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WATER MANAGEMENT FOR GOLD RECOVERY USING ALTERNATIVE LIXIVIANTS TO CYANIDE

By

[1]S R La Brooy and [2]P Smith

[1]Ausenco, Australia
[2]Proxa Australia (Pty) Ltd, Australia

Presenter and Corresponding Author

Stephen La Brooy
stephen.labrooy@ausenco.com

ABSTRACT

Research on alternative lixiviants for gold extraction is ongoing. This paper looks at where an engineering company fits into the matrix of people working on alternative lixiviant technology.

Typically developers focus on discrete aspects of a process. The big advantage that engineering companies bring is that they are used to looking at the complete process. Recycle streams and the effect of the impurities that they contain need to be taken into account.

Alternative lixiviants are typically applied at concentrations 50 to 100 times those required for cyanidation. Higher concentrations make recycle and what might happen in the TSF significant considerations. Further complications come with systems where preg-robbers are present so that no lixiviant can be tolerated in the comminution circuit.

Carryover of the approaches used with cyanide, such as lixiviant kill before water recycle would result in a huge operating cost. The solution to this could be to incorporate membrane treatment to provide clean water for the comminution circuit and also concentrate up lixiviant for recycle to the leach circuit. It is likely that at closure membrane treatment will again be required to recover the significant concentrations of reagent in the TSF back into the process, to minimize future liability.

Bleed streams can create significant issues at plant scale, especially if environmental pressures or climate preclude evaporation ponds. A solution to this could be to use a MVC falling film evaporator and crystallizer system to produce a mix of solids for recycle and offsite disposal.

To further increase what Ausenco can offer it has recently formed a joint venture with Proxa, a South African water treatment company specializing in custom solutions involving membrane processes, ion exchange and energy efficient zero discharge options.

INTRODUCTION

There is ongoing interest in development of alternative lixiviants for gold recovery as evidenced by papers by Barrick, CSIRO and Outotec at this conference. This paper looks at where an engineering company fits into the matrix of people working towards the application of alternative lixiviant technology.

Technology developers often seem to think that after they have had their eureka moment and sorted out one aspect of the process such as leaching, recovery onto an adsorbent, or an elution process, that a viable process is just around the corner. Even when they set out to review the issues and impediments to use of a reagent it is still easy to miss issues such as recycling of water and reagents. For instance Muir and Aylemore(1) reviewed the issues and impediments to use of thiosulfate as an alternative to cyanide. They considered the mechanism of leaching, the kinetics, the stability of the reagent, the options for gold recovery, but the nearest that they got to reagent recycle was the buildup of polythionates and environmental considerations from de-oxygenation of waterways and oxidation to toxic species if it was released into the environment.

The truth is that each phase of development just contributes another link to the overall process chain. Barrick's recent report(2) on work towards the commercialization of thiosulfate processing provides a good example of the range of inputs required from many people. There can be no viable process until all the links are in place. It is also very important that engineering companies work very closely with their clients, especially when the project involves a new breakthrough technology. The big advantage that engineering companies bring is that they are used to reviewing mass / water / energy balances for a complete process in order to be able to design plants. This helps see any missing links and some of their implications.

In reality it is usually quite difficult to simulate a complete process incorporating all the recycle loops. Often the best that can be arranged are locked cycle batch tests. Recycle streams and the effect of the impurities that they contain can have a significant effect on operability and the operating cost of a process. Even when companies go to the expense of building a demonstration plant it is unlikely that they are able to fully simulate all the recycle loops. The only option then is to rely on computer modeling of the process in a program such as SysCAD or MetSim to derive the design data for engineering the process. It is vital that enough reality checks are carried out to try and reconcile model output with the pilot / demonstration plant data to ensure as far as possible that model predictions are realistic. The model predictions can then be used to add the required chemicals to spike solutions to simulate recycling solution from the tailings storage facility (TSF). SysCAD or MetSim are excellent at keeping track of the species that they told about, but they are totally at the mercy of the process chemistry and extent of reactions that are included in the programming. Hence it is not unusual to need several iterations of modeling to try and get the model predictions and process observations to converge.

BASIC ISSUES WITH ALTERNATIVE LIXIVIANTS

Concentrations

Researchers often point out that the unit cost of alternative lixiviants is less than that of cyanide. However, alternative lixiviants are typically applied at concentrations 50 to 100 times higher than those required for cyanidation eg in the case of thiosulfate(1), if not thiocyanate(3). Compare 25-150 mg/L (0.001-0.006 M) cyanide with 0.1 M (15.8 g/L $Na_2S_2O_3$)(1). Higher concentrations make recycle and what might happen in the TSF significant considerations.

Corrosion

Cyanide and the alkaline solutions required for its use are easily processed in normal carbon steel equipment. Corrosion issues with chloride systems are well known. Reagents such as thiourea and thiocyanate are actually used as corrosion inhibitors for steel and thiosulfate can be used for solution deoxygneation to prevent corrosion. However, under the pH and concentration ranges necessary for gold dissolution there are corrosion issues. At anything more than trace levels for deoxygneation thiosulfate is corrosive to steel, as is the case for acid conditions required for use of thiourea and even thiocyanate can under certain conditions cause stress corrosion cracking. Hence additional steel protection is required wherever these reagents are used throughout the circuit. For any system other than a heap leach with dry crushing corrosion protection will need to be considered starting from the grinding circuit. While it is possible to address the corrosion issues as

Ausenco did at the Sepon copper plant, where grinding is carried out in acid solution, such options are yet to be applied in gold processing. Further complications arise with systems where preg-robbers are present, necessitating essentially total absence of lixiviant in the comminution circuit.

Water Recycle

With cyanide systems it is conventional to use some form of reagent destruction before the slurry is sent out to the TSF, with possibly further lixiviant kill on the process water coming back to the plant, in circuits where flotation preconcentration is used. This approach makes sense as cyanide concentrations are relatively low, so that operating costs for cyanide destruction reagents are manageable. However for alternative lixiviant systems, where the reagent concentrations are much higher this approach would have a large operating cost.

Given the much more benign nature of the alternative reagents, there is not the same need for reagent destruction on the slurry going out to the TSF. In fact if this was required the cost of reagent destruction by a process such as Inco air/SO_2 oxidation, and the lixiviant replacement cost, would probably kill a project. Gos and Rubo[(4)] had previously pointed out that the cost of oxidation of thiosulfate to sulfate to generate lixiviant free water was likely to be much higher than the cost with cyanide due to the much higher reagent concentrations and the number of molecules of oxygen required per molecule of thiosulfate.

Fortunately significant reagent recovery can be achieved as in the cyanide system by using a tails thickener to recycle solution to the plant.

REVERSE OSMOSIS

Background

While a tails thickener significantly reduces the reagent recycle issues, it does not solve the need for clean water for the comminution circuit, where most of the process water needs to be added. The solution to this could be to incorporate membrane treatment to provide clean water for the comminution circuit and at the same time concentrate up lixiviant for recycle to the leach circuit. Conceptually this is no different to the use of reverse osmosis (RO) to treat plating rinse solution to recycle reagents to the plating bath and supply clean water for rinsing that was proposed by Hauck[(5)] over 40 years ago as illustrated in Figure 1.

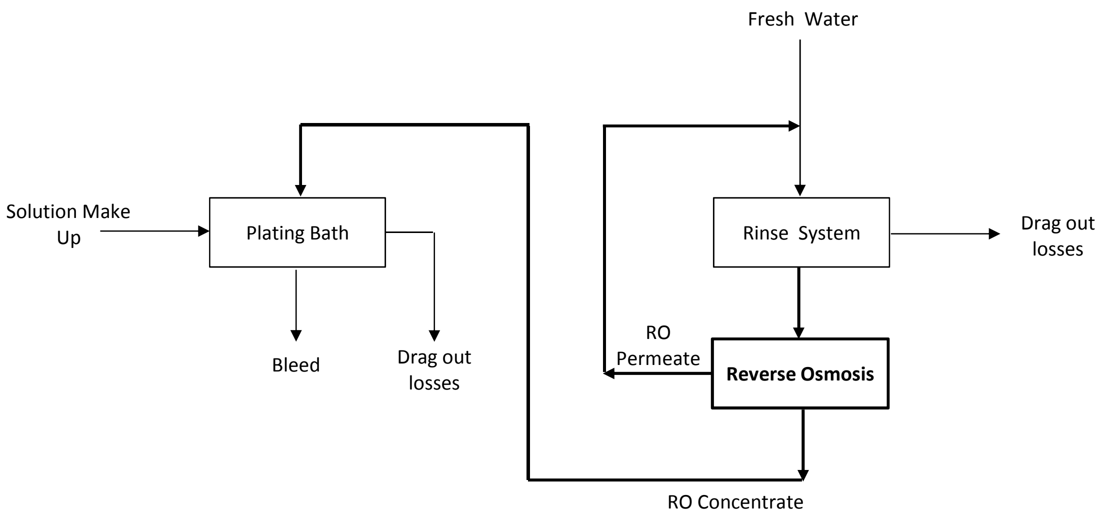

Figure 1: Application of RO into a plating rinse system for rinse water and reagent recycle

It is important to ensure that potential show stoppers are captured at the Scoping Study stage of the project, as the ability to impact on a project and its design typically diminishes rapidly through the project assessment process as illustrated in Figure 2 (after Lane et al)[(6)].

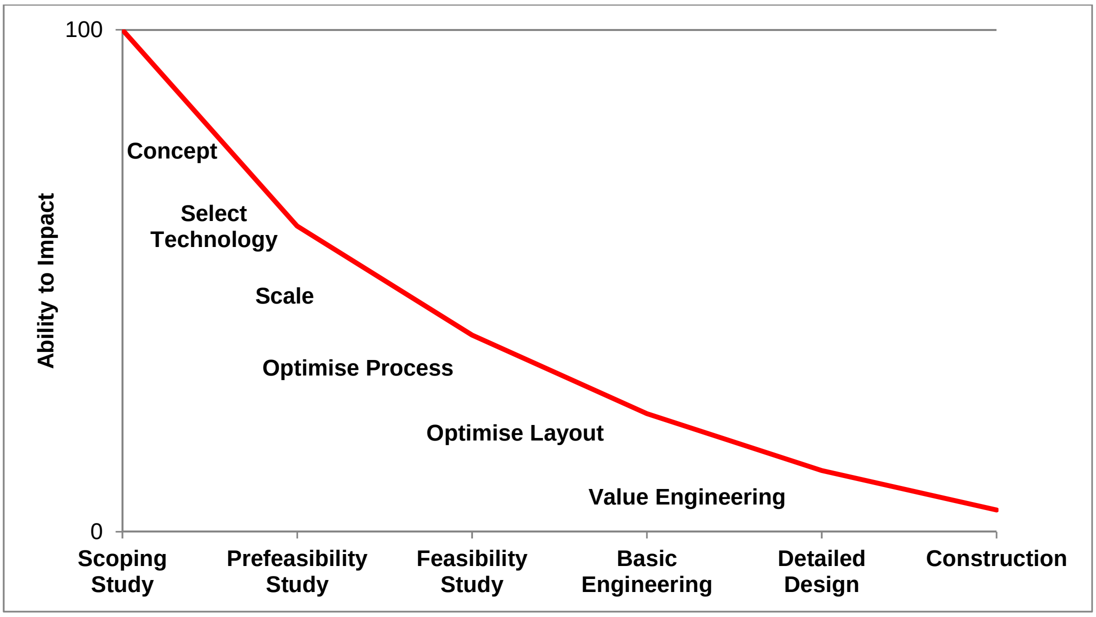

Figure 2: Ability of ingenious solutions to impact capital and operating costs at different stages of project(6)

In the face of pressures from climate change and population growth, people in many parts of the world have become more dependent on membrane processes for supply of potable water, especially from sea water. This has been driven by the ability of RO to offer a lower energy consumption route than multistage flash distillation. The high chloride concentrations encountered in such plants have ensured that corrosion resistance issues have been considered, to provide useful background for the corrosion issues that can arise with alternative lixiviants due to the lixiviants themselves or need for acid conditions. This is another area that engineering companies can assist in the deliberations on acceptable materials of construction from issues that have arisen on other projects.

Membrane applications in metallurgical industries are generally less well known but Lien(7) has provided information on a number of applications for metal recovery, in conjunction with acid or alkali recovery. These include:

- 400 m³/h system installed in 1992 at rod mill in USA, to recover copper, sulfuric acid and water for rinsing
- 900 m³/h Mexican system treating acid mine drainage containing 0.7 g/L copper to enable copper recovery the concentrate that paid for the system within 6 months
- copper refinery groundwater pollution control system upgrade installed in 1993 in USA to reduce the volume of solution ahead precipitation treatment
- 40 m³/h NF / RO plant for boron removal from Australian zinc refinery process water bleed to generate boiler feed make up water and allow zero discharge with brine sent to an evaporation pond.
- 600 m³/h UF / RO Spanish alkaline mine drainage treatment to recovery clean water for use as process water
- 750 m³ Spanish UF / RO system to treat pit perimeter dewatering bore flow to produce desalinated water for re-injection to recharge the downstream aquifer.

There have been at least two RO gold industry applications to treat excess water for offsite disposal, to provide higher quality water than could be achieved by conventional water treatment. The first RO plant at Yanacocha Norte was installed in 2003(7), treating Merrill Crowe (MC) barren solution to generate permeate that could be released to the environment after chlorination to destroy the residual cyanide. This provided high quality water that could be discharged to local rivers that downstream communities rely on for farming and agriculture.

In addition there were process benefits from the return of the cyanide and gold content of the MC barren solution to the leach process. Since the MC barren had already been filtered to recover the precipitated gold and silver, RO pretreatment requirements were limited to the (blue) bag filtration units adjacent to the feed pumps in the foreground in Figure 3(8). Lien(7) pointed out that the payback period on the initial RO plant was less than four months, thanks to cyanide savings, a 75% reduction in chlorine requirement for cyanide destruction and 96.5% recovery of residual gold and silver present in the barren solution. The latter safety net was particularly useful under 'upset' conditions.

Hence it is no surprise that the International Cyanide Code 2011 Recertification Audit Report noted that in 2011 there were five RO treatment plants operating at Yanacocha to treat excess water in addition to five conventional excess water treatment plants[9]. The earlier Golder International Cyanide Code Verification Audit report[10] noted that the RO plants were based on 250 m³/h modules and operated independently of the conventional excess water treatment plants. Figure 3 shows the second RO plant at Yanacocha Norte installed in 2004. The two level 1000 m³/h plant[6] is reported to have cost $50M[11].

Figure 3: Yanacocha 2004 reverse osmosis water treatment plant (after Elbuenminer)[8]

At Waihi[7,12] the driving force for membrane treatment has been its ability to remove specific contaminants such as selenium and antimony to lower levels than can be achieved by chemical precipitation. The 240 m³/h Waihi RO[7] plant receives feed from the metal precipitation plant that is passed through multimedia filtration and bag filtration ahead of a two parallel train RO system. Each RO system has two stages with the first operating at less than 200 psi and the second higher pressure stage at less than 400 psi. The two stage system allows an overall water recovery to permeate across RO of about 87%, with the brine sent to the tailings storage facility (TSF). The higher quality of the permeate compared to the previous conventionally treated water has allowed a relaxation in the restrictions on discharge to the local river.

Process Design

One of the significant issues with RO is the need for pretreatment of the feed water to remove components that the membranes cannot cope with, such as suspended solids. Even with optimum operation of a tails thickener and a target of say 100 ppm total suspended solids (TSS), some form of pre-treatment will required ahead of RO to ensure stable operation. There has been much progress in this area of water treatment as evidenced by the different technology used for pre-treatment in the two Perth seawater desalination plants. The initial Kwinana plant was designed with the conventional approach of coagulation and settling followed by multimedia filtration and polishing cartridge filtration ahead of RO. The second southern plant has taken advantage of more recent developments to simplify the pretreatment to membrane filtration in a short cycle spaghetti type system eliminating the need for coagulation, settling and multimedia filtration. This approach is viable given the relatively low TSS content of seawater.

However in mining applications it is not unknown for tails thickeners to have hiccups or for the TSF decant water to acquire colour on windy days. Hence the more conventional and conservative approach of multimedia filtration will probably provide a more robust front end to a water treatment plant. Additional protection against potentially high TSS inputs from the TSF decant water on windy days could be achieved by routing it through the tails thickener to provide a safety net, as well as assist with the feed slurry dilution for optimum thickener performance.

As a further precaution to protect the RO system from fine TSS material and potential bacterial fouling issues it is probably a good idea to incorporate a UF stage ahead of RO.

The TDS values that need to be considered for RO in a system with alternative gold lixiviants are not that different to what sea water plants deal with. Conventional sea water plants typically operate at water recoveries around 43%, with initial stage with equipment rated to around 300 psi (2 070 kPa) and a second stage with 600 psi (4 140 kPa) equipment. This relatively low water recovery is adequate as there is plenty of sea from which to extract more water and limiting the brine concentration also reduces environmental impacts around the area where it is returned to the ocean. Typical gold plants require most of the recycled process water to be added to the dry ore coming into the comminution circuit, with a smaller fraction being added in the leach circuit. Hence for optimum operation a much higher recovery of clean reagent free water is required, necessitating a third stage of RO at higher pressures with equipment rated to 1000 psi (6 900 kPa) to achieve the required water recovery.

In addition the ionic speciation of such solutions is completely outside the envelope of chemical experience of most membrane treatment suppliers. Hence initial guesses by membrane suppliers as to what would be required and what it might be possible to achieve are likely to be way off the water recovery and concentration factors that a metallurgical plant operation would require. Thus testwork is absolutely necessary before suppliers can contemplate achieving the targets that a project is likely to require. This testwork may well have to be carried out on simulated solutions, using TDS values predicted from computer modeling, to try and avoid the usual issue with membrane treatment systems in mining applications. Most plants report that recovery is below the nameplate capacity as there was inadequate allowance for buildup in TDS with solution recycle, so that achieving the design permeate flow would require higher pressures / more membrane modules than are available.

FURTHER ISSUES WITH ALTERNATIVE LIXIVIANTS - CLOSURE

Significant research has been carried out on naturally generated low concentrations of thiosalts formed when processing sulfide ores[13,14]. These papers, albeit looking at much lower concentrations, have flagged potential acid generation on oxidation of thiosalts to sulfate. In addition to chemical processes the literature show that thiospecies are also amenable to bacterial oxidation[15].

This should not be a significant issue during plant operation as solutions are recycled controlling the solution residence time in the TSF and stabilizing the pH. However, depending on the acid neutralization capacity of the tailings, in some cases it is likely that further membrane treatment may be required to recover the significant concentrations of reagent in the TSF back into the process to minimize future liability before closure. Researchers have noted that[4,1], although thiosulfate is generally regarded as relatively non-toxic, it is also metastable and can decompose to polythionates and sulfate whilst consuming oxygen, or to toxic sulfide ion under anaerobic or reducing conditions.

In the later stages of mine operation typically throughput decreases as the availability of ore decreases. This should free up capacity in the water treatment plant, to allow for additional treatment of the TSF decant water to reclaim reagents.

FURTHER ISSUES WITH ALTERNATIVE LIXIVIANTS – BLEED STREAMS

Background

Technology developers often gloss over the need for process bleed streams to remove unwanted reaction products. If these are not removed or at least controlled they could build up and stop the process. At laboratory or pilot scale usually only minor quantities of solution need to be removed. However bleed streams can create significant issues at plant scale, especially if climate or environmental issues preclude evaporation ponds.

One way around this is to use an evaporator / crystallizer system. This could incorporate a mechanical vapour compression (MVC) evaporator as a first stage to concentrate up the solution, followed by a two stage crystallizer system to produce some salts that could be recycled back into the process before a final stage of evaporation to dryness to produce solids for offsite disposal. A two stage cystalliser approach would reduce the mass of material for offsite disposal, but the overall system will nevertheless add to the process energy requirements. There can also be issues with the salts for disposal if there are solution components that could result in the salts being classified as hazardous wastes. In that case a more robust solution could be to try and eliminate the need for the process bleed, by revision to the flowsheet changing process chemistry to eliminate addition of the ions that would later need to be bled from the system.

Given the experience at other mining operations utilizing RO for treatment of water for disposal, where the buildup of total dissolved salts (TDS) in the process solutions has ultimately limited treatment capacity, it is still possible that in the longer term some form of solution bleed may still be necessary. It is possible that despite using computer modeling to try and ensure that adequate capacity is built into the initial RO system, model limitations or inadequate validation may still result in the recycle solution TDS exceeding the model predictions. In turn this may result in the membrane technology not being able to deliver the required water recovery. This could require extracting salts from a bleed stream of the concentrate, or alternatively using some form of chemical precipitation to remove the problem ions, before returning the treated concentrate back to the RO process for the final stage of treatment. Brine treatment before further RO treatment has been proposed by a number of researchers(16,17) to allow increased water recovery by RO.

The potential process options will depend on the ions that need to be removed and their concentrations. In some cases selective removal may be possible by chemical precipitation or ion exchange to produce a treated stream that is amenable to further RO treatment. In other cases due to the concentrations involved or high solution TDS some form of concentration and crystallization may be required. The problem is that the concentrations required for crystallization are usually well beyond what can be achieved in the RO concentrate. Hence additional process stages such as evaporation are required to raise the concentration so that crystallisation can occur. Evaporation / crystallization systems treating effluents at best produce low value products, However, given the mix of species in these high TDS streams it is unlikely that any saleable ‘products’ are extractable by crystallization. It is possible that the most valuable product could be the water recovered by condensation of the vapour.

Available Technology

To further increase what Ausenco can offer it has recently formed a joint venture with Proxa, a South African water treatment company specializing in custom solutions involving membrane processes, ion exchange and energy efficient zero discharge options. Proxa has developed expertise on zero discharge systems for mining applications where the bleed stream salts need to be evaporated to dryness to produce dry material for disposal.

Evaporators

Solutions are normally concentrated by application of heat at reduced pressures leading to evaporation. The main types of evaporators are(18):

- falling film
- forced circulation and
- seed recycle.

The essential difference between the falling film units and the forced recirculation approach is where the evaporation occurs. In falling film systems the evaporation occurs at the same time as the solution trickles down the sides of a heated tube. On the other hand in the forced recycle units boiling is suppressed in the heated sections which are flooded, with flashing occurring above the bulk liquid in a separate section of the unit. The forced circulation approach is better able to deal with crystal formation and is generally the preferred approach for effluent systems. Forced circulation units are easier to operate and can run for longer before the system needs to be taken off line for descaling. However, this has to be traded off against a higher capital cost. Where scale formation is more serious than a forced recirculation system can cope with, then it is worth considering seed recycle systems. These incorporate an extra stage to capture and return crystals to the flow to provide seed on which scale can form rather than on the tube walls. However the need to conserve and recycle the seed crystals adds to the complexity of operation.

The amount of energy, eg steam required to power the evaporation can be reduced by using multiple (stages) effects, where the energy in the vapour generated in one stage is used in the following stage. In theory it is possible to design systems with 2-10 effects, but in practice capital cost and temperature differences usually limit systems to no more than 5-7 effects. An alternative approach is to use MVR between stages to enable evaporation in the subsequent stage without the need for application of additional heat. Electrical power can be used to drive the compressor or it could be coupled to a steam driven turbo. The choice of approach will depend on the relative costs of steam and electricity. In general the key factors that need to be considered during process development include:

- steam quality, availability and cost
- electrical energy and cost
- materials of construction
- nature of salts
- scale formation and nature of scale.

Given the complex mix of species present in these bleed streams, pilot or at least laboratory testing is required to determine suitable operating parameters for the system. Pre-treatment may also be required to deal with problem species in the salt load on the system prior to evaporation and crystallization.

Crystallizers

Once the bleed solution has been brought to saturation by evaporation, cooling or both, species can be removed by crystallisation. The two basic types of crystallizers are forced circulation and growth units. Forced circulation units are simpler and common, accounting for around 90% of effluent duties where crystallisation is required. They are similar in concept to the forced circulation evaporators. Boiling is suppressed in the heat exchanger and supersaturation is generated by flashing recirculating slurry in the crystallizer body. Recirculation rate, crystallizer volume and slurry density are all important design parameters and distinguish a forced circulation crystallizer from a forced circulation evaporator.

Growth crystallizers are designed specifically to grow large crystals with a defined size distribution to meet specific market requirements. The best known and most successful of these is the draft tube baffle (DTB) crystallizer. This design enables extremely low levels of supersaturation within this unit, combined with an ability to destroy fine crystals. It is however, more expensive than the simpler forced circulation type and hence is only used for marketable products with a defined size distribution.

Materials of Construction

Solution parameters particularly the chloride concentration and pH strongly influence the choice of materials. In general more exotic materials are required as the pH goes down and/or the chloride concentration goes up.

Case Study

Proxa in partnership with Process Plant Technology (PPTech) has installed a zero liquid discharge application on a brine stream at the Sasol plant at Secunda, South Africa. The brine feed contains carbonate, sulfate, calcium, chloride, sodium and magnesium. It is treated by MVR evaporation and crystallisation. In this case it was possible to develop a process to recover four products, including boiler feedwater. The revenue from the sale of the products and the elimination of the previous dumping costs provided significant economic benefits to the process.

The main evaporation duty (MVR) is performed in an 8 600 mm diameter forced circulation evaporator fabricated in 904L. The recovered water is then sent back to the boilers. The concentrated brine is reacted at high pH to recover a mixed magnesium / calcium sulfate product that is sold into the fertilizer industry. The filtrate is pumped to a much smaller second forced circulation crystallizer for the recovery of a 98.5% pure sodium sulfate which is centrifuged and flash dried. A purge from the crystallizer to control the level of impurities is then cooled to crystallize hydrated sodium sulfate to maximize the recovery of the sodium sulfate. A fourth crystallizer recovers sodium chloride that is used internally by Sasol for regeneration of ion exchangers.

Alternative Approaches

People have looked at the relative amounts of heat that must be added or removed from a solution to extract water as vapour or ice and wondered at the potential application of cooling for concentration(19). While it is a well-established approach for producing heat sensitive products such as in the food industry(20), and has been proposed for zero discharge paper industry applications(21) it is yet to find application for low or zero value products. Nevertheless it could be considered and may offer a more cost and energy effective option for some solutions.

CONCLUSIONS

Alternative lixiviants for a gold extraction are generally applied at much higher concentrations than cyanide. This makes reagent recycle an important consideration. Inclusion of a tails thickener in the circuit can assist with reagent recycle, but that will only work if the lixiviant can be tolerated in the comminution circuit. Unfortunately the conditions / concentrations required to get the alternative lixiviant systems to extract gold are also generally far more corrosive to steel than alkaline cyanide solutions.

The traditional approach of reagent destruction and replacement as used for low concentrations of cyanide would result in an operating cost that would kill an alternative lixiviant based project. The only viable approach to generate clean water for use in the comminution circuit and recycle reagents back to the leach is to incorporate a membrane treatment step into the flowsheet.

In some cases alternative lixiviant extraction systems may result in the need for bleed streams to remove solution components that would ultimately stop the process. Depending on environmental and climatic factors these could result in the need for application of evaporation and crystallisation to enable zero discharge operation.

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