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KINETICS OF PYRITE OXIDATION IN ACIDIC POTASSIUM DICHROMATE SULUTIONS

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The kinetics of pyrite oxidation in potassium dichromate solution was investigated. The effect of stirring rate, temperature and particle size have been examined. In addition the solid phases before and after leaching were examined by SEM, electron microprobe and chemical analysis. The rate of pyrite oxidation was found to be independent of the stirring speed. The consumption of dichromate ions in the initial solutions showed that at all temperatures under consideration sulphide sulphur was oxidized to sulphate. The value of the apparent activation energy of 43.5 ± 1.5 kJmol^{-1}, the independence of reaction rate on the stirring speed, the linear relationship between the rate constant, and the inverse of the initial particle diameter are in good agreement with a mechanism controlled by chemical reaction.

Key words: pyrite, oxidation, potassium dichromate, reaction kinetics

INTRODUCTION

Pyrite is the most abundant of all sulphide minerals. It occurs in most sulphide ore deposits, often as a major phase. It is also commonly associated with coal and gold deposits. Pyrite is one of the most refractory and difficult to leach minerals. Its exceptional stable electronic structure is responsible for this behaviour (Nowak, 2006). The literature data show that leaching of pyrite requires elevated temperatures and pressures in the presence of oxygen (Long and Dixon, 2004) or strong oxidizing agent such as nitric acid (Karaca et al., 2003)

Sulphuric acid containing dichromate ions is a powerful oxidizing agent with a pH-dependent oxidation potential. The first studies applying sulphuric acid solution of

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sodium dichromate were connected with copper concentrates (Shantz and Morris, 1974; Murr and Hiskey, 1981).

Our previous works dealt with the nickel sulphides leaching in acidic dichromate solutions (Mulak, 1983 and 1992). Another relevant papers on the leaching of sulphide minerals with dichromate are those on pyrite, molybdenite concentrates (Ruiz and Padilla, 1998) and copper converter slag (Altundogan et al., 2004).

In this paper the effect of stirring, temperature and particle size on the dissolution rate of pyrite have been examined.

EXPERIMENTAL

CHARACTERIZATION OF PYRITE SAMPLES

Pyrite used in the experimental work was obtained from *Smolnik* (Slovak Republic). The results of its semi-quantitative spectral analysis were as follows (in wt. % as the element): 10^1 Fe; 10^{-1} Si; 10^{-2} Al, Bi, Ca, Mg; 10^{-3} Co, Pb, Ti, Cu. The chemical analysis showed that it contained 45.0% iron, 42.1% sulphur as sulphide and 2.5% sulphur as sulphate (the iron and sulphur were determined gravimetrically as Fe_2O_3 and $BaSO_4$, respectively). The X–ray diffraction patterns of the sample showed only pyrite lines.

LEACHING EXPERIMENTS

All experiments were performed with grains of the size <0.056 mm, except those relating to the effect of the particles size on the reaction kinetics. All reagents used were prepared from analytical grade chemicals and distilled water. In every experiment a flask containing 200 ml of acidic dichromate solution was submerged in a tank, the temperature of which was kept constant to within 0.1°C. When the required temperature had been reached, a charge of 0.2 g of pyrite was added and the stirring was started.

The leaching was carried out for 120 min during which seven 1 mL samples of the solution were taken for determination of the iron concentration by an atomic absorption method. The degree of dichromate reduction in the final solution was determined iodometrically.

RESULTS AND DISCUSSION

MORPHOLOGY OF UNREACTED PYRITE SAMPLE

SEM micrograph of unreacted pyrite particles presented in Fig.1 shows two different grain types (indicated by *a* and *b*). The first type (indicated by *a*) corresponds to a solid with a dense structure, smooth surfaces and sharp edges. In turn, the second type (marked by *b*) shows a solid with more round-shaped edges and porous surface. However, the inspection of cross-sections of the grains revealed the presence of micropores of various sizes beneath the surface (Fig.2.).

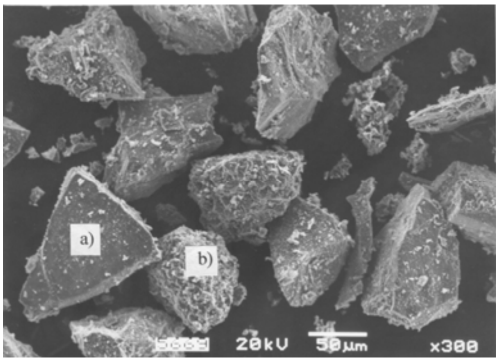

Fig. 1. SEM micrograph of unreacted pyrite sample

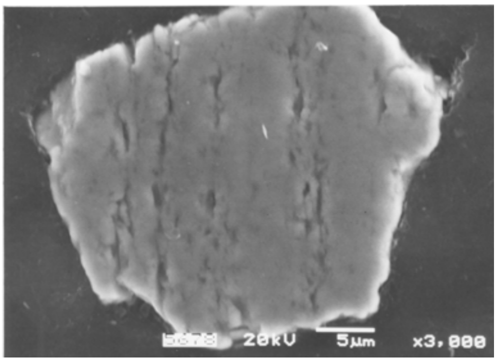

Fig. 2. SEM micrograph of unreacted pyrite grain cross-section

The electron microprobe analysis of the grain surface indicated by *a* in Fig.1 shows only iron and sulphur (Fig.3a), but the grain surface marked by *b* in Fig.1 indicates the presence of iron, sulphur and small peak of oxygen (Fig.3b).

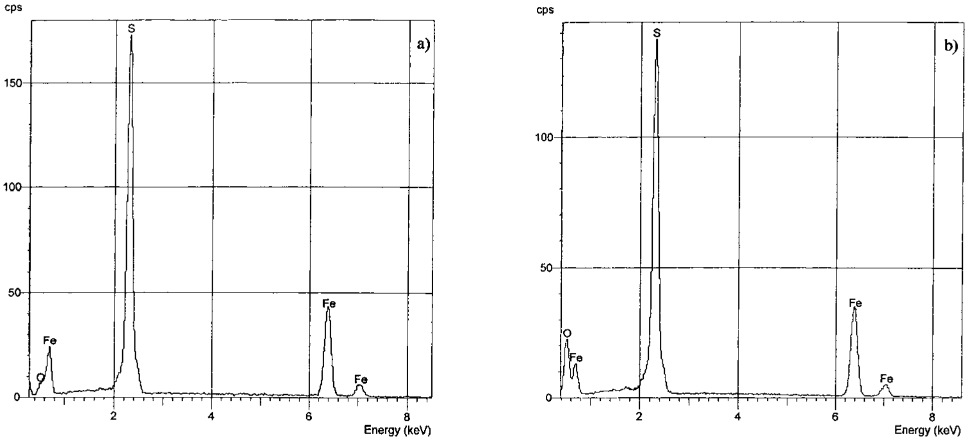

Fig. 3. Microprobe analyses of the grains marked by *a* and *b* in Fig.1

EFFECT OF STIRRING SPEED

The effect of stirring speed on the extraction of Fe from pyrite was investigated in a solution of 0.025 M $K_2Cr_2O_7$ and 0.5 M H_2SO_4 at 50°C. The variation of the stirring speed within the range 400–1200 min^{-1} had no effect on the rate. This indicates that the diffusion of the reactants from the solution toward the surface of the particle, and the products away from the particle, were fast, and hence did not control the leaching rate within the range of stirring speeds tested. All subsequent experiments were carried out at a stirring speed of 900 min^{-1} to assure invariance of this parameter.

EFFECT OF TEMPERATURE

The leaching was performed within the temperature range 30–90°C with an initial concentration of dichromate ions of 0.025 M and 0.5 M sulphuric acid at a constant stirring speed of 900 min^{-1}. The dissolution curves are shown in Fig.4. The high dissolution rate observed in the initial stage can be caused by soluble compounds already present in the raw material or oxides formed during grinding. The experimental data were analysed in terms of several models connecting the fraction reacted (α) and time (*t*) (Wadsworth, 1979).

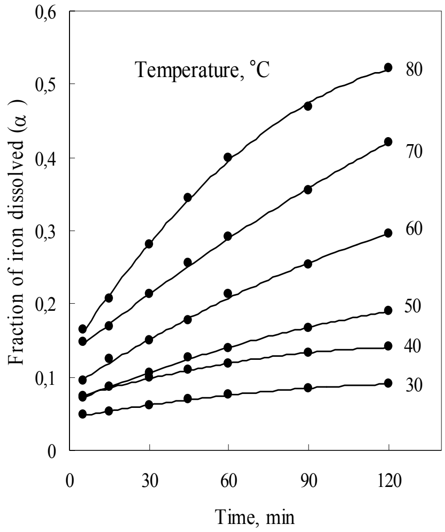

Fig. 4. Effect of temperature on the fraction of iron dissolved from pyrite in 0.025 M $K_2Cr_2O_7$ and 0.50 M H_2SO_4

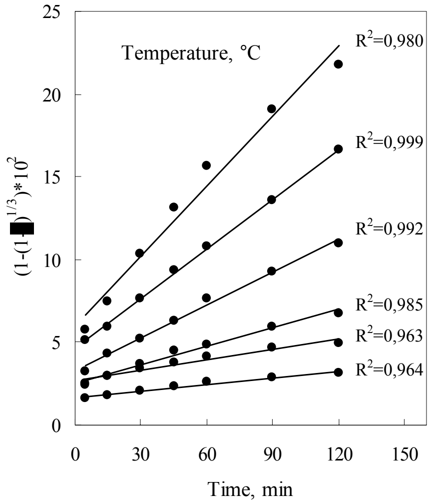

Fig. 5. A plot of the data in Fig.4 according to Eq. (1)

It seems that the model assuming chemical reaction on the surface of particles as the rate-limiting step of the process is correct. The following relationship *α(t)* is established:

$$1-(1-\alpha)^{1/3}=kt\,, \tag{1}$$

where $k\ [\text{min}^{-1}]=\dfrac{const}{d_0}$ is the rate constant, d_0 denotes the initial particle diameter (Wadsworth, 1979).

It is evident from Eq.(1) that the left-hand side plotted vs. *t* should result in a straight line. A plot of the data from Fig.4 for temperature range 30–90°C, made according to Eq.(1), is shown in Fig.5. The apparent rate constant, *k*, obtained from the slopes of the straight lines in Fig.5 was used to determine an activation energy of 43.5 ± 1.5 kJmol $^{-1}$, as shown in Fig.6. This confirms that the chemical reaction on the surface of particles is the rate-limiting step of the dissolution process. The results of microprobe analysis of the cross-sections of partially leached pyrite in acidic dichromate solutions do not show any elemental sulphur layer on the pyrite surface.

The degree of dichromate ion reduction in the final solutions showed that at all temperatures sulphide sulphur was oxidized to sulphate according to the following reaction:

$$2FeS_2 + 5Cr_2O_7^{2-} + 38H^+ = 2Fe^{3+} + 4SO_4^{2-} + 10Cr^{3+} + 19H_2O \qquad (2)$$

The influence of temperature on the consumption of the dichromate ions after 2 hours of pyrite dissolution is shown in Fig.7. A satisfactory agreement with the experimental data on the consumption of the dichromate ions and the theoretical ones calculated according to Eq.(2) is observed.

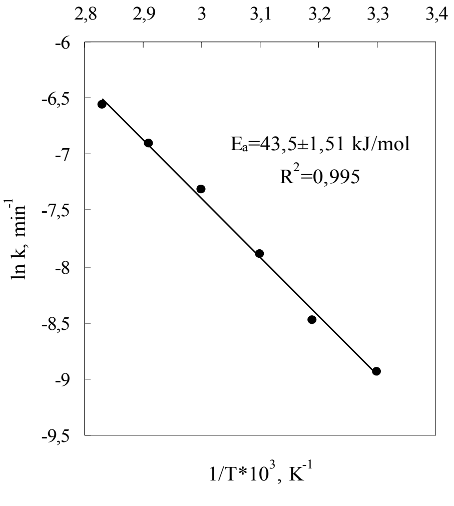

Fig. 6. Arrhenius plot for the dissolution of iron from pyrite in 0.025 M $K_2Cr_2O_7$ and 0.50 M H_2SO_4

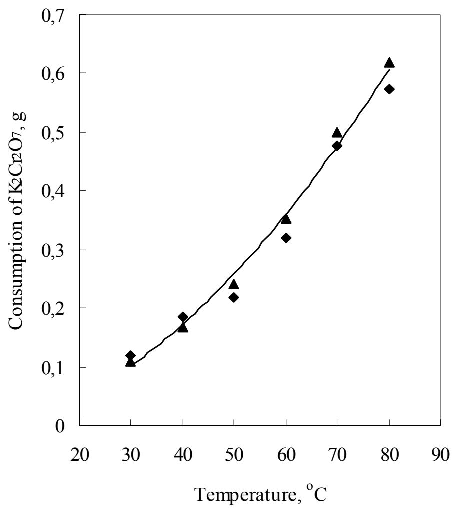

Fig. 7. Influence of temperature on the consumption of $K_2Cr_2O_7$, after 2 h of pyrite dissolution in 0.025 M $K_2Cr_2O_7$ and 0.5 M H_2SO_4, ▲ – experimental points, ■ – according to equation (2)

The oxidation of pyrite in acidic dichromate solution leads to a creation of large pits (Fig. 8). These pits may exhibit defined geometry and orientation. For instance, the pyramidal pits characterize the intercept of dislocation with (001) planes of cubic crystals (Ciminelli and Osseo-Asare, 1995).

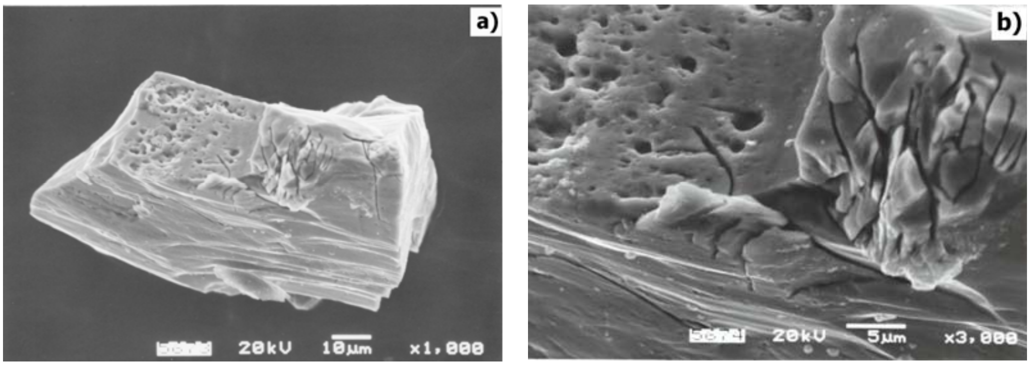

Fig. 8. SEM photograph of pyrite reacted in 0.5 M H_2SO_4 solution with 0.025 M $K_2Cr_2O_7$ addition at temperature 50°C ($\alpha = 21.2\%$): a) pyrite grain, b) fragment of the surface of this grain

EFFECT OF PARTICLE SIZE

The influence of particle diameter on the rate of iron extraction was examined by measuring the reaction rate for fractions of four sizes (in mm): <0.056, 0.040 – 0.056, 0.063 – 0.071 and 0.071 – 0.080, with 0.025 M $K_2Cr_2O_7$ in 0.5 M H_2SO_4 solution at 50°C.

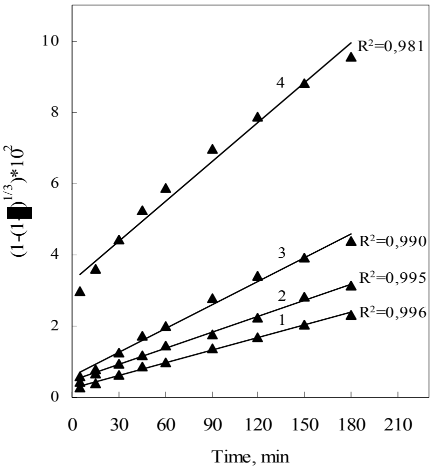

Fig. 9. The variation of $1 - (1 - \alpha)^{1/3}$ with time at various initial particle diameter d_0 of FeS_2

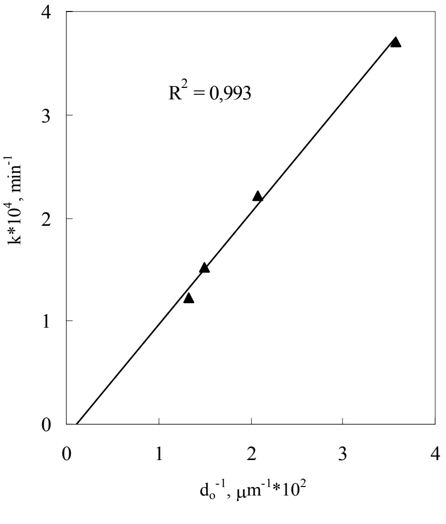

Fig. 10. A plot of the rate constant versus an initial particle diameter d_0 of FeS_2

The plot of $1-(1-\alpha)^{1/3}$ for various particle diameters is shown in Fig.9. As expected, the smaller is the particle size the faster the dissolution of pyrite is. Fig.10 shows the calculated apparent rate constants vs. the initial particle diameter d_0. The linear relationship between the rate constant k and the inverse of d_0 indicates that the chemical reaction on the surface of particles is, indeed, the rate-limiting step of the dissolution process.

CONCLUSIONS

From the results of these examinations the following conclusions can be drawn.

1. The oxidation of pyrite in acidic dichromate ion solutions results in the formation of sulphate ions.
2. The rate of pyrite dissolution was found to be independent on the stirring speed.
3. A linear relationship between the rate constant k and the inverse of the initial particle diameter was established.
4. The value of the apparent activation energy of 43.5 ± 1.5 kJ mol^{-1} supports the conclusion that the rate of dissolution is limited by the chemical reaction on the surface of particles.

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Chojnacka M. Wawrzak D., Mulak W., **Szymczycha-Madeja A.,** *Kinetyka ługowania pirytu w kwaśnym roztworze dichromianu potasu,* Physicochemical Problems of Mineral Processing, 41 (2007) 117-124 (w jęz. ang.).

Określono wpływ temperatury, wielkości ziaren oraz warunków hydrodynamicznych w roztworze na szybkość ługowania pirytu w kwaśnym roztworze $K_2Cr_2O_7$. W celu zbadania składu i morfologii powierzchni faz stałych przed i po ługowaniu wykonano analizy skaningowym mikroskopem elektronowym z mikrosondą rentgenowską. Na podstawie krzywych kinetycznych stosując zależność $f(\alpha)=1-(1-\alpha)^{1/3}$ od czasu obliczono stałe szybkości reakcji oraz energię aktywacji równą 43,5 ± 1,5 kJ/mol. Wartość energii aktywacji oraz liniowa zależność stałej szybkości reakcji od odwrotności średnicy ziaren wskazuje, że najwolniejszym etapem procesu jest reakcja chemiczna na powierzchni pirytu. Stwierdzono również, że w całym badanym zakresie temperatur (30-70^{o}C) jony S^{2-} utleniają się do jonów SO_4^{2-}.