Original Article

MgSO₄ carbothermic reductive decomposition to produce a highly reactive MgO powder

Bruno Souza a, Rodrigo Souza a,*, Irnildes Santos b, Eduardo Brocchi a

a Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, Rua Marquês de São Vicente, 225 CEP, 22453-900, Rio de Janeiro, RJ, Brazil
b Instituto Tecnológico Vale, Avenida Juscelino Kubitschek, 31, 35400-000 Ouro Preto, MG, Brazil

ARTICLE INFO

Article history:
Received 23 August 2019
Accepted 5 December 2019
Available online 16 January 2020

Keywords:
Reductive decomposition
Magnesium oxide
Magnesium sulphate
Charcoal
Neutralizing agent

ABSTRACT

Magnesium sulphate is commonly present in industrial wastes due to Mg’s presence in the structure of various minerals and the fact that sulphuric acid leaching is widely used. MgO appears as a possible pH neutralizing agent that can be obtained by decomposition of MgSO₄. However, at 1500 K, the temperature where this decomposition occurs, the oxide formed cannot be used for this purpose. The thermodynamic study suggests that in the presence of reducing agents, such as carbon, decreasing the decomposition temperature makes the formed oxide viable for this use. The objective of the work is an evaluation of the behaviour of the reaction system constituted by MgSO₄ and charcoal. The study also contemplates the obtained materials characterization to verify the MgO formation and evaluating how the properties of the material are suitable for its use as a pH regulator. Thus, in addition to the scanning and X-ray diffraction electron microscopy techniques, the quantification of the reactivity of the product in acid solutions is also expected. The analysis performed with the variables of excess reducing agent and temperature showed that temperature is the variable that most influences the decomposition of MgSO₄. The experiments at 1173 K and 20, 25 and 30 min were the ones that indicated the best experimental results of conversion, reaching a conversion close to 100%. The characterization analysis, in XRD and SEM/EDS, indicated that MgO was formed at the end of the reaction. Reactivity test indicates that the obtained MgO can be used as a pH regulator.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

In various segments, such as paper mills, textile industries, mining, agrochemical and aluminium industries, sulphate ions are commonly present in its process effluents [1,4]. Compared with toxic metals, sulphate is only mildly hazardous, however, it can affect the taste of water and can also have laxative effects at concentrations above 600 mg L⁻¹ [4]. To deal with its deleterious effects, the use of magnesium for sulphate removal through precipitation is suggested [3], since usually SO₄²⁻ and Mg²⁺ coexist in some industrial waste [2]. In mining waters, for instance, magnesium can amount up to thousands of milligrams per liter [3]. In this context, other studies indicate the presence of magnesium in industrial waste [5],
especially within the mineral industry [6,7], increasing the possibility of its occurrence in conjunction with sulphate. Another reason for the presence of sulphate in industrial effluents is the use of sulphuric acid (H₂SO₄) as a leaching agent [8].

In parallel to this, Magnesium oxide (MgO), which can be obtained by decomposition of magnesium sulphate (MgSO₄), can be used as a pH regulator within acid leaching operations if it has the necessary characteristics [9,10]. It is known that MgO can be easily produced through MgSO₄ thermal decomposition. However, it should be noted that this decomposition occurs in high temperatures, and the formed oxide does not meet the characteristics required for its use as a pH regulator. For this use it is necessary that the obtained MgO has high reactivity in acid media, probably associated with a consequent high surface area [10]. For processes with temperatures above 1372 K (1100 °C), the formed MgO does not have such characteristics [11]. Still, it is possible to decrease this temperature up to 773 K (500 °C) with the presence of a reducing agents such as CO(g), C and H₂(g) [12]. In this context, the reductive decomposition could be used as an alternative chemical process to transform MgSO₄ in MgO in lower temperatures [12-15].

Moreover, considering the recent interest in nickel laterites, in which the magnesium content could be very high, it has been observed that H₂SO₄ acid leaching is being considered for high pressure and atmospheric processes for nickel extraction [16,19-21]. In this scenario, the magnesium content tends to report to acid liquors and consume high quantities of sulphuric acid [17,18,22,23]. Some alternatives have been proposed to remove magnesium from such liquors [22,23], however, there is a paucity of information regarding its technological reuse within acid leaching flowcharts.

For that reason, the motivation for this research work is associated with the study of a chemical process in which magnesium sulphate, a possible by-product of sulphuric acid leaching flowcharts, is transformed in its respective oxide and its potential application as pH neutralizing agent.

Under this general perspective, the present study deals with the assessment of the reaction system behaviour constituted by MgSO₄ heptahydrate in the presence of charcoal in order to evaluate the effectiveness of the produced oxide as a pH regulating agent. To achieve that, a thermodynamic evaluation of the reaction system and experimental studies of the reductive decomposition of MgSO₄ heptahydrate with charcoal were carried out. Subsequently, the obtained products were characterized through scanning electron microscopy (SEM/EDS), x-ray diffraction (XRD) and its reactivity in acid media tested to appreciate its applicability.

2. Materials and methods

2.1. Thermodynamics assessment

To assess the thermodynamics features of magnesium sulphate decomposition in reductive and non-reductive conditions, it was performed calculations of the equilibrium composition as a function of temperature. These were carried out using the software HSC Chemistry [24].

### Table 1 - Relationship between sulphate and distilled charcoal masses within the prepared mixture in each temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Boudouard equilibrium CO percentage (%)</th>
<th>Boudouard equilibrium CO₂ percentage (%)</th>
<th>Charcoal / sulphate ratio (wt% / wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>25.7</td>
<td>74.3</td>
<td>0.0306</td>
</tr>
<tr>
<td>973</td>
<td>61.8</td>
<td>38.2</td>
<td>0.0394</td>
</tr>
<tr>
<td>1073</td>
<td>88.9</td>
<td>11.1</td>
<td>0.0460</td>
</tr>
<tr>
<td>1173</td>
<td>97.4</td>
<td>02.6</td>
<td>0.0480</td>
</tr>
</tbody>
</table>

2.2. Reductive decomposition experimental procedure

Commercial grade charcoal was used as a reducing agent to promote the decomposition of an analytical grade magnesium sulphate heptahydrate sample, manufactured by Merck. The charcoal was milled, dehumidified and distilled according to the methodology presented at ASTM D1762-84 standard. The magnesium sulphate also was milled for in order to diminish particle size effects in reaction conversion. The experiments were carried out in a tubular furnace, where 0.5 g of the mixture of MgSO₄·7H₂O and charcoal was placed in a boat-type porcelain crucible within the isothermal zone. The temperatures of 873 K (600 °C), 973 K (700 °C), 1073 K (800 °C) and 1173 K (900 °C) were studied as function of time until 30 min using a high-purity argon at 0.33 L.min⁻¹. In addition, experiments were carried out to determine the effect that the excess reducing agent may cause in the final conversion of the reducing decomposition of MgSO₄, experiments were carried out with the stoichiometric reducing agent (charcoal), and conditions of excess of 10%, 20% and 30% with a time of 30 min [25]. Fig. 1 shows a graphical representation of the experimental line used during the experiments.

Both solids were mechanically mixed according to the proportionality of the Boudouard Equilibrium as shown in reactions (1) and (2) as well as Table 1. This was made to respect the correct stoichiometry of each reaction within the studied temperatures.

\[
\text{MgSO}_4 + C \rightarrow \text{MgO(s)} + \text{SO}_2(g) + \text{CO(g)} \tag{1}
\]

\[
\text{MgSO}_4 + 0.5\text{C} \rightarrow \text{MgO(s)} + \text{SO}_2(g) + 0.5\text{CO}_2(g) \tag{2}
\]

2.3. Materials characterization methods

To characterize the hydration levels of the synthetic MgSO₄·7H₂O, as well as the thermal behaviour of the sample, it was used as a Netzsch thermogravimetric analyser model STA 449 F3 Jupiter, from the Department of Chemical and Materials Engineering of the Pontifical Catholic University of Rio de Janeiro (DEQM / PUC-Rio). The analysis was performed in an inert atmosphere of ultra-pure nitrogen at a heating rate of 15 K (15 °C) min⁻¹ from room temperature until 1173 K (900 °C). The reductive decomposition was also characterized through thermogravimetric analysis.

The Hitachi TM-3000 Scanning Electronic Microscope/X-ray Scattering Spectroscopy (SEM/EDS) was used to study the particle morphology as well as to appreciate the chemical
composition of the obtained product to verify sulphur removal after the reductive decomposition.

The Bruker X-ray diffraction model D8 Discover was used for an evaluation of the mineralogical composition of the product obtained to assess the sulphate transformation in its respective oxide.

The reactivity tests of the product obtained by the reductive decomposition of MgSO₄ were carried out in the presence of analytical grade citric acid and were based on the methodology described by Yi et al. [26]. A solution of 100 mL of 0.07 m.L⁻¹ citric acid was prepared and maintained at 313 K (40 °C) under constant stirring in a 500 mL beaker. For each test, 0.85 g of MgO was poured into the citric acid solution. pH meter, mPA-210 from MS Tecnopon Instrumentation, was used to measurement of pH and was calibrated to cover a variation of 0.01 in pH.

3. Results and discussion

3.1. Thermodynamics assessment

Figs. 2 show the equilibrium species distribution diagrams, as a function of temperature and initial chemical composition of the decomposition of magnesium sulphate with or without reducing agent.

It is possible to identify MgO as the only product of the decomposition containing magnesium. The analysis also allowed the observation that while the decomposition of MgSO₄ without the reducing agent only occurs from 1100 K (827 °C), in the presence of the reducing agent the decomposition occurs from 300 K (27 °C). This reduction in the MgO formation temperature is very important because it could promote the formation of an MgO with distinct characteristics. In
part b) it is possible to verify around 873 K (600 °C) that the only species containing magnesium is MgO, so the decomposition experiments were performed as temperatures higher than that.

3.2. Reductive decomposition

By the analysis of Table 2, it is possible to evaluate the behaviour of the decomposition in relation to the temperature over time of 30 min.

For the experiments performed at 873 K (600 °C) the maximum conversion value reached was 8.69%, for those performed at 973 K (700 °C) the maximum conversion was 11.35%, the tests at 1073 K (800 °C) show a maximum conversion of 29.48%. The best results, as expected, were for the tests at 1173 K (900 °C), where the conversion to the 20–30 min intervals was close to 100%. By analysing the behaviour of the reductive decomposition over time it can be observed that for the temperatures of 873 K (600 °C) and 973 K (700 °C) the conversion of the reaction does not present a gradual evolution in relation to the increase of time in the tests, this occurs due to the difficulty of decomposing MgSO4 at these temperatures. While at temperatures of 1073 K (800 °C) and 1173 K (900 °C) it is possible to observe the influence of time on the conversion of the decomposition, in the first 15 min of the tests the rapid increase of the conversion indicates a strong initial reactivity, already for experiments with more than 20 min the conversion variation with time decreases, indicating a milder reaction.

The effect of the excess of the reducing agent on the final conversion of the MgSO4 decomposition is presented in Fig. 3.

These values confirm the excess reducing agent has no direct influence on the final conversion of the reducing decomposition, since the difference between the largest and the smallest recorded conversion does not reach 10% per temperature, being 3.6% in the tests at 873 K (600 °C), 4.1% in the tests at 973 K (700 °C), 8.5% in the tests at 1073 K (800 °C) and 0.6% in the tests at 1173 K (900 °C). Since the excess of reducing agent does not influence the final conversion of the decomposition reaction, the other experiments were carried out under stoichiometric conditions.

3.3. Materials characterization

3.3.1. Thermogravimetric analysis

The Figs. 4 present the data of the mass percentage variation of the MgSO4.7H2O obtained through the TGA, during a non-reductive decomposition and a reductive decomposition respectively.

In part a), MgSO4.7H2O shows a significant mass variation between approximately 373 K (100 °C) and 623 K (350 °C). This variation represents a loss of total mass of 51.57%, which is close to the expected loss of mass of the MgSO4.7H2O molecule since the seven molecules of water bound to sulphate represent 51.16% of the total mass. After approximately 623 K (350 °C) the magnesium sulphate becomes anhydrous and stable up to 1350 K (1077 °C) when MgSO4 begins to decompose. In part b), MgSO4.7H2O shows practically the same mass variation between 373 K (100 °C) and 623 K (350 °C) than in part a). The difference between the reductive system is the temperature to decompose begins, after 1050 K (777 °C).

3.3.2. Chemical and morphological characterization of MgO

Fig. 5 shows the morphological structure of the product obtained at 1173 K (900 °C), 25 min and presence of the reducing agent, probably MgO, in four magnifications: ×200, ×400, ×800 and ×1500. From these images, it can be observed that the material presents a homogeneous morphology formed of small particles. By the analysis of the image with the highest magnification, it can be find out that these particles are smaller than 10 µm. It can be can state that, despite the for-
mation of small crystals, visually the material appears to have certain porosity in its structure.

To assert the product formed in the reductive decomposition a region of the sample was analysed by EDS, Fig. 6. This analysis determined that the material produced contained magnesium and sulphur in its elemental chemical composition, Fig. 7. This result was expected since this method of analysis does not capture a signal of any element equal to or less than oxygen.

What enables the completion of the formed product is the percentage of each element in the final product, since both are present in the reagent, MgSO₄. Considering the detection limitation for only magnesium and sulphur, in the reactant, it was identified a theoretical proportion of 43.2% of the weight for magnesium and 56.8% of the weight for sulphur, whereas in the product it was detected an amount of 94.7% of magnesium and 5.3% sulphur. This discrepancy in proportion indicates that about 4.0% of magnesium belongs to an amount of unreacted MgSO₄, while the other 90.7% are dissociated from sulphur, probably as MgO.

Analysing the diffractogram resulting from the X-ray diffraction analysis of the product obtained at 1173 K (900 °C), 25 min and presence of the reducing agent assays and comparing this result with the databases of known crystal structures, it was possible to determine that the product obtained is composed of three phases of magnesium oxide. This result is in line with that expected after the thermodynamic analysis and the chemical composition found by the EDS analysis. The adjustment that enabled this analysis of the mineralogical composition of the product obtained can be observed in Fig. 8.

The grey line, present in the lower region of the image, represents a difference between the signal captured by the diffractometer from the analysed material and the value calculated from the known databases. This is an indication of the existence of other crystalline structures that have not been adjusted. Due to the low amplitudes in the grey line, it is plausible to admit that these unidentified structures are on a smaller scale than those of magnesium oxide, the existence of most of these peaks between 16° and 38° can be observed. By the nature of the reaction studied, these peaks probably represent compounds found in charcoal ashes.

3.3.3. Reactivity test of MgO obtained by the reducing decomposition

After confirming that the product of the reducing decomposition was MgO, tests were performed on three different compositions to verify the reactivity of the MgO formed. Test 1 was performed with the MgO formed at 1173 K (900 °C), 25 min and presence of the reducing agent, subjected to a stirring of 200 rpm. Test 2 was performed with the MgO formed at 1173 K
(900 °C), 25 min and presence of the reducing agent, subjected to a stirring of 500 rpm. Test 3 was performed with the product of the decomposition of MgSO₄ at a temperature of 1273 K (1000 °C) and without the presence of the reducing agent, subjected to a stirring of 500 rpm. The three tests were performed on a solution of citric acid with pH 2.29.

In test 1 the MgO was able to raise the pH of the solution to the desired point (pH 8.5), however, this value was reached after 360 s, time over than necessary (120 s). With this test 2 was carried out with increased agitation, in it, the MgO raised the pH of the solution to 8.5 in 93 s, enough time to determine the MgO formed as highly reactive. Test 3 was performed to analyse the influence of temperature on the reactivity, where the pH of the solution was raised to 2.51 after 120 s and remained unchanged during the test period, 600 s, demonstrating the importance of the temperature decrease decomposition of MgSO₄ in the reactivity of its product. The test data are in Table 3.
Fig. 5 – Morphological structure of the product of the reductive decomposition obtained by SEM.

Fig. 6 – Morphological structure of the product of the reductive decomposition obtained by SEM of the region analysed by EDS.

4. Final remarks

The evaluation of the thermodynamic assessment performed showed a total decomposition temperature of pure magnesium sulphate at temperatures above 1500 K (1227 °C) and indicated that the total decomposition of magnesium sulphate in the presence of the reducing agent at temperatures above 873 K (600 °C).

Although the thermodynamic appreciation indicates that MgSO_4 could decompose from 873 K (600 °C) in the presence of the reducing agent, experiments have shown that at less than 1073 K (800 °C) there is no significant decomposition of
Table 3 – Results of reactivity tests in the presence of an acid solution.

<table>
<thead>
<tr>
<th>Test</th>
<th>pH t=0</th>
<th>pH t=2 min</th>
<th>pH t=6 min</th>
<th>Time to reach pH 7</th>
<th>Time to reach pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.29</td>
<td>4.40</td>
<td>9.07</td>
<td>300</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>2.29</td>
<td>8.75</td>
<td>9.10</td>
<td>60</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>2.29</td>
<td>2.51</td>
<td>2.51</td>
<td>Not reached</td>
<td>Not reached</td>
</tr>
</tbody>
</table>

The same. The tests carried out at 1173 K (900 °C) were the ones that achieved the best conversion results in the tests with more than 20 min, reaching a conversion above 94%.

The TGA analysis, during non-reducing decomposition and reductive decomposition, shows that both have a mass variation between approximately 373 K (100 °C) and 623 K (350 °C), a variation due to loss of mass of the molecules of water in MgSO₄·7H₂O. These analyses also indicate a different behaviour regarding the decomposition of MgSO₄, indicating a decrease of 300 K at the initial decomposition temperature, 1350 K (1077 °C) in the non-reducing and 1050 K (777 °C) in the reducing agent. This behaviour confirms the thermodynamic appreciation.

The evaluation of the SEM product indicated that the product obtained has a homogeneous morphology composed of particles smaller than 10 µm. Visually the material appears to have porosity in its structure that may be suitable for use as a pH adjuster. The DR-X characterization test of the product obtained in the chosen assays indicates that the MgO is being formed at the end of the reaction. Since the diffractogram indicates that the mineral composition of the analysed product is formed by MgO.

The reactivity tests of the MgO formed in the reductive decomposition indicated that it can be used as a pH regulator since it was able to raise the pH of the solution to the desired levels in the two agitations studied. The reactivity test with the product of simple decomposition at 1273 K (1000 °C) con-
firms that the material obtained does not have the necessary characteristics to act as a pH regulator.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors are also grateful to the Instituto Tecnológico Vale (ITV) and the Vice-Reitoria para Assuntos Acadêmicos (VRAC / PUC-Rio) for the partnership and support throughout this research.

References