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SINTERING OF MAGNESIUM OXIDE OBTAINED FROM SEAWATER AT 1600 °C

SINTERIRANJE MAGNEZIJEVA OKSIDA IZ MORSKE VODE PRI 1600 °C

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ABSTRACT

This study has examined the process of sintering of Mg0 samples (80 % precipitation) obtained from seawater at a temperature of 1600 ºC with time until the sintering temperature is obtained, in order to examine their properties (density, porosity) and chemical composition after sintering.

The prepared magnesium oxide samples are distinguished by the method of treatment of the magnesium hydroxide precipitate in the technological process of obtaining magnesium oxide from seawater. The examination results indicate that the method of rinsing of the magnesium hydroxide precipitate in the technological process of obtaining magnesium oxide from seawater does not significantly affect the density and porosity of sintered samples, but it does significantly affect the chemical composition of samples, primarily with regard to the CaO and B_2O_3 *content.*

Keywords: magnesium oxide from seawater, substoichiometric precipitation, sintering

SAŽETAK

U ovom radu ispitivan je proces sinteriranja uzoraka MgO (80 %-tno taloženje) iz morske vode pri temperaturi 1600 ºC uz vrijeme do postizanja temperature sinteriranja, sa svrhom da se ispitaju njihova svojstva (gustoća, poroznost) te kemijski sastav nakon sinteriranja.

Pripremljeni uzorci magnezijeva oksida međusobno se razlikuju po načinu obrade taloga magnezijeva hidroksida u tehnološkom postupku dobivanja magnezijeva oksida iz morske vode.

Rezultati ispitivanja ukazuju da način ispiranja taloga magnezijeva hidroksida u tehnološkom postupku dobivanja magnezijeva oksida iz morske vode ne utječe značajnije na gustoću i poroznost sinteriranih uzoraka, ali značajno utječe na kemijski sastav uzoraka prvenstveno s obzirom na sadržaj CaO i B_2O_3*.*

Ključne riječi: magnezijev oksid iz morske vode, nestehiometrijsko taloženje, sinteriranje

1. INTRODUCTION

Seas and oceans that cover 71% of the total surface of the Earth contain inexhaustible and endless supplies of mineral resources. In the last fifty years, the exploitation of mineral resources of the sea and the seabed has aroused special international interest. The exploitation and study of the potentials of the sea is, as a whole, a huge opportunity for the humanity on the way of amicable overcoming of major contradictions that agitate the modern world and threaten its future. This hope is justified only provided a reasonable approach to exploitation of the sea and its protection from pollution. Although the results of oceanographic research indicate that seawater contains various dissolved inorganic salts and metals, there are only a small number of them that is industrially extracted from seawater, either due to the fact that their concentration is too low for economic production, or to the fact that these minerals can be found in sufficient quantities in the land. If it turns out that the existing technologies and free-trade economy can be used to mine, process, and use the mineral deposits of the sea, these deposits are then classified as potential mineral resources. This also relates to the use of sea/ocean water for obtaining magnesium oxide, since the content of magnesium in the total mass of seawater amounts to 0.13 % [1,2]. The process of obtaining magnesium from seawater [2-5] involves the precipitation of magnesium hydroxide ($Mg(OH)_2$), which is formed by the reaction of magnesium salts ($MgCl_2$ and $MgSO_4$) dissolved in seawater with a suitable base reagent such as calcined dolomite or calcined lime, in the form of a solution or sludge.

Magnesium oxide is an excellent high-temperature resistant refractory material due to its high-grade refractoriness, as MgO melts at (2823±40) ^{o}C, to its chemical resistance to many acids, acid gases, base slags and neutral salts, and it reacts with carbon only above 1800 ºC.

Magnesium oxide obtained from seawater contains boron (III) oxide as impurity whose mass fraction can be reduced by using the appropriate method of rinsing the magnesium hydroxide precipitate in the process of decanting and after the filtering process.

Magnesium oxide used in this study was obtained by substoichiometric precipitation, with the addition of 80% of dolomite lime as a precipitation agent, with different methods of rinsing the magnesium hydroxide precipitate.

MgO samples (80 % precipitation) were sintered at 1600 ºC until the sintering temperature was reached, in order to determine the properties (density, porosity) and chemical composition of sintered samples (CaO, MgO and B_2O_3) relative to the method of their preparation.

2. EXPERIMENTAL

Seawater used to obtain magnesium oxide was taken at the location of the Oceanographic institute in Split.

The composition of seawater used for precipitation of magnesium hydroxide was:

MgO = 1.997 g dm^{-3} and CaO = 0.530 g dm^{-3}.

Dolomite used as the precipitation agent in obtaining magnesium hydroxide from seawater was taken from the Đipalo – Sinj location.

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

CaO = 59.03%, MgO = 40.69 %, SiO_2 = 0.108 %, Al_2O_3 = 0.093 % and Fe_2O_3 = 0.071 %.

In order to prevent lime contamination of the magnesium hydroxide precipitate the seawater was pre-treated to remove bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. After the pre-treatment of the seawater, a calculated amount of dolomite lime was added to the magnesium hydroxide precipitate. The experiments were carried out with substoichiometric precipitation, with the addition of 80 % of the stoichiometric quantity of dolomite lime. The experimental procedure used to pre-treat seawater as well as the experimental procedure used to obtain the magnesium hydroxide precipitate was similar to that employed in our previous studies [6].

After sedimentation of the magnesium hydroxide precipitate, the precipitate was decanted and rinsed with the rinsing agent.

The following were used as the rinsing agent:

- Distilled water with pH value of 5.66 and

- Alkalized distilled water with pH value of 12.50 (obtained by dissolving NaOH p.a. granules, with pH values determined by a pH-meter).

In these experiments, operating conditions were altered with respect to the method and number of rinses of the precipitate formed. Rinsing by decanting was performed with about 1 dm^3 of the rinsing agent. The duration of contact with the rinsing agent was about 30 min, i.e. until the precipitate settled again before the following decanting.

After rinsing by decanting, the samples were rinsed in the process of filtering on multiple funnels.

The rinsing by decanting used distilled water (5 times) or the combined rinsing method (3+2), i.e. the magnesium hydroxide precipitate was rinsed 3 times by alkalized distilled water (pH = 12.50) and 2 times by distilled water (pH = 5.66). The rinsing on filter paper used distilled water (5 times) or the combined rinsing method (2+3), i.e. the magnesium hydroxide precipitate was rinsed 2 times by alkalized distilled water (pH = 12.50) and 3 times by distilled water (pH = 5.66).

Thus, two samples of magnesium hydroxide were prepared relative to the method and number of rinses of the magnesium hydroxide precipitate.

- SAMPLE 1 – after rinsing by decanting with distilled water with pH value of 5.66, the magnesium hydroxide sample was rinsed five times by distilled water with pH of 5.66 on filter paper.

- SAMPLE 2 – after rinsing by decanting by the combined method (3+2), i.e. 3 times by alkalized distilled water with pH = 12.50 and 2 times by distilled water with pH = 5.66, the magnesium hydroxide sample was rinsed by the combined method (2+3), i.e. 2 times by alkalized distilled water of pH = 12.50 and 3 times by distilled water pH = 5.66 on filter paper.

After completion of filtration, the rinsed precipitate was dried in an oven at 105 °C, and then calcined in a muffle furnace at 950 °C for 5 hours. This process yields calcined magnesium oxide that contains impurities.

Table 1 shows the chemical composition of calcined magnesium oxide obtained from seawater by substoichiometric 80%-precipitation, with operating conditions of rinsing the magnesium hydroxide precipitate.

Table 1: Chemical composition (mass %) of magnesium oxide obtained from seawater by substoichiometric 80 % precipitation.

No. of sample	Rinsing agent	No of rinses	CaO	MgO	B_2O_3
			mass %		
1.	Distilled water (pH = 5.66)	by decanting 5 on filter paper 5	1.73	97.36	0.328
2.	Alkalised distilled water (pH = 12.50) + Distilled water (pH = 5.66)	by decanting* 3+2 on filter paper* 2+3	2.45	97.31	0.108

*in the first phases of combined rinsing method, alkalized distilled water with pH of 12.50 was used

Magnesium oxide samples were subjected to the process of cold pressing. To obtain compacts, the pressing pressure p = 625 MPa was applied. Pressing was performed in a “Maschinenfabrik Herzog Osnabrück” hydraulic press, model TP 40.

All compacts were sintered at a temperature of 1600 ºC until the sintering temperature was reached. The time to reach that temperature in the furnace was about 2 hours. After sintering, samples were left to cool in the furnace. A gas furnace by the French company “Mecker”, type 553, with a coating of zirconium (IV) oxide, was used for sintering.

Dimensions of the baking chamber are 20 cm in diameter and 30 cm in height. The furnace is heated by burning propane-butane gas mixture with air, with the addition of oxygen to achieve high temperatures.

The following tests have been done on sintered magnesium oxide samples (80% precipitation): determination of density, porosity and chemical composition.

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 magnesium oxide samples examined was determined potentiometrically. The variation coefficient for the method applied [7] is ± 1 %. The results shown represent the average of a number of measurements (5 analyses in each case).

3. RESULTS AND DISCUSSION

The experimental part of the study has examined the process of sintering of magnesium oxide obtained from seawater by substoichiometric precipitation. The addition of dolomite lime in the precipitation process amounted to 80% of the stoichiometrically required quantity. The precipitation of magnesium hydroxide with a lower quantity of the precipitation agent than stoichiometrically required, the so-called substoichiometric precipitation, elaborated by B. Petric and N. Petric [8], has significant advantages in the so-called wet phase, resulting in significant increase of plant capacity (thickener productivity). Substoichiometric precipitation with 80% of the stoichiometrically required quantity of dolomite lime as the precipitation agent increases the thickener productivity (calculated according to the Kynch theory) by 86.5% as compared to full (stoichiometric) precipitation. However, with this precipitation method, the boron content in the form of B_2O_3 is somewhat increased in the final product, i.e. magnesium oxide. Specifically, if 80% quantity of dolomite lime is added to seawater for the purpose of precipitation of magnesium hydroxide, alkalinity of seawater assumes a pH value of about 9,60. This favours greater adsorption of ionic forms of orthoborate acid from seawater (primarily $H_2BO_3^-$) onto the magnesium hydroxide precipitate during the precipitation reaction according to the equation (1) and therefore the increased fraction of B_2O_3 in calcined magnesium oxide.

$$2CaO \cdot MgO(s) + 2Mg^{2+}(aq) + SO_4^{2-}(aq) + 2Cl^-(aq) + 4H_2O(l) = 4Mg(OH)_2(s) + CaSO_4(s) + Ca^{2+}(aq) + 2Cl^-(aq) \quad (1)$$

Rinsing of the magnesium hydroxide precipitate greatly contributes to the reduction of boron (III) oxide content in calcined magnesium oxide, and consequently of its content in sintered magnesium oxide, if subjected to sintering at high temperatures. Boron (III) oxide is a common impurity in seawater derived magnesia that increases the solubility of dicalcium silicate in the liquid phase, thus lowering the hot strength of the magnesia product. According to N. Heasman [5] good quality sintered magnesium oxide contains ≤ 0.05 mass % B_2O_3.

Two samples of magnesium oxide (80% precipitation) were prepared in order to examine the effect of the method of rinsing of magnesium hydroxide precipitate.

– **SAMPLE 1,** prepared by multiple (5 times) rinsing of the magnesium hydroxide precipitate both in decanting and on filter paper by fresh distilled water with pH value of 5.66.

– **SAMPLE 2,** prepared by the combined method of rinsing the magnesium hydroxide precipitate (3+2) in decanting and by the combined method of rinsing (2+3) on filter paper.

In order to determine the efficiency of this method of rinsing of the magnesium hydroxide precipitate, the chemical composition of samples prepared was examined for their mass fraction of B_2O_3, CaO and MgO.

The results (Table 1) indicate that the MgO content in both samples examined is only slightly different, i.e. it is 97.36 mass % in SAMPLE 1, and 97.31 mass % in SAMPLE 2.

The examinations also indicate that the CaO content in SAMPLE 1 is 1.73 mass %, which is by about 29 % less than the CaO content in SAMPLE 2 (CaO = 2.45 mas. %). The application of alkalized distilled water with the increased pH value of 12.50 in the first phases of rinsing in the combined method (3+2) in decanting and (2+3) on filter paper favours the retention of CaO in the magnesium oxide sample (80% precipitation) obtained from seawater. Specifically, increased pH favours greater adsorption of Ca^{2+} ions onto the magnesium hydroxide precipitate, due to increased stability of $Ca(OH)_2$ in a highly alkaline medium, i.e. at pH = 12-13.

As for the B_2O_3 content, Table 1 shows that the application of the combined method of rinsing in decanting and on filter paper significantly reduces the B_2O_3 content in samples examined. The repeated application of alkalized distilled water with a high pH value of 12.50 very favourably affects the reduction of the boron (III) oxide in calcined magnesium oxide. The comparison of the results indicate that the B_2O_3 content in SAMPLE 2 amounts to 0.108 mass %, which is by 67 % less than the B_2O_3 content in SAMPLE 1 (B_2O_3 = 0.328 mass %).

Prepared magnesium oxide samples, differing from each other by the method of treatment of the magnesium hydroxide precipitate in the technological process of obtaining magnesium oxide from seawater, were sintered at 1600 ºC until the sintering temperature has been reached, in order to determine their properties (density, porosity) and chemical composition after sintering.

Table 2 shows the results of examination of the chemical composition of magnesium oxide samples derived from seawater by 80% precipitation, with the described operating conditions in rinsing of the magnesium hydroxide precipitate, after sintering at a temperature of 1600 ºC until the sintering temperature has been reached. Table 3 presents the results obtained for density and porosity (total, apparent and closed) of magnesium oxide samples (80% precipitation).

The comparison of results before (Table 1) and after sintering (Table 2) shows that the B_2O_3 content in the magnesium oxide is reduced during the process.

This is due to boron volatility as already at 1000 ^oC during the process of sintering of magnesium oxide from seawater the boron present evaporates from the sample into the atmosphere in the form of B_2O_3 [9]. Considering the chemical composition of samples examined after sintering (Table 2), it is evident that the mass fraction of B_2O_3 is slightly reduced in the samples examined. It may also be observed that the B_2O_3 fraction changes during sintering in the samples examined depending on the method of obtaining magnesium oxide for the specified operating conditions. The comparison of results indicates that the B_2O_3 content in SAMPLE 1 after sintering amounts to 0.304 mass %, which is by 7.32 % less than the B_2O_3 content in the same sample before sintering. The B_2O_3 content in SAMPLE 2 after sintering amounts to 0.101 mass %, which is by 6.48 % less than the B_2O_3 content in the same sample before sintering. This indicates that the sample heated to the sintering temperature of 1600 ^oC still retains the B_2O_3 fraction above the limit of maximum pollution according to N. Heasman [5], and that retaining the sample at the sintering temperature for a certain period is necessary for the B_2O_3 content to get below 0.05 mass%.

Table 2. Chemical composition of magnesium oxide samples obtained from seawater (80% precipitation) after sintering at 1600 ºC until the sintering temperature has been reached, p = 625 MPa.

Sample	Sample number	Rinsing method	CaO	MgO	B_2O_3
			mass %		
MgO (80% precipitation)	1.	Multiple rinsing (5 times) by distilled water (pH = 5.66) in decanting and on filter paper	1.75	97.85	0.304
	2.	*Combined method (3+2) in decanting, combined method (2+3) on filter paper	2.41	96.65	0.101

*In the first phases of the rinsing process in decanting and on filter paper alkalized distilled water was used with pH of 12.50, followed by fresh distilled water with pH of 5.66.

Table 3: Density (ρ), apparent (P_a), total (P_t), and closed (P_c) porosities of sintered samples of MgO (80% precipitation) obtained at different methods of treatment the magnesium hydroxide precipitate, t = 1600 ºC until the sintering temperature has been reached, p = 625 MPa.

Sample	Sample number	Rinsing method	ρ	P_a	P_t	P_c
			g cm^{-3}	mass %		
MgO (80% precipitation)	1.	Multiple rinsing (5 times) by distilled water (pH = 5.66) in decanting and on filter paper	3.433	0.12	4.16	4.04
	2.	* Combined method (3+2) in decanting, combined method (2+3) on filter paper	3.427	0.13	4.35	4.22

* In the first phases of the rinsing process in decanting and on filter paper alkalized distilled water was used with pH of 12.50, followed by fresh distilled water with pH of 5.66.

A smaller percentage of evaporated B_2O_3 in SAMPLE 2 is due to the increased CaO content in the sample examined (CaO = 2.41 mass %). Keeping the samples for about 2 hours in the sintering process until the temperature of 1600 ^{o}C is reached is a relatively short time during which only a slight evaporation of B_2O_3 from the sample into the atmosphere takes place.
Table 3 shows the results for density and porosity (total, apparent and closed) in sintered samples of magnesium oxide (80% precipitation)
As for results for density (Table 3) of sintered samples of magnesium oxide, it is evident that both samples have approximately the same density (ρ = 3.433 g cm^{-3} for SAMPLE 1, ρ = 3.427 g cm^{-3} for SAMPLE 2). The relative density of sintered samples of MgO (80% precipitation) obtained under different methods of treatment of the magnesium hydroxide precipitate, relative to the theoretical density (ρ_t = 3.576 gcm^{-3}) amounts to approximately 96% for both samples.

Results for porosity (Table 3) of examined sintered samples of MgO (80% precipitation) also show low values. This indicates that the increase of temperature to 1600 ^{o}C leads to formation of elements of a crystal lattice and formation of contact surfaces between the particles, which leads to increased density and reduced porosity in the sintered material.

4. CONCLUSIONS

- The process of sintering of magnesium oxide obtained from seawater by substoichiometric 80% precipitation at 1600 ^{o}C until the sintering temperature was reached has been examined.

- The method of rinsing the magnesium hydroxide precipitate in the technological process of obtaining magnesium oxide from seawater does not significantly affect the density and porosity of sintered samples, but it does significantly affect the chemical composition of the samples, specifically with respect to the CaO and B_2O_3 content.

5. REFERENCES

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