STRESS IN FULL DEPOSIT ELECTROWON NICKEL

*K. Voogt, J. H. W. M. Brits and L. Bryson

Anglo American Technical Solutions
8 Schonland Street,Theta, Johannesburg, South Africa, 2025
*(*Corresponding author: karen.voogt@angloamerican.com)*

ABSTRACT

The Anglo American Platinum's Rustenburg Base Metals Refinery (RBMR) has the world's first full deposit nickel plating tankhouse. Impurities in the nickel electrolyte can induce stresses in the electrowon nickel deposits that could lead to delamination of the deposit. Identifying the impurities that contribute to increasing internal stresses in the nickel deposit is key to successful operation and automation of the tankhouse.

Impurities were introduced in the plant electrolyte and the effects on the full-scale nickel deposits evaluated. The impurity-adjusted electrolyte solutions were also analyzed using commercially available bench-scale methods to determine the induced stress. A correlation between impurity-induced deposit stress and full-scale delamination was developed. A direct correlation can now be made between feed quality, i.e. impurity concentrations, and degree of delamination in the plant. This methodology has the potential to rapidly predict the effect of new reagents, upstream process upset conditions and synergistic interactions between impurities on deposit stress and delamination of nickel deposits.

KEYWORDS

Nickel, Electrowinning, Full Deposit, Stress, Delamination

INTRODUCTION

Nickel electrowinning in sulphate media was first pioneered by Outokumpu in its Harjavalta refinery in 1960 (Saarinen and Seilo, 1985). The original process was very manual with starter sheets plated onto “acid resistant” steel for 36 hours and then manually stripped and cut into sheets which could be inserted into the main production cells for a further 4–5 days. The starter sheet stripping and manufacture process was later automated. The same technology was subsequently implemented on a number of plants around the world. Anglo American Platinum’s Base Metal Refinery (BMR) began nickel electrowinning in the early 1980’s.

The recent expansion of Anglo American Platinum’s Base Metals Refinery necessitated the construction of a new nickel tankhouse to achieve two primary objectives. The first to increase the capacity to 32 400 tpa nickel and the second to reduce employee occupational exposure to nickel aerosols. The new tankhouse has been commissioned and is in the process of ramp-up; more details are given by Hagemann et al. (2016). Fundamental to lowering employee exposure to aerosols was automating both harvesting and final handling of cathode. In order to accomplish this a bold move was taken to plate up to 10 days on permanent titanium blanks which are harvested by automatic crane and automatically stripped. The original development work for the plating nickel on titanium blanks over a ten day cycle is given by Bryson et al. (2006).

During the development work little consideration was given to the relationship between the nickel deposits residual stress developed during deposition and the roughness of the prepared titanium blanks. Bryson et al. (2006) showed that roughness preparation alone could not sustain adherence of full-scale cathode for periods longer than 6 days and anchor points were drilled through the titanium cathode to allow growth between the two metal deposits on either side of the blank.

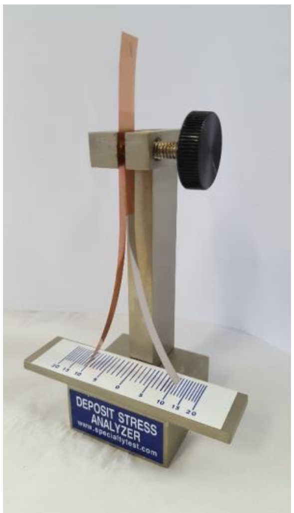
Nevertheless the relationship is important since the ability for the nickel deposit to adhere to the titanium substrate for the duration of the deposition cycle depends on the competition between the residual stress and the roughness providing sufficient anchor points for the nickel deposit to adhere to. Obviously the substrate could not be infinitely rough as then stripping the deposit would be impossible. Interesting work by Gendron and Ettel (1975) defined an exfoliation index in an attempt to map a region where deposits of nickel will adhere to or delaminate from a substrate under a specific set of conditions.

A substantial amount of work has also been published regarding the effect of impurities in nickel solutions on deposit morphology and stress. Holm and O’Keefe (2000) have evaluated the effects of pH, temperature and nickel ion concentration. Kittelty and Nicol (2001) also conducted a similar study evaluating the same parameters, however, including the effects of sodium sulphate. Kittelty and Nicol (2003) went on to investigate the impact of various organics used for solvent extraction as well as various metal cations: aluminium, chrome, copper, iron, manganese and zinc. Recently, Freire et al. (2017) examined the impact of various organic additives on the cyclic voltametric response as well as resultant deposit morphologies. It should be noted that most of these tests were conducted on bench-scale apparatus and hence do not assist in answering questions regarding the impact on the actual stresses developed over commercial scale cathodes over a complete deposition cycle.

The work presented in this paper attempts to combine the methodology of defining an exfoliation index as defined by Gendron and Ettel (1975) by performing testwork on Anglo American Platinum’s nickel tankhouse. Impurities were manually introduced into the BMR nickel tankhouse feed solutions and the effect thereof on delamination followed. The nickel tankhouse uses cathode bags to control the pH around the cathode at the required level. This configuration allows the catholyte in each cathode bag to be dosed individually without it affecting the rest of the cathodes in the cell. The positive head in each cathode bag result in a net outflow of electrolyte from each bag thereby making the background catholyte around each cathode fairly unique to that cathode.

EXPERIMENTAL

The nickel deposit needs to adhere to the blank during the plating cycle without delamination but should be easy to strip off at harvesting. The titanium blanks needs to be rough enough to counteract the tensile stress in the nickel deposit that promotes delamination. The Gendron and Ettel (1975) exfoliation index visually demonstrates the area for safe plating. The patent does state, however, that the exfoliation index must be determined empirically for each different thickness or area of deposit. Although the patent describes the use of a spiral contractometer to measure the deposit stress a second method, the bent strip method, was found to be used in the electro-forming and -plating industry. The bent strip and spiral contractometer in use are shown in Figure 1 (a) and (b), respectively.

a 

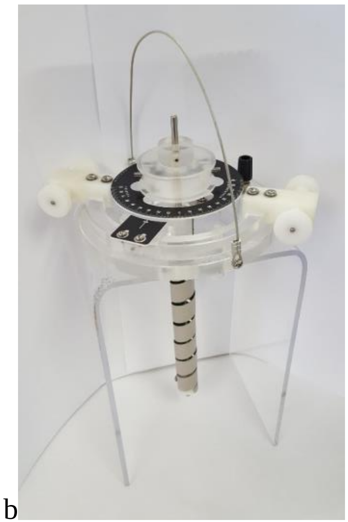
b 

Figure 1. The bent strip (a) and the spiral contractometer (b).

Two approaches were followed in the experimental section of this work. In the first instance stock solutions of the impurities: selenium as Na_2SeO_3 and Na_2SeO_4, FC1100, copper as $CuSO_4$, cobalt as $CoSO_4$ and zinc as $ZnSO_4$ were prepared and pumped into selected cathode bags at 1% of the flowrate of the nickel electrowinning feed solution for the full harvest cycle. Freshly sandblasted titanium blanks with a known surface roughness, Ra, of between 9 and 13 µm, were inserted into the selected test positions for each test. During the harvest cycle the feed and catholyte were sampled daily. The cathodes and cells were measured for current, flowrate, temperature and sampled during the harvest cycles to ensure normal process conditions were maintained. Delamination of the cathodes was an important parameter to validate in this study and cathodes were checked daily for signs of delamination. Once a cathode delaminated it was pulled, stripped and returned for further plating into the same bag at the same conditions thereby providing additional data. After harvesting the catholyte in each cathode bag was sampled for subsequent testing with the spiral contractometer and/or the bent strip. In the second instance synthetic solutions matching the catholyte in the bags were prepared from reagents and the Na_2SO_4 concentration varied. The synthetic catholyte solution was made to match the catholyte solutions collected from the plant and its composition shown in Table 1.

Table 1. Synthetic electrolyte composition for Na_2SO_4 tests.

Component	Concentration
Ni (g/L)	63
H_3BO_3 (g/L)	11
Na_2SO_4 (g/L)	0, 40, 80, 120, 170, 220
pH	3.5

The conditions for the spiral contractometer and bent strip tests were selected to match the plant's conditions. An electrolyte temperature of 60°C and current density of 220 $A.m^{-2}$ were used throughout. A BK Precision model 1696 direct current power supply was used in all tests.

Copper-iron alloy (PN 1194 test strips from Speciality Testing and Development) was used in all the bent strip tests. The test strips were weighed to four decimal places, cleaned by dipping in ethanol at 40°C for 1 minute and allowed to air dry before use. The test strip was clamped to a bar and placed into the test beaker and allowed to equilibrate to the electrolyte temperature for 30 seconds before the current was started for the predetermined time. All tests were conducted to plate to a deposit thickness of approximately 2.7 µm (approximately 6 minutes). Bent strip tests were conducted in triplicate.

The spiral contractometer and stainless steel helix (Material Testing Technology) was used to conduct all spiral contractometer tests. The helices were weighed to four decimal places before use, rinsed in ethanol at 40°C and allowed to air dry before use. The helix was then mounted on the contractometer, calibrated as per the manufacturer's recommendations, placed in the electrolyte and allowed to equilibrate to temperature for approximately 1 minute before the current was started for the predetermined time. All tests were conducted to plate to a deposit thickness of approximately 12.7 µm (approximately 28 minutes). Most spiral contractometer tests were conducted only once with selected tests conducted twice due to a limited number of helices available and the limited lifetime of the inside non-conductive coating that deteriorated with each test under the experimental conditions used. Contractometer results were corrected, according to the instrument's manual, for the large difference between Young's modulus of elasticity for the substrate and the coating.

RESULTS AND DISCUSSION

Two main commercial methods exist to determine the stress in metallic deposits namely the spiral contractometer and the bent strip method. Both these methods were used for comparative purposes. Catholyte samples collected from the tests conducted on the plant where impurities were dosed into the cathode bags with feed were used to conduct the bench-scale stress tests, the results of which are discussed below.

Sodium Sulphate

The Base Metal Refinery process treats sulphide smelter products with sulphuric acid. This result in process solutions throughout the plant containing a background of Na_2SO_4. The conductivity of the electrolyte is enhanced by the background of Na_2SO_4 and improves current efficiency. However, should the Na_2SO_4 concentration be too high it negatively impacts mass transport. Kittelty and Nicol (2001) found that nickel deposit strain increased 21% at low (0 g/L) and 59% at high (160 g/L) concentrations of Na_2SO_4 from a minimum at around 80 g/L. The target for Na_2SO_4 in the BMR nickel electrowinning feed is 120 g/L which is on the upper end of the range investigated by Kittelty and Nicol. This raised questions around the role and impact of Na_2SO_4 concentration on deposit stress.

The solubility limits of Na_2SO_4 at room temperature prevented the addition of high concentrations thereof in low volumes to cathode bags. Concentrations of Na_2SO_4 lower than the concentration already in the feed could not be tested in the plant either, making synthetic electrolyte solutions with varied Na_2SO_4 concentrations the only option to test stress over a wider range of Na_2SO_4 concentrations. The deposit stress results (Figure 2) determined by the bent strip show a similar trend and minimum to that of Kittely and Nicol (2001). In this study, however, the stress at 0 g/L Na_2SO_4 is 40% higher than at the minimum at 80 g/L and it increases by 34% from the minimum at 170 g/L. The greater number of data points tested provide more resolution around the minimum and suggests a gradual increase in stress around the minimum rather than a steep increase with the change in Na_2SO_4 concentration. This result highlights which parameters are important in the management of stress in the nickel tankhouse in terms of feed quality. The results, however, only speaks to deposit stress and not morphology; as well as failing to emulate the effects of any interactions of other species with Na_2SO_4 on these same properties. The synthetic solution results correspond well with a plant catholyte reference that contains 177 g/L Na_2SO_4 confirming that the bent strip methodology can be directly applied to plant solutions.

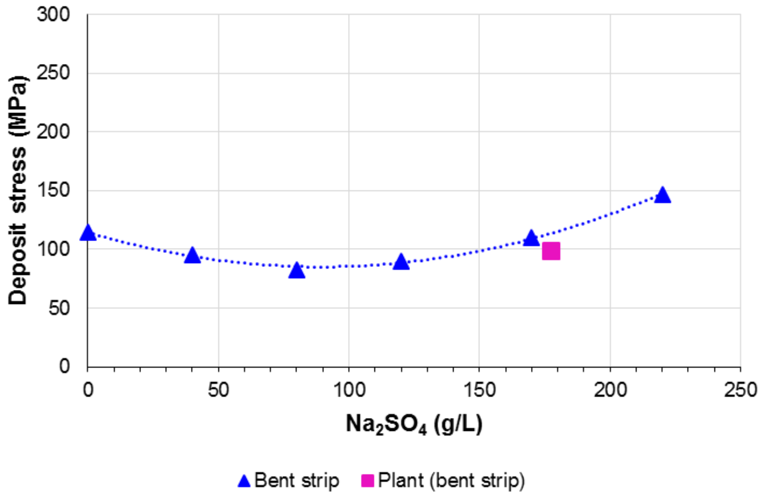


Figure 2. The effect of Na_2SO_4 on nickel deposit stress as determined by the bent strip.

Copper, Cobalt and Zinc

Other metallic impurities present in the BMR electrolyte feed such as Cu, Co and Zn were also tested under typical plant and slightly higher concentrations to determine their impact on deposit stress. Kittelty and Nicol (2003) investigated the effect of Cu, Co and Zn at 20 mg/L and found that the addition of Cu increased the strain by approximately 60% over the strain induced by Co and Zn. The bent strip results for the three metallic impurities performed over a wider range, shown in Figure 3, indicate little or no impact on deposit stress measured and no significant difference between Cu and the other two metallic impurities. There was also no delamination observed on the plant for any of the concentrations of metallic impurities tested.

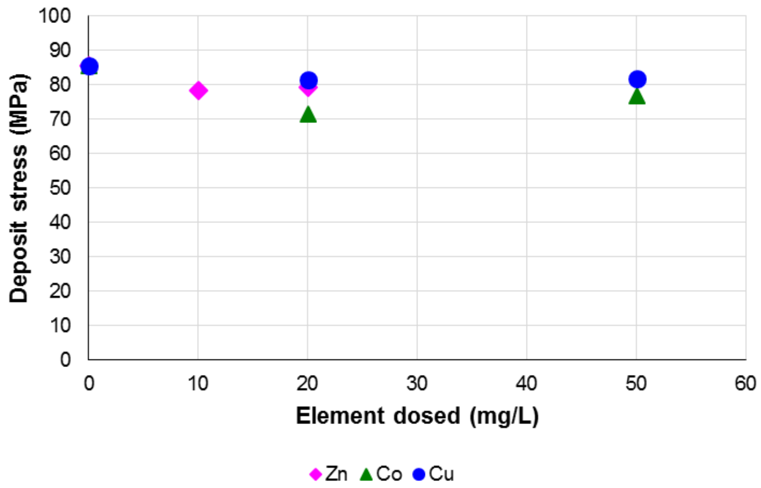


Figure 3. The effect of Zn, Co and Cu on nickel deposit stress as determined by the bent strip.

Selenium

The impact of selenium was also tested and was found to have the biggest effect on deposit stress and delamination of all the impurities and additives tested. It has been found that both selenite, Se^{4+}, and selenate, Se^{6+}, are generated in the oxidising pressure leaching sections of the refinery and hence an attempt was made to test both species independently. The effect of selenite, Se^{4+}, on deposit stress is shown in Figure 4. The bent strip results suggest that the relationship between Se concentration and stress is linear. The spiral contractometer, however, plateaus off at deposit stresses above 250 MPa. The reason for this is unclear. Full scale deposit delamination from the blank occurred in all deposits to which more than 15 mg/L Se^{4+} or more was added, as indicated by the red line on the graph.

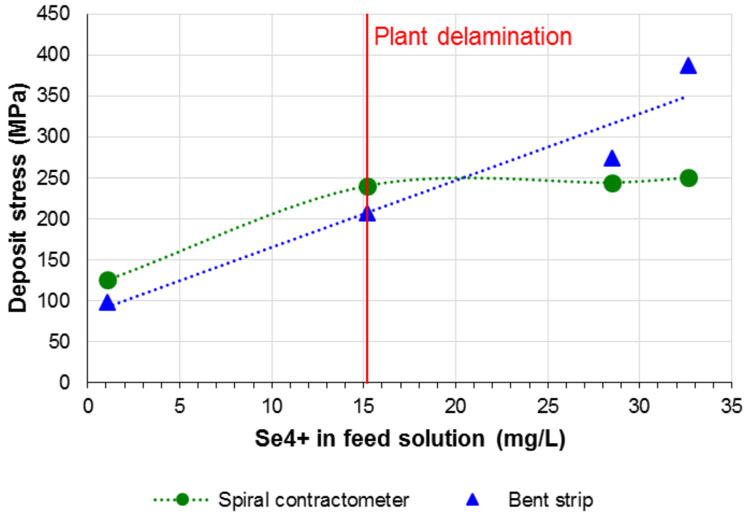


Figure 4. The effect of Se^{4+} on nickel deposit stress as determined by the bent strip and spiral contractometer.

Both the cathodes to which 15 and 28 mg/L Se^{4+} were added delaminated making it possible to relate the bent strip stress results to actual full-scale delamination. In this instance delamination from titanium at a surface roughness, Ra, of 9–13 µm occurs when the stress in the deposit is greater than 207 MPa. All deposits that delaminated did so 4–5 days into the harvest cycle.

Selenate or Se^{6+} were also added to selected cathode bags at different concentrations in another cell during the same harvest cycle. The effect of Se^{6+} and Se^{4+} on deposit stress as measured using the bent strip method is shown in Figure 5. The cathode exposed to the highest concentration of Se^{6+} tested (31 mg/L) delaminated and grew through the cathode bag. The cathode bag had to be cut off during harvesting resulting in a loss of the catholyte and thereby the deposit stress data point. Delamination on the plant as a result of Se^{6+} occurred at concentrations above 15 mg/L, as indicated by the red line on the graph. The deposit stress of 203 MPa was measured as a result of exposure to Se^{6+} at 15 mg/L. All delamination occurred after 2–3 days into the harvest cycle.

Exposure to both Se^{4+} and Se^{6+} at $\geq$ 15 mg/L resulted in delamination on the plant. Based on observation on the plant Se^{6+} had a more pronounced effect that resulted in faster delamination. Regardless of the exact speciation of selenium in the feed and cathode bag the total selenium concentration need to be controlled to less than 15 mg/L to eliminate delamination.

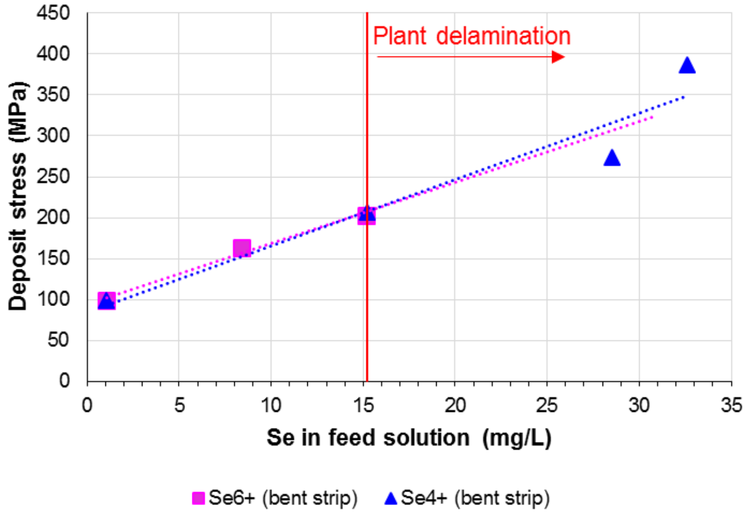


Figure 5. The effect of Se^{6+} and Se^{4+} on nickel deposit stress as determined by the bent strip.

Acid mist reagent, FC-1100

Aerosols in nickel electrowinning are a significant occupational health concern as soluble nickel has an occupational exposure limit of only 0.1 $mg.m^{-3}$ (Bryson et al., 2008). In a continued quest to reduce aerosols Fluorad FC-1100, an acid mist suppressant used in copper tankhouses to great effect, was tested. Freire et al. (2017) reported delamination of deposits at FC-1100 additions of 50 and 100 mg/L, respectively. The decrease in crystal size of the deposits were thought to increase the internal stress of the deposits exposed to FC-1100 causing the delamination. The tests conducted on the plant with FC-1100 added at concentrations of 10, 20 and 50 mg/L to selected cathode bags for a harvest cycle confirmed Freire et al.'s hypothesis. Bent strip analysis of the catholyte from the tests, shown in Figure 6, indicate a linear increase on deposit stress over the range tested as the FC-1100 concentration increases. Full scale deposit delamination from the titanium blank occurred in all deposits to which 20 mg/L FC-1100 or more was added, as indicated by the red line on the graph.

The deposit exposed to 10 mg/L FC-1100 was very rough and started delaminating at the top of the titanium blank. The 20 and 50 mg/L deposits were smoother but both delaminated on harvesting and displayed signs of "honey-combing" as shown in Figure 7. Delamination occurred at FC-1100 concentrations above 20 mg/L with an associated deposit stress of more than 160 MPa in the deposits. All deposits that delaminated due to FC-1100 did so at harvesting on the seventh day of plating.

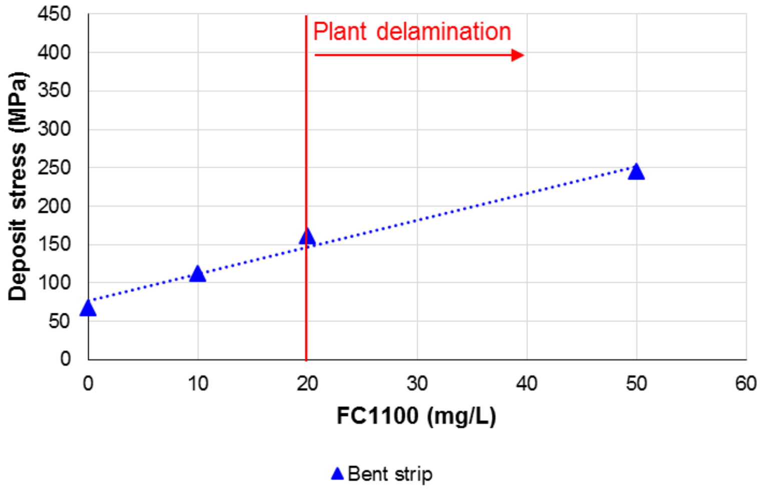
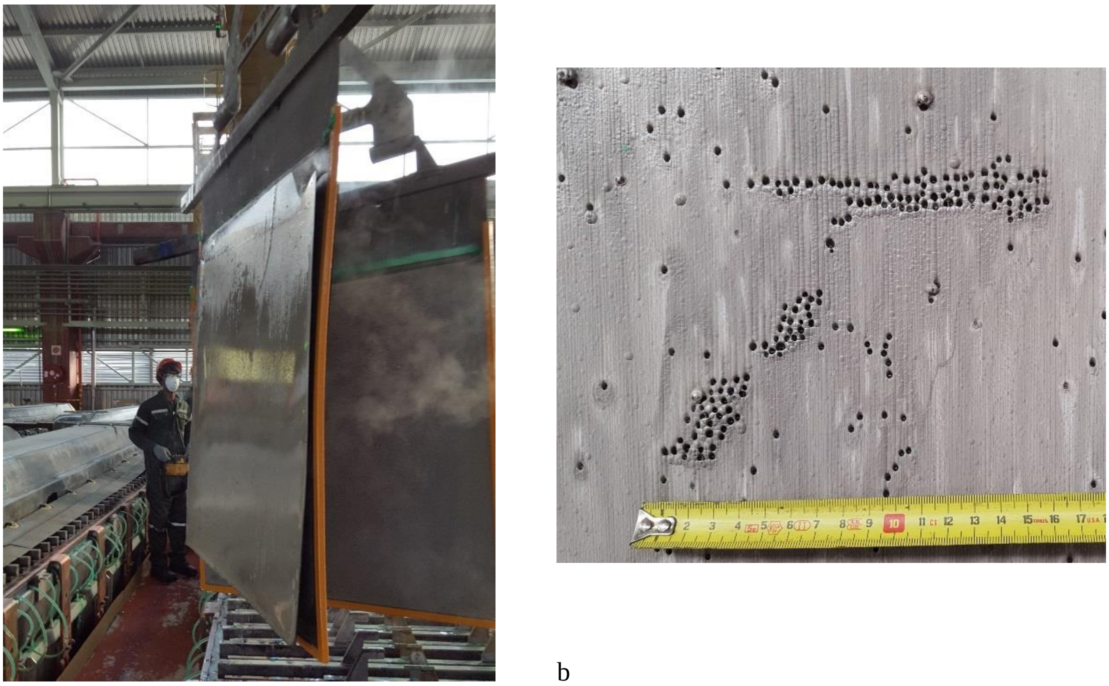


Figure 6. The effect of FC1100 on nickel deposit stress as determined by the bent strip method.



a b

Figure 7. Delamination (a) and “honey-combed” nickel deposit (b) as a result of FC-1100.

Exfoliation Index

The experimental data for Se suggests that there is good correlation between the bent strip and spiral contractometer results at stress values lower than 250 MPa. It is therefore possible to represent the bent strip results obtained in an exfoliation index for the BMR’s new nickel tankhouse in comparison to the one published by Gendron and Ettel (1975) that was developed using the spiral contractometer. The exfoliation indices are shown in Figure 8. Above the exfoliation area, the deposit delaminates due to high internal stress. Below the exfoliation area, the deposit strongly adheres to the substrate and can not be stripped.

The solid horizontal lines on the BMR exfoliation index areas for Se (blue) and FC-1100 (green) in Figure 8 indicate the limits of delamination at high internal stress values as measured. The undefined edges of the exfoliation squares indicate limits that were not specifically tested in this work. This includes the lower limit of the index area, at which the deposits cannot be stripped, and the vertical edges that define the surface roughness limits for the blanks. The surface roughness of the titanium blanks was not varied beyond the 9–13 µm Ra values the plant specifies for its newly sandblasted blanks.

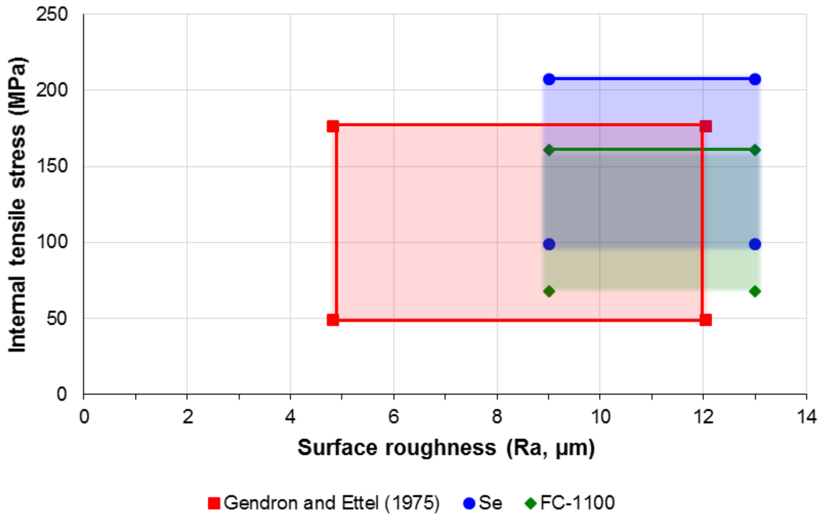


Figure 8. Comparison of the BMR and patent exfoliation indices.

CONCLUSIONS

A relationship between full-scale electrowon nickel deposit stress and the bent strip test results was developed. The ability to determine the deposit stress from a solution, be it a synthetic or plant solution, in a quick and simple way to predict whether deposits will delaminate on full scale is an invaluable tool. It allows for off-line plant process upset scenario testing as well as the determination of the impurity parameters and synergistic effects within which the full scale operation needs to operate to minimise delamination issues. It can also be used as a diagnostic tool to allow the operation to anticipate delamination. Deposit stress increases as plating progresses and the bent strip method can therefore be used as an early warning tool to predict delamination and allow the operation time for corrective action.

The bent strip method was shown to be a robust, quick and simple method to use for determining deposit stress in nickel on a routine basis. The method uses disposable test strips that give reproducible results. It was shown to have a practical application on a nickel electrowinning full deposit plant.

ACKNOWLEDGEMENTS

This paper was published by permission of Anglo American and Anglo American Platinum Ltd.

The Technical Solutions team would like to thank the following people specifically: Cobus Meyer, Metallurgical Technical Engineer at the new nickel tankhouse, who trusted us to pump stress-causing impurities into his production cathodes, and Tito Sepoloane, Metallurgist, and Willie van Heerden, Day Shift Leader, who assisted us with organising the harvests and manual stripping of the cathodes. The project would have been impossible without their assistance.

REFERENCES

Bryson, L.J., Graham, N.J., Bogosi, E.P., & Erasmus, D.L. (2008). Nickel electrowinning tank house developments at Anglo Platinum's Base Metal Refinery. Paper and presentation at ALTA 2008.

Freire, N.H.J., Majuste, D., Angora, M.A. and Ciminelli, V.S.T. (2016). Effect of organic impurities and additive on nickel electrowinning and product quality. Hydrometallurgy 169, 112-123.

Gendron, A. S., & Ettel, V. A. (1975). U.S. Patent No. 3883411. Washington, DC: U.S. Patent and Trademark Office. Electrodeposition of thick nickel deposits on permanent cathode blanks.

Hagemann, J.P., Ndlovu, J., Nelson, L.R., Bryson, L.J., Gilmore, M.W., Hines, K., Peyper, B., Varty, R.N. & Sepoloane, T. (2016). Full deposit nickel electrowinning at Rustenburg Base Metals Refiners. XXVIII International Mineral Processing Congress September 11-15, Quebec City, Canada.

Holm, M. & O'Keefe, T.J. (2000). Electrolyte parameters effects in the electrowinning of nickel from sulfate electrolytes. Minerals Engineering 13 (2), 193–204.

Kittelty, D., & Nicol, M.J. (2001). The electrocrystallization of nickel and its relationship to the physical characteristics of the metal. In Kelsall, G.H. (Ed.). Electrometallurgy 2001, (p. 217Megabytes). Canada: Metallurgical Society of CIM.

Kittelty, D., & Nicol, M.J. (2003). The effects of solution impurities on the properties of nickel cathodes .In: Hydrometallurgy 2003 – Volume 2: Electrometallurgy and Environmental Hydrometallurgy TMS, 1205–1217.

Saarinen, H., Seilo, M., (1983). Production of the cathode nickelin the Outokumpu process. Refining Processes in Metallurgy (Raffinationsverfahren in der Metallurgie), Hamburg, FRG,October 20–22. Verlag Chemie, D-6940 Weinheim, FRG, pp. 267–283.