11-18:Template Journal 6/25/09 11:52 AM Page 329

Increasing the capacity of existing and new exothermic autoclave circuits

by G.M. Dunn*

Synopsis

Pressure leach autoclave circuits are employed in the leaching of ores, concentrates, mattes, alloys and intermediates for the recovery of metals into solution. Once the metals are extracted into solution, the value metals can be recovered by hydrometallurgical means such as by purification followed by electrowinning, hydrogen reduction, pyrohydrolysis, crystallization and other unit operations. In many of these integrated flowsheets the pressure leach step is pivotal to the recovery of the value metals from the host material.

Furthermore, the autoclave circuit invariably is a high capital cost component of the plant and an area that is carefully scrutinized when debottlenecking and capacity increases are being considered. This paper identifies a unique proven way of increasing the capacity of existing or new exothermic pressure oxidative leach autoclave circuits by as much as two or three times.

Introduction

Pressure leach autoclave circuits are employed in the leaching of ores, concentrates, mattes, alloys and intermediates for the recovery of metals into solution. Once the metals are extracted into solution, the value metals can be recovered by hydrometallurgical means such as by purification followed by electrowinning, hydrogen reduction, pyrohydrolysis, crystallization and other unit operations. In many of these integrated flowsheets (refer Figure 1) the pressure leach step is pivotal to the recovery of the value metals from the host material.

The exothermic leaching process

The leaching of sulphide concentrates and intermediates as well as alloys is often accompanied by the release of energy, which has to be removed from the autoclave slurries in order to avoid the slurry temperatures within the vessel exceeding the design operating values. For example, in the pressure leach of chalcopyrite the reaction could be represented by the following relationship:

$$CuFeS_2 + H_2O + 8\tfrac{1}{2}O \rightarrow CuSO_4 + \tfrac{1}{2}Fe_2O_3 + H_2SO_4$$

The energy release, as calculated from heats of formation (25°C), is approximately 1 690 kilojoules per gram mole. This exothermic heat release can limit the capacity of an autoclave to 1.1 to 1.3 tonnes of concentrate per active cubic metre per day where a retention time of approximately 1.2 hours has been prescribed. There are chalcopyrite concentrate autoclave circuits that have been subjected to feasibility studies and designed to operate in this capacity range (approximately 8–12% (w/w) feed solids).

At higher feed concentrations the energy release is such that the autoclave temperature will exceed the 210–230°C typical operating range being considered for POX autoclaves treating chalcopyrite. This condition triggers the need to remove energy from the autoclave in order to maintain temperature control and the desired oxygen partial pressure in the vessel.

There are a variety of heat removal processes that are available to the autoclave designer, and these will be examined individually.

Quenching

The quenching processes appear to be favoured by most engineers involved in autoclave design. The general concept is captured in Figure 2. It is simple to configure and has relatively simple control features. Quench liquor, in the leaching of copper concentrates, can be a solvent extraction raffinate or spent electrolyte. The CCD 2 liquor can be considered for the quench in cases where there is a countercurrent decantation solid-liquid separation circuit. The cool aqueous liquor is normally fed to the autoclave compartments on temperature control. In cases where there are little solids present in the

* *Hydromet (Pty) Ltd, South Africa, hydromet@hydromet.co.za, hydromet@mweb.co.za.*

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11-18:Template Journal 6/25/09 11:52 AM Page 330

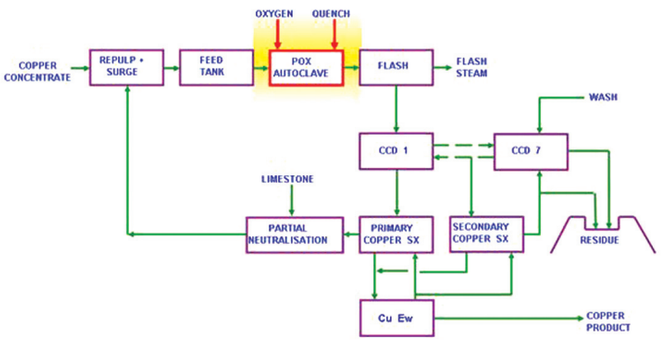

Figure 1—Example of hydrometallurgical flowsheet for the recovery of copper from a flotation concentrate

quench fluid, multistage centrifugal pumps can be employed and, where this is not the case, an appropriate positive displacement pump may be suitable.

The quench circuit of Figure 2 is also employed in the leaching of nickel and nickeliferous sulphides and mixed nickel and copper sulphides.

The use of a quench liquor does require an increase in the autoclave active volume and can result in dilution of the pregnant leach solution (PLS) if water or some diluted liquor is employed in this duty.

Internal cooling coils

In some autoclaves, internal cooling coils have been fitted into the compartments to abstract heat. These cooling coils are often fixed to the dividing walls of the autoclave and are serviced by cooling water or other process fluids. There are numerous limitations associated with the use of coils, which include:

- Difficulties in fixing the coils to the vessels internals
- Designing the coils and their supports for the thermal stresses
- Deprivation of reactor volume by the coils
- A low degree of flexibility in being able to accommodate an increase in reaction extent and its concommitant impact on where the heat is generated within the autoclave, and
- Scaling of heat transfer surfaces by precipitates or gangue from the feed materials.

Cooling coils are employed in the mixed mineral millerite, chalcocite and covelite leach autoclaves of Southern Africa[1] and the USA. They are also used extensively in the Norilsk pyrrhotite-pentlandite leach autoclaves[2]. Figure 3 provides the cooling system concept employed in some Southern African autoclaves.

External coolers

An enhancement of the internal cooling coil concept is to be found in the use of external coolers. The slurry is removed from the autoclave and pumped through a heat exchanger before being returned to the same compartment of the autoclave.

Some of the disadvantages of the internal cooling coils are addressed in the use of these external heat exchangers, however:

- Scaling of the heat transfer surfaces can still occur, albeit to a lesser extent. This reduced scale propensity is as a consequence of the higher tube side velocities that can be achieved within the heat exchanger
- The pumps required to circulate the autoclave contents through the external heat exchangers have certain temperature and pressure limitations, resulting in this concept being limited to low and medium pressure autoclave circuits, and
- Significant wear to isolation valves can be experienced on the pump suction and heat exchanger discharge lines.

One acceptable feature of external pumped coolers is that additional cooling surface can be added, thereby improving their flexibility with respect to varying or unpredictable reaction extents during the operation phase.

Figure 4 provides a simple flowsheet of the external cooler employed in a copper-cobalt leach autoclave in Zambia[3].

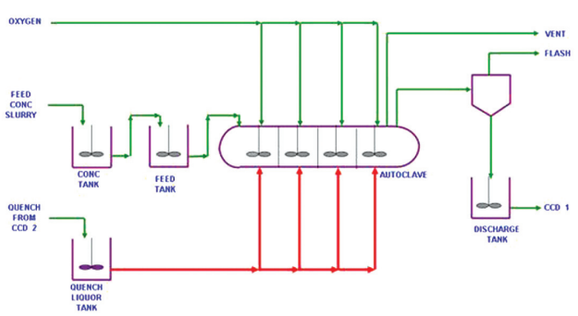

Figure 2—Flowsheet of autoclave with quench cooling

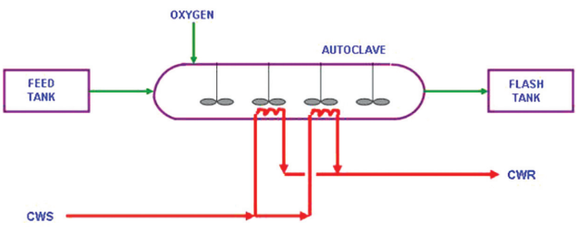

Figure 3—Flowsheet of autoclave with internal cooling coils

11-18:Template Journal 6/25/09 11:52 AM Page 331

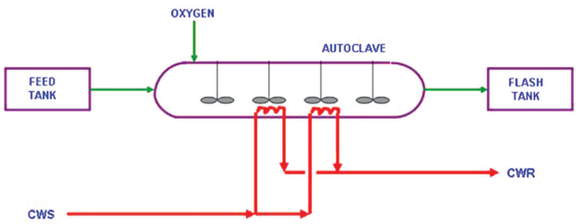

Figure 4—Flowsheet of autoclave with external coolers

Flash-recycle

In most exothermic autoclave circuits a majority of the energy is liberated in the first compartment, with only smaller quantities being generated in the downstream compartments. An alternate approach to the removal of heat from exothermic autoclaves was introduced in South Africa in the mid 1980s in a pressure leach step for a blend of chalcocite, covelite and small quantities of millerite. Since then it has been installed in two other operations in South Africa[1], one in Zimbabwe[4], the USA[5] and Australia. The flowsheet for some Southern African operations is given in Figure 5.

Any energy release in the first compartment that will result in the slurry exceeding the design temperature is abstracted by removing slurry from the first compartment to the feed tank via a flashing process and returning it to the autoclave. The feed tank becomes an extension to the first compartment in this circuit and while a recycle loop is established between this tank and the autoclave, the overall retention time of the autoclave is related to the net new feed rate entering the circuit from the concentrate tank and is not influenced by the recycle loop flow rates.

There are several control methods available to the autoclave engineer for the flash-recycle circuit and these serve, in a well designed system, to maintain the temperature in the first compartment at the set point with a tolerance of +3°C. This temperature control is normally acceptable for most brick lined, alloy or alloy clad autoclaves.

Some of the advantages of this system compared to the three options above are that it provides:

- For optimal utilization of the installed reactor volume
- For enhanced water balance control
- The ability to concentrate the reactor contents, if required, through the evaporation of water flashed as steam
- The potential to use the flashed steam as an energy source elsewhere in the operation, and
- For an opportunity to introduce first compartment reagent addition into the feed tank. The flashed slurry recycle loop can provide a lower cost vehicle for reagent additions to the first compartment of an autoclave.

The flash recycle (FR) circuit can be retrofitted to autoclaves employing any of the alternate heat removal systems listed above. Invariably, any exothermic heat carried over into the second and ensuing compartments can be removed, for example, by the use of coils as this normally constitutes a small portion of the overall exothermic heat load.

When the above heat removal interventions are considered holistically only the FR circuit provides the autoclave designer with the maximum degrees of freedom.

A disadvantage, for example, of the quench process is that the fluid introduced into the first compartment for temperature control can often contain the products of the autoclave discharge, which may disturb the desired equilibrium conditions in that first compartment. It could also, for example, as in some matte leach circuits, be a spent electrolyte, which introduces an acidic liquor into the first compartment. The acid concentration in this and ensuing compartments is therefore influenced by the thermal quench and may result in a condition where the operator is not able to control this parameter. He may in fact require a different acid concentration for the optimal leach conditions over that which is delivered by the quench temperature control.

A further disadvantage in the case of the internal and external cooler system is that any feed density fluctuations above the set point may result in the introduction of a larger feed mass, for example, of the slurry to the autoclave. The temperature rise in the autoclave first compartment may be excessive and the energy release greater than what the coolers can handle. In continuous operations the reaction extent in the first compartment could be reduced and consequently the second and ensuing compartments' heat

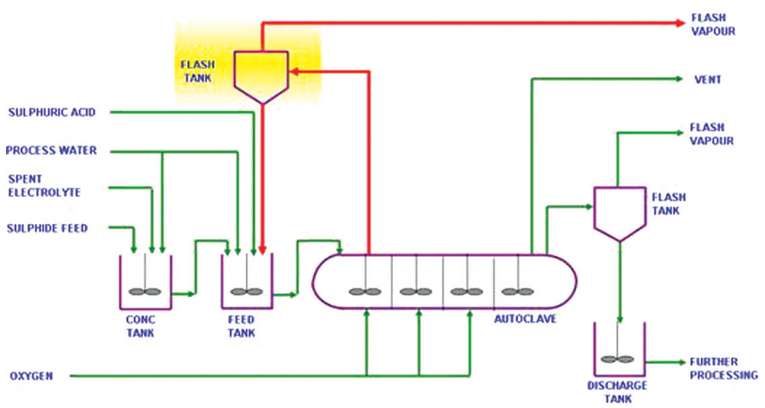

Figure 5—Flash-recycle flowsheet

11-18:Template Journal 6/25/09 11:52 AM Page 332

removal circuits may not be able to abstract the extra heat load thrust on them by the feed density fluctuation in this case. Unless design flexibility is provided, the temperatures can 'run away' and an incomplete leached product can be discharged from the autoclave.

However, in the flash-recycle circuit:

- Temperature control is achieved without disturbing or changing the process variables within the first compartment by the return of another process fluid
- The leachate can be concentrated, if required, by not replacing all the water that is flashed as steam in the flash step
- If the feed mass is higher to the autoclave as a consequence, for example, of poor density control then the automatic level adjustment of the feed tank can be invoked to ensure the design reaction extent is achieved in the first compartment, thereby preventing conditions developing in which unreacted product is discharged from the autoclave, and
- The mean autoclave retention time is the highest of all the known methods of abstracting heat from the autoclave, thereby increasing the autoclave productivity (tonnes per day per cubic metre of autoclave volume).

Autoclaves in matte leach circuits today have been increased in capacity by in excess of 45 per cent employing the flash recycle system whereas others have been derated in pressure and temperature without affecting the original treatment rate.

In autoclaves operating at temperatures close to the atmospheric boiling point of the aqueous fraction, Norilsk have proposed their patented vacuum flash. This circuit was in operation at its Tati Nickel demonstration plant in Botswana[6]. The first compartment flash vessel is operating at partial vacuum, which allows the flash underflow slurry to be reduced in temperature below the atmospheric boiling point. This generates a higher sensible heat loss than would otherwise occur in a flash-down to an atmospheric boiling condition. Additional mechanical equipment in the form of condensers, vacuum pumps and sealing fluid cooling circuits, etc. are required in this variant of the flash-recycle circuit.

Flash-thickener-recycle (FTR) circuit

An extension of the flash-recycle circuit is to be found in the incorporation of a solid-liquid separation step after the flash. This solid-liquid separation step can be on the first compartment flash but it can also be on the flash from any compartment of the autoclave. This solid-liquid separation is often best achieved with a thickener but it can be effected with other equipment such as a classifier or a filtration step. This flow sheet modification will be referred to as the flash-thickener-recycle or FTR circuit.

The FTR circuit provides a means of increasing the retention time of the solids fraction within the autoclave over that of the liquid fraction.

A further embellishment of the flowsheet concept of Figure 5 incorporates a thickener in the flash-recycle loop. In circumstances where there is a mass reduction of the feed concentrate in the leach, the incorporation of a thickener in the flash cooling circuit permits the removal of a fraction of the leachate. The partially leached solids are returned from the thickener to the autoclave via the feed tank. The thickener thus provides a means of increasing the solids' retention time in the autoclave over that of the liquid phase. Alternately, for a fixed retention time, the capacity of an autoclave can be increased subject to the impellers delivering sufficient oxygen mass transfer.

Figure 6 depicts this concept of the FTR circuit.

The FTR circuit not only permits the abstraction of leachate from the first compartment, but also provides a means of restoring some water to the feed tank to drive the equilibrium in favour of the leach extraction. Alternately, in the absence of water addition, salt hydrolysis can occur if this is desired.

In the design of or a modification of an existing autoclave, the first compartment is sized to achieve in excess of 50 per cent but typically 85 to 95 per cent of the overall reaction extent. This can and often results in the thickener overflow being very similar in composition to the autoclave discharge stream after flash.

The mean mass flow rate in the first and ensuing compartments of the autoclave is:

$$\text{Concentrate feed}(1) + \text{Process water}(2) - \text{Flash}(3) - \text{Thickener overflow}(4)$$

In the FTR circuit the net feed rate (5) through the autoclave can be adjusted to suit the required mass flow and extraction simply by adjusting the volumetric flow at stream

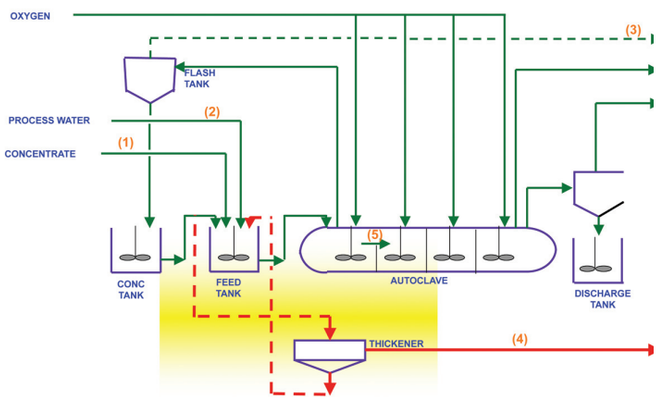

Figure 6—Flash-thickener-recycle flowsheet

11-18:Template Journal 6/25/09 11:52 AM Page 333

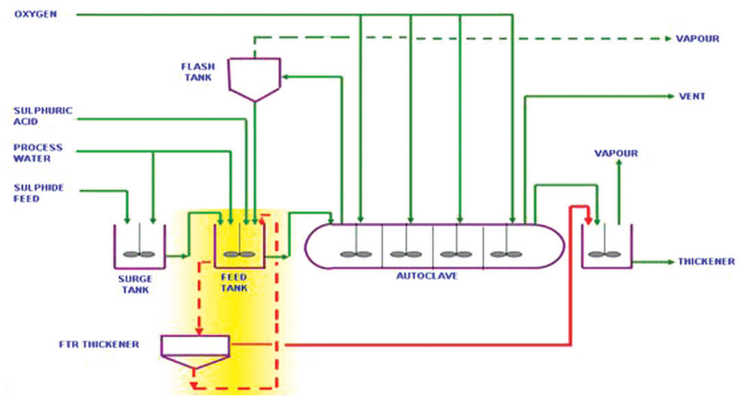

Figure 7—Covellite-chalcocite POX leach

(4) subject to thickener underflow viscosity and density constraints. By diverting the thickener overflow to the discharge tank it has been possible to increase the retention time by as much as 200 per cent before the autoclave slurry density increases to a point where it is not economical to increase it any further. Other factors such as oxygen mass transfer at the autoclave impellers may become rate limiting.

The flash-thickener-recycle (FTR) concept has been patented by Hydromet[7].

Applications

Covellite-chalcocite pox leach

The flowsheet of Figure 7 has been considered and tested by an operation processing nickel-copper sulphide mattes. The autoclave was operated as a bulk leach to provide an approximately 90% mass reduction in the feed. It was followed by a polishing leach autoclave circuit. This modification was made to an existing three compartment autoclave and:

- Increased the retention time of the solids fraction from 3.0 hours to an excess of 7.5 hours, and
- Increased the capacity of the autoclave from 0.71 to 1.32 tonnes of feed per cubic metre (active volume) per day at an operating temperature of 150°C.

The impellers in the autoclave were not upsized for the FTR duty. These agitators became 'rate limiting' in their oxygen transfer rate and were responsible for a capacity increase significantly below what would have been expected for the additional retention time that was achieved with this modification.

The extraction of copper and oxidation of sulphide sulphur at the higher capacity in the FTR circuit is given in Figure 8 and Figure 9. It needs to be noted that this was a three compartment autoclave possessing the normal deficiencies of such a vessel.

In this case the overall reaction extent in the first compartment was in excess of 80%.

When the circuit was operated as a standard flash recycle cooling circuit (without the thickener in service) and with a mean solids retention time of 3 hours, the copper extraction profile was typically that shown in Figure 8 with a first compartment copper extraction of 97%.

The lower copper extraction in the FTR circuit is attributed to the rate limiting features of the agitation systems, which was unchanged in both cases.

Chalcopyrite leach

The pressure oxidative leach of chalcopyrite is a strongly exothermic process. The classical approach with quench

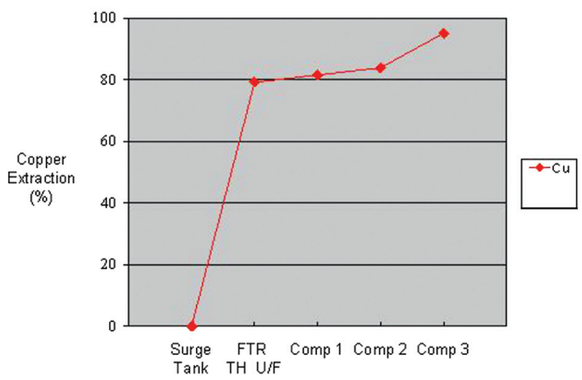

Figure 8—Extraction of copper in the FTR circuit for a covellite-chalcocite leach

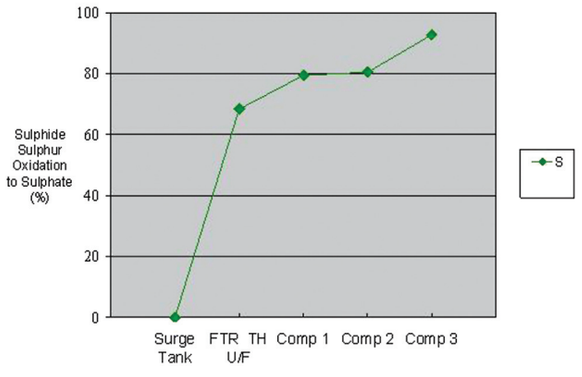

Figure 9—Oxidation of sulphide sulphur in the FTR circuit for a covellite-chalcocite leach

11-18:Template Journal 6/25/09 11:52 AM Page 334

cooling can result in the feed density being reduced to between 8 and 12% feed solids equivalent on a weight basis. In Zambia, Kansanshi Mining plc (a company 80% owned by First Quantum Minerals Limited) installed a chalcopyrite pressure oxidation (POX) process to the flowsheet in Figure 10. An atmospheric leach of oxidized copper ore is being undertaken on the present site and the plan is to integrate the sulphide POX leach into the atmospheric leach circuit to provide sulphuric acid, energy and some ferric iron as a lixiviant for some secondary sulphides in the oxide ore. The PLS from the atmospheric leach CCD circuit is fed to a copper SX circuit. The raffinate from this SX circuit is returned, in part, to the POX circuit for the repulp of concentrate and the quench.

The POX circuit has been designed to operate:

- At 210°C and approximately 3.0 MPa(g)
- With a first compartment mean solids residence time of just under one hour and an overall residence time of approximately 1.7 hours, and
- With two autoclaves for a concentrate treatment rate of 105 kt/annum.

Kansanshi Mining are considering the FTR circuit on a single POX autoclave employing the flowsheet of Figure 11. The FTR circuit will:

- Operate at 210°C and approximately 3.0 MPa(g), i.e. at identical conditions as those in the quench concept
- With the same mean solids retention time distribution as the quench circuit, and
- With one autoclave designed to treat approximately 130–150 kt/annum.

The specific process factors of the circuit are summarized in Table I.

In the FTR circuit, in excess 75% of the leached copper in the autoclave will be removed in the thickener overflow and diverted directly to the discharge tank. This is approximately 80% of the total copper leached in the first compartment. The remaining leached copper is in the slurry overflowing from the first compartment to the second and ensuing compartments of the autoclave.

The leaching of nickel sulphides

Nickel sulphides mattes have been leached in Southern African matte POX circuits for over 35 years[8,9].

The leaching of nickeliferous sulphide concentrates has been practised at Outokumpu using the Hitura concentrate[10] and is currently practised at Norilsk on pyrhhotite-rich concentrates. Inco are considering a pressure leach circuit for its Voisey Bay concentrate.

The flowsheet in Figure 12 has merits where there is a significant mass loss from the feed concentrate in the leach. It is, for example, suited to the acid pressure oxidative leaching of mixed nickel and cobalt sulphides generated from a hydrogen sulphide precipitation process of a laterite leachate. The autoclave capacity can be reduced by over 200% of that employed in the classical quench cooling process.

Kinetically different leach systems

The platinum group metals are known to respond more slowly than the base metals in the acid leach of a mix of base metal sulphides and PGM sulphides, selenides, tellurides, arsenides, bismuthides, etc.

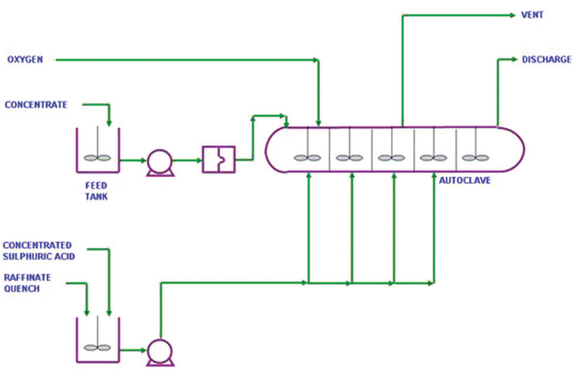

Figure 10—Kansanshi Mining's chalcopyrite POX circuit with quench cooling

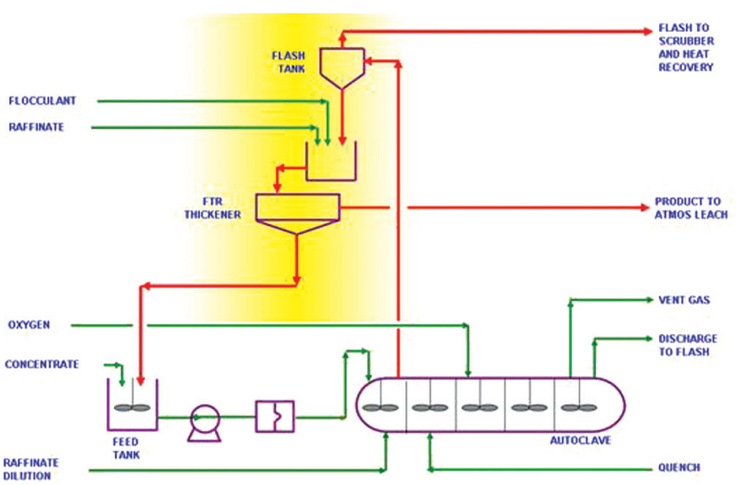

Figure 11—Kansanshi Mining's chalcopyrite POX circuit with FTR

11-18:Template Journal 6/25/09 11:52 AM Page 335

Table I

Process factors of the circuit

		Quench concept	FTR concept
Specific autoclave feedrate at 1.7 hours	(t.concentrate/day m³)	1.14	3.04
Overall retention time	(t.Cu/day m³)	0.33	0.89
	(t.S=/day m³)	0.37	0.97
Sulphuric acid requirements	(t/tonne concentrate)	0.43	~nil
First compartment mean solids retention time	(h)	0.94	0.94
First compartment slurry feed rate	(m³/h)	7.2	78
First compartment dilution feed rate	(m³/h)	65	110–140
First compartment oxygen transfer rate	(kg/m³h)	62	147

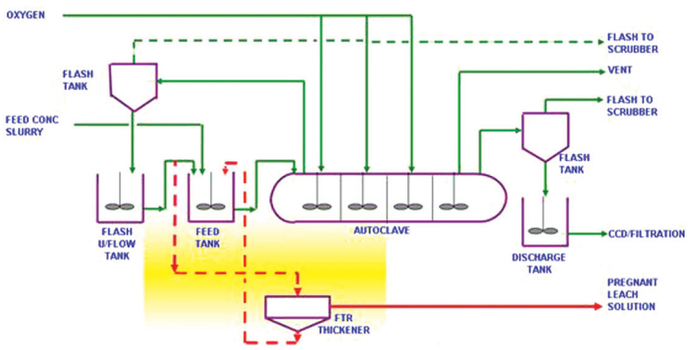

Figure 12—Pressure oxidation of nickeliferous sulphides with FTR

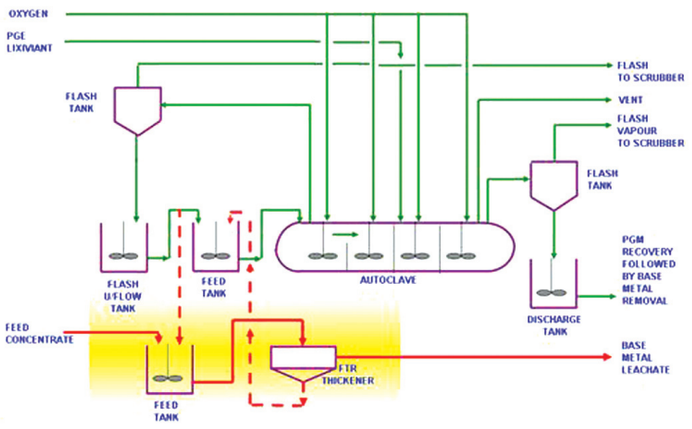

Figure 13—FTR circuit for minerals displaying different leach kinetics

Where it is the intent to dissolve both the base metals and the precious metals, it may be appropriate to separate a majority of the base metal leachate in a first compartment FTR circuit. The extraction of the precious metals can then be made in the downstream compartments of the autoclave in a considerably smaller autoclave volume.

The circuit of the type shown in Figure 13 has some merits in that:

- A large part of the base metals is removed in the leachate overflow from the FTR thickener
- Any PGE that do dissolve in the first compartment are precipitated on the concentrate, which is blended with the first compartment leach slurry prior to thickening. The thickener overflow will therefore be low in precious metals concentration
- The lixiviant that is employed for PGE dissolution e.g. chloride ions in the Platsol process may need to be added only into the second compartment of the autoclave. This could reduce the material and maintenance costs of the autoclave significantly, and
- The volume of leachate containing PGE is much smaller, as is the autoclave itself.

11-18:Template Journal 6/25/09 11:52 AM Page 336

Conclusions

The introduction of the thickener in the flash front end cooling circuit increases the retention time of the solids fraction over that of the aqueous stream.

The FTR circuit can be retrofitted to existing POX circuits to increase the capacity of these circuits at minimal capital and operating cost.

The FTR concept can be designed into new POX circuits to reduce the size of the autoclave or reduce the operating complement of autoclaves where parallel units are being considered for a plant.

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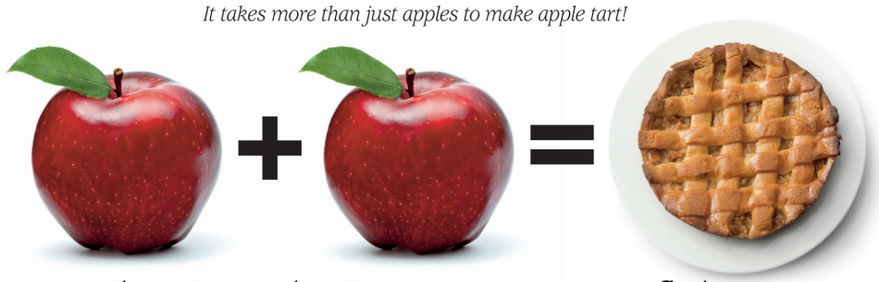
It takes more than just apples to make apple tart!



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Globally, gold, coal, diamond, uranium, iron ore and mineral sands mines are currently benefitting from Reconcilor's simple to use and comprehensive feature set.

From resource and reserve estimates, grade control, truck dispatch, survey pickup and plant production systems through to final production processing, or shipping, Reconcilor accumulates, checks and reports on mining activities against budgeted plans and metrics.

Reconcilor can manage activities from a single site, single commodity mine, to a multi-national operation spanning the globe.

Current implementations have process proven the value of the solution and delivered substantial benefits to both large and small mining organisations.

Snowden is well positioned to respond quickly and effectively to on site demands through a network of worldwide offices, ensuring efficient global solutions delivered locally.

For more information on Reconcilor, please contact your nearest Snowden office.

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