

Article

Influence of Water Quality on Sulphide Ore Oxidation and Speciation of Sulphur Anions during Autogenous Milling

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Abstract: Earlier studies at the Kevitsa Cu-Ni concentrator plant have indicated that seasonal variations of the properties of the process water affect the oxidation of the surface of the minerals, and further, the pentlandite flotation performance. However, it is not clear whether the differences in flotation performance are solely due to changes in the mineral surface oxidation, and/or also due to surface oxidation-induced changes in the aqueous phase of the pulp. This paper investigates the effects of the mineral surface oxidation of Kevitsa Cu-Ni ore on the properties of the aqueous phase of the slurry. A systematic study was formulated to monitor the surface oxidation related changes in the mill circuit of the Kevitsa concentrator plant. The study was timed to coincide with a seasonally observed drop in the concentrator plant's flotation performance, which happens during the summer months (June, July, and August). Both physicochemical parameters, as well as sulphur oxyanions in the plant process water, mill discharge, and hydrocyclone overflows were monitored. Also, the bubble size in selected rougher and cleaner cells was monitored. The results show that season-related changes in mineral surface oxidation cause clear differences in the aqueous phase chemistry of the mill circuit. The increased concentration of reduced sulphur species in the mill discharge is an indication of extensive oxidation of the ore during milling. Also, the bubble size of the flotation cells reacts to the observed seasonal change. The findings of the study confirm that the consequences expected, based on the theory of mineral surface oxidation, are observable downstream in the aqueous phase of the milling circuit. Based on these results, it is not yet possible to say whether the poor flotation performance is caused solely by the oxidation of the mineral surface or also by the properties of the aqueous phase of the slurry after milling. However, the results show that the plant needs both to find ways to limit oxidation rates in the summer, and to consider installing a more robust frother, capable of maintaining efficacy during the warm season. The findings of this study may help the plant to develop ways to enable a timely response to changes in the recycled process water quality, to prevent harmful impacts on pentlandite flotation. The former could be achieved by lowering the temperature of the process water and flotation air, whereas the latter could mean using a different frother.

Keywords: sulphuroxy anions; oxidation products; plant performance; flotation; pentlandite

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1. Introduction

Based on previous studies, process water quality seems to play an important role in influencing the flotation behaviour of sulphide minerals. In a closed process water loop, the process water quality increasingly changes with the number of loops and seasonal temperatures. Recent studies have shown, e.g., a cyclic pattern for water parameters such as conductivity, pH, redox potential, metals, and sulphur oxyanion species [1–3]. In particular, the possible impacts of thiosalts on the flotation of sulphide minerals have been widely studied by numerous researchers [4–6]. The focus has been on understanding how sulphuroxy

species influence the flotation behaviour of sulphide minerals. Kasymova et al. concluded that only sulphite had a detrimental effect on the flotation of sulphide minerals [4]. Another researcher reported that increasing the amounts of thiosulphate up to 78 ppm showed improved flotation performance for nickel minerals [5]. Mhonde et al. found that thiosulphate ions negatively affected collector adsorption on sulphide minerals [6]. Furthermore, other researchers have also reported that surface oxidation rates can be affected by various factors such as dissolved oxygen concentration, pH, temperature, ferric iron concentrations, galvanic effects, and surface area [7–10].

When studying the effect of sulphuroxy anions on flotation performance, researchers have typically used synthetic water with varying amounts of sulphuroxy anions, or real process water with spiked amounts of sulphuroxy anions. Although these two approaches have aimed to produce research data and knowledge on the effects of sulphur oxyanions on flotation performance, they do not necessarily take into account the fact that the composition of the water phase of the pulp can change significantly within the milling circuit. As a result, when the first flotation stage finally begins, the composition of the aqueous phase of the pulp may differ significantly from the composition of the original recycled process water.

In well-controlled laboratory conditions, such changes in the composition of the aqueous phase of the pulp may remain minor, but on a plant scale, the changes may become significant. For example, the wide operating temperature range of plants can affect the reactivity of mineral surfaces [2], e.g., seasonal variations of the temperature of the process water, and an increase in the temperature of the pulp during grinding, can significantly contribute to the oxidation rates of the mineral surfaces, and further to the composition of the aqueous phase of the pulp. However, few studies have examined how the composition of the aqueous phase of the pulp changes as the processing progresses under variable conditions. Thus, it remains unclear which effect is ultimately more significant in terms of flotation performance, the quality of the recycled process water before grinding or the composition of the aqueous phase of the pulp just before the start of flotation.

At Kevitsa mine, the weak flotation performance of pentlandite during the warm summer months has been related to the changing properties of the recycled process water [2]. Not only does the temperature of the recycled process water increase towards the warm summer months, but the temperature increase also speeds up oxidation reactions in the tailings pond during the summer months, resulting in a significant drop in the pH of the recycled process water [3,11]. Then, the quality of the recycled process water is also characterized by the increased concentration of dissolved metals and higher-oxidation state sulphur compounds. A more detailed study at the Kevitsa plant also showed that the change in the quality of the recycled process water resulted in a clear increase in the surface oxidation of sulphide minerals during grinding, which then apparently reduced the flotation recovery of pentlandite [3]. Given the context, the rationale for this work arises from the question: how much do these significant changes in mineral surface oxidation during grinding affect the chemistry of the aqueous phase of the pulp just prior to flotation. However, studies on the oxidation kinetics of mineral surfaces processed in concentrators, and its consequences, are strongly dependent on the plant's conditions and residence times. These conditions and phenomena are very difficult to imitate in laboratory experiments, and therefore this research was carried out as an industrial case study at the Boliden Kevitsa concentrator plant.

In this study, an approach was taken to monitor how the quality of the aqueous phase of the pulp changes in the grinding circuit of a full-scale concentrator plant. Special emphasis is placed on the months when the most significant decline in pentlandite flotation recovery has been observed. In more detail, it is of interest to study how the electrochemical changes in the mineral surfaces during grinding are manifested in the aqueous phase chemistry of the mill circuit, and especially in the sulphur oxyanion concentrations. Therefore, the study focused on the following plant streams: recycled process water, mill discharge, and hydrocyclone overflow. This study was based on previous findings showing that in the warm season, extensive oxidation of pentlandite minerals occurs before the flotation

process begins [3]. It is expected that changes in the aqueous phase composition caused by oxidative dissolution of sulphide minerals can be verified with this approach. All in all, this study is most likely to help direct future studies to answer the important question of whether the flotation performance is more dependent on the degree of oxidation of the mineral surfaces and the products of the oxidation reactions formed during grinding, or only on the properties of the process water fed to the grinding.

2. Materials and Methods

2.1. Case Description

The Boliden Kevitsa concentrator plant is located in northern Finland and processes low-grade Cu-Ni-PGE ores. Due to its geographical location, approximately 140 km north of the Arctic Circle, the plant experiences extreme weather conditions. The difference in temperatures from summer to winter is +35 degrees Celsius to −40 degrees Celsius, respectively.

Commissioned in 2012, the plant produces copper and nickel concentrate through sequential flotation. Prior to Cu-Ni sequential flotation, the ore is milled in autogenous mills using recycled process water from the tailings pond. The plant recirculates over 90% of the process water through a tailings pond. Since its commissioning, the plant has focused on improving its fines recovery, since it struggles with high losses of pentlandite minerals in the fine fraction.

Over the years, the plant has repeatedly identified a decline in the flotation performance that coincides with a seasonal change. To match the study with the problematic season, this study was carried out during that season, from June to August. This helped us to study what kind of changes the oxidative dissolution of sulphide minerals causes in the aqueous phase of the milling circuit.

This case study was based on industrial data obtained from manual sampling campaigns and from the plant's historian. Even though researching the topic in a laboratory would be more scientific in many ways, a case study was decided on for many reasons: As changes in conditions and physicochemical parameters promote the surface oxidation and possibly also affect the speciation of oxidation products in the grinding circuit, mimicking all these factors at a laboratory scale is difficult, if not impossible. Therefore, an industrial case study approach was selected.

2.2. Materials

Table 1 shows the mineralogy and chemical assays of the ore during the sampling campaign. The major non-sulphide gangue minerals include the pyroxene group [12]. The ratio of pyrrhotite to pentlandite (Po/Pn) has been included in the table.

Table 1. Mineral assays for Kevitsa Ore.

| Sampling Week | Chalcopyrite (%) | Pentlandite (%) | Pyrrhotite (%) | Po/Pn | Non-Sulphide Gangue (%) |
|---------------|------------------|-----------------|----------------|-------|-------------------------|
| Week 1 | 0.52 | 0.49 | 0.49 | 1.0 | 98.43 |
| Week 3 | 0.31 | 0.21 | 0.30 | 1.4 | 99.19 |
| Week 5 | 0.88 | 0.28 | 0.23 | 0.8 | 98.60 |
| Week 7 | 0.45 | 0.31 | 0.83 | 2.7 | 98.41 |
| Week 9 | 0.68 | 0.44 | 0.69 | 1.6 | 98.19 |
| Week 11 | 0.88 | 0.51 | 0.86 | 1.7 | 97.75 |
| | Cu (%) | Ni (%) | Fe (%) | Co | S (%) |
| Week 1 | 0.25 | 0.23 | 5.40 | 0.01 | 1.14 |
| Week 3 | 0.18 | 0.21 | 4.36 | 0.01 | 0.89 |
| Week 5 | 0.29 | 0.23 | 5.29 | 0.01 | 1.13 |
| Week 7 | 0.21 | 0.25 | 5.20 | 0.01 | 1.20 |
| Week 9 | 0.30 | 0.22 | 5.88 | 0.01 | 1.52 |
| Week 11 | 0.35 | 0.23 | 6.19 | 0.01 | 1.62 |

X-ray diffraction (XRD, CubiX³, Malvern Panalytical Ltd., Malvern, UK) analysis was used to determine the mineral distribution in the mill discharge. Slurry samples were collected, filtered, dried, and submitted for XRD analysis.

2.3. Sampling Scheme for Plant Sampling Campaign

The samples were taken on a bi-weekly basis from 1 June to 10 August. The sampling period was chosen to coincide with the seasonally observed drop in the plant's flotation performance.

The Kevitsa concentrator's flowsheet is described by Musuku et al. [12]. The process begins with the crushing of ore from the open pit and stockpiling it for milling. The crushed ore is milled by four autogenous mills and the mill discharge classified using hydrocyclones, as shown in Figure 1. The cyclone overflow is fed to the Cu circuit, where Cu concentrates are produced. The tailings from the Cu circuit are fed as feed to the Ni circuit, and Ni concentrates are produced. The Ni tailings are separated into high and low sulphur tailings and stored in separate tailings ponds for environmental reasons. The recycled process water used for milling and flotation is reclaimed from the tailings ponds.

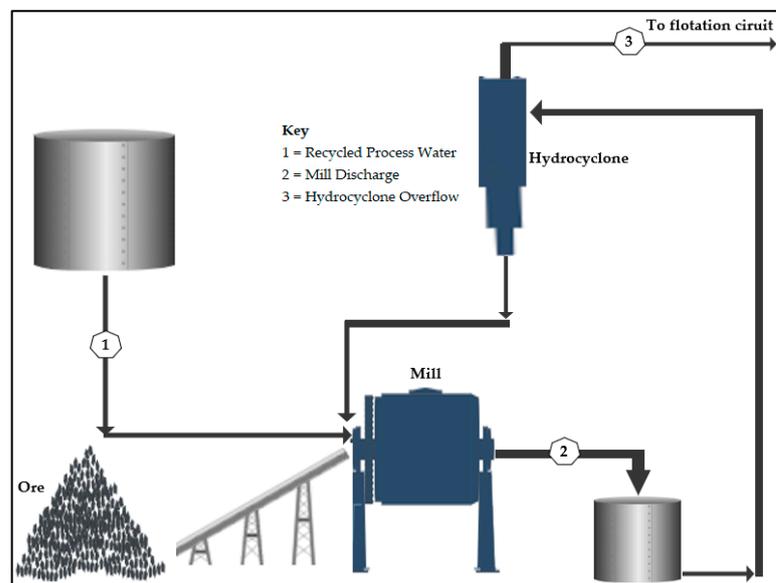


Figure 1. Sampling points around the autogenous primary mill (8.5 m × 8.5 m, 7000 KW). Sampling point 1 is process water, sampling point 2 is mill discharge and sampling point 3 is hydrocyclone overflow.

The main reagents used during flotation are Aerophine 3418A, Nasfroth 240, lime, and sodium isopropyl xanthate. No reagents are added during milling. In this study, representative samples were taken for chemical analyses from various locations of this mill circuit, as numerically indicated in Figure 1.

2.4. Measurements of Physicochemical Parameters

Water and slurry samples were collected from the respective sampling points shown in Figure 1 and immediately measured for their physicochemical parameters (pH, ORP, dissolved oxygen, conductivity, and temperature) by using a calibrated YSI ProDSS multi-parameter probe (YSI, Xylem Inc., Yellow Spring, OH, USA). The readings were recorded in 30 s measurement periods for a total period of 10 min. The objective was to observe the change in parameters with time. However, Table 2 presents 2-minute averages of the parameters, as these can be better considered as the in-situ parameters of the process.

Table 2. Physicochemical parameters of process water and slurry samples.

| Process Water | Temperature (°C) | Dissolved Oxygen (ppm) | SPC $\mu\text{S}/\text{cm}$ | pH | Redox Potential mV |
|-------------------------|------------------|------------------------|-----------------------------|-----|--------------------|
| Week 1 | 12 | 8 | 2870 | 7.3 | 124 |
| Week 3 | 13 | 8 | 3087 | 7.1 | 273 |
| Week 5 | 19 | 5 | 3112 | 6.6 | 355 |
| Week 7 | 17 | 6 | 3061 | 6.9 | 368 |
| Week 9 | 18 | 4 | 3137 | 6.7 | 282 |
| Week 11 | 16 | 4 | 3219 | 8.0 | 107 |
| Mill Discharge | | | | | |
| Week 1 | 29 | 3 | 1464 | 9.3 | 189 |
| Week 3 | 31 | 4 | 1867 | 9.4 | 210 |
| Week 5 | 34 | 1 | 1669 | 9.4 | 115 |
| Week 7 | 34 | 2 | 1546 | 9.2 | 243 |
| Week 9 | 32 | 2 | 1738 | 9.4 | 250 |
| Week 11 | 30 | 2 | 1696 | 9.5 | 207 |
| Cyclone Overflow | | | | | |
| Week 1 | 25 | 6 | 2272 | 9.4 | 63 |
| Week 3 | 26 | 7 | 2548 | 9.5 | 81 |
| Week 5 | 31 | 5 | 2620 | 9.5 | 84 |
| Week 7 | 30 | 6 | 2351 | 9.4 | 103 |
| Week 9 | 29 | 6 | 2578 | 9.5 | 159 |
| Week 11 | 27 | 6 | 2719 | 9.6 | 90 |

2.5. Chemical Analysis of Water and Slurry Samples

Water and slurry samples were immediately stored in clean bottles after sampling and deep frozen at $-20\text{ }^{\circ}\text{C}$ to preserve the integrity of the samples. The deep-frozen samples were sent to the laboratory for further preparation and analyses (Metso Outotec Dewatering Technology Center (DTC) in Lappeenranta, Finland). The water and slurry samples were thawed just before analysis. The samples were left thawing at room temperature overnight but did not thaw properly by morning and were therefore placed in a sink with lukewarm water and shaken from time to time until defrosted. The slurry samples were vacuum filtered immediately after thawing. About 100 mL of the thawed water samples and filtrates of slurry samples were additionally filtered with $0.45\text{ }\mu\text{m}$ syringe filters and immediately analysed for thiosalts concentrations. The rest of the water samples and the slurry filtrates was sent to an accredited laboratory for the determination of total and dissolved calcium (Ca) and magnesium (Mg), sulphates (SO_4^{2-}), and total sulphur (S). The samples were kept cold until analysis.

2.5.1. Determination of Thiosalts, Sulphate and Total Sulphur

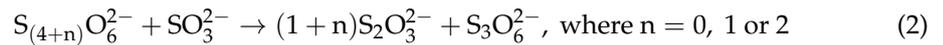
The iodometric titration method was used to determine thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and polythionates (as a sum of $\text{S}_4\text{O}_6^{2-}$, $\text{S}_5\text{O}_6^{2-}$, and $\text{S}_6\text{O}_6^{2-}$) ions. The method is based on a redox reaction between iodine and thiosulphate in the sample. The part of the added iodine that did not react with thiosulphate in the sample is then titrated with thiosulphate standard solution. The end point of the titration is determined potentiometrically, and the results are calculated based on the amount of the thiosulphate standard solution that was consumed by reaction with the excess iodine that was left in the sample. One sample was subjected to a series of two titrations, in which some of the analytes were masked or pre-treated prior to the addition of iodine and subsequent titration. The first series shows the amount of thiosulphate in the sample, while the second series shows the sum of thiosulphate and polythionates in the sample. By subtracting one from the other, separate values for thiosulphate and polythionates can be calculated.

In the first series of titrations, part of the added iodine reacts with thiosulphate according to reaction (1) below [13,14]:



The sample is then subjected to a titration with a thiosulphate standard solution. The part of the iodine that does not react with thiosulphate in the sample, reacts with the titrant, as described above. Once the end point is determined, the volume of titrant is recorded and used for calculating the amount of thiosulphate in the sample.

In the second series, the sample is first treated with an excess of sulphite to produce thiosulphate from polythionates according to reaction (2):



The excess of sulphite is masked with formaldehyde to avoid a reaction between sulphite and iodine [13,14]. Added formaldehyde forms formaldehyde bisulphite with the sulphite ions present in the sample according to reaction (3):



The thiosulphate is then treated with iodine and titrated as described above.

Sulphite (SO_3^{2-}) ions were analyzed spectrophotometrically Hach DR6000 UV/Vis spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany) with LCK654 cuvette tests were used to determine concentration of sulphite. An aliquot of a 0.45 μm filtered sample was added directly to the Hach LCK cuvettes. The detailed procedure for LCK cuvette tests can be found on the Hach web site. After the sample was prepared in a cuvette according to the procedure, it was placed in the Hach Lange DR6000 UV/Vis spectrophotometer and analyzed automatically by reading the barcode on the side of the cuvette. For analyzing sulphite with LCK654 cuvette tests, only the visible light spectrum is needed. Thus, the cuvettes do not have to be analyzed with a DR6000 that is equipped with a UV lamp as well, and smaller equipment with only the visible spectrum can be used, such as a Hach Lange DR3900 or DR1900 (Hach Lange GmbH, Düsseldorf, Germany).

Sulphate (SO_4^{2-}) ions were determined with 930 Compact IC Flex ion chromatographer (Metrohm, Herisau, Switzerland).

Total sulphur was determined by ICP-OES (inductively coupled plasma optical emission spectrometry) method with Thermo iCAP 6500 Duo analyzer (Thermo Scientific, Rugby, England).

2.5.2. Determination of Total and Dissolved Calcium and Magnesium

Total and dissolved Ca and Mg were determined by an ICP-OES (inductively coupled plasma optical emission spectrometry) method with Thermo iCAP 6500 Duo analyzer (Thermo Scientific, Rugby, England). To determine the dissolved metal concentrations in the aqueous phase, the samples were filtered through a 0.45 μm Millipore filter before ICP-OES determination.

2.6. Bubble Size Measurement

The Kevitsa process plant is equipped with froth cameras (FrothSense™, Metso Outotec, Espoo, Finland) on selected rougher and cleaner cells. The cameras are capable of measuring froth velocity and speed, bubble size distribution, stability and collapse rate, bubble loading, etc. The bubble-size data was collected from the Kevitsa plant's historian and analysed.

2.7. Plant Flotation Response

Plant performance data was collected from the Kevitsa plant historian for all the days of sampling. The plant performance was calculated using the following Equation (4):

$$\text{Plant Performance} = \frac{\text{Ni Recovery (\%)}}{\text{Ni Concentrate grade (\%)}} \quad (4)$$

2.8. Sulphur Compounds Speciation in Process Water, Mill Discharge and Hydrocyclone Overflow

The sulphur species were determined by calculating the amount of sulphur in sulphates and expressing it as a percentage of total sulphur. It was then assumed that the difference between total sulphur, and sulphur in sulphates, accounts for the reduced sulphur species. Equations (5) and (6) show how the sulphur species were calculated:

$$\% \text{ Sulphur in Sulphate} = \frac{0.33 \times (\text{Sulphate Concentration})}{\text{Total Sulphur concentration}} \quad (5)$$

$$\% \text{ Sulphur in Thiosalts} = 100\% - \% \text{ Sulphur in Sulphates} \quad (6)$$

3. Results

3.1. Sulphur Speciation in Process Water, Mill Discharge and Hydrocyclone Overflow

Table 3 shows the concentrations of total sulphur and calculated sulphur species using the ratio of sulphur in sulphate (0.33).

Table 3. Distribution of percent sulphur in sulphates and thiosalts in process water, mill discharge, and hydrocyclone overflow.

| Process Water | Sulphate ppm | Total Sulphur ppm | % Sulphur in Sulphate | % Sulphur in Thiosalts |
|-------------------------|--------------|-------------------|-----------------------|------------------------|
| Week 1 | 600 | 230 | 87 | 13 |
| Week 3 | 700 | 280 | 83 | 17 |
| Week 5 | 730 | 280 | 87 | 13 |
| Week 7 | 1100 | 410 | 89 | 11 |
| Week 9 | 790 | 290 | 91 | 9 |
| Week 11 | 820 | 290 | 94 | 6 |
| Mill Discharge | | | | |
| Week 1 | 540 | 230 | 78 | 22 |
| Week 3 | 610 | 260 | 78 | 22 |
| Week 5 | 640 | 260 | 82 | 18 |
| Week 7 | 570 | 240 | 79 | 21 |
| Week 9 | 630 | 270 | 78 | 22 |
| Week 11 | 690 | 310 | 74 | 26 |
| Cyclone Overflow | | | | |
| Week 1 | 550 | 230 | 80 | 20 |
| Week 3 | 620 | 250 | 83 | 17 |
| Week 5 | 660 | 270 | 81 | 19 |
| Week 7 | 580 | 230 | 84 | 16 |
| Week 9 | 650 | 270 | 80 | 20 |
| Week 11 | 720 | 280 | 86 | 14 |

3.2. Plant Performance Bubble Sizes, and Metastable Sulphur Oxyanions

The plant performance was calculated using Equation (1) and is presented in Table 4. The bubble sizes of nickel in the rougher and cleaner flotation cells were also monitored. The average bubble size diameters are reported in Table 4.

Table 4. Plant performance and bubble size of rougher and cleaner flotation cells.

| Sampling Week | Plant Performance | Bubble Size mm Rougher Cells | Bubble Size mm Cleaner Cells |
|---------------|-------------------|---------------------------------|---------------------------------|
| Week 1 | 7.8 | 50 | 32 |
| Week 3 | 7.6 | 38 | 29 |
| Week 5 | 6.7 | 27 | 22 |
| Week 7 | 6.5 | 32 | 19 |
| Week 9 | 5.9 | 25 | 25 |
| Week 11 | 6.1 | 31 | 25 |

Thiosulphate ($S_2O_3^{2-}$), polythionates (as a sum of $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$), sulphite (SO_3^{2-}), and sulphate (SO_4^{2-}) were analysed in the process water, mill discharge, and hydrocyclones overflow samples. Table 5 shows the concentrations of sulphuroxy anions in the process water, mill discharge, and hydrocyclones overflow.

Table 5. Sulphuroxy compounds in process water, mill discharge, and hydrocyclones overflow.

| Process Water | Sulphate ppm (SO_4^{2-}) | Sulphite ppm (SO_3^{2-}) | Thiosulphate ppm ($S_2O_3^{2-}$) | Polythionates ppm (as a Sum of $S_4O_6^{2-}$, $S_5O_6^{2-}$ and $S_6O_6^{2-}$) * |
|-------------------------|---------------------------------|---------------------------------|---------------------------------------|---|
| Week 1 | 600 | 4 | 13 | 23 |
| Week 3 | 700 | 5 | 27 | 15 |
| Week 5 | 730 | 0 | 28 | 12 |
| Week 7 | 1100 | 4 | 24 | 10 |
| Week 9 | 790 | 4 | 26 | 6 |
| Week 11 | 820 | 4 | 12 | 6 |
| Mill Discharge | | | | |
| Week 1 | 540 | 7 | 60 | 6 |
| Week 3 | 610 | 8 | 50 | 4 |
| Week 5 | 640 | 8 | 71 | 5 |
| Week 7 | 570 | 7 | 61 | 5 |
| Week 9 | 630 | 8 | 76 | 2 |
| Week 11 | 690 | 8 | 59 | 7 |
| Cyclone Overflow | | | | |
| Week 1 | 550 | 6 | 45 | 10 |
| Week 3 | 620 | 7 | 46 | 13 |
| Week 5 | 660 | 8 | 58 | 0 |
| Week 7 | 580 | 7 | 76 | 0 |
| Week 9 | 650 | 7 | 53 | 4 |
| Week 11 | 720 | 7 | 30 | 7 |

* Total concentration of polythionates presented as $S_4O_6^{2-}$ -equivalent.

3.3. Total and Dissolved Calcium and Magnesium

The total and dissolved calcium (Ca) and magnesium (Mg) were analysed for all the process water, mill discharge, and cyclone overflow samples. The values are presented in Table 6.

Table 6. Concentrations of magnesium and calcium in process water, mill discharge, and hydrocyclones overflow.

| Process Water | Total Magnesium ppm (Mg) | Total Calcium ppm (Ca) | Dissolved Magnesium ppm (Mg) | Dissolved Calcium ppm (Ca) |
|-------------------------|-----------------------------|---------------------------|---------------------------------|-------------------------------|
| Week 1 | 69 | 160 | 69 | 160 |
| Week 3 | 78 | 190 | 76 | 190 |
| Week 5 | 75 | 210 | 73 | 210 |
| Week 7 | 99 | 310 | 99 | 310 |
| Week 9 | 72 | 230 | 70 | 220 |
| Week 11 | 77 | 230 | 70 | 220 |
| Mill Discharge | | | | |
| Week 1 | 52 | 210 | 45 | 200 |
| Week 3 | 25 | 270 | 24 | 270 |
| Week 5 | 38 | 280 | 29 | 280 |
| Week 7 | 33 | 250 | 29 | 250 |
| Week 9 | 30 | 270 | 29 | 270 |
| Week 11 | 43 | 280 | 41 | 280 |
| Cyclone Overflow | | | | |

Table 6. Cont.

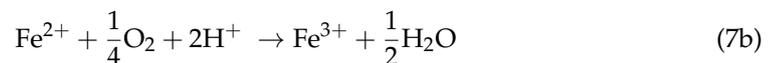
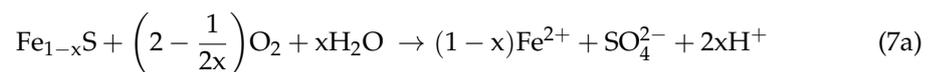
| Process Water | Total Magnesium ppm (Mg) | Total Calcium ppm (Ca) | Dissolved Magnesium ppm (Mg) | Dissolved Calcium ppm (Ca) |
|---------------|--------------------------|------------------------|------------------------------|----------------------------|
| Week 1 | 59 | 180 | 59 | 180 |
| Week 3 | 40 | 240 | 39 | 240 |
| Week 5 | 41 | 260 | 36 | 260 |
| Week 7 | 51 | 220 | 44 | 220 |
| Week 9 | 41 | 250 | 40 | 240 |
| Week 11 | 49 | 260 | 47 | 260 |

4. Discussion

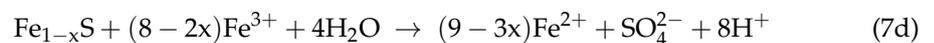
4.1. Sulphur Speciation of Species in Process Water, Mill Discharge, and Hydrocyclone Overflow

The oxidative properties of the Kevitsa process water, characterized as a quotient of temperature and pH (T/pH), increase towards the warm summer months. This parameter can be assumed to describe the oxidative properties of the water for the following reasons; firstly, the effect of temperature on mineral surface oxidation is twofold; based on van't Hoff's law, the increase of temperature shifts the endothermic reaction equilibrium to increase the concentration of products; thus, to increased formation of H⁺ (Equations (7)–(9)).

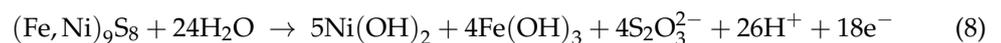
Pyrrhotite-initial oxidation, pH decrease [15–17]:



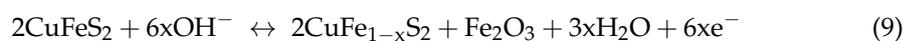
Pyrrhotite-further oxidation, pH decrease:



Pentlandite-oxidation, pH decrease [18]:



Chalcopyrite oxidation [19]:



In addition, based on the Arrhenius rate law, the reaction rate constants of the oxidation reactions increase as a function of temperature, meaning the oxidation reaction rate increases rapidly with increasing temperature. The pH of the recycled process water decreases towards the warm season due to the increased rate of oxidation reactions in the pond area. This results in a pH-drop-related increase in the concentration of dissolved metals. These dissolved metals serve as catalysts, enhancing the rates of surface oxidation reactions. Consequently, the increase of this simple index should indicate a tendency for enhanced mineral surface oxidation [3]. Figure 2a compares the T/pH index to plant performance, and Figure 2b the distribution of sulphur species in the process water.

As the graph shows, the plant performance seems to deteriorate when the process water corrosiveness increases towards the warm summer months (Figure 2a). This observation is in line with the earlier study [3] showing that the increasing corrosiveness of the recycled process water increased mineral surface oxidation and depressed pentlandite flotation.

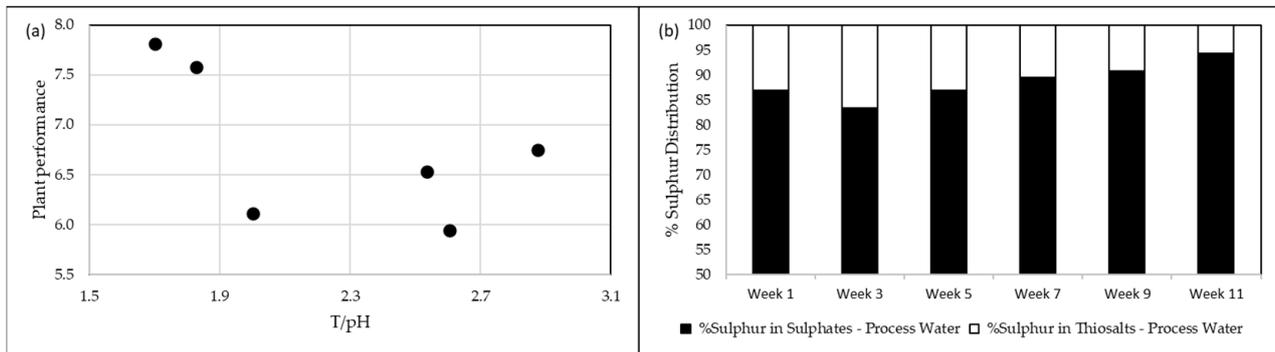


Figure 2. (a) Comparison between process water corrosiveness and plant performance, and (b) distribution of sulphur species in process water.

At the same time as the oxidative properties of the recycled process water increase, the distribution of sulphur species in the recycled process water changes towards the more oxidized species; there is an evident increase in the concentration of sulphate in the recycled process water (Figure 2b), whereas the concentration of reduced sulphur species (thiosalts) decreases. This change of sulphur speciation towards a more stable sulphur compound, sulphate, confirms the earlier findings by Muzinda and Schreithofer [11].

Interestingly, sulphur speciation in the mill circuit is completely different from the sulphur speciation in the process water. Figure 3 shows the percentage of the sulphur in the aqueous phase of the process water, and in the aqueous phase of the mill discharge, is bound to thiosalts.

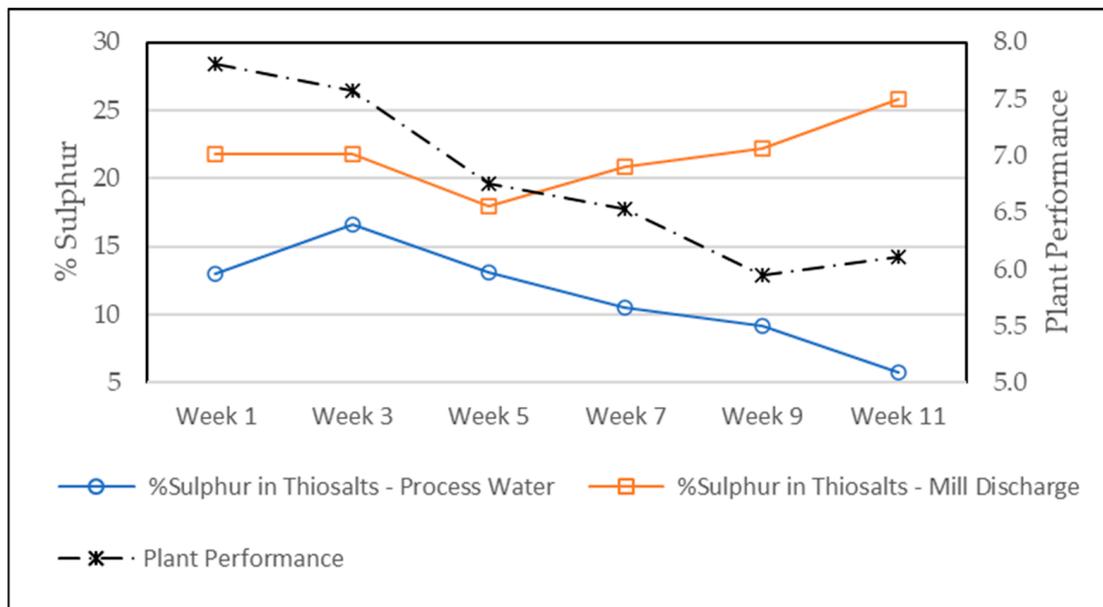


Figure 3. Thiosalts generation during milling compared to plant performance.

As Figure 3 shows, under highly oxidizing and poor performance conditions there is an increased formation of reduced sulphur species in the milling circuit. The formation even increases as we move towards the warm summer months with more oxidative conditions (week 5 to week 11). This increase in reduced sulphur species during milling is a clear indication of an enhanced mineral surface oxidation, and follows what is described in the scientific literature as well. This observation therefore confirms the conclusion drawn in the previous studies that, despite autogenous milling, the Kevitsa milling process is an electrochemically active environment that defines the degree of mineral oxidation [3]. Furthermore, the distribution of sulphur species in the hydrocyclone overflow was compared

to the respective values for the mill discharge as shown in Figure 4. It appears to be that the proportion of reduced sulphur species starts decreasing with an increasing residence time. This decrease in the proportion of thiosalts probably results from the continued oxidation of reduced sulphur species to sulphates. This is supported by the results, that show a simultaneous increase in the proportion of sulphur in sulphate. However, the difference is small, and the oxidation of the ore in the hydrocyclone appears to be minimal compared to the oxidation during milling. It can therefore be deduced that, under warm summer conditions, extensive oxidation of the ore already happens during the milling process. Thus, grinding can be considered an important processing stage, as it defines both the degree of mineral oxidation for flotation and the plant performance.

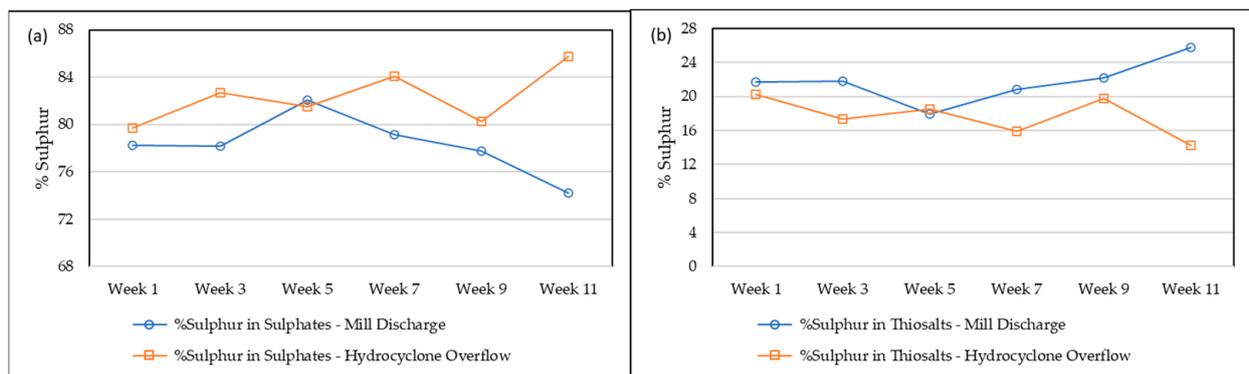


Figure 4. (a) Percent Sulphur in sulphates distribution in mill discharge and hydrocyclone overflow. (b) Percent Sulphur in sulphates distribution in mill discharge and hydrocyclone overflow.

Furthermore, the result shows that the reduced sulphur species in the recycled process water cannot be the root cause for the observed flotation performance decline. Actually, the concentration of reduced sulphur species in the recycled process water is at a minimum during the problematic season. Instead, the enhancement of mineral surface oxidation due to increasing water corrosiveness leads to the generation of reduced sulphur during the milling. Then, the highest concentration of reduced sulphur species occurs not in the recycled process water but in the mill circuit.

4.2. Relationship between ORP and Sulphur Speciation during Milling

Eh-pH dependence of both collectorless and collector flotation recovery is well-known, as it has been determined for various sulphide minerals and mineral–thiol collector systems by various researchers. Previous studies on the Kevitsa case [3] also concluded that the ORP of the nickel flotation feed has an impact on the recovery of pentlandite minerals. However, what was not considered in that study was how the ORP value of the recycled process water drops towards the nickel flotation feed value, and how the sulphur speciation relates to the foreseen change. In this study, the ORP drop during milling was plotted against the percentage of reduced sulphur species present in the aqueous phase of the slurry. Figure 5 shows that a clear drop in the ORP value is seen when the percentage of reduced sulphur species increases. As discussed earlier, sulphur oxyanions are intermediate products in the sulphur oxidation cycle [4]. Therefore, the increase in their concentration suggests that oxidation/reduction reactions are happening in the aqueous phase and at the mineral surface [20]. In this case, the higher the generation of reduced sulphur species in the milling circuit, the higher the drop in the ORP value.

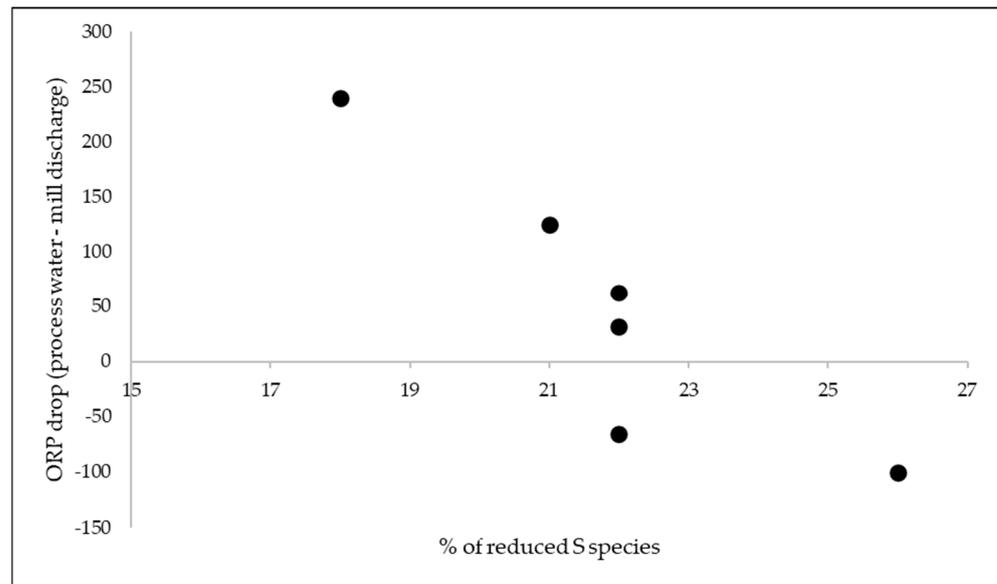


Figure 5. Relationship between ORP and sulphur speciation during milling.

4.3. Presence of Metastable Sulphur Oxyanions in Milling Circuit Streams

Sulphates, polythionates, thiosulphate, and sulphite anions were analysed in the process water, mill discharge, and hydrocyclone overflow. However, based on Pourbaix diagrams for aqueous sulphur systems, most of these species are metastable at the given Eh-pH-T conditions. Therefore, due to this metastability, there is very little value in investigating their correlations to the plant performance. The metastability of these species is also a challenge for their determination; even slight changes in sampling, sample pretreatment, and/or analysis procedures might result in radical changes in the concentrations of the individual sulphur species. Therefore, the determined results of intermediate sulphur species should be treated with caution, and all far-reaching conclusions should be avoided. Some experiments ignore the metastability of spiked ions (e.g., sulphur oxyanions), and misleading conclusions arise because no measurements have been carried out to check the speciation and concentrations after spiking. However, assuming that most of the analytical uncertainties are minimized, then some trends might be discussed. For example, the observed trend of sulphate in this study (Figure 6a) is inconsistent with what other researchers have observed [5,21,22]. Dzingai et al. [5] concluded that an increase in sulphate concentrations up to 2400 ppm had no impact on nickel recovery, while the concentrate grade was slightly impacted negatively, consistent with Corin et al. [21]. Bulut and Yenial [22] made a similar observation on galena. Furthermore, other researchers have concluded that thiosulphate anions inhibited the adsorption of hydrophilic compounds on the mineral surface, thereby improving sulphide mineral floatability [5,23,24].

However, in this study, most of the analytical uncertainties could be successfully minimized by validated sampling and determination methods. Therefore, some general trends can be discussed, and the results can be used to indicate the presence of these metastable sulphur species in the grinding circuit. Comparing sulphuroxy concentrations of all three samples, sulphates and polythionates tend to decrease from the process water to the mill discharge, while thiosulphate and sulphite show the opposite trend. It becomes apparent that their concentration increases from the process water to the hydrocyclone overflow. Also, a general increase in the total concentrations of reduced sulphur species was observed, indicating the increased surface oxidation rate of the ore in the mill circuit. The most important observation regarding these metastable species is that during the warm and problematic summer conditions, these reduced sulphur species do not originate from the recycled process water. Instead, they are generated in the milling circuit due to the

enhanced oxidation of mineral surfaces. The concentrations measured for these species are significantly higher than in the process water used for processing.

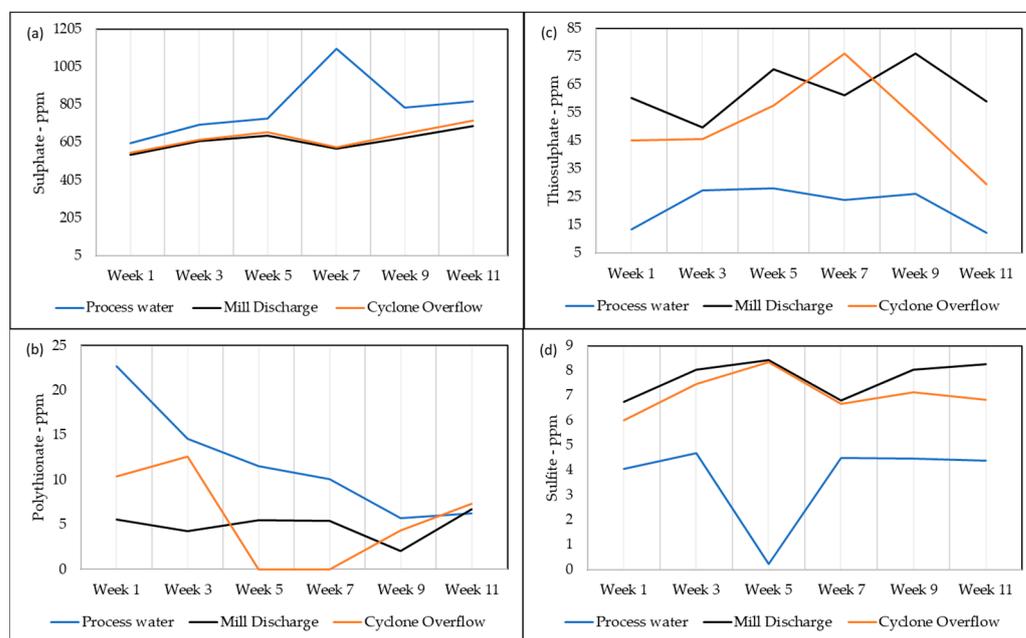


Figure 6. (a) Sulphate concentration in process water, mill discharge and hydrocyclone overflow. (b) Polythionates concentration in process water, mill discharge and hydrocyclone overflow. (c) Thiosulphate concentration in process water, mill discharge and hydrocyclone overflow. (d) Sulphite concentration in process water, mill discharge and hydrocyclone overflow.

It should be noted that plant operations are aimed at producing a good and saleable concentrate grade. Therefore, the impact on plant performance is mostly from recovery change in maintaining the concentrate grade. A poor plant performance implies low nickel recovery and vice versa. In this study all the individual sulphur oxyanion species in the milling circuit streams showed very poor correlations with the plant performance, inconsistent with the findings of other researchers. For example, the impact of tetrathionate on the recovery of sulphide minerals was studied by Mhonde et al. [25]. They concluded that tetrathionate had a negative impact on flotation due to its tendency to consume xanthate. Kasymova et al. [4] observed that only sulphite deteriorated flotation performance. For example, all the other researchers referred to in this study spiked respective sulphur oxyanions and performed lab-scale flotation tests to study the impact. Furthermore, they all used much higher concentrations compared to what has been observed in this study. And although it is well known that these species are metastable by nature, few studies even measured the real concentrations after spiking. As mentioned earlier, spiking was only done to synthetic waters and not to the mill discharge. All these factors could lead to different conclusions as to the exact effect of sulphur oxyanions on plant performance. The different findings from different researchers imply that the impact of sulphur oxyanions can be better-understood case by case and by studying actual plant processes.

4.4. pH and ORP of Good, Moderate, and Poor Plant Performance

Sulphide minerals easily oxidises when in contact with oxygen and water [26]. For ores containing pyrrhotite, the rate of oxidation is higher, since pyrrhotite is highly reactive [7,8,26–29]. The oxidation of sulphide minerals in tailings results in acid production, thereby lowering the pH [30]. It must be noted that at the Kevitsa concentrator, the pH of tailings leaving the flotation plant is around 9.5. As described by Musuku et al. [12], the tailings are stored in a tailings pond, and the water is recovered for reuse in the process plant. Figure 7 shows the pH and ORP, of the recycled process water (tailings discharge),

mill discharge, and hydrocyclone overflow. The data is classified into three classes using plant performance (PP) data: good (PP–7.8), moderate (PP–6.5), and poor (PP–5.9) plant performance.

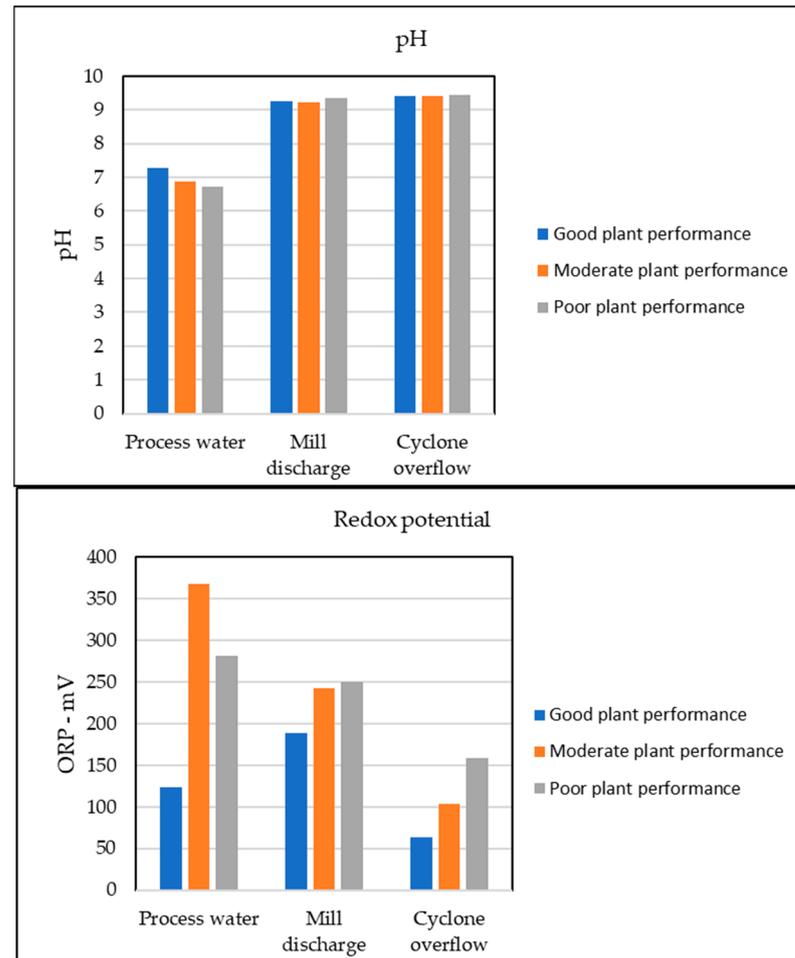


Figure 7. pH and ORP during good, moderate, and poor plant performance.

The pH of the recycled process water varies seasonally and is typically much lower than that of the mill discharge and hydrocyclone overflow. As discussed earlier, the seasonal lowering of pH of the recycled process water is an indication of increased oxidation activity in the sulphide tailings during the warm season. This pH drop in the recycled process water enhances the dissolution of both settled and non-settleable fine solids, resulting in increased concentrations of dissolved metals in the recycled process water. Interestingly, when the process water is added to the mill, the pH starts increasing, and eventually there is hardly any difference in the pulp pH of the mill discharge and hydrocyclone overflow. Since pH modifiers are not added to the grinding circuit, this pH increase is attributed to the oxidative dissolution of gangue minerals (carbonates, silicates). It is therefore hypothesized that gangue minerals, such as dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), undergo oxidative dissolution, resulting in the release of carbonates, which in turn buffer the pH to about 9.5. The consequence of this oxidative dissolution is also seen as an increase in both the total and soluble calcium in the mill discharge (Table 6). In fact, the concentrations of calcium in both the mill discharge and cyclone overflow increase as we move from good to poor plant performance. This trend was actually expected to happen towards the problematic warm season with poor pentlandite recovery; the pH of the recycled process water is much lower, thus enhancing the oxidative dissolution of carbonate minerals, resulting in increased Ca and Mg concentrations. Similarly, an increase in lime dosing has been

found to impact pentlandite recovery due to the presence of hydrophilic calcium species on the mineral surface [31]. These findings are consistent with the observations made in this study; the increase of dissolved calcium concentration correlates with poor plant performance. Therefore, it can be postulated that the low pH in process water affects the oxidation of both sulphide and non-sulphide gangue minerals. Although some of the calcium in process water is attributed to the recycled calcium from the lime added during flotation, the data show evidence of the oxidative dissolution of calcium during milling. On the other hand, the redox potential shows a general increase in the ORP from good to bad plant performance. This observation is in line with recent studies which showed a correlation between the ORP and pentlandite flotation performance [3]. The study revealed that pentlandite flotation was negatively impacted by a high ORP.

4.5. Consumption of Dissolved Oxygen

The dissolved oxygen demand test determines the rate of oxidation of minerals in the pulp [32–34]. Figure 8 shows the curves of the rapid decrease in the dissolved oxygen concentration with measurement periods of 2 and 10 min. The data shows that a lot of oxygen is depleted during the first 2 and 5 min for the mill discharge and hydrocyclone overflow, respectively.

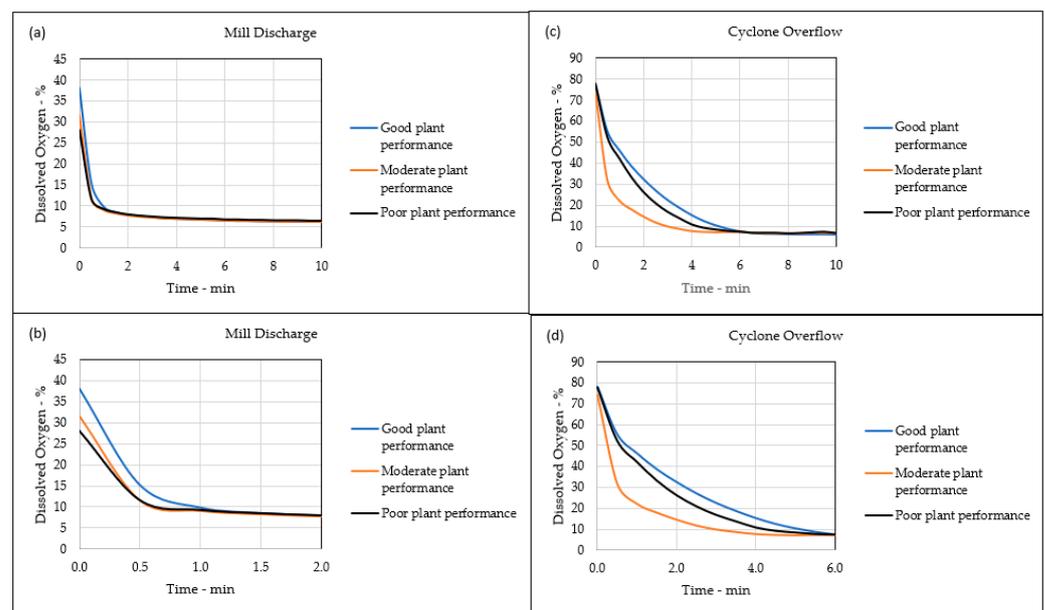


Figure 8. Consumption of dissolved oxygen in mill discharge and cyclone overflow. (a) Change of oxygen concentration in mill discharge during 10 min measurement period, (b) Change of oxygen concentration in mill discharge during first 2 min measurement period, (c) Change of oxygen concentration in hydrocyclone overflow during 10 min measurement period, (d) Change of oxygen concentration in hydrocyclone overflow during first 6 min measurement period.

As expected, the mill discharge consumes dissolved oxygen at a faster rate than the hydrocyclone overflow. This is to be expected, as the ore surfaces after milling are fresh and prone to surface oxidation. In addition, the tests performed for the mill discharge sample show a clear trend of the dissolved oxygen concentration dropping when moving from good to poor plant performance. This trend suggests that the poor plant performance is attributed to the high oxidation rate of the mineral surfaces. This observation is consistent with what was recently reported on the oxidation of Kevitsa ore [2,3]. It also confirms the conclusions drawn by the researchers, that under highly oxidative conditions, the Kevitsa ore is over-oxidized in less than 20 min, i.e., already during milling.

4.6. Froth Structure during Warm Summer Months and Plant Performance

Previously, researchers have found a correlation between the ionic strength of process water and froth stability [5,21,35–38]. Manono et al. concluded that the increase in ionic strength caused a reduction in bubble size [38]. They further observed that the increase of ions in process water created a more stable foam, due to bubble coalescence. These are interesting observations as they agree in part with our findings, despite the use of synthetic water. Figure 9 shows how the bubble sizes of selected rougher and cleaner cells changed during the period of the study. Both rougher and cleaner flotation cells showed a decrease in bubble size when the plant performance was poor. Based on plant metallurgists’ experience, a reduction in bubble size, and froth instability, happen at the same time and coincide with poor plant performance. It has been observed that the reduction of bubble size in the rougher cells is much higher than in the cleaner cells.

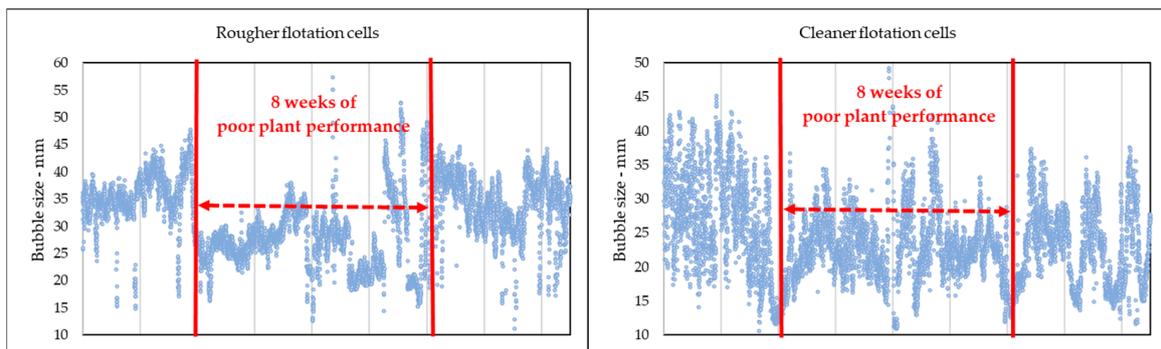


Figure 9. Rougher and cleaner cells bubble size reduction during the poor performance.

It is evident that the observed bubble size reduction coincided with the high temperature seasons and poor plant performance, as shown in Figure 10. Some researchers have concluded that, generally an increase in temperature resulted in an increase in the rate of pyrite recovery and the sulphur grades, and a decrease in the water recovery and size of the bubbles in the pulp [39]. Issaoui and Mansour also reported that increasing the temperature leads to the decrease of bubble diameter [40]. Similarly, plant metallurgists at the Kevitsa process plant have observed a reduction in bubble size as a result of the premature rupturing of the bubbles. With the type of frother used, an increase in dosage does not translate into bubble stability.

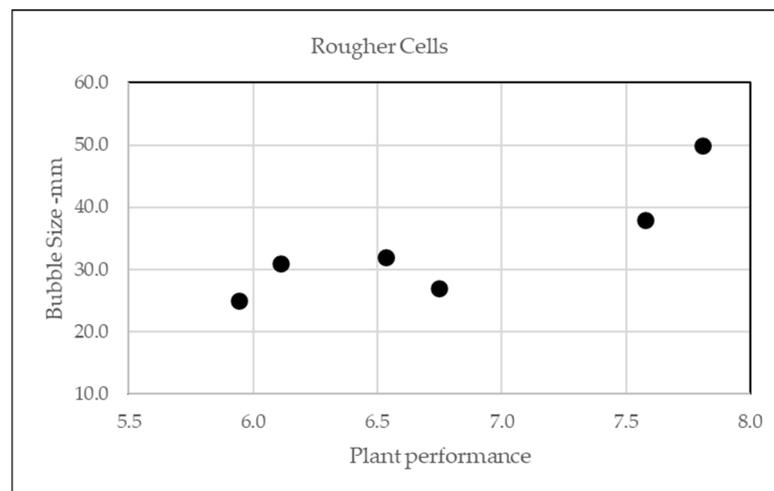


Figure 10. Plant performance plotted against rougher bubble size.

Therefore, the poor plant performance is partly attributed to froth instability as well. It is apparent that as the recycled process water temperature increases, the bubbles become unstable and rupture prematurely, with an impact on the flotation performance. Therefore, it can be deduced that the effect of temperature on the flotation performance may be multifaceted: (a) high temperatures accelerate oxidation reactions, thereby increasing oxidation products that are detrimental to flotation, (b) high temperatures may have a direct impact on some frothers by reducing their efficiency and compromising froth stability.

5. Conclusions

The study confirms that the consequences of the oxidation of mineral surfaces of the Kevitsa Cu-Ni ore are clearly visible in the properties of the aqueous phase of the pulp in the grinding circuit. More specifically, the results show that the most significant changes in the properties of the aqueous phase of the pulp in the grinding circuit coincide with the poor flotation performance conditions. Based on the results obtained, it becomes clear that when the oxidation rates in the grinding circuit increase towards the warm summer conditions, a strong formation of reduced sulphur species takes place. This is manifested with a sharp drop in the ORP values during the mineral processing. The results also show that the proportion of the reduced sulphur compounds in the grinding circuit starts to decrease as the residence time of the pulp in the circuit increases. This decrease in the proportion of reduced sulphur compounds is probably due to the continuous oxidation of reduced, metastable sulphur compounds to more stable sulphates. Owing to the strong oxidative dissolution of gangue minerals, calcium concentrations in the mill circuit also increase significantly towards the poor plant performance conditions. In addition, it can be observed that the bubble size of the nickel froth also decreases when moving to oxidizing, poor plant performance conditions. Consequently, the findings of this study confirm that the consequences expected, based on the theory of mineral surface oxidation, are observable downstream in the aqueous phase of the milling circuit. The observations regarding the metastable sulphur species also show that during the warm and problematic summer conditions, these reduced sulphur species do not originate from the recycled process water. Instead, they are generated in the milling circuit due to the enhanced oxidation of mineral surfaces.

Based on these results, it is not yet possible to say whether the poor flotation performance is caused solely by the oxidation of mineral surfaces or also by the properties of the aqueous phase of the slurry after milling. However, the results show that the plant needs both to find ways to limit oxidation rates in the summer, and to consider installing a more robust frother, capable of maintaining efficacy during the warm season. The findings of this study may help the plant to develop ways to enable a timely response to changes in the recycled process water quality, to prevent harmful impacts on pentlandite flotation. The former could be achieved by lowering the temperature of the process water and flotation air, whereas the latter could mean using a different frother.

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