

**THE SELECTION OF A HYDROXIDE PRECIPITATION /
AMMONIACAL RELEACH CIRCUIT FOR METAL
RECOVERY FROM ACID PRESSURE LEACH LIQUORS**

by Dr. M.L. Steemson

**Hydrometallurgy Research Laboratories
MIM Holdings Ltd.**

**THE SELECTION OF A HYDROXIDE PRECIPITATION / AMMONIACAL
RELEACH CIRCUIT FOR METAL RECOVERY FROM ACID PRESSURE LEACH
LIQUORS**

by Dr. M.L. Steemson

TABLE OF CONTENTS

1.0	INTRODUCTION	3
2.0	HYDROXIDE PRECIPITATION / AMMONIACAL RELEACH CIRCUITS	4
3.0	TECHNICAL AND CHEMISTRY RELATED ISSUES IN THE SELECTION OF MgO OR LIME AS A METAL PRECIPITANT	8
4.0	AREAS FOR FURTHER INVESTIGATION	16
5.0	CONCLUSIONS	17

1.0 INTRODUCTION

It is interesting to note that most of initial flowsheets developed for metal recovery from acid pressure leach liquors over the past 5 years involved significant differences in processing routes. The major flowsheets that have been developed can be classified into the following areas:

- (1) Nickel/cobalt sulphide precipitation followed by oxidative pressure leaching of the nickel/cobalt sulphide to form nickel and cobalt products (e.g. the Sherritt processing route as practised at Anaconda Nickel).
- (2) Nickel/cobalt hydroxide precipitation followed by ammoniacal leaching of the nickel/cobalt hydroxide. Nickel is then subsequently extracted from the ammoniacal liquor via solvent extraction and electrowinning, with cobalt extracted as an oxide or sulphide from the nickel raffinate.
- (3) Direct solvent extraction of nickel and cobalt from acid pressure leach liquors. The major current projects following this route include Bulong (Resolute / Preston Mining) and Goro (Inco).

The first nickel laterite project to investigate a basic hydrometallurgical flowsheet involving hydroxide precipitation using MgO and subsequent ammoniacal leaching was Nical in the late 1980's. This work did not progress to the recovery of nickel via solvent extraction from the ammoniacal leaching liquors. With input from Henkel and Alta Metallurgical Services³, Highlands Gold Ltd. (with Hydrometallurgy Research Laboratories (HRL)) were the first Australasian based company to develop an MgO based nickel/cobalt hydroxide precipitation and ammoniacal leaching circuit for metal recovery in their Ramu nickel laterite project. This incorporated the production of nickel metal from ammoniacal leachates using solvent extraction and subsequent electrowinning. As per the earlier Nical work, an ammonia / ammonium carbonate leachate was employed to leach nickel and cobalt from nickel/cobalt hydroxides. More recently, other nickel laterite projects (such as Cawse (Centaur Mining) and Marlborough (Preston Resources)) have adopted this flowsheet in their metal recovery circuits.

In an effort to reduce operating costs in the nickel/cobalt hydroxide precipitation and ammonia leaching stages of the Ramu nickel project, HRL and Highlands Gold Ltd. have developed a modified circuit based on the use of lime as the nickel/cobalt hydroxide precipitant followed by ammoniacal leaching in an ammonia / ammonium sulphate leachate. The impetus for this modified circuit was the high cost of caustic MgO when delivered to site as compared to on-site production of lime. In their recently completed feasibility study on the Ramu nickel laterite, Highlands Pacific Ltd. has adopted this modified flowsheet. The feasibility study involved further testing at pilot plant scale of the lime based hydroxide precipitation / ammonia leaching circuit at Lakefield Research Ltd. in Canada based on design criteria supplied by HRL⁴.

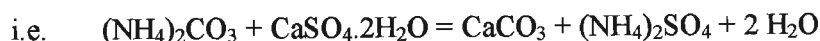
The current paper is a discussion of issues involved in the selection of an appropriate hydroxide / ammoniacal leaching processing route. The focus of the current discussion will be on the alternative use of caustic MgO or lime as the nickel/cobalt hydroxide precipitant, and the subsequent processing and cost issues involved.

2.0 NICKEL / COBALT HYDROXIDE PRECIPITATION / AMMONIACAL RELEACHING CIRCUITS

2.1 GENERAL

The objective of a hydroxide precipitation / ammoniacal releaching circuit in the metal recovery stage of a nickel laterite acid pressure leach circuit is to produce a suitable ammoniacal leach liquor for nickel solvent extraction and electrowinning, with maximum recovery of the nickel and cobalt. This involves two stages:

- (1) The production of a nickel / cobalt hydroxide precipitate. Conventionally, MgO has been the preferred metal precipitant for nickel and cobalt recovery, owing to the ready filterability of MgO based hydroxide precipitates, and the compatibility of the nickel / cobalt hydroxide precipitant with ammonia leaching using an ammonia / ammonium carbonate leachate. However, the cost of MgO is high, with consumable costs ranging from 10 to 25 US c/lb of nickel, depending on the project location and MgO source. This makes MgO generally the second highest consumable cost in an acid pressure leach project. A second alternative, pioneered by HRL in the Ramu nickel project was the use of low cost lime as the primary nickel / cobalt hydroxide precipitate. This is particularly attractive if suitable quality lime can be produced from local limestone deposits.
- (2) The releaching of the nickel / cobalt hydroxide in ammoniacal leach liquor to produce a suitable feed for nickel solvent extraction, typically 12 gpl Ni. A key advantage of the ammoniacal releach is its capacity to reject any co-precipitated manganese and iron in the hydroxide feed. For an MgO based hydroxide precipitate an ammonia / ammonium carbonate based releach can be implemented. For a lime based hydroxide precipitant, the ammonia / ammonium carbonate based releach cannot be employed owing to reaction by ammonium carbonate on gypsum contained in the hydroxide cake,



The net effect is a rapid buildup in ammonium sulphate in the leachate, and an accompanied depletion in ammonium carbonate. In order to overcome this problem, HRL have developed an ammonia / ammonium sulphate based releach circuit, as implemented in the Ramu nickel project flowsheet.

2.2 NICKEL / COBALT HYDROXIDE PRECIPITATION

In order to achieve maximum nickel and cobalt recovery, with minimum manganese co-precipitation to the hydroxide precipitant, HRL have employed a two-stage hydroxide precipitation circuit for use with both lime and MgO as the metal precipitant in acid pressure leach projects. A third stage is also implemented if soluble manganese control is required in the leach circuit.

Figure 1 presents a schematic of the hydroxide precipitation circuit. In the first stage, the objective is maximum nickel and cobalt recovery with minimum manganese

carryover. Typical process parameter parameters are an operating temperature of 60 to 90 °C, with a total residence time of 2 to 4 hours. Generally, 90-98% of the nickel and 85-95% of the cobalt can be recovered, alongside with 15-35% of the manganese. Either MgO or lime can be employed as the metal precipitant. The major difference, apart from cost, is the mass of hydroxide cake formed, with lime based hydroxide cake having about twice the mass of an MgO based hydroxide cake, owing to the presence of extra gypsum in the hydroxide cake. A typical dried MgO based hydroxide cake, using high quality commercial MgO, assayed at 38% Ni, 1.4% Co, 4% Mg and 2.5% Mn. A similar dried lime based hydroxide cake, with high quality commercial lime, assayed at 19% Ni, 0.8% Co, 0.7% Mg and 2.1% Mn. The actual analysis of the cake will depend on the leach liquor characteristics, and the quality of the precipitating agent.

The objective of the second nickel / cobalt hydroxide precipitation stage is to recover the bulk of the un-precipitated nickel and cobalt in solution, whilst rejecting manganese. Lime is the preferred choice of precipitant, owing to its significantly lower cost than MgO. Typically, well over 99.5% nickel and cobalt total recovery (hydroxide precipitation stages 1 and 2) can be achieved, with 30-50% of the total manganese being co-precipitated.

An important issue in the second precipitation stage is the disposition of the nickel / cobalt precipitate. Two options are available:

- (1) Mild acid leaching to recover the nickel and cobalt, for example, recycling the second stage nickel / cobalt precipitate to be re-dissolved in autoclave discharge liquor.
- (2) Recycling the second stage precipitate to the first stage. In continuous experimental trials, HRL has noted that manganese oxides can partly be used to precipitate soluble nickel and cobalt, thus lowering the amount of manganese deportment to the first stage nickel / cobalt hydroxide precipitate.

The final hydroxide precipitation stage involves the use of lime to precipitate soluble manganese, in order to satisfy environmental constraints, and/or to prevent manganese buildup in the leach circuit if spent leach liquor is employed as CCD wash water. Using aerated reactors, the final soluble manganese level can readily be reduced to 50-100 ppm.

2.3 AMMONIA LEACHING OF MgO BASED HYDROXIDE PRECIPITANTS

Figure 2 presents a schematic of a typical ammonia / ammonium carbonate based re-leach circuit treating nickel / cobalt hydroxide produced using MgO, which has been adopted, or proposed, in several current nickel laterite projects. This involves the following stages:

- (1) An ammonia leach stage to redissolve nickel, cobalt, zinc and copper in the nickel / cobalt hydroxide, but to reject manganese and iron. Important issues are that sulphate present in the nickel / cobalt hydroxide will deport to the ammoniacal leach liquor, in the form of ammonium sulphate, and that cobalt is required to be in the cobaltic state in the ammoniacal liquor in order to

minimise subsequent nickel organic poisoning. Aeration can be employed to assist in manganese precipitation during the leach, and to assist in cobalt oxidation, but at the cost of higher ammonia losses to the offgas. Typical ammonia leach temperatures are 40 to 60 °C, with residence times of 1 to 3 hours (lower residence times will most likely require a partial stripping stage).

- (2) Thickening and filtration of the ammonia leach residue, after washing. The ammonia leach residue can be recycled to either a mild acid leach, or introduced into the pressure acid leach autoclaves, to recover any unleached nickel and cobalt.
- (3) A partial strip of ammonia and carbon dioxide can be employed to reduce the ammonia content in the feed to nickel solvent extraction, and to further assist in manganese precipitation.
- (4) Nickel solvent extraction and electrowinning to produce nickel cathode. A review of issues relevant to nickel solvent from ammoniacal solutions produced from nickel laterites is discussed in Mackenzie et al².
- (5) The production of a mixed cobalt / zinc sulphide from nickel raffinate.
- (6) Recycle of ammoniacal liquor after recovering ammonia and carbon dioxide from a bleed stream via steam stripping. Ammonia is also recovered from vent gases in the ammonia leaching plant via scrubbers. Ammonia makeup can be provided by additional ammonia addition to the circuit, or the use of ammonium sulphide as the sulphide precipitant. Carbon dioxide can be added as a CO₂ supplement, or using offgases from limestone neutralisation stages. Issues which require consideration are the ammonia losses via ammonium sulphate formation and the environmental impact of ammonium sulphate containing effluents, and the impact of ammonium sulphate on ammonia and carbon dioxide recovery (this may limit the amount of ammoniacal liquor which can be recycled without steam stripping of the ammonia and carbon dioxide).

In general, an ammonia / ammonium carbonate based re-leach circuit is amenable to the processing of an MgO based nickel / cobalt hydroxide to produce nickel metal and cobalt intermediates. Significant issues (apart from maximising nickel and cobalt extraction during ammonia leaching) are sulphate deportment, the oxidation of cobaltous ammine (Co²⁺) to cobaltic ammine (Co³⁺) in order to prevent organic poisoning, manganese control, and the design of the ammonia recovery and regeneration circuits.

2.4 AMMONIA LEACHING OF LIME BASED HYDROXIDE PRECIPITANTS

A schematic of an ammonia / ammonium sulphate based re-leach circuit treating nickel / cobalt hydroxide produced using lime as the precipitant is shown in Figure 3. Although similar to the ammonia / ammonium carbonate based re-leach circuit, there are a number of noted differences:

- (1) A significantly higher mass of releach residue is produced owing to the carryover of gypsum. This increases the size of the releach thickener and filters. Additionally, ammonia losses to the releach residue become significant. This is exacerbated by difficulties in washing the residue, owing to the presence of a significant amount of fines. The net effect is a requirement to recover entrained ammonia from the releach residue in a lime boil stage (alongside of a bleed stream which is most likely governed by the overall water balance).
- (2) The recovery of nickel and cobalt from releach residue is more difficult. During the Ramu pilot plant⁴, 95% of the nickel and 80% of the cobalt in the ammonia leach residue were recovered in a mild acid leach. This can represent a significant cobalt loss of 2.5-3% of the feed material to ammonia leaching. To improve this loss of metal, HRL have developed a nickel / cobalt dissolution stage, utilising sulphur dioxide / air, which improved nickel and cobalt recoveries from the releach residue to over 99% for the nickel, and 96-97% for the cobalt. Such a metal recovery strategy is shown in Figure 3.
- (3) Sulphate carryover is not a significant issue, thus impurity buildup and the overall water balance govern the bleed.
- (4) The use of a partial strip for manganese scavenging control may not be effective. However, this can be achieved during the ammonia leach via an appropriate choice of residence time and aeration strategy. The use of either peroxide addition or oxygenation of ammoniacal leach liquor prior to nickel solvent extraction is recommended to ensure that cobalt is in the form of cobaltic ammine (Co^{3+}).
- (5) Vent gases from the ammonia leach circuit can be scrubbed in acidified water, thus reducing the volume of scrubber water to be recycled.

Thus, although much of the ammonia / ammonium sulphate based releach circuit is similar to that of a comparable ammonia / ammonium carbonate based circuit, noted differences are evident in residue handling and the design of the ammonia recovery system. Additionally, the extra filtration capital costs can be significant.

3.0 TECHNICAL AND CHEMISTRY RELATED ISSUES IN THE SELECTION OF MgO OR LIME AS A METAL PRECIPITANT

3.1 GENERAL

Having discussed some of the more important flowsheeting issues relating to the use of MgO or lime in hydroxide precipitation and ammonia re-leaching, an analysis of some of the key technical and chemistry related issues pertaining to the selection of a hydroxide precipitant is warranted. The data used in the current discussion is a compilation of batch and continuous data collected from hydroxide precipitation / ammonia re-leach information generated in process development work undertaken on several nickel laterite projects at HRL. Also included are Ramu project pilot plant data, generated at Lakefield Research Ltd. using HRL design data, and published Cause project process development data.

3.2 NICKEL / COBALT HYDROXIDE PRECIPITATION

A summary of nickel / cobalt hydroxide precipitation data using MgO and lime is presented in Tables 1 and 2. The data includes information from both batch and fully continuous experimental trials. With hydroxide precipitation, it is not possible to completely reject manganese from nickel laterite leach liquors, and some manganese will deport with nickel and cobalt to a hydroxide precipitate.

In general, the metal precipitation behaviour of nickel and manganese using lime and MgO is similar in a stage 1 precipitation (Figure 1), with over 90% of the nickel and 20-40% (typically 30%) of the manganese being precipitated. For cobalt, MgO may be slightly superior, with cobalt recoveries generally over 90% using MgO and 80-90% using lime. In a two stage precipitation circuit, over 99.5% of the nickel and 99% of the cobalt can be recovered using either MgO or lime. An MgO based nickel / cobalt hydroxide cake has a significantly higher nickel and cobalt content than a comparable lime based precipitate, owing to the presence of gypsum in a lime based nickel / cobalt hydroxide.

The precipitation behaviour of both lime and MgO is kinetically determined, with higher reaction times generally increasing the recovery of nickel and manganese. The kinetics of MgO precipitation are marginally slower than that of lime (significantly slower if coarse MgO is employed). The behaviour of cobalt is more complex, with cobalt-manganese interactions occurring during precipitation. Typically, 3 hours residence time is typically required for a first stage hydroxide precipitation.

During continuous lime precipitation trials using lime, when the second stage hydroxide precipitate was recycled to the first stage, it was observed that both the lime requirement was slightly lower, and a reduction in manganese precipitation was noted. This effect is illustrated in Table 1, whereby stage 1 manganese extraction was reduced from the typical 30% to 13%, when stage 2 nickel / cobalt hydroxide product was recycled in continuous trials. This suggests that manganese hydroxides can

Table 1 : Nickel / Cobalt Hydroxide Precipitation Results using MgO as the Precipitating Agent

Test Type	Feed Liquor Composition	Precipitation Conditions			Metal Recovery (%)			Hydroxide Dry Analysis
		Temp. (°C)	Residence Time / Batch Time (hrs)	MgO Addition ¹	Nickel	Cobalt	Manganese	
BATCH	5.1 gpl Ni, 0.19 gpl Co, 1.1 gpl Mn, 34 gpl Mg	75	3	106% stoich to Ni+Co	92	98	39	38% Ni, 1.4% Co, 4% Mg, 2.4% Mn
	6.4 gpl Ni, 0.23 gpl Co, 2 gpl Mn, 22 gpl Mg	75	3	110% stoich to Ni+Co	95	94	30	27% Mg, 1.3% Co, 1% Mg, 2.9% Mn
	3 gpl Ni, 0.3 gpl Co, 2.5 gpl Mn, 2.7 gpl Mg	60	7	170% stoich to Ni+Co	>99	97	34	
CONTINUOUS: STAGE 1	2.8 gpl Ni, 0.3 gpl Co, 2.5 gpl Mn, 2.6 gpl Mg	60	3 (3 vessels in series)	pH 7.3 final reactor	98	98	15-20	
		60	3 (3 vessels in series)	pH 7.5 final reactor	>99	98	28-30	

1 Different sources of MgO have been employed in the current summary, with different quality characteristics.

Table 2 : Nickel / Cobalt Hydroxide Precipitation Results using Lime as the Precipitating Agent

Test Type	Feed Liquor Composition	Precipitation Conditions			Metal Recovery (%)			Hydroxide Dry Analysis
		Temp. (°C)	Residence Time / Batch Time (hrs)	Lime Addition ¹	Nickel	Cobalt	Manganese	
BATCH	5.4 gpl Ni, 0.19 gpl Co, 2 gpl Mn, 19 gpl Mg	75	3	110% stoich to Ni+Co	89	90	27	19% Ni, 0.84% Co, 0.7% Mg, 2.1% Mn
CONTINUOUS: STAGE 1	3 gpl Ni, 0.3 gpl Co, 6.5 gpl Mn, 8 gpl Mg	60	3 (3 vessels in series)	pH 7.2 aim in final vessel	98	75-80	28	
	2.8 gpl Ni, 0.22 gpl Co, 1.7 gpl Mn, 2.1 gpl Mg ²	60	3 (3 vessels in series)	pH 7-7.2 aim	>90	>85	25	
	3.6 gpl Ni, 0.35 gpl Co, 2.4 gpl Mn, 5.4 gpl Mg ³	60	3 (3 vessels in series)	6 gpl	98	93	13	
CONTINUOUS: STAGE 2	2.8 gpl Ni, 0.22 gpl Co, 1.7 gpl Mn, 2.1 gpl Mg ²	60	2 (2 vessels in series)	pH 7.7-7.8 aim	>99	>99	40	
	3.6 gpl Ni, 0.35 gpl Co, 2.4 gpl Mn, 5.4 gpl Mg ³	60	2 (2 vessels in series)	3 gpl	>99	>99	50 ⁴	

- 1 Different sources of lime have been employed in the current summary, with different quality characteristics.
- 2 Ramu pilot plant data⁴.
- 3 Second stage hydroxide product recycled to the first stage.
- 4 Additional manganese containing stream included in the feed to stage 2 in this trial.

precipitate nickel and cobalt from laterite leach liquors. Such a strategy may be an effective way of producing a higher quality nickel and cobalt intermediate product, but requires further development.

3.3 AMMONIA RELEACHING

Ammonia Leaching

The main similarities and differences between an ammonia / ammonium carbonate releaching system (treating an MgO based nickel / cobalt hydroxide) and an ammonia / ammonium sulphate releach (treating a lime based nickel / cobalt hydroxide) are summarised in Table 3. Supporting this data are summaries of the key results from a range of ammonia releach tests conducted on both MgO based hydroxides (Table 4) and lime based hydroxides (Table 5).

Both ammonia / ammonium carbonate and ammonia / ammonium sulphate releaching effectively recover nickel and cobalt from their respective hydroxides, with excellent rejection of manganese and iron. Both the final nickel and cobalt recoveries, and the leach kinetics are slightly better with an ammonia / ammonium carbonate leach. In general, 95-98% of the nickel and 84-95% of the cobalt can be extracted from an ammonia / ammonium carbonate leachate treating an MgO based hydroxide, as compared to 91-96% of the nickel and 80-90% of the cobalt from an ammonia / ammonium sulphate leachate treating a lime based hydroxide. This accentuates the need for an effective releach residue treatment scheme when treating lime based hydroxides (discussed further in Section 2.3). In terms of manganese, the sulphate based ammonia leach was interesting in that an initial burst of soluble manganese (up to 1000 mg/l) was observed, which quickly precipitates. This effect has not as yet been observed in the ammonium carbonate based ammoniacal leach.

An advantage of an ammonia / ammonium carbonate based leachate is that low levels of magnesium and calcium are observed in leach liquors. However, any sulphate in the feed hydroxide cake is solubilised (experimental data indicates close to 100% sulphate dissolution), and will deport as ammonium sulphate. In contrast, sulphate deportment to an ammonia / ammonium sulphate leachate is not an issue. However, calcium (from calcium sulphate in the feed) is solubilised to saturation level (500-700 mg/l), and magnesium is extracted (50-70%). Magnesium will need to be removed from the ammoniacal leachate via a bleed stream. In current test data using a lime based hydroxide feed, the magnesium build-up was about 200 mg/l per leach pass, which can be readily handled in bleed streams. It is clear that magnesium buildup would be excessive if an ammonia / ammonium sulphate leachate were treating an MgO based nickel / cobalt hydroxide.

An interesting observation in the ammonia / ammonium sulphate leaching of lime based hydroxides were the differences in cobalt recovery when comparing a stage 1 hydroxide feed to a mixed stage 1 and stage 2 feedstock (whereby the stage 2 hydroxide was recycled to stage 1). Table 5 indicates that the cobalt extraction was reduced from 87-92% to 81% by recycling stage 2 material. Clearly there are chemistry differences in the form of the stage 2 cobalt hydroxide, most likely due to manganese – cobalt interactions (in stage 2 a significantly higher proportion of manganese is precipitated when compared to the first stage). It is interesting to

Table 3 : Summary of Key Technical Issues Observed in Nickel / Cobalt Hydroxide Ammonia Based Releach Circuits

Ammonia Releach Stage	Ammonia / Ammonium Carbonate System Treating MgO Based Ni/Co Hydroxide	Ammonia / Ammonium Sulphate System Treating Lime Based Ni/Co Hydroxide
Ammonia Leach	Leach liquor content limited by Nickel SX requirements. 95-98% Ni, 84-95% Co recovery (Table 4)	Leach liquor content limited by Nickel SX requirements. 91-96% Ni, 80-90% Co recovery (Table 5)
	Fast nickel and cobalt kinetics (1-3 hours)	Slightly slower leach kinetics (3-5 hours)
	Good manganese rejection (< 20 ppm)	Good manganese rejection (< 20 ppm). Initial manganese peak, which quickly precipitates.
	Good iron, magnesium and calcium rejection	Good iron rejection. Magnesium extractions of 50-70% noted. Saturated calcium (500-700 mg/l)
	Close to 100% sulphate redissolution.	Sulphate transfer not an issue.
Ammonia Leach Thickening	Slow thickening to about 20% w/w solids density.	Slow thickening to 20-25% w/w solids density.
Residue Filtration	Slow filtration rate owing to fine manganese containing solids.	Slow filtration rate owing to fine manganese containing solids. Greater mass (3-4 x) owing to gypsum. Potentially higher ammonia losses.
Nickel Solvent Extraction	3 Extraction / 4 Stripping stages.	3 Extraction / 5 Stripping stages recommended owing to slower strip kinetics.
Cobalt Sulphide Precipitation	Stoichiometric sulphide addition.	Stoichiometric sulphide addition.
Ammonia Recovery	Steam strip of ammonia and carbon dioxide. Lime boil of ammonium sulphate?	Lime boil.

Table 4 : Summary of Ammonia / Ammonium Carbonate Releach Results treating an MgO based Nickel/Cobalt Hydroxide

Ni/Co Hydroxide Feed Liquor or Cake Composition	Type of Hydroxide Precipitation	Ammonia Leach				Metal Recovery (%)		Solution Impurity Level (mg/l)			
		Temp. (°C)	Time (hrs)	Initial Leachate (gpl)		Nickel	Cobalt	Mn	Fe	Ca	Mg
				NH ₃	CO ₂						
38% Ni, 1.4% Co, 4% Mg, 2.4% Mn	Stage 1	50	3	102	88	97	94	22	<1	7	67
27% Mg, 1.3% Co, 1% Mg, 2.9% Mn	Stage 1	50	3	102	88	97	84	53		2	55
30% Ni, 8% Co, 4% Mg, 12% Mn ¹						>98	90	40	1		30
3 gpl Ni, 0.3 gpl Co, 2.7 gpl Mg, 2.5 gpl Mn ²	Stage 1	40	3	100	100	95-98	82-95 ³	10-20			

1 Cawse nickel laterite project published data¹

2 A range of ammonia leach trials were conducted, at scales ranging from 1 to 20 L.

3 Most commonly 90-95% cobalt extraction.

Table 5 : Summary of Ammonia / Ammonium Sulphate Relach Results treating a Lime based Nickel/Cobalt Hydroxide

Ni/Co Hydroxide Feed Liquor or Cake Composition	Type of Hydroxide Precipitation	Ammonia Leach				Metal Recovery (%)		Solution Impurity Level (mg/l)			
		Temp. (°C)	Time (hrs)	Initial Leachate (gpl)		Nickel	Cobalt	Mn	Fe	Ca	Mg
				NH ₃	SO ₄						
19% Ni, 0.84% Co, 0.7% Mg, 2.1% Mn	Stage 1	50	5	80	100	96	90	<1	<1	520	220
3.6 gpl Ni, 0.35 gpl Co, 2.4 gpl Mn, 5.4 gpl Mg	Stage 1	45	3	80	100	96	92	2			
3.6 gpl Ni, 0.35 gpl Co, 2.4 gpl Mn, 5.4 gpl Mg	Two stage	40	4	80	100	91	81	<1		700	
3.6 gpl Ni, 0.35 gpl Co, 2.4 gpl Mn, 5.4 gpl Mg	Two stage	60	5	80	100	91	81	<1		520	
2.8 gpl Ni, 0.22 gpl Co, 1.7 gpl Mn, 2.1 gpl Mg ¹	Stage 1	60	3	100	100	94	87	<15			

¹ Ramu pilot plant data⁴.

note that Raman spectroscopic analyses of solid ammonia leach residues produced from the leaching of lime based hydroxides in an ammonia / ammonium sulphate leachate indicate that a bridging bidentate structure of some of the gypsum is formed, with elemental substitution of manganese (and possibly cobalt) for calcium in the crystal lattice. This, and cobalt absorption onto manganese hydroxides, may account for the lower cobalt recoveries observed.

Ammonia Leach Residue Thickening and Filtration

The leach residue thickening and filtration behaviour of lime and MgO based hydroxide feedstock to ammonia leaching was similar. The major difference is that the residue mass is significantly higher with a lime based leach residue, by a factor of 3-4, owing to the presence of insoluble gypsum in the feed. In both cases, a thickened solids density of 20-25% w/w solids was achieved, with slow filtration noted owing to the presence of fine manganese containing solids.

Nickel Solvent Extraction

During continuous nickel solvent extraction trials on both ammonia / ammonium carbonate and ammonia / ammonium sulphate containing leach liquors, HRL have observed slower stripping kinetics with the sulphate based feed. Using a 30% v/v LIX 84I nickel extractant (In Shellsol 2046), it was not possible to completely neutralise the acid in nickel strip liquor (60 gpl Ni, 100 gpl Na₂SO₄, 42 gpl H₂SO₄) in 4 stages of stripping treating an ammonia / ammonium sulphate feed liquor (12-13 gpl Ni). In contrast, a similar continuous solvent extraction trial, using ammonia / ammonium carbonate feed liquor, reduced the nickel strip liquor acidity to below detectable levels (pH 2.5-3) in 4 stripping stages. Further stripping tests indicated that a fifth stripping stage was required for the sulphate based feed in order to achieve the required pH levels for nickel electrowinning.

The above findings contrast with batch stripping data by Henkel², but are similar to Ramu nickel solvent extraction pilot plant data⁴.

For the extraction stages, over 99.8% nickel recovery was observed when treating both an ammonium carbonate, or an ammonium sulphate based feed liquor.

Cobalt Sulphide Precipitation

Using nickel raffinate produced from both sulphate and carbonate containing ammonia leach liquors, it was found that sulphide addition was an effective method for precipitating a mixed cobalt / zinc sulphide. In both cases, the sulphide addition was close to stoichiometric.

4.0 AREAS FOR FURTHER INVESTIGATION

The current analysis of ammoniacal leaching of nickel / cobalt hydroxides produced from the acid pressure leaching of nickel laterites has indicated a number of areas which warrant further investigation. These areas are:

- (1) A better understanding of sulphate deportment in hydroxide precipitation using MgO, with the objective of minimising sulphate deportment to nickel / cobalt hydroxide intermediate products.
- (2) An improved understanding of cobalt-manganese-gypsum interactions during hydroxide precipitation and ammonia leaching. This may lead to higher cobalt extractions in the ammonia leaching of lime based nickel / cobalt hydroxides and/or an improvement in the filtration characteristics of ammonia leach residues.
- (3) An improved understanding of the effect of sulphate in ammonia and carbon dioxide gas recovery systems.
- (4) Additional information quantifying the kinetic differences in both extraction and stripping between an ammonia / ammonium carbonate based leachate and an ammonia / ammonium sulphate based leachate during nickel solvent extraction.
- (5) Further studies quantifying the conversion of cobaltous ammine (Co^{2+}) to cobaltic ammine (Co^{3+}) in ammonia leaching. These studies would investigate the effect of the ammoniacal leachate type (carbonate or sulphate based), the ammonia leach process conditions (e.g. residence time and temperature), and the impact of aeration and oxygenation on the conversion.

Some of the above areas will be developed as current nickel laterite projects advance in development stages. Other areas warrant specific targeted studies.

5.0 CONCLUSIONS

The current paper presents a technical analysis of two potential metal recovery options employed in current nickel laterite projects:

- (1) Nickel / cobalt hydroxide precipitation using MgO followed by ammonia leaching using an ammonia / ammonium carbonate leachate.
- (2) Nickel / cobalt hydroxide precipitation using lime followed by ammonia leaching using an ammonia / ammonium sulphate leachate.

Ammonia / ammonium sulphate re-leaching of a lime based nickel / cobalt hydroxide offers significant potential operating cost savings by eliminating MgO (particularly if good quality lime can be locally produced), but has the following process disadvantages (when compared to carbonate buffered ammonia leaching of MgO based hydroxides):

- (1) Nickel and cobalt recoveries (particularly cobalt) are reduced during ammonia leaching, requiring the establishment of an appropriate re-leach residue treatment scheme. One such scheme, using readily available sulphuric acid and sulphur dioxide is introduced.
- (2) A higher mass of re-leach residue is produced, owing to inert gypsum.
- (3) A lime boil stage is required to recover ammonia from the re-leach residue and bleed streams, in lieu of steam stripping.
- (4) Nickel solvent extraction strip kinetics are slower, requiring 5 stripping stages instead of 4 as in the carbonate buffered amine leach.

Apart from these disadvantages, the lime based system has advantages in terms of eliminating sulphate carryover problems, and offering the potential for reduced manganese carryover to the hydroxide precipitate by utilising a two stage hydroxide precipitation strategy with recycle of the second hydroxide product to the first stage.

The selection of a hydroxide precipitation / ammonia re-leach scheme for a nickel laterite project will depend on local cost and reagent availability issues. However, both an MgO and a lime based option should be considered in individual projects.

Suggestions for areas which warrant further investigation and development in nickel / cobalt hydroxide precipitation and ammonia leaching are presented.

ACKNOWLEDGMENTS

The author wishes to acknowledge the support of Highlands Pacific Ltd. in the development of a lime based hydroxide precipitation and ammonia re-leaching processing route for treating acid pressure leach product liquors, and International Process Development Services for helpful discussions over the course of several nickel laterite projects. Further thanks are due to the efforts and advice provided by a number of HRL support staff, notably Mr Shayne Smail, Mrs Nicolette Canal, and Ms Jane Kilgour.

REFERENCES

- 1 Kyle, J.H. and Furfaro, D., "The Cawse Nickel/Cobalt Laterite Project Metallurgical Process Development", Proceedings of the Nickel- Cobalt 97 International Symposium, Volume 1, August, 1997, Sudbury, Ontario, Canada
- 2 Mackenzie et. al., "Extraction of Nickel from Ammoniacal Leach Solutions: Extractant and Solution Chemistry Issues", Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, May, 1997, Perth, Western Australia
- 3 Mackenzie et. al., "Recovery of Nickel from Ammoniacal Solutions using LIX 84-I", Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, May, 1996, Perth, Western Australia
- 4 Mason, P. and Hawker, M., "Ramu Nickel Process Pilot", Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum, May, 1997, Perth, Western Australia

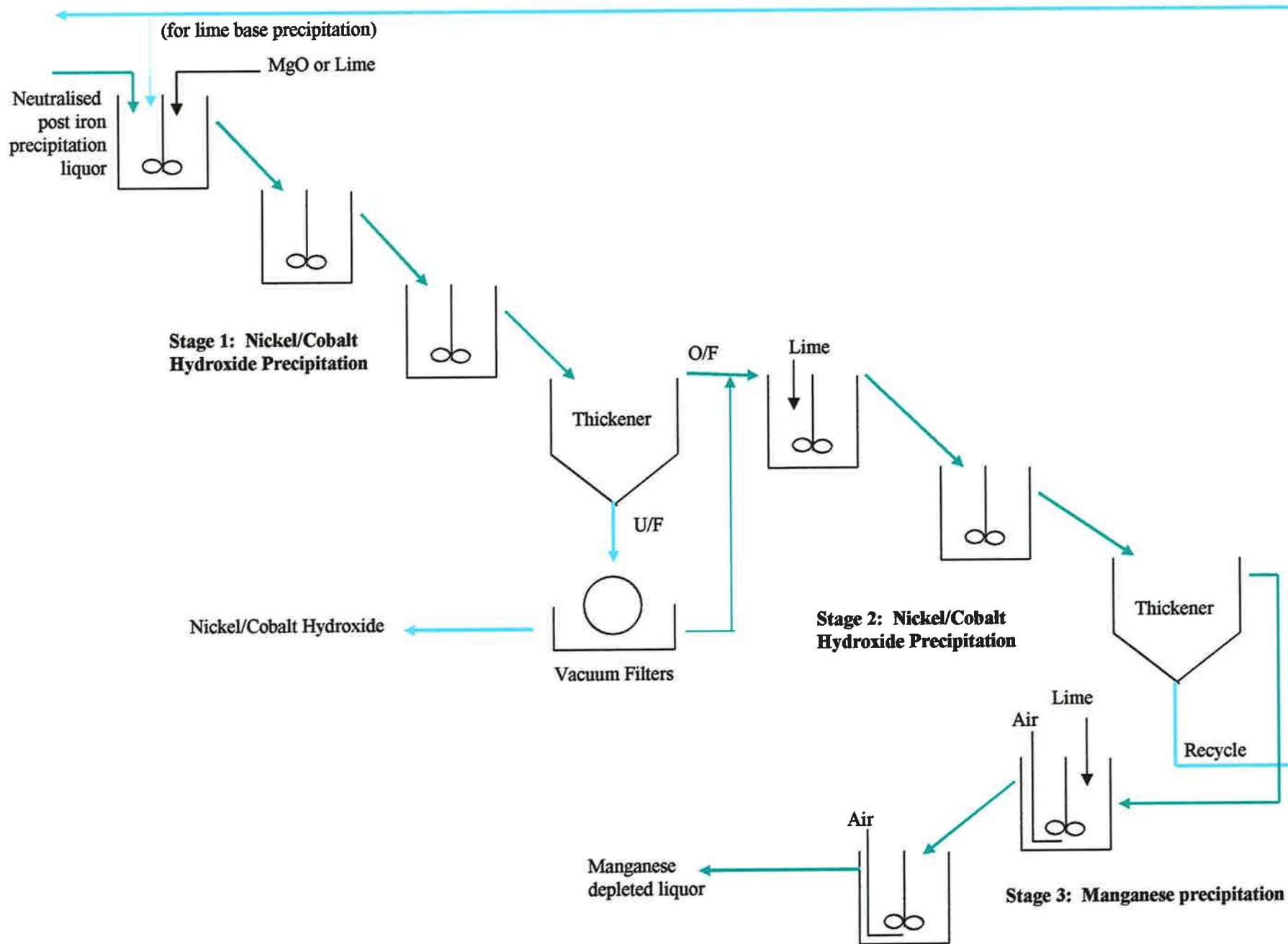


Figure 1: Schematic of Nickel/Cobalt Hydroxide Circuit

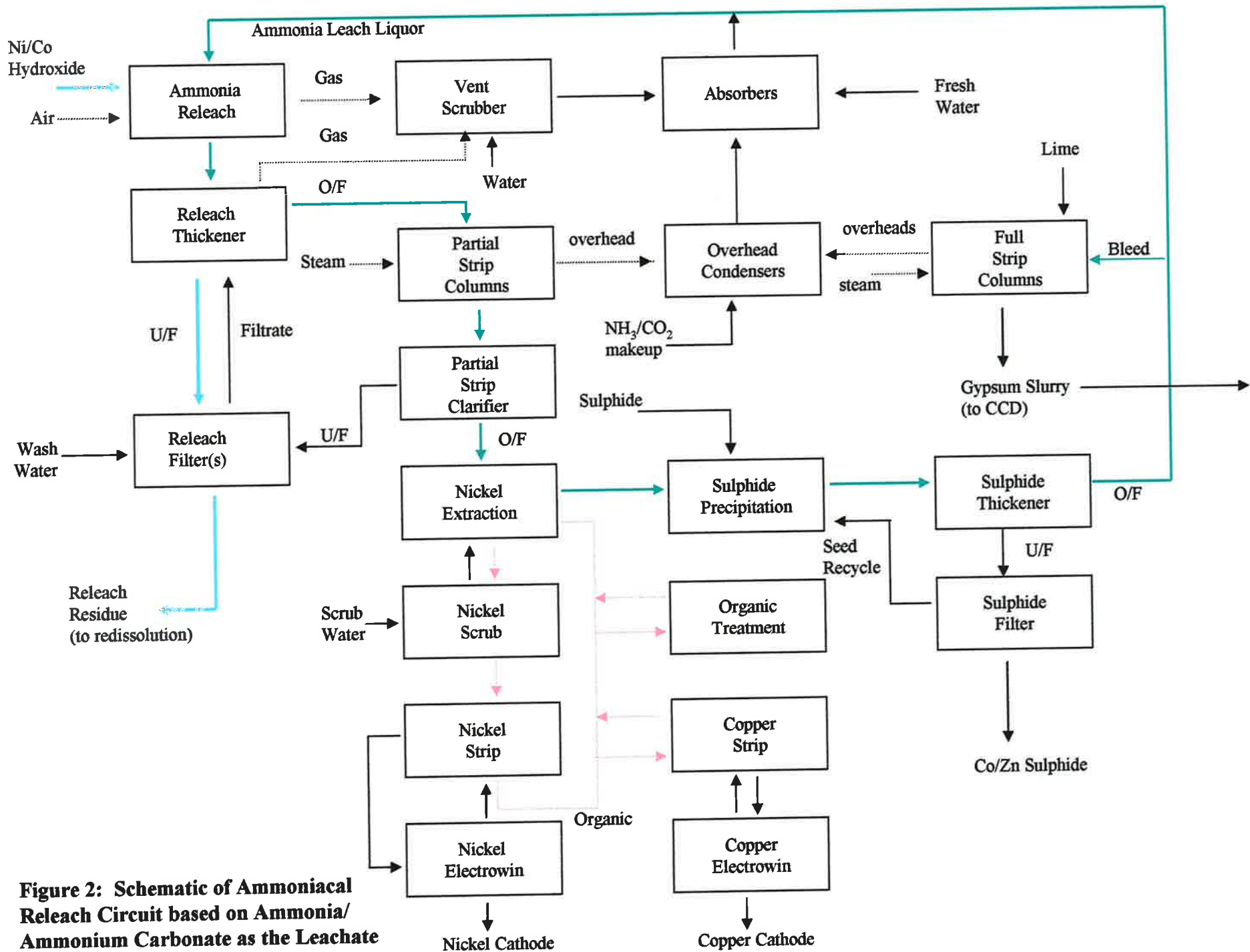


Figure 2: Schematic of Ammoniacal Releach Circuit based on Ammonia/Ammonium Carbonate as the Leachate

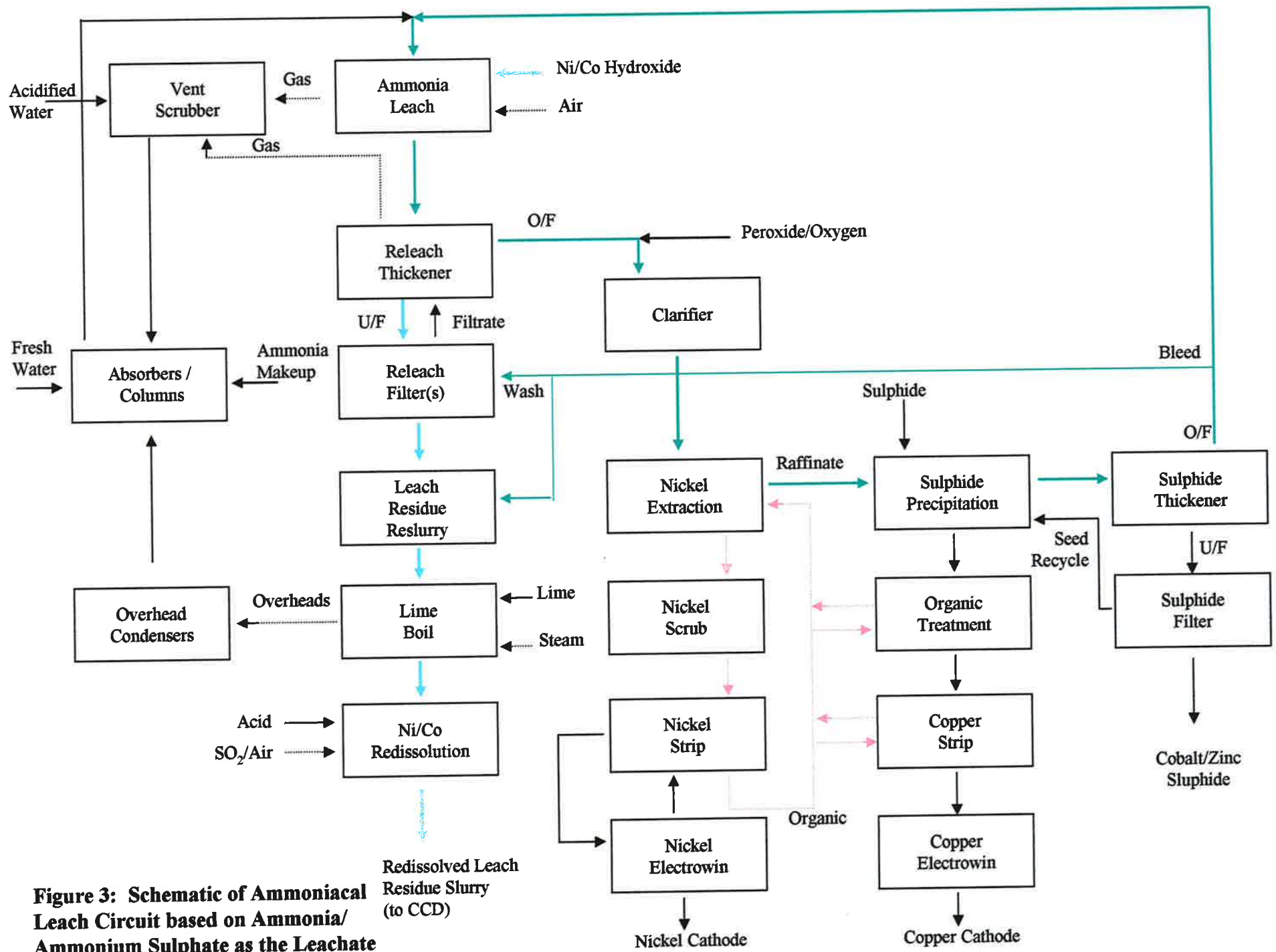


Figure 3: Schematic of Ammoniacal Leach Circuit based on Ammonia/Ammonium Sulphate as the Leachate

Redissolved Leach Residue Slurry (to CCD)