AmmLeach®
A New Paradigm in Copper–Cobalt Processing

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The predominant current processes for the treatment of oxidized copper–cobalt ores use a reductive acid leach to bring the desired metals into solution. However, the indiscriminate nature of acid leaching results in a solution, akin to a metal soup, containing not only the Cu and Co but also an extensive suite of other metals. These other metals, notably Fe, Mn, Al, Ca, Mg and Si, all have to be eliminated from solution before the copper and cobalt can be recovered. Generally precipitation processes are used, but these tend to result in significant losses of copper and/or more usually cobalt from solution, leading to reduced recoveries. The AmmLeach® process uses ammonia-based chemistry to selectively leach the target metals, leaving the rest behind in the leach residue. This approach eliminates any need to clean the solution of unwanted metals and the consequent metal losses. After solid–liquid separation, the leach solution is immediately subjected to separation and concentration of the copper and cobalt using solvent extraction and electrowinning.

INTRODUCTION

The Copper Belt extends through the northern part of Zambia and the southern province of Katanga in the Democratic Republic of Congo (DRC) and contains the richest and highest grade deposits of copper and cobalt remaining in the world. Whilst there are a number of mines that produce sulphide concentrates, using froth flotation, the largest deposits are those where near-surface sulphides have been weathered over time to form oxides. The oxides cannot be concentrated by conventional physical means to give high recoveries. Despite this, a number of dense medium separation plants have been installed and used to produce a higher grade concentrate which is typically exported (while the rejects, typically 2 to 3% Cu are stockpiled for treatment at a later date). These plants generally have low recoveries and can only be used on the dwindling supply of high grade materials. In exporting the concentrate, little value adding is undertaken within the country, thus greatly reducing the economic benefits to the country. Recent changes to the regulations in the DRC will effectively ban the export of low value ores, concentrates and intermediates in favour of high value metals. This will necessitate mines to install new processing circuits in order to comply with these regulations.

The head grade of ores currently being treated in the DRC is slowly decreasing as the extremely high grade materials are being selectively mined out. In many cases, the removal of a small volume of high grade materials leaves a much larger volume of economically marginal ore behind. This is due to a desire for short-term profits overtaking long-term prosperity. The remaining ore, which in many cases is still of relatively high value by world class standards, is likely to be only treatable by low cost heap leaching. There are some initial trials of heap leaching within the DRC, but implementation at a large scale has yet to be adopted.
The copper is commonly present in the ores mostly as malachite, but a number of other minerals have also been identified, including pseudomalachite, azurite, diopside and chrysocolla (Gauthier & Deliens, 1992). Several of these copper minerals are green and frequently misidentified as malachite with the resulting leaching results being somewhat unexpected.

In oxidised ores, cobalt is generally present in two different populations, as a discrete mineral heterogenite, CoOOH, the cobalt analogue of goethite and within a powdery, black, largely noncrystalline manganese oxide phase, often termed wad. Sulphides may also be present in transition ores. Heterogenite has been shown to occur in at least two different physical or crystallographic forms with the same chemical composition but the difference does not appear to affect leaching (Apua & Mulaba-Bafubiandi, 2011; Burlet et al., 2011). The vast majority of the cobalt in the ore is present in the trivalent state, Co$^{3+}$, which is insoluble in purely acidic solutions and necessitates using a reductant in the presence of an acidic solution in order to effect dissolution.

The plants which process the ores to produce a higher value product, either cathode or intermediate, use acid leaching. The flowsheet is largely the same for all plants (Sole & Cole, 2002), and summarised in Figure 1. After ore preparation, a reductive acid leach is used to solubilise the copper, cobalt and numerous other metals (Apua & Mulaba-Bafubiandi, 2011; Ferron & Henry, 2008; Miller, 2008). The most common reductant used is sodium metabisulphite (SMBS) but liquid SO$_2$ is now being examined by a number of operations to reduce costs (Mwema et al., 2002). Ferrous ions have also been proposed as reductants (Apua & Mulaba-Bafubiandi, 2011; Ferron & Henry, 2008).

![Figure 1. Typical reductive acid flowsheet for copper-cobalt ores using SO$_2$ as the reductant.](image)

The tailings are separated and the acidic pregnant leach solution (PLS), which contains high levels of a range of different metals, passes to copper removal using solvent extraction (SX). The copper-free raffinate solution is then treated to remove, Fe, Mn, Al and Si by a series of precipitation steps, each of which has a solid–liquid separation step. Finally, the cobalt-bearing solution is subjected to a recovery step, shown here as SX–electrowinning (EW) but precipitation is also used. In some plants, the copper and cobalt are leached sequentially, with copper recovered by SX after an acid leach and the residue is then reductively acid leached to recover the cobalt. The two-stage process does not remove the necessity to precipitate the assortment of metals dissolved during the leach.

Each of the precipitation stages between copper and cobalt recovery involves a loss of cobalt. The loss
during iron and manganese precipitation can be especially substantial since the cobalt will be both
coprecipitated into the precipitate and adsorbed onto the surface. Cobalt losses during aluminium
precipitation are lower but nevertheless add to the total loss. In some plants, there is no attempt to even
try to recover the cobalt as the capital costs and losses incurred during solution clean-up are too high
to warrant recovery. In these plants, there is a circulating inventory of cobalt amounting to at least 1 g/L.

Elimination of the precipitation steps will result in a greater fraction of the cobalt solubilised during the
leach reported to cobalt recovery. However, this cannot presently be achieved after an acidic leach.

The host rock of deposits between Likasi and Tenke in the DRC Copper Belt is carbonate-based (Geco,
2015; Unrug, 1988) and, as a consequence, acid leaching of such ores is expected to lead to high acid
consumptions as the host rock will also react with the acid being used. For some operating deposits, it
is only the high head grade of the copper and cobalt and high commodity prices which allow economic
processing. As head grade and metal prices fall and acid becomes more expensive, these operations
will rapidly become uneconomic and close down. Clearly, for such deposits, a process which does not
require acid utilization will allow a more sustainable operation with a longer life span.

It was in this environment of low cobalt recoveries, decreasing metal prices and high acid
consumptions that the AmmLeach® process (Johnston et al., 2009, 2010a, 2010b, 2011a, 2011b, 2011c)
was developed. The use of an ammonia-based leach can be expected to increase cobalt recovery,
because the precipitation steps are not required, and lower costs, by eliminating the significant cost of acid. These technoeconomic advantages will open up opportunities for the processing of lower grade and higher carbonate deposits at lower cost than acid-based processes.

**AMMLEACH® PRINCIPLES**

The potential–pH diagrams in Figure 2 show the basic principles of the AmmLeach process. In the
presence of ammonia, cobalt and copper form soluble ammine complexes whilst the undesirable
metals, represented here by Fe and Mn, do not. Thus, using an ammonia-based leach process
will result in a PLS containing only those metals which form ammine complexes whilst leaving the
impurity metals within the leach residue. By doing this, the resultant leach solution contains only the
target metals and eliminates any requirement to purify the solution by precipitation, thereby ensuring
that any cobalt leached will be recovered as the final product.

It is important to note that, in acid solutions, cobalt only has a single stable valence, Co²⁺, but in
ammoniacal solution, there are two stable ammine complexes, the divalent Co(NH₃)₅²⁺ and the
trivalent Co(NH₃)₆³⁺. In the ammoniacal system, aerial oxidation will convert all of the cobalt to the
trivalent form and this forms the basis of the separation of copper and cobalt.

Although copper can also be present in a monovalent form, the ammine complex is almost impossible
to form except under anaerobic conditions. In the presence of, for example, native copper, the
copper(II) ammine complex will act as an oxidation mediator by reducing to copper(I) ammine which
is immediately oxidised by air back to copper(II) ammine (Black, 2006). This chemistry has been used
to recovery copper from printed circuit boards (Oishi et al., 2007). The cyclical nature of the
copper(I/II) ammine system does provide some oxidising capability in the AmmLeach process, but it
is not an essential component for most ores. There are currently no reports of the same redox mediator
effect in cobalt-ammonia solutions.
The AmmLeach process has a stage immediately prior to leaching that is tailored to the mineralogy of the metals targeted. As a consequence, precise identification and quantitation of the minerals present is critical for the best results. Thus far, it has been found that almost all minerals can be pre-treated such that the target metals are rendered soluble in ammoniacal solutions. The pre-treatment uses a small volume of reagent at a high concentration to rapidly and effectively change the unleachable minerals into a leachable form. The volume used is sufficient to fill the pores and cover the surface of the ore particles with a thin layer whilst the high concentration provides a highly aggressive chemical environment which increases rate and extent of reaction compared with a single-stage leach.

Every mineral present has a different optimum pre-treatment and, where possible, positively identified mineral specimens have been trialled using many different pre-treatment options to allow different suites of minerals to be treated so as to obtain the best possible recovery. For some suites of minerals, there may well be counteracting optimum pre-treatments (e.g., acid vs. alkaline, oxidative vs. reductive) and a different (neutral, non-redox) pre-treatment may well give better overall results than targeting one mineral or the other. It should be noted that the use of a small volume of reagent at high concentration does not significantly affect the subsequent leaching stage as the total dose used remains small. Depending upon the ore texture and the dissemination of the target minerals it is eminently possible to use AmmLeach in a heap-leach scenario. In arid environments, covering the heap is recommended to minimise both water and ammonia losses by evaporation.

Table I shows typical solution tenors for acid and AmmLeach solutions after leaching a range of difference copper-cobalt ores. The levels of copper and cobalt are the same for both leaching processes but the impurity elements are very significantly lower for AmmLeach than for acid leaching. The lower impurity levels preclude the need to undertake any solution purification prior to separation and recovery of the copper and cobalt. The low levels are due to the low solubilities of the metals across the typical operating pH range (8 to 11) and the undesirable metals not forming soluble ammine complexes. It should be noted that during testwork substantially higher copper and cobalt concentrations have been achieved with no increase in the impurity elements.
Table I. Typical solution tenors in ppm obtained from acid leaching and AmmLeaching of ores.

<table>
<thead>
<tr>
<th>Element</th>
<th>Acid (mg/L)</th>
<th>Ammleach (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1000–5000</td>
<td>1000–5000</td>
</tr>
<tr>
<td>Co</td>
<td>500–1000</td>
<td>500–1000</td>
</tr>
<tr>
<td>Fe</td>
<td>2000–6000</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Mn</td>
<td>1000–7000</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Si</td>
<td>50–200</td>
<td>1–20*</td>
</tr>
<tr>
<td>Ca</td>
<td>500–2000</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mg</td>
<td>500–2000</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Al</td>
<td>50–500</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

*believed to be colloidal rather than dissolved

A schematic AmmLeach flowsheet is shown in Figure 3. As can be seen, by using a selective leach process there is no requirement for any precipitation stages in order to eliminate unwanted elements from solution. All of the copper and cobalt that is leached reports to the recovery stages without any losses to tailings. Indeed, the only metal and ammonia losses are due to entrainment in the tailings due to insufficient washing.

![Schematic AmmLeach flowsheet.](image)

The near-perfect recycle of ammonia is a key factor in the significant economic benefits of AmmLeach® process, compared with acid processes where the leachant acid has to be continually replaced due to consumption. The AmmLeach process also does not produce gypsum or other hard-to-handle precipitates, leaving the tailings largely unchanged from the ore. The residual ammonia present in the tailings promotes revegetation by acting as a fertiliser.

**AMMLEACH® PRACTICE**

A sample of oxidised copper cobalt ore was obtained from a working operation; the head grades were unusually high at 5.14% Cu and 0.64% Co. The copper was observed to be present as predominantly malachite; no specific cobalt mineral could be identified by X-ray diffraction. The powdery black nature of the ore suggested the cobalt was likely present as heterogenite (CoOOH) or within a manganese wad.
Samples of ore were cured by adding just enough of a variety of different solutions to form a paste. The pastes were rested for 24 h in order for the pre-treatment to take effect. A solution of 20 g/L (NH₄)₂CO₃ + 20 g/L NH₃ (AAC) was then added and the solution agitated for 24 h, after which time the solution was analysed for copper and cobalt. The results are shown in Figure 4.

![Figure 4](image_url)

Figure 4. Extent of leaching of copper and cobalt in AAC after pretreatment in stated solutions. The red and blue lines show the respective recovery of cobalt and copper after leaching without any pretreatment.

From these results, it can be seen that copper dissolution is unaffected by pre-treatment with almost all runs, achieving >80% dissolution. However, the cobalt dissolution is highly dependent upon the pre-treatment step. The two most effective pre-treatments were those containing reductants. The ineffectiveness of non-reductive acid pretreatment is shown by the poor recovery after pre-treatment in 1 M HCl.

The same ore was pretreated using Na₂SO₃ solution at pH 2 and then then rested for different times up to 24 h. After the required resting time, AAC was added and the leach continued for 24 h under constant agitation. The recovery of copper and cobalt as a function of pre-treatment time is shown in Figure 5. The x-axis is logarithmic to show the effect of short times more clearly, the data at 1 min are for ore without any pre-treatment and the data at 1000 min are actually for 1440 min (24 h). Copper recovery is unaffected by pre-treatment with >90% consistently being leached, but there does seem to be a slight reduction in leaching extent for pre-treatments longer than 120 min. The extent of cobalt dissolution is clearly affected by the pretreatment process, with only 5 min of pretreatment necessary to increase recovery from <20% to >80%. This clearly indicates an extremely rapid reaction involving reduction of the cobalt-bearing mineral. Beyond the initial time, the data become more scattered than is desirable but the data show that >70% cobalt recovery can be achieved, regardless of pre-treatment time. Unlike copper, there is no clear decrease in recovery for longer pre-treatment times.

From an operational point of view, the rapid effect of pre-treatment is excellent as there is no need to include a large tank in which the paste can be allowed to have a long pre-treatment time. The minimal effect on extent of cobalt recovery for longer pre-treatment times also allows much greater flexibility in operations by being able to hold up the repulping of the paste in the event of problems elsewhere in the plant. The maximum rest time for this ore would seem to be around 2 h as, after this, copper recovery slowly reduced.

Following on from this, a further set of leaching runs were made on pre-treated ore to examine the leaching kinetics. The results are summarised in Figure 6.
Figure 5. Extent of leaching of copper and cobalt after pretreatment in Na$_2$SO$_3$ for different times. The data shown at 1 minute is without any pretreatment.

Figure 6. Extent of metal leaching as a function of leach time.

The cobalt leaching is extremely rapid with >80% in solution within 30 min and then a slow increase in leaching up to at least 24 h. Copper dissolution was somewhat slower, with a more classic kinetic look to the curve. These results suggest that the pre-treatment renders a high proportion of the cobalt very rapidly soluble, leaving a fraction which leaches more slowly. Copper is unaffected by the pre-treatment and leaches more slowly in the ammoniacal solution. After 24 h, both metals leach to >90% from this ore.

In commercialisation of the AmmLeach process for copper and cobalt, the quantity and cost of reductant is the key reagent cost as the ammonia is almost 100% recycled. This is the key economic difference from the acid-reductive process where acid is consumed during the leaching step and then neutralised using lime forming gypsum. The acid process pays for acid and then has to pay for lime to neutralise it whilst also losing dissolved cobalt during the precipitation processes. AmmLeach is conspicuously different in that there is no such consumption of leaching reagents, thereby greatly lowering operating costs.

The mineralogy of the ore largely determines the quantity of the reductant which is required during the pre-treatment. It should be noted that, for the same ore, the AmmLeach process will use the same dose of reductant as the acid process to give the same extent of copper and cobalt dissolution. Thus, whilst the AmmLeach process gives the same (or in some cases better) extents of copper and cobalt dissolution than a reductive acid leach, the cobalt losses are essentially eliminated because, unlike the acid processes, there are no precipitation stages.
In theory, only one electron is required to reduce the Co$^{3+}$ to Co$^{2+}$. However, in reality there are two other reducible elements in the ore, Mn$^{4+}$ and Fe$^{3+}$. Cobalt is often associated with manganese and both need to be reduced if the maximum cobalt recovery is to be achieved. Consequently, there is no simple way to predict the required dose on the basis of chemical analyses and test work is essential to optimise the reductant dose in both acid and AmmLeach processes.

Figure 7 shows the extent of metal recovery as a function of the dose of reductant. Two reductants were trialled, ferrous ions and sulphite ions. Ferrous ions are less powerful reductants than sulphite but are substantially less expensive, being capable of manufacture on site from scrap iron and sulphuric acid whilst sulphites are typically transported to site from a remote location. More recent use of liquid SO$_2$ offsets some of the costs by reducing the transport cost by moving sulphur instead of SMBS. A second advantage of using ferrous ions is that the oxidised form, ferric ions, are insoluble in the ammoniacal solution and do not add an unwanted cation (sodium if SMBS is used) which necessitates a bleed stream to keep solution levels in check.

Copper recovery is affected to some extent by both reductants, especially higher doses of ferrous ions which seem to limit the recovery to around 85%. As would be expected, cobalt is much more sensitive to the use of a reductant. When a reductant is absent, <20% of the cobalt is leached. As the reductant dose increases, the extent of cobalt dissolution is increased to near 100% for sulphite and a maximum of ~80% for ferrous ions. The ferrous ion appears to have greater efficacy than the sulphite at lower doses but is limited to ~80% cobalt extraction. Excessive dosing of ferrous is actually counterproductive, with cobalt dissolution decreasing. This is likely due to the same mechanism as seen in acid leaching, whereby precipitation of ferric ions leads to losses of cobalt from solution by coprecipitation and/or adsorption. Sulphite does not have this particular problem.

The separation of copper and cobalt in the PLS is achieved by the remarkably simple expedient process of solvent extraction using LIX®-84I (BASF). This reagent has been used to recover copper and nickel from ammoniacal solutions for over twenty years in copper recycling plants and nickel–cobalt refineries (Cognis, 1998). The extractant almost quantitatively loads the divalent metals, leaving the trivalent cobalt behind in solution. It is important to ensure that the cobalt is present as Co(III) prior to contact with the extractant or else Co(II) will load and immediately oxidise to Co(III) which can only be extracted using a strongly acidic highly reductive leach (Fittock, 2009; MacKenzie et al., 2006).

A sample isotherm for copper extraction from ammoniacal solution using LIX-84I is shown in Figure 8. The isotherm is extremely steep at low aqueous concentrations, resulting in very high recoveries per stage. The simple McCabe–Thiele diagram construction, assuming 95% stage efficiency, shows that it is possible to get from 5 g/L to ~12 mg/L in two loading stages, a recovery of >99.7%. Stripping is also equally efficient, with >99% of the copper stripped in two stages to produce an acid electrolyte suitable for electrowinning.
An additional advantage is the substantially higher transfer of copper possible when using LIX-84I from ammoniacal solution than from acid solution. LIX-84I is composed of two stereoisomers, only one of which is active in acidic solutions but both of which are active in ammoniacal solutions. This allows a much smaller inventory of extractant to be used in ammoniacal systems for the same mass transfer.

The raffinate contains only Co(III) ammine which can be recovered in a variety of ways, depending upon local conditions. It can be precipitated as sulphide using NaHS, as a hydroxide by heating with NaOH (Fittock, 2009) or extracted using an organophosphorus extractant, such as D2EHPA or Cyanex® 272 and transferred into acid solution for electrowinning.

After the cobalt is recovered, the ammoniacal solution can be recycled back to the leaching stage or concentrated by steam stripping part or all of the stream. Steam stripping effectively resolves the water balance by recycling the ammonia in a much smaller volume of water. Any solution impurities remain behind in the ammonia-depleted solution and can be discarded, effectively bleeding these out of the circuit and preventing any build-up within the circuit.

If the multiple precipitation steps are eliminated, the AmmLeach flowsheet is very similar to the acid leach flowsheet. As a consequence, it is possible to convert an acid plant into an AmmLeach® plant with relatively little additional capital. The major additions are a mixer and the ammonia-recovery circuit, both of which are commonly used in mining and other industries.

CONCLUSIONS

The AmmLeach process provides a number of major advantages over an acid process. The circuit is significantly simpler as there is no need to clean up the acid solution after leaching in order to recover the copper and cobalt. The primary leaching reagent, ammonia, is almost completely recycled, whereas acid is consumed by the carbonate host rock and then neutralised by adding lime during precipitation of unwanted metals. The AmmLeach leach solution proceeds directly to metals recovery after separation from the tailings, ensuring recovery of all of the metal leached; cobalt losses during the precipitation stages in an acid process can be as high as 50% of the dissolved metal. The residue after AmmLeach is neutral and is easily revegetated, with any residual ammonia acting to fertilise the regrowth; acid residue may well require ongoing monitoring to ensure environmental compliance.
REFERENCES


