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S. E. Ghazy[a]; M. A. Kabil[a]; A. M. Abeidu[a]; N. M. El-Metwally[a]
[a] DEPARTMENT OF CHEMISTRY FACULTY OF SCIENCE, MANSOURA UNIVERSITY, MANSOURA, EGYPT

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Selective Separation of Magnesium from Olivine Minerals

S. E. GHAZY, M. A. KABIL, A. M. ABEIDU,
and N. M. EL-METWALLY
DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
MANSOURA UNIVERSITY
P.O. BOX 66, MANSOURA, EGYPT

ABSTRACT

The aim of this investigation was the selective separation of Mg(II) from olivine, $(Mg,Fe)SiO_4$. The feasibility of leaching of Mg^{2+}, Fe^{2+}, and Fe^{3+} from olivine and serpentinized olivine with HCl or H_2SO_4 solutions of pH $\sim$ 2 or 3.5 has been examined. The results obtained showed that, under identical conditions, HCl solution is more effective than H_2SO_4 in leaching of Mg^{2+} as well as Fe^{2+}, and that the optimum pH is <3.5. Magnesium ions are selectively and quite effectively separated from the leaching solution by precipitation of $Mg(OH)_2$ at pH $\sim$ 11.5 since most, if not all, other metal ions that exist in natural samples are pre-precipitated as hydroxides and separated by filteration. Alternatively, Mg^{2+} is selectively separated from the leaching solution by flotation as magnesium oleate in the 7.0–8.5 pH range.

INTRODUCTION

Magnesium is the lightest of the industrial metals employed on a large scale (1–4). It finds extensive uses in bombs, pyrotechnics, photographs, cameras, and a number of household gadgets; as a reducing agent for the production of Zr, Hf, U, Be, etc.; as cathodic protection for steel pipelines; and as a negative electrode in primary electric cells. Moreover, its alloys are used in the manufacture of many machinery parts for various industries: automotive, textile, and aircraft. Hence, the recovery of magnesium from its natural sources is a vital process.

Magnesium does not occur naturally as a native element but always in the combined state in the form of such minerals and salts as magnesite, $MgCO_3$; dolomite, $CaMg(CO_3)_2$; talc, $Mg_3SiO_4O_{10}(OH)_2$; brucite, $Mg(OH)_2$; chrysotile, $Mg(Si_2O_5)(OH)_4$; tremolite, $Ca_2Mg_5Si_8O_{22}(OH)_2$; epsomite, $MgSO_4{\cdot}7H_2O$; carnallite, $MgCl_2{\cdot}KCl{\cdot}6H_2O$; olivine, (Mg,Fe)-$SiO_4$; and serpentine, $(Mg,Fe)_3Si_2O_5(OH)_4$ (5, 6). Of these, magnesite and dolomite are presently considered to be of commercial importance. This may due to their occurrence in vast quantities coupled with the ease of extraction of magnesium from them. However, no data are available in the literature about the extraction of magnesium from silicate minerals. Therefore, the objective of this investigation is to study the feasibility and amenability of selective separation of Mg^{2+} from olivine and serpentinized olivine. This goal is achieved by leaching with HCl at $pH < 3.5$. Then the pH of the leachate is increased to an extent permitting the precipitation of most concomitant species (especially Fe^{2+} and Fe^{3+}) with magnesium, followed by filtration. Magnesium ions in the filtrate are collected in the pure state by either precipitation with lime or flotation using the very cheap and available oleic acid soap as a collector after adjusting the pH to the optimum.

EXPERIMENTAL

Reagents

All chemical reagents used were of analytical or equivalent grades. Oleic acid used for the preparation of sodium oleate was of technical grade.

Minerals

Olivine minerals consist of transparent round pebbles with a green or yellowish-green color. Distributed rocks of magnesium minerals occur in the Eastern Desert of Egypt (7). Reasonably pure crystals of olivine and serpentinized olivine were used throughout this investigation. Infrared analyses showed that the samples used were clean and free from locked particles and gangue. They were crushed, ground in an agate mortar, and screened to a $-100+200$ mesh fraction for leaching tests and to a -300 mesh fraction for infrared studies.

Apparatus

A Perkin-Elmer 2380 atomic absorption spectrophotometer was used throughout for quantitative determination of metal ions. The infrared spectra were recorded on a Perkin-Elmer 1430 ration spectrophotometer. The pH measurements were carried out using a Hanna Instruments 8519 digital pH meter.

Procedure

Leaching of Mg^{2+} and Fe^{2+}

The feasibility of leaching Mg^{2+} and Fe^{2+} from the surface of olivine particles was studied as follows: 5 g of an olivine −100+200 mesh fraction was introduced into a 250-mL beaker. To this olivine sample, 100 mL of aqueous hydrochloric or sulfuric acid solution of the desired pH was added. The pulp was stirred by means of a magnetic stirrer for the required time. The leaching rate (dissolution) of Mg^{2+} and Fe^{2+} and/or Fe^{3+} was determined by periodically pipetting a 25-ml aliquot from the supernatant solution for quantitative determination of Mg^{2+} and Fe^{2+} (Fe^{3+}) as described previously (8–10).

The selective separation of Mg^{2+} from the leachate was achieved either by precipitation of Mg^{2+} as $Mg(OH)_2$ at pH ~ 11.5 after filtration of the hydroxides of the contaminated metals or by ionic flotation of it as magnesium oleate.

Ionic Flotation

Ionic flotation of Mg^{2+} from the leaching solution of olivine or serpentinized olivine was carried out by precipitating metal hydroxides (especially that of iron) and filtering. To 50 mL of the filtrate (2.5 g/L Mg^{2+}) in a 100 mL beaker, 12 mL of sodium oleate (1 g/L) was added and the pH was adjusted to the optimum pH range (7.5–8.5). The magnesium oleate formed is self-floatable and does not need any air bubbles. The optimum time of flotation was 5 minutes, after which the floated magnesium oleate was separated from the mother liquor by means of separating funnels. The recovery and effectiveness of selective separation were calculated by quantitative determination of Mg^{2+} in the residual solution from the relation, $R = (C_i - C_r)/C_i \times 100\%$, where C_i and C_r denote the initial and residual concentrations of Mg^{2+} in the mother liquor as described previously (11). Alternatively, the recovery may be calculated by quantitative determination of Mg^{2+} in the float after dissolving it in a mixture of concentrated HNO_3 and methyl alcohol (1:3).

RESULTS AND DISCUSSION

Leaching of Mg^{2+} and Fe^{2+}

Figures 1 and 2 report the feasibility of leaching of Mg^{2+}, Fe^{2+}, and Fe^{3+} from olivine and serpentinized olivine with HCl and H_2SO_4 solutions of pH 2 and 3.5 at different times. Note that there is a direct and close relationship between the amount of Mg^{2+} and that of Fe^{2+} leached, but the rate of dissolution is not constant. The rate of dissolution is relatively

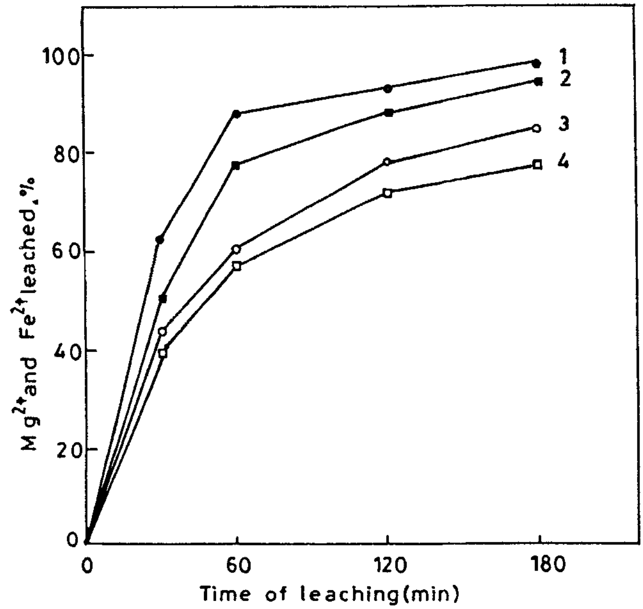

FIG. 1 Leaching of Mg^{2+} and Fe^{2+} from olivine (−100+200 mesh fraction) by HCl as a function of time and pH. Curves 1 and 3: Mg^{2+} and Fe^{2+} at pH 2, respectively. Curves 2 and 4: Mg^{2+} and Fe^{2+} at pH 3.5, respectively.

high during the initial 60 minutes, after which it increases regularly up to 2 hours. Any further increase of the time of leaching has only a slight effect.

An increase of pH of the leaching solutions from 2 to 3.5 caused a substantial change in the rate and in the total amount of leachable Mg^{2+}, Fe^{2+}, and Fe^{3+}. An interpretation of these results may be possible if we take into consideration the chemical characteristics of olivine- and serpentine-forming cations, namely Mg^{2+}, Fe^{2+}, and Fe^{3+} in acid medium. Since magnesium only exists in one valence state (1), whereas iron is capable of existing in more than one valence state in combination with anions, there is a difference in the solubilities between the valence states of iron in acid medium, and the prevailing redox potential may seriously affect the mobility of iron. Indeed, it has been well established that precipitation of $Fe(OH)_3$ occurs in the pH range 2.1–3.5 whereas precipitation of Fe^{2+} as $Fe(OH)_2$ requires a much higher pH value (pH 7.5–9.5) (12, 13).

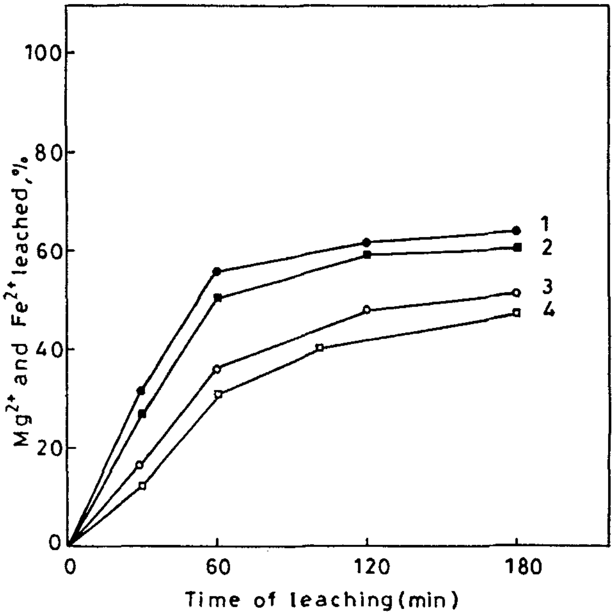

FIG. 2 Leaching of Mg^{2+} and Fe^{2+} from olivine (– 100 + 200 mesh fraction) by H_2SO_4 as a function of time and pH. Curves 1 and 3: Mg^{2+} and Fe^{2+} at pH 2, respectively. Curves 2 and 4: Mg^{2+} and Fe^{2+} at pH 3.5, respectively.

It seems reasonably to assume that at pH ≤ 3.5, olivine and serpentine break down to the individual cations (Mg^{2+}, Fe^{2+}, and Fe^{3+}) contained therein, which would be expected to assume their preferential octahedral structures: $[Mg(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$, and $[Fe(H_2O)_6]^{3+}$. This is in accord with the well-established phenomenon that dissolution of minerals is enhanced by reagents able to complex minerals which form cations (14, 15). This may also explain the sensitivity of serpentine, which contains Fe^{3+}, to the pH values of the leaching solutions (Figs. 3 and 4). Thus, $[Fe(H_2O)_6]^{3+}$ is a fairly strong acid and undergoes acid ionization such as (16):

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + H^+ \qquad (pK = 2.21)$$

The first ionization constant for $[Fe(H_2O)_6]^{3+}$ is comparable to the second ionization constant for sulfuric acid, being about 2.1×10^{-2}.

Accordingly, when conditions are suitably reducing and the pH is ≤ 3.5, much of the iron may be leached from olivine, whereas if the environment

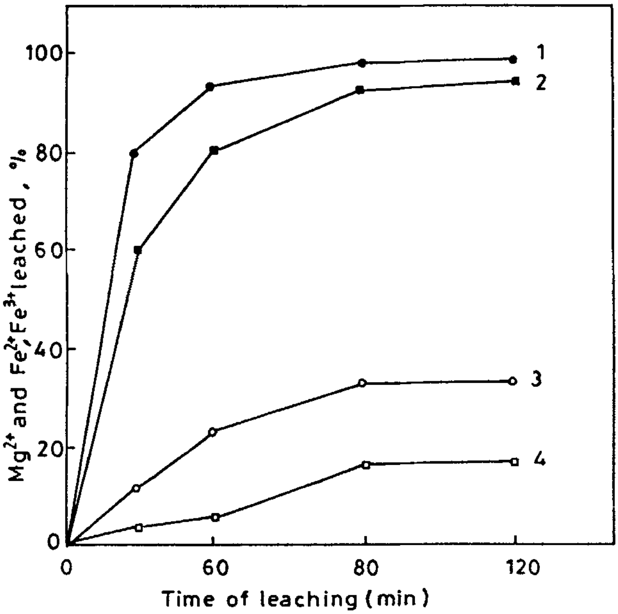

FIG. 3 Leaching of Mg^{2+} and $Fe^{2+}(Fe^{3+})$ from serpentinized olivine (−100+200 mesh fraction) by HCl as a function of time and pH. Curves 1 and 3: Mg^{2+} and $Fe^{2+}(Fe^{3+})$ at pH 2, respectively. Curves 2 and 4: Mg^{2+} and $Fe^{2+}(Fe^{3+})$ at pH 3.5, respectively.

is oxidizing and the pH is ≥3.5, iron is rendered immobile and is stabilized in the Fe(III) state. Moreover, it has been reported that solutions of salts of tervalent metal ions are acidic due to their hydrolysis. Only the formation of mononuclear hydrolysis products was considered for a long time, but Bjerrum and others assumed that in the hydrolysis of some metal(III) cations, polynuclear complexes, e.g., $M_2(OH)_2^{4+}$ and $M_2(OH)_4^{2+}$, are also formed. In the last two decades the hydrolysis of different metal ions has been extensively investigated (15). Moreover, it is also well established that metal cations exist in acidic solution as aquo complexes and that different mono- and polynuclear oxo- and hydroxo-complexes are formed on adding alkali.

The role played by hydrogen ion in leaching cannot be ignored. Not only does it initiate distribution of the crystal structure but its concentration also influences the solution and precipitation of some of the released ions. However, hydrogen ion concentration is not an independent variable in leaching but rather is a function of several interrelated factors: composi-

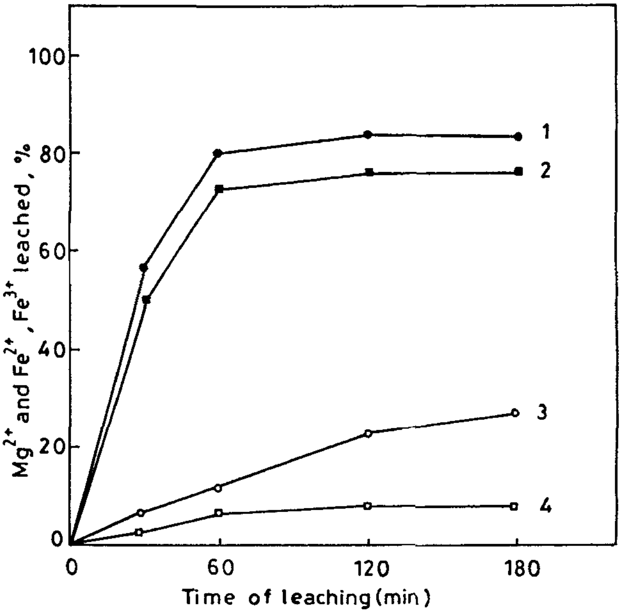

FIG. 4 Leaching of Mg^{2+} and $Fe^{2+}(Fe^{3+})$ from serpentinized olivine (– 100 + 200 fraction) by H_2SO_4 as a function of time and pH. Curves 1 and 3: Mg^{2+} and $Fe^{2+}(Fe^{3+})$ at pH 2, respectively. Curves 2 and 4: Mg^{2+} and $Fe^{2+}(Fe^{3+})$ at pH 3.5, respectively.

tion and structure of the minerals to be leached, the rate of leaching, the nature and, in particular, the cation-exchange capacity of the residual mineral product. Minerals break down primarily because some of their constituent atoms and ions are dissolved and effectively removed from the environment. The loss of those constituents renders the existing mineral structure unstable, and new crystalline phases tend to form. Thus, when conditions are suitable for reduction and the pH < 3.5, iron may be leached from iron-bearing minerals such as olivine and serpentine. In contrast, if the environment is suitable for oxidation, iron is stabilized even in a fairly strong acid media (pH <3.5) (Figs. 1–4).

It has been reported that the dissolution and behavior of various ion-leaching reactions can be related directly to their ionic potential, which is a fundamental property of the element because it is closely related to the element's electronegativity. Ionic potential is expressed numerically as the ratio of the charge in valency units to the ionic radius in Angstrom units. Consequently, both Mg^{2+} and Fe^{2+} have an ionic potential of 2.6

(14), i.e., less than 3, making them tend to pass to the leaching solution in ionic form (14). On the other hand, Fe^{3+} has an ionic potential of 4.5, i.e., much greater than 3 and less than 9, which makes it precipitate and become concentrated in the residue (14).

Figures 1–4 indicate the superiority of HCl over H_2SO_4 in leaching olivine and serpentinized olivine. This may be attributed to its nonoxidizing properties coupled with the ability of Cl^- ions to form complex soluble anions with olivine-forming cations, namely Mg^{2+} and Fe^{2+}, of the type $MgCl_4^{2-}$, $FeCl_3^-$, $FeCl_4^{2-}$ (16). Moreover, H_2SO_4 may oxidize Fe^{2+} to the potentially immobile species Fe^{3+}.

Selective Separation of Mg^{2+}

By Precipitation

The results of selective separation of Mg^{2+} from leachate by precipitation are graphically illustrated in Fig. 5. It is noted that Mg^{2+} is selectively

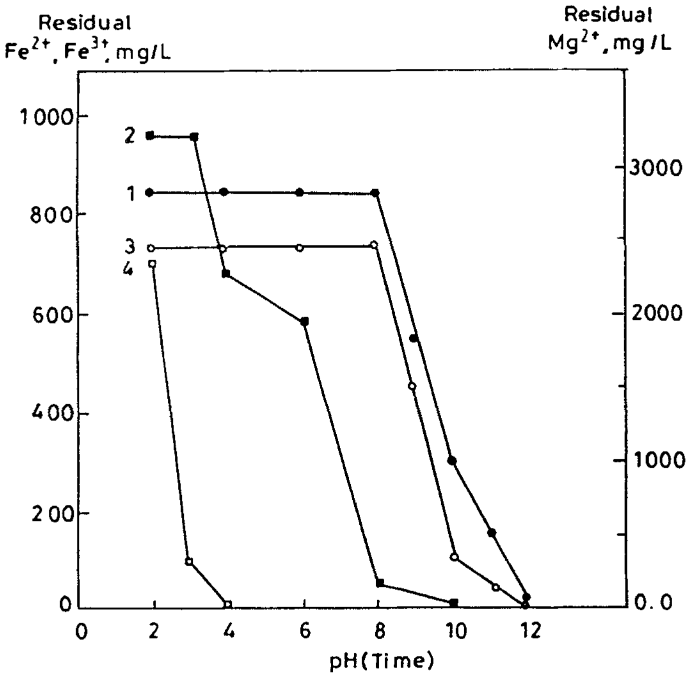

FIG. 5 Selective separation of Mg^{2+} by precipitation from leaching solution of olivine (Curves 1 and 2 for Mg^{2+} and Fe^{2+}, respectively) and serpentinized olivine (Curves 3 and 4 for Mg^{2+} and Fe^{3+}, respectively) as a function of pH.

and quite effectively separated by precipitation of $Mg(OH)_2$ at pH ~ 11.5. It is fortuitous that $Mg(OH)_2$ precipitates at pH > 10, and hence most, if not all, other metal ions are pre-precipitated and separated as hydroxides by filtration. This favors and enhances the precipitation of Mg^{2+} as $Mg(OH)_2$ without contamination due to coprecipitation.

By Ionic Flotation

The contaminated metal ions, especially Fe^{2+} and Fe^{3+}, are precipitated from the leaching solutions of olivine and serpentinized olivine and filtered. The effect of pH on the floatability of Mg^{2+} from the filtrate of the leaching solutions was investigated to select the optimum pH for maximum flotation efficiency. The results are shown in Fig. 6. As can be seen, the maximum flotation efficiency is obtained in the 7–8.5 pH range. Separation by flotation is characterized by being less time consuming. Self-flotation of magnesium oleate eliminates the need for air bubbles. It is simple with magnesium oleate to obtain pure magnesium metal.

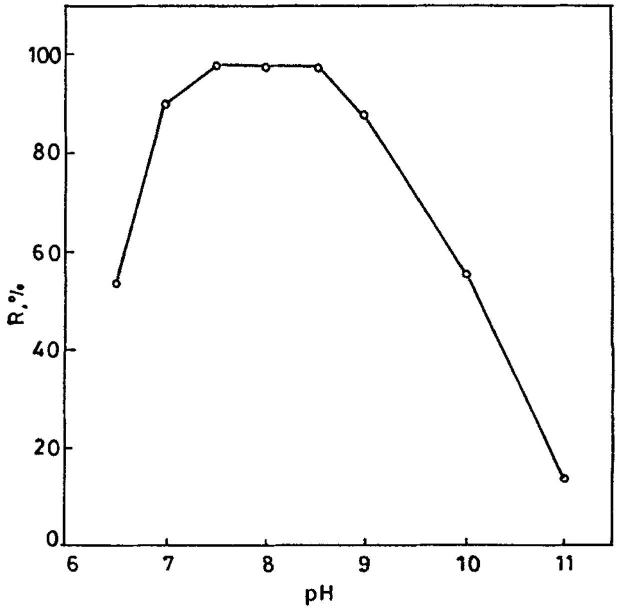

FIG. 6 Ionic flotation of Mg^{2+} from the filtrate of the leachate of olivine or serpentinized olivine (containing 2.5 g/L) as a function of pH.

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