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Porvali, Antti

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VTT Technical Research Centre of Finland Ltd
P.O. box 1000
FI-02044 VTT
Finland

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RESEARCH REPORT

VTT-R-00324-24



Bench-scale continuous leaching pilot of raw material bearing Ni and Zn sulfides

Authors: Antti Porvali

Confidentiality: VTT Public

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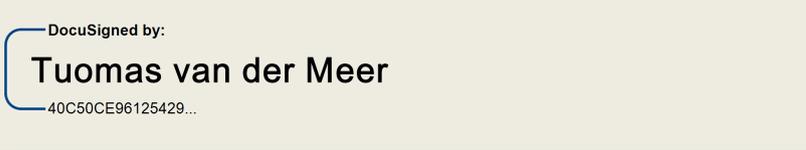
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<p>Summary</p> <p>In this report, a single bench-scale leaching piloting experiment performed is reported. The pilot was conducted as part of the jointly funded project BATCircle2.0.</p> <p>In this work, a continuous cascade leaching (1 L x 3) was performed over a time of 45 hours. Under ideal conditions, hydraulic retention time of 9 h was planned to be used with $T = 70\text{ }^{\circ}\text{C}$, air purging as oxidant with slight excess sulfuric. Intermittent calcium lignosulfonate adding was tested to contain foaming. The slurry was pumped from a pulper to reactor 1 from which the slurry overflow to RC2, RC3 and collection vessel. Mass balance was recorded, and elements analysed in streams.</p> <p>The pilot was operated successfully for 45 hours. However, process stability was not achieved. In the post-mortem analysis shown in this report we hypothesize that the cause was likely the pulper and its pump. Mass-flow out of the pulper remained stable, but the mass balance derived from the process indicated that the quality of feed from pulper was not equal to initial material added to pulper. It appears that gravity-assisted classification may have occurred. In particular, the elemental sulfur whose content was high in the material, appeared to preferentially exit the pulper.</p> <p>Despite the issues and the lower than intended ZnS and NiS content in in the reactors due to classification, Zn extraction worked as intended, and low Zn content was detected in leach residues (<0.5 wt%). Zn and Ni content in leach residue and Zn content in the end filtrate began to increase in the final 11 h of the experiment as pulper now contained larger relative quantity of Zn and Ni than initially. This caused decrease in operating ORP and pH as reagent consumption increased.</p>	
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Espoo 15.8.2024	
Written by	Reviewed by
Antti Porvali Research Scientist	Tuomas van der Meer Research Team Leader
VTT's contact address VTT Technical Research Centre of Finland Ltd, P.O. Box 1000 (Vuorimiehentie 2K), FI-02044 VTT, Finland	
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Name: Tuomas van der Meer

Title: Research Team Leader



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1. Introduction

In BATCircle2.0 project, VTT undertook research pertaining to the processing of sulfidic secondary raw material. In prior work whose results will be published separately, the material was characterized, a leaching process to be explored decided, and various hypotheses were studied to ascertain the extractability of the main components Ni and Zn with the said leaching process.

Characterization revealed the material to contain millerite, sphalerite, and mixed sulfides in small particle size. It was decided that oxidative sulfuric acid leaching would be investigated under atmospheric conditions. In the course of the work, it was decided that the selective extraction of Zn, while utilizing as mild conditions as possible in terms of temperature and oxidant, would be the goal. Therefore, the goal was to maximize Zn extraction while keeping leaching conditions such that Ni extraction was limited. Air was utilized as an oxidizing agent and no further milling was performed on the material and temperature was kept at 70 °C.

In this work report, the results from continuous leaching pilot performed on secondary raw material containing Ni and Zn sulfides as its main component is outlined.

2. Goal

In this work, extractability of Zn in stable continuous mode according to the parameter choices from the to-be-published work was undertaken. The stability of the leaching pilot was observed numerically by means of sensors and mass balance related analyses and data. The goal of the research was to show that the Zn is extractable to a level indicated by the batch experiment data. The recycling of solutions was not taken into consideration in the pilot.

3. Methods

3.1 Materials & Analytics

The chemicals used in this work was H₂SO₄ (8.39 M), calcium lignosulfonate (LS, 99%), de-ionized H₂O and NaOH (in scrubbers). Raw material was dried and characterized in previous work that will be published at later date. Lignosulfonate was prepared into DI water at 50 g/L. The raw material contained ca. 16 wt.% of Zn, 15 wt.% of Ni and 50% of S. The rest is silicates, iron, and some oxygen from small quantity of sulfates present in the dry material.

The leaching reactors were made of acid-resistant steel (904L) and contained integrated baffles with overflow nozzle at 1 L level. In each of the leaching reactor, two integrated pH, T and ORP probe (Endress-Hauser, Memosens CPS16D) were placed. The condition of the electrodes was periodically checked with an external third electrode. Scales were utilized in the mass flow-based monitoring of the pumping rates of solutions (acid, surfactant, pulper slurry). Mass-flow controllers (MFC) were utilized in monitoring and controlling of the supplied technical grade air into the leaching reactors. Data was collected with in-house datalogging system to which the probes, mass-flow controllers and scales were connected to. Solution densities were determined with solution density measurement device (Anton Paar, DMA 35 Version 3).

Solution samples were analyzed with inductively coupled plasma optical emissions spectroscopy (ICP-OES, Agilent, SVDV 5110).



3.2 Pilot Flow Design

The system was composed of three 1 L reactors. With sensors and stirrers, the total volume of each reactor before overflow was 0.8585 L. Thus, the leaching system had a total volume of 2.58 L.

$$V_{system} = 0.8585 \text{ L} \cdot 3 = 2.58 \text{ L}$$

The hydraulic retention time (HRT) was designed to be $t_{HRT} = 9 \text{ h}$ in ideal system. Therefore, the total volumetric flow of an assumed ideal system, barring any changes in volume due to solvation, would be:

$$q_{Tot} = \frac{V_{system}}{t_{HRT}} = \frac{2.58 \text{ L}}{9 \text{ h}} = 286.17 \frac{\text{mL}}{\text{h}}$$

The desired S/L ratio in the RC1, prior any leaching reactions, was $SL_{RC1} = 125 \text{ g/L}$. Therefore, the mass flow of the raw material could be calculated:

$$\dot{m}_s = q_{Tot} \cdot \frac{SL_{RC1}}{1000} = 35.77 \text{ g/h}$$

The individual volumetric flow rate of the raw material could be also calculated as the estimate for the density of the raw material was known $\rho_s = 2.46 \frac{\text{g}}{\text{cm}^3}$:

$$q_s = \dot{m}_s \cdot \rho_s = 14.57 \frac{\text{mL}}{\text{h}}$$

Since the S/L ratio determined the material mass flow, it will also determine the mass flow of the acid into the system as acid to sample mass ratio of 0.6 (g/g) was to be utilized as per the batch experiments. It was determined that steady-state acid concentration of 75.03 g/L would result in the ratio of 0.6:

$$\dot{m}_{pure, H_2SO_4} = 75.03 \frac{\text{g}}{\text{L}} \cdot q_{Tot} = 21.47 \frac{\text{g}}{\text{h}}$$

The pre-made H_2SO_4 solution was determined by titration and density measurement to be 8.39 M and was utilized as is. Therefore, the volumetric and subsequently the mass flow rate, based on volumetric flow and known density ($\rho_{H_2SO_4} = 1.456 \text{ g/mL}$) for the solution was required to be as:

$$q_{H_2SO_4} = c_{H_2SO_4} \cdot \dot{m}_{pure, H_2SO_4} = 822.88 \frac{\text{g}}{\text{L}} \cdot 21.47 \frac{\text{g}}{\text{h}} = 26.09 \frac{\text{mL}}{\text{h}}$$

$$\dot{m}_{H_2SO_4} = q_{H_2SO_4} \cdot \rho_{H_2SO_4} = 26.09 \frac{\text{mL}}{\text{h}} \cdot 1.456 \frac{\text{g}}{\text{mL}} = 37.99 \frac{\text{g}}{\text{h}}$$

Since the RC1 was required to have SL ratio of 125 g/L, and some of the solution was supplied via the sulfuric acid solution, it was necessary to utilize higher SL ratio in the pulper. The required pulper S/L ratio which would fulfil the condition in RC1 (SL = 125 g/L) was determined as follows:

$$SL_{pulper} = \frac{\dot{m}_s}{\frac{\dot{m}_s}{\rho_s} + q_{H_2O}} = 137.5 \frac{\text{g}}{\text{L}}$$

where \dot{m}_s is the mass flow rate of the solid raw materials, ρ_s is the raw material density (2.46 g/cm³) measured by displacement method, q_{H_2O} the pulper water flow rate. This gives the pulper solid liquid ratio. The volumetric water flow rate for the pulper was determined from the fact that the total flow rate is known by design, as well as the acid flow rate and the raw material flow rate. Ergo, the remaining volumetric flow is related to the water from the pulper:

$$q_{H_2O} = \dot{m}_{H_2O} = q_{tot} - q_{H_2SO_4} - q_s = 245.51 \frac{mL}{h}$$

And the total pulper flow rate q_{pulper} and mass flow rate \dot{m}_{pulper} would therefore be:

$$q_{pulper} = q_{H_2O} + q_s = 245.51 \frac{mL}{h} + 14.57 \frac{mL}{h} = 260.08 \frac{mL}{h}$$

$$\dot{m}_{pulper} = \dot{m}_s + \dot{m}_{H_2O} = 35.77 \frac{g}{h} + 245.51 \frac{g}{h} = 281.28 \frac{g}{h}$$

The designed hydraulic retention time was 9 hours for the whole system – i.e., in ideal case, 3 hours per reactor in the cascade. The calculated flow rates to which the pumps were calibrated to are presented in Table 1 in mL/min, calculated from mL/h values presented previously. The surfactant dosing was not included in this calculation due to the small overall quantity added over the whole experiment: 22 mL of 50 g/L calcium lignosulfonate solution was utilized. The required addition rate to maintain suitable surfactant levels as per pre-tests by calculation was 0.488 mL/h which would have required smaller capillary tubes than at the time was available in facility. The entirety of 22 mL was added as bursts over period of 1 minute in 2 h 1 min 44 s intervals. Pulp and acid flow rates include the water in both.

Table 1: The designed flow rates in volumes as well as in masses. Surfactant was not included.

Acid Flow Rate ($q_{H_2SO_4}$)	0.43	mL/min
Acid Flow Rate ($q_{H_2SO_4}$)	0.63	g/min
Total Pulp flow rate	4.33	mL/min
Total Pulp flow rate	4.69	g/min

3.3 Pilot Execution

The pulper was loaded with 1716 g of raw materials with 11776 of DI H₂O. The RC1 was filled up with 734.4 g DI H₂O as well as 107 g of raw materials. 113.6 g or 78 mL of the acid solution was required to be added into the RC1. Acid pump was kept on at the desired flow rate until 113.6 g of the acid was pumped into the RC1, after which the slurry pump from the pulper was switched on as well. This denotes the starting point of the experiment $t = 0$ h where $t = 45$ h denotes the end of the experiment. All pumps were calibrated and tested before the ramp-up.

The leaching pilot was planned to last 45 hours with hydraulic retention time (HRT) of 9 h under ideal flow conditions. These 45 hours included the ramp-up phase of the test which lasted the 9 h. In total, 3.75 cycles (not including the ramp-up) were completed during the work. From the RC1, the slurry overflowed to the RC2 and from RC2 to RC3. All reagents were added only into the RC1, apart from the air which was purged into all reactors. Sampling of the slurry was performed at even intervals from the outflow of the RC3. The experimental setup is schematically explained in Fig. 1. All RCs had airflow supplied into them. From RCs, the airflow was directed into condensers after which the gases were scrubbed by solutions of NaOH in containers.

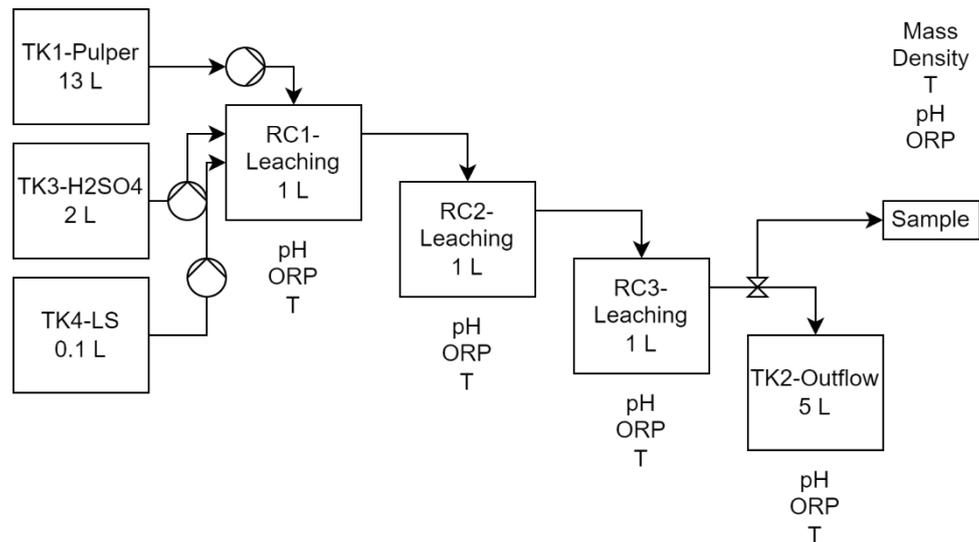


Fig. 1: Schematic representation of the leaching pilot and its measurements.

The time schedule of the experiment is outlined in Table 2. The experiment lasted ca. 45 hours in total, including the ramp up. Sampling was undertaken every 4.5 hours. Every 9 hours, i.e., when a cycle was completed, the collected bulk sample was filtered, repulped, and washed. Every 2 hours a slurry sample was retrieved from the mixed pulper, and its wet content measured with a moisture analyzer. Although the moisture analyzer will not give completely correct value due to the dissolved species present in the pulper water, it should be stable and make it possible to monitor the wet-content change throughout the experiment.

Table 2: The sampling time-schedule of the test.

Datetime	Cycle	Note
11.2.2024 21:19	-	Ramp up
12.2.2024 1:49	-	
12.2.2024 6:19	0.00	Ramp up end
12.2.2024 10:49	0.50	
12.2.2024 15:19	1.00	
12.2.2024 19:49	1.50	
13.2.2024 0:19	2.00	
13.2.2024 4:49	2.50	
13.2.2024 9:19	3.00	
13.2.2024 13:49	3.50	
13.2.2024 16:05	3.75	Exp. end

4. Results

4.1 Mass and volumetric flow balance

According to the designed total flowrate $q_{Tot} = 302.75 \frac{g}{h}$ the total mass flow over the 45 hours of feeding time would equal to 13623.76 g of mass flow. However, the recovered masses (overflow and reactor

beyond the obvious



contents) only summed up to 11055 g of masses. Of all the masses pumped into the reactor system, 13263.8g were recovered, and the 400 g is loss due to washing and repulping (which could potentially be calculated backwards to recover the masses dissolved therein – this was not done) as well as losses during filtration and repulping. In particular, the first repulping caused losses, causes which were then fixed for subsequent repulping. However, losses cannot explain the discrepancy between the planned outflow and realized outflow. The masses are summarized below in Table 3.

Table 3: Mass recoveries in the pilot. Both solution and solid masses from all units.

Expl.	Site	Mass in the Site	Unit
Initial			
Initial solids in	Pulper	1716	g
Initial solutions in	Pulper	11776	g
Initial solutions in	RC	848	g
Initial solids in	RC	107	g
SUM	RC+Pulper	14447	g
Mass recoveries			
Final	Input	2209	g
Final	Output	10725	g
	Total	13264	g
Solids in	OF	571	g
Solids in	RC	330	g
Solids in	Pulper	424	g
Solutions in	OF	7749	g
Solutions in	RC	2406	g
Solutions in	Pulper	1785	g
Recovered	Solutions	11939	g
Recovered	Solids	1325	g
Mass in	OF+RC	11055	g
Mass in	Pulper	2209	g

As there was discrepancy in the masses recovered and what was designed, flow rates were inspected. During the experiment, flow rates were monitored and recorded for the process stability. Overall, the experiment was executed successfully over 45 hours. However, the process stability was not achieved during the leaching, despite appearing so for the first 28 hours appearing so. First, the pulper mass flow stability was monitored with the help of the scale upon which the entire pulper resided. The scale had a resolution of tens of grams which allows for limited data resolution due to the limited flow rate out. Based on the pre-determined pulper mass flow rate ($\dot{m}_s = 4.69 \text{ g/min}$), the resolution was as follows:

$$t_{res_s} = \frac{10 \text{ g}}{4.69 \frac{\text{g}}{\text{min}}} = 2.13 \text{ min}$$

Furthermore, the resolution was impacted by the requirement of having constant stirring. Therefore, the value itself has inherent uncertainty but over a period of time, should predict the steadiness of mass flow and even allow estimation whether the slope would be changing over time periods greater than more than 2 minutes. The value was recorded from the scale manually every 30 minutes.

The flowrate out of the pulper ranged throughout the experiment and decreased from 280 g/h to 237 g/h and 243 g/h at closer to the end of the experiment. The cutoff points have been chosen based on visible changes to the chemical conditions in the system that were observed as well. The designed pulp flow rate was 281 g/h. Initially, the mass flow out of the pulper has worked as intended and calibrated. Although the pulper flow rate was initially as designed, there were indications that the system was not working as it was intended. For instance, decrease on pulper tank water content was observed, i.e., the solid concentration in the pulper was increasing. This is the first indication of classification occurring. This was plotted as well as a function of time.

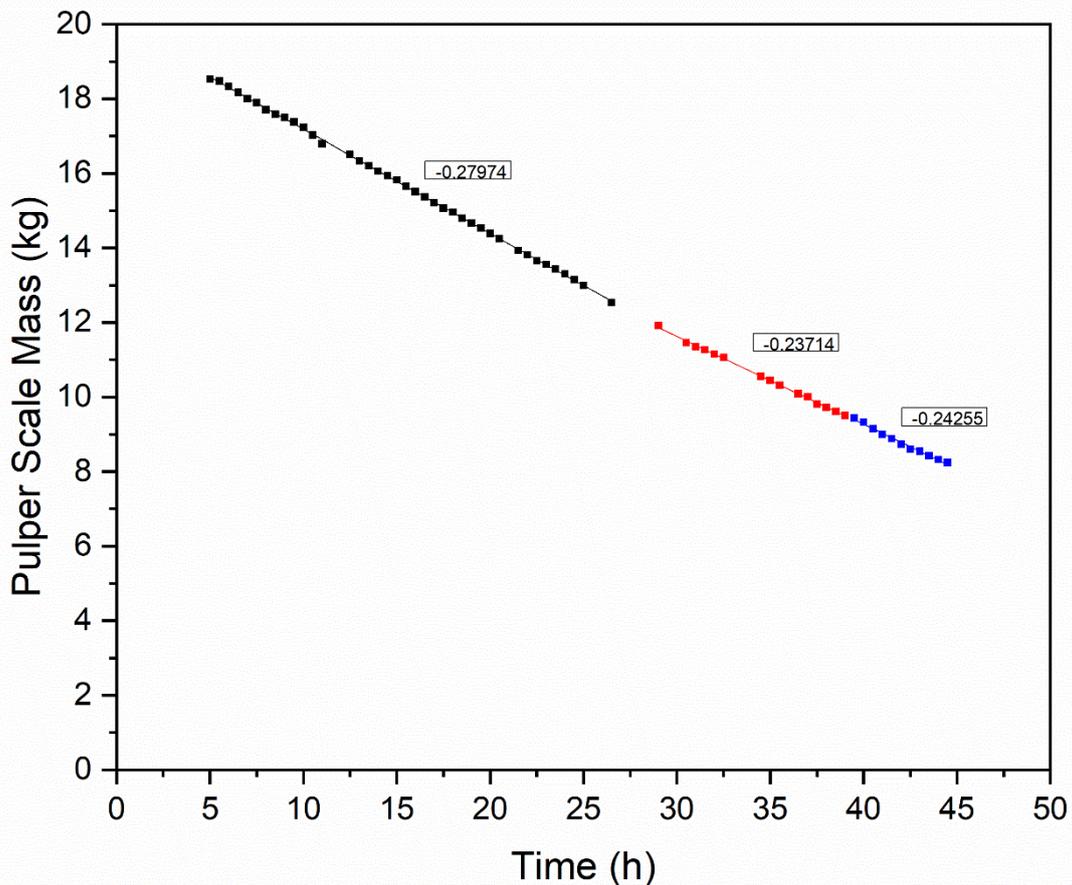


Fig. 2: The pulper mass change. The slope of the plotted lines is in boxes, indicating the kg/h pump differential.

H₂SO₄ feed was recorded throughout the experiment. Sufficient quantity of acid solution was placed on a scale in a graduated cylinder. A linear line was fitted into the data as a function of time (h). The slope therefore indicates the real mass flow rate of the acid, which was 38.365 g/h, Fig. 3. Therefore, the feed rate of the acid was higher than what was designed by 0.366 g/h. This, in turn, would result in slightly shorter hydraulic retention time as well as higher steady-state acid concentration than designed: 75.77 g/L vs. 75.03 g/L, respectively. The error in steady-state acid concentration was less than 1%, a relatively



minor deviation. Of the two different major pumps, it appears the pulper pump is the likely culprit for the imbalance between designed mass flow rate vs. realized mass flow rate.

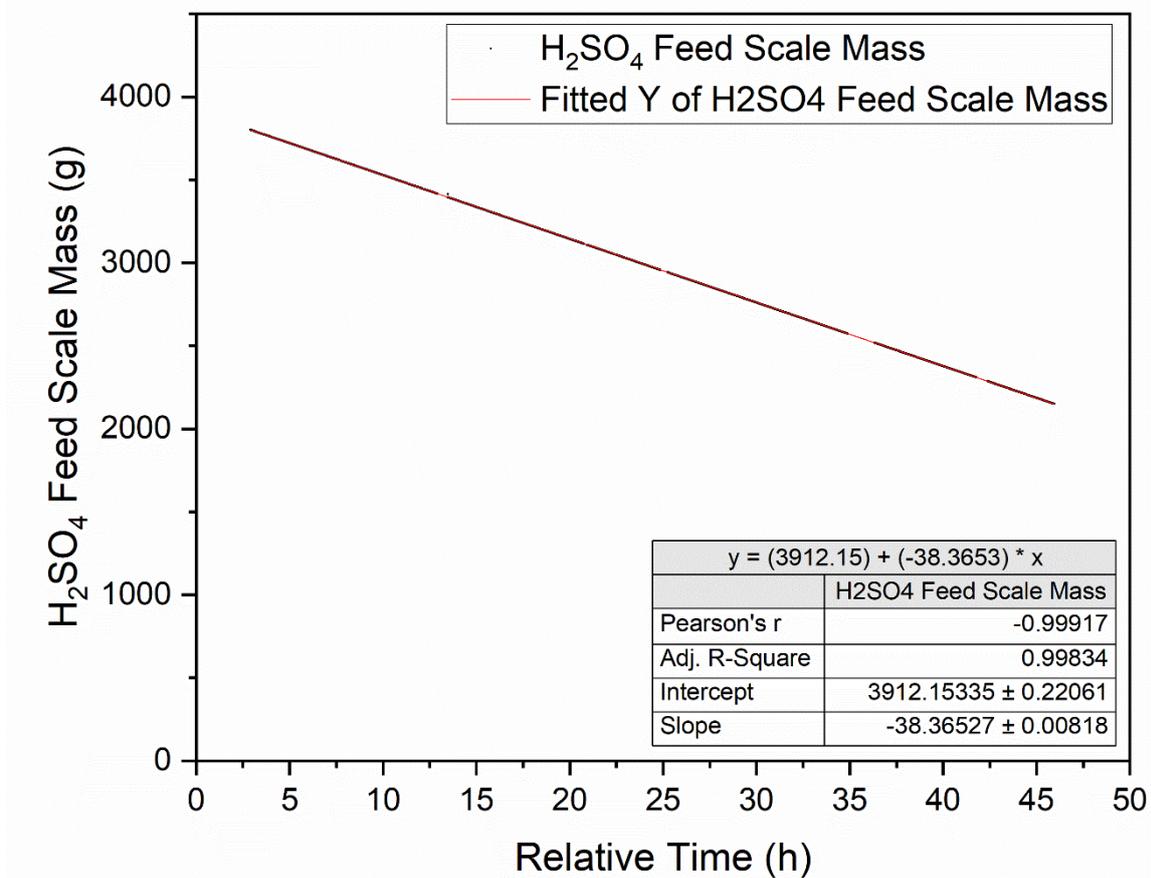


Fig. 3: The acid feed scale mass change graph.

Since the issue in the experiment appeared to occur in the pulper pump side the individual subsamples per HRT cycle was measured: solution and solid masses as well as solution densities. This allows comparison of mass recoveries between the cycle time points of 1, 2, 3 and 3.75. The results are presented in Table 4. There are two distinct changes occurring during the experiment: the recovered masses per HRT cycle. HRT1 and HRT2 had identical functioning, as was also indicated by the pulper scale (Fig. 2). However, the recovered masses decreased for HRT3. Compared to HRT3, HRT3.75 had anomalously high mass recovery considering it was not a full HRT cycle. Second difference is in the ratio of recovered solution volume per mass of solids; however, this can change due to many things: changes in process conditions and extraction kinetics vs. flow-rate changes or compositional changes.



Table 4: mass and solution recoveries per HRT from filtration.

Mass Recoveries per HRT

HRT1	Solution	2090.8	g	2261	Mass sum (g)
HRT1	Density	1.0818	g/cm ³	12.3	Mass ratio
HRT1	Volume	1933	cm ³	0.924	Ratio (g/L, solids/solution)
HRT1	Solids	170.0	g		
HRT2	Solution	2161.4	g	2296	Mass sum (g)
HRT2	Density	1.0831	g/cm ³	16.1	Mass ratio
HRT2	Volume	1996	cm ³	0.923	Ratio (g/L, solids/solution)
HRT2	Solids	134.3	g		
HRT3	Solution	1799.0	g	1937	Mass sum (g)
HRT3	Density	1.094	g/cm ³	13.0	Mass ratio
HRT3	Volume	1644	cm ³	0.914	Ratio (g/L, solids/solution)
HRT3	Solids	138.1	g		
HRT3.75	Solution	1721.3	g	1850	Mass sum (g)
HRT3.75	Density	1.113	g/cm ³	13.4	Mass ratio
HRT3.75	Volume	1547	cm ³	0.898	Ratio (g/L, solids/solution)
HRT3.75	Solids	128.5	g		

Finally, the pulper wet content (and therefore, relative solid content) was monitored throughout the experiment. The wet content clearly decreased over the experiment, seen in Fig. 4. This likely signifies that there was an issue with homogeneous flow out of the reactor, and more solution was taken up from the pulper by the pump than solids than intended. This was potentially indicated as well by the measured ratio of obtained solution volume per obtained solid residue, shown in Table 4. As the relative mass of liquid phase present in the pulper decreased, it was more likely that solids would be taken up by the pump over time. This would negatively impact the process stability as well as cause improper raw material feed into the RC1.

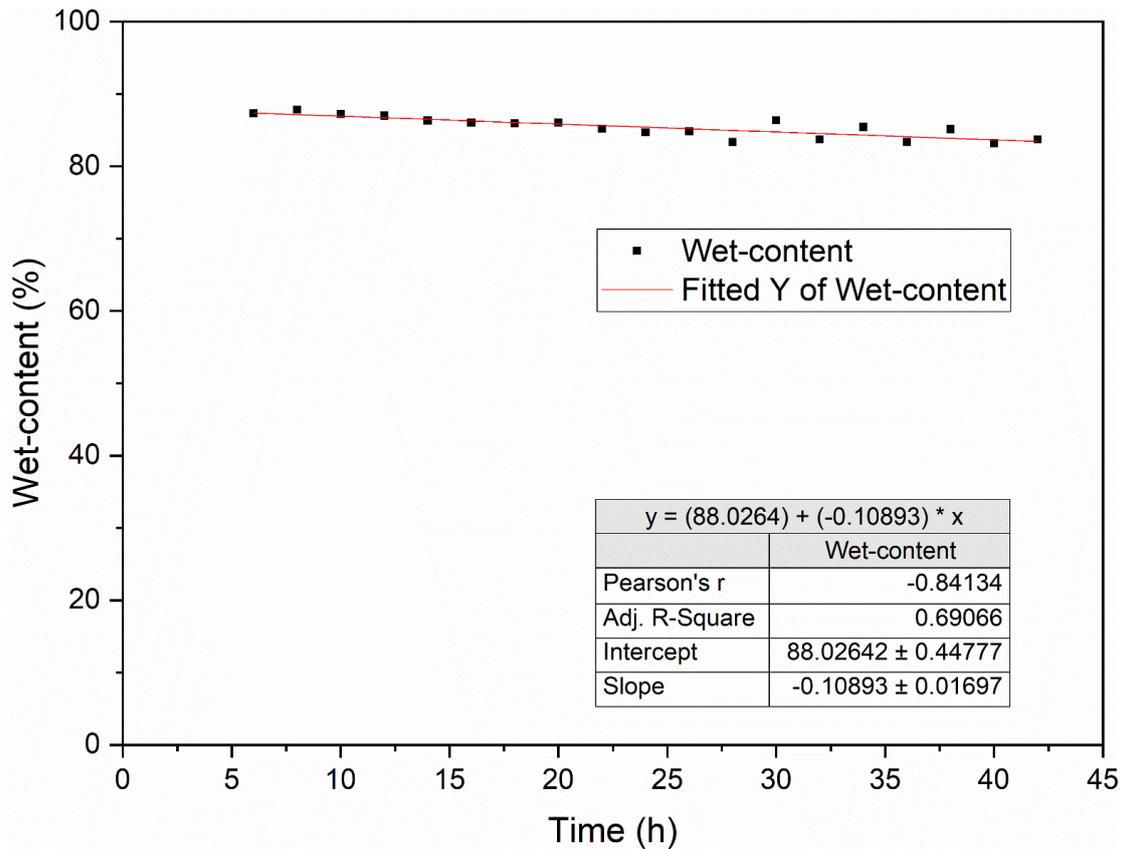


Fig. 4: Pulper wet-content over the duration of the experiment.

4.2 Process Chemical Conditions

The pH, ORP and temperature was recorded for all the reactors throughout the leaching pilot with two sensors present in each reactor. It was expected that the pH of the RC3 should be in the range of 0.5 – 1.0 at the end, and lower in RC1 and RC2 at steady-state. The pilot was designed to run at sufficient acid excess to trigger acid attack on the material. The realized, measured pH values are presented in Fig. The acidity is high enough that the values can't be considered too reliable. In conjunction with the pH values, ORP was recorded and offers valuable information on the process conditions and in their stability. Drastic changes could be observed to have occurred in the system in two places. The first change occurs slightly before HRT cycle 2 ends, around midnight between 12.2. and 13.2. This was likely due to the adjustments made to the pump tubing in the pulper as unintended bubbling was detected from the support structures. The second change was after HRT cycle 3 completed and was caused the need to adjust the height of the pulper vs. the stirrer. As limited raw materials were available for this experiment, it was not possible to fill up the pulper over time. Filling the pulper would have improved the process stability in two ways: first, the abrupt changes caused by the second manual adjustment would have been avoided. Second, the mixing conditions in the pulper likely changed over time which may have impacted how the pulper pump functions. As was discussed in previous section, the small scale of the experiment (1 L reactors in cascade) likely exacerbated the issue and could therefore be improved by utilizing slightly larger (e.g., 3 L or 5 L) reactors, which would significantly increase all the flow rates and make the whole system more resistant to small deviations.

In terms of pH, a clear change was associated with both breakpoints where adjustments were made, causing increase in pH and therefore decrease in acidity, i.e., acid was simply consumed. The only material consuming acid in the system is the raw material. Therefore, either less acid was supplied than previously or more acid-consuming materials were provided into the system. As was seen in Fig. 3, there was no issues with the acid feed according to the scale nor reported by the operators in the laboratory log.

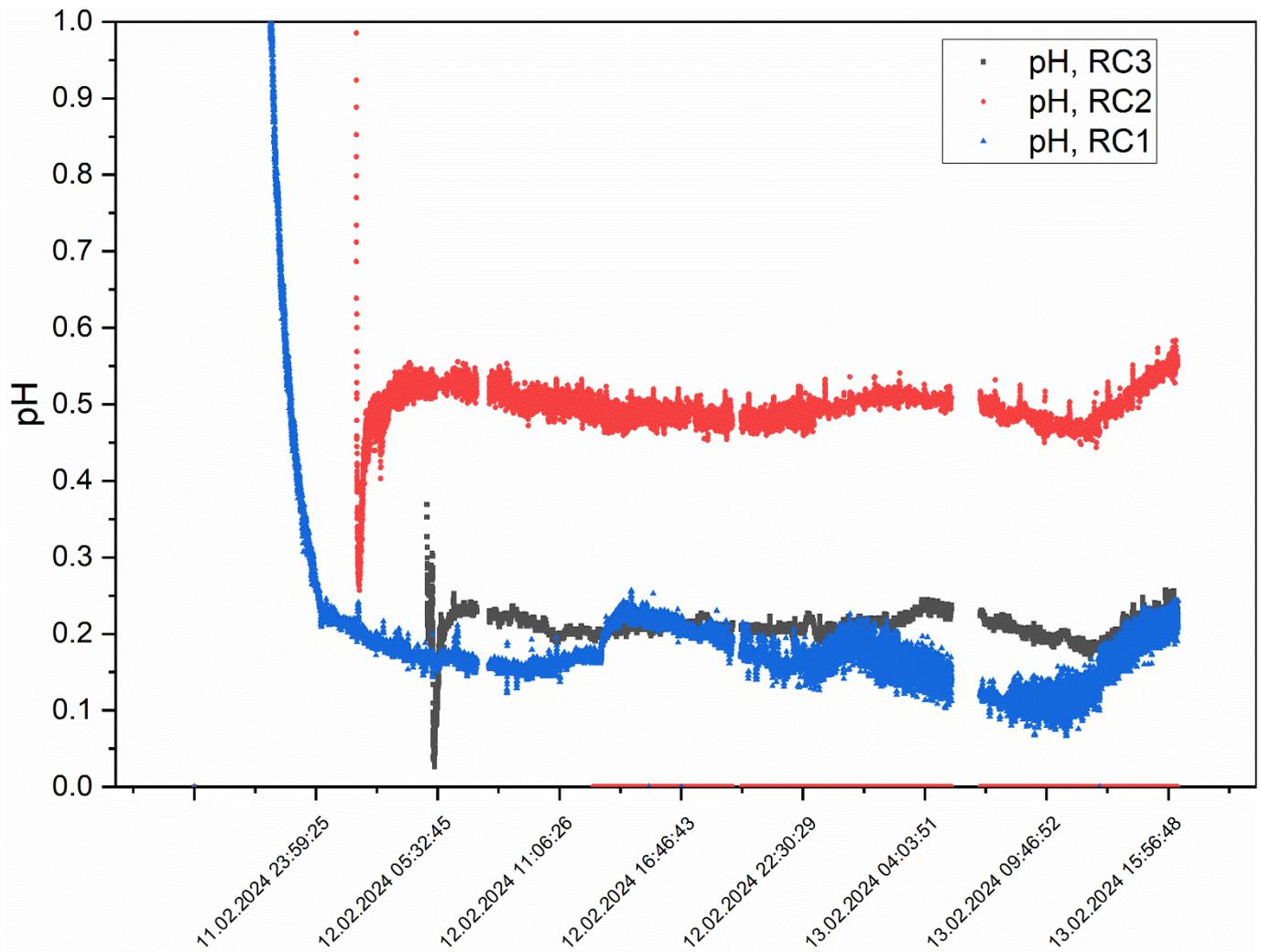


Fig. 5: pH data from the three different reactors. Single channel data.

ORP data indicated stability issues in the process at the previously mentioned stages of leaching: just before HRT cycle 2 when the tubing was adjusted and just after HRT cycle 3 when the pulper stirrer height was adjusted. Both instances caused clear disturbances to mass flow rate (Fig. 2), pH (Fig. 5) and ORP (Fig. 6). Change in ORP to lower level is indicative of breakup of steady-state equilibrium at which the dissolved species reside in the solution. The only significant source of reductive reagents is the raw material from the pulper. ORP change therefore indicates increase in uptake of reductive materials such as ZnS and NiS from the pulper into RC1. The more dramatic change of ORP in RC1 and RC2 and only minor in RC3 indicate that the additional materials react well before arriving to RC3, and ORP remained high therein. The second disruption caused catastrophic collapse in ORP. This is a clear indication that unreacted reductive raw materials are reaching RC3 and possibly the overflow container.

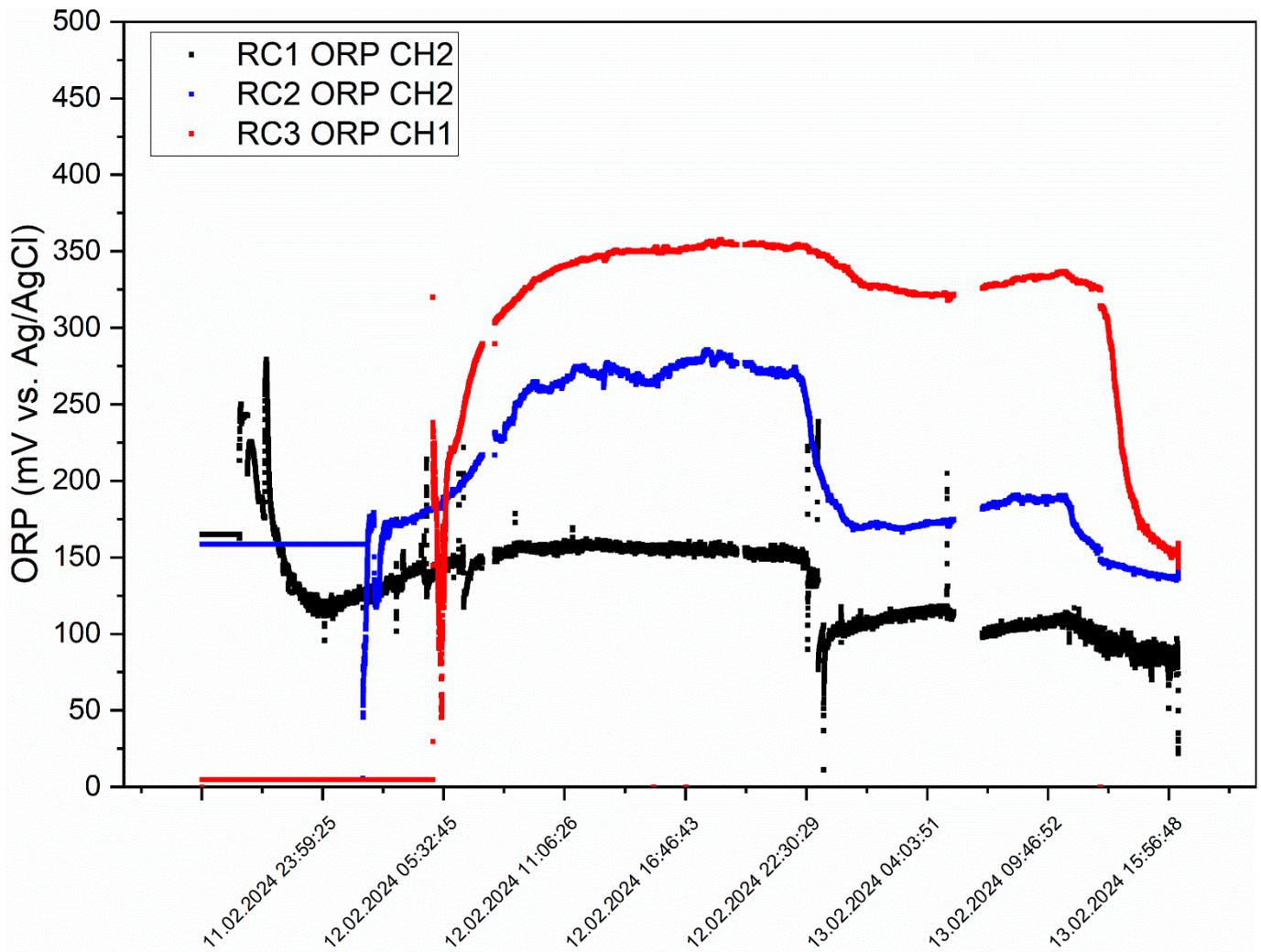


Fig. 6: ORP data from the three different reactors. Single channel data.

The recovered HRT samples from the overflow every 0.5 cycles were analyzed and are reported in Fig. 7. The results herein support the assertion discussed previously that the primary reason for the unstable functioning of the experiment was the inconsistency with the pulper. As the pulper pump tubing was adjusted shortly before HRT cycle 2 sampling, there is a dramatic change in the trend of Zn concentration in the solution and Ni concentration in the leach residue. Remarkably, it appears the change is similar in magnitude for both Zn and Ni. As it was known and expected that NiS present in the material would not dissolve, and for ZnS the opposite was true, the result supports the hypothesis that the amount of solid phase present in the pulper pump feed increase at the expense of liquid phase. Overall, Zn concentration was lower than expected at the designed SL ratio of 125 g/L. Between HRT0 – HRT2 there is steady decrease of Zn content in solution, a clear indication that solids are not transferred from the pulper at the homogeneous composition. In terms of leaching efficiency, Zn was efficiently extracted, and the goal of < 5000 ppm was achieved until the HRT cycle 3, where the second disruption caused by lifting of the pulper caused changes to solids uptake. Despite the surfactant, it is believed that there were shift to non-ideal overflow and solids were carried all the way to the collection vessel in 0.5 cycles already. The non-ideal overflow was caused by foaming phenomena occurring due to the increase of reactive Ni and Zn bearing sulfidic raw material from the pulper.

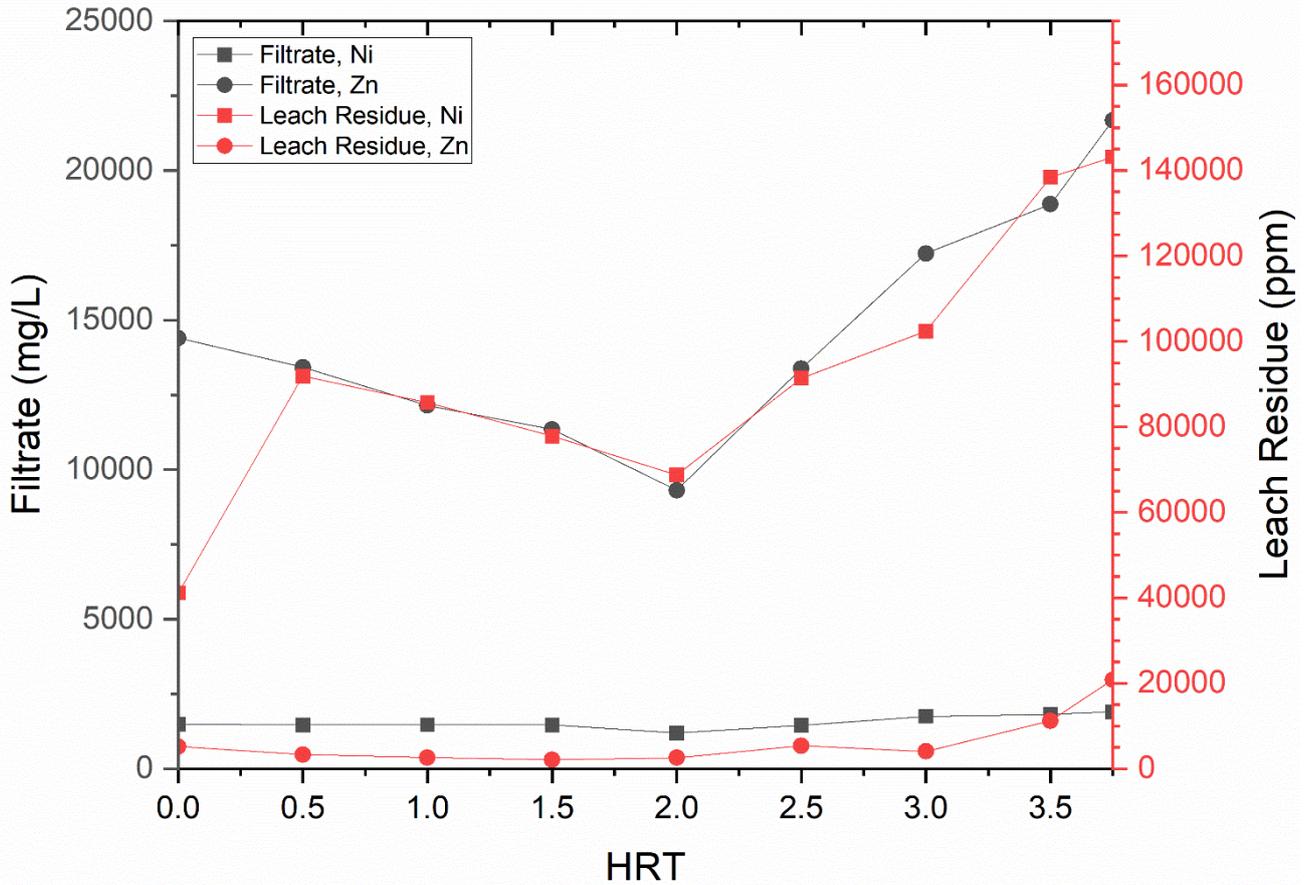


Fig. 7: The Zn and Ni concentrations in the solution (mg/L) as well as in solids (ppm, mass fraction).

4.3 Element Recovery and Mass Balance

After the experiment, all solids, and selected solutions (PLS and first pulping or washing solution) were analysed. First, the Zn and Ni elemental recoveries were inspected. The whole system (pulper, reactors, overflow samples) contained initially 297 g of Zn and 268 g of Ni. These quantities should be found dispersed into filtrates, leach residues, and solids still in pulper. In terms of solids and solutions, distribution and recoveries shown in Table 5 was seen. As was seen in the mass flow inspection (Table 3), there is only 25% of the solid mass remaining in the pulper at the end of the experiment, whereas 31% of Ni was still present in the pulper. 1716 grams of solids were initially set into the pulper, and 424 g remained in the pulper after the experiment as was shown in Table 3. Therefore 24.7% of the solids remained in the pulper while the rest, 75.3% was removed by the pump. Therefore, if the mass flow had been homogeneous mixture of the solids from the pulper from the beginning, it should be possible to observe that 75.3% of Ni is either in the OF solutions or OF leach residues. Now only 20.5% was found in the overflow. This is potentially an indication of enrichment of NiS into the pulper. In terms of densities, pure sphalerite has density of 4.04 g/cm³ while pure NiS has density of 5.5 g/cm³ [1]. It is possible that NiS has more strongly classified in the pulper.



Table 5: Distribution of Zn & Ni in the pilot, and their total mass recovery. OF is the sum of all the overflowed solid and liquid phases, and so on.

Solid phase	Zn (g)	Ni (g)	Zn %	Ni %
OF	3.8	54.9	1.3	20.5
RC	38.1	92.6	12.8	34.5
Pulper	75.4	83.4	25.4	31.1
SUM	117.3	230.8	39.4	86.1
Liquid phase	Zn (g)	Ni (g)	Zn %	Ni %
SUM	155	20	52.3	7.3
Total	Zn (g)	Ni (g)	Zn %	Ni %
SUM	273	250	91.8	93.4

Peculiarly, largest fraction of Ni was present in the reactors at the time of the end of the experiment. As no unusually high Ni concentration was detected in the leach residues of the HRT cycle samples, it is likely that the second abrupt change to the pulper pump functioning caused after HRT cycle 3 is the likely culprit: large fractions of NiS and ZnS was suddenly taken in into the RC1, which caused the dramatic changes observed in ORP Fig. 6. As the raw material contained elemental S, which is very light compared to the sulfides (~2 g/cm³), it is also possible that in the initial stages of the experiment elemental S was preferentially up taken. This was confirmed by the ICP-OES analysis of the solids, Fig. 8. Over 90% S content was detected in the very first sample. Although part of the S is sulfidic, majority of the S present in the raw material was elemental. 36 wt% of the raw material was elemental S.

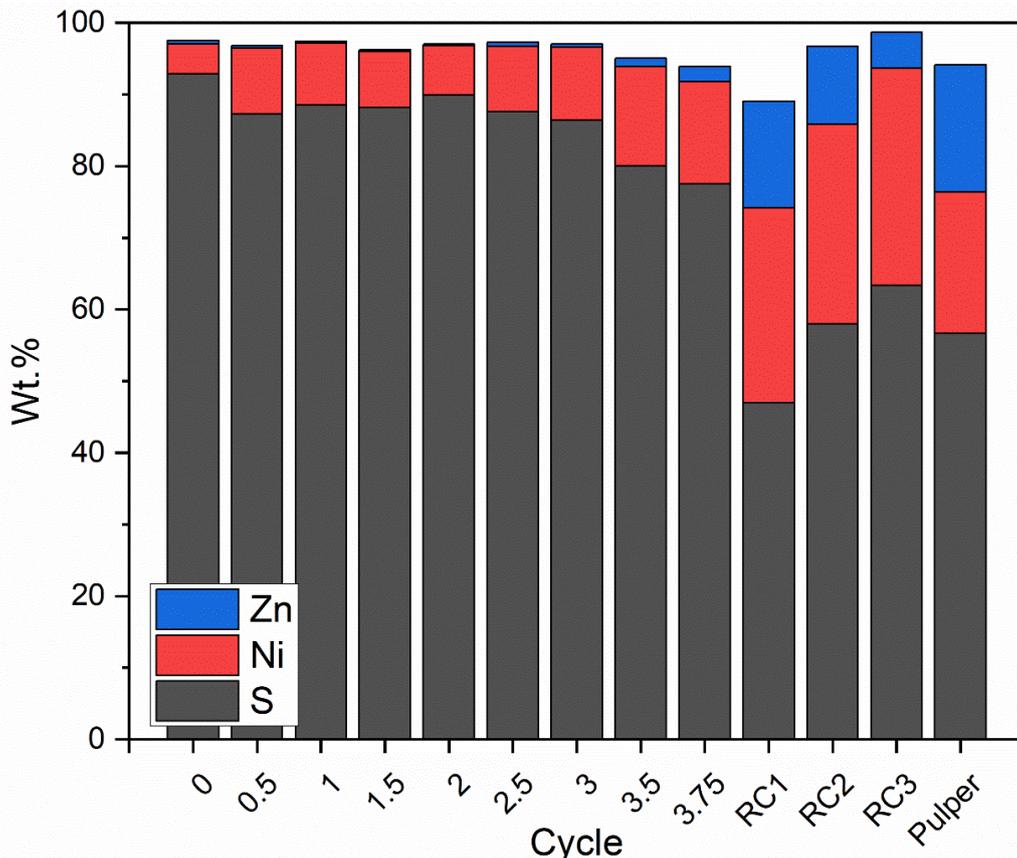


Fig. 8: The % concentration of S in the analysed residues. The number indicates a cycle sample. RC1, RC2, RC3 and pulper indicate the solids present in each vessel at the end of the experiment.



4.4 Technical Improvements

The project allowed a single piloting run from the perspective of raw materials and resources. Despite the initially correct mass flow out of the pulper at the time and shortly after of the calibration, there were clear issues that were centrally related to the peristaltic pump and pulper. First, if pulper overflow is operated by pump, the flow rates should be sufficient. In this work, 4.33 mL/min was the flow rate from pulper to the reactor. A peristaltic pump with Masterflex LS 16 tubing was utilized with inner diameter of 0.12 mm, or 0.012 cm. This is flow velocity of ca. 1.6 m/s. Decreasing the tubing size to increase the flow velocity is not an option as the particle size could become a limiting factor if it wasn't already in this case. Based on particle-size analyses reported elsewhere (unpublished manuscript, 2024), D100 of the material was smaller than 0.01 cm.

Increasing the scale of the experiments from 1 L reactors to 3 L reactors (i.e., at least tripling the system total volume), would at least triple the needed volumetric flow rate and hence flow velocity. Increase in the flow velocity may help facilitate the cleanup and transport of solids alongside the solution. The sufficiency of the pumping system should be tested in the future with similar material. The study was also limited by the quantity of raw material available which necessitated the scale of the operation to 1 L x 3 reactor cascade.

Another option would be to transform the equipment setup to utilize gravimetric overflow from the pulper to the RC1 with the help of the screw feeder. However, here the raw material quantity available for the test was also a limiting factor and the use of screw feeder was rejected.

5. Conclusions

A single leaching piloting experiment was undertaken based on batch experiments. Small-scale (1 L x 3) continuous cascade was utilized due to the limitations in the raw material availability, allowing experimentation and evaluation of technical challenges presented such experimental setup. Overall, Zn was extracted as indicated by the batch experiments and < 0.5 wt.% Zn mass fraction was achieved apart from the final moments of the experiment (HRT cycle of 3.5, 3.75). Technical challenges were encountered, and based on the process-wide data analysis, the main culprit was likely the pulper pump. Although mass flow rate was initially as designed, the flow rate slowed down. Additionally, it appears likely that the pulper pump flow rate was not appropriate for the material and gravity-assisted separation of NiS and ZnS occurred from the lighter material. Less solids flowed into the reactor than was expected from the design point. To avoid such issues in the future utilizing such small scales, it would be important to avoid pumping of slurry against gravity and either utilize a screw feeder or increase the scale of the experiments to allow faster slurry pumping rates.

6. Summary

- A pilot was operated successfully for 45 hours.
- Technical challenges were encountered. Based on extensive process-wide data analysis, the likely culprit was the pulper pump setup which caused uneven mass flow rate as well as classification of particles.
- S was preferentially up taken by the pulper pump, while leaving NiS and ZnS into the pulper.
- As raw material quantity available for the experiment was limitation, small-scale had to be utilized. This caused following challenges:



- Screw feeder was too larger for the material quantity.
- Slurry pump rate was low, and clearly insufficient the way it was set up.

The challenges may be alleviated by utilization of sufficient raw material quantity to allow for the use of 5 L reactors, ensuring by scale the sufficient slurry flow rate in the pumping and avoiding pumping against gravity by experimental design.

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8. References

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