

THE APPLICATION OF THE CESL NICKEL PROCESS TO LATERITES

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1 Introduction

Cominco Engineering Services Ltd previously developed a process for treating sulphide concentrates of nickel and cobalt to produce both refined nickel and cobalt. The process was tested in an integrated pilot plant campaign in 1996.¹ More recently, CESL has adapted the process to treat lateritic ores. Acid pressure leaching of laterite ores is quite different from oxidative pressure leaching of sulphide concentrates; autoclave conditions, oxidation requirements, solids handling and impurity levels vary considerably. In both cases, however, nickel and cobalt report to an impure solution, and must be recovered separately in purified forms. This paper discusses the application of the CESL Nickel Process to laterites, limiting the discussion to the treatment of the impure nickel/cobalt solution after the pressure acid leach (PAL).

2 Background

Cominco Engineering Services Ltd. (CESL) is a wholly – owned subsidiary of Cominco Ltd., an integrated mining and metallurgical company producing zinc, copper, and lead, together with precious metals and various byproducts. Cominco operations originated in the Kootenay region of British Columbia, Canada, centred around the venerable Sullivan mine at Kimberley, and the lead – zinc smelting and metallurgical complex in Trail, which recently celebrated its 100th year.

Cominco has a long history of innovation in hydrometallurgical processes beginning as far back as 1908 with the world's first hydrometallurgical refinery for lead, using the then-untried Betts process, followed by Canada's first zinc electrorefinery (1916). In more recent times, Cominco has been one of the pioneers in pressure oxidation of base metals, having developed and built the world's first pressure leach processes for zinc sulphide concentrates (1982) and copper matte (1988).

CESL was formerly a full – service engineering company providing EPCM to the mining industry, but in 1994 the bulk of CESL's assets and personnel were transferred to the mining division of H.A.Simons Ltd. of Vancouver (now part of AMEC E&C Services). However, CESL continues to operate as a company that is focussed on technology development, primarily consisting of a large group in Vancouver that is engaged in process development research.

The CESL process research group was formed in 1992 with the express purpose of developing a hydrometallurgical alternative to smelting of base metal sulphides, and the group continues to focus on this objective today. CESL now operates two integrated pilot plant facilities in the Vancouver area, with a total staff of about 100 people. Approximately \$50 million (\$Cdn) has been spent on the Refined Metal Project to date, and much of that has been devoted to identifying engineering problems **before** building the full-scale plant, and then demonstrating the validity of proposed solutions.

¹ Jones, David, Jackie Hestrin and Rachel Moore. CESL Process for Nickel-Cobalt-Copper Sulphides: Testing in An Integrated Pilot Plant. Alta 1998 Proceedings. Perth, Australia. May 1998.

3 History of the CESL Copper and Nickel Processes

3.1 Copper Process

With the aim of developing and selling hydrometallurgical technology, CESL began benchscale testwork on copper sulphide concentrates in 1992. Successful results from the testwork allowed a tentative flowsheet to be developed, and justified the construction of the pilot plant in 1993. The integrated pilot plant was operated in a series of three campaigns on different concentrates throughout 1994 and 1995. Due to discoveries that resulted from the pilot plant operations, the initial flowsheet was extensively modified.

In 1995, Cominco decided it would be wise to build a larger pilot plant (the demonstration plant) before building a commercial plant. At thirty times the size of the pilot plant, the demonstration plant is capable of utilizing commercially-available equipment and providing reliable engineering data that could be used to build the full-scale plant. Construction was completed in early 1997, and was operating by the second quarter of that year. Since that time, the demonstration plant has been run on four different concentrates, producing a total of 280 tonnes of copper cathode. Feasibility studies have been conducted on two different projects, using results provided by the demonstration plant. These projects have not gone ahead to commercialization due to both political and economic reasons. At present, two further projects are at the feasibility stage.

3.2 Nickel-Copper-Cobalt

In 1995, CESL commenced benchscale testwork on pressure oxidation of nickel-copper-cobalt sulphide concentrates. Initial results were favourable, and a flowsheet was developed. Additional unit operations were built at the copper pilot plant in early 1996 to allow for nickel – cobalt recovery and a campaign was run in the last half of 1996.

4 Process Objectives

In designing both the Copper Process and the Nickel Process, a few simple objectives have been kept in mind:

- Use known technology as much as possible. The uniqueness of the process is based on the particular combination of unit operations; however, the unit operations in of themselves have been in use previously in commercial plants. The purpose of this is to reduce the risks associated with starting up a new process. In addition, CESL has attempted to test all equipment to be included in the commercial plant at the demonstration level. This allows for proper assessment of the equipment, and the gathering of sufficient engineering data for scale-up.
- Maximize metal recoveries.
- Minimize the use of expensive reagents. While acid, lime rock, lime and oxygen are used in significant quantity, the addition of more costly reagents such as caustic, ammonia and soda ash is limited, or avoided completely.
- Byproducts must be amenable to tailing ponds storage.
- Minimize energy consumption.
- Rugged Process.

5 Process Description

5.1 Overview of Existing Sulphide Flowsheet

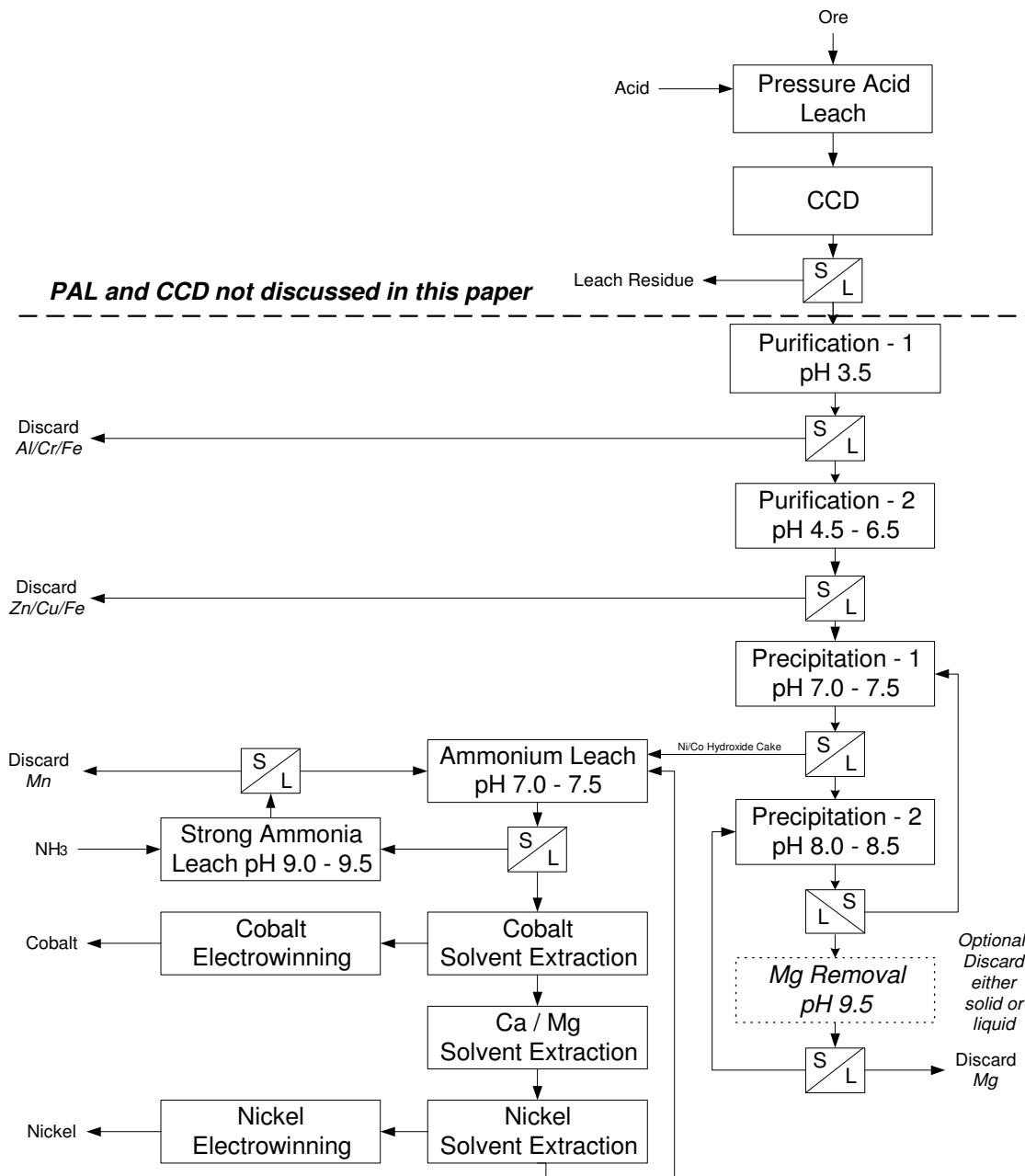
The CESL Nickel process for sulphides commences with an oxidizing pressure leach in a chloride-sulphate media to put nickel and cobalt into solution. This is followed by a series of purification steps to remove copper, zinc and iron. The purified solution is then treated with lime to selectively precipitate a nickel/cobalt hydroxide solid in the presence of magnesium. This solid is then re-dissolved in an ammonium sulphate solution at comparatively low pH (7 – 7.5) to produce a relatively pure solution of nickel and cobalt as diammines. Cobalt and then nickel are separately recovered from the diammine solution by individual SX/EW circuits, producing the respective metals as refined cathodes. Details of this process have been published previously.

5.2 Laterite Flowsheet

Treatment of nickel laterite ores by pressure leaching is in use at several commercial plants including three now in operation in Western Australia. While the pressure leach step is similar in all plants, the processes vary considerably in the treatment of the leach solution. The CESL Nickel process for sulphide concentrates has been adapted to treat pressure leach solution from laterite ores and offers an alternative to the existing flowsheets. The pressure leach step is not discussed in this paper.

The CESL Nickel Laterite flowsheet is shown in Figure 1.

Figure 1: CESL Nickel Laterite Flowsheet



Purification

The slurry from the autoclave is thickened and clarified to produce a solution with the following typical composition:

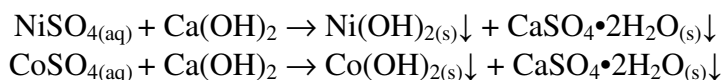
Ni	Co	Mg	Fe ³⁺	Fe ²⁺	Mn	Cr	Zn	Cu	Al
g/L	g/L	g/L	g/L	g/L	g/L	ppm	ppm	ppm	ppm
3.5	0.3	2.0	2.5	0.7	2.0	120	15	60	150

The solution is neutralized and purified in two operations; the first operation utilizes limestone to achieve a pH of 3.5 which is followed by a second operation which utilizes lime to reach a pH of 6.5. Solid from the first operation is discarded and constitutes an outlet for aluminum, chromium and iron. Solid from the second operation is discarded and constitutes an outlet for copper and zinc. The second operation itself has two stages at pH 4.5 and 6.5, with intermediate liquid solid separation and the solid from the second stage (pH 6.5) is recycled to the first stage (pH 4.5) in a counter current fashion to recover the nickel and cobalt values. A purified leach liquor is produced with the following composition:

Ni	Co	Mg	Fe ³⁺	Fe ²⁺	Mn	Cr	Zn	Cu	Al
g/L	g/L	g/L	ppm	ppm	g/L	ppm	ppm	ppm	ppm
3.0	0.3	1.85	<1	<1	1.85	<1	<1	<1	<1

Precipitation

The purified solution from the second neutralization stage is sent to precipitation where nickel and cobalt are precipitated almost quantitatively as hydroxides, according to the following reactions:



Manganese, another impurity of considerable importance in laterite ores, is precipitated as a hydroxide along with nickel and cobalt. Magnesium is partially precipitated along with the nickel and cobalt; typically only 5% of the magnesium in solution precipitates. The amount of magnesium precipitated is controlled by using a two-stage countercurrent circuit, in the same manner as the purification circuit. The first stage is conducted at pH 7.0 - 7.5 followed by the second stage at pH 8.0 – 8.5. Second stage solids are recycled to the first stage. Lime is the precipitation agent. In general, it is desirable to minimize the amount of magnesium which is precipitated; however, a small amount of magnesium is required to ensure subsequent separation of nickel and cobalt during solvent extraction.

The hydroxide slurry from precipitation is washed thoroughly in a CCD circuit to minimize the amount of contained chloride, and then is filtered to produce the nickel cobalt hydroxide cake which typically has the following composition:

Ca	Ni	Mn	Co	Mg	Fe	Al	Cr	Zn	Cu
%	%	%	%	%	%	%	%	%	%
15	11	8	1.1	0.6	0.03	0.01	0.01	0.01	0.01

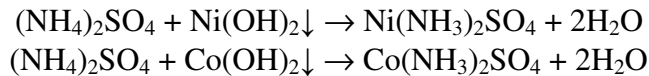
Magnesium Removal

The filtrate from the precipitation step, still containing a small amount of nickel, is subjected to a final stage either to partly remove the magnesium from the solution (if the stream is recirculated to the autoclave) or to recover the remaining nickel (if the solution is disposed of). At pH 9 to 9.5, magnesium hydroxide is partly precipitated, along with the remaining nickel and cobalt. A liquid-solid separation step following the precipitation produces a solid which is recycled to the precipitation unit operation. The final filtrate from this step can either be recycled back to the autoclave or disposed of. This decision would be largely determined by climate conditions at site; in an area of net evaporation (Western Australia) disposal is likely to be the best option.

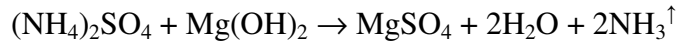
Ammonium Leach

The nickel and cobalt solid hydroxides from the precipitation step are selectively released in an ammonium sulphate solution to form diammine sulphate complexes. Nickel and cobalt diammine complexes are easier to separate by solvent extraction than sulphate complexes, and therefore represent a significant advantage inherent in the process.

The leach is conducted at about pH 7.0 - 7.5 in 200 g/L ammonium sulphate solution; minimal free ammonia (~ 1 g/L) is present under these conditions. The complexes are formed according to the following reaction:



Any magnesium present in the solid also dissolves, according to the following reaction:



As can be seen from the above reaction, any magnesium present in the solid hydroxide cake results in the release of ammonia. For this reason, the amount of magnesium present in the cake is carefully controlled in the precipitation step described above.

Manganese hydroxide, also present in the hydroxide cake, is only partially leached into the ammonium sulphate solution under these conditions. As a result, the leach solution contains a minimum amount of manganese (5 – 10 ppm).

A liquid/solid separation step following the leach produces a solid residue, which still contains significant amounts of nickel and cobalt, and a leach liquor which is the fed to the solvent extraction circuits. The leach liquor has the following typical composition:

Ni	Co	Mg	Fe	Ca	Mn	Cr	Zn	Cu	Al	Cl	Cd
g/L	g/L	g/L	ppm	g/L	ppm	ppm	ppm	ppm	ppm	ppm	ppm
13	1.2	0.5	<1	0.5	9	1	7	3	1	500	0.1

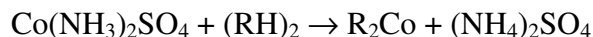
Overview of Cobalt – Nickel SX/EW

The product liquor from the ammonium leach contains divalent cobalt, as well as nickel, and some impurities. Solvent extraction with a phosphinic reagent, Cyanex 272, is used to selectively remove about 90% of the cobalt from the liquor, and produce a purified cobalt electrolyte. About 10% of the cobalt is deliberately left in the cobalt raffinate in order to get sufficient cobalt nickel selectivity. A second solvent extraction circuit, also with Cyanex 272, is used to remove the remaining cobalt, as well as the calcium and magnesium. Finally, solvent extraction with a ketoxime reagent, LIX 84I, is used to selectively recover the nickel to a purified nickel electrolyte. The barren leach liquor, nickel raffinate, is recirculated to the ammonium sulphate leach. Since the raffinate is recirculated, it is not necessary to achieve a low nickel concentration in the raffinate, thus improving the efficiency of the nickel solvent extraction circuit (higher loading with fewer stages). While a small amount of ammonia is added to make up for ammonia losses, no neutralization agents such as soda ash or caustic are required.

The magnesium / calcium solvent extraction circuit acts as a buffer between the nickel and cobalt solvent extraction units. In the cobalt solvent extraction circuit, a fully loaded organic is targeted to minimize coextraction of nickel along with the cobalt, and hence ensuring a high quality cobalt product. As a result, some cobalt remains in the raffinate. The magnesium / calcium solvent extraction circuit recovers this trace amount of cobalt, ensuring that the feed to the nickel solvent extraction circuit is free of cobalt.

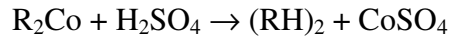
Cobalt Solvent Extraction and Electrowinning

The cobalt PLS, ammonium leach liquor, primarily contains nickel, cobalt and several impurities. Three extraction stages are required to selectively recover the cobalt from the nickel bearing leach liquor using a phosphinic organic reagent, Cyanex 272. The extraction proceeds according to the following reaction:



Following extraction, a single low acid wash stage is used to remove physically entrained ammonium sulphate solution from the organic reagent. The washed organic reagent is then scrubbed in three stages with a bleed of cobalt electrolyte (30%) under slightly acidified conditions. The scrub stages successfully remove any nickel that has loaded along with the cobalt onto the organic reagent.

The scrubbed organic reagent is then stripped in two stages to recover the cobalt into a purified cobalt electrolyte. The stripping reaction is as follows:



The pregnant electrolyte is carefully controlled to pH 3 – 4 by ensuring the pregnant electrolyte is contacted by loaded organic to produce a satisfactory cobalt pregnant electrolyte. The pregnant electrolyte is then fed to an electrowinning circuit to produce cobalt metal.

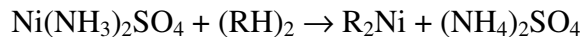
Following cobalt stripping, the stripped organic reagent is subjected to a second stage of stripping with dilute sulfuric acid to remove trace impurities (Zn / Cu / Mn /Fe) that would otherwise build up in the organic. This is followed by a water wash stage to remove physically entrained sulfuric acid. The organic reagent is recirculated back to the extraction stages to complete the loop.

Magnesium / Calcium Solvent Extraction

Following the cobalt solvent extraction circuit is a second solvent extraction circuit utilizing Cyanex 272. The purpose of this circuit is to remove the cobalt still remaining in the ammonium leach liquor. In effect, the circuit acts as a buffer between the cobalt and nickel solvent extraction circuits. Inevitably this also extracts about 10% of the nickel but it allows the cobalt raffinate to <1 ppm cobalt, thus ensuring high nickel to cobalt ratio in the nickel PLS. This is the price paid for having good cobalt nickel separation. About 10% each of the nickel and cobalt is recirculated back to the PAL sulphate circuit. In addition to removing the last of the cobalt, the circuit also removes the majority of the magnesium and calcium present in the ammonium leach liquor. Three stages of extraction are followed by two stages of washing with dilute sulfuric acid to remove physically entrained ammonium sulphate solution. The organic reagent is stripped with hydrochloric acid in two stages, and is then washed in one stage with water to remove any entrained hydrochloric acid. The hydrochloric acid strip solution is recirculated to the autoclave to recover the nickel and cobalt values.

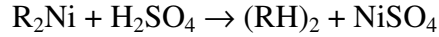
Nickel Solvent Extraction and Electrowinning

The ammonium leach liquor, with the cobalt removed, is the feed to the nickel solvent extraction circuit. Using LIX 84I as the organic reagent, nickel is extracted according to the following reaction:



Four stages of extraction are followed with two wash stages to remove physically entrained ammonium sulphate solution.

The washed organic is stripped into a pregnant electrolyte according to the following reaction:



The pregnant electrolyte is fed to nickel electrowinning to produce nickel metal. Four stages of stripping are required to meet the dual requirements of a low stripped organic and a high pH in the nickel pregnant electrolyte. The stripped organic is then washed in two stages in remove any physically entrained acidic solution, and recirculated back to the extraction stages.

Strong Ammonia Leach

The solids produced from the liquid solid separation following the ammonium leach step still contain significant amounts of nickel and cobalt (10-20% of feed Ni/Co). The solids are leached at high % solids with a small volume of ammoniacal ammonium sulphate at pH 9- 9.5 to recover the nickel and cobalt into solution while leaving the manganese in the solids. A liquid solid separation produces a solid gypsum product which is discarded (providing an efficient outlet for manganese), while the liquid added to the ammonium leach circuit as makeup.

6 Process Changes for Laterites

There are significant process changes to adapt the CESL Nickel Process for sulphides to laterites. These are summarized as follows:

- Oxidation of feed material in the autoclave is not required with laterites (not discussed in this paper).
- Precipitation of additional impurities (aluminum, chromium, increased iron) in the purification and precipitation stages.
- Much higher magnesium in the autoclave leach liquor is removed either via a magnesium hydroxide byproduct in the magnesium removal step or via discharge of the solution after the magnesium removal step.
- Releach of ammonium leach solids in strong ammonia instead of acid to reject manganese.
- Lower nickel and cobalt concentrations in the autoclave leach liquor resulting in different operating conditions in the purification and precipitation, and less co-precipitation of nickel and cobalt in the purification byproducts.
- Higher cobalt to nickel ratio in all solutions and solids.

7 Impurity Department

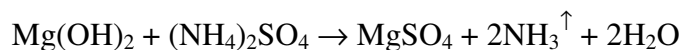
As mentioned above, the impurities inherent in treating a lateritic ore are substantially more complex than treating a sulphide concentrate. In particular, manganese, magnesium, aluminum and chromium are present in much higher quantities. Zinc, copper and cadmium are reduced, however. Cobalt is generally higher, which is beneficial as the cobalt to impurity ratio is improved. The department of these impurities is discussed in this section.

7.1 Manganese

The manganese to nickel ratio in lateritic ores can vary substantially. As much of the manganese present in the ore leaches under the autoclave conditions, it can be seen that manganese is a significant impurity. Present as manganese sulphate in the autoclave leach liquor, manganese is precipitated quantitatively as a hydroxide along with the nickel and cobalt in the precipitation step. However, the manganese does not leach significantly in the ammonium leach circuit but remains in the solid, allowing for the separation of the nickel and cobalt from the manganese. This solid is subjected to a strong ammonia leach to recover the remaining nickel and cobalt, but again the manganese does not leach under these conditions. The solid remaining after the strong ammonia leach can be disposed of, providing a final outlet from the circuit for the manganese. The small amount of manganese that does leach in the ammonium sulphate circuit constitutes a significant impurity to the cobalt. Careful control of the manganese in the Cyanex 272 circuit is maintained by acid stripping as described.

7.2 Magnesium

Magnesium is also present in considerable concentrations in lateritic ores. Present as magnesium sulfate in the autoclave leach liquor, magnesium remains in the leach liquor through the purification stage. At the precipitation stage, however, careful control of the circuit allows nickel and cobalt hydroxide precipitation while minimizing magnesium precipitation. A certain amount of magnesium in the hydroxide cake is desirable as it provides a buffer between the nickel and cobalt solvent extraction circuits, and enhances separation. Significant amounts of magnesium are undesirable as they result in the loss of ammonia from the ammonium sulphate loop. As shown in the following reaction, magnesium hydroxide in the cake combines with the ammonia sulphate, freeing up ammonia ions which are then lost from the solution.



Following nickel cobalt hydroxide precipitation, magnesium can be precipitated as magnesium hydroxide in the magnesium removal step.

7.3 Aluminum and Chromium

While neither aluminum nor chromium is present in sulphide concentrates, they are both present in lateritic ores, and partially leach in the autoclave. Sufficient ferrous in the autoclave ensures that the chromium is reduced from Cr^{+6} to Cr^{+3} , where it can be removed by hydrolysis. Both elements are then removed by precipitation in the neutralization / purification stages at pH 3.5.

8 Process Advantages and Disadvantages

The CESL Nickel Process offers some important advantages for laterites. The advantages are as follows:

- Production of both nickel and cobalt as cathode metal in the same plant
- Very high recovery **and** grade of both nickel and cobalt
- Reagent use (such as ammonia / soda ash / caustic) minimized as no significant pH adjustments are required other than the lime/limestone in the sulphate purification and precipitation stages
- Low pH of ammoniacal sulphate solution (ie low free NH_3), reducing environmental as well as health and safety considerations
- No need for ammonia stripping/adsorption circuits nor ammonia containment in ammonium sulphate leach or solvent extraction circuits
- Avoidance of sulphide precipitation and re-oxidation steps
- Enhanced impurity rejection by formation of intermediate hydroxide product hydroxide
- Efficient nickel cobalt separation by formation of diammines
- No need to oxidize or reduce cobalt to avoid extraction in the nickel solvent extraction

The disadvantages of the CESL Nickel Process for laterites include the following:

- Multiple solvent extraction circuits with several mixer settlers in each circuit
- Less than optimal selectivity for cobalt over nickel at pH 7 rather than pH 5
- Careful operation of the precipitation and purification circuits is required to ensure impurity rejection and hydroxide cake quality.