

ACID LEACHING OF ZINC FROM ZnO/Al_2O_3 CATALYST

Nadia Alane, Souad Djerad and Lakhdar Tifouti

Department of Chemical Engineering, University of Annaba, B.P. 12 El Hadjar, Annaba
23000, Algeria
s_djerad@hotmail.com

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ABSTRACT

In this study a simple process has been developed for zinc recovery from ZnO/Al_2O_3 catalyst in acidic milieu. The results have shown that a high dissolution efficiency of zinc was achieved with H_2SO_4 (2M) at ambient temperature with a liquid/solid ratio of 10/1 while alumina support was left unaffected. The dissolution of ZnO reached 81% in the first 4 hours. The rate of dissolution increased slowly after that and reached 90% after 24h. Leaching process was found to be controlled by diffusion through a product layer. After separation, alumina with high purity (99,5%) was obtained. Zinc was precipitated in leach liquor by pH-controlled precipitation using sodium hydroxide. The resulting solid was purified and dried at 120°C. Zinc powder in the form of ZnO with 100% purity was produced with recovery efficiency of 72,2%.

Keywords: zinc recovery, acid leaching, separation, alpha alumina, caustic precipitation

INTRODUCTION

Metal residues discarded by industrial processes figure among the most important sources of environmental contaminations. Some of these are recyclable, others are toxic, constituting hazardous wastes. Recycling the valuable part of these wastes instead of landfill depositing is an important issue from an environmental point of view. For this reason many industrial processes have focused research on the development of methods for their recovery from waste materials (Prakash *et al.*, 2000; de Souza *et al.*, 2006; Ruiz *et al.*, 2002; Ullari, 2000; Kim *et al.*, 2006). Furthermore, this conversion also implies economical benefits.

Spent catalysts contribute a significant amount of the solid wastes. The spent catalyst wastes generated especially in the petrochemical industry (Anon, 2000) have become an environmental problem, and it has presented a challenge task for the mineral engineers to recycle and convert these materials to useful products. Several alternative methods for the reuse and utilization as raw materials are available to the industrials to deal with the spent catalyst problem (Chang, 1998).

Zinc, the 25th most abundant element, is widely distributed in nature, making up between 0,0005% and 0,02% of the Earth's crust (Irwin *et al.*, 1997). The estimated world production of zinc is 7,1 million metric tons. Zinc is used in vast variety of products, primarily in the production of brass, noncorrosive alloys, and in galvanization of iron and steel products. The most widely used zinc compounds are the oxide, the sulfide, and the

chloride. The oxide is used as a reinforcer in rubber tires, a white paint pigment, a ceramic glaze, and an opaque base in cosmetics. It is also used in catalysis and as adsorbent evolved in steam reforming process (Chen & Tang, 2007; Kim *et al.*, 1997; Kim *et al.*, 1995; Evgenidou *et al.*, 2007; Srinivasan *et al.*, 2006).

Million tons of zinc wastes are discarded every year without control and poses enormous environmental hazards. Zinc is listed by the Environmental Protection Agency as one of the 129 priority pollutants. In humans, prolonged excessive exposure to zinc can lead to deficiencies in iron and copper, nausea, fever, headache, tiredness, and abdominal pain (Irwin *et al.*, 1997). Therefore, recovering zinc from the industrial wastes which are considered as vast mineral wealth is important in terms of metal recycle and environmental protection.

Among the vast variety of the available methods for metal recovery, hydrometallurgical method can be a viable wet technique. Promising results can be obtained by combining relatively difficult and expensive methods like conventional liquid-liquid extraction, ion exchange, and/or electrochemical separations used for some metals (Kim *et al.*, 2000; Wódzki & Sionkowski, 1999; Gupta *et al.*, 1987).

The literature reports only few works on zinc found in soil resulting from industrial discharges like spent catalysts (Hsu *et al.*, 2005; Dvorak & Jandova, 2005; Leclerc *et al.*, 2002).

In general, the active phase is considered as the most valuable element in the catalyst to be recovered, however the carrier support which is the main body of the catalyst, failed to have a good recovery. The aim of this paper is to recover both components from ZnO/Al₂O₃ catalyst with sulfuric acid and the study of the leaching kinetic. This work investigated the influence of the leaching time on the zinc recovery. The process consisted of five stages: (1) acid leaching at pH=1 with H₂SO₄; (2) liquor/residue separation; (3) support recovery after washing and drying; (4) zinc precipitation in caustic milieu; (5) several successive rinsing steps of the precipitate with distilled water.

EXPERIMENTAL

Materials and Methods

The catalyst was a 5%ZnO/Al₂O₃ (n/n) in fresh form with 68µm particles size. The catalyst was dried at 110°C overnight before the experiments. Qualitative X-ray diffraction analysis (XRD) was performed on powder material using an X'Pert Pro MPD, Philips diffractometer. Diffraction patterns were measured in 2θ-scale using CuKα radiation (λ = 1,5406 Å) at 40 kV and 30 mA with scanning speed of 0,02°/s. Identification of the crystalline phases was done by the Joint Committee for Powder Diffraction Standards (JCPDS) file of the instrument.

The analysis of solid composition was realized by AAS method. Sulfate ions were analyzed with a spectrophotometer UV-Visible Anthelie 5 Secomam using the Beer's law calibration plot at the maximum absorption wavelength of 650 nm. pH measurements of the solutions were performed using HANNA 931401 pH-meter.

In the leaching experiments, sulfuric acid from Organics with a purity of 96,98% and a density of 1,84g/ml was used. Sodium hydroxide from Alfa Aesar with a purity of 99,99% was used as precipitation agent. Distilled water was used for all solution preparation and rinsing.

Dissolution studies were carried out in a (20ml-capacity) glass flask fitted with a seal. H_2SO_4 (2M) with a liquid to solid ratio (l:s) of 10:1 was used. Leaching was tested at the laboratory temperature under reaction conditions which were characterized by a relatively high excess of the acid to eliminate possible effects of the changes in lixiviant composition during individual runs on the rate of leaching. The reaction mixture was left for various selected periods (1, 2, 4, 8, 18 and 24h) in order to study the effect of leaching time on the dissolution process.

Figure 1 shows the flowsheet of the recovery and separation of zinc from the $\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst.

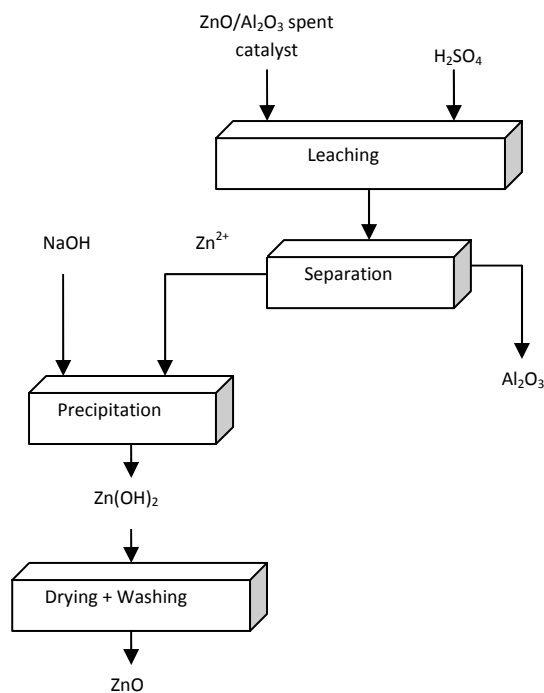
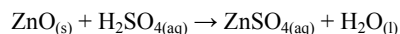


Figure 1. The flowsheet of the recovery and separation of zinc from $\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst.

RESULTS AND DISCUSSION

Leaching experiments

The dissolution reaction of zinc oxide with sulfuric acid can be written as follows:



After the completion of each leaching test, the liquor was separated from insoluble residue by decanting. The residue was washed with distilled water several times until no more SO_4^{2-} ions were detected, dried in oven at 110°C overnight, weighted, and preserved to await analysis. The wash solutions were added to main liquor. The experiments were run duplicates, and the mean values were considered.

The dissolved zinc into the aqueous phase was analyzed by chelatometric titration in order to subsequently determine the percentage of the zinc leached. The dried leaching residues and original sample were analyzed by XRD. The leaching yields were calculated with the aid of analysis and weight of the original and residue samples.

In the original sample, corundum was identified as a major component by X-ray diffraction analysis (Fig. 2) whereas ZnO (Zincite) was determined as a minor component.

In Figure 3 is plotted the variation of the dissolved ZnO as a function of leaching time. It is clear that there are two distinct stages in the ZnO dissolution process, an initial stage of dissolution (up to 4h), during which the dissolution rate increased and attained 81%, and an advanced stage (beyond 4h) during which the dissolution rate decreased rapidly and the curve became almost flat. In fact, the leaching continued very slowly up to 24h, the maximum time used, where it reached 90%. Thus, using high acid concentration and increasing the reaction time do not necessary result in higher dissolution efficiency in this case.

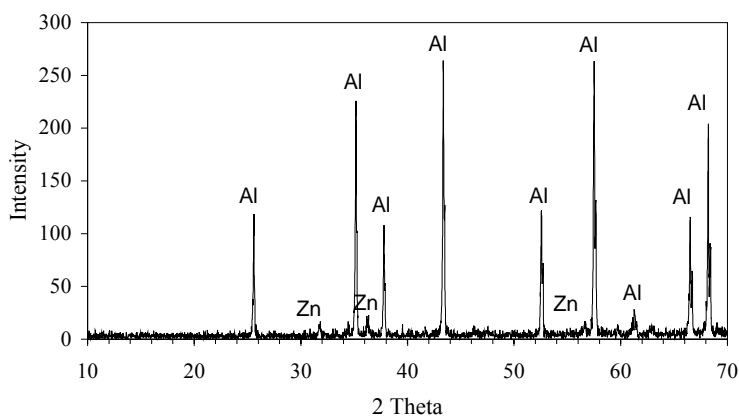


Figure 2. X-ray diffraction pattern of ZnO/Al₂O₃ catalyst.

A DRX analysis was applied on the residue of the catalyst treated for 24h after total removing of sulfate ions by washing with distilled water (Fig. 4). The Figure shows peaks corresponding to alpha alumina, those corresponding to ZnO disappeared. Alumina support was chemically analyzed giving a composition of 99,5% (n/n) for Al_2O_3 and 0,5% (n/n) for ZnO. The absence of ZnO peaks from alumina support was simply due to the detection limit of the XRD method.

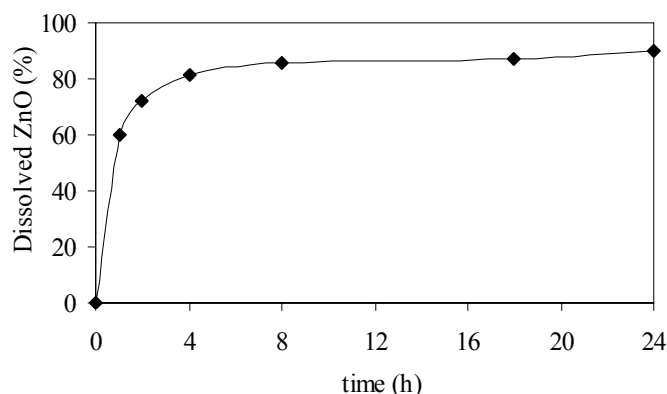


Figure 3. Plot of zinc recovery as a function of leaching time, ambient temp, l:s=10:1, H_2SO_4 (2M).

Furthermore, it can be observed that concentrated acid did not alter alumina support even after 24h of leaching treatment. This was confirmed by analyzing the aluminum ions by atomic absorption spectrometry in the leach liquor of 24h which gave negative result. Alumina exists in many structures. The most stable and common being $\alpha\text{-Al}_2\text{O}_3$ (corundum), in which the oxygen anions are arranged in a hexagonally close-packed lattice within which the aluminum cations occupy octahedral sites. All alumina structures are irreversibly transformed into corundum if annealed at high enough temperatures as demonstrated in literature (O'Della *et al.*, 2007). In this case, leaching alumina was not needed since the separation of the two metal oxides was possible through ZnO dissolution.

The experiment was repeated once more without withdrawing the support for analysis. The residue was dried and weighed. The result indicated that the recovery of the support was accompanied by 1,5% mass loss.

Kinetic study

The rate of a reaction between a solid and a fluid such as the system considered here can be expressed by homogeneous and heterogeneous models (Levenspiel, 1972). In a heterogeneous system, the overall rate expression becomes complicated because of the interaction between physical and chemical processes.

To interpret the results of ZnO dissolution in H_2SO_4 , the kinetic has been assessed on the basis of the shrinking core model in which, the solid reactant is considered to be non-porous

and is initially surrounded by a fluid film through which mass transfer occurs between the solid and the bulk of the fluid. As the reaction proceeds, a layer forms around the unreacted core. According to this model, the following three steps are considered to occur in succession during the dissolution:

- 1- Transport of the reactant through the solution and the product layer to the surface of the solid.
- 2- Reaction on the surface between the reactant and the solid.
- 3- Formation of the solid products on the surface layer of the reaction zone and transport of the soluble products from the interface into the bulk of solution.

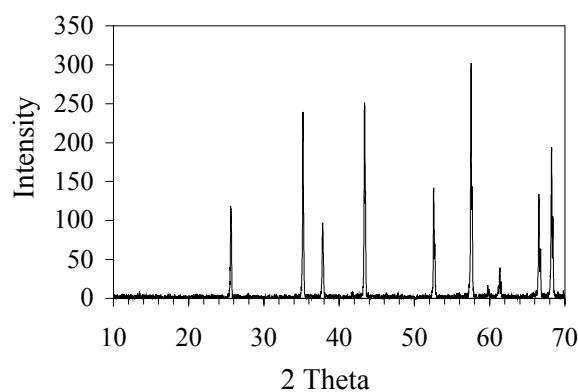


Figure 4. X-ray diffraction pattern of alumina support after ZnO separation and washing.

Thus, the overall leaching process may be controlled by intrinsic chemical reaction or by external mass transfer. The following expressions can be used to describe the dissolution kinetics of the process:

$$\begin{array}{ll}
 1 - (1-x)^{2/3} = k.t & \text{for liquid film diffusion control} \quad (1) \\
 1 - 3(1-x)^{2/3} + 2(1-x) = k.t & \text{for solid product diffusion control} \quad (2) \\
 1 - (1-x)^{1/3} = k.t & \text{for reaction control} \quad (3)
 \end{array}$$

Where “x” is the fractional conversion of ZnO, “t” is the reaction time (h) and “k” the apparent rate constant (h^{-1}).

The rate of the process is controlled by the slowest of these sequential steps.

Applicability of the shrinking core model to the reaction system studied was checked using the experimental data up to 4h as shown in Figure 5. In this Figure, the three expressions $[(1 - (1-x)^{2/3})]$, $(1 - 3(1-x)^{2/3} + 2(1-x))$ and $(1 - (1-x)^{1/3})$ are reported on the y axis as a function of time which is reported on the x axis.

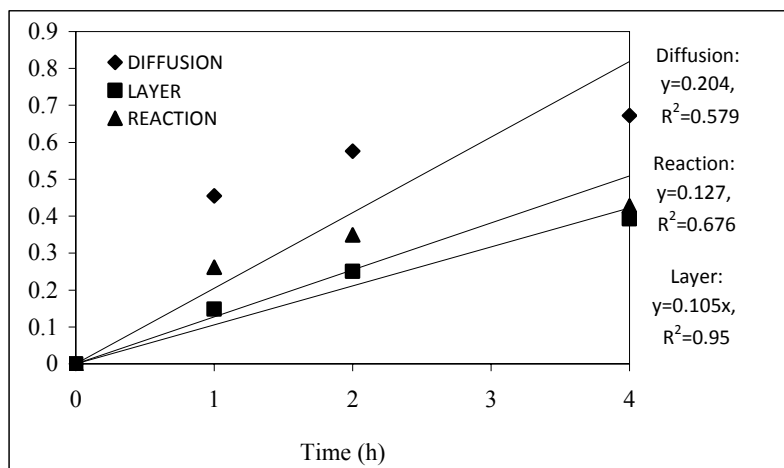


Figure 5. Fit of shrinking particle model to experimental data.

The apparent reaction rate k is then the slope of each line plotted. The fit of all experimental data was tested by calculating the regression coefficients for the three expressions. The results show that experimental data did not fit to the surface reaction and film diffusion controlled heterogeneous rate models. Data fit to the diffusion control through product layer model with a regression coefficient $R^2=0,95$. This statement seems to be evident. In fact, under conditions used in the present work where agitation was absent, the dissolution can be explained as follows: in the beginning of the reaction there is a direct interaction between the surface of the solid and the reaction media giving as result the formation of a barrier formed by Zn^{2+} that obstructs the diffusion of dissolved species and reagents. Consequently, the reactants would have to overcome the resistance of this layer before reaching the surface of the solid and the dissolution process slowed down. After 4h, the leaching process is too low due probably to the thickness of the layer which increased with time that the dissolution of ZnO could be considered as stopped.

Recovery of leached zinc by caustic precipitation

Precipitation experiment was performed on the solution obtained after 24h of leaching time. The experiment was carried out at ambient temperature in a glass beaker of 200ml capacity in which pH electrode was plunged to follow the variation of pH during zinc precipitation with NaOH (0,5M). The extract obtained was precipitated in the form of hydroxide according to the reaction (Marcos, 2001):

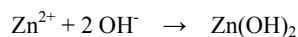
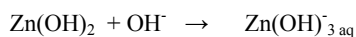


Figure 6 shows the $Zn(OH)_2$ formation as a function of pH of the solution. The initial pH of $ZnSO_4$ solution was 1. A pH of 9.5 was the maximum value at which 100% of Zn^{2+} was deposited. Beyond this value, the precipitate started to dissolve due to the formation of aqueous $Zn(OH)_3$ according to the following reaction (Dutra *et al.*, 2006):



The solution became clear when the pH was higher than 13. The dissolution of zinc in acidic zone and its re-dissolution in alkaline zone were due to its amphoteric behavior.

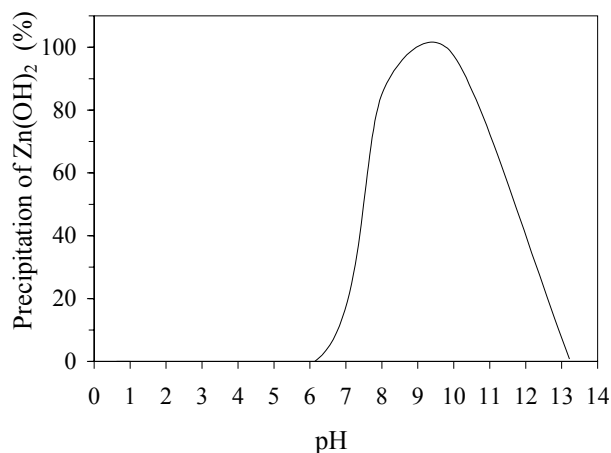
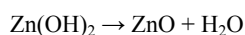


Figure 6. The effect of pH on the zinc precipitation in leached liquor at ambient temperature.

The zinc hydroxide Zn(OH)_2 obtained by precipitation contained Na^+ and SO_4^{2-} resulting from the former operations. These ions are considered as impurities which should be removed to get high quality product of zinc. To separate Zn(OH)_2 from these ions, the sample mixture was first dried overnight in oven at 120°C to transform zinc hydroxide into zinc oxide known to be insoluble in water according to the reaction:



And after that the impurities were separated by washing the obtained solid with distilled water for several times.

The dried product (without any washing) was analyzed by DRX. The obtained spectrum (Fig. 7) showed a very crystalline structure with a multitude of peaks due to the presence of crystallites containing sulfate, sodium and zinc. After that, the washing operations of the solid were applied. It is worth noting that the operations were carried out on unique samples. Indeed, the original residue was divided into equal amounts and each amount has undergone a predetermined number of washing. One gram was used for each washing experiment. At the end of the washings, sulfate ions were analyzed by spectrometry method and the solids after drying were analyzed by XRD. Sodium content in the solutions was not analyzed. This method was applied to avoid the decrease in the SO_4^{2-} content in leachates due to the decrease in the solid amount after it was taken for XRD analysis.

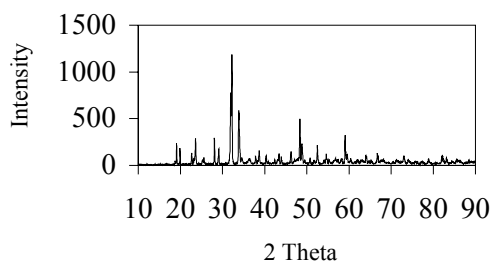


Figure 7. X-ray analysis for ZnO precipitate unwashed and dried at 120°C.

The operation consisted in adding in a beaker 150 ml of distilled water to the weighted solid and stirring magnetically the suspension at 200rpm for 10 minutes. The solid was separated from the liquid phase by centrifugation. The procedure was repeated on the recovered solid until reaching the desired number of washing.

The results show that removing sulfates completely needs 6 washing operations as shown in Figure 8. X-ray diffraction analyses were applied to samples obtained after the first, third and sixth washings, to follow the variation of their structures if any. The results are presented in Figures 9 a-c. Thus, as leaching progressed, some peaks disappeared indicating the dissolution of the crystallites formed by sulfate and sodium.

It should be noted that all X-ray spectra are presented in this paper without any accumulation and that the noise signals observed on some of them are due to the nature of the samples. In fact, in Figure 4, noise signal is very weak which indicates that the sample contains only alumina. On the contrary, Figures 7a and 9 show important noise signals which indicate in reality the formation of different kind of crystallites due to the presence of impurities. The crystallites were difficult to identify because of their complicated form.

At the end of the sixth washing, only structure of pure ZnO (zincite) was left (Fig. 9c). Thus, zinc could be efficiently recovered and separated from the impurities by a simple drying of the solution. Transforming Zn^{2+} to ZnO was possible without the need of calcination.

Once the awaited result was obtained, all steps of the experiment were applied once more on one sample without withdrawing the zinc precipitate for analysis. The aim was to leave intact the zinc amount in order to calculate the percentage of ZnO recovered from the original catalyst. The precipitate was then dried overnight at 110°C and weighed.

Based on 10g of the ZnO/Al_2O_3 treated in this experiment, the mass of ZnO weighed at the end of the experiment was 0,278g. From AAS analysis, the initial mass of ZnO in the catalyst was 0,385g.

Thus, yield of about 72,2% for ZnO with respect to the original zinc content of the catalyst was obtained. From the dissolution data, 90% (n/n) from initial ZnO was leached which should give 0,346g as ZnO at the end of the experiments if no mass loss occurred. This indicates that 17,8% of zinc oxide were lost during the experiments.

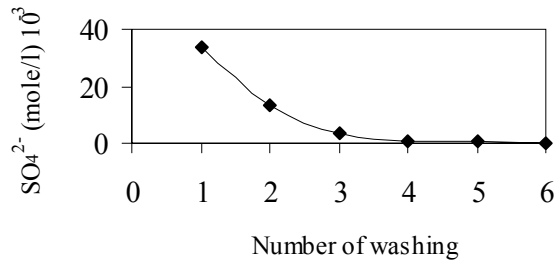


Figure 8. Diminution of the sulfates concentration with washing the ZnO precipitate.

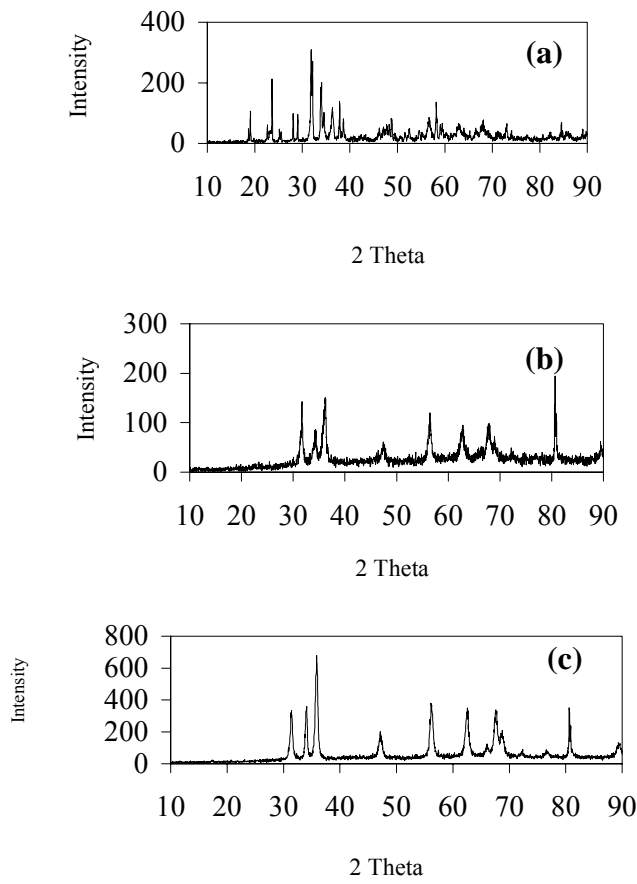


Figure 9. X-ray analysis for ZnO precipitate washed 1 time (a), 3 times (b) and 6 times (c).

CONCLUSION

Metal oxides recovery is possible to safeguard the environmental problems caused by the heavy metal contamination to the soil and high cost incurred for the landfill.

ZnO acid leaching is a slow process since significant dissolution was obtained within time scale of several hours. Kinetic of ZnO dissolution in H₂SO₄ was investigated by using the shrinking core model. It was found that the dissolution was controlled by the diffusion through the solid product layer.

The obtained products have a good potential to be reused as raw materials since they were recovered with 100% purity for ZnO and 99,5% for alumina.

It is evident that precipitation method used for purification of zinc proceeds with zinc loss as it is apparent from the comparison of the composition of the original leach liquor and the amount of the recovered ZnO.

Dissolution of zinc is a slow solid-liquid reaction which depends on several factors. In this paper, the effect of reaction time was studied. This work will be continued. The proposed experiments will be focused on increasing the leaching kinetic at ambient temperature using micro wave and ultrasound methods.

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