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AN EXAMINATION OF B_2O_3 IN MAGNESIUM OXIDE OBTAINED FROM SEAWATER

DOLOČANJE B_2O_3 V MAGNEZIJEVEM OKSIDU IZ MORSKE VODE

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The study has been examining the possibility of a repeated application of the agent used to rinse the precipitate of magnesium hydroxide obtained from seawater by substoichiometric precipitation with the addition of 80% of the stoichiometric quantity of dolomite lime as the precipitation agent. The purpose of the study has been to ensure a high-purity product i.e. magnesium oxide, particularly regarding the B_2O_3 content, because the hot-strength properties of certain magnesia refractory products are significantly affected by their boron content.

The rinsing agent was alkalized distilled water with a pH=12.5, which was alkalized by the addition of concentrated NaOH prior to each use.

The aim of the study was to reduce the amount of magnesium hydroxide rinsing agent, while retaining satisfactory level of purity for the magnesium oxide product. The product quality was established by determining the concentrations of MgO, CaO and B_2O_3 in the calcined magnesium oxide.

Examinations were carried out with magnesium oxide samples prepared by rinsing the precipitate with:
- fresh alkalized distilled water
- recycled alkalized distilled water
- non-alkalized distilled water
- and without previous rinsing of the magnesium hydroxide precipitate.

The results indicate that by using the recycled alkalized distilled water with a pH=12.5, the B_2O_3 content in the MgO samples (80% precipitation) amounts to 0.0807 mass %, which is 58% less than the B_2O_3 content in samples prepared without rinsing of the magnesium hydroxide precipitate (B_2O_3 = 0.1937 mass %).

Key words: substoichiometric precipitation, B_2O_3 content, rinsing agent, magnesium oxide from sea water

Preiskovana je bila možnost večkratne uporabe sredstva za izpiranje usedlin magnezijevega hidroksida, dobljenega iz morske vode z nestehiometričnim načinom usedanja, z dodatkom 80% stehiometrične količine dolomitnega apna kot usedalnega reagenta. Namen postopka je dobivanje čim večje čistote končnega proizvoda, to je magnezijevega oksida, predvsem glede na vsebino B_2O_3, ker je lastnost dobljenega magnezijevega oksida za posebne namene, to je visoka trdnost, zelo odvisne od vsebine bora v produktu.

Sredstvo za izpiranje je lužnata destilirana voda vrednosti pH 12,5, ki se pred vsako uporabo luži z dodatkom konc. NaOH.

Cilj preiskave je varčevanje sredstva za izpiranje usedlin magnezijevega hidroksida pod pogojem, da čistota končnega proizvoda magnezijevega oksida ustreza zahtevam. Kvaliteta proizvoda se spremlja z določanjem vsebine MgO, CaO in B_2O_3 v kalciniranem magnezijevem oksidu.

Poskusi so bili narejeni na vzorcih magnezijevega oksida, ki so bili pripravljeni z izpiranjem usedline magnezijevega hidroksida s svežo lužnato destilirano vodo, reciklirano lužnato destilirano vodo ter tudi na vzorcih magnezijevega oksida, ki so bili pripravljeni z izpiranjem z nelužnato destilirano vodo in brez predhodnega izpiranja usedline magnezijevega hidroksida.

Rezultati preiskave kažejo, da z uporabo reciklirane lužnate destilirane vode pH=12,5 vsebina B_2O_3 v vzorcih MgO(80% usedanje) 0.0807 mas.%, kar je za 58% manj v primerjavi z vsebino B_2O_3 v vzorcih, pripravljenih brez izpiranja usedline magnezijevega hidroksida (B_2O_3 = 0,1937 mas.%).

Ključne besede: nestehiometrično usedanje, B_2O_3 vsebina, sredstvo za izpiranje, magnezijev oksid, morska voda

1 INTRODUCTION

Magnesia (MgO) is produced from two sources: natural [1-4] and synthetic [5-13]. Magnesia from natural sources constitutes 82% of the world's magnesia installed capacity. The dominant source is magnesite ($MgCO_3$) which occurs in both a macro and a cryptocrystalline forms[2,3]. Less significant are dolomite ($CaCO_3 \cdot MgCO_3$), hydromagnesite ($3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), brucite ($Mg(OH)_2$) and serpentine ($Mg_3(Si_2O_5)(OH)_4$). Synthetic materials are manufactured either from seawater [5-11] or from magnesia-rich brines [12,13]. The production of magnesium oxide from seawater is a well-known industrial process. The process involves the extraction of dissolved magnesium, which has a concentration of around 1.3 g dm^{-3} in seawater, and 3 to 40 times this value for brines, and the reaction of magnesium salts (chloride and sulfate) with lime or dolomite lime to produce a magnesium hydroxide precipitate. The precipitate is washed and calcined to form caustic magnesia. Boron is a particularly problematic impurity for the magnesia used as a high-quality refractory material. Thus, boron can be a problem in refractory magnesia for specialized refractory applications where a high hot strength is required.

Boron occurs in seawater partly as non-dissociated boric acid (H_3BO_3) and partly as borate ions ($H_2BO_3^-$), and during the magnesia precipitation process boron is adsorbed onto the magnesia.

This paper aims to determine the operating conditions that might be used for the production of good quality caustic magnesia, i.e. caustic MgO with a low B_2O_3 content.

2 EXPERIMENTAL

The composition of the seawater used for magnesium hydroxide precipitation was as follows:

MgO = 2.4269 g dm^{-3} ; CaO = 0.6533 g dm^{-3}

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

MgO = 42.27% Al_2O_3 = 0.042%

CaO = 57.55% SiO_2 = 0.076%

Fe_2O_3 = 0.062%

The seawater was first treated to remove bicarbonate and carbonate ions by adding a quantity of sulfuric acid with online control using pH measurement (from 8.2 to 4.0) and degassing of the acidified water. Degassing was accomplished by rinsing the stream of air in a desorption tower packed with Raschig rings.

The flow rate of induced air was 120 dm^3 h^{-1} and the volumetric flow rate of seawater through the desorption tower was 6 dm^3 h^{-1}. In this way, the seawater derived lime contamination of the magnesia can be minimized.

Precipitation of magnesium hydroxide took place with 80% of the stoichiometric quantity of dolomite lime.

The precipitation reaction took 30 min., using a magnetic stirrer. After the magnesium hydroxide precipitation, settling took place. The sedimentation rate was increased by the addition of an optimum amount of the flocculant Flocal B (polyacrylamide). The experimental procedure used to determine the optimum quantity of Flocal B has been described in a previous investigation [8].

Three types of rinsing water were used: alkalized distilled water with pH = 12.50; recycled alkalized distilled water of previously determined pH = 12.50 and distilled water (pH = 5.95). The rinsing and decanting procedure was repeated five times with approximately 1 dm^3 of the rinsing agent. After that, the magnesium hydroxide precipitate was filtered through a number of funnels. The rinsing agent used with the magnesium hydroxide precipitate on the filter paper was the same as the agent used for rinsing by decanting. The procedure was also repeated five times, i.e. until the rinsing was completed. The magnesium hydroxide obtained was dried at 105 °C and then calcined at 950 °C for 5h to form caustic magnesia.

The boron content in the samples examined was determined potentiometrically. The uncertainty for the applied method is ± 1% [14]. The results represent the average value of a series of measurements - an average of five analyses in each case.

3 RESULTS AND DISCUSSION

In **table 1** the experimentally obtained values for the composition of the magnesium oxide obtained by precipitation with 80% of the stoichiometric quantity of dolomite lime, under the described operating conditions are shown.

In **tables 2 and 3** the changes in the pH value of the rinsing water relative to the number of rinses are shown.

Table 1: Chemical composition (mass %) of magnesium oxide (80% precipitation) after calcining at 950 °C / 5 h

Tabela 1: Kemijska sestava (mas.%) magnezijevega oksida (80% usedanje) po kalcinaciji na 950 °C / 5 h

No. of samples	Rinsing water	pH of the rinsing water	CaO	MgO	B_2O_3
			mass %		
1	distilled	12.50	1.307	97.71	0.0589
2	recycled distilled	12.50	2.178	97.08	0.0807
3	distilled	5.95	0.85	97.53	0.1764
4	without rinsing		2.613	96.77	0.1937

Table 2: Change in the pH of the rinsing water relative to the number of rinses. The rinsing water is fresh alkalized distilled water with pH = 12.50

Tabela 2: Sprememba pH-vrednosti sredstva za izpiranje v odvisnosti od števila izpiranj. Sredstvo za izpiranje je sveža lužnata destilirana voda pH = 12,50

Number of rinses	Rinsing by decanting	Rinsing on the filter paper
	pH	pH
1	11.50	12.00
2	11.50	12.00
3	12.00	12.00
4	12.00	12.00
5	12.00	12.00

Table 3: Change in the pH of the rinsing water relative to the number of rinses. The rinsing water is recycled alkalized distilled water with pH = 12.50

Tabela 3: Sprememba pH-vrednosti sredstva za izpiranje v odvisnosti od števila izpiranj. Sredstvo za izpiranje je reciklirana lužnata destilirana voda pH = 12,50

Number of rinses	Rinsing by decanting	Rinsing on the filter paper
	pH	pH
1	11.50	12.50
2	12.00	12.50
3	12.00	12.50
4	12.50	12.50
5	12.50	12.50

The experimental part of this study has examined the possibility of recycling the rinsing agent used for rinsing the precipitate of magnesium hydroxide obtained from seawater by substoichiometric 80% precipitation.

Examinations have been carried out in order to conserve the rinsing agent and to keep the purity of the final magnesium oxide product at a satisfactory level. Previous investigations [8,9] have shown marked advantages of the substoichiometric precipitation of magnesium hydroxide from seawater, i.e. the precipitation with less precipitation agent than needed stoichiometrically. This method of precipitation increases the thickener capacity (calculated according to Kynch) by approximately 86.5% in comparison with the stoichiometric precipitation. Substoichiometric precipitation significantly increases the sedimentation rate of the magnesium hydroxide precipitate formed, due to the decreased thickness of the double electrical layer around the magnesium hydroxide particle. A consequence of the increased adsorption of Mg^{2+} ions onto $Mg(OH)_2$ particles is a decrease in the zeta-potential. Therefore, substoichiometric precipitation increases the coagulation stability of the given $Mg(OH)_2$-seawater system.

One of the advantages of substoichiometric (80%) precipitation lies in the reduced quantity of concentrated HCl needed to neutralize waste seawater after sedimentation. This quantity amounts to only 1.1 g of concentrated HCl per kg of MgO, while it is 210.5 g of concentrated HCl per kg of MgO with the overstoichiometric (120%) precipitation [15].

With 80% precipitation, however, the B_2O_3 content in the product increases, i.e. in the magnesium oxide obtained from the seawater. Boron is present in seawater in part as the non-dissociated orthoborate acid H_3BO_3, and in part as the borate ion $H_2BO_3^-$. The concentration of the higher oxidation level ions HBO_3^{2-} and BO_3^{3-} is very low. The orthoborate acid is a weak acid with the following dissociation constants:

$$H_3BO_3 = H^+ + H_2BO_3^- \qquad K_1 = 5.8 \cdot 10^{-10}$$

$$H_2BO_3^- = H^+ + HBO_3^{2-} \qquad K_2 = 1.8 \cdot 10^{-13}$$

$$HBO_3^{2-} = H^+ + BO_3^{3-} \qquad K_3 = 1.6 \cdot 10^{-14}$$

By calculating the dissociation rate, one can establish the molal concentration of $H_2BO_3^-$, HBO_3^{2-}, and BO_3^{3-}, as well as the molal dissociation rate for every degree of dissociation of the orthoborate acid.

The aim of this study has been to examine the possibility of recycling the solution used to rinse the magnesium hydroxide precipitate, i.e., of the repeated use of the rinsing agent with appropriate alkalizing of the solution. In order to determine the efficiency of repeated use of the rinsing solution, the chemical composition of the samples prepared was analyzed regarding the B_2O_3, CaO, and MgO content.

The aim was mainly to determine how the recycled rinsing agent, with appropriate alkalizing to the pH value of 12.50, affects the reduction of the boron (B_2O_3) content in the final product - magnesium oxide, and also to determine how it affects the CaO and MgO contents.

Experimental results (**Table 1**) indicate that the MgO content in the sample prepared by rinsing the magnesium hydroxide precipitate with recycled alkalized distilled water with pH = 12.50 amounts to 97.08 mass %, being slightly lower than the MgO content in the sample prepared by rinsing the magnesium hydroxide precipitate with fresh alkalized distilled water with a pH = 12.50 (97.71 mass %). They differ for 0.64% only. In the magnesium oxide sample prepared without rinsing the magnesium hydroxide precipitate, the MgO content is markedly lower (96.77 mass %) due to a higher impurity content.

Examinations also indicate that the CaO content in the sample prepared with fresh alkalized distilled water with a pH = 12.50 used to rinse the magnesium hydroxide precipitate is 1.307 mass %, which is approximately 50% less than the CaO content in the sample prepared without rinsing the magnesium hydroxide precipitate (CaO = 2.613 mass %).

If recycled alkalized distilled water with a pH = 12.50 is used, the CaO content is 2.178 mass %, which is only 16.65% less than the CaO content in the sample prepared without rinsing the magnesium hydroxide precipitate. Therefore, the repeated use of alkalized distilled water with pH = 12.50 does not significantly affect the reduction of CaO in the final product.

The CaO content in the sample rinsed with the recycled rinsing agent is approx. 40% higher than in the sample rinsed with the fresh rinsing agent.

If the recycled rinsing agent is used to rinse the magnesium hydroxide precipitate, the final product - magnesium oxide - will have a high CaO content, slightly lower than in the sample prepared without rinsing the magnesium hydroxide precipitate. If the fresh rinsing agent is used to rinse the magnesium hydroxide precipitate, the CaO content is lower by half than in the sample prepared without rinsing the magnesium hydroxide precipitate.

As for the B_2O_3 content, Table 1 indicates that it is significantly reduced if the magnesium hydroxide precipitate is rinsed with a rinsing agent of high pH value, i.e. with alkalized distilled water with a pH value of 12.50.

The results obtained indicate that rinsing with alkalized distilled water (pH = 12.50) significantly reduces the quantity of boron adsorbed.

A comparison of results shows that the B_2O_3 content in the sample prepared by rinsing the magnesium hydroxide precipitate with the fresh prepared rinsing agent amounts to 0.0589 mass %, which is 69.59% less than the B_2O_3 content in the sample prepared without rinsing of the magnesium hydroxide precipitate (B_2O_3 = 0.1937 mass %).

When recycled distilled water with a pH = 12.50 is used to rinse the magnesium hydroxide precipitate, the B_2O_3 content in the final product - magnesium oxide - is lower by 58.34% than in the sample prepared without rinsing the magnesium hydroxide precipitate.

From this we can conclude that the B_2O_3 content is significantly lower in the sample prepared with repeated use of the rinsing agent than in the sample prepared without rinsing of the precipitate, but it is for 37.01% higher than the B_2O_3 content when the fresh prepared rinsing agent is used to rinse the magnesium hydroxide precipitate.

The high pH value of the rinsing agent (pH = 12.50) provokes fuller dissociation of the orthoborate solution, i.e. an increased concentration of higher dissociation degree ions. This process provides for the possibility of adsorption of ionic boron species. However, this does not happen: in a highly alkaline medium (pH = 12.50) small, negatively charged OH-ions, present in high quantities, are preferentially adsorbed onto the magnesium hydroxide precipitate, thereby preventing further pollution of MgO with boron.

Tables 2 and 3 indicate the effect of the number of rinses on the change of the pH value of the rinsing agent. Experimental results indicate that when fresh alkalized distilled water with a pH = 12.50 is used to rinse the magnesium hydroxide precipitate, the pH of the rinsing agent changes after each rinse (it is lower than 12.50) which means that the rinsing water adsorbs a certain amount of impurity ions during each rinse.

If the recycled rinsing agent is used to rinse the magnesium hydroxide precipitate, even after the fourth rinse the pH value of the rinsing agent does not change (12.50) and remains constant after each subsequent rinse. The rinsing water is already sufficiently saturated with impurity ions, and cannot absorb new quantities, so its pH value remains constant, which means that there is no point in rinsing after the fourth rinse.

All above mentioned leads to the conclusion that recycled distilled water with a pH = 12.50 is not suitable for rinsing the magnesium hydroxide precipitate, as the condition of the purity of the final magnesium oxide product has not been fulfilled.

The final magnesium oxide product contains a significant CaO content (2.178 mass %) as an impurity, and the B_2O_3 content is higher by 37% than when the fresh prepared rinsing agent is used to rinse the magnesium hydroxide precipitate.

Therefore, although recycling provides for conserving the rinsing agent, the magnesium hydroxide precipitate should be rinsed each time with fresh prepared alkalized distilled water with a pH value of 12.50, in order to achieve the purity of final magnesium oxide product.

4 CONCLUSION

The possibility of the repeated application of the agent used to rinse the precipitate of magnesium hydroxide obtained from seawater by substoichiometric 80% precipitation has been examined. The rinsing agent was alkalized distilled water with a pH value of 12.50.

Repeated application of the rinsing agent in rinsing the magnesium hydroxide precipitate with appropriate alkalizing of the solution to a pH value of 12.50 does not achieve a significant reduction in the CaO content in the final product.

A significant quantity of CaO (2.178 mass. %) remains in the final product as an impurity, and the B_2O_3 content is higher by 37% than when the recycled rinsing agent is used to rinse the magnesium hydroxide precipitate.

Although recycling provides for conserving the rinsing agent, the magnesium hydroxide precipitate should be rinsed each time with fresh alkalized distilled water with a pH of 12.50 in order for the final magnesium oxide product purity to be obtained.

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