

THE EFFECT OF THE pH OF THE RINSING SOLUTION ON THE PROPERTIES OF MAGNESIUM OXIDE FROM SEAWATER

VPLIV pH RAZTOPINE ZA IZPIRANJE NA LASTNOSTI MAGNEZIJEVA OKSIDA IZ MORSKE VODE

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We have investigated the effect of the pH of the rinsing agent on the content of B_2O_3 , CaO and MgO in magnesium oxide obtained from seawater by substoichiometric precipitation (where the precipitation of magnesium hydroxide took place with 80% of the stoichiometric quantity of dolomite lime as the precipitation agent). In such a case, i.e. when this precipitation method is employed, the boron content adsorbed onto the magnesium hydroxide during the precipitation process is somewhat higher than during stoichiometric precipitation, and should therefore be reduced.

The purpose of the study was to ensure high-purity magnesium oxide, particularly with respect to the B_2O_3 content, because boron causes problems in refractory magnesia for specialized refractory applications where a high hot-strength is required.

The rinsing agents were alkalized distilled water with pH = 11.0 and 12.5, which were alkalized by the addition of concentrated NaOH prior to each use, and non-alkalized distilled water with pH = 5.95. It was established that the content of B_2O_3 in magnesium oxide samples is significantly reduced when the pH value of the agent used for rinsing the magnesium hydroxide precipitate increases. The magnesium oxide samples obtained were then sintered with the addition of TiO_2 (1, 2 and 5 mass %) in order to determine the properties of the sintered samples (density, porosity, the B_2O_3 content) relative to the method used for rinsing the magnesium hydroxide precipitate and to the quantity of added TiO_2 . The results indicate that all the samples, sintered at 1650 °C for 3 hours, had very low porosity, and densities up to 95 % of the theoretical density. Also, the B_2O_3 content in the products was much lower than in the samples prior to sintering.

Key words: substoichiometric precipitation, rinsing solution, magnesium oxide, seawater, TiO_2 addition, activated sintering

Raziskovan je bil vpliv pH raztopine za izpiranje na vsebnost B_2O_3 , CaO in MgO v magnezijevem oksidu, dobljenem iz morske vode z nestehiometričnim načinom usedanja (usedanje je napravljeno z dodatkom 80-odstotne stehiometrične količine dolomitnega apna kot usedalnega reagenta). Pri tem načinu usedanja je količina bora, ki se adsorbira na usedlino magnezijevega hidroksida med usedanjem, nekoliko večja v odnosu na stehiometrično usedanje in jo je treba zmanjšati.

Namen postopka je dobiti magnezijev oksid visoke čistote, predvsem glede na vsebnost B_2O_3 , ker bor povzroča težave v ognjevarnem magnezijevem oksidu za posebne namene, ker je potrebna visoka čvrstota (raziskovanje na toploti).

Sredstvo za izpiranje je lužnata destilirana voda pH = 11,0 in 12,5, ki je lužena z dodatkom koncentrirane NaOH pred vsako uporabo, kot tudi destilirana voda pH = 5,95. Dokazano je, da se vsebnost B_2O_3 v vzorcih magnezijevega oksida občutno zmanjšuje s povečanjem pH-vrednosti sredstva za izpiranje usedline magnezijevega hidroksida. Dobljeni vzorci magnezijevega oksida so potem sintrani z dodatkom TiO_2 (masni deleži: 1, 2 in 5 %) z namenom, da se določijo lastnosti sintranih vzorcev (gostota, poroznost, vsebnost B_2O_3), odvisno od načina izpiranja usedline magnezijevega hidroksida in količine dodanega TiO_2 . Rezultati raziskovanja kažejo, da imajo vsi vzorci, sintrani pri 1650 °C v trajanju 3 ur, zelo majhno poroznost, a dosežene gostote so do 95 % teoretične. Tudi vsebnost B_2O_3 je v produktu precej manjša, kot je v vzorcih pred sintranjem.

Ključne besede: nestehiometrično usedanje, sredstvo za izpiranje, magnezijev oksid, morska voda, dodatek TiO_2 , aktivirano sintranje

1 INTRODUCTION

Magnesium oxide is one of the most important materials used in the production of high-temperature-resistant ceramics. Besides its high refractoriness, MgO ceramic is non-toxic and chemically inert in basic environments at elevated temperatures.

Today, in large-scale technical processes, magnesia (MgO) for refractories is produced from three basic sources: natural magnesite, extraction from seawater and extraction from inland brine. The production of magnesium oxide from seawater is a well-know industrial process¹⁻⁸ and has been studied all over the world for a number of years. In principle it is chemically a very simple process, requiring only the addition of an alkaline

base, such as calcined dolomite or calcined limestone, to precipitate the magnesium salts present in seawater as magnesium hydroxide. The precipitate is then washed and calcined to form caustic magnesia. The apparently simple chemistry of the process is unfortunately complicated in practice because seawater is not a pure solution of magnesium salts and dolomite or limestone, although abundant, are never found free of impurities. Taking into consideration that B_2O_3 is a common impurity in seawater-derived magnesia, the purpose of this study was to examine the effect of the pH of the rinsing solution as well as the possibility of adding TiO_2 in quantities of 1, 2 and 5 mass % for reducing the boron content in the product, i.e. magnesium oxide sintered at 1650 °C.

2 EXPERIMENTAL

The composition of the dolomite lime used for precipitating the magnesium hydroxide from seawater was as follows (mass %):

MgO = 40.90 %

CaO = 57.89 %

SiO₂ = 0.102 %

Al₂O₃ = 0.866 %

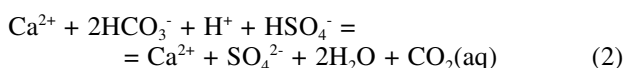
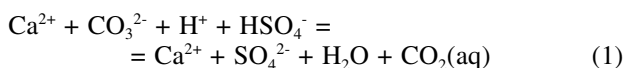
Fe₂O₃ = 0.319 %

and the composition of the seawater was as follows:

MgO = 2.179 g dm⁻³; CaO = 0.556 g dm⁻³.

In order to prevent lime contamination on the precipitate of magnesium hydroxide the seawater was pretreated to remove bicarbonate and carbonate ions. This was done by acidifying the seawater with sulfuric acid to approximately pH 4, followed by the removal of the liberated carbon dioxide by aeration in a desorption tower. The flow rate of the induced air was 120 dm³ h⁻¹, and the volumetric flow rate of the seawater through the desorption tower was 6 dm³ h⁻¹.

The chemical reactions are:



The calcium sulfate formed remained in the solution.

After the pretreatment of the seawater, a calculated amount of dolomite lime was added to precipitate the magnesium hydroxide.

The experiments were carried out with substoichiometric precipitation, with the addition of 80% of the stoichiometric quantity of dolomite lime. The experimental procedure was similar to that employed in our previous investigation⁹.

The rinsing agent was:

- distilled water, pH = 5.95
- alkalized distilled water, pH = 11.00 and 12.50, which was alkalized by the addition of concentrated NaOH.

The magnesium hydroxide thus obtained was dried at 105 °C and then calcined at 950 °C for 5 h to form caustic magnesia. Mixtures of magnesium oxide were then prepared with 1, 2 and 5 mass % of added TiO₂. The dopant oxide used was analytical reagent grade titania (TiO₂ p.a.) in the rutile form, produced by Merck. Its analysis is shown in **Table 1**. Samples were homogenized by manual stirring in absolute ethanol (C₆H₅O p.a.) for 30 min. The mixtures were then dried at 80 °C until all the alcohol had evaporated. The mixtures were cold pressed into compacts in a hydraulic press at a pressure of 625 MPa. The compacts were then sintered at 1650 °C for a duration of τ = 3 h. The sintering was carried out in a gas furnace, made by a French firm, Mecker (type 553), with a zirconium (IV)-oxide lining. It took approximately 2 h to reach the maximum tempera-

ture in the furnace. After sintering, the samples were left to cool in the furnace. The sample density after sintering (ρ) was determined from the volume of water displaced from a calibrated cylinder. The total (P_t), apparent (P_a) and closed (P_c) porosities in the samples examined were determined according to standard methods (HRN: B. D8. 302, B. D8. 312, B. D8. 313). The boron content in the samples examined was determined potentiometrically. The variation coefficient for the method applied was ±1 %¹⁰. The results listed represent an average value of a number of measurements - an average of five analyses in each case.

Table 1: Chemical analysis (mass %) of TiO₂ p.a. (Merck)

Tabela 1: Kemijska analiza (masni delež) TiO₂ p. a. (Merck)

	TiO ₂ (99 %)
Water-soluble matter	0.3 %
Chloride (Cl)	0.01 %
Sulphate (SO ₄)	0.05 %
Heavy metals (such as Pb)	0.001 %
Iron (Fe)	0.005 %
Arsenic (As)	0.0002 %

3 RESULTS AND DISCUSSION

Table 2 shows the operating conditions during the rinsing of the magnesium hydroxide precipitate, as well as the experimental results for the determination of the chemical composition of the magnesium oxide obtained by precipitation with 80 % of the stoichiometric quantity of dolomite lime. The above results indicate that the method of rinsing the magnesium hydroxide precipitate significantly affects the chemical composition of these samples, primarily in terms of the CaO and B₂O₃ contents in the calcined magnesium oxide. Rinsing the magnesium hydroxide precipitate with alkalized water, especially at pH = 12.50, contributes to a noticeable reduction in the quantity of boron adsorbed in the final product, i.e. calcined magnesium oxide.

Table 2: Chemical composition (mass %) of magnesium oxide (80 % precipitation) after calcining at 950 °C / 5 h

Tabela 2: Kemijska sestava (masni delež) magnezijevega oksida (80-odstotno usedanje) po kalcinaciji na 950 °C / 5 h

Rinsing agent	pH of the rinsing water	CaO	MgO	B ₂ O ₃
		mass %		
distilled water	5.95	0.85	98.62	0.1764
alkalized distilled water	11.00	0.95	97.89	0.1198
	12.50	1.28	97.83	0.0518

Boron occurs in seawater, partly as non-dissociated orthoborate acid (H₃BO₃) and partly as borate ions (H₂BO₃⁻, HBO₃²⁻ and BO₃³⁻), and during the magnesia-precipitation process boron is adsorbed onto the

magnesia. H_3BO_3 is a weak acid with the following dissociation constants ¹¹:



The increased pH in the rinsing agent increases the degree of dissociation of the orthoborate acid. At pH 12.50 the first-stage dissociation is complete, with about 1/3 dissociated in the second stage, while the BO_3^{3-} concentration is very low. Owing to the alkalinity of the medium, H_2BO_3^- ions are adsorbed to a much lesser degree. This can be explained by the fact that the increased pH of the medium (12.50) when rinsing the magnesium hydroxide precipitate with alkalized distilled water first affects the preferred adsorption of OH^- ions, and consequently the reduction of B_2O_3 in the final product (in seawater-derived magnesia). However, the increased pH also increases the adsorption of Ca^{2+} ions onto the $\text{Mg}(\text{OH})_2$ precipitate, as the stability of $\text{Ca}(\text{OH})_2$ is higher in a very alkaline medium, i.e. at pH 12-13.

In order to determine the properties of the samples examined relative to the precipitate-rinsing method and the B_2O_3 content in the magnesium oxide, samples of magnesium oxide containing additions of TiO_2 , and samples without TiO_2 , were sintered at 1650 °C for 3 hours. **Table 3** presents the values of the density and the porosity for sintered magnesium oxide samples (80% precipitation) sintered at 1650 °C for 3 h with various quantities of sintering agent (in mass %). The experimentally obtained values for the density of the sintered samples indicate a favorable effect of the TiO_2 addition on product densification during the isothermal sintering of the magnesium oxide from the seawater. The density amounts to 95-98% of the theoretical density ($\rho_t = 3.576 \text{ g cm}^{-3}$). Magnesium oxide compacts with TiO_2 were found to be denser than the undoped samples, after being fired under the same thermal conditions. However, this increase in density was not very significant.

Data on the apparent porosity of the sintered samples indicate the presence of very few open pores in the

system. The pores that are present are mainly of the closed type. As a result, the total porosity is almost identical to the closed porosity. The low values obtained for densification during isothermal heating in the samples examined indicate that densification occurred even before the maximum sintering temperature was reached, which may be attributed to the activity of the TiO_2 at lower temperatures. It is evident that the addition of TiO_2 promotes low-temperature densification of magnesium oxide, in proportion to the extent of solid-solution formation and vacancy formation. In this case the sintering was intensified in the presence of the liquid phase in the MgO-TiO_2 system ^{12,13}.

Table 4 shows the results of an examination of the effect of TiO_2 on the boron content in sintered magnesium oxide samples for the operating conditions described. Although the addition of TiO_2 is known to reduce the quantity of boron adsorbed during isothermal sintering of the magnesium oxide obtained from seawater ¹⁴⁻¹⁷, the purpose of this work was to relate these two aspects, i.e. the effect of the precipitate-rinsing method and the effect of the addition of TiO_2 on the B_2O_3 content in the samples of magnesium oxide from seawater that were sintered for 3 hours at 1650 °C. The results obtained for the effect of TiO_2 addition on the B_2O_3 content in sintered samples show that the B_2O_3 content changes during sintering, depending on the method of magnesium oxide preparation for the operating conditions described. The effect of added TiO_2 is higher in magnesium oxide samples obtained by rinsing the magnesium hydroxide precipitate with distilled water, pH 5.95, than in the samples obtained by rinsing the precipitate with alkalized distilled water, pH 12.50, which is related to the quantity of CaO in the examined samples. In our previous paper ¹⁸ the content of dicalcium borate ($\text{Ca}_2\text{B}_2\text{O}_5$) was determined in sintered samples by means of X-ray diffraction, i.e. it was found that during sintering B_2O_3 reacts with CaO to form $\text{Ca}_2\text{B}_2\text{O}_5$. Also, the studies ^{12,13,19} show that the methods of X-ray diffraction and EDAX analysis indicate that in the sintering process the added TiO_2

Table 3: Density (ρ), apparent (P_a), total (P_t) and closed (P_c) porosity for sintered magnesium oxide samples (80% precipitation) with 1, 2 and 5 mass% TiO_2 added, and no sint. aid, $t = 1650 \text{ }^\circ\text{C}$, $\tau = 3 \text{ h}$, $p = 625 \text{ MPa}$

Tabela 3: Gostota (ρ), odprta (P_a), ukupna (P_t) in zaprta (P_c) poroznost za sintrane vzorce magnezijevega oksida (80-odstotno usedanje) z masnimi deleži TiO_2 1, 2 in 5 % in brez dodatka TiO_2 , $t = 1650 \text{ }^\circ\text{C}$, $\tau = 3 \text{ h}$, $p = 625 \text{ MPa}$

No. of sample	Rinsing water	pH of the rinsing water	TiO ₂ addition	ρ	P_a	P_t	P_c
			mass%	g cm^{-3}			
1	distilled water	5.95	no sint. aid	3.392	0.09	5.42	5.33
2			1	3.433	0.08	4.16	4.08
3			2	3.450	0.07	3.65	3.53
4			5	3.481	0.02	2.73	2.71
5	alkalized distilled water	12.50	no sint. aid	3.358	0.09	6.49	6.40
6			1	3.388	0.09	5.55	5.46
7			2	3.399	0.08	5.21	5.13
8			5	3.497	0.05	2.26	2.21

reacts with the CaO from the MgO-CaO solid solution and transforms into calcium titanate, CaTiO₃. Thus, two reactions cause the B₂O₃ content to reduce during sintering. These reactions are:



Therefore, TiO₂ binds a part of the CaO in the CaTiO₃, and thus reduces the CaO content that reacts with B₂O₃. Thus, the higher the CaO content, the more B₂O₃ is retained in the sintered samples.

In order to examine this effect of TiO₂ on the reduction of B₂O₃ content in the sintered samples, experimental results were processed, i.e. the percentage of B₂O₃ liberated during sintering (J_1) was calculated from the experimental data on the B₂O₃ content in the sintered samples and the B₂O₃ content in the calcined magnesium oxide, as well as the percentage of CaO that had reacted with the TiO₂ (J_2). Based on the experimental data for the boron determination by potentiometrical titration in magnesium oxide samples sintered at 1650 °C, the reaction yield degree, ξ , was calculated for the dicalcium borate formation reaction in all the samples examined, relative to the quantity of boron present in the calcined magnesium oxide. **Table 5** presents the results obtained. The results shown in Table 5 indicate that the dicalcium borate formation reaction yield degree decreases when the addition of TiO₂ increases. Thus, an increased TiO₂ addition leads to

increased boron evaporation from the sample into the atmosphere. Also, the dicalcium borate formation reaction yield degree is higher in samples obtained by rinsing with alkalized distilled water, pH 12.50, which may be attributed to the increased CaO content in the sample (1.28 mass %). While with magnesium oxide obtained by rinsing with distilled water, pH 5.95, the addition of 1 mass % of TiO₂ binds all of the CaO ($J_1 = 84.30\%$; $J_2 = 80.63\%$) with magnesium oxide obtained by rinsing with alkalized distilled water, pH 12.50, a higher addition of TiO₂ is needed to bind excess CaO into CaTiO₃, i.e. only the addition of 5 mass % TiO₂ causes greater evaporation of B₂O₃ during sintering ($J_1 = 82.24\%$; $J_2 = 96.41\%$).

Although the magnesium oxide samples obtained by rinsing the magnesium hydroxide precipitate with alkalized distilled water, pH 12.50, have a much lower B₂O₃ content (0.0518 mass %), owing to the increased CaO content in the specified sample (1.28 mass %) the sintered samples contain a higher quantity of B₂O₃ ($J_1 = 24.52\%$ in samples with 1 % TiO₂ added, $J_1 = 62.74\%$ in samples with 2 % TiO₂ added, and $J_1 = 82.24\%$ in samples with 5 % TiO₂ added). Therefore, one should take into account the CaO content in the initial sample in order to choose the optimum TiO₂ addition that will bind the excess CaO during sintering and thereby significantly affect the quantity of B₂O₃ evaporated from the sample into the atmosphere.

Table 4: Effect of TiO₂ on the B₂O₃ content in the sintered magnesium oxide samples (80% precipitation) at 1650 °C, $\tau = 3$ h, $p = 625$ MPa

Tabela 4: Vpliv TiO₂ na vsebnost B₂O₃ v sintranih vzorcih magnezijevega oksida (80-odstotno usedanje) pri 1650 °C, $\tau = 3$ h, $p = 625$ MPa

No. of sample	Rinsing water	pH of the rinsing water	TiO ₂ addition	B ₂ O ₃
			mass%	
1	distilled water	5.95	no sint.aid	0.0387
2			1	0.0277
3			2	0.0142
4			5	0.0028
5	alkalized distilled water	12.50	no sint. aid	0.0486
6			1	0.0391
7			2	0.0193
8			5	0.0092

Table 5: Dependence of J_1 , J_2 and ξ on the different quantities of sintering aid and the method employed for rinsing the magnesium hydroxide precipitate in the sintered magnesium oxide samples (80% precipitation) at 1650 °C, $\tau = 3$ h, $p = 625$ MPa

Tabela 5: Odvisnost J_1 , J_2 in ξ od količine dodanega TiO₂ in načina izpiranja usedline magnezijevega hidroksida v vzorcih MgO (80-odstotno usedanje) pri 1650 °C, $\tau = 3$ h, $p = 625$ MPa

No. of sample	Rinsing water	pH of the rinsing water	TiO ₂ addition	J_1	J_2	ξ
			mass %	%		
2	distilled water	5.95	1	84.30	80.63	15.70
3			2	91.95	95.02	8.05
4			5	98.41	97.13	1.59
6	alkalized distilled water	12.50	1	24.52	53.54	75.48
7			2	62.74	95.17	37.25
8			5	82.24	96.41	17.76

4 CONCLUSIONS

The B₂O₃ content is significantly reduced if the magnesium hydroxide precipitate is rinsed with a high-pH rinsing agent, i.e. with alkalized distilled water with a pH value of 12.50.

All samples sintered at 1650 °C for 3 hours had a very low porosity, and the densities were up to 95 % of the theoretical density.

The optimal TiO₂ quantity needed to bind CaO into calcium titanate, and thus cause greater evaporation of B₂O₃ from the sample into the atmosphere during sintering, depends on the method used for rinsing the magnesium hydroxide precipitate, i.e. the CaO content in the initial sample.

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