HYDROMETALLURGICAL TREATMENT OF NON-SULFIDE ZINC ORE FOR PRECIPITATION OF ZINC OXIDE NANOPARTICLES

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Abstract: Acid leaching of Egyptian zinc ore from the Um Gheig area was carried out with sulfuric acid. This study determines the optimum conditions for dissolution of non-sulfide zinc ore. The optimum conditions are 25% -74μm particle size, 45 °C temperature, 2 h leaching time, 1.1 stoichiometric molar ratio of H_2SO_4 to Zn, 1:3 solid/liquid ratio. The maximum filtration rate is 1.6 Mg Zn·m^{-2}·day^{-1}at pressure difference of 0.80 bar. The zinc recovery is about 90%. As the zinc ore contains zinc silicate, some additives were tested to enhance filtration and prevent formation of silica gel. To increase the added value of the product, zinc oxide was precipitated by a co-precipitation method in a nanosize powder with average particle size ~ 20 nm. Photocatalytic degradation of methylene blue dye under UV light using ZnO nanopowders produced at different conditions was investigated. Photocatalytic efficiency with methylene blue (MB) concentration was reduced as much as 85% in 240 min with the produced nanoparticles.

Keywords: zinc ore, sulfuric acid leaching, filtration rate, zinc sulfate, zinc oxide nanoparticles, MB photocatalytic degradation

Introduction

The Um Gheig area is a part of the coastal plain of the Red Sea Coast of Egypt. It lies 38 km south of the city of Quesier. The area can be reached by the Quesier-Marsa Alam asphalt road. Um Gheig ore is nonsulfide Zn (Pb) about two teragrams in capacity deposit with an average grade of 10% Zn and 2% Pb. The zinc ore of Um Gheig is called "calamines". It consists of a mixture of zinc carbonates (smithsonite, hydrozincite) and zinc silicates (hemimorphite) (Farag et al., 2012). The carbonates (smithsonite and hydrozincite) and the silicates (hemimorphite, willemite) as well as Zn smectite have an economic importance. The economic value of zinc nonsulfide ores is thus dependent not only on the geologic setting of deposit but also on the

specific characteristics of the mineralogical association and the nature of the gangue minerals (De Wet et al., 2008; Woollett, 2005; Farag et al., 2012). Zinc extraction is performed mainly by direct acid leaching as magnesite, dolomite ores (hydrometallurgical route) in sulfuric acid or alkaline solution (Abdel-Aal et al., 1994, 1995, 1996, 2000; Ibrahim et al., 1995; Abdel-Aal and Rashad, 1997; Hongsheng et al., 2010; Licun-Xiong et al., 2010). The amount of zinc extraction in sulfuric acid solution is high in comparison with other methods and the concentration of silica and other undesirable elements are low. It was observed that the dissolution of zinc ores was diffusion controlled and that the dissolution of zinc silicates was chemically controlled during the acid leaching. If the dissolved silica is treated incorrectly, it will turn to gel, causing a problem in filtration. There are a variety of processes to overcome the filtration difficulty such as quick leaching (Abdel-Aal and Shoukry,1997), use of flocculants (Perry, 1966; Dufresne, 1976; Kumar et al., 1986; Bodas, 1996; Corriou et al., 1988; Huaa et al., 2002), microwave radiation leaching (Sciacca, 1963), hydrothermal leaching (Wood et al., 1977) and controlling the amounts of water (Dufresne, 1976).

It is worth mentioning that zinc oxide nanoparticles of different applications can be synthesized from zinc acetate salt via hydrothermal technique (Ismail et al., 2005).

In the present work, Egyptian zinc ore is evaluated, beneficiated and leached with sulfuric acid. The difficulty of filtration was overcame by making the slurry sufficiently stable under the acidic leach conditions (pH about 2) and finally the zinc sulfate solution was used for precipitating zinc oxide nanoparticles by co precipitation method which relatively popular since it is easier, low-cost, environmentally friendly, large-scale production, low-temperature process and no catalyst is required (Nouneh et al., 2015).

Experimental

A representative sample from Um Gheig mine, Egypt, was subjected to crushing and grinding by a jaw crusher. The sample was separated from their gangues by several beneficiation techniques such as shaking table tests and Falcon gravity concentrator (Farag et al., 2012).

A desired amount of zinc ore was added gradually into agitated sulfuric acid solution in reactor of 1 dm^3 capacity. The slurry pH was kept at 2 to prevent silica polymerization and improve filterability. The slurry was filtered from silica. The clear solution was chemically analyzed. Filtration times were recorded to calculate the filtration rate.

A desired amount of zinc sulfate solution was mixed with NH_4HCO_3 solution while stirring and the reaction mixture was kept at 50 ºC. Diethyl amine was used as a stabilizer to attain the desired pH value of 11. A slurry of zinc basic carbonate in the form of white precipitate was obtained. Then, it was filtered, washed with deionized water for several times and dried at 60 ºC for 24 h.

Results and discussion

Characterization of zinc ore

Farag et al. (2012) presented the X-ray diffraction (XRD) and chemical analysis which were used to determine the main components of the non-sulfide zinc minerals and their associated gangue minerals. The smithsonite is the major non-sulfide zinc mineral where it represents about 50.7% by weight, whereas hydrozincite and hemimorphite represent ~18.8% and 14.8% respectively. On the other hand, calcite (15.8% in weight) is the major gangue mineral with minor amounts of goethite (2.8%). Liberation study indicated that high degree of mineral liberation (> 90%) can be attained at 0.106 mm in size, where individual component are distinctly separated. The experimental beneficiation techniques involve crushing, grinding, and classification to prepare a feed suitable for the separation process. Gravity separation process using "shaking table" was applied to separate the zinc bearing minerals from their associated gangues. Shaking table technique is applied on the feed size of -0.125 +0.080 mm size fractions. At such optimum conditions, a maximum operational recovery and grade of 93.8% and 62.2% ZnO respectively are obtained. On the other hand, Falcon technique was applied for treatment of fines below 0.080 mm. At such optimum conditions, maximum operational recovery and grade of 76.6% and 54.85% ZnO respectively are obtained.

The samples obtained by the two gravity separation techniques was mixed well and characterized by using x-ray diffraction, sieve analyses and chemical analysis. Figure 1 and Table 1 show the X-ray diffraction of the concentrate sample. X-ray diffraction analysis indicates that the concentrate contains hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$], willemite [$Zn_2SiO_4$] and smithsonite [$ZnCO_3$] are the major minerals, calcite [$CaCO_3$], goethite [$FeO(OH)$] and enstatite [$MgSiO_3$] are the minor minerals. Particle size distribution of the concentrate sample is given in Table 2.
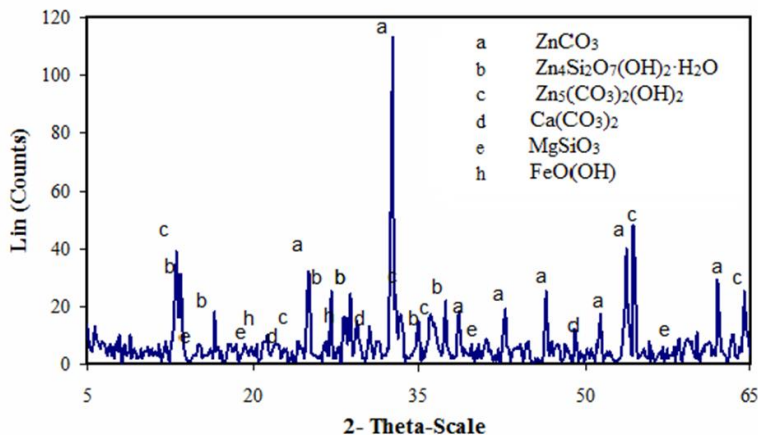

Fig. 1. X-ray diffraction pattern of Egyptian zinc concentrate

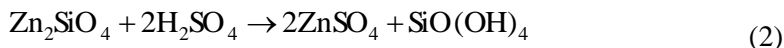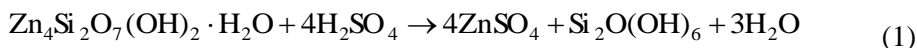Table 1. Chemical analysis of the tested zinc concentrate

Constituent	wt, %
ZnO	56.1
CaO	9.52
Fe_2O_3	1.11
MgO	0.33
SiO_2	18.0
L.O.I., 900 ºC	12.0
Others	2.94

Table 2. Particle size distribution of the concentrate sample

Particle size, mesh	wt, %
+100	0
-100 +120	3.18
-120 +150	59.47
-150 +170	7.88
-170, +200	4.05
-200, +230	9.28
-230, +270	0.40
-270	15.74

Leaching of zinc ore

The leaching experiments were carried out according to the following equations:

$$Zn_4Si_2O_7(OH)_2 \cdot H_2O + 4H_2SO_4 \rightarrow 4ZnSO_4 + Si_2O(OH)_6 + 3H_2O \tag{1}$$

$$Zn_2SiO_4 + 2H_2SO_4 \rightarrow 2ZnSO_4 + SiO(OH)_4 \tag{2}$$

$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + CO_2 + H_2O. \tag{3}$$

Based on the industrial scale limits given in Table 3, the conditions used for leaching are liquid: solid ratio 3:1 g·cm^{-3}, temperature 45 ºC (ambient temperature), reaction time 2 h, particle size 25% -200 mesh. The H_2SO_4 stoichiometry was studied by changing this ratio from 1.0 to 1.2 (H_2SO_4 to total Zn, Ca and Mg) under the optimum conditions. The results are given in Table 4. The increase in H_2SO_4 stoichiometry leads to increase of zinc recovery which reach to 90% at 1.1 but there no significant increase was observed at 1.2 (zinc recovery 90.9%).

Table 3. Optimum conditions of leaching process

Optimum conditions and results	Value	
	Umm Geig Zn Concentrate	Industrial Limits
Particle size, % -200 mesh	25	9-100
Temperature, °C	45	40-50
Reaction time, h	2.0	2.0 -4.5

Table 4. Effect of sulfuric acid stoichiometry on Zn recovery

H_2SO_4 Stoichiometry	Zinc Recovery, %
1.0	52.6
1.1	90.0
1.2	90.9

Filtration

The slurry obtained after leaching, was filtered and washed three times. The filtration and washing conditions (Abdel-Aal, 1997) are given in Table 5.

Table 5. Conditions of filtration

Type of filter	Buchner-type funnel; effective filter area: 43 cm^2
Filter cloth	Polypropylene; aperture of filter cloth: 200 mesh

Effect of pressure difference

Different filtration operations were carried out under various pressure difference ranging from 0.66 to 0.80 bar as reported by Abdel-Aal (1997). The results are given in Table 6. The optimum pressure difference achieved is 0.80 bar which gives the highest filtration rate (1.17 Mg Zn·m^{-2}·day^{-1}). Higher pressure difference (>0.80 bar) results in boiling of the filtrate.

Table 6. Effect of pressure difference on filtration rate

Pressure Difference	Filtration Rate		
bar or Pa·10^{-5}	m^3·m^{-2}·h^{-1}	Mg Zn·m^{-2}·day^{-1}	dry residue, kg·m^{-2}·h^{-1}
0.66	0.37	0.65	57.7
0.69	0.44	0.76	67.1
0.71	0.50	0.87	76.8
0.74	0.55	0.97	85.3
0.77	0.62	1.08	94.7
0.80	0.67	1.17	102.9

Effect of aluminum powder addition

Different filtration operations were carried out under the addition of different amounts of aluminum powder (0.0–2.0% related to zinc ore). Aluminum powder reacts with free sulfuric acid to form aluminum sulfate (Abdel-Aal, 1997). Al^{3+} ions decrease the solubility of silica, which are adsorbed on the colloidal silica (Corriou et al., 1988; Perry, 1966). The results are given in Table 7 and reveal that with increasing aluminum powder addition; the filtration rate is increased reaching to 0.94 m^3·m^{-2}·h^{-1} at 0.3% addition of aluminum powder related to ore. Further increase in aluminum powder leads to insignificant increase in filtration rate.

Table 7. Effect of aluminum powder addition on filtration rate
Pressure difference: 0.80 bar

Filtration Rate	Al Powder to Ore, %							
	0.0	0.1	0.2	0.3	0.5	1.0	1.5	2.0
$m^3 \cdot m^{-2} \cdot h^{-1}$	0.25	0.67	0.86	0.95	0.95	0.99	0.96	0.95
megagram $Zn \cdot m^{-2} \cdot day^{-1}$	0.43	1.17	1.50	1.63	1.71	1.66	1.66	1.63
acid insoluble cake, $kg \cdot m^{-2} \cdot h^{-1}$	39	103	132	144	144	151	145	144

Quality of product and residue

The produced zinc sulfate solution was chemically analyzed and the residue was analyzed using EDAX. The results are given in Table 8 and Figure 2.

Table 8. Chemical analysis of $ZnSO_4$ solution and residue

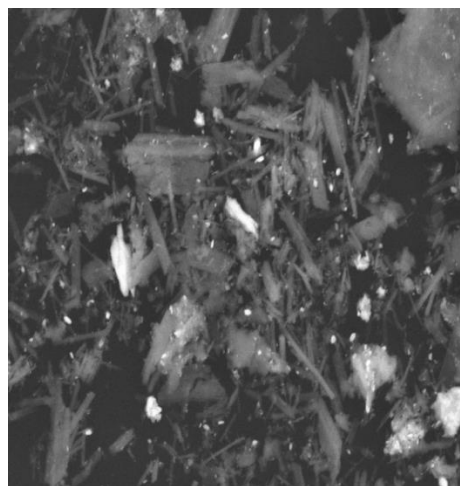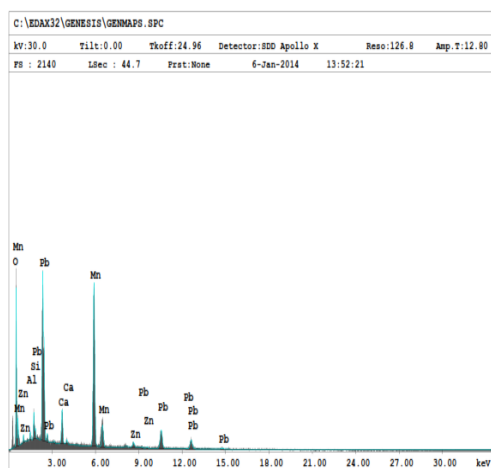| Constituent	$ZnSO_4$, %	Residue, %
Zn	10.90	1.46
Ca	0.439	3.50
Fe	0.01	0.55
Al	0.01	1.18

Fig. 2. SEM and EDX of the residue of the leaching process

Precipitation of zinc oxide nanoparticles

The powder obtained after precipitation and calcination was characterized by using transmission electron microscope (TEM) to determine the morphology and size of nanoparticles. The results are given in Figure 3. These results show that the precipitated and calcinated zinc oxide powder has a hexagonal structure with average particle size of ~20 nm. The produced powder was tested for the photocatalytic

degradation of methylene blue (MB) which occurs on the surface of photocatalyst. The time-dependence of UV–Vis spectra of MB during the irradiation under UV light with ZnO nanoparticles are shown in Figure 4. It can be observed that the maximum absorbance of 664 nm decreases gradually according to the photocatalysts after 240 min. The photocatalytic degradation of MB was carried out using the prepared photocatalysts ZnO nanoparticles molar ratio (Figure 5).
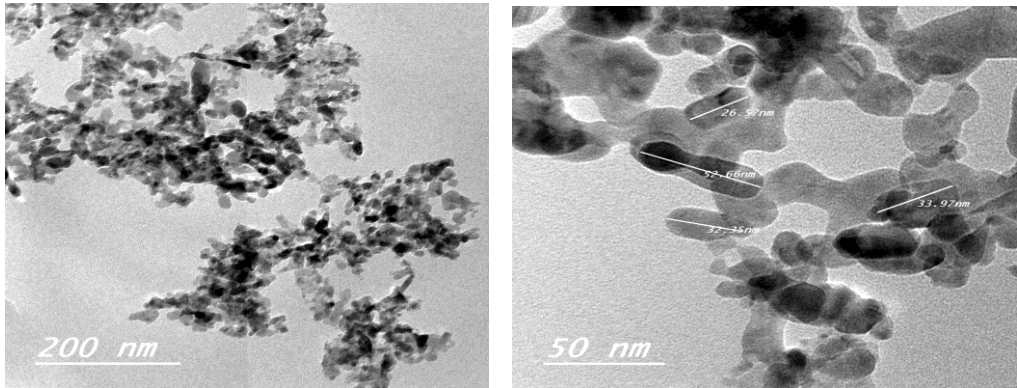

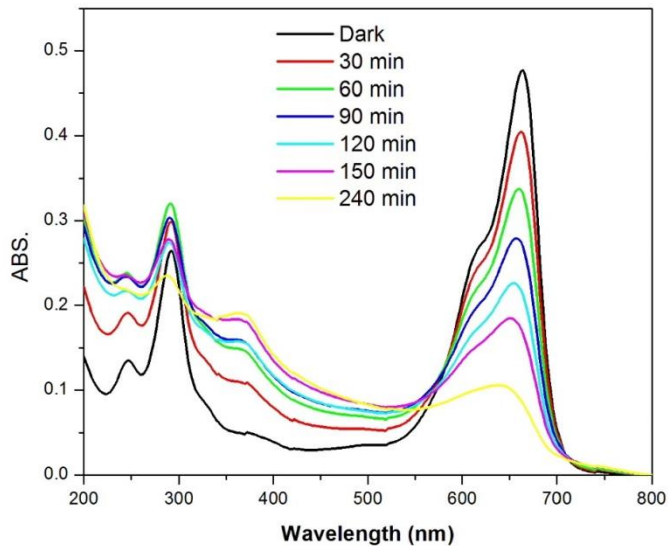Fig. 3. HR-TEM of zinc oxide nanoparticles

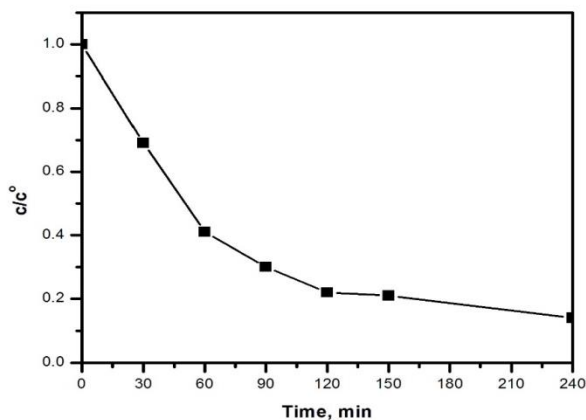Fig. 4. The absorbance spectra changes of MB solution in ZnO sample

Fig. 5. Photocatalytic de-colorization kinetics of MB using ZnO sample

Conclusions

The Um Gheig nonsulfide deposit in the Red Sea Coast of Egypt consists mainly of smithsonite, hydrozincite and hemimorphite. Calcite and goethite are the main gangues minerals. The experimental beneficiation techniques involve crushing, grinding and classification to prepare a feed suitable for the separation process using shaking table and falcon. The results showed that a second concentrate with 54.85% ZnO and operational recovery 76.6% was obtained. The results indicated that shaking table technique is efficient for treatment of course fractions while the Falcon technique is ideal for treatment of fine feed samples. Zinc concentrate was leached with sulfuric acid and a recovery of 90% was achieved under the following conditions: particle size 100 % -100 mesh that contains about 25% -200 mesh; liquid/solid ratio 3:1 $g \cdot cm^{-3}$; temperature 45 °C; reaction time 2 h; H_2SO_4 stoichiometry 1.1. The obtained slurry was filtered. The achieved filtration rate was 1.63 megagram of zinc $\cdot m^{-2} \cdot day^{-1}$ at 0.80 bar pressure difference with 0.3% aluminum powder addition. ZnO nanoparticles were synthesized by using co-precipitation method with average particle size ~20 nm and tested for the photocatalytic degradation of MB dye.

References

ABDEL-AAL E.A., IBRAHIM I.A., RASHAD M.M., ISMAIL A.K., 1994, *Hydrometallurgical processing of Egyptian magnesite ore for production of magnesium sulfate*, Physicochemical Problems of Mineral Processing Journal, 28, 165–175.

ABDEL-AAL E.A., 1995, *Possibility of utilizing Egyptian dolomite ores for production of magnesium oxide by acid leaching*, Physicochemical Problems of Mineral Processing Journal, 29, 55–65.

ABDEL-AAL E.A., IBRAHIM I.A., RASHAD M.M., ISMAIL A.K., 1996, *Hydrometallurgical processing of Egyptian magnesite ore*, Physicochemical Problems of Mineral Processing Journal, 30, 207–216.

ABDEL-AAL E.A., RASHAD M.M. 1997, *Hydrometallurgical processing of Egyptian magnesite ore with nitric acid*, Physicochemical Problems of Mineral Processing Journal, 31, 7–17.

ABDEL-AAL E.A., SHOUKRY Z.E. 1997, *Application of quick leaching method to an Egyptian zinc silicate ore*, Transactions-Institution of mining and metallurgy. Section C. Mineral processing & extractive metallurgy, 106.

ABDEL-AAL E.A., 1997, *Direct leaching of oxidized zinc ore*, The Institution of Engineers India, Journal-MM 78, 25–29.

ABDEL-AAL E.A., 2000, *Kinetics of sulfuric acid leaching of low-grade zinc silicate ore*, Hydrometallurgy 55, 247–254.

BODAS M.G., 1996, *Hydrometallurgical treatment of zinc silicate ore from Thailand*, Hydrometallurgy 40, 37−49.

CORRIOU, J.P., GELY, R., VIERS, P., 1988, *Thermodynamic and kinetic study of the pressure leaching of zinc sulfide in aqueous sulfuric acid*, Hydrometallurgy, 21, 85–102.

DE WET K., SINGLETON J.D., 2008, *Development of a viable process for the recovery of zinc from oxide ores*. The Southern African Institute of Mining and Metallurgy, Proceedings of LEAD and ZINC '08, Durban, 177–192.

DUFRESNE R., 1976, *Quick leach of siliceous zinc ores*, JOM 28, 8–12.

FARAG M.Z., ABDEL-KHALEK N.A., HASSAN M.S., El AREF M.M., El MANAWI A.W., 2012, *Upgrading of Egyptian nonsulfide zinc ore by gravity separation techniques*, Journal of Metallurgical Engineering, 1, 6–13.

HONGSHENG X., CHANG W., CUNXIONG L., GANG F., ZHIGAN D., MINTING L., XINGBIN L., 2010, *Sulfuric acid leaching of zinc silicate ore under pressure*, Hydrometallurgy 105, 186–190.

HUAA Y., LINA Z., YAN Z., 2002, *Application of microwave irradiation to quick leach of zinc silicate ore*, Minerals Engineering 15, 451–456.

IBRAHIM I.A., ABDEL-AAL E.A., El-SAFTY N.A., ISMAIL A.K., 1995, *Hydrometallurgical beneficiation of manganese ore from Sinai*, Physicochemical Problems of Mineral Processing Journal, 29, 73–79.

ISMAIL A.A., EL-MIDANY A., ABDEL-AAL E.A., EL-SHALL H., 2005, *Application of statistical design to optimize the preparation of ZnO nanoparticles via hydrothermal technique*, Materials Letters 59, 1924–1928.

KUMAR R., BISWAS A.K., 1986, *Zinc recovery from Zawar ancient siliceous slag*, Hydrometallurgy 15, 267−280.

LICUN-X., XU H., DENG Z., LI X., LI M., WEI C., 2010, *Pressure leaching of zinc silicate ore in sulfuric acid medium*. Transactions of Nonferrous Metals Society of China, 20, 918–923.

NOUNEH K., AJJAMMOURI T., LAGHFOUR Z., MAAROUFI A., ABD-LEFDIL M., CHAUMONT D., SEKAT Z., 2015, *Structural and spectral properties of ZnO nanorods by wet chemical method for hybrid solar cells applications*, Materials Letters 139, 26–30.

PERRY W., 1966, *Refining zinc silicate ore by special leaching technique*, Chemical Engineering, 73, 182−184.

SCIACCA F., 1963, Brazilian patent 65, 790.

WOOD J.T., KEM P.L., ASHDOWN N.C., 1977, *Electrolytic recovery of zinc from oxidized ores*, Journal of Metals, 29, 7–11.

WOOLLETT, A., 2005, *The processing of non-sulfide zinc deposits*. In: Boni, M., Gilg, H.A. (Eds.), *European Science Foundation (ESF) Workshop on Nonsulfide Zn–Pb Deposits*, Iglesias.