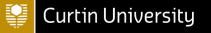
Development of alkaline glycine processing technology & its evaluation within the circular hydrometallurgy context



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1st International Circular Hydrometallurgy Symposium Mechelen, Belgium 9-11 September 2024



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Natural Flake Graphite

The Circular Economy and Critical Minerals

- The dominant use of Critical Minerals in the Energy Transition requires that the minerals, and their associated metals and materials are extracted, converted and refined in sustainable ways to ensure that we don't pollute the earth under the banner of achieving clean energy.
- Sustainability in processing requires a circular approach to everything we do.
- Historically our metallurgical technological approaches have been linear value chains:
 - We used the cheapest extractants (sulfuric acid, cyanide, lime) irrespective or the carbon footprint of their production, or that their production were associated with fossil fuels (sulfur from oil refineries, NH₃ from Haber-Bosch process).
 - The back end of the process often led to large waste/tailings heaps and toxic residues from leaching, still bearing some associated reactants e.g., red mud from bauxite, gold ore leach residues, etc., and neutralization products e.g. jarosite, gypsum and Na₂SO₄.
 - Water was seldom recovered, recycled and reused with loss of excess reactants.
 - Energy integration (in metallurgical processes) have been minimal
 - Toxicity and environmental impacts were often related to lower priority than economic benefit.



Spodumene (Li)



HPA (Alumina)



Pentlandite (Ni)



Platinum

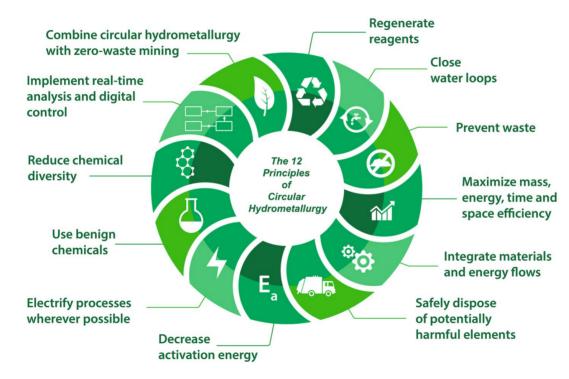


The need for a new chemical-metallurgical approach

- <u>Water scarcity</u> (and water of the appropriate quality) has raised the value of water and has incentivized <u>recovery of water</u> (and water-soluble reagents). Conversely water rich areas cannot afford the pollution of their waterways.
- The reducing cost trend of <u>renewable energy</u> (with energy storage) has shifted the costs <u>manufacturing bulk reagents</u> (such as H₂, O₂, NaOH, CL₂ and HCL, green ammonia) and has made them worthwhile to consider as alternative reagents.
- Conventional fossil fuels will not disappear, but there is a big driver to rather convert them into value-added products of higher complexity than burning them to CO₂. This includes the manufacture of benign <u>organic reagents for the metallurgical industry</u>.
- The <u>recovery</u> of effluent <u>water</u> implies that more expensive <u>reagents</u> can be considered as they themselves can be recovered (assuming they are stable and can be concentrated from water).
- Many <u>organic acids are crystalline and allows easy reconcentration</u> in cheap materials of construction. On the other hand, most inorganic acids (H₂SO₄, HCl, HNO₃, H₂SO₃, HF, and HCN) are difficult to reconcentrate, either because of their extreme affinity for water or due to the formation of high boiling azeotropes, or extreme corrosivity or decomposition (HNO₃). Conversely, the volatility of some (HCN, HF decomposition of H₂SO₃) creates challenges.



The 12 Principles of Circular Hydrometallurgy: Process development towards circularity



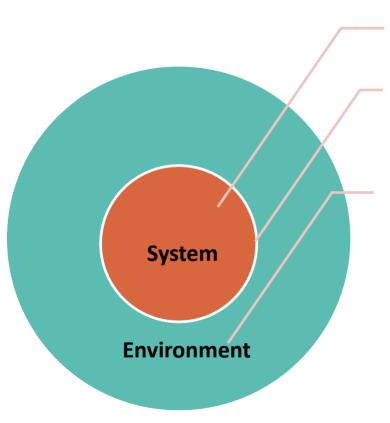
From: Binnemans, K., and Jones, P.T., 2022. The Twelve Principles of Circular Hydrometallurgy. Journal of Sustainable Metallurgy, p. 1-25 <u>https://doi.org/10.1007/s40831-022-00636-3</u>,



The constraints created by the resources to be processed

- Our choice of reagents and processing options are typically highly constrained by the nature of the solid material we need to treat:
 - Rapidly deteriorating grade of metals of interest
 - Polymetallic nature of resources (complexity of separation without losses)
 - Difficulty in physical upgrading of oxide/silicate ores
 - Finely disseminated mineralization and emulsion mineral textures
 - Large amounts of acid-consuming gangue
 - Large amount of acid-leachable Mg & Fe & large uptake in leachates
 - Oxygen demand linked to reactive (but non-valuable) sulfides
 - Stability and leachate retention of the leach residues
 - The electrochemical, semiconductor and passivation characteristics of minerals
 - The shear quantity of material to be treated (e.g. gold ore vs e-waste, iron ore vs. Rare-earthore)
- The attributes of the solid material to be leached often is the biggest constraint in our freedom to select reagents, and is often associated with the biggest cost, safety and environmental impacts.
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The Controlled System & its Uncontrolled Environment



The System:

The process chemistry & development that we can influence through design, manufacture and control. Principles of Circular Hydrometallurgy essential

The Interface:

Qualify & quantify as much as possible

The Environment:

Disturbances we need to manage while minimising the impacts on it. We cannot control our environment, only adjust & adapt to it. Examples include:

Ore/raw materials / feed attributes

Water quality and quantity

Energy attributes (Renewable? / reliability? / Affordability?/ CO2 Footprint)

Legal Frameworks

Community

Surrounding Industry

Customer Specifications

Waste / effluent /emissions constraints



The challenges of polymetallic ores: Au-Cu example

- Many of the world's precious metal (Au, Ag, PGMs) ores are polymetallic. Thus, they co-occur with base metals such as Cu, Fe, Zn, Pb and Ni/Co in their oxide, silicate, sulfide or arsenide forms.
- A prime example is gold ores with nuisance copper (where Au grades may be 1 ppm and Cu grade at 0.1%). On it own the Cu grade often doesn't justify economic recovery.
- However, copper is a major consumer of cyanide reagent during gold leaching (and there is often >1000x more Cu than gold, but it's is worth only 0.00011 of the value of gold).
- Also, Cu forms higher order complexes of cyanide than Au; Compare: $[Cu(CN)_4]^3$ to $[Au(CN)_2]^-$.
- While the Au-CN complex is very stable, the [Cu(CN)₄]³⁻ complex releases cyanide with changing pH, making it dangerous (so called "weak-acid-dissociable cyanide" or WAD cyanide).
- CN^{-} recovery and detoxification of the $[Cu(CN)_{4}]^{3-}$ is expensive and a "linear" (end-of-pipe) approach
- Cyanide costs are high and pH excursions may lead to dangerous and volatile HCN to form.
- To extract Cu before Au, often involves expensive and inefficient pretreatment with H₂SO₄ and pH swings as the process progresses from base metal extraction to precious metal extraction.
- Many ores are located in dry/arid areas where water management and recovery is essential.



In the Cu-Au example, cyanide-based processes fail the test of the 12 principles of circular hydrometallurgy

- 1. Regenerate reagents
- 2. Close water loops
- 3. Prevent waste
- 4. Maximize mass, energy, space, and time efficiency
- 5. Integrate materials and energy flows
- 6. Safely dispose of potentially harmful elements
- 7. Decrease activation energy
- 8. Electrify processes wherever possible
- 9. Use benign chemicals
- 10. Reduce chemical diversity
- 11. Implement real-time analysis and digital process control 11. Measurement of free CN and complexes difficult
- 12. Combine circular hydrometallurgy with zero-waste mining

- 1. Reagents consumed with poor or no recovery
- 2. Water is mostly not recovered
- 3. Significant cyanide bearing waste
- 4. Detoxification, pretreatment leads to plant complexity, excess reagent consumption
- 5. No integration
- 6 Problematic
- 7. No catalytic action by Cu, rather it can decrease overall Au recovery to CIP.
- 8. Little opportunity for electrification
- 9. Chemicals are highly toxic and used in large amounts
- 10. Diverse range of chemical by-products (Cu-Cn complexes)
- 12. CN-Tailings hard to reintegrate back into mining



Developing a new process achieving circularity for Cu-Au ores

- 1. During 2012-2013 J.J. Eksteen and E.A. Oraby investigated a process to extract, recover and refine precious metals and base metals that either eliminated or minimised the use of cyanide for precious metals and sulfuric acid for base metals.
- 2. Under optimised alkaline conditions precious metals such as Au, Ag and Pd could be leached in the absence of cyanide, or under cyanide starved conditions using amino acids.
- 3. While several amino acids were evaluated, it was found that the simplest one, glycine (NH₂CH₂COOH), was the most suitable given kinetics, reagent cost and reagent consumption.
- 4. Under alkaline conditions, base metals could be leached from the sulfide minerals (with an oxidant) and oxide minerals. By raising the temperature and redox potential, Au, Ag and Pd could be leached in alkaline glycine in the absence of cyanide, or at room temperature in the presence of only a fraction of the cyanide used conventionally.
- 5. It didn't form higher order complexes with copper, as for cyanide.
- 6. The presence of copper glycinate catalysed the leaching of gold.
- 7. Silver could be leached as well.
- 8. The pH and leach conditions were similar to current industrial leaching.
- 9. The Au and Ag glycinates adsorbed well onto activated carbon, making CIP and CIL technology possible.
- 10. Cyanide detoxification could be minimised or eliminated.
- 11. pH changes between base metals and precious metal leaching could be averted.
- 12. Copper can be recovered by sulfide precipitation, IX and SX.
- 13. Reagent is easily recoverable and recyclable and follows recycled tailing water.
- 14. Direct electrowinning of copper possible from glycinate solutions.



Glycine Chemistry versus Cyanide Chemistry

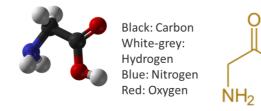
Gold-copper-glycinate speciation	Gold-copper-cyanide speciation						
Au(Gly) ₂ -	Au(CN) ₂ -						
Cu(Gly) ₂	Cu(CN) ₂ ⁻ , Cu(CN) ₃ ²⁻ , Cu(CN) ₄ ³⁻						
Other:	Other						
GlyH, Gly⁻	CuCN (s), HCN(aq), CNO ⁻ , CNS ⁻ , HCN(g), CN ⁻ , [Fe(CN) ₆] ⁴⁻ .						
# Species: 4	# Species: 11						
Gly = Glycinate anion, i.e. $NH_2CH_2COO^2$ GlyH = Glycine, i.e. NH_2CH_2COOH							



Why Glycine at Alkaline pH?

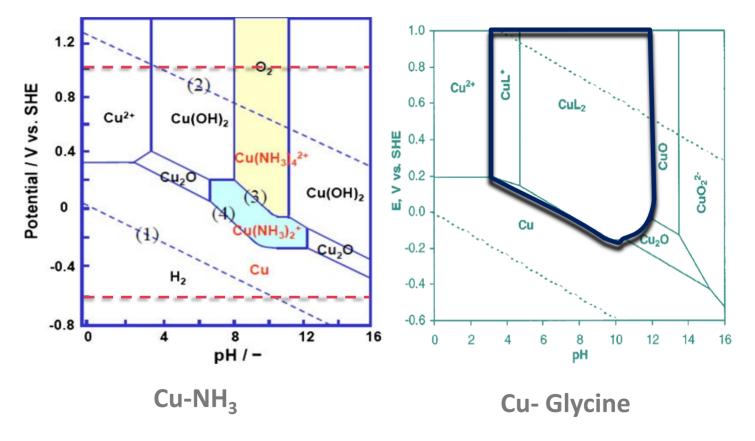
Non-toxic (edible)	Crystalline, Non-volatile, High melting point (with decomposition): 233°C	Reagent Cost ~USD \$1.5 – \$1.7 /kg
Non-flammable	Non-oxidising/non-reducing	Highly water soluble (250g/L)
Stable over wide temperature, pH an Eh range	Can be synergistic with cyanide, thiourea and ammonia: accelerated Au, Cu, Ni, Pd leach rates	High adsorption of Au, Ag onto activated carbon. Ease of AARL-type elution
No interaction with acid consuming gangue	Application to various leaching modes (ISL, Heap, vat, tank)	Cheap materials of construction (mild steel)
Selective over non-sulfide gangue minerals	No transport, logistics, or trade restrictions	Ease of base metals removal / recovery
Operated under dilute and concentrated modes	Easy reagent recovery, recycle and reuse	High affinity for Au, Ag, Cu, Zn, Pb, Pd, Cd, Ni, Co
pK _a : 2.35; and 9.78	Cu- glycinate good oxidant	No pH swings, Simple chemistry
Insignificant Fe, Mn, Cr, Mg, Al, Si dissolution	No elemental sulfur, no silica gels, no jarosites	Pyrite not dissolved (unless mechano- chemically activated).

ЮH





Cu-NH₃ vs Cu-Glycine

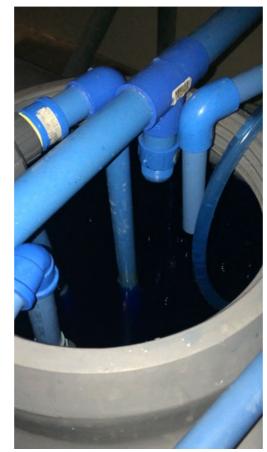


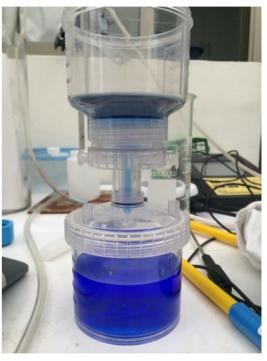
Extending the stability zone for both pH and Eh



A pilot plant example (heap leach of highly carbonaceous oxide ores with alkaline glycine using sea water in Atacama desert)









Leaching of copper ores and concentrates





Glycine Leaching of Metals and their Sulfide Minerals

The glycine leaching of chalcophile metals and their sulfide minerals and precious metals entails multiple chemical levers:

- Reduction-oxidation (of oxygen to water and metals to their divalent ions and sulfide sulfur to sulfates).
 - Raising the Dissolved Oxygen (DO), using H₂O₂ or strong oxidants such as KMnO₄
- Acid-base interactions.
 - Reactions typically in alkaline domain (pH 8-12)
 - Hydroxyl anions converted to water in combination with redox reaction
 - Form of speciation of glycine is pH dependent
- Complexation
 - Formation of glycinate complexes that can either be neutral (e.g. for copper) or anionic (e.g. gold, silver, nickel, cobalt).
 - Complex is moderately strong, but weak enough that cationic IX/SX can strip the metal cation from the complex, thereby releasing free glycine / glycinate
 - Formation of stereoisomers (*Cis* and *Trans* isomers) which have different solubilities (influence crystallisation) and hydrates.
- Temperature



Chalcopyrite Leaching in a Glycine Environment

Direct Leach (without alkaline peroxidation):

CuFeS₂ (s) + 2 NH₂CH₂COOH (aq) + 4.25 O₂ (aq) + 4 OH $^-$ (aq) \rightarrow

 $Cu(NH_2CH_2COO)_2$ (aq) + Fe (OH)₃ (s) + 2 SO_4^{2-} (aq) + 1.5H₂O (l)

Leaching following atmospheric alkaline preoxidation (2 step process)

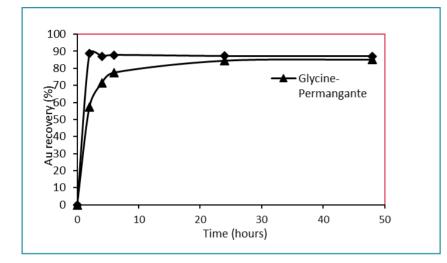
Alkaline Preoxidation

 $CuFeS_2(s) + 4.25 O_2(aq) + 4 OH^-(aq) \rightarrow CuO(s) + Fe(OH)_3(s) + 2 SO_4^{2-}(aq) + 0.5 H_2O(l)$

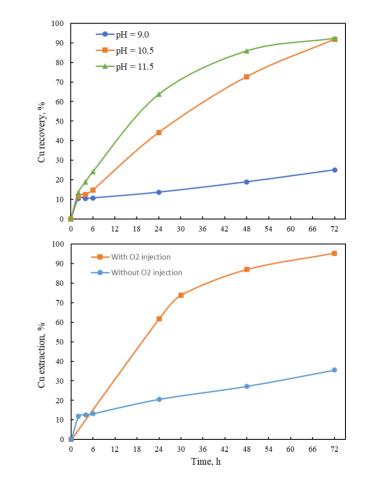
Glycine Leaching

 $CuO + 2 \text{ NH}_2CH_2COOH \rightarrow Cu(NH_2CH_2COO)_2 + H_2O$

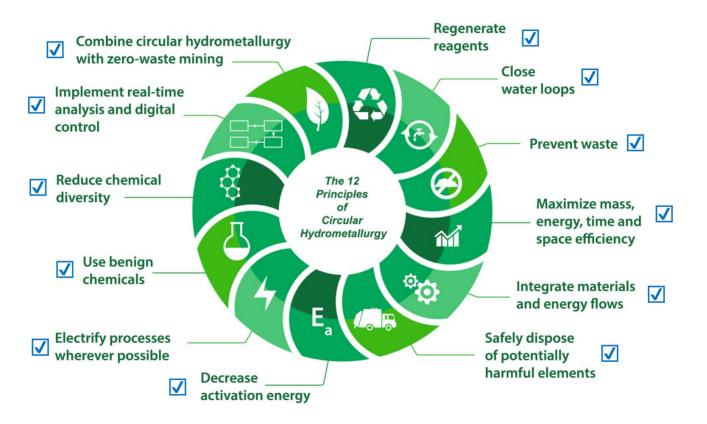
Copper and gold leaching in cyanide-free alkaline conditions



Gold extraction by cyanidation and glycinepermanganate from gold oxide ore at leach conditions of 2 g/L glycine, 30% solids content, 100% -75 μ m, pH 10.5, 2.0 g/L permanganate at room temperature

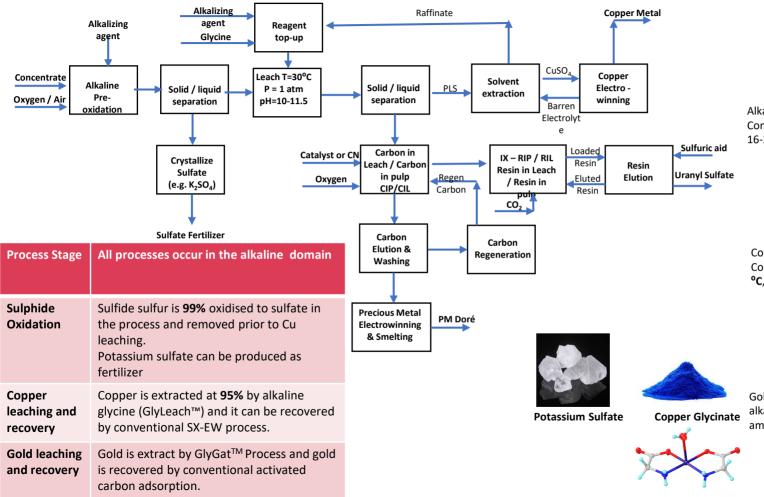


Novel glycine systems satisfying the 12 Principles of Circular Hydrometallurgy





Glycine leach to extract value from polymetallic (Au-Cu-U) concentrates



Alkaline Pre-oxidation (**99% S conversion**) Conditions: 75 °**C**, 2:1 K:S molar ratio, KOH, 16-24h



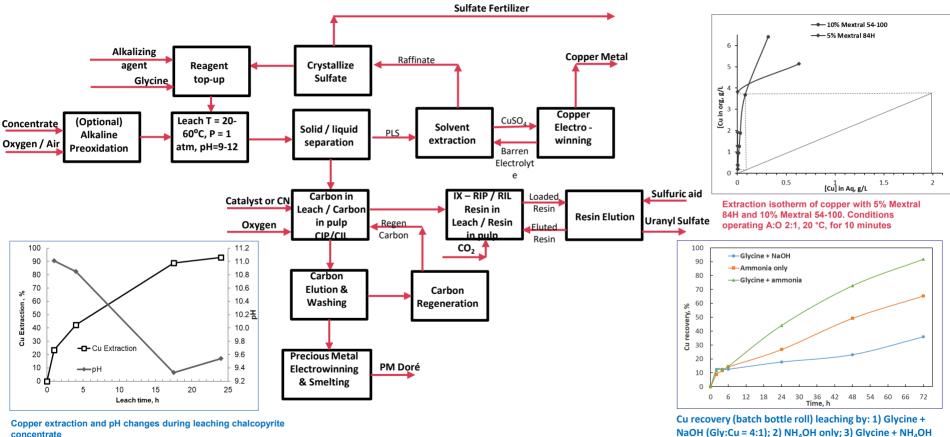
Copper leaching (**95% Cu extraction**) Conditions: glycine-Cu 4:1 molar ratio 30 ^oC, pH 10.5-11, 24-30 hours (**GlyLeach™**)



Gold leaching: Gold will be extracted by alkaline glycine in the presence of small amount of cyanide (**GlyCat™** Process)



High level process block flow : Cu-Au-U polymetallic concentrate



concentrate

Conditions: UFG (80% –10 µm), after alkaline pre-oxidation, 9% (w/w) solids, 40 a/L alvcine, 60 °C 0.75 mL/min O₂, 500 rpm

(Glv:Cu = 4:1). T = 23°C. Rolling speed =100 rpm. pH

=10.5.

Glycine leach extraction of Ni and Co from ores, tailings and concentrates

Leach Conditions:

- Room Temperature
- Atmospheric Pressure
- Controlled dissolved
 oxygen levels / Redox
- Controlled (maintained) pH
- Results reflect outcomes of batch tests
- Resin-in-pulp / resin-inleach and counter-current transfer can further improve results
- Different alkalizing agents used, depending on nature of material treated

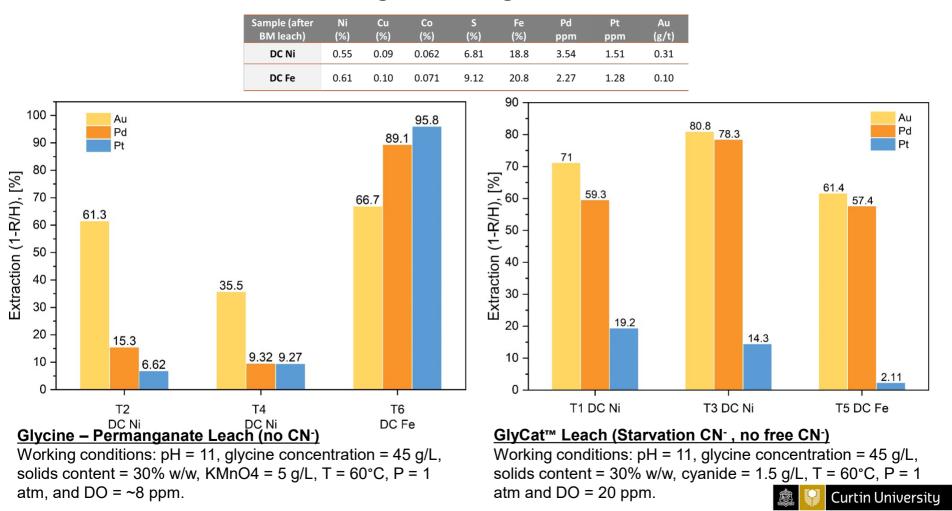
		INI allu	CUTIC	<u>, 111 (</u>	0163), ιαι	iiiigs a			1125	
	Sample	Rougher concentrate 1	Rough concentra		Or	e 1	Ore2	Cleaner Tails 1	Cleaner Tails2	High Pyrrhotite slimes	
	Ni	6.13	6.02		0.	78	1.67	0.886	0.79	4.075	
	Fe	9.12	33.5		5.	89	11.4	5.24	6.43	26.50	
	Ca	0.49	0.33		0.	55	1.49	0.39	0.20	2.975	
	Mg	16.29	4.04		22.9 0.83		5.92	22.25	22.2	4.465	
	S	6.04	27.6				7.04	1.15	1.70	15.30	
	Mn	0.08	0.09	0.0		05	0.11	0.06	0.06	0.120	
	Со	0.11	0.179)	0.014 0.008		0.048	0.021	0.019	0.132	
	Zn	0.03	0.012	2			0.011	0.001	.023	0.021	
	As	0.03	0.007	,	0.0	07	0.005	0.0045	.007	BDL	
	Cu	0.29	0.301		0.	13	0.10	0.0185	0.215	2.00	
	Tes	t ID	Rougher Concentrate 1		ıgher ntrate 2	Ore 1	Ore 2	Cleaner Tailings 1	Cleaner Tailings 2		
	Solid, %		30	10		40	30	30	30	10	
	Initial pH Gly:Ni mole ratio Residence time, hours Ni Extraction, % of total Ni		10.2	10.2		10.2	10.2	10.2	10.2	10.2	
			4:1	4:1		4:1	4:1	4:1	4:1	4:1	
			72	72		48	72	48	48	72	
			90.2	8	1.9	69.1	74.8	62.5	80.1	81.5	
Co Extraction, % of total Co		, % of total Co	85.7	16.5		65.3	27.5	64.5	72.6	71.9	

Selectivity of Ni-Co-Cu leaching versus gangue co-leaching

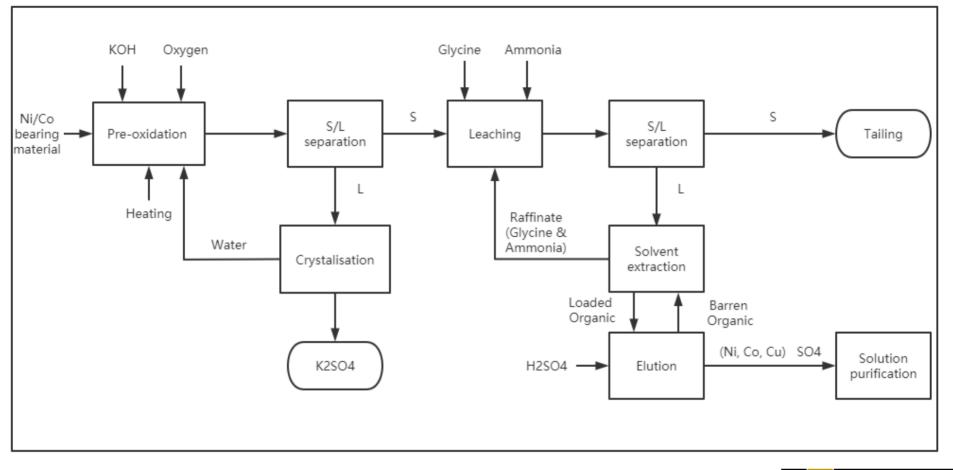
								-			
Test ID	Element	Ni	Со	Fe	Са	Mg	S	Mn	Zn	As	Cu
Cleaner Tails 1	Final solution assay, mg/L	2070	52.8	BDL	118	79.8	3200	BDL	0.8	BDL	48.8
Cleaner Tails 2	Final solution assay, mg/L	2805	63.8	1.5	30.5	25.3	3860	BDL	11.0	BDL	118
High pyrrhotite Slimes	Final solution assay, mg/L	3500	100	19.6	12.8	7.4	3770	BDL	BDL	BDL	646
Ore 1	Final solution assay, mg/L	4100	80.5	BDL	50.6	36.5	4820	BDL	2.5	BDL	318
Ore 2	Final solution assay, mg/L	4020	27.2	11	78.6	78.4	7760	BDL	9.0	0.11	213
Rougher Concentrate 1	Final solution assay, mg/L	7560	147	3.4	10.8	22.4	9860	DBL	15.8	0.07	316
Rougher Concentrate 2	Final solution assay, mg/L	5080	30.8	115	5.5	2.6	9750	BDL	0.4	0.21	169



PGM Leaching from low grade concentrates

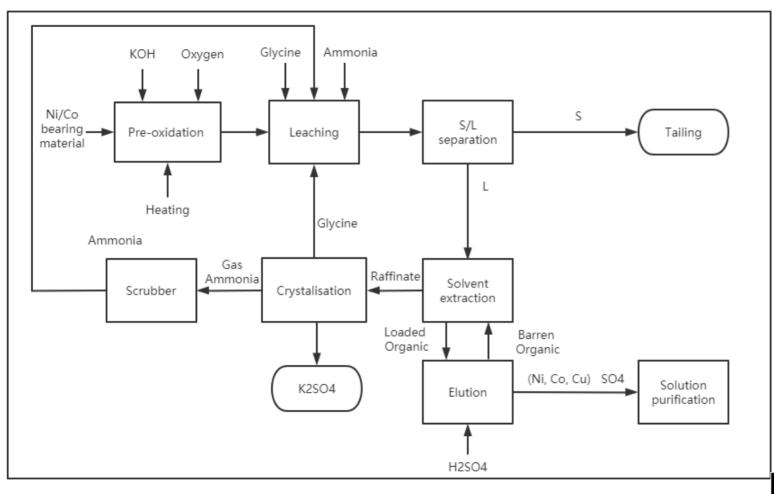


High Level Process Options: Pre-oxidation (concentrates & high pyrrhotite materials)



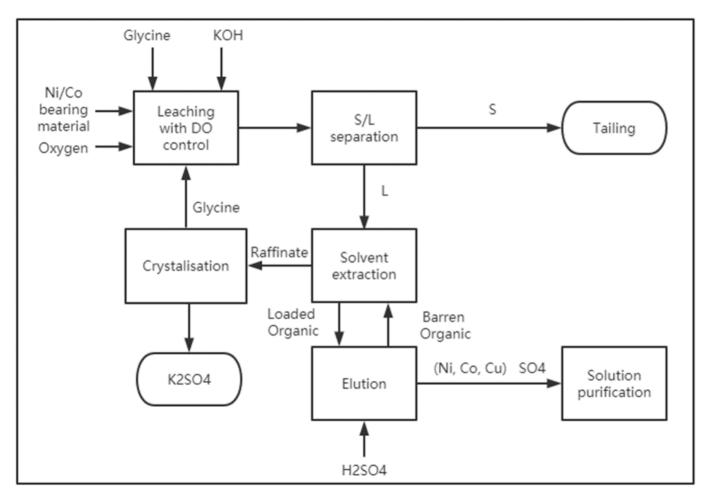


Option 2 (for Concentrates and high sulfide materials): Low-Ammonia addition



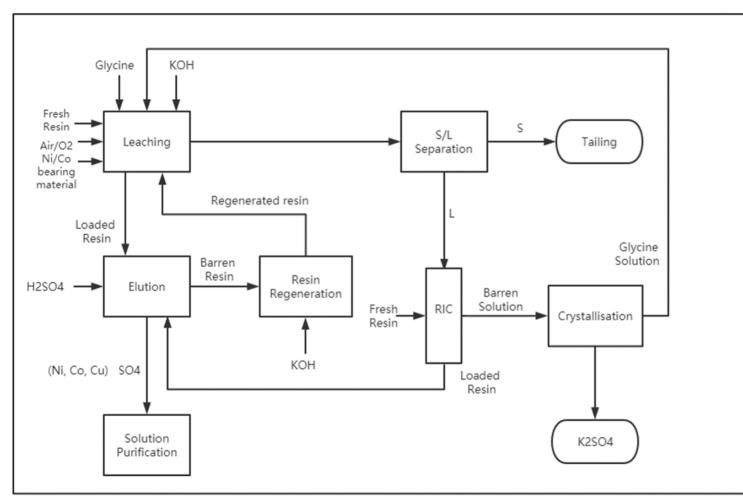
Curtin University

Option 3: High level conceptual flowsheet for rougher concentrate leach:





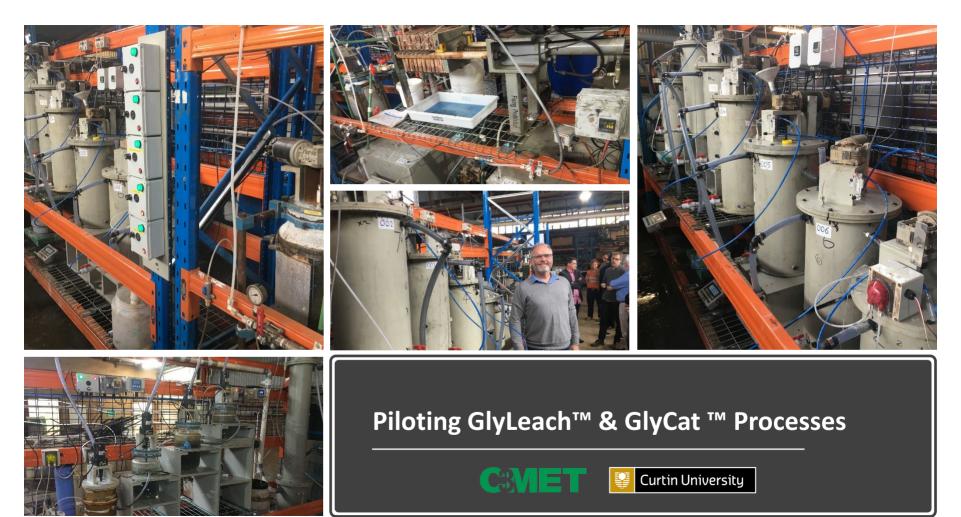
Option 3: Ore / Tailings leach with ion-exchange recovery of Ni/Co/Cu from solution





Alkaline glycine technology provides an ideal pathway for the production of "Green" nickel and cobalt, particularly for lower grade and polymetallic resources.

- It allows maximum recovery of Ni & Co with minimal co-extraction of impurities
- It allows pathways directly to Ni & Co sulfate without the need for smelting, converting, or pressure leaching
- It eliminates most of the typical problematic contaminants, such as Fe, Mg, Ca, Al, Si, Mn from the first extraction stage
- It operates under similar processing conditions, and with similar equipment to gold leaching circuits
- A detracting factor is leach residence time (around 24-48 hours) leading to more tankage
- Glycine recycle is simple, minimising reagent costs
- Processes can be used with saline / hypersaline water
- Applicable to various grades, but optimal for ores & concentrates with nickel grades of between 0.3% 7.0% Ni
- Various alkalising agents can be considered (hydroxides/carbonates of K, Na, NH₄⁺, Ca)



Invention, innovation and commercialization

- The glycine and amino-acid based leach technologies has been invented by Jacques Eksteen and Elsayed Oraby with the original priority dates dating back to 2013.
- Since then, 5 patent families and more than 80 international national phase patents have been registered.
- The research to date has been published in more than 40 peer reviewed journal papers.
- Initially the technology was commercialised through Mining & Process Solutions Pty Ltd (MPS).
- MPS was acquired by the Czech multinational company Draslovka a.s. in 2022.
- Draslovka is currently deploying the GlyCat[™] and GlyLeach [™] technologies at an industrial scale globally.
- The process, in various modifications have been piloted for Au, Au-Cu, Cu, Ni/Co operations
- Many international operating licences have been issued and the process is being trialled at industrial scale at multiple sites in Africa, South and North America, Australia and Asia.
- The technology applies to the leaching, extraction, refining and recovery of metals from solutions for Au, Ag, Pd, Pt, Zn, Cu, Pb, Ni & Co.
- The challenge was to find holistic, integrated process solutions that covered the leaching, purification and recovery of metals from solution as well as reagent recycle and reuse.
- The development took a decade and is still ongoing.
- It is an example of a sustainable, "green" process that can be used for some key Critical Metals such as Ni, Co, Cu, Pd, Ag and Pt while satisfying the 12 criteria for "Circular Hydrometallurgy".



MINING.COM

Barrick cuts cyanide by 80% by adding glycine leach for gold recovery

Staff Writer | March 4, 2024 | 11:16 am Suppliers & Equipment Top Companies Africa Gold



The Bulyanhulu gold mine, opened in 2001. (Archive image courtesy of Acacia Mining.)

Barrick Gold (TSX: ABX: NYSE: GOLD) and Draslovka have achieved their goal – an 80% reduction in cyanide use by adding the GlyCat technology to the processing plant. Gold recovery remains comparable to traditional cyanidation.

Glycine leaching technology (GLT) uses glycine, a non-toxic, recyclable and biodegradable amino acid that is commonly used as a food additive, to recover gold, copper, nickel, and cobalt.

Unlock tomorrow's battery metals

Achieve optimal recovery with GlyLeach™



Draslovka

Thank you!

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