

AmmLeach® is a proprietary ammonia based process for the selective leaching and extraction of base metals from high acid consuming or complex ores under ambient temperature and pressure conditions.

Version 11

Technical Overview

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The AmmLeach® Process



The AmmLeach® process (patents granted and pending) is a new process developed by MetaLeach Limited, a wholly owned subsidiary of Alexander Mining plc, for the extraction of base metals, especially copper, zinc, nickel and cobalt from ore deposits and concentrates. The process utilises ammonia-based chemistry to selectively extract metals from ores under ambient conditions of temperature and pressure. The target ores will typically be high acid consuming, although AmmLeach® is also a viable alternative to acid leach processes as it is far more selective and offers a considerable number of technical and economic benefits.

The technology consists of the same three major stages as acid processes i.e. leaching, solvent extraction (SX) and electrowinning (EW). The leaching occurs in two steps, an ore-specific pre-treatment which converts the metals into a soluble form and the main leaching step, which uses recycled raffinate from the solvent extraction stage. Solvent extraction is used to separate and concentrate the metals, whilst also changing from ammoniacal media to acid sulphate media from which metals can be directly electrowon using industry standard unit operations. One of the key benefits of the AmmLeach® process is that, unlike some new technologies, it requires no special purpose built equipment. The AmmLeach® process can directly replace acid leaching in an existing operation.

AmmLeach® technology is suitable for both low grade heap leaching and higher grade tank leaching; the choice is dictated by the grade and deposit economics. Polymetallic deposits can be readily handled using standard solvent extraction and solution purification techniques.

The difference from acid leaching is that the leaching is conducted in moderately alkaline solution with ammonia present to selectively leach base metals. The use of alkaline conditions allows the use of AmmLeach® on high-carbonate ores where acid consumption would be prohibitive.

The AmmLeach® process has an extremely high selectivity for the target metal over iron, aluminium and manganese, which are insoluble under AmmLeach® conditions. Calcium and magnesium solubilities are also significantly suppressed by the presence of carbonate and extremely low sulphate levels in the leaching solutions. These features ensure that there are no potential problems due to jarosite or gypsum precipitation reducing permeability in the heap or scaling problems in the solvent extraction plant. Additionally, silica is also insoluble in the AmmLeach® process, removing problems associated with formation of unfilterable precipitates within an acid leach plant during pH adjustment and the need to handle high viscosity solutions. Ammonia, unlike acid, doesn't react with aluminosilicates and



ferrosilicates, whose products can cause drainage and permeability problems in heaps.

Compared with previous ammoniacal processes, almost any ore mineralogy can be treated as the pre-treatment step is specific to each orebody. The whole AmmLeach® process is tailored to individual ore bodies and consequently has substantially lower ammonia losses than earlier processes. In theory, all the ammonia can be recovered, however in practice small losses do occur.

Decommissioning of the heap is extremely simple as no neutralisation is necessary and the potential for acid mine drainage is virtually eliminated. After final leaching the heap is simply washed to recover ammonia and then left to revegetate, with the residual ammonia acting as a fertiliser.

The alkaline residue allows immediate application of cyanide leaching of gold and silver in ores where there is an economic precious metal content after removal of high cyanide consuming metals such as copper.

Typical Capital and Operating Costs for Copper Heap Leaching

An analysis of the economics of the AmmLeach® process compared with conventional acid leaching for high acid consuming copper ores is dependent upon a multitude of parameters specific to the mineralogy of the deposit and its location. Suffice it to say that the capital and operating cost savings can be major, particularly for high acid consuming ore bodies located in remote locations with long transport distances. This is because the safe supply of sulphuric acid is logistically difficult and expensive as the transport costs of bulk chemicals in-country to site can be as much again as, or more than, the FOB cost.

In many instances, economics will dictate that the mine will have to build an expensive sulphur burning sulphuric acid plant for the supply of acid. In addition, to regulate supply variations and for acid plant maintenance, acid storage tanks for around one month's consumption, whether the mine makes its own or buys in acid, will be required, significantly adding to the capital cost. As well as a substantial capital cost saving, this is where AmmLeach® has a major operating cost advantage too, due to the order of magnitude difference in reagent consumption per tonne of ore processed.

For example, for even a moderately high acid consuming ore, ten to fifteen times as much acid (50kg/t) as ammonia will be consumed. This is due to the fundamental difference between the two leaching processes in that whereas acid is consumed by gangue minerals during leaching, ammonia is not. The reagent is can be recycled and only relatively small losses of ammonia need to be made up.

Capital costs comparisons for the AmmLeach® technology and conventional acid leaching assume that certain aspects are common to both leach systems i.e. mining, mine infrastructure, mine waste disposal, process plant residue disposal, project buildings (administration, laboratories, workshop, warehouse etc), site access roads, the power transmission line and the water supply line. Hence any comparison is limited to the process plant itself.

Typically for copper only oxide ores, process plant capital costs for AmmLeach® and acid heap leach operations of the same size are similar as, excluding reagent production and storage/handling costs on site, essentially the same equipment is used for both processes. However, importantly, where economics dictate that



sulphuric acid is made on site, there can be a major differential associated with reagents and, in particular, the differential costs of ammonia and sulphuric acid.

The AmmLeach® process can achieve much higher copper solution concentrations in the pregnant leach solution (PLS) than are typically seen in acid plants. Typical copper concentrations for an acid leaching operation are of the order of 1-2g copper (Cu)/L compared to PLS concentrations for the AmmLeach® process of 6-12g Cu/L. This, coupled to the much greater copper transfer between aqueous and organic, allows the efficient handling of high copper tenors in PLS (in acid plants this would necessitate larger volume mixer-settlers due to the higher volume of PLS and lower transfer between aqueous and organic phases); i.e. more metal produced per unit capacity of plant than in a corresponding acid leach-SX-EW plant.

Moreover, in ores where cobalt is a valuable bi/co-product (eg DRC and Zambia), AmmLeach® offers additional significant capital and operating cost savings. This is because in the case of the acid leach circuit the cobalt recovery circuit is complex in that the main leach solubilises a range of metals. The raffinate bleed will therefore contain unextracted copper, iron (both ferrous and ferric), manganese and aluminium. Other species may also be present and these will need to be examined and potentially dealt with as well. Such metals include nickel and cadmium. For the production of metal a multiplicity of unit operations are required ahead of cobalt metal production.

In the case of the alkaline leach circuit, the requirements for purification ahead of final cobalt recovery are much less complex. The leach itself is highly selective for copper and cobalt since not all metals will produce ammines. In this respect there is negligible iron and manganese present in the liquor. A number of possibilities exist for recovery of cobalt from the ammoniacal solution.



Potential Applications

The following metals are particular targets for the AmmLeach® process:

- Copper and Copper/Cobalt oxide deposits
- Zinc oxide deposits
- Gold/Copper oxides and Silver/Zinc oxides (alkali leaching)
- Molybdenum oxides

Of these, the copper process has already been demonstrated at pilot plant scale for heap leaching and at bench scale for agitated leaching (a more comprehensive description can be found below). The cobalt (or copper and cobalt oxide ore) process has been bench tested successfully for both heap and agitated leaching.

Further development of the zinc process has led to a new solvent extraction process for zinc from ammoniacal solutions, for which patents are granted and pending. This patent application is for the recovery of zinc from ores which do not require pretreatment before ammoniacal leaching. A patent covering a process allowing selective leaching of zinc from sideritic ores has also been applied for.

Because of the tailored pre-treatment step, almost any ore type is amenable to the AmmLeach® process. Thus far, it has been demonstrated on predominantly oxide ores but sulphides have also been shown to leach after appropriate pre-treatment. This advance allows the treatment of mixed oxide-sulphide ores which are often present in the transition from weathered to unweathered ore. As a project proceeds, the AmmLeach® process can be modified to cope with the changing mineralogy from oxide to sulphide without substantial capital expenditure.

Polymetallic ores can also be processed by AmmLeach® with separation achieved using solvent extraction to separate metals and produce multiple revenue streams. The minimisation of ammonia transfer allows these metals to be recovered directly from their strip solution by precipitation, crystallisation or electrowinning.

The alkaline conditions used in the AmmLeach® process allow precious metals to be recovered from the base metal depleted heap using a secondary leach step. The heap can simply be washed to recover ammonia and subjected to standard alkaline cyanidation to recover gold and silver. Work is currently underway to incorporate precious metal recovery within the AmmLeach® process. Preliminary work on the leaching of cyanide consuming metals prior to precious metal leaching with cyanide looks highly promising.



Copper

The León copper deposit in northern Argentina is a sediment-hosted, stratabound copper/silver deposit comprising two north-trending sub-parallel zones, hosted by a limestone unit termed the Yacoraite Formation and is in the basic form of a horseshoe, open to the northwest. The eastern zone is termed El Plomo and the western zone called El Cobre. The predominant copper minerals in both deposits are the common carbonates malachite and azurite.

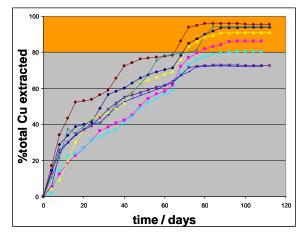
Leaching tests indicated sulphuric acid consumptions ranging from 300 to >1,000kg acid per tonne for a number of samples from León. A composite ore sample ground to <75 microns leached 86.2% of the total copper, whilst consuming 1,150kg acid per tonne of ore. The same sample was leached in ammoniacal solution giving 81.2% Cu recovery in 72 h, 94% of the acid leachable copper. This leach did not involve the application of an ore specific pre-treatment stage which is a key feature of the patent pending AmmLeach® process.

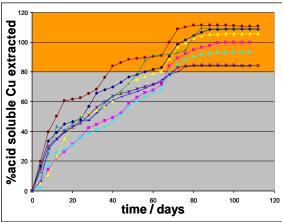
This result compares extremely well with acid heap leach operations where copper recoveries of 55-100% of leachable copper were reported (Jackson et al, Cobre '99, vol. IV, p.493-566). The high fraction of leachable copper is also comparable with the published data from operating acid plants (*ibid.*) which had leachable copper contents ranging from 20-98 %.

The recovery of copper during column leaching of pure and blended ore is shown below left. As is clear, the extraction of copper is very rapid, with one column achieving >80% recovery within 70 days. The other columns reached 80% recovery within 80 days, the only two columns which did not achieve 80% recovery were duplicates of one ore type. These results compare very favourably with acid heap leach plants where leach times of 45-540 days are used. The shorter leach cycle times mean earlier cash flow.

The right hand graph shows the fraction of "acid leachable" copper, clearly, the AmmLeach® process is more effective than acid leaching with most columns showing >100% acid leachable copper. The improvement in both rate and extent of recovery is due to the use of the ore specific AmmLeach® pre-treatment step.

Copper recoveries from Leon ore during column leaching





The data shown in the graph does not adhere to the standard shrinking core model, which is typically used for heap leach operations. This indicates that the leaching



rate is not controlled by diffusion into or out of the rock particles. The near linear recovery with time after an initial rapid leaching period indicates that the rate controlling step is reagent supply – i.e. stronger leaching solutions will increase the rate of recovery. However, the use of stronger solutions can also result in greater ammonia losses so optimising the leaching rate using economics is important.

The reason for this leaching behaviour is that the pre-treatment step has mobilised the copper within the ore and redeposited it onto the surface where it is much more readily and rapidly accessible to the leaching solution. This is clearly shown in the photograph below left which shows a broken 4" ore particle from the early stages of the Leon heap leach. The particle shows a clear coating composed of malachite / azurite whilst the centre of the particle is essentially barren. The right hand photograph shows the surface of the heap after the initial pre-treatment stage, the drippers are in place to apply the leaching solution.

Broken ore particle from the Leon heap leach (left) and overview of the heap (right) after the ore-specific pre-treatment stage

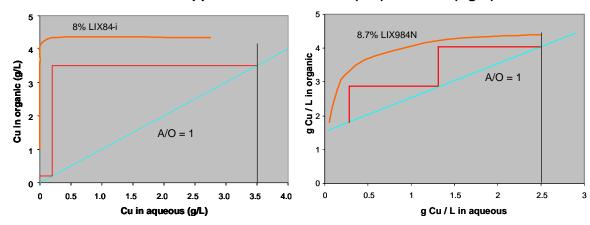




The capability of tailoring the rate of recovery is an important feature of the AmmLeach® process and allows the plant to operate more flexibly with the rate of leaching matched to the operating capacity of the solvent extraction plant. Alternatively, production can be increased at low cost by using a stronger leach solution, coupled with a higher extractant concentration in the SX plant.

A typical isotherm for solvent extraction of copper from ammoniacal solution is shown below left and an isotherm for acid solution is shown below right (Cognis Redbook, 2007, p.33).

Isotherms for SX of copper from ammoniacal (left) and acid (right) solutions





The very steep initial rise and sharp inflection point for the ammoniacal system indicates that high copper extractions leaving a very low raffinate are achievable. The overlaid McCabe-Thiele diagram shows that a single stage will reduce the PLS from 3.5g/L to <0.2g/L. A similar construction for the acid system shows two stages are required to reduce copper from 2.5g/L to 0.22g/L – a third stage would be needed for a PLS containing 3.5g/L. The net transfer from ammonia is much greater with 0.41g Cu/L/vol% LIX84-I compared with 0.26g Cu/L/vol% LIX984N allowing a smaller SX plant to recover the same quantity of copper.

Ammonia transfer from leach solution to the organic can be a problem as this builds up in the electrolyte until ammonium sulphate precipitates. However, a further feature of the AmmLeach® process is that the ammonia transfer is minimised during solvent extraction so that it cannot build up to levels that cause significant transfer to the organic phase and formation of precipitates during stripping.

The solvent extraction is stripped using sulphuric acid based depleted electrolyte from the electrowinning plant. This stage is common to all copper electrowinning operations and presents no design or operational difficulties.

Electro winning cells at Leon pilot plant







Comparison of AmmLeach® with acid leaching of copper

Parameter	Acid	AmmLeach®	
Mineralogy	Oxides, carbonates, silicates, some sulphides	Almost any – dependent upon pre- treatment stage	
Selectivity	Low: iron, manganese, calcium and silica are likely problems	High: no iron, manganese, calcium or silica dissolution	
Rate of extraction	Limited by acid strength and diffusion	ammonia concentration in leach solution matched to leaching rate	
Recovery	80% of leachable metal	>80% in 50 days	
Heap lifetime	~55-480 days	~60-130 days	
Sulphate precipitation	Reduced permeability in heap, break down of clays and plant scaling due to precipitation of gypsum and jarosite	Calcium and iron solubilities too low for precipitation, also low sulphate levels in leach solution	
Leachant consumption	Depends upon carbonate content but 30 to over 100kg/t reported for operating heaps	Depends on concentration used but range of 3-5kg/t measured at Leon	
Safety	Large volumes of concentrated acid required	On-demand systems using hydrolysis of urea to minimise onsite risks	
Precious metals	Heap to be neutralised before cyanidation	Neutralisation not required, potential for simultaneous recovery using thiosulphate or sequential leaching using cyanide	
Decommissioning	Heap requires washing, neutralisation and long term monitoring to avoid acid mine drainage (AMD)	Heap can be washed and left, residual ammonia acts as fertiliser for vegetation regrowth, minimal likelihood of AMD.	

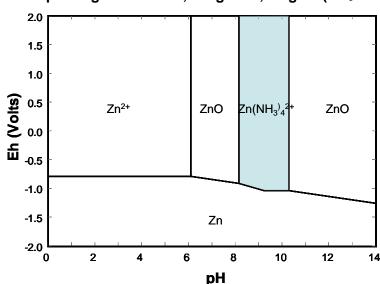


Zinc

The general flow sheet for the zinc process is straightforward and consists of leaching, purification and recovery stages. The nature of the leach stage depends upon a number of factors, notably the grade of ore and leaching kinetics. High grade, fast leaching ore would be readily accommodated by an agitated tank leach, whilst low grade, slow leaching ores would be better suited to heap leaching. Depending upon the product desired, there may be no need for a solution purification stage, further simplifying the overall process flow sheet.

Leaching

The potential-pH diagram below shows zinc is soluble in ammoniacal solutions as the tetra-ammine complex. For these conditions, the upper and lower pH boundaries are approximately 1 pH unit either side of the pH where there are equimolar concentrations of ammonia and ammonium. For lower zinc (Zn), or higher ammonia, concentrations in the PLS these boundaries will expand, giving a wider pH range. The range of solubility is lower than for copper but the use of the ammoniacal - ammonium carbonate leach will buffer the leaching solution within the required window.



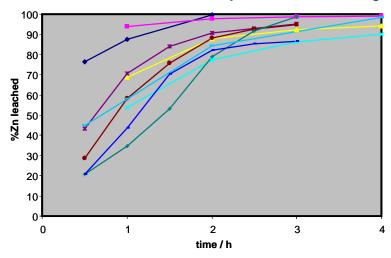
Potential-pH diagram for zinc, 6.3 g/L Zn, 17 g / L (NH₃ + NH₄⁺)

A wide range of different oxide zinc mineralogies can be treated by AmmLeach®, including those with significant hemimorphite content which presently can only be treated using acid. The acid route requires ore containing >10% zinc to be economically viable. The co-dissolution of silica and iron in the acid results in a very complex flow sheet, as typified by that used at the Skorpion mine in Namibia. The tailings from Skorpion are typically >4% Zn showing that acid leaching can be extremely inefficient.

In AmmLeach® solutions, the leaching can be extremely rapid provided the conditions are appropriately matched to the ore. The graph below shows the extent of leaching for several different oxide zinc ores pre-treated according to the mineralogy. The head grades ranged from 5.2 to 19 % Zn and the mineralogy ranged from pure smithsonite to predominantly hemimorphite. The highest solution tenor achieved was >100g/L and higher tenors should be achieved with further optimisation.



Leaching curves for different zinc oxide ores pre-treated according to mineralogy



Separation and recovery

The tenor of the zinc in the leaching solution also determines the subsequent options for purification and recovery. Ideally, the solution would be of sufficiently high tenor to go directly to a recovery stage and this may well be the case for high grade, fast leaching ores. There are several options for recovery and the selection of the particular method is likely to be site dependent.

The potential processes for zinc recovery from AmmLeach® solutions are summarised in the table below.

		leach solution zinc tenor		
recovery method	product	<10 g/L	10-50g/L	>50g/L
pH adjustment	ZnO / ZnCO ₃	no, too high cost	possible	yes
sparging with CO ₂	ZnCO ₃	no, too high cost	possible	yes
steam stripping	ZnO / ZnCO ₃	possible	possible	yes
spray drying	ZnO	no, too high cost	no, too high cost	yes *
crystallisation by cooling	ZnCO ₃	no, too high cost	no, too high cost	possible
solvent extraction	high Zn solution	yes	yes	maybe **
SX with acid strip / EW	Zn metal	yes	yes	yes

^{*} may also be performed after SX to produce zinc sulphate crystals

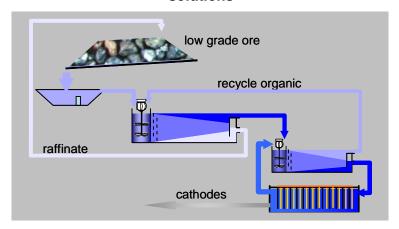
As can be seen, for low tenor solutions, such as those from heap leaching, the most viable route is to increase the solution tenor using solvent extraction and then use a second process depending upon the desired product.



^{**} SX may be used to transfer the zinc from ammoniacal to acid sulphate solution whilst removing some impurities reducing cementation costs before electrowinning.

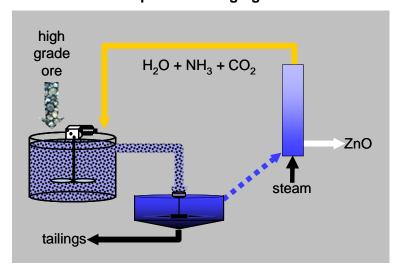
MetaLeach has developed a novel (patents applied for) process for the solvent extraction of zinc from ammoniacal solutions. An example flow sheet for this is shown below.

Example process flow sheet for the solvent extraction of zinc from ammoniacal solutions



The ultimate aim is to produce commodity Special High Grade zinc metal by an electrolytic process. However, this requires a cell house and an available local source of low cost power. Many operations will be too small to justify this level of capital investment so an intermediate product may be desirable. The ammoniacal zinc solution can be steam stripped to remove the ammonia and carbon dioxide (both of which are captured and recycled into the leaching stage), resulting in the precipitation of a zinc oxide-carbonate-hydroxide solid. The solid can then be calcined to produce zinc oxide which is readily saleable either to existing Roast-Leach-Electrowin (RLE) plants or as an intrinsic value added product. Steam stripping of ammoniacal carbonate solutions is commonly used within the Sherritt-Gordon process for nickel and cobalt and presents no technological challenges. This flow sheet option for a high grade ore is shown below.

Flow sheet option for a high grade zinc ore





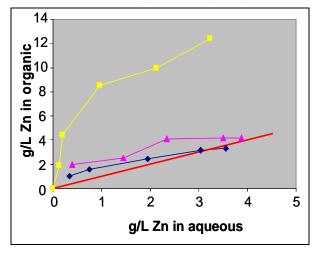
The direct recovery from solution will result in an oxide containing any impurities which are present within the ore and which also leach at the same time as the zinc. Potential contaminants reporting to the recovery process include copper, cadmium, nickel and cobalt. They may be at a sufficiently low level to not be of concern to either an end user of ZnO or an RLE plant, which has to purify the solution in any event. If the impurities are high then a separation process may be required to remove them from the zinc product and produce a potentially valuable co-product.

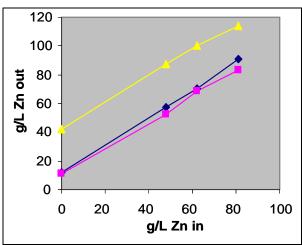
There is potential to use steam stripping to produce a zinc product and then to produce a higher impurity co-product by using several stages of stripping. However, this adds to process complexity and is undesirable. It is not anticipated that high grade, fast leaching zinc ores will contain such high levels of impurities that selective recovery is essential. The AmmLeach® process can be tailored to give selective dissolution of zinc minerals but leave behind most or all minerals containing other metals. However, such selectivity is ore specific and test work is required to assess the potential for selective leaching.

If a high grade zinc oxide is essential, zinc dust may be added to the PLS to cement out most of the major impurities likely to be leached. This process is commonly used in the RLE process to remove the elements which cause deleterious effects in the electrowinning process. After cementation, the purified solution can be steam stripped.

Lower tenor solutions are more problematical as steam stripping is unlikely to be commercially viable. Therefore, it is highly desirable to upgrade the solution. This can be achieved using MetaLeach's patents applied for solvent extraction process.

Test work has shown that zinc can be efficiently extracted from ammoniacal solutions using commercially available reagents in a single stage and stripped with acid solutions, with better efficiency and greater selectivity than has previously been reported. The isotherm for three extractants are shown below left, the most promising reagent has an isotherm similar to that for copper shown above and would only require a single loading stage.





Stripping from the three reagents is shown above right, a range of different synthetic spent electrolytes with up to 80g/L zinc in sulphuric acid were tested. Clearly, the solution tenor produced by stripping is sufficient for conventional electrowinning. The best reagent gave an increase in zinc tenor of around 25g/L, making it ideal for recirculation through an electrowinning cell house.



Comparison of AmmLeach® with acid leaching for zinc

Parameter	Acid (Skorpion)	AmmLeach®
mineralogy	oxides, carbonates, silicates	oxides, carbonates, silicates, sulphides
ore grade	cut off at Skorpion ~6-8% (tails reportedly >4%)	lower limit dependent upon economics
leaching	tank leach in >40g/L sulphuric acid, heated to 50-60°C	heap, vat and tank leach possible, solution tenor 0.5 to >100g/L
leaching efficiency	70-80% Zn leached in agitated tanks	70 to >98% depending upon leach method
selectivity	iron, manganese, calcium and silica are known problems	no iron, manganese, calcium or silica dissolution
silica control	careful control of conditions, pH, temperature, concentration etc	insoluble, no special measures needed
iron control	solvent extraction or precipitation	insoluble, no special measures needed
other impurities	very complex, multi-stage solvent extraction	depends upon desired product, maybe none, SX or cementation all viable
rate of extraction	limited by acid strength and diffusion	ammonia concentration in leach solution matched to leaching rate
sulphate precipitation	some plant scaling due to precipitation of gypsum and jarosite	calcium and iron solubilities too low for precipitation, also low sulphate levels in leach solution
leachant consumption	ore dependant but potentially very high	reagents recycled so losses are very low (3-5kg/t typical, <1kg/t in pilot plant)
solvent extraction / stripping	requires considerable solution manipulation, involving cementation/precipitation to remove iron, manganese and calcium because of low selectivity for zinc extraction into the organic phase	highly selective for zinc and significant advance over previously reported extraction efficiencies
recovery	electrowinning	see table above for options
product	metal	oxide, carbonate, sulphate or metal
safety	concentrated acid required, in large amounts	gaseous ammonia main hazard, on-demand systems using hydrolysis of urea minimises transport risks low consumption reduces make up requirements







MetaLeach Limited is a wholly owned subsidiary of Alexander Mining plc (www.alexandermining.com)

UK office:

Martin Rosser

Alexander Mining plc Salisbury House London Wall London

EC2M 5PS

England

Tel: +44 (0) 20 7078 9564 martinrosser@metaleach.com

