Insights on the impact of NaSH reagent dosing strategy in molybdenum selective flotation

Fernandez, B.[1], Soto. F.[2], Montes-Atenas G.[2,3(*)]

[1] Integral Solutions for Mineral Processing Co.
[2] Empirica Co.
[3] Department of Mining Engineering, University of Chile

1. Introduction

The success of froth flotation operations relies heavily on the correct selection of different types of reagents (Lynch, 2010). Sodium hydrosulphide (NaSH), for instance, is known to promote the depression of copper sulphide minerals floatability, and is successfully used in the selective flotation of molybdenum (Gupta, 1992). However, dosing strategies for reagents are often inadequately addressed by both suppliers and mine sites. Indeed, the common practice of adding large concentrations to achieve a target average after mixing creates a problem: a relatively significant portion of the slurry is exposed to excessively high reagent concentration levels. This can be detrimental if high concentrations trigger side reactions or accelerate consumption, leading to reagent overuse.

While dosing at lower concentrations could mitigate this, it risks significant pulp dilution that may even negatively influence the throughput of an operation. This is a critical consideration in Chilean Cu-Mo concentrators, where NaSH can represent up to 70% of the selective flotation circuit implementation costs. Furthermore, NaSH exhibits multiple roles in flotation, including sulphidising oxide minerals, modifying froth stability and pH, and reducing redox potential, among others (Kalichini, 2015; Rousseau, 1987; Wills and Finch, 2015; Gupta, 2000; Nagaraj and Gorken, 1989; Goktepe, 2010). Despite its well-documented functions, there is limited information on the side reactions it triggers. Recent studies have shown that NaSH can promote the precipitation of mackinawite-like salts (FeS) and other species. Staged dosing may reduce losses to such parallel reactions (Fernandez et al., 2014). This study aims to understand this behaviour and provide insights for maximising the reagent's usefulness in these systems.

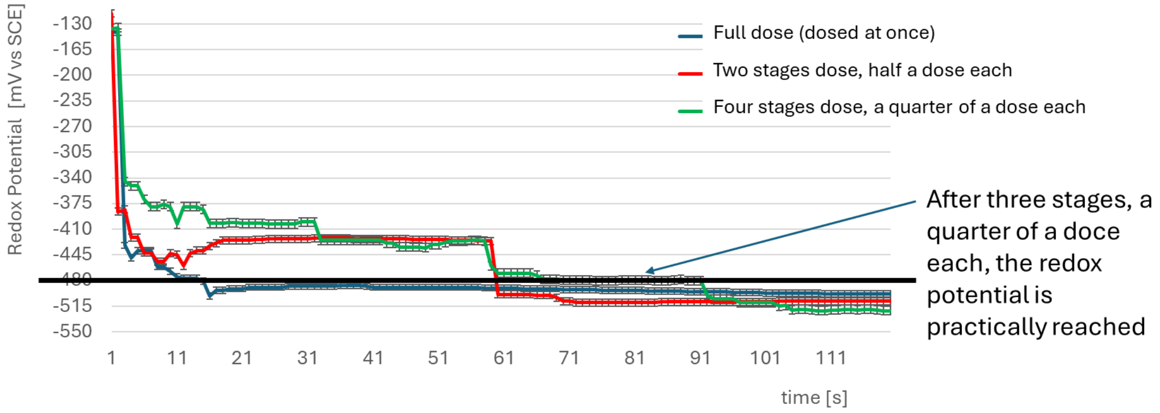
2. Methodology

Pulp samples were obtained from a mine site in northern Chile. The sampling was performed in a location just prior to NaSH dosing. The pulp was filtered to isolate the process water for experimentation. This water was kept at 4°C and as soon as possible tests were carried out by contacting it with the NaSH reagent under varying pH conditions while the redox potential and pH value were monitored at a constant temperature. The operational target for copper sulphide depression at this site is a redox potential of -480 mV vs SCE. This study evaluated both single-dose and stage-dosing strategies.

If any precipitates formed, they were characterized using classical chemical analysis techniques, including atomic absorption spectroscopy (AAS) model GBC 908, X-ray diffraction (XRD) Siemens D5000 and Scanning Electron Microscopy coupled with X-ray Energy dispersion (SEM-EDX) FEI Quanta 250. A more detailed analysis of these samples was conducted using X-ray photoelectron spectroscopy (XPS) at the Laboratory of Surfaces and Nanomaterials. XPS measurements were performed at room temperature on powder samples under high vacuum using a Physical Electronics 1257 X-ray system equipped with a SPECS hemispherical analyzer. The system used non-monochromatized Al-Kα radiation (1486.6 eV) operating at 300 W, with working pressures in the range of 10^{-7} Pa. High-resolution scans were acquired with a pass energy of 44.75 eV and a step size of 100 meV. The resulting XPS spectra were fitted with Gaussian/Lorentzian curves using the Multipack software.

3. Results and Discussion

i. The impact of stage dosing of NaSH on the redox potential achieved



After three stages, a quarter of a doce each, the redox potential is practically reached

Figure 1. Redox potential results obtained are different dosing methods (modified from Fernandez et al., 2024).

Figure 1 shows the redox potential results for various NaSH dosing strategies. A stage dosing of the reagent may allow reaching the redox potential to inhibit the floatability of copper sulphide minerals at lower overall dosing amounts. In fact, as shown in the text enclosed, the redox potential achieved after three doses of a quarter of the full dose is equivalent to that required by the operation. It is important to highlight that the observed redox potential in the system is likely to increase in aerated systems due to the mixed potential resulting from the oxidation reaction of hydrosulphide to sulphate ions (Equation 1), coupled with oxygen reduction. This coupling with the oxygen reduction reaction leads to the slightly higher redox potentials measured.

$$HS^{-}_{(aq)} + 9OH^{-}_{(aq)} \rightarrow SO^{2-}_{4(aq)} + 5H_2O_{(l)} + 8e^{-} \tag{1}$$

The Nernst equation in this case, in standard conditions (25 °C, 1 atm), can be written as Equation 2.

$$E = 0.252 + 0.0074 log \frac{a_{SO^{2-}_{4(aq)}}}{a_{HS^{-}_{(aq)}}} + 0.0665pOH \tag{2}$$

Chemical speciation studies confirm that within a pH range of 8 to 12, the $NaSH$ reagent exists predominantly in the form of $HS^{-}_{(aq)}$. This was verified through chemical speciation modeling using ChemEql® software with the Davies correction.

The impact of adding extra NaSH significantly depends on the resultant change in redox potential. As shown in Figure 2, the magnitude of the redox potential change is greatest when the argument of the logarithm in the Nernst equation is smallest.

The high initial NaSH concentration (approximately 4.2 M) at which the reagents is dosed is relatively constant and it does not allow reducing significantly the magnitude of the argument of the logarithm function. Therefore, the decrease of the redox potential depends significantly on the concentration of sulphate ions appearing at the numerator of the argument of the logarithm function. The smaller the concentration of sulphate ions the closer the function is to zero and the steepest is the slope of the function in those conditions.

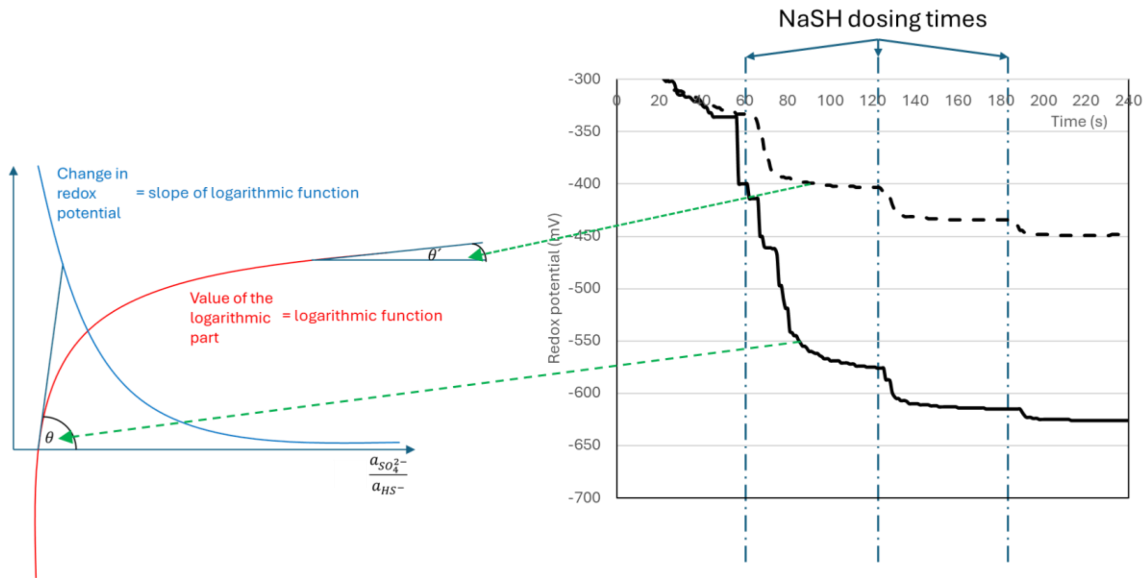


Figure 2. Impact of the sulphate to hydrosulphide ratio onto the redox potential drop when dosing NaSH. Left hand-side figure: the logarithm function and its slope as a function of the concentration ratio of the relevant species, Right hand-side: redox potential drop as function of accumulative NaSH dosis.

Furthermore, the latter analysis was confirmed in separate experiments. The decrease of redox potential occurs in steps that become less pronounced as the NaSH concentration increases. This behavior may also be associated with the reagent's oxidation, which increases sulphate concentration and thereby attenuates the drop in redox potential.

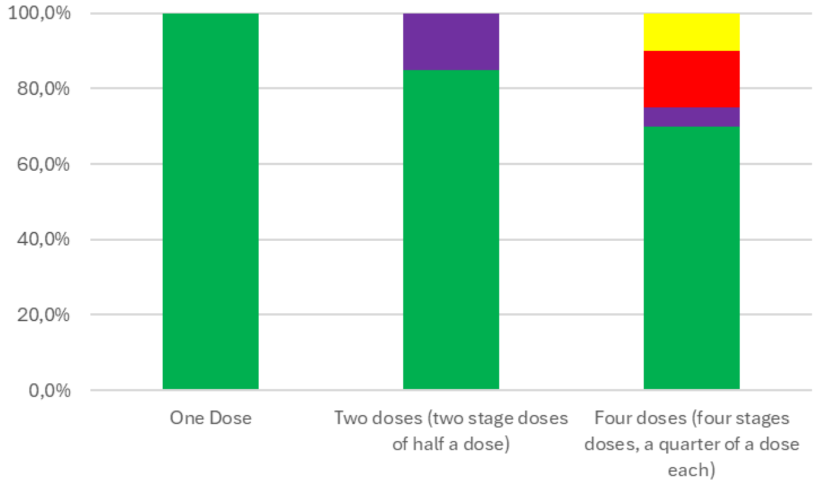


Figure 3. Mass percent of precipitate formed using different NaSH dosing strategies. In all cases, the mass of precipitate formed is equivalent.

ii. The parallel precipitation reaction and the species being formed as a function of NaSH dosis.

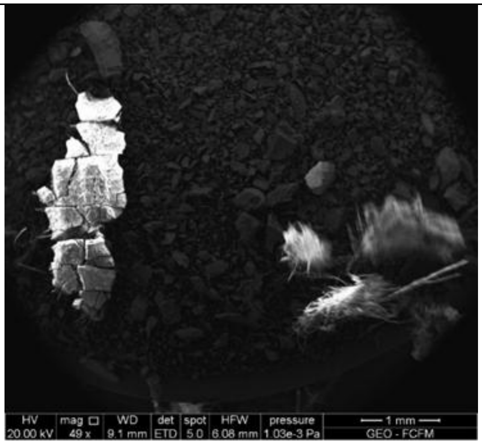
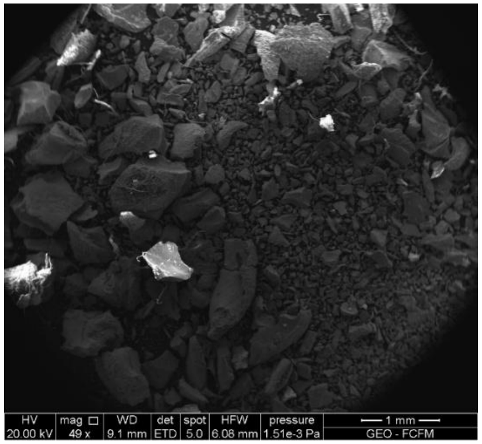
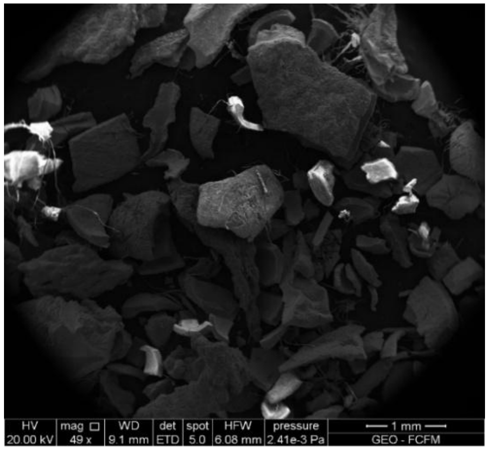
The quantity of solid precipitation proved to be consistent regardless of the NaSH dosing strategy followed (Figure 3). The amount of precipitate is relatively high when comparing the three strategies of NaSH dosing regardless the amount of the reagent dosed. This is, in principle an indication that the operation is running at high sulphide concentrations. Table 1 shows the structural composition of precipitates formed after the first dose in each strategy. Most of the solids species formed are amorphous in nature.

However, the composition of the precipitates differs in each case. X-ray diffraction qualitative analysis of the precipitates indicates the formation of sulphur which may be related to the low initial pH of the aqueous solution coupled with metal hydrolysis from local dissolution of metal-sulphides. They could also be associated to meta-stable species. This species is formed along with iron sulphide structures. The observed precipitation of iron (II) sulphide appears inconsistent with its high reported solubility product (Lide, 2005). This anomaly may be explained by a reduction in solubility due to seed precipitation, whereby colloidal initiators assist in the nucleation of metal sulphide and subsequent crystal growth.

On the other hand, as expected, when increasing the NaSH dosis the particles formed increase in size. This means nucleation may be the original mechanism that later shifts to a crystal growth mechanism. The SEM-EDX analysis shows that when the NaSH dosis starts, the metal oxide species are formed with more intensity than the corresponding sulphides.

Preliminary X-ray photoelectron spectroscopy (XPS) studies have proven that the sulphide precipitates readily oxidise at the surface, possibly inhibiting the redissolution of the precipitates ultimately reducing the availability of sulphide ions.

Table 1. SEM-EDX microphotograph of the precipitates formed after NaSH different dose strategies (full dose, half dose and a quarter of a full dose), and X-ray diffraction (XRD) characterisation.

NaSH dose		A quarter of NaSH dose	Half NaSH dose	Full dose
Microphotographs				
SEM-EDX	C	17.60	8.67	22.20
	O	31.09	23.62	21.49
	Na	0.70	9.77	2.67
	S	7.93	24.68	26.32
	Ca	0.09	0.93	3.18
	Fe	39.43	32.33	24.15
	Al	3.61	0.00	0.00
DRX most probable species		S_8, Fe_3S_4	S_8	S_8, FeS

iii. Mass transport model

A one-dimensional mass transport model was developed for iron sulphide precipitation, treating it as a second-order reaction. The application of scaling factors yields the relevant dimensionless number. (Equation 3).

$$\varphi = \frac{8Pe^3}{8Pe^2 - Da} \tag{3}$$

Here, Pe and Da are the dimensionless Péclét and Damkhöler numbers, respectively. As the precipitation reaction is irreversible, precipitate formation inevitably leads to reagent loss. This study will also incorporate further analysis of reaction relaxation times for multiple simultaneous reactions. Combined with experimental and modeling data, this analysis will help identify trends for optimizing reagent dosage. Ultimately, this approach aims to help reagent companies improve their services and enable mine sites to achieve greater process efficiency.

4. Conclusions

The main findings of this study are:

a) A fraction of the NaSH dosed in the selective molybdenum flotation circuit may precipitate as metal sulphides, depending on pH and process water quality. This mechanism is particularly relevant at lower pH values, where Mo flotation is more efficient.

b) Although metal sulphide formation involves fast equilibrium reactions, the precipitation is irreversible. The reagent consumed in this process does not contribute to lowering the redox potential.

c) The irreversibility is likely due to the formation of metal oxides on the metal sulphide surfaces. The resulting species are predominantly amorphous, and XRD analysis indicates that different compounds form depending on the NaSH dose magnitude.

d) Under these conditions, the reduction of redox potential is controlled by the sulphate-to-hydrosulphide ratio and oxygen concentration. Consequently, flotation operations running at lower redox potentials require less NaSH.

5. References

Fernandez, B., Montes-Atenas, G., Valenzuela, F., & Yarmuch, J. L. (2024). Insights on Determining Improved Conditions for Multipurpose Reagent Dosing to Increase Froth Flotation Efficiency: NaSH in Cu-Mo Selective Flotation Case Study. Minerals, 14(3), 240. https://doi.org/10.3390/min14030240

Goktepe F. (2010) Effect of H2O2 and NaSH Addition to Change the Electrochemical Potential in Flotation of Chalcopyrite and Pyrite Minerals, Mineral Processing and Extractive Metallurgy Review. An International Journal, 32(1), 24-29.

Gupta CK (2000) Extractive Metallurgy of Molybdenum, CRC Press, Taylor and Francis Group, 404 p.

Kalichini M.S. (2015) A study of the flotation characteristics of a complex copper ore, MSc thesis in Chemical Engineering, University of Cape Town, 178 p.

Lide DR (2005) CRC Handbook of Chemistry and Physics (86th ed.). CRC Press, Taylor & Francis, p. 8-120.

Lynch AJ, Harbort GJ, Nelson MG (2010) History of Flotation, AusIMM, The Minerals Institute, Spectrum Series No. 18., Carlton Victoria, Australia, 348 p.

Nagaraj, D.R., Gorken, A. (1989) Potential controlled flotation and depression of copper sulphides and oxides using hydrosulphide in non-xanthate systems. Processing of Complex Ores, Proceedings of the International Symposium on Processing of Complex Ores, Proceedings of Metallurgical Society of Canadian Institute of Mining and Metallurgy, Halifax, August 20–24, 203-213.

Rousseau W (1987) Handbook of Separation Process Technology, Wiley-Interscience Pub., 1024 p.

Wills B.A., Finch J.A. Wills'. (2015) Mineral Processing Technology. An Introduction to the Practical As-pects of Ore Treatment and Mineral Recovery, Elsevier Ltd., 512 p.