consumption to more than 100kg/t which was uneconomical. Roasting of these ores has become the preferred option

Interestingly it has been found that the pressure oxidation treatment can reduce the impact of pregrobbing material. A recent innovation in this area has been Newmont's high-temperature pressure oxidation process⁽³⁹⁾. This has been installed at the Twin Creeks operation in Nevada to treat whole ore and employed at the Macraes in New Zealand⁽⁴⁰⁾ to process finely ground auriferous flotation concentrates. In this process the temperature, oxidation potential and acidity of the finely ground ore or concentrate are closely controlled in the autoclave to establish conditions under which the sulfides are oxidized and the carbonaceous material is passivated⁽³⁹⁾.

It is claimed that certain types of bacteria can passivate the carbon in preg-robbing ore⁽⁹⁾. Not much is known about the mechanism and there does not appear to be a commercial operation using this technology.

Some Alternative Treatment Options for Treating Preg–Robbing Gold Ores

Penjom Gold Mine

The Penjom mine employs kerosene but combines this with the use of a commercial ion-exchange resin to adsorb the gold ⁽³⁶⁾. The advantages of the resin over activated carbon are the much higher equilibrium gold loadings that can be achieved coupled with a greater resistance to fouling in the presence of kerosene. The kerosene addition rates at Penjom are reported to be up to 8L/t of ore.

Gravity separation is used on the ball mill cyclone underflow stream to preferentially remove both free gold and gold containing sulfides. This concentrate is then subjected to intensive cyanide leaching⁽³⁶⁾.

Stawell Gold Mine

LTA2012Free Paper The Stawell Gold Mines in Victoria, Australia treats partially refractory pyrite-arsenopyrite gold ores that contain various quantities of a preg-robbing carbonaceous material. The process developed by the metallurgist at the mine to deal with these ores consists of a combination of gravity separation to remove as much free gold as possible, ultrafine grinding (10 to 20 microns) of the sulfides removed by flotation, kerosene addition to blind the preg-robbing component, an activated carbon adsorption step to remove residual kerosene to prevent fouling of the activated carbon in the gold adsorption step, oxygen is also sparged into this part of the circuit as a pretreatment step and finally a 'true' carbon-in-leach circuit (cyanide added in the carbon circuit). The flowsheet gives between 10-15% extra gold recovery and the recovery is sensitive to the amount of preg-robbing component in the feed.

Jundee Gold Mine

The Jundee operation located in Western Australia contains preg-robbing carbonaceous shales. Laboratory and plant trials showed that significant improvements in overall gold recovery could be obtained by maximizing 'free' gold recovery by gravity, ensuring that no 'free' cyanide was present in the plant process water (this would result in some gold in the feed being dissolved and adsorbing onto the preg-robbing material) and finally adding cyanide in the CIL tanks (true CIL operation) only⁽⁴¹⁾. It was also found that mixing non preg- robbing ore with preg-robbing ore would result in lower gold recovery for the non preg-robbing ore. This flowsheet demonstrated that 7-15% extra gold recovery could be obtained on moderately preg-robbing ores. For highly preg-robbing ores the circuit was ineffective. All the preg-robbing ore that were stockpiled over the years was treated under the same operating parameters employed during the plant trials.

THOUGHTS ON FUTURE CHALLENGES AND OPPORTUNITIES

The introduction of pressure and biological oxidation as well as some innovations to roasting in the mid 1980's has revolutionized the way that refractory gold ores are treated. These technologies allowed previously uneconomical gold ore deposits to be processed. As with all new technologies there were huge learnings along the way with a lot of heartache followed by jubilation as the participants on this journey solved the seemingly unsolvable problems encountered along the way. The refractory treatment processes are complex from a flowsheet perspective as there are many interactive unit operations, as well as complex chemistry associated with high temperature and biological systems. This paper gives a brief glimpse on the progress made over the years to find new solutions to treat more complex refractory gold ores and importantly ways to reduce both operating and capital costs.

The challenges of the future will be undoubtedly focused on environmental issues and operating and capital cost reductions. Environmental focus will be on how the industry deals with the minor toxic elements (mercury, selenium, tellurium, antimony and arsenic to name a few) released during the extreme operating conditions encountered when treating refractory gold ores. How these are collected and disposed of will be the focus of government agencies and other interested external parties. Water usage, treatment and disposal will receive a lot of attention also. Capital and operating costs have increased dramatically over the last couple of years and have outpaced the gold price on a percentage basis. The question of how to reduce these given the long term critical shortage of skilled manpower and increases in energy costs that have a 'roll on effect' to increase consumable costs will be the challenge

So given the above what are the possible opportunities in the future. Clearly at the moment there seems to be a trend for small operations treating refractory gold to use the biooxidation process possibly due to its 'relative' simplicity and lower capital cost. Flotation concentration is an essential part of the front end of biooxidation and some ores not amenable to flotation. So are there ways to improve this or use a combination of other processes as demonstrated by the smaller operations dealing with preg-robbing ores to improve recovery? Also are there opportunities to consider other options to oxidise the sulfides, for example the Albion or similar technologies, or other chemical oxidation process such as the chloride system? Furthermore are there opportunities for considering alternatives to cyanide that will leach gold in an acid environment and will be less of an issue to dispose of into the environment? There are undoubtedly many more ideas that people will and can think of and pursue in the future. It will be an interesting time for the gold industry as the challenges of the future will not only be around technology but will include social issues as well.

Lastly as always there will be ways to incrementally make improvement to the current process and some of these have been or are being developed. As an example of this is the progress made in biooxidation to reduce cyanide consumption and detoxification costs. The next step along these lines is considering ways to reduce the capital and energy costs around the 'conventional' agitated tank reactors used in the biooxidation.

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