IJAAR PUBLISHING®
DOI: 10.46654

Engineering Research Journal | ISSN: **2782-8212**
Vol. 1, Issue 7 (July, 2021) | www.ijaar.org

EFFECT OF PROCESSING PARAMETERS ON ZINC RECOVERY FROM SPHALERITE CONCENTRATE IN FERROUS SALT

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Abstract

In this study, zinc was leached from sphalerite in ferrous sulphate at varied concentrations of hydrogen peroxide (H_2O_2), stirring speed and temperature; this is with a view to investigating the effects of these parameters on zinc recovery. 200g of comminuted sphalerite sample was wet sieved at -180+125, -125 +90, -90 +63 and -63 +38µm particle sizes to determine the optimum particle size range. Thereafter, 1 gram of sample from the optimum size range was leached in 1.0M of iron sulphate ($FeSO_4$) at the varied concentration of the oxidant (0.5-3.5M), stirring speed (150-330rpm) and temperature (20-105^oC). From the results, the least and highest zinc contents were obtained at the particle sizes of -180+125 and -90 +63µm with concentrate amounts of 12.38% and 17.56% respectively. Weight percent of zinc leached at the optimum particle size (-90 +63µm) was variedly influenced by the parameters.Optimum weight percent were obtained at 2.5MH_2O_2,210 rpm stirring speed and 110^oC temperature with the values 78%, 69% and 72 % respectively after the experimental period (120 minutes) of leaching time.

Keywords: Sphalerite; leached; Hydrogen peroxide, stirring speed; temperature; oxidant

1. Introduction

Sphalerite is brownish, yellowish, or black and mainly associated with other metal sulphide minerals such as chalcopyrite ($CuFeS_2$), galena (PbS) and pyrite (FeS_2). The common zinc-containing minerals are the zinc sulfide known as zinc blende or sphalerite (ZnS), a ferrous form of zinc blende known as marmatite [(ZnFe)S], and a zinc carbonate known as calamine or smithsonite ($ZnCO_3$). Zn is widely used in different area of industrial applications (Ma *et al.*, 2016; Onyemaobi, 1990). It is used as an alloying metal with copper to make brass, as corrosion-protection coatings on steel (galvanized metal), as chemical compounds in rubber, ceramics, paints, and agriculture (Mubarok *et al.*, 2018; Li *et al.*, 2010). Also, it is used in wide area of industrial applications and as die castings.

Pyrometallurgy has been the conventional route for sulphide concentrate processing, but this route is associated with myriad of problems, including pollution, high energy cost, shortage of high grade ores, processing of lean and complex ores and exploitation of smaller deposits. These problems have necessitated the development of low temperature hydrometallurgical route, which involves metal dissolution (leaching), separation, concentration and reduction to the metal at low temperature (Abdel-Aal, 2000). However, hydrometallurgical processes are usually more favourable at higher temperatures, making it necessary to measure the parameters of variables of the process.Leaching process is electrochemical in nature, involving selective dissolution of soluble constituents of a solid in aqueous solution and subsequently isolation of metal from the leached dissolution. The dissolution takes place by diffusion of reactant through the diffusion layer, adsorption of the reactant on the solid, chemical reaction between the reactant and the solid, desorption of the product from the solid and diffusion of the product through the diffusion layer (Ikechukwu *et al.*, 2020; Onukwuli *et al.*, 2018).

Generally, sulphide minerals are inert in water, dissolution of these minerals are aided by the employment of acid, alkaline or certain salts alongside water (Aydoğan *et al.*, 2006). There are several innovative leaching processing developed for zinc extraction, including copper catalyzed ammonia leaching, pressure leaching, heap leaching and ferrous sulphate leaching in hydrogen peroxide medium (Michael, 2020; Crundwell, 1987). Hydrogen peroxide is widely used in this respect due to its high oxidation- reduction potential value (1.77 V, vs SHE), and very cost-effective substitute for the leaching out of zinc sulphides (Olubambi *et al.*, 2006; Adebayo *et al.*, 2006; Aydoğan, 2005). Oxidative leaching has eliminated the roasting step associated with conventional hydrometallurgical processes for the extraction of a base metal from a sulphide concentrate; it also produces elemental sulphur, instead of sulphur dioxide.

A plethora of study on copper catalyzed ammonia leaching, pressure leaching, and heap leaching of sphalerite exists in literature (Asim *et al.*,2013; Li *et al.*, 2010; Aydoğan *et al.*, 2005; Salih *et al.*, 2005; Babu *et al.*, 2002). While study on leaching with acid and hydrogen peroxide is still relatively scanty, this is in spite of the important role of ferrous sulphate and ferric iron in the overall leaching process of sphalerite. Consequently, effort was made in this work to leach sphalerite concentrate in ferrous salt under the conditions of varied concentration of hydrogen peroxide, stirring speed and temperature.

2. Methodology

2.1. Material

The experimental sphalerite sample was crushed and grind in jaw crusher and ball mill respectively. 200g of the ground sample was wet sieved to -180+125, -125 +90, -90 +63 and -63 +38 µm particle sizes, and the main chemical composition of the sized sample for each of the fraction was determined using atomic absorption spectrometer (AAS). The result is presented in Table 1. This is the liberation size at which the ground sample would be leached.

Table 1: Chemical Analysis of the sphalerite

Particle Size (µm)	% Composition					
	Zn	Fe	Mg	S	Si	O_2
-180 +125	12.38	7.02	0.98	24.20	24.10	0.006
-125+90	15.41	7.06	0.78	24.43	23.09	0.009
-90 +63	17.56	7.06	-	26.06	22.05	-
-63	16.49.	7.06	-	25.21	22.07	-

2.2 Leaching Procedure

The reactor used for the leaching experiment is a 1 litre Pyrex beaker, which was closed by a rubber cover, equipped with a mechanical stirrer and housed in a water bath. The temperature was monitored and controlled by passing water through the bath. A mixture of 50ml ferrous salt and 50ml hydrogen peroxide was introduced into the reactor, 1.0g of the sphalerite at particle size range -90 +63 µm was added at desired the temperature. The contents of the reactor were stirred at the desired speed. After which, 2ml of the pregnant solution was withdrawn from the reactor 60 minutes diluted with distilled water to 25ml in a standard flask and analysed for zinc using atomic absorption spectrometry (AAS). The conditions involved varying a parameter and keeping the others constant at a time was repeated for varying hydrogen peroxide concentration, stirring speed and temperature (Adebayo *et al.,* 2006). Depicted in Table 2 is the summary of the experimental procedure.

Table 2: Summary of the experimental procedure

Run	Varied parameter	Range of the varied parameter and unit	Constant parameters	Values of the constant parameters and unit
1.	Hydrogen peroxide	0.5-3.5M	sphalerite concentrate stirring speed temperature Ferrous salt particle size	1.0g 150rpm 80^{o}C 50ml 100% passing -90 +63 µm
2	Stirring speed	150-330rpm	sphalerite concentrate Temperature Hydrogen peroxide Ferrous salt particle size	1.0g 80^{o}C 2.5M 50ml 100% passing -90 +63 µm
3.	Temperature	20-110°C	sphalerite concentrate Hydrogen peroxide stirring speed Ferrous salt particle size	1.0g 2.5M 180rpm 50ml 100% passing -90 +63 µm

3. RESULTS AND DISCUSSION

3.1 Chemical analysis of the sphalerite

Result of the chemical composition (Table 1) shows sphalerite concentrate contains zinc sulphide (ZnS) as its major constituent. Other constituents in relative minor quantities are silica (SiO_2) and alkaline gangue (MgO). The least and highest zinc contents were obtained at the particle sizes of -180+125 and -90 +63µm with concentrate amounts of 12.38% and 17.56% respectively. Also, the sulphur and iron contents in all the size fractions were similar.

3.2 Influence of varying concentration of hydrogen peroxide

The sphalerite concentrate was leached at varying hydrogen peroxide concentrations of 0.50, 1.0, 1.50 2.0, 2.50, 3.0 and 3.5M under the conditions of constant stirring speed (150 rpm) and temperature (80^oC). And the results as presented in Fig. 1 reveals increase in weight % of zinc leached in the range of 0.5-2.5 M and subsequent decrease in the range of 2.5-3.5M. The leaching of sphalerite concentrate in ferrous salt by H_2O_2 was made possible as a result of the relative high redox potential of H_2O_2. In congruence, Adebayo *et al.,* (2006) have shown that redox potential of hydrogen peroxide is higher as compared to redox potential of sulphur / metal sulphide pair. The increased dissolution of the zinc concentrate in the range of 0.5- 2.5M of H_2O_2 from 41-72% after 120 minutes leaching time can be attributed to the accompanied rapid decomposition of H_2O_2, which resulted the action of ferrous salt (Crundwell, 1987;Dutrizac and MacDonald, 1974; 1978).

The catalytic reaction, involving H_2O_2 decomposition and subsequent oxidation of soluble ferrous salt (Fe^{2+}) to ferric salt (Fe^{3+}) is described by the four stages reactions in Eqns. 1-4. The resulting dissolution of zinc from zinc sulphate is described by Eqns. 5 and 6, while the latter is the form. During the process, ferric salt (Fe^{3+}) reacted sphalerite concentrate, forming ferrous salt (Fe^{2+}), elemental sulphur (S^0) and zinc sulphate ($ZnSO_4$), which is soluble and dissociates in aqueous solutions (Olubambi *et al.,* 2006; Perez and Dutrizac, 1991).

$$Fe^{2+} + H_2O \rightarrow Fe^{3+} + OH + OH \qquad (1)$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \qquad (2)$$

$$HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH \qquad (3)$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH \qquad (4)$$

$$Fe_2(SO_4)_3 + ZnS \rightarrow 2FeSO_4 + ZnSO_4 + S^o \qquad (5)$$

$$ZnS + 2Fe^{3+} \rightarrow Zn^{2+} + 2Fe^{2+} + S^o \qquad (6)$$

In addition, increase in sphalerite concentrate dissolution in the range of 0.5-2.5M, may have been partly influenced by the removal of elemental sulphur during leaching. Microscopic studies of sphalerite ore during leaching revealed blocking of sphalerite surface by elemental sulphur (Olubambi *et al.,* 2006). On the other hand, decreased dissolution of the zinc concentrate in the range of 2.5-3.5M of H_2O_2 from 41-72% after 120 minutes leaching time may have resulted from increased presence of emerging ferric ions and, in consequence, reduction in local concentration of H_2O_2 (Olubambi *et al.,* 2008; Souza, *et al.,* 2007).

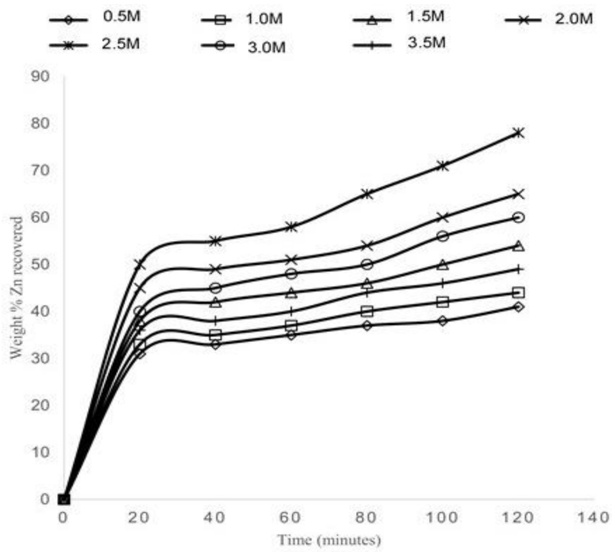

Fig. 1: Effect of varied H_2O_2concentrationon Zn recovery from sphalerite in ferrous salt at stirring speed of 180 rpm and temperature of 80°C temperature.

3.3 Effect of varying stirring speed

The effect of stirring speed variation (150-330 rpm) on weight percent of zinc leached under the experimental conditions of constants temperature (80^{o}C) and 2.5M H_2O_2 is depicted in Fig. 2. From the result, the rate of zinc leached was increasingly and decreasingly sensitive to stirring speeds in the range of 150- 210 rpm and 270- 330 rpm respectively over the experimental period of 120 minutes. The highest weight percent of zinc leached (72%) was obtained at the agitation rate of 210 rpm and the least (44%) at 330 rpm. Increased weight percent of zinc leached in the range 150- 210 rpm may be attributed to less rapid agitation, during which, better contact between the leachants and sphalerite particles was established (Olubambi *et al.,* 2006 Adebayo, *et al.,* 2006).

In converse, the decrease in sensitivity of zinc leaching, and hence, low weight percent of zinc leached in the 270- 330 rpm was attributed to rapid agitation, during which, the less contact between the leachants and sphalerite particles was established. Also, at such a high agitation rate (270- 330 rpm), particle/solvent interaction may have been reduced by the molecular oxygen that accompanied rapid decomposition of H_2O_2, which absolved on to the particle surface (Olubambi *et al.,* 2006). In addition, increased leachant viscosity in the range 270- 330 rpm may have partly accounted for the low weight percent of leached. With increase in stirring speed, there was rapid collision of small particles and formation of larger ones and, in consequence, the number of particles per unit area was increased.

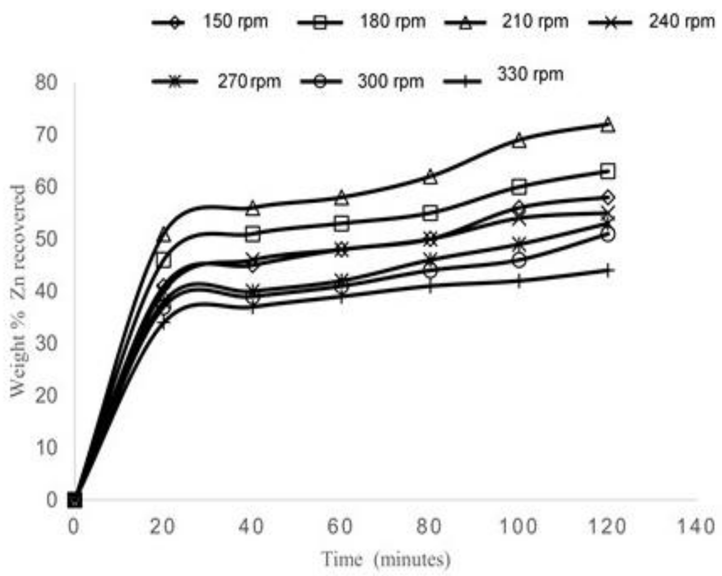

Fig. 2: Effect of stirring speed on Zn recovery from sphalerite inferrous salt at temperature of 80°C and H_2O_2 concentration of 1M

3.4 Effect of varying temperature

Fig. 2 depicts effects of temperature in the range of 20-11°C on the leaching yields of zinc from sphalerite ore under the conditions of constants H_2O_2 and stirring speed of 2.5 M and 180 rpm respectively. It had been shown that the leaching efficiency of sphalerite in nitric acid was enhanced by increased temperature (Adebayo *et al.*, 2006). Souza *et al*. (2007) have shown that leaching efficiency of hemimorphite increased with increasing of temperature from 30 to 60 °C. Abdel-Aa, (2000) showed that with increase in leaching temperature from 40 to 70 °C, the leaching efficiency of Zn was increased from 70 to about 95%. In agreement with the results of the previous findings, it is obvious that zinc dissolution increases appreciably with increasing temperature over the experimental period of 120 minutes (Fig. 3). The appreciable increase in weight percent of zinc leached from minimum of 49% to maximum of 69% at 20°C and 110°C respectively over the 120 minutes of the experimental period, may be attributed to increasing decomposition of H_2O_2 (Eqn. 7) and, in consequence, gradual rise in the available oxygen and diffusion coefficient.

$$H_2O_2 \rightarrow \frac{1}{2}O_2 + H_2O \qquad 7$$

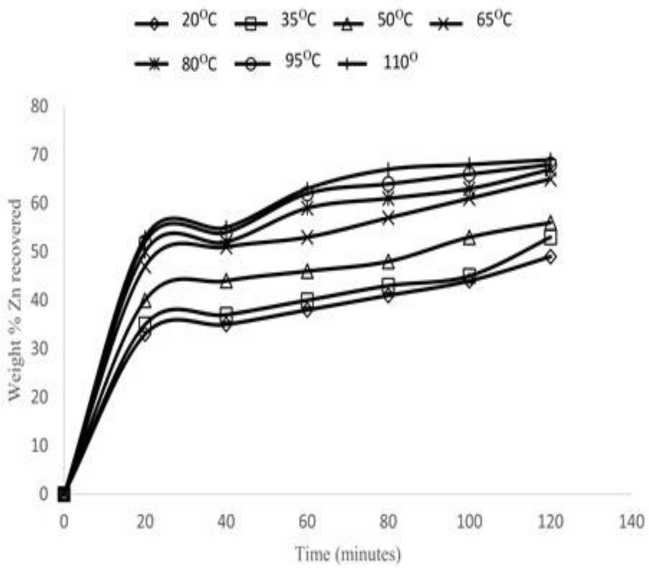

Fig. 3: Effect of varied temperature on Zn recovery from sphalerite in ferrous salt at H_2O_2 concentration of 1M and stirring speed of 180 rpm

4. CONCLUSIONS

From the results of the investigation, the following conclusions were drawn:

1. The recovery yield of Zn from sphalerite in Fe_2SO_4 over the experimental period of 120 minutes was to some considerable extents dependent on H_2O_2 concentration, stirring speed and temperature.
2. Weight % of zinc leached was increased in the range of 0.5-2.5 M hydrogen peroxide concentration and decreased with subsequent increase in the range of 2.5 - 3.5M.
3. Weight % of zinc leached was more sensitive to stirring speeds in the range of 150-210 rpm and less sensitive in the range of 270- 330 rpm.
4. Temperature was found to have appreciable effect on the weight % of zinc leached over the experimental period of the leaching time.
5. Highest Zn recovery of 78%, 69% and 72 % were obtained at the optimum leaching conditions of; (i) hydrogen peroxide concentration of 2.5M), (ii) stirring speed of 210 rpm and (iii) temperature of 105°C.

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