

NOVEL DESIGN ASPECTS OF THE TATI ACTIVOX® PROJECT AMMONIA RECOVERY CIRCUIT.

G.J. Nel
Norilsk Nickel

D A van den Berg
Hatch

ABSTRACT

The Tati Activox® Project (TAP) utilises the Activox® technology to selectively recover base metals from low-grade base metal sulfide concentrates from the Tati Nickel Mining Company. The base metal-containing liquor produced in the leach process is processed through solvent extraction, precipitation and electrowinning circuits to extract, concentrate and produce LME grade copper metal, cobalt carbonate cake and LME grade nickel metal. Ammonia is used as neutralization agent in the cobalt and nickel solvent extraction plants to selectively extract the base metals.

Ammonia forms a soluble ammonium sulfate product which reports to the raffinate stream. The ammonia has to be recovered from the raffinate stream before disposal or re-use of the process solution. Historically, operation of an ammonia recovery or limeboil circuit has been problematic due to severe scaling. Norilsk Process Technology (NPT) developed a novel ammonia recovery circuit using vibrating mills to contact the ammonium sulfate with calcium oxide (fine quick lime) followed by stripping of ammonia from the slurry and upgrading the ammonia product in a stripping column. The process flowsheet was extensively tested at NPT and the Tati Hydrometallurgical Demonstration Plant (HDP) for three years and significant reduction in scaling and improved reagent utilizations were reported. The TAP design recovered a significant portion of the input energy, using heat exchangers and thermo compressors. The recovered heat was utilised in the iron removal circuit.

The ammonia recovery circuit was designed for a recovery of 90%. The design included a redundant train and ageing tanks to simplify change over, plant turn down, reagent inefficiencies, process upset and the risk due to commercially unproven technology.

1. Introduction

In early 2003 a decision was made to design, install and operate a fully integrated Activox® Hydrometallurgical Demonstration Plant (HDP). The HDP employed Norilsk Nickel Process Technology's (NPT) proprietary Activox® leaching technology to extract base metals from a nickel sulfide concentrate produced at the Phoenix operation in Botswana. The HDP plant was designed to process 7 tonnes per day of concentrate and

produce 270 kg of nickel cathodes and 150 kg of copper cathodes. The quality of both nickel and copper cathodes has been consistently above target at 99.9% and 99.99% respectively and information generated by the Tati HDP was used as design information for a full scale commercial plant.

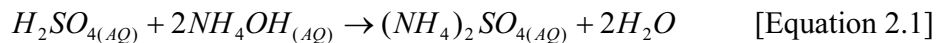
Execution of the Tati Activox® Project (TAP) started in October 2006 with Hatch Africa chosen as the EPCM contractor. TAP is the first project to employ NPT's proprietary Activox® leaching technology to produce annually 25 000 ton of LME grade nickel, 22 000 ton of LME grade copper and 640 tonnes of cobalt as a carbonate from the Phoenix operation's 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 cobalt and nickel Solvent Extraction (SX) circuits require neutralization to selectively extract cobalt and nickel from the pregnant leach liquors into a high grade, pure loaded liquor for final metal production. Aqueous ammonia is used for neutralization in SX and ammonium sulfate is produced that remains the SX raffinate solution.

The ammonia recovery circuit was designed to recover aqueous ammonia from the SX raffinate solution. Recovering the ammonia reduces reagent make-up requirements, plant water consumption by producing recyclable process water and the hazardous nature of the plant tails streams.

This paper will outline the novel design aspects of the ammonia circuit to ensure that the plant design criteria were met at acceptable risk to the project.

2. The Tati Activox Plant

In the SX circuits the PLS are contacted with organic solvents that selectively extract the metals from the aqueous solutions. The metal is then stripped from the organic using spent electrolyte from the electrowinning (EW) circuits or spent loaded strip liquor from cobalt precipitation. A portion of the copper raffinate is recirculated to the concentrate preparation area for repulping and for temperature control inside the autoclaves. The cobalt loaded strip liquor (LSL) is filtered and pumped to the cobalt precipitation circuit. The rich electrolytes from copper and nickel SX are sent to EW to produce the cathodes. The pH in the cobalt and nickel SX circuits is maintained using aqueous ammonia. The ammonium hydroxide neutralizes the sulfuric acid in the SX circuit and produces a soluble ammonium sulfate product which reports to the SX raffinate stream, as shown in equation 2.1



The TATI ammonia recovery circuit uses vibrating mills to contact the ammonium sulfate with calcium oxide (fine quicklime). The ammonium sulfate is converted to calcium sulfate (fine gypsum precipitate) and aqueous ammonia. A series of seeded reaction and ageing tanks are used in the BMR design to further encourage crystal growth

prior to the steam stripping columns, where aqueous ammonia is stripped to the column overheads and condensed to a 10 percent aqueous ammonia solution for re-use. The soluble ammonium sulphate concentration in the raffinate varied between 7 and 9 g/l NH₃ depending on the Co and Ni concentrations in SX. The quicklime utilization, based on HDP testwork, was 82% compared to 65% with conventional limeboil process. The consumption of quicklime is between 20 and 35 g/ liter raffinate. The ammonia losses in the circuit are topped up with anhydrous ammonia or ammonium sulfate crystals. The barren gypsum slurry reports to a thickener and the thickener underflow to the tailings dam, supernatant solution is recovered for use as process water.

2.2 The Traditional Lime Boil Process

The recovery of ammonia from ammonium sulfate is historically referred to as a lime boil and consists of two operations, preparing the slaked lime and reacting to recover ammonia as discussed by Regan (1999)⁶.

The lime slaking process is exothermic and the milk of lime is then pumped to a stirred reactor tank containing the ammonium sulfate solution. The ammonium sulfate 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. Historically the commercial lime boil process equipment have poor operability and low reagent utilizations due to severe scaling,

blockages, ammonia vapour leaks, the risks associated with descaling the reactor tanks and coating of the unreacted lime particles resulting in high reagent consumptions and costs (Regan, 1999)⁶.

2.3 The Tati Ammonia Recovery Circuit

2.3.1 The Tati Ammonia Recovery Circuit Developments

The ammonia recovery process utilised in the TAP design was developed by Norilsk Process Technology (NPT) to overcome the main drawbacks of the traditional lime boil process, particularly lime utilization and gypsum scaling, while minimising steam consumption as discussed by Johnson and Zhuang (1999)⁴ and later by Harrison (2008)³. The process uses vibrating mills, reaction tanks, stripping columns, vapour condensers and off-gas scrubbers as illustrated in Figure 2.3.

The circuit was designed with a complete redundant slurry train to ensure the design circuit availability is met and the risks associated with the commercialization of a new process circuit are minimized. The ammonia condensing, separation and scrubbing system was not duplicated and utilized conventional technology with almost no scale risk.

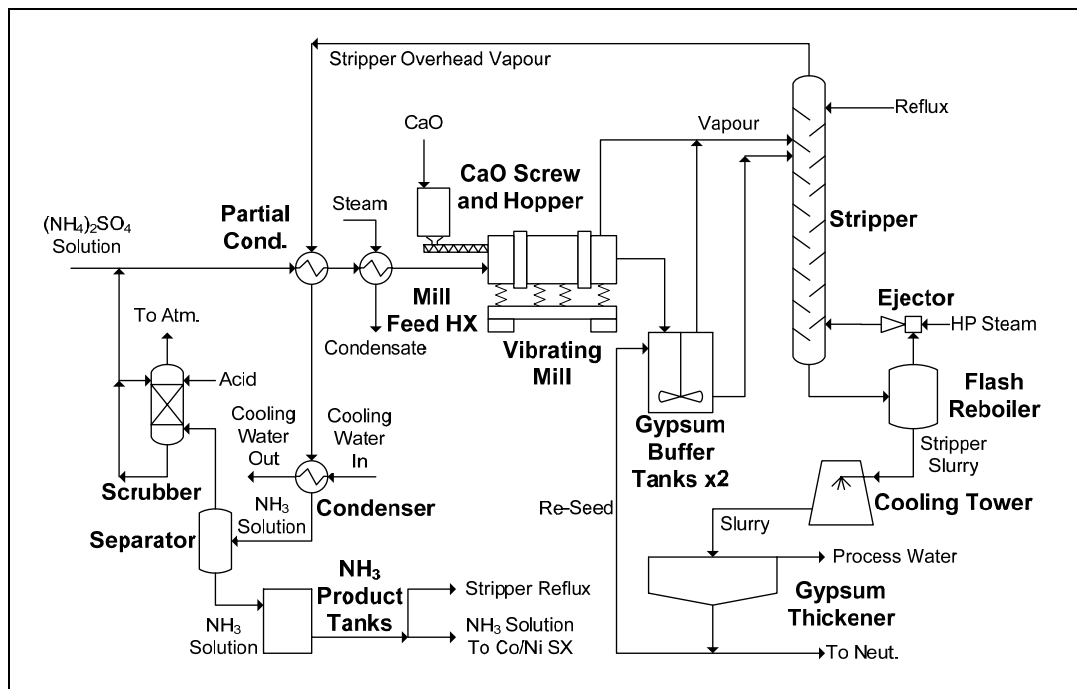


Figure 2.3: TAP ammonia recovery circuit design.

2.3.2 *Quicklime and Ammonium Sulfate Solution Contact*

The nickel raffinate solution, rich in ammonium sulfate, is pre-heated to 90°C and fed through a sealed port into either of the vibrating mills. The ports are located on the feed side of the mills in the vapour area to prevent quicklime, product or media flowing back into the nickel raffinate line. This eliminated the need for check valves, strainers or exotic material for the line. The plant design and layout allowed for parallel lines to the two vibrating mills and easy access to the valves for quick change over and process flexibility. The nickel raffinate could be fed to either or both vibrating mills depending on the process requirements. The mill residence times were 1 minute per mill. The vapour seals on the nickel raffinate feed lines are achieved using viton rubber bellows.

Dry quicklime (CaO) powder is screwed into the vapour area of the vibrating mills from the storage silo using an extended screw inside the mill. The quicklime reacts with the moisture in the vapour area to form a “quicklime plug” that acts as a vapour seal. The “quicklime plug” is continually broken by the screw action and fed into the vibrating mills. One of the layout constraints for the ammonia circuit was to ensure horizontal entry of the screw feeders into the vibrating mills. The horizontal screw feeder increases the vibrating mill vapour seal life; prevents moisture and water build-up and permanent blockage of the screws. The major disadvantage of the horizontal screw feeders was increased height to the vibrating mills. The quicklime reacts exothermically with the aqueous solution to form soluble calcium hydroxide.

This exothermic reaction maintains the mill temperature above 95°C. The quicklime particles react with the ammonium sulfate to release 95% of the ammonia into solution while producing gypsum precipitate.

The application of vibrating mills for ammonia recovery is unique (Western Minerals Technology, 2000)⁵. The gypsum scale that forms on the mill walls is continuously removed due to the abrasive action of the milling media. The media also abrades the gypsum coating off any unreacted quicklime particles improving the reagent utilization to as high as 91% compared to some utilization of 50% (Harrison, 2008)³ achieved with the conventional Lime Boil Process.

The direct contact of the quicklime with the nickel raffinate solution is also unique to the design compared to the Lime Boil Process where lime slaking happens prior to ammonia recovery. This reduces the amount of water dilution, size of process equipment and energy requirements to recover the ammonia. All the equipment is kept at a slight negative pressure to prevent ammonia leaks from the seals using a blower on the stripping column off-gas.

2.3.3 Reaction Tanks

Analysis of the Tati HDP stripping column showed scaling on the slurry feed plate in the ammonia stripping column during start-up and upset conditions potentially due to incomplete reactions in the vibrating mill caused by flowrate surges and short circuiting. Two reaction tanks with a total residence time of 30 minutes were included in the TAP design to act as buffer capacity during upset conditions by ensuring complete reaction prior to the stripping columns.

Approximately 50% of the thickener underflow (containing solids residue from process) is recycled back to the first reaction tank. The seeding provides surface areas for crystal growth and minimizes gypsum precipitation on the reaction tank walls, agitators, pipes and pumps. Seeding is a recommended method for reducing gypsum scale on equipment as discussed by Cooper and Slabbert (2005)². The reaction tank vapours are combined with the vibrating mill vapours before reporting to the stripping column.

The plant design allowed for both vibrating mills to feed either of the reaction tank trains. The ability to feed either reaction tank train using one of the vibrating mills improves process flexibility, assists during cleaning of the standby equipment and will improve plant availability. The disadvantage of the switch over system was the increased complexity of the pipe routing, instrumentation and control.

The layout of the circuit is demonstrated in Figure 2.4. Transfer points and line lengths were minimized in the design by arranging the equipment into two parallel trains and by gravity feeding the second reaction tanks from the first tanks. Using a pump box system as transfer point between the vibrating mills and the reaction tanks was not ideal but necessary to limit the height of the vibrating mills and quicklime silo structure; and to ensure the operational requirements were met.

2.3.4 Ammonia Stripping Column

In the Lime Boil Process the ammonia in solution is stripped from the gypsum slurry using steam in the reaction tanks and the ammonia vapour concentrated using distillation columns. For the TAP design, the gypsum slurry, containing the ammonia solution is pumped to ammonia stripping columns where the ammonia in solution is stripped, using steam.

The ammonia and water vapours exit the top of the stripping column and are condensed in a series of condensers. The feed nickel raffinate is used as cooling medium in the first condenser and preheated prior to the vibrating mills in a shell and tube type heat exchanger. The first and second condensate from the condenser is pumped via heat exchangers to the ammonia scrubbers for optimal heat balancing. The partially condensed ammonia vapour is further condensed and cooled with cooling water as part of the heat recovery process. The hot water from the second condenser is used in the iron removal circuit to preheat the copper raffinate.

The non-condensable gas from the second condenser is drawn into the ammonia scrubber. The condensed aqueous ammonia is further cooled using water and flows into the ammonia separation tank. A portion of the condensed ammonia solution is removed as final product while the remainder is refluxed back to the top of the stripping column to improve the final ammonia concentration. The stripping column, condensers and scrubber were designed by Process Plant Technology PTY LTD¹. 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 Tati BMR stripping column design was optimised to reduce the plant steam consumption. This was achieved by using a higher Liquid to Vapour (L/V) ratio in the column, larger tray spacing, column diameter and improved liquor flows. The final tray efficiency selected for the TAP design was 15%.

The ammonia scrubber design utilised a three stage scrubber, where the first two stages used dilute ammonia condensate and the final stage diluted sulfuric acid to reduce the ammonia concentration in the off gas to less than 25 ppm prior to venting to atmosphere.

The underflow from the ammonia stripping column is discharged into a vacuum flash cooler. The flash cooler was unique to the TAP design and incorporated a thermo-compressor which recovered heat from the discharge slurry and reduced the live steam requirements by 30%. The vacuum flash cooler was designed for the highly scaling environment. The flash cooler discharge is cooled to 30°C in slurry cooling towers prior to thickening.

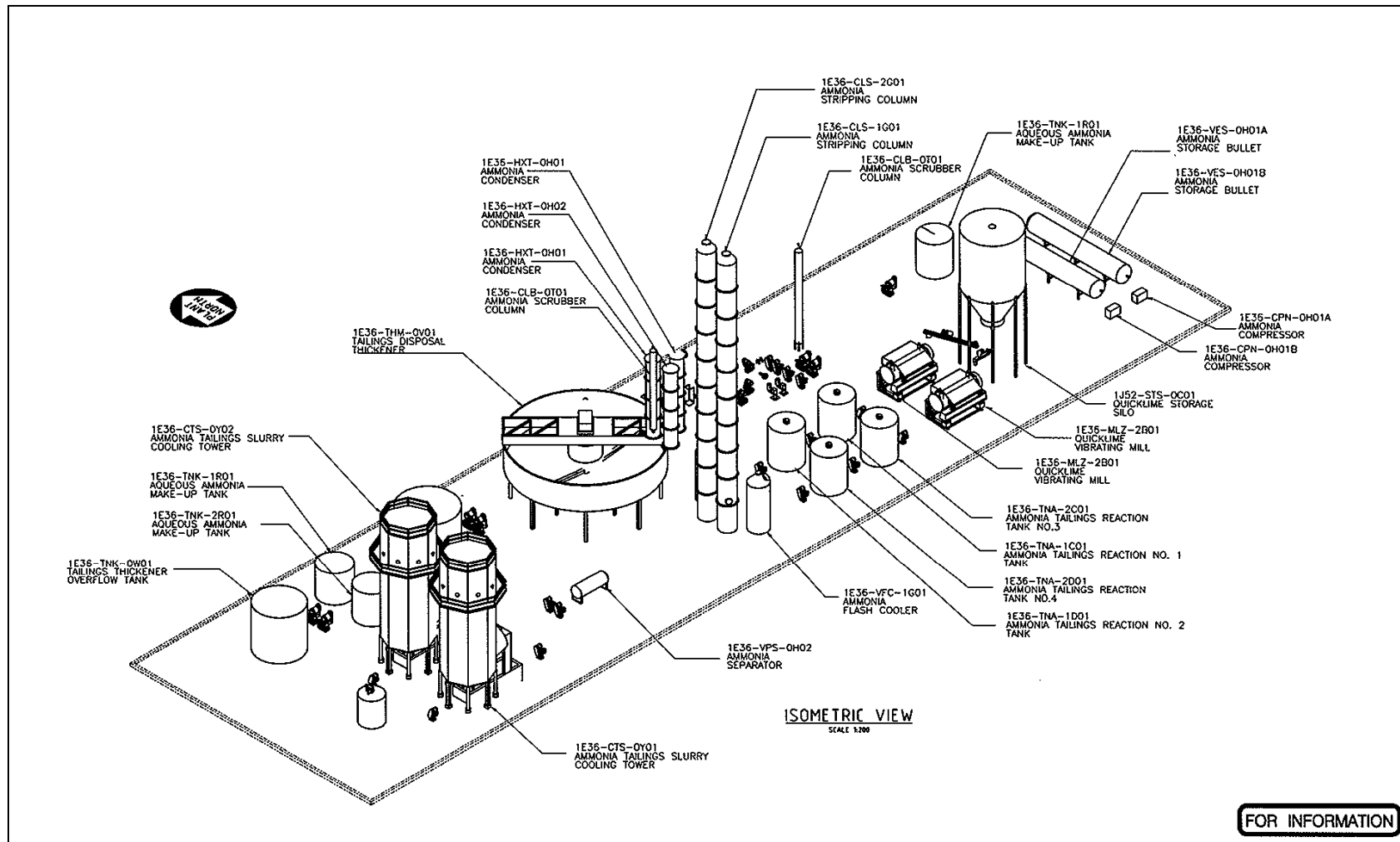


Figure 2.4: Ammonia circuit layout.

Gypsum scaling of the thickener and potential equipment damage (due to high feed temperatures) were identified as major risks associated with the ammonia tails thickening process. Installing a slurry cooling tower prior to the thickener contained the scaling problem inside the cooling tower and controlled the feed temperature to the thickener. The ammonia slurry cooling towers were designed with minimal internal components to minimize scale build-up inside the column and some of the cooling tower discharge is recycled back to the cooling tower feed to act as seeding. Cooling tower valves and spray nozzles were accessible from outside the cooling tower and could be replaced with the cooling tower in operation. The cooling tower chamber was designed for easy access and de-scaling with a standby cooling tower to ensure plant availabilities were met.

The ammonia tails thickener overflow is diluted with clean water prior to transferring the overflow to the process water dam to prevent potential scaling of the thickener overflow line. The thickener underflow is combined with the CCD circuit underflow and pumped to the tailings dam.

All the equipment in contact with the nickel raffinate and process slurry was made of SAF 2205 stainless steel or SAF 2205 clad carbon steel due to the high chloride content in the nickel raffinate.

The vibrating mill did not require descaling over a three year period, only the discharge lines, piping and ammonia stripping column in the HDP was taken off line once every six months for de-scaling.

The energy requirements to separate the ammonia from the slurry were significantly reduced by installing flash coolers on the column underflow. In total 90% of the ammonia in the raffinate stream are recovered using the process.

2.4 Applications of the NPT ammonia recovery process

NPT have investigated, through testwork, process simulation and engineering the application of ammonia recovery to:

- Barren strip bleed liquor for two uranium flowsheets. One flowsheet designed for all ammonia make-up to the plant to be made as ammonium sulphate to the ammonia recovery plant. This removed the need to transport anhydrous ammonia to a very remote location.
- Impurity bleed for a nickel reduction circuit (hydrogen)

Some of the drivers for using the NPT ammonia process technology include:

- Reduction in the quicklime consumption per mole ammonia recovered leading to significant operational cost saving.
- Reduced dilution prior to the ammonia recovery process leading to a reduction in the equipment sizes.

- TAP design meets World Bank Guidelines and the bulk of the water from the circuit is recycled back into the process. Minimizing the fresh water make-up to the circuit and size of tailings disposal facilities.
- High process efficiency to recover ammonia. This reduced the makeup anhydrous ammonia consumption, storage requirement and costs.
- Either anhydrous ammonia or ammonium sulfate crystals can be used for makeup. The flexibility reduces the dependence on reagent supply and enables the operation to take full advantage of market conditions.
- There is a limited market for ammonium sulfate by-products. The NPT process recovers the ammonia in the process effluent into a reusable form that can be directly recycled back to the process.

3. Conclusion

The TAP ammonia recovery process was developed by NPT over several years to eliminate the operational problems experienced with the conventional Lime Boil Process. The NPT process incorporated several new technologies, resulting in higher quicklime utilizations, smaller equipment and lower operating costs.

Extensive work was done in the TAP design phase to ensure the plant design availability and process flexibility was met. Some of the key design aspects was the fully redundant train with flexibility to switch over between equipment, heat recovery from the ammonia stripping column tails, three stage condensation with condensate recycle to control final product grade and to minimize dilution in the ammonia scrubber, and cooling of the ammonia stripping column tails prior to thickening.

NPT is constantly refining the ammonia recovery process and looking for ways to improve the operation and economics. The main areas of development focus include reducing vibrating mill size, alternative mill media and improving energy utilization.

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The Author



Gerhardus Johannes Nel, *Project Manager Hydrometallurgy*, Norilsk Nickel Africa

Gerhard Nel completed his B.Eng in Chemical Engineering in 2001 and started his career at Nkomati Mine as Engineer in Training in the Massive Sulphide Concentrator. He was later promoted to Metallurgist, Senior Metallurgist and Metallurgical Superintendent. In 2004 he moved to Anglovaal Head Office as Project Engineer and worked on the Nkomati Activox® Project. He joined Tati Nickel Mine in 2004 as Senior Metallurgist on

the Tati Activox® Hydrometallurgical Pilot plant where the Activox® hydrometallurgical technology was tested on various nickel sulphide concentrates from Tati, Nkomati and BCL. He was transferred in 2006 to Norilsk Nickel Africa Head Office (formerly LionOre) as Process Lead to work on the Bankable Feasibility Study for Tati commercial Activox® plant. The project was approved in June 2006 and execution started in October 2006. Norilsk Nickel Africa decided in June 2008 to suspend the TAP project. He has worked since on TAP close out, metallurgical consulting at Tati and Nkomati.

