The relationship between phase composition and conditions of sintering seawater derived magnesium oxide

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Abstract. This study has focused on the favourable effect of the TiO_2 addition (1, 2 and 5 wt%) on the reduction of B_2O_3 content during activated sintering of magnesium oxide from seawater at temperatures of 1400, 1500 and 1700°C for the duration of 1, 2 and 4 h. A mathematical model of dependence between the B_2O_3 mass fraction in the sintered sample, the temperature of isothermal sintering, the isothermal sintering time and the mass fraction of TiO_2 added have been proposed. Magnesium oxide was obtained from seawater by substoichiometric precipitation, with the addition of 80% of dolomite lime as the precipitation agent. New phases formed in magnesium oxide samples were examined by the XRD and SEM/EDS analysis. The results indicate that during activated sintering of seawater-derived magnesium oxide with a TiO_2 addition, reactions of formation of $\text{Ca}_2\text{B}_2\text{O}_5$, CaTiO_3 and Mg_2TiO_4 took place simultaneously. The thermodynamics analysis of experimental results, based on the Onsager reciprocity relations (symmetry relations), was applied and phenomenological coefficients were calculated to describe the interference of these three irreversible processes.

Keywords. Sintering of MgO ; seawater; TiO_2 ; mathematical model; Onsager's principle; phenomenological coefficients.

1. Introduction

Due to the reduction in magnesite reserves (in Great Britain and Japan), and consequently the ability to produce pure and high quality magnesium oxide, chemical processes for obtaining high purity magnesium oxide from seawater or saline waters rich with magnesium have been researched worldwide for a long time. A significant part of the world's production of synthetic magnesium oxide (by precipitation of magnesium hydroxide from seawater or salty waters) is nowadays produced in about twenty plants in industrially developed countries (China, France, Ireland, Israel, Jordan, South Korea, USA, Brazil, Mexico), amounting to about 14% of the world's production of magnesium [1]. Magnesium oxide has a number of applications in the industry and is used as an addition in the production of artificial fertilizers, as fillers in the manufacture of rubber, plastics, paper, magnesium, chemicals and medicines. Due to its excellent physical and chemical stability at high temperatures, sintered magnesium oxide has its wide application as a high-temperature refractory construction and insulating material. Seawater represents a major reservoir and an inexhaustible source of magnesium oxide due to the high mass concentration of magnesium in seawater, which averages 1.35 g dm^{-3} i.e., 0.13% magnesium in the total mass of

seawater [1, 2]. The precipitation of magnesium hydroxide from seawater with the addition of a lesser amount of the precipitation agent than stoichiometrically required still poses a challenge when it comes to the selection of the precipitation method and the starting raw material.

Magnesium oxide obtained from seawater by substoichiometric precipitation, with the addition of 80% of dolomite lime as the precipitation agent was used in the present study. The sintering process was conducted at temperatures of 1400, 1500 and 1700°C for the duration of 1, 2 and 4 h and the addition of 1, 2 and 5 wt% TiO_2 with the purpose of establishing a mathematical model between the B_2O_3 mass fraction as the dependent variable and independent variables of the temperature of isothermal sintering, the isothermal sintering time and the mass fraction of the added TiO_2 .

The aim of this study was to investigate the correlations of sintering conditions and solid state reactions which take place simultaneously during the sintering of magnesium oxide from seawater.

2. Experimental

Seawater used for the precipitation of magnesium hydroxide in this study was taken from the location of the Oceanographic Institute in Split, Croatia. The composition

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of seawater, determined by the complexometric method [3], with respect to the contents of MgO and CaO, was as follows:

$$2.3293 \text{ g L}^{-1} \text{ MgO and } 0.6229 \text{ g L}^{-1} \text{ CaO}$$

Dolomite lime was obtained by the calcination of dolomite (location Đipalo-Sinj, Croatia) at 950°C for 5 h. The composition of dolomite lime used as the precipitation agent was as follows [4]:

$$\begin{aligned} &40.69 \text{ wt\% MgO; } 59.03 \text{ wt\% CaO; } 0.1083 \text{ wt\% SiO}_2; \\ &0.0705 \text{ wt\% Fe}_2\text{O}_3; 0.0925 \text{ wt\% Al}_2\text{O}_3. \end{aligned}$$

Seawater was pre-treated with sulphuric acid in order to remove bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, followed by the removal of the liberated carbon dioxide (CO_2) by aeration in a desorption tower. The flow rate of the induced air was 120 L h^{-1} and the volumetric flow rate of seawater through the desorption tower was 6 L h^{-1} . After the pre-treatment of 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 precipitation reaction took 30 min with magnetic stirring. Sedimentation was improved by the addition of the optimum amount ($6.8 \text{ cm}^3/2 \text{ L}$) of the anionic 818 A flocculent (polyacrylamide) produced by the Dutch firm Hercules. The optimum quantity of the anionic 818 A flocculent has already been described in a previous study [5].

After sedimentation of the magnesium hydroxide precipitate, the precipitate was decanted and rinsed. Distilled water ($\text{pH} = 5.86$) and alkalized distilled water ($\text{pH} = 12.50$) were used as the rinsing agent. The rinsing by decanting used the combined rinsing method (2 + 3), i.e., the magnesium hydroxide precipitate was rinsed 2 times by distilled water ($\text{pH} = 5.86$) and 3 times by alkalized distilled water ($\text{pH} = 12.50$). 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 using repeated rinsing (5 times) with distilled water ($\text{pH} = 5.86$).

The rinsed precipitate was dried in an oven at 105°C, and then calcined in a muffle furnace at 950°C for 5 h to form caustic magnesia.

The chemical composition of the magnesium oxide product (80% precipitation) was: 98.98 wt% MgO, 0.83 wt% CaO and 0.1888 wt% B_2O_3 .

Mixtures of magnesium oxide were then prepared with the addition of mass fractions of 1%, 2% and 5% TiO_2 . The doping oxide used was analytical reagent grade titanium (TiO_2 p.a.) in the rutile form—produced by Carlo Erba

Reagent. Samples were homogenized by manual stirring in absolute ethanol for 30 min. The mixtures were dried at 80°C until all the alcohol was evaporated. Mixtures were cold pressed into compacts at a pressure of 625 MPa. Pressing was performed in a “Maschinenfabrik Herzog Osnabrück” hydraulic press, model TP 40. All compacts were sintered at temperatures of 1400, 1500 and 1700°C for the duration of 1, 2 and 4 h. The time of reaching these temperatures in the gas furnace was about 2 h. After sintering, samples were left to cool down in the furnace (type 553, French company “Mecker”). The boron content in the samples examined was determined using the potentiometric method. The variation coefficient for the method applied [6] is $\pm 1\%$. Results represent the average number of measurements (5 analyses in each case).

Phase compositions were analysed by X-ray powder diffraction (program MAUD) [7] using an ItalStructures diffractometer APD2000 with monochromatised Cu K α radiation (graphite monochromator). Silicon (Koch-Light Lab. Ltd.) was used as an internal standard (space group $m\bar{3}m$, for $a = 5.43088 \text{ \AA}$). The magnesium oxide samples were also examined by scanning electron microscopy (JSM-6510 LV, JEOL) equipped with an attached energy dispersive X-ray spectrometer (Oxford INCA X-act.) for the semi-quantitative elemental analysis.

3. Results and discussion

Table 1 shows the test results for the B_2O_3 mass fraction in sintered magnesium oxide samples with and without the TiO_2 addition under the operating conditions described. The B_2O_3 mass fraction in sintered magnesium oxide samples changes with the change in the parameters of activated sintering. A significant decrease of the B_2O_3 content in sintered samples is observed after the addition of 2 mass% TiO_2 at all sintering temperatures from 1400 to 1700°C while the addition of 1 mass% has no major impact.

Table 1. The B_2O_3 content in MgO samples derived from seawater (80% precipitation) sintered at 1400, 1500, 1700°C for 1, 2 and 4 h with different additions of TiO_2 .

MgO (80% precipitation)		$w(\text{B}_2\text{O}_3)$, wt%		
$t/^\circ\text{C}$	τ/h	1% TiO_2	2% TiO_2	5% TiO_2
1400	1	0.1805	0.0772	0.0582
	2	0.1425	0.0364	0.0328
	4	0.1239	0.0283	0.0273
1500	1	0.0997	0.0270	0.0228
	2	0.0933	0.0206	0.0171
	4	0.0836	0.0154	0.0138
1700	1	0.0785	0.0174	0.0119
	2	0.0598	0.0106	0.0103
	4	0.0280	0.0087	0.0071

Compared to the B_2O_3 mass fraction in calcined magnesium oxide sample, the percent of B_2O_3 evaporated from the sintered samples increases both with the increase of the duration of isothermal sintering and with the increase of the sintering temperature and the mass percent of TiO_2 added. The results presented in table 1 have been analysed in order to perform the regression analysis to obtain a mathematical model.

The mathematical package ‘Statistics 7’ was used to perform the correlation and regression analysis of experimental data (table 1) in order to obtain the relationship between the B_2O_3 mass fraction in sintered MgO as the dependent variable and independent variables.

- temperature of isothermal sintering, t : 1400°C, 1500°C, and 1700°C,
- duration of isothermal sintering, τ : 1, 2, and 4 h, and
- mass fraction of added TiO_2 , z : 0, 1, 2, and 5%.

The correlation between the B_2O_3 mass percent (w) and temperature t , duration of isothermal sintering τ and the mass fraction of added TiO_2 z was examined. The results are shown in table 2. The correlation matrix (table 2) shows that, for examined magnesium oxide samples (80% precipitation), there is no correlation between the temperature, duration or TiO_2 mass fraction, and therefore a regression equation can be obtained. There exists a significant ($p = 0.05$) negative correlation of medium strength between the B_2O_3 mass fraction and temperature and between the B_2O_3 mass fraction and mass fraction of TiO_2 , and there exists a significant weak correlation between the B_2O_3 mass fraction and duration of isothermal sintering.

A model of multiple regressions has been proposed.

$$w = b_0 + b_1 \cdot t + b_2 \tau + b_3 \cdot z + b_4 \cdot z^2 + \varepsilon \quad (1)$$

where w is the mass fraction of B_2O_3 , t is the temperature (°C), τ is the time of isothermal sintering (h), z is the mass fraction (%) of added TiO_2 , b_0 , b_1 , b_2 , b_3 , b_4 are unknown coefficients and ε is the random error in the model.

The regression equations:

$$w = 0.45598 - 0.000207 \cdot t - 0.009356\tau - 0.04868 \cdot z + 0.005882 \cdot z \quad (2)$$

where $s = 0.02588$; $R^2 = 0.76525$; $R = 0.87478$; $F(4, 139) = 113.28$; $p = 0.00$.

The value of the multiple correlation coefficient indicates that 87.5% of the B_2O_3 mass fraction variation may be attributed to the effect of variation of these factors: temperature, duration and mass percent of the TiO_2 addition. Only 12.5% of the B_2O_3 mass fraction variation is due to some other factors and random influences. Consequently, the proposed model is acceptable for predicting the B_2O_3 mass fraction in the temperature range 1400–1700°C, duration of isothermal sintering 1–4 h and the TiO_2 addition from 0–5% because the statistic F is significant at the level of $p = 0.00$.

Earlier research [8–10] has already shown a positive effect of the TiO_2 addition on the B_2O_3 content in sintered MgO samples, due to $CaTiO_3$ formation during sintering. The TiO_2 reaction with CaO reduces the amount of CaO available to react with B_2O_3 , therefore a higher amount of B_2O_3 can evaporate during the sintering process. The increase in temperature and duration of sintering also increases the percentage of evaporation of B_2O_3 from the samples into the atmosphere. According to Hesmanu [11] good quality sintered magnesium oxide used in the refractory industry contains ≤ 0.05 mass% B_2O_3 . This condition is met already at lower sintering temperatures (1400°C) with the addition of 2 mass% TiO_2 or 5 mass% TiO_2 depending on the sintering duration [10].

The results of the phase analysis at 1500 and 1700°C for 4 h (figures 1 and 2) obtained by the XRD analysis show periclase to be the main crystalline phase in all the samples. In the sample without any addition no other phase was detected. It is assumed that the amounts of CaO and B_2O_3 in this sample are too small to be detected by the XRD analysis. In a previous study [12], it has been found that B_2O_3 reacts with CaO during sintering to form $Ca_2B_2O_5$. The addition of TiO_2 leads to formation of $CaTiO_3$ and $MgTiO_4$ which has been detected by the XRD analysis. The microstructural effect of titania addition to magnesium oxide from seawater is evident from figures 3 and 4. A certain quantity of $CaTiO_3$ and Mg_2TiO_4 appeared in the form of globular segregations within the grains of MgO. The addition of TiO_2 to seawater derived magnesia results in the formation of small quantities reactive liquid that promotes sintering and grain growth. The SEM/EDS analysis (figures 3 and 4) of MgO samples detected the

Table 2. The correlation matrix for MgO (80% precipitation) samples.

Variable	Correlation for MgO (80% precipitation) samples			
	$t/^\circ\text{C}$	τ/h	TiO_2 addition, wt%, (z)	B_2O_3 , wt%, (w)
$t/^\circ\text{C}$	1.00	0.00	– 0.00	– 0.49
τ/h	0.00	1.00	0.00	– 0.22
TiO_2 addition, wt%	– 0.00	0.00	1.00	– 0.63
B_2O_3 , wt%	– 0.49	– 0.22	– 0.63	1.00

Figure 1. Powder diffraction patterns of MgO samples (80% precipitation) containing different additions of TiO_2 sintered at 1500°C for 4 h. (M-4-15—MgO without any addition of TiO_2 sintered at $1500^\circ\text{C}/4$ h; M1T-4-15—MgO with the addition of 1% TiO_2 sintered at $1500^\circ\text{C}/4$ h; M2T-4-15—MgO with the addition of 2% TiO_2 sintered at $1500^\circ\text{C}/4$ h; M5T-4-15—MgO with the addition of 5% TiO_2 sintered at $1500^\circ\text{C}/4$ h).

Figure 2. Powder diffraction patterns of MgO samples (80% precipitation) containing different additions of TiO_2 sintered at 1700°C for 4 h. (M-4-17—MgO without any addition of TiO_2 sintered at $1700^\circ\text{C}/4$ h; M1T-4-17—MgO with the addition of 1% TiO_2 sintered at $1700^\circ\text{C}/4$ h; M2T-4-17—MgO with the addition of 2% TiO_2 sintered at $1700^\circ\text{C}/4$ h; M5T-4-17—MgO with the addition of 5% TiO_2 sintered at $1700^\circ\text{C}/4$ h).

presence of CaO and confirmed the results obtained by the XRD analysis. The chemical analysis detected the presence of CaO and B₂O₃ as impurities.

In previous study [9] we have studied the mutual relationship of two interdependent reactions, i.e., reactions of formation of Ca₂B₂O₅ and CaTiO₃ so that this study is a continuous investigation with the purpose to connect all the factors that take effect on sintering of magnesium oxide from seawater.

Since the results of the XRD analysis indicated the formation of the Mg₂TiO₄ phase, the system of two interdependent reactions of formation of Ca₂B₂O₅ and CaTiO₃ has been extended to include the reaction of formation of Mg₂TiO₄. Thus, during the process of activated sintering of seawater-derived MgO with the addition of TiO₂, three interdependent reactions take place:

The consideration of the above mentioned three relationships has not been reported in literature. A system of phenomenological equations, dealt within the open system thermodynamics [13–16], has been applied to reactions (3), (4), and (5) in order to link all the factors affecting the process of activated sintering of seawater-derived magnesium oxide, and the ability to control the process itself.

The non-equilibrium thermodynamics approach is widely recognized as a useful phenomenological theory that describes the coupled transport without the need for examining detailed coupling mechanisms of complex processes. The principles of non-equilibrium thermodynamics for the systems not far away from the thermodynamic equilibrium are expressed in linear forms [13–15]. Linear relations can be expressed between flows J_i , and driving forces X_i . If a non-equilibrium system consists of several flows caused by various forces, the general expression for J_i is:

$$J_i = \sum_j^n L_{ij} \cdot X_j \quad (i, j = 1, 2, \dots, n) \quad (6)$$

or for X_i

$$X_i = \sum_j^n K_{ij} \cdot J_j \quad (i, j = 1, 2, \dots, n) \quad (7)$$

where: L_{ij} , K_{ij} are phenomenological coefficients. Equations (6) and (7) are phenomenological equations which

Figure 3. SEM/EDS images of the MgO sample without any addition of TiO₂ sintered at 1700°C/4 h.

Figure 4. SEM/EDS images of the MgO sample with the addition of 5% TiO₂ sintered at 1700°C/4 h.

describe the multi-flow systems and the effect of non-conjugate forces on a flow. The “proper” phenomenological coefficients with the same indices relate the conjugated forces and flows. The “mutual” phenomenological coefficients L_{ij} or K_{ij} ($i \neq j$) describe the interference, i.e., characterize the mutual effect of the two irreversible processes “i” and “j”. According to the principle of microscopic reversibility, Onsager has defined “mutual” phenomenological coefficients and postulated that the matrix of “mutual” phenomenological coefficients is symmetrical [16].

$$L_{ij} = L_{ji} \text{ i.e. } \left(\frac{\partial J_i}{\partial X_j} \right)_{X_i=0, i \neq j} = \left(\frac{\partial J_j}{\partial X_i} \right)_{X_j=0, i \neq j} \quad (i, j = 1, 2, \dots, n) \quad (8)$$

$$K_{ij} = K_{ji} \text{ i.e. } \left(\frac{\partial X_i}{\partial J_j} \right)_{J_i=0, i \neq j} = \left(\frac{\partial X_j}{\partial J_i} \right)_{J_j=0, i \neq j} \quad (i, j = 1, 2, \dots, n) \quad (9)$$

The system of these three interdependent reactions has been analysed by linear non-equilibrium thermodynamics, based on an important theorem due to Onsager. For a system with three flows caused by three driving forces, i.e., with three simultaneous irreversible processes ($n = 3$), phenomenological equations can be expressed based on Onsager reciprocity relations [13–15]:

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \quad (10)$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \quad (11)$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \quad (12)$$

where J_1, J_2 and J_3 denote the flows; and X_1, X_2 and X_3 denote the forces causing these flows. The “mutual” coefficients are equal according to Equations (8) and (9), which reduces the number of phenomenological coefficients. The phenomenological coefficients have to meet the following conditions [15]:

$$L_{11} \geq 0, L_{22} \geq 0, L_{33} \geq 0 \quad (13)$$

$$L_{11}L_{22} - \frac{1}{4}(L_{12} + L_{21})^2 \geq 0 \quad (14)$$

$$L_{22}L_{33} - \frac{1}{4}(L_{23} + L_{32})^2 \geq 0 \quad (15)$$

$$L_{11}L_{33} - \frac{1}{4}(L_{13} + L_{31})^2 \geq 0 \quad (16)$$

The “proper” coefficients are always positive because the entropy production can never be negative. The “mutual” coefficients are limited by Equations (14), (15) and (16). The matrix of phenomenological coefficients L_{ij} and K_{ij} , is related by

$$K = L^{-1} \quad (17)$$

where L^{-1} is the inverse of the matrix L .

The phenomenological equations can also be expressed in terms of forces:

$$X_1 = K_{11}J_1 + K_{12}J_2 + K_{13}J_3 \quad (18)$$

$$X_2 = K_{21}J_1 + K_{22}J_2 + K_{23}J_3 \quad (19)$$

$$X_3 = K_{31}J_1 + K_{32}J_2 + K_{33}J_3 \quad (20)$$

The phenomenological coefficients are related by the following relations:

$$\begin{aligned} K_{11} &= \frac{(L_{22}L_{33} - L_{23}^2)}{|L|}; K_{22} = \frac{(L_{11}L_{33} - L_{13}^2)}{|L|}; \\ K_{33} &= \frac{(L_{11}L_{22} - L_{12}^2)}{|L|}; K_{12} = \frac{(L_{13}L_{23} - L_{12}L_{33})}{|L|}; \\ K_{13} &= \frac{(L_{12}L_{23} - L_{22}L_{13})}{|L|}; K_{23} = \frac{(L_{13}L_{12} - L_{23}L_{11})}{|L|} \end{aligned} \quad (21)$$

$$L = L_{11}L_{22}L_{33} + 2L_{12}L_{13}L_{23} - L_{13}^2L_{22} - L_{23}^2L_{11} - L_{12}^2L_{33} \quad (22)$$

where $|L|$ is the determinant of the matrix L .

Coefficients L_{12}, L_{23} and L_{13} have been calculated from Equations (10), (11), (12), (13), (14), (15) and (16) using the mathematical program Wolfram Alpha. They are defined as:

$$\begin{aligned} L_{12} &= \frac{J_1J_2}{J_1X_1 + J_2X_2 - J_3X_3}; \\ L_{23} &= \frac{J_2J_3}{-J_1X_1 + J_2X_2 + J_3X_3}; \\ L_{13} &= \frac{J_1J_3}{J_1X_1 - J_2X_2 + J_3X_3} \end{aligned} \quad (23)$$

or

$$\begin{aligned} L_{12} &= \frac{J_1J_2}{J_1X_1 + J_2X_2 + J_3X_3}; \\ L_{23} &= \frac{J_2J_3}{J_1X_1 + J_2X_2 + J_3X_3}; \\ L_{13} &= \frac{J_1J_3}{J_1X_1 + J_2X_2 + J_3X_3} \end{aligned} \quad (24)$$

Equations (23) and (24) give different results for the same coefficient but the result used in further calculation is the one that gives a better match at the end of the experiment. The combination of the mean values method with the least square method was used in determining all the phenomenological coefficients. Coefficients L_{22}, L_{33} and L_{11} have been calculated using the mathematical program Mathcad 2000 Professional from Equations (10), (11) and (12). They are defined as:

$$\begin{aligned}
 L_{11} &= \frac{\sum_{ij} J_1 X_1 - L_{12} \sum_{ij} X_1 X_2 - L_{13} \sum_{ij} X_1 X_3}{\sum_{ij} X_1^2}; \\
 L_{22} &= \frac{\sum_{ij} J_2 X_2 - L_{12} \sum_{ij} X_3 X_2 - L_{23} \sum_{ij} X_2 X_3}{\sum_{ij} X_2^2}; \\
 L_{33} &= \frac{\sum_{ij} J_3 X_3 - L_{13} \sum_{ij} X_1 X_3 - L_{23} \sum_{ij} X_2 X_3}{\sum_{ij} X_3^2}
 \end{aligned} \quad (25)$$

If phenomenological equations (10), (11) and (12) are applied to the three reactions (3), (4) and (5) that describe the process of sintering of MgO samples (80% precipitation) obtained from seawater, it follows:

$$J_1 = L_{11}t' + L_{12}\tau + L_{13}\gamma \quad (26)$$

$$J_2 = L_{21}t' + L_{22}\tau + L_{23}\gamma \quad (27)$$

$$J_3 = L_{31}t' + L_{32}\tau + L_{33}\gamma \quad (28)$$

where J_1 represents the fraction of B_2O_3 evaporated, J_2 the fraction of CaO that reacts with TiO_2 and J_3 the fraction of TiO_2 that reacts with MgO. These fractions are a function of the temperature of sintering (t'), time (τ) and additives (γ). According to Equations (23), (24) and (25), phenomenological coefficients were calculated by using the experimental data shown in table 1. The theoretical approximation for J_1, J_2 and J_3 is replaced with the experimental results for J_1^o, J_2^o and J_3^o . It has also been assumed that $t' = t \cdot 10^{-2} \text{ } ^\circ\text{C}$ to achieve the appropriate adjustment of numerical expressions obtained. The obtained values for J_1^o, J_2^o and J_3^o are shown in table 3.

After calculating all the phenomenological coefficients, phenomenological equations result in two sets of solutions

(first set—29a, 30a, and 31a; second set—29b, 30b, and 31b).

$$J_1 = 1.625 \cdot t' + 4.707 \cdot \tau + 0.126 \cdot \gamma \quad (29a)$$

$$J_1 = 1.626 \cdot t' + 4.676 \cdot \tau + 0.089 \cdot \gamma \quad (29b)$$

$$J_2 = 4.707 \cdot t' + 7.781 \cdot \tau - 0.144 \cdot \gamma \quad (30a)$$

$$J_2 = 4.676 \cdot t' + 7.774 \cdot \tau + 0.101 \cdot \gamma \quad (30b)$$

$$J_3 = 0.126 \cdot t' - 0.144 \cdot \tau + 0.153 \cdot \gamma \quad (31a)$$

$$J_3 = 0.089 \cdot t' + 0.101 \cdot \tau + 0.153 \cdot \gamma \quad (31b)$$

Relative errors are shown in table 4. The deviations of the theoretical data and the corresponding experimental data in both cases are within the reasonable limits because the relative errors for individual equations are relatively small. Equations (29a), (30a), (31a) match the experimental values better than equations (29b), (30b), (31b) and give slightly more accurate results. Therefore equations (29a), (30a), (31a) are more appropriate for this technological process of sintering MgO samples (80% precipitation) obtained from seawater.

These phenomenological equations can also be expressed in terms of forces for the final results:

Table 4. Relative errors for individual values of all flows.

MgO (80% precipitation)						
Relative errors/%	First set of results			Second set of results		
	J_1	J_2	J_3	J_1	J_2	J_3
$\bar{\delta}$	0.69	0.12	6.44	0.69	0.12	6.20

Table 3. The experimental values of J_1^o, J_2^o and J_3^o in dependence on temperature, duration of heating and additions of TiO_2 .

MgO (80% precipitation)										
		MgO + 1% TiO_2			MgO + 2% TiO_2			MgO + 5% TiO_2		
$t/^\circ\text{C}$	τ/h	J_1^o	J_2^o	J_3^o	J_1^o	J_2^o	J_3^o	J_1^o	J_2^o	J_3^o
1400	1	4.40	64.75	0.20	59.11	84.69	0.85	69.17	88.36	3.40
	2	24.52	72.09	0.12	80.72	92.57	0.77	82.63	93.26	3.35
	4	34.38	75.68	0.09	85.01	94.13	0.76	85.54	94.32	3.33
1500	1	47.19	79.39	0.04	85.70	93.26	0.75	87.92	94.06	3.29
	2	50.58	80.61	0.03	89.09	94.48	0.73	90.94	95.15	3.28
	4	55.72	82.46	0	91.84	95.47	0.72	92.69	95.78	3.28
1700	1	58.42	82.46	0	90.78	94.41	0.72	93.70	95.45	3.22
	2	68.33	82.46	0	94.39	95.69	0.70	94.54	95.75	3.22
	4	85.17	82.46	0	95.39	96.05	0.70	96.24	96.36	3.21

$$t' = -0.656 \cdot J_1 + 0.414 \cdot J_2 + 0.928 \cdot J_3 \quad (32)$$

$$\tau = 0.414 \cdot J_1 - 0.131 \cdot J_2 - 0.463 \cdot J_3 \quad (33)$$

$$\gamma_3 = 0.928 \cdot J_1 - 0.463 \cdot J_2 + 5.325 \cdot J_3 \quad (34)$$

The phenomenological equations allow the usage of computer programs in order to predict the B_2O_3 content in sintered samples and the phase composition in the final product of MgO in dependence on temperature, duration of heating and additives. Modelling the process of sintering MgO from seawater is most important for predicting the content of B_2O_3 in the final product because the content of B_2O_3 has to be ≤ 0.05 wt% for getting the good quality refractory materials based on MgO [11].

4. Conclusions

The proposed mathematical model is acceptable for predicting the B_2O_3 mass fraction in the temperature interval 1400–1700°C, duration of isothermal heating 1–4 h and the TiO_2 addition of 0–5%.

The concept of non-equilibrium thermodynamics has been successfully applied to the process of sintering MgO from seawater in order to establish the relations of mutual influence of simultaneous irreversible processes during sintering. The phenomenological equations are defined with phenomenological coefficients in dependence on temperature, duration of heating and additives. This relationship among all the factors of sintering makes it possible to use computer programs to predict the B_2O_3 content in the sintered samples and the phase composition in the final product of MgO.

The phenomenological coefficients were calculated from the experimental data in the temperature range of 1400–1700°C for the duration of 1–4 h and with the addition of max 5% of TiO_2 . Since the same phenomenological coefficients have given dual results, relative errors were taken as an indicator of accuracy of the proceedings. As the values of relative errors were similar for both the results obtained, the phenomenological equations that are in better agreement with the experimental values obtained were chosen as more appropriate for the description of this technological process of sintering of MgO (80% precipitation) obtained from seawater.

Nomenclature

J_i, J_j flows
 L_{ij}, K_{ij} phenomenological coefficients

X_i, X_j driving forces
 t' temperature of sintering, °C
 τ time, h
 γ addition of TiO_2 , wt%

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