Optimisation of platinum recovery from the Copper Boil Process

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Abstract

BHP Billiton Nickel West Pty Ltd (Nickel West) operates a nickel refinery based on the Sherritt-Gordon process. The nickel matte feed contains copper which requires removal for the refinery to produce premium grade nickel briquettes and powder. The copper is removed via the copper boil process, precipitating out of solution with elemental sulphur to form copper sulphide. Platinum group metals (PGMs) such as platinum, rhodium, and palladium are recovered via co-precipitation with the copper sulphide. However, PGM recovery is inconsistent especially concerning platinum and rhodium, which has meant that Nickel West is unable to receive any realisable income. It is unknown why the recovery in the copper boil process is so low; a possible reason is due to the vast array of process variables that affect the chemistry in the system. Through analysing Nickel West's annualised data, sulphur has been identified as a process variable that affects the recovery of platinum. Subsequently, tests have been conducted on a laboratory scale in which the sulphur concentration was adjusted using elemental sulphur, sodium hydrosulphide, and thiourea. Current observations indicate that improved platinum recovery is attainable in an economically viable manner to reach the desired 99 % recovery.

1. Introduction

BHP Billiton Nickel West Pty Ltd (Nickel West) operates a nickel refinery based on the Sherritt-Gordon process that commenced operation in 1970. It is one of two refineries in the world that operate using this nickel extraction method. The process involves leaching nickel matte with ammonia to form metal amine sulphate solutions. These solutions can then be further processed via oxidation and hydrolysis (oxydrolysis) and hydrogen reduction to produce high purity nickel products of powder and briquettes. Figure 1 demonstrates how these processes are incorporated in the Sherritt-Gordon process.

The feed grade of the nickel matte varies depending on the ore supplied from the mines. Consequently, in addition to nickel, several other species are found in the matte which require removal to achieve a high purity nickel product. These include copper, cobalt, iron, platinum group metals (PGMs) and other precious metals (OPMs). Copper and the PGMs are removed in the Copper Boil (Cu Boil), which consists of 4 tanks in series with a reboiler, representing a rectifying column of four plates (Wishaw 1980). Liquor flows down through these tanks to the reboiler, where the mixture is heated, resulting in the ammonia and water vapours being sent counter-currently in the circuit. The purpose of the copper boil is to:

1. Remove excess ammonia from the process liquor to meet the ammonia:metal ratio for nickel reduction
2. Increase the ammonium sulphate concentration required for oxydrolysis
3. Precipitate copper impurities via reacting with sulphur to form Copper sulphide

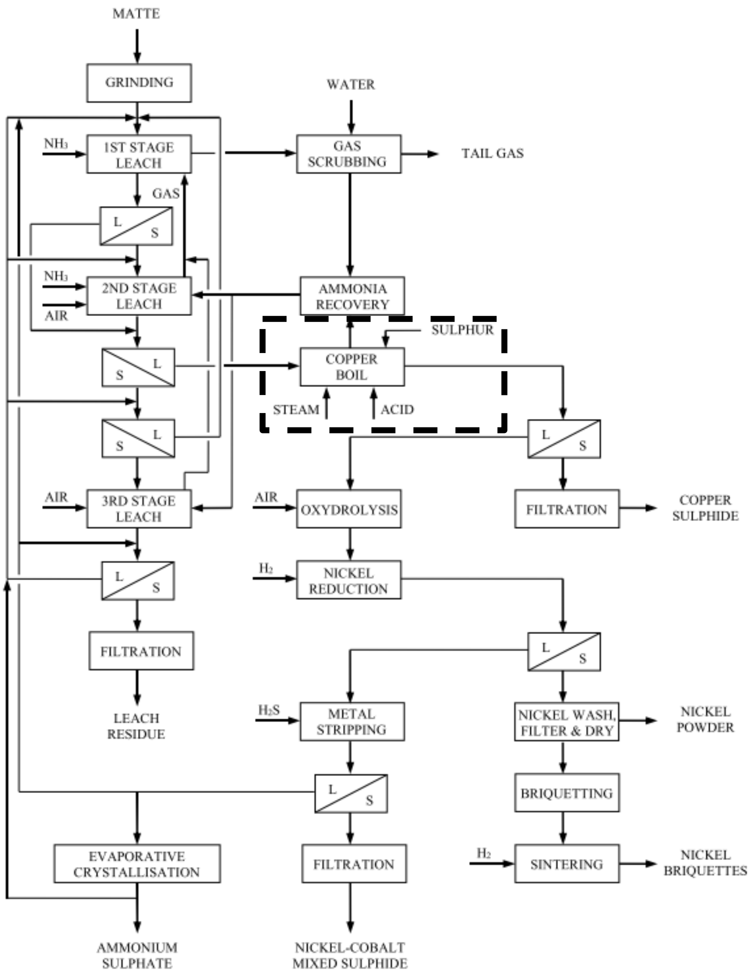

Figure 1 Nickel West's Sherritt-Gordon refining process with the Cu boil process highlighted (Woodward 2014)

The feed liquor to the Cu boil consists of the overflow from the three thickeners used at Nickel West's refinery. This liquor is pre-heated and fed to the first tank with the liquor cascaded down to the second tank, where sulphur is added. The amount of sulphur added is dependent on the requirements of the precipitation of copper. The resulting slurry is then agitated and cascaded down the remaining two tanks to the reboiler. The reboiler operates at elevated temperatures to promote Copper sulphide precipitation in the tanks (Wishaw 1980). The addition of steam and sulphuric acid helps with reaching these temperatures. The overheads of the process are then further separated, with the ammonia and water vapours fed back to the reboiler to provide heat. The remaining liquor is fed to a Copper sulphide circuit feed tank before being separated to copper-free liquor (CFL) and Copper sulphide.

PGMs such as platinum, rhodium and palladium and OPMs such as silver and gold, are also recovered at this stage via co-precipitation with Copper sulphide. The literature on the mechanisms and kinetics of co-precipitation of metal sulphides is very limited, and not well understood (George, Gaylard & Lewis 2009). Consequently, it is unknown how the co-precipitation occurs in the Cu boil. However, most of the PGMs and OPMs are recovered at sufficiently high concentrations with the Copper sulphide product via this mechanism. Platinum and rhodium, however, have limited recovery, which has meant that Nickel West is unable to generate any realisable income for these species.

The low recovery of these species has been consistent throughout the 49 years the refinery has been in operation, with no solution or clear reason proposed as to why this occurs. What makes this problem so intricate is that the concentration of PGMs is dispersed throughout the Sherritt-Gordon process, making them difficult to recover due to the low concentrations. The last known study on improving the recovery was completed in 1987 by B.F. Wishaw to determine methods on a laboratory scale to improve the recovery of platinum. However, conclusions could not be drawn due to *"numerous potential sources of error"* and *"non-representative"* data (Wishaw 1987). Consequently, this problem is complicated by the limited data and poor knowledge of the system. This has provided more incentive to investigate platinum recovery to understand why the recovery is limited and how it can be improved. This project seeks to identify and propose a possible solution to increasing the recovery of platinum to 99 % in a manner which is economically viable and neither modifies nor affects downstream processes in the Sherritt-Gordon process.

2. Process

Due to the uniqueness of the Sherritt-Gordon process, there is no clear solution outlined in industry nor literature to increasing platinum recovery. However, inspiration was drawn from literature to find an appropriate resolution.

2.1 Data Acquisition

Upon reviewing other scenarios where the recovery of PGMs have been low, the solution to resolving this matter has been modifying operational parameters of the system. George, Gaylard, and Lewis (2009) investigated the mechanism of rhodium co-precipitation with Copper sulphide; where the rhodium concentration was two orders of magnitude lower than the copper. Process variables were identified that affected the co-precipitation mechanism such as temperature, cupric copper concentration and metal sulphide solubility which were then altered under laboratory conditions to achieve improved recovery. Similarly, Mulwanda and Dorfling (2015), investigated different operating conditions in a copper sulphate leach residue to recover rhodium, ruthenium, and iridium. By adjusting the temperature and agitation of the solution, recovery was increased. Hence, it is suggested that potential mechanisms for improved platinum recovery could be identified by analysing process variables, as currently there is a poor understanding of how the Cu boil's conditions affect the mechanism of platinum recovery.

Consequently, Cu boil process parameter data was obtained from Nickel West. This included 45+ process parameters such as reboiler temperature, tank pressure, and sulphur addition. The data obtained was then "cleaned" by removing periods of shut-down, start-up and intermittent periods when the Cu boil was operating out of the desired operating conditions. The data was then annualised to determine the average and associated fluctuations for the variables throughout the corresponding year. Each process variable could then be correlated against the respective recovery of platinum. Hypotheses were then proposed that reflected what variable could be adjusted in the Cu boil process. From this, an experimental methodology was designed to test whether the hypotheses were true and applicable to the Cu boil process. It is noted though, that hypotheses that would affect downstream circuits in the Sherritt-Gordon process such as oxydrolysis and reduction, were ignored as this would then affect the purity of the nickel products that the refinery produces.

2.2 Experimental Methodology

From the data acquisition, experimental tests were designed to test the suggested hypotheses. These tests were designed in four stages:

1. Establish a base case of Cu Boil
   It was necessary that the experiments appropriately reflected the Cu boil process. To ensure this, several different experimental setups were reviewed to ensure the heating of the vessel used in the laboratory was sufficient. This was to allow excess ammonia from the process liquor to be evaporated to meet the ammonia:metal ratio required in the Sherritt-Gordon process. The liquor used was the copper boil feed (CBF) liquor, which came from the adjustment thickener overflow (ATO).

2. Batch Test of Cu Boil
   The established base case set-up was then used in a series of tests replicating the Cu boil process whilst increasing the amount of sulphur added. The reactor was run for a period of 4 hours, similar to the residence time of liquor in the full-scale Cu boil. Samples were taken hourly to determine how the recovery of the PGMs changes with time.

3. Bottle Roll
   Several bottle roll tests were conducted in a hybridisation oven using liquors of Copper Boil Discharge (CBD) and CFL. These experiments were to reflect if further recovery of platinum could occur at the end of the Cu boil process instead of adjusting throughout the entirety of the process. These bottles were agitated for a period of 24 hours in the oven instead of 4 hours, as the residence time of the selected liquors would not affect the functionality of the Cu boil.

4. Scale-Up of Bottle Roll
   From the results achieved in the bottle roll testing, scale-ups of the promising tests were completed. The 24-hour residence time remained, with samples taken hourly to map the kinetics of the process. This would assist in selecting the best residence time and reagent to potentially implement to the Cu boil.

3. Results and Discussion

3. 1 Process Variable Selection

Analysing the annual composite data found several correlations between process variables and the platinum recovery in the Cu boil. The most significant correlation was with the amount of sulphur in the Cu boil. The concentration of sulphur present in the Cu boil system appears to impact the percentage of platinum recovered as indicated by Figure 2. This suggested that an increase in the sulphur concentration will allow platinum to co-precipitate out of solution in larger concentrations as PtS. This encouraged an investigation into adding various amounts of elemental sulphur to the Cu boil to determine whether a 99 % recovery is possible. This was in addition to exploring whether other sulphur species, such as sodium hydrosulphide (NaSH) or thiourea, could be added to CBD and CFL at the end of the process to assist in improving the recovery of platinum under the current operating conditions of the Cu boil. It is suggested that these species only be added to the final Cu boil liquors due to their strong reducing nature. If added throughout the Cu boil, the chemistry required to form copper sulphide could be affected.

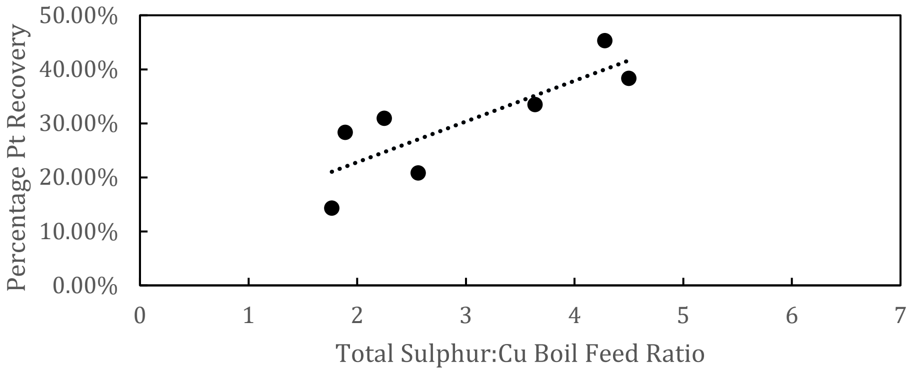

Figure 2 Annualised trend data of sulphur concentration in Cu boil with the respective platinum recovery

Further correlations were found with other process variables, but none as notable as the impact sulphur has on the Cu boil. Additionally, most of the other process variables identified would affect the operability of the Cu boil and consequently, downstream processes, and thus could not feasibly be altered.

3.2 Experimental Testing

At the time of publication, 3 of the 4 stages of testing have been completed. From establishing a base-case of the Cu boil, it was determined that the laboratory set-up would require external heating. This would allow the liquor to obtain enough heat for ammonia to evaporate off. This method was implemented when conducting the batch testing of the Cu boil. Several different elemental sulphur dosages were added with the respective recoveries of platinum evaluated. The results indicate that an increase in sulphur will increase the platinum recovery, supporting the previously established hypothesis. However, the curve does not correlate with the annualised data as demonstrated in Figure 3. It is suggested that this has occurred due to insufficient mixing and heating of the solution, which in turn could affect the mechanism of platinum recovery. The differences in the mixing between the Cu boil and laboratory set up is reflected in the evaluated tip shear and Reynolds Number (Table 1). To resolve this, the Cu boil will be remodelled to ensure the laboratory set up better reflects the mixing occurring in the Cu boil. From here, a more realistic evaluation on the recovery level that can be achieved can occur.

Bottle roll test results indicate that the addition of NaSH and thiourea to CBD and CFL does improve the recovery of platinum. From these initial results, tests can be developed and scaled up to a reactor size to further assess whether these reagents and liquors can achieve as high of recovery as elemental sulphur in the copper boil feed (CBF).

Set-Up:	Cu Boil Process	Laboratory Reactor
Average Shear Rate (s^{-1})	2.63	70.07
Reynolds Number	$2.12x10^5$	$1.12x10^4$

Table 1 Comparison between tip shear and Reynolds number for the Cu boil and laboratory reactor set-up

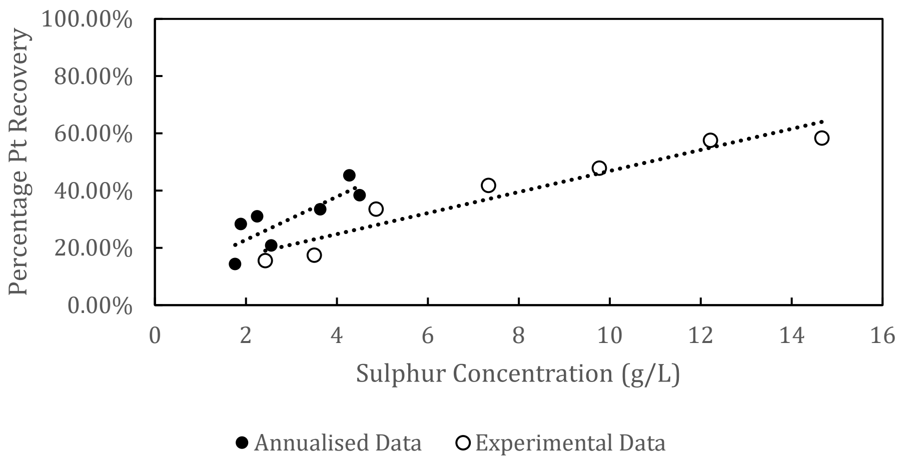

Figure 3 Comparison between the annual platinum recovery trend and the experimental platinum recovery trend

4. Conclusions and Future Work

Based on the preliminary findings, platinum recovery within the Cu boil can potentially be improved by increasing sulphur concentration. However, further testing is required with enhanced heating and mixing to see if recovery can be further improved and reproduce the annualised data trend. Ongoing work includes evaluating whether adding NaSH or thiourea to CBD or CFL will further improve the platinum recovery. It is suggested that the findings from this project be used to develop a pilot plant of the Cu boil process. This will assist in determining the most viable option to increase platinum recovery, as this would best reflect the Cu boil process and hence, give a more accurate evaluation on how the recovery can be increased.

5. Acknowledgements

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6. References

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