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Oxidative Dissolution of Low-Grade Ni-Cu Ore and Impact on Flotation of Pentlandite

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Abstract: This paper investigated the effect of mineral surface oxidation on the floatability of Kevitsa low-grade Ni-Cu ore. Physicochemical measurements, ethylene diamine tetra acetic acid (EDTA) extraction, and oxygen uptake experiments were carried out with slurry and recycled process water samples obtained from the Kevitsa Cu-Ni sequential concentrator plant. The pH of recycled process water, copper flotation feed, and nickel flotation feed dropped by 0.7, 0.4, and 0.7 points, respectively, from May to July. The oxygen demand increased from recycled process water to the copper flotation feed, then dropped for the nickel flotation feed. The nickel flotation feed Redox potential (ORP) was lowest for July, while EDTA extractable metals increased from May to July. There was a 20% drop in nickel recoveries from May to July. Based on ORP measurements of the nickel flotation feed, good nickel flotation takes place in a moderately oxidizing (75–170 mV) and alkaline (9.2–9.7 pH) environment. Therefore, the ORP/pH of the nickel flotation feed is important to the nickel flotation. The results showed that at the Kevitsa plant, the grinding process is an electrochemically active environment, which, together with the incoming recycled process water quality, defines the degree of mineral surface oxidation for flotation. The increasing corrosiveness of the recycled process water increased mineral surface oxidation and depressed pentlandite flotation. Laboratory flotation experiments confirmed the observed poor plant flotation response when the corrosiveness of recycled process water increased. Total dissolved solids (TDS) was proven to be a reliable online parameter for the corrosiveness of the recycled process water and was inversely proportional to the pentlandite recovery. The findings of this study may help the plant develop ways to enable a timely response to changes in recycled process water quality to prevent harmful impacts on pentlandite flotation.

Keywords: total dissolved solids; physicochemical parameters; oxidation; nickel flotation; EDTA

1. Introduction

Copper and nickel minerals are recovered by flotation from different sections of the Kevitsa Ni-Cu-(PGE) deposit. The process flowsheet and ore mineralogy of the Kevitsa Mine were well documented by Musuku et al., 2016 [1], and accordingly, the main sulfide minerals are chalcopyrite, pentlandite, and pyrrhotite. Note that the Kevitsa concentrator plant comprises a sequential flotation process aiming to recover copper minerals (chalcopyrite and cubanite) and nickel minerals (pentlandite). The tailings are deposited into the tailing ponds where most of the solids settle, and over 90% of the water is recycled back to the milling and flotation process as recycled process water. Retention time as well as the quality of the process water in the tailings pond vary by the season. In addition, the accumulation of certain compounds in the pond water is obvious as there is an overall increase in conductivity values over time (Muzinda and Schreithofer, 2018) [2]. Over the years, the plant has repeatedly identified a decline in the flotation performance that coincides with a seasonal change. Accordingly, the lowest recoveries have typically been

recorded for the warmest summer months. Even though the scientific literature discusses ionic species, solids, and bacteria and their detrimental impacts on flotation performance, previous studies and literature reviews have not succeeded in explaining the observed decline in Kevitsa plant recoveries [2,3]. It was, therefore, hypothesized that recycled process water quality changes might somehow affect pentlandite oxidation and cause the observed decline in flotation recovery.

It is broadly agreed that the nature and floatability of sulfide minerals are greatly controlled by the degree of surface oxidation (Rosso and Vaughan, 2006; Hu et al., 2009; Ekmekçi et al., 2010) [4–6]. As electrochemical investigations show, floatability is supported by slight surface oxidation, which increases the hydrophobicity of the surface through the formation of elemental sulfur or polysulfides (Ralston, 1991; Hu et al., 2009) [5,7]. It also affects dixanthogen formation, which is responsible for inducing hydrophobicity on the mineral surface (Mendiratta, 2000) [8]. Extreme oxidation of sulfide mineral surfaces, on the other hand, reduces floatability as surface hydrophobicity is lost through progressive oxidation of elemental sulfur to sulfur oxyanions and sulphate [7], as well as due to the formation of metal oxy-hydroxide precipitates (Ralston, 1991) [5]. Nowadays, the Eh-pH dependence of both collectorless and collector flotation recovery is well-known as it has been determined for various sulfide minerals and mineral–thiol collector systems by various researchers. According to Grano, 2010 [9], Eh-pH dependence also helps us understand pulp chemistry and its impact on the flotation response at operating plants. Despite its significance, data on concentrator plants' electrochemical conditions and their variation due to varying operating conditions are limited. For example, in the Kevitsa case, the qualitative reactivity order of pure sulfide minerals is known, e.g., the pyrrhotite mineral oxidizes more rapidly than pentlandite and chalcopyrite minerals (Buckley and Woods, 1984; Belzile et al., 1997) [10,11]. However, it is not known how and to what extent the changes in the Kevitsa mineralogy (pyrrhotite-dominated vs. normal ore) and related galvanic interactions affect the reactivity and oxidation rates. Likewise, operating concentrator plants are prone to climatic conditions, and especially in the arctic region, recycled process water temperatures may easily vary between 0 °C and 25 °C. It is well known that thermodynamic stability is sensitive to temperature; however, thermodynamic models depicted by Pourbaix diagrams for the effect of processing temperature changes on mineral stability are mostly missing. In addition, kinetic data describing the impact of plants' temperature variation on water corrosiveness and mineral oxidation are sparse. Therefore, it is difficult to predict if the recycled process water quality changes by season affect mineral reactivity and oxidation rates. In addition, as discussed by Corin et al., 2013 [12], it is often believed that the surface properties of the minerals can be adjusted during flotation rather than during grinding. This is reflected in the recent research activity that places more emphasis on investigations to study the impact of water quality and specific ions on the floatability of sulfide minerals [12]. Such studies imply that, e.g., alkaline earth metal cations, sulfur anions [13,14], and reagent residues [2] have significant impacts on flotation performance.

For industrial processing operations, the ability to understand and maintain flotation performance in varying operating conditions would be of great economic importance. Innovating chemistry control concepts beyond the state of the art would require a plant-specific understanding of aquatic chemistry of mineral-selective adsorption as well as selective redox reactions at mineral–solution interfaces [15]. Recent results by Le et al., 2020 [16], however, show that plant context is a mine-specific, multidimensional, and inherently complex system with interaction effects between conversion steps as well as interactions between the process water, minerals, and processing chemicals. Furthermore, the system is dynamic by nature and typically characterized by incomplete, high-uncertainty information [16]. Given the context, this work's rationale arises from a question concerning how to generalize existing research findings to understand and maintain the flotation chemistry of the Kevitsa concentrator plant in varying operating conditions. It is essential to understand that, despite the available knowledge of sulfide minerals' aquatic chemistry and molecule-level understanding of water–flotation interactions, many fundamental reactions

occurring at a specific processing plant's scale and related to sulfide mineral–water–air interfaces remain unresolved or poorly understood. Up until now, there has been very little effort devoted to answering what factors or factor combinations have the most significant impact on the flotation performance at a real processing plant, and how the quality of the process water changes the pulp chemistry already before flotation.

This study aims to challenge the previous studies conducted at Kevitsa, which mostly overlooked the influence of the grinding stage on the mineral surface oxidation, and consequently on the flotation performance. Those previous studies focused more on investigating how certain specific species affect flotation performance [2,14]. Those findings are valuable as well, but few of them discuss or question the impact of mineral surface oxidation on the outcome. In addition, as is typical for research, most studies also rely on laboratory experiments as a primary choice for studying the impacts of water on flotation performance. Then, the translation of laboratory findings into plant-scale operations becomes a challenge as lab studies are usually conducted under strictly controlled experimental conditions that ignore the true fluctuation in the plant-related variables. Laboratory testing also utilizes much shorter retention times compared to the real plant scale, and consequently, the mineral surface properties achieved may differ from the actual properties achieved at the plant scale, thus raising the possibility of wrong conclusions.

This study investigates the effect of mineral surface oxidation on the flotation performance of the Kevitsa low-grade Ni-Cu ore. Special emphasis is on the nickel flotation performance and the study bases mostly on slurry samples obtained from the operating plant. In more detail, it is of interest to investigate how the mineral surface oxidation is affected by the varying electrochemical conditions that possibly derive from the seasonal variation in recycled process water quality. It is anticipated that through this approach, the relationship between specific minerals' reactivity, electrochemical conditions, and pentlandite flotation performance will be better understood.

2. Materials and Methods

2.1. Materials

Ore Samples for Laboratory Testing

Representative low-grade ore for the study was obtained from Boliden Kevitsa Ni-Cu-PGE Mine. Experimental tests were carried out using ore that was crushed and sieved through 4 mm mesh. Crushed and sieved ore was riffled and split into 1 kg portions with a rotary sample splitter. The portions were immediately sealed in plastic, frozen, and stored in the freezer until needed for the experimental work. A representative sample was taken for mineralogical and chemical analysis. Elemental composition and mineralogy were analyzed at the Metso Outotec Research Centre in Pori. A polished resin section was prepared for mineralogical studies utilizing a JEOL JSM-6490LV scanning electron microscope (SEM) equipped with an Oxford Instruments energy-dispersive spectrometer (EDS).

The imaging and EDS analyses were performed under routine conditions using a 20 kV acceleration voltage and 1 nA beam current. Mineral quantification was performed using HSC Chemistry® software version 10.0.8.3 (module HSC Geo 9, Metso Outotec, Tampare, Finland). Additionally, the powder samples were analyzed crystallographically using a PANalytical Aeris diffractometer. The main elements of the sample were analyzed using ICP-OES (inductively coupled plasma optical emission spectrometer) after total dissolution. Nickel and iron contents after bromine methanol dissolution were analyzed to differentiate between Ni and Fe content in sulfides and silicates. Sulfur and carbon contents were measured using an Eltra CS-2000 automatic analyzer. The quantity of silica was analyzed colorimetrically using a Hach DR 5000 UV-Vis spectrophotometer. The results are given in Table 1.

**Table 1.** Mineral and Chemical Assays in Kevitsa Ore.

Minerals/Elements	Assays (%)
Chalcopyrite	1.29
Pentlandite	0.63
Pyrrhotite	1.34
Non-Sulfide gangues	96.74
Cu	0.36
Ni	0.23
Fe	9.00
S	1.24

2.2. Laboratory Experiments

The purpose of this work was to study the problems at the plant scale using samples taken from the actual process and in real-time. As the plant process is dynamic and one cycle of laboratory experiments was taking more than 3 h 30 min, the conditions of the plant samples would not be the same. Therefore, no replicates were conducted in this study. However, the same procedure was maintained for all experiments.

2.3. Laboratory Flotation Tests

All the experimental work except for the chemical analytics was performed at the Kevitsa concentrator plant laboratory. For the experiments, each sealed and frozen 1 kg ore sample was milled for 26 min at 60% solids with a Kevitsa laboratory rod mill, targeting a fineness of 75% passing 75 microns. The slurry was then transferred to a 2.5 L flotation cell and diluted to 39% solids. Sequential flotation tests were carried out in the alkaline region with an Outotec GTK Labcell lab cell flotation machine, by first recovering copper minerals at pH 10.5 and then nickel minerals at pH 9.5. The rotor mixing speed was set to 900 rpm and a 6 L/min air flow for all flotation experiments. The sketch and details of the experimental setup are shown in Figure 1.
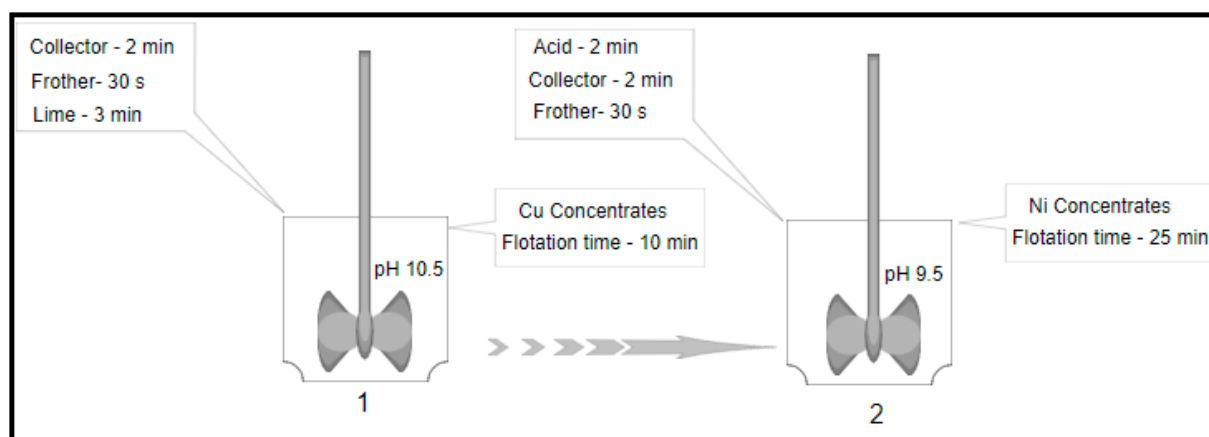
Figure 1. Sketch of the experimental setup used for laboratory flotation experiments.

Reagents for the flotation tests were prepared at different solution strengths. Table 2 shows the reagents prepared, their solution strengths, and their purpose. All reagents selected for the study were of industrial grade. The following were purity levels for the reagents used: Aerophine 3418A 50–60%, Sodium Isopropyl xanthate 85–90%, Nasfroth 240 96–100%, and lime and sulfuric acid 70%. To match with the expected decline in the plant's metallurgical performance that typically occurs between late spring to warm summer months, the flotation experiments were carried out using recycled process water sampled from the plant from May to July. That enabled us to capture the seasonal quality change of the recycled process water, to investigate its impact on the oxidative dissolution of the ore.

Consequently, a recycled process water sample for testing was collected from the plant's recycled process water tank in May, June, and July.

Table 2. Reagents and their solution strengths.

Reagent	Strength (%)	Purpose
Aerophine 3418A	1	Copper Collector
Sodium Isopropyl Xanthate (SIPX)	1	Nickel Collector
Nasfroth 240	100	Frother
Lime	50	pH Modifier
Sulphuric Acid	98	pH Modifier

To prevent further quality changes, water sampling was conducted immediately before conducting the flotation experiments. The recycled process water sample taken was then used immediately for milling, dilutions, and physicochemical analysis purposes.

2.4. Sampling Scheme for a Plant Sampling Campaign

A Kevitsa concentrator plant comprises a sequential flotation process aiming to recover copper minerals (chalcopyrite and cubanite) and nickel minerals (pentlandite). To carry out the experiments, both recycled process water, as well as copper and nickel flotation feed streams, were sampled on a bi-weekly basis for 3 months. The sampling scheme is presented in Figure 2.
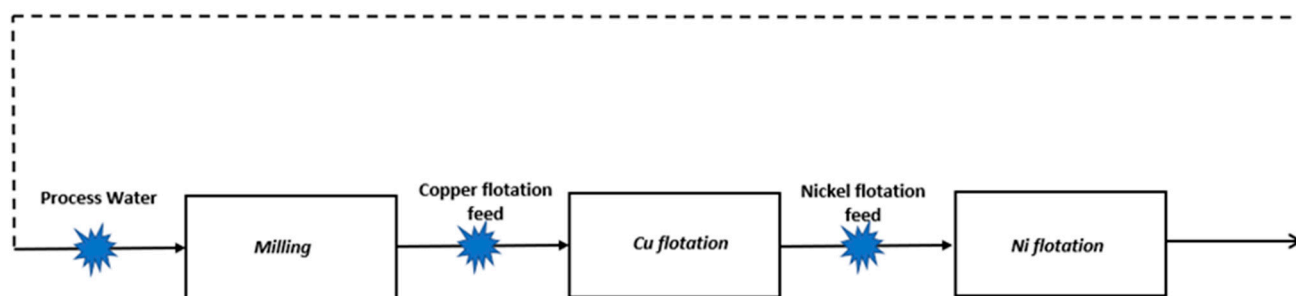
Figure 2. Sampling scheme for the Kevitsa plant sampling campaign.

Water samples were then divided into two portions. The first portion was utilized for laboratory flotation tests and the second portion was stored in clean bottles and deep-frozen at −20 °C to preserve the integrity of the sample before chemical analytics. Slurry samples were divided into two portions. The first portion was targeted for dissolved oxygen demand and EDTA extraction tests, and the second portion was targeted for chemical analytics purposes. Prior to sending the sample for further analysis, solid samples were filtered with a bottle-top vacuum filter and dried overnight in the oven at 80 °C.

2.5. Dissolved Oxygen Demand Experiments

Dissolved oxygen demand tests were carried out on recycled process water, copper flotation feed, and nickel flotation feed samples according to the method devised by Greet and Brown, 2000 [17]. Tests were monitored over the 90 min testing period with the YSI ProDSS Multiparameter probe (YSI, Xylem Inc., Yellow Springs, OH, USA) for specific conductance, ORP, pH, dissolved oxygen, and temperature.

2.6. EDTA Extraction Experiments

EDTA metal ions extraction tests were conducted on both copper flotation feed and nickel flotation feed samples. Amounts of 24 mL of fresh slurry sample and 250 mL of 3% EDTA solution whose pH was adjusted to 7.5 with NaOH solution were mixed and

conditioned for 30 min in a covered beaker using a magnetic stirrer. The slurry mixture was filtered using 0.45 μm filter paper and both solids and liquid were analyzed for Ni, Cu, and Fe by atomic absorption spectrometry.

2.7. Chemical Characterization of Solid and Water Samples

The physicochemical characteristics of the samples are presented in Table 3. Physicochemical parameters were determined immediately after primary sampling with the YSI ProDSS Multiparameter probe (YSI, Xylem Inc., Yellow Springs, OH, USA).

Table 3. Physicochemical parameters and elemental compositions of water and slurry samples.

Process Water	May	June	July
T °C	8	12	22
SPC μS/cm	2362	2564	2667
Dissolved Oxygen mg/L	11.5	10.0	7.9
Oxygen Demand %	3	6	10
pH	7.6	7.4	6.9
ORP mV	136	123	146
Total Cu μg/L	1	43	2
Total Fe μg/L	960	8100	210
Total Ni μg/L	140	430	170
Total Ca μg/L	140,000	180,000	190,000
Langelier saturation index	−1	−1	−2
Larson–Skold index	44	51	61
Copper Flotation Feed			
T °C	27	30	31
SPC μS/cm	2037	1240	2662
Dissolved Oxygen mg/L	4.2	3.7	5.1
Oxygen Demand %	45	53	30
pH	9.4	9.2	9
ORP mV	81	41	111
Total Cu μg/L	n/a	n/a	n/a
Total Fe μg/L	n/a	n/a	n/a
Total Ni μg/L	n/a	n/a	n/a
Total Ca μg/L	n/a	n/a	n/a
Langelier saturation index	n/a	n/a	n/a
Larson–Skold index	n/a	n/a	n/a
Nickel Flotation Feed			
T °C	28	30	33
SPC μS/cm	1666	1593	2716
Dissolved Oxygen mg/l	6.2	5.7	5.6
Oxygen Demand %	20	23	22
pH	9.4	9.3	8.7
ORP mV	88	69	12
Total Cu μg/L	3400	5400	7400
Total Fe μg/L	790,000	760,000	460,000
Total Ni μg/L	57,000	29,000	13,000
Total Ca μg/L	2,400,000	2,500,000	660,000
Langelier saturation index	n/a	n/a	n/a
Larson–Skold index	n/a	n/a	n/a

The elemental composition of the water and slurry samples was analyzed at the Outotec Research Centre in Pori. Metals were determined by ICP-MS and sulfur and carbon contents were determined using an Eltra CS-2000 automatic analyzer.

Slurry samples from the plant sampling campaign were analyzed for Cu, Fe, Ni, and Ca. Before ICP-MS determination, microwave-assisted acid digestion was used to rapidly extract the elements from the solid samples. To determine dissolved Cu, Fe, and Ni concentrations in the aqueous phase, water samples were filtered through a 0.45 μm Millipore

filter before ICP-MS determination. To determine total Cu, Fe, and Ni concentrations in the aqueous phase, water samples were not filtered before microwave-assisted acid digestion. Prior to ICP-MS determination, microwave-assisted acid digestion applicable for siliceous matrices was used. Concentrate and tailing samples from laboratory flotation tests were analyzed for Cu, Ni, and Fe by ICP-MS. The same method was used for the determination as for the determination of the slurry samples from the plant sampling campaign. Flotation feed grades for each laboratory flotation test were then back-calculated using concentrate and tailing assays.

2.8. Total Dissolved Solid Online Measurements

Total dissolved solids (TDS) is considered a water quality parameter used to describe the sum of inorganic salts and small amounts of organic matter present in an aqueous solution (WHO, 1996) [18]. According to the definition, the principal inorganic constituents are usually, e.g., calcium, magnesium, sodium, and potassium cations and carbonate, hydrogen carbonate, chloride, sulphate, and nitrate anions. Although conductivity is often used for this purpose, it is based on the measurement of the inorganic ionic species in the aqueous phase. Thus, conductivity does not directly measure the organic phase, e.g., process chemical residues. It was, therefore, expected that, as water corrosiveness is a function of total dissolved solids, TDS data might correlate with the increased mineral surface oxidation. The Vaisala PR-23 inline process refractometer was installed in the recycled process water stream for TDS monitoring for the entire period of the study. The refractometer determines the refractive index nD of the aqueous solution and converts it to the concentration of total dissolved solids.

3. Results

3.1. Plant-Scale Studies

3.1.1. Nickel Flotation Recovery Results

For reasons of confidentiality, Ni recoveries were presented in cluster form using the following formula:

$$Cl\ (1\text{--}5) = X + Y\ (1\text{--}5) \tag{1}$$

where X is the plant's lowest Ni recovery and Y (1–5) is a 0–20% increase in Ni recovery.

Ni recovery data were collected from the Kevitsa plant historian over a period of five months and clustered into five classes: Cl-1 (X + 0%), Cl-2 (X + 5%), Cl-3 (X + 10%), Cl-4 (X + 15%), and Cl-5 (X + 20%).

3.1.2. Process Water Quality Results

The timing for the study was selected so that the impact of the predicted recycled process water quality change on mineral surface oxidation and flotation performance of the low-grade Kevitsa ore could be investigated. Consequently, the investigations were performed between May and July because, historically, this is one of the most difficult periods for the Kevitsa concentrator plant. The physicochemical composition of the recycled process water samples (Table 4) characterizes the change in the water properties over that period. It is evident that not only does water temperature increase significantly toward the end of the period, but the corrosiveness of water in relation to minerals also increases. In addition, elevated temperature also enhances oxidative dissolution reactions in the tailings pond area, thus decreasing pH and increasing the concentration of dissolved metal ions that are capable of catalyzing mineral surface oxidation in the plant. It is then obvious that, toward the end of the period and based on the properties of the recycled process water, it can turn the grinding electrochemically more active environment where both thermodynamics and kinetics then favor oxidative dissolution of the minerals.

Table 4. Physicochemical composition of the recycled process water.

Cluster	TDS	°C	%DO	SPC	pH	ORP	Turbidity
Cl-1	1.3342	21	96	2731	7.1	122	9
Cl-2	1.3325	15	96	2501	7.4	145	16
Cl-3	1.3309	7	94	2709	7.4	267	12
Cl-4	1.3302	4	94	2855	7.8	250	12
Cl-5	1.3303	8	63	1843	7.5	111	6

3.1.3. Oxygen Uptake Results

As discussed in the introduction, several studies have shown that the flotation performance of sulfide minerals depends on the reactivity of the ore and the resulting degree of surface oxidation. In this study, oxygen uptake experiments were conducted for the samples taken from the Kevitsa plant to investigate if the reactivity of the low-grade Kevitsa ore varies depending on the recycled process water quality. The spatial data obtained show (Table 3) that oxygen demand values obtained for copper flotation feed samples are significantly higher compared to those of nickel flotation feed and recycled process water samples. This indicates that rapid and extensive surface oxidation already takes place during the grinding stage and before Cu flotation. Then, in the next processing stages, the reactivity starts decreasing, and oxygen demand is already significantly lower before Ni flotation. Temporal data show that oxygen demand and mineral surface reactivity before Cu flotation decrease toward the end of the plant sampling period, which is discussed in detail in Section 4.1.

3.1.4. EDTA Extraction Results

The ability of EDTA to solubilize oxidation products but not metal sulfides from mineral surfaces is well known [9,19,20]. The EDTA extraction method was, therefore, used to solubilize oxidation products from the surface of mineral particles to determine the extent of mineral surface oxidation. The objective was to investigate if the surface oxidation of low-grade Kevitsa ore varies depending on the recycled process water quality. EDTA extractable metals in nickel flotation feed samples taken from the Kevitsa plant in May, June, and July are shown in Figure 3. Elevated levels of EDTA extractable iron, copper, and nickel in the nickel flotation feed sample indicates an increased oxidation degree of the mineral surfaces toward the end of the sampling period. The elevation in extractable metal ions is attributed to oxidation as there was no change in grinding media (autogenous milling), and the ore mineralogy was similar. The main sources of Cu and Ni are chalcopyrite/cubanite and pentlandite, respectively. A comparison of EDTA extractable metals also indicates that chalcopyrite and cubanite do not become oxidized as much as pentlandite and pyrrhotite under the same conditions.
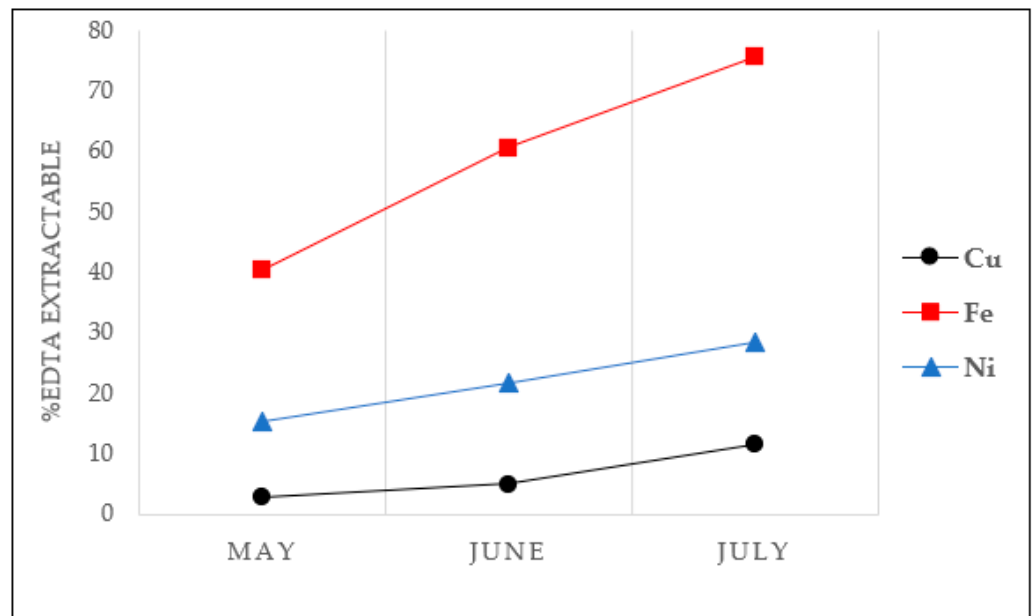
Figure 3. EDTA extractable Cu, Fe, and Ni in nickel flotation feed samples taken from the Kevitsa plant.

### 3.1.5. Correlation between TDS and Plant Nickel Recovery

Refractive index nD was measured using the Vaisala PR-23 inline process refractometer. The data obtained were clustered into five classes based on nickel recoveries as follows: Cl-1 (X + 0%), Cl-2 (X + 5%), Cl-3 (X + 10%), Cl-4 (X + 15%), and Cl-5 (X + 20%). An average TDS-nD for each cluster was then calculated. In Figure 4, the TDS of recycled process water is plotted against the actual plant nickel recoveries. The nickel recovery is inversely correlated with TDS in recycled process water.
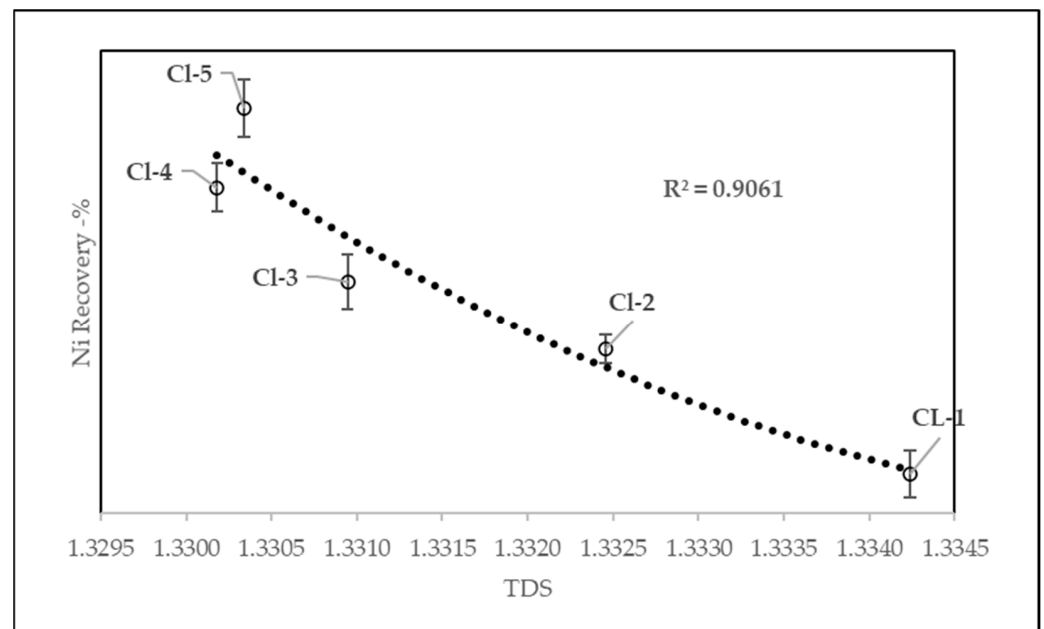
Figure 4. Effect of TDS in recycled process water on the plant recovery of nickel.

3.2. Laboratory Flotation Results

In addition to the plant survey, laboratory flotation experiments were also conducted to investigate if the seasonal quality variation of recycled process water affects the oxidative dissolution of the low-grade Kevitsa ore. Consequently, laboratory flotation experiments for low-grade Kevitsa ore were conducted using recycled process water samples taken from the Kevitsa plant between May and July. The objective was to study if the laboratory findings confirm the plant observations, i.e., whether the nickel flotation performance varies depending on the recycled process water quality. To prevent the change in the water quality before testing, all flotation experiments were performed immediately after the withdrawal of a water sample from the plant's water system. Table 3 shows the physicochemical characteristics of the recycled process water used for the flotation experiments. The nickel recovery and grade data given in Figure 5 show a clear decline in nickel flotation response toward the end of the sampling period. The flotation kinetics was also slower in July compared to May and June.
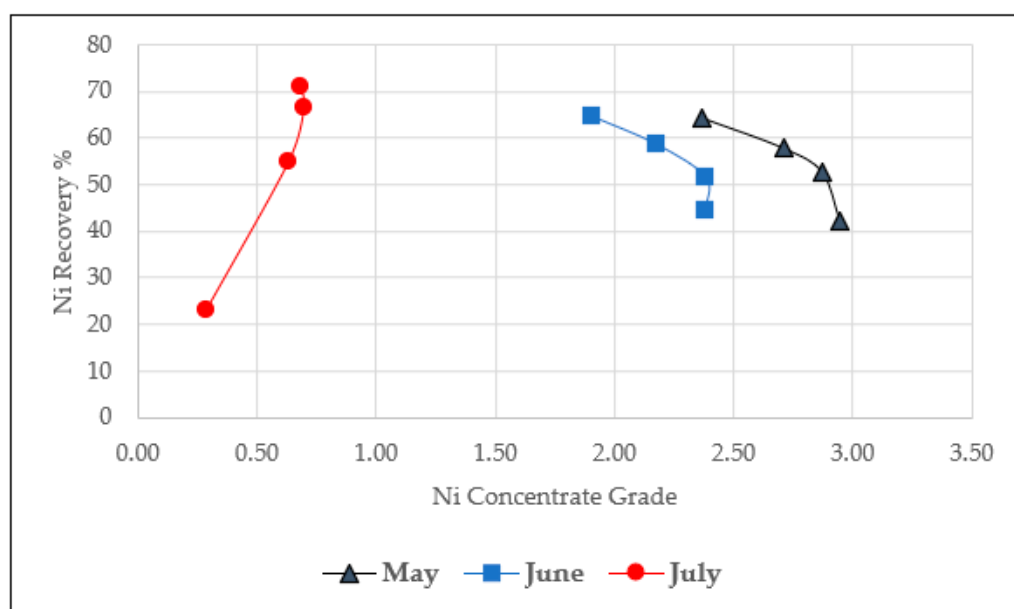
Figure 5. Nickel grade-recovery results from flotation experiments conducted with recycled process water samples taken in May, June, and July.

4. Discussion

4.1. Relationship between Process Water Quality, Surface Oxidation, and Pentlandite Flotation Recovery

Some knowledge of the expected electrochemical reactions possibly occurring in the Kevitsa slurry exists to understand the fundamentals of mineral oxidation and to determine the potential effects of recycled water quality on mineral surface oxidation. Several research groups have conducted electrochemical studies on chalcopyrite, pentlandite, and pyrrhotite oxidation [4,11,21]. Despite the fundamental research carried out, it does not yet help us understand the reactivity at dynamic plant conditions. First, thermodynamic and kinetic models describing the reactivity of Kevitsa main minerals under the plant's typical temperature range are mostly missing. Secondly, the main minerals' surface oxidation is not a result of separately occurring oxidative dissolution reactions but depends also on the galvanic interactions, which again are affected by the dynamic variation occurring in the incoming mineralogy, water quality, and grinding conditions. Indeed, such fundamental studies linking the reactivity, resulting surface oxidation, and flotation recovery are mostly missing. In this study, the focus was not on fundamental research but on characterizing the resulting surface oxidation with the real process samples obtained from the operating Kevitsa plant. To scale down the complexity, the impacts deriving from the incoming mineralogy and grinding changes were minimized by selecting the plant sampling times so

that there would not be any significant changes in the incoming mineralogy and grinding. Then, the observed changes in mineral surface oxidation would mostly derive from the water quality changes.

As the dissolved oxygen demand tests shows in Figure 6, it is obvious that excessive mineral surface oxidation occurs already before Cu flotation. After that stage, the dissolved oxygen consumption values decrease and, before the nickel flotation circuit, the surface oxidation has already slowed down.
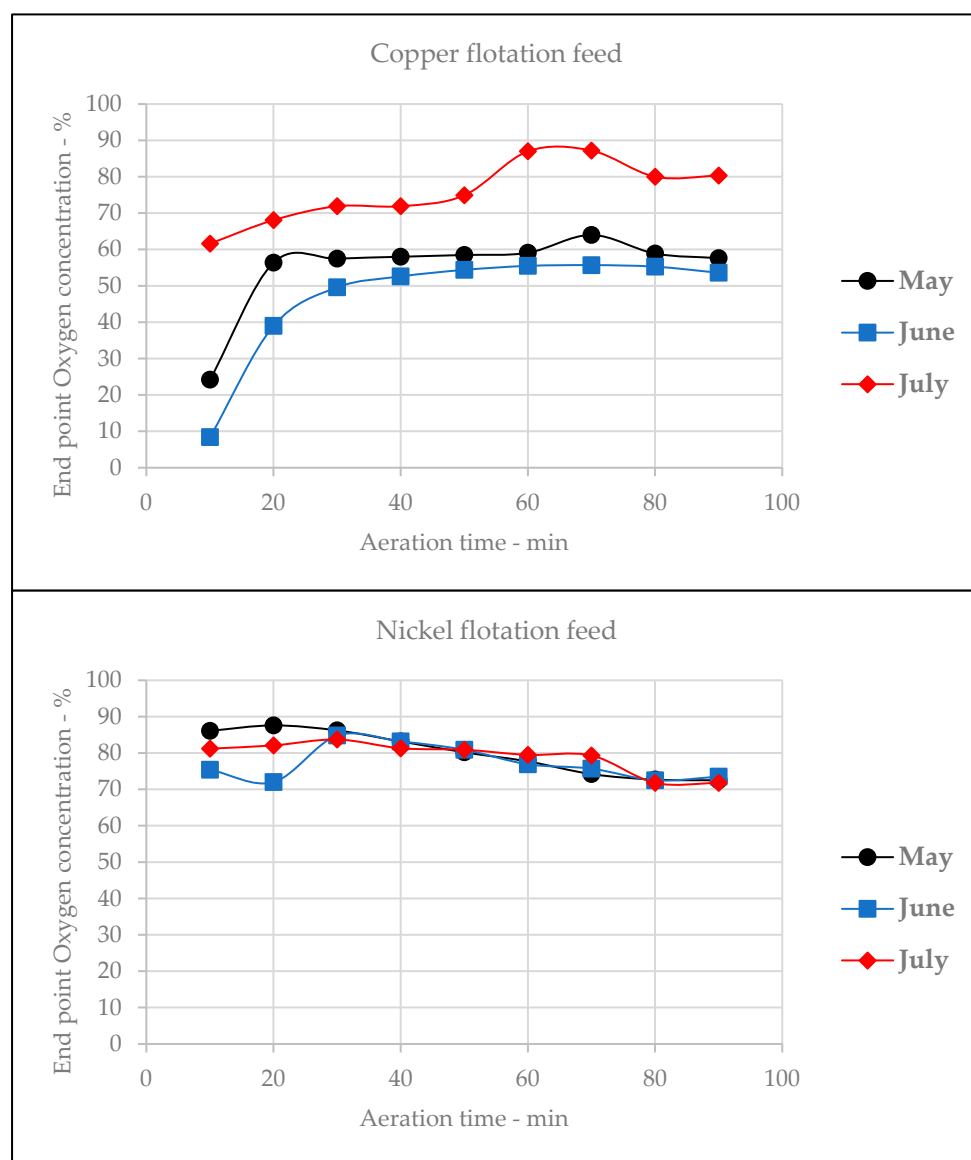
Figure 6. Dissolved oxygen endpoint for copper and flotation feed for different months.

Temporally, it appears that the dissolved oxygen consumption and mineral surface oxidation at the copper flotation feed decrease as water corrosiveness increases. However, this just indicates that when the corrosiveness of water increases, mineral surface oxidation reaches its maximum already much earlier in the grinding process, and due to that, the surface oxidation has already slowed down before the copper flotation circuit. This observation is also consistent with the EDTA test results (Figure 3), which confirm that the degree of mineral surface oxidation increases with the increasing corrosiveness of the process water. It is, therefore, evident that in the case of Kevitsa, the grinding process forms an electrochemically active environment, which, together with the incoming recycled process water quality, defines the degree of mineral surface oxidation for flotation. This is

consistent with the findings by Grano, 2010, which confirm that the oxidative dissolution of metal ions is rapid due to the generation of fresh minerals surfaces and the constant presence of air during grinding. Furthermore, the low amount of extractable Cu indicates that chalcopyrite and cubanite, which are the main copper minerals in Kevitsa ore, do not become oxidized as much as pentlandite and pyrrhotite under the same conditions. This aligns with the plant's earlier observations that indicate that Cu recovery is much less affected by the seasonal change in recycled process water quality. A significantly higher amount of extractable Fe and Ni ions is, however, observed, which could derive from the rapid and excessive oxidation of pentlandite and pyrrhotite.

Previous studies by Abramov et al. (1989) [21] showed that high oxidation rates and the overoxidation of pentlandite result in a mixture of Ni and Fe –hydroxides. In addition, violarite ($FeNi_2S_4$), $Ni(OH)_2$, and $NiSO_4$ are found in the pentlandite-oxidized overlayer, and Fe(III)-S and polysulfide species are found in the overlayers of both minerals. As indicated by Kelebek and Nanthakumar, 2007 [22], this overoxidation of pentlandite then results in flotation losses by transforming the fast-floating particles into slow-floating particles and those, in turn, into nonfloatable particles. These are consistent with the findings of this study and with the plant's earlier observations, which indicate that Ni recovery is heavily affected by seasonal change. Our findings confirm that recycled process water corrosiveness is inversely proportional to the pentlandite recovery. Laboratory flotation test results are consistent with actual plant flotation performance and demonstrate poor nickel flotation in July.

Physicochemical Parameters of Process Water, Copper Flotation Feed, and Nickel Flotation Feed

Physicochemical parameters of process water, copper flotation feed, and nickel flotation feed were monitored on specific dates in May, June, and July and are reported in Table 3. Figure 7 shows how the ORP changes from the process water to nickel flotation feed.
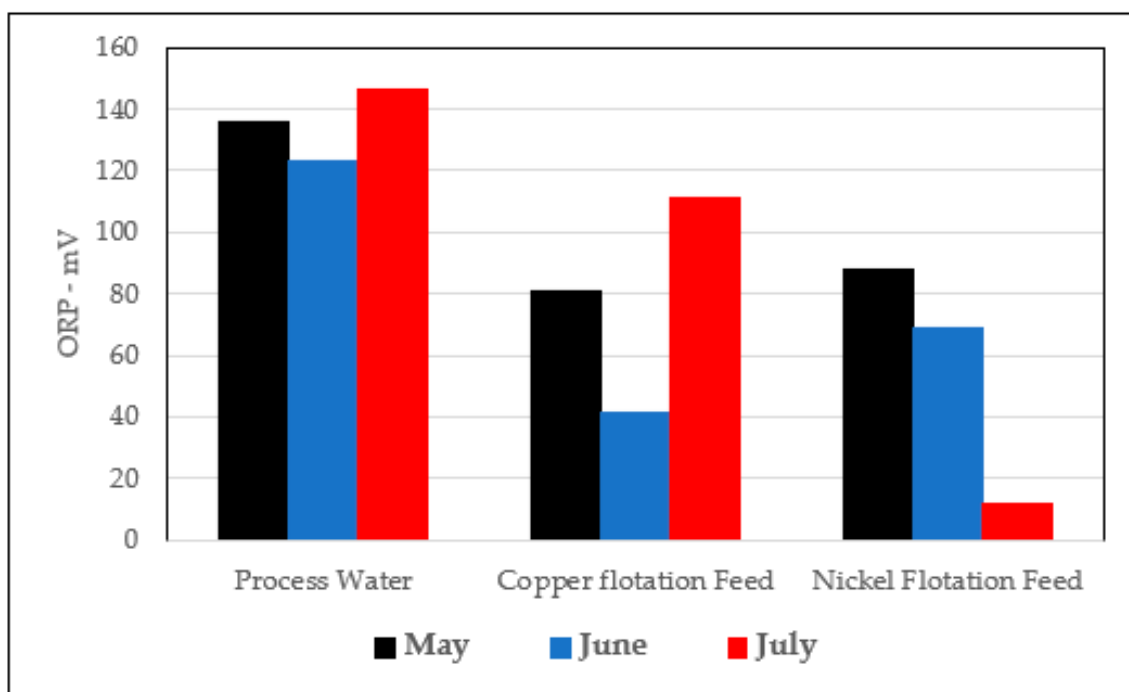

Figure 7. ORP change from process water to nickel flotation feed.

Compared to the values measured for the nickel flotation feed in May and June, there appears to be a strong decline (>100 mV) in the ORP of the nickel flotation feed in July. Then, nickel recovery on the plant was also at its lowest in July. As discussed by Hu et al. (2009) [5] and Tayebi-Khorami (2018) [23], it is well known that under strong oxidation, metastable sulfur oxyanions form. Based on Kasymova (2021), the presence of these metastable species, especially sulfite, results in a significant drop in ORP. Consequently, the poor performance recorded in July can be attributed to the excessive pentlandite surface oxidation and related unfavorably low ORP. On the other hand, good nickel flotation performance in May is attributed to a more moderate oxidation and higher ORP. As expected, the ORP/pH of the process water and nickel flotation feed are different for the same period, as shown in Figure 8. Based on ORP measurements of the nickel flotation feed, good nickel flotation takes place in a moderately oxidizing (75, 170 mV) and alkaline (9.2, 9.7 pH) environment. It appears that the ORP/pH of the nickel flotation feed is important to the nickel flotation.
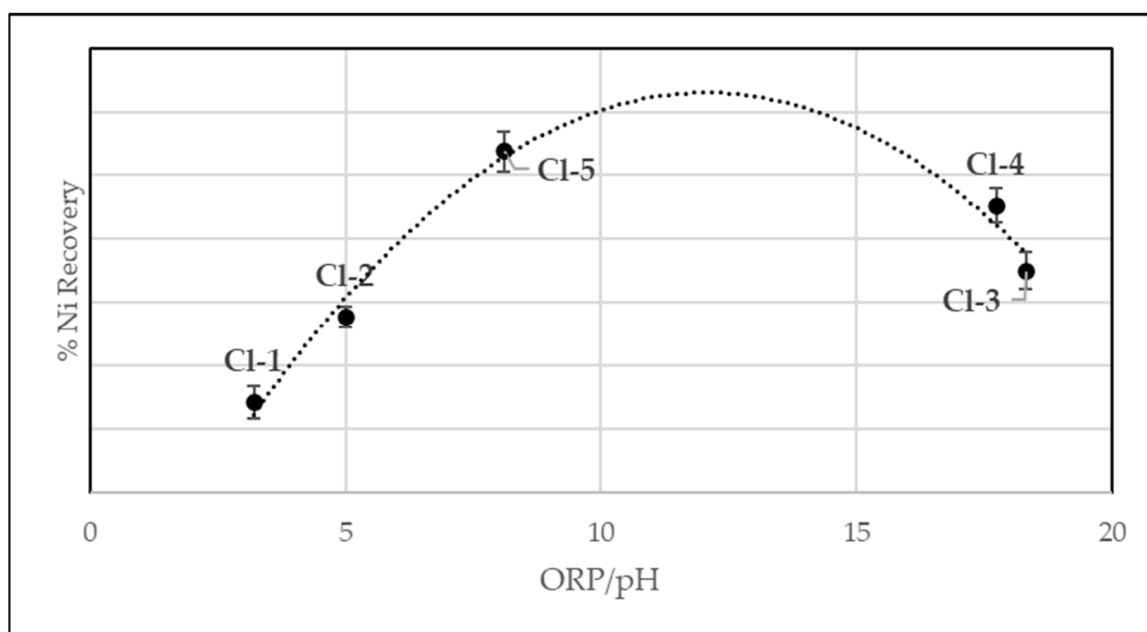
Figure 8. Effect of ORP/pH of nickel flotation feed on recovery of pentlandite.

Specific conductance (SPC) and pH were measured for the nickel flotation feed and is plotted as shown in Figure 9. The data indicate that in July, the SPC is significantly higher and the pH is lower than in both June and May. This is consistent with the finding that there is rapid and extensive oxidation occurring in July compared to both June and May.
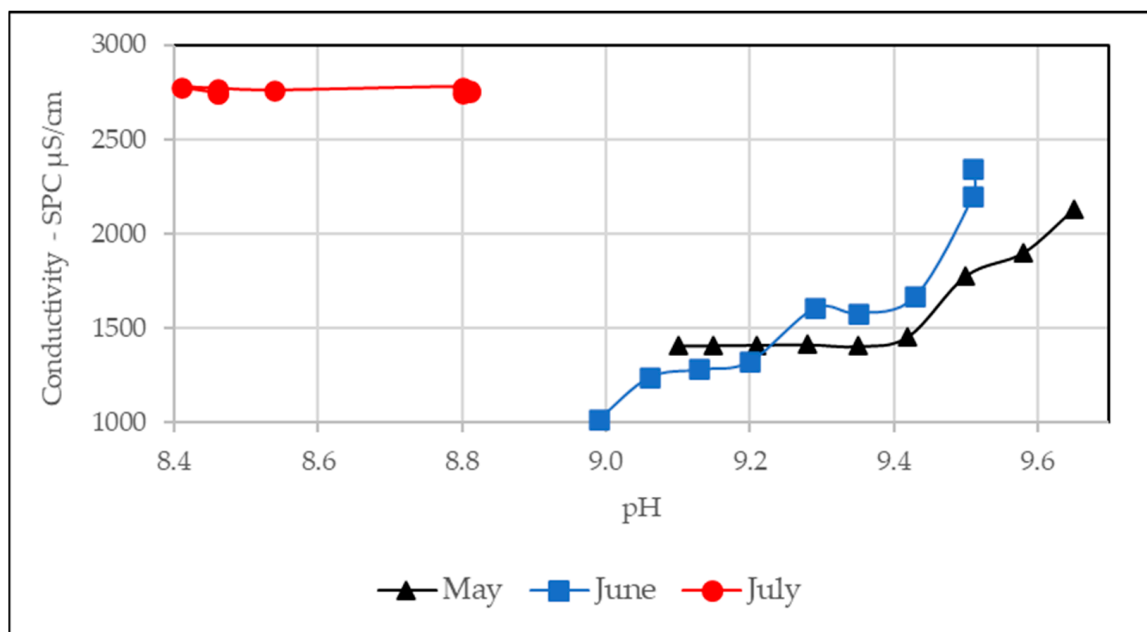
Figure 9. Effect of pH on SPC of nickel flotation feed.

### 4.2. Laboratory Flotation Experiments Using Recycled Process Water

Laboratory flotation experiments were performed to validate the plant-scale observations. Laboratory flotation test results (Figure 5) are consistent with actual plant flotation performance, which demonstrates poor nickel flotation in July. Although the overall recoveries were comparable, the nickel flotation performance significantly suffered from poor selectivity, consistent with studies conducted elsewhere, which have shown poor selectivity of pentlandite against pyrrhotite at low Eh/pH (Kelebek and Nanthakumar, (2007)) [22].

4.3. Relationship between TDS and Pentlandite Flotation Recovery

Based on theory, the degree of surface oxidation controls the floatability of sulfide minerals. However, as EDTA and oxygen demand tests are time-consuming lab experiments, they are not optimal for process control purposes to support operators to react to process changes affecting the surface oxidation. Because water corrosiveness is a function of TDS and temperature, it was considered that the TDS measurement installed at the plant could be used as a proxy for water corrosiveness.

According to the results illustrated in Figure 4, TDS data correlate inversely with the nickel recovery. However, as TDS is just a sum parameter, it does not yet give insight into what the species or elements for increasing TDS are. Therefore, the concentration of both total and dissolved metal ions in the aqueous phase was measured both for recycled process water and nickel flotation feed samples. According to Figure 10, there is a significant increase in total and dissolved metal concentrations from the recycled process water to nickel flotation feed. Most of the dissolved calcium is derived from the addition of lime. The high concentration of metals in the nickel flotation feed can be attributed to the high oxidation degree of minerals before nickel flotation with the consequent release of oxidative dissolution products to the aqueous phase.
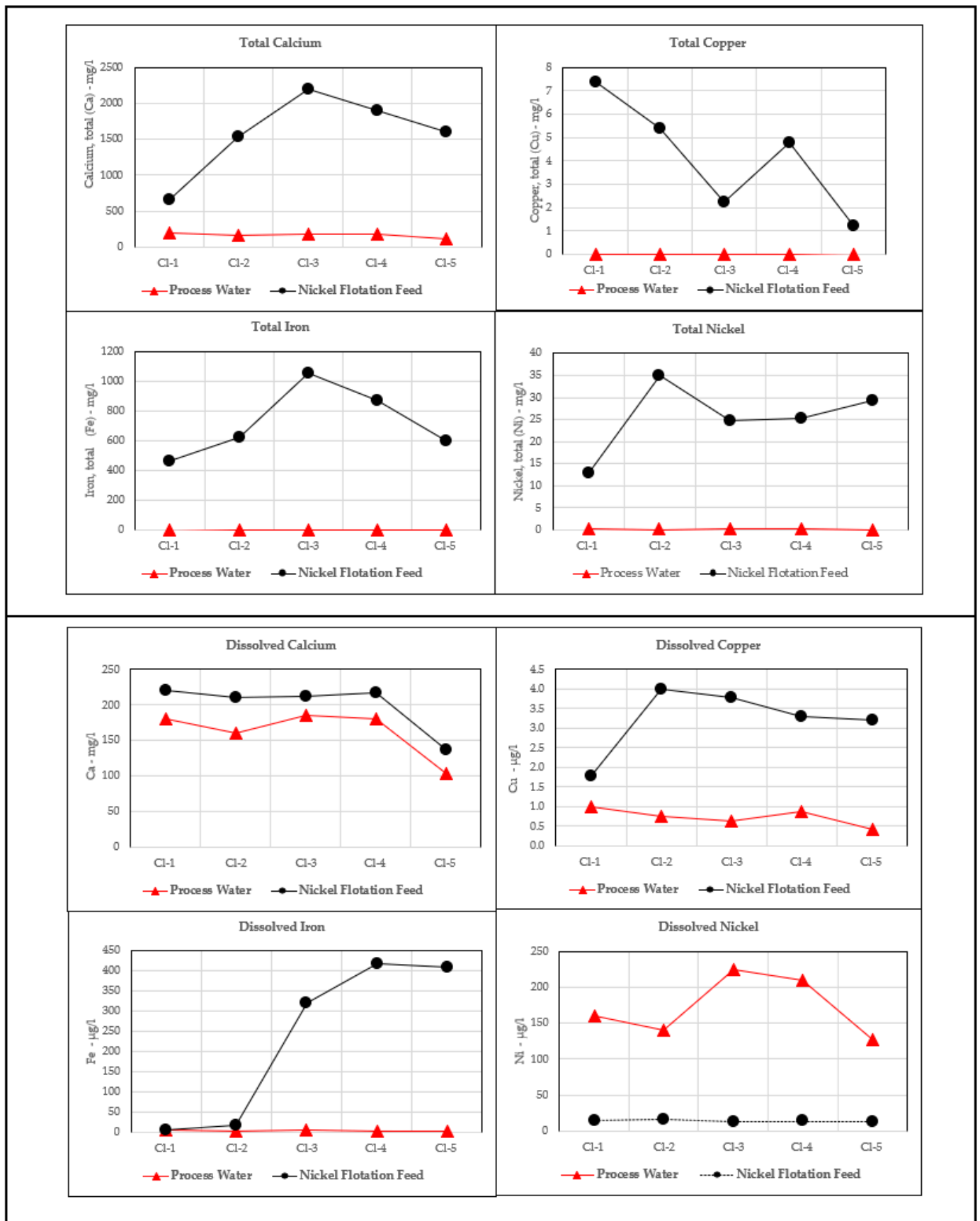
Figure 10. The comparison of the total and dissolved metal concentrations between process water and nickel flotation feed.

5. Conclusions

As the results show, the seasonal variation in recycled process water quality has a significant role in pentlandite flotation. The plant sampling campaign showed that increasing corrosiveness of the process water toward the warm summer months results in rapid and extensive oxidation of pentlandite surfaces. This overoxidation, which occurs already during the grinding stage, reduces pentlandite floatability as surface hydrophobicity is lost through progressive oxidation. The findings explain why pentlandite recovery at the Kevitsa plant is heavily affected by seasonal change. Based on ORP measurements of the nickel flotation feed, good nickel flotation occurs in a moderately oxidizing (75–170 mV) and alkaline (9.2–9.7 pH) environment. It, therefore, appears that the ORP/pH of the nickel flotation feed is important to the nickel flotation. The results also show that the TDS of recycled process water inversely correlates with pentlandite recovery. Furthermore, TDS increases during summer months when oxidation rates of the ore are expected to be high. Consequently, online TDS measurement can be utilized for process control purposes and to support operators to react to process changes affecting surface oxidation. The laboratory flotation tests performed on the same ore using different recycled process water qualities confirmed that water quality is responsible for poor pentlandite flotation. The results obtained from the laboratory showed poor selectivity for July, which coincides with poor plant nickel recoveries.

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