

LEACHING OF ZINC OXIDE IN AQUEOUS SULPHURIC ACID SOLUTIONS

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LOUŽENÍ OXIDU ZINEČNATÉHO VE VODNÝCH ROZTOCÍCH KYSELINY SÍROVÉ

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Abstrakt

Cílem práce bylo zjistit průběh rozpouštění rozdílných druhů práškových ZnO v 0,25, 0,5 a 1,0 M H₂SO₄ při 20, 40 a 60°C. Studované vzorky ZnO byly připraveny sintrováním analyticky čistého ZnO nebo kalcinací zinkových hydroxidových sloučenin na vzduchu při teplotách 800 a 1000°C po dobu 3h. Hydroxidové sloučeniny byly vysráženy z čistého roztoku ZnSO₄, z modelových různě znečištěných roztoků ZnSO₄ nebo z výluhů po loužení odpadních galvanických kalů ve zředěné H₂SO₄ 50% roztokem NaOH. Experimentální data, která vyjadřují vliv přípravy, chemického, mineralogického a morfologického složení práškových vzorků ZnO a vliv rozdílných podmínek loužení na rychlost rozpouštění ZnO ve vodných roztocích H₂SO₄, byly použity pro výpočet rozpouštěcích charakteristik. Zvolené experimentální podmínky studia kinetiky rozpouštění ZnO, způsob jejich přípravy a znečištění, koncentrace a teplota loužících roztoků modelují přepokládané podmínky navrhované metody recyklace zinkových kalů, pro kterou budou získané výsledky využity.

Abstract

The dissolution of four types of powdered ZnO samples, which were prepared by sintering of analytical grade ZnO or by air-calcination of zinc hydroxides, was studied in 0.25, 0.5 and 1M H₂SO₄ at 20, 40 and 60°C. Zinc hydroxides were precipitated from pure solution of ZnSO₄ or from a model contaminated solution of ZnSO₄ or from leach liquors originated from leaching waste galvanic sludges in 0.5 M H₂SO₄ with 50% solution of NaOH. The sintering or calcination was performed at temperatures of 800 or 1000°C within 3 hours. The experimental data expressing the influence of the conditions of preparation of oxide samples, their chemical and phase composition and the different conditions of leaching on the rate of ZnO dissolution were used for the calculation of the additional

dissolution characteristics according the grain model. The obtained data will be utilised in processing of zinc waste galvanic sludges.

1. Introduction

The dissolution of ZnO in solutions of sulphuric acid has been investigated by many authors from the point of view both theory and practice [1-5]. Most studies are related to solving practical problems arising from the hydrometallurgical production of zinc and therefore, are focused on the investigation of the dissolution of pure ZnO and/or of ferrites which are formed during the oxidative roasting of zinc sulphide concentrates.

Terry [1] conducted a critical analysis of published data on acid dissolution of ZnO, Zn_2SiO_4 and $ZnFe_2O_4$ and established correlations relating the specific chemical rate for acid dissolution of these compounds. Doyle, Ranjan and Peters [2] developed a mathematical model to describe the leaching kinetics of ZnO in dilute acid solutions which assumed that the leaching rate is controlled by mass transport.

Due to the homogenous composition of bulk oxides which would not change during the dissolution there are no difficulties in the experimental determination of dissolution rate. However, here the difficulties for a kinetic investigation consist in the experimental technique and particularly in the lack of information about the real surface and its microstructure which may change during the dissolution process. If the rate of dissolution is fast, transport of the reagents or the products in the solution is rate determining. If the rate of the interfacial reaction is slow, a large surface area is required for measuring the rate by chemical analysis of the dissolved material. For this purpose, powdered oxides or sintered pellets with a large surface area have been commonly used.

The dissolution or leaching behaviour of pure bulk zinc oxide and/or of zinc ferrite in sulphuric acid solution have been studied in wide range of sulphuric acid concentration and temperatures. Leaching tests with powder specimens were used to study the dissolution behavior of ZnO [2, 5] and of zinc ferrite [6,7]. Investigations of the dissolution kinetics using the rotary disc technique with samples of sintered pellets were performed for ZnO in the study [4]. In experiments with powders, however, the surface area varies during the dissolution and the influence of transport processes hardly can be analyzed correctly. The experiments with sintered pellets suffer from lack of information about the real surface structure. These shortcomings were eliminated in the study [3] in which the authors investigated the anodic dissolution of zinc oxide single crystals on the electrolyte composition. The crystals were strongly n-type and the rate of dissolution was instantaneously measured at anodic bias an electric current.

Generally, the findings of the dissolution investigations of ZnO and zinc ferrite using different techniques are in a good agreement. The overall rate of ZnO dissolution appears to be controlled by mass transport of species between the bulk solution and the particle surface, whereas zinc ferrite dissolves at a chemically controlled rate that is dependent on the acidity. However, the results achieved are exactly valid only for the samples measured due to the fact that the dissolution kinetics is significantly influenced by the properties of the oxide surface which depends both on the way of oxide sample preparation and of its purity.

The objective of this work was to examine the leaching behaviour of powdered zinc oxide within a wide range of experimental parameters such as conditions of preparation of the oxide samples, their chemical and phase composition as well as different concentrations and temperatures of leaching liquor/aqueous solutions of H_2SO_4 . The knowledge obtained will be utilised in processing zinc waste sludges by the method which is developed in the Department of Metals and Corrosion Engineering. This methods is based on acid leaching of zinc sludges, precipitation of contaminated zinc hydroxides from leach liquors, air-calcination of the hydroxide precipitates at 800 or 1000°C within 3h during which impurities such as Al, Cr, Fe, Mn and partly Cu, Ni and Mg are transferred into sparingly soluble spinels. The resulting oxide mixture is leached in dilute solution of sulphuric acid under conditions which make possible an efficient zinc extraction into solution while the impurities bonded spinels remain in the leach residue. Finally, the refined zinc hydroxide is precipitated from the solution. In contrary to the published studies related to the hydrometallurgical production of zinc the aim of this study was to seek proper conditions under which free zinc oxide dissolves efficiently while bound metals including zinc are kept in the insoluble residue. No publication concerning the dissolution

reactivity of sintered ZnO containing admixtures of Al, Cr, Ni, Mn, Ca, Mg and Mn was found in the literature.

The reason for using pure, synthetic contaminated and industrial samples of ZnO in the dissolution tests performed was to obtain an idea of how the impurities which commonly occurred in waste sludges will affect the leaching behaviour of ZnO prepared under the conditions which simulate the proposed regime of zinc waste sludges processing. The range of H₂SO₄ concentrations, 0.25, 0.5 and 1.0 M H₂SO₄, and of leaching temperatures, 20, 40, 60°C, was chosen in agreement with the published data on ZnO dissolution. According to this knowledge, powdered ZnO dissolves rapidly even at low acid concentration and at relatively low temperatures. Experimental conditions mentioned above make possible to determine the lowest concentration of H₂SO₄ and leaching temperature under which more than 90% of ZnO will go into solution while the spinels, the dissolution of which is promoted by high acid concentrations and high temperatures, will be kept in insoluble residues. Further, the experimental conditions allow to determine the linear dissolution rate, half-period of dissolution and apparent activation energy of dissolution of selected samples.

2. Experimental

The dissolution tests were performed with four different types of zinc oxide samples:

- (I) pure ZnO obtained by sintering the analytical grade chemical in air
- (II) ZnO obtained by air-calcination of zinc hydroxide precipitated from pure solutions of ZnSO₄ (II) containing 12 g Zn/l with a solution of 50% NaOH up to pH=8
- (III) ZnO obtained by air-calcination of contaminated zinc hydroxide precipitated from model solutions of ZnSO₄ (III) with a solution of 50 % NaOH up to pH=8
- (IV) ZnO obtained by air-calcination of contaminated zinc hydroxide precipitated from leach liquors (IV, IV^{*}) originating from the leaching waste zinc galvanising sludges in 0.5 M H₂SO₄ with a solution of 50% NaOH up to pH=8. In the following text these samples will be denoted as industrial samples.

Model zinc sulphate solutions were prepared by dissolving accurately weighed amounts of analytical grade ZnSO₄·7H₂O, Al₂(SO₄)₃·18H₂O, Cr₂(SO₄)₃·6H₂O, CuSO₄·5H₂O, Fe₃(SO₄)₄·9H₂O, NiSO₄·7H₂O, MgSO₄·2H₂O and MnSO₄·5H₂O. The leach liquors were prepared by leaching waste galvanising sludge in 0.5M H₂SO₄ under oxidative conditions up to pH=3.9 or 4.6. The exact composition of model ZnSO₄ solution and of leach liquors which are given Table 1, were determined by the AAS method.

Table 1 Composition of zinc sulphate solutions prepared for precipitation of zinc hydroxides

^x leaching up to pH=4,6

Samples of pure ZnO and of precipitated hydroxides were sintered or calcinated in air under the conditions given in Table 2. The conditions of the preparation of the oxide samples were chosen following the results of thermogravimetric analysis of individual hydroxide precipitates and the knowledge concerning the formation of sparingly soluble spinels [8].

Table 2 Procedure for the preparation of the ZnO samples

All the ZnO samples prepared were dry ground in a laboratory vibration mill. Their chemical compositions after their dissolution were determined by the AAS method. Mineralogical and morphological examination of individual samples was carried out by X-ray diffractometry (XRD), electron microprobe analysis and scanning electron microscopy (SEM). The cumulated distribution of the grain size was determined by the grain size analysis on vibrating screens following the DIN 4188 norm. All fractions were used in the leaching tests.

Leaching experiments were carried out in a closed thermostated 1l glass reactor. Standard mixing was accomplished by means of an impeller. For every experiment the reactor was filled with 250 or 500 ml of leaching solution of 0.25 M, 0.5 M or 1 M H_2SO_4 following the dissolution regime of the individual samples. Once the desired temperature of 20, 40 or 60°C was reached again following the dissolution regime, an accurately weighed amount of solids was added into the reactor. The solid to liquid ratio was kept low in order to avoid any significant decrease in the acid concentration during the experiment and to produce a final zinc concentration in solution in the range between 8-10 g Zn/l. At regular time intervals, samples were withdrawn from the reactor to be analysed by AAS for zinc and impurities. In the case of the leaching experiments conducted with the contaminated ZnO, the leach residues were filtered, water-washed, weighed, dried and examined by XRD.

3. Results and discussion

The chemical composition of the ZnO samples investigated is given in Table 3.

Table 3 Chemical composition of the ZnO samples

The mineralogical examination by XRD showed that the main phases of the unleached zinc contaminated oxide particles prepared from model solution were: ZnO, spinel - $Mn_{1-x}(Zn, Mg, Ni)_x(Al, Cr)_2O_4$. The main phases of the unleached zinc contaminated oxides prepared from leach liquors were: ZnO, spinel - $Mn_{1-x}(Zn, Mg, Ni)_x(Al, Cr)_2O_4$; $ZnSiO_4$ and $(Mg, Ni)O$ (only in samples IV/2; IV^x/2). The zinc oxides originated from $ZnSO_4$ solution which were calcinated at 800°C contained depending on the calcination time a small amount of $Zn_3O(SO_4)$ which did not occur in any oxides calcinated at 1000°C. However, the position of ZnO reflections does not reveal any changes. That leads to the conclusion that impurities do not substitute for Zn^{2+} in its oxide but form their individual oxides or spinels. Further, it was found that the leach residues which were separated from solutions after completing the leaching of contaminated ZnO (group III, IV, IV^{*}) consist in all cases of only from the spinel $Mn_{1-x}(Zn, Mg, Ni)_x(Al, Cr)_2O_4$. The comparison of powder patterns of the calcinated sample IV^x/1 (1) and its leach residue (2) is given in Fig.1. It is seen that ZnO and $ZnSiO_4$ dissolved completely, while the spinel-like structure $Mn_{1-x}(Zn, Mg, Ni)_x(Al, Cr)_2O_4$ remained in the insoluble residue.

The point electron microscope analysis showed that the unleached contaminated zinc oxide particles are formed by two main phases which differed in the content of ZnO. In the case of the oxides prepared from model solutions the main phase contained 86-92% ZnO; 1.5-4.9% NiO; 2.1-2.3% CuO; 1.0-3.3% MnO; 2.1-3.2% Al₂O₃; 0.8-1.5% Cr₂O₃; 0.1-0.2% Fe₂O₃; 0.1-0.4% MgO. The second phase contained 62-65% ZnO, 13.4-15.6% Al₂O₃; 4.9-6.8% MnO; 4.9-6.3% NiO; 4.2-5.4% Cr₂O₃; 2.6-3.4% CuO; 0.3-0.5% Fe₂O₃; 0% MgO. In the case of oxides prepared from leach liquors the main phase contained 81-83% ZnO; 2.7-4.1% NiO; 1.5-2.0% CuO; 1.7-3.5% MnO; 2.6-4.6% Al₂O₃; 0.4-1.0% Cr₂O₃; 0.2-0.3 %Fe₂O₃; 0.2-0.8% MgO; 1.6-6.2% SiO₂; 0.4-1.0% CaO . The second phase contained 50-62% ZnO, 8.3-12.1% Al₂O₃; 3.4-5.3% MnO; 2.7-3.8% NiO; 0.5-14.2% Cr₂O₃; 1.3-2.8% CuO; 0.1-0,3 % Fe₂O₃; 1.2-3.0 % MgO; 5.8-6.2% SiO₂; 0.1-0.9.2% CaO.

Fig.1 The comparison of powder patterns of calcinated sample IV^X/1 (1) and its leach residue (2)

Finally, the examination by SEM showed that the all zinc oxide samples independent on the method of their preparation and on their purity were non-porous like-spherical particles (Fig.2a, b).

Fig.2 Typical unleached contaminated zinc oxide particles observed under SEM: (a) sample III/1; (b) sample IV/2

The results of the leaching tests performed are given in Figs.3-9 as a time dependence of the dissolved zinc in weight percentages related to the initial content of zinc in the samples treated. The survey of the leaching conditions, mean grain diameter of particles together with the calculated values of the half-period of dissolution $t_{1/2}$ and the linear dissolution rate k_{LIN} are listed in Table 4.

Fig.3 Plot of ZnO dissolution (40°C; 0.25, 0.5, 1 M H₂SO₄)

Fig.4 Plot of ZnO dissolution (60°C; 0.25, 0.5, 1 M H₂SO₄)

Fig.5 Plot of ZnO dissolution (20°C; 0.5 M H₂SO₄)

Fig.6 Plot of ZnO dissolution (40°C; 0.5 M H₂SO₄)

Fig.7 Plot of ZnO dissolution (60°C; 0.5 M H₂SO₄)

Fig.8 Plot of ZnO dissolution (40, 60°C; 0.5 M H₂SO₄)

Fig.9 Plot of ZnO dissolution (40°C; 0.5 M H₂SO₄)

Dissolution of ZnO belongs to heterogeneous reactions at a solid-liquid interface. The rate controlling step is a mass transport of dissolved reactants (H₂SO₄) from the bulk solution to a surface, mass transport of products into the bulk of the solution or the surface chemical reaction, depending on acid concentration, temperature and stirring rate. In special cases the mixed transport-surface reaction controlled kinetics may develop. Guspil and Riesenkamp [4] have found that the ZnO dissolution rate is diffusion-controlled in a wide range of acid concentrations and temperatures and that the formal reaction order of ZnO dissolution in 0.1-2 M H₂SO₄ is 0.1 This leads to the deduction that considerable adsorption of the anions on the oxide surface will take place and that surface complexes will be formed. These complexes contain hydroxide groups and also considerable amounts of anions which markedly reduce the effect of hydrogen ion concentration on the dissolution rate.

Since reaction products do not form an insoluble protective layer at the surface, the dissolution rate r is related to the surface area and concentration of active substances in the electrolyte [9].

Considering solubility of products and nearly constant concentration of reactants and products in the solution with time the reaction has the linear kinetics. Under the assumption of the steady dissolution of ZnO and the constant concentration of active sites at the oxide surface the rate of the

reaction interface movement dL/dt is constant and therefore the reaction rate is a function of the actual surface area S [10].

$$(1)$$

where k' is the rate constant in $\text{mol}\times\text{m}^{-2}\times\text{s}^{-1}$, M the molar weight of ZnO, ρ the density of hexagonal ZnO ($5606 \text{ kg}\times\text{m}^{-3}$, [11]) and k_{LIN} the linear rate constant in $\text{m}\cdot\text{s}^{-1}$.

In experiments with powders the surface area varies during the process. To calculate the rate of ZnO dissolution, the grain model was used [9, 12]. Samples were considered to be composed of several groups of non-porous spherical particles with the same diameter. Considering validity of the described model the conversion of ZnO X is a function of the grain diameter decrease ΔL as

$$(2)$$

where m_0 is the initial (i.e. at time $t = 0$) mass of the sample, $L_{0,i}$ the initial mean grain diameter in a group i . Number of grains a_i was evaluated by the equation

$$(3)$$

where p_i is the initial weight percent of ZnO in a group i . The dependence of X on ΔL for samples I/1, II/3 and III/1 is shown in Fig.10.

Fig.10 Dependence of ZnO conversion on the particle diameter decrease

The time dependence of the particle diameter decrease which is illustrated for samples I/1, II/3, III/1 and IV/1 in Fig.11 was calculated on the basis of the known cumulative distribution of the grain size and the dependence of X on time. The slopes of the lines in Fig.11 were obtained by the linear regression and correspond to the linear rate constant k_{LIN} in $\text{m}\times\text{s}^{-1}$. The linear rate constants for all the investigated samples are given in Table 4 together with the half-periods of dissolution. From the dissolution curves measured (Figs.3-9) and from the values of the linear rate constant which is independent on the grain size, it is evident that the dissolution of ZnO samples investigated proceeds relatively fast and is not practically influenced by the way of their preparation. It also appears obvious that the presence of impurities does not influence the rate of dissolution of model contaminated and industrial samples of ZnO. However, in contrast to the samples containing only ZnO, the samples of contaminated ZnO did not dissolve completely because Zn^{2+} ions are partly bound in the spinel Mn_1 .

$x(\text{Zn, Mg, Ni})_x(\text{Al, Cr})_2\text{O}_4$ which remains undissolved in the leach residue. The yield of zinc into solution which ranged between 93-99 % increased with decreasing calcination temperature and with elevated leaching temperature.

Due to the higher ratio of Mn:Al in the original industrial oxides compared with that in the model contaminated oxides, the amount of undissolved ZnO which is bound in $\text{Mn}_{1-x}(\text{Zn, Ni, Cu})\text{Al}_2\text{O}_4$ spinel is lower. The detailed study of the formation of insoluble spinels containing impurities which occur in zinc waste galvanic sludges and their leaching behavior will be the aim of a further study.

For variable temperature, $k_{L/N}$ (generally a rate constant) is known to be an exponential function of T^{-1} (an Arrhenius relationship, [13])

$$(4)$$

where E_a is the activation energy and A the pre-exponential factor. Because of diffusion control of the ZnO dissolution, only the apparent activation energy could be evaluated, which does not correspond to the activation energy of the surface chemical reaction. The apparent activation energy E_a was calculated for dissolution of model contaminated ZnO in 0.5 M H_2SO_4 at temperature ranges from 40 to 60°C. The calculated values of $7.9 \text{ kJ}\cdot\text{mol}^{-1}$ (III/1) and $24.2 \text{ kJ}\cdot\text{mol}^{-1}$ (III/3) confirm the assumption of diffusion control of the process.

The effect of temperature on the reaction kinetics for samples I is minimal. The dissolution of samples III is slightly accelerated with the increasing temperature. However, in the case of dissolution of samples II the temperature increase from 20 to 40°C causes an increase of $k_{L/N}$ but the additional solution temperature increment leads to a decrease in the dissolution rate. There is presently no explanation for this effect.

Dissolution in acid solutions is supported by proton adsorption onto the solid-liquid interface. It weakens critical metal-oxygen bonds and leads to release of ions into the solution. The influence of the concentration of hydrogen ions on the dissolution rate of ZnO was examined only for the sintered ZnO- samples I/1, I/2, Fig.3 and 4. From the results obtained it is obvious that the increase of acid concentration above 0.5 M has no significant effect on the reaction rate. Based on the findings mentioned above, the leaching behaviour of the industrial samples of ZnO (IV, IV^x), Fig.9, was studied only in 0.5 M H_2SO_4 at 40°C.

4. Conclusion

The results obtained in this work indicate that the leaching of powdered ZnO in dilute aqueous solutions of H_2SO_4 at elevated temperatures is diffusion controlled. This process runs relatively fast and is not significantly influenced by the conditions used for the preparation of the samples investigated. The increase of dissolution temperature results only in an insignificant increase of the dissolution rate. The increase of acid concentration above 0.5 M has no significant effect on the

reaction rate. Both the rise of sintering or calcination temperature and the elongation of the calcination time result in decreased dissolution rate of ZnO and depressed overall dissolution of impurities bound in sparingly soluble spinels. However, independent of the temperature of preparation of the individual ZnO samples, their dissolution in 0.5 and 1 M H₂SO₄ was completed within 10 to 15 min. The presence of impurities does not influence the rate of ZnO dissolution due to the fact that they do not substitute Zn²⁺ in its oxide but form their individual oxides or spinels. However, in contrast to the samples containing only ZnO, the samples of contaminated ZnO did not dissolve completely because Zn²⁺ ions are partly bound in the spinel Mn_{1-x}(Zn, Mg, Ni)_x(Al, Cr)₂O₄ which remains undissolved in the leach residue. The optimum leaching regime which will be applied on processing zinc waste galvanic sludge was found to be 0.5 M H₂SO₄ and 40°C.

Acknowledgements

The present study was supported by the Grant no. 104/97/0705 and no. 203/96/0111 of the Grant Agency of the Czech republic and by the research intention CEZ: 19/28 223111100002.

Literature

- [1] B. Terry: Specific chemical rate constants for the acid dissolution of oxides and silicates, *Hydrometallurgy*, 11 (1983), pp. 315-344
- [2] F. M. Doyle, N. Ranjan and E. Peters: Mathematical model of zinc oxide leaching in dilute acid solutions, *Trans. Instn. Min. Metall (Sect. C: Mineral Process. Extr. Metall.)* 96 (1987)pp. C69-C78
- [3] H. Gerinsher and N. Sorg: Chemical dissolution of zinc oxide crystals in aqueous electrolytes-an analysis of the kinetics, *Electrochimica Acta* 37 (1992) pp. 827-835
- [4] J. Guśpiel and W. Riesenkauf: Kinetics dissolution of ZnO, MgO and their solid solutions in aqueous sulphuric acid solutions, *Hydrometallurgy*, 34 (1993) pp.203-220
- [5] G.L. Pashkov , R.B. Nikolaeva, S.V. Salkova and E.V. Karpacheva: Effect of zinc oxide preparation method on dissolution rate during sorption leaching, *Zh. Prikl. Khim.* 67 (1994) pp.1029-1031
- [6] K. Rycaj, W. Riesenkauf: Kinetics of the dissolution of zinc-magnesium ferrites in sulphuric acid solutions related to zinc leach process, *Hydrometallurgy*, 11 (1983) pp. 363-370
- [7] D. Filipou, G. P. Demopoulos: *The Canadian Journal of Chemical Engineering*, 71 (1993) pp. 790-801
- [8] Powder Diffraction File (1997). JCPDS-international Center for Diffraction Data, Newtown square Corporate Campus, 12 Campus Boulevard, Newstone Square, PA 19073-3273 USA
- [9] M. E.Wadsworth: Reactions at surfaces, in: *Physical Chemistry - An Advanced Treatise*, vol. VII, Academic Press, 1975, pp. 413-472
- [10] T. Grygar , J. Hostomský: Effect of Particle Size Distribution on Dissolution Kinetics; Dissolution of Iron (III) Oxides, will be published
- [11] R. H. Perry, D. Green : *Perry's Engineers' Handbook*, McGraw-Hill, 1984
- [12] W. Stumm : *The Kinetics of Surface Controlled Dissolution of Oxide Minerals; An Introduction to Weathering*, in: *Chemistry of the Solid-Water Interface*, John Wiley & Sons, 1992
- [13] Moore W. J.: *Fyzikální chemie*, SNTL, Praha 1979
- [14] Gmelins *Handbuch der Anorganischen Chemie* 6 B2, Verlag Chemie Weinheim, 1960