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Original research article

SELECTIVE SEPERATION OF MAGNESIUM FROM SLOVENIAN DOLOMITES

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ABSTRACT – Although magnesium is one of the most abundant elements on Earth by weight, the demand for magnesium is constantly increasing due to its widespread use in a diverse range of industries such as metal alloys, electronics, batteries, agricultural and pharmaceutical compounds. For this reason, magnesium is categorised as a critical raw material by the European Union. Dolomite $CaMg(CO_3)_2$ is one of the most important mineral sources of magnesium, which in its pure form contains 13.18 % magnesium by weight. Various pyrometallurgical and hydrometallurgical processes have been developed and are used to extract magnesium from dolomite and other magnesium ores. In this study, samples of dolomite of different geological ages were collected in Slovenia and their elemental composition was analysed by microwave-assisted acid digestion and ICP-OES. Magnesium was then extracted by selective leaching and selective precipitation. Leaching was carried out with inorganic and organic acids. The separation of magnesium and calcium in a solution prepared by dissolving dolomite with acid was carried out by precipitation with hydroxide and oxalate. High extraction yields of magnesium and a significant separation between the two metals were achieved with both methods.

Keywords: Magnesium, Dolomite, Extraction, Selective Leaching, Selective Precipitation.

INTRODUCTION

Magnesium (Mg) is an alkaline earth metal and one of the most abundant elements by weight in Earth's crust and oceans. The most important mineral sources are magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), and talc ($Mg_3Si_4O_{10}(OH)_2$). The other important source is seawater, which contains the soluble magnesium cation Mg^{2+}. Mg has many desirable properties and is therefore used in various industries (e.g., alloys, electronics, energy storage, agriculture, construction, pharmaceuticals). Mg is extracted from all its source materials and produced in large quantities [1,2]. With the ever-increasing demand and its current and other potential uses, the EU has categorised Mg as a critical raw material.

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Mg production is largely centred on two processes: molten salt electrolysis of $MgCl_2$ salt extracted from seawater [3] and thermal reduction of carbonate minerals magnesite and dolomite [4]. Both processes are energy intensive, as they require high temperatures, and produce toxic emissions [1]. As an alternative, hydrometallurgical processes are used to extract Mg from its sources. These processes are being used more and more frequently, and new approaches are being developed. Mg is extracted and dissolved from its ores using various chemical solutions. The Mg-rich leachate is then either evaporated to obtain Mg salts or electrolysed to recover Mg metal [1,5].

Dolomite is a common mineral that is widely distributed in its rock form. Its molecular formula is $CaMg(CO_3)_2$, which corresponds to the molar ratio of Mg to Ca of 1:1. For this reason, pure dolomite contains 13.18 % Mg by weight. Dolomite is formed by dolomitisation, a process in which calcite or limestone ($CaCO_3$) undergoes cation exchange with Mg ions under certain conditions [6].

The territory of Slovenia is mostly covered by sediments, especially two sedimentary rocks – limestone and dolomite. Dolomites cover about 10 % of the surface and were formed by the process of dolomitisation in all geological periods (from the Permian to the Cretaceous) [7].

EXPERIMENTAL

Dolomite samples

Dolomite samples were collected throughout Slovenia where there are known dolomite deposits. The samples were collected from active and disused quarries and other natural areas. Five of the samples that were identified as pure dolomite rock and that correspond to all geological periods in which dolomite was formed on the territory of present-day Slovenia were included in this study (Table 1). The samples were collected in bulk and then ground into fine powder, which was stored in transparent plastic containers for further analysis.

Table 1 List of dolomite samples, their geological period and their appearance (colour) in powder form. Samples are arranged from oldest to youngest.

dolomite sample	**geological period**	**appearance (colour)**
D1	Permian	dull white
D2	Early and Middle Triassic	pure white
D3	Late Triassic	dull white
D4	Late Jurassic	light grey
D5	Cretaceous	light grey

Elemental analysis

Dolomite samples were prepared by microwave-assisted acid digestion in a microwave system (Ethos UP, Milestone, Italy). The samples were weighed into PTFE vessels with an approx. mass of 250 mg. Then 8 mL conc. hydrochloric acid (HCl, 37 %, pro analysi, KEFO, Slovenia) and 2 mL tetrafluoroboric acid (HBF_4) solution were added. HBF_4 was prepared in-house by dissolving boric acid (H_3BO_3, pro analysi, Honeywell, USA) in concentrated hydrofluoric acid (HF, 48 %, pro analysi, Merck, Germany). Acid digestion was carried out using a three-stage temperature programme: the samples were heated to 220 °C (over a period of 30 min), the set temperature was maintained for 15 min, and then the samples were allowed to cool to near room temperature before opening. The digested solutions were quantitatively transferred to 50 mL graduated polypropylene centrifuge tubes (Sarstedt, Germany) and diluted to the 50 mL mark with ultrapure water. The blank sample was prepared using the same procedure. The samples were digested in triplicate.

Selective leaching

Selective leaching of magnesium was carried out using solutions of sulfuric(VI) acid (H_2SO_4, 95-97 %, pro analysi, Honeywell, USA), tartaric acid (DL, $C_4H_6O_6$, ≥99 %, Merck, Germany), and oxalic acid ($C_2H_2O_4 \times 2H_2O$, pro analysi, Merck, Germany). The dolomite samples were weighed into centrifuge tubes with an exact mass of 1 g (±0.5 %). Then 10 mL H_2SO_4 solution or 20 mL organic acid solution was added. The centrifuge tubes were placed in a stand and shaken on an orbital shaker (Orbit 1900, Labnet, USA) for 30 min at 240 rpm. For the first 15 min the tubes were upright and open, then the tubes were closed and placed horizontally until the end of shaking. The resulting mixture was filtered through a filter paper (white mark, IDL, Germany) into a new centrifuge tube. The centrifuge tube was washed twice with 5 mL ultrapure water and the filter paper was washed once with 5 mL ultrapure water. The filtrate was acidified by adding 1 mL of conc. nitric(V) acid (HNO_3, 65 %, pro analysi, KEFO, Slovenia) and diluted to the 50 mL mark with ultrapure water. The samples were prepared in triplicate.

Selective precipitation

Hydroxide and oxalate solutions were prepared from sodium hydroxide (NaOH, pro analysi, Avantor, USA) and ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 \times H_2O$, pro analysi, Carlo Erba, Italy), respectively. They were used to selectively precipitate magnesium and calcium ions. First, dolomite samples with an exact mass of 1 g (±0.5 %) were weighed into centrifuge tubes. The samples were dissolved by adding 10 mL HNO_3 solution. The centrifuge tubes were shaken open for 15 minutes at 240 rpm in a vertical position. Then a further 15 minutes at 240 rpm in the horizontal position and closed. Then 10 mL NaOH solution or 20 mL $(NH_4)_2C_2O_4 \times H_2O$ solution was added, and shaken for 15 minutes at 240 rpm in horizontal position and closed. The suspension was centrifuged at 4000 rpm for 5 minutes (Centric 350, Domel, Slovenia). The supernatant was decanted into a new centrifuge tube and the suspension was washed twice with 5 mL ultrapure water, centrifuged and the supernatant collected. The collected supernatant was acidified by adding 1 mL of concentrated HNO_3 and diluted to the 50 mL mark with ultrapure water. The samples were prepared in triplicate.

ICP-OES measurements

The concentrations of the elements in the sample solutions were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100 SVDV, Agilent Technologies, USA). The sample solutions were appropriately diluted with

1 % HNO_3 solution. Calibration standards were prepared in 9 concentrations ranging from 0.1-1000 µg/L, by mixing and diluting two certified multi-element standard solutions Periodic table mix 1 for ICP (33 elements, 10 mg/L, Merck, Germany), and VAR-CAL-1 (4 elements, 100 mg/L, Inorganic Ventures, USA) with 1 % HNO_3 solution. The elements measured were Li, Be, Na, Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, In, Sn, Sb, Te, Ba, Tl, Pb, and Bi.

Preparation of solutions

In the case of H_2SO_4, tartaric acid, oxalic acid, and HNO_3, the solutions of the reagents were prepared so that the volume of solution added to 1 g of dolomite sample contained 105 % of the molar equivalent required for the total reaction between the reagent and the combined amount of magnesium and calcium in 1 g of ideal dolomite. For NaOH and $(NH_4)_2C_2O_4$, the solutions were prepared so that each addition contained 105% of the molar equivalent of only Mg and Ca (i.e., half the total amount). This resulted in the preparation of the following solutions: H_2SO_4 1.144 M, tartaric acid 0.570 M, oxalate acid 0.570 M, HNO_3 2.294 M, NaOH 1.140 M, and $(NH_4)_2C_2O_4$ 0.285 M.

All solutions of reagents or dilutions of concentrated acids were prepared with ultrapure water (resistivity >18.2 MΩ cm, Synergy Water Purification System, Merck Millipore, Germany).

RESULTS AND DISCUSSION

The results of the elemental analysis (Table 2) confirm that the identification of the samples as dolomite was correct. Samples D1 to D4 are almost pure dolomite, with the mass percentage w of magnesium and calcium being very close to the ideal values and the molar ratios of the metals being almost the same. The exception is the youngest dolomite D6, whose composition and molar ratio (m. r.) of only 0.8 Mg to 1 Ca shows incomplete dolomitisation. All samples contain less than 1% of impurities consisting of other common mineral elements such as Si, Al, Fe, Na, K, and Zn. The lowest amount of impurities, less than 0.1%, is present in D2, which is consistent with its appearance – sample D2 is pure white.

Table 2 Mass percentages w of Mg, Ca, and impurities in dolomite samples.

	w_{Mg} [%]	w_{Ca} [%]	m. r. (Mg:Ca)	*total* and main elemental impurities (ppm)
$CaMg(CO_3)_2$	13.18	21.74	1:1	/
D1	13.001 ± 0.023	22.203 ± 0.040	0.966:1	*(6020)* – Si (4000), Fe (733), Al (700), K (215), Na (191)
D2	12.75 ± 0.055	21.94 ± 0.13	0.959:1	*(970)* – Zn (354), Fe (142), Mn (121), Si (110), Al (83)
D3	12.82 ± 0.17	22.30 ± 0.21	0.948:1	*(3120)* – Si (1100), Al (653), Fe (579), K (427), Na (131)
D4	12.998 ± 0.085	22.29 ± 0.14	0.962:1	*(3060)* – Si (1860), Al (314), K (238), Na (221), Fe (203)
D5	11.690 ± 0.086	24.05 ± 0.10	0.802:1	*(1310)* – Si (709), Na (175), Sr (117), Al (93), Fe (48)

The aim of the selective leaching experiments was the selective solubilisation of magnesium ions, while calcium ions remained in solid form. This was done with three reagents H_2SO_4, tartaric acid and oxalic acid, whose Mg and Ca salts sulphate(VI), tartrate and oxalate show large differences in their solubility. In all cases, the Mg salt is the more soluble of the two [8].

The results are given as extraction efficiency η and molar ratio (m. r.) of the two metals in solution (Table 3). Of the three, H_2SO_4 extracted the largest amount of Mg – 70-75 % of the total mass percentage, and about 5 % of Ca for all dolomite samples. The Mg:Ca molar ratio improved to the lowest ratio of 10.6:1 and the highest ratio of 19.2:1. While both organic acids extracted less Mg, they outperformed H_2SO_4 in extraction selectivity. In both cases, the molar ratio increased strongly in favour of Mg.

Table 3 Extraction efficiencies η of Mg and Ca from dolomite samples with solutions of H_2SO_4, tartaric acid, and oxalic acid.

sample	**H_2SO_4**			**tartaric acid**			**oxalic acid**		
	η_{Mg} [%]	η_{Ca} [%]	m.r. (Mg:Ca)	η_{Mg} [%]	η_{Ca} [%]	m.r. (Mg:Ca)	η_{Mg} [%]	η_{Ca} [%]	m.r. (Mg:Ca)
D1	75.77	4.96	14.8:1	23.44	0.26	86.1:1	29.81	0.06	448:1
D2	76.61	3.82	19.2:1	45.57	0.17	259:1	26.80	0.14	184:1
D3	75.20	5.33	13.4:1	18.93	0.24	74.8:1	20.76	0.38	51.3:1
D4	74.87	5.24	13.7:1	14.99	0.32	45.7:1	21.00	0.15	137:1
D5	70.26	5.29	10.6:1	11.93	0.43	22.3:1	18.95	0.05	288:1

Dissolution of the dolomite samples with HNO_3 solution, in preparation for selective precipitation, was complete for all samples. The solutions contained >95 % of the mass percentages of magnesium and calcium in the dolomite samples as determined by elemental analysis. All solutions were clear, some were pale yellow, and all contained very small amounts of grey or brown coloured solid residues.

Selective precipitation, like selective leaching, was based on differences in the solubility of Mg and Ca salts of hydroxide and oxalate. While both Mg and Ca hydroxide are insoluble, the solubility product of the former is six orders of magnitude greater than the K_{sp} of the latter. The opposite is true for Mg and Ca oxalate. [8]

Table 4 Percentage η of precipitated Mg and Ca with hydroxide and percentage η of Mg and Ca remaining in solution after precipitation with oxalate.

sample	**NaOH**			**ammonium oxalate**		
	precipitate			*solute*		
	η_{Mg} [%]	η_{Ca} [%]	m.r. (Mg:Ca)	η_{Mg} [%]	η_{Ca} [%]	m.r. (Mg:Ca)
D1	72.70	5.11	13.7:1	94.46	5.43	16.8:1
D2	75.56	2.01	36.0:1	96.03	5.91	15.6:1
D3	73.80	5.34	13.1:1	93.14	5.83	15.1:1
D4	71.42	6.91	9.9:1	94.79	5.46	16.7:1
D5	80.72	0.17	391:1	95.89	10.15	7.6:1

The results for precipitation with hydroxide are given as a percentage η of the precipitated metals and with oxalate as a percentage η of the remaining metal ions in the solution. 70-80 % of Mg precipitated when hydroxide solution was added to the solution of dissolved dolomite. Small amounts of Ca also precipitated together with Mg, resulting in an improvement of the Mg:Ca molar ratio in the precipitate. For sample D6, the molar ratio changed significantly to 391:1 for Mg, while for all other samples it improved to around the order of 10 to 1. During precipitation with oxalate, most of the Ca precipitated (approx. 95 %) and approx. 5 % of Mg. The solution remained rich in Mg – the Mg:Ca molar ration was increased to about 15 to 1.

CONCLUSION

This study explored hydrometallurgical methods for Mg extraction from Slovenian dolomite, focusing on selective leaching and precipitation. Elemental analysis confirmed the composition of dolomite, and leaching with various acids and precipitation with hydroxide and oxalate demonstrated successful Mg enrichment. These results suggest that hydrometallurgical approaches offer viable pathways for Mg recovery from dolomite, with potential for optimisation to enhance efficiency and selectivity.

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