Development of the Tati Activox® BMR ammonia recovery circuit

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The TATI Base Metal Refinery (BMR) was designed to be a hydrometallurgical processing plant employing Norilsk Nickel Process Technology’s Activox® leaching technology, solvent extraction and electrowinning to annually extract and recover 25 kt of LME grade nickel, 22 kt of LME grade copper and 640 tonnes of cobalt as a carbonate. The BMR requires acid neutralization in the cobalt and nickel solvent extraction (SX) circuits where pH control is crucial for selective extraction of the base metal sulphides from the pregnant leach liquors. The choice of neutralizing reagent and treatment of the resultant neutralization product affect the overall plant design.

This work discusses the criteria used to select ammonia as the neutralizing reagent for the BMR design, as well as the development of an ammonia recovery circuit.

The ammonia forms a soluble ammonium sulphate neutralization product, which reports to the SX raffinate stream. The BMR ammonia recovery circuit uses vibrating mills to contact the ammonium sulphate with calcium oxide (fine quicklime). The ammonium sulphate is converted to CaSO₄ (fine gypsum precipitate) and aqueous ammonia. A series of seeded reaction tanks are used to further encourage the gypsum precipitation and crystal growth. Aqueous ammonia is then stripped from the slurry in steam stripping column, and condensed to a 10% solution for reuse. The barren gypsum slurry reports to the tailings dam, where supernatant solution is recovered for use as process water.

Anhydrous ammonia is used as top-up to account for losses due to the ammonia recovery circuit.

Introduction

The Tati Base Metal Refinery (BMR) has been designed as a greenfield project close to Francistown in Botswana. The remote site location in Sub-Saharan Africa introduces several challenges specific to the BMR design including logistics, as well as water and power constraints. An ammonia recovery circuit was designed for the BMR specifically to ease these constraints.
The BMR project is a hydrometallurgical processing plant employing Norilsk Nickel Process Technology’s proprietary Activox® leaching technology, solvent extraction and electrowinning to extract and recover annually 25 kt of LME grade nickel, 22 kt of LME grade copper and 640 tonnes of cobalt as a carbonate from the Tati Nickel Mine concentrates. The process consisted of ultra fine milling, low pressure and temperature leach, solid liquid separation, solvent extraction, electrowinning, iron removal, cobalt precipitation and ammonia recovery. The BMR requires acid neutralization in the cobalt and nickel solvent extraction (SX) circuits to selectively extract Co and Ni from the pregnant leach liquors into a high grade, pure loaded liquor for final metal production. Ammonium sulphate is produced during the SX neutralization process and remains in the SX raffinate solution.

The ammonia recovery circuit is designed to recover aqueous ammonia from the SX raffinate solution for reuse in the SX as a neutralization agent. Recovering the ammonia reduces reagent make-up requirements and reduces the plant fresh water consumption by producing recyclable process water. The process solution from the ammonia recovery circuit can be reused as wash water in the solid liquid separation step.

This paper will outline the decision to use ammonia as the SX neutralizing agent, the decision to use an ammonia recovery circuit, and the overall role played by ammonia recovery in the BMR design.

The Tati Activox plant

Tati Plant process description

The Tati process is outlined in Figure 1, including the ammonia recovery and ammonia dosing.

Tati mine concentrates are repulped from 90 to 50% solids using copper raffinate from the CuSX and fed to an ultra-fine grinding mill circuit where the concentrate is ground to 80% less than 10 microns. Milled slurry is then fed into the Activox® autoclaves where it is reacted in the multi-compartment horizontal autoclave, using oxygen at elevated pressures of 11 bar (g) and moderate temperatures of 105°C to produce copper, cobalt and nickel sulphates in

Figure 1. Tati Activox BMR process flow
solution for downstream recovery. The leach discharge slurry proceeds to the solid-liquid separation section that includes a 7-stage CCD washing circuit, where the leach residue solids are washed with recycled process water. The washed leach solids are then pumped to the PGE flotation circuit to recover the PGEs from the wash leach residue. The pregnant leach solution (PLS) from the CCD train is clarified prior to reporting to the copper PLS pond.

The PLS is contacted with an organic solvent that selectively extracts copper from the aqueous solution in copper solvent extraction. Copper is stripped from the organic using spent electrolyte from the copper EW circuit. A portion of copper raffinate is recirculated to the concentrate preparation area for repulping the concentrate and for temperature control inside the autoclaves. The remainder of the copper raffinate is advanced to the iron removal circuit where the iron is precipitated using limestone. The thickener overflow is passed through clarifiers before it reports to the Co PLS pond.

Cobalt PLS is contacted with an organic solvent that selectively extracts cobalt from solution in cobalt solvent extraction. Cobalt is stripped from the loaded organic phase with an acidic strip solution and the resultant loaded strip liquor (LSL) is filtered and pumped to the cobalt precipitation circuit. The pH in the cobalt SX circuit is maintained using aqueous ammonia. The LSL from the cobalt SX circuit is treated with sodium carbonate (soda ash) to recover cobalt as a carbonate product.

The cobalt raffinate is then contacted with an organic solvent that selectively extracts nickel from the process solution in nickel solvent extraction. Nickel is stripped from the loaded organic phase with spent nickel electrolyte recirculated from nickel EW. The pH in the nickel SX circuit is maintained using aqueous ammonia addition. The nickel raffinate stream is transferred to the ammonia recovery circuit.

Ammonia is dosed for pH control in the cobalt and nickel SX circuits. The ammonia forms a soluble ammonium sulphate neutralization product, which reports to the SX Raffinate stream. The TATI ammonia recovery circuit uses vibrating mills to contact the ammonium sulphate with calcium oxide (fine quicklime). The ammonium sulphate is converted to CaSO₄ (fine gypsum precipitate) and aqueous ammonia. A series of seeded reaction tanks is used in the BMR design to further encourage crystal growth. The slurry stream is then pumped into a steam stripping column, where aqueous ammonia is stripped to the column overheads and condensed to a 10% solution for reuse. The recovered aqueous ammonia is topped up with anhydrous ammonia to account for losses and recycled for pH control in the SX circuits. The barren gypsum slurry reports to the tailings dam, where supernatant solution is recovered for use as process water in the solid liquid separation step.

The Tati reagent selection

Reagent types

The acid neutralization in the SX circuits of hydrometallurgical facilities generally utilize ammonia, sodium hydroxide or sodium carbonate. The choice of pH control reagent is largely driven by economic factors, logistics and availability.

Ammonium hydroxide

Ammonia is supplied as liquid anhydrous ammonia, which is stored under pressure. The anhydrous ammonia is diluted in water to form aqueous ammonium hydroxide; the solution is easier to handle and simplifies dosing and pH control. The ammonium hydroxide neutralizes the sulphuric acid in the SX circuit and produces a soluble ammonium sulphate product, as shown in Equation [1].
The ammonium sulphate can be crystallized and sold as fertilizer, or reacted with quicklime to recover the ammonia for reuse while forming a gypsum by-product.

\[ H_2SO_4(aq) + 2NH_4OH(aq) \rightarrow (NH_4)_2SO_4(aq) + 2H_2O \]  

[Sodium hydroxide]

Sodium hydroxide is generally provided as a 50% solution and stored in stainless steel tanks. It is similarly diluted to lower concentrations to simplify usage. The sodium hydroxide reacts with sulphuric acid to produce a soluble sodium sulphate product, as shown in Equation [2].

\[ 2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \]  

The sodium sulphate is typically crystallized, as is the case of Rustenburg Base Metals Refinery, and sold for use in detergents, Kraft sulphate pulping, and glass manufacturing.

[Sodium carbonate]

Sodium carbonate is generally delivered as an anhydrous solid and dissolved in tanks to around 30% solution. These tanks are mild steel, and must be heated above 36°C to prevent heptahydrates and decahydrates from precipitating. The sodium carbonate reacts similarly to sodium hydroxide to produce a soluble sodium sulphate neutralization product, as shown in Equation [3].

\[ Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2 \]  

The sodium sulphate is similarly sold for use in detergents, Kraft sulphate pulping, and glass manufacturing.

[Ammonia as the reagent of choice for Tati]

The remote plant location in Francistown Botswana resulted in high transportation costs for all reagents—ammonia, sodium carbonate and sodium hydroxide. The use of ammonia provided the lowest cost option, provided that 90% of the ammonium sulphate product was recovered and reused to reduce the fresh reagent make-up requirements. The option to produce ammonium sulphate crystals, which could be upgraded to a saleable product, was not feasible for the BMR project due to the lack of market in Botswana. Therefore the choice of neutralizing reagent for the Tati plant was selected due to financial drivers, and largely to reduce logistics costs.

[The ammonia recovery process]

The traditional lime boil process

The recovery of ammonia from ammonium sulphate is historically referred to as a lime boil. The lime boil consists of two operations, preparing the slaked lime and reacting to recover ammonia, as discussed by Regan (1999).

Typically quicklime is reacted with water in a slaker to form milk of lime. The reaction is exothermic and the solution temperature increases. The milk of lime is then pumped to a stirred reactor tank containing the ammonium sulphate solution. The ammonium sulphate and lime mixture reacts and is brought to the boil by direct steam injection. Ammonia has a lower partial pressure than the solution and will concentrate in the vapour phase. The vapours are condensed and ammonia recovered.
The traditional lime boil process equipment is subject to poor operability due to severe scaling and the risks associated with descaling the reactor tanks. Furthermore, the gypsum tends to coat any unreacted lime particles leading to reagent utilizations as low as 50%, resulting in high reagent consumptions and costs (Regan, 1999).7

**The Tati ammonia recovery circuit**

**The Tati ammonia recovery developments**

The ammonia recovery process utilized in the BMR design was developed by Norilsk Process Technology to overcome the main drawbacks of the traditional lime boil process, particularly lime utilization and gypsum scaling, while minimizing steam consumption as discussed by Johnson and Zhuang (1999)4 and later by Harrison (2008)3.

The BMR ammonia recovery circuit is presented in the Figure 2 as a block flow diagram. It includes the vibrating mills, reaction tanks, stripping columns, vapour condensers and off-gas scrubbers.

The detailed design of the ammonia recovery circuit called for materials of construction that could handle the high chloride levels in the nickel raffinate stream. This necessitated the use of SAF2205 as the primary material of construction for the mill reactors, reaction tanks and stripping columns in contact with nickel raffinate. The stripping column vapours did not contain chlorides and therefore the condensing systems were constructed from 304L stainless steel.

The innovations in the BMR ammonia recovery process are intended to manage gypsum scaling. The high scaling probability and process risk demanded that the circuit be designed with 100% redundancy to allow for descaling on line and 95% plant availability.

**Vibrating mills**

The barren nickel raffinate solution, rich in ammonium sulphate, reports to the ammonia recovery circuit. The raffinate is preheated to 90°C and fed into a vibrating mill with dry quicklime (CaO) powder. The quicklime reacts exothermically with the aqueous solution to form soluble calcium hydroxide, as shown in Equation [4].

![Figure 2. Block flow diagram of the Tati ammonia recovery circuit](image-url)
This exothermic reaction maintains the mill temperature and reduces the mill steam requirement. The fine quicklime particles further react with the ammonium sulphate to release 95% of the ammonia into solution while producing gypsum precipitate, as shown in Equation [5].

\[
(NH_4)_2SO_4(aq) + Ca(OH)_2(aq) \rightarrow 2NH_4OH(aq) + CaSO_4(s)
\]  

[5]

The use of vibrating mills is unique for this process (Western Minerals Technology, 2000) and is intended to reduce gypsum scale from forming on the milling media or the vibrating mill walls. Furthermore, the agitation of the milling media serves to abrade the gypsum coating off any unreacted quicklime particles, improving the reagent utilization to as high as 91% (Harrison, 2008).

The direct addition of quicklime to the ammonium sulphate solution is a second significant departure from the traditional lime boil process, where the quicklime is first slaked with water. This reduces the amount of water dilution and utilizes the significant lime hydration energy. This results in lower steam consumption, smaller equipment requirements, and improved stripping column ammonia purity.

The mills are maintained at a temperature close to the solution boiling point by the reaction energy (and steam as required), thus favouring the liberation of an ammonia rich vapour. The mill off-gas is vacuum extracted to draw any ammonia gas into the ammonia stripping column.

**Reaction tanks**

Analysis of the pilot plant stripping column showed scaling on the slurry feed plate during start-up and upset conditions, suggesting that complete gypsum precipitation had not occurred in the vibrating mills during upset conditions. A series of two reaction tanks was included in the design to provide additional gypsum precipitation residence time and to limit scaling to the vibrating mill and reaction tanks.

The first reaction tank is seeded with recycled gypsum particles. The seeding serves to discourage gypsum precipitation on the reaction tank walls, agitators, pipes and pumps by improving crystal growth. The seeding of precipitation tanks is a recommended method for reducing gypsum scale on equipment as discussed by Cooper and Slabbert (2005). The reaction tank vapours contain some ammonia and are combined with the vibrating mill vapours before reporting to the stripping column.

**Stripping column**

The gypsum slurry, containing ammonia in solution, is pumped from the reaction tanks into the countercurrent steam stripping column. The ammonia in solution is preferentially stripped, as shown by Equation [6].

\[
NH_4OH(aq) \rightarrow NH_3(g) + H_2O(g)
\]  

[6]

The ammonia and water vapours exit the top of the stripping column and are condensed in a series of condensers. A portion of the condensed ammonia solution is removed as a 10% ammonia product while the remainder is refluxed back to the top of the stripping column to improve the final ammonia concentration. The product ammonia solution is combined with fresh anhydrous ammonia to account for the 10% ammonia losses in the plant.
The stripping column, condensers and scrubber were designed by Process Plant Technology PTY LTD. The stripping column was designed to achieve a 95% stripping efficiency and combined with the 95% reaction efficiency in the vibrating mills, results in an overall ammonia recovery of 90% in the ammonia recovery circuit. The stripping column design also minimized steam requirements and catered for the highly scaling gypsum slurry.

The Tati BMR stripping column design was optimized to reduce the plant steam consumption. This was achieved by using a higher liquid to vapour (L/V) ratio than in the Tati Hydrometallurgical Demonstration Plant (HDP) plant. The BMR design tray efficiency was higher than the HDP tray efficiency, due to larger tray spacing, column diameter and improved liquor flows. The final tray efficiency selected for the Tati BMR design was 15%.

The theoretical number of stages was initially predicted using a McCabe Thiele diagram, as shown in Figure 3, and later confirmed with ASPEN™ modelling. The theoretical number of stages was corrected using the predicted tray efficiency to calculate the actual number of stages and the design column height.

The BMR column discharged slurry into a vacuum flash cooler. The flash cooler incorporated a thermo-compressor, which could recover steam from the discharge slurry and reduce the live steam requirements by almost 30%. The discharged gypsum slurry is thickened and sent to the tailings pond. The gypsum is settled and the solution recovered for reuse as gypsum saturated process water in the solid liquid separation step.

Condensers and scrubber

The ammonia vapours are drawn from the top of the stripping column, through a primary cooler and secondary condenser system. The resultant ammonia rich solution proceeds to a product tank, with the non-condensable gas and entrained ammonia vapour reporting to a multi-stage scrubber.

The primary condenser was designed to cool the ammonia vapours and preheat the nickel raffinate feed to the vibrating mills. The secondary condenser was designed to condense ammonia vapours while preheating cooling water to provide a hot water utility for use elsewhere. These design constraints complicated the condenser and scrubber design. The BMR design utilized a three-stage scrubber, where the first two stages utilized dilute ammonia

![Figure 3. McCabe thiele diagram for ammonia-water system with Tati operating parameters](image-url)
condensate to improve the overall ammonia recovery while meeting the cooling constraints. The final scrubbing stage used sulphuric acid to reduce the ammonia concentration in the off gas to allow venting to atmosphere.

Conclusion

The choice of neutralizing reagent for the SX circuits affects the overall plant design. The logistic and economic drivers for BMR favoured the use of ammonia integrated with an ammonia recovery circuit. The ammonia recovery circuit incorporated several new technologies over the traditional lime boil operations, resulting in higher quicklime utilizations, improve plant availabilities, smaller equipment, lower energy requirements, and improved management of gypsum scale.

References

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Dylan is a process engineer with two years of experience in the design and engineering of mineral processing, pyrometallurgical and hydrometallurgical facilities. He has developed specialist technical expertise in areas that include METSIM process modelling and managing mass balance tables. Dylan has been involved as a graduate process engineer on two significant hydrometallurgical execution projects in Africa, namely the Kamoto Redevelopment Project in the DRC (Copper and Cobalt) and the TATI Activox Project in Botswana (nickel, copper, cobalt). Recently Dylan has been involved in several concept level studies for both pyrometallurgical and hydrometallurgical projects, including the Eastplats furnace expansion Project in Marikana (PGM smelter/converter) and Akanani Project (PGM and base metal refinery/roaster/smelter/converter).