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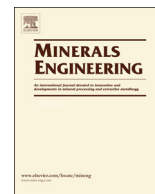
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# Water quality effects on flotation: Impacts and control of residual xanthates

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## ABSTRACT

For increasing the sustainability and cost effectiveness of their operations Boliden Kevitsa Mining Oy in collaboration with academic research partners aims to develop a holistic approach to water management in its mineral processing operation. This paper describes one of the first steps taken in this process, namely the monitoring and control of residual collectors in their flotation circuits.

Boliden Kevitsa Mining Oy, a Cu-Ni-PGE concentrator recycles 90–95% of its water for use in the plant. The quality of recycled water tends to deteriorate as various elements and compounds such as Ca, Na, Mg, K,  $\text{SO}_4^{2-}$  and residual reagents accumulate. The accumulation shows seasonal cyclic variation that has an impact on flotation performance.

UV/VIS Spectrophotometry was employed to measure residual xanthates in key process streams and process return water from the Tailings Storage Facility. This allowed the implementation of dosage monitoring and control strategy with the objective of performance control and optimization throughout the seasonal changes during the year.

## 1. Introduction

Conservation and management of freshwater resources is one of the major challenges facing humanity in this century. The mining and mineral processing industries use water in all of their operations, from exploration, through mining and processing to closure. Limited availability of freshwater resources, government regulations, civil actions as well as the corporate sustainability policies and goals, put serious pressure on the mining industry. Therefore some minerals processing operations started evaluating and implementing water recycling to reduce fresh-water intake already in 1970s (Bailey, 1970; Pickett and Joe, 1974), bringing benefits both from cost effectiveness and sustainability points of view.

The quality of the water plays an important role in determining the performance of the flotation process. This has led to significant amount of research initiatives dealing with the impact of water re-use and water quality on flotation. Summaries of the findings have been published by Rao and Finch (1989), Johnson (2003), Liu et al., (2013). There is now a strong push for this aspect to be included in plant design as well.

The quality of water that is reused by recycling it back into the process tends to deteriorate as various inorganic and organic species accumulate in it altering the chemistry of the system. The accumulation of different species can have positive and negative effects as well. Pickett and Joe (1974) have found that water recycling in monometallic

or bulk flotation circuits such as the nickel-copper mills in Sudbury area does not cause serious problems. However, this is not the case for multistage circuits where selective flotation needs to be achieved. Residual collectors, such as xanthates and their oxidation products, activators or depressants can cause activation or depression when not desired.

Alkali metal ions such as  $\text{Ca}^{2+}$  can activate gangue minerals. Sulphate and thiosulphate generated during grinding can increase froth stability and decrease the grade of the concentrate (Biçak et al., 2012; Forssberg and Hallin, 1989; Johnson, 2003; Levay and Schumann, 2006; Rao and Finch, 1989).

Recycling of reagents can lower reagent consumption and therefore costs, however it can also have negative effect causing loss of selectivity between minerals. For example, the oxidation and degradation products of residual xanthates can be surface active, thus their adsorption in mineral surfaces could lead to loss of selectivity between minerals. The kinetics and mechanism of degradation is dependent on the pH and the temperature of the system as well as the residence time and the amount of UV light penetrating the liquid phase (Dautzenberg et al., 1984; Mustafa et al., 2004; Rao and Finch, 1989; Shen et al., 2016).

Research efforts are now focused on developing protocols for conserving water through reuse and recycling (Bridging North to South, 2016; ITERAMS, 2017) without suffering from the negative impacts of such practices whilst amplifying the positive aspects. These efforts

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amongst others, attempt to tackle the issues related accumulation of inorganic and organic species such flotation reagents that interfere with the optimal operation of the process.

This paper describes the approach we used at the Boliden Kevitsa mine for the monitoring and control of collector concentrations to improve the process performance.

## 2. Operational and environmental factors affecting process water quality at kevitsa operation

Boliden Kevitsa Mine treats low grade Cu-Ni-PGM ore in a sequential operation, with copper being floated first followed by nickel to produce two concentrates.

At the Boliden Kevitsa plant, water from precipitation, seepage groundwater and raw water from the water dam enters the site water inventory requiring some portion of the inventory to be treated and discharged to maintain the site water balance.

Notable elements that have been observed to accumulate in Kevitsa process water in a seasonal cyclic manner are Ca, Na, Mg, K and  $\text{SO}_4^{2-}$  and residual reagents i.e. frother and xanthate collectors. The seasonal variation in the water quality is clearly illustrated by the variation in the conductivity of the process water as shown in Fig. 1.

As it can be seen on the graph, the highest conductivity values are always detected in February–March, followed by a sharp decrease in the late spring and summer months. Nevertheless, the graph also shows an overall increase in conductivity values due to the accumulation of ionic constituents over time.

Seasonal variations with extreme winter conditions that prevail in winter have a direct impact on process water quality used at Kevitsa. Process water is reclaimed from the decant pond that forms at the centre of the Tailings Storage Facility (TSF). Inorganic substances and residual reagents are at their lowest in the spring and summer months because of dilution and decomposition especially for xanthate collectors. In summer with abundant sunlight from the long days, higher temperatures and significant water inventory (1.7 Million cubic metres) decomposition of residual xanthate is complete as the residence time in the tailings pond is longer, and the sunlight provides the UV light and elevated temperatures that speed up the decomposition reactions.

In winter, sub-zero temperatures prevail for 5–6 months during

which an ice cap forms on the decant pond. Elevated levels of residual reagents are observed in these months due to the formation of an ice cap on the process water pond which locks a significant amount of the decant pond inventory into the ice thus short circuiting the freshly deposited water to the decant pumps. With reduced residence time, lack of UV light and low temperatures in the dark and cold winter months to aid decomposition, more reagents and unsettled tailings are recycled back into the process with the water, which affects the flotation circuit performance. Additional to lack of UV, xanthate decomposition rate reduces with increase in pH and reduction in temperature (Mustafa et al., 2004). With final tails deposited at the Tailings Storage Facility (TSF) averaging pH 9.5 and sub-zero temperatures in the winter, xanthate decomposition in the TSF decant pond is severely inhibited.

Therefore the need to control the xanthate concentrations in the process was recognised earlier, however the systematic monitoring, evaluation and adjustment of xanthate dosages to suit the particular ore blend was only introduced in early 2017.

## 3. Water recirculation and process performance

Kevitsa water recycling rate ranges from 86% to 97% and the variation is driven by the amount of fresh raw water entering the site inventory for treatment to provide potable water and for mill motor cooling system heat exchangers. With potable water consumption being constant, the mill cooling water is the main variant and thus the recycling rate is dependent on this.

For purposes of evaluating circuit performance KPIs and operational conditions' relation to the amount of recycling taking place, the 'Water Intensity' parameter was derived. Water intensity in this case is simply the amount of fresh water taken into the inventory per day divided by the milled tonnage for that day, in other words, higher water intensity means more freshwater intake into the process. Plotting recycling rate against water intensity gave a linear relationship as shown in Fig. 2.

The period following commissioning and achievement of commercial production, the flotation performance of the plant varied significantly with changes in seasons. The circuit being a sequential Cu-Ni flotation requires limiting the flotation of Ni into the Cu concentrate. This is achieved by using a Cu selective collector (Aerophine) and high pH in the final cleaning stage. In winter recycling rates are at their

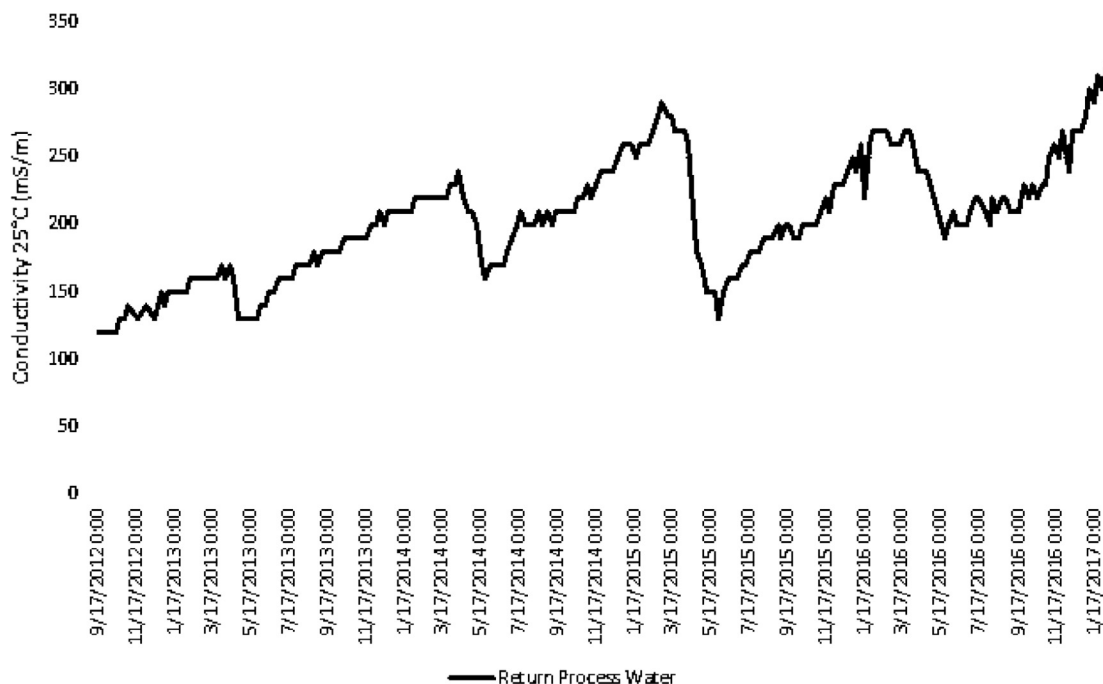


Fig. 1. Seasonal variation in Kevitsa process water conductivity between 2012 and 2017.

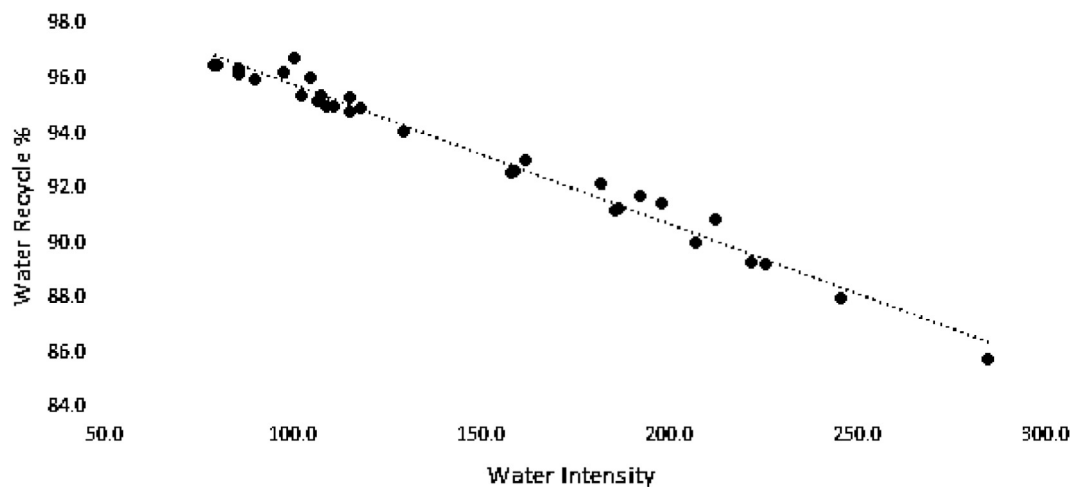


Fig. 2. Recycling rate vs water intensity.

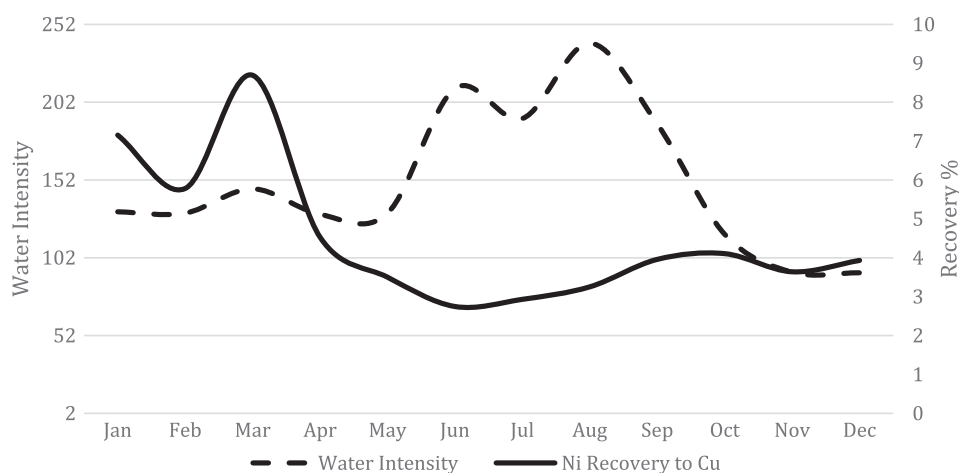


Fig. 3. Water intensity vs Ni recovered into the Cu concentrate.

highest owing to less demand of raw water for the mill motor cooling systems. Coupled with the poor quality of the water from the decant pond as a result of the winter conditions, it was observed that the Ni recovery in the Cu rougher and scavenger circuits increased significantly. Ultimately this led to the loss in selectivity in the Cu circuit as the concentrate produced contained higher amounts of Ni. Ni recovered to the copper concentrate is considered a loss because smelters do not pay for it. Fig. 3 shows a typical copper flotation performance varying in winter with respect to Ni recovered to copper concentrate in

the absence of any monitoring and corrective action to minimise this.

Figs. 4–6 show the recovery of Cu to Cu, Ni to Cu and Ni to Ni concentrates as a function of water intensity.

These figures clearly show, that lower water intensity viz. higher volume of recirculated water in the process results in loss of selectivity between Cu and Ni in the copper flotation (increased loss of Ni to the copper concentrate). Nevertheless both Cu and Ni recoveries have been observed to increase during this period whilst overall reagent consumption was reduced.

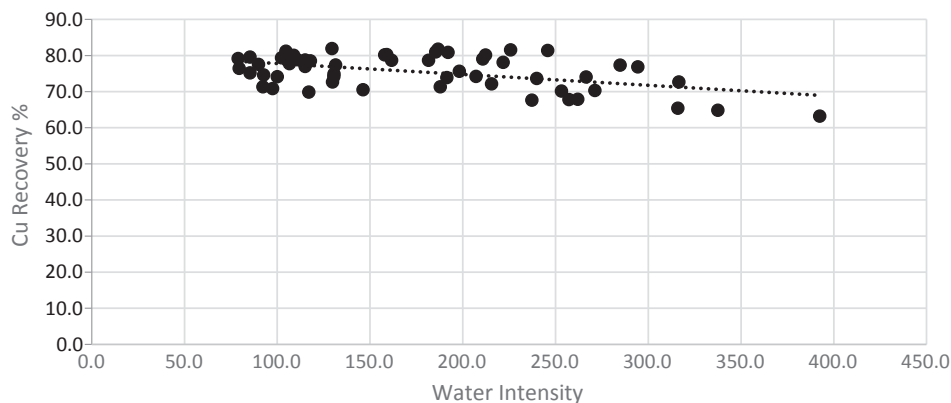


Fig. 4. Cu recovered to Cu concentrate vs. Water intensity observed in the Kevitsa operation.

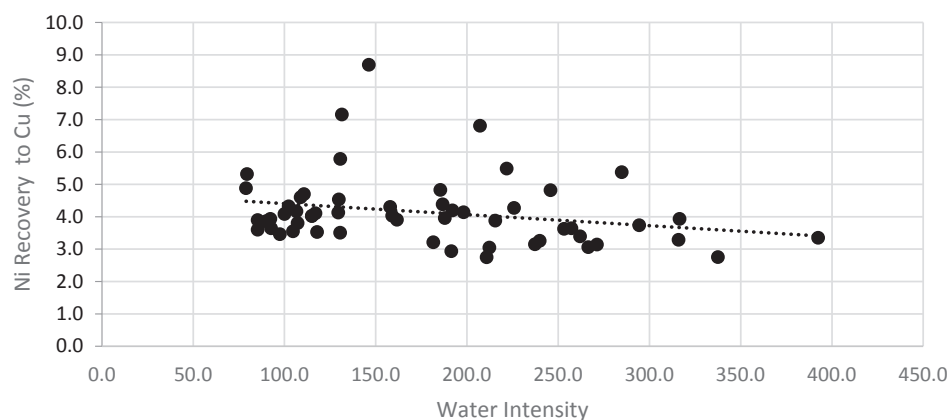


Fig. 5. Ni recovered to Cu concentrate as a function of Water intensity observed in the Kevitsa operation.

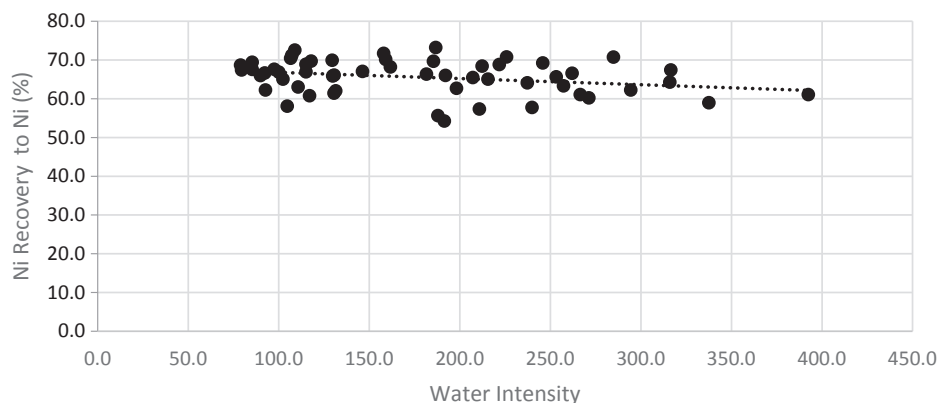


Fig. 6. Ni recovered to Ni concentrate vs. Water intensity observed in the Kevitsa operation.

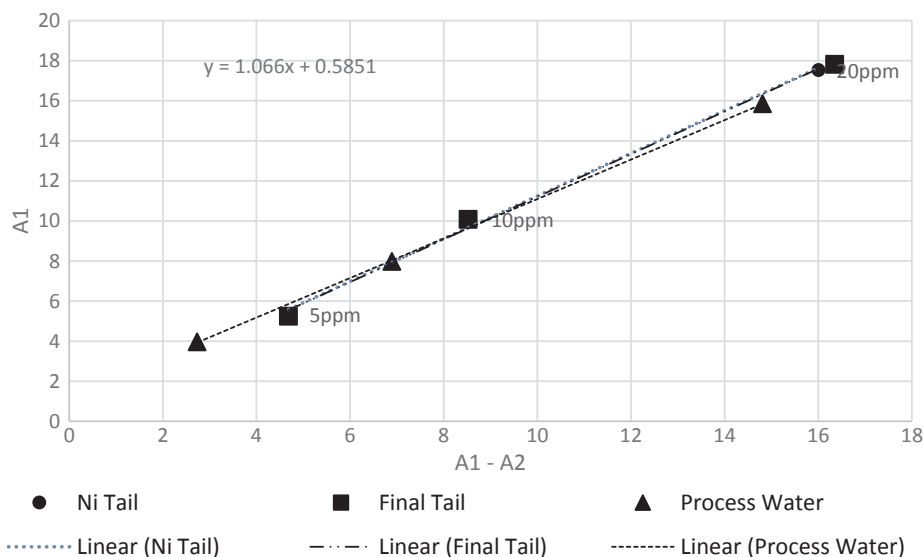


Fig. 7. Validation curves for Ni tailings, final tailings and process water.

#### 4. Xanthate concentration monitoring

In order to minimise the negative effects of the water recirculation caused by the residual reagents recirculated from the tailings pond, as described above, a systematic residual xanthate monitoring and control scheme was developed. The xanthate analysis methodology was based on the one described by (Jones and Woodcock, 1973). Even though this method is not suitable for quantifying the concentration of xanthate

degradation products also present in the process waters, that might have an effect on the flotation efficiency, the methodology was chosen as it is a relatively easy and cheap. Compared to more sophisticated technologies, such as capillary electrophoresis (Kemppinen et al., 2015) or GC-MS (Shen et al., 2016) that require highly trained personnel and sophisticated equipment, this method gives good indication on the xanthate concentrations present in the process waters based on which the reagent dosage rates can be decided.

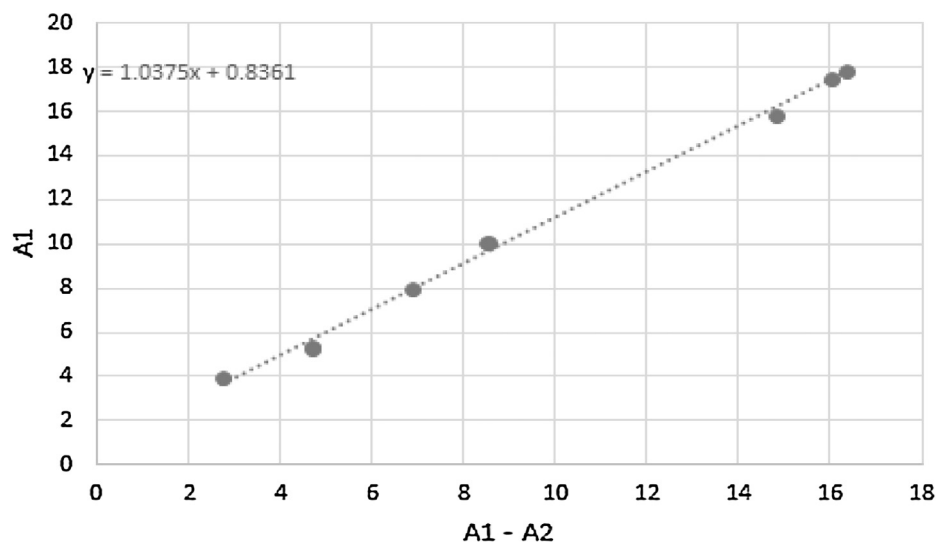


Fig. 8. Combined validation curve.

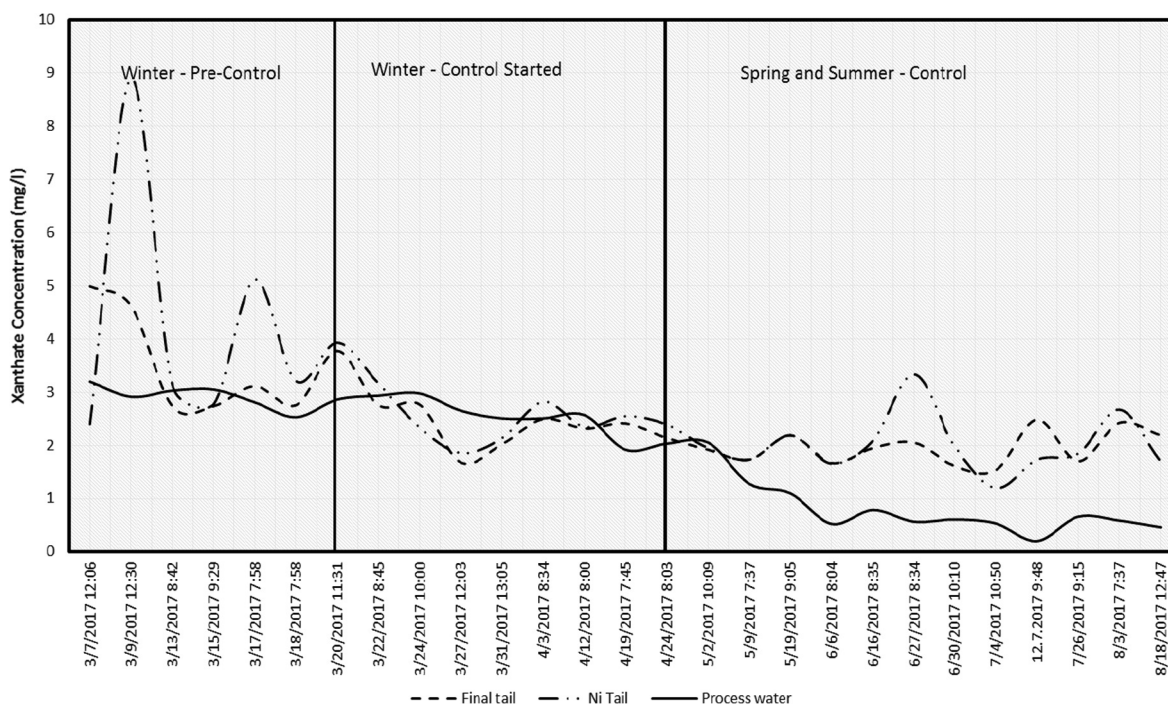


Fig. 9. Graph showing before and after control of xanthate and the change in season.

#### 4.1. Sampling

Water samples for the Nickel rougher scavenger tail, Final tails and Process return water are taken for xanthate analysis with the UV/VIS method. All three samples are filtered with a 20  $\mu\text{m}$  filter and the filtrate is collected and analysed.

#### 4.2. Xanthate analysis

A Hach DR 6000 UV–Vis Spectrophotometer is used at Kevitsa for xanthate analysis. The main xanthate in use at the concentrator is Sodium Isopropyl Xanthate (SIPX) which is used as a Ni collector. The spectrophotometer was first calibrated using known concentrations of SIPX collector made up using distilled water and measuring the absorbance (Absorbance range 200–450 nm). 301 nm is normally the wavelength where xanthate ions exhibit maximum absorption peak and

is used as a measure of xanthate concentrations (Jones and Woodcock, 1973).

A cuvette with distilled water is first read on the machine as a blank followed by the sample itself to give a xanthate concentration reading in mg/litre based on the calibration curve shown below.

$$y = 9.5907 \times \text{Measured Absorbance}$$

Special care is taken to ensure that the cuvette is clean and the water sample is filtered well enough not to contain any solids. This simple method as applied at Kevitsa assumes that there are no suspended solids or dissolved elements in the water that have the same absorbance at 301 nm under any pH condition.

However most samples have elements in solid form or in solution that have an absorbance at 301 nm under different states as follows:

1. Suspended solids or dissolved substances in the normal state of the



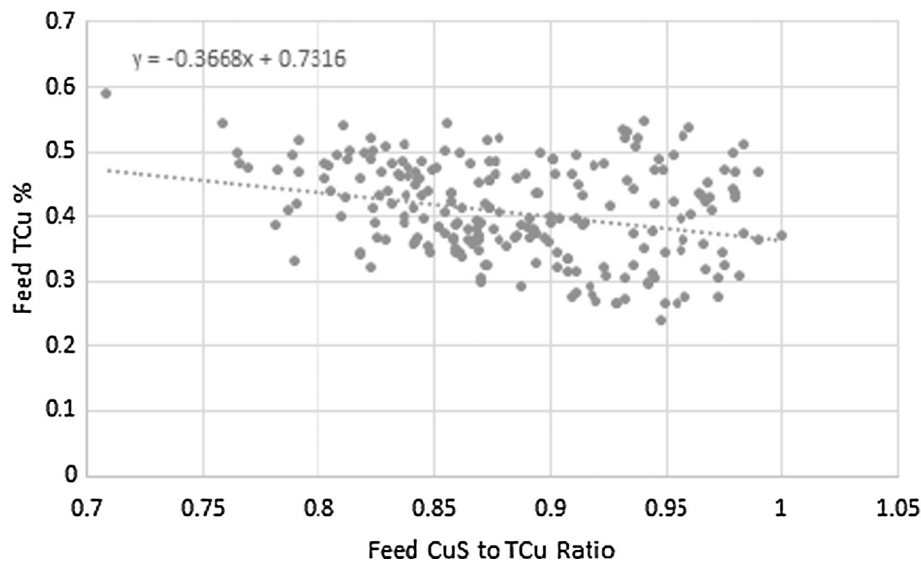


Fig. 10. Total Cu in Feed vs. Feed CuS/TCu.

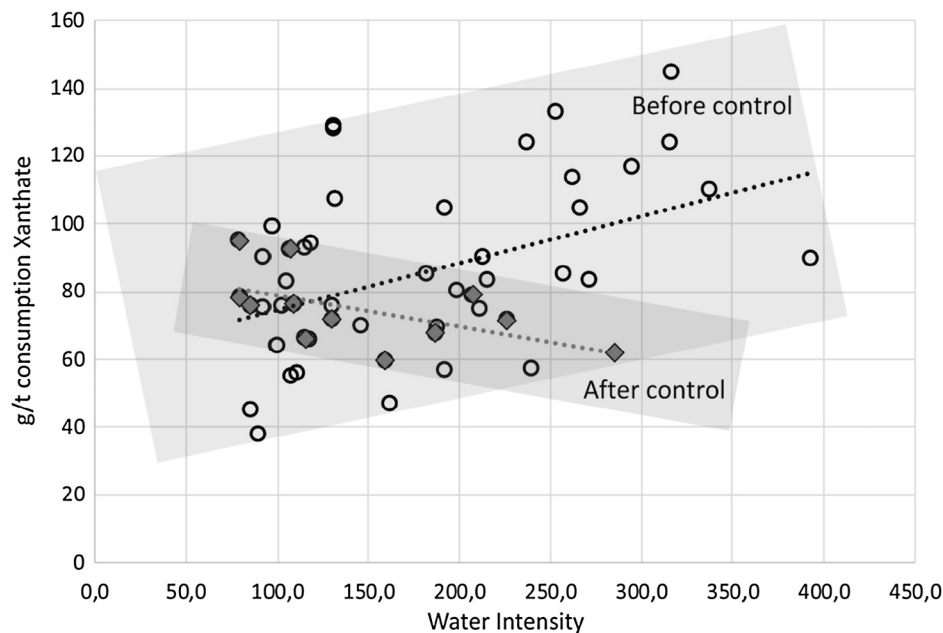


Fig. 11. Water intensity correlation with xanthate g/t consumption.

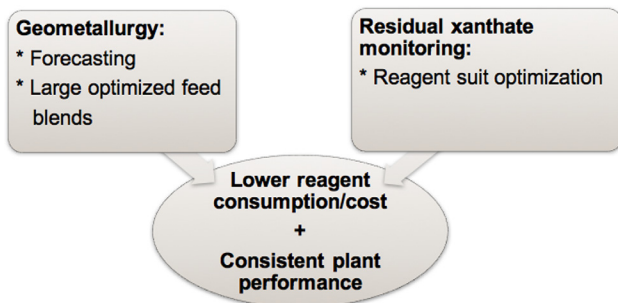


Fig. 12. Overview of the Kevitsa plant practice on combining geometallurgy with residual xanthate monitoring.

3. Suspended solids or dissolved substances with pH dependence in acidic solutions.
4. Suspended solids or dissolved substances with pH dependence in both alkaline and acidic solutions.

The effect of the suspended solids is not easily dealt with by filtration of the sample as there remain very fine suspended solids even after passing through a 0.05  $\mu\text{m}$  filter. For Kevitsa, validation tests were done by assuming that the water sample solutions had solids or elements with absorbance at 301 nm in both alkaline and acidic solutions.

#### 4.3. Validation procedure

Jones and Woodcock (1988, 1973) described four procedures for dealing with a wide variety of interfering compounds in solutions with unknown composition. Method 4 was chosen in this study, as the most generally applicable and suitable for solutions with unknown composition. The method consists of the following steps:

- water sample.
2. Suspended solids or dissolved substances with pH dependence in alkaline solutions.

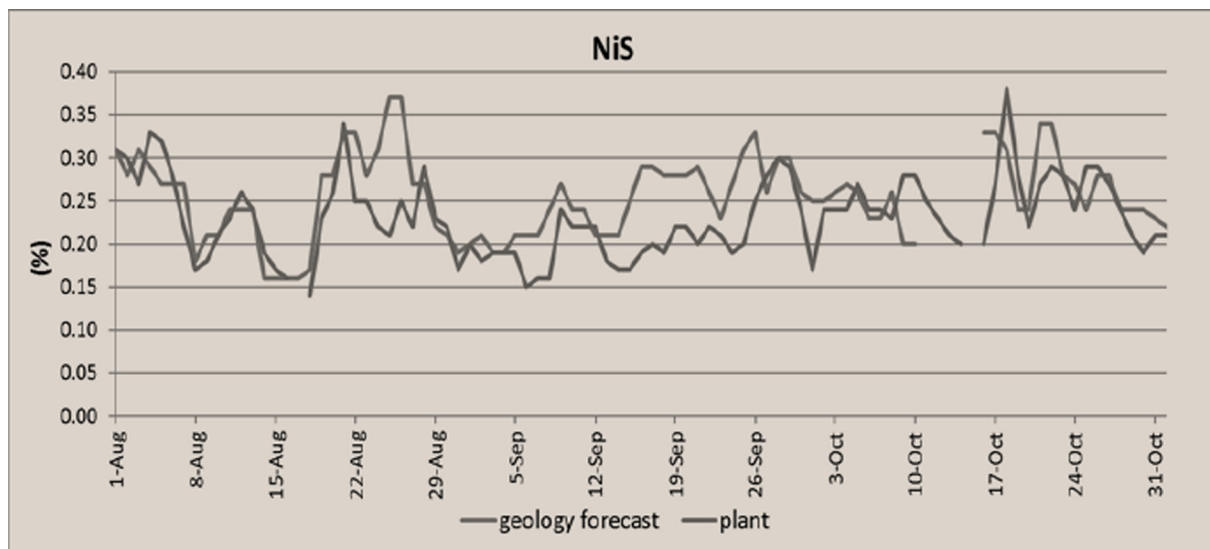


Fig. 13. Feed grade variation before ore control.

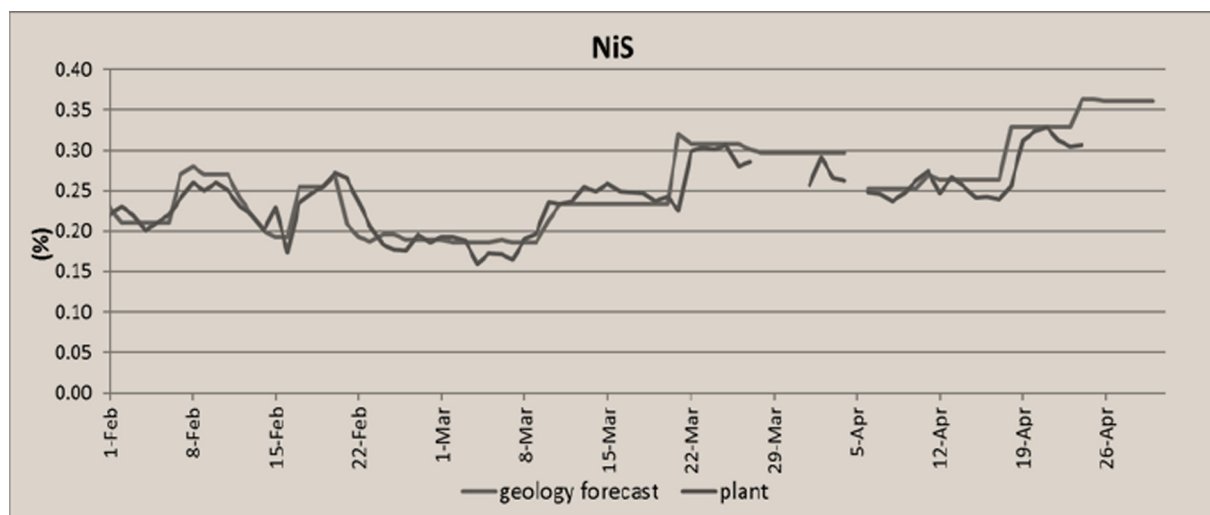


Fig. 14. Feed grade variation after ore control.

- The water sample is first filtered, pH measured and its absorbance measured at 301 nm as with the normal procedure.
- Following this, the pH of the same sample is adjusted to 6.5–6.8 using HCl and the absorbance A1 is measured at 301 nm.
- In the next step the pH is adjusted to less than 2. The sample is allowed to stand for at least 1 min to decompose the xanthate. NaOH is then added to bring the pH back to 6.5–6.8, the standard background condition and the absorbance A2 is measured.
- A1–A2 is a measure of the xanthate present in the original sample.

The validation tests were performed at such a time that there was little or no residual xanthate in the waters as it was the summer season. This required the modification of the validation procedure were the filtered sample water is used to make up 20, 10 and 5 ppm xanthate solutions before measuring A1, doing then pH adjustments and measuring A2.

#### 4.4. Application of the validation model

A1–A2 is the measure of the absorbance allocated to the xanthate which is dissolved by taking the pH down to 2. The assumption is that all the xanthate in the sample is dissolved at this pH. However this

seems not be the case based on the results of the validation. The results of the quick straight procedure plotted against the measurements done using the validation procedure for the three samples is shown in Fig. 7 for the different concentrations.

Because the three models for the 3 samples were quite similar it justified to combine of all the readings for the 3 samples over the three xanthate concentrations to get one model as shown in Fig. 8.

The validation procedure used exposed the following points:

- There is residual xanthates in the Ni tails and Final Tails samples and very little in Process water sample.
- The higher the xanthate concentration, the higher the background absorbance measured, indicating incomplete xanthate decomposition at pH 2. The time allowed for decomposition was identified as a factor and was targeted for investigation in forthcoming tests.

## 5. Results and discussion

### 5.1. Effect of feed mineralogy – increase of cut-off grade in 2017

Measurements of the xanthate concentrations in the process water recycled from the tailings pond and two plant slurry tailings samples



was initiated in March 2017 for the purposes of monitoring and control. Fig. 9 shows the residual xanthate measurements from March to date. It can be seen that owing to summer conditions, dilution from water release during the spring melt and the increased raw water intake for mill motor cooling systems, the xanthate concentration values in the process water recycled from the tailings drop significantly.

It can also be observed that with the monitoring procedure and dosage control in place there is tighter control on xanthate addition and thus the xanthate concentration readings in the tailings stream measured fluctuate less. Improvements in flotation performance are less apparent owing to the ore feed mineralogy changes that occurred late 2016 into 2017. Cut-off grade was increased and with it the presence of a secondary copper mineral Cubanite. It is apparent that the increase in the cut-off grade has more Cu deported into non-sulphide mineral species (silicates) as shown in Fig. 10.

Elevated levels of Cubanite have the effect of reducing Cu recovery to copper concentrate owing to the slower floatability of Cubanite to Chalcopyrite the main Cu mineral. The presence of Cubanite requires operating the Cu circuit at a lower point on the concentrate grade vs. recovery curve. Cubanite with the formula  $\text{CuFe}_2\text{S}_3$  has more iron and sulphur for one atom of Cu compared to chalcopyrite  $\text{CuFeS}_2$ . The concentrate grades achieved for the same feed grades and mineral recovery are lower as a result.

Total reagent consumption with higher recycling reagents in winter is lower than in the summer months. An evaluation correlating water intensity vs. xanthate g/t consumption before and after the implementation supports this finding. Fig. 11 shows the reduced variation in the dosage rates and consumption rate of xanthate. This is attributed to implementation of control and also the change to a stronger xanthate type done for improved Ni recoveries.

Residual xanthate control implementation was coupled with the Ore control project which was already running to reduce feed variability in with respect to grade and mineralogy (Fig. 12).

The improvements arising from ore control is illustrated by Figs. 13 and 14, before and after ore control, showing forecasted vs plant feed grade trends.

Consistent feed quality over a longer period allowed operations to set optimum xanthate dosages at the onset of a new feed blend. This was then maintained for the duration of the feed blend (several days) before any changes were required giving less variations in dosage rates and residual xanthate measured in the 3 streams.

## 6. Conclusions

UV/VIS is simple and easy method to measure residual xanthate concentrations in critical flotation concentrator streams where xanthate is the primary collector. This allows for better control of dosage rates to prevent either over or under dosing which is detrimental to a flotation performance from a reagent cost, xanthate recirculation (over collection and loss in selectivity) and recovery point of view.

Measurement and control of xanthate addition also allows for different strategies to be adopted to mitigate against some of the adverse effects brought about by seasonal climate conditions. Kevitsa now intentionally takes in raw water into the inventory in winter to improve

the quality of the water. This enables the maintenance of some selectivity between Cu and Ni in the Cu circuit.

Loss of selectivity is weighed against the benefits in improved recovery and thus an optimum water intensity point needs to be established for each plant and would require a cost benefits analysis to be performed. Another aspect for recycling is the overall reduction in reagent g/t consumption of xanthate and even frother for that matter an aspect not focused on in this paper. This ability to measure xanthate in the process water opens up possibilities to recycle some xanthate in the waters for the benefits mentioned above.

Lower overall reagent consumption for a concentrator like the likes of Kevitsa means reduced environmental impact be it the need to use energy and more chemicals in water treatment before discharging into the environment. Cost savings are realised from power and operational costs associated with running these plants.

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