

B₂O₃ AND CaO IN THE MAGNESIUM OXIDE FROM SEAWATER

B₂O₃ IN CaO V MAGNEZIJEVEM OKSIDU IZ MORSKE VODE

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We have examined the effect of distilled water with a pH of 12.50 during the rinsing of a precipitate of magnesium hydroxide, obtained from seawater by sub-stoichiometric precipitation with 80% of the stoichiometric quantity of dolomite lime as the precipitation reagent. However, with this precipitation method the content of B₂O₃ in the product increases, i.e., magnesium oxide obtained from seawater. The purpose of this study was not only to reduce the B₂O₃ quantity as much as possible, but also to determine the minimum number of rinses needed to obtain calcined magnesium oxide with a satisfactory quality. Specifically, boron causes significant disturbances in the electrolysis of magnesium chloride used to obtain metal magnesium if magnesium chloride obtained from seawater is used as the cell charge, and it also adversely affects the quality of the refractory material produced from the sintered magnesium oxide obtained from seawater. The results indicate that if this method of rinsing the magnesium hydroxide precipitate is used, the B₂O₃ content in the MgO samples (80% precipitation) is 0.069 mass %, which is 66% less than the B₂O₃ content in samples prepared without rinsing the magnesium hydroxide with alkalized distilled water (B₂O₃ = 0.200 mass %).

We found that it is sufficient to carry out the rinsing by decantation three times, as further rinsing does not cause a further reduction in the amount of B₂O₃ in the sample. This rinsing method does not change the CaO content in calcined magnesium oxide, which indicates that further rinsing should be done with non-alkalized distilled water.

Key words: substoichiometric precipitation, B₂O₃ content, rinsing agent, magnesium oxide from seawater

Raziskan je vpliv destilirane vode s pH 12.50 pri izpiranju usedline magnezijevega hidroksida pridobljenega iz morske vode z nestehiometrijskim obarjanjem in z dodatkom 80 % stehiometrijske količine dolomitnega apna kot obarjalnega reagenta. Pri tem načinu obarjanja je v magnezijevev oksidu povečana vsebnost B₂O₃.

Namen dela je bil zmanjšati vsebnost B₂O₃ na najmanjšo možno mero in določiti minimalno število izpiranj, da bi nastal kalcinirani magnezijev oksid zadovoljive kakovosti.

Borov oksid povzroča precejšnje motnje pri elektrolizi magnezijevega klorida, če se kot polnilo celice uporabi magnezijev klorid pridobljen iz morske vode. Borov oksid tudi zmanjša kakovost ognjevzdržnega materiala proizvedenega iz magnezijevega oksida pridobljenega iz morske vode.

Rezultati raziskave kažejo, da pri standardnem načinu izpiranja usedline magnezijevega hidroksida znaša vsebnost B₂O₃ v vzorcih MgO (80%-tno usedanje) 0.069 mas. %, kar je za 66 % manj kot v vzorcih, pripravljenih brez izpiranja magnezijevega hidroksida z bazično destilirano vodo (B₂O₃ = 0.200 mas. %). Trikratno izpiranje zmanjša vsebnost B₂O₃ na konstantno vrednost, ki se ne spremeni več pri povečanju števila izpiranj.

Pri opisanem načinu izpiranja se ne spreminja vsebnost CaO v kalciniranem magnezijevev oksidu.

ključne besede: nestehiometrično usedanje, vsebnost B₂O₃, sredstvo za izpiranje, magnezijev oksid, morska voda

1 INTRODUCTION

Magnesium oxide is a very important refractory material. It is currently produced from mineral sources in the earth, primarily magnesite¹⁻³, and from alternative sources like seawater⁴⁻¹² and natural salt waters¹³⁻¹⁵. Seawater can be economically used as a raw material in the production of magnesium oxide if the magnesium mass concentration¹⁶ in it is at least 1.3 g dm⁻³. This condition is met in numerous places in seas and oceans. For most of the second half of the twentieth century, seawater provided almost 50% of the magnesium produced in the western world, and today it still remains a major source of magnesium oxide in many countries. The process involves the extraction of dissolved magnesium and the reaction of magnesium chloride and magnesium sulfate with lime or dolomite lime to produce a magnesium hydroxide precipitate. The precipitate is washed and calcined to caustic magnesia.

Boric oxide is a common impurity in seawater-derived magnesia; it is capable of reacting with silicates that can be present in refractory grades of magnesia.

The purpose of this work was to examine how and to what extent the rinsing of a magnesium hydroxide precipitate using alkalized distilled water with a pH of 12.50 affects the reduction of the B₂O₃ content in magnesium oxide obtained from seawater by substoichiometric precipitation (precipitation of magnesium hydroxide with 80% of the stoichiometric quantity of dolomite lime as the precipitation agent).

2 EXPERIMENTAL

The content of MgO and CaO in the seawater used for the magnesium hydroxide precipitation was:

MgO = 2.490 g dm⁻³; CaO = 0.605 g dm⁻³

The composition of the dolomite lime used as the precipitation agent was as follows (mass %):

CaO = 57.17 %	MgO = 42.27 %
SiO ₂ = 0.099 %	Al ₂ O ₃ = 0.051 %
Fe ₂ O ₃ = 0.079 %	

The seawater was acidified (by sulfuric acid) to lower its pH from the normal value of 8.2 to 4.0. Seawater was then passed through the desorption tower packed with Rasching rings, where it flowed downward against a stream of air. At low pH, the bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) were converted to CO₂ gas, which was stripped out of the falling water drops by the ascending airflow. The flow rate of the induced air was 120 dm³h⁻¹, and the volumetric flow rate of the seawater through the desorption tower was 6 dm³ h⁻¹.

The precipitation of magnesium hydroxide took place after the pretreatment of the seawater with 80% of the stoichiometric quantity of dolomite lime. The experimental procedure was similar to that employed in our previous investigations^{7,9}. The sedimentation rate was increased by the addition of an optimum amount of anionic 818A flocculent (polyacrylamide). The experimental procedure used to determine the optimum quantity of the anionic 818A flocculent has been described in a previous study¹⁰. The rinsing agent was alkalized distilled water with a pH = 12.50, which was alkalized by the addition of concentrated NaOH.

In the experiments the operating conditions were varied in terms of the number of rinses of the magnesium hydroxide precipitate by the decantation.

The rinsing and decanting procedure was carried out once, twice, three, four or five times, always with approximately 1000 cm³ of the rinsing agent.

After that, the magnesium hydroxide precipitate was filtered through a number of funnels. In order to establish the efficiency of the alkalized distilled water with a pH = 12.50 as the rinsing agent, the magnesium hydroxide precipitate was collected for further processing after each decantation.

The prepared magnesium hydroxide samples, which differed from one another in terms of the number of times they were rinsed by decantation, were dried at 105 °C after filtering, and then calcined at 95 °C for 5 h to form caustic magnesium. The boron content in the samples examined was determined potentiometrically. The uncertainty of the applied method is ± 1%¹⁷. The results represent the average values of a series of measurements (an average of five analyses in each case).

3 RESULTS AND DISCUSSION

In the experimental part of the work the application of alkalized distilled water with a pH of 12.50 as a rinsing agent used to rinse the magnesium hydroxide precipitate obtained from seawater by substoichiometric 80% precipitation was investigated.

Table 1 shows the chemical composition (mass %) of the magnesium oxide obtained from seawater with 80% of the stoichiometric quantity of dolomite lime, after calcining at 950 °C for 5 h, and operating conditions during the rinsing of the magnesium hydroxide precipitate by alkalized distilled water with pH = 12.50. **Table 2** shows the change in the pH value of the rinsing agent relative to the number of rinses.

Table 1: Chemical composition (mass %) of magnesium oxide (80% precipitation) after calcining at 950 °C for 5 h, and operating conditions during rinsing of the magnesium hydroxide precipitate with alkalized distilled water with a pH = 12.50

Tabela 1: Kemijska sestava (mas. %) magnezijevega oksida (80 % obarjanje) po 5 urni kalcinaciji pri 950 °C in delovni pogoji med izpiranjem magnezijevega hidroksida dobljenega z bazično destilirano vodo s pH = 12.50

No. of sample	No. of rinses by decantation	CaO	MgO	B ₂ O ₃
		mass %		
1	1	3.73	94.44	0.125
2	2	3.58	94.97	0.095
3	3	3.73	94.97	0.069
4	4	3.82	94.29	0.070
5	5	3.79	94.59	0.070
6	0	3.08	94.21	0.200

Table 2: pH of the rinsing agent (alkalized distilled water with a pH = 12.50) versus the number of rinses

Tabela 2: Sprememba pH reagenta za izpiranje (bazična destilirana voda s pH = 12,50) glede na število izpiranj

Number of rinses	1	2	3	4	5
pH of the rinsing agent	11.50	12.09	12.09	12.50	12.50

This work is a continuation of our previous research^{9,11,12} into the effect of the method of rinsing the magnesium hydroxide precipitate obtained from seawater by substoichiometric 80% precipitation. The substoichiometric precipitation^{7,9-12} of magnesium hydroxide from seawater, elaborated by B. Petric and N. Petric, has significant advantages in the so-called "wet phase".

If a substoichiometric quantity of the precipitate agent is added, the coagulation (aggregation) stability of the observed colloid system observed is reduced, which leads to an increased sedimentation rate, and therefore to an increased thickener capacity. In the presence of surplus, i.e., non-precipitated Mg²⁺ ions, the electrokinetic potential is reduced, which makes the magnesium hydroxide sedimentation process faster. This may be explained by the Mg(OH)₂ particle model. However, during substoichiometric precipitation, an increased adsorption of ionic boron forms present in seawater (primarily H₂BO₃⁻, and HBO₃²⁻ and BO₃³⁻ to a lesser degree) occurs onto the magnesium hydroxide precipitate. Consequently, the B₂O₃ content is increased in calcined magnesium oxide obtained from seawater by substoichiometric precipitation. Experimental results

(Table 1) indicate that the B₂O₃ part in MgO (80% precipitation) amounts to 0.200 mass %.

It is therefore necessary to apply a proper method of rinsing the magnesium hydroxide to reduce the B₂O₃ content in the final product, as the special-purpose magnesium oxide properties are significantly affected by the boron content in the product. Specifically, the mechanical resistance of refractory materials at high temperatures decreases with the increase of the B₂O₃ content, and the elasticity module of such refractory materials is also reduced. According to N. Heasman⁹ the boron impurity limit should not be higher than 0.05 mass % B₂O₃ in sintered magnesium oxide obtained from seawater.

Previous research^{9,11} has shown that an increased pH of the rinsing agent reduces the content of boron adsorbed (expressed as B₂O₃) onto the precipitate of magnesium hydroxide obtained from seawater.

This study aimed at finding the optimum number of rinses by decantation of the magnesium hydroxide precipitate with alkalized distilled water with a pH of 12.50.

In order to determine the efficiency of the application of the alkalized distilled water of pH 12.50, the B₂O₃, CaO, and MgO contents were determined in the magnesium oxide samples after each decantation.

The results obtained (Table 1) show that the increased number of rinses reduced the B₂O₃ content in the examined MgO samples, while it does not affect significantly the CaO content, which remained in the range of 3.73 to 3.82 mass %.

The increased pH of the rinsing agent helps the desorption of ionic boron species from the surface of the magnesium hydroxide precipitate. Specifically, the high pH value of 12.50 of the rinsing agent enhances the dissociation of the orthoboric acid, i.e., it reduces the concentration of ions of a higher dissociation degree. This process creates the possibility of the adsorption of ionic boron forms. However, it does not happen, as primarily small, negatively charged OH⁻ ions, present in high quantities, adsorb onto the magnesium hydroxide precipitate in the highly alkaline medium, thereby preventing further pollution of the MgO by boron.

After the first rinsing by decantation with alkalized distilled water with a pH of 12.50 (sample 1), the B₂O₃ content was reduced to 0.125 mass %, which is 38% less than the B₂O₃ content in samples prepared without rinsing the magnesium hydroxide precipitate (0.200 mass %). If the rinsing by decantation took place twice (sample 2), the B₂O₃ content was reduced by an additional 24%, attaining the value of 0.095 mass %.

Further rinsing by decantation with alkalized distilled water with a pH of 12.50 (sample 3) does not change the content of B₂O₃ in the magnesium oxide. The experimental results show that after the third rinsing the B₂O₃ content was of 0.069 mass %, which is approximately 66% less than the B₂O₃ content in the sample prepared without rinsing the magnesium hydroxide precipitate (0.200 mass %).

A further increase in the number of rinses by decantation to four or five (samples 4 and 5) does not diminish the B₂O₃ content and shows that the number of rinses by decantation should be limited to three. Thus, the rinsing of magnesium hydroxide with alkalized distilled water with a pH of 12.50 above three rinses does not affect the chemical composition of the obtained magnesium oxide.

After the first rinsing by decanting, the pH value of the rinsing agent falls to 11.50 (Table 2). After the second and third rinses by decantation, the pH value of the fresh rinsing agent falls to 12.09, and remains unchanged after the fourth and fifth rinsings by decantation. The reduction of the pH value suggest a desorption of ionic boron forms from the surface of the magnesium hydroxide particles. The rinsing agent with the pH of 12.09 is a strong alkaline medium; it is expected that no desorption of Ca²⁺ ions will take place because of the increased stability of Ca(OH)₂ in the alkaline medium.

During the isothermal sintering of magnesium oxide obtained from seawater, CaO reacts with B₂O₃ forming Ca₂B₂O₅, and in sintered samples the B₂O₃ is retained. It is therefore also important to reduce the CaO content in the initial sample, i.e., the calcined magnesium oxide, and thus reduce the CaO content which reacts with the B₂O₃. So a smaller quantity of Ca₂B₂O₅ is formed, which remains in the sintered sample so that a greater part of B₂O₃ evaporates.

The results of this work show that after the third rinsing of the precipitate with alkalized distilled water with a pH of 12.50, further rinses should make use of non-alkalized distilled water.

4 CONCLUSIONS

1. The application of alkalized distilled water with a pH of 12.50 in rinsing the magnesium hydroxide precipitate leads to a reduction in the B₂O₃ content in MgO (80% precipitation) from 0.200 mass % to 0.069 mass %, i.e., the B₂O₃ content is reduced by 66%.
2. The number of rinses by decantation should not be higher than three.
3. Further rinsing of the magnesium hydroxide precipitate with alkalized distilled water with a pH of 12.50 after three rinses does not affect the chemical composition of the magnesium oxide.
4. The application of alkalized distilled water as a precipitate rinsing agent does not lead to a reduction in the CaO content.

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