

# New reagents for controlling of $H_2O_2$ by metal sulfide and its effect in sulfide mineral floatation

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## ABSTRACT

Our recent studies revealed that the ground sulphide minerals in contact with water generate  $H_2O_2$  but its effect on the oxidation of pulp components and hence in deteriorating the concentrate grade and recovery in flotation has not been explored yet. The use of  $Na_2S$  reductant at the grinding stage is thought to control the deleterious effects of  $H_2O_2$  in the pulp liquid. Therefore, the effect of  $Na_2S$  addition during grinding stage on the formation of  $H_2O_2$  and its influence on sulphide complex ore flotation was investigated. The results showed that the presence of  $Na_2S$  increases the formation of  $H_2O_2$  but decreases the dissolved oxygen. An increase in  $Na_2S$  dosage in grinding, the Pb grade and recovery in Cu-Pb concentrate is decreased while pyrite is depressed marginally better. These changes in flotation response of sulphides have been discussed and explained with the formation of  $H_2O_2$  quantitatively.

**Keywords :** *Sulphide complex ore,  $Na_2S$ , Depressant, Flotation*

## 1. Introduction

Our recent studies have illustrated the formation of hydrogen peroxide ( $H_2O_2$ ) by metal-sulphides during grinding in the presence and absence of oxygen [1-4]. In the absence of oxygen, it was found that pyrite surface is catalytically active and able to breakdown water molecules to form  $OH^\cdot$  free radical and thereby deriving oxygen in the formation of  $H_2O_2$  from water molecules. The in-situ formation of  $H_2O_2$  and its influence on sulphide flotation has not been addressed yet. The presence of strong  $H_2O_2$  oxidant in the pulp liquid and its selective oxidation of pyrite would be beneficial in depressing pyrite flotation. Therefore, it is important to build correlation between percentage of pyrite in the concentrate, grinding conditions and concentration of  $OH^\cdot/H_2O_2$  in the pulp as well as to study possible ways of flexibly controlling the formation of these species through known chemical means for depressing the generation of the oxidant. One of such ways for controlling of effect  $H_2O_2$  could be the addition sodium sulphide during grinding.

Sodium sulphide (as  $Na_2S$  or  $NaHS$ ) or sodium sulfite ( $Na_2SO_3$ ) has been used as modifier in copper circuits but is rarely added during grinding. Freeman et al. (2000) found that the addition of  $NaHS$  to the mild steel mill increased froth stability and hence improved copper flotation kinetics. They showed that copper recovery generally increases with increasing  $NaHS$  levels (up to 100 g/t) for particle sizes between 10  $\mu m$  and 100  $\mu m$  [5]. Orwe et al. (1998) showed that the use of  $NaHS$  in the flotation improved recovery of fine copper particles ( $\sim 10 \mu m$ ) [6]. Houot and Duhamet (1992) reported that sodium sulphide depressed galena and increases selectivity of copper sulphide from other sulphides [7].

Sodium sulphite was used to improve the separation of copper-activated sphalerite from pyrite in mildly alkaline pH conditions [8]. For depressing pyrite, galena and sphalerite in copper circuits in neutral pH conditions sodium sulphite has been used and similar sulfoxy species

such as sodium bisulphite, metabisulphite or sulphur dioxide gas have also been applied [7-11].

In our recent studies was found that pyrite ( $FeS_2$ ), chalcopyrite ( $CuFeS_2$ ), sphalerite ( $(Zn,Fe)S$ ), and galena ( $PbS$ ), which are the most abundant sulphide minerals on Earth, generated  $H_2O_2$  in pulp liquid during wet grinding in the presence or absence of dissolved oxygen in water and also when the freshly ground solids are placed in water immediately after dry grinding. Pyrite generated more  $H_2O_2$  than other sulphide minerals and the order of  $H_2O_2$  production by the minerals found to be pyrite > chalcopyrite > sphalerite > galena [1-4]. However, participation of these oxidising  $H_2O_2$  species formed by sulphide minerals, to build correlation between percentage of pyrite in the concentrate, grinding conditions and concentration of  $OH^\cdot/H_2O_2$  in the pulp liquid on flotation grade and recovery, the effect of depressant and collector additions during grinding on the formation of  $H_2O_2$  by metal sulphides and its influence on complex ore flotation was investigated. The results showed a decrease in the generation of  $H_2O_2$  with the addition of depressants during grinding while the addition of depressant and collector together increased  $H_2O_2$  formation in the flotation pulp liquid [13].

In this study, the effect of sodium sulphide addition during grinding on formation of  $H_2O_2$  and its influence on complex ore flotation was investigated. The results are presented and discussed in terms of  $H_2O_2$  generation vis-à-vis concentrate grade and recovery in flotation.

## 2. Method and materials

### 2.1. Sample and reagents

The sulphide ores were from Renström mine of Boliden Mineral AB, Sweden. A bulk ore sample was received in a drum in wet condition and it was dried and crushed in three stages to < 3 mm size and divided into 1 Kg sub-samples using a rotary splitter. These 1 Kg samples were stored in sealed polyethylene bags in a freezer at temperature minus 18 °C. All

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chemicals used are technical grade. The flotation reagents that are being used at Boliden concentrator for treating complex sulphide ores have been obtained. Potassium amyl xanthate (KAX), Isobutyl xanthate (IBX) and Danafloat 871 (dialkyle dithiophosphate mercaptobenzothiazole) were used as collectors. Dowfroth 250 (polypropylene oxide methanol) was used as frother. Dextrin, sodium hydrogen sulphite ( $\text{NaHSO}_3$ ), and zinc sulphate ( $\text{ZnSO}_4$ ) were used as pyrite and sphalerite depressants respectively in flotation. Copper sulphate ( $\text{CuSO}_4$ ) was used as a source of copper ions for activation of sphalerite. Deionised water was used in the processes of both grinding and flotation. Solutions of 2, 9-dimethyl-1, 10-phenanthroline (DMP) (1%), copper (II) ions (0.01 M), and phosphate buffer (pH 7.0) were used for estimating  $\text{H}_2\text{O}_2$  amount in pulp liquid by UV-Visible spectrophotometer.

## 2.2. Pulp chemistry measurement

The pH, Eh (pulp potential), and dissolved oxygen (DO) were measured before and after grinding of the complex sulphide ore. The Eh was measured at room temperature in all experiments using a platinum electrode and KCl (3 mol/litre) reference electrode and expressed relative to the standard hydrogen electrode, SHE. The pH was measured using a glass electrode. A DO meter (SevenGo (Duo) proTM/OptiOXTM) was used for measuring the dissolved oxygen.

## 2.3. Assessment of $\text{H}_2\text{O}_2$ production in pulp liquid

One Kg ore sample is wet-ground with 0.6 liter of water in a laboratory stainless steel rod mill. The slurry samples were collected at a pre-determined time intervals, filtered and the liquid (filtrate) was immediately analysed by spectrophotometric method using copper (II) ion and 2, 9-dimethyl-1, 10-phenanthroline (DMP) for  $\text{H}_2\text{O}_2$  concentration in solution [14]. The solids after grinding are subjected to FTIR-DRIFT spectral analysis to judge the extent of surface oxidation and their species.

## 2.4. Bench-scale flotation tests

The procedure followed for flotation tests is a standard optimised method at Boliden laboratory in the treatment of complex sulphide ores. For each flotation test, 1 Kg of ore of  $-3$  mm is wet ground with 0.6 litre of water for 20 min. The  $d_{80}$  size of the ground material is  $65\mu\text{m}$  which material is subjected to flotation test in a WEMCO cell of 2.5 litre capacity. The sequences of reagent additions were pH regulator, depressants, collectors, frother, and flotation. The dosages of depressants are; 1500 g/t  $\text{ZnSO}_4$ , 300 g/t  $\text{NaHSO}_3$  and 200 g/t of dextrin. Copper and lead minerals were floated simultaneously, followed by zinc mineral flotation. Dosages of collectors in a three stage sequential Cu-Pb flotation are 30+20+10 g/t Danafloat and 10+5+0 g/t KAX. The conditioning times for pH regulator, depressants, and collectors are 5 min, 1 min and 2+1+1 min respectively. Dosages of zinc activator and collectors in a three stage flotation were 400 g/t  $\text{CuSO}_4$  and 40+20+20 g/t IBX. The conditioning times for zinc activator and collectors are 2 min, 1 min and 1+1+1 min respectively. The frother dosage was 20 g/t Dowfroth. The pH was regulated to  $\sim 10.5$  at copper-lead flotation and to  $\sim 12$  at zinc flotation with powdered calcium oxide. Experiments were performed at room temperature of approximately  $22^\circ\text{C}$ . Total flotation time in successive three stages was 4.5 min (1+1.5+2) as shown in Fig. 1. The three float products in each test were analysed chemically at Boliden laboratories using PANalytical AXIOS XRF spectrometer. Table 1 shows the reagent conditions of the flotation tests that were discussed in this paper.

Table 1. Addition of  $\text{Na}_2\text{S}$  that added to mill

Test no.	Reagents added during grinding in 600 ml water
F1	Reference (normal flotation test)
F10	$\text{Na}_2\text{S}$ (440 g/t = 3.053 mM)
F9	$\text{Na}_2\text{S}$ (850 g/t = 5.898 mM)
F16	$\text{Na}_2\text{S}$ ( 1570 g/t=10.895 mM)

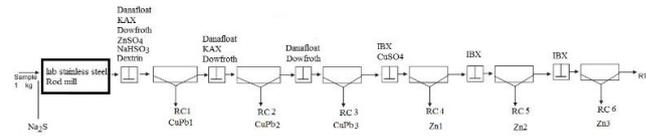


Fig. 1. Schematic diagram of flotation test procedure.

## 2.5. Analysis of flotation product

For analysis of flotation products was used X-ray fluorescence (XRF) equipment that located in Boliden AB company in Skellefteå. The samples were analysed by PANalytical AXIOS XRF Spectrometer. To examine the samples were 10 ml of each sample and further mixed with 0.8 to 1 gram powder paper (0.8 gram for ore and tail samples and 1 gram for concentrate samples). Furthermore, the samples were ground in a laboratory mill kind Herzog in 45 seconds. Steel rings that shaped briquettes were filled with ground material and compressed using briquet hydraulic press with strength of between 11 and 12 tonnes. The briquettes were cleared also not provide non compacted material in the spectrometer during analysis. Finished pellets were placed in the spectrometer to analyse. The device was programmed by the computer and in this case chosen references for the investigation of copper and zinc concentrates.

## 2.6. Diffuse reflectance FTIR studies

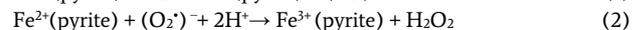
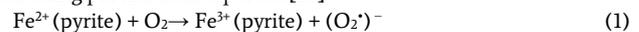
The Bruker FTIR spectroscope model IFS 66 v/s was used for FTIR-DRIFT analysis. Solid fractions of dried ground products were subjected to record infrared spectra. Diffuse reflectance infrared Fourier transform (DRIFT) method was used in measurement with 2.8 wt% concentration of mineral sample in potassium bromide (KBr) matrix. Each spectrum was recorded after 256 scans.

## 3. Results and discussion

### 3.1. Effect of $\text{Na}_2\text{S}$ on Formation of $\text{H}_2\text{O}_2$ in pulp liquid

Fig. 2 shows the effect of  $\text{Na}_2\text{S}$  dosage on Eh and pH of the pulp liquid before and after grinding. The results show with increasing  $\text{Na}_2\text{S}$  concentration, Eh value decreases successively until 3 mM and above which concentration, a significant decrease from positive to negative potential is noticed. The Eh value became constant above 6 mM concentration of  $\text{Na}_2\text{S}$ . The increase in Eh value after grinding is obviously due to the formation of  $\text{H}_2\text{O}_2$ . However, there is no marked variation in pH value of pulp liquid before and after grinding because of  $\text{Na}_2\text{S}$  addition.

Fig. 3 shows that with increasing  $\text{Na}_2\text{S}$  concentration, the formation of  $\text{H}_2\text{O}_2$  in pulp liquid after grinding increases and there is a corresponding decrease in the dissolved oxygen concentration due to a consumption of oxygen in the generation of hydrogen peroxide. Cohn et al. (2006) showed that ferrous iron associated with pyrite in the presence of dissolved molecular oxygen could form superoxide anion ( $\text{O}_2^-$ ) (eq. 1), which further reacts with ferrous iron to form  $\text{H}_2\text{O}_2$  (eq. 2) [15]. The addition of sodium sulphide during grinding is seen to increase the formation of hydrogen peroxide and this could be due to an increase in pH (Fig. 3b) and the formation of  $\text{H}_2\text{O}_2$  increases with increasing pH has been reported [16].



### 3.2. Effect of $\text{Na}_2\text{S}$ dosage on flotation

Fig. 4a shows that the Cu grade and recovery in Cu-Pb concentrate is seen to decrease. It could be due to increasing of pyrite content as shown in Fig. 4c that pyrite depresses chalcopyrite recovery flotation [17]. However, the Pb grade and recovery in Cu-Pb concentrate is seen to decrease (Fig. 4b) and earlier studies showed that the  $\text{H}_2\text{O}_2$  acts as a depressant for galena [18]. This is in agreement with other study where it was observed that sodium sulphide depresses galena [7].

Fig. 5a shows that with increasing of sodium sulphide amount during grinding greatly increases Zn grade and recovery in Zinc concentrate and in this case H<sub>2</sub>O<sub>2</sub> might have favoured the collector adsorption as dixanthogen. Fig. 5b shows that the pyrite content significantly decreases in Zinc concentrate. It is not very clear of this extremely beneficial effect of Na<sub>2</sub>S addition during grinding on Zn flotation, first improved depression during Cu-Pb flotation and then better flotation during Zn flotation and the H<sub>2</sub>O<sub>2</sub> might have effectively depressed pyrite [18].

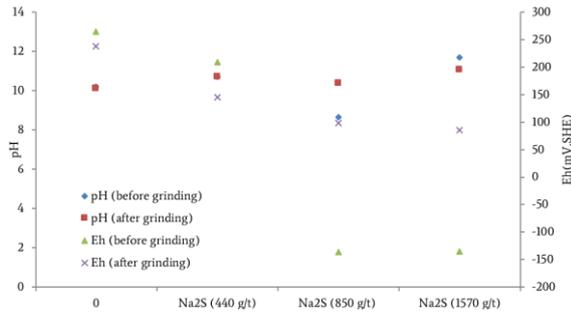


Fig. 2. Effect of Na<sub>2</sub>S on pH and Eh of the pulp liquid before and after grinding.

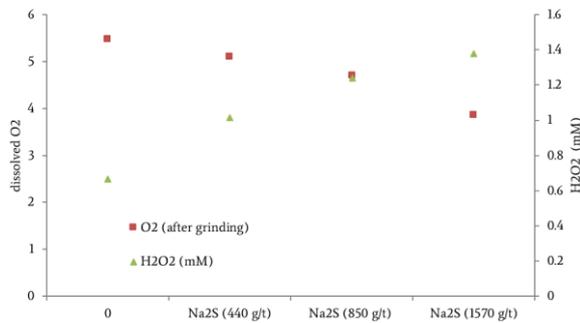


Fig. 3. Effect of Na<sub>2</sub>S dosage on H<sub>2</sub>O<sub>2</sub> concentration and dissolved oxygen in the pulp liquid.

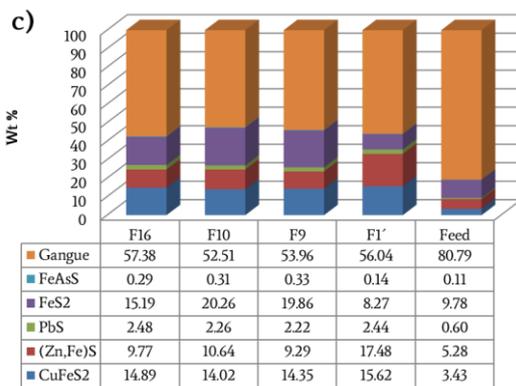
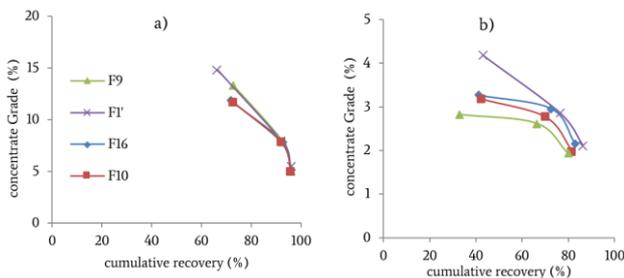


Fig. 4. Effect of Na<sub>2</sub>S addition during grinding on Cu-Pb concentrate: a) Cu grade and recovery, b) Pb grade and recovery and c) Mode of occurrence of minerals in different products of the compared with the feed samples.

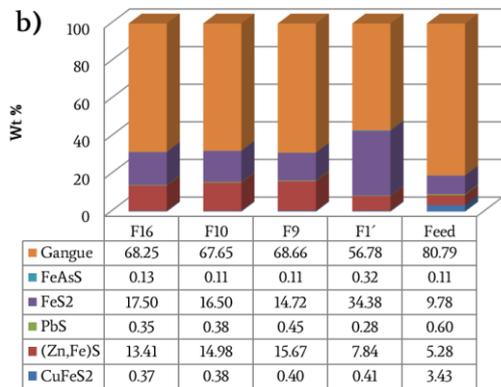
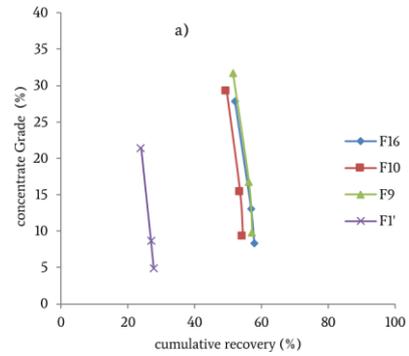


Fig. 5. Effect of Na<sub>2</sub>S addition during grinding on Zn concentrate: a) Zn grade and recovery, b) Mode of occurrence of minerals in different products of the compared with the feed samples.

Fig. 6a shows the Cu-Pb flotation selectivity against Zn (sphalerite) up on the addition of Na<sub>2</sub>S concentration during grinding. The results indicate that selectivity has increased and the Na<sub>2</sub>S dosage more than 3 mM has no further improvement in selectivity. Fig. 6b shows that there is no influence on the Cu-Pb selectivity against Fe (pyrite) with the addition of Na<sub>2</sub>S concentration during grinding.

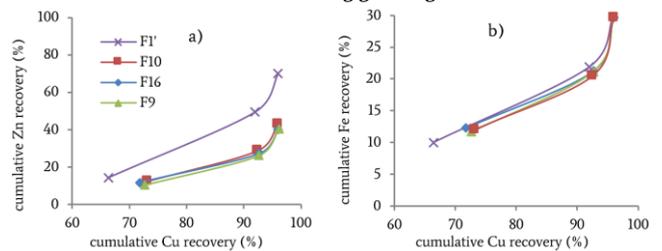


Fig. 6. Effect of Na<sub>2</sub>S addition on Cu-Pb flotation: a) selectivity against Zn, b) selectivity against Fe (pyrite).

Fig. 7 shows the effect of Na<sub>2</sub>S addition during grinding and its dosage on the flotation selectivity between Zn versus Fe (pyrite). The results indicate a significant increase in flotation selectivity up on the addition of Na<sub>2</sub>S although no further improvement with increasing Na<sub>2</sub>S amount. It is agreement that sodium sulphite was used to improve the separation of copper-activated sphalerite from pyrite in mildly alkaline pH conditions [8].

### 3.3. Diffuse reflectance FTIR studies

Solid fractions of grinding products were subjected to FTIR-DRIFT analysis which were conducted on dried samples. The FTIR spectrum of complex sulphide ore before and after conditioning with Na<sub>2</sub>S is presented in Figure 8. five visible absorption peaks were detected on the complex sulphide ore surface. As discussed, addition Na<sub>2</sub>S during grinding and increased dosage of Na<sub>2</sub>S is seen to increase H<sub>2</sub>O<sub>2</sub> concentration, Fig. 8 Shows that addition of sodium sulfide increases of intensity how increasing of sodium sulfide concentration increased

intensity. The bands at 666, 1,160, 1,454  $\text{cm}^{-1}$  are S–O vibrations in sulfate, and the band at 989  $\text{cm}^{-1}$  can be assigned to S=O stretching in sulfite and sulfate [19-20]. Fig. 8 confirm that Pb grade and recovery in Cu-Pb concentrate decreased with increasing of sodium sulfide concentration due to increase intensity S=O and S–O stretching in sulfate, sulfite. The FTIR spectrum of complex sulphide ore in Fig. 8 confirm that higher amounts of  $\text{Na}_2\text{S}$  have depressed pyrite during Cu-Pb flotation due to increase intensity S=O and S–O stretching in sulfate, sulfite and sulfate.

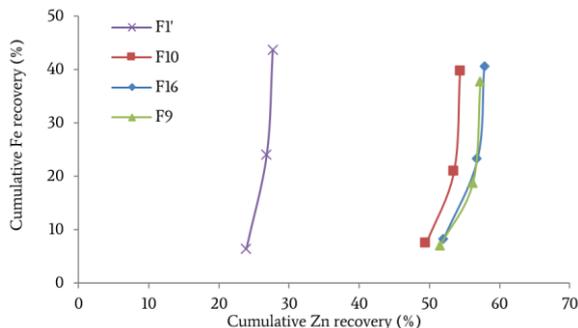


Fig. 7. Effect of  $\text{Na}_2\text{S}$  addition on flotation selectivity between Zn and Fe (pyrite).

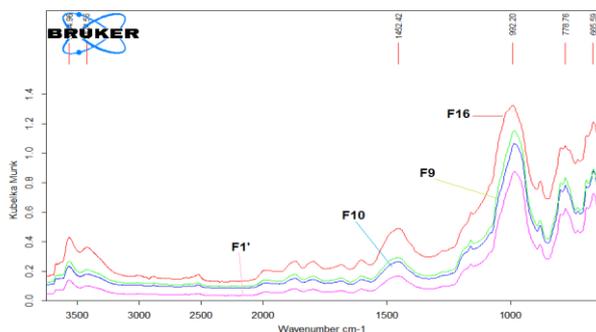


Fig. 8. DRIFT spectra of corresponding ore solid residue separated from solution after grinding for 60 minutes in solution.

#### 4. Conclusion

Formation of  $\text{H}_2\text{O}_2$  in the pulp liquid increases with the addition  $\text{Na}_2\text{S}$  during grinding and increased dosage of  $\text{Na}_2\text{S}$  is seen to increase  $\text{H}_2\text{O}_2$  concentration. Increasing formation  $\text{H}_2\text{O}_2$  led to a decrease in dissolved oxygen content. Sodium sulphide has no effect on Cu flotation but decreased Pb grade and recovery in Cu-Pb concentrate. Higher amounts of  $\text{Na}_2\text{S}$  have depressed pyrite during Cu-Pb flotation. However, Zn flotation is seen better at higher dosages of  $\text{Na}_2\text{S}$ . The results suggest beneficial effect of  $\text{Na}_2\text{S}$  addition during grinding for pyrite depression and better sphalerite flotation. The pyrite depression is due to sulphite species generated by the oxidation of  $\text{Na}_2\text{S}$  by  $\text{H}_2\text{O}_2$ .

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