EFFECT OF TEMPERATURE ON THE SELECTIVITY OF LEACHING OF HIGH-CALCIUM DEAD-BURNED MAGNESITE USING HYDROCHLORIC ACID

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Abstract
Leaching of particulate dead-burned magnesite with 0.5 M and 2.8 M hydrochloric acid was investigated with special regard to the effect of temperature (from 30°C to 60°C) on the rate of chemical dissolution of magnesium, calcium and iron. The leaching process was found to be selective at a given temperature, but no significant effect of temperature on the selectivity was observed. Maximum selectivity was reached in the initial stage of leaching and the differences in dissolution rates decreased with increase in fraction of dead-burned magnesite reacted. The difference between the “initial” fractions of the iron dissolved in diluted and concentrated hydrochloric acid is probably caused by much faster (“step-wise”) dissolution of the iron in the initial stage of leaching of dead-burned magnesite using 2.8 M hydrochloric acid solution.

Keywords: oxides, yield phenomena, magnesium, calcium, iron, chemical dissolution.

1 Introduction
Significance of hydrometallurgical processes for magnesium extraction from Slovak magnesites was explained in our recently published paper [1]. Though various chemical routs using solutions of acids to leach the raw or burned magnesite are referred to in the literature [2-11], the authors focused mostly on the leaching behaviour of the magnesium and the dissolution of other components was investigated rarely [1, 12-15]. Hence, there is a lack of relevant engineering data, which could be used to increase the overall efficiency of such processes by cutting the production costs related to the iron, calcium and other impurities removal.

In our previous work [1], the effect of acid concentration (from 0.1 M to 4.8 M) on the leaching of dead-burned magnesite with hydrochloric acid at 45°C was investigated with special regard to the rate of chemical dissolution of magnesium, calcium and iron. It was found out that the leaching of dead-burned magnesite with hydrochloric acid is selective in the initial stage of the process and the selectivity of leaching decreases with increase in fraction of dead-burned magnesite reacted; the initial difference in dissolution rates of iron and magnesium increased with increase in acid concentration.

The aim of the present work was to contribute to better understanding of the effect of temperature on the dissolution rates of magnesium, iron and calcium during the leaching of iron- and calcium-rich dead-burned magnesite.

Chemical dissolution of dead-burned magnesite in hydrochloric acid may be controlled by external mass transfer or by surface chemical reaction according to Eq. (1):
\[ Me_x O_y (s) + 2yH^+(aq.) \rightarrow xMe^{(2y/x)+} (aq.) + yH_2O(l) \],

where \( x=y=1 \) for MgO and CaO, \( x=2 \) and \( y=3 \) for Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\).

2 Materials and experimental methods

The bulk rotary-kiln product from the Jelšava plant, Slovakia was used in the present study. Sized fractions of the dead-burned magnesite were obtained by dry-milling and dry-screening. The physico-chemical characteristics of the sample used for the leaching experiments are given in Table 1. The sample was analysed by two different analytical methods (atomic absorption and X-ray fluorescent spectrometry), the specific surface area was determined by the BET nitrogen adsorption technique. Analytical reagent grade chemicals and distilled water were used in all experiments.

Table 1  Physico-chemical characteristics of the sample of dead-burned magnesite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle diameter (µm)</th>
<th>Specific surface area (m(^2).g(^{-1}))</th>
<th>Chemical composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSJE</td>
<td>90 - 200</td>
<td>0.11</td>
<td>MgO 85.4, CaO 7.2, Fe(_2)O(_3) 6.6, Al(_2)O(_3) 0.3, SiO(_2) 0.5</td>
</tr>
</tbody>
</table>

Leaching behaviour of the samples of dead-burned magnesite was tested in a 1.1 L isothermal well-mixed glass batch reactor (for more details see ref. [11]). When the HCl solution in the reactor had reached the required temperature, 1.0 g of dead-burned magnesite was added. 15 mL to 30 mL samples of the reaction mixture were withdrawn from the reactor at appropriate time intervals (2, 5, 10, 20, 40 and 60 minutes), filtered and the solutions were analysed. The calcium, magnesium and iron contents of the liquors were determined by atomic absorption, using model calibrating solutions.

The leaching experiments were carried out under reaction conditions, which were: temperature from 30°C to 60°C and concentration of HCl 0.5 M and 2.8 M.

Relatively high excess of the acid was used in all leaching experiments, to eliminate possible effects of the changes in lixiviant composition during individual runs on the rate of leaching. It was shown elsewhere [13,14] that the dissolution is practically isothermal, i.e. surface chemical reactions (1) took place at the temperature of bulk liquid.

3 Results and discussion

Dissolution of magnesium

The rate of dissolution of the magnesium is very sensitive to leaching temperature and there is practically no difference between the dissolution behaviour of the magnesium in 0.5 M and 2.8 M hydrochloric acid solution, as can be seen from Fig. 1a and b, respectively. Two sets of results obtained at the same temperature indicate the accuracy of the experimental method used in the present work.

Dissolution of calcium

Dissolution of the calcium in 0.5 M and 2.8 M HCl solutions at various temperatures is shown in Fig. 2a,b. The effect of temperature was stronger at higher HCl concentration. Furthermore,
significantly higher fractions of calcium dissolved (85% – 95%) were observed in the initial stage of leaching with 2.8 M HCl (Fig. 2b) if compared with those obtained for 0.5 M HCl solution (60% – 90%), especially at lower temperatures. Fig. 2a,b also indicates higher accuracy of the results obtained at the higher concentration of hydrochloric acid solution.

**Fig. 1** Effect of temperature on fraction of magnesium dissolved in hydrochloric acid solutions: a) 0.5 M HCl, b) 2.8 M HCl

**Fig. 2** Effect of temperature on fraction of calcium dissolved in hydrochloric acid solutions: 0.5 M HCl, b) 2.8 M HCl

**Dissolution of iron**

From Fig. 3a,b it is seen that the rate of dissolution of the iron is very sensitive to leaching temperature at both lower and higher HCl concentration, but there is a significant difference in the leaching behaviour of the iron in the initial stage of leaching. While the iron is dissolved continuously in 0.5 M HCl solution, a step-wise increase in fraction of the iron dissolved was observed in the initial period of the leaching process, especially at lower temperatures.

In the present work, the selectivity was measured using the three ratios

\[ Y_{Fe-Mg} = \frac{X_{Fe}(t)}{X_{Mg}(t)} , \]  

(2)
\[ Y_{\text{Ca-Mg}} = X_{\text{Ca}}(t):X_{\text{Mg}}(t), \]  
\[ Y_{\text{Ca-Fe}} = X_{\text{Ca}}(t):X_{\text{Fe}}(t), \]  

where \( X_{\text{Mg}}(t), X_{\text{Fe}}(t) \) and \( X_{\text{Ca}}(t) \) are the fractions of magnesium, iron and calcium, respectively, dissolved at 45°C in a solution of hydrochloric acid of defined concentration, during the same period of leaching time \( t \) \([1]\).

**Figs. 4, 5 and 6** reveal that no significant effect of leaching temperature on the selectivity of the leaching process was observed. In general, maximum selectivity was observed in the initial stage of the process and the difference in the dissolution rates decreased with increase in fraction of dead-burned magnesite reacted - the time behaviour of the selectivity of leaching is similar to that referred to in our previous work \([1]\).

It can be seen from **Fig. 4a,b** that the maximum (initial) values of \( Y_{\text{Fe-Mg}} \) ratio 3.6 and 5.0 were reached for 0.5 M and 2.8 M HCl, respectively. The \( Y_{\text{Fe-Mg}} = 1 \) asymptote was reached for \( X_{\text{Mg}} \geq 0.6 \) using 0.5 M HCl and \( X_{\text{Mg}} \geq 0.84 \) using 2.8 M HCl.

**Fig.4** \( Y_{\text{Fe-Mg}} \) vs. \( X_{\text{Mg}} \) dependence for leaching of the sample OSJE with hydrochloric acid solutions: a) 0.5 M HCl, b) 2.8 M HCl
Qualitatively identical results were obtained for $Y_{Ca-Mg}$ (Fig. 5a,b): the maximum values of $X_{Ca}:X_{Mg}$ ratio 16 and 13 were reached using 0.5 M and 2.8 M HCl, respectively. The $Y_{Ca-Mg} = 1$ asymptote was reached for $X_{Mg} \approx 1$ for both 0.5 M and 2.8 M HCl.

Different situation is shown in Fig. 6a,b: during the leaching with 0.5 M HCl solution, maximum (initial) values of $X_{Ca}:X_{Fe}$ ratio up to 5.5 were obtained for $X_{Fe} \approx 0.1$, while the initial values of $X_{Ca}:X_{Fe} \approx 2.7$ were obtained for $X_{Fe} \approx 0.3$ using 2.8 M HCl; the $Y_{Ca-Fe} \approx 1$ asymptote was reached for $X_{Fe} \approx 1$ in both cases. The difference between the “initial” fractions of the iron dissolved (i.e. the conversions of iron measured at $t = 120$ s) is caused by much faster (“step-wise”) dissolution of the iron in the initial stage of leaching of dead-burned magnesite with 2.8 M hydrochloric acid solution.

![Graph](a)

![Graph](b)

**Fig. 5** $Y_{Ca-Mg}$ vs. $X_{Mg}$ dependence for leaching of the sample OSJE with hydrochloric acid solutions: a) 0.5 M HCl, b) 2.8 M HCl

![Graph](a)

![Graph](b)

**Fig. 6** $Y_{Ca-Fe}$ vs. $X_{Fe}$ dependence for leaching of the sample OSJE with hydrochloric acid solutions: a) 0.5 M HCl, b) 2.8 M HCl

### Conclusions

In the present work, leaching of dead-burned magnesite with 0.5 M and 2.8 M hydrochloric acid solutions was investigated with special regard to the effect of leaching temperature (from 30°C...
to 60 °C) on the rate of chemical dissolution of magnesium, calcium and iron. Selectivity of the leaching process is presented in terms of ratios defined using Eqs. (2) to (4). The conclusions are as follows:

a) There is a significant difference in the leaching behaviour of the iron in the initial stage of leaching. While the iron is dissolved continuously in 0.5 M HCl solution, a step-wise increase in fraction of the iron dissolved was observed in 2.8 M HCl solution during the initial period of the leaching process, especially at lower temperatures.

b) The leaching of dead-burned magnesite with hydrochloric acid is selective, but no significant effect of leaching temperature on the selectivity of the leaching process was observed under the conditions considered in the present work.

c) Selectivity of leaching decreases with increase in fraction of dead-burned magnesite reacted.

d) Maximum selectivity can be observed in the initial stage of the process; related values of the ratios $Y$ are: $Y_{Fe-Mg} = 3.6$ and 5.0, $Y_{Ca-Mg} = 16$ and 13, and $Y_{Ca-Fe} = 5.5$ and 2.7 for 0.5 M and 2.8 M HCl, respectively.

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