

Sulphidization to improve the nickel oxide recovery by froth flotation

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Abstract-This study aimed to investigate the sulphidization-flotation of nickel oxide. Sulphidization was conducted before froth flotation to convert the surface of nickel oxide to nickel sulphide. Key variables considered were type of sulphidization reagent, sulphidization Eh, time of sulphidization, and flotation Eh. Ammonium sulphide ((NH₄)₂S) was more effective in decreasing the Eh of nickel oxide suspension than sodium hydrogen sulphide (NaSH) and calcium sulphide (CaS_x) and selected for sulphidization-flotation. With potassium amyl xanthate (PAX) addition, nickel oxide recovery increased after sulphidization with (NH₄)₂S. Increasing the time of sulphidization (> 5 min) decreased nickel oxide recovery. Flotation at Eh of -450 mV SHE produced the maximum recovery of 63%, from 37% without sulphidization (2x10⁻⁴ M PAX). The developed sulphidization-flotation method was identified as a good potential option to enhance the recovery of nickel oxide from natural ores.

Keywords: reagent, Eh, sulphidization time, ammonium sulphide

1. INTRODUCTION

Although the flotation of metal oxide minerals with long chain collectors can be used, sulphidization of metal-oxides containing for example copper, cobalt before their flotation with thiol collectors were also reported [e.g. 1]. As a result, mineral separation by flotation can be improved with the sulphidization of these metal oxides and the attachment of thiol collectors become more selective. There are several articles reporting sulphidization (using polysulphide, ammonium sulphide and sodium sulphide/hydrosulphide) of oxide minerals such as malachite [1,2], heterogenite [1], nickel-copper oxide and copper-cobalt oxide ores [3,4], and oxidised pentlandite [5]. The majority of the works performed on the sulphidization assisted flotation dealt with the copper mineral and ores [e.g. 6-12] while the investigations on nickel bearing oxide minerals/particles are still missing while a very limited number of works reported with oxidized iron-nickel sulphide mineral, pentlandite and ores containing it [3,13,14]. Thus we have lack of basic understanding of nickel oxide sulphidization and its effect on froth flotation. This study gives more insight about the effect of different operational variables on the sulphidization of nickel bearing mineral particles followed by the flotation.

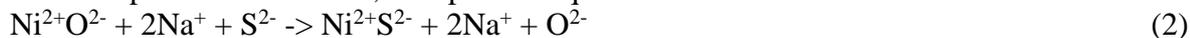
For example, it was shown that using sulphidization to restore the flotation of oxidised nickel minerals [5,15] with the addition of sodium hydrosulphide (NaSH) to maintain a sulphidization potential of -315 mV SHE and xanthate as a collector, pentlandite recovery was increased from 35% to 75% after sulphidization. On the other hand, some researchers also pointed out challenges associated with the application of sulphidization as an upstream operation prior to flotation [e.g. 16].

A general sulphidization reaction using a (major) sulphidizing reagent, sodium sulphide, for

example, can be written in the following Eq. 1 [17]:



where M^{2+} is a surface metal ion, A^{2-} is an anion resulting from the oxidation. Thus, in the case of the sulphidization of NiO, the specific Eq. 2 can be written.



With ammonium sulphide, the sulphidization reaction can be written as:



In this study, NiO was used as a model mineral bearing the nickel content. Its flotation performances in the absence and presence of sulphidization were compared to further understand and optimize the sulphidization process of NiO with the specific application to enhance its flotation recovery. The effects of variable parameters in the sulphidization and flotation steps, i.e. type of sulphidizing reagents, sulphidization Eh and time, and flotation Eh (just before collector addition) on the NiO recovery were investigated.

2. MATERIALS AND METHODS

The nickel oxide Ni(II)O (99% purity) was purchased from Sigma-Aldrich. Its dry sieved fraction between 38 and 75 μm , common flotation feed particle size, was used for the series of experiment in this study. Ammonium sulphide ($(\text{NH}_4)_2\text{S}$), sodium hydrogen sulphide (NaSH) and calcium sulphide (CaS_x) from Sigma-Aldrich were used as sulphidizing reagents. Potassium amyl xanthate (PAX), Dow Froth 250, and potassium nitrate (KNO_3) were used as a collector, frother, and electrolyte, respectively.

The zeta potential of NiO was measured as a function of pH using a Zetasizer Nano (Malvern). The sample was conditioned in the presence of 1×10^{-2} M KNO_3 for 30 min, and the small portion of its supernatant was collected and fed into a measurement cell.

Sulphidization of NiO was conducted in a closed cell with N_2 purging (0.5 L/min) for 5 min with different sulphidizing reagents, NaSH, CaS_x or $(\text{NH}_4)_2\text{S}$ at pH 8.5 in 1×10^{-2} M KNO_3 followed by the aeration with air (1 L/min) before the collector addition. Nitrogen gas was purged to eliminate dissolved oxygen and increase the formation efficiency of a coherent and compact sulphidized layer on the oxide mineral surface. It can also reduce the consumption of a sulphidizing reagent [16,17]. The schematic diagram of the sulphidization process is shown in Fig. 1. The sulphidization parameters studied were the sulphidization Eh (to form a sulphide layer on the mineral surface), the sulphidization time at a fixed sulphidization Eh (to stabilise the formed sulphide layer) and the flotation Eh just before the collector addition. An optimum Eh should be reached with the aeration for the maximum adsorption of thiol collector and thus flotation recovery. Also, the excessive aeration or too high Eh may re-oxidise the sulphidized metal oxide mineral, resulting in low recovery [18].

Flotation was conducted in an IMN flotation machine at pH 8.5 using a gas flow rate of 1 L/min and 200 g/t of frother, Dow Froth 250. The NiO (38-75 μm) pre-conditioned in the absence or presence of sulphidization was transferred to the flotation cell (0.3 L) and a collector, potassium amyl xanthate (PAX), was added and conditioned for two minutes followed by the frother addition and conditioning for 1 min. The concentrates were collected after 0.5, 2, 4, 8 min (cumulative) of flotation, filtered and dried in an oven. The feed mass was 2 g.

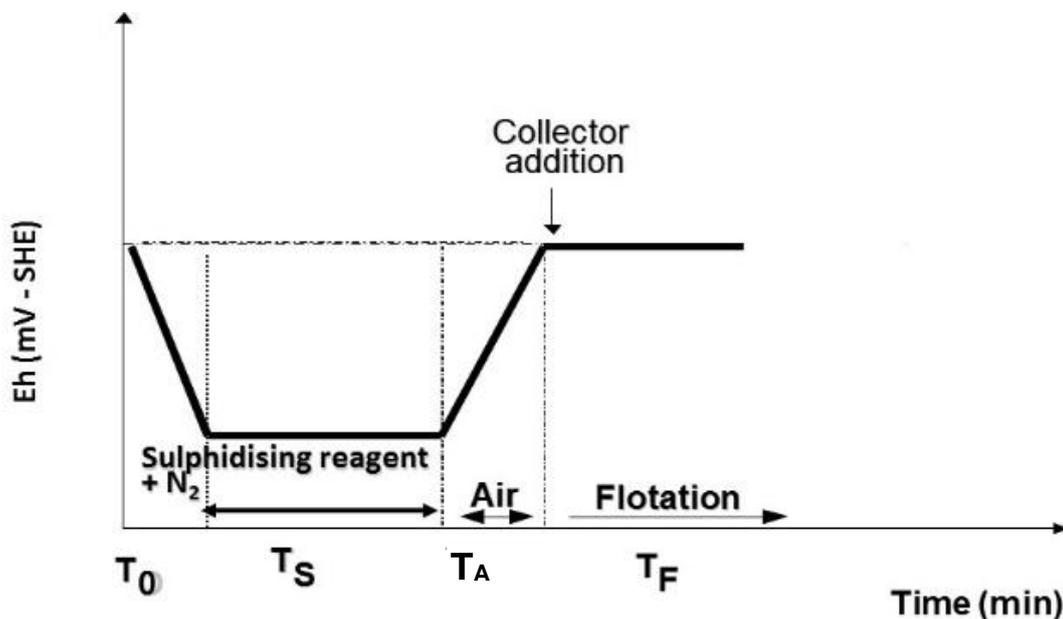


Fig. 1: Schematic diagram of the sulphidization process. T_S , T_A and T_F represent the sulphidization, aeration and flotation times, respectively.

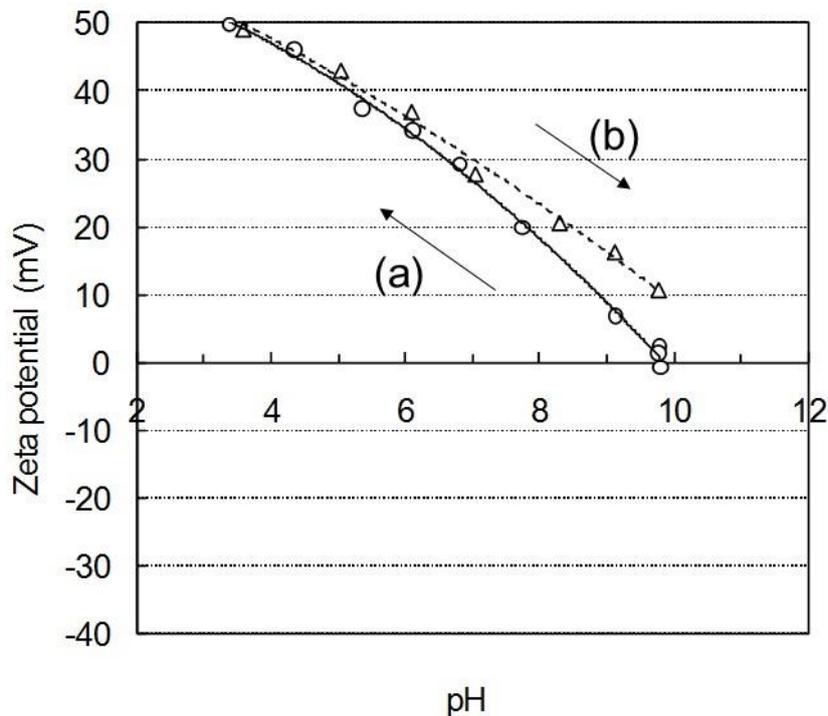


Fig. 2: Zeta potential of NiO as a function of pH in the presence of 1×10^{-2} M KNO_3 for (a) acid and (b) base titration. The arrows show the progression of titration. The sample was conditioned for 30 min before the zeta potential measurement.

3. RESULTS AND DISCUSSION

3.1 Zeta potential measurement

Zeta potential measurements of NiO were conducted in order to characterize its surface charge. Figure 2 shows the zeta potential of NiO in the presence of 1×10^{-2} M KNO_3 as a function of pH. The isoelectric point, IEP, was found at pH 9.8, which agreed with the reported values of NiO [e.g. 19]. It positively increases with decreasing pH (acid titration). In the base titration, the zeta potential follows closely that in the acid titration except for a small deviation in the pH between neutral and alkaline range where the zeta potential is slightly more positive. This deviation can be the result of the Ni dissolution at low pH values and formation/precipitation of nickel hydroxide in alkaline pH. Another explanation can be the slower protonation/deprotonation of nickel oxide surface sites compared to change in pH values.

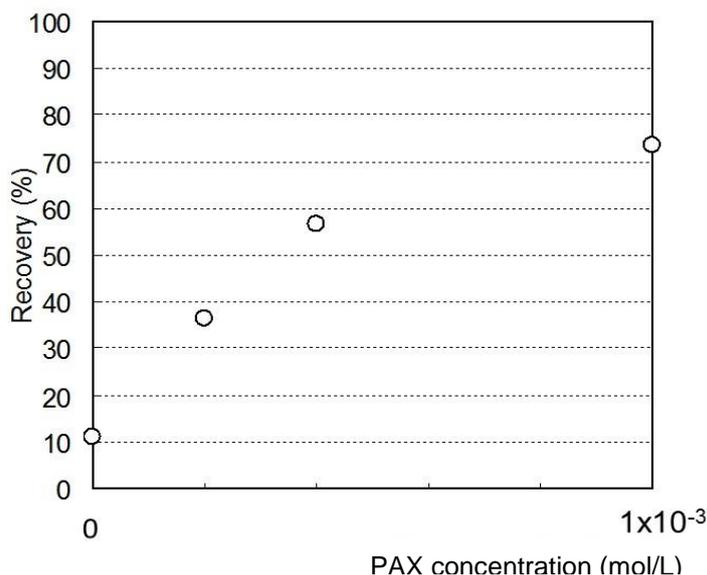


Fig. 3: NiO recovery after 8 min of flotation as a function of PAX concentration at pH 8.5 in the presence of 1×10^{-2} M KNO_3 (Flotation Eh = 10-20 mV SHE).

3.2 Effect of PAX concentration on NiO recovery (no sulphidization)

Figure 3 shows the flotation recoveries of NiO as a function of PAX concentration. With increasing the PAX concentration, the NiO recovery (after 8 min of flotation) increased from 11% (no collector) to 37% and to 70% with the addition of 2×10^{-4} M and 1×10^{-3} M PAX, respectively. Similar results were reported by Naklicki et al. (2002) [20], and Rao and Finch (2003) [21]. A PAX concentration of 2×10^{-4} M was selected in all subsequent experiments as this low concentration corresponds more closely to that commonly used in flotation plants. The Eh before collector addition was 10-20 mV SHE in these experiments.

3.3 Changes in suspension Eh with different sulphidizing reagents

Figure 4 shows the effect of the concentration of sulphidizing reagents, (NaSH , CaS_x or $(\text{NH}_4)_2\text{S}$), on the Eh of NiO suspension. For similar concentrations, $(\text{NH}_4)_2\text{S}$ was more effective in decreasing Eh until a concentration of 2048 g/t where the Eh of the NiO suspension became

similar to $(\text{NH}_4)_2\text{S}$ and CaS_x . The reagent consumed the least amount to effectively reduce Eh and to sulphidize the oxide surface was selected, by following the proposition by other researchers (e.g. Bulatovic, 2010 [22]). In terms of the detail mechanism explaining their different sulphidization behavior, there was no study to the best of authors' knowledge at this moment and it is out of focus of this study. It can be a good future study in order to further understand the basics as well as the application/practical point of view to effectively manipulate and optimize the sulphidization processes. Based on the results, $(\text{NH}_4)_2\text{S}$ was selected and used for the further experiments.

The results obtained this study agreed with the results previously reported for copper oxides and cobalt oxides. Kongolo et al. (2003) [1] reported that for cobalt oxides the $(\text{NH}_4)_2\text{S}$ achieved the higher metal recovery with less selectivity while NaHS achieved the good selectivity with poor recovery. They also reported the mixture of those two reagents provided the better selectivity and metal recovery. Such reagent mixture can be tested in the future to study the separation performance of actual nickel ore systems that contains both nickel minerals and other minerals.

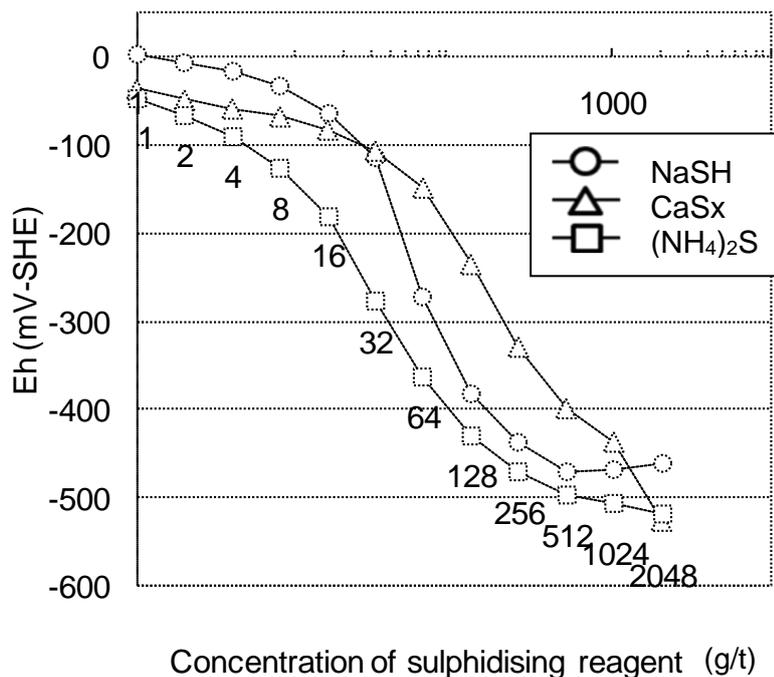


Fig. 4: Eh of NiO suspension at pH 8.5 as a function of concentration of sulphidizing reagents (i.e. NaSH, CaS_x and $(\text{NH}_4)_2\text{S}$) with the continuous nitrogen addition to avoid the oxidation of newly formed NiS on the surface of NiO. The values below the graph indicate the exact concentration of sulphidizing reagents.

3.4 Optimization of experimental conditions for sulphidization-flotation of NiO

In order to maximize the NiO recovery, experimental conditions in the sulphidization and flotation steps were optimized. The parameters studied were sulphidization Eh, sulphidization time and Eh of flotation (just before PAX addition).

3.4.1 Effect of sulphidization Eh on the NiO recovery

As many researchers pointed out, one of the major challenges in sulphidization is to find and maintain the optimum sulphide concentration [e.g. 16]. That is the reason why we monitored and adjusted the suspension Eh instead of the concentration of sulphidizing reagent, in order to optimise the subsequent flotation performance. Figure 5 shows the flotation recovery of NiO as a function of sulphidization Eh. The NiO recovery with 2×10^{-4} M PAX increased from 36% (without sulphidization) to 56% (at the Eh of -500 mV SHE). This sulphidization Eh for the maximum flotation of NiO was close to the Eh reported by Kongolo et al. (2003) [1] for the CoO sulphidization. The results indirectly indicated the formation of NiS on the NiO surface and thus the enhancement of xanthate collector adsorption, leading the increase in the NiO recovery. Another potential explanation of this increase can be discussed with the change in zeta potential of NiO. According to Newell et al. (2007) [15], decreasing the suspension Eh of oxidised pentlandite negatively increased its zeta potential from -12 mV (at -65 mV SHE) to -35 mV (at -465 mV SHE). Such zeta potential change can lead the surface charge of the NiO particles used in this study to nearly zero from around 20 mV at pH 8.5 (Fig. 2). It can lead the particle coagulation, and enhance the particle collection efficiency by increasing the probability of particle collision with air bubbles [23].

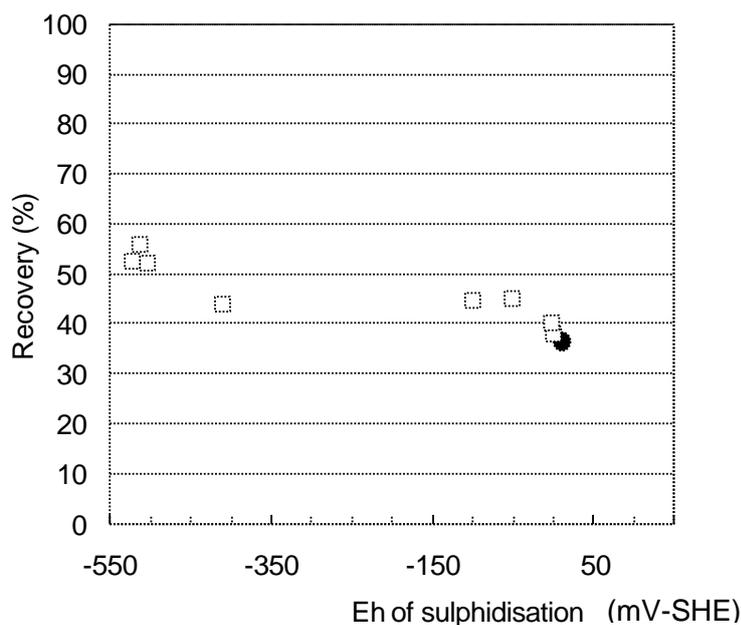


Fig. 5: NiO recovery after 8 min of flotation as a function of sulphidization Eh adjusted with $(\text{NH}_4)_2\text{S}$ and a sulphidization time of 5 min. The filled symbol represents the recovery without sulphidization (pH = 8.5; $[\text{KNO}_3] = 1 \times 10^{-2}$ M; $[\text{PAX}] = 2 \times 10^{-4}$ M).

3.4.2 Effect of sulphidization time on the NiO recovery

Figure 6 shows the flotation recovery of NiO as a function of sulphidization time at a fixed sulphidization Eh of -500 mV SHE selected from the above results (Fig.5). The maximum recovery of 60% was obtained after 5 min sulphidization. Increasing sulphidization time decreased the NiO recovery. This decrease can be explained by the oxidation of the freshly

sulphidized surface with the longer sulphidization time and enhancement of surface dissolution rather than sulphidization under the intense sulphidization process [15]. Another possible explanation can be the depressant action of sulphide ions with the excess sulphide [16] due to the prevention of anionic collector (xanthate) adsorption onto a particle with the high negative charge given by S^{2-} .

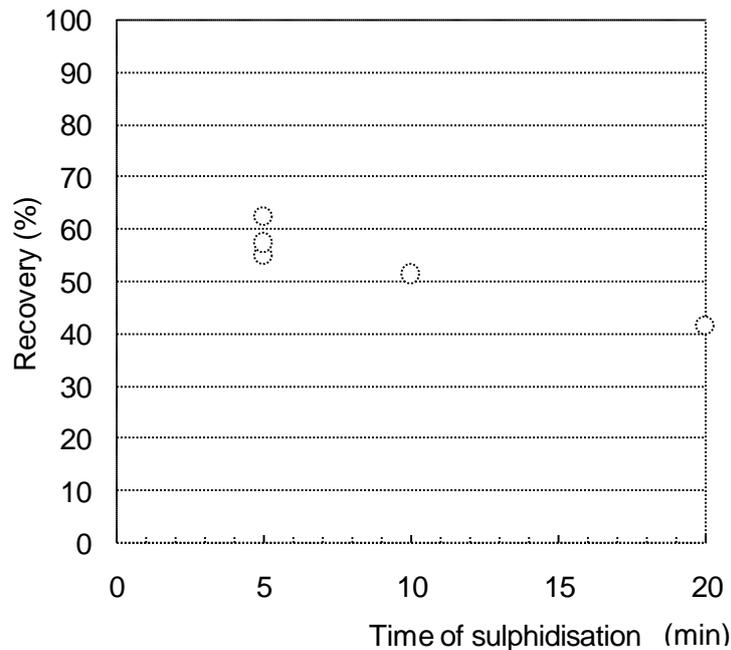


Fig. 6: NiO recovery after 8 min of flotation as a function of sulphidization time and at a sulphidization Eh of -500 mV SHE (pH = 8.5; $[KNO_3] = 1 \times 10^{-2}$ M; $[PAX] = 2 \times 10^{-4}$ M).

3.4.3 Effect of flotation Eh after sulphidization on the NiO recovery

Figure 7 shows the flotation recovery of NiO as a function of flotation Eh (just before the collector addition). The sulphidization Eh was -500 mV SHE which was maintained constant for 5 min optimised from the previous experimental step (Fig.6). The maximum recovery around 60% was obtained at flotation Eh values between -490 to -450 mV SHE while higher flotation Eh depressed recovery. This trend can be explained by the excessive oxidation producing unstable sulphate on mineral surface and xanthate can be easily detached [24]. A similar trend was reported by Soto and Laskowski (1973) [18] for the flotation of malachite ($CuCO_3 \cdot Cu(OH)_2$). They showed that maximum recovery was obtained at the optimum flotation Eh, and lower recoveries were found for longer aeration time or higher flotation Eh.

Based on these flotation results at pH 8.5 with potassium amyl xanthate as a collector, the optimum sulphidization conditions for maximizing the NiO recovery are: Sulphidization Eh = -500 mV SHE; Flotation Eh = -490 to -450 mV SHE; Sulphidization time = 5 min.

In terms of sulphidization Eh, previously -315 mV SHE for restoring the pentlandite flotation recovery was reported by Newell et al. (2007) [15]. The difference with the current investigation might be explained by the difference in size and type of mineral particles examined in two different investigations (38-75 μm of nickel oxide in this study; 38-106 μm of oxidised pentlandite in Newell et al. (2007) [15]), leading the difference in surface area available for

sulphidizing reagent to react with. In other words, a suspension with the finer oxide particles requires more sulphidizing reagent to formulate sulphides on their surfaces than the other with the coarser originally sulphide particles. Figure 8 shows the summary of this investigation comparing the flotation kinetics of NiO with and without sulphidization, and was observed the improvement in terms of the flotation kinetics and recovery (from 37% to 63%).

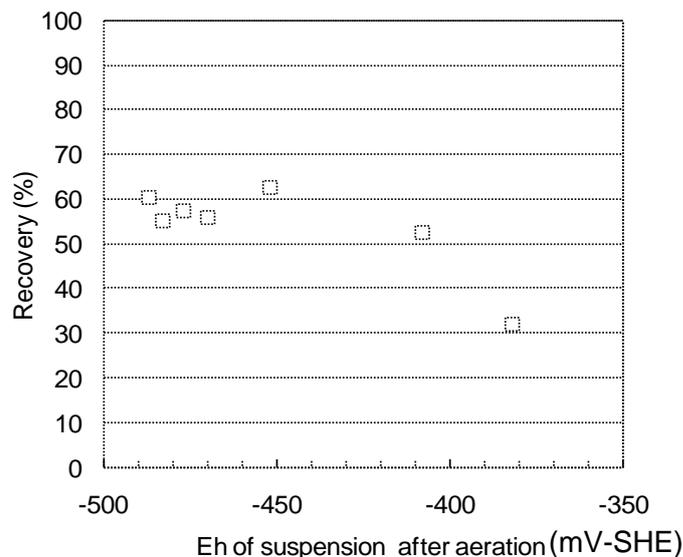


Fig. 7: NiO recovery after 8 min of flotation as a function of suspension Eh after aeration. The sulphidization Eh was kept at -500 mV SHE for 5 min (pH = 8.5; $[KNO_3] = 1 \times 10^{-2} M$; $[PAX] = 2 \times 10^{-4} M$).

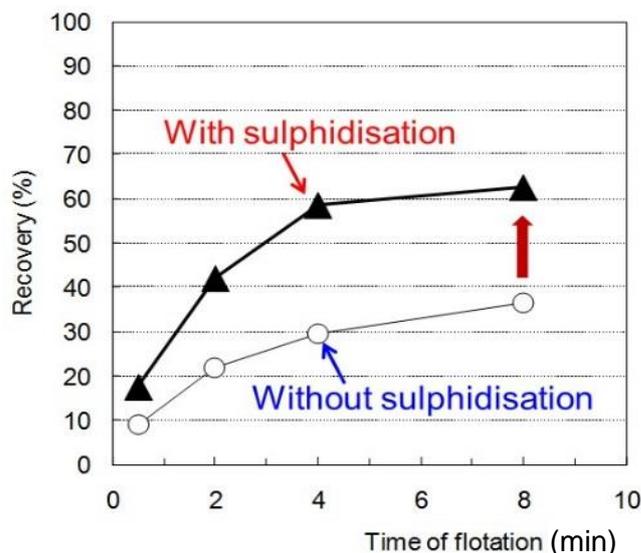


Fig. 8: NiO recovery (38 -75 μm) in the absence and presence of sulphidization as a function of flotation time with $2 \times 10^{-4} M$ PAX at pH 8.5 in the presence of $1 \times 10^{-2} M$ KNO_3 . For sulphidization, suspension Eh was kept at -500 mV SHE for 5 min, and flotation Eh was -450 mV SHE.

4. CONCLUSIONS

Flotation experiments were performed in the absence and presence of sulphidization to compare the results. Sulphidization of NiO with $(\text{NH}_4)_2\text{S}$ prior to xanthate addition can further improve the NiO recovery, and the key parameters (i.e. sulphidization Eh, sulphidization time and flotation Eh (before collector addition)) were optimised to improve the NiO flotation performance. The proposed combination of sulphidization and flotation can be a potential option to enhance the nickel recovery from complex nickel ores.

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DECLARATION OF CONFLICTING INTERESTS

The authors declare that there is no conflict of interest.

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