

IS ALKALINE GLYCINE A CONTENDER FOR DIRTY COPPER CONCENTRATE?

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ABSTRACT

A new hydrometallurgical approach to extracting gold, silver and copper from various sources has recently been proposed. This approach uses alkaline glycine as the lixiviant, and the results of an appreciable amount of exploratory laboratory-scale work have been published.

This paper presents an early-stage evaluation of the process economics potentially associated with the application of alkaline glycine to the processing of a copper sulphide concentrate that is not suitable for smelting because of its high arsenic content. This work uses process and capital cost modelling to evaluate:

- Conventional POX processing, in which the sulphide is oxidised under pressure.
- Alkaline glycine chemistry applied to the extraction of copper, at ambient pressure.

The results of this study are presented as calculated variable, fixed operating and capital costs and simple cash flow analyses, comparing the POX and alkaline glycine technologies.

Keywords: Alkaline glycine, POX, copper, arsenic, sulphide, costs

INTRODUCTION

In a keynote address to the Alta 2016 Nickel-Cobalt-Copper Conference, Ken Baxter of SNC-Lavalin, Australia, presented a review of copper production technology and addressed the question of whether or not hydrometallurgy is likely to replace pyrometallurgy as the dominant means of producing copper ⁽¹⁾. His review covered a number of developing hydrometallurgical technologies for the production of copper from concentrate and presented a case study of pressure oxidative leaching (POX) technology, currently the only commercially established hydrometallurgical route for treating concentrate that is too high in arsenic for conventional smelting.

Recently proposed novel chemistry, not mentioned in the above review, uses alkaline glycine as the lixiviant for processing copper ore or concentrate ^(2,3). An early-stage comparison of the alkaline glycine approach to conventional cyanidation, presented at the 2016 Alta Gold-PM Conference, indicated that the alkaline glycine approach may well be competitive with cyanide, at least for the copper-bearing gold ore assumed ⁽⁴⁾. From that, a logical question would be whether or not the alkaline glycine chemistry might be worth developing for the extraction of copper from feeds not amenable to pyrometallurgy.

This paper presents a comparative early-stage study of the extraction of copper from an arsenic-bearing copper sulphide concentrate that is not suitable for smelting. The study examines the application of alkaline glycine chemistry and established POX technology to the recovery of metallic copper from this concentrate, along with gold and silver as a precious metal concentrate.

The purpose of this work is to help determine whether or not the alkaline glycine chemistry merits the extensive effort and cost that would be required to develop it from concept to viable technology for the production of copper.

CONCENTRATE

The concentrate chosen for this study was copied from the third case study presented by Ken Baxter (complete hydrometallurgical processing) at the 2016 Alta NCC Conference ⁽¹⁾. Table 1 shows the elemental analysis of this concentrate and Table 2 lists a suite of minerals that back-calculates to the elemental analysis in Table 1.

Table 1 - Concentrate assay

Cu	28%
As	8.84%
Fe	23%
S	32.5%
Ag	300 g/t
Au	10 g/t

Table 2 – Concentrate mineralogy

Cu ₃ AsS ₄	46.5%
CuFeS ₂	15.9%
FeS ₂	22.1%
FeOOH	12.5%
SiO ₂	3.0%
Ag	300 g/t
Au	10 g/t

ASSUMPTIONS AND APPROACH

For the purposes of this study, the annual processing rate was set to 530 000 tonnes of concentrate per year, at 8 000 operating hours per year. The location was assumed to be North America and the plant was assumed to be a greenfield project, but to not include the mining and concentrate

production facilities, nor other infrastructure such as an electrical sub-station, as those would be common to the various processing options. For the circuits examined, copper dissolution was assumed to be 97 percent, gold dissolution 95 percent and silver dissolution 90 percent (as in the abovementioned case study).

For each circuit, a numerically-rigorous mass-energy balance was built using commercially available flowsheet simulation software known as AspenPlus®. The mass-energy balance was then electronically exported to commercially available cost estimation software known as Aspen Process Economic Analyzer® (APEA), in which the various volumetric flows are mapped to the appropriate process equipment for each unit operation and materials of construction and the required residence time or equipment dimensions are specified. The APEA software uses the volumetric flows and other inputs to size each item of process equipment and calculate the amounts of material and manpower needed to fabricate and install that piece of equipment. It then draws on databases of material and labor costs to calculate the installed cost of each item of process equipment and the entire circuit. The APEA software uses correlations based on a large number of actual projects to assign allowances for process piping, valves and electrical systems. It also applies civil engineering rules to calculate quantities of concrete for foundations and steel for supporting structures, and it calculates estimates of engineering design and EPCM costs, etc. Further details on this have been presented previously ⁽⁵⁾, along with examples showing that this approach generates capital cost estimates that are within the normal uncertainty of preliminary engineering studies.

CIRCUITS

Established POX technology similar to the third case study of the 2016 review ⁽¹⁾ by Ken Baxter was chosen as a baseline for this work. The newcomer, an approach using alkaline glycine chemistry, is based on information published by Curtin University ^(2,3).

POX

Figure 1 illustrates the circuit using POX technology. The incoming sulphide concentrate is slurried with recycled water and pumped into the autoclave stage. The solids content of the slurry entering the autoclave is set to make the pressure leach autogenous at 220°C. The corresponding pressure is 32.5 bar absolute. Oxygen is injected into the autoclave, causing the reactions listed in Table 3. The fractional conversions refer to the first component listed for each reaction. The last two reactions are modelled as equilibrium reactions, using the data in the AspenPlus database, to account for residual iron and arsenic in the solution leaving the autoclave.

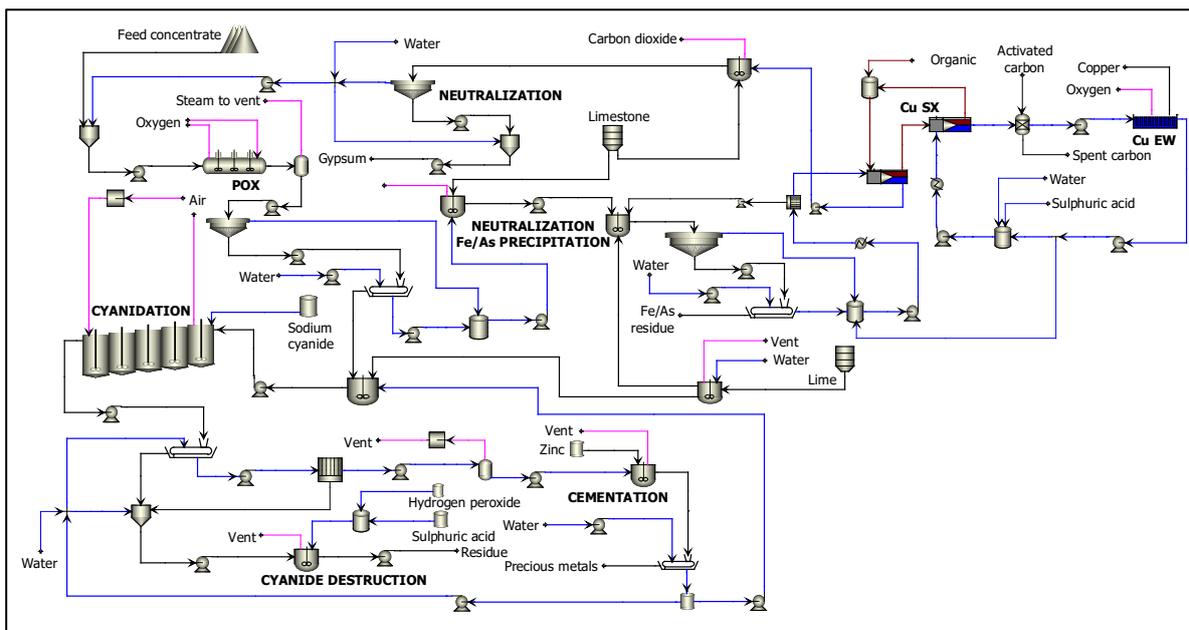


Figure 1 - POX circuit

Table 3 – POX stoichiometry

Stoichiometry	Conversion
$\text{Cu}_3\text{AsS}_4 + 2\frac{1}{2}\text{H}_2\text{O} + 8\frac{3}{4}\text{O}_2 \rightarrow 3\text{CuSO}_4 + \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4$	0.970
$2\text{CuFeS}_2 + 2\text{H}_2\text{O} + 8\frac{1}{2}\text{O}_2 \rightarrow 2\text{CuSO}_4 + \text{Fe}_2\text{O}_3 + 2\text{H}_2\text{SO}_4$	0.970
$2\text{FeS}_2 + 4\text{H}_2\text{O} + 7\frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4$	0.970
$\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$	Equilibrium
$2\text{H}_3\text{AsO}_4 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + 3\text{H}_2\text{O}$	Equilibrium

The slurry leaving the POX step is flashed to atmospheric pressure and thickened. The thickener underflow is filtered, the filter cake is washed with fresh water and the combined filtrate is added to the thickener overflow. The washed leach residue is mixed with a slurry of slaked lime and recycled barren solution, and pumped to the cyanidation train, where sodium cyanide and air are added to dissolve the gold and silver via the conventional chemistry shown in Table 4.

Table 4 – Cyanidation stoichiometry

Stoichiometry	Conversion
$4\text{Au} + 8\text{CN}^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow 4\text{Au}(\text{CN})_2^- + 4\text{OH}^-$	0.950
$4\text{Ag} + 8\text{CN}^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow 4\text{Ag}(\text{CN})_2^- + 4\text{OH}^-$	0.900

The slurry exiting the cyanidation train is filtered and the filter cake is washed with recycled barren solution, then re-slurried with more recycled barren solution and treated with Caro's acid (hydrogen peroxide and sulphuric acid) to destroy the cyanide prior to final disposal of the residue. The filtrate is passed through a polishing filter and a vacuum de-gassing step to remove dissolved oxygen, then contacted with zinc powder to recover the gold and silver by cementation, the zinc addition being twice the stoichiometric amount. The resulting cementation slurry is filtered and the filter cake is washed with fresh water and recovered as a precious metal concentrate for onward processing elsewhere. The filtrate, now barren, is recycled.

The supernatant from the thickener after the POX step, combined with the filtrate from the thickener underflow, is contacted with limestone to neutralize the free acid, then with lime to precipitate the residual iron and arsenic as ferric hydroxide and arsenical ferrihydrite⁽⁸⁾. The resulting slurry is thickened, the thickener underflow is filtered, the filter cake is washed with water and the washed filter cake leaves the circuit.

The iron- and arsenic-free thickener overflow and filtrate are combined with a small bleed of spent electrolyte from the electrowinning section, cooled and passed through a polishing filter, any solids captured being sent back to the Fe/As precipitation step. The polished filtrate goes to the copper solvent extraction section, where it is contacted with conventional copper extractant/diluent in four parallel trains, each with two mixer-settler stages in series, extracting essentially all of the copper into the organic phase. The loaded organic phase is stripped with spent electrolyte in four parallel trains of two mixer-settlers in series. The stripped organic phase is recycled to the extraction step. The copper-loaded aqueous phase is passed through activated carbon to remove entrained or dissolved organic compounds, and the resulting advance electrolyte is passed through conventional copper electrowinning, the resulting copper cathodes being the copper product. The spent electrolyte, less a small bleed (to the aqueous feed tank ahead of the solvent extraction section) and with replenishment of water and sulphuric acid, returns to stripping in the solvent extraction section.

The barren raffinate from the extraction step of the solvent extraction section is neutralised with limestone, the resulting slurry is thickened and the thickened gypsum leaves the circuit. The supernatant is used to slurry the incoming sulphide concentrate ahead of the POX step.

Alkaline glycine

Figure 2 illustrates the first alkaline glycine circuit examined. This circuit is based on research published by the Western Australian School of Mines at Curtin University^(2,3). Incoming sulphide concentrate is slurried with recycled solvent extraction raffinate and milled from its initial particle size range of about 80% passing 40 μm to about 80% passing 7 μm . The fine-milled slurry is then pumped into a leach train in which the copper minerals are dissolved via the stoichiometry listed in

Table 5. Make-up glycine is added to hold the total glycinate concentration at 0.1 M in the solution exiting the leach and slaked lime is added to hold the pH of the leach at 11. The incoming lime is slaked with raffinate from the copper solvent extraction section. The conversion of the copper minerals was assumed to be 97 percent, the dissolution of gold was assumed to be 95 percent and the dissolution of silver was assumed to be 90 percent (the same as in the POX circuit). For simplicity, the iron and arsenic leached were assumed to reprecipitate completely as solid goethite and johnbaumite, but the actual chemistry, especially the arsenic chemistry ⁽⁹⁾, is likely to be more complex than this and should be investigated properly if this technology is to be developed further.

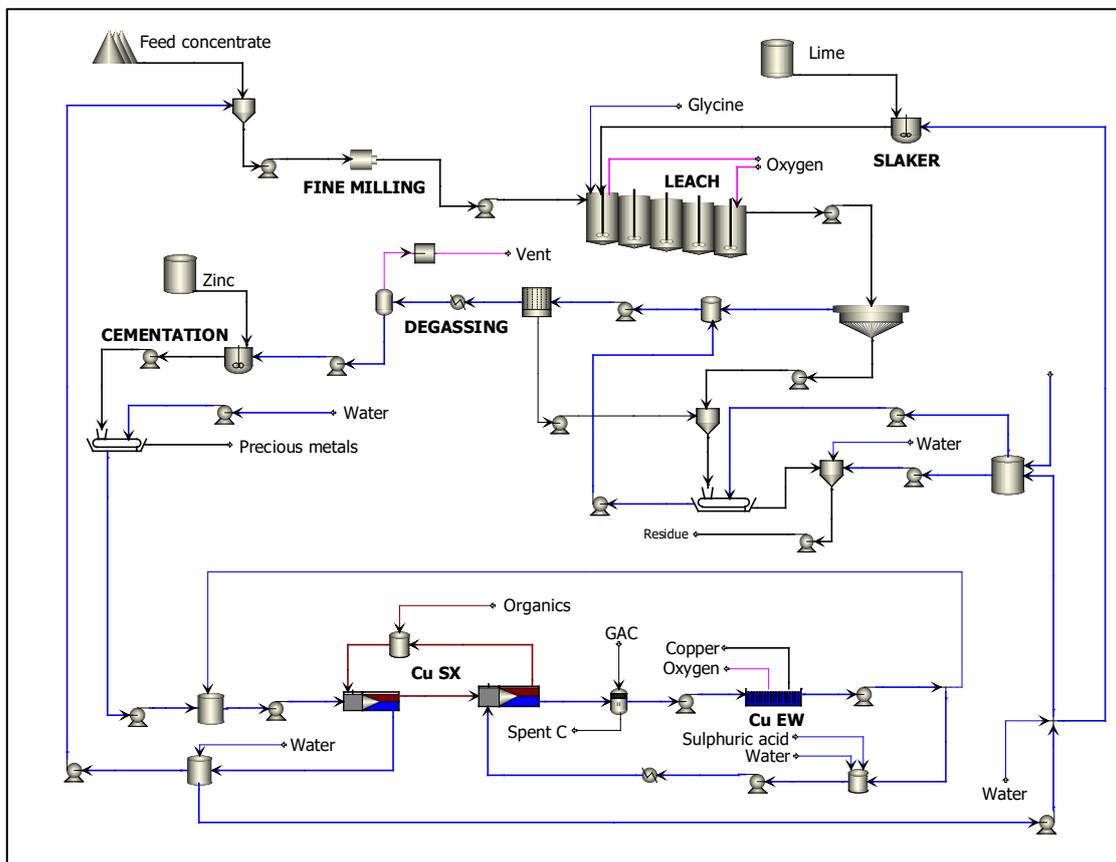


Figure 2 – Alkaline glycine circuit 1

Table 5 – Alkaline glycine leach stoichiometry

Stoichiometry
$\text{Cu}_3\text{AsS}_4 + 2\text{OH}^- + 8\frac{3}{4}\text{O}_2 + 6\text{H}_2\text{NCH}_2\text{COO}^- + \frac{1}{2}\text{H}_2\text{O} \rightarrow 3\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2 + \text{H}_3\text{AsO}_4 + 4\text{SO}_4^{2-}$
$2\text{CuFeS}_2 + 4\text{H}_2\text{NCH}_2\text{COO}^- + 8\frac{1}{2}\text{O}_2 + 4\text{OH}^- \rightarrow 2\text{Cu}(\text{H}_2\text{NCH}_2\text{COO})_2 + 4\text{SO}_4^{2-} + 2\text{FeOOH} + \text{H}_2\text{O}$
$3\text{H}_3\text{AsO}_4 + 5\text{Ca}(\text{OH})_2 \rightarrow \text{Ca}_5(\text{AsO}_4)_3\text{OH} + 9\text{H}_2\text{O}$
$4\text{Au} + \text{H}_2\text{NCH}_2\text{COO}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Au}(\text{H}_2\text{NCH}_2\text{COO})_2^- + 4\text{OH}^-$
$4\text{Ag} + \text{H}_2\text{NCH}_2\text{COO}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Ag}(\text{H}_2\text{NCH}_2\text{COO})_2^- + 4\text{OH}^-$

The leached slurry is pumped to a thickener, the thickener underflow is filtered, the filter cake is washed with raffinate from the solvent extraction section, re-slurried with the remaining raffinate and water, and pumped to disposal. The filtrate is combined with the supernatant from the thickener, passed through a polishing filter and sent on to degassing and cementation of the gold and silver with zinc powder. Any solids captured in the polishing filter join the solids going to the thickener underflow filter.

In the cementation section the gold and silver are recovered according to the stoichiometry shown in Table 6, zinc addition being twice the stoichiometric amount. This chemistry has not been experimentally demonstrated; it is merely a convenient assumption for this exercise. If a process such as this is to be developed, experimental verification of the cementation step would be prudent. The resulting slurry is filtered, the filter cake is washed with water and the washed filter cake leaves as a precious metal concentrate for further treatment elsewhere.

Although it might not be necessary in reality, for this work the assumption was that glycine, being an amino acid, could degrade if heated too much, so the evaporation step was assumed to require sub-atmospheric pressure with the concentrated solution boiling at 60°C, the same temperature as the leach. The steam evolved is then recompressed and used to supply the evaporation energy on the hot side of the evaporation heat exchanger. (While this works in cyberspace, it is a risky assumption for reality, as fouling of the heat exchange surfaces could be a significant challenge. The reason for using this assumption was to evaluate the effect of glycine capture and recycle from the residue leaving the circuit.) The remaining concentrated liquid is pumped back to atmospheric pressure and recycled via the lime slaker. The extent of water evaporation from the raffinate is manipulated to maintain the desired overall water balance, and the condensate from the hot side of the evaporation heat exchanger is used to re-slurry the washed leach residue before it is pumped to disposal, with some extra water added to make the slurry suitable for pumping.

Reverse osmosis was also evaluated for removing water from the raffinate, but calculations showed the pressure required for the necessary water separation to be over 400 atmospheres, which is unrealistically high, therefore reverse osmosis was dropped in favor of the evaporation approach.

RESULTS

Table 8 lists the variable operating costs calculated for the circuits illustrated in Figure 1, Figure 2 and Figure 3. The column headed POX is the numbers for the POX circuit. The column headed AG1 is for the alkaline glycine circuit illustrated in Figure 2, allowing glycine to leave the circuit in the final residue. The column headed AG2 is for the alkaline glycine circuit illustrated in Figure 3, in which evaporative concentration is used to prevent loss of glycine in the residue leaving the circuit. The column headed AG3 is for the circuit illustrated in Figure 2, assuming 20 percent instead of about 5 percent solids in the slurry entering the leach. The experimental work was done at about 5 percent solids into the leach, hence this value in the first two alkaline glycine cases. The point of case AG3 was to see whether or not reducing the total volume of the leach reactor train would make an appreciable difference to the cost of the process. Making the slurry entering the leach train four times higher in its solids content makes the leach train's required volume correspondingly smaller for the same residence time, reducing the capital cost. The modelling work used the assumption that mixing power is 0.5 kW per m³ of mixed reactor volume, so lower total volume also means lower operating costs for that section. (It might be that a more-dense slurry requires more agitator power per unit volume, but for this exercise the assumption used was 0.5 kW/m³ of active volume regardless of slurry density.)

Table 8 – Operating costs, \$/lb Cu

Reagent/utility	POX	AG1	AG2	AG3
Incoming concentrate (\$17/t)	0.029	0.029	0.029	0.029
Oxygen (\$80/t)	0.109	0.072	0.072	0.072
Glycine (\$1500/t)	-	0.071	0.000	0.210
Sodium cyanide (\$2500/t)	0.004	-	-	--
Lime (\$150/t)	0.013	0.117	0.116	0.117
Limestone (\$60/t)	0.099	-	-	-
Sulphuric acid (\$200/t)	0.008	0.000	0.000	0.000
Hydrogen peroxide (\$1000/t)	0.002	-	-	-
Zinc powder (\$2500/t)	0.001	0.001	0.001	0.001
Electricity (\$0.1/kWh)	0.130	0.156	0.172	0.117
Fresh water (\$2/m ³)	0.012	0.012	0.015	0.015
Cooling water make-up (\$1/m ³)	0.002	0.007	0.007	0.006
Variable operating cost	0.410	0.464	0.412	0.566
Fixed operating cost	0.024	0.022	0.036	0.019

The oxygen cost is higher in the POX circuit than in the alkaline glycine circuits because all the pyrite in the feed is oxidized in the autoclave step, while the alkaline glycine leach does not attack pyrite.

The first glycine circuit, in which glycine is lost in the leach residue (AG1), has a higher variable operating cost than the second glycine circuit (AG2), because of the amount of fresh glycine required. The variable operating cost calculated for the POX circuit is lower than those of all the alkaline glycine cases examined.

In case AG3 the concentrate slurry enters the leach at 20 percent solids, approximately four times higher than the other two alkaline glycine cases. Although that does make the overall electricity cost lower, by lowering the cost for agitation in the leach, it makes the circuit run at higher copper, and thus also higher glycinate levels, resulting in a higher loss of glycine to the final tailings and thereby negating any potential advantage to be had from the lower capital and leach agitation costs.

Table 9 lists the capital costs calculated for the POX circuit and the variations of the alkaline glycine circuit. Cases AG1 and AG2 were assumed to leach at the solids content used in the laboratory tests on which these models are based, i.e. about 5 percent solids into the leach, which is lower than might be considered efficient because it makes the leach reactors rather large and thus more expensive than necessary. Cases AG3 assumed 20 percent solids in the slurry entering the leach.

Table 9 – Capital costs, \$ per annual tonne Cu capacity

Category	POX	AG1	AG2	AG3
Purchased Equipment	834	658	1720	649
Equipment Setting	6	5	8	6
Piping	768	746	767	730
Civil	161	130	138	105
Steel	199	199	200	196
Instrumentation	317	304	310	302
Electrical	140	135	144	126
Insulation	99	100	105	92
Paint	15	13	13	12
Other	694	635	771	603
G & A Overheads	93	84	121	81
Contract Fee	92	85	112	81
Contingencies	615	557	794	537
Total Project Cost, \$/t-y Cu	4031	3650	5203	3520

Table 10 is a listing of the fabrication and installation costs of the process equipment, for the various cases examined in this study. All of the cases were set up to produce the same amount of copper, so the electrowinning section would be expected to be the same and to have the same cost in all cases. Similarly, the solvent extraction section processes the same amount of copper in all the circuits, if at different feed tenors, so the cost of that section would also be expected to not differ substantially.

Table 10 – Equipment fabrication and installation costs, \$/tonne annual Cu capacity

Section	POX	AG1	AG2	AG3
Cu electrowinning	1338	1334	1334	1340
Cu solvent extraction	462	436	439	458
Precious metal recovery	29	68	66	34
Cyanide destruction	10	-	-	-
Fine milling, leach	-	295	294	185
Glycine recovery, water recycle		4	777	4
Cyanidation	187	-	-	-
POX and solid-liquid separation	299	-	-	-

The capital cost calculated for the POX circuit in this exercise is lower than the corresponding number (about \$5200 per annual tonne of copper production) from the study presented in 2016 ⁽¹⁾. That study did not present a breakdown of the capital cost estimate, so explaining that difference is

not possible. It may be due to differences in the choice and sizing of the equipment chosen, or the capital cost for the 2016 study might include items that were not included in this study because items common to all the circuits cancel out in the comparative evaluation for which the costs were generated in this exercise. The absolute numbers generated in this exercise matter less than the differences between the costs calculated for the various cases examined. These costs were all calculated by the same method, so while the absolute results quite probably differ appreciably from other studies, the relative differences remain meaningful.

As might be expected, case AG3, with the concentrate slurry entering the leach at about 20 percent solids instead of the 5 percent solids assumed for the other alkaline glycine cases, has smaller, and thus less expensive, leach reactors. However, the installed equipment cost, and therefore also the total capital cost, is dominated throughout by the capital costs of the electrowinning and solvent extraction sections, which are almost the same throughout. That diminishes the impact of differences between cases in the capital costs of the other sections on the relative economics of the various cases.

DISCUSSION

The calculated capital costs are restricted to the process equipment illustrated in Figure 1, Figure 2 or Figure 3. For an actual project, there would be other items in the costing, for example infrastructure such as buildings, access roads, fencing, tailings disposal facilities, electrical sub-station, etc., but these would be the same throughout and would therefore cancel out in differential comparisons.

The calculated capital and operating costs of the different cases are conveniently compared by simple cash flow analysis. Figure 4 shows the internal rate of return (IRR) numbers calculated for the different cases examined, versus the duration of the project. The assumptions used for these calculations are listed in Table 10. Depreciation was included in the cash flow analyses via the declining balance method ⁽⁹⁾. The IRR curves flatten out between about ten and fifteen years of project duration, meaning that project durations longer than that would not really alter the profitability, if the internal rate of return is the primary determinant.

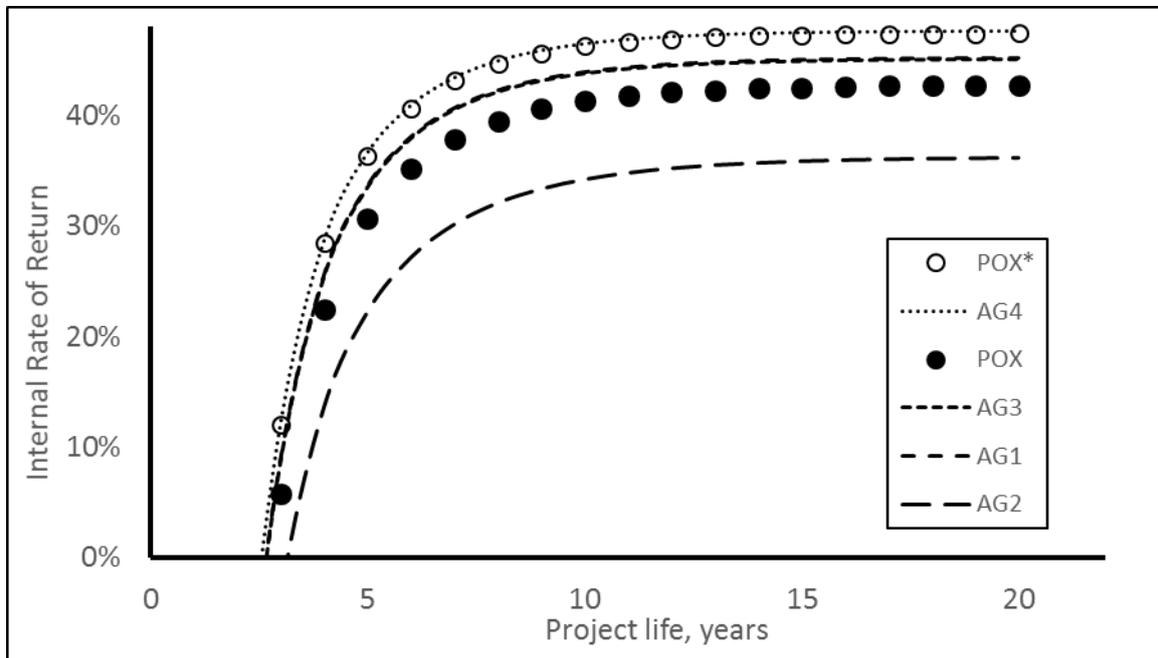


Figure 4 – IRR results

While the actual IRR numbers calculated in this exercise make it look like a rather profitable project, items that would be common to all the cases (sub-station, buildings, tailings facility, etc.), are not included in the costs, thus the calculated IRR numbers are higher than they would be were all the common equipment included, and only the differences between cases are meaningful.

Simplistically, the higher the internal rate of return, the more economically attractive the project. By that measure, it would appear that the POX technology could be matched by the alkaline glycine technology, at least for the concentrate used in this exercise, but not by a significant margin.

Table 11 – Cash flow assumptions

Capital expenditure in year -1	50%
Capital expenditure in year 0	50%
Production in year 1	25%
Production in year 2	50%
Production in year 3	75%
Production in year 4 onwards	100%
Copper selling price (\$2.7/lb)	\$5952/t
Silver selling price (\$13/oz)	\$434/kg
Gold selling price (\$607/oz)	\$19514/kg
Tax rate	35%

Intuitively, one might expect that limiting the loss of glycine from the alkaline glycine circuit would lead to better overall economics, but the numbers generated in this exercise show that the extra capital cost associated with not allowing glycine out with the final residue outweighs the savings in glycine, at least if the required process equipment is as assumed for case AG2.

The IRR curves for cases AG1 and AG3 are virtually identical. The reduced capital cost of case AG3, at 20 percent solids into the leach versus about 5 percent solids in case AG1, is balanced by increased loss of glycine to the final tailings. That is because at the higher solids into the leach, the circuit operates at a higher copper concentration after the leach, thus also at a higher glycinate concentration. Without some as-yet undiscovered cost-effective way of reclaiming glycine from the tailings, as the in-circuit concentrations go up, so does the concentration of glycine in the tailings because the tailings are washed with solvent extraction raffinate.

The curves labelled POX and POX* (the open and filled symbols, respectively) are for the POX case with and without the contingency allowance in the capital cost. The difference between these two curves is, simplistically, a measure of the uncertainty in the IRR calculations. By that evaluation, the IRR curves for cases AG1 and AG3 are within the uncertainty range of the POX case, and thus not economically stronger. The IRR curve for case AG2 is below the lower POX curve by more than the uncertainty in the POX curve.

The curve labelled AG4 in Figure 4 is a spurious variation on case AG3, with the cost of make-up glycine set to zero. Even this spurious case, assuming either zero-cost make-up glycine or some presently undefined way of preventing glycine loss that does not entail any extra capital or operating cost, does not lift the alkaline glycine approach above the upper POX curve.

CONCLUSIONS

The results of this study indicate that the alkaline glycine chemistry does not offer process economics that are superior to the established pressure oxidation technology. Unless the assumptions used in this exercise are incorrect, the ongoing expenditure of significant effort, time and money on developing the alkaline glycine technology for processing arsenic-bearing chalcopyrite concentrates like the one assumed for this exercise is probably not warranted. The associated resources would be better applied to the processing of other copper feeds such as low grade oxides and/or to copper-bearing gold ores.

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