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Probing the Effect of Water Recycling on Flotation through Anion Spiking Using a Low-Grade Cu–Ni–PGM Ore: The Effect of NO_3^-, SO_4^{2-} and $S_2O_3^{2-}$

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Abstract: Water scarcity necessitates the recycling of process water within mineral processing practices. This may however come with its disadvantages for unit operations such as froth flotation as this process is water intensive and sensitive to water chemistry. It is therefore important to monitor the water chemistry of the recycle stream of process water and any other water source to flotation. Monitoring the concentrations of the anions in recycled process water is therefore important to consider as these are speculated to impact flotation performance. Batch flotation tests were conducted using synthetically prepared plant water (3 SPW) with a TDS of 3069 mg/L as the baseline experiment. 3 SPW contained 528 mg/LNO_3^- and 720 mg/L SO_4^{2-}, other anions and cations, and no $S_2O_3^{2-}$. Upon spiking 3 SPW with selected anions, viz, NO_3^-, SO_4^{2-} and $S_2O_3^{2-}$, it was noted that NO_3^- and SO_4^{2-} exhibited threshold concentrations while $S_2O_3^{2-}$ did not show a threshold concentration for both copper and nickel grade. Spiking 3 SPW with 352 mg/L more of NO_3^- to a total 880 mg/L NO_3^- concentration resulted in the highest copper and nickel grade compared to 3 SPW while increasing the $S_2O_3^{2-}$ from 60 to 78 mg/L increased nickel and copper grade. 720 to 1200 mg/L SO_4^{2-} and 528 to 880 mg/L NO_3^- were deemed the concentration boundaries within which lies the threshold concentration above which flotation performance declines with respect to metal grades, while for $S_2O_3^{2-}$ the threshold concentration lies outside the range considered for this study. Anion distribution between the pulp and the froth did not seem to impact the recovery of copper or nickel. Notably, the correlation between the concentrate grades and anion distribution between the froth and the pulp seemed to be ion dependent.

Keywords: froth flotation; ion accumulation; ion concentration spiking; ionic strength; water recycling

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1. Introduction

With the drive to reduce water usage globally, the mining sector must reassess its water usage; in the past, it has contributed greatly to environmental degradation, due to effluent discharge and tailings disposal [1]. To minimize freshwater usage and effluent discharge, the mining sector considers recycling to effect closed water circuits within mineral processing [2,3]. The recycled water may contain anions that affect the mineral surface, pulp chemistry balance, and reagent action, hence the need to establish whether threshold concentrations exist beyond which the flotation performance will be adversely affected by these anions common in mineral processing plant water. The presence of ions has been shown to either increase or decrease the floatability of sulfide minerals, depending on both the mineral type and the water chemistry [4,5]. This makes the addition of reagents such as depressants, activators, frothers, and collectors pertinent to enhancing the hydrophobicity of the desired mineral [6] or promoting the hydrophilicity of the gangue material [7]. Furthermore, there is limited literature concerning the effect of anions such as NO_3^-, SO_4^{2-} and $S_2O_3^{2-}$ on the floatability and recovery of sulfide minerals, and this research considers these anions. These concerns have led to the proposed spiking protocol to ascertain the impact that individually selected anions have on flotation performance [8].

Finkelstein and Lovell [9], Davis et al. [10], and Bradshaw et al. [6] suggested that dissolved ions, frothers, depressants, and activators, in addition to collectors and other chemical species, affect flotation performance. Collectors are added to the pulp to induce the hydrophobicity of the valuable minerals. Part of the trident factors of flotation operating parameters, adapted from Klimpel [11], demonstrate that flotation chemistry also has a substantial effect on flotation performance; this was supported by Ikumapayi et al. [12] and Muzinda and Schreithofer [13], who demonstrated that certain ions have potentially adverse effects on flotation performance. More recently, Dzingai et al. [8] investigated the effect of cationic spiking on the flotation performance of a low-grade Cu–Ni–PGM (Platinum Group Mineral) bearing ore and showed that certain cation concentrations may have affected valuable mineral recoveries marginally, although a marked difference was observed in the grade of the recovered concentrates. This behavior was attributed to the impacts of the hydroxo species adsorbing onto the target mineral and inadvertently affecting the collector-particle action on the valuable mineral or enhancing the depression of gangue minerals.

As previous studies have shown, flotation reagents may have their efficacy affected by the ionic nature of the solution in their interaction with mineral particles [2,7,13–18]; common reasoning, therefore, suggests that inorganic electrolytes present in process water may affect the ion–reagent–particle interactions occurring in the pulp phase and in turn, the implications of these effects could be seen in the froth phase phenomenon. Manono et al. [19], while investigating the effect of electrolytes present in process water on the flotation behavior of a Cu–Ni–containing ore, considered the effect of ion type, focusing on Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, SO_4^{2-}, and Cl^-, using single salts at a constant ionic strength of 0.0213 $mol \cdot dm^{-3}$ (an ionic strength of standard synthetic plant water prepared at the University of Cape Town (UCT) to mimic typical clean plant water from a South African concentrator). They found that some divalent ions (e.g., SO_4^{2-} and cations) resulted in higher water recoveries than the monovalent ion; this finding was said to be in line with the existing literature which suggests that divalent ions have a stronger froth stabilizing power than monovalent ions. Of the anions, NO_3^- ions resulted in a considerable increase in copper and nickel grades compared to Cl^- and SO_4^{2-}. It was speculated that NO_3^- ions promoted the depression of gangue [20]. However, the mechanism of this effect is yet to be investigated. This paper therefore presents research data that will form a basis for more in-depth and fundamental investigations into the mechanisms through which anions such as NO_3^- affect critical aspects of the flotation process.

To better understand the influence of water recycling in flotation, a low-grade Cu–Ni–PGM sulfide ore was used. This study investigated the effects of increasing ionic strength as well as increases in specific anion concentrations to determine whether these anions had beneficial or deleterious effects on the flotation process. Copper and nickel were the target metals, floated as chalcopyrite and pentlandite, respectively. Their recovery and grade under different conditions were used as measures to quantify whether a threshold ion concentration existed. To complement the flotation performance tests which considered concentrate recoveries and grades, electrical conductivity measurements were taken on both the pulp and the froth to determine the distribution of ions between the two phases.

2. Materials and Methods

2.1. Synthetic Plant Water Preparation

SPW in this study stands for synthetic plant water, while I.S stands for ionic strength. The standard UCT SPW was first developed by Wiese et al. [21], which had a total dissolved solids (TDS) concentration of 1023 mg/L, more recently referred to as 1 SPW. To achieve this recipe, different chemicals are added to deionized water. The slurry pH for the results presented in this paper was ~9. It is important to note that no pH modifier was added to this slurry because it was self-buffering, owing to the gangue minerals in the ore. To study the influence of ionic strength on flotation, the standard 1 SPW was multiplied 3, 5, and 10-fold, and the appropriate spiking levels were achieved by adding the specific ion concentration, as shown in Table 1.

Table 1. Concentrations of ions for the various water qualities, showing the TDS and I.S for each water type.

Water Type	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	NO_3^{-} (mg/L)	SO_4^{2-} (mg/L)	$S_2O_3^{2-}$ (mg/L)	CO_3^{2-} (mg/L)	TDS (mg/L)	I.S. (M)
1 SPW	80	70	153	287	176	240	-	17	1023	0.024
3 SPW	240	210	459	861	528	720	-	51	3069	0.073
5 SPW	400	350	765	1435	880	1200	-	85	5115	0.121
10 SPW	800	700	1530	2870	1760	2400	-	170	10230	0.242
Spiked 3 SPW										
3 SPW + 352 mg/L NO_3^{-}	240	210	772	861	880	720	-	51	3734	0.082
3 SPW + 1232 mg/L NO_3^{-}	240	210	1555	861	1760	720	-	51	5397	0.106
3 SPW + 480 mg/L SO_4^{2-}	240	210	647	861	528	1200	-	51	3737	0.087
3 SPW + 1680 mg/L SO_4^{2-}	240	210	1118	861	528	2400	-	51	5408	0.122
3 SPW + 60 mg/L $S_2O_3^{2-}$	240	210	479	861	528	720	60	51	3149	0.074
3 SPW + 78 mg/L $S_2O_3^{2-}$	240	210	485	861	528	720	78	51	3173	0.075

In considering the increase in the concentration of one ion at a time while maintaining a complex background process water-matrix, 3 SPW, selected anions were spiked to represent the accumulation of that specific anion over and above all other ions present in the complex background process water matrix (3 SPW). This spiking was informed by actual site water compositions. This 3 SPW was considered best to represent average current on-site TDS levels, and was thus used as the baseline in the experiment. All spiking tests were therefore performed with this baseline of the complex background process water matrix at the 3 SPW level. Each ion was spiked to its concentration level of 5 and 10 SPW, respectively. Additionally, 60 and 78 mg/L of $S_2O_3^{2-}$ was added to 3 SPW (which does not contain any $S_2O_3^{2-}$ anions), to mimic onsite water containing $S_2O_3^{2-}$.

2.2. Ore Preparation

In this study, a low-grade Cu–Ni–PGM sulfide sample was obtained and used. The bulk sample was crushed to reduce particle size, blended for homogeneity, riffled, and split using a rotary splitter into 1.3 kg samples. The 1.3 kg ore samples were finely ground in SPW, at the required ionic strength using a laboratory-scale stainless steel rod mill, to achieve a grind of 70% passing 75 µm. This represents the typical on-site grind size of the selected ore.

For the ore used in this study, the sulfides accounted for less than 5% of the overall deposit's mineralogy. Chalcopyrite is the primary copper-bearing mineral of interest, while pentlandite is the nickel-bearing mineral of interest. Approximately 20% of the nickel and up to 10% of the copper is contained in the non-sulfide minerals, which qualifies the ore body as low grade. Schreithofer and Muzinda [22] found that pyroxene is the most abundant non-sulfide gangue mineral; they used a similar ore as the one used in this investigation. The most abundant sulfide gangue mineral is pyrrhotite [23].

2.3. Batch Flotation

After milling, the slurry was transferred to a 3 L Barker flotation cell. The volume of the cell was made up to generate 35% solids using synthetic plant water of appropriate ionic strength. The cell was fitted with a variable speed rotor and the pulp level was controlled manually by the continuous addition of water. The impeller speed was set to 1200 rpm, while an airflow rate of 7 L/min was maintained for all flotation experiments. A constant froth height of 2 cm was sustained manually throughout. The cell height was constantly corrected to 2 cm by the addition of synthetic plant water at the relevant ionic strength. Concentrates were collected at 5, 10, 17.5, 25, 37.5, and 50 min by scraping the froth into a collecting pan every 15 s. A feed sample was taken before, and two tails samples were taken after each flotation test. Water usage was monitored throughout.

For all the batch flotation tests, tests were conducted in duplicates in order to maintain reproducibility to within 5% standard error. Aerophine 3184A copper collector dosages of 50 g/t was added to the float cell for a two-minute conditioning time, while carboxy methyl cellulose (CMC) depressant for pyrite, pyrrhotite, and non-sulfide-gangue (NSG) was added at dosages of 35 g/t and 20 g/t Nasfroth 240 frother to the float cell. These were specifically needed for the first 10 min to recover copper; immediately after 10 min of copper flotation, nickel flotation was initiated; 50 g/t of sodium iso-propyl xanthate (SIPX = 97% purity) was added into the cell as a nickel collector, 15 g/t CMC depressant and 10 g/t Nasfroth 240 frother were added, and at 25 min, 30 g/t SIPX was added to collect the final two concentrates. Reagents were used as supplied by Univar, Van Horne, BC, Canada. Feeds, concentrates, and tails were filtered, dried, and weighed before copper and nickel analysis by a Bruker S4 Explorer XRF Spectrophotometer (Bruker AXS GmbH, Karlsruhe, Germany). Each reagent was conditioned for two minutes. This procedure is as described by Dzingai et al. [8].

2.4. Electrical Conductivity Measurements

Electrical conductivity (EC) in water is a measure of its ability to conduct current. Current can be carried by ions in an electrolyte solution; the more ions there are in solution, the higher the EC. In this study, the froth was removed from a frothing column shown in Figure 1 using a vacuum pump into a collecting flask. The electrical conductivity was measured for the pulp and collected froth. EC was measured using a HANNA® Instruments' conductivity multiprobe (H17634-00, HANNA® JHB, Johannesburg, South Africa). It is important to note that the measured EC was used as a proxy for ionic strength.

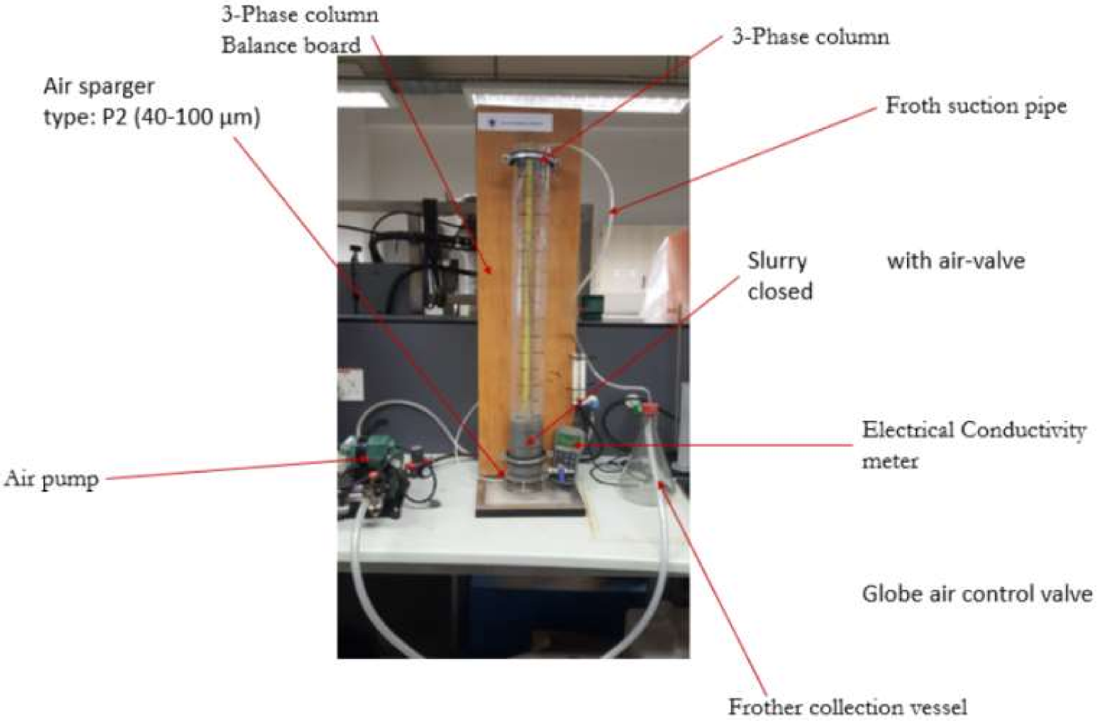


Figure 1. Three-phase froth column set up.

Figure 1 shows the experimental setup for a three-phase froth column. A total of 400 mL of the slurry was thoroughly stirred in a 500 mL beaker to condition the 10 g/t Nasfroth 240 and 2.5 g/t Aerophine 3418A before being transferred to the column; this was meant to be replicated for the copper flotation time only. The initial height of the slurry in the column was noted before air was introduced. Air was introduced to the column at a flow rate of 3 L/min from the bottom of the column through a constant pore size air sparger, type P2, which allowed the development of the froth phase until an equilibrium froth height was attained. A control globe-valve was used to maintain the air flowrate at 200 kPa. This height was noted. A vacuum pump was used to remove the froth after an equilibrium froth height was achieved.

2.5. ANOM of Selected Ions

The analysis of means (ANOM) is a statistical method that is used for comparison purposes between the treated means and the overall mean. The ANOM is used to test the significance, if any, between the means in comparison to the grand mean. Treated means is the average/mean of the groups under investigation. The grand mean is defined as the sum of all the means of the samples under consideration divided by the number of means. The ANOM compares the samples' mean to the grand mean and boundary lines called the upper decision line (UDL) and lower decision line (LDL). The UDL shows a positive statistical difference, while the LDL shows a negative statistical difference, both of which are compared to the grand mean. A typical ANOM chart has three lines: the UDL, the grand mean, and the LDL. The assumed level of confidence of these tests was 95%. As with confidence interval estimation, when computing the UDL and LDL, a measure of sampling error is added and subtracted around the statistic of interest. Specifically, Equation (1) shows the grant mean, Equation (2) shows how UDL is calculated, and Equation (3) shows how to obtain the LDL. Minitab version 18.1 was used to evaluate the ANOM.

$$\overline{\overline{y}} = \pm h_{c,n_j}\sqrt{\left\{\frac{S_p^2(c-1)}{n}\right\}} \tag{1}$$

where c is the number of groups of study, j is the representation of a particular group, n_j is the sample size for group j, n is the total number of observations where all of the sample sizes are equal, i.e., $n = n_1 + n_2 + \ldots + n_c$, $\overline{\overline{y}}$ is the overall or grand mean, i.e., $\overline{\overline{y}} = \frac{\overline{x_1} + \overline{x_2} + \ldots + \overline{x_c}}{c}$, S_p^2 is the pooled variance, an estimate of the inherent variability in the data computed by averaging the c group variances $S_p^2 = \frac{S_1^2 + S_2^2 + \ldots + S_c^2}{c}$, and h_{c,n_j} is the critical value of Nelson's h statistic with c groups and equal observations per group obtained from the table of the h statistic.

This leads to the UDL being calculated, as shown in Equation (2).

$$UDL = \overline{\overline{y}} + h_{c,n\,j}\sqrt{\left\{\frac{S_p^2(c-1)}{n}\right\}} \tag{2}$$

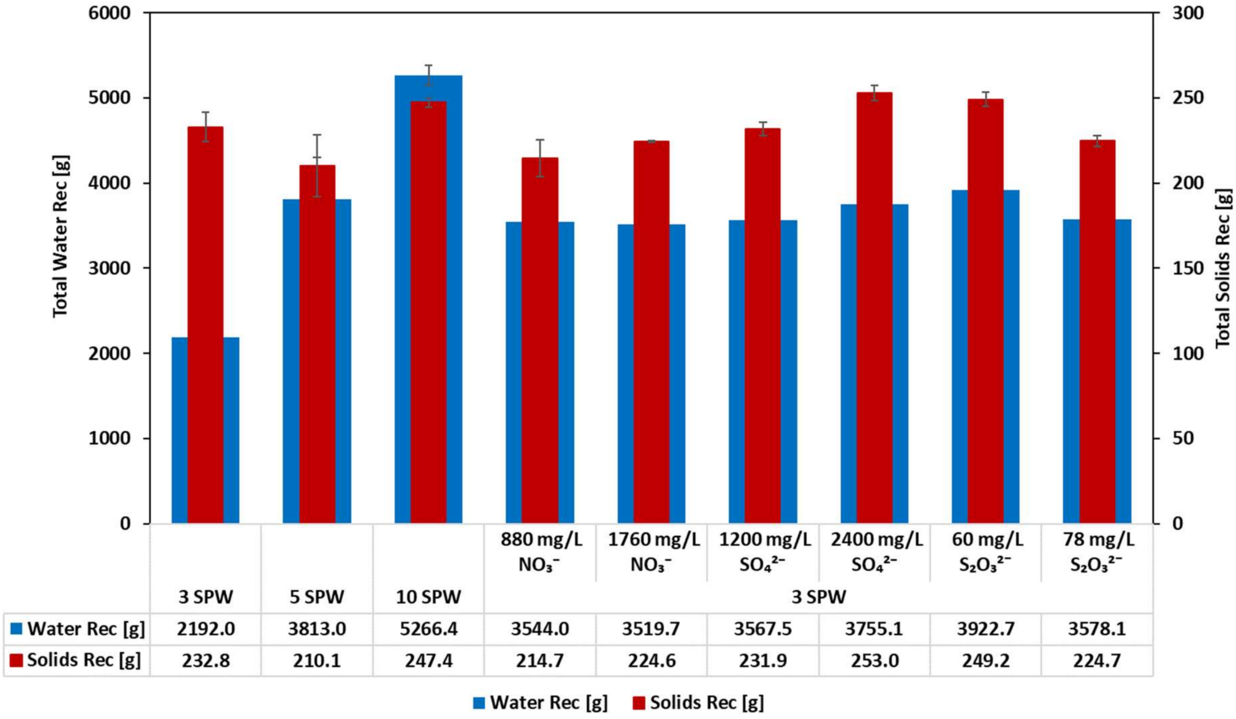
The LDL is evaluated using Equation (3).

$$LDL = \overline{\overline{y}} - h_{c,n\,j}\sqrt{\left\{\frac{S_p^2(c-1)}{n}\right\}} \tag{3}$$

3. Results

3.1. Effect of Increased NO_3^-, SO_4^{2-} and $S_2O_3^{2-}$ Concentration in Process Water on Solids and Water Recoveries: Implications on the Stability of the Froth

Figure 2 shows the variation of total water and solids recovery with the type of synthetic plant water used. The water recovery increases as the ionic strength of water increase from 3 SPW to 10 SPW. It is important to note that the fact that all the inorganic ions are added to the maximum level of what they would be in 10 SPW without spiking; this is done for comparison purposes. Adding NO_3^- to 3 SPW results in higher water recovery compared to 3 SPW. Adding 352 and 1232 mg/L NO_3^-, in addition to the 528 mg/L NO_3^- in the original background matrix (3 SPW), practically recovered the same amount of water above the 3 SPW total water recovery. Spiking 3 SPW with SO_4^{2-} resulted in more water being recovered in comparison to 3 SPW. The 10 SPW SO_4^{2-} (2400 mg/L) concentration equivalent resulted in a slightly higher total water recovery than the 5 SPW SO_4^{2-} (1200 mg/L) concentration equivalent. Of the anions used, $S_2O_3^{2-}$ recovered the most water at 60 mg/L, having recovered 173.1 g more water than 3 SPW. Spiking with 78 mg/L $S_2O_3^{2-}$ resulted in water recovery in the same range as spiking 3 SPW with the 352 mg/L and 1232 mg/L NO_3^-, as well as with 480 mg/L SO_4^{2-}. The general observation is that as 3 SPW is spiked with specific anions, the ionic strength increases, and so does the water recovery, as can be seen in Table 1 and Figure 1. The water recovery follows the order: 10 SPW > 60 mg/L $S_2O_3^{2-}$ > 5 SPW > 2400 mg/L SO_4^{2-} > 78 mg/L $S_2O_3^{2-}$ > 1200 mg/L SO_4^{2-} > 880 mg/L NO_3^- > 1760 mg/L NO_3^- > 3 SPW.



	3 SPW	5 SPW	10 SPW	3 SPW					
				880 mg/L NO_3^-	1760 mg/L NO_3^-	1200 mg/L SO_4^{2-}	2400 mg/L SO_4^{2-}	60 mg/L $S_2O_3^{2-}$	78 mg/L $S_2O_3^{2-}$
■ Water Rec [g]	2192.0	3813.0	5266.4	3544.0	3519.7	3567.5	3755.1	3922.7	3578.1
■ Solids Rec [g]	232.8	210.1	247.4	214.7	224.6	231.9	253.0	249.2	224.7

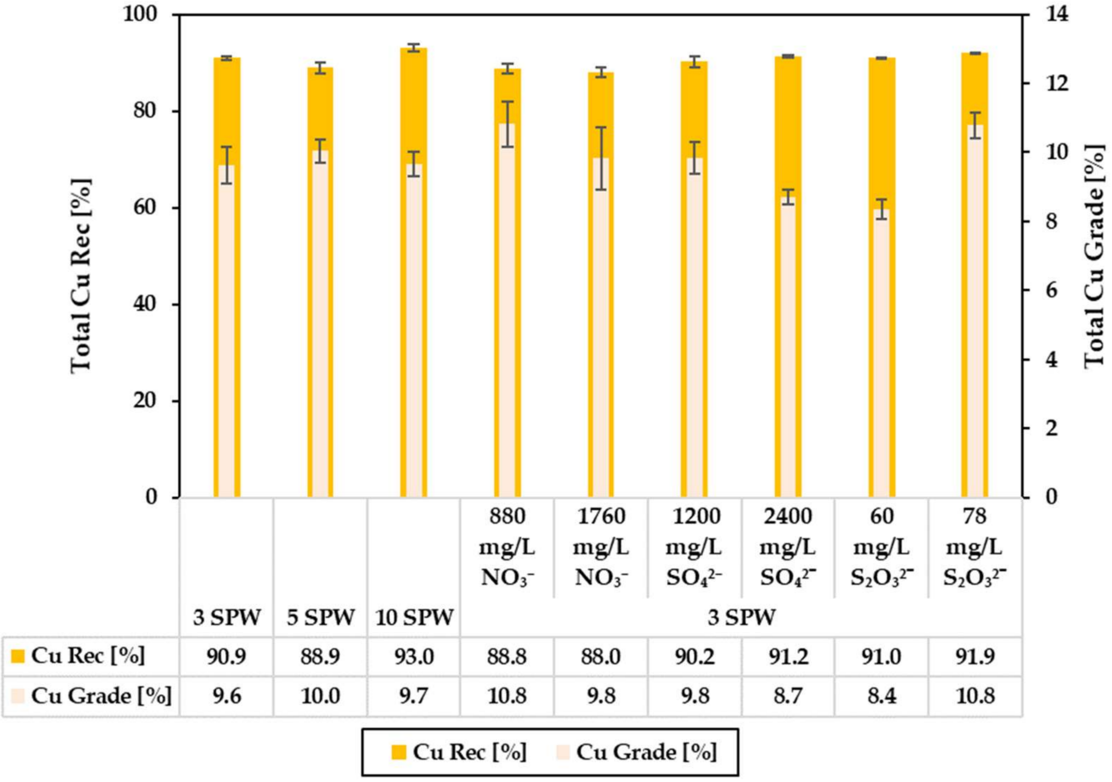
Figure 2. Final Water Rec vs. Solids Rec at different anion spiking concentrations, where 'Rec' refers to recovery.

Increasing the I.S. from 3 SPW to 5 SPW resulted in a decrease in solids recovery. However, an increase in I.S. from 10 SPW resulted in an increase in solids recovery in the order 10 SPW > 3 SPW > 5 SPW. Spiking 3 SPW with 352 mg/L and 1232 mg/L NO_3^- resulted in a decrease in solids recovery compared with 3 SPW; the decrease was within the same range despite the concentration of NO_3^- used (for the two compared anion concentrations). Spiking 3 SPW with 480 mg/L SO_4^{2-} showed no effect on solid recoveries. However, when 3 SPW was spiked with 1680 mg/L SO_4^{2-}, an increase in solids recoveries occurred. As 60 mg/L $S_2O_3^{2-}$ was added to 3 SPW, the amount of solids recovered increased, and a further increase in the $S_2O_3^{2-}$ concentration from 60 to 78 mg/L resulted in a decrease in mass of the solids recovered below that of 3 SPW. The general trend on solids recovery is that SO_4^{2-} and $S_2O_3^{2-}$ have a greater impact on solids recovery compared to NO_3^-; the basis of comparison is the 3 SPW water background matrix. The solids recovery followed the order: 2400 mg/L SO_4^{2-} > 60 mg/L $S_2O_3^{2-}$ > 10 SPW > 3 SPW > 1200 mg/L SO_4^{2-} > 78 mg/L $S_2O_3^{2-}$ $\geq$ 1760 mg/L NO_3^- > 880 mg/L NO_3^- > 5 SPW.

3.2. Effect of Increased NO_3^-, SO_4^{2-} and $S_2O_3^{2-}$ Concentration in Process Water on Recoveries and Grades

Copper recovery for each spiked anion concentration is shown in Figure 3. From 3, 5 and 10 SPW, copper recovery increased, although a dip is seen at 5 SPW compared with 3 SPW, showing a similar trend with that of the solid recoveries shown in Figure 2.

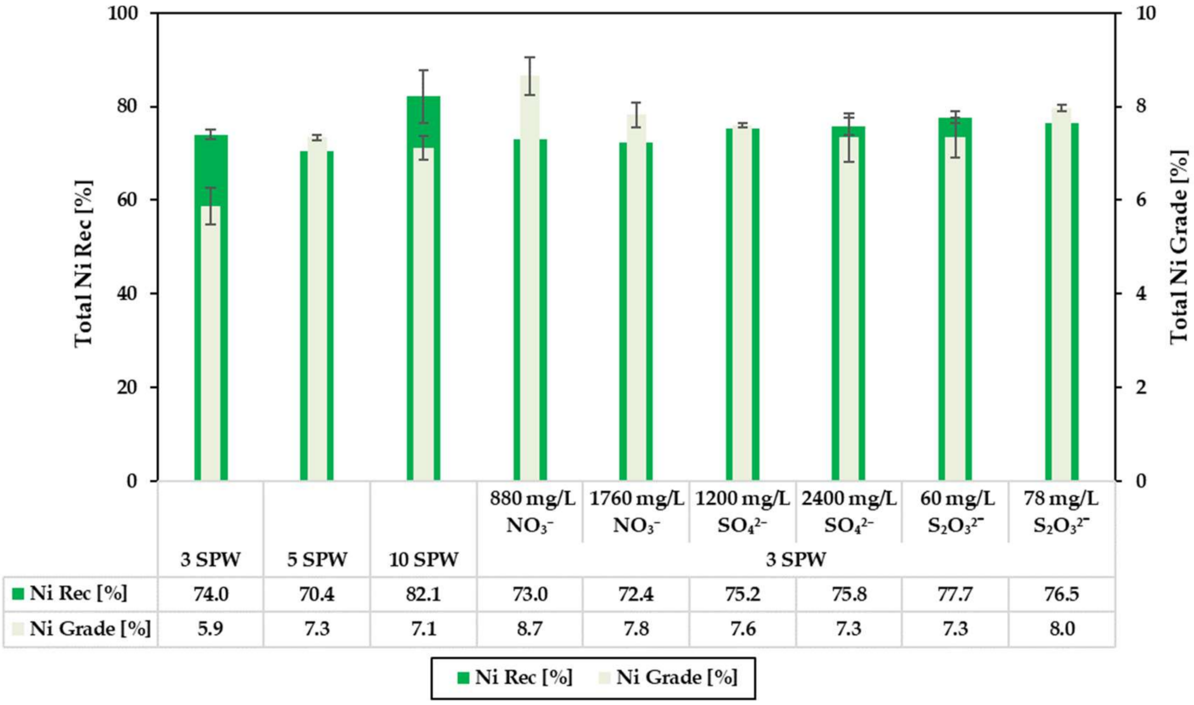
The 5 SPW shows a slight increase in grade, while 3 and 10 SPW show the same copper grade. Adding 352 mg/L and 1232 mg/L NO_3^- to 528 mg/L NO_3^- already contained in the complex background water matrix (3 SPW) resulted in a slight decrease in copper recovery; although this may seem as though it is a recognizable difference, it is statistically insignificant. There was no significant increase in copper grade upon spiking the 3 SPW with the NO_3^- anion. Spiking 3 SPW to levels of 1200 mg/L SO_4^{2-} and 2400 mg/L SO_4^{2-} resulted in no change in copper recovery. The grade of copper also remained unaffected when 3 SPW was spiked to 2400 mg/L SO_4^{2-}. As already mentioned, the $S_2O_3^{2-}$ anion was added separately to 3 SPW. Adding 60 mg/L $S_2O_3^{2-}$ resulted in no increase in copper recovery, while adding 78 mg/L $S_2O_3^{2-}$ constituted a slight increase in copper recovery. The lower spiking level of 60 mg/L $S_2O_3^{2-}$ resulted in a slight decrease in copper grade, while when 3 SPW was spiked with 78 mg/L $S_2O_3^{2-}$, there was a slight increase in copper grade. The impact of anion spiking showed no significant effect on copper recovery and grade. Copper recovery followed the order: 10 SPW > 78 mg/L $S_2O_3^{2-}$ > 2400 mg/L SO_4^{2-} > 60 mg/L $S_2O_3^{2-}$ > 3 SPW > 1200 mg/L SO_4^{2-} > 5 SPW > 880 mg/L NO_3^- > 1760 mg/L NO_3^-, while copper grade followed the order: 880 mg/L NO_3^- $\geq$ 78 mg/L $S_2O_3^{2-}$ > 5 SPW > 1760 mg/L NO_3^- $\geq$ 1200 g/L SO_4^{2-} > 10 SPW > 3 SPW > 60 mg/L $S_2O_3^{2-}$ > 2400 mg/L SO_4^{2-}.



				880 mg/L NO_3^-	1760 mg/L NO_3^-	1200 mg/L SO_4^{2-}	2400 mg/L SO_4^{2-}	60 mg/L $S_2O_3^{2-}$	78 mg/L $S_2O_3^{2-}$
	3 SPW	5 SPW	10 SPW	3 SPW					
■ Cu Rec [%]	90.9	88.9	93.0	88.8	88.0	90.2	91.2	91.0	91.9
■ Cu Grade [%]	9.6	10.0	9.7	10.8	9.8	9.8	8.7	8.4	10.8

Figure 3. Copper Rec and grade at different anion concentrations, where 'Rec' refers to recovery.

The variation of the nickel recovery and associated grade at different synthetic plant water conditions is shown in Figure 4. Increasing the ionic strength of water through 3, 5 and 10 SPW resulted in a dip in nickel recovery at 5 SPW, with 10 SPW recovering most of the nickel. An interesting phenomenon was observed at 5 SPW; although it had a considerably low nickel recovery compared to 3 SPW, it exhibited better nickel grade compared to 3 and 10 SPW. Spiking 3 SPW with 352 mg/L and 1232 mg/L NO_3^- results in nickel recoveries of 73.0% and 72.4%, respectively, compared to 74.0% observed at 3 SPW. NO_3^- did not seem to have a pronounced effect on the recovery of nickel. There was no significant recovery difference between 3 SPW containing 880 mg/L and 1760 mg/L NO_3^-. SO_4^{2-} and $S_2O_3^{2-}$ spiking showed recoveries of nickel to be in the same region, with 60 mg/L $S_2O_3^{2-}$ showing a slight improvement in recovery, i.e., 77.7% nickel recovery compared to 74.0% nickel recovery at 3 SPW. The nickel recovery followed the order: 10 SPW > 60 mg/L $S_2O_3^{2-}$ > 60 mg/L $S_2O_3^{2-}$ > 2400 mg/L SO_4^{2-} >1200 mg/L SO_4^{2-} > 3 SPW > 880 mg/L NO_3^- > 1760 mg/L NO_3^- > 5 SPW.



	3 SPW	5 SPW	10 SPW	880 mg/L NO_3^-	1760 mg/L NO_3^-	1200 mg/L SO_4^{2-}	2400 mg/L SO_4^{2-}	60 mg/L $S_2O_3^{2-}$	78 mg/L $S_2O_3^{2-}$
				3 SPW					
🟩 Ni Rec [%]	74.0	70.4	82.1	73.0	72.4	75.2	75.8	77.7	76.5
⬜ Ni Grade [%]	5.9	7.3	7.1	8.7	7.8	7.6	7.3	7.3	8.0

Figure 4. Nickel Rec and grade at different anion concentrations, where 'Rec' refers to recovery.

Contrary to negligible differences in recovery upon changes in inorganic anion spiking, the grade showed marked improvement for the anions under study in comparison to the baseline experiment—3 SPW, which has a nickel grade of 5.8%. NO_3^- at 880 mg/L (i.e., adding 352 mg/L NO_3^- to 3 SPW) gave the highest nickel grade of 8.7%. Adding 1232 mg/L NO_3^- to 528 mg/L NO_3^- already contained in the baseline experiment (3 SPW) resulted in a nickel grade of 7.8%, which is a 1.9% improvement in nickel grade compared to 3 SPW; however, comparing the two spiking conditions (880 and 1760 mg/L NO_3^-), a decrease in grade (0.9%) was observed at 1760 mg/L NO_3^-. Because 5 and 10 SPW are used as boundary ionic strengths, a comparison was made in relation to 3 SPW, and 78 mg/L showed the second-best nickel grade. The nickel grade followed the order: 880 mg/L NO_3^- > 78 mg/L $S_2O_3^{2-}$ > 1760 mg/L NO_3^- > 1200 mg/L SO_4^{2-} > 2400 mg/L SO_4^{2-} ≥ 60 mg/L $S_2O_3^{2-}$ ≥ 5 SPW > 10 SPW > 3 SPW.

A statistical analysis of the means was conducted as shown in Figure 5. The confidence interval was kept at 95%, and only selected conditions were analyzed. The ANOM of the copper grade revealed that when 3 SPW was spiked with the NO_3^- anion, there was no significant difference (Figure 5a). On the other hand, the NO_3^- anion spiking resulted in a statistically significant increase in nickel, as shown in Figure 5b; the nickel grade at 3 SPW was 5.9%, while at 880 mg/L NO_3^- it was 8.7%, and at 1760 mg/L NO_3^- it was 7.8%. A more positive impact was shown at 880 mg/L NO_3^-. The copper grade results presented in Figure 5c show that spiking 3 SPW with the $S_2O_3^{2-}$ anion had no statistically significant impact. The $S_2O_3^{2-}$ anion showed a positive impact on the low-grade-Cu–PGM ore (Figure 5d) with respect to nickel, because 3 SPW showed a nickel grade of 5.9%, while adding 60 mg/L $S_2O_3^{2-}$ to 3 SPW increased the nickel grade to 7.3%, and 8.0% when 78 mg/L $S_2O_3^{2-}$ was added to 3 SPW; therefore, 3 SPW resulted in a statistically different nickel grade compared to the grand mean.

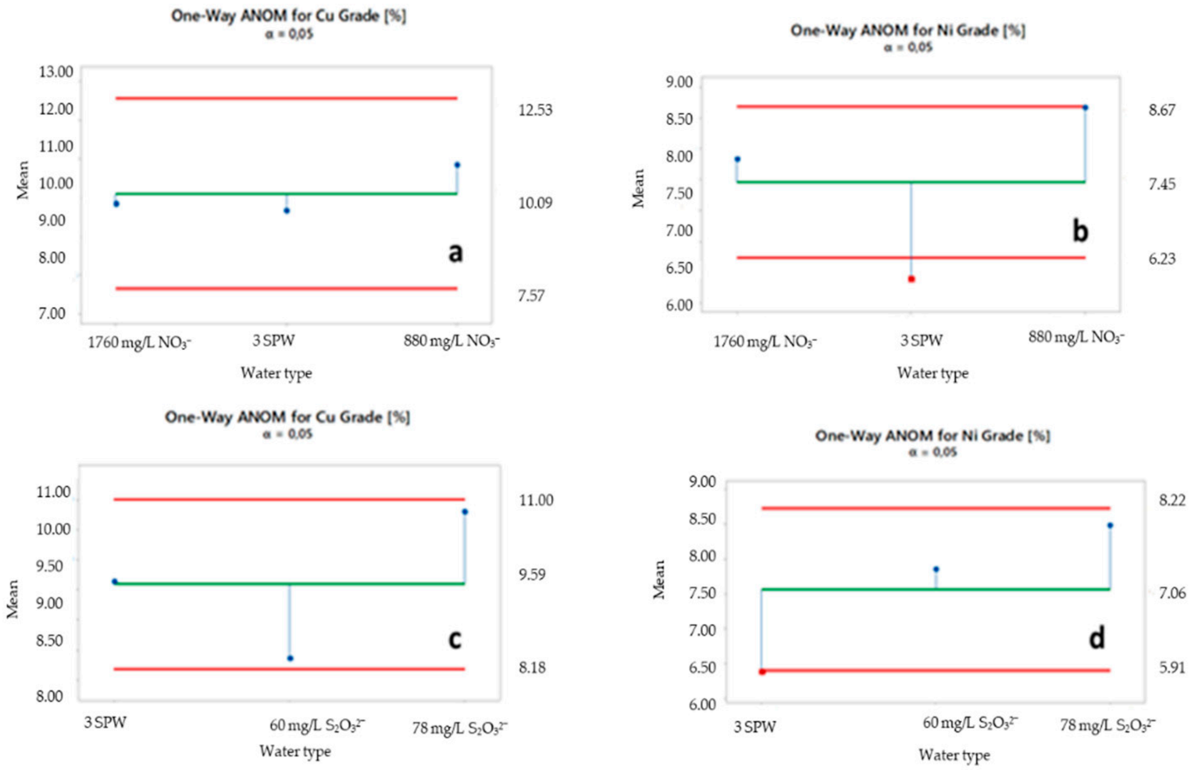
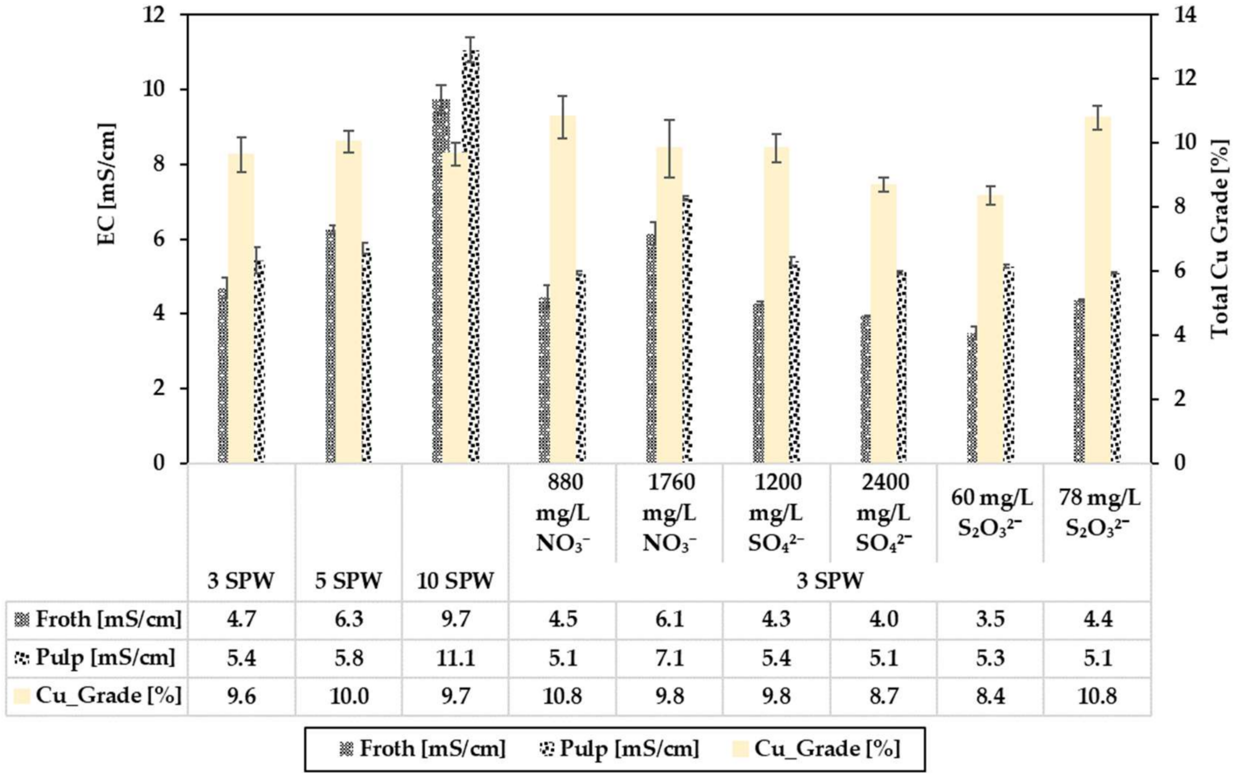


Figure 5. Statistical analysis of means (ANOM) on selected anions at 95% confidence intervals: (**a**) comparison between the baseline experiment 3 SPW with respect to copper grade and varied $NO_3{}^-$ anion concentration; (**b**) comparison between the baseline experiment 3 SPW with respect to nickel grade and varied $NO_3{}^-$ anion concentration; (**c**) comparison between the baseline experiment 3 SPW with respect to copper grade and varied $S_2O_3{}^{2-}$ anion concentration; and (**d**) comparison between the baseline experiment 3 SPW with respect to nickel grade and varied $S_2O_3{}^{2-}$ anion concentration.

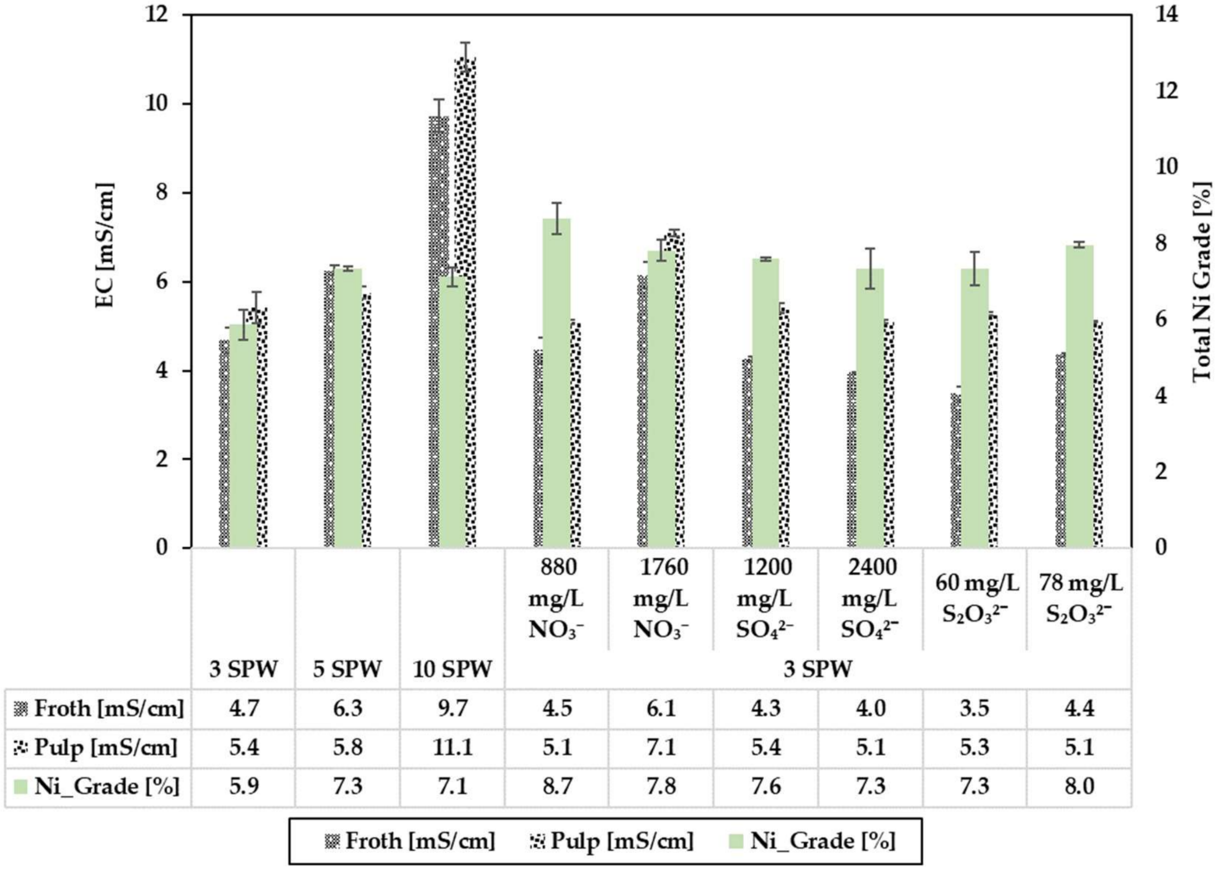
3.3. *Relating the Effect of Spiking* $NO_3{}^-$, $SO_4{}^{2-}$ and $S_2O_3{}^{2-}$ *on the Electrical Conductivity (EC) to Flotation Performance*

The variation in ionic distribution as measured by the EC and the correlation with the concentrate grades is shown in Figures 6 and 7. As the ionic strength of water increased from 3 SPW to 10 SPW, the froth EC was lower compared to the pulp EC at 3 SPW, while at 5 SPW, the froth EC was slightly higher than the pulp EC, and at 10 SPW, the froth EC was lower than the pulp EC. Spiking 3 SPW with $NO_3{}^-$ resulted in a pulp EC greater than the froth EC, particularly at 880 mg/L $NO_3{}^-$ (i.e., adding 352 mg/L to 3 SPW) resulted in a 0.6 mS/cm pulp EC higher than its froth EC, and at 1760 mg/L the pulp EC was 1.0 mS/cm higher than the froth EC; this change in pulp EC was accompanied by a 1.0% decrease in copper grade. Adding 480 mg/L to the 720 mg/L $SO_4{}^{2-}$ already contained in the background complex water matrix (3 SPW) to make the total concentration of the $SO_4{}^{2-}$ anion 1200 mg/L, resulted in a 1.1 mS/cm increase in the pulp compared to its froth; the same difference was observed when 1680 mg/L was added to the 720 mg/L already contained in 3 SPW to make up 2400 mg/L $SO_4{}^{2-}$. Despite the same difference in pulp EC and froth EC between 1200 mg/L and 2400 mg/L, the copper grade decreased by 1.1% and that of nickel decreased by 0.3%. Adding $S_2O_3{}^{2-}$ to 3 SPW generally had a positive impact on the copper and nickel grades. At 60 mg/L $S_2O_3{}^{2-}$, the difference between the froth and pulp EC was 1.8 mS/cm, with pulp EC being higher, while the EC difference at 78 mg/L $S_2O_3{}^{2-}$ as 0.7 mS/cm, with the pulp EC being higher than the froth EC. Between these two conditions of $S_2O_3{}^{2-}$ additions to 3 SPW, the copper grade improved by 2.4%, and that of nickel improved by 0.7%. A notable trend was that, when spiking with 3 SPW with $S_2O_3{}^{2-}$ anion, the pulp EC was always higher compared to the froth EC.



	3 SPW	5 SPW	10 SPW	880 mg/L NO_3^-	1760 mg/L NO_3^-	1200 mg/L SO_4^{2-}	2400 mg/L SO_4^{2-}	60 mg/L $S_2O_3^{2-}$	78 mg/L $S_2O_3^{2-}$
				3 SPW					
▩ Froth [mS/cm]	4.7	6.3	9.7	4.5	6.1	4.3	4.0	3.5	4.4
▨ Pulp [mS/cm]	5.4	5.8	11.1	5.1	7.1	5.4	5.1	5.3	5.1
🟨 Cu_Grade [%]	9.6	10.0	9.7	10.8	9.8	9.8	8.7	8.4	10.8

Figure 6. Relating the electrical conductivity to Cu grade.



	3 SPW	5 SPW	10 SPW	880 mg/L NO_3^-	1760 mg/L NO_3^-	1200 mg/L SO_4^{2-}	2400 mg/L SO_4^{2-}	60 mg/L $S_2O_3^{2-}$	78 mg/L $S_2O_3^{2-}$
				3 SPW					
▩ Froth [mS/cm]	4.7	6.3	9.7	4.5	6.1	4.3	4.0	3.5	4.4
▨ Pulp [mS/cm]	5.4	5.8	11.1	5.1	7.1	5.4	5.1	5.3	5.1
🟩 Ni_Grade [%]	5.9	7.3	7.1	8.7	7.8	7.6	7.3	7.3	8.0

Figure 7. Relating the electrical conductivity to Ni grade.

4. Discussion

4.1. Effect of Spiking 3 SPW with NO_3^- on Flotation Performance

Figure 2 shows the water and solids recovery. It was shown that although 3 SPW had slightly higher solids recovery than NO_3^- at 880 and 1760 mg/L NO_3^-, 3 SPW recovered far less water than either 880 or 1760 mg/L NO_3^-. This showed that the NO_3^- spiking caused the froth to be significantly more stable. This was due to an increase in ionic strength of water and was similarly found by Corin et al. [16], Manono et al. [17,24], and Corin and Wiese [25], where an increase in ionic strength resulted in an increase in water recovery through enhancing the stability of the froth, which was enabled further by the addition of more ions to a certain concentration. The water recovery was in the order 3 SPW < 880 mg/L NO_3^- $\leq$ 1760 mg/L NO_3^- < 5 SPW < 10 SPW. A phenomenon observed here is that increasing the I.S. of water resulted in increased water recovery above the baseline experiment (3 SPW), bubble diameter reduces as the I.S increases [19], and smaller bubbles recover more water. The solids showed a minimum at 5 SPW and followed the order 5 SPW < 880 mg/L NO_3^- < 1760 mg/L NO_3^- < 3 SPW < 10 SPW. As explained by Dzingai et al. [8], the solids percentage (w/v) of the concentrates when combined decreased with I.S. increase, i.e., 3 SPW 10.6%, 5 SPW 5.5%, and 10 SPW 4.7%. Therefore, although 5 SPW may seem to be an outlier by giving the lowest solids recovery for the synthetic plant water test, it fits the solids percentage trends.

Copper and nickel grades increased above that of 3 SPW when the baseline 3 SPW was spiked with NO_3^-, showing an agreeing trend to those the literature on the effect of NO_3^- on copper and nickel grades [19]. Other studies such as Corin et al. [16], Manono et al. [17], and Corin and Wiese [25] have simply stated that as the I.S. of water increases, the grade decreases, owing to increased water recovery and therefore increased gangue entrainment. The observed behavior is indicative of the impact of NO_3^- on gangue depression. The copper and nickel recoveries were not impacted, while the copper grade was higher for the spiked samples and followed the order 10 SPW $\leq$ 3 SPW < 5 SPW < 1760 mg/L < 880 mg/L, and the nickel grade order was 3 SPW < 10 SPW < 5 SPW < 1760 mg/L < 880 mg/L. The increase in nickel grade upon spiking 3 SPW with NO_3^- could be due to some degree of increased collector selectivity at 880 mg/L NO_3^- owing to pulp chemical species which may be present, as well as a reported association of nickel-bearing sulfides with gangue composites [26]. However, beyond 880 mg/L NO_3^-, it was speculated that, for this ore, the gangue material surface became saturated with the ion such that it became difficult for CMC to attach, and as a result, at 1760 mg/L NO_3^-, this gangue material experienced less depression and therefore reported to the concentrate, diluting the purity of the nickel recovered, as shown by the sharp decrease in the grade of nickel (Figure 4). This behavior could be attributed to the increased total ionic strength effect of froth stability which counter-acted the depressive effect of NO_3^- on gangue.

The concentrate grade as a function of EC, observed in Figures 6 and 7, suggests that for a three-phase system, the NO_3^- ions are more concentrated around the mineral surface as compared to the froth phase at 1760 mg/L, as exemplified by higher ECs in the pulp phase. However, a huge difference between the froth and solution at 880 mg/L could indicate the reagent interaction with the NO_3^- ion before the introduction of the ore, and as such results in a slightly higher grade of copper and nickel compared to 1760 mg/L. The NO_3^- could be enhancing the mineral–ion–reagent (Aerophine 3184A) interaction, but beyond the 880 mg/L point there could be over-saturation of the ion, resulting in the activation of the gangue; hence, the grade starts to decrease or the froth stability enhances as a result of an increase in total ionic strength playing more of an important role. More precisely, it could be a "twin-effect" of the NO_3^- depressive effect and the increase in total I.S. which increases froth stability.

Maintaining that the outcomes of this study are ore-dependent, the peak NO_3^- concentration which exhibited higher copper and nickel grades was 880 mg/L, and beyond this concentration the grade decreased. This means that in plant operations when monitoring recycled concentrator water, it is important to consider concentrations of NO_3^- to be below 880 mg/L, because beyond this point, the grade of copper and nickel may start to decrease. Therefore, for this given ore, between 528 and 800 mg/L NO_3^-, lies what could be deemed the threshold NO_3^- concentration beyond which the concentrate grades would be negatively affected.

4.2. Effect of Spiking 3 SPW with SO_4^{2-} on Flotation Performance

Corin et al. [16] observed that increasing ionic strength for a Merensky reef ore did not affect the recovery of the sulfide mineral as measured by copper and nickel recovery, however the grade was impacted negatively due to the increase in ionic strength which resulted in high solids and water recovery and introduced more naturally floatable gangue (NFG) to the final concentrate. The increase in solids and/or NFG recovery was attributed to the gangue activating and froth stabilizing nature of ions present in process water such as SO_4^{2-}. This is akin to the observation made in this research; the ionic strength was increased by spiking 3 SPW with SO_4^{2-} from 0.073 to 0.122 mol·dm^{-3}, as shown in Table 1. As the concentration of SO_4^{2-} ions increased, the overall ionic strength of water also increased, recovering more water compared to 3 SPW due to a more stable froth.

Furthermore, it is important to note that, upon increasing the concentration of the SO_4^{2-} from 1200 to 2400 mg/L, overall copper and nickel recovery remained practically the same, with only a slight decrease in grade owing to higher solids recovery, which can be attributed to gangue material recovery. The decrease in grade is hypothesized to be a result of the complex species formed by SO_4^{2-} on the mineral surface or in the bulk solution, and these species lower the surface area available for hydrophobic bonding, reducing mineral floatability by inhibiting the collector adsorption [8,12].

A concentration of 1200 mg/L SO_4^{2-} was the peak, beyond which the copper and nickel grades decreased. This implies that for recycling streams using concentrator water, it is imperative to maintain the concentration of the SO_4^{2-} ions below 1200 mg/L, and countermeasures should be taken when this concentration has been exceeded.

Bulut and Yenial [27] investigated the effects of major ions in recycled water on sulfide mineral flotation using a complex sulfide ore; each ion was added separately with different concentrations, from 10^{-5} to 10^{-1} M, and in the microflotation tests they showed that as ion concentrations increased from 10^{-5} M to 10^{-3} M, galena recovery also increased, although it decreased at concentrations over 10^{-3} M. Recycled water, which included 567 mg/L (5.5×10^{-3} M) SO_4^{2-} ions, increased galena flotation, but as the concentration rose beyond 10^{-3} M, the galena recovery started decreasing. In our case, the SO_4^{2-} ions showed a decrease in the grade of copper at 2400 mg/L compared to 1200 mg/L but did not show considerable difference between the two spiked conditions, despite the grade being above the baseline experiment (3 SPW).

The EC (see Figures 6 and 7) does not seem to influence the nickel recovery or grade. The difference between the pulp EC and froth EC is 1.1 mS/cm (with pulp being higher) for the two concentrations, i.e., 1200 mg/L SO_4^{2-} (Cu grade = 9.8%, Ni grade = 7.6%) and 2400 mg/L SO_4^{2-} (Cu grade = 8.7%, Ni grade = 7.3%) compared to 3 SPW which contains 720 mg/L SO_4^{2-} (Cu = 9.6%, Ni grade = 5.9%); beyond 1200 mg/L SO_4^{2-} concentration, the copper grade dropped by 1.1%, while that of nickel dropped by 0.3%. This could be explained by the fact that at 1200 mg/L SO_4^{2-}, there is better bubble–sulfide–particle attachment. Similar studies by October et al. [28] considered a fundamental study of specific ion effects on the attachment of sulfide minerals to air bubbles, where the SO_4^{2-} showed better performance with regards to particle–bubble attachment; however, in Ikumapayi et al. [12], it was shown that beyond 1400 mg/L SO_4^{2-} the anion starts affecting the collector efficacy on the sulfide mineral, and consequently, the grade decreased. The difference in these three findings may be attributed to the differences in water type used as well as different ore types and grades.

4.3. Effect of Spiking 3 SPW with $S_2O_3{}^{2-}$ on Flotation Performance

Figure 2 shows that although 3 SPW was spiked with $S_2O_3{}^{2-}$, water the recovered for the two conditions (i.e., 60 mg/L and 78 mg/L $S_2O_3{}^{2-}$) was 60 mg/L $S_2O_3{}^{2-}$ > 78 mg/L $S_2O_3{}^{2-}$ > 3 SPW, showing that 60 mg/L $S_2O_3{}^{2-}$ presented the most stable froth compared to the other conditions. As $S_2O_3{}^{2-}$ increased from 60 to 78 mg/L, water recovery slightly decreased, presumably due to increased bubble coalescence as the recovery of solids followed a slightly similar trend [29].

For hydrophobic particle–bubble attachment to take place, the contact angle and surface tension should thermodynamically possess a decreasing change in free energy, and to achieve optimal attachment, the particle diameter and bubble diameter should be comparable [9,29]. The increase in $S_2O_3{}^{2-}$ concentration in flotation circuits was reasoned to increase bubble coalescence following findings from Kirjavainen et al. [29]; this means that the froth was more stable, and as a consequence resulted in increased water recoveries. According to Corin et al. [16] and Manono et al. [18], an increase in overall ionic strength will result in increased froth stability (derived from increased water recovery) and a decrease in sulfide grade. However, this was contrary to spiking 3 SPW with $S_2O_3{}^{2-}$ from 60 to 78 mg/L. Comparing copper grade in the form 3 SPW: 60 mg/L: 78 mg/L = 9.6%: 8.4%: 10.85%, the higher the $S_2O_3{}^{2-}$ anion concentration (at least for the conditions considered for this study), the better the grade, which is postulated to be due to gangue depression effect of the $S_2O_3{}^{2-}$ anion. The addition of the $S_2O_3{}^{2-}$ anion improved the nickel grade not only in the order: 78 mg/L $S_2O_3{}^{2-}$ (8.0%) > 60 mg/L $S_2O_3{}^{2-}$ (7.3%) > 3 SPW (5.9%) but also showed that the nickel circuit can be operated with $S_2O_3{}^{2-}$ concentrations above 78 mg/L $S_2O_3{}^{2-}$, at this concentration the froth of the low-grade Cu-Ni-PGM ore seemed stabilized and better grades are observed. $S_2O_3{}^{2-}$ improved the gangue depression associated with nickel sulfide flotation as there is a statistically significant (see Figure 5b) nickel grade increase between 3 SPW, 60 mg/L $S_2O_3{}^{2-}$ and 78 mg/L $S_2O_3{}^{2-}$.

Agar [30] conducted electrochemical studies to determine the interaction of $S_2O_3{}^{2-}$ on pentlandite and pyrrhotite surfaces and concluded that $S_2O_3{}^{2-}$ competes with xanthate for adsorption on the mineral, thereby controlling the onset of the induced mineral hydrophobicity of the sulfide mineral. It is important to note that even though the $S_2O_3{}^{2-}$ competed for surface adsorption with the xanthate, it did not consume the xanthate. Xanthate chemisorption takes place at the active nickel sites; this xanthate can be oxidized to form dixanthogen, which then enhances hydrophobicity [30]. This is akin to Kirjavainen et al. [31], who claimed that the $S_2O_3{}^{2-}$ improves sulfide floatability by decreasing the likelihood of the adsorption of hydrophilic compounds, such as hydroxides formed through redox processes. This was also confirmed in Figures 6 and 7, which show that the $S_2O_3{}^{2-}$ was concentrated in the pulp phase compared to its froth phase (observing the EC distribution between the pulp and froth), and as such there was a statistically significant increase in the grade of copper and nickel. There were more ions concentrated in the pulp phase compared to the froth phase, as shown by higher EC in the pulp phase, further suggesting that there is a possible improvement of xanthate attachment to the target sulfide mineral enhanced by the presence of $S_2O_3{}^{2-}$ in the pulp. The $S_2O_3{}^{2-}$ tests showed that the threshold concentration was not yet reached within the range considered in this study, because copper and nickel recoveries and grades were higher than the baseline experiment—3 SPW.

The findings of this study suggest that the increase in $S_2O_3{}^{2-}$ concentration is good for flotation, at least within the range considered in this investigation. This was exemplified by increases in copper and nickel grade upon increases in $S_2O_3{}^{2-}$ concentration. It could be assumed that plant operations can operate using recycled water at $S_2O_3{}^{2-}$ concentrations well within 60 and 78 mg/L, because the threshold seemed to lie outside this range.

5. Conclusions

Recycling process water within spiked anion concentrations did not show much impact on the recoveries of copper and nickel, however a marked effect on the concentrate grade was shown when certain concentrations of specific anions were present. This means that there is a need to manage the number of anions that are recycled to the concentrator before they become detrimental to the overall flotation performance. The impact shown on the grade of the valuable mineral is dependent on the type of ion under consideration and its effect on froth stability and gangue; hence, there is a need to understand and operate within thresholds of each ion to maximize performance. Following the findings of this study, below are the notable conclusions.

NO_3^- spiking: 880 mg/L NO_3^- showed a higher nickel grade and recovery, however further increase to 1760 mg/L NO_3^- resulted in a decrease in nickel grade. The pulp phase showed an increase in the ions at 1760 mg/L. This was similar to what was observed with regards to copper hence the NO_3^- concentration threshold is deemed to be between 528 and 880 mg/L for copper and nickel grade for this given ore.

SO_4^{2-} spiking: 1200 mg/L SO_4^{2-} resulted in similar copper recoveries and grades as 3 SPW, while spiking it to 2400 mg/L SO_4^{2-} resulted in a decrease in copper grade. The 1200 mg/L SO_4^{2-} showed a positive impact on nickel grade, more so than 2400 mg/L SO_4^{2-} when compared to 3 SPW, which had a lower nickel grade. This suggested that between 720 and 1200 mg/L SO_4^{2-} (in comparison to 3 SPW) lies the threshold concentration beyond which the copper and nickel grade was impacted.

$S_2O_3^{2-}$ spiking: Spiking 3 SPW with 60 and 78 mg/L $S_2O_3^{2-}$ resulted in improved floatability of the valuable nickel mineral. Nickel recovery and grade showed an improvement when spiked from 60 to 78 mg/L $S_2O_3^{2-}$. Beyond 60 mg/L $S_2O_3^{2-}$, both copper and nickel grade increased; hence, the threshold was deemed to lie outside of the concentrations considered in this study.

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