

DEVELOPMENT IN BATTERY METALS SOLVENT EXTRACTION PROCESS DESIGN AND SIMULATION

By

Hannu Laitala

Metso Finland Oy, Finland

Presenter and Corresponding Author

Hannu Laitala

hannu.laitala@metso.com

ABSTRACT

During the last decade we have seen a big demand increase for the battery metals like nickel, cobalt, manganese and lithium. At the same time market is demanding higher quality products. Higher quality requirements put pressure on the process design practices. Process design practices must be developed so, that one can not only predict the amount of production, but also the quality of the production.

This means, that modern process design for a solvent extraction plant must be done using a process simulator. A modern SX plant's accurate mass balance can't be calculated manually. Solvent extraction process simulator must be able to calculate not only the main process flows and their compositions, but also calculate the solvent extraction circuit's performance with different feed compositions and amounts. Simulator must also be able to predict how the critical impurities behave in the different circuits. One very important detail is also to model the entrainments in the circuits.

Especially in battery metals solvent extraction processes accepted impurity levels are given in mg/L and this means, that solvent extraction entrainments have big impact how well the SX circuit is performing. Also, SX simulator must be able to predict how the changing process conditions in the different solvent extraction stages changes the chemical equilibrium. Organic phase's metal loading in different stages also affects the chemical equilibrium calculation. Highly loaded organic phase extracts metals differently than a partly or not-loaded organic phase.

Simulator design is also very fast. For a standard SX process, simulator model can be normally done in a few hours. Little bit more complicated cases can be simulated in a few days and even a totally new simulator can be done in less than a week if the base information is readily available. Simulation result accuracies are far better than compared to the process mass balance calculations done without a simulator. Modern simulators can also predict problems in a SX circuit design.

Metso's HSC Sim process simulator is an excellent tool for SX process simulation. HSC Sim is one of the few process simulators, where you can simulate both phases, aqueous and organic, in changing process conditions and given entrainments in every stage and combine the different SX stages to a fully functional SX process. Today HSC Sim models have been used in the process design of several operational SX plants. Several SX plants are being constructed where process simulation has been done by HSC Sim.

Keywords: Solvent extraction, simulation, battery metals, Metso, HSC Sim

INTRODUCTION

Process modelling, especially in the field of hydrometallurgy, has developed very fast during last couple of years. Less than 10 years ago it was quite common to calculate even big process flowsheets using very simple calculation routines. In worst case a whole SX plant's mass balance calculation was done with a couple of main static reactions without any information about the organic phase's features.

Nowadays hydrometallurgical plant's process model contains all unit process equipment separately and different parts of the model can be connected so, that for example SX process is getting the data from the leaching model. SX model in turn can send the calculated results for example to a crystallization or electrowinning process model, where these results can be used as feed data for the simulation.

Most of the models today are static process models. These models can calculate very complicated chemical reactions and equilibriums. Most of the current process models are lacking the dynamical calculation possibility. Current SX models can't usually calculate how temperature changes are affecting the reaction kinetics. Ion cross effects in different process conditions in different phases and between the phases are also missing from the current models. All these features will be added to the simulation models in the future.

SX process models today can already be used for mass balance calculations and operator and metallurgical training. Models can be also used very easily to simulate new process balances. Operator can follow what happens and where if some certain change is made in the feed or the controls.

Metallurgist can calculate SX process balance and verify the simulation result to the data from the actual plant. If more data from the process is achieved later, all these values can be updated easily to the process model.

When a reaction extent closes to 0 %, 100 % or reaction changes direction or reaction happens in conditions where acid or base concentrations are very low, simulator must overcome several difficulties affecting the equilibrium calculations. In these cases, the solution equilibrium and pH calculations are very sensitive.

Very small change in the acid concentration can have a big change in the solution's pH value and thus the metal transfer reaction degree. Acid balance calculation must be very robust, because if simulator's acid concentration goes negative in any of the calculated streams, simulation stops in error. In real life this doesn't happen, because in real SX process acid concentration can go to zero, but not negative.

In this paper a few design examples are presented, where SX simulators have been used to simulate some special SX design cases and these simulated results have had a critical impact on the process design.

ORGANIC PHASE'S TOTAL METAL LOADING EFFECT ON EQUILIBRIUM

When extracted target metal mass flow per time unit is big, but the last extraction stage contains very small amount of the target metal, organic phase can start to extract a different metal because organic phase's activity is high. Usually it is assumed, that solvent extraction equilibrium curves are constant, but in reality, equilibrium curves can change according to the SX process operating point.

This can cause problems in some certain situations. In the example below the target metal was Co and the next metal in the extraction series was calcium. In this case incoming feed solution didn't contain magnesium. In figure 1 below it's shown the base equilibrium curves for a Co SX process using Cyanex 272 (C272) as an extractant. In normal Co SX extraction conditions with Cyanex 272 cobalt is extracted well before calcium.

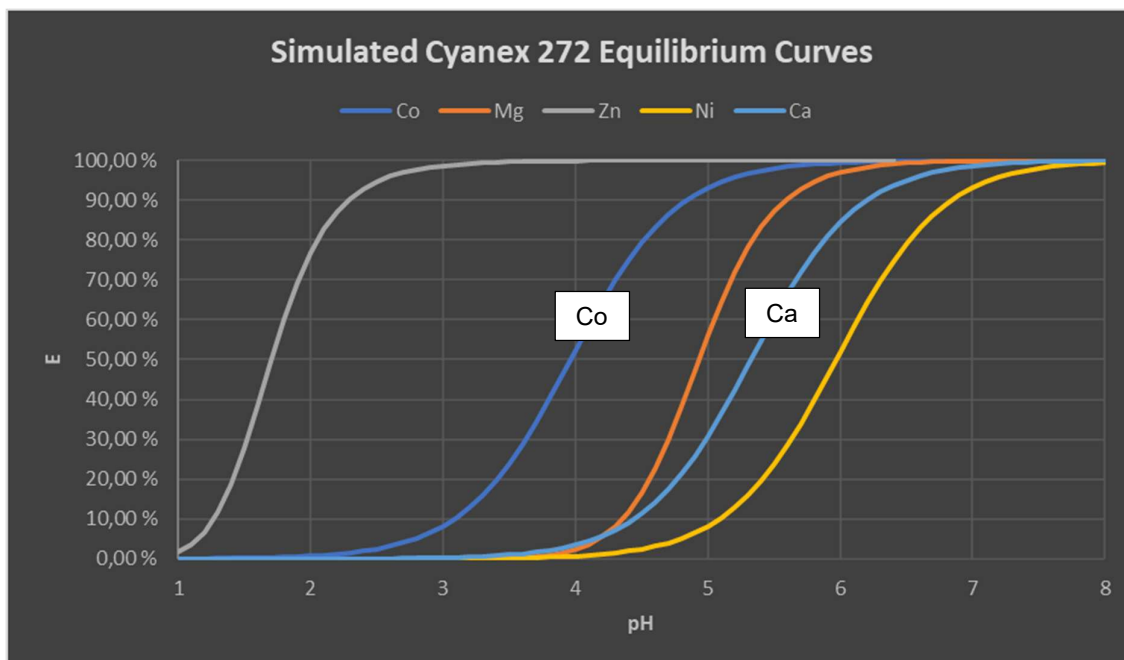


Figure 1: SX Simulator's Cyanex 272 Base Equilibrium Curves

If in the last extraction stage Co concentration in the aqueous phase is low (less than 95 % of the incoming value) and the incoming organic phase's metal concentration is zero, then calcium starts to be extracted if magnesium is not present in the system.

In figure 2 it is shown how calcium's equilibrium curve shifts location in these conditions in the last extraction stage. If organic phase has been preneutralized before organic feeding to the extraction stages, this loading is not calculated as organic phase metal loading.

Calcium starts to be extracted at an aqueous solution pH very close to the Co extraction pH. This can be an operational problem especially when the incoming feed is calcium saturated.

If calcium is extracted excessively in the last extraction stage, calcium concentration increases in the last extraction stage's organic phase much higher than it normally would. When this organic phase flows to the second-last extraction stage, the extra calcium extracted in the last extraction stage will be stripping down from the organic phase to the aqueous phase.

Now there can be a problem if the aqueous phase contains already calcium. Calcium's solubility in sulphate solution is limited and gypsum can start to precipitate easily if the extra calcium stripping down from the organic phase increases calcium concentration in the aqueous phase over calcium's solubility limit.

If water phase's calcium concentration is low or water phase is chloride based, calcium's water phase concentration is not usually a problem. To check if gypsum precipitation will be a problem to a Co SX process different feed and pH profiles can be simulated with a Co SX simulator, which uses the changing extraction equilibrium curves.

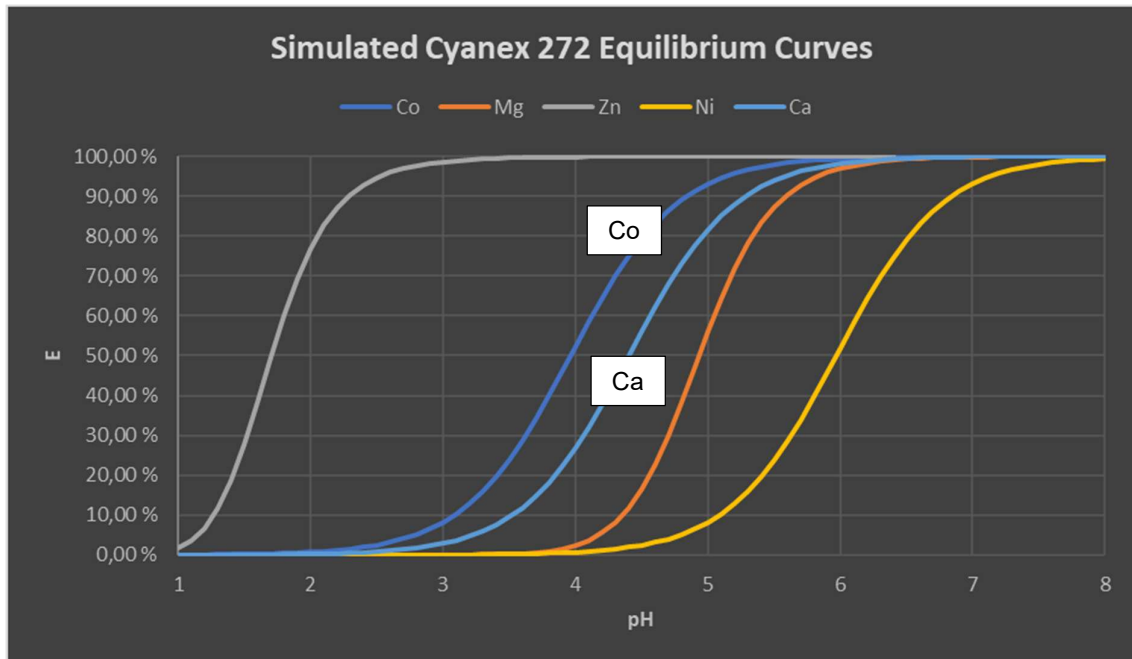


Figure 2: Co SX Simulator's Changed Ca C272 Equilibrium Curve

VERSATIC 10 SOLUBILITY IN Ni SOLVENT EXTRACTION

Versatic 10 (V10) is a carboxylic acid reagent, which is commonly used to extract nickel especially from magnesium and calcium containing solutions. V10's nickel extraction efficiency is excellent, but in the pH range, where Ni extraction happens, V10's solubility to the aqueous phase is high and this can lead in problems at the raffinate treatment plant. V10's high solubility can also affect the operating cost of the SX plant. In figure 3 below some Ni SX simulator's equilibrium base curves are shown.

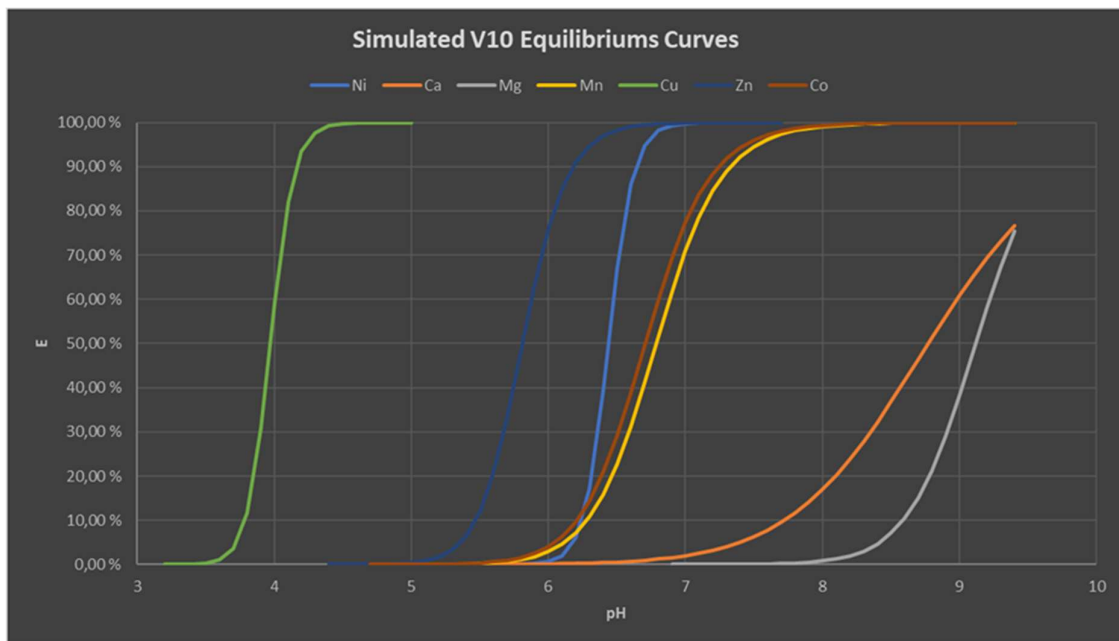


Figure 3: Ni SX Simulator's Versatic 10 (V10) Equilibrium Curves

Aqueous phase pH for a V10 Ni SX extraction stages is 6,0 – 6,5. Equilibrium curves shown in the figure 3 will be adjusted automatically during the simulation based on the organic phase reagent concentration and organic phase's total metal loading degree.

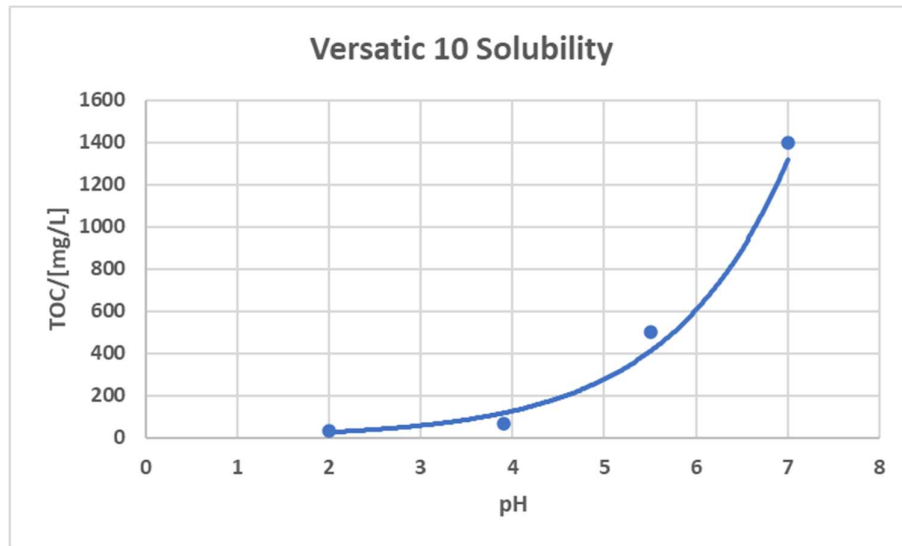


Figure 4: Versatic 10 Solubility

From figure 4 it can be seen, that V10's solubility in the Ni SX operating pH is high. V10's aqueous phase solubility is a function of pH, temperature and ionic strength. At a real SX plant SX process operating temperature and raffinate flow's ion strength can be assumed to be constant with a reasonable confidence, so at the SX plant level V10's aqueous phase solubility is mainly function of aqueous phase pH.

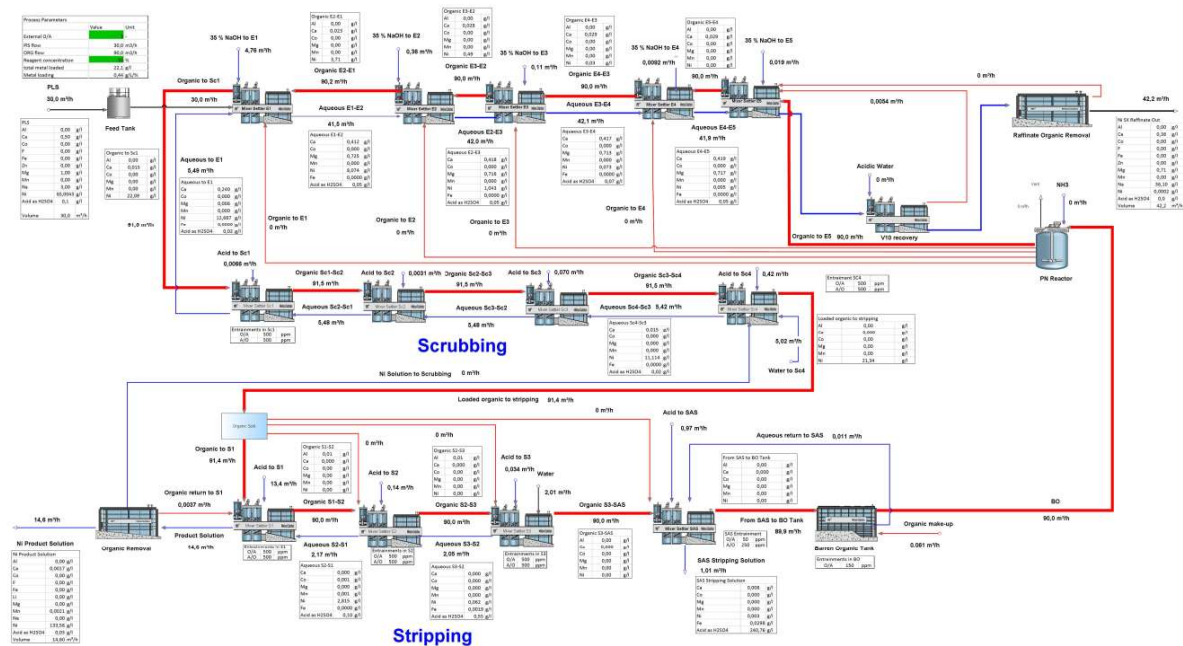


Figure 5: Ni SX Simulator

In this simulation Ni SX feed contained 65 g/L Ni and total PLS flow was 30 m³/h. Nickel transfer to crystallization was 1 950 kg/h. After the last extraction stage, extraction stage E5 in this simulation, there was an extra mixer settler. In this unit V10's concentration in the aqueous phase was decreased by adjusting the pH of the raffinate. This Versatic solubility reduction stage is usually called a VR stage (VR = Versatic Recovery). First simulation was done without pH adjustment to find out the V10 loss in a case where V10 was not recovered.

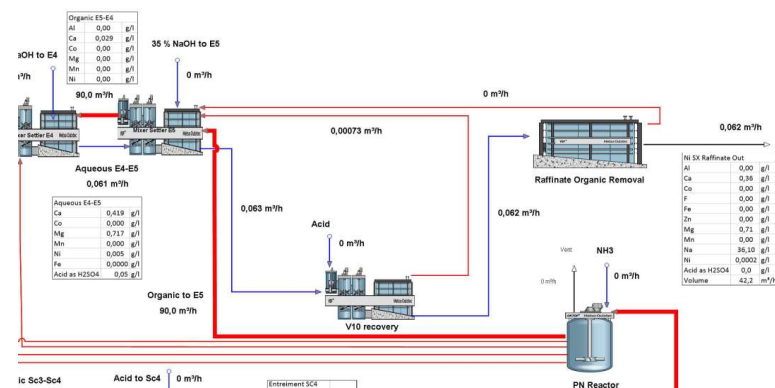


Figure 6: Ni SX without V10 Recovery

According to the simulation organic entrainment in the raffinate stream increases to 1 500 mL/m³ and V10 loss with raffinate out from the process is over 60 L/h. This V10 loss alone is over 90 % of the total organic loss for the whole simulated system.

Second simulation was done assuming that pH control for the raffinate stream in the VR stage was on. pH of the incoming raffinate was adjusted to 3. No other changes were made in the simulation.

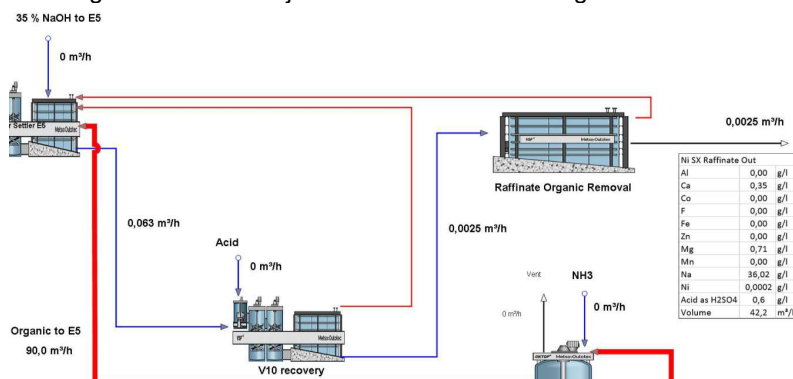


Figure 7: Ni SX with V10 Recovery

When V10 recovery is operational more than 95 % of the soluble V10 can be turned to insoluble organic and returned to the process. Amount of the soluble organic in the raffinate stream drops from 62 L/h to 2,5 L/h. Total organic consumption of the circuit was also reduced more than 90 %.

COPPER REMOVAL SOLVENT EXTRACTION

When producing battery grade manganese, cobalt and nickel salts, one common impurity in the solution coming from the leaching stage is copper. Copper mass flow is usually quite small ranging from 100 to 3 000 t/a Cu. For this kind of case copper production is usually considered to be a by-product production. At a full-size copper production plant plant's main target is to maximize the copper production at the same time when copper unit costs are minimized.

In a Cu removal solvent extraction process copper removal efficiency is maximized so, that battery metals production unit operating costs are minimized. In battery metals production copper solvent extraction's extracted solution (raffinate) is not normally circulated back to the leaching process. In some cases, part of the Cu SX raffinate can be returned to the leaching stage to be used as make-up water and to return part of the acid formed in the SX process back to the leaching stage.

In this example Cu SX is connected to the main process so, that the Co SX process will get its feed solution after the leaching stage's solids removal process. Process block diagram is shown in figure 8.

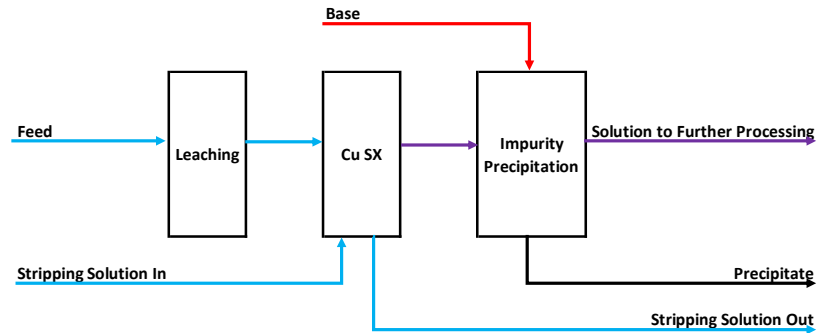


Figure 8: Cu Removal SX Main Process Connection

In this simulation example the main aqueous phase impurities were iron, chloride and manganese. Important feed values for the solution coming from the leaching stage are:

1. Volumetric flow 50 m³/h and sulphuric acid concentration 5,0 g/L.
2. Minimum temperature +25 °C and maximum temperature +40 °C.
3. Copper concentration 8,0 g/L.
4. Iron concentration 20 g/L
5. Chloride concentration 100 g/L.
6. Manganese concentration 10 g/L.

Cu SX Configuration

Because this Cu SX is cleaning the feed for battery metal salt production, the Cu removal efficiency must be as high as technically and economically possible. Main target of this process is to remove as much copper as possible and produce an easily marketable copper product. Even if in the simulated case copper mass flow is quite small, approximately 320 t/a, copper's economical value is still over two million dollars and worth to recover.

First stage of the simulations is to choose a correct base model for this case. In this case you have high iron, chloride and manganese concentrations and intermediate concentration of copper in the incoming feed. Cu SX simulator was updated to be able to handle high chloride concentration in the feed^(1,2).

Cu SX Simulations

Used Cu SX simulator was designed to simulate a Cu SX process with a configuration 3E+LOT+1W+2S in given feed conditions.

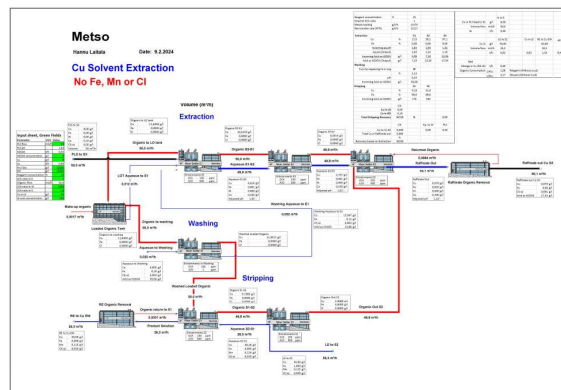


Figure 9: Cu SX HSC Sim Simulator

Input sheet, Green Fields		
Parameter	Unit	Value
PLS flow	m ³ /h	50,0
PLS pH	-	1,83
H2SO4	t/h	0,25
H2SO4 concentration	g/l	5
Cu	g/l	8
Cu	t/h	0,40
Fe (+3a)	g/l	0,002
Mn	g/l	0,001
Reagent concentration	%	25
O/A ratio in E	-	1
Organic Flow	m ³ /h	50,0
O/A ratio in W	-	2000
O/A ratio in S	-	50
Cu in LE	g/l	13
LE acid concentration	g/l	180

PLS to SX	
Cu	8,00 g/l
Fe	0,00 g/l
Ni	0,00 g/l
Co	0,10 g/l
Cl(-a)	0,00 g/l
Volume	50 m ³ /h

PLS to SX	
50,0 m ³ /h	

Figure 10: Cu SX Feed Solution's Composition

First simulation was done with two extraction stages connected in series and without any organic phase washing and no chlorides, iron or manganese in the feed. This simulation indicates how high recovery we can get with only two extraction stages.

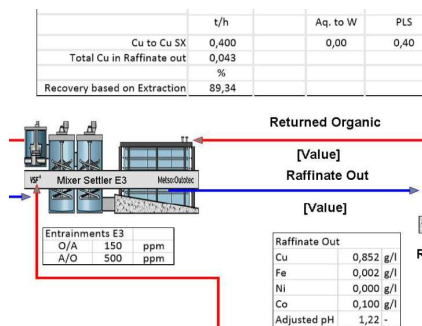


Figure 11: Cu Extraction with 2E+2S Configuration

As it can be seen from the results Cu recovery is below 90 % and the simulated raffinate Cu concentration is 0,85 g/L. This is not acceptable for a Cu removal SX. Second simulation used configuration 3E+2S and simulated copper recovery was 99 % with a raffinate Cu concentration below 0,1 g/L. This was considered as an acceptable result.

For the third simulation all impurity components were added to the feed. Cu recovery was unaffected, but iron and chloride concentrations increased in the product solution. Iron concentration increased 116 mg/L and chloride 86 mg/L. Fourth simulation was done with one washing stage added to the simulator. Addition of the one washing stage decreased the total copper recovery from 99 % down to 95 %, but iron and chloride concentrations in the product solution increased anymore 21 and 14 mg/L. Washing was better, but not good enough.

In the fifth simulation a second washing stage was added to the simulator. According to the simulation copper recovery dropped from 95 % to 94 %, but now iron and chloride concentrations increased in the product solution only 7 and 5 mg/L. Now washing result is acceptable, but we still must compensate the drop in the copper extraction efficiency.

There are three ways how this drop in the copper extraction efficiency can be compensated; Increase reagent concentration, increase organic flow or neutralize acid from the extraction stages. Usually, acid neutralization is not an option for a normal Cu SX process, because acid is circulated back to leaching. However, in this case Cu SX raffinate was the feed solution for battery metal salts production, so acid will be neutralized anyway and thus acid neutralization was an option for this case.

Easiest way to compensate the drop in the copper extraction efficiency is to increase the organic flow if you have the extra pumping capacity available. In the sixth simulation organic flow was increased by 8 % and then copper recovery increased back to 99 %. In the last simulation a base addition was added to the first extraction stage and with this base addition Cu recovery was increased to over 99,7 % and raffinate's Cu concentration dropped down to 0,023 g/L.



Table 1: Cu SX Main Simulation Results

*** = Concentration change in the stripping solution

In this case manganese's oxidation stage will be controlled at the leaching plant so, that manganese's oxidation state will be +2. Manganese's higher oxidation states can be a problem for a SX process and especially if manganese is entering an electrowinning process after the Cu SX, where manganese could be oxidized to a level of +7. Permanganate ion (MnO_4^-) is a very strong oxidant and could negatively affect Cu SX's organic phase.

In some cases, organic phase preloading is the preferred method, but not always. To use or not to use the organic phase preloading must be considered case by case.

In figure 13 below is shown a process block diagram, which was proposed to be used for a project in China. This block diagram was developed by a local engineering company in China for this particular project.

Metso

28.2.2024

Hannu Laitala
Chief Metallurgist - Hydrometallurgy
Metso Finland Oy
Original Impurity SX Configuration

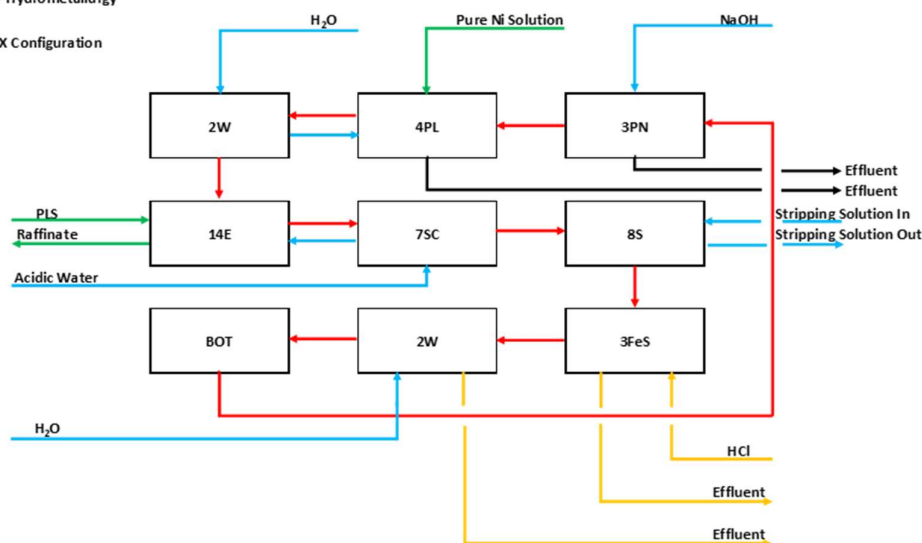


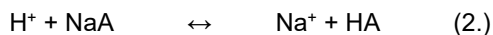
Figure 13: Client's Impurity SX Configuration

Total number of SX contactors was 43 pcs; three preneutralization (PN) stages, four preloading (PL) stages, two base cation washing (W) stages, 14 extraction (E) stages, seven scrubbing (SC) stages, eight stripping (S) stages, three iron stripping (FeS) and two chloride washing (W) stages. This block diagram presents quite standard impurity SX configuration for a manual operated impurity SX circuit.

Manual operation in this case means, that process control is done mainly by controlling the main process flows. In this case manual operation doesn't mean, that client doesn't use DCS. High number of mixer settlers makes this process very robust to operate, but it also makes this plant's investment cost high. Some downsides of this process configuration are discussed below.

Separated Preneutralization and Preloading Stages

Preneutralization and preloading stages are separated increasing the number of the required mixer settlers. In proposed configuration organic phase is first preneutralized according to the reaction 1. After preneutralization organic phase is fed to the preloading stages, where the organic phase is preloaded with pure Ni solution and any remaining acid in the incoming Ni solution is neutralized with the preneutralized organic phase according to the reactions 2 and 3.



Caustic soda solution's concentration can't be high because mixing devices used for the mixing are not suitable for this kind of service. Extra water is needed to dilute down the caustic soda. Nickel solution used for the organic phase preloading is pure nickel solution suitable for battery grade nickel sulphate production. Nickel solution's quality is too high for this kind of use.

Preloaded Organic's Washing Stages

Pure water is used in the washing stages to wash the base cation away from the organic phase. Its ionic strength is low and pH is high. Because of these points phase separation is slow and water entrainments are very high in the washing stages. This leads to low washing efficiency in the washing

stages and low washing efficiency in turn means base cation contamination of the incoming aqueous phase in the extraction stages.

Scrubbing Stages

Proposed process configuration uses preloading to avoid the water phase base cation contamination and the aqueous phase dilution in the extraction stages. Used scrubbing water return to the extraction stages doesn't contaminate the extraction stages' aqueous phase with base cation. However, this return causes aqueous phase dilution.

Because of this dilution effect scrubbing stage's external O/A ratio must be high and the number of the scrubbing stages must be increased leading to a higher capital investment cost of the plant.

Stripping Stages

Without properly designed pH control in the stripping stages number of the stripping stages must be increased leading to a higher capital investment cost of the plant. Iron stripping is done with hydrochloric acid leading to usage of very expensive and corrosive chemical. Because of the hydrochloric acid two extra water washing stages must also be installed to remove the entrained chloride from the organic phase before the organic phase is returned to the preneutralization stages.

Modified Impurity SX Configuration

Impurity SX configuration was modified so, that the number of the mixer settlers and consumptions of pure water, sulfuric acid and caustic soda were minimized at the same time while the plant's capacity stayed the same. Modified SX configuration is shown in the figure 14 below. Instead of original amount of 43 mixer settlers, this new configuration will be using only 15 mixer settlers. This new configuration doesn't use hydrochloric acid at all.

Metso

28.2.2024

Hannu Laitala
Chief Metallurgist - Hydrometallurgy
Metso Finland Oy
Metso Impurity SX Configuration

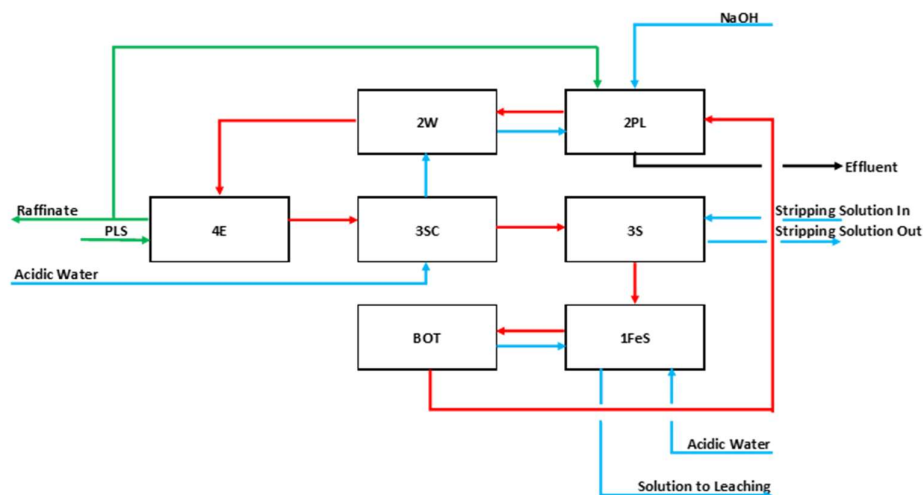


Figure 14: Improved Impurity SX Configuration

This new impurity SX configuration was first simulated with a HSC Sim simulator. After simulations this new configuration was tested in a client pilot plant test run at Metso's research center in Pori, Finland, 2023. This new Metso configuration will be taken into service next year in a project in China.

This new, Chinese plant will use new configurations for their impurity and Co SX circuits. Both configurations were developed by Metso Finland Oy in less than one year.

New Preloading Stages

Because main target is to load the organic phase with the metals from aqueous feed coming in and not to load sodium in the organic phase, preloading process has been changed by combining the preneutralization and preloading stages.

Main reactions happening in the preloading stages are given in the reactions 4 and 5 below. From these reactions it can be seen, that used base cation is not entering the organic phase and this will increase the base cation washing efficiency.



Metal containing feeds are coming from the main process scrubbing and extraction stages. Used scrubbing solution is flowing first through the base cation washing stages, where this solution is washing entrained base cation away from the loaded organic phase.

Metal containing solution can contain any metal, which is not extracted in the SX circuit in question. In this impurity SX case preloading can be made with a solution containing Ni, Co and Mg. Clean Ni solution is not needed for this purpose. In fact, if pure nickel solution would be used for this purpose, it would be a waste of good quality nickel solution.

Caustic soda solution's concentration can be increased because used equipment is specially designed to use base concentration. Currently Metso is using over 10M NaOH solutions for this service. The higher concentration caustic soda can be used, the lower amount of water is needed and because sodium sulphate concentration is also increased in the effluent stream, organic entrainment from the preloading stage will also be lower.

Scrubbing Stages

In this new process configuration used scrubbing solution is used as a base cation wash solution. With the new connection the used scrubbing solution is not diluting the extraction stages' aqueous phase. Because there is no dilution effect, scrubbing stages' external O/A can be increased and the number of scrubbing stages can be reduced.

Scrubbing solution's target in the scrubbing stages is to wash the valuable metals away from the loaded organic phase. In this case the valuable metals are Ni and Co. In base cation washing stages aqueous phase's target is to wash base cation away from the preloaded organic phase. Because used stripping solution doesn't contain base cation and it contains metals, which will be loaded to the organic phase in the preloading stages, used scrubbing solution is a perfect solution to be used as a base cation washing solution after the scrubbing stages.

Stripping Stages

With proper pH control the number of the required stripping stages can be decreased from the original eight to three. Also, iron stripping is done with sulphuric acid in one stage. In the original configuration iron stripping was done with three stripping stages using hydrochloric acid.

Because of the hydrochloric acid two water washing stages were needed for the organic phase. Now iron can be stripped with one sulphuric acid using mixer settler and no extra washing stages are needed. Used iron stripping solution can be easily returned to the leaching plant to be used as a make-up acid for the process. With hydrochloric acid this can not be done and used iron stripping solution must be discarded from the process a waste stream.

REFERENCES

1. Ekman E. (1997). The behaviour of chloride in the extraction of copper from sulphate liquors. Master's Thesis, Lappeenranta University of Technology. Lappeenranta, Finland; 1997.
2. Yanez H, Ardiles L, del Rio C. (2017). High Chloride in PLS and their Impact on Copper Solvent Extraction. In: 9th International Seminar on Process Hydrometallurgy (Hydroprocess) • International Conference on Metal Solvent Extraction (ICMSE). Santiago, Chile; 2017.