PREPARATION OF ZINC OXIDE FROM INDIGENOUS BESHAM (FATA AREA) LEAD ZINC ORE

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ABSTRACT: *Zinc oxide also known as zincite has variety of remarkable properties. It was prepared from indigenous Besham (FATA area) lead zinc ore. Representative sample was analyzed after passing through jaw, roll mill for mesh of liberation. Flotation feeds were prepared by subjecting the ore sample to primary and secondary crushing followed by wet grinding. Flotation reagents, frother, collector and pH were used in flotation practice. The rougher concentrate of zinc was obtained which was further subjected to four cleaning operations to obtain final concentrate containing 60% zinc content. The complete analysis of concentrate was performed. ZnS concentrate was leached with nitric acid, resulting in the formation of zinc nitrate. The solution was filtered out and sodium carbonate was added with constant stirring to precipitate zinc carbonate. Dried zinc carbonate was heated in furnace at 800-850^oC. The optimum parameters were determined after a series of trials. The purity of zinc oxide was 94-96% and the grade was commercial.*

Keywords: Indigenous, Preparation, zinc oxide, ore

1. INTRODUCTION

Zinc oxide is a chemical compound with formula ZnO. It occurs as white hexagonal crystals or a white powder commonly known as zinc white which is used as a pigment in paints. It is nearly insoluble in water but soluble in acids or alkalis. Chinese white is a special grade of zinc white and used in artists' pigments. Zinc oxide and stearic acid are important ingredients in the commercial manufacture of rubber goods. Zinc oxide is valuable and growth-oriented product both for direct application and production of other zinc compounds. Two main processes for producing zinc oxide are direct and indirect methods. In the direct or American method, zinc ore is heated in air with coke or anthracite, and the resulting zinc vapors are subjected to the controlled oxidation. In the indirect or French process the zinc vapors to be oxidized are obtained by boiling zinc.

Zinc ores are widely distributed throughout the world, although more than 40 percent of the world's output originates in North America and Australia. Some deposits of lead-zinc ore were reported from Duddar, Basham, and Azad Kashmir. Lead and zinc ores were present in nature in the form of sulphides, Galena and sphalerite mainly.

P.C.S.I.R reported in 1978 that a number of lead-zinc occurrences had been identified in Lasbela and Khuzdar districts. Three of these occurred at Duddar, Gunga and Surmai had been evaluated by the Geological Survey of Pakistan [1]. Butter B.S. explained the common zinc-containing minerals are the zinc sulfide known as zinc blende or sphalerite, a ferrous form of zinc blend known as marmatite [(ZnFe)S], and a zinc carbonate known as calamine or smithsonite ($ZnCO_3$) [2]. Hydrometallurgical process was introduced by Nguyen K. D. for the manufacture of zinc oxide from wasted zinc sulfide concentrate. The process provided roasted zinc sulfide (ZnS) concentrate [3]. In 1989, Shuomingshu prepared high purity zinc oxide by melting and vaporizing Zn-containing ore powders in rotary Kiln equipment to separate Zn from other metals. The purity of ZnO obtained was >99.7% [4]. Gongkai manufactured high purity zinc oxide by zinc containing raw material. The material was crushed, leached with aqueous NH_3 and $(NH_4)_2CO_3$ and filtered. The impurity free filtrate was heated at 80 – 100^oC, then basic $ZnCO_3$ was sintered at 900^oC to obtain ZnO and the gaseous NH_3 and CO_3 were adsorbed and recovered [5]. Faming, Z. and Gongkai (1994) prepared pure active ZnO (97.5%) from direct decomposition of $ZnSO_4$ with H_2SO_4 [6]. Kitakaname prepared in 1995 an active ZnO from zinc ore by a series of steps such as lixiviating, purifying, hydrolyzing, drying, calcining and ammonium chloride as a leaching agent instead of currently used H_2SO_4. Optimum process conditions and factors affecting the results were obtained; temperature of leaching was 60°C, and time two hours. Zinc content of the solution was 15g/L with more than 96% hydrolyzed ratio [7]. Preparation of ZnO and red lead from low grade Pb-Zn ore was studied by Liu, 1997 [8]. Zhong in 1998 prepared an activated zinc oxide from Zn ore by acid leaching, purifying and calcining process. The effect of acid leaching temperature and pH value on leaching rate of Zn was studied. Fe impurity in $ZnSO_4$ solution was removed by oxidizing with $KMnO_4$. The high purity $ZnCO_3$ was calcined to obtain activated ZnO. [9]

The manufacturing technology of activated zinc oxide through leaching from lead zinc oxide mineral by H_2SO_4, purifying of leaching liquor, synthesizing basic carbonate, dyeing and calcining was studied by Okada in 2000 [10]. Huaxue in 2000 treated Ore from different mining spot individually based on their characteristics and the products were high quality lead concentrates, high quality zinc concentrate and bulk concentrates lead and zinc [11]. Wang and Wentiang manufactured high purity zinc oxide by dissolving high purity metal zinc in acid mixed sodium carbonate or sodium bicarbonate with the acidic solution. High purity zinc oxide was manufactured by using a simple process. Zinc oxide was used in the manufacture of light amplifier [12]. Zinc from low-grade zinc oxide ores was recovered by solvent extraction [13].

In present work Zinc oxide was prepared from indigenous Besham (FATA area) lead zinc ore.

2. MATERIAL AND METHODS

2.1 Preparation of Head Sample of Lead-Zinc Ore

The head sample of the ore was prepared by crushing the lumps of ore in the size range 4-12 inches in a jaw crusher. The product of the jaw crusher was secondary crushed in a rolls crusher to a size of 4 mesh. The roll's product was subjected to conning and quartering. The head sample was analyzed for further processing work.

2.2 Flotation Sequence

Basham lead-zinc ore was a complex ore having Galena, Pyrite, along with Sphalerite as major minerals. Galena was removed prior to the flotation of Sphalerite. Galena was floated at pH 8.5. After the removal of Galena, Sphalerite was activated with copper sulphate and was floated using potassium amyl xanthate as collector. Floatation of Sphalerite was carried out at pH 11-12.

2.3 Preparation of Zinc Oxide

Raw material utilized was Zinc Concentrate (60%) ZnS, Nitric Acid and Soda Ash.

2.4 Reaction of ZnS & HNO_3

4-6 mL of nitric acid was added in grinded zinc sulfide concentrate and diluted to 100 mL at 80-90°C along with constant stirring. The reaction was completed in one hour at pH of the solution 5 - 5.5 .The solution was filtered out.

$$ZnS + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 3S + 2NO + 4H_2O$$

2.5 Reaction of $Zn(NO_3)_2$ & Na_2CO_3

3-4 grams of 15% sodium carbonate was added into the filtrate to precipitate zinc carbonate. The precipitates were dried at 110-120°C to obtain zinc carbonate.

$$Zn(NO_3)_2 + Na_2CO_3 \longrightarrow ZnCO_3 + 2NaNO_3$$

2.6 Decomposition of $ZnCO_3$

Zinc carbonate produced was then heated at 800-850°C in a muffle furnace till the effervescence ceased on the addition of hydrochloric acid solution to obtain the final product ZnO.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

The developed zinc oxide was evaluated to find out its percentage purity, moisture, total zinc content. Trace elements such as Fe, Pb, Na were also detected using the same procedures as described in the analysis of head sample of ore.

3. RESULTS AND DISCUSSION

3.1 Reserves of Lead Zinc Ore

The two significant reserves are located near Basham in FATA and Khuzdar in Balochistan. In Pakistan lead-zinc based chemicals are produced on a very limited scale. The only source of zinc in Pakistan for the production of zinc based chemicals is sphalerite. Basham lead zinc ore was simple in composition and easy to upgrade.

3.2 Chemical Analysis of Head Sample

Gravimetric and titrimetric methods were used for the determination of different constituents in head sample of ore. The sample was ground in a pulverizer and the different constituents were evaluated. The chemical composition of head sample has been shown in the Table 1 as well as Figure 1.

3.3 Chemical Evaluation of Zinc-Concentrate

The grade of zinc concentrate was determined through its chemical evaluation, Zn, Pb, Fe, Al, S and trace elements such as Mn, Cd, Cu were detected. The chemical composition of head sample has been shown in the Table 1 as well as Figure 2.

3.4 pH

pH plays an important role in flotation as well as in leaching the concentrate. pH of the leaching concentrate was adjusted at 5 – 5.5 by adding nitric acid. By adding more acid there was no precipitation and below pH = 5 reaction was very slow.

It was seen that under similar conditions of leaching, the percentage of zinc in the leach solution increased with increasing nitric acid concentration. At pH = 5.5, the concentration of zinc in leach solution reaches 97.90% after which it became constant.

3.5 Effect of the liquid to solid ratio on the leaching of concentrate

The effect of the liquid to solid ratio on the leaching of concentrate was studied in which at a liquid to solid ratio of 2:1 the zinc leached was 97.79% and at 10.0 the zinc leached was slightly higher after which it became constant. After 60 minutes the percentages of zinc leached become constant.

3.6 Effect of Temperature

Zinc carbonate was precipitated out at 110 - 120°C after that precipitation became constant. At higher temperature precipitates started to dissolve in the solution. Cracking of zinc carbonate was done at 800 - 850°C.

Table – 1: Chemical Composition of minerals in the head sample and zinc concentrate

Minerals	Head Sample (%)	Zinc Concentrate (%)
SiO_2	38.47	9.34
Al_2O_3	ND	5.82
CaO	9.52	ND
Cu	0.11	ND
Fe_2O_3	ND	19.85
K_2O	0.87	ND
Moisture	0.52	0.52
Na_2O	1.01	ND
PbO	2.47	0.3
R_2O_3	26.05	ND
S	12	ND
ZnO	3.35	61.69

ND: Not Determined

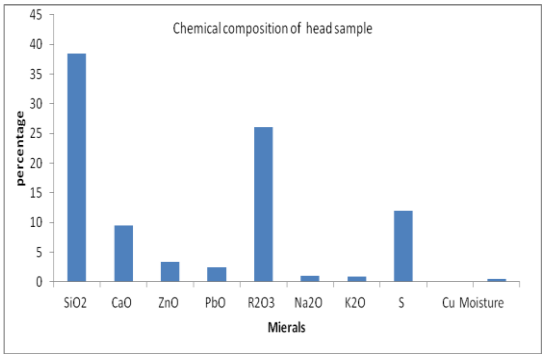

Figure – 1: Chemical composition of Head Sample

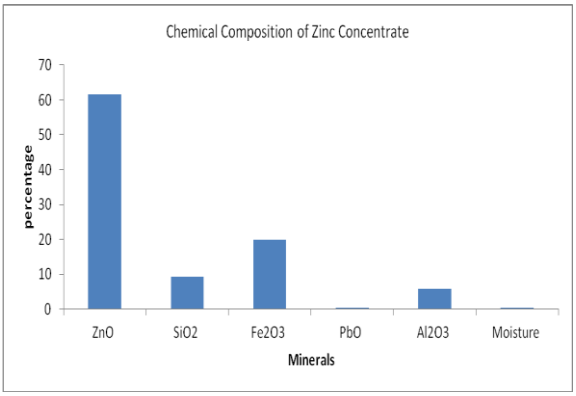

Figure – 2: Chemical composition of zinc concentrate

4. CONCLUSION

An attempt was made to produce a zinc-based chemical zinc oxide (ZnO) by utilizing the ore as a raw material. Zinc concentrate, after flotation contained 50 - 60% zinc, and 30% sulphur, the principal mineral was sphalerite (ZnS). The roasting of zinc sulfide was quite harmful due to the liberation of SO_2 which constitutes a health hazard for the surrounding areas. This method for the production of zinc oxide was based on the chemical process because good anthracite coal is not available indigenously and good quality sphalerite is not found in appreciable quantity within the country. Zinc sulfide was leached with nitric acid solution resulting in the formation of zinc nitrate. The insoluble matter was removed by filtration in the first stage along with the unreacted mass and elemental sulfur. Zinc nitrate was then converted into zinc carbonate by treating with sodium carbonate after the removal of iron. The optimum pH for the precipitation of zinc carbonate was found to be 8. The zinc carbonate was then ignited to obtain 96% pure zinc oxide with 80% recovery.

5. REFERENCES

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