State of the Art of Solvent Extraction and Electrowinning Design.

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Abstract

Solvent Extraction and Electrowinning design has evolved over the last 5 decades and a brief history of novel designs that have come and gone and the reasons some fundamentals have remained are discussed.

State of the Art designs are discussed that involve mixer settler arrangements with piping that is re-configurable to suit any changes in processing requirements and or chemistry as an operation expands.

Minimalist designs, which have a reduced degree of instrumentation and are designed for self regulation have evolved from multiple implementations in Africa. Such State of the Art designs include elements to minimise the chance of an SX fire and the preservation of other assets nearby in the event of a fire.

Considering that the EW product in a SXEW operation is the most critical output, quality issues due to antagonistic relationship between SX and EW processes are discussed on a practical and chemical level. Design and operating solutions to overcome such are discussed with the incorporation of best practice on mixer settler arrangements, inherent process control and fire risk minimisation.

Background

Commercial Solvent Extraction (SX) facility design has evolved over the past five decades with a number of types of mixer settler and column arrangements tried and tested in pilot and commercial operations. Some fundamentals have however not changed and are often not properly addressed or even considered in some commercial operations, leading to high risk installations, possible catastrophic failure and or fire.

Fundamentals that are often poorly addressed in SX design include:

- Plant layout in-order to minimise piping and electrical routes and for simpler operability and lower CAPEX;
- Inter-stage piping and unit layout;
- Design for re-configuration of the units should the chemistry or flows require such;
- Design for operability issues in commercial plants – extreme organic or aqueous flows needed to change mixer continuity;
- Material selection, earthing, piping, instrumentation and civils;
- The positioning of SX plants relative to other SX plants, process plant and buildings that would be damaged or involved in the event of a SX fire;
- Fire hazards created by static electricity generated via the flow of organic (especially in plastic pipes);

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• Contamination and organic degradation from oxidation reaction(s) in the closed electrolyte circuit as a result of high Eh generated in Electrowinning (EW) circuit;
• Crud removal access and crud handling facilities;

Commercial Electrowinning (EW) design has changed to a lesser degree than SX design over the same period although there have been small progressive improvements. An understanding of the interactions that EW has with SX under certain conditions has resulted in more specific operating and design criteria to maintain a healthy synergistic relationship between the two.

**Mixer Settler Designs**

The ‘conventional’ mixer settler design has gone full circle and now is fundamentally the same as used in uranium plants in the 1950’s albeit with many improvements. Novel designs such as Krebs settlers, external organic depth control and pulsed columns have come and gone. After 50 years of innovation, the conventional mixer settler design is the most commonly implemented in the minerals industry today.

The traditional head to tail arrangements have been reconfigured with some smart piping and nozzle designs so that the mixers are all the same side resulting in considerable operability improvements as well as a reduction in electrical and piping reticulation. The result is a reduced footprint and a reduced CAPEX of the plants. Reverse Flow and the MMS SideFeed™ mixer settlers are now the most commonly used head to head arrangement. Better layouts with these arrangements facilitate reconfiguration of the units to suit any revised duty.
A 3E+1S SX design head to head

Piping detail with on-line bypassing

An initial 3E+1W+1S configuration converted to a 3E+2S or 2E+1PE+2S configuration

The multi-nozzle discharge of the MMS SideFeed™ settler allows neat piping in a head to head layout

The most recent installations of the MMS designed mixer settlers in Australia and Africa now incorporate piping designs to include the flexibility to change the duty of a mixer settler unit should the need arise. These installations are reconfigurable so that mixer settler units can be changed, from or to; Strip (S), Wash (W) or Extract (E).
Being originally designed to be reconfigurable allows changes in piping that avoid the delays and costs associated with shutdowns for hot work (welding).

Such piping also allows a mixer settler unit to be converted easily and without the need for hot work, from a series unit to a parallel unit. In addition to these improvements, the modern mixer settler units have superior flow distribution from the mixer into the settler. Advanced picket fence designs minimise turbulence and achieve better aqueous organic separation with lower entrainments.

Other modern head to tail arrangements are provided by Outotec. These installations are generally very compact and difficult to operate and sample. The use of higher unit settler flow rates has resulted in an increase in organic depth to limit the space velocity. The increased inventory costs are significant in the overall CAPEX profile.

**Columns**

Uranium, phosphate and nickel SX are the only major metal recovery SX operations where pulsed columns have competed with mixer settlers. The extraction kinetics of ion exchange extractants commonly used for uranium recovery are faster than those of the chelating oxime extractants used for copper recovery. This has meant that while column contactors are not considered for copper SX operations, they have been installed for the extraction stages in a limited number of uranium operations. For uranium SX there is no technical imperative for the use of columns.

While columns have been used for the extraction stages of uranium SX plants, they have not to date been used in the stripping and scrubbing stages. There are examples where the use of columns in pilot plant stripping and scrubbing operations has been met with difficulties due to the requirement of stage by stage pH control (3). As a result the scrubbing and stripping activities of base metals processes are all conducted in mixer settlers.

**Materials of Construction**

Settler fabrications over the years have ranged from fiber reinforced plastics (FRP) lined concrete, anchored polyethylene (PE) lined concrete, full FRP and full stainless steel in no particular order. The choice between full stainless steel and full FRP has usually been one of price although chloride or fluoride content of acid process liquors has also affected selection. Major teething problems have regularly been experienced in projects where a transition of different materials occurs; for example where stainless steel mixers transition into FRP lined concrete settler.

Composite materials and transitions suffer from differential rates of thermal expansion causing leaks and cracks. Anchored PE lined concrete has been successful in Chile but few other places. Compatible materials include polyvinyl chloride (PVC) nozzle’s and piping in FRP tanks. Full stainless steel fabrications do not have this issue and have proven to be far more robust than FRP units.
Fire Prevention and Containment

Fire risks management in SX plants have justifiably been scrutinised due to the number and severity of such fires during the last fifteen years. Poor layout and or selection of piping material have resulted in several major SX fires around the world. Two of these being at Olympic dam, where they were found to be the result of minimal compliance with the standards for control of static electricity (5).

The diluent used in copper SX typically has a high flash point and thus copper SX plants could be classified as non-hazardous areas. From a general survey by Miller (5), over 50% of copper SX plants were found to be unclassified or unrated for electrical apparatus fire initiation. Many of the advances made in the understanding and minimisation of fire risks in copper SX are directly transferrable to other SX plants including:

- The use of fire plume analysis to position other assets outside the fire affected zone from an SX fire and should be applied to all new SX plants.
- Understanding and implementing the standards on static electricity generation and relaxation. The conductivity of uranium SX organic is two to three orders of magnitude higher than copper SX organic. This means that in theory the static electricity codes could be applied; but the risk of a static accumulation is in any case much lower.
- Application of the appropriate hazardous area rating codes. With the use of isodecanol, other alcohols or other modifiers, in an SX plant the effective flash point is often lowered and the plant must be hazardous rated appropriately.
- Attention to the detailed design of the mixer settlers and other elements to eliminate the generation of aerosols that could lower the effective flash point even further.

Crud prevention and treatment

The acid leach processes commonly used in uranium, copper and other base metal leaching can dissolve significant amounts of silica from the ore. Along with suspended solids (SS), dissolved SiO$_2$ concentrations in the resulting PLS can range from a few hundred ppm up to several thousand ppm.

For this reason alone, SX circuits are best equipped with PLS clarification and silica removal circuits which should always be conservative in design to cope with plant upsets (No one has complained yet that the PLS feeding an SX plant is too low in silica and suspended solids …or that the crud processing plant is not being utilised fully!).

Crud and organic recovered from Electrowinning (EW) cells should under no circumstance be returned to crud processing or the SX. The extractant has most likely been oxidised and chemically altered in the EW cell, and will only serve to create issues of crud, reduced chemical capacity of the SX organic and slow phase disengagement issues. Such organic must be disposed of.
Antagonistic Reactions in SXEW

Permanganate degradation of SX extractants occurs by a now well understood mechanism as follows (4):

- Manganese in the PLS is transferred by entrainment (or more often silica based floating crud) into the electrolyte;
- Contamination with traces of other extractants such as Cyanex 272 will chemically transfer Mn;
- \( \text{Mn}^{2+} \) is oxidized to \( \text{Mn}^{7+} \) in the EW operation;
- The \( \text{Mn}^{7+} \) returns in the spent electrolyte sent to the SX strip and oxidizes the organic, forming surface active polar products;
- The oxidized organic has lower chemical capacity and slower phase separation times leading to more entrainment of the PLS in the organic and thus to the electrolyte;
- The higher entrainment of manganese in the electrolyte gives a faster degradation of the SX organic finally leading to a catastrophic collapse of the SX operation due to less than one percent degradation of the organic.

Prevention of permanganate degradation of the extractant is relatively easy and has been covered previously (4, 6).

Contamination from other SX extractant(s) used at the same location.

A significant example of this is that experienced at the Olympic Dam Operation which has a sequential Cu SX and U SX circuit. The problem was chloride transfer into the EW; resulting in pitting corrosion of the stainless steel cathodes which causes the copper sticking and not being easily stripped from the cathode (2).

The eventual culprit was found to be the U SX reagent that was entrained in the raffinate in such quantities that it was returning to the copper PLS via the leach and CCD circuit. In the Cu SX, the trace of U SX extractant was transferring the chloride to the EW electrolyte with disastrous consequences for the stainless steel cathodes.

The cause of the high losses was not purely entrainment but physical transfer during start and stop transients. The column extraction system released much of the contactor organic contents to the raffinate tank on shut down; due to poorly sealing aqueous discharge valves.

Conclusions

Design improvements to the conventional mixer settler including: flow distribution, picket fence designs based on CFD modelling, smart piping layouts combined with extensive practical experience have resulted in numerous operating improvements such as higher unit capacities and lower reagent losses. These refined conventional mixer settler designs have proved to be the best all round performers for a wide range of SX duties in the minerals industry. State of the art SX plant design allows for both reconfiguration and flexibility as well as fire risk minimisation.
Crud management must start at the front end with conservative designs for the maximum possible removal of suspended solids and dissolved silica. Crud processing is part and parcel of any commercial SX operation and should always be well catered for.

SX designs need to cater for the prevention of all possible sources of contamination; and such designs also need to be conservative. Prevention of SX cross contamination may involve diluent washing or activated carbon processing of raffinate prior to the next SX stage.

EW design and commissioning needs to be mindful of the relationship EW has with SX and steps need to be taken to ensure an ongoing healthy synergy, especially for Eh control of the spent electrolyte.

New SX extractants and associated technologies will develop over the coming years, but prior to successful commercialisation, the SX system should be verified against, and designed for, the many lessons already learnt in SX operation over the past five decades.

References