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KINETICS OF ALKALINE PRESSURE LEACHING OF MECHANICALLY MODIFIED ZIRCON CONCENTRATE

Received March 15, 2006; reviewed; accepted May 15, 2006

Hydrometallurgical processing of zircon concentrate separated from Egyptian black sands is attained through leaching with sodium hydroxide of mechanically pretreated zircon concentrate under relatively high temperature (260°C). The effects of temperature, sodium hydroxide concentration, grinding time, grain size, and leaching time were studied as well as the kinetics of the leaching process.

Key words: zirconium, zircon, mechanical activation, pressure leaching

INTRODUCTION

Zirconium is present fairly abundantly in the earth's crust but it is difficult to remove and has limited use outside the nuclear industry. The industrially important zirconium minerals are baddelyite (ZrO_2) and zircon ($ZrSiO_4$). Baddeleyite is relatively scarce, but zircon is available in abundant quantities in concentrated form and is the most important raw material for producing metallic zirconium, its alloys, and its compounds. Main occurrence of zircon in Egypt is a constituent of beach sands along with ilmenite and monazite. Zircon concentrate is separated from its heavy minerals by a gravity concentration followed by magnetic and electrostatic processing. (El-Hinawi, 1964).

Pyrometallurgical methods are used for processing of zircon concentrate which include fusion with caustic soda with the formation of acid soluble zirconate (MacDonald, et al 1982), sintering with lime or chalk and formation of calcium zirconate (Krisham et al, 1986; Mohammed and Daher, 2002). Thermal dissociation by plasma are commonly used for the production of technical and pure grade ZrO_2 in addition to the chlorination of a mixture of zircon and carbon to produce $ZrCl_4$ and has

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become the most popular method for producing $ZrCl_4$ (Abdel-Rehim and Khalil, 1975; Staumbaugh and Miller, 1983).

The aim of this work is to discuss a new process for extraction of zirconium from zircon concentrate instead of pyrometallurgical processing using mechanochemical treatment where grinding is carried out in the presence of sodium hydroxide and is followed by pressure leaching in autoclave.

Mechanical activation, usually done via energetic milling, has been demonstrated to accelerate the leaching of sulphide minerals (Welham 2001a) as well as of non sulphide minerals (Amer, 2000; 2001; 2002).

EXPERIMENTAL

The studied zircon concentrate was separated from black sands. The chemical analysis of studied concentrate is given in Table 1.

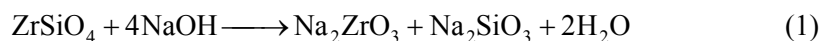
Table 1. Chemical analysis of zircon concentrate

Component	%
ZrO_2	64.50
SiO_2	32.58
Fe_2O_3	1.14
Al_2O_3	0.22
K_2O	0.03
TiO_2	0.9

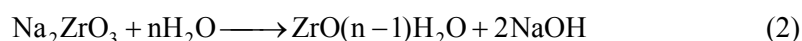
APPARATUS AND PROCEDURE

A stirred ball mill with a vertical attritor (PE 0.75, Netzsh, Selb) was used with steel balls of 2.0 mm diameter. The rotation rate was maintained at 1200 min^{-1} . Grinding was carried out in the presence of sodium hydroxide solution. The pulp from the attritor was charged into the autoclave and agitated by an impeller at 1200 min^{-1} . A complete description of the leaching system was given elsewhere (Levenspiel, 1972).

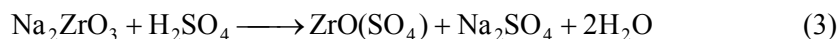
The reaction of zircon with caustic soda solution lead to formation of sodium zirconate and sodium silicate.



With dilution, sodium silicate is removed while sodium zirconate is hydrolysed to hydrated zirconia.



The resultant hydrated cake is dissolved in sulphuric acid as given in the following reaction:



After the complete dissolution of the cake, sulphate solution was filtered off and the impurities (Fe, Cu, Mg, Ti, Al, Na and Si) were analyzed in the solution by atomic spectrometry while zirconium was gravimetrically analyzed using mandelic acid as precipitant.

Effects of the following factors on the course of leaching of zircon concentrate were studied:

Temperature	200°-260°C
Concentration of sodium hydroxide	0.1-0.8M
Grinding time	0-5 hrs
Leaching time	30-300 min
Grain size	12-58 μm

RESULTS AND DISCUSSION

EFFECT OF TEMPERATURE

Figure (1) shows leaching results of zircon at the temperature ranging from 200 to 260°C. Temperature has a significant effect on the dissolution of zirconium. About 85% of zirconium present in zircon concentrate is leached at 260°C after 90 min. The surface reaction model was applied to determine the activation energy. Data presented in Figure (1) are plotted according to the following equation:

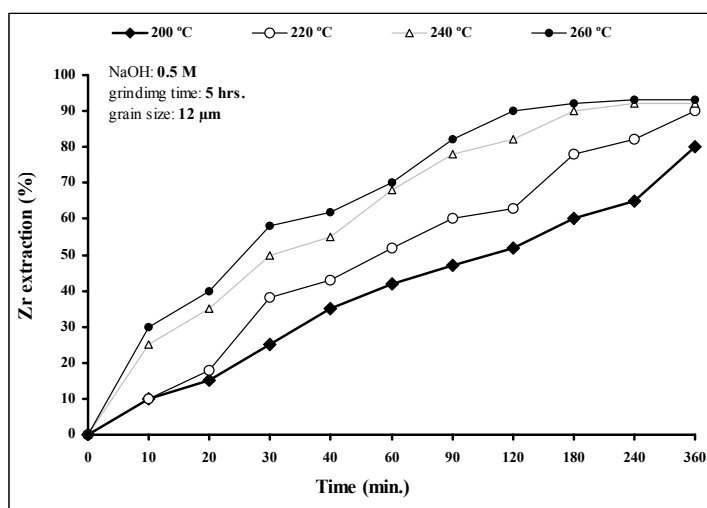


Fig. 1. Course of zirconium leaching at different temperatures

$$1 - (1 - \alpha)^{1/3} = k t \quad (4)$$

where:

- k – the apparent reaction rate constant,
- α – the fraction of zirconium leached,
- t – leaching time in sec^{-1} .

and presented in Figure (2). Slopes of curves in Figure 2 according to $d[1 - (1 - \alpha)^{1/3}] / dt$ represent the apparent rate constants (k). These constants as plotted according to the Arrhenius equation are shown in Figure (3). The activation energy was found to be equal to 72 kJ/mole. Its magnitude confirms a surface reaction-control mechanism.

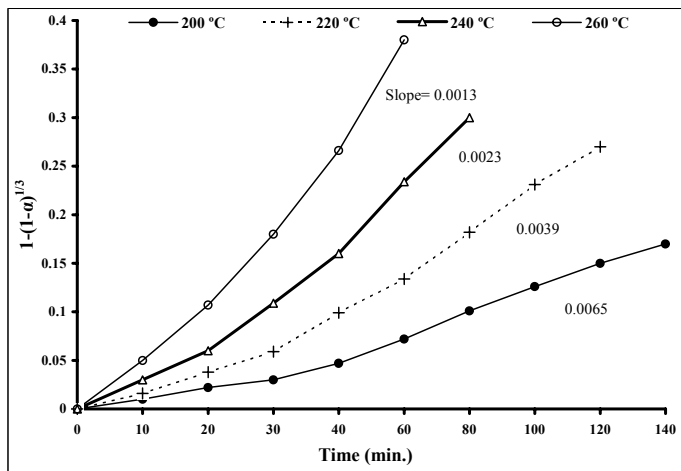


Fig. 2. A plot of $1-(1-\alpha)^{1/3}$ versus time for various temperatures

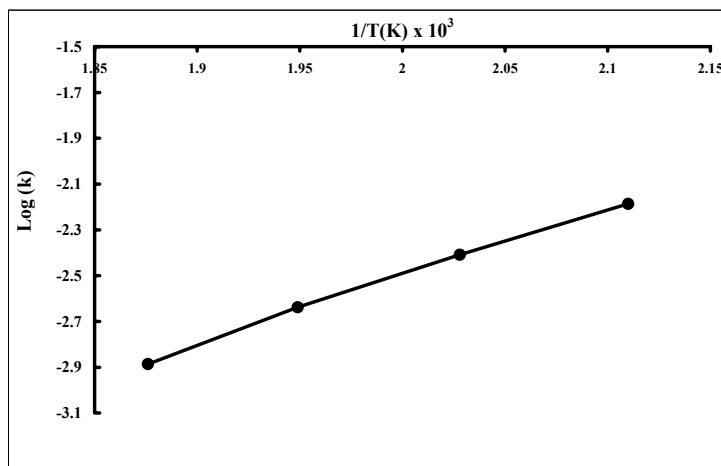


Fig. 3. Arrhenius plot for determination of activation energy

EFFECT OF PARTICLE SIZE

Figure (4) shows the experimental results obtained for particle size fractions of mean diameter: 12, 36, and 58 μm . The particle size effect is clearly seen since the first leaching stage consists of a series of straight lines.

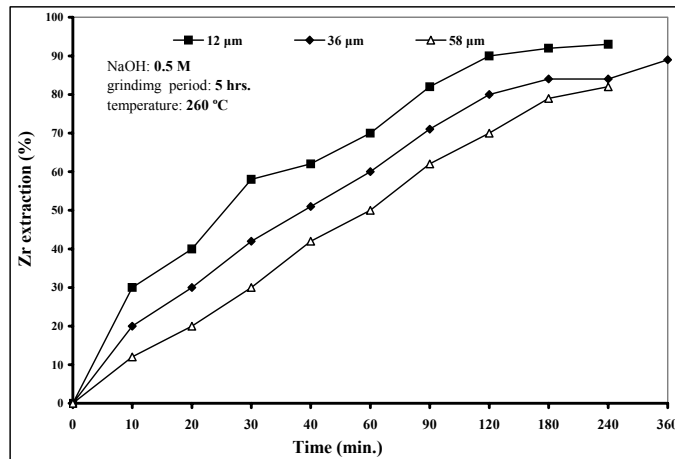


Fig. 4. Course of zirconium extraction at different particle sizes

The apparent rate constants (k) were calculated according to Eq. (1) and the external surface areas were calculated for different particle sizes using the following equation:

$$S = \frac{6m}{\rho D} \quad (5)$$

where:

S – the external surface area for the particles (see Table 2),

m – the mass of the leached sample,

ρ – the density of the sample 4.6 g/cm^3 ,

D – the particle mean diameter.

The specific apparent rate constants k/S were calculated and are shown in Table (2) which shows that the smaller the particle size the smaller the specific apparent rate constant. It is known that smaller particle size makes the boundary layer surrounding a particle thinner. Therefore under chemical control, the values of specific apparent rate constant increased with the decrease of particle size. So, the controlling step of leaching process seems to be chemically controlled.

Table 2. Rate constants for various particle sizes in the first leaching stage

D(μm)	S (cm^2)	K (min^{-1})	K/S
12	1786	0.1326	7.43×10^{-5}
36	595	0.0558	9.38×10^{-5}
58	369	0.0383	10.39×10^{-5}

EFFECT OF SODIUM HYDROXIDE CONCENTRATION

Figure (5) shows results of experiments with sodium hydroxide concentration varying from 0.4 to 0.8 M. The increase in sodium hydroxide concentration from 0.1 to 0.5 M led to an increase of zirconium leaching but further increase (>0.5M) gave no practical increase.

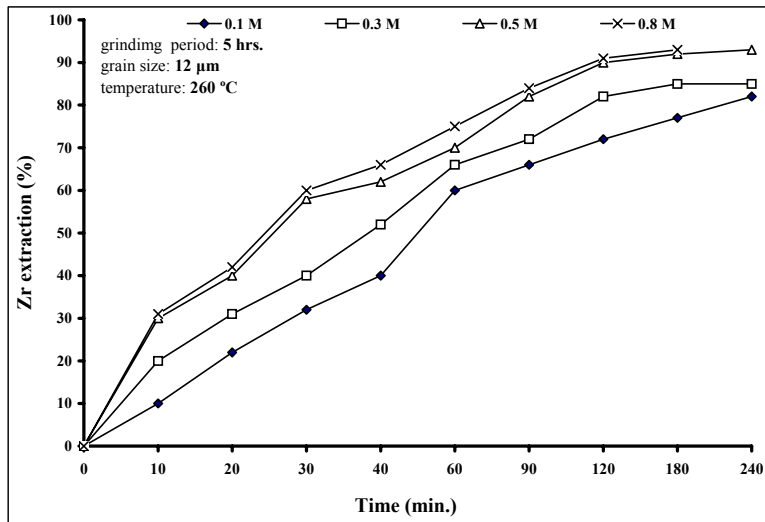


Fig. 6. Course of zirconium extraction at different grinding periods

The Langmuir-Hinshelwood equations may be used to evaluate the effect of sodium hydroxide concentration on leaching of zircon concentrate:

$$\Theta = \frac{KC_A}{1 + KC_A} \quad (6)$$

and

$$\Theta = C_A / C_{\max} \quad (7)$$

where:

Θ is the fraction of grain surface of zircon occupied by sodium hydroxide molecules.

C_A – the concentration of sodium hydroxide in the bulk solution (mol/L)

C_{\max} – the hydroxide adsorbed on zircon interface (mole/m²). Effect of grinding time.

The dependence of zircon leaching on grinding time is illustrated in Fig. (6). The apparent rate constant is directly proportional function of grinding time varying from 0 to 5 hrs. Such a dependence is consistent with the theory of leaching (Levenspiel, 1972).

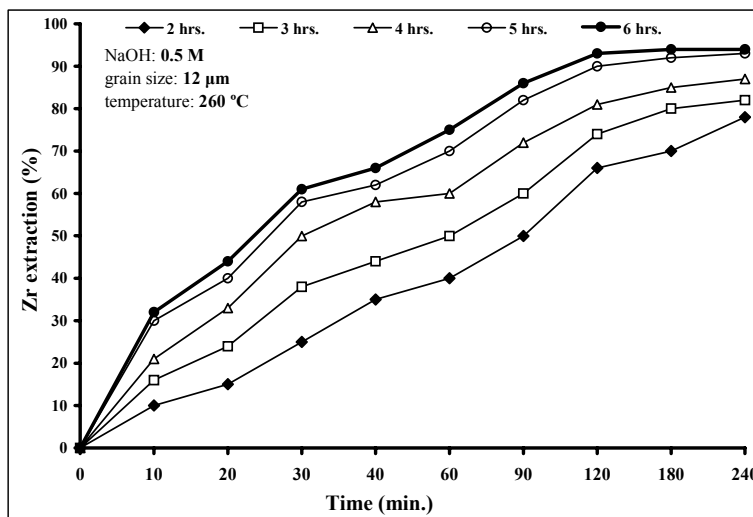


Fig. 5. Course of zirconium extraction at different sodium hydroxide concentrations

CONCLUSIONS

A new possibility of intensive zirconium removal from zircon concentrate is the mechanochemical activation which integrates mechanical and chemical processing operations in one step.

Results of investigation reveal that even a short leaching time (90 min) at 260°C led to removal of over 85% of zirconium after 5 hrs of grinding in the attritor using sodium hydroxide of 0.5 M zircon concentrate with particle size of 12 μm. The overall leaching reaction was found to be chemically rate controlled.

REFERENCES

- ABDEL-REHIM, A.M., KHALIL, S.O. (1975), *Sintering of Rosetta Zircon with calcite*, Acta Mineralogica, Petrographica, Szeged XX 11 / 1, 147-55.
- AMER, A.M. (2000), *Investigation of the direct hydrometallurgical processing of mechanically activated low-grade wolframite concentrate*, Hydrometallurgy, 58, 251-259.
- AMER, A.M. (2001), *Kinetics of acid pressure leaching of mechanically activated cassiterite concentrate*, Erzmetall, 54 (a) 446-449.
- AMER, A.M. (2002), *Processing of Egyptian boilerash from extraction of vanadium and nickel*, Waste Management, 22, 515-520.
- EL-HINAWI, E.E.; (1964), *Mineralogical and geochemical studies in Egyptian black sands*, Beitrage Zur Mineralogie and petrographic, 9, 519.
- KRISHNAN, T.S.; BABU, R.S., CAPTA, C.K. (1986), *Extended abstract*, Zirconia 86, Ceram. Soc. Jpn, 200-201.
- LEVENSPIEL, O. (1972), *Chemical reaction engineering*, New York (Wiley).
- MacDONALD, D.J.; GUIDOTT, R.A., HENRG, H.G. (1982), U.S. Bur Mines. Rep. Invest., 8718.
- MOHAMMED, N.A., DAHER, A.M. (2002). *Preparation of high purity zirconia from Egyptian zircon: an anion-exchange purification process*, Hydrometallurgy, 65, pp. 103-107.

- STAUMBAUGH, E.P., MILLER, J.F. (1983), Proceedings of 1st Int. Symposium on hydrothermal Research, p. 859.
- WELHAM, N.J. (2001), *Effect of extended grinding on the dissolution of Ta/Nb concentrate*, Can. Metall. Q, 40(2), 143-154.

Amer A.M., *Kinetyka alkalicznego ciśnieniowego ługowania mechanicznie modyfikowanego koncentratu cyrkonowego*, Physicochemical Problems of Mineral Processing, 40 (2006), 61-68 (w jęz. ang.).

Przeprowadzono hydrometalurgiczną przeróbkę koncentratów cyrkonowych wydzielonych z czarnego piasku pochodzącego z Egiptu poprzez ługowanie za pomocą wodorotlenku sodu przy względnie wysokiej temperaturze (260 °C). Koncentraty były mechanicznie aktywowane przed ługowaniem. Badano wpływ temperatury, stężenia wodorotlenku sodu, czasu mielenia, rozmiaru ziaren i czasu ługowania jak również kinetykę procesu ługowania.