

Effect of hydrochloric acid concentration on the selectivity of leaching of high-calcium dead-burned magnesite

Pavel Raschman¹, Marianna Špáková and Alena Fedoročková²

Leaching of particulate dead-burned magnesite with hydrochloric acid at 45 °C was investigated with special regard to the effect of acid concentration (from 0.1 M to 4.8 M) on the rate of chemical dissolution of magnesium, calcium and iron. The leaching process was found to be mostly selective in the initial stage and the differences in dissolution rates decreased with an increase in the fraction of dead-burned magnesite reacted.

Key words: magnesium; calcium; iron; chemical dissolution.

Introduction

A decreasing consumption of refractory materials and increasing demand for their purity in modern steelmaking push the producers of burned magnesite to improve their technological processes, and to look for new applications of their products in the industry, agriculture and the environment protection, as well.

The iron in the iron-rich magnesites mined in Austria and Slovakia is of the isomorphous type since it has replaced some magnesium ions in the carbonate lattice and its content can only be marginally reduced by physical separation. Hence, the family of so-called “chloride” hydrometallurgical processes has been developed for upgrading Slovak magnesites during past three decades. The common feature of these processes is that burned magnesite is leached with acidic chloride solutions. In the “primary chloride process”, for example, magnesite flue-dusts (trapped in dust-collectors of rotary and shaft kilns for producing dead-burned magnesite) are dissolved in hydrochloric acid to produce a magnesium chloride solution from which the impurities are removed using precipitation, filtration and extraction. The solution is then thermally decomposed to recover the high-grade magnesia with an extremely low boron content (Sehnálek and Raschman, 1992). However, various chemical routs using other acids to leach the raw or burned magnesite are also referred to in the literature (Bakan et al., 2006; Bayrak et al., 2006, 2010; Demir and Dönmez, 2008; Dönmez et al., 2009; Lacin et al., 2005; Özbek et al., 1999; Ranjitham and Khangaonkar, 1990; Raschman, 1997, 2000; Sučík et al., 2009).

The overall efficiency of such a hydrometallurgical or chemical process can be enhanced by increasing the yield of magnesium (especially in the leaching stage) and/or cutting the production costs related to the iron, calcium and other impurities removal. The dissolution behaviour of magnesium during the leaching of dead-burned magnesite with hydrochloric acid under various reaction conditions has been intensively studied (Fedoročková et al., 2007; Raschman et al., 2001; Raschman and Fedoročková, 2004a, 2004b). It was observed that the dissolution of MgO is strongly affected by the temperature and particle size, while the effect of composition of the solid is weak. The dissolution of MgO is controlled by the chemical reaction of MgO with H⁺ ions at the liquid-solid interface. The apparent activation energy is 58-64 kJ.mol⁻¹. The acid concentration (higher than 1.0 M) was surprisingly found to have a decelerating effect on the dissolution rate of MgO, resulting in the negative reaction order for H⁺ ions (Raschman and Fedoročková, 2004a). Another question is how to operate the leaching process selectively. It would be advantageous, in general, to reach a maximum yield of the magnesium and minimum yields of the iron and calcium dissolved during the leaching, because the expenses for the impurities removal could be decreased. Unfortunately, there is a lack of relevant engineering data.

The aim of the present work was to study the effect of hydrochloric acid concentration on the dissolution rates of magnesium, iron and calcium during the leaching of iron- and calcium-rich dead-burned magnesite. Prospective raw-materials for an actual technological process are, in general, mixtures of fine particles of (reactive) calcined magnesite (characterised by a high content of reactive MgO) and dead-burned magnesite (with MgO of low reactivity) (Hančulák and Bobro, 2004; Sehnálek and Raschman, 1992). The reactivity of calcined magnesite is much higher, therefore the dissolution of dead-burned magnesite component in hydrochloric acid can, under certain conditions, control the overall output of the leaching reactor.

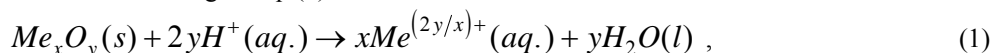
¹ prof. Ing. Pavel Raschman, CSc., Mgr. Marianna Špáková, Technical University of Košice Faculty of Metallurgy Department of Ceramics Park Komenského 3, Slovak Republic

² doc. RNDr. Alena Fedoročková, Technical University of Košice Faculty of Metallurgy Department of Chemistry Letná 9, Slovak Republic (Review and revised version 15. 1. 2011)

Theoretical

Chemical dissolution of burned magnesite in hydrochloric acid is a liquid-solid reaction in which no solid product is formed. Due to sintering, dead-burned magnesite is practically non-porous, which means that the rates of dissolution of individual species may be controlled by the intrinsic chemical reaction or by the external mass transfer (Sohn and Wadsworth, 1979). Dissolution of each component involves the following steps in series:

1. diffusion of H^+ ions through the liquid film at the liquid-solid interface to the surface of the solid particles;
2. surface chemical reaction according to Eq. (1):



where $x=y=1$ for MgO and CaO, $x=2$ and $y=3$ for Fe_2O_3 and Al_2O_3 ;

1. diffusion of liquid products of the reactions (1) from the interface through the film to the bulk liquid.

Experimental

Materials

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.

Tab. 1. Physico-chemical characteristics of the sample of dead-burned magnesite.

Sample	Particle diameter (μm)	Specific surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Chemical composition (wt.%)				
			MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2
OSJE	90 - 200	0.11	85.4	7.2	6.6	0.3	0.5

Leaching procedure and measuring kinetic data

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. (Raschman, 2000).

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 45 °C and concentration of HCl from 0.1 M to 4.8 M.

Results

Dissolution of magnesium

The experiments showed that the rate of transfer of the magnesium into the solution increased with increase in HCl concentration up to 0.5 M and then decreased with further increase in HCl concentration. The situation is illustrated in Fig. 1. The results shown in Fig. 1 are very similar to those observed in the previous studies (Raschman and Fedoročková, 2004a), which supports the hypothesis that the inhibiting effect of HCl concentration on the dissolution rate of magnesium oxide in concentrated solutions is a characteristic feature of the system MgO-HCl- H_2O .

Dissolution of calcium

It was observed that the fraction of calcium dissolved reached 65-100 % before the first sample of the reaction mixture was withdrawn from the reactor. The situation is shown in Fig. 2.

Dissolution of iron

From Fig. 3, it is seen that an initial period of the iron dissolution characterised by relatively high dissolution rates was observed, followed by a period of lower (and continuously decreasing) dissolution rate. High initial dissolution rates were observed at higher HCl concentrations.

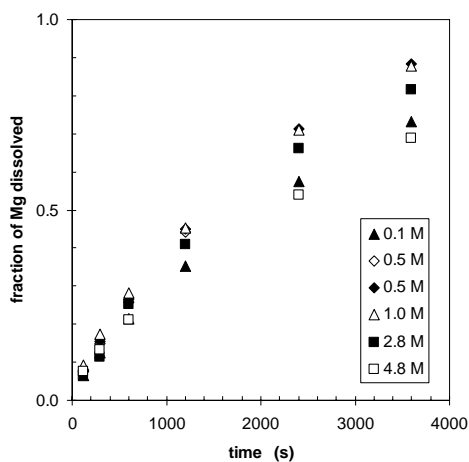


Fig. 1. Effect of hydrochloric acid concentration on fraction of magnesium dissolved at 45°C.

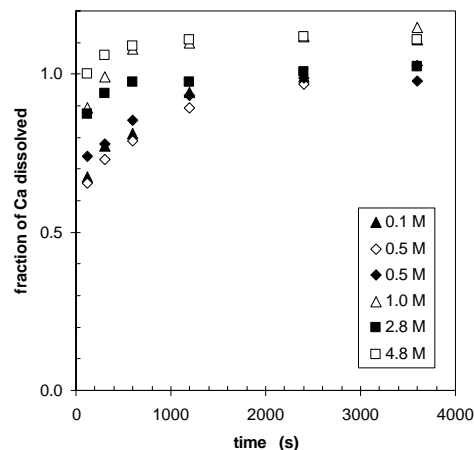


Fig. 2. Effect of hydrochloric acid concentration on fraction of calcium dissolved at 45°C.

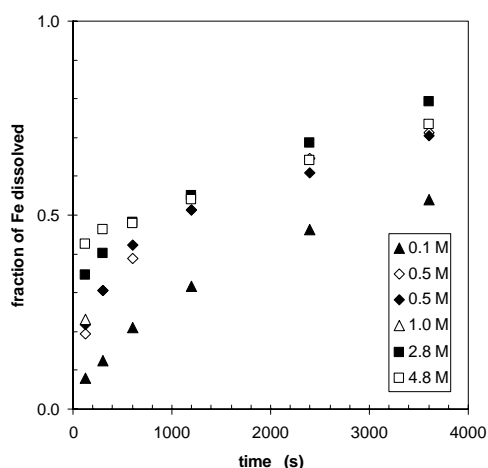


Fig. 3. Effect of hydrochloric acid concentration on fraction of iron dissolved at 45 °C.

Discussion

Experimental method

Leaching behaviour of dead-burned magnesite was tested under reaction conditions which were characterised 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.

It was shown elsewhere (Raschman and Fedoročková, 2004a) that the dissolution is practically isothermal, i.e. surface chemical reactions (1) took place at the temperature of bulk liquid.

Two sets of results presented for 0.5 M HCl indicate the accuracy of the experimental method used in the present work.

Selectivity of leaching

In general, the leaching process is selective when different dissolution rates of the magnesium, iron and calcium are observed under given reaction conditions (temperature, HCl concentration, particle size). In the present work, the selectivity was measured using three ratios defined as

$$Y_{Fe-Mg} = X_{Fe}(t):X_{Mg}(t), \quad (2)$$

$$Y_{Ca-Mg} = X_{Ca}(t):X_{Mg}(t) \quad (3)$$

$$Y_{Ca-Fe} = X_{Ca}(t):X_{Fe}(t), \quad (4)$$

where $X_{Mg}(t)$, $X_{Fe}(t)$ and $X_{Ca}(t)$ 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 . The leaching process is not selective if

$$Y_{Fe-Mg} = Y_{Ca-Mg} = Y_{Ca-Fe} = 1. \quad (5)$$

Figs. 4, 5 and 6 reveal that the leaching of the sample OSJE with hydrochloric acid is selective. 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. For example, it can be seen from Fig. 4 that the values of $X_{Fe}:X_{Mg}$ ratio up to 6.7 were obtained for $X_{Mg} \approx 0.06$, while practically no difference in fractions of the magnesium and iron dissolved (i.e. $Y_{Fe-Mg} \approx 1$) was observed for $X_{Mg} \geq 0.6$. Furthermore, the maximum values of Y_{Fe-Mg} increase with increase in acid concentration; $Y_{Fe-Mg} = 1.4$ and 6.7 were obtained for HCl concentration 0.1 M and 4.8 M, respectively.

Fig. 5 shows that $X_{Ca}:X_{Mg}$ ratio up to 15 was obtained for $X_{Mg} \approx 0.06$, while practically identical fractions of the magnesium and calcium dissolved (i.e. $Y_{Ca-Mg} \approx 1$) were observed for $X_{Mg} \geq 0.8$. Unlike Y_{Fe-Mg} , no significant effect of HCl concentration on Y_{Ca-Mg} was observed due to bigger error (up to $\pm 10\%$ rel.) of measurement of the calcium concentration in the liquor. Similar situation is shown in Fig. 6; $X_{Ca}:X_{Fe}$ ratio up to 8.4 was obtained for $X_{Fe} \approx 0.08$, the $Y_{Ca-Fe} \approx 1$ asymptote was reached for $X_{Fe} \geq 0.85$ and no significant effect of HCl concentration on Y_{Ca-Fe} was observed.

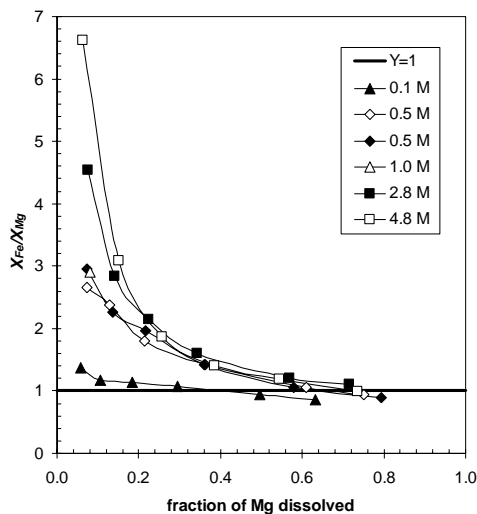


Fig. 4. Y_{Fe-Mg} vs. X_{Mg} dependence for leaching of the sample OSJE with 0.1, 0.5, 1.0, 2.8 and 4.8 M hydrochloric acid at 45°C.

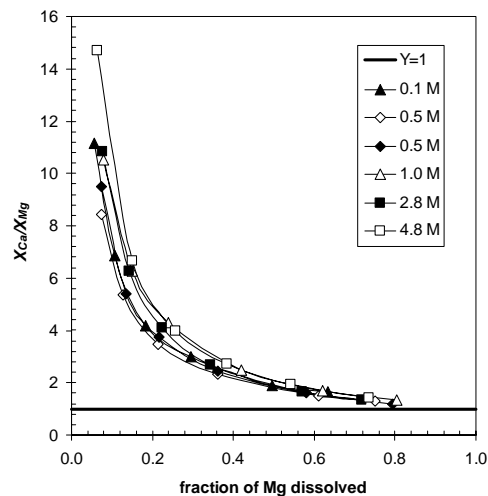


Fig. 5. Y_{Ca-Mg} vs. X_{Mg} dependence for leaching of the sample OSJE with 0.1, 0.5, 1.0, 2.8 and 4.8 M hydrochloric acid at 45°C.

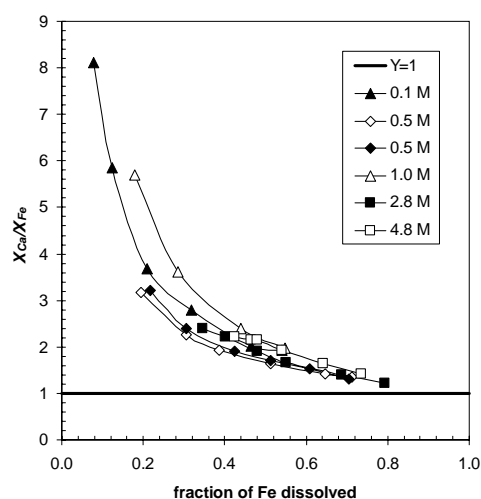


Fig. 6. Y_{Ca-Fe} vs. X_{Fe} dependence for leaching of the sample OSJE with 0.1, 0.5, 1.0, 2.8 and 4.8 M hydrochloric acid at 45 °C.

Conclusions

In the present work, leaching of dead-burned magnesite with hydrochloric acid at 45°C was investigated with special regard to the effect of acid concentration (from 0.1 M to 4.8 M) 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:

- The leaching of dead-burned magnesite with hydrochloric acid is selective.
- Maximum selectivity can be observed in the initial stage of the process; related values of the ratios Y are: $Y_{Fe-Mg} = 6.7$, $Y_{Ca-Mg} = 15.0$ and $Y_{Ca-Fe} = 8.4$.
- Selectivity of leaching decreases with an increase in the fraction of dead-burned magnesite reacted.
- While the maximum values of Y_{Fe-Mg} increase with the increase in the acid concentration ($Y_{Fe-Mg} = 1.4$ and 6.7 were obtained for the HCl concentration 0.1 M and 4.8 M, respectively), no significant effect of HCl concentration on Y_{Ca-Mg} and Y_{Ca-Fe} was observed under the conditions considered in the present work.

Acknowledgements: This publication is the result of the project implementation OPVaV-2008/2.1/01-SORO "Research Excellence Centre on Earth's sources extracting and treatment (Project No. 26220120017)" supported by the Research & Development Operational Programme funded by the ERDF.

References

- Bakan, F., Lacin, O., Bayrak, B., Sarac, H.: Dissolution kinetics of natural magnesite in lactic acid solutions. *Int. J. Miner. Process.* 80, 27-34, 2006.
- Bayrak, B., Lacin, O., Bakan, F., Sarac, H.: Investigation of dissolution kinetics of natural magnesite in gluconic acid solutions. *Chemical Engineering Journal* 117, 109-115, 2006.
- Bayrak, B., Lacin, O., Sarac, H.: Kinetic study on the leaching of calcined magnesite in gluconic acid solutions. *Journal of Industrial and Engineering Chemistry* 16, 479-484, 2010.
- Demir, F., Dönmez, B.: Optimization of the dissolution of magnesite in citric acid solutions. *Int. J. Miner. Process.* 87, 60-64, 2008.
- Dönmez, B., Demir, F., Lacin, O.: Leaching kinetics of calcined magnesite in acetic acid solutions. *Journal of Industrial and Engineering Chemistry* 15, 865-869, 2009.
- Fedoročková, A., Raschman, P., Sučík, G., Briančin, J.: Changes in the surface morphology of magnesia particles due to the leaching using hydrochloric acid. *Acta Montanistica Slovaca* 12(3), 212-216, 2007.

- Hančulák, J., Bobro, M.: Influence of Magnesite Industry on Emission Load by Solids in the Area of Jelšava. *Acta Montanistica Slovaca* 9(4), 401-405, 2004.
- Lacin, O., Dönmez, B., Demir, F.: Dissolution kinetics of natural magnesite in acetic acid solutions. *Int. J. Miner. Process.* 75, 91-99, 2005.
- Özbek, H., Abali, Y., Colak, S., Ceyhun, I., Karagölge, Z.: Dissolution kinetics of magnesite mineral in water saturated by chlorine gas. *Hydrometallurgy* 51, 173-185, 1999.
- Ranjitham, A. M., Khangaonkar, P. R.: Leaching behaviour of calcined magnesite with ammonium chloride solutions. *Hydrometallurgy* 23, 177-189, 1990.
- Raschman, P.: Kinetics of leaching of burned natural magnesite. *Acta Metallurgica Slovaca* 3(4), 284-291, (in Slovak), 1997.
- Raschman, P.: Leaching of calcined magnesite using ammonium chloride at constant pH. *Hydrometallurgy* 56, 109-123, 2000.
- Raschman, P., Fedoročková, A., Sučík, G.: Applicability of kinetic leaching data to the phase analysis of complex oxides. *Acta Metallurgica Slovaca* 4, Special Issue 2001/4, 140-147.
- Raschman, P., Fedoročková, A.: Study of inhibiting effect of acid concentration on the dissolution rate of magnesium oxide during the leaching of dead-burned magnesite. *Hydrometallurgy* 71, 403-412, 2004a.
- Raschman, P., Fedoročková, A.: Relationship between composition and leaching behaviour of dead-burned magnesite in hydrochloric acid. *Acta Metallurgica Slovaca* 10, Special Issue 2004/2, 231-238 (in Slovak) 2004b.
- Sehnálek, F., Raschman, P.: Production of pure magnesite refractories. *Chemické listy (Chemical Papers)* 86, 611-616, (in Slovak) 1992.
- Sohn, H. Y., Wadsworth, M. E., (Eds.): Rate Processes of Extractive Metallurgy. *Plenum Press, New York, 1979.*
- Sučík, G., Hreus, M., Fedoročková, A., Hršák, D.: Dehydroxylation of the serpentinite before its chemical treatment. *Acta Montanistica Slovaca* 14(1), 33-37, 2009.