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Gold-PM Keynote

TREATMENT OF REFRACTORY GOLD ORES IN CHINA

By

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ABSTRACT

The treatment of refractory gold ores has been a major challenge in China's Gold Industry for the past two decades. The low gold extraction recovery and high operating cost of conventional flotation and cyanidation processes make it not a viable approach. Different pre-treatment technologies such as roasting, bio-oxidation and pressure oxidation were developed and commercialized to make the utilization of the refractory gold ores more efficient and environmentally friendly.

The distribution of refractory gold ores in China, as well as the respective resources, are summarized in this paper. The mineralogy characteristics of the refractory gold ores are presented. The dominant pretreatment technologies of roasting, bio-oxidation and pressure oxidation are reviewed and compared in terms of their capability, capital and operating costs. The respective advantage and disadvantage of these technologies are discussed as well. The typical case studies of each technology are described and analyzed. Ultra-fine grinding and cyanidation is the other option but not commonly adopted in China depending on the gold ore liberation.

The recent efforts and studies to improve of the efficiency and effectiveness of all these technologies are reviewed. A novel process integrating pressure oxidation and non-cyanide leaching is introduced. Some key research topics that promote the development of refractory gold ores in China are proposed and discussed. The application of these technologies depends mainly on the size of resources, gold extraction recovery, sound environmental solutions and competitive capital and operating costs.

Keywords: refractory gold ores, pre-treatment, roasting, bio-oxidation, pressure oxidation, ultra-fine grinding, non-cyanide leaching, gold ore processing in China

INTRODUCTION

China has been the world's largest gold producer since 2007. According to the data source of the Annual Book of Gold in China[1], China produced 8.70 million ounces of gold in 2007 and 14.58 million ounces of gold in 2016 with average growth rate of 7.5%. The production growth rate has slowed down since 2014, as result of increasing operation costs, strict environmental regulation, and low gold prices. The portion of gold production by treatment of refractory gold ores has increased from 3.22 million ounces in 2007, accounting 37% of total gold production, to 7.88 million ounces in 2016, accounting for 54% of total gold production, respectively[1][2].

With the development of gold resources and the depletion of high grade and easy treatable gold ores in China, the development and treatment of refractory gold ores has become very important for the Gold Industry of China. The refractory gold ores could be classified initially in China as two types: 1) Gold is finely encapsulated with pyrite or arsenopyrite, easily recovered by flotation of a gold bearing concentrate but not viable for direct cyanidation .The concentrates then need to be pretreated by roasting or bio-oxidation to exposure gold to cyanidation; 2) Gold which is very finely, encapsulated with pyrite or arsenopyrite (gold particles ~ 5 to 10 micron size), but also interacted with gangue minerals, such as silicate or carbonates, leading to a poor flotation recovery. In addition, gold can occur as antimony, bismuth sulfide and telluride ores, or carbonaceous-sulfidic ores – these ores are defined as double refractory gold ores. Roasting of whole ore or pretreatment by caustic followed by roasting were studied for this kind of gold ore, but achieved with a lower gold recovery of 70-80%.

MINERALOGY CHARACTERISTICS OF REFRACTORY GOLD ORES

The classification of refractory gold ores was more clearly defined by Zhou, Marsden & House in three major categories[3][4]: The refractory gold ores include 1) iron sulfide or arsenic sulfide ores; 2) antimony, bismuth sulfide and telluride gold ores; and 3) carbonaceous ores. Typical refractory gold ores in China and representative mines are listed in Table 1.

Table 1: Refractory gold ore types and gold occurrence

#	Ore Type	Mode of Occurrence of Gold	Example
1	Iron sulfide and/or arsenic ores	Gold occurs as liberated particles, attachments to or as inclusions in sulfide (commonly in pyrite and arsenopyrite, and less commonly in marcasite and pyrrhotite), and as submicroscopic gold in sulfide minerals	Carlin type and Carlin-like type gold ores: Zimudang, Baidi, Danzhai, Jinya, Longhe, Sijia, Mingshan, Gaolong,, Lianhecun, Manaoke, Gaojiaao, Yangshan Epithermal gold ores: Hatu, Axi
2	Antimony, bismuth sulfide and telluride gold ores	Gold occurs mainly as native gold, gold tellurides, aurostibite or maldonite, with minor to moderate amounts of gold particles locked in sulfides. Submicroscopic gold can also be present in sulfide.	Antimony gold ore: Hechi (Guangxi), Bismuch gold ore: Tongguan (Gansu) Telluride gold ores: Dongping (Hebei), Kunyu (Henan)
3	Carbonaceous-sulfidic ores	Gold occurs mainly as fine-grained gold particles and submicroscopic gold in sulfides, and surface gold absorbed onto the surface of carbonaceous, matter and FeOX.	Lannigou, Shuiyindong, Yata, Getang, Banqi, Qiaoqiaoshan, Dongbeizhai, Laerma, Pingding, Qiuluo

Gold in iron sulfide or arsenic sulfide ores is associated predominantly with the sulfide minerals and occurs both as fine-grained gold particles and/or submicroscopic gold, such as some epithermal gold ores and most Carlin type gold ores. Acceptable extraction of gold in this type of ore can only be achieved by employing a pre-oxidation process prior to cyanide leaching.

Antimony, bismuth sulfide and telluride gold ores are often somewhat refractory due to the presence of slow-dissolving gold minerals such as aurostibite, maldonite and gold tellurides.

Gold in carbonaceous ores is fine, and, usually, is predominantly associated with the sulfides (pyrite or arsenopyrite) that are present in carbonaceous ores. Some is in the form of colloidal size grains (<0.1μm) in carbonates or microcrystalline quartz particles[3] (Fleming, 1998). Gold recovery from the carbonaceous sulfidic ore is more difficult because the gold is "robbed" from the cyanide solution by the carbonaceous matter[5] (Wan, 2001). These ores are pretreated by pressure oxidation (POX) (Shuiyindong), Bio-oxidation (BIOX) (Lannigou) and roasting (Zimudang) prior to cyanide leaching.

GOLD RESOURCES IN CHINA

In 2007, it was estimated that 30-40% of gold reserves in China are refractory gold, corresponding to 1500 to 2000 tons of gold[2] (Song, 2009). Most of the refractory gold occurs in two groups in southwest China: one in Guizhou, Yunnan, and Guangxi provinces near the southwest margin of the Yangtze craton, and another in northwest Gansu, Shanxi, and Sichuan provinces near the east and south margin of the Aba craton (Fig.1)[6] (Hu, 2002). Minor amounts of refractory gold occur in Liaoning, Jiangxi, Guangdong, Hunan[2] (Song, 2009).

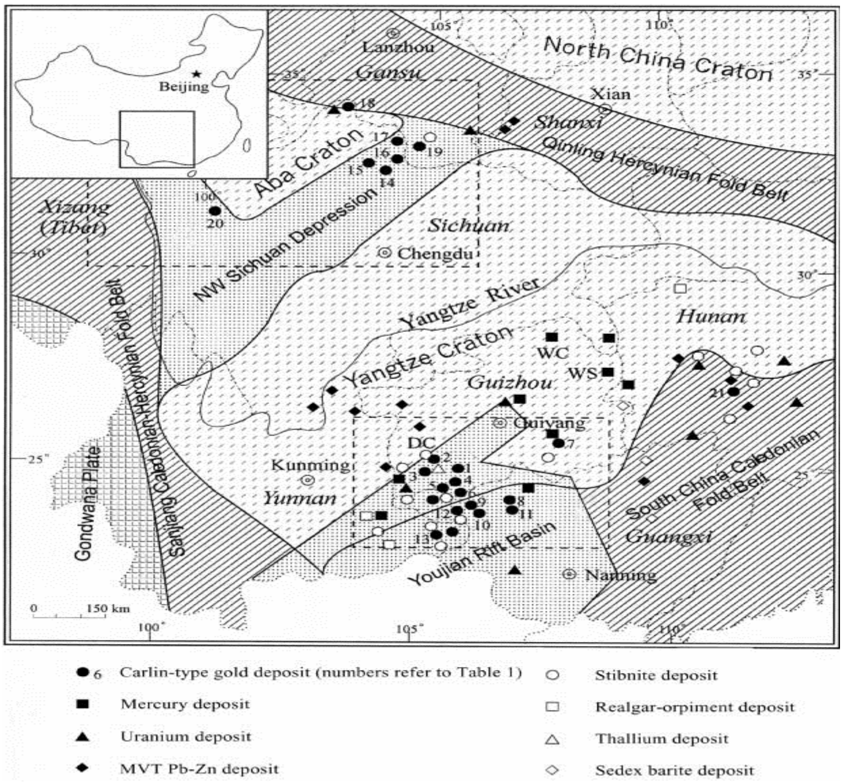

Figure 1: The Occurrence and Distribution of Refractory Gold Ores in China

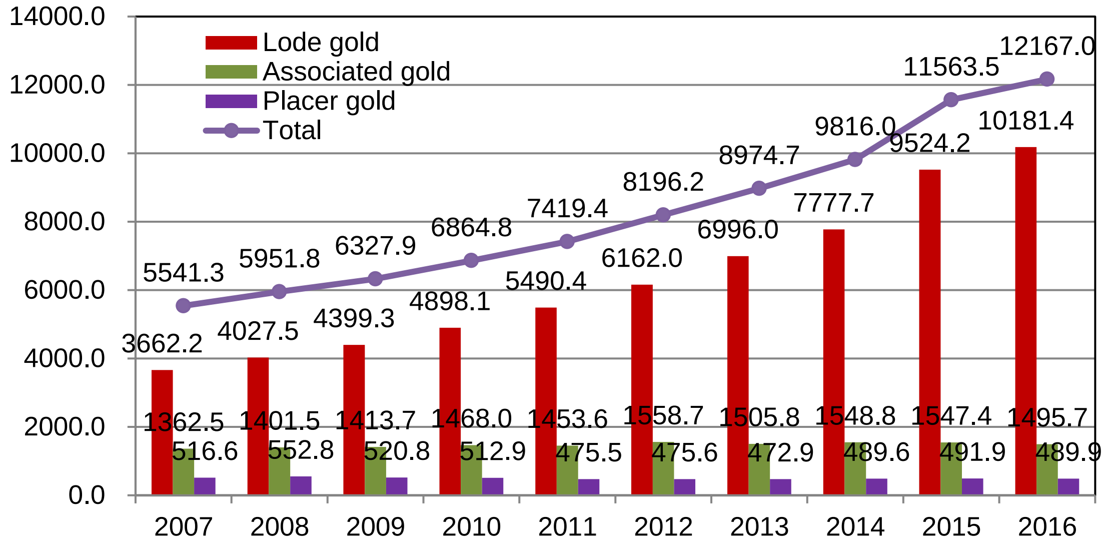

Figure 2: Gold Resources in China from Year of 2007 to 2016

The gold resources were recently summarized and published by the Annual Book of Gold in China[1]. As shown in Fig. 2, the gold resources have increased significantly from 5,540 tons to 12,167 tons. It is estimated that over 50% of the gold resources are now in refractory gold ores.

PRETREATMENT TECHNOLOGIES OF REFRACTORY GOLD ORES

The study of pre-treatment technologies of refractory gold ores has been conducted in China since the early 1990s by several organizations such as Beijing General Research Institute of Mining & Metallurgy (BGRIMM), Changchun Gold Research Institute (CCGRI), General Research Institute for Nonferrous Metals (GRINM), and Zijin Research Institute of Mining & Metallurgy (ZRIMM). Roasting, followed by bio-oxidation and pressure oxidation, are the three major pre-treatment technologies that have been carried out at lab bench or pilot scale. This research work has provided a sound foundation for the commercialization of these technologies in China.

Roasting was the first pre-treatment technology commercialized in China in 1986 by Shandong Guoda Gold Smelter at a capacity of 50 t/d. There is a total of 24 roasting plants for refractory gold in China with current total capacity of 9,750 t/d[7-10].

Bio-oxidation technology was developed in China during the 2000s[11-18]. The first pilot bio-oxidation plant was built in 2000 at Yantai Gold Processing Plant with a capacity of 50 t/d in Shandong Province. The first commercially successful bio-oxidation plant was built in 2001 with capacity of 100 t/d, adopting Bac-tech technology at Laizhou Gold Processing Plant in Shandong Province. CCGRI developed a bio-oxidation technology and commercialized it at Liaoning Tianli with capacity of 100 t/d in 2003. There are total of 7 processing plants in operation with total capacity of 1400 t/d. The largest bio-oxidation plant is in Guizhou Jinfeng with a capacity of 750 t/d, adopting BIOX technology in 2007.

The commercialization of pressure oxidation technology has been an interesting story for the last two decades[19-29]. During 1997 to 1999, CCGRI cooperated with Beijing Research Institute of Chemical Engineering & Metallurgy (BRICEM) to conduct a pilot plant operation with a capacity of 1t/d ,adopting low pressure oxidation of whole ores under non-acidic conditions. The technology was only applicable to low sulphide and high carbonate gold bearing ores with a cyanidation recovery of 90%. The approach was not applied at a large commercial scale.

In 2002, Institute of Process Engineering, and Chinese Academy of Sciences (IPE),cooperated with Shangdong Jinchiling Gold Mine to construct a pilot plant with capacity of 1 t/d, adopting a low temperature Nitric Acid Catalytic Oxidation Acid Leaching (COAL) process at 100°C and 0.4 MPa oxygen partial pressure. It was reported that 93% of gold recovery was achieved during the pilot campaign[19]. The problem of how to deal with the elemental sulphur formed during the oxidation was a challenge for this process. Poor engineering and unstable continuous operation conditions of the process led to the shutdown of the plant in the same year.

Zijin Mining Group Co., Ltd. built a Pressure Oxidation (POX) pilot plant with a capacity of 1t/d in 2012 and ran a couple of continuous pilot test campaigns on the gold concentrates from its Shuiyindong Gold Mine to achieve 98% sulfide oxidation and 96% gold cyanidation recovery in 2013. A POX plant with a capacity of 450 tons of gold concentrates per day at Zijin Guizhou Shuiyindong Gold Mine was designed in 2014 and constructed in 2015 to 2016. The plant was commissioned in November 2016 and reached its designed capacity within 3 months. This is the first commercial POX plant for refractory ore in China[20-21].

Roasting

There are two phases in the development and application of roasting technology in the pre-treatment of gold refractory ores in China.

From 1980 to 2000, single stage roasting technology was very popular to pre-treat copper and gold pyrite concentrates. The roasted ore is leached with sulphuric acid to digest copper into the leach solution, followed by solvent extraction and electrowinning to recover copper. The leached residue is washed in CCD thickeners then neutralized with lime to pH10-11, followed by cyanidation to recover gold. The final leach residues could be sold to cement plant as raw materials. The off-gas from the roaster is absorbed and used to produce acid.

The one stage roasting technology is relatively simple and reliable to recover gold from the refractory ores and associated copper as a by-product. This technology is not applicable to arsenic containing gold concentrates.

The typical one stage roasting plants are summarized in Table 2 as follows: Shandong Guoda Gold Smelter, China Gold Group Zhongyuan Gold Smelter, Liaoning Chaoyang Xindu Gold Smelter, Henan lingbao Gold Smelter, Shandong Henbang Gold Smelter and China Gold Group Tongguan Gold Smelter. The roasting capacity is ranging from 150 to 350 t/d.

Table 2: Summary of Gold Smelters Adopting One and Two Stage Roasting in China

No.	Company	capacity,t/d	Stages	Set	Remarks
1	Shandong Guoda Gold Smelter	200	Two	2	
		200	One	3	
		600	One	1	Pyrite to produce acid
2	Qinghai Dachaidan Mining Ltd.	480	Two	1	
3	Jingshan Gold Smeter, Zijin Mining Group Co., Ltd.	200	Two	1	
4	Xinjiang Xingta Mining Ltd.	100	One	1	
		200	Two	1	
5	Western Gold Yili Ltd.	200	Two	1	
6	Gansu Zhaojin Precious Metals Smelter	400	Two	1	
7	Liaoning Chaoyang Xindu Gold Smelter	100	One	1	
8	Hunan zhongnan Gold Smelter	200	Two	1	
9	Shandong Henbang Metallurgy Co., Ltd.	200	One	1	
		200	Two	2	One plant shut down
		200	One	1	
		400	Two	1	
		300	Two	1	
10	China Gold Tongguan Gold Smelter	200	Two	1	
		150	One	1	
11	Yantai Jinao Gold Ltd.	200	Two	1	
12	Guangxi Tianyang Gold Ltd.	200	Two	1	Shut down
13	Luoyang Zijin Yinghui Gold Smelter	400	One	1	
14	Shanxi Jinzhong Gold Smelter	50	One	1	
15	Henan Zhongyuan Gold Smelter	250	One	1	Shut down
16	Lingbao Jinyuan Mining Co., Ltd.	150	One	1	
		200	One	1	
17	China Gold Songyuan Gold Smelter	170	One	1	
		350	One	1	
18	Guizhou Jinxing Gold Ltd.	1000	Whole Ore	1	
19	Gansu Mingxian Mining Ltd.	500	Whole Ore	1	
20	Jiangxi Hongji Precious Metal Smelter	50	One	1	
21	Kaiyuan Mining Ltd.	300	One	2	
22	Lingbao Gold Co., Ltd.	1000	One	5	
23	Lingbao Boyuan Mining Ltd.	300	One	2	
24	Yichun Yongfeng Gold Smelter Ltd.	100	One	1	

Two stage roasting technology was developed successfully in China in 2002. The technology is applied to pretreat gold bearing arsenopyrite concentrates to recover arsenic and gold at different stages. The two stage roasting plants are also summarized in Table 2. The typical plants include Shandong Guoda Gold Smelter, Shandong Henbang, Zijin Mining Group Fujian Jinshan Gold smelter, Qinghai Dachaidan Mining Ltd., Hunan Zhongnan Gold Smelter and China Gold Tongguan Gold Smelter. The capacity of two stage roasting ranges from 100 to 480t/d. A gold recovery of 88-90% can be achieved, depending on mineralogy and operating conditions.

Whole ore roasting technology was studied and developed by BGRIMM in 1999 and a pilot plant with a capacity of 500t /d was built to pretreat those low sulfide carboneous refractory gold ores containing arsenic not viable for flotation and direct cyanidation. 67% of sulfur and 83% of arsenic were fixed in the calcine and 70% of gold recovery was achieved in the pilot test[1]. The calcium and magnesium in the gange could be used to fix arsenic and sulfur if the ratio of CaO to sulfur is higher than 1.75. CCGRI constructed and commissioned a whole ore roasting demonstration plant at Guizhou Jinxing Gold Ltd. with capacity of 1000 t/d in 2008. It is reported that 98% of arsenic and 90% of sulphur could be fixed in the calcine and 85% of gold cyanidation recovery could be achieved[2].

Roasting Capital and Operating Costs

The capital and operating costs of typical refractory gold smelters are summarized in Table 3.

The capital investment of a roasting plant depends on the specified project timing, site infrastructure conditions and construction schedule management. The capital cost of a 200t/d roasting plant cost USD 19 to 24 million before the year of 2010 and USD 29 to 33 million after year of 2010, respectively.

The operating cost varies with site power tariffs, infrastructure conditions, labor cost, and tax polices etc. The operating cost for one stage roasting ranges from USD 87 to 142 per ton of concentrates, and those for two stage roasting is between USD 119 to 175 per ton of concentrates, respectively.

Table 3: Summary of Capital and Operating Costs of Typical Roasting Plants in China

Plant	Year of Commissioning	Feed material	Capacity t/d	S%	Au g/t	Stages	Capex In million USD	Opex In USD/t conc
Jinshan Gold Smelter, Zijin Mining Group Co., Ltd.	2008	conc.	200	23-27	-	Two	21	146
Qinghai Dachaidan Mining Ltd.	2009	conc.	480	23-26	20	Two	45	-
Hunan Zhongnan Gold Smelter	2008	conc.	200	23	65	Two	24	159
China Gold Dongguan Gold Smelter	2009	conc.	200	24-26	50	Two	31	-
Guizhou Jinxing Gold Ltd.	2006	whole ores	1,000	5-7	3-5	One	27	29

Roasting Industrial Application

Pretreatment of Refractory Gold Concentrate by multi-stage roasters at Jinshan Gold Smelter

ZiJin Jinshan Gold Smelter (hereafter “Jinshan”) was built in 2006 and commissioned in the first quarter of 2008 with the purpose of processing gold concentrate from the gold mines within ZiJin Mining Group or concentrates from the south eastern part of China. Jinshan adopted two stages of roasting with a capacity of 200 tonnes per day to treat various arsenic, carbonaceous, copper-bearing refractory gold concentrates. Roasting integrated with downstream hydrometallurgical and off-gas treatment circuits has become a flexible, economically viable and environmentally acceptable treatment for such refractory gold concentrate[9].

Mineralogy

The two types of gold concentrate being processed at Jinshan are described below:

- High copper bearing gold concentrate. Copper occurs predominantly as primary sulphide such as chalcopyrite, accounting for about 74%, and secondary copper sulphide and copper oxide, accounting for about 14% and 11% respectively. Copper encapsulated by silicate minerals accounts for less than 1%. Gold occurs mainly as native gold attached to or encapsulated by sulphide minerals such as pyrite, accounting for 86%, liberated native gold, gold encapsulated by carbonate gangue and silicate mineral accounting for 14%.

- High arsenic and carbonaceous bearing gold concentrates**.** Gold is encapsulated within the crystal matrix of iron sulphide minerals such as pyrite and arsenopyrite. Gangue minerals are mainly silicate and carbonate. Carbonaceous components are mainly organic carbon such as hydrocarbon, humic acid and activated elemental carbon, which will cause a pre-robbing issue. A small minority of gold occurs as liberated gold.

Process Description

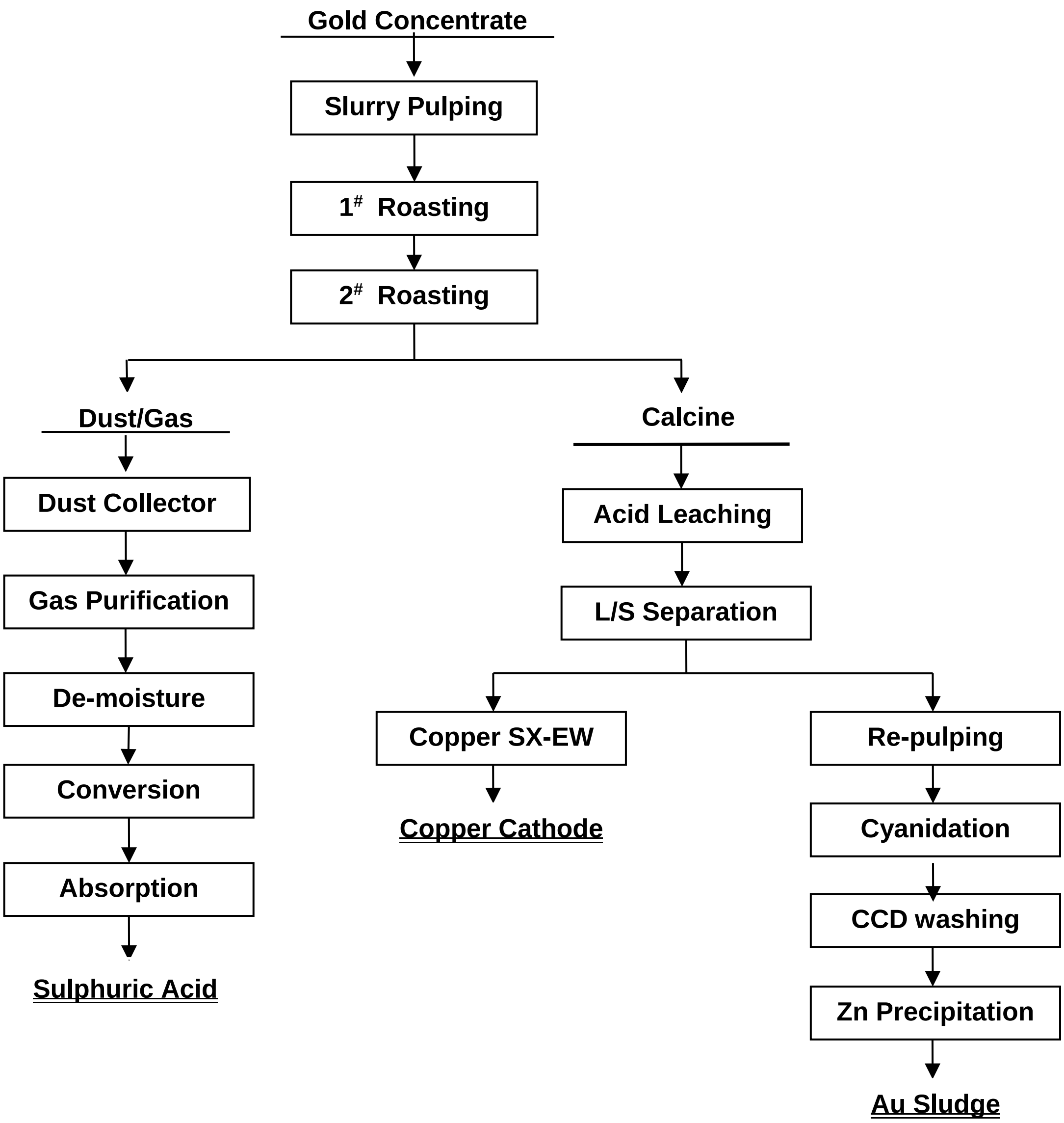

Figure 3: Principle Process Flow Chart of ZiJin Jinshan Smelter

As discussed above, there are mainly two kinds of concentrate processed by this smelter:

- High copper bearing gold concentrate, containing Au>30 g/t, Cu>2.5~4.0%, S 26%, As<0.4%, and C<0.4%;
- High arsenic bearing gold concentrate, containing Au> 30 g/t, Cu <0.3%, S 26%, As 2.0-3.5%, and C<0.4%.

The principle flow chart of Jinshan Smelter is shown in Figure 3. The key operating parameters are summarized in Table 4.

To process copper bearing gold concentrate, the concentrate was pulped to a slurry concentration of 70% and pumped to the two stage roasters. The dust and gas from the roasters were treated by high efficient cyclone precipitator and high temperature electric dust collector. It was then passed into a two stage converter to convert sulphur dioxide into sulphur trioxide and absorbed by sulphuric acid to produce concentrated acid. The calcined stream is combined with the collected dust and then leached by dilute acid solution of 10-15 g/L to recover copper. The resultant leach liquor was pumped to a copper Solvent Extraction Electrowinning (SX-EW) circuit to produce copper cathode. The copper leached residue was re-pulped and pumped to the cyanidation leaching circuit and followed by Counter Current Decantation (CCD) washing. The resultant liquor was treated by zinc precipitation to produce gold sludge, which was sent to gold refinery to produce gold bullion.

One of major characteristics of this technology is to integrate two stage roasting together and to be readily switched from single stage roasting, under oxidizing condition, to two stage roasting with the first stage operated under slightly reducing condition, mainly depending on the arsenic content in the gold concentrate. In other words, single stage roasting was adopted to process high copper bearing gold concentrate, while two stage roasting was used to process high arsenic containing concentrate. This process configuration makes it a flexible treatment for gold concentrate from different gold mines in China.

The switch from two stage roasting to one stage roasting was achieved by installation of venturi gas washing and purification units attached to arsenic collector bags. When arsenic bearing concentrate was processed, the dust and gas were passed through arsenic collector bags first while the dust and gas from copper bearing concentrate, without arsenic, bypassed the arsenic collector bags and went through to the venturi washing circuit.

Table 4: Key operation parameters of one/two stage roasting at ZiJin Jinshan Smelter

Feed	Mode	Parameters	Recovery
Copper bearing Gold concentrate	Single stage roasting under oxidizing condition	Roasting at 630℃ Calcine leached at 95℃ for 2h Slurry concentration: 40%, Initial acidity: 20 g/L H_2SO_4 Cyanidation for 32 h Slurry concentration: 33% NaCN concentration: 0.3%	Cu: 89 % Au: 90 %
Arsenic bearing Gold concentrate	First stage roasting under slightly reducing condition + second stage roasting under oxidizing condition	1# Stage roasting at 580-600℃, 2# Stage roasting 650℃, Cyanidation leach for 32 h Slurry concentration: 33% NaCN concentration: 0.3%	As Removal: 96 % Au: 88 %

Jinshan Gold Smelter was commissioned in 2008 and achieved the designed nameplate of gold concentrate 66,000 t/a to produce 86,000 ounces of gold bullion, silver 806,000 ounces, copper cathode 780 t/a, arsenic oxide 2,500 t/a and sulphuric acid 37,000 t/a. The total investment was USD 21 million and the total operating cost is USD 146 per tons of concentrates.

Bio-oxidation

Compared with roasting, bio-oxidation technology was reported to be more environmentally friendly, relatively easier to operate at smaller scale, and more applicable to arsenic containing complex gold refractory ores. Thus, bio-oxidation was commercialized quickly during 2000 to 2010 in China and a total of 11 bio-oxidation plants were built and 7 are active in operation. The bio-oxidation plants are summarized in Table 5.

Table 5：Summary of Bio-Oxidation Plants in China

No.	Plant	Location	Capacity (t/d)	Remarks
1	Yantai Gold Processing Plant	Yantai, Shandong	80	Shut down
2	Laizhou Gold Processing Plant	Laizhou, Shandong	100	Shut down
3	Dandong Shixing Gold Processing Plant	Dandong, Liaoning	30	Shut down
4	Benxi Dongda Gold Tech Development Co., Ltd.	Benxi, Liaoning	50	Shut down
5	Liaoning Tianli Ltd.	Fengcheng, Lioaning	150	
6	Zhenan Gold Processing Plant	Zhenan, Shanxi	50	
7	Jiangxi Sanhe Gold Ltd.	Dexing, Jiangxi	80	
8	Xinjiang Axi Gold Mine	Xinjiang	100	
9	Xingjiang Hatu Gold Mine	Xinjiang	80	
11	China Gold Guizhou Jingfeng Gold Mine	Jingfeng, Guizhou	790	
12	Wulaga Gold Mine	Helongjiang	150	
13	Honghe Gold Mine	Yunnan	100	In construction

A typical bio-oxidation plant has 3 stages of agitation tanks in parallel for primary oxidation, and three to four stages of agitation tanks in series as a secondary oxidation step. Air is introduced into the tanks and dispersed by agitator to mix with slurry to achieve oxidation of the sulphur in the pyrite concentrates. The temperature of the tanks usually is controlled at 38-45°C using cooling water by indirect heat exchanger to provide a good environment for bacteria, and the pH is controlled at 1.5-2.0 by limestone to neutralize acid produced by oxidation of sulphur. The bacteria under suitable conditions can be adopted to oxidize gold arsenopyrite concentrates with an arsenic content of less than 3%.

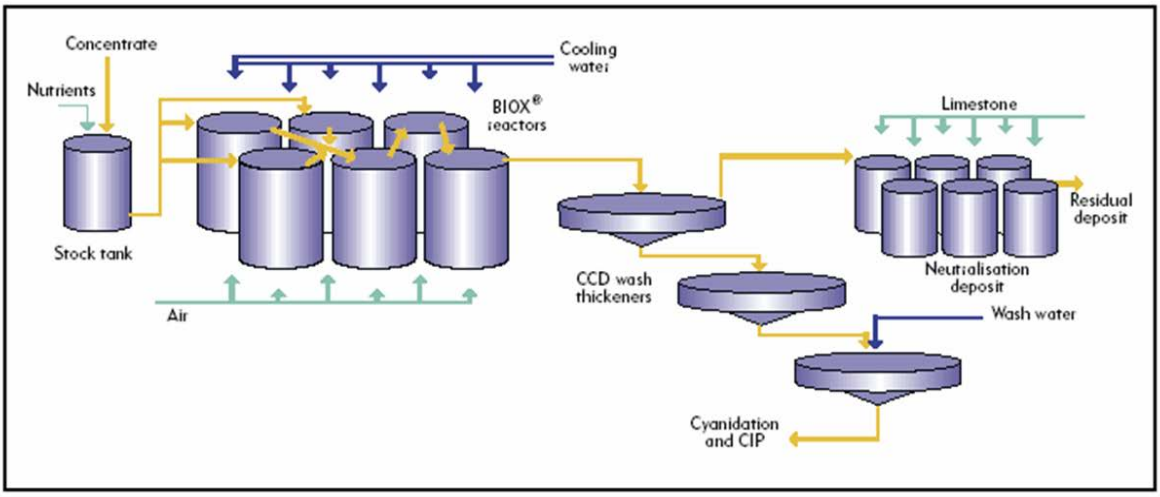

Figure 4: Typical Bio-oxidation Process Flow Chart

Bio-oxidation Capital and Operating Costs

Table 6：Bio-oxidation Plant Capital and Operating Costs

Plant	Year of Commissioning	Location	Capacity t/d	Capital Cost in million USD	Operating cost USD/t cocn.
Laizhou Gold Processing Plant	2001	Shandong	100	10	NA-
Axi Gold Mine	2005	Xinjiang	100	6.3	173
Sanhe Gold Ltd.	2006	Jiangxi	150	13.4	141
Jingfeng Gold Mine	2007	Guizhou	790	15.9	159
Hatu Gold Mine	2008	Xinjiang	80	NA	152
Huibao Gold Mine	2012	Liaoning	100	14.3	NA

The capital and operating costs of typical refractory gold bio-oxidation plants are summarized in Table 6.

Similar to the roasting smelter, the capital investment of a bio-oxidation plant depends on the specific required timing, site infrastructure conditions and construction schedule management. The capital cost of a 100t/d bio-oxidation plant was USD 6.3 to 10 million before year of 2010 and USD 14.3 million after year of 2010, respectively.

The operating cost varies with the sulphide content of the concentrates, site power tariffs, infrastructure conditions, labor cost, and tax polices etc. The operating cost ranges from USD 141-173 per ton of concentrates.

Bio-oxidation Industrial Application

Pretreatment of Refractory Gold Concentrate by Bio-oxidation at China Gold Guizhou Jingfeng Gold Mine

Mineralogy

Gold mineralization is typically associated with highly carbonaceous gangue material or cataclastic breccia. Quartz and sulphide (pyrite, arsenopyrite) veins are common, occurring as either steeply-dipping or shallowly-dipping sheeted sets preferentially within sandstone beds. Quartz rich veins contain trace amounts of dolomite, and become more carbonate rich distal to mineralization. Sulfides present in mineralized zones are pyrite, arsenopyrite, cinnabar, stibnite, orpiment, and realgar.

The Jinfeng deposit has many geological and geochemical characteristics in common with the renowned sediment-hosted deposits of the Carlin district in the Western United States, and is best classified as a Carlin-like gold deposit.

The gold concentrates contain gold of 20-40g/t，sulphide of 10-17%, Arsenic of 3-4% and organic carbon of 0.5%. Gold is finely locked in the matrix of pyrite, arsenopyrite or gangue minerals. The direct cyanidation of concentrates, even ground to P80 less than 38 mircon, yields a very poor gold recovery of less than 18%.

Process Description

The bio-oxidation plant was built in July 2005, and commissioned in April 2007 by adopting BIOX technology. The designed capacity is 750 t/d but the actual throughput has dropped to only 400 t/d as result of a significant decrease in mining production.

The principle flow chart of is shown in Figure 5.

The gold concentrate is re-pulped with process water at a slurry content of 20% and pH of 7, depending on the sulphide content and oxidation performance, then pumped into two trains of bio-oxidation in parallel. Each train has eight agitation tanks with four for the first stage oxidation and four for the second stage. The first stage is controlled at pH of 1.6-1.8 and redox potential of 500-600 mv, while the second stage is controlled at pH of 1.2 to 1.6 and redox potential of above 600 mv, using lime stone. The retention time for the first and second stages of oxidation is 2 to 3 days, depending on the sulphide content and oxidation performance. The oxidized slurry is then sent to 3 stages of CCD washing thickeners.

The upflow of the thickener is sent to the solution neutralization circuit to be neutralized using carbonate containing tailings to pH of 5 then further to pH above 7 by using lime, respectively. The neutralized tailings is pumped to tailing dam.

The underflow of thickener with slurry content of 30%, is pumped to an oxidized slurry neutralization circuit using lime, then sent to CIL tanks and leached using cyanide for 24 hours to recover gold. The leaching residues are filtered by a filter press then stacked in a dedicated tailing dam. The free cyanide and arsenic content in solutions of tailing dams are monitored to ensure the water quality meet the environmental permit conditions.

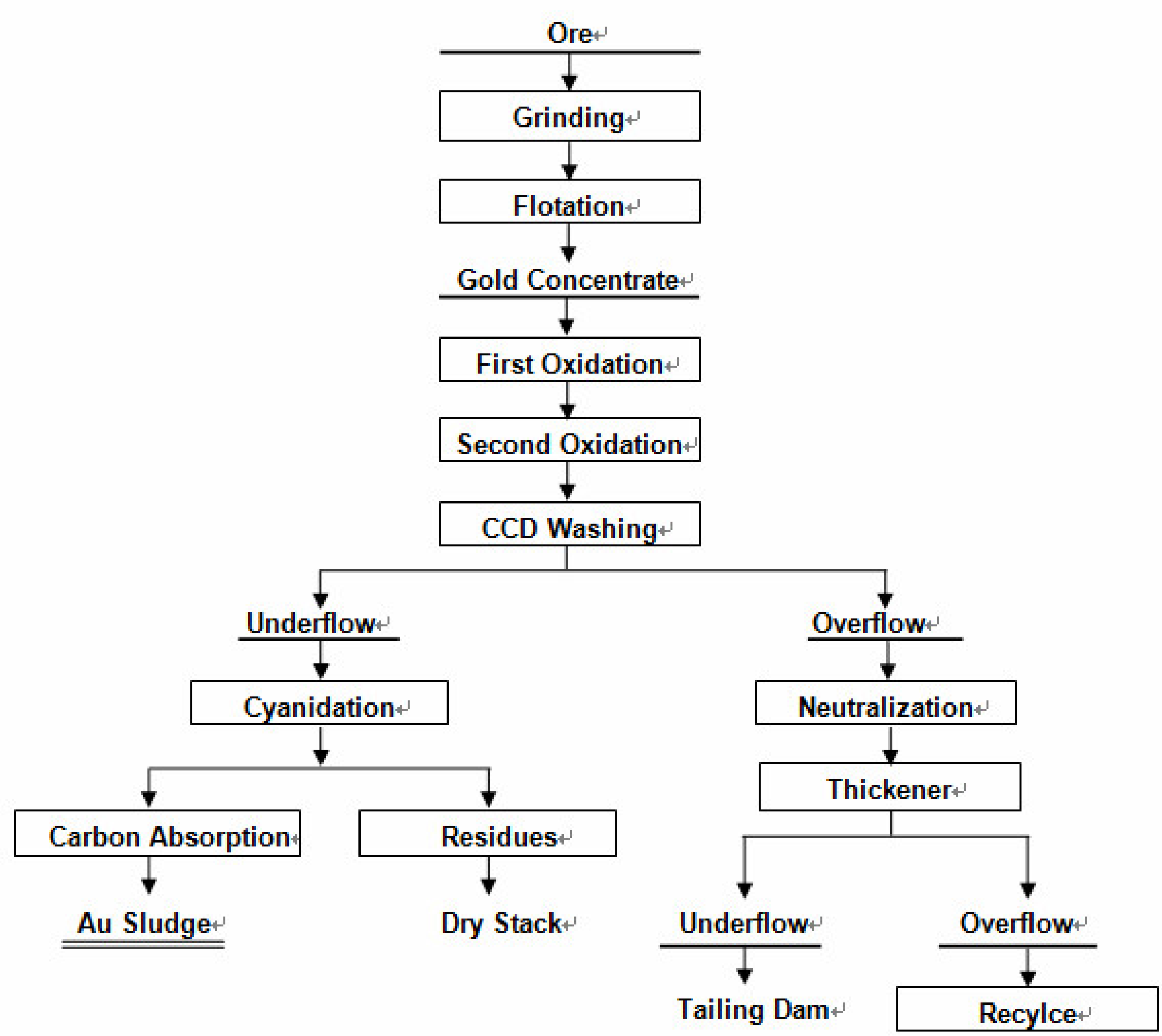

Figure 5: Principle Process Flow Chart of China Gold Guizhou Jingfeng Gold Mine

Pressure Oxidation

The pre-treatment of refractory gold ores by pressure oxidation technology has been studied by research organizations and gold industry since 1995. CCGRI, BRICEM and IPE were quite active in developing different low pressure and high pressure oxidation processes under nonacidic and acidic conditions(19,22). However， there was no successful commercial application of pressure oxidation of refractory gold ores until 2016.

During 2012 to 2014, the State key laboratory for the "comprehensive utilization of refractory gold ores" at Zijin Mining Group Co., Ltd. conducted a couple of continuous tests on pressure oxidation of refractory gold concentrates at its 1 t/d pilot plant and achieved 96% of gold recovery.

Based on the good understanding of the POX process and key equipment such as the autoclave, feed pumps and critical valves, Zijin cooperated with ENFI to design a first POX plant with capacity of 450 t/d at Zijin Guizhou Shuiyindong Gold Mine in 2014. The plant was commissioned successfully in November 2016 and is the first commercial POX plant in China.

Mineralogy

Gold occurs mainly with iron sulphide such as pyrite and arsenopyrite. Carbonate and quartz are gangue minerals. Carbonate accounts for 50% of gangue materials, which indicates that ore needs to be pre-treated with acid to remove carbonate from the slurry fed to the autoclave. Gold occurs as very fine particle with pyrite or homogenously with carbonate or carbonaceous minerals such as hydrocarbon or humic acid. The typical gold mineralogy of ore and concentrate is shown in Table 7.

Table 7: Gold Mineralogy at Shuiyindong Gold Mine

Sample	Unit	Native gold	Encapsulated with Carbonate	Encapsulated with Sulphide	Encapsulated with Silicate	Total Au
Gold conc.	g/t	0.24	0.33	27.1	0.38	28.05
	%	0.86	1.18	96.61	1.35	100.0
Ore	g/t	0.12	0.006	4.3	0.2	4.626
	%	2.59	0.13	92.95	4.32	100.0

Process Description

The principle process flow chart of POX plant at Guizhou Shuiyindong Gold Mine is shown in Figure 6.

The ore slurry with particle size of P90 less than 74 micron is blended with gold concentrates slurry with a particle size of P80 less than 45 microns in a mixing thickener then a storage surge tank. The sulphur content and organic carbon in the mixed slurry are set at 14-18% and less than 4%, respectively. The mixed slurry is pumped into a pre-acidification tank to remove 90% of carbonate by controlled pH at 1.5 using acidic upflow from CCD 1. The acidified slurry is then pumped to a thickener to deliver a slurry with relatively stable sulphur content at a solid content of 40% by weight to a storage surge tank of acidified slurry.

The acidified slurry is pumped into an autoclave operated at temperature of 200-210°C and total pressure of 2400-2800 kPa for an oxidation for an hour. There are four compartments in the autoclave and five agitators, of which two agitators are in the first compartment. The oxygen with purity of 90% produced by a VPSA plant is introduced from the bottom of each autoclave compartment by a sparge gun.

The oxidized slurry is discharged from the autoclave into a flash vessel. The flashed slurry is at about 102°C then flows by gravity into a hot cure circuit. The offgas from the autoclave and flash vessels are vented into a quench tower to be washed by water then discharged into the atmosphere via a stack.

The upflow from the acidification thickener goes to two stages of solution neutralization to neutralize the acid and precipitate metal ions before being discharged to a tailings dam. The first stage of neutralization is conducted using carbonate containing tailings from the flotation circuit to pH 3.5-4, and the second stage neutralization using lime to control pH at 7-9. The solution is then sent to a solution neutralization thickener. The upflow from the thickener is used as process and cooling water. The underflow is pumped to the tailings dam.

The oxidized slurry is pumped into 5 stages of hot cure agitation tanks at a temperature of 95°C, where the basic iron sulphate is broken down to release acid and iron into the solution. Then the slurry is pumped to 3 stages of CCD thickeners. A liquor of 5 g/L free sulphuric acid is used to scrub iron and acid from the oxidized slurry to achieve 98% of washing efficiency. The upflow from the CCD1 is sent to the acidification circuit to digest carbonate gangue materials from the slurry. The underflow of CCD3 is pumped to an oxidizing slurry neutralization circuit then CIL circuit to recover gold with cyanidation. The residue from the CIL circuit is detoxed and then pumped to the tailings dam.

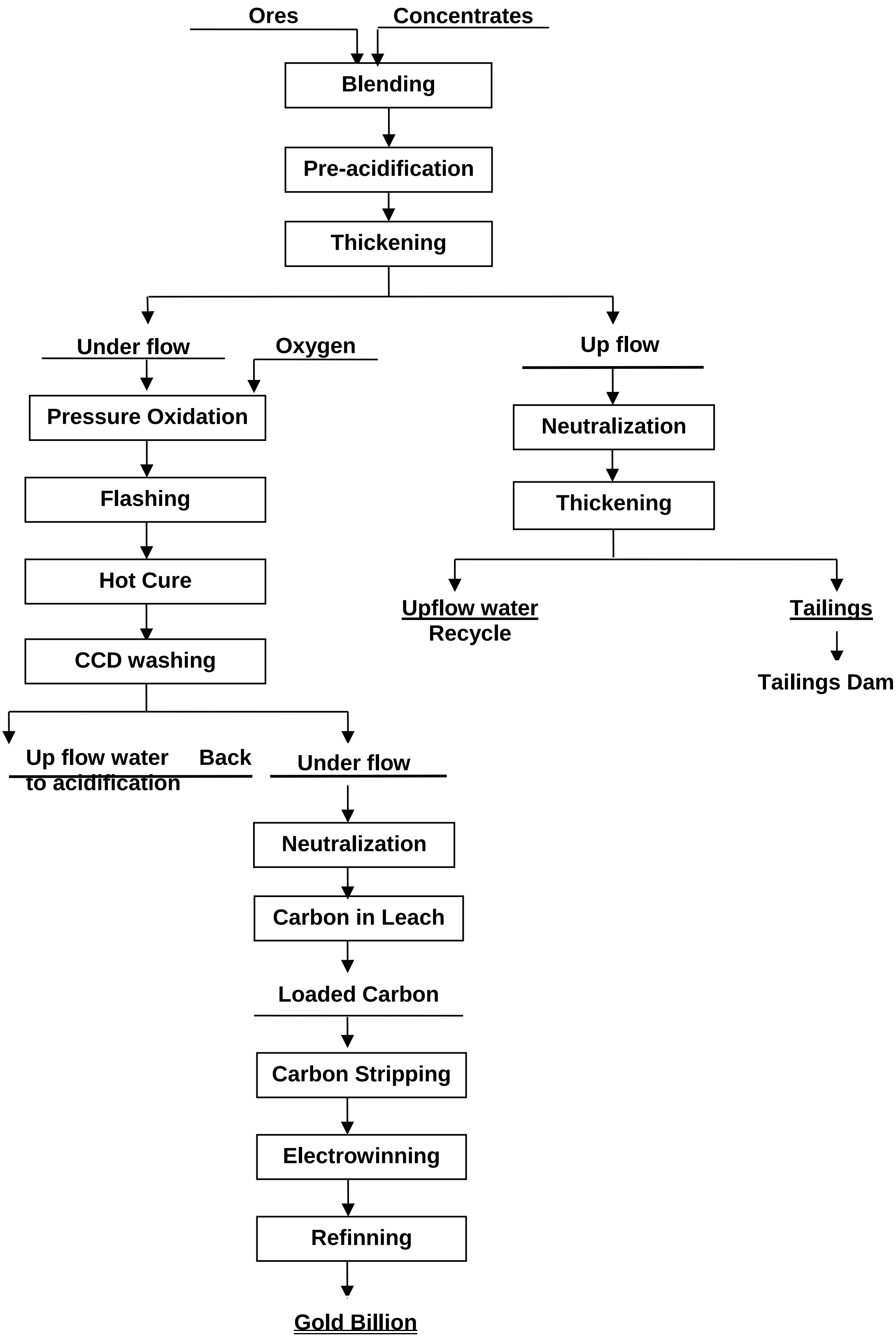

Figure 6: Principle flow chart of Pressure Oxidization Process at Shuiyingdong Gold Mine

The key operating parameters of the POX plant are summarized in Table 8. The operating cost is shown in Table 9.

The total capital for Guizhou Shuiyindong Gold POX Plant is USD 43.4 million (not including CIL circuit).The total throughput in 2017 was 123,590 tons mixed ores containing 17,800 tons of sulphur. A total of 1,670 kg of gold was produced. The total operating cost for oxidation was USD 114/t concentrate.

The POX plant was operated for 300 days in 2017 and reached its designed throughput. The unstable feed of blended refractory gold concentrates has direct bearing on the gold recovery and operating cost. Jarosite was observed in the oxidized slurry and lime boiling was adopted to improve gold recovery by 2-3%.

Table 8：Key Parameters of Guizhou Shuiyindong POX Plant

Circuit	Parameters	Design	Acutal	Remarks
Feed Preparation	Thoughput t/d	400	413	Organic carbon and chloride in slurry higher than design criteria
	S %	18	14.38	
	Au g/t	18.7	13.46	
	Organic carbon%	＜4	4.56	
	Chloride, ppm	＜40	20~100	
Pre-acidification	Temperature℃	80	65	
	Time h	3	4	
	End pH	1.5	1.5~2	
	Removal of Carbonate%	90	85	
Pressure Oxidation	Temperature℃	215~225	200~210	Temperature is reduced to about 210 to avoid impact of chloride on gold preg-robbing.
	Pressure Kpa	3300~3800	2400~2800	
	Time min	60	60	
	S Oxidation %	97	98	
	Free acid in slurry g/L	~40	~50	
Hot Cure	Temperature℃	90~100	80~90	
	Timeh	12	12	
CCD Washing	Stages	3	3	
	Ratio	4	5	
	Washing efficiency	98	96	
Solution Neutralization	Iron removal %	~100	~100	
	As removal %	~100	~100	
CIL	Time h	24	24	Jarosite is observed to be formed in the oxidized slurry and have impact on gold recovery, and lime boil is adopted to improve gold recovery by 2%.
	pH	10~11	10~11	
	Gold recovery%	94	92	

Table 9: The Average Operating Cost of Guizhou Shuiyindong POX Plant in 2017

Item	Total throught t conc.	USD/t conc.	USD/t sulphur
Concentrates processed	123,588.86		
C1 cost		78.3	544.6
Total cost		114.3	795.4

Comparison of Pretreatment Technologies for the Refractory Gold Ores

The comparison of different pretreatment of technologies for the refractory gold ores, namely, roasting, bio-oxidation and pressure oxidation is summarized in Table 10.

Table 10: Comparison of Different Technologies on Pretreatment of Refractory Gold Ores

No	Pre-treatment Technology	Characteristics
1	Roasting	• Treatment of arsenic, antimony and telluride containing carbonaceous gold ores or concentrates. • Has long application history but has become less attractive since 2010. • Applicable to treat different kinds of ores of sulphide contents with variability. • SO_2 and As_2O_3 are emitted during the roasting，need to be absorbed and treated before discharge. • The strict environmental regulations on air emission makes the capital and operating costs of roasting and emitted off-gas treatment increasingly high.
2	Bio-oxidation	• Treatment of arsenic containing gold concentrates not applicable to ores as yet. • Slow oxidation kinetics and takes 48-72 hours to achieve oxidation of 80% plus • Not applicable to high sulphide content gold concentrates • Applicable to partial oxidation of sulphide to deliver a good gold recovery depending on gold mineralogy. • To control gold and sulphide ratio at 1 g/t Au to 1% S to achieve an economic return. • Relatively high capital and operating cost but small scale • Environmentally not as attractive as pressure oxidation for arsenic treatment.
3	Pressure oxidation	• Treatment of arsenic containing refractory gold ore and concentrates. • Treatment of carbonaceous refractory gold ores needs to be integrated with downstream process to ensure gold recovery. • High oxidation efficiency and gold recovery. 5-10% higher than roasting or bio-oxidation. • Arsenic is oxidized a stable scorodite that could be stored safely in tailing dam. • Applicable at large scale compared with roasting and bio-oxidation • Relatively high capital cost and complex technology, high maintenance requirements but with highest gold recovery.

CONCLUSIONS

The treatment of refractory gold ores has been a major challenge in China's Gold Industry for the past two decades. Different pre-treatment technologies such as roasting, bio-oxidation and pressure oxidation were developed and commercialized to make the utilization of the refractory gold ores more efficient and environmentally friendly.

Roasting was the first pretreatment technology developed and commercialized in China. The application of two stage roasting technology provided a viable route for gold recovery from the arsenic bearing refractory gold ores or concentrates but the further treatment or storage of derived arsenic oxide imparts huge pressure on the roasting plants. With the strict environmental regulations on air emission implemented by the Chinese Government, the capital and operating costs of roasting and emitted off-gas treatment has become increasingly high. Roasting has become less attractive and is in decline since 2010.

Bio-oxidation was the second technology commercialized for pre-treatment of refractory gold concentrates but at a relatively small scale of less than 150 t/d. There was a trial of bio-heap leach of refractory gold ores in China, developed by Northeastern University, but it was not commercialized at industrial scale. Depending on the gold mineralogy, bio-oxidation has the advantage of partial oxidation of sulphide to deliver a good gold recovery and reduces the downstream neutralization cost of the oxidized solution. The arsenic treatment by this technology is not as good as pressure oxidation.

Pressure oxidation is the latest method applied in China for the pretreatment of refractory gold concentrates. The first POX plant was commissioned successfully by Zijin Mining Group at Guizhou Shuiyindong Gold Mine in 2017. Although POX is very mature technology for the pre-treatment of gold whole ores or concentrates, there are many challenges in its application, which have restricted its adoption in China. These include:

- Manufacture, transportation and installation of autoclaves in remote mine sites.
- Small gold mines have difficulty in maintaining stable sulphur and gold feeds to the autoclave
- Lack of experienced process engineers and operators for POX plants.
- Relatively high operating cost of POX compared with other technologies such as BIOX.
- Expensive componentry such as isolation valves, discharge and let down valves. The high wear rate on these components, due to high temperature and acidity conditions, requires the plant to have some (more) scheduled downtime. These critical components often have long delivery times.
- Relatively high content of organic carbon and sensitivity to chloride concentration can lead to gold loss in tailings

Some key lessons learned from the commissioning this first POX plant are as follows:

- Provide oxidized environment for the autoclave circuit during hot and acid commissioning
- Material selection and testing for pipeline and valves is vital for POX operation
- The acidity of the underflow of CCD3 and carry over in the vent gas need to be monitored to maintain a good scrubbing efficiency to reduce the lime consumption
- A feed mixing and preparation system is critical to maintain stable sulphur containing feed and operation of autoclave
- The chloride and sodium content in the feed needs to be monitored and controlled to reduce the gold loss in the tailings

Zijin is cooperating with the Central South University to develop a process integrating pressure oxidation and non-cyanide leaching. The oxidized acidic slurry is leached directly by thiourea without neutralization. The technology is now being studied at laboratory scale.

With the increasing ratio of refractory gold resources of over 50% in total gold resources, there will be huge potential for development and application of pretreatment technology in China. At this stage, POX is believed to be the most viable and competitive technology for the treatment of refractory gold ores or concentrates at large scale and offers an acceptable environmental solution.

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