BREAKTHROUGH IN HALIDE LEACHING

By

Dave Sammut

Loop Hydrometallurgy, Australia

Presenter and Corresponding Author

Dave Sammut

dave@loophydromet.com.au

ABSTRACT

The extraction of minerals using chloride lixiviants has been thoroughly investigated and proven to offer major advantages in low-cost, highly versatile minerals processing, with an extremely low carbon footprint.

Loop Hydrometallurgy continues to innovate in advanced halide-based minerals processing. The Halion Loop[™] employs mixed halides to extract copper, nickel, cobalt, lead, zinc, silver, gold, PGMs REEs and other metals from a broad range of concentrates, tailings and industrial waste materials. It operates at atmospheric pressure and less than 100 degrees Celsius, with no noxious gas emissions and no liquid effluents.

In its latest breakthrough, Loop Hydrometallurgy has proposed an entirely new form of leaching that significantly extends the capabilities of economic and efficient processing for refractory materials. This new form of leaching has undergone successful initial trials in the extraction of cobalt from pyrite tailings.

This new technology offers the prospect of near reagent-less leaching for materials that would otherwise be expected to be highly acid- or alkali- consuming by conventional hydrometallurgical processes.

By extending the capabilities of the extraction step, the Halion Loop[™] has also been shown to enable significant efficiencies to be captured upstream of the concentrate, at the mine and mill.

This paper will discuss the outcomes of initial studies of the breakthrough technology, as well as some of the broader potential applications in critical and battery minerals, gold processing, the stabilisation of arsenic, and beyond. It will also discuss the outcomes of economic analysis for processing non-traditional concentrate feedstocks, including low grade and polymetallic bulk concentrates, and materials containing high levels of arsenic.

Keywords: Critical minerals, chloride leaching, halide leaching, cobalt process, hydrometallurgy

INTRODUCTION

Halide hydrometallurgy is widely recognised for its versatility⁽¹⁻⁴⁾. It is capable of unlocking value from a very broad range of resources (ores, concentrates, tailings and industrial wastes) at low cost and with minimal environmental impact.

Halides are a significantly stronger lixiviant than sulphate, and significantly safer and cleaner than cyanide. Leaching in halide can be performed swiftly at atmospheric pressure, at less than 100°C, using air as the oxidant, producing no noxious gas emissions and no liquid effluents. By comparison, most sulphate-based processes require high temperatures and pressures, or long leach times to achieve similar levels of extraction.

The Halion LoopTM is based on these thoroughly-established principles of **Hal**ide **Ion** minerals extraction technology. Using a mixed halide liquor, the Halion LoopTM has been proven to achieve >99% copper extraction from a 'conventional' chalcopyrite concentrate in 4-6 hours. For the same feedstock, sulphate-based pressure oxidation would require in excess of 220°C and 35 bar to achieve similar leaching in the same period, also requiring an expensive oxygen plant; bio-oxidation would require 48 hours of leaching; and heap leaching would take up to 200 days to achieve ~60% extraction.

Additionally, halides can dissolve and extract a much broader range of metals than sulphate. Halides form soluble chelates with copper, nickel, cobalt, lead, zinc, gold, silver, PGMs and rare earth elements – plus other metals.

Chloride hydrometallurgy produces environmentally stable residues for safe and low-cost disposal, being primarily composed of hematite, elemental sulphur and (where arsenic is present in the feed) scorodite.

Given these major advantages, multiple technologies have been developed over the last 50 years that use halides exclusively or in combination with sulphate to extract copper from chalcopyrite and other minerals, none of which were ever commercialised. These developments have proven the process engineering, using common and inexpensive materials of construction including fibreglass, HDPE and PVDF, as well as some titanium.

The primary factor keeping multiple chloride technologies from getting to market was the inability of any of the previous technologies to <u>directly</u> recover the copper from the cuprous state in a practical and efficient manner. Maintaining the cuprous state is critical to minimising power consumption on electrowinning, requiring only one electron per atom of copper instead of two.

That problem has been solved by the Halion[™] electrowinning cell, presented at ALTA 2023⁽⁵⁾. This novel design is the world's first <u>practical</u> electrowinning cell design for the continuous production and recovery of high purity copper metal from the cuprous chloride state, producing copper as dendritic powder for melting/pressing into product. It is estimated to require 70% less power than conventional sulphate electrowinning, with less than 20% of the tankhouse footprint.

Loop Hydrometallurgy's breakthrough provides the key unit operation that now makes closed-loop metal extraction in a halide lixiviant practical, effective and cost-efficient. It leverages the broad and thoroughly established global knowledge of chloride leaching and purification, then brings to application new developments for the recovery of key co-products and by-products. The company is currently commercialising that technology.

THE HALION[™] LOOP

The 2023 ALTA paper⁽⁵⁾ described the status of the Halion Loop[™] technology and the breakthrough Halion[™] electrowinning cell for the continuous production of high purity copper from mixed halide electrolyte.

The Halion[™] Loop is a mixed-halide closed-loop hydrometallurgical process for the extraction and recovery of copper, silver, gold, PGMs and REEs from mineral concentrates.



Figure 1: The Halion[™] Loop Flowsheet

Table 1: Halion Loop [™] Process Parameters			
Operating conditions	Atmospheric pressure		
	<100 °C		
	>5M CI / Br		
	pH~2		
	4-6 hours leach residence time		
Primary reagents	Air		
	Sulphuric acid (if needed)		
	Limestone (if needed)		
Residues	Hematite		
	Elemental sulphur		
	Alkaline precipitate		

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Commercialisation of the Halion Loop[™]

The overwhelming majority of the Halion Loop[™] has already been proven to TRL 7 (Figure 1). The leaching and purification of metals in chloride lixiviants has been widely studied, with pilot and demonstration plants run by multiple companies including Metso, JX Nippon Mining & Metals and Intec.

The invention of the HalionTM electrowinning cell represents the first practical opportunity to close the loop on a full process to leach, purify and electrowin metals in a single co-ordinated process.

This technology is complemented by a range of demonstrated techniques to recover a range of coproduct and by-product metals: gold, silver, PGMs, nickel, cobalt, lead, zinc and potentially REEs, uranium and/or thorium.

As a direct application of these multi-element technologies, the existing and proven unit operations are available and ready to be applied at commercial scale. There are a range of immediate project opportunities to produce metal-bearing products (high grade oxide or hydroxide concentrates, sulphates or other intermediates) that could be developed swiftly and relatively inexpensively.

Some of the most immediate opportunities involve the processing of materials that are contaminated with arsenic. As a penalty element in any concentrate or intermediate product, arsenic can have a major adverse effect on operations – not just the economic penalty on sale of the product, but also the negative effect on the operation of the mill, particularly through increased costs and a reduction in total metal recovery while attempting to minimise the arsenic contamination of the concentrate.

This offers a major opportunity for the Halion $Loop^{TM}$ and halide hydrometallurgy more generally. Under oxidising acid conditions and with the right liquor composition, leached arsenic can be swiftly oxidised and reprecipitated as scorodite (FeAsO₄), which is stable and safe for disposal to tailings.

This can be leveraged to advantage at the mill by changing the operating principle to maximise metal recovery (over arsenic grade and potentially also metal grade) and minimise mill operating cost. The proven and market-ready unit operations (leaching and purification/recovery) could then be applied for the processing of that material.

In principle, this approach could be applied to unlock value from a range of 'stranded' medium- to high-arsenic resources that are currently uneconomic across the full range of base and precious metals.

Over the last 12 months, studies have continued into the various use cases of the Halion Loop[™] process for metals extraction. Two particular use case studies are presented here:

- 1. (Fast to market) Metal extraction and recovery without electrowinning;
- 2. Low-grade, polymetallic, arsenic-contaminated concentrate

These studies have demonstrated the ability to unlock value from a 'stranded' copper resource that is low-grade, polymetallic (Pb/Zn) and contaminated with arsenic; and the ability to extract cobalt from low-grade pyritic tailings.

Most particularly, the first case represents a potentially significant extension of halide leaching capabilities to a broader range of low-grade concentrates and tailings, with Loop Hydrometallurgy's second major technology development. This is a new form of leaching apparatus that offers the prospect of significantly reducing the acid/base reagent requirement for the leaching of materials (such as tailings).

CASE STUDY 1: COBALT LEACHING FROM PYRITIC TAILINGS

Case Study Background

Early in 2024, Loop Hydrometallurgy was provided with a sample of cobaltiferous pyrite tailings that is known to be resistant to / uneconomic for conventional processing.

The tailings material graded <0.8% Co and >0.2% As in a 95% pyrite matrix. While no details were provided regarding the specific mineralogy of the cobalt, it can be inferred from available literature such as Holley et $al^{(6)}$ that the cobalt may be present as iron substitution in the pyritic host mineral.

Over the last 10 years, the cobalt price has commonly traded between US\$25,000/tonne and US\$35,000/tonne. (It peaked twice in excess of US\$80,000/tonne). Accordingly, a viable process for these tailings needs to have an operating cost less than the minimum contained metal value (approximately US\$200/tonne tailings at a cobalt price of ~US\$30,000/tonne), with an allowance for both profit and repayment of capital: say US\$100/t opex.

This expense limitation is exacerbated because - in the case of tailings, where the target mineral might typically be <1% of the tailings mass, instead of >40% - most of the reagent consumption will be lost to the leaching of non-value-producing pyrite, rather than extraction of valuable metals.

While it might be feasible for some tailings to roast the pyrite to form hematite – particularly as the sulphuric acid produced from the necessary capture of the resulting SO_2 gas could be reused for the cobalt leaching – this is impractical when the tailings are also contaminated with arsenic.

Understandably, few hydrometallurgical technologies seek to leach highly-refractory pyrite. Generally, leaching of pyrite only represents a cost to a given process via the consumption of oxidant, with no economic return.

Further, even if a given process only oxidises the sulphur to its elemental form rather than sulphate, and thereby only requires two electrons per sulphur atom rather than eight, every tonne of pyrite could equate to a wasted tonne of reagent. For most hydrometallurgical processes, this would require either highly-oxidising reagents or an oxygen plant.

There are many papers which discuss the use of chlorine (Cl₂), hypochlorous acid (HClO) or perchloric acid (HClO₄) to leach chalcopyrite, which is among the most refractory forms of copper mineral. Few of these papers mention the ability to leach pyrite.

Halide leaching could potentially provide the solution.

Experimental work – Novel Leach Approach

Loop Hydrometallurgy conducted initial testwork that confirmed that the pyrite would leach in the presence of a mixed halide electrolyte using hypochlorous acid as a reagent. As expected, the reagent consumption rates were excessive, and therefore unlikely to be economic.

This provided an opportunity to consider a new technology concept that Loop Hydrometallurgy had been developing at the time. A prototype was constructed of a novel leaching apparatus.

Scouting leach / extraction tests were conducted at 70°C and using a 'standard' Halion Loop[™] lixiviant of ~6M NaCl + NaBr at 70°C, at pH <2 to 10. These tests were conducted from 3 hours to 20 hours with varying slurry densities of tailings.

The tests showed immediate and significant colour-conversion of the tailings from the original greyish colour to a very distinctive rusty brown that is characteristic of the hematite that is formed in conventional Halion LoopTM application from the hydrolysis of leached Fe^{3+} .

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$$
(1)

XRD analysis from the early tests barely showed the evolution of the observed hematite phase, most likely because the hematite particle size in short batch tests (3-6 hours) was too small to detect. A detailed study⁽⁷⁾ of the precipitation of iron phases from comparable mixed halide systems has previously shown that short batch tests of this system may variously precipitate hematite or goethite, but that the latter is a metastable state.

During routine continuous closed loop halide hydrometallurgical processing, small particles of iron oxide that pass through the leach filter are recycled to the beginning of the leach, and ensure hematite formation via a combination of particle aging and seeding effects. This growth of larger hematite crystals also aids in settling and filtration.

Accordingly, future batch tests may use hematite seeding to better enable hematite particle detection by XRD, with some support to filtration.

All of the successful scouting tests were conducted under highly oxidising conditions, as would be expected to be required for pyrite leaching: typically >800mV (vs Ag/AgCI).

Under these conditions, gold, silver and PGMs would also be expected to leach from any typical copper, nickel or other base metal concentrate. This is 'standard' behaviour for materials being leached in the Halion Loop[™]. Furthermore, under such conditions, most of the sulphur leached from the minerals would form elemental sulphur, with only a minority (typically <5%) oxidising through to sulphate.

In this application, the data suggests that the sulphur leached from the pyrite was mostly oxidised to sulphate. As example, a 20 hour leach test was conducted on a larger quantity of leach residue, to allow for periodic sampling and analysis. XRF assay of the residues and ICP analysis of filtrate samples show good mass balance closure for sulphur (2.7g difference).

These data suggested that 61% of the sulphur in the original solid (entirely present as pyrite) was leached into solution (presumably as sulphate).



Figure 2: Change in Sulphur Content of Solids/Residues

The mineral / sulphur leaching is based on redox reactions. Indicatively, the leach half-cell reactions may include some combination of:

$FeS_2 \rightarrow Fe^{3+} + 2S^0 + 3e^{-}$	(2)
Cl₂Br + 2e ←→ 2Cl + Br	(3)
S ⁰ + 4H ₂ O + 6e ⁻ → SO ₄ ²⁻ + 8H ⁺	(4)

Based on the testing to date, it would appear that the atypically high levels of oxidation of sulphur through to sulphate are an intrinsic property of either the pyrite mineral or the conditions required to achieve pyrite oxidation. While this higher oxidant requirement is not ideal, it does have the advantage that the resulting residues will contain no species that are vulnerable to acid mine drainage. The costs of tailings management should, therefore, be commensurately lower.

For one of the alkaline test residues, a test was then conducted on the leached residue to determine the effect of reducing pH after leaching. In this test, 70% of the mass dissolved in an acid brine matrix, leaving mostly a grey-white residue of needle-like crystals, possibly gypsum or an oxidised aluminosilicate precipitate such as orthoclase or alunite.

In principle, once the pyrite host matrix is broken down, the contained metal should be liberated. Collective extraction of cobalt in this test was 64%, which corresponds to the pyrite destruction noted in the test shown in Figure 2. Similar results were obtained in testing at different pH levels.

Accordingly, it is hypothesised that as the conditions and settings of the prototype are optimised for maximum pyrite leaching, then cobalt extraction should be proportionally increased.

It is notable that throughout the entire test sequence using the prototype equipment, no chemical oxidant addition was required. While these results are not yet definitive, all indications from the scouter testing are that the new Halion[™] prototype is prospective for effective and efficient leaching of pyritic tailings without the need for substantial reagent addition.

This, in turn, is prospective for a cost-effective process for cobalt extraction from the tailings. An updated prototype for the novel leaching approach has been designed for further testing.

Cobalt Recovery

The two oxidation states of cobalt (Co^{2+} and Co^{3+}) precipitate at different pH levels, just as the differing Fe²⁺ and Fe³⁺ states do. This might offer an opportunity for separation of the iron and cobalt.

Under the conditions of operation in the Halion[™] liquor, gold and platinum are both known to leach, particularly in the presence of excess chloride as shown in reactions (5) to (8). Due to the concentrated salts and complex multi-element chemistry of a typical Halion Loop[™] mineral leach, thermodynamic and electrochemical theoretical data has limited application. They can be used as a guide, but not absolute predictors. Using standard reduction potentials, it is not highly likely that cobaltate might form (9) under Halion Loop[™] redox conditions. The standard oxidation potential for reaction (9) is more negative than that of gold or platinum:

$Au_{(s)} \leftrightarrow Au^{3+} + 3e^{-}$	$E^0 = -1.52V$	(5)
$Au_{(s)}$ + 4Cl ⁻ $\leftarrow \rightarrow$ AuCl ₄ ⁻ + 3e ⁻	E ⁰ = -1.00V	(6)
Pt _(s) ←→ Pt ²⁺ + 2e ⁻	E ⁰ = -1.2V	(7)
$Pt_{(s)}$ + 4Cl ⁻ $\leftarrow \rightarrow$ $PtCl_{4^{2^{-}}}$ + 2e ⁻	$E^0 = -0.73V$	(8)
Co ²⁺	E ⁰ = -1.92V	(9)

Separation via ion exchange might be an option, and it is conceivable that cobalt metal could be produced using the Halion[™] electrowinning cell. Either of these alternatives would be subject to testwork.

Additionally, it is entirely possible that the pyrite matrix could be broken down in such a fashion as to leave the cobalt entirely in the hematite residue. After filtration, the hematite residue might be reacidified in a sulphuric acid solution to create cobalt sulphate as a product which might be recovered by simple crystallisation. (As noted below, elemental sulphur can be extracted from the residue to make inexpensive acid directly at site, if needed for cobalt sulphate production).

All of these options should be considered during further testwork.

CASE STUDY 2: LOW-GRADE, POLYMETALLIC, ARSENIC-CONTAMINATED CONCENTRATE

Loop Hydrometallurgy's second 2024 study concerned a use-case application of the Halion Loop[™] to a stranded polymetallic copper resource.

Previous feasibility studies have found that the processing of this ore to prepare a conventional smelter-grade copper concentrate with silver and gold credits (for export) is uneconomic, because the resources is low-grade, polymetallic and contaminated with arsenic.

The mill capital and operating costs to separate lead, zinc and arsenic from the copper concentrate had proved uneconomic in previous studies. The current study examined two cases of Halion Loop[™] concentrate processing:

- a 'base case' processing the smelter-grade copper concentrate (inclusive of by-product zinc, lead, silver and gold, with low penalty arsenic) to copper metal and other products; and
- an 'enhanced case' processing a bulk copper-lead-zinc concentrate (inclusive of by-product silver and gold, with high arsenic) into copper, lead and zinc metal and other products.

Basic parameters of the two study cases are shown in Table 2. Across both cases, the mineralogy was primarily enargite and tennantite, with chalcopyrite, bornite, chalcocite, covellite, sphalerite and galena, with substantial pyrite and non-sulphur gangue phases. Of these, the enargite is known to be a particularly refractory copper mineral, but has been previously proven to be highly amenable to halide leaching.

Parameter	Base Case	Enhanced Case
Concentrate		
- Tonnage	250ktpa	350ktpa
- Cu	~30%	~20
- Pb	~1%	~3%
- Zn	~4%	~11%
- As	~5%	~4%
Products		
- Cu	Metal (99.99%)	Metal (99.99%)
- Ag	Metal	Metal
- Au	Metal	Metal
- Pb	Pb/Zn concentrate	Metal (98%)
- Zn	Pb/Zn concentrate	Metal: (99%)
		Prime Western Grade
- S	Not recovered /	Not recovered /
	(Optional recovery)	(Optional recovery)
- As	Stabilised for disposal	Stabilised for disposal

Table 2: Study Parameters

Process flowsheets were laid out for both cases, mass and energy balances, equipment lists, capital cost and operating cost estimates. Cost assumptions were based primarily on independent modelling performed on Halion Loop[™] copper processing for the Think & Act Differently ('TAD') Ingenious Extraction Challenge in 2021 and data supplied by the project proponent.

The key outcomes of the modelling are shown in Tables 3 and 4.

Table 3: Summary of Comparative Opex Data

	Base Case US\$/Ib Cu	Enhanced Case US\$/Ib Cu
Mine & Mill	\$1.47	\$1.30
Halion Loop™	\$0.31	\$0.45
Less by-product credit	(\$0.80)	(\$1.45)
Total Cost	\$0.99	\$0.31

		Base Case	Enhanced Case	
Total revenue	US\$M	751	855	
Total operating costs	US\$M	294	292	
EBITDA	US\$M	469	577	
NPV	US\$M	2,900	3,600	
IRR	%	76%	77%	
Payback	mth	23	23	

Table 4: Profit & Loss Comparison

Existing technology offered no economic solution for the ore. The application of the Halion Loop[™] to this stranded resource is transformative to the site economics. Processing just a conventional copper concentrate, the Halion Loop[™] offers the production of high purity copper metal on site for a total mine-to-metal production cost of less than US\$1 per pound of copper, an IRR of 76% and payback period of less than 2 years.

Leveraging the advantages of the Halion Loop[™] for the processing of a low-grade, polymetallic bulk concentrate alternative improves the project revenues by over US\$100 million per annum, reducing operating cost to just US\$0.31/lb from mine to metal.

There are many equivalent opportunities at projects in Australia and beyond. Loop Hydrometallurgy is actively investigating opportunities to unlock value from such stranded assets.

CONCLUSION

The Halion Loop[™] has closed the loop on a clean, versatile and economic approach to the extraction and recovery of copper and a broad range of co-product metals.

The use of halide hydrometallurgy for leaching and purification is thoroughly established, proven and ready for implementation at commercial scale. The HalionTM electrowinning cell provides the final – and critical – unit operation to make the process completely cyclic.

The Halion Loop[™] now offers the possibility of creating a paradigm shift in copper metal production, unlocking value from a range of stranded resources and greatly extending the ability to more thoroughly utilise the existing resources – even as global ore grades continue to drop.

This capability can be extended to other critical and strategic metals – notably including cobalt, nickel and REEs – and to tailings and other secondary materials.

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