

# PILOT PLANT EVALUATION OF A HYBRID BIOLOGICAL LEACHING-PRESSURE OXIDATION PROCESS FOR AURIFEROUS ARSENOPYRITE/PYRITE FEEDSTOCKS

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## ABSTRACT

A process has been evaluated, on a continuous pilot plant scale, to treat refractory gold arsenopyrite/pyrite concentrates. The process consisted of biological leaching to partially oxidise sulphides, followed by pressure leaching for complete sulphide oxidation and arsenic precipitation, followed by liquor neutralisation and cyanidation of the autoclave residue for gold recovery. This paper provides a brief description of the treatment flowsheet and discusses some of the main parameters and results of the process.

During integrated pilot plant campaigns, it was confirmed that acceptable sulphide oxidation and gold extraction of 96-98% could be achieved by a two-stage oxidation with BIOX<sup>®</sup> (4 days total retention time) followed by POX (40 minutes retention time at 220°C). Only partial arsenic precipitation was achieved in the autoclave, followed by complete precipitation by neutralization under atmospheric conditions.

The overall process could be significantly simplified, and capital and operating costs reduced, with a flowsheet modification allowing all of the BIOX<sup>®</sup> liquor to bypass the autoclave directly to the neutralization circuit.

## INTRODUCTION

For several years, TVX Hellas Company has been developing the Olympias property in Greece. The deposit consists of a pyrite concentrate stockpile, a zinc flotation tailings stockpile and in-situ ore reserves. Run-of-mine ore was proposed to be milled and floated in a two-stage flotation circuit to produce lead and zinc concentrates, followed by flotation of the remaining sulphides in the zinc tailings to produce a gold-containing arsenopyrite/pyrite concentrate.

Previous studies indicated that pressure oxidation of the Olympias pyrite concentrate, as compared to bacterial oxidation, resulted in similar or slightly higher gold recovery at significantly lower cyanide consumption. Capex estimate of the pressure oxidation process was higher than bacterial oxidation, but a significant portion of the arsenic was precipitated in the autoclave as an environmentally stable compound.

A feasibility study was conducted at SGS Lakefield facilities to investigate the possibility of treating the refractory pyrite concentrates using a combina-

tion of bacterial oxidation (BIOX<sup>®</sup>) and pressure oxidation (POX) technologies. By combining the two technologies, the majority of the sulphide sulphur present in the concentrate (approximately 70%) could be oxidised with air by applying the BIOX<sup>®</sup> process. This left a relatively small portion of the sulphides to be oxidised with oxygen in an autoclave to complete the oxidation and precipitate the arsenic.

The BIOX<sup>®</sup> section of the dual process could be designed to produce a partially oxidised product containing sufficient residual sulphur to ensure autothermal operation of the autoclave. Based on extensive bench scale testwork and previous pilot plant campaigns, the recommended process flowsheet is illustrated in Figure 1.



showed that the stockpile concentrate contained mostly pyrite, while the ROM and PEC concentrate blends contained a larger percentage of arsenopyrite. The gold was present as submicroscopic particles in arsenopyrite and arsenic-rich pyrite. There was virtually no free gold present and only a small percentage of the gold was associated with gangue minerals.

Continuous flotation pilot plant campaigns were conducted at SGS Lakefield on the ROM 2001-2003 and PEC ores. The flowsheet involved the use of cyanide as pyrite depressant during base metal flotation. It was observed that the cyanide reacted with sulphides to form thiocyanate, which 'adsorbed' onto the pyrite concentrate surfaces. Thiocyanate is highly toxic to the BIOX® bacteria, even at a fairly low concentration of above 2 mg/L CNS in solution. Therefore, washing of the concentrate prior to the BIOX® circuit was found to be extremely important.

## PILOT PLANT DEMONSTRATIONS

### BIOX® CIRCUIT

The BIOX® program and circuit operation were directed by TVX Hellas and GoldFields Mining Services Ltd. representatives. The circuit was operated on a 24-hour basis for 160 days by TVX and SGS Lakefield personnel. The main objective of the continuous BIOX® circuit

was to produce semioxidised BIOX® product as feed to the continuous POX circuit. These pilot plant campaigns presented the first opportunity to treat the fresh concentrate blends in a continuous mode. All previous piloting had been conducted on the stockpile concentrate only. The BIOX® process uses a mixed culture of thiobacillus ferrooxidans, thiobacillus thiooxidans and leptospirillum ferrooxidans to break down the sulphide mineral matrix. The active inoculum produced during small pilot plant operations in Greece was shipped to Lakefield for reactivation and inoculation in the pilot plant reactors.

The BIOX® plant consisted of two identical trains of one primary reactor and two secondary reactors fabricated from stainless steel. Figure 2 is a photograph showing the BIOX® pilot plant, and Figure 3 - the continuous autoclave.

The primary reactors had an un-aerated volume of 622 litres each and the secondary reactors, 208 litres each. The plant was designed to treat 100 kg concentrate per day, at a retention time of 5 days, 3 days in the primary stage and 1 day per each secondary stage. This arrangement allowed a reduction in retention time by taking the secondary reactors off line, should this prove to be necessary.

The pilot plant was controlled at the following operating conditions:

Liquid/Solid Ratio 4/1 and 5.7/1
Liquid/Solid Ratio 4/1 and 5.7/1
Slurry pH 1.2 to 1.8
Dissolved Oxygen Concentration 2 to 6 mg/L

The pilot plant was fed on a continuous basis at a pre-determined rate to give a specific retention time. The required nutrient salts, consisting of ammonium sulphate, ammonium phosphate and potassium sulphate, were added to the feed make-up tank.

The slurry pH was controlled by manual addition of limestone slurry. Limestone was also added to the feed make-up tank to give a total carbonate content of 3% in the feed to the plant. The average limestone consumption, depending on the feed composition, was in the range of 125-250 kg/t.

The oxygen uptake rate (which is an instant measurement of the rate of oxygen depletion in an active inoculum and probably the most important criterion in assessing bacterial activity) was measured routinely. Ferric and ferrous iron concentrations were also measured routinely, as well as redox potential.



Figure 2 – Continuous BIOX®



Figure 3 – Continuous Autoclave Agitator Assemblies

The following samples were regularly taken from the circuit: feed samples, profile samples from each reactor, and final products from each train. Typical results from the continuous operation are illustrated in Figure 4 and summarised in Table 2.

BLEND	TANK	RETENTION TIME DAYS	SOLIDS ANALYSES						SOLUTION ANALYSES		
			S <sup>=</sup>	S <sup>0</sup>	S <sup>SO4</sup>	S <sub>TOTAL</sub>	As	Fe	As	Fe	SO <sup>4</sup>
			%	%	%	%	%	%	g/L	g/L	g/L
	Feed	-	39	-	-	-	9.0	39	-	-	-
1	Primary	3	17	6	8	31	2.1	20	19	69	44
	Secondary R1	1	5	9	12	26	1.3	13	21	78	48
	Secondary R2	1	2	9	13	24	1.0	11	22	80	49
2	Feed	-	29	-	-	-	11.3	31	-	-	-
	Primary	3	16	6	28	28	3.4	20	30	67	41
	Secondary R1	1	5	8	23	23	1.4	11	35	82	48
3	Feed	-	32	-	-	-	11.0	33			
	Primary	3	14	7	28	28	5.3	21	28	63	36
	Secondary R1	1	8	8	26	26	2.8	15	41	86	46

Table II – BIOX® Pilot Plant Results

sulphides and other sulphur species. A percentage of the BIOX® solution was decanted from the slurry and bled directly to the neutralisation circuit. The design target of the bleed was 10% volume, with the actual volume varying between 10 and 25%, depending on the BIOX® discharge slurry density. The BIOX® product must contain enough residual sulphides and elemental sulphur to maintain auto-thermal operation of the autoclave. Therefore, it was established that the BIOX® plant only required a primary and one secondary stage to achieve the required level of sulphide oxidation. The residual sulphide grade in the BIOX® discharge was controlled by varying the number of reactors on-line and the reactor configuration.

Based on the pilot plant results, the following plant operating parameters were recommended by GoldFields Mining Services:

Feed Slurry Density 20% solids
Operating pH in primary and secondary reactors 1.2 to 1.7
Operating Temperature 40 to 45°C
Retention Time Primary reactors 3 days Secondary reactors 1 day

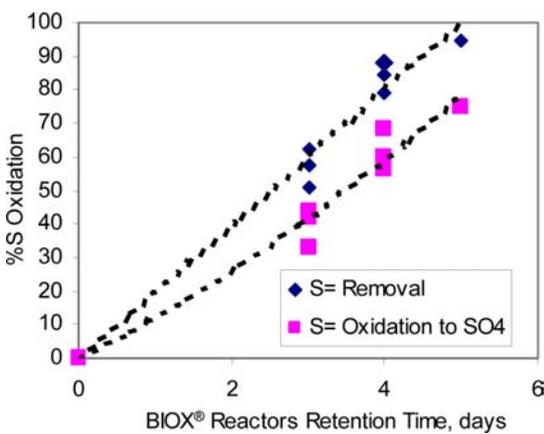


Figure 4 – Sulphide Oxidation as a Function of Retention Time

correlation between the operating pH, iron and arsenic Figure 2 – Continuous BIOX® Figure 3 – Continuous Autoclave Agitator Assemblies dissolution and the formation of elemental sulphur. It is likely that the formation of elemental sulphur in the BIOX® discharge is due to the slower kinetics of the last step of conversion of elemental sulphur to sulphate. More elemental sulphur is produced as the overall sulphide removal increases, but only a fraction of the elemental sulphur further reacts to form sulphate. It is generally expected that thiobacillus thiooxidans would oxidize sulphur to sulphate but, surprisingly, this was not demonstrated during the pilot plant campaign. The high levels of oxygen uptake rate have indicated that the bacteria was quite active in all reactors, therefore it is unlikely that the sulphur production resulted from direct ferric leaching without bacteria. The precise mechanism is, however, not known. The iron and arsenic dissolution averaged 60- 75% and 80-90% respectively, with the BIOX® liquor containing up to 85 g/L Fe (mostly as ferric) and 40 g/L As.

The bacterial activity was very high during the pilot plant operation, with an average sulphide sulphur removal over 90% after 5 days; however, the sulphide oxidation to sulphate was considerably lower due to the formation of elemental sulphur or polysulphide species.

The elemental sulphur content in the BIOX® discharge was initially in the order of 10-11%, but later stabilised between 7-9%. The reasons for the presence of so much elemental sulphur were not clearly understood. The analytical data suggested that there was no clear

The BIOX® circuit discharge was forwarded to a pressure oxidation stage to complete the oxidation of residual

**POX CIRCUIT**

The main objective of the POX circuit was to oxidise all residual sulphides and sulphur present and to expose gold for extraction by cyanide leaching. Additional objectives were to precipitate out arsenic as a stable precipitate and to produce final effluents meeting industrial standards. The test program was designed in consultation with SNC-Lavalin and TVX Hellas representatives.

SGS Lakefield’s continuous horizontal autoclave, constructed of Grade 12 titanium, is 172.7 cm in length with an inside diameter of 25.0 cm, and is divided into six compartments by means of weir plates. Oxygen gas is sparged at controllable flow rates into all compartments. The oxygen is normally

PARAMETERS	CAMPAIGN 1		CAMPAIGN 2				CAMPAIGN 3			
	POX FEED	POX DISCHARGE	POX FEED	POX DISCHARGE			POX FEED	POX DISCHARGE		
A/C Conditions										
Temperature, °C	-	225	-	225	225	225	-	225	225	225
Time, min	-	70	-	70	40	30	-	65	50	36
Solution Analyses										
As, g/L	20	13	15	5	8	9	14	7	7	10
Fe, g/L	65	60	48	22	24	34	48	34	35	45
SO <sub>4</sub> , g/L	140	300	80	190	190	200	93	190	185	230
FA, g/L	<10	47	<10	62	56	44	<10	41	46	37
Fe/As Molar Ratio	4.4	6.2	4.3	5.9	3.9	5.2	4.6	6.5	6.7	6
Solids Analyses										
As, %	3	6	2	5	5	5	2			
Fe, %	20	22	16	22	21	22	18			
S <sup>=</sup> , %	15	0.2	6-11	0.1	0.1	0.7	11	0.23	0.19	0.19
S <sup>o</sup> , %	10	<0.5	7-10	<0.5	<0.5	<0.5	9	<0.5	<0.5	<0.5
Results										
Au Extraction, %		98		98	98	97		96	97	98
S <sup>=</sup> Oxidation %	-	99	-	99	98	85	-	96	98	98
As precipitation, %	-	50	-	85	79	72	-	86	85	75

Table III – Pressure Oxidation Pilot Plant Results

distributed with greater than 80% of the total flow directed into the first two compartments. Total oxygen flow is typically in the order of 28-40 litres per minute.

Three continuous integrated pilot plant campaigns were conducted on each pyrite concentrate blend, partially oxidised by the BIOX® process. Autoclave feed comprised principally of BIOX® product, with small additions of untreated pyrite concentrate in order to achieve the target sulphide plus sulphur grade of ~15%. This value was determined by the MetSim model as the minimum amount of sulphide sulphur for auto-thermal autoclave operation. The target solid content varied between 15 and 20% solids. The autoclave feed contained approximately 10% elemental sulphur. Quebracho or Lignosol were added at a rate of 5 kg/t and 2.5 kg/t respectively, as an elemental sulphur dispersant, to prevent occlusions by sulphur of unreacted sulphide particles. Autoclave target operating conditions were 225°C, 100 psig oxygen overpressure and 30 to 70 minutes nominal residence time.

Filtered and washed autoclave discharge and compartment samples were submitted for neutralisation-cyanidation/CIL for the recovery of gold and silver. The tests were conducted in a batch mode. The samples were neutralised at 30% solids with hydrated lime to pH 11, for at least 12 hours in order to reach a stable pH prior to cyanidation. Activated carbon was added at 10 g/L solution and CIL was carried out at 0.5 g/L NaCN for 24 hours. A summary of the autoclave campaign results is presented in Table 3. The results indicated that sulphide sulphur oxidation was typically greater than 95% after 30 minutes in the autoclave. Elemental sulphur conversion to sulphate was greater than 98% after 10 minutes in the autoclave.

The fast kinetics of oxidation of sulphide and elemental sulphur indicated that the risk of sulphide occlusion by elemental sulphur was minimised by the addition of Lignosol. In association with the sulphide and sulphur oxidation, iron conversion from ferrous to ferric was greater than 98%. Similarly, arsenic oxidation to As(V) was greater than 98%; the residual As(III) solution concentration was about 120 mg/L. Kinetic profiles of sulphide

oxidation versus gold and silver recovery are illustrated in Figure 5 and 6.

The results showed that gold recoveries closely followed the sulphide sulphur oxidation profile. Gold extraction from the autoclave discharge was excellent and averaged 96-98%, leaving a residue assaying 0.3-0.9 gAu/t cyanidation residue. Silver extraction was in a range of 50% only. Silver extraction was around 50% only, probably due to formation of silver jarosite. No attempts were made to improve silver extraction in this testwork campaign. Sodium cyanide and lime consumptions for the autoclave discharge composites were in the range of 1 kg/t and 80-90 kg/t of cyanidation feed, respectively. Lime consumption versus autoclave retention time is illustrated in Figure 6. Mineralogical analysis of selected autoclave discharge and compartment samples suggested that the major phase present was a basic iron sulphate, which is a fairly unstable compound that reacts with lime during the neutralization stage prior to cyanidation.

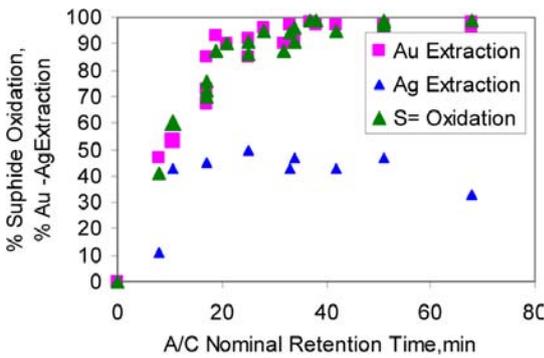


Figure 5 – S<sup>=</sup> Oxidation and Gold Extraction as a Function of A/C Retention Time

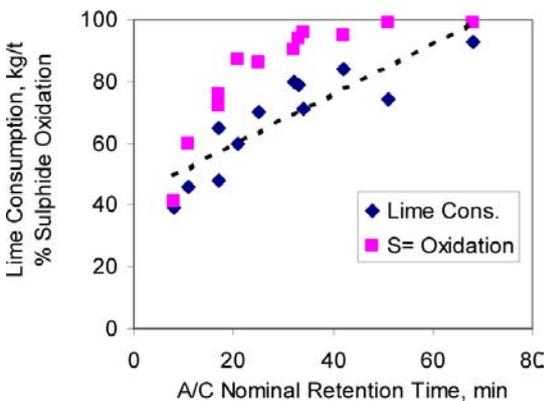


Figure 6 – Lime Consumption as a Function of A/C Retention Time

Arsenic precipitation efficiency was evaluated based on arsenic distribution between the solid and solution phases. The distribution of arsenic to the solids increased from 20 to 40% in the feed to 60-80% in the discharge as illustrated in Figure 7.

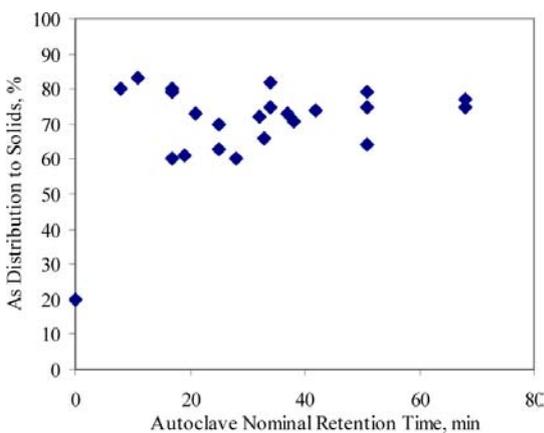


Figure 7 – As Distribution to Solids as a Function of Autoclave Retention Time

The profile of arsenic precipitation across the autoclave suggested that arsenic precipitated as an unstable compound in the first compartment, followed by redissolution in the second compartment and re-precipitation as a stable compound in the last two

compartments. The re-dissolution of the precipitate in the second compartment appeared to coincide with an increase in free acid formation through sulphur oxidation.

In simple arsenic-acid systems, it is well known that the solubility of arsenic increases with increasing acidity, with a minimum solubility in the pH range 3 to 5. The high acid level in the autoclave discharge, 40-60 g/L, must be one of the reasons for the high residual arsenic in solution.

The results obtained during the autoclave pilot plant campaigns indicated that the residual arsenic and iron in the autoclave discharge depended to a certain extent on the initial arsenic and iron concentration in the POX feed/BIOX<sup>®</sup> discharge, with relatively high soluble iron and arsenic in the feed to POX (campaign 1) leading to relatively high arsenic in solution in the POX discharge. Arsenic precipitation in the autoclave was only ~50% in campaign 1, versus ~85% in campaigns 2 and 3.

The iron to arsenic ratio is probably also important, since work by Monhemius and Swash (1) has shown that the precipitation of scorodite or other ferric-arsenate components is inhibited at higher Fe/As ratios, in the presence of sulphuric acid. Mineralogical analyses indicated that the arsenic department was poorly defined; arsenic was present as a low-level constituent of the iron sulphate; there was no evidence of calcium arsenate.

Arsenic-rich Fe sulphate formed rounded radial structures ranging from 4 to 25µm in diameter, as shown in Figure 8. This phase was the primary host for arsenic in the sample.

The structures may represent intimate intergrowth of basic Fe-sulphate and hydronium jarosite, but incorporated arsenic in their lattice. Arsenic was also identified as "Type 1" Fe arsenate.

SEM-EDS analysis of these grains identified a composition rich in iron and sulphur, with minor amounts of arsenic.

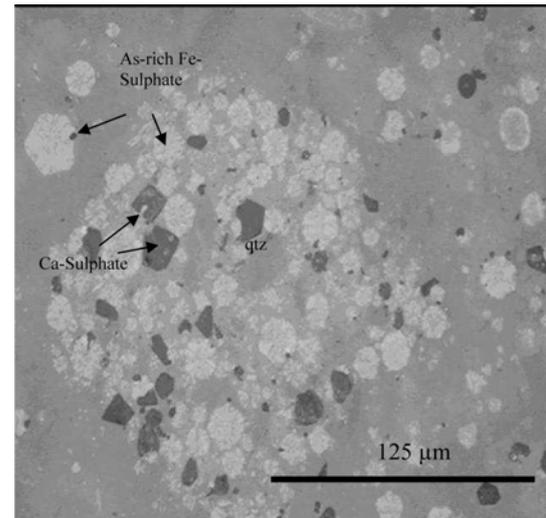


Figure 8 - Autoclave Discharge - As-Rich Fe-Sulphate

### SOLID/LIQUID SEPARATION AND LIQUOR TREATMENT

The autoclave discharge slurry and the small bleed of the BIOX<sup>®</sup> liquor that by-passed the autoclave were combined and treated in a multi-stage continuous CCD/neutralisation circuit. The feed to the oxidation/neutralization circuit contained 7-10 g/L As(V), 125 mg/L As(III), 20-30 g/L Fe and 90-140 g/L SO<sub>4</sub>. The main objectives of this stage of the pilot program were to: demonstrate at a pilot plant scale, that the residual As(III) present in solution can be effectively oxidised to As(V) using SO<sub>2</sub> and air as an oxidant; precipitate arsenic as a stable product suitable for disposal; and produce final effluent that meets industrial regulatory limits.

As(III) oxidation was carried out in a series of three cascading 45L tanks, with additions of sodium metabisulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) and air into each oxidation tank. The results of preliminary scoping testwork indicated that the SO<sub>2</sub> requirements for complete conversion of As(III) at a pH of ~0.4 was 10-15 times the stoichiometric requirements for the amount of As(III) in solution. Gas addition was kept at 1 vessel volume per minute, and the SO<sub>2</sub> concentration at 1% of the gas (v/v).

Overall equivalent SO<sub>2</sub> consumption during the pilot plant test was 2.5 g/L of oxidation feed. This consumption equates to an average addition of 27 moles of SO<sub>2</sub> per mole of As(III). The SO<sub>2</sub> consumption was not optimised during

the pilot plant campaign. Retention time within the oxidation circuit was 4.2 hours.

Liquor neutralisation was conducted in two stages with the use of "high density sludge" recycle mode. Each neutralisation stage was carried out in three 60L neutralisation tanks with mechanical agitators. Compressed air was sparged into all tanks in order to maintain the oxidising environment, the temperature was maintained at 40°C.

During the first stage of neutralisation, the pH of the blended feed solution was adjusted to pH 5.5-6 by introducing limestone from the Olympias mine site. The second stage of neutralisation was carried out with commercial hydrated lime additions to pH ~9.2. Retention time within each neutralisation stage was approximately 3 hours.

The second stage neutralisation discharge was transferred to a thickener for solid-liquid separation. The thickener underflow was divided, with approximately 66% being recycled to the first tank.

Overall alkali consumption, during the neutralisation stage, including limestone and lime (CaO equivalent), was in the range of 600 kg/t limestone and 200 kg/t lime per tonne of autoclave discharge solids. The final neutralised solution met industrial effluent standards for the required elements.

In order to determine the stability of the final waste products, samples of the neutralised sludge, the CCD underflow and the CIL residue were submitted for TCLP 1311 leachate testing. The results showed that the concentrations of all the elements in the leachates for the samples tested were below regulatory limits. However, elevated concentrations of manganese (Mn) and zinc (Zn) were observed in the leachates of the neutralisation sludge samples.

## CONCLUSIONS

From intensive and integrated pilot plant campaigns, it was confirmed that:

- Acceptable sulphide oxidation could be achieved by two-stage oxidation with BIOX® (4 days) followed by POX (40 minutes at 220°C).
- Gold extractions from the POX discharge were excellent, ranging from 96-98%, with only 1 kg/t NaCN consumed but lime consumption was high at 80-90 kg/t under the conditions tested.
- Arsenic precipitation in the autoclave varied between 50-80% due to the high acidity. Complete precipitation was achieved by neutralisation.
- As(III) in the BIOX liquors could be readily oxidised to As(V) by SO<sub>2</sub>/air
- Neutralisation of the plant liquors (BIOX® and POX) was successful, resulting in effluents meeting effluent standards.
- The results of TCLP 1311 testing of the final waste products yielded leachates that were below regulatory limits, confirming that arsenic had been stabilised.

The Olympias process could be simplified, and capital and operating costs significantly lowered, if all of the BIOX® liquor was allowed to bypass the autoclave directly to the neutralisation circuit. In this regard, the following factors are pertinent:

- The precipitate produced during neutralisation under atmospheric conditions can be as stable as the ferric arsenate compound produced in the autoclave, as indicated by the most recent research findings (Monhemius and Swash).
- The total residence time in the autoclave was determined by the rate of ferric arsenate precipitation (50-70 minutes) rather than the rate of sulphide and sulphur oxidation (30-40 minutes). The autoclave size could therefore be significantly reduced, if the autoclave design was based solely on the requirement for efficient gold recovery.
- Bypassing the BIOX® liquor around the autoclave will reduce the iron, arsenic and sulphate concentration in the feed

to POX, which will in turn decrease the acid generated by iron precipitation and increase the efficiency of precipitation of any remaining arsenic in the autoclave.

- It will also allow the feed to the autoclave to be adjusted to the required density and sulphide plus sulphur concentrations for auto-thermal autoclave operation. Therefore, it will not be necessary to blend untreated pyrite concentrate with BIOX® discharge in the POX feed to achieve the required heat balance. This will further reduce the size of the autoclave and lower capital costs.

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