# SX CONTACTORS FOR THE FUTURE

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1. ABSTRACT

A number of alternate designs of contactors are available for solvent extraction in the minerals industry. Of these only mixer-settlers and pulsed columns have any significant commercial installations. Some advocates of tubular reactors are creating interest in alternate mixing systems but in general no real economic alternative to the conventional mixer-settler has appeared. Advances in the engineering of these units and their peripherals will continue to provide the mainstream processing options.

The engineering design of conventional mixer-settler units has been the subject of significant improvements over the last five to ten years. CFD analysis has enabled the visualization of the flow patterns within the units; and the development of internal systems to maximize performance. Specific items have been identified as leading to large macro flow mal-distribution; including the feed spout and the feed in the upper half of the settler depth.

The detailed design of internal elements has also been progressed to minimise local production of vortices and dead areas. More attention is being paid to the development of smooth transitions and stream flow patterns as tools in achieving good design elements.

With the recent SX fires increased attention is being paid to minimization of: fire ignition risk elements, slowing the propagation of a fire and preservation of other settlers near by in the event of a fire. This involves use of alternate design approaches and materials of construction. Recent fire engineering advances have enabled accurate modelling of the fire event and selection of appropriate systems to either suppress or prevent further fire propagation.

The process design will also take advantage of new concepts in circuit integration and optimisation of operating costs. Overall the mixer-settlers will tend to include all the things that make them work better, cheaper and more effectively with shorter shut downs and fewer clean outs.
2. INTRODUCTION

Mineral processing solvent extraction has generally been undertaken with only a few different types of equipment. These are considered in the light of the use to which the solvent extraction process is put. In many cases the drivers for equipment selection are competing priorities of cost, complexity and effectiveness. As a result, the equipment selected tends to polarise to a few unit types; that show consistently better balance of outcomes. Many contactor types have been proposed but used in only a few specific cases.

Advances in the understanding of the drivers of poor performance in existing contactors have been made and performance improved significantly over the last five years. However no really fundamentally new contactor has yet been put forward that seems to show the promise of meeting the competing priorities with better outcomes. The two main protagonists are still mixer-settlers and pulsed columns.

3. CONTACTOR OPTIONS

3.1 MIXER-SETTLERS

Mixer-settlers have been the work horse of the minerals industry with the majority of plants using them in whole or in part. They are robust physically and can tolerate a reasonably wide range of throughput up to maxima set by the effect of entrainment on downstream processes. They have their drawbacks but these are outweighed by the other benefits that they show. In fact installations that might be considered ‘ideal’ for pulsed columns have used mixer-settlers for multiple stage contacts (May 1990). The Greenbushes plant used five stages of extraction, five of stripping, five of scrubbing and five of back washing. A similar multiple stage installation at the Gallium plant in Wagerup used many multiple stages of SX for extraction, scrubbing, stripping and washing (Goodman 1992).

Cusack et al (2002) have applied basic Chemical Engineering principals to the issues of liquid-liquid contact and phase separation. They have come up with a novel arrangement using plug flow reactors for mixing and pressure settlers and coalescers for phase separation. The overall concept of the mixer-setter has been retained but with alternate in-line mixing and pressure vessel settling to enhance the unit rates. There has been nothing published recently on the developments of this system probably due to the high cost of pressure vessels and pumping systems. Part of the cost impacts are the need for intensive explosion proof instrumentation; as well as high integrity equipment for the high temperatures and pressures involved. This concept is likely to be restricted to very specific situations where it may be cost effective.

The settlers themselves are of simple geometry with more or fewer enhancements for feed distribution and improved coalescing. The simplest use a few picket fences for feed distribution while others have a wide range of performance enhancement equipment. The better known of these enhancements include:

- IMI tray filled settlers
- The CRA interface baffles developed at Cockle Creek
- The PIP structured packing in place at Quebrada Blanca in Chile
• The MMS random packed media used in Australia and SE Asia

• The Davy CMS using a material called Knitmesh™ that enhanced coalescing of both phases.

Many of these are less tolerant of crud, particularly those with small interstitial gaps such as CMS and IMI. This is one of the major reasons that such systems have not become universally used.

Other settling enhancements have been practiced such as electro-static coalescing and settling in the Krebs SX at the Wagerup gallium recovery facility. This technique has been developed by Rhone Polenc as part of their proprietary Ga SX recovery process.

3.2 PULSED COLUMNS

Pulsed columns are claimed to provide a significant advantage over mixer-settlers:

• When multiple contact stages are required

• Plant space is at a premium and a smaller footprint is necessary

• Lower entrainment solvent loss in raffinate streams from the lower shear environment

• Ease of providing enclosure for inert atmosphere and for managing organic vapour emissions.

These aspects are really part of trying to put a positive spin on a higher cost process equipment option. The reality of a number of metallurgical installations is that the only claim that has held water is the lower footprint required. All the other aspects are readily addressed by alternate mixer-settler designs. Pulsed columns have shown in fact some distinct negative attributes:

• Limited unit throughput around 200 m3/h; for the largest unit yet installed (Grinbaum 2002). Thus for a throughput of 2 400 m3/h twelve units would be needed, plus one for maintenance/clean out. The equivalent mixer-settler plant would only need two trains to comfortably treat the same flow rate.

• Extreme difficulty in clean out after major scale build up. One operation needed to replace the full column internals as it proved impossible to remove the scale without damaging the discs and donuts.

• The total operating organic entrainment loss can be quite high especially with numerous starts and stops. The column contents are maintained by a tailings (raffinate) valve and if this does not seal 100% (scale or valve material failure etc) then the whole contents of the column can end up in the raffinate tank.

• Different process solution combinations need separate columns. Extraction, scrubbing, washing and stripping are done in separate columns (or mixer-settlers as at Olympic Dam). Some progress on addressing this situation has occurred but is not yet proven in commercial practice.

• Columns need fast reaction kinetics to be effective; as longer residence times come at the expense of fewer equilibrium stages for a given column height. This is OK for uranium
extraction but not very effective for uranium stripping – where mixer settlers are still used with their long residence times.

- As yet there is no commercial application of columns that need intermediate stage pH managements for the process to work. The large installations, both existing and planned, are without pH control through the column (Olympic Dam and Goro Nickel).

- The high installed cost of the units is such that the alternate mixer-settler train(s) can be more than 50% less. This is a large economic driver to continue with mixer-settlers.

The inert atmosphere situation has already been addressed by plants using mixer-settlers. The QNI Ni-Co separation using LIX83 has gas tight mixers and settlers with water seals to control emissions of ammonia from the PLS. The gallium SX plant at Wagerup in WA uses nitrogen blanketing in mixer-settlers to control the oxidation of the extractant. Figure 1.0 shows the fully enclosed and sealed gallium SX plant.

![Figure 1.0 Gallium SX Plant with Nitrogen Blanketed Mixer-Settlers](image)

There are developments with pulsed columns to reduce the severity of some of their limitations. A demonstration column has been run with intermediate pH control; as well as an attempt to combine
extraction and stripping in the same column. No results have been published to date as to the success or otherwise of these steps.

In general there will be limited use of pulsed columns for hydrometallurgical operations except where multiple contacts are required such as Nb-Ta separation. Even then multiple small mixer-settlers were used at the Greenbushes operation. Large volume flow rates will generally dictate a small number of very large mixer-settler units to minimise the plant costs incurred.

4. MIXING

Mixing designs are already very mature and there is little more that is likely to be developed in terms of improved efficiency. One area that will probably be looked at closely is the proper scale up of mixing residence time and mixer mass transfer. To date there has not been very much published on the interactions of the mixing conditions with the interfacial kinetics, and the required scale up of the batch residence time to the continuous residence time distribution of single and multiple mixers.

Most scale up is on the basis of batch mixing tests (if done at all) using standard impellor conditions (tip speed and impellor type). This is ‘converted’ into a mixing time requirement by rules of thumb. A more rigorous method should really be applied that involves

- Production of a batch conversion vs time curve that allows selection of an appropriate approach to equilibrium. Generally the test should be carried out to reach +98% approach to equilibrium in order to provide the necessary range of information.

- Selection of the number of mixers to be used in the plant. This is an engineering decision that can be based on experience and the physical size of the plant. It is common to use:
  - One for short residence times (fast kinetics) or low flow rate < 100 m3/h
  - Two for intermediate flow rates < 800 m3/h and relatively slow kinetics.
  - Three for high flow rates > 800 m3/h

- Calculate of the mixer scale up from the CSTR residence time distribution function and the target conversion. For a 95% approach to equilibrium (typical of hydrometallurgical operations) the total residence time required for first order reactions are:
  - Single mixer  6.4 x the batch reaction time
  - Two mixers in series  2.3 x the batch reaction time
  - Three mixers in series  1.8 x the batch reaction time

In terms of engineering ‘efficiency’ at least two mixers generally give a better economic outcome.

These factors increase substantially when a 99% approach to equilibrium might be required. Such situations have arisen recently in copper-cobalt projects where advance copper concentrations less
than 10 ppm are desirable into the cobalt recovery circuit. One such project used two mixers in series with x 10 the batch residence time to reach the target approach to equilibrium.

The use of residence time distribution analysis and the inherent kinetics of the solvent extraction process is the only way to get a reasonable estimate of the appropriate mixer residence times. If this is not done then there a endless debates as to whether two or three minutes are required and how close the equilibrium the design is achieving.

Other areas of mixer engineering design progress are those of minimising the effect of aqueous locking and of minimum energy input into the mixing activity.

Aqueous locking has been subject to analytical analysis (Miller 2000) as to the causes and methods of elimination. It is now possible to design mixer down-comers to eliminate the symptoms caused by early phase disengagement and shut down accumulation in the mixers. The greatest issue is still the accumulation of the aqueous phase in the mixer during a shutdown situation. The mixer needs to be able to re-start and eliminate the accumulated aqueous otherwise a mixed phase situation will prevail. The easy way to eliminate the issue is to have the mixer exit at a height larger than the settler inter-phase interface. This then retains the problem of settler feed distribution from a stream of partial depth coming into the settler.

The minimisation of mixing energy has been the focus of two main groups: Outokumpu and Lightnin. Outokumpu have develop the Spiroc mixer with dispersion overflow pumping (DOP) to generate the required hydraulic head through the settler train. There are some issues with this arrangement especially when production pressures require larger and larger throughputs in the SX. Some of the plants have not been easily upgraded due to limitations in the mixing effectiveness and capacity of the DOP.

Lightnin improved the design of their impellors to reduce the amount of fine haze produced and to increase the hydraulic efficiency. Both aims were achieved with some spectacular results when the impellors were retrofitted to existing operations. The impellors provided the required pumping power and the necessary inter-phase surface area, but with much reduced power input. One of the consequences of the re-design was the shortening of the impellor blades. With the inside and outside diameters much closer the differential tip speeds were less and the production of fine droplets reduced. In fact one unforeseen result was the appearance of aqueous locking in many plants during commissioning; as the emulsion separated due to the absence of the fine droplets.

Another area of some debate has been the use of small primary mixers and larger secondary / tertiary mixers. The use of a smaller primary is in an effort to reduce the amount of fine haze produced; by limiting the residence time of the emulsion in the primary mixer. This is thought to reduce the number of passes through the pump-mixer and the formation of finer and more stable emulsions. CFD modeling of the standard pump-mixer by both Lightnin and CSIRO has shown that there is only very limited recirculation of emulsion back through the mixer itself. Significantly less than 10% is re-entrained through the mixer. The vast majority circulates around in the tank above the impellor and does not become involved in any re-mixing. This was not the case with the old Davy B-B design where the impellor was mounted on a draft tube 0.5 D off the bottom of the tank. The adverse effects were somewhat limited by having the impellor both top and bottom shrouded so that the re-entrainment was reduced.
Good engineering design now has all mixers of the same overall geometry so that construction costs are minimised and layout simplified for operators.

5. PHASE SEPARATION

The phase separation process is generally scaled up from batch testing and engineering design based on previous good experience. The biggest inherent assumption that is made in many of the designs is that the settler operation is plug flow – with both phases going down the length of the settler at constant velocities. This has been shown by many workers to be quite the contrary (Miller 2000). CFD modelling has again shown the importance of elimination macro, micro and meso scale eddy formation; and that settler feed distribution is critical to the overall performance of the units.

The phase separation process itself sets up pressure gradients and large scale vertical eddy formation in both the aqueous and organic phases. All of the contributing factors lead to a multi pronged approach to settler design:

- Settler feed systems that do not aqueous lock on shut down
- Settler feed systems that distribute the feed over the full width and depth of the settler with minimal eddy formation.
- Elimination of stream line concentration within the settler body. Aqueous or organic recycle extraction can have major influences on local stream lines when extracted from the body of the settler. The practice of aqueous recycle from a pipe at the bottom of setter, and organic recycle from a decant point on top of the organic layer; are two situations that set up adverse stream line flow.
- Enhanced coalescing devices including
  - More picket fences
  - Structured packing media (baffles, PIP System)
  - Random packing media (MMS coalescing media)
- Detailed design of the settler internals to eliminate the smaller eddy formations that can lead to local re-mixing of separated phase –
  - non-spouting picket fence: designs of Outokumpu and MMS.
  - Rounded exit launders to promote stream line concentration without local eddy formation
  - Elimination of sharp edges in flow streams and sharp changes of flow direction.

All of these attributes can enhance the settler performance to allow capabilities of between 25% and 40% higher than previously used.
Other phase separation enhancements are used externally to the settler proper and are related to the need to control entrainments in down stream processes (Miller and Readett 2003). Many have been in use for some time and others are gaining popularity due to ease of operation.

- Coalescers on loaded organic: both Chuquicamata and the MMS designs
- Raffinate and electrolyte after-settlers for recovery of larger excursions of organic entrainment. Again the designs have included random packed media (Chuquicamata and MMS) and structured packing such as the Pacesetter™.
- Regular recovery of organic from the surface of tanks and ponds using continuous rope mops.
- Pressure coalescers such as those of Otto York have appeared to be poorly performing in long term service due to blockage of the fine passages by crud and entrained solids such as insect wings and plastic swarf.

The use of coalescing units is generally restricted to those cases where some severe upset conditions are evident (silica, chloride or manganese management required) or the cost of the SX reagent loss is justification for the installation.

6. INHERENT SAFETY IN DESIGN

The inherent safety aspects of the mixer-settler design have now been highlighted by a number of authors as requiring improvement (Miller 2005). This is being accomplished by changes to the vessel internals, as well as the external environment, to minimise the risk of a fire event; and manage the potential escalation to the rest of the facility.

One of the major criticisms of the mixer-settler concept has been the need for provision of access for monitoring and removal of crud. By changing the operating paradigm in two key areas this has been addressed while still allowing crud to be removed. The organic- aqueous interface level is fixed at a design level i.e. no aqueous adjustable weir. This allows installation of fixed crud withdrawal systems from the now fixed interface. Figure 2.0 shows the fixed weir and the installed crud extraction System.
Figure 2.0: Fixed Settler Weirs and Crud Extraction System

Clear sections in the withdrawal pipe allow visual inspection as to whether crud is present or not at the interface. With fixed crud extraction systems using piping alone, the roof structure can be made to fully encode the settler; and even gas tight as at QNI and Wagerup.

With an enclosed roof system that has inherently few outlets, a system of cooling sprays can be deployed to minimise the risk of escalation from one SX vessel to another. This heat dump system is a classic practice in hydrocarbon processing when using metal tanks and pipes. Heat modelling of non
combusting materials eg FRP and metal show that simple heat dump by water sprays can preserve the vessel even when it is as close as one meter to a one that is on fire (Miller 2005).

Further inherent safety measures are possible but sometime not often practiced due to adverse effects in the process.

- Use of conductivity modifiers to lessen the production of static electricity; have some issues with the affects on the SX chemistry and phase dis-engagement.
- Changes to reagents and diluents are not possible without significant developments from the petroleum industry. Some moves have been made in Africa with the availability of higher flash point aromatic diluents and 100% aliphatic diluents.

Materials of construction have also moved forward, recognizing that non-combustible and conductive substrates need to be in contact with the process organic solutions. Greater use of 316 SS has been made in African projects where chloride corrosion is not a significant issue. Where non-metals are preferred due to the high cost of chemically compatible metals, the use of conductive and fire retardant FRP has become more important.

The greatest perceived threat to the inherent safety is the production of static electricity. A number of recommendations have been made at recent ALTA conferences. The main one is to read, understand and apply the existing codes and standards for the control of static electricity. By doing this simple thing most of the risk elements in the design can be eliminated or at least minimised.

The general look of the mixer-settlers will not change much, but the level of inherent safety in their design will be significantly increased; by attention to the interface between operations and fire safety management. The one aspect that has gained almost universal adoption is the siting of the SX plant so that in a fire event the fire plume will not engage any other significant assets on the site. SX plants are being placed remotely from the other process steps including tank farm, crud treatment and electrowinning.

7. OPERATIONAL ACTIVITIES

Other operational activities will change to improve in the way that they are undertaken so that the inherent safety is maintained. It will no longer be acceptable for process fluids to be dumped into the bunded area as part of a handling strategy during a shut down. Alternative methods of handling them will be implemented to allow lower risk of fires, OH&S issues and corrosion of the plant.

Organic handling will be done almost entirely by the process pumps provided with the plant. The usual means of emptying a settler if organic is to flood it with aqueous and decant the organic into the next mixer-settler unit. This will continue. However handling of the contents of the mixer will be done with the crud extraction pump and/or the loaded organic aqueous entrainment pump. Suitable reticulation from the mixer drains will be connected to these pumps; to allow the mixer contents to be pumped to an appropriate destination.

Evaporation management of organic from settlers and mixers is now integrated with the permanent cud extraction facilities. Fixed roof structures, with few if any penetrations, can be designed to minimise evaporative loss and the emission of VOC’s. The risk of an accumulation of an explosive atmosphere is also minimised outside the mixer-settlers.
Addition of the diluent is generally acceptable using a pump from the diluent storage tank. Addition of the reagent has been an issue in handling from the large IBC’s into the plant. By using peristaltic sump pumps it is quite easy to add another suction off-take to one or more of them. This is connected to the IBC drain valve with a short flexible hose (1.0 m or so) and the contents pumped directly into the plant. The IBC is then washed with diluent that is reticulated to the IBC decant site. No reagent sees the light of day in the whole process.

Handling of the other aqueous solutions can also be integrated with the process piping to eliminate the need to transfer via the spillage sumps and pumps. Settlers can be drained to their appropriate aqueous discharge pipes.

- Extraction settlers can drain to the raffinate pond via the main raffinate pipe. They are re-filled using the PLS pumps
- Wash / scrub settlers can also drain to the raffinate pond or similar. Refilling needs to be with a relatively large make up water supply to reduce the time to get back on line.
- The strip settlers drain into the advance electrolyte tank; from where the electrolyte is pumped into the downstream process for storage. The electrolyte is returned with the large process pumps
- For solutions that need to be stored due to long make up times e.g. wash solution using RO water; a utility tank is provided for storing this material. Return of the solution using one of the larger process pumps will minimise shut down times.

Crud extraction has been mentioned as an integral part of the settler inherent safety in design. The other part to this is the elimination of hoses from the crud process and to replace them with a permanently installed reticulation. This eliminates the OH&S issues of handling the heavy hoses and trips from the hoses across walkways. It also makes the crud extraction process easy to do; so it gets done. In combination with an efficient crud treatment process some operations have reported a 50% reduction in reagent use and an increase in hydraulic capability of the settlers. The ability to do daily crud extraction eliminates the crud layer and improves phase disengagement.

Crud treatment with decanter (two or three phase) centrifuges is now the preferred method. This allows a non-line extraction and treatment process to be implemented that has minimum operator intervention needs. The centrifuges, due to their higher fire risk from fast rotation and vee belts (on some models) will be located away from the SX plant so that any fire in the crud treatment will be contained to that area alone. By keeping the total organic inventory low the fire plume from the crud plant will be modest and separation distances of 20 m or 30 m will be appropriate to prevent escalation to the other SX facility(s).

8. PROJECT RELATED DESIGN

Some project benefits can be integrated to allow synergistic project design and risk management. By adopting new circuit concepts like the Split-Circuit™ (Miller and Nisbett 2007) the SX fire risk management is enhanced. The Spilt-Circuit needs an SX facility capable of treating two different PLS streams of high and lower grade. When this is provided by two separate SX plants they can be separated physically so that one at least will survive a fire event (Miller 2003). The plants themselves
incorporate enough mixer-settler units to allow re-configuration in a series – parallel arrangement that will provide up to 75% production tonnage continuity at the cost of lower overall recovery.

Other spin offs come from the consideration of alternate process arrangements using the SX facility. More circuits will include the SX flexibility in generating lower costs and higher recoveries. One such is the integration of the cobalt recovery process into the copper SX plant (Miller and Nisbett 2007). Primary copper extraction is done and the portion of the raffinate for cobalt recovery is sent for iron precipitation. This involves neutralisation to pH 4.5 to remove Fe, Al SIO$_2$ and some Mn. The copper is left largely in solution. The iron free stream at high pH, is returned to copper SX for removal of the copper to <10 ppm in two stage of extraction. In this way the integrated circuit can be used to lower the advance copper concentration to an order of magnitude (nearly two orders) less than ‘normal’; with consequent savings in copper loss and cost of the plant to remove it in the cobalt process.

9. CONCLUSIONS

The future mineral processing solvent extraction plant will superficially not look much different from the present hardware. What will have changed is the detailed internal design, to improve performance and reduce fire and escalation risks.

Mixing design will focus more on the inherent chemical engineering principals of scale up of CSTR’s from batch kinetic reaction data. The mode of mixing will develop with more emphasis on tighter drop size distribution and faster phase separation.

The mixer-settler will probably continue to be the work horse of the industry with some specific installations opting for pulsed columns for particular needs – foot print, multiple staging and inert gas atmosphere. More design developments of internals will be the result of CFD analysis of alternatives before physical testing.

The SX plant will become far more inherently safe with better design for vapour management, solution transfer, crud extraction and treatment and reagent handling.

The process design will also take advantage of new concepts in circuit integration and optimisation of operating costs.

Overall the mixer-settlers will tend to include all the things that make them work better, cheaper and more effectively with shorter shut downs and fewer clean outs.

10. REFERENCES


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