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# Prediction of flotation behavior of sulphide ores by oxidation index

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#### ABSTRACT

In addition to size, density, composition and mineralogy (mineral type, texture, liberation, etc.), surface characteristics of sulphide minerals affects flotation behavior of sulphide ores considerably. The variations in surface characteristics of sulphide minerals can be related to the variations to the degree of surface oxidation which is known to influence the flotation performance. Surface oxidation affects dissolution behavior of sulphide minerals, activation/depression and adsorption of collectors, i.e. their flotation behavior. Therefore, a methodology, called "Oxidation Index" was developed to measure surface oxidation of sulphide minerals quantitatively and predict flotation behavior of different ore types. The methodology is based on derivation of an ore specific calibration curve and prediction of flotation performance of different ore types from the same deposit by using the calibration curve. The results of the test works performed using a complex Cu–Zn sulphide ore from Çayeli Bakır İşletmeleri A.Ş., Turkey are discussed in this paper.

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#### 1. Introduction

Mineralization in sulphide ore deposits is generally not homogenous. In the same ore deposit, it is likely to observe ore types with different mineralization, different degree of liberation and also surface oxidation (Ekmekci et al., 2010; Bojcevski et al., 1998; Vink, 1997; Jones, 1987). These variations affect flotation performance significantly depending on the structure of ore. In most of the sulphide ore flotation plants, chemical and mineralogical properties of the flotation feed are periodically measured to control the flotation process. However, it is likely to observe drastic changes in the flotation response with the same chemical and mineralogical characteristics. This is generally attributed to the changes in surface properties of the sulphide minerals in the ore due to surface oxidation. Therefore, measurement of surface oxidation of sulphide minerals has a crucial importance for plant control. Flotation of sulphide ores are strongly affected by chemical parameters like pH, Eh, dissolved ions and surface oxidation. Low degree of surface oxidation may enhance the flotation of sulphide minerals by forming surface coatings of metal deficient sulphides (Buckley and Walker, 1988), elemental sulphur (Trahar, 1984) or polysulphides (Luttrell and Yoon, 1984). However, extensive surface oxidation generally reduces flotation recovery and selectivity (Senior and Trahar, 1991; Smart, 1991) by coating the surface of the minerals with hydrophilic and stable metal oxide/hydroxide species.

Oxidation of sulphide ores may occur due to weathering process during formation, mining, stockpiling, crushing, milling or flotation. In literature there has been many techniques used to determine the degree of oxidation which are basically Eh (Baker et al., 1991), dissolved oxygen demand test (Houot and Duhamet, 1990), EDTA extraction technique (Rumball and Richmond, 1996; Kant et al., 1994), XPS and Auger surface analysis (Smart, 1991), optical mineralogy, infrared spectroscopy, flotation, contact angle and zeta potential. However, most of these techniques have some limitations particularly in plant scale applications.

Ethylene diamine tetra acetic acid, widely abbreviated as EDTA is a polyamino carboxylic acid and a colorless, water-soluble solid acetate. EDTA has the ability to dissolve and form complex with the oxidation products of sulphide minerals, however does not react with metal sulphides (Shannon and Trahar, 1986; Grano et al., 1988; Rumball and Richmond, 1996). EDTA extraction was found to be the most suitable method for measurement of surface oxidation both in laboratory and plant scale applications (Bicak et al., 2008).

Therefore, the aim of this work was to develop a new measure based on EDTA extraction technique to determine the degree of oxidation of sulphide ores quantitatively. The surface oxidation as measured by the new methodology was then related to the changes in flotation performance.

#### 2. Materials and methods

### 2.1. Material

In this paper, a copper-zinc massive sulphide complex sulphide ore from Çayeli Bakır İşletmeleri A.Ş., Turkey, containing about 70% sulphide minerals is used. The average composition of the ore are given in Table 1.

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In Çayeli ore, chalcopyrite, pyrite and sphalerite are the main sulphide ore minerals. In addition to that bornite, galena and chalcocite are found in variable proportions in different ore types in the same deposit.

#### 2.2. Experimental methods

#### 2.2.1. EDTA extraction test

There are many techniques to measure degree of oxidation in literature but among these techniques, EDTA extraction was found to be the most suitable for plant applications (Bicak, 2011).

In the EDTA extraction technique, 10–20 g of dry sample is added into a beaker containing 200 ml of 3% EDTA solution at pH 7.5 and stirred vigorously for 30 min. The beaker is sealed during extraction to prevent contact with atmosphere. After the extraction, the pulp is filtered to separate the solution and the solid for chemical analysis. 3% EDTA solution was used as a standard solution in all of the tests. pH of the solution was adjusted to 7.5 with NaOH to prevent the formation of metal–EDTA precipitates (Rumball and Richmond, 1996).

Degree of oxidation is evaluated based on two methods of calculation, Es and Em. Es (Kant et al., 1994) represents the amount of metal oxidized on the mineral surface which is accepted as an indication for mineral oxidation, whereas Em (Eq. (1)) value represents oxidation degree of the ore in total. In this paper, all evaluations are made on the basis of Em Total values.

$$Em_{(Cu,Zm,Fe)} = \frac{Amount\ of\ metal\ in\ solution\ (mg)_{(Cu,Zn,Fe)}}{Amount\ of\ solid\ (g)} \tag{1}$$

#### 2.2.2. Flotation tests

Flotation tests are conducted in a 3 l modified Leeds type flotation machine. Flotation feed is ground at 60% w/w pulp density for 15 min to obtain particle size 80% passing 38  $\mu m$ . Aerophine (3418A) and MIBC obtained from Çayeli flotation plant were used as collector and frother respectively. The flotation tests were performed at 30% w/w pulp density and pH 11.5 by adding CaO to the mill.

The flotation products were assayed for Cu, Zn and Fe using AAS. Flotation rate constants calculated by using first order flotation rate equation.

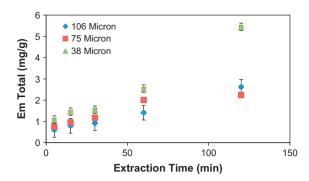
## 3. Optimization of EDTA extraction test

Factorial design was used to test the influence of different parameters in the optimization tests and the results were evaluated by using Design Expert 7.1.5. Surface area of the different size fractions was measured using BET technique.

Fig. 1 shows the change of Em Total (mg/g) values according to the changes in extraction time and P80 passing size of material. Em Total values changes as a function of extraction time and particle size. The results of EDTA extraction tests showed that the particle size (surface area) was a significant parameter determining the amount of extracted metal from the mineral surface (Bicak,

**Table 1**Mineralogical and chemical characteristics of a typical Çayeli ore.

Mineral	(%)	Element	(%)
Chalcopyrite	7	Cu	3.5-4
Bornite	0.4	Zn	5-7
Sphalerite	12.72	Fe	28-30
Pyrite	60	Pb	0.5-1.2
Galena	0.6		
Others	19.28		



**Fig. 1.** The changes in Em Total values with extraction time and P80 values of solid used. (P80: 80% of material passing size).

2011). Therefore, the equations used to calculate Es Cu and Em total were modified to include surface area (Eqs. (2)–(4)).

$$Em_{total} = Em_{Cu} + Em_{Zn} + Em_{Fe} \tag{3}$$

$$Em \ Total_{BET} = \frac{EmTotal}{BET \ surface \ area \ (m^2/g)} \eqno(4)$$

In the calculation of Es Cp, chalcopyrite was assumed as the only copper mineral in the ore. Similar calculations can be done for the other minerals (sphalerite, galena, pyrite, etc.) by using the concentrations of the other metals (Zn, Pb, Fe, etc.). Em Total can be calculated as the ratio of total amount of dissolved metal by EDTA to the amount of ore used in the extraction and unit surface area (Eq. (4)).

Another significant parameter for extraction is the time of extraction. Fig. 1 shows clearly that even after two hours, the Em Total values continue to increase linearly. Similar finding is compatible with literature. According to Rumball and Richmond (1996), complete dissolution of iron takes eight hour. Therefore for practical reasons, the extraction time was taken as 30 min and kept constant for all experiments. Particle size which is 80%  $-38~\mu m$  (also flotation size in the plant) were also kept constant in all tests.

## 4. Derivation of Oxidation Index

There has been many research works in the literature investigating the effects of surface oxidation on flotation performance. Some of these techniques are qualitative or at best semi-quantitative and does not give a quantitative index representing the degree of oxidation of a sulphide ore. Therefore, a quantitative measurements method is required to establish the relationship between oxidation and flotation performance of a given ore.

Flotation tests were conducted in a 3 lt modified Leeds flotation machine. The flotation tests were performed at pH 11.5 and 30% w/ w pulp density. 15 g/t MIBC was used in the experiments, the collector dosage was determined according to the copper content of the feed. Air rate is adjusted to 3 lt/min and the flotation time is 0.5–1.5 – 7 min. The products of the flotation tests were analyzed for Cu, Zn and Fe. Flotation rate constants calculated by using first order flotation rate equation (Eq. (5)).

$$R = R_{\infty} \chi (1 - e^{-kt}) \tag{5}$$

where, R is the Flotation Recovery (%),  $R_{\infty}$  the Flotation Recovery at infinity (%), k the Flotation rate constant (1/min), t is the Flotation Time (min).

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