

THE HALION LOOP: COPPER MADE GREEN

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ABSTRACT

Halide hydrometallurgy is widely recognised as offering superior economic and environmental outcomes for the leaching of a wide range of mineral concentrates: copper, nickel, rare earths, lead, zinc, silver, gold, PGMs and more.

Halide leaching is significantly faster than sulphate. Extremely high extraction can be achieved without the need for high pressures, high temperatures, or complicated bacterial processes. The smaller, faster, more efficient leach processes therefore offer capital and operating costs that are only a fraction of conventional sulphate leaching or smelting.

With significantly stronger chelating power, halides can effectively leach a broader range of (more refractory) minerals. Halides can be used for direct extraction of gold, PGMs and other valuable by-products. They are also ideally suited to polymetallic or low-grade concentrates, as well as those that are contaminated with elements such as arsenic.

Metso-Outotec, JX Nippon Mining & Metals and Intec have collectively spent over \$100 million demonstrating fast and effective halide leaching processes for copper and other minerals. It can be fairly described as established technology.

However, halide leaching has until now been limited to very niche commercial applications because of difficulties in the direct recovery of the target metals via electrowinning. Unlike sulphate systems, halide electrolytes produce dendritic copper crystals rather than flat plates, and this has hampered E/W cell designs. Accordingly, most proponents of halide leaching have sought to use solvent extraction to allow conventional sulphate electrowinning, but the significant compromises required to make that possible have impeded commercialisation.

Loop Hydrometallurgy has developed a revolutionary new electrowinning cell design that makes practical the direct production of high purity copper from purified halide leachate. Starting from the Cu(I) state and operating at over 1,000A/m², this cell uses less than half the power required for conventional E/W. The anolyte is then fully recycled to the leach, which aids in the direct extraction of gold and PGMs.

Leveraging the extensive prior demonstration of halide leaching and more than 50 years of combined experience in the field, Loop Hydrometallurgy's E/W cell is now poised to bring to market the first commercially viable complete cyclic process for the production of high-grade copper from concentrates: at the bottom decile of the industry cost curve; at site; at atmospheric pressure, <100°C; with no noxious gas emissions or liquid effluents, and producing an environmentally stable hematite residue for on-site disposal.

This paper will discuss breakthrough technology for copper processing, and the opportunities to unlock value from Australian and international resources.

Keywords: Copper electrowinning, halide leaching, copper process, hydrometallurgy

INTRODUCTION

For much of the 20th century, a significant portion of copper demand was based on its use in infrastructure, particularly electricity and telecommunications. It is natural, then, that usage in these applications was proportionately greater in developing nations over the last decades, particularly in the rapid urbanisation and industrialisation of China and other Asian nations.

The last decade has seen a major swing in developed nations for the development and uptake of energy-efficient and renewable energy technologies, both in generation and usage. These newer technologies tend to be much more dependent on copper.

Speaking at 'Copper to the World 2022', Bloomberg Senior Metals Analyst Yi Zhu said that "copper demand arising from clean energy technologies may double by 2030 vs 2020 levels."⁽¹⁾

As example, electric cars typically contain more than four times as much copper as the previous generation of vehicles. Each vehicle now contains approximately 90kg of copper. Copper is used extensively in the transformers, connectors and switches for the underlying electricity infrastructure. The International Copper Study Group notes that EV usage had tripled in 2021 to 16.5 million vehicles, since just 2018⁽²⁾.

The massive growth in electric vehicle sales, both in China and in western nations; together with the associated copper-based upgrades in the infrastructure required to supply electricity to these vehicles, are both forecast to significantly enhance growth in demand. Goldman Sachs forecasts⁽³⁾ that green demand will rise four-fold over the decade from 2020, representing over 16% of the total copper demand by 2030. Of the forecast annual growth of 500kT in growth of the global copper market, 300kT is directly attributable to growth in demand for green applications.

With 80% of the world's copper supply still coming from bronze age technology, the positive environmental credentials of these green applications is seriously compromised. The world needs greener sources of copper. But the fundamental divalent chemistry of copper in the sulphate processes that dominate both electrorefining (post-smelting) and electrowinning (inherent to virtually all leaching operations) puts a severe limitation on any attempts to save power – and therefore carbon footprint – from all current metal production.

It has long been understood that chloride hydrometallurgy offers a major breakthrough for that limitation. Copper forms a monovalent ion in chloride, the immediate effect of which is to halve the number of electrons required for reduction to metal, and therefore to halve the power required.

Until recently, no practical electrowinning cell had been designed that could efficiently produce high grade copper metal directly from cuprous chloride solution.

CHLORIDE HYDROMETALLURGY

Advantages

High Metal Solubility / Strong Chelation

The advantages of chloride hydrometallurgy have been well established⁽⁴⁾⁽⁵⁾⁽⁶⁾⁽⁷⁾. Chlorides and/or mixed-halides can effectively and thoroughly leach a broad range of minerals, including many that are considered too refractory for other processes.

Metal chlorides are typically highly soluble, particularly with enhanced solubility via the formation of soluble chelates / complexes. This makes chloride processes significantly more efficient, with much smaller process liquor volumes compared to sulphate.

The strong chelating effect of chloride, together with its effect on ion activity⁽⁴⁾, means that chloride leaching does not require high pressure and temperature. All of the 'typical' copper minerals: chalcocite, covellite, bornite and chalcopyrite can be leached to 99.5%+ extraction at atmospheric pressure and less than 100°C, in most cases without the need for ultra-fine grinding. Quoted timing varies, but residence times of <6 hours are typical for published chloride processes.

Feedstock Flexibility

This leaching power extends to more refractory copper minerals such as enargite. It also allows the direct leaching of gold and PGMs from mineral feedstocks, without the need for separate processing operations.

Unlike most sulphate leaching technologies, chloride leaching does not require the addition of pure or upgraded oxygen supply. Untreated air is sufficient, representing a significant reduction in capital cost compared to other hydrometallurgical technologies.

Polymetallic Extraction

Major companies including JX Nippon Mining & Metals and Metso-Outotec have developed processes (the Nikko-Chloride⁽⁸⁾ and HydroCopper⁽⁹⁾ processes, respectively) based upon chloride leaching. Australian variations including the Intec Copper Process⁽⁷⁾⁽¹⁰⁾ have also been developed, including multiple years of pilot plant and demonstration plant operations that have scaled up the technologies, and have successfully demonstrated the principles of chloride leaching of copper, as well as lead, zinc, nickel, silver, gold and PGMs. In doing so, these operations have thoroughly established the engineering and materials of construction suitable for chloride systems.

These companies have also demonstrated a range of other key 'upstream' advantages. Chloride hydrometallurgy can effectively and economically process much lower grade concentrates. The Intec Copper Process⁽⁷⁾ could process concentrates at 15% Cu grade, and lower grades are likely also possible. This could be a major benefit at mines with poor grade recovery curves.

The same benefit can be leveraged at mines with polymetallic ore bodies. Significant extra metal can be captured between ore and concentrate if there is no need to compromise multiple competing grade-recovery curves to achieve smelter-grade products. Significant capital and operating cost could be saved if, as example, a given mine no longer required a cleaner circuit during flotation. Significant cost, power, and carbon footprint could also be saved where the need for fine- or ultra-fine grinding could be eliminated before leaching.

Furthermore, chloride processes can leach co-product and by-product metals directly, including non-cyanide extraction of gold and PGMs. This can have major advantages in environmentally sensitive areas and in well-regulated jurisdictions.

Monovalent Copper

Of all the advantages of chloride hydrometallurgy, perhaps the most clear and prominent is the massive power saving that could be leveraged from direct electrowinning of the monovalent copper ion. Additional power savings are then possible from the power savings of lower voltages (power = voltage x current).

Operating at very high comparative current density: 1,000+ A/m² vs <400 A/m² – will yield both energy and operating cost advantages, reducing the cathode area per tonne of copper production by more than 50%.

Table 1: Advantages of Chloride/Mixed-Halide Hydrometallurgy

Parameter	Primary Advantages	Secondary Advantages
High metal solubility	High extraction	No oxygen plant Reduced energy consumption Smaller physical plant Reduced OPEX Reduced CAPEX
Stronger chelation	Rapid leach kinetics	Atmospheric leaching Low temperature Reduced OPEX Reduced CAPEX

Feedstock flexibility	Lower grade concentrates Less grinding Refractory minerals	Improved grade/recovery Energy savings Higher recoveries
Polymetallic extraction	Direct gold & PGM recovery Pb, Zn, Ni, Co, Ag, REEs	Improved grade/recovery
Monovalent copper	50%+ electrowinning power reduction	Reduced carbon footprint

Disadvantages

Materials of Construction

Among the disadvantages of chloride systems is that the materials of construction are more problematic than conventional sulphate. The chloride-enhanced galvanic couple between copper ions and iron means that chloride systems will rapidly corrode virtually any ferrous metal, including most ferrous alloys that would otherwise be considered 'chloride resistant'. This disadvantage has been largely overcome with the advent of modern materials, most particularly the diverse range of polymers that have become ubiquitous in industrial application over the last 30 years.

Metal Separation

A greater challenge lies in the chelating strength of chloride. While this is immensely useful for achieving rapid and thorough leaching, the fact that most metal chloride salts are soluble - particularly in high chloride systems where there is an excess of chloride supporting the formation of soluble metal chloride complexes - results in complex polymetallic process liquors.

In turn, this makes the purification of the liquors more complicated from chloride. Sulphate systems generally rely on a combination of the low solubility of most metal sulphates and the rejection of non-target metals during solvent extraction to achieve copper sulphate solutions of sufficient purity for electrowinning or electrorefining. This inherent solubility differential between copper and other metals is the basis of the formation of 'anode slime' waste.

Over the last fifty years, techniques have been developed and proven to selectively recover other metals from chloride systems. These use a combination of pH, temperature, redox chemistry, solvent extraction, ion exchange and more. On one hand, these add complication to chloride processing; but on the other hand, they unlock the possibility for the direct production of a broad range of co-products and by-products from a single process.

Copper Recovery via Electrowinning

While both the materials of construction and metal separation issues have now been effectively dealt with in chloride systems, the actual recovery of copper from chloride has remained as the persistent problem that has challenged chloride technologies for several decades.

Copper produced electrolytically from divalent copper sulphate naturally forms a flat plate on a cathode. Conventional operations add various smoothing agents to enhance this natural propensity, with the current density at the cathode limited to less than 400A/m² to further maintain this property.

By contrast, copper electrowon from chloride forms dendrites – crystalline 'tree-like' structures that grow chaotically from the cathode at uneven and difficult-to-control sites. These dendrites have high surface area, making them subject to oxidation. Their complex structures make physical handling difficult.

Chloride electrowinning is further complicated by the fact that the anode reaction during electrowinning produces high volumes of hot, wet, highly corrosive chlorine gas. The Intec Copper Process⁽⁷⁾ overcame this by using two halides – chloride and bromide – which alters the anodic reaction to produce a soluble chloride-bromide complex that can be leveraged on its return to the leach circuit to maximise metal leaching, particularly Au and PGMs. The bromide also enhanced the leaching of by-product metals, such as Ag.

Until recently, no practical electrowinning cell had been developed that could reliably produce dendritic copper directly from the chloride liquor. In the absence of a viable direct route to copper recovery, most developing processes have sought to approach the problem indirectly.

Taking the Nikko-Chloride and HydroCopper Processes as example, both attempted to use solvent extraction to transfer the copper from the chloride system to sulphate. Massive amounts of research capital was expended on these attempts, with neither sufficiently successful to produce a viable commercial process. The problem is that even trace amounts of chloride contaminate sulphate electrowinning (interrupting the production of smooth copper plate), and solvent extraction is not sufficiently selective to achieve the multiple orders of magnitude change in chloride concentration required. Accordingly, both processes were required to make changes to the leach process that ultimately compromised the advantages inherent to chloride leaching.

Loop Hydrometallurgy is the first company to develop an efficient, practical electrowinning cell design for the direct electrowinning and recovery of copper from a halide electrolyte.

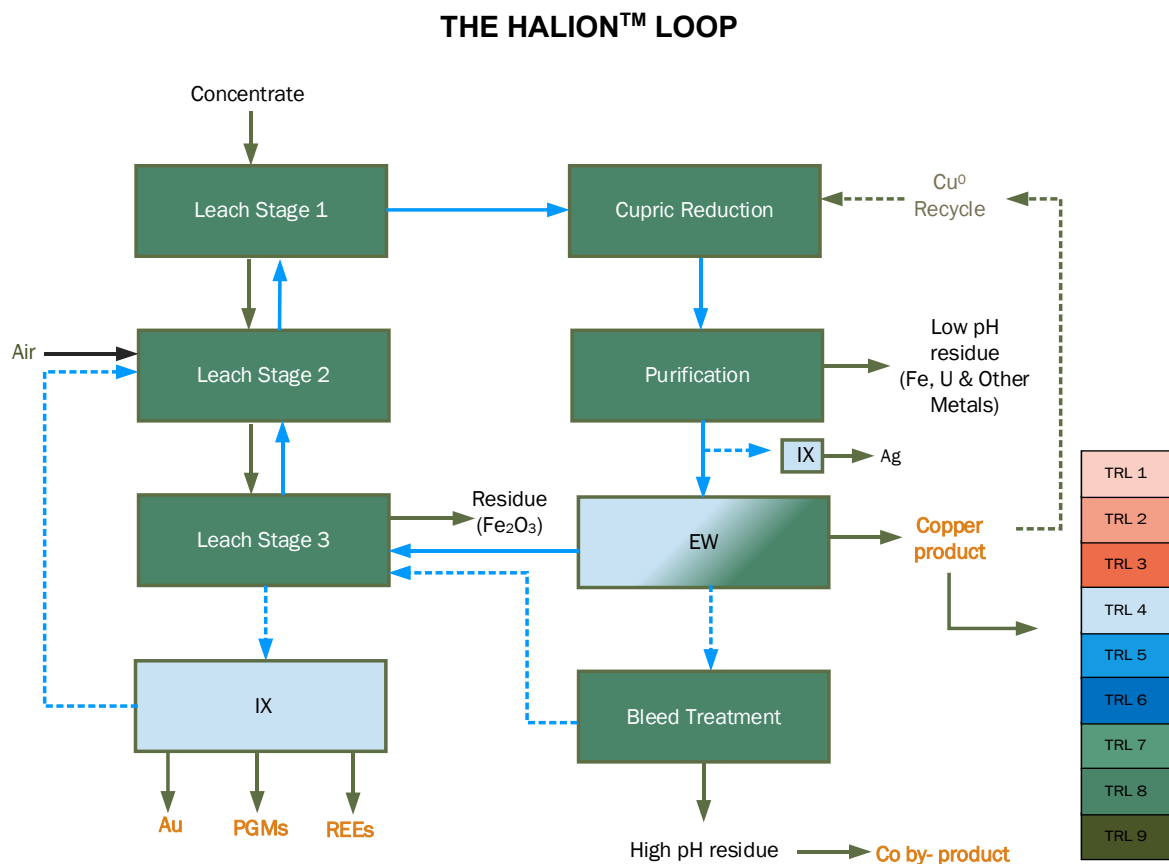


Figure 1: The Halion™ Loop Flowsheet

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.

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.

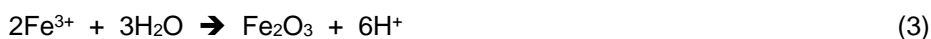
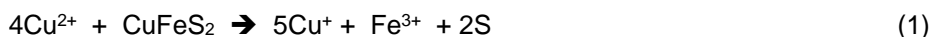
Most particularly, it leverages Loop Hydrometallurgy’s breakthrough electrowinning cell design to close the process loop, so that a single process can extract and recover all of the key value metals contained in the concentrate feedstock.

Table 2: Halion™ Process Parameters

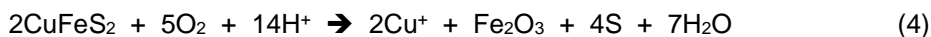
Parameter	Primary Advantages
Feedstock	15-65% Cu 25-75 µm Pb, Zn, Ni, Co ✓ Ag, Au, PGMs ✓ High As ✓ REEs ✓
Minerals	Chalcopyrite Bornite Chalcocite Covellite Bastnasite (more)
Operating conditions	Atmospheric pressure <100 °C >5M Cl / Br pH~2
Primary reagents	Air Sulphuric acid Limestone
Residues	Hematite Elemental sulphur Alkaline precipitate

Leaching

Various copper leaching processes claim to be either a copper chloride or a ferric chloride leach. In reality, these are both the same, because copper and iron both extract each other into solution. Once there is any level of copper in solution, then the chemistry is dominated by the redox chemistry of the cupric-cuprous ferric-ferrous 'couple':



Effectively, the net reaction is the cupric-catalysed partial oxidation of the mineral (with ~95% of the sulphide oxidised only to elemental sulphur, rather than to sulphate).



This chemistry has been thoroughly demonstrated. It is highly flexible for application to a very broad range of copper and other mineral concentrates, including bastnasite (for REE leaching). Loop Hydrometallurgy is currently developing a variation for monazite resources as well.

The reaction products are simple and stable: primarily hematite and elemental sulphur. A detailed environmental study of operating residues was published in 2002⁽¹⁰⁾.

Notably, the leach can also handle very high levels of arsenic in the concentrate feedstock. If the conditions are controlled correctly, the arsenic is leached and immediately reprecipitated as stable

scorodite (FeAsO₄). This can be managed such that no arsenic is detectable in solution, so that the risk of any arsenic escaping the process as liquid effluent or gaseous emission is eliminated altogether.

In the Halion™ Loop, leaching is separated into three counter-current stages. In Stage 1, fresh, incoming concentrate is contacted with process liquor under relatively reducing conditions. By leveraging the redox effect of the mineral leaching, no reagents are required in this stage to achieve the desired reduction of cupric ions to cuprous.

The mineral then progresses to Stage 2, where the bulk of the mineral leaching occurs with air as the primary reagent. By the end of Stage 2, the oxygen has converted at least 99% of the copper in solution to the cupric state.

In Stage 3, the depleted mineral is contacted with recycled high-oxidation potential liquor that has been recycled back from the anode chamber of the electrowinning cell. Gold and PGMs are leached under these conditions, and can be recovered directly from the oxidised liquor using ion exchange. Where REEs are present in the copper concentrate, these will be recovered from the same process stream.

Purification and By-Product Recovery

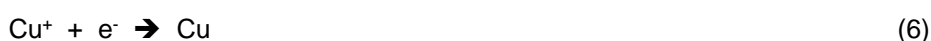
Process liquor moves in a closed cycle around the Halion™ Loop, proceeding 'backwards' through the leach and becoming increasingly reduced. By the end of Leach Stage 1, 85-90% of the copper in solution will be in the cuprous state, maintained in solution by the significant excess of chloride ions. The remaining cupric is then eliminated using recycled copper metal product.



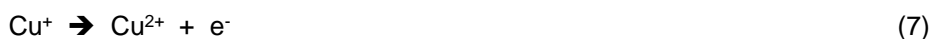
The cuprous chloride then has quite different chemical properties to the other divalent and trivalent metal ions that have been leached from the concentrate. Lead, zinc, uranium and other metals can be recovered, while other non-value or contaminant metals (including excess iron) can be rejected as an alkaline precipitate.

Electrowinning

As with any conventional electrowinning, the cell has a catholyte and anolyte separated by a permeable membrane. Purified cuprous chloride process liquor is fed continuously to the catholyte at high concentration, where copper is reduced at the cathode from the monovalent cuprous state.



The depleted catholyte passes through the membrane to the anode chamber, where the remaining copper is oxidised to cupric, and an oxidised halide complex is formed⁽¹⁰⁾.



This anolyte is recycled to Leach Stage 3, closing the loop for the process cycle.

Process Summary and Economics

Overall, the Halion™ Loop has no gaseous emissions or liquid effluents. The residues are primarily hematite and elemental sulphur, which have been demonstrated⁽¹⁰⁾ to be stable and suitable for on-site disposal.

Independent modelling indicates that the cost of production will be just 17.6 US c/lb. This represents the processing of concentrate to metal. By comparison, the cost of transport, treatment and refining charges, and discounts on payable metal is currently 50 US c/lb for the site used in the modelling exercise.

BREAKTHROUGH ELECTROWINNING CELL

Loop Hydrometallurgy's key breakthrough is its revolutionary electrowinning cell design. Using this new cell, it now becomes practical to close the loop for a continuous process cycle for the direct leaching and recovery of copper and by-products, without having to extract any of the metals away from the chloride system.

For the first time, the Halion™ cell is able to utilise a flat plate cathode to produce dendritic copper. The key to making this possible is by creating controlled growth sites, without the use of secondary materials or complicated manufacturing techniques.

In previous chloride electrowinning process attempts, both of these issues made the resulting cells impractical for use.

The most advanced cell previously developed was that used by the Intec Copper Process (7). It used a 'sawtooth' cathode, which needed to be precisely matched to a set of sawtooth wiper blades, which were in turn mounted to an articulated vertical wiping mechanism that periodically wiped the cathodes clean. The approach had multiple challenges:

- the wiping mechanism required a high-precision match in the sawtooth formations of the wiper and cathode, significantly increasing the cost of manufacture and compromising performance wherever that match was imperfect;
- the combination of high surface area and periodic wiping meant that the effective current density at the cathode could change by several orders of magnitude at each wiping cycle, affecting product quality, morphology and cell voltage;
- the periodic wiping also 'dumped' a large load of copper dendrite to the bottom of the cell in bulk, creating mechanical handling problems for product removal;
- the vertical movement of the wiping mechanism carried cuprous catholyte upwards on every wetted surface during wiping, allowing for oxidation in the air. Carrying this oxidised liquor back into the cell on the downward movement compromised the cell efficiency by several percent;
- this vertical arrangement also required significant space above the cell for the movement of the mechanism; and
- the cell used a conveyor system. This did not handle the smaller copper particles in the particle size range, resulting in accumulation of the cell. The recovered copper was exposed to air and oxidation during the removal process.

All of these issues have been overcome in the Halion™ cell. A key aspect is that the copper is removed from the cathode continuously, but slowly, yielding a product that can best be described as 'coarse copper sand'.

The continuous movement ensures that the electrical conditions within the cell stay stable (and at the lowest possible voltage); and it maintains a permanent quantity of copper on the cell, ensuring that the effective current density is at least 1-2 orders of magnitude lower than the nominal current density (1,000+ A/m²). Further testing is required to determine how high the nominal current density can be raised.

The simple removal mechanism does not require any complicated articulated mechanism, as a result of which the anode-cathode distance can be narrowed by more than 50%. This reduces the cell voltage.

Moving horizontally, the removal mechanism never 'breaks surface', minimising the air ingress into the cell. It may be practical to cover the cell to prevent air ingress altogether, maximising the cell efficiency. It is expected that the cathodes will be capable of operating and producing copper product continuously for long periods of time (up to 6-12 months), without needing removal from the cell other than for scheduled preventative maintenance.

The copper can then be removed continuously from the bottom of the cell using conventional methods, avoiding exposure of the high surface area product to air before it is washed and dried.

This design represents the first practical method of directly electrowinning copper from the chloride system, that can be applied effectively at the commercial scale.

COPPER MADE GREEN

Electrowinning: Halide vs Sulphate

Taking into account the effects of electrowinning from the cuprous state, current density and other advantageous operating factors, it is estimated that the Halion™ cell will reduce the electrowinning power consumption by as much as 70% compared to conventional copper sulphate electrowinning.

Table 3: Comparison of Electrowinning Technologies

	Halion™ Cell E/W	Sulphate E/W
Copper valence state	Cu(I)	Cu(II)
Notional current density	>1,000 A/m ²	<400 A/m ²

Process Environmental Comparison

The CSIRO⁽¹¹⁾ has modelled the whole-of-process life cycle impact of the dominant copper production technologies. Of the technologies modelled, the Halion™ Loop has the strongest commonality with the Intec Copper Process – both atmospheric, low-temperature, cyclic, mixed-halide processes.

The environmental impacts of smelting (as the current dominant copper production technology) are harder to assess for comparative purposes because much of the energy used in smelter copper production comes from the oxidation of sulphide to sulphur dioxide, rather than from electricity and carbon sources. Effectively, smelting gets a very large ‘cheat’ on its carbon footprint, at the expense of either producing acid rain (unregulated jurisdictions) or large volumes of sulphuric acid (typically requiring neutralisation).

The life cycle assessment showed that the carbon emissions of the mixed-halide hydrometallurgy were the lowest of the hydrometallurgical techniques for a ‘standard’ 25% copper concentrate using power supplied from black coal, slightly higher than smelting.

This ratio versus smelting changes in favour of hydrometallurgy for lower-grade concentrates, or when using hydro power. The ratio was also affected by transport distance. Where the hydrometallurgical processes are based at the mine site, the conventional long transport distances associated with transport to smelter and refining added over 2.6MJ/kg to the total energy consumption.

In all scenarios, the acidification potential of smelting was vastly higher (up to 290%) than mixed halide hydrometallurgy.

Table 4: Global Warming Potential (kg CO₂-e/kg-Cu)

	Mixed Halide + Direct E/W	Pressure Oxidation (average)	Bacterial Oxidation (average)	Flash Smelting
25% con. Black coal	4.9	7.3	8.2	4.3
15% con. Black coal	5.0	8.8	10.4	5.2
25% con. Natural gas	3.4	5.3	6.1	3.2
25% con. Hydroelectric power	1.5	2.9	3.6	1.8
25% con. 5,500km transport	4.9	7.3	8.2	4.5

Table 5: Acidification Potential (kg SO₂-e/kg-Cu)

	Mixed Halide + Direct E/W	Pressure Oxidation (average)	Bacterial Oxidation (average)	Flash Smelting
25% con. Black coal	0.033	0.044	0.047	0.057
15% con. Black coal	0.034	0.048	0.051	0.089
25% con. Natural gas	0.010	0.013	0.014	0.039

The improved performance of the Halion™ cell will improve the total energy consumption from the mixed-halide process considered in the CSIRO study.

Depending on concentrate grade, electricity generation source and comparative transportation distance, it is estimated that the Halion™ Loop would be almost equal to or lower than smelting in both total energy consumption and carbon footprint, and significantly lower than all other competing hydrometallurgical process options.

COMMERCIALISATION OF THE TECHNOLOGY

Loop Hydrometallurgy is currently undertaking a commercialisation program to bring this technology to market. The preferred first project for this project may include the following characteristics, which best leverage the advantages of the technology:

- 20-40 kTpa Cu production
- 15-25% Cu grade and/or poor grade recovery curve
- REE, Au, PGM and/or Co co-product credits
- Polymetallic: Pb, Zn, Ni and/or Co
- Arsenic contamination
- Hydroelectric or gas power supply

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