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SIMULATION SOFTWARE METHODOLOGIES FOR HYDROMETALLURGICAL PROCESS EVALUATION APPLIED TO SELECTIVE ACID LEACHING OF MIXED HYDROXIDE PRECIPITATE

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ABSTRACT

Flowsheet simulation is widely used in metallurgical design to provide data for equipment sizing and specifications. Sufficiently defined mass and energy balances can also be used to specify process operating strategies, compare plant performance and bottlenecking with different ore types and estimate reagent usage and costs.

In hydrometallurgical design in particular, prediction of plant water balance, dissolved salt recirculating load and bleed requirements are required during scoping, feasibility and engineering study stages to truly assess the process.

There are a number of different flowsheet simulation software programs available such as AspenPlus, SysCAD, JKSimMet, METSIM, IDEAS, LIMN, HSC. Different methodologies and approaches are required to carry out simulations with these software programs.

In this paper, the Selective Acid Leaching of MHP (Mixed Hydroxide Precipitate) process has been simulated using both AspenPlus and SysCAD. The similarities and differences in results, the methods/procedures and benefits or disadvantages of setting up the balances in the different flowsheet simulation software packages are discussed. The results of the simulations are compared and then used to provide a comparison of the Selective Acid Leaching process with alternative MHP to metal process options.

Keywords: MHP, selective acid leach, nickel, cobalt.

INTRODUCTION

Flowsheet balances and simulations are ubiquitously used at some level throughout metallurgical design. In the initial options or scoping stages of engineering design, the simulation is typically based on generic or assumed data, and used to estimate overall factors such as energy requirements, reagent and raw material requirements, plant scale. In these stages, simple block flow calculations can often provide sufficient information to inform the design and comparison.

During pre-feasibility and feasibility stages of design, the simulation accuracy is steadily improved by incorporating additional validated data, such as from pilot studies and industrial benchmarks. It is at this stage that the simulation needs to consider carefully the role of recycle streams and control strategies for process stability. Modern metallurgical plants have highly complex flowsheets and often operate continuously with varying feed parameters. These complexities mean that calculating a plant mass and energy balance at the level of detail required for design cannot be done manually with sufficient confidence in the accuracy of the calculations. There are a number of different flowsheet simulation software programs available now which are all capable of handling the complexities of metallurgical processing plant design. These flowsheet simulation programs are all based on the same general principles however the specific program details often mean that different methodologies and approaches are required to carry out simulations with each.

Taylor (2014) and Dry (2014, 2015, 2016) presented a series of papers providing a technical and cost comparison of laterite treatment process routes (Dry 2014, 2015, 2016; Taylor 2014). The comparisons were supported by flowsheet simulations developed in AspenPlus for each process option. The initial process comparison, through part 1, 2 and 3, examined processes such as High Pressure Acid Leaching (HPAL), Heap Leaching, Caron Processing, Rotary Kiln Electric Furnace Smelting and Sinter-Smelting, as well as developing technologies including chloride and nitric acid. These processes were examined through to production of mixed nickel and cobalt oxide/hydroxide (MHP), nickel oxide, mixed nickel and cobalt sulfide (MSP), Ferronickel and Nickel Pig Iron (NPI)(Dry 2014, 2015; Taylor 2014). The results presented in part 3 indicated that, for the general scenario used for the purposes of the comparison, the HPAL processing route through to MHP appeared to provide the best overall economics for laterite treatment. The fourth paper in the series examined three processing routes to take the MHP intermediate product through to nickel and cobalt metals, using various solvent extraction systems, again supported by AspenPlus simulations(Dry 2016). Comparatively, Vaughan et al. (2013) presented technical comparison of some MHP refining processes along with a technical and economic argument for the UQ developed Selective Acid Leach (SAL), which was supported by flowsheet simulations developed in METSIM (Vaughan, J et al. 2013).

The UQ Hydrometallurgy group developed a novel method for treating MHP in a selective acid leaching (SAL) process (Byrne, Hawker & Vaughan 2016), (Vaughan, J et al. 2013), (Vaughan, J., Hawker & White 2011), (Vaughan, James & Hawker 2012) (Williams, Hawker & Vaughan 2013). The SAL process is based on selective oxidation of cobalt and manganese, which means that the nickel can be selectively leached, and therefore separated from these elements without the need for a solvent extraction process. This involves contacting MHP with sufficient amount of strong oxidant to oxidize all of the cobalt and the manganese from their divalent to their trivalent states, while also contacting the MHP with a sufficient amount of acid to leach the majority of the divalent nickel. The process yields a concentrated nickel sulfate solution at a moderate pH suitable for direct recovery of a final nickel product and a cobalt concentrate. The solid product from the SAL process typically contains significant cobalt, manganese and a small amount of un-leached nickel relative to the MHP feed. This solid can be processed further to pure cobalt, manganese and nickel products, or may be considered for direct refining to produce an NCM (Nickel, Cobalt and Manganese) battery electrode material (Chong, Hawker & Vaughan 2013; CleanTeQ 2016; Williams, Hawker & Vaughan 2013).

Due to experience and software availability, further investigations and development of the SAL process at UQ have been carried out using the SysCAD flowsheet simulator. The use of the three different flowsheet simulation software packages on relatively similar processes therefore provides an interesting opportunity to compare the methodologies and outcomes from the different software packages. Hence in this paper, the SAL process flowsheet development in the two software packages, AspenPlus and SysCAD, will be discussed. The simulation outcomes will then be used to compare the SAL process with the alternative MHP treatment processes described in Dry (2016).

PROCESS SIMULATION SOFTWARE

All the process simulation software packages have relatively similar setup and user interfaces. They will have one or many flowsheet tabs where the user specifies a certain model and representative image for that model (icon, in modelling jargon). These models simulate the required unit operations which can then be connected with lines/streams/pipes. Behind the flowsheet, the simulation requires a chemical and thermodynamic database which contains all of the relevant chemistry properties for that particular simulation. From there, the feed or input streams, along with the operating parameters and reactions of the unit operation models can be specified. Once these are all selected, the flowsheet will generally solve and provide a mass and energy balance. However, many of the feed streams, such as the reagent addition requirements and the recycle flows, are not initially known as they depend on the rest of the simulation. Hence the simulation software programs include model controller capabilities where input variables can be controlled based on a measured variable elsewhere in the flowsheet. Correct setup of these controllers is required to solve the simulation in the first place and optimally, they are flexible enough for the model to be able to simulate varying feed and operating conditions.

SAL INCORPORATED PROCESS FLOWSHEET

The simplicity of the SAL process, shown in
Figure 1, is one of the reasons that this flowsheet simulation comparison can easily be carried out.

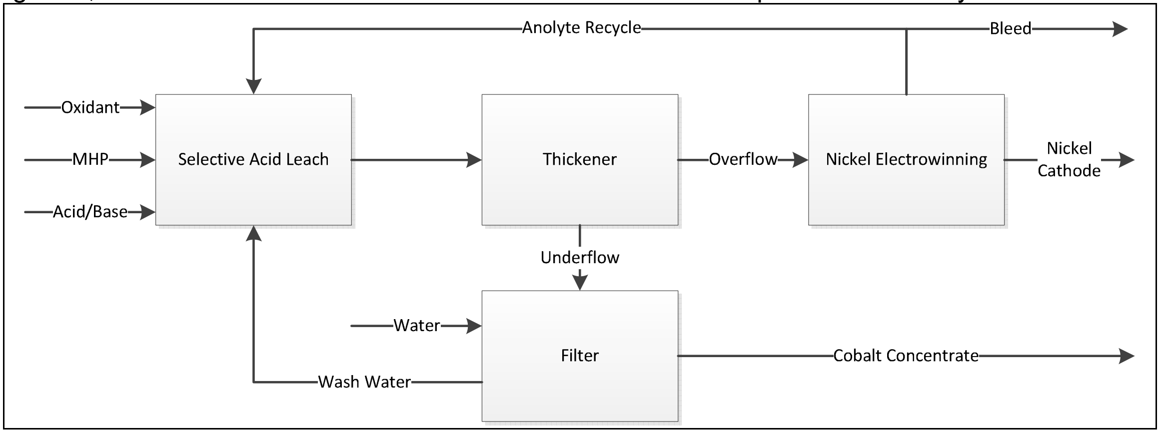

Figure 1 – Simple SAL Incorporated Flowsheet

The process entails a leaching step in which nickel is solubilized and the cobalt and manganese are stabilized to the solid phase. In general, in the selective acid leaching stage any nickel and magnesium sulfate salts will readily dissolve, as will any basic magnesium and calcium compounds which may be present in the MHP from its precipitation stage. If present in sufficient quantity, the dissolution of a calcium compound will then result in the crystallization of gypsum. At SAL process conditions, Nickel hydroxide will also dissolve readily with typical recovery to solution at 90% or greater (Byrne, Hawker & Vaughan 2016). Cobalt and manganese sulfates and hydroxides, on the other hand, will quickly be oxidized to produce solid oxyhydroxides or trivalent hydroxides, with no measurable manganese or cobalt reporting to the leach solution provided sufficient oxidant is supplied and the leach pH remains above approximately pH 2 (Vaughan, J., Hawker & White 2011).

The resulting slurry can then be thickened and filtered to produce a cobalt concentrate saleable as a battery electrode precursor and a clarified solution directly suitable for conventional nickel electrowinning. Anolyte from the electrowinning can be recycled to provide acid for the leaching stage and a small solution bleed will be required to maintain the acid, trace element or water balance.

Because the SAL stage directly leaches the nickel from the MHP, it is possible to target very high nickel concentrations out of this leach. Leach solutions above 100 g-Ni/L have been produced in previous test work. Nickel electrowinning is generally carried out at 60-80 g-Ni/L with the anolyte reduced to approximately 30-50 g-Ni/L, therefore with a Δ[Ni] of 30 g-Ni/L. The Harjavalta nickel refinery in Finland operates nickel electrowinning in the sulfate system with 130 g-Ni/L in the catholyte. In Crundwell et al. (2011), the Harjavalta refinery is reported to achieve a Δ[Ni] of 65 g-Ni/L, however this appears to be incorrect as a Δ[Ni] of 30 g-Ni/L is reported in Knuutilla (1997) and has been confirmed by personal communication (Knuutila et al. 1997; Luoma 2017). These concentrations are important considerations as they will impact on the recirculating load and therefore equipment sizing within the circuit.

The basis for this simulation comparison is the same as that used in the hydroxide to metal processing simulations presented in Dry (2016). The composition of the MHP used in those simulations is shown in Table 1. The capacity assumed was 30 kt/y of Ni contained in the feed laterite and the production of MHP was 101.6 kt/y (8000 h/y), or 12.7 t/h MHP.

Table 1 – AspenPlus MHP Composition (Dry 2015)

Compound	Wt.%	Element	Wt.%
$Ni(OH)_2$	23.90%	Ni	43.1
$NiSO_4{\bullet}3Ni(OH)_2$	51.50%	Co	6.1
$Co(OH)_2$	3.40%	Mn	0.03
$CoSO_4{\bullet}Co(OH)_2$	7.30%	S	0.6
$Mn(OH)_2$	0.04%	O	42.9
$MgCO_3$	2.00%	H	2.8
H_2O	12.00%	C	0.3

The water associated with the MHP feed also contained a small amount of dissolved salts such as Ni^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Na^{+} and SO_4^{2-}. The dissolved salts constitute less than 0.01 Wt.% of the feed and hence are not included in this summary.

This particular MHP has a significant amount of nickel as sulfate, which will dissolve without the need for any acid in the SAL stage, but will still generate acid in the electrowinning stage. This means that this MHP will likely be net acid generating and require a significant electrolyte bleed. To avoid losing significant amounts of nickel in this bleed, a nickel hydroxide precipitation (NHP) stage can be included, to neutralize the bleed and recover the contained nickel. The precipitated nickel hydroxide can then be re-introduced to the electrowinning circuit by leaching. Introducing this back into the SAL directly is possible, although this may introduce some additional nickel loss due to incomplete dissolution. Alternatively, it can be re-dissolved in the anolyte recycle in a separate stage before the combined solution is fed to the SAL stage, which should result in near complete re-dissolution of the nickel in the NHP. This adaptation of the SAL incorporated flowsheet is shown in Figure 2.

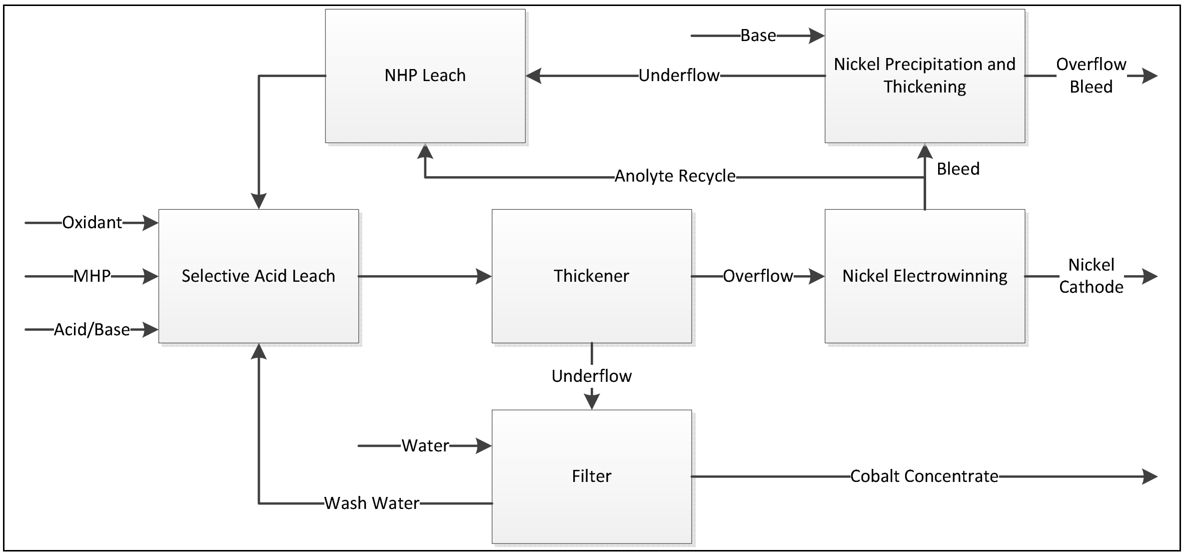

Figure 2 – SAL incorporated flowsheet for acid generating MHP

SIMULATION DEVELOPMENT

Initial setup in SysCAD

When starting a new simulation project in SysCAD, the first step is to set up the project configuration file with all of the relevant chemical data required for that simulation. This requires the specification of all chemical components that will be required in the system by adding them to the project configuration from the SysCAD or any other suitable thermodynamic database, or manually specifying the chemical components and their thermodynamic properties. It is very important to ensure that all of the correct chemical components are included and that the required thermodynamic data is correct and specified.

When specifying the chemical components, the user is faced with an important decision that will carry on through the rest of the model development and results. The user can choose whether to specify the dissolved chemical components as electrochemically neutral species, such as $NiSO_4(a)$, or individually charged ions such as $Ni^{2+}(a)$ and $SO_4^{2-}(a)$, or both. While this appears to be a very minor decision, it will have a significant impact on the process simulation later because the software does not appear to recognize that nickel can exist as both an individual $Ni^{2+}(a)$ ion or as a neutral $NiSO_4(a)$ species when calculating the balance and reactions and therefore will treat them as separate components. Because the software does not recognize both, it is important to select either the ionically charged or the neutral species, but not both, as this will make the simulation calculations confusing.

This choice of ionically charged or neutral has the obvious and direct impact of having the rest of the simulation operate in terms of either the individual ions or the complete neutral species, so all flows are therefore reported in terms of the individual ion or the neutral species. It also has a less obvious impact on the thermodynamic calculations as the thermodynamic data related to the individual ion may also be different to that associated with the neutral species. User experience has shown that the individual ions may not always have as many thermodynamic properties specified in the database as the overall neutral species do. As an example, during this simulation exercise the simulation was configured to use the individual ions rather than the neutral species as shown in Table 2.

Table 2 – SysCAD Solution Species Component Specification

Individual Ion Species	Neutral Species
Ni^{2+} (a)	$NiSO_4$ (a)
Mg^{2+} (a)	$MgSO_4$ (a)
Co^{2+} (a)	$CoSO_4$ (a)
Mn^{2+} (a)	$MnSO_4$ (a)
Na^{+} (a)	Na_2SO_4 (a)
H_2SO_4 (a)	H_2SO_4 (a)
HSO_4^{-} (a)	
SO_4^{2-} (a)	
H^{+} (a)	
OH^{-} (a)	

However, the concentration-density correlation for the individual $Ni^{2+}(a)$ ion was not properly specified in the database. This meant that the catholyte fed to the nickel electrowinning unit had a density very close to water, while the spent electrolyte leaving the electrowinning unit had a significantly higher density, due to the formation of sulfuric acid. Higher density out means that a fixed concentration of Ni^{2+} out carries less kg/h Ni^{2+} . Because the model had a fixed concentration of nickel in and a fixed ΔNi, that made the per-pass conversion of Ni^{2+} to metal too high. This had the flow on effect of appearing to over produce nickel metal from the nickel electrowinning unit. Once identified, this issue was solved by correctly specifying the concentration-density correlation for the ion.

Therefore, depending on the process simulation requirements and thermodynamic data availability, it may be more appropriate to use neutral species. However, if the downsides can be avoided, the use of individual ions rather than neutral species can make it easier to operate the simulation as it allows the user to view and directly control factors such as the dissolved nickel concentration for process control. This also illustrates why the user needs to critically review the numbers emanating from any database and process model to investigate and correct any anomalies.

Once the SysCAD project configuration is complete and all relevant chemical components are included and thermodynamically specified, the user can then specify the flowsheet inputs, unit models and flows. The most important step is specifying the reactions occurring in each unit. In SysCAD, simulating a unit with reactions is done through an add-on reaction editor program bundled with the SysCAD program. When inputting all of these reactions in SysCAD, it is very important to consider how the reaction extents will be specified as this has a huge impact on how the unit operation will solve and how the process can be controlled. The various methods of specifying the reaction extent in the SysCAD reaction editor are outlined in Table 3. It is also important to consider the order that the reactions will occur in, as by default, the software will solve the reaction extents sequentially. While it is possible to have the software solve the reactions for a unit simultaneously, there are a number of disadvantages such as the speed of solving that unit and the inability to use products from one reaction in a sequential reaction.

Table 3 – SysCAD Reaction Extent Specifications

Extent	Control Based On
Fraction	Fraction of one of the reactants that must react
Ratio	Molar or mass ratio of a product to a reactant
Equilibrium	Equilibrium constant (K) for the reaction
Final Concentration	Concentration of a particular species required at the end of the reaction
Final Fraction	Mass or mole fraction of a particular species required at end of the reaction
Dynamic Rate	Fraction and a fractional rate at which one of the reactants will react, for use in dynamic simulations
Dynamic Fraction	Fraction and a time period in which this fraction of the reactant will react, for use in dynamic simulations

Initial setup in AspenPlus

In AspenPlus, a simulation can be set up as either “apparent component approach” or “true component approach”. In the apparent component approach the chemistry is reported as neutral species, such as H_2SO_4 and $NiSO_4$, for example, for sulfuric acid and dissolved nickel sulfate in water. In the true component approach the species reported are H_3O^+, HSO_4^-, SO_4^{2-} and Ni^{2+}, along with some un-dissociated H_2SO_4 at high concentrations of sulfuric acid. The software calculates the true species in both approaches; the apparent component approach merely converts the true species distribution back to the equivalent neutral compounds in the output.

AspenPlus allows the user to specify global chemistry. In the context of hydrometallurgy, that means a set of aqueous equilibrium reactions that are applied to all streams by default, unless the global chemistry is deliberately turned off at any particular point in a simulation. This is most easily illustrated by way of an example, a convenient one being sulfuric acid and nickel sulfate in water. To set up a simulation using sulfuric acid, nickel sulfate and cobalt sulfate in water, one would first specify the main constituents of the system, as illustrated in Table 4.

Table 4 – Initial AspenPlus input

Component ID	Type	Component name	Alias
H2O	Conventional	WATER	H2O
H2SO4	Conventional	SULFURIC-ACID	H2SO4
NISO4	Conventional	NICKEL-SULFATE	NISO4
COSO4	Conventional	COBALT-SULFATE	COSO4

The next step entails using a chemistry wizard, which is a facility in AspenPlus that takes the input components, searches a set of databases for chemical equilibrium reactions involving these components and adds any other components involved, equilibrium constants for individual reactions, etc. Table 5 illustrates the input component list after running the wizard, using the true component approach. The additional compounds are from equilibrium reactions stored in the software’s databases;

Table 6 lists these reactions. There are three types of reaction, equilibrium, salt and dissociation. The component types, conventional or solid, mean, respectively, dissolved/liquid/gaseous or solid components

Table 5 – AspenPlus input after running the chemistry wizard

Component ID	Type	Component name	Alias
H2O	Conventional	WATER	H2O
H2SO4	Conventional	SULFURIC-ACID	H2SO4
NISO4	Conventional	NICKEL-SULFATE	NISO4
COSO4	Conventional	COBALT-SULFATE	COSO4
CO++	Conventional	CO++	CO+2
H3O+	Conventional	H3O+	H3O+
OH-	Conventional	OH-	OH-
HSO4-	Conventional	HSO4-	HSO4-
SO4--	Conventional	SO4--	SO4-2
COSO4(S)	Solid	COBALT-SULFATE	COSO4
SALT1	Solid	COSO4*7H2O	COSO4*7W
SALT2	Solid	COSO4*6H2O	COSO4*6W

Table 6 – Aqueous equilibrium reactions

Reaction	Type	Stoichiometry
1	Equilibrium	H2SO4 + H2O <--> H3O+ + HSO4-
2	Equilibrium	H2O + HSO4- <--> H3O+ + SO4--
3	Equilibrium	2 H2O <--> OH- + H3O+
SALT2	Salt	SALT2 <--> CO++ + SO4-- + 6 H2O
SALT1	Salt	SALT1 <--> CO++ + SO4-- + 7 H2O
COSO4(S)	Salt	COSO4(S) <--> CO++ + SO4--
COSO4	Dissociation	COSO4 --> CO++ + SO4--

The equilibrium reactions are reactions between conventional components only. Each salt reaction simulates the solubility of the individual salt and the dissociation reactions simply convert the neutral species concerned completely, to the individual ionic species.

There is a caveat here, illustrating a risk in allowing databases to do the "thinking". Note that the component list in Table 5 does not contain the divalent nickel ion, and the list of reactions in Table 6 does not contain anything involving nickel sulfate. That is because the software's databases do not "know" that, at least at low concentrations, NiSO□ dissociates to Ni^{2+} and SO_4^{2-} in water. To model a system containing nickel sulfate in water, the missing components need to be added manually. As a general rule of thumb, anything emanating from a database should be subjected to scrutiny and correction as necessary. Table 7 shows the corrected component list and global chemistry. If necessary, nickel salts such as $NiSO_4 \cdot 4H_2O$ and $NiSO_4 \cdot 7H_2O$ could be added, along with the corresponding salt equilibrium reactions, but if that were required, it would also be necessary to calibrate those salt reactions against measured solubility data. While quite possible and not difficult, that is unnecessary for the exercise presented in this paper because the circuit modelled does not precipitate any nickel or cobalt sulfate salts. The cobalt salts could be removed from the global chemistry in this exercise, but leaving them there does no harm, in that their formation will not be predicted because the dissolved cobalt concentration remains too low.

Table 7 – Corrected component list and global chemistry

Component ID	Type	Component name	Alias
H2O	Conventional	WATER	H2O
H2SO4	Conventional	SULFURIC-ACID	H2SO4
NISO4	Conventional	NICKEL-SULFATE	NISO4
COSO4	Conventional	COBALT-SULFATE	COSO4
NI++	Conventional	NI++	NI+2
CO++	Conventional	CO++	CO+2
H3O+	Conventional	H3O+	H3O+
OH-	Conventional	OH-	OH-
HSO4-	Conventional	HSO4-	HSO4-
SO4--	Conventional	SO4--	SO4-2
COSO4(S)	Solid	COBALT-SULFATE	COSO4
SALT1	Solid	COSO4*7H2O	COSO4*7W
SALT2	Solid	COSO4*6H2O	COSO4*6W

Reaction	Type	Stoichiometry
1	Equilibrium	H2SO4 + H2O <--> H3O+ + HSO4-
2	Equilibrium	H2O + HSO4- <--> H3O+ + SO4--
3	Equilibrium	2 H2O <--> OH- + H3O+
COSO4(S)	Salt	COSO4(S) <--> CO++ + SO4--
SALT2	Salt	SALT2 <--> CO++ + SO4-- + 6 H2O
SALT1	Salt	SALT1 <--> CO++ + SO4-- + 7 H2O
COSO4	Dissociation	COSO4 --> CO++ + SO4--
NISO4	Dissociation	NISO4 --> NI++ + SO4--

Feed composition in SysCAD

The feed composition used in this exercise is as listed in Table 1. When setting up the SysCAD configuration however, it was noted that neither the SysCAD or HSC databases included any data for the nickel and cobalt mixed hydroxyl-sulfate compounds noted in the composition table. While it is possible to add new chemical components to the databases, it was far simpler to modify the feed composition specification to include the hydroxy-sulfate compounds as separate hydroxide and sulfate compounds rather than mixed compounds. In addition to being a simpler approach, there is a certain level of trust and consistency associated with using the chemical components already available in the database. As long as the chemistry change is carried through to the way that the reactions are specified, this change will not affect the mass balance of the process simulation. It may, however, have a slight impact on the calculated energy balance of the simulation as the mixed compounds may have slightly different thermodynamic properties to the single anion salts. The modified feed composition used in the SysCAD simulation is shown in Table 8.

Table 8 – SysCAD MHP Composition

Compound	Wt.%	Element	Wt.%
$Ni(OH)_2$	57.00	Ni	43.1
$NiSO_4$	18.40	Co	6.1
$Co(OH)_2$	8.00	Mn	0.03
$CoSO_4$	2.60	S	0.6
$Mn(OH)_2$	0.04	O	42.9
$MgCO_3$	2.00	H	2.8
H_2O	12.00	C	0.3

Feed composition in AspenPlus

The AspenPlus databases include many solid compounds, but very often a particular solid is not covered. In this case, the compounds NiSO□•3Ni(OH)□ and CoSO□•3Co(OH)□ are absent. However, adding new compounds is easy; the software has a means whereby the chemical formula can be specified for a new component, and there are group-contribution methods for estimating the thermodynamic properties of new components. In the example used in this paper, the thermodynamic properties of NiSO□•3Ni(OH)□ and CoSO□•3Co(OH)□ were estimated using a method developed by Mostafa (Mostafa, Eakman & Yarbro 1995). This method is embedded inside the software, making it convenient to use. Alternatively, if the properties are available from elsewhere, they can be input as the relevant values.

SYSCAD SIMULATION

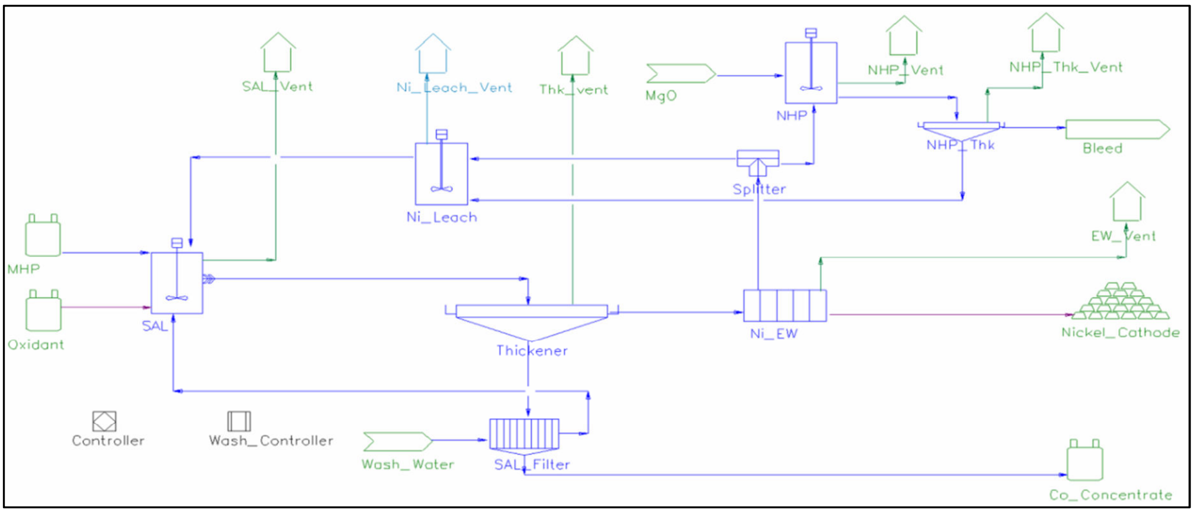

Figure 3 – SysCAD Diagram

Figure 3 is the diagram generated in SysCAD, representing the circuit modelled in this exercise.
In the SAL unit, the MHP, oxidant, anolyte recycle (via nickel hydroxide leaching), and cobalt concentrate wash water are mixed and reacted. The specified leaching and oxidation reactions were:

$MgCO_3(s) + H_2SO_4(a) \rightarrow Mg^{2+}(a) + SO_4{}^{2-}(a) + H_2O + CO_2(g)$ EXT:100%
$Ni(OH)_2(s) + H_2SO_4(a) \rightarrow Ni^{2+}(a) + SO_4{}^{2-}(a) + 2H_2O$ EXT:90%
$NiSO_4(s) \rightarrow Ni^{2+}(a) + SO_4{}^{2-}(a)$ EXT:90%
$2Co(OH)_2(s) + Na_2S_2O_8(s) \rightarrow 2CoOOH(s) + 2Na^+(a) + SO_4{}^{2-}(a) + H_2SO_4(a)$ EXT:100%
$2CoSO_4(s) + Na_2S_2O_8(s) + 4H_2O \rightarrow 2CoOOH(s) + 2Na^+(a) + SO_4{}^{2-}(a) + 3H_2SO_4(a)$ EXT:100%
$2Mn(OH)_2(s) + Na_2S_2O_8(s) \rightarrow 2MnOOH(s) + 2Na^+(a) + SO_4{}^{2-}(a) + H_2SO_4(a)$ EXT:100%

Because the SysCAD simulation used a slightly different feed composition to the AspenPlus simulation, to simplify and keep the inputs consistent between the different programs the dissolution of the nickel hydroxide and nickel sulfate were both fixed at extents of 90%.

The amount of anolyte recycled to the NHP and then into the SAL was controlled to maintain a pH of 3.5 out of the SAL. The slurry ex SAL is thickened, the underflow is filtered and the filter cake is washed with water. The washed filter cake leaves the circuit as a cobalt concentrate. The thickener overflow is directed to the nickel electrowinning section. The stoichiometry in the nickel electrowinning section is:

$Ni^{2+}(a) + SO_4{}^{2-}(a) + H_2O \rightarrow Ni(s) + H_2SO_4(a) + \frac{1}{2}O_2(g)$ Δ[Ni] of 30 g-Ni/L
$H_2O \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ 5% Current Inefficiency

The cathode nickel is harvested and removed. The reaction extent was controlled to maintain a Δ[Ni] of 30 g-Ni/L. The extent of the water decomposition reaction is manipulated to make the overall current efficiency for nickel deposition 95 percent. The spent electrolyte is split to either the NHP precipitation stage to recover bled nickel and bleed for water, acid or minor element balance, or to the SAL, via the NHP leaching stage, based on the acid requirement to maintain the SAL leach at pH 3.5.The part going to the nickel precipitation step is neutralized with magnesium oxide slurry to precipitate the nickel as nickel hydroxide via the following stoichiometry:

$$MgO(s) + H_2SO_4(a) \rightarrow Mg^{2+}(a) + SO_4{}^{2-}(a) + H_2O \qquad \text{EXT:100\%}$$
$$Ni^{2+}(a) + MgO(s) + H_2O \rightarrow Ni(OH)_2(s) + Mg^{2+}(a) \qquad \text{EXT:100\%}$$

The precipitation reactions go to completion and the amount of magnesium hydroxide added is manipulated to maintain 2w.t.% magnesia in the solid phase product. The resulting slurry is thickened and the overflow solution is bled from the circuit.

The NHP thickener underflow is mixed with the recycled spent electrolyte. The nickel hydroxide and any unreacted magnesia are re-dissolved via the following stoichiometry, the reactions proceeding to completion:

$$MgO(s) + H_2SO_4(a) \rightarrow Mg^{2+}(a) + SO_4{}^{2-}(a) + H_2O \qquad \text{EXT:100\%}$$
$$Ni(OH)_2(s) + H_2SO_4(a) \rightarrow Ni^{2+}(a) + SO_4{}^{2-}(a) + H_2O \qquad \text{EXT:100\%}$$

The resulting solution then feeds to the SAL.

Both SAL slurry and NHP thickeners were specified to operate with 40% solids in the underflow and 0% solids in the overflow. The cobalt concentrate filter was specified to produce a filter cake at 60% solids, operating at 90% wash efficiency with the wash water to water in the filter cake at 2:1.

All vapors generated in reaction tanks, thickeners and the electrowinning cell house were vented in vapor-liquid equilibrium, meaning the gases vented were saturated in water.

ASPENPLUS SIMULATION

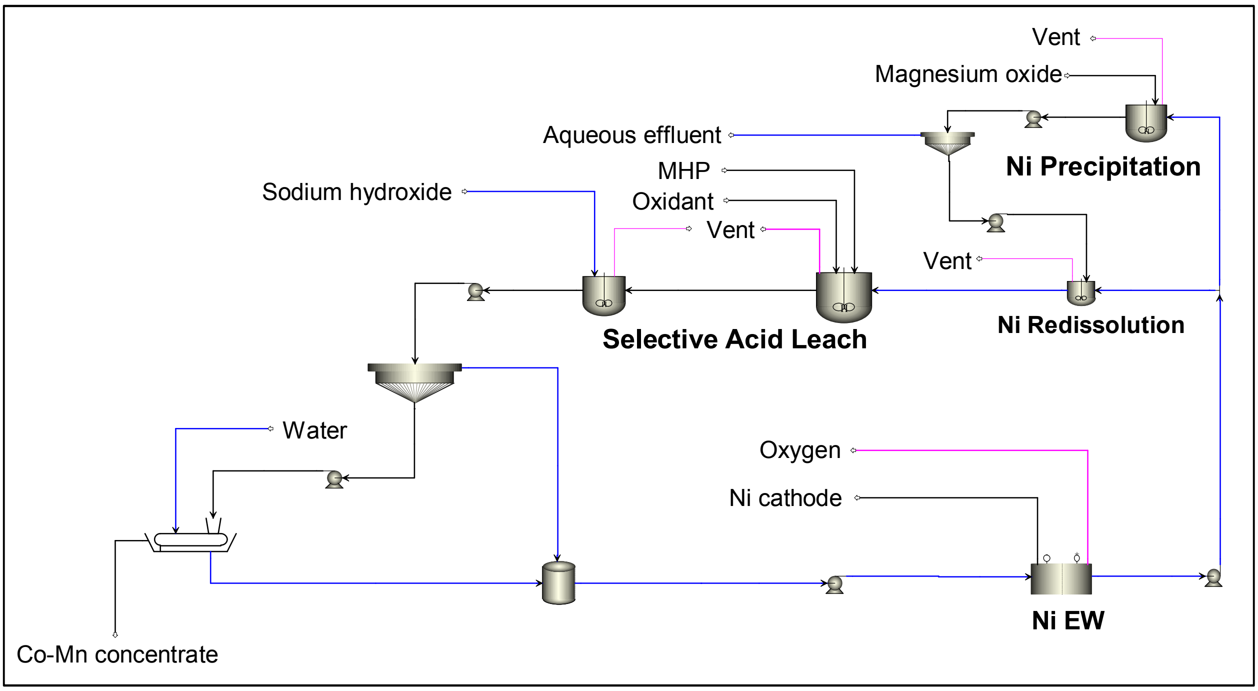

Figure 4 – AspenPlus diagram

Figure 4 is the diagram generated in AspenPlus, representing the circuit modelled in this exercise. The incoming MHP and oxidant are mixed with recycled anolyte. The leach stoichiometry is:

$CoSO_4 \bullet 3Co(OH)_2 + 2Na_2S_2O_8 + 8H_2O \rightarrow 4CoOOH + 4Na^+ + 6H_3O^+ + 5SO_4^{2-}$	100%
$2Co(OH)_2 + Na_2S_2O_8 + 2H_2O \rightarrow 2CoOOH + 2Na^+ + 2H_3O^+ + 2SO_4^{2-}$	100%
$2Co(OH)_2 + Na_2S_2O_8 + 2H_2O \rightarrow 2CoOOH + 2Na^+ + 2H_3O^+ + 2SO_4^{2-}$	100%
$NiSO_4 \bullet 3Ni(OH)_2 + 6H_3O^+ \rightarrow 4Ni^{2+} + SO_4^{2-} + 12H_2O$	90%
$Ni(OH)_2 + 2H_3O^+ \rightarrow Ni^{2+} + 4H_2O$	90%

The amount of spent electrolyte entering the selective acid leach is manipulated to make the advance electrolyte entering the nickel electrowinning section contain 130 g/L Ni^{2+} . Any vapor formed is vented. The pH of the resulting slurry is adjusted to 3.5 with sodium hydroxide and any vapor formed is vented. The neutralized slurry is thickened, the underflow is filtered and the filter cake is washed with water. The washed filter cake leaves the circuit as a cobalt concentrate. The thickener overflow is combined with the filtrate and the combined solution is pumped to the nickel electrowinning section. The stoichiometry in the nickel electrowinning section is:

$$Ni^{2+} + 3H_2O \rightarrow Ni + 2H_3O^+ + \tfrac{1}{2}O_2$$
$$Co^{2+} + 3H_2O \rightarrow Co + 2H_3O^+ + \tfrac{1}{2}O_2$$
$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$

The cathode nickel is harvested. The oxygen and hydrogen evolved are vented, saturated with water vapor. The conversion of Ni^{2+} to metal is manipulated to make the spent electrolyte contain 100 g/L nickel. While the model allows for cobalt to be deposited, the conversion being the same as for nickel, the advance electrolyte contains essentially no cobalt. The extent of the water decomposition reaction is manipulated to make the overall current efficiency for nickel deposition 95 percent. The spent electrolyte is split, part being sent to a nickel precipitation step and the bulk returning to the selective acid leach via a nickel re-dissolution step. The part going to the nickel precipitation step is neutralized with magnesium oxide to precipitate the nickel as nickel hydroxide via the following stoichiometry:

$$H_2SO_4 + MgO \rightarrow Mg^{2+} + SO_4^{2-} + H_2O$$
$$Ni^{2+} + MgO + H_2O \rightarrow Ni(OH)_2 + Mg^{2+}$$
$$Co^{2+} + MgO + H_2O \rightarrow Co(OH)_2 + Mg^{2+}$$

While the model includes cobalt precipitation from the spent electrolyte, there is essentially no cobalt present. Any vapor released is vented. The precipitation reactions go to completion. The amount of magnesium hydroxide added is manipulated to give a final pH of 5.5. The resulting slurry is thickened and the supernatant leaves the circuit. The underflow is mixed with the bulk of the spent electrolyte and the precipitated hydroxide is re-dissolved via the following stoichiometry, the reactions proceeding to completion:

$$Ni(OH)_2 + H_2SO_4 \rightarrow Ni^{2+} + SO_4^{2-} + 2H_2O$$
$$Co(OH)_2 + H_2SO_4 \rightarrow Co^{2+} + SO_4^{2-} + 2H_2O$$

Any vapor released is vented and the resulting solution returns to the selective acid leach.

COMPARISON OF MODEL RESULTS

Table 9 shows selected parameters extracted from the AspenPlus and SysCAD process models. Both models were set up to use the same feed quantity and elemental composition. Both models were set up to recover nickel from the spent electrolyte bleed by neutralization and precipitation of nickel hydroxide that is then recovered by thickening and re-dissolved in the remainder of the spent electrolyte. The overall recovery of nickel to the cathode product, therefore, is the same as the dissolution of nickel in the selective acid leach. i.e. 90 percent, with very slight variation arising from differences in moisture content of the cobalt concentrate.

The only significant differences between the simulations arise from the control methods used. The AspenPlus model was set up to manipulate the amount of spent electrolyte returning to the leach to give a nickel concentration of 130 g/L in the advance electrolyte entering the electrowinning section, and to manipulate the per-pass deposition of nickel in the electrolysis step to give 100 g/L of nickel in the spent electrolyte. The AspenPlus model therefore included a neutralization stage to adjust the pH to 3.5 after the SAL.

Table 9 – Process parameters

Parameter	AspenPlus	SysCAD
Incoming MHP feed, dry basis	11.17 t/h	11.17 t/h
Ni in MHP feed	5.46 t/h	5.46 t/h
Ni in cathodes	4.91 t/h	4.90 t/h
Ni in Co concentrate	0.55 t/h	0.56 t/h
Ni re-precipitated with MgO	0.52 t/h	0.78 t/h
Ni recovery to cathodes	90.0%	89.7%
Ni in advance electrolyte	130 g/L	128 g/L
Ni in spent electrolyte	100 g/L	98 g/L
Per-pass Ni deposition	19.1%	28.0%
pH of advance electrolyte	3.5	3.5

Conversely, the SysCAD simulation was setup to manipulate the amount of spent electrolyte returning to the leach to give a final pH of 3.5. The concentration of nickel in the electrolyte was not directly controlled, rather it was solved based on the plant water balance. In both cases, the plant water balance was affected by the water input via the MHP, the neutralization streams and the cobalt concentrate wash, and the water output via the vents, the bleed and in the cobalt concentrate. The water balance worked out to achieve a concentration of 128 g/L nickel in the advance electrolyte at the conditions specified and the nickel electrowinning model therefore achieved 98 g/L of nickel in the spent electrolyte. Varying the water inputs, with the most influential being independent variable of the cobalt concentrate wash water ratio, had an impact on the simulated nickel concentration. Increasing the wash water ratio in the simulation decreased the nickel concentration, while decreasing the wash water ratio increased the nickel concentration, despite a minor increase of nickel in the cobalt concentrate.

The key result of this difference in control is that the AspenPlus simulation has slightly higher recirculating loads through the SAL and electrowinning circuit than the SysCAD simulation, because more acid is returned to SAL and then neutralized. This means that the AspenPlus SAL circuit is larger than the SysCAD SAL circuit, however conversely, the SysCAD NHP circuit is larger than the AspenPlus NHP circuit. In terms of reagents, this means that the SysCAD simulation requires more magnesia than the AspenPlus simulation, and while the AspenPlus simulation required less magnesia, it also requires sodium hydroxide addition.

COMPARISON OF ECONOMICS – SYSCAD AND ASPENPLUS

Table 10 lists the reagent and utility requirements of the circuit, as calculated by the different process models. Table 11 lists the calculated variable costs. The AspenPlus software has a facility whereby the balance can be exported into related software that calculates capital costs, known as Aspen Process Economic Analyzer™ (APEA). For each step in the circuit, the AspenPlus unit operation is mapped to the relevant process equipment (e.g. a train of agitated tanks, or centrifugal pump) and where required the necessary residence time is specified for that equipment, as well as the material of construction (e.g. rubber lined steel, plastic or stainless steel). The APEA software uses the required residence time and the volumetric flows from the balance to size the process equipment and calculate the amounts of material and manpower needed to fabricate and install that item of equipment. The APEA software estimates the costs of peripherals like process piping, instrumentation and electrical wiring from a large database of actual projects, and it uses civil engineering rules to calculate the costs of concrete and structural steel. It also estimates engineering and other indirect costs. More on this has been published previously (Dry 2013) . This was done to generate a capital cost estimate for the AspenPlus simulation.

The APEA software also allows the user to enter an equipment list, specifying materials of construction and dimensions (volume, diameter or height of an agitated tank, for example, or volumetric flow for a pump). This was done for the SysCAD simulation, using equipment dimensions calculated externally from the SysCAD balance, to generate a capital cost estimate for the SysCAD simulation.

Table 10 – Reagent and utility consumption, per tonne cathode nickel

Reagent/utility	Consumption	
	AspenPlus	SysCAD
Oxidant (100% Na□S□O□)	359 kg	352 kg
Sodium hydroxide (50% NaOH)	215 kg	-
Electricity	12.4 GJ	12.4 GJ
Fresh water	264 t	

Table 11 – Variable costs, $ per tonne cathode nickel

Reagent/utility	Unit cost	Variable cost	
		AspenPlus	SysCAD
Oxidant (100% Na□S□O□)	$1000/t	318	319
Sodium hydroxide (50% NaOH)	$500/t	70	-
Magnesium oxide (100% MgO)	$300/t	27	47
Electricity	$28/GJ	349	348
Fresh water	$2/t	11	5
Calculated variable cost		775	719

Table 12 lists the capital costs estimated for the two simulations. The two estimates agree to well within the normal uncertainty for estimates of this nature. Table 13 lists the estimated fixed costs for the process.

Table 14 lists the calculated revenue, assuming the cathode nickel to be sold at the long-term average nickel price ($7.33/lb) and the cobalt concentrate to be sold at 80 percent of the long-term average cobalt price (i.e. 80% of 26.52/lb) (Dry 2016).

Table 12 – Capital cost estimates, $ million

Item	AspenPlus	SysCAD
Purchased Equipment	37.5	35.7
Equipment Setting	0.2	0.2
Piping	42.4	41.1
Civil	13.0	3.0
Steel	0.2	0.1
Instrumentation	25.3	24.9
Electrical	25.8	25.0
Insulation	4.6	5.1
Paint	0.6	0.6
Other	42.3	35.1
G & A Overheads	0.0	0.0
Contract Fee	5.3	4.8
Contingencies	36.4	32.4
Total Project Cost	238.8	212.7

Table 13 – Fixed cost estimates
(same for both AspenPlus and SysCAD models), $ million/year

Operators (2/shift)	$20/h	0.3
Supervisors (1/shift)	$35/h	0.3
Annual maintenance costs		0.5
Total fixed costs		1.1

Table 14 – Calculated revenue, $ million/year

Revenue stream	AspenPlus	SysCAD
Ni cathode (100% of Ni price)	635	634
Co concentrate (80% of Co price)	288	288
Total revenue	923	922

Table 15 and Table 16 show the results of simple cash flow calculations for the circuit, as based on the AspenPlus and the SysCAD models, respectively, assuming the input cost of the MHP to be 75 percent of the price of the contained nickel and cobalt. The slightly lower IRR for the AspenPlus simulation is because that model assumed a neutralization step using sodium hydroxide after the selective acid leach, while the SysCAD simulation did not. Consequently, the capital cost estimated based on the AspenPlus model is higher than the estimate based on the SysCAD model. Replacing the capital cost from the AspenPlus simulation with that from the SysCAD simulation in the AspenPlus cash flow calculation changes its IRR to 27 percent, the same as in the SysCAD cash flow calculation.

Table 15 – Simple cash flow analysis (AspenPlus model)

Cash flow, $ million	Years 1&2	Years 3-22
Capital expenditure	119.4	
Fixed operating cost		1.1
MHP feed cost		799.7
Variable operating cost		30.5
Revenue	0.0	923.4
Gross margin	-119.4	92.5
Tax (30%)		27.8
Net margin	-119.4	64.8
Internal rate of return		24%

Table 16 – Simple cash flow analysis (SysCAD model)

Cash flow, $ million	Year 1&2	Years 3-22
Capital expenditure	106.3	
Fixed operating cost		1.1
MHP feed cost		799.7
Variable operating cost		28.2
Revenue	0.0	921.5
Gross margin	-106.3	92.5
Tax (30%)		27.7
Net margin	-106.3	64.7
Internal rate of return		27%

COMPARISON OF MHP TREATMENT METHODS

The SAL process would compete with other processes for converting the MHP into metallic nickel and cobalt. In (Dry 1016) the economically strongest option for converting MHP to cathode nickel and cathode cobalt entailed dissolving the MHP in fresh sulfuric acid and spent electrolyte from the nickel electrowinning section. Figure 5 illustrates the circuit found to be economically the strongest, in a previous exercise (Dry, 2016). The MHP is dissolved using fresh sulfuric acid and spent electrolyte from the nickel electrowinning section. The residual solids are filtered from the resulting slurry, washed with water and discarded. The wash filtrate is returns to the main laterite circuit to maintain the water balance and to purge magnesium and manganese. The primary filtrate goes to the cobalt solvent extraction section, which uses Cyanex 272 to extract the cobalt, the manganese and a part of the nickel.

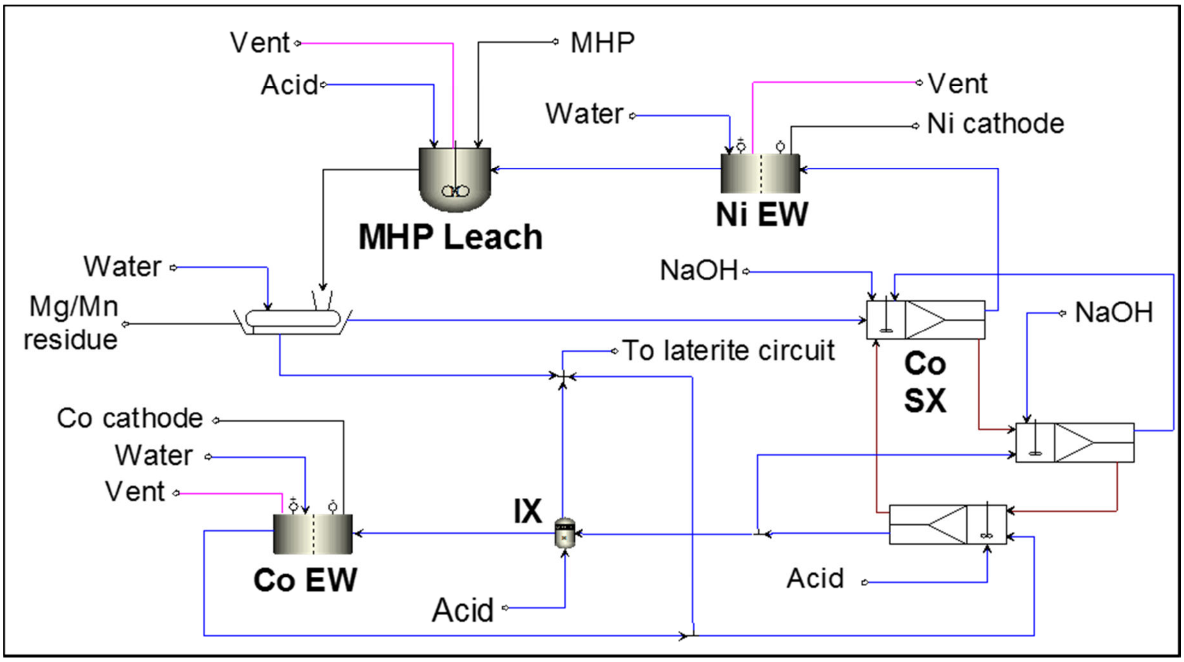

Figure 5 – Acid leach, Co SX-EW and Ni EW

The loaded organic phase is scrubbed with some of the loaded strip liquor from the subsequent stripping section to remove the co-extracted nickel, the spent scrub solution returning to the feed to the extraction section. The scrubbed organic phase proceeds to the stripping section where it is stripped with spent electrolyte from the cobalt electrowinning section. The loaded strip liquor, less the part used as scrub solution, goes to the cobalt electrowinning section via an ion exchange stage to remove any residual nickel. The loaded resin is stripped with sulfuric acid, the spent eluate returning to the laterite circuit. Cobalt is recovered from the purified solution by electrowinning. The spent electrolyte, minus a small bleed to the laterite circuit to purge manganese, is replenished with fresh sulfuric acid and returned to the solvent extraction section.

In this circuit, a substantial part of the nickel and cobalt are returned to the MHP precipitation section in the main plant to avoid a buildup of dissolved magnesium and manganese. For an equivalent comparison with the SAL circuit in the exercise of this paper, the circuit in Figure 5 was modified as shown in
Figure 6, with the various streams that previously went back to the MHP precipitation section in the main laterite plant (the wash filtrate, the eluate ex the ion exchange step and a bleed of cobalt spent electrolyte) instead being combined and neutralized with magnesium oxide, precipitating the nickel and cobalt as hydroxides. The resulting slurry is thickened, the supernatant leaves the circuit, removing dissolved magnesium and manganese. The underflow, containing the nickel and cobalt hydroxide, is returned to the MHP leach.

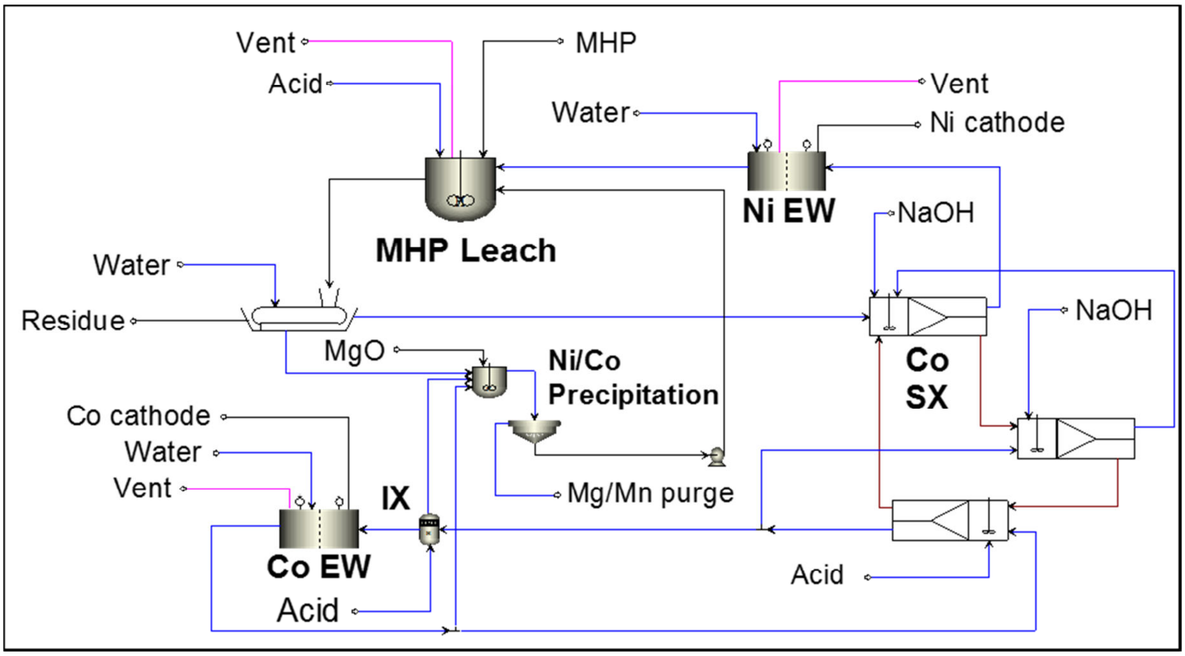

Figure 6 – Modified MHP acid leach circuit

The reagents and utilities consumed in this circuit are sulfuric acid to the MHP leach and the ion exchange step, sodium hydroxide to the cobalt solvent extraction section, magnesium oxide to the precipitation step, make-up water and electricity to the electrowinning of cobalt and nickel, which would be sold for their full metal prices. Table 17 lists the reagent and utility consumptions calculated for this circuit, their respective unit costs and the resulting variable costs per tonne of cathode nickel produced. For comparison, the variable costs calculated for the SAL circuit are $775 and $719 per tonne of cathode nickel (Table 11).

Table 17 – Reagent and utility consumption, per tonne cathode nickel, modified MHP acid leach baseline

Reagent/utility	Consumption	Unit	Variable cost
Sulfuric acid (96% H_2SO_4)	320 kg	$65/t	$231
Sodium hydroxide (50% NaOH)	4.6 kg	$500/t	$26
Magnesium oxide (100% MgO)	112.3 kg	$300/t	$375
Water	887.3 kg	$2/t	$20
Electricity	12.5 GJ	$28/GJ	$391
Calculated variable cost			$1,043

Table 18 lists the capital cost estimate for this circuit and Table 19 lists the fixed operating costs calculated. Table 20 shows the results of a cash flow analysis of the numbers generated for this circuit, assuming for the sake of equal comparison with the SAL circuit that 90 percent of the incoming MHP dissolves in the leach and all of the recycled hydroxide dissolves. Although the revenue is somewhat higher because of the full price for the cobalt, the capital and operating costs are also higher than the corresponding numbers for the SAL circuit, which causes the total MHP leach IRR to be a little lower than that calculated for the SAL circuit (Table 15 and Table 16; 24% from AspenPlus and 27% from SysCAD). The difference, though, is not great enough to be definitive at this level of analysis and with the current assumptions on the value of the cobalt concentrate.

Table 18 – Capital cost estimate, modified MHP acid leach baseline, $ million

Item	AspenPlus
Purchased Equipment	49.2
Equipment Setting	0.3
Piping	58.8
Civil	16.7
Steel	0.2
Instrumentation	35.5
Electrical	44.9
Insulation	0.5
Paint	2.2
Other	57.9
Subcontracts	0.0
G and A Overheads	7.4
Contract Fee	7.0
Escalation	0.0
Contingencies	50.5
Total Project Cost	331.0

Table 19 – Fixed costs, modified MHP acid leach baseline

Operators (3/shift)	$20/h	$0.5 million/year
Supervisors (1/shift)	$35/h	$0.3 million/year
Annual plant maintenance		$0.5 million/year
Total fixed costs		1.1 million/year

Table 20 – Cash flow calculation, modified MHP acid leach baseline

Cash flow, $ million	Years 1&2	Years3-22
Capital expenditure	165.5	
Fixed operating cost		1.3
MHP input cost		799.7
Variable operating cost		40.9
Revenue		959.1
Gross margin	-165.5	117.1
Tax (30%)		35.1
Net margin	-165.5	82.0
Internal rate of return (20 year)		22%

The argument for simulating the SAL process with production of the cobalt concentrate rather than further processing the solid leach product and separating the nickel, cobalt and manganese is that these three components exist in the solid at stoichiometric ratios and chemical forms very similar to those required in production of Lithium-NCM batteries. Hence this solid product could quite easily be refined directly into battery electrode material. This would alleviate the need to separate the nickel, cobalt and manganese, crystallize each out as sulfate salts, and then recombine the three salts to precipitate them as the mixed hydroxides and oxyhydroxides required for the battery electrode material. If this is taken into account when considering the value of the cobalt concentrate, it seems reasonable to assume that the value of the cobalt concentrate, which also contains significant nickel, is at least the same as the MHP if not greater. Table 21 shows an economic comparison of the MHP Leach-CoSX-NiEW-CoEW process against the two versions of the SAL process with the cobalt concentrate valued at the same terms as the MHP, i.e. 75% of contained nickel and cobalt value. Considering this value for the cobalt concentrate, the revenue from the SAL process is virtually the same as that from the total MHP leach, while the project capital and variable operating costs are still considerably lower. Hence, when this still conservative value of the cobalt concentrate is taken into account, the SAL process appears to have a distinct economic advantage with a 20 year IRR of 32-36% compared with the MHP leach 20 year IRR of 22%.

Table 21 – New calculated revenue, $ million/year, project costs $ million and resulting 20 year IRR

Product	MHP Leach	SAL	
		AspenPlus	SysCAD
Ni cathode (100% of Ni price)	635	635	634
Co cathode (100% of Co price)	324	-	-
Co concentrate (75% of Ni and Co price)	-	323	323
Total Revenue	959	958	956
Total Project Cost	331	239	213
Internal rate of return (20 year)	22%	32%	36%

CONCLUSION

Selective Acid Leaching of MHP has been simulated using both AspenPlus and SysCAD. The two models developed for the same process in separate programs resulted in similar final process flows, equipment size requirements and overall project economics. The only differences in the process flows and resulting equipment and economic considerations arose from variations in how the two different simulations were setup by the users, in terms of process control and design criteria. This indicates that it does not matter which program is used, but rather that the process to be simulated and the philosophy behind the process design is clear and well specified. Further, it’s vital that the people doing the modelling fully understand the chemistry and the technology being modelled, that the numbers generated are scrutinized by appropriately experienced people, and that the various inputs (e.g. extents of leaching) have to be validated by measured data at a level appropriate for that stage in the overall development of the project. One must always consider that all flowsheet simulation software programs are merely powerful calculators, and any error or inconsistency in the input data will cause errors in the output.

One of the key considerations for the user when setting up these kinds of simulations in the different software programs that have been discussed, is the need to critically review the thermodynamic data used in the simulations to avoid unrealistic simulation results. This again highlights the need to have an experienced user who is familiar with the process and the software so that potential anomalies can be easily identified, investigated and corrected.

In terms of using the simulation results for economic analysis of the process and project, the Aspen Process Economic Analyzer™ (APEA) add on to the AspenPlus package is a very useful tool to get more out of the simulation and modelling exercise.

Finally, a range of competing process routes for treatment of MHP have previously been proposed. A previous study found that the total MHP Leach-CoSX-NiEW-CoEW process was economically strongest option for converting MHP to cathode nickel and cathode cobalt, however that comparison did not consider the SAL process route. This economic comparison places the SAL process slightly ahead of the total MHP leach option and therefore all the other options previously studied, mainly due to the significantly lower project capital and variable operating costs. Further, if a less conservative value of the cobalt concentrate is considered in the economic calculations, the SAL process has a significant economic advantage over all of the other MHP treatment processes previously considered. Hence, the SAL circuit does appear to merit further development, particularly if a reasonable value can be achieved for cobalt concentrate, for example through its interest to lithium-ion battery manufacturers.

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