Milling in Acidic Raffinate Solution in Copper–Cobalt Hydrometallurgical Circuits — The Next Step Towards Reducing Operating Costs

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The major contributors in operating costs in copper–cobalt hydrometallurgical process plants are power and reagents. Concentrated sulphuric acid and lime contribute between 20% and 30% of the reagent and consumable costs, as experienced by Central African copper–cobalt hydrometallurgical plants. A split solvent extraction (SX) circuit developed by Cognis (now BASF), the SplitCircuit™, has resulted in a reduction in consumption of these two reagents. This consumption was further reduced by using milling in acidic raffinate solution. This paper narrates experiences gained from designing and executing milling in acidic raffinate process plants, examines benefits and key challenges, and proposes milling in acidic raffinate as a serious alternative to conventional milling for copper–cobalt hydrometallurgical circuits.

INTRODUCTION

The major contributors in operating costs (OPEX) in copper–cobalt hydrometallurgical plants on the Central African Copperbelt are power and reagents. With regard to reagents, concentrated sulphuric acid and lime contribute between 20% and 30% of the reagent and consumable costs of the OPEX.

Typically, the costs of these reagents fluctuate according to demand and oil prices. From 2010 onwards, there has been a significant upsurge in copper and cobalt production, owing to many projects being brought online in Zambia and the Democratic Republic of the Congo (DRC). Consequently, in the DRC, for instance, the landed cost of 98% concentrated sulphuric acid alone fluctuated from a low of USD 250/t to a high of USD 480/t. Similarly, the cost of quicklime varied from USD 125/t to USD 320/t.

HISTORICAL TECHNOLOGIES

The first-generation copper SX plant on the African Continent was plagued with high costs for concentrated sulphuric acid and lime owing to the high acid losses associated with leached tailings, resulting in high quantities of lime required for neutralisation prior to disposal to the tailings storage facilities.

The high acid losses (and associated high lime consumption) were, in part, due to the existing circuit configuration not utilising the acid generated from the SX raffinate for leaching. This acid was not utilised for leaching because the large volume of raffinate generated from the SX operations created a process solution volume imbalance. Therefore, additional concentrated sulphuric acid (98 % concentration) had to be used for leaching.

The SX Split Circuit developed by Cognis (now BASF) (Nisbett *et al*., 2009), which splits the pregnant leach solution (PLS) into high-grade (HGPLS) and low-grade (LGPLS), addressed this issue.

The HGPLS and LGPLS are fed to the high- and low-grade copper SX circuits, respectively. The processed solution from the high-grade copper SX plant generates high-grade raffinate (which contains a high concentration of acid), which is routed to the leach circuit for leaching of the slurry feed. The LGPLS, processed through the low-grade copper SX circuit, produces a low acid-bearing solution termed low-grade raffinate. The low-grade raffinate solution is then used for counter-current decantation thickener (CCD) washing to reduce acid and copper/cobalt losses to the tailings storage facility or, where this configuration is not possible, it is bled directly to the tailings neutralisation circuit and pumped to the tailings storage facility.

The incorporation of the SX Split Circuit into later SX operations has brought about a significant reduction in acid and lime consumptions.

RECENT TECHNOLOGICAL DEVELOPMENTS

A resurgence of copper and cobalt mining production on the DRC–Zambia Copperbelt saw the copper production increase from 380 000 tonnes in 2000 to 1.8 million tonnes in 2014. The increased number of copper–cobalt hydrometallurgical plants resulted in a corresponding increase in the demand for concentrated sulphuric acid and lime.

The demand for these two reagents was such that the existing production facilities in both the DRC and Zambia could not meet the requirements, thus necessitating importation of these reagents in most cases. This increased demand, coupled with other factors, such as the price of sulphur, caused the prices of these reagents to increase. At peak demand, the landed costs in the DRC were as high as USD 480/t for 98% sulphuric acid and as high as USD 320/t for quicklime in the third quarter of 2013.

The high landed cost of these two reagents negatively impacted the OPEX of the copper–cobalt hydrometallurgical plants. Table I provides a comparison of the OPEX based on different acid costs.

Table I: Operating cost comparison based on acid costs.

Description	Unit	Scenario 1	Scenario 2
Acid consumption	t	2.1	2.1
Copper cathode produced	t	1	1
Acid cost	USD/t copper	150	400
PEX	c/lb copper	14	42

Assuming that these two reagents constitute 20% of the OPEX, the OPEX at 42c/lb copper would translate to USD 2.1/t of copper produced. This would reduce the profit margin (the average London Metal Exchange cash settlement price for copper in 2013 was USD 7350/t or USD 3.3/lb copper).

This laid the foundation for milling in raffinate using duplex stainless-steel mills and then proceeding to the execution stage. Milling in raffinate, as a process in copper hydrometallurgy, was already in operation in the Sepon mine in Laos in the Savannakhet Province in 2004 (Elphinston *et al*., 2015). A similar process operation, which was brought online in 2011 (MMG Kinsevere, 2016), existed at Kinsevere in the DRC.

The two above-mentioned plants used mills with shells lined with epoxy coating for protection against acid corrosion; however, epoxy lining protection failures in these mills resulted in the mill shells leaking. Consequently, the design engineering team considered a change in the material of construction from epoxy-protected carbon steel shells to duplex stainless-steel shells for the grinding mills.

FLOWSHEET DESIGN

Literature Review

Based on an extensive literature review conducted on alternative circuits that would reduce acid and lime consumption, the option of milling in raffinate was selected. In one of the papers on various copper–cobalt hydrometallurgical circuit configurations for optimum process selection, Reolon *et al.*, (2009) identified that one of the disadvantages of milling in raffinate (MIR) was the stainless-steel mill delivery schedule of 20 weeks. The stainless-steel mill requires a longer delivery time (20 weeks) than a conventional carbon steel mill, since there are not many mill fabricators that work with stainless steel and, in particular, duplex stainless steel. Therefore, specialised mill fabricators are required, resulting in the long delivery time. According to Reolon, further arguments that worked against the MIR option were the expensive mill shell and prolonged shutdowns due to maintenance. It must be noted that at the time of publication, the only copper MIR plant in operation was the Sepon mine in Laos, which had a mild steel mill that was epoxy-lined. The prolonged shutdowns were related to the prolonged epoxy lining maintenance requirements (curing period). Reolon also noted that the health and safety issues relating to milling in raffinate increased due to corrosion and acid handling. In his recommendation, milling in raffinate was potentially a higher-risk option, both technically and commercially, when compared with milling in water.

Option Selection

A noticeable reduction in acid and lime consumption has been reported from a number of recent SX/electrowinning (EW) plants in both the DRC and Zambia that have utilised the SX Split Circuit. It was, therefore, decided that the MIR option should be used in combination with the SX Split Circuit to lower the OPEX associated with concentrated sulphuric acid and lime consumption.

The first hydrometallurgical circuit where this selected option was executed was a copper–cobalt circuit in the DRC. The resultant smaller cobalt circuit footprint, as a result of a volume reduction in a LG raffinate feed to cobalt circuit, was an added benefit. The smaller cobalt footprint provided real estate capacity for future circuit expansions.

Milling in Raffinate Design Modifications

As noted from MIR operations at Kinsevere as well as Sepon, epoxy lining caused prolonged mill shutdown. The prolonged shutdown was for curing of epoxy lining protection.

The use of duplex stainless steel has overcome this aspect of maintenance. The choice of a duplex over 316L stainless steel was based on its superior mechanical strength. The duplex steel exhibits superior fatigue, corrosion resistance, as well as higher resistance to stress corrosion and cracking when compared with 316L.

In the first MIR installation with duplex stainless steel, the mill grinding media was specified as high chrome; however, high chrome specification in terms of chrome content from various suppliers ranged from 10–20% by chemical composition. The first mill that was installed experienced high grinding media consumption, in excess of 1.6 kg/t ore, as well as high wear rate. Worn grinding media samples were collected and analysed by Mintek, where it was found that chrome specification was in the region of 18%. When datasheet for grinding media was first sent out for the high chrome, the specification was based on a supplier definition of high grinding media chrome ranging from 25 % to 35.5 %. It was then decided, following from the Mintek grinding media chemical analysis and prior experience at Sepon, and to specify the minimum chrome content for grinding mill balls to not to be less than 27%.

Subsequent mill grinding media were ordered based on the revised specification, which resulted in the grinding media consumption falling within the 0.9–1.1 kg/t milled ore. Typical Split Circuit without MIR is shown in Figure 1 and typical Split Circuit incorporating an MIR configuration is depicted in Figure 2.

KEY BENEFITS OF MILLING IN RAFFINATE

The key benefits of using the MIR option has been the reduction in plant OPEX as well as capital expenditure (CAPEX) (Note: CAPEX figures withheld due to client confidentiality) due to reduced sulphuric acid and lime consumptions on both Split SX circuit and conventional SX–EW hydrometallurgical plant. These benefits are outlined in Table II.

Table II: Benefits of milling in raffinate.

Equipment/area	CAPEX	OPEX
Pre-leach thickener	No pre-leach thickener	Pre-leach power reduction and associated flocculant consumption. No associated maintenance costs.
Lime handling/slaking	Reduction in lime handling/slaking plant footprint	Reduction in lime usage, lime dust emissions.
Cobalt plant	Reduction in cobalt plant footprint.	Reduction in power requirement for agitators due to smaller precipitation tanks.
Acid	Reduction in acid handling storage capacity or reduced acid plant size	Reduced acid consumption.
Copper/cobalt losses		Gain in copper and cobalt recoveries
Raw/process water		Reduced intake of raw water uptake (no raw water to mill)

One of the motivating factors for utilising the MIR configuration is that no pre-leach thickening and pre-leach filtration are required before leaching circuit, which is beneficial, especially when treating copper–cobalt ores with high clay content, which possess filtration difficulties and water balance issues, as experienced on certain mine sites in the DRC.

Table III outlines copper losses from a *METSIM*™ mass balance on a simulated plant mass throughput of 100 t/h based on copper head grade of 1.90%. Table IV shows copper and cobalt losses as well as a cobalt bleed stream size based on a *METSIM*™ mass balance of 100 t/h and on copper and cobalt head grades of 1.90% and 0.40%, respectively.

One of the motivating factors of utilisation of the MIR configuration has been based on certain high clay copper–cobalt feedstock experienced on certain mine properties in DRC. The reported high clay levels in some of these ores have meant that pre-leach dewatering alone would not achieve required water balance issues unless used in conjunction with pre-leach filtration. Indeed, another plant elsewhere within DRC has incorporated a pre-leach displacement wash thickener train (CCD) ahead of leaching to try and maintain a water balance that does not result in a big cobalt circuit footprint.

Table III shows that for a copper circuit only, the immediate benefit that is the acid saving. Table IV shows that for a copper–cobalt circuit, the acid and associated lime savings are not as large when compared with the copper-only circuit; however, the benefit is seen in the smaller cobalt footprint of the MIR circuit compared with conventional milling with a Split Circuit. The bleed volume to the cobalt circuit for the conventional milling is 53% larger than for the MIR circuit.

The resulting increase in cobalt circuit footprint is the associated CAPEX of large-volume precipitation tanks, large precipitation tanks agitator drives, large SO_2/air spargers and larger civils for the tanks. OPEX associated with precipitation tank agitator increased power consumption is also escalated.

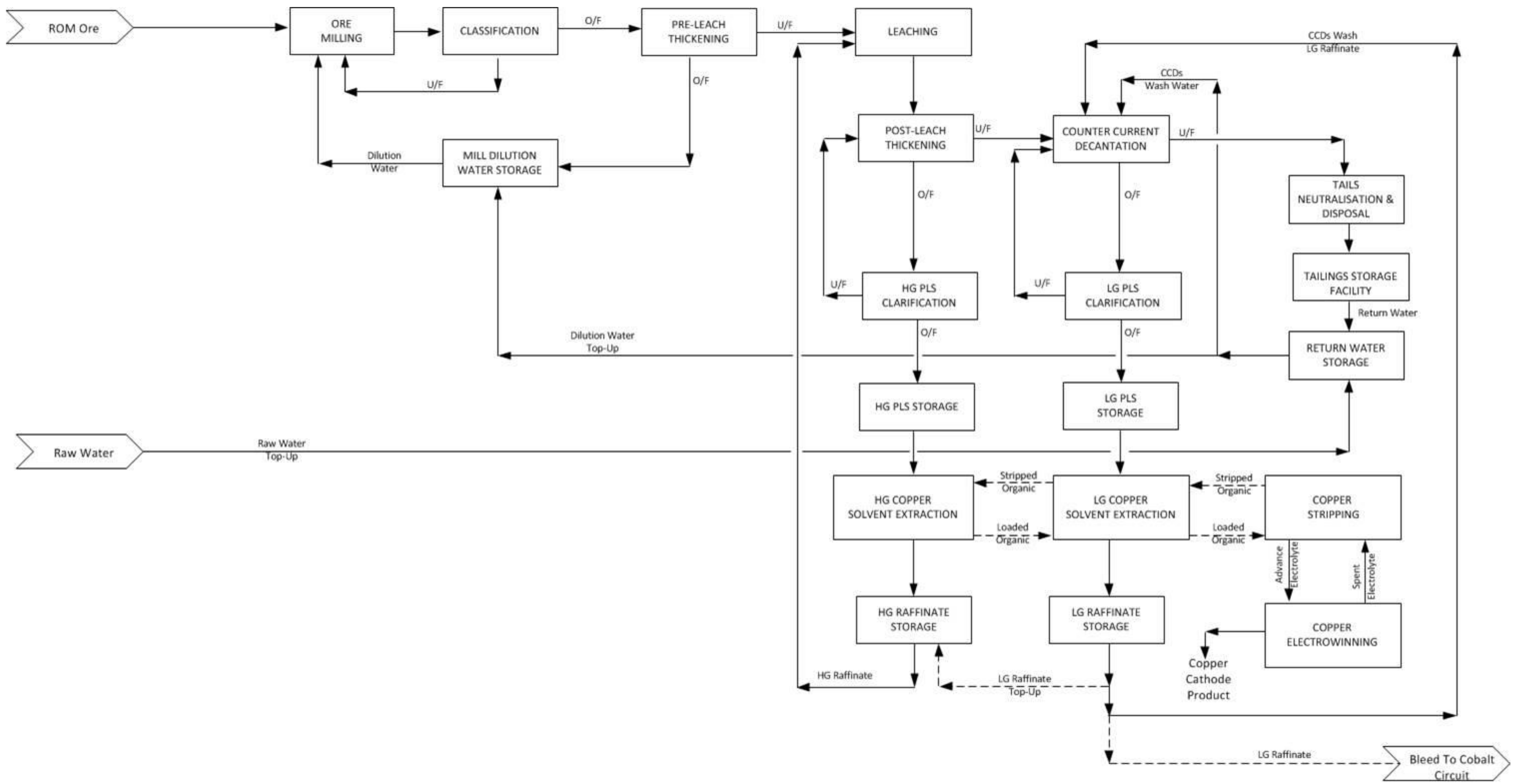

Figure 1. Conventional Split Circuit for copper-only circuit configuration.

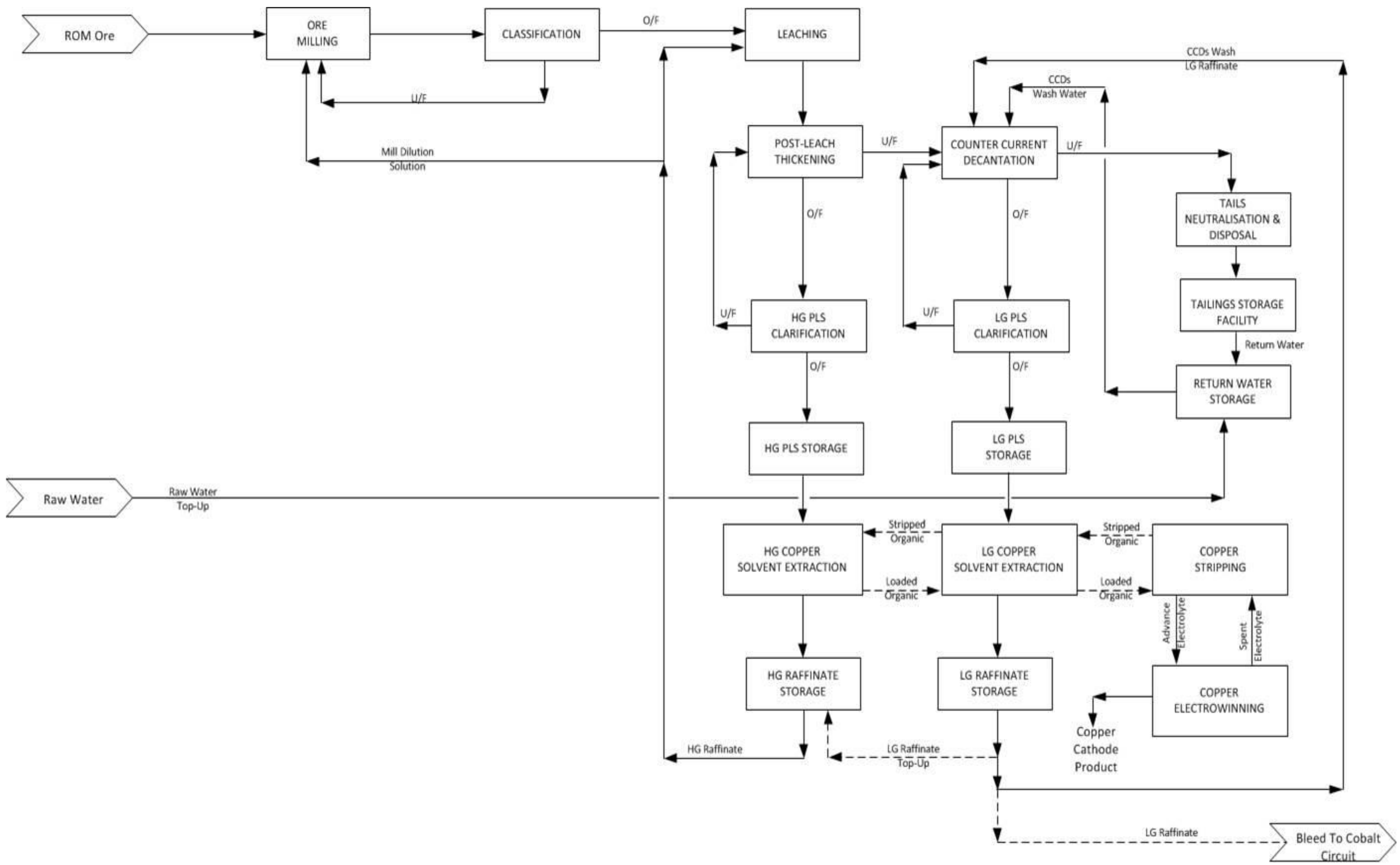

Figure 2. Milling in raffinate copper-only circuit incorporating the Split Circuit configuration.

Table III: Acid and copper losses for milling in raffinate compared with conventional milling.

	Unit	Milling in raffinate (copper circuit only)	Conventional milling (copper circuit only)
Typical copper head grade	%	1.90	
Acid losses to tails	t/h	0.70	1.29
Copper losses to tails	t/h	0.05	0.06
Acid saved	t/a	4 652	–

Table IV: Acid, copper, cobalt losses and cobalt circuit bleed volumes for milling in raffinate and conventional milling.

	Unit	Milling in raffinate (copper–cobalt circuit)	Conventional milling (copper–cobalt circuit)
Typical copper head grade	%	1.90	
Typical cobalt head grade	%	0.40	
Acid loses to tails	t/h	0.06	0.14
Copper loses to tails	t/h	0.04	0.09
Cobalt loses to tails	t/h	0.05	0.07
Bleed volume to cobalt circuit	m^3/h	92.9	141.0
Bleed [Co] to cobalt circuit	g/L	3.7	1.8
Acid saved	t/a	630	–

Table V shows that an annual OPEX saving of 30 c/lb is realised for an MIR circuit compared with a conventional milling circuit. The figures outlined in Table V are for the 4th quarter of 2013 for landed costs of USD 380/t for sulphuric acid and USD 140/t for quicklime. The lime reduction was due to the elimination of the neutralisation step.

Table V: Operating costs for milling in raffinate compared with conventional flowsheet.

Consumable	Conventional milling (c/lb copper)	Milling in raffinate (c/lb copper)	Reduction (%)
Acid cost (98% H_2SO_4)	45	37	18.8
Quicklime	24	0	100
Pre-leach flocculant	1	0	100
Carbon steel grinding media/liners	11	0	–
High chrome (27% Cr) grinding media/liners	0	14	−29.2
Total cost USD	81	51	
MIR OPEX saving annual (c/lb)	30		

KEY CHALLENGES

One of the key challenges that was encountered in the MIR design was selecting a competent mill fabricator for fabrication of a mill shell out of duplex steel and subsequent mill designs would require fabrication of mill body requiring stainless steel plates larger than 100 mm (Elphinston *et al.*, 2015). The increase in the number of mill vendors with a capacity to fabricate mills shells from LDX2101 duplex steel or equivalent duplex steels has meant that mill turn-around fabrication time and delivery have fallen into the same fabrication timeframes as conventional carbon steel mills. Because of the special fabrication requirements, during the first three years or so only one fabricator was available to fabricate the mills from duplex steel. The situation has now changed, with an additional fabricator also being able to manufacture mills from duplex stainless-steel plates.

Previous operational challenges that were identified during ramp-up period, such as slipper bearing on the MIR semi-autogenous (SAG) mills that were failing at a rapid rate because of material of construction incompatibility (Miller *et al*., 2013)were replaced with new generation of polyether-etherketone (PEEK) polymer type.

The first installed duplex mill with a nominal throughput of 203 t/h experienced corrosion issues due to mill slurry exiting at pH greater than 2.5. The corrosion was attributed in part to pseudomalachite and apatite, which caused precipitation of jarosite, leading to copper cementation. Subsequent process design parameters were adjusted to maintain the mill discharge slurry pH of less than 2.5 by including a static inline mixer to contact the mill dilution acidic raffinate solution with concentrated sulphuric acid.

MIR circuit configuration for a copper-only flowsheet requires an acid-lined tailings storage facility (TSF), while the MIR circuit configuration for copper–cobalt flowsheet requires two TSFs, one being an acid-lined TSF and the second one being the basic TSF for storage of cobalt effluent, which is mainly the magnesium hydroxide and gypsum that precipitate at pH greater than 10.5.

The two separate TSFs pose different challenges. The acidic tailings storage facility, the return solution of which accumulates deleterious elements such as iron, manganese, nickel and aluminium that remain in solution at pH of <2.5, is used as part of the CCD wash solution and will likely cause quality issues in the copper EW circuit (for copper-only circuit configuration). The basic TSF, the return solution of which is used as make-up solution for process water mainly in the cobalt circuit, is likely to cause pipe scaling with gypsum due to calcium saturation in solution (>600 mg/L). Further, the two TSFs increase both CAPEX and OPEX.

The perceived arguments have been that, over a long period of time, the returning CCD wash solution from the TSF will contained increased amount of impurities, which results in process upsets further downstream. Because the MIR configuration is water-balance negative, addition of fresh water or raw water overcomes these challenges.

The calcium saturation problem associated with return solution is offset by letting the basic TSF function as a maturation storage dam with a maturation cycle of 28 days or more. The long maturation period enables most of the gypsum to precipitate.

Health and Safety Issues: Some concern raised around adopting the MIR circuit was the handling of acidic spillage. Implied, but not stated explicitly, is the issue of acidic mist generated from the mill, largely due to elevated slurry temperature in the mill. Acid mist generated from the mill is extracted and scrubbed with low grade raffinate and discharged into the leach train. All operating personnel as well as maintenance staff in all MIR mill operations are trained on hazards related to dilute acidic solutions.

CONCLUSION

Concerns raised previously regarding perceived risk around costs associated with milling in raffinate, as well as health and safety issues, have been addressed as evidenced in four (Mutanda Mining, Glencore: 3; Chemaf: 1) installations in the DRC. MIR used in conjunction with the Split Circuit has further reduced acid and copper losses as well as reduction in water usage.

Calculated (using *METSIM*) annual saving of 30 c/lb on a typical copper-only circuit (one operating plant has reported OPEX of USD 1.43/lb) is an added advantage as it enables copper producers with low-grade ores to achieve better returns than would otherwise be possible without this advance.

Incorporation of MIR for copper–cobalt plant configuration results in substantial reduction in cobalt circuit plant footprint as well as associated reduction in motor power for agitation in both iron precipitation and cobalt precipitation stages.

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