Nuorivaara, Ted; Klemettinen, Anna; Serna-Guerrero, Rodrigo

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Improving the flotation recovery of Cu from flash smelting slags by utilizing cellulose-based frother formulations

Ted Nuorivaara, Anna Klemettinen, Rodrigo Serna-Guerrero *

Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, PO Box 16200, FI-00076 Aalto, Finland

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ABSTRACT

Froth flotation is an operation currently used for the recovery of Cu from pyrometallurgical smelting slags due its simple operation and relatively low operational costs. While it has been utilized for many decades, it may be necessary to develop strategies that improve Cu recovery from slags, as the unprecedented increase in Cu demand has made industrial waste and side streams economically relevant sources of metals.

This study presents a novel chemistry-based approach for the flotation of Cu from smelting slags by utilizing an amphiphilic cellulose-surfactant mixture as a flotation frother, hereby referred to as CellFroth. The present work pursues two main objectives: i) to improve the performance of flotation for the treatment of smelting slags and ii) to accomplish a first proof of concept for frothers produced from renewable sources in the context of industrial waste treatment. The flotation performance of CellFroth was compared with a commercially available additive (i.e., DowFroth250) and hydroxypropyl methyl cellulose (HPMC).

The results showed significant advantages in performance for CellFroth. At the highest collector concentration, Cu recovery was higher with CellFroth compared to DowFroth 250 and pure HPMC (73%; 62% and 65% respectively). A 75% reduction in xanthate concentrations had negligible effects on Cu recovery for CellFroth (70%), while recoveries decreased drastically with DowFroth250 (47%) and pure HPMC (50 %). Finally, CellFroth consistently reached comparable concentrate productivity (grade and recovery) as DF250 within significantly shorter flotation times. The use of CellFroth thus offers the possibility of increasing the Cu recovery from flash smelting slags, while reducing the environmental impact of the process by using a frother produced from sustainable sources and simultaneously reducing xanthate consumption.

1. Introduction

Copper has been an essential metal in the development of our modern society and its role will be more critical as a larger manufacturing capacity and a growing world population further increase its demand. To help meeting the exponentially rising global needs, it is necessary to further improve the efficiency of Cu production processes. Currently, the majority of primary Cu is produced by enriching sulfidic Cu-bearing ores with froth flotation and subsequently processing the concentrates via pyrometallurgical operations, typically via flash smelting (Najdenov et al., 2012; Tian et al. 2021).

In the pyrometallurgical production and beneficiation of primary Cu, the formation of smelting slags is a necessary by-product. It is estimated that ca. 2–3 tons of slag are generated for each ton of Cu produced (Tian et al., 2021). However, slag formation enables an efficient collection of a copper-rich matte in the smelting procedures (Sibanda et al., 2020). In practice, this is achieved by adding a fluxing agent, typically SiO₂, which forms the slag phase by its combination with other oxides, thus enabling the isolation of the Cu-rich matte (Gorai and Premchand, 2003; Potysz et al., 2015). The density of the slag phase is lower compared to that of the matte, allowing an efficient separation in preparation for further beneficiation steps. As the separation of slag and matte is not perfect, a significant proportion of Cu is inevitably lost into the slag formed during smelting (Shen and Forssberg, 2003; Wang et al., 2013). For these reasons, the efficient recovery of Cu from slag, which would otherwise be considered a waste stream, may have a considerable economic and ecological impact.

The three most common approaches to recover Cu from smelting slags are hydrometallurgy, pyrometallurgy and froth flotation (Liu et al., 2020; Tian et al., 2021; Zhou et al., 2021). While hydrometallurgical slag cleaning has been demonstrated as an efficient extraction technique for Cu and other heavy metals present in the slag, it is often not preferred.
due to its need for complicated waste management procedures and its operational costs are considered high (Liu et al., 2020; Tian et al., 2021). Alternatively, the pyrometallurgical cleaning processes offer advantages in geographical areas where electricity is inexpensive (Demetrio et al., 2000) and/or when a particularly high-grade matte can be produced (Acuna and Sherrington, 2005). However, the pyrometallurgical route also presents some limitations, e.g., low Cu recovery, and comparatively high energy and water consumption (Karimi et al., 2013).

One of the biggest motivations behind using froth flotation as the preferred slag cleaning method is the comparatively high levels of Cu recovery it provides (Schleisinger et al., 2011). Indeed, historical accounts of a Finnish smelting operation already showed that Cu recovery with an electric furnace was of 77% but with the introduction of flotation as the slag cleaning process, the overall Cu recovery increased to 88% (Lakkarinen, 1967). Furthermore, the principles for Cu slag flotation (i.e. chemical reagents and standard operating procedures) are considered analogous to typical sulfidic Cu ore flotation (Shen and Forsberg, 2000), and thus, shares its well-known benefits, namely, low operational costs, low energy consumption, high production efficiency and vast knowledge generated throughout the years (Goral and Premchand, 2003; Liu et al., 2020). Nevertheless, with increasing raw materials demands and the need to minimize permanent losses of valuable materials as dictated by philosophies in vogue such as the circular economy, it is worth exploring alternatives to further improve the flotation efficiency for slag treatment (Liu et al., 2020; Sibanda et al., 2020).

While there are various operational aspects that have a significant impact on the flotation behavior of Cu smelting slags, such as the cooling schedule of the slag, the composition of the slag, particle size, pH, solids content, etc. (Tian et al., 2021), the topic of this manuscript is to study the effect of a novel frother formulation that has been recently developed in our research group (Nuorivaara and Serna-Guerrero, 2019; Nuorivaara and Serna-Guerrero, 2020a; Nuorivaara and Serna-Guerrero, 2020b; Nuorivaara and Serna-Guerrero, 2020c). This new type of froth stabilization reagent, hereby referred to as “CellFroth” is based on a combination of an amphiphilic cellulose derivative, namely hydroxypropyl methyl cellulose (HPMC), and commercial polyglycol surfactants, which effectively form an interactive polymer-surfactant (PS) mixture. In previous interfacial characterization studies, a synergistic adsorption at the air–liquid interface was identified for the PS-mixture (CellFroth), manifested as accelerated diffusion rates. Such faster initial adsorption may have improved coalescence prevention, resulting in bubble size reductions and improved control over foam stability (Nuorivaara and Serna-Guerrero, 2020b).

The use of CellFroth has reportedly improved the flotation of a synthetic Zn ore, synthetic Cu ore, natural Cu ore and Cu-bearing tailings in terms of improved recovery of the valuable mineral, faster flotation kinetics and improved tolerance towards varying operational conditions (Nuorivaara and Serna-Guerrero, 2019; Nuorivaara and Serna-Guerrero 2020a; Nuorivaara and Serna-Guerrero, 2020c).

The aim of the present study is to systematically study the use of CellFroth as an aid in the flotation of Cu smelting slags, supported by the evaluation of mineralogy that are successfully beneficiated with it. Consequently, the current study presents the first ever experimental research manuscript on the flotation of Cu containing smelting slags with PS-mixtures as flotation frothers. In this manner, it is expected to demonstrate whether this chemical additive with lower environmental impact also offers the possibility to reduce the losses of Cu into waste.

2. Materials and methods

2.1. Materials

The studied Cu slag samples were collected from the flotation feed of a real industrial Cu slag flotation site and were received as a ground, dry powder. Based on XRF-measurements carried out with an Oxford Instruments, X-Met5100 XRF gun with a specific setting for mineral samples, the main constituents of the slag samples were Fe (37.86 %); Zn (2.29 %); Cu (1.64 %); Ca (0.83 %), Pb (0.54 %), and a minor presence (>0.5%) of elements such as Mo, As, Co, Ba, Ni and Sn.

The HPMC used in this study was purchased from Sigma-Merck (Product No. 423238), with a nominal molecular weight of 10 kDa, a methoxyl content of 29% and a hydroxypropyl content of 7%. The CellFroth sample was produced in a similar manner as previously reported for the flotation of Cu ore (Nuorivaara and Serna-Guerrero, 2020c). The performance of pure HPMC and CellFroth was compared to an industrial grade DowFroth 250 (DF250) (from Dow Chemical). The collector used in all aspects of this study was an industrial-grade sodium isobutyl xanthate (SIBX). All Chemicals were used without any further purification. Mother solutions of the reagents were prepared by diluting the chemicals in ultra-pure water (UPW), purified with a Millipore Q-3 water purification system down to a resistivity of 18.2 MΩ. The water used in the flotation experiments was municipal tap water from Espoo, Finland.

2.2. Methods

The Cu slag samples were divided into representative samples of approximately 600 g using a Retsch rotary sampling machine. The mass of the samples was verified with a Precisa XB 6200D laboratory scale.

Further characterization of the feed samples was conducted by energy-dispersive X-ray spectroscopy (EDS). The samples were mounted in epoxy (Struers, Denmark), ground and polished using the traditional wet metallographic method. The samples thus prepared were carbon coated with a vacuum evaporator (JEOL IB-29510V) in order to achieve sufficient electrical conductivity of sample surfaces.

Elemental mapping of the sample microstructure was carried out with a Scanning Electron Microscope (SEM, Mira3, Tescan, Czech Republic) equipped with an UltraDry Silicon Drift Energy Dispersive X-Ray Spectrometer and NSS Microanalysis Software (Thermo Fisher Scientific, Waltham, MA, USA). In all measurements, an acceleration voltage of 15 kV and a beam current between 9 and 10nA on the sample surface were used. The principle for Cu slag flotation (Lukkarinen, 1967). Furthermore, the principles for Cu slag flotation (i.e. chemical reagents and standard operating procedures) are considered analogous to typical sulfidic Cu ore flotation (Shen and Forsberg, 2000; Roy et al., 2015). The consequent lower collector concentrations were selected with an aim to observe the flotation performance of DF250 as a benchmark against which the new frother formulations (HPMC and CellFroth) were compared. The total frother concentration in all aspects of the study was 20 parts per million (ppm), in relation to the amount of water in the suspension, with varying collector (SIBX) concentrations.

The highest collector concentration was based on levelsakin to previous studies, which are also common in industrial practice (Stirbanovic et al., 2011; Roy et al., 2015). The consequent lower collector concentrations were selected with an aim to observe the flotation performance of each frother as the hydrophobicity of valuable minerals.
decrease, similar as previous studies made by the authors (Nuorivaara and Serna-Guerrero, 2020a; Nuorivaara and Serna-Guerrero, 2020c).

The full set of experimental conditions are compiled in Table 2. In order to help identifying each experiment, they have been labeled based on the frother chemical species (D = DF250; H = HPMC; C = CellFroth), frother concentration (20 ppm) and xanthate concentration in g/t (i.e., X30/X60/X120). Finally, the letter R in selected experiment stands for the word “repetition”. For example, D20-X120 means that the experiment was run with 20 ppm of DF250 and 120 g/t of xanthate.

Before flotation, each sample was ground with a laboratory-scale ball mill (Technical research center of Finland, type 14MK3/9) with a volume of 5.67 l using a ball charge of 5.5 kg and a solids content of 50 % for 5 min to reach a nominal particle size of d80 = 45 μm. The particle sizes of the samples were confirmed by performing laser diffraction particle size analysis (Mastersizer 3000) on five randomly selected samples. It is worth noting that the main aim of this grinding procedure was to polish possibly tarnished surfaces rather than significantly altering the particle size of the feed.

After grinding, the slurry was transferred to the flotation cell with sufficient additional water to reach a solids content of 33 %. The conditioning procedure was conducted directly in the flotation cell as follows: 1) the slurry was stirred for five minutes at 1300 rpm; 2) the impeller speed was lowered to 900 rpm and collector was added after which the slurry was stirred for three minutes; 3) frother was added and the slurry was stirred for three minutes. Once the latter stirring period was over, the impeller speed was increased back to 1300 rpm and air flow was started, marking the beginning of the flotation experiment (t = 0).

Five froth fractions were collected at 0–3; 3–6; 6–10; 10–14, and 14–20 min intervals. For the first 10 min of the flotation experiments, froth was manually scraped 10 times every 30 s and between 10 and 20 min the froth was collected by scraping 15 times every 60 s. A video of the froth was manually scraped 10 times every 30 s and between 10 and 20 min intervals. For the first 10 min of the flotation experiments, the tailings were filtered using filter paper with 0.45 μm pores and the collected tailings and froth fractions were dried in a 100°C oven. After each flotation experiment was recorded with a digital camera to have a qualitative comparison on froth properties for each frother species. As seen, the model also considers the squared effect of collector concentration.

3. Results and discussion

3.1. SEM EDS

The SEM-EDS characterization images of the feed are exemplified in Fig. 1, with further EDS analyses available in the Supplementary Information, S1. Upon investigation, the association of elements in specific groups was identified. As seen in Fig. 1, the main groups are formed by: 1) Cu, Pb and S 2) Fe, Co and O 3) Al, Si, Ca and O

EDS results indicate that Pb and Cu are mostly found in the form of sulfides, and the other elements are present as oxides. While the results presented in Fig. 1 cannot be directly used to determine the exact mineralogy of the sample, it can be used to reasonably predict the most likely mineralogies present in the slag. For the purposes of the present study, the most relevant piece of information to be extracted was the mineralogy of Cu containing species.

As stated above, the grains of sulfidic minerals contain both Cu and Pb. However, it is known that Cu and Pb are rarely present in the same sulfide mineral structure. Furthermore, the main sulfidic species containing Cu in smelting slags reported in the literature are: bornite ((Cu9FeS8), chalcopyrite (CuFeS2), and chalcocite (Cu2S) (Potysz et al., 2015; Tian et al., 2021). According to such studies, Cu may also be present in some complex oxide and hydroxide species. Based on the results presented in Fig. 1, neither Fe nor O are strongly associated with Cu. Furthermore, Potysz et al. (2015) stated that sulfidic species such as cubanite (Cu9Fe2S8), covellite (CuS), digenite (Cu9S5), trolley (FeS), and pentlandite ((Fe,Ni)9S8) are not typical of Cu slags. Thus, it is reasonable to assume that Cu is mostly present in the form of chalcocite (Cu2S), as it is the only listed sulfidic Cu species that does not include Fe. Thus, for the purposes of calculating the flotation performance in terms of SE, it was assumed that all Cu is found in the form of chalcocite.

3.2. Flotation results

3.2.1. Flotation behavior of elements other than Cu

To have a good understanding on the floatability of the slag under study, the behavior of elements other than Cu will be analyzed in the first place. Table 3 displays the average values for the grades in froth and tailings from all conducted flotation experiments. The results represent a simplified compilation of the overall flotation behavior of each element. A more thorough compilation of experimental results for these elements is presented in the Supplementary Information (S2). While variations in operational conditions affected the recoveries of each element, their grades were comparable throughout all flotation experiments. This facilitates the evaluation of flotation behavior for each specific element. As can be seen in Table 3, As and Pb were moderately enriched to the froth fraction, while Zn, Fe and Co were not.

Table 2

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Experiment name</th>
<th>Frother</th>
<th>SBIX (g/t)</th>
<th>sample mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>D20-X30</td>
<td>DF250</td>
<td>30</td>
<td>60.9</td>
</tr>
<tr>
<td>2</td>
<td>D20-X30-R1</td>
<td>DF250</td>
<td>30</td>
<td>61.3</td>
</tr>
<tr>
<td>3</td>
<td>D20-X30-R2</td>
<td>DF250</td>
<td>30</td>
<td>57.3</td>
</tr>
<tr>
<td>4</td>
<td>D20-X60</td>
<td>DF250</td>
<td>60</td>
<td>60.4</td>
</tr>
<tr>
<td>5</td>
<td>D20-X120</td>
<td>DF250</td>
<td>120</td>
<td>61.0</td>
</tr>
<tr>
<td>6</td>
<td>H20-X30</td>
<td>HPMC</td>
<td>30</td>
<td>59.8</td>
</tr>
<tr>
<td>7</td>
<td>H20-X30</td>
<td>HPMC</td>
<td>60</td>
<td>59.0</td>
</tr>
<tr>
<td>8</td>
<td>H20-X120</td>
<td>HPMC</td>
<td>120</td>
<td>60.7</td>
</tr>
<tr>
<td>9</td>
<td>C20-X10</td>
<td>CellFroth</td>
<td>10</td>
<td>56.9</td>
</tr>
<tr>
<td>10</td>
<td>C20-X30</td>
<td>CellFroth</td>
<td>30</td>
<td>59.2</td>
</tr>
<tr>
<td>11</td>
<td>C20-X30-R1</td>
<td>CellFroth</td>
<td>30</td>
<td>59.6</td>
</tr>
<tr>
<td>12</td>
<td>C20-X30-R2</td>
<td>CellFroth</td>
<td>30</td>
<td>57.1</td>
</tr>
<tr>
<td>13</td>
<td>C20-X60</td>
<td>CellFroth</td>
<td>60</td>
<td>60.0</td>
</tr>
<tr>
<td>14</td>
<td>C20-X120</td>
<td>CellFroth</td>
<td>120</td>
<td>59.6</td>
</tr>
</tbody>
</table>
As Pb is found in a sulfidic form according to the results presented in Section 3.1, its enrichment into the froth fraction is understandable, since the collectors used in this work are known to promote hydrophibization of sulfidic species. Indeed, Cu smelting slag flotation is typically designed similarly to sulfide ores flotation (Shen and Forssberg, 2003; Bulut et al., 2007). On the other hand, the enrichment of As into the froth implies that a proportion of As can be associated with sulfidic Cu species as proposed in by previous studies (Potysz et al., 2015; Tian et al., 2021; Zhou et al., 2021). Certainly, Fig. 1 shows that As is evenly spread throughout the slag sample. Further contemplations regarding the behavior of As are however considered to be outside the scope of this manuscript.

Contrarily to As and Pb, the rest of the monitored metallic elements enriched to the flotation tailings. As mentioned above, Cu smelting slag flotation resembles sulfide ore flotation, which consequently means that the species that do not enrich to the froth fraction are likely present in the form of oxides. The SEM-EDS images in Fig. 1 show a strong correlation between Fe, Co and O. The poor floatability of both Fe and Co in Cu-smelting slags is well documented (Shen and Forssberg, 2003; Bulut et al., 2007). For Fe, this behavior arises from being found in mineralogies such as fayalite (Fe2SiO4), magnetite (Fe3O4), and hematite (Fe2O3) (Tian et al., 2021), whereas Co is known to be dispersed throughout the slag (Bulut et al., 2007). Finally, while Zn appears to moderately enrich into the tailings (Table 3), it is distributed throughout the slag sample, both into oxide and sulfidic minerals (Fig. 1) and thus, it reports evenly into froth and tailings fractions.

### Table 3
Flotation result compilation of elements other than Cu, with standard deviation in parentheses.

<table>
<thead>
<tr>
<th>Element</th>
<th>Avg grade in froth (%)</th>
<th>Avg grade in tailings (%)</th>
<th>Enriches to froth fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.37 (0.05)</td>
<td>0.22 (0.01)</td>
<td>Yes</td>
</tr>
<tr>
<td>Pb</td>
<td>0.66 (0.07)</td>
<td>0.48 (0.02)</td>
<td>Yes</td>
</tr>
<tr>
<td>Zn</td>
<td>2.13 (0.16)</td>
<td>2.09 (0.07)</td>
<td>No</td>
</tr>
<tr>
<td>Fe</td>
<td>33.03 (2.4)</td>
<td>36.77 (1.1)</td>
<td>No</td>
</tr>
<tr>
<td>Co</td>
<td>0.13 (0.01)</td>
<td>0.16 (0.01)</td>
<td>No</td>
</tr>
</tbody>
</table>

As Pb is found in a sulfidic form according to the results presented in Section 3.1, its enrichment into the froth fraction is understandable, since the collectors used in this work are known to promote hydrophibization of sulfidic species. Indeed, Cu smelting slag flotation is typically designed similarly to sulfide ores flotation (Shen and Forssberg, 2003; Bulut et al., 2007). On the other hand, the enrichment of As into the froth implies that a proportion of As can be associated with sulfidic Cu species as proposed in by previous studies (Potysz et al., 2015; Tian et al., 2021; Zhou et al., 2021). Certainly, Fig. 1 shows that As is evenly spread throughout the slag sample. Further contemplations regarding the behavior of As are however considered to be outside the scope of this manuscript.

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#### 3.2.2. Flotation of Cu

Direct comparison of flotation results between slag samples from different origins can be challenging, as the efficiency of slag flotation is affected by many variables outside flotation chemistry, such as cooling schedule, slag composition, particle size, liberation, etc. (Tian et al. 2021). However, since the results hereby obtained using the designated benchmark conditions are in line with previous studies (Shamsi et al., 2015; Stirbanovic et al., 2011), it is considered that the choice of reagent dosages and operating conditions was adequate. Therefore, the results obtained with DF250 can be used as a foundation for comparative performance analysis between the different studied frother formulations (Fig. 2).

The first performance comparison between different frothers can be done at the highest collector concentration (120 g/t) (Fig. 2a). Under these conditions, DF250 and CellFroth achieved better grades compared to pure HPMC. Interestingly, higher recoveries were observed with HPMC at shorter flotation times (<6 min), although with consistently lower grades, as per the usual trade-off between grade and recovery. After 20 min flotation, the use of CellFroth produced the highest final recovery while the best final grade was measured using DF250. A comparison of grade-recovery curves in Fig. 2 shows a better overall performance of CellFroth, consistently resulting in higher separation efficiency.

In previous studies, the influence of frother formulation on improved
flotation performance was attributed to a better control over bubble coalescence and froth stability (McFadzean et al., 2016; Chipfunhu et al., 2019). This seems like a reasonable explanation for the flotation results hereby obtained, as the previously mentioned properties have been identified in earlier interfacial characterization for PS-mixtures similar to the current CellFroth, which resulted in better SE than commercial frothers (Nuorivaara and Serna-Guerrero, 2020b).

Fig. 2b shows the flotation results after collector concentration was reduced to 60 g/t. As seen, significant reductions in both grade and recovery were observed in the presence of pure HPMC. In the case of DF250 the grade increased slightly during early flotation times, but its recovery was notably decreased compared to the higher SIBX concentration. This was not the case for CellFroth, for which only minor reductions in grade occurred at early stages of flotation, while recovery remained mostly unaffected.

When the collector concentration was even further reduced, down to 30 g/t, a further decline in performance was observed in the presence of both DF250 and HPMC (Fig. 2c). The same tendency was not observed with CellFroth, as once again only minor reductions in Cu grade and an almost unchanged recovery were measured.

With the aim of analyzing productivity of Cu, Fig. 3 shows the evolution of grade and recovery throughout the flotation experiments for DF250 and CellFroth. As seen in Fig. 3a (i.e., 120 g/t collector concentration), CellFroth appears to accelerate the flotation separation with values of recovery and grade of the product after 10 min comparable to those reached with DF250 after 20 min. The same tendency was not observed with CellFroth, as once again only minor reductions in Cu grade and an almost unchanged recovery were measured.

The low sensitivity of CellFroth to changes in collector concentration is a behavior not reported before in the context of Cu flotation from slag. For example, Roy et al., (2015) studied the effect of different collectors on Cu recovery in flotation of Cu smelting slag over a wide concentration range. Their results showed a clear, direct correlation between collector concentration and the obtained Cu recovery, regardless of collector type (i.e., sodium iso-propyl xanthate, sodium di-ethyldithiophosphate and alkyl hydroxamate). It is generally known that reductions in collector concentration have a negative effect on the recovery of valuables and thus, the lower recoveries with DF250 were not unexpected. However, a similar strong correlation is not followed when a PS-mixture such as CellFroth is used.
CellFroth is used. Based on the results of previous studies by the authors, the robust flotation performance throughout a wide range of conditions with CellFroth has been attributed to a combination of small bubbles and an interfacial stability of the froth phase that is less dependent on the hydrophobicity of mineral particles (Nuorivaara and Serna-Guerrero, 2020a; Nuorivaara and Serna-Guerrero, 2020b; Nuorivaara and Serna-Guerrero, 2020c).

To further describe the experimental behavior observed, the first-order kinetic model with rectangular distribution of floatabilities was used (Dowing et al., 1985; Yuan et al., 1996):

\[ R(t) = R_{\text{max}}[1 - \frac{1}{k_t}(1 - \exp(-k_t t))] \]  

(3)

where \( R \) is the recovery at time \( t \), \( R_{\text{max}} \) is the maximum theoretical recovery, \( k \) is the kinetic constant and \( t \) flotation time in seconds.

While the classical first order kinetic equation is considered to represent an average flotation rate, the first order kinetics with rectangular distribution of floatabilities describes the flotation rate in terms of the fastest floating component (Polat and Chander, 2000). Previous studies preferred this approach due to a better fit to experimental data (Dowing et al., 1985; Yuan et al., 1996; Azizi et al., 2013), which was also the case in the present work.

Although the mathematical form of Equation (3) describes the kinetic behavior based on the evolution of recoveries up to \( R_{\text{max}} \) its form does not take into consideration whether \( R_{\text{max}} \) is comparatively higher or lower. Considering the complex nature of flotation and that the values of \( R_{\text{max}} \) and \( k \) are known to be susceptible to changes in both chemical and operational conditions, some authors have proposed the use of a modified flotation rate constant, \( k_m \) which is defined as the product of \( R_{\text{max}} \) and \( k \) (Equation (4)) (Xu, 1998; Nguyen and Schulze, 2004). The calculated values for the rate constant and the modified rate constant are presented in Table 4.

\[ k_m = k^*R_{\text{max}} \]  

(4)

While the fast early-stage recoveries of pure HPMC were reflected as higher \( k_m \) values than DF250 or CellFroth, a thorough investigation of its kinetic behavior was not pursued due to the inferior relative flotation performance observed in the presence of pure HPMC (Figs. 2 and 3).

However, at first glance, there may be an apparent contradiction regarding the values of kinetic constants of DF250 and CellFroth (Table 4) and the faster flotation previously claimed for CellFroth. Indeed, while it was observed that similar recoveries were obtained faster with CellFroth than with DF250, particularly at low collector concentrations, the calculated values for \( k \) in Table 4 is always higher for the commercial frother. Nevertheless, the higher value of the kinetic constant with DF250 is in this case associated with a lower \( R_{\text{max}} \) which is reached earlier than the comparatively higher \( R_{\text{max}} \) for CellFroth. This is a prime example demonstrating that the phenomena surrounding flotation kinetics are not trivial and the use of kinetic models based solely on recovery may have its limitations. While the technical usefulness of recovery-based kinetic models in the design of operations is acknowledged, the results hereby presented suggest that the phenomenological analysis of flotation kinetics may require more comprehensive equations. In comparison, \( k_m \) values favor DF250 only at the highest xanthate concentration (Table 4). However, as the collector concentration decreases, the \( k_m \) values of CellFroth start to match those of DF250.

While the flotation rates in the current study were determined based on a chemical-kinetics-analogy model, and as such is not directly related to quantifiable properties (Nguyen and Schulze, 2004), their relative values can still be used in the interpretation of flotation behavior based on known connections to flotation kinetics. Indeed, as Chipfunhu et al. (2019) described, flotation kinetics are expected to increase with decreasing bubble sizes, due to the connection between flotation rates and bubble surface area flux. Furthermore, flotation kinetics are often described as a function of froth recovery (Savassi et al., 1997), and as such kinetics can be interpreted as a proxy for froth stability. While the experimental methods utilized within this study did not enable the quantifying of froth recovery, it is important to note that there is a strong correlation between froth stability and recovery (Farrokhpay, 2011). Thus, improved froth recovery can be claimed as an important factor behind the superior flotation performance of CellFroth. As supported by a simple visual analysis on the froth quality (videos of froth during each experiment; see Supplementary Information: S13), CellFroth produced more stable froths also with the slags hereby studied, reflecting the synergistic self-stabilizing interfacial property characteristic of PS-mixtures (Nuorivaara and Serna-Guerrero, 2020a; Nuorivaara and Serna-Guerrero, 2020b).

Finally, as explained in Section 2.2, it was of interest to study the statistical sensitivity of each frother to changes in collector concentration. This was conducted by creating PLS models for each frother, in which Cu recovery and Cu grade were established as responses on changes in collector concentration. The coefficients obtained for each model represent the sensitivity each frother system has with respect to collector concentration, at least within the studied range. The coefficient values of each frother and for grade and recovery are presented in Fig. 4. The error bars indicate the statistical relevance of the coefficients. Although the error bars should be smaller than the coefficient value to represent objective statistical significance, they are admittedly larger in this study, likely due to the complexity of flotation and the limited number of repetitions carried out. Nonetheless, the smaller error bars observed with CellFroth are indicative a more stable flotation behavior.

When observing the effect of collector concentration on Cu, it was found that collector concentration has an overall positive impact with all studied frothers. However, there is a clear difference between the sensitivity of pure frother components (DF250 & HPMC) and that of CellFroth, as the coefficient values of the latter are considerably lower. This implies that CellFroth is better able to maintain flotation performance in terms of grade with varying collector concentrations.

When considering the coefficients in regards of Cu recovery (Fig. 4b), the coefficient values for CellFroth are significantly smaller compared to those of DF250 and HPMC. These findings provide statistical evidence that CellFroth offers a superior robustness towards reductions in collector concentration compared with the state-of-the-art polyglycol-based frothers.

4. Conclusions

In this study, the flotation performance of a novel cellulose-based frother formulation, namely CellFroth, was evaluated in the flotation of Cu smelting slags. The behavior of CellFroth was compared to a commercial frother, DF250 and the pure cellulose component that is used in the CellFroth formulation, HPMC. Firstly, the results of this study demonstrated for the first time that PS-mixtures such as CellFroth are capable of selectively and efficiently separating Cu containing species.
from associated slag. Thus, presenting the first proof of concept for utilizing such chemicals produced from sustainable sources in the flotation of Cu smelting slags.

The next major finding from this study was that using CellFroth further improved the flotation performance compared to the commercial benchmark of DF250. Indeed, overall Cu recovery was higher in the presence of CellFroth in all aspects of this study. Furthermore, it was noticed that CellFroth was able to maintain a good level of selectivity, as it demonstrated higher Cu recoveries with similar grades as with DF250. These improvements in flotation performance were associated to previously identified synergistic interfacial properties observed in the presence of CellFroth that facilitated the formation small bubbles and improved the control over bubble coalescence.

The current study also corroborated previous results by the authors, where the performance of CellFroth was significantly more robust to the combined effects of available factors. In this study, the performance of CellFroth was considered superior due to its higher robustness was connected to the self-stabilizing interfacial property previously identified with PS-mixtures such as CellFroth. If the CellFroth technology is integrated industrially, this finding can have a significant positive impact when applying for a mining permit. Further improved the control over bubble coalescence.

Finally, CellFroth demonstrated superior productivity when comparing how much flotation time was required to reach a certain froth quality (i.e. recovery and grade). CellFroth obtained a similar or better froth quality in half or less the time required for DF250 (depending on collector concentration). Due to the higher robustness of CellFroth, its relative performance improved as collector concentration decreased. This is theorized to be a combination of faster transfer of materials to the froth fraction and an improved froth recovery provided by CellFroth.

Interestingly the flotation rate constants, in isolation, showed faster kinetic values for DF250. However, the kinetic constants do not consider whether the achieved maximum recovery is higher or lower. Thus, the observed flotation performance should always be assessed by considering the combined effects of available factors. In this study, the performance of CellFroth was considered superior due to its higher recoveries, faster flotation productivity and exceptionally robust performance towards changes in chemical conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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