

PREPARATION OF ZINC SULPHATE ELECTROLYTE FROM ZINC SULPHIDE CONCENTRATE

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(Received April 2, 1991; revised May 28, 1992)

A process is described for the preparation of zinc sulphate solution from a zinc sulphide concentrate that was obtained by flotation of a local lead-zinc ore. It has been shown that 97% ZnO is obtained at a temperature of 925°, while at a lower temperature of 750°, the same percentage of ZnO is obtained if air is passed over the zinc sulphide during roasting. The dissolution of zinc oxide has been studied using sulphuric acid concentrations of 20.5–50.5 gm/l at liquid to solid ratios varying from 11.25–31.50. It has been shown that 97.9% Zn is leached at a H₂SO₄ concentration of 48 gm/l with a liquid to solid ratio of 13.75 in 60 mins. The leach solution has been purified by raising its pH from 2.97–5.80 which resulted in the precipitation of iron and aluminium. Heating the solution during precipitation helps in the coagulation of precipitate for easier filtration.

Key words: Electrolyte, Flotation concentrates, Leaching, Roasting.

Introduction

Zinc ranks third with respect to non-ferrous metals consumption in the world [1]. Metallic zinc is extracted from ores by two distinct methods, both starting with oxide formed by roasting the ores and/or concentrates [2-5]. (i) The pyrometallurgical or distillation process wherein the ZnO is reduced with carbon in retorts from which the resultant zinc is distilled and condensed; and (ii) the hydrometallurgical and electrolytic process wherein the ZnO is leached from the roasted or calcined material with H₂SO₄ to form ZnSO₄ solution which is electrolyzed in cells to deposit zinc on cathodes. The electrolytic process currently produces about two thirds of the world's primary zinc [1].

There are many zinc bearing minerals but only a few of them are the commercial source of metal. The principal among them is zinc sulphide (ZnS) known as sphalerite or zinc blende. Zinc deposits, mostly in veins, occur at several places in Pakistan. The two most significant reserves are located near Besham in district Swat (NWFP) and Khuzdar in district Kalat (Baluchistan) [6,7]. The Baluchistan ore contains around 6.0% zinc while Besham ore contains 5.6-7.8% [8].

At present, Pakistan imports all its requirements in zinc and zinc based chemicals. During the years 1985-88, zinc ingots, waste and scrap worth Rs. 533 million was imported while the import of zinc chemicals amounted to Rs. 31 million [9]. In order to make use of the indigenous lead-zinc ores, a project entitled Substitution of Imported Minerals and Mineral Based Products was undertaken by the Minerals and Metallurgy Research Centre (MMRC) which resulted in a process for the production of zinc sulphide concentrate on a pilot plant scale.

The paper deals with the utilization of zinc concentrate through roasting and leaching to prepare solution for electro-winning of metallic zinc.

Experimental

Material. The zinc concentrate used in the investigation had the characteristics given in Table 1 (a,b,c).

Analytical. The analyses of the solid materials and solution was carried out using atomic absorption spectrophotometer (Hitachi Model 8000), X-ray fluorescence spectrometer (Jeol Model 603) and X-ray diffractometer (Siemens Model D-5000).

Roasting of zinc concentrate. Twenty grams of zinc concentrate, placed in a porcelain dish, was roasted in a muffle furnace with a thermostatic temperature control. The combustion chamber of the furnace measured 29.0 x 13.5 x 8.5cm (LxWxH) and had a 1cm hole in the gate to admit air. The roasting behaviour was studied from 550°–1000° for 15, 30, 60 and 90 mins. The concentrate bed was stirred manually from time to time during roasting. The results of roasting are given in Table 2(a,b,c).

Leaching of roasted zinc concentrate. A series of batch tests was conducted to determine optimum leaching conditions. In these tests the roasted concentrate, which looked agglomerated when taken out of the furnace, was crushed and leached with H₂SO₄ in pyrex glass beakers. The pulp was stirred manually from time to time with the help of a glass rod. At the end of the leaching operation, the leach residue was separated prior to purification of the solution. The leaching results are presented in Table 3 (a,b,c).

Purification of leach solution. The acidic leach solution containing impurities such as iron, aluminium and others like

Cu, Cd, As, Sb was subjected to neutralization by raising the pH from 2.97–5.80. The pH was adjusted by the addition of one of the following four neutralizing agents, viz. roasted ZnS (calcine) pure ZnO, zinc dross (a mixture of zinc oxide and zinc dust in 1:1 ratio) and CaO. After the addition of neutralizing agent the solution was heated to coagulate the precipitate. The iron was converted from ferrous to ferric state, during heating, by the addition of H_2O_2 . The resulting precipitate was filtered off in a vacuum filter and washed with distilled water. After the removal of iron, the solution was reconstituted to contain 150 gm/l zinc. The solution was analysed for the remaining impurities and further purification was carried out with zinc dust. The data on the purification of solution is presented in Tables 4 and 5.

Results and Discussion

Data presented in Table 2a indicate the percent conversion of zinc sulphide into zinc oxide when the sulphide is heated for different time intervals at different temperatures under natural draught conditions.

It is seen that when the sulphide concentrate is heated for 15 mins at temperatures from 550–925°, the formation of zinc oxide increases slowly to 39.28% at 900° then suddenly jumps to 93.1% at 925°.

The roasting of sulphide for 30 mins. in the same temperature range shows quicker rates of conversion to the oxide reaching a maximum of 97.90% at 925°.

In the case of roasting for 60 and 90 mins. under similar conditions of temperature, the conversion to oxide shows much higher rates upto a temperature of 925°. At this temperature, it reaches 92.12 and 91.09% for 60 and 90 mins. respectively.

Data presented in Table 2b show the results of roasting zinc sulphide in a current of air. It is seen that for a duration of 30 mins., the conversion of zinc sulphide into zinc oxide rises with increase in temperature till it reaches 86.57% at 900°.

It is apparent from this table that the conversion at 750° is about double as compared to that obtained at the same temperature and time interval when roasting was conducted under natural draught conditions. This would mean that the passage of air over the hot mass accompanied by rabbling reduces the use of energy to a large extent.

In order to optimise the time required to obtain a reasonably higher conversion at 750°, a set of experiments was carried out. The results are shown in Table 2c.

It is seen that the roasting of zinc sulphide in a current of air yields 97.01% zinc oxide when roasting is carried out for 60 mins. at 750°.

This temperature appears to be useful practically. The ignition point of pure sphalerite is reported to be 646° [10]. At

the same time, the formation of ferrite starts around 650° [11] which increases with rising temperature. Beyond 800°, the rate is very fast. But it was noticed that when roasting was carried out beyond 750° in a current of air, followed by acid leaching, the zinc that remained unleached in the form of ferrite and/or sulphide did not exceed 2.1%. It would mean the formation of zinc ferrite was insignificant even at high temperature. Actually marmatite (Zn, Fe)S is ignited at low temperatures than sphalerite and the largest quantity of zinc ferrite is produced in roasting zinc concentrates containing marmatite for the reason that in marmatite, sulphides of zinc and iron make up an isomorphous mixture [12]. Another point in favour of such a temperature is the formation of sulphates at 500–600° [10,11]. At higher temperatures the sulphate starts breaking yielding oxide [10]. Thus, it was noticed that roasting

TABLE 1a. CHEMICAL COMPOSITION OF ZINC CONCENTRATE.

Constituents	Percent
Zn	50.26
Pb	00.03
S	33.0
Fe ₂ O ₃	9.7
Al ₂ O ₃	5.00
SiO ₂	1.01
Cu	0.04
Ni	0.01
Cd	0.03
Mn	0.15
Sb	0.76

TABLE 1b. MINERALOGICAL COMPOSITION OF ZINC CONCENTRATE.

Constituents	Percent
Sphalerite	75.0
Galena	00.04
Pyrite	16.50
Aluminates	5.00
Silicates	1.01
Others	2.45

TABLE 1c. SIZE ANALYSIS OF ZINC CONCENTRATE.

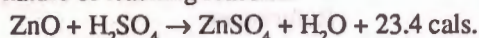
Particle size (microns)	Wt.% retained	Cum. Wt.% (retained)	Cum. Wt.% (passing)
+150	0.30	0.30	99.70
-150+105	1.49	1.79	98.21
-105+75	4.11	5.90	94.10
-75+63	8.09	13.99	86.01
-63+53	5.51	19.50	80.50
-53	80.50	100.00	—

at 750° in a current of air produced some sulphate also. This was determined by first dissolving the roasted mass with water followed by acid leaching for zinc oxide and locked zinc. The quantity of zinc sulphate was found to be 9-10%.

Table 3a shows the effect of H₂SO₄ concentration on the leaching of zinc from the roasted concentrate. It is seen that under similar conditions of leaching, the percentage of zinc in the leach solution increases with increasing H₂SO₄ concentration. At 48 gm/l H₂SO₄, the concentration of zinc in leach solution reaches 97.90% after which it becomes constant.

Table 3b shows the effect of liquid to solid ratio on the leaching of roasted concentrate. It is seen that at a liquid to solid ratio of 12.50 the zinc leached is 97.79% and at 13.75 the zinc leached is slightly higher, i.e., 97.79% after which it becomes constant.

Table 3c shows the leaching of zinc as a function of time keeping the acid concentration at 48 gm/l and liquid to solid ratio at 13.75. It is seen that there is no significant difference between the values of zinc leached as the time interval is increased. However, it may be observed that the percentage of zinc leached becomes constant for a time of 60 mins and thereafter. The results of leaching study indicate that the maximum extraction of zinc from the roasted material, containing 97.01% zinc in the form of oxide and sulphate, amounts to be 97.9%. It was observed during leaching that the temperature of the solution rose to 50° (Table 3b,c) due to the exothermic nature of leaching reaction.



At lower concentrations (< 45gm/l), the temperature of the solution was less than 50°. It was also observed that agitation of the solution during leaching greatly helped leaching. Thus when the solution was not agitated, the zinc extraction in 60 mins was only 50% while with agitation it was 97.9%.

Table 4 shows the results of purification of the leach solution by using different materials for the removal of impurities. It is seen that calcine and zinc dross remove impurities to an extent of 99% while pure zinc oxide removes them upto 99.90%. Calcium oxide is slightly less effective and results in an impurity removal of 98.50%. It was observed that purification of the solution with zinc dust did not improve the results.

Table 5 shows that impurities like Cu, Cd, Pb and Sb have been removed. Nickel is another deleterious impurity which has a permissible limit of 0.0001 gm/l. It is seen from Table 5 that Ni has been removed to permissible limits. Mn does not have serious effect rather its presence may improve the electrowinning process [15].

It was observed that at lower pH values (<5) the precipitate started dissolving and at higher values (>6) zinc was lost

in the precipitate. A pH of 5.8 was found to be a good compromise value for the precipitation of iron and aluminium. It was also seen that the heating of solution to a temperature of >70, <100° assisted in the coagulation of precipitate for easy filtration. Also heating of the solution promotes the coagulation of silicic acid which would otherwise cause filtering problems [12]. Impurities like Sb and As are removed during roasting to a large extent. Part of the rest alongwith Cu and Pb are removed with iron which is precipitated out as 2Fe(OH)SO₄ or FeO.OH or Fe₂O₃.H₂O [13,14].

TABLE 2a. ROASTING WITHOUT AIRFLOW.

Temperature (°C)	Zn Conversion%			
	15 mins.	30 mins.	60 mins.	90 mins.
550	8.95	9.95	14.37	21.19
600	10.64	30.60	36.49	50.71
650	12.44	38.84	42.36	57.70
700	14.07	42.36	63.03	63.17
750	35.81	44.73	78.77	85.58
800	37.38	49.82	84.56	86.17
850	37.52	71.71	84.89	86.25
900	39.28	75.31	85.05	86.30
925	93.91	97.90	92.12	91.09
950	74.79	← Sintering and fusion →		

TABLE 2b. ROASTING WITH AIRFLOW AT CONSTANT TIME.

Temperature (°C)	Zn Conversion (%)
550	10.13
600	30.60
650	56.49
700	57.79
750	75.33
800	78.62
850	85.56
900	86.57

Time = 30 mins.

TABLE 2c. ROASTING WITH AIRFLOW AT CONSTANT TEMPERATURE.

Time (mins.)	Zn Conversion (%)
15	52.03
30	75.33
45	93.51
60	97.01

Temperature = 750°.

TABLE 3a. EFFECT OF ACID CONCENTRATION ON EXTRACTION OF ZINC.

H ₂ SO ₄ (gm/l)	Zn % leached
20.50	36.50
30.00	61.44
40.50	87.12
48.00	97.90
50.50	97.90

Liquid to solid ratio = 13.75, time = 1 hr.

TABLE 3b. EFFECT OF LIQUID TO SOLID RATIO ON EXTRACTION OF ZINC.

Liquid to solid ratio	Zn % leached
11.25	96.80
12.50	97.79
13.75	97.90
14.00	97.90
15.25	97.90
31.50	97.90

H₂SO₄ (gm/l) = 48.0, time = 1 hr.

TABLE 3c. EFFECT OF TIME ON EXTRACTION OF ZINC.

Time (min.)	Zn % leached
15	97.50
30	97.81
45	97.85
60	97.90
90	97.90
24 hrs	97.90

Liquid to solid ratio = 13.75, H₂SO₄ (gm/l) = 48.0

TABLE 4. CONSUMPTION OF NEUTRALIZING AGENTS.

Neutralizing agent	Consumption (gm/l)	Impurities removed (%)
Calcine	12.50	99.05
Zinc oxide	10.80	99.90
Zinc dross	11.61	99.50
Calcium oxide	10.95	98.50

Coagulation end-point, pH = 5.8.

TABLE 5. CHEMICAL COMPOSITION OF ZINC SULPHATE PURIFIED SOLUTION.

Constituents	gm/l
Zn	50.00
Mn	5.21 x 10 ⁻³
Ni	3.0 x 10 ⁻⁴
Cu, Cd, Pb, Sb	Nil

Conclusion

The experimental results reported in the preceding pages have led us to the conclusion that it is possible to produce purified electrolyte from the zinc sulphide concentrate obtained from a local lead-zinc ore.

It has been shown that when the zinc sulphide concentrate is roasted at 750° in a current of air for a time period of 60 mins, the roasted material contains soluble zinc upto 97.9%. An XRD analysis of the remaining 2.1% unleached material shows the presence of Franklomite (Zn, Fe₂SO₄), having the same formula as zinc ferrite, which is difficult to leach.

The leaching of the roasted concentrate has shown that around 98% of the zinc passes into solution when the roasted mass is leached with 48 gm/l of H₂SO₄ keeping the liquid to solid ratio at 13.75 for a duration of 60 mins. During leaching, impurities such as Pb, Sb, Cu, As and Fe also report in the leach solution. Their quantities depend upon the roasting conditions and the presence of the various mineral species in the original concentrate. It is, however, attempted to remove as much of the impurities in the purification stage as possible.

The leach solution can be purified by the precipitation of iron and aluminium by raising the pH to 5.8. At this pH not only Fe and Al are removed but coagulation of their precipitate by heating between 70° and 100° carries with them major part of the remaining impurities. The purified solution can be subjected to electrolysis.

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the ethanol production of amyloglucosidase by solid substrate fermentation.

Zachwajewicz cerevisiae was used for the ethanol production. The organism was maintained on MYPG - medium (malt-extract 0.2%, yeast-extract 0.3%, peptone 0.3%, glucose 1.0%, agar-agar 2.0%).

Enzyme synthesis and assay. Amyloglucosidase was synthesized by solid substrate fermentation of which data are reported previously [1]. The enzyme assay was carried out by a modified method of Kainuma et al. [8].

Inoculum preparation. Twenty four hours old yeast cells were transferred from the slants to inoculate 50 ml of sterilized MYPG - medium in a 250 ml Erlenmeyer flask and incubated at 30° on a rotary shaker with 120 rpm. The 24 hrs old inoculum was used for ethanol fermentation of raw starch.

For anaerobic cultivation of yeast cells the inoculum was placed under aseptic conditions at 30°, without shaking. Fermentation technique. Twenty grams of raw corn starch (based on reducing value), 120 IU of amyloglucosidase, 50 ml of distilled water and 10 ml of 24 hrs old yeast inoculum were added simultaneously into 250 ml flask. pH of the medium was adjusted to 3.5 with 0.1N H₂SO₄. The fermentation was allowed to proceed at 30±2° with and without shaking.

Samples for the estimation of reducing sugars, pH and ethanol were taken out after 24 hrs. interval.

Analytical methods. Reducing sugars were determined by Somogyi-Nelson method [11] with glucose as standard. Ethanol was measured by the dichromate method of Bernard and Kraybill [12] and pH with a pH meter.

Results and Discussions

Effect of enzyme concentration. Three concentrations of enzyme i.e. 120, 90 and 60 IU were studied for their effect on the hydrolysis and subsequent ethanol fermentation of raw starch (Fig. 1). The maximum quantity of ethanol (4.0% v/v) was produced, after 72 hrs. when 120 IU of enzyme were

Introduction

In the conventional alcoholic fermentation of starch, cooking is first necessary to hydrolyse the starch and to sterilize the broth. This process requires a large amount of heat, which accounts for 30 - 40% of the total energy input. In order to reduce the cost of this processing and cooking extensive research work is being carried out on the production of ethanol from starch materials through a non-cooking system. Raw starch hydrolyzing amyolytic enzymes are being extensively used for this purpose [1-8]. These enzymes are capable of hydrolyzing starch to fermentable sugars, at ambient temperatures. The sugars being subsequently used in the manufacture of ethanol by yeast *Zachwajewicz cerevisiae*.

Ueda et al. [4] reported the use of *Aspergillus niger* and *Aspergillus awamori* for hydrolysis of raw starches. Park and Rivera [9] conducted a comparative study on the alcohol production from various enzymes converted starches without cooking. Yamamoto et al. [10] observed that hydrolysis of Potato tubers was enhanced by the addition of Pectin depolymerase. The present paper describes optimum reaction conditions for the ethanol production from raw starch by simultaneous saccharification and fermentation process. This process combines the unit operations of liquefaction, saccharification, yeast-fermentation, cooking and anaerobic into a single step, thus making the production of ethanol more cheap and economical.

Materials and Methods

Materials. Corn starch was of commercial grade, potatoe yeast extract and malt extract were from Dico Laboratories, England. All other chemicals were of analytical grade. Micro-organisms. A strain of *Aspergillus niger* PCSIR-10 maintained on Potato - dextrose agar medium was used for

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