

Systematic Precipitation of Magnesium Hydroxide Using NH₄OH to Preparing MgO-PSZ Precursor Powder

Chieko Yamagata^{1, a}, Jose O. A. Paschoal¹

¹Instituto de Pesquisas Energéticas e Nucleares, Centro de Ciência e Tecnologia de Materiais (CCTM), Av. Prof. Lineu Prestes, 2242, CEP-05508-000, Universidade de São Paulo, São Paulo-SP, Brazil.

^ayamagata@ipen.br

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Abstract. The wide range of applications of zirconia based ceramics is due to stabilization of its tetragonal and cubic structures at room temperature, by controlled adding of dopants such as yttria, magnesia, calcia, ceria and some rare earth oxides. The advantage of the use of magnesia as dopant is not only due to its low cost, but fact that by controlling its ceramic processing, it is possible to control a specific microstructure for the specific application. The precipitation of magnesium hydroxides, using NH₄OH as a precipitant, presents some difficulties due to the formation of a variety of soluble complexes of ammonia with magnesium, which inhibits the total precipitation of magnesium. In the present work, the influence of precipitant and metals concentrations and pH on the magnesium hydroxide precipitation was investigated. Magnesium chloride, zirconium oxychloride and NH₄OH were used as starting materials. The precipitation of magnesium hydroxide depends on concentrations of OH⁻, Cl⁻ and Mg²⁺. To achieve specific precipitation yield, lower the concentration of Mg²⁺ high molar ratio of [OH⁻]/[Cl⁻] is required. The pH measure is not enough to control Mg(OH)₂ precipitation. The use of molar ratio of [OH⁻]/[Cl⁻] = 4.4, resulted in 95 % of Mg(OH)₂ precipitation. The co-precipitation of Zr and Mg hydroxides, using the optimized molar ratio of [OH⁻]/[Cl⁻], the precipitation of Mg(OH)₂ achieved in range of 97.6 to 98.3 %.

Introduction

In the simultaneous precipitation of zirconium and magnesium hydroxides, the precipitant generally used is NH₄OH solution because of its low cost easily removed by calcining. While zirconium is almost totally precipitated, magnesium is never completely precipitated [1]. This is related to the solubility of magnesium hydroxide, which is markedly high in a solution of ammonium salts because of formation of ammonia-magnesium complexes [2], which inhibit the precipitation of Mg²⁺ ion. For zirconium and magnesium simultaneous precipitation, solutions of ammonium hydroxide, sodium hydroxide, ammonium carbonate, and ammonium oxalate are some of possible precipitants [3]. With NH₄OH, magnesium ion (Mg²⁺) give partial precipitation of Mg(OH)₂. Mg(OH)₂ is very sparingly soluble in water, but readily soluble in ammonium salts solutions. With sodium hydroxide, the Mg²⁺ is practically completely precipitated resulting Mg(OH)₂, which is insoluble in excess of the reagent, but also readily soluble in solutions of ammonium salt. Basic magnesium carbonate is obtained with ammonium carbonate solution, but its complete precipitation takes place only on boiling or on long standing. No precipitate is obtained in the presence of ammonium salts, since the latter reduces the carbonate ion concentration because of the

common ion effect. NH_4OH and NaOH solutions precipitate zirconium hydroxide. Solutions of $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitate basic zirconium carbonate and zirconium oxalate respectively, which are soluble in excess of the reagent. Both precipitations do not happen in presence of sulfate ion [4]. NaOH is a good precipitant for both magnesium and zirconium, but calcining does not volatilize it. Therefore, but even some previous mentioned inconvenient of NH_4OH , it is considered a suitable precipitant for simultaneous precipitation of magnesium and zirconium. The precipitation of zirconium in chloride solution starts at 1.9 pH and ends at 4.2 pH [4]. The reaction between Mg^{2+} and NH_4OH may be represented by following reaction [5]:



By the progress of the reaction, the concentration of ammonium ions increases due to the complete dissociation of the ionized ammonium salt, and consequently the concentration of hydroxyl ions decreases remaining to the common ion effect. The hydroxyl ion concentration, already low, is decreased still further so that much of magnesium salt remains in solution. In the presence of a sufficient concentration of ammonium salts, the ionization of the ammonium hydroxide is depressed to such an extent that the solubility product of $\text{Mg}(\text{OH})_2$ is not exceeded, hence magnesium is not precipitated by ammonium hydroxide solution in the presence of ammonium salts. Because of the difficulties to establish the magnesium precipitation conditions when NH_4OH solution is used as precipitant, other methods such as polymeric [6], acetate [7], alkoxide [8], sol-gel [9] and melting salts [10,11], mechanical milling [12] processes have all been used for synthesize MgO-PSZ powders. In this work, the optimization of magnesium precipitation was studied. The influence of Mg^{2+} and NH_4OH concentration and molar ratio of $[\text{OH}^-] / [\text{Cl}^-]$ on the precipitation of $\text{Mg}(\text{OH})_2$ was investigated.

Experimental

The solutions of MgCl_2 obtained by dissolving $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water, ZrOCl_2 obtained by dissolving of zirconium hydroxide (produced at IPEN- Instituto de Pesquisas Energéticas e Nucleares) [13] in 6M HCl and NH_4OH were used as starting materials. The study of $\text{Mg}(\text{OH})_2$ precipitation with NH_4OH , performed following the procedure as follows. In volumetric glassware, a volume of magnesium chloride solution was added. After that a calculated volume of NH_4OH solution, following the previous fixed molar ratio of $[\text{OH}^-] / [\text{Cl}^-]$, was added. The mixture content in the volumetric glassware was carefully stirred and the nominal volume of the recipient was completed with distilled water. After 30 min resting, a clear aliquot of mother solution was separated to determine the value of pH and the concentration of Mg^{2+} not precipitated. The $\text{Mg}(\text{OH})_2$ precipitation yield was calculated from the relation of the difference between starting mass of Mg^{2+} and the mass of Mg^{2+} not precipitated on the starting mass of Mg^{2+} . The analysis of Cl^- and Zr^{4+} were carried out by gravimetric method by using AgNO_3 and NH_4OH solutions as precipitant respectively. The concentrations of Mg^{2+} and OH^- in solutions were determined by atomic absorption and volumetric techniques, respectively. To study the simultaneous precipitation of Zr and Mg, the above described procedure was followed, using a mixture of zirconium oxychloride and magnesium chloride solutions. After established the optimum simultaneous precipitation of Mg^{2+} and Zr^{4+} , this condition was used for preparing MgO-ZrO_2 precursor powders. The

mixture of $ZrOCl_2$ and $MgCl$ solutions was added dropwise to a vigorously stirred NH_4OH solution, following the molar ratio of $[OH^-]/[Cl^-]$, established in the optimum co-precipitation (simultaneous precipitation) of Mg^{2+} and Zr^{4+} . The resulting gel was filtered by vacuum and washed with distilled water until no indication of Cl^- , determined by $AgNO_3$ test. After that the gel was washed with ethanol, filtered, dried at $100^\circ C$ for 1h, crushed in a mortar and pestle and calcined at $550^\circ C$ for 1h. The calcined powders were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD). BET technique was used for surface area determination and Quasi Light Scattering (QELS) technique for particle size distribution characterization.

Results and discussion

The main objective of this work was to investigate the precipitation of $Mg(OH)_2$ with NH_4OH solution and to establish the optimum condition of precipitation and applying this condition for co-precipitating of Mg^{2+} and Zr^{4+} . The precipitation of Mg^{2+} , in NH_4OH , may be controlled by concentration of OH^- and ammonium salt related to the system. The starting solution used in the present work was $MgCl_2$ solution. In this case, Cl^- ion is the responsible for the presence of ammonium salt (NH_4Cl) in the precipitation environment. Therefore, the influence of OH^- concentration relative to total concentration of Cl^- , in the precipitation environment, i.e., $[OH^-]/[Cl^-]$ and concentration of Mg^{2+} , in the precipitation of $Mg(OH)_2$ were studied. Figure 1 shows the results of $Mg(OH)_2$ precipitation varying the molar ratio of $[OH^-]/[Cl^-]$ in the range of 1 to 10 times of stoichiometric value, 2.92. The concentration of $196\text{ mg}\cdot\text{L}^{-1}\text{ Mg}^{2+}$ was set. The precipitation of $Mg(OH)_2$ increases with increasing the molar ratio of $[OH^-]/[Cl^-]$. The variation of pH was too slight, from 10.6 to 11.0, compared with the variation of precipitation yield, which varied from 39.3 to 98.8%. This fact indicates that the pH measure is not enough to control the $Mg(OH)_2$ precipitation.

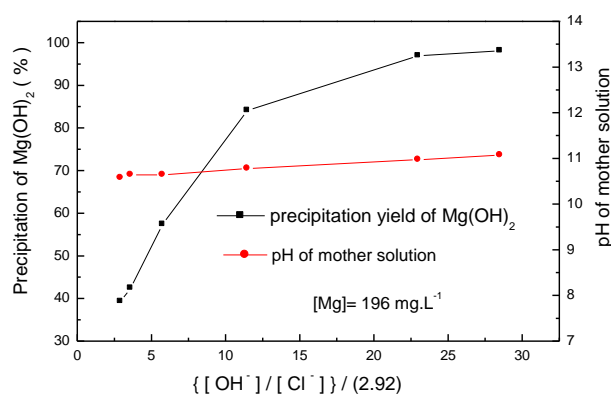


Figure 1. Precipitation of $Mg(OH)_2$ and pH as a function of $[OH^-]/[Cl^-]$ molar ratio

In Fig 2, it is observed the effect of Mg^{2+} concentration on the precipitation of $Mg(OH)_2$, when the $[OH^-]/[Cl^-]$ was fixed at 2.96 (slightly greater than the stoichiometric value, 2.92). Fig. 2 shows that the precipitation of $Mg(OH)_2$ increases with increasing the concentration of Mg^{2+} . Fig.1 and Fig.2 have shown that high concentration of Mg^{2+} and high $[OH^-]/[Cl^-]$ values promote the $Mg(OH)_2$ precipitation.

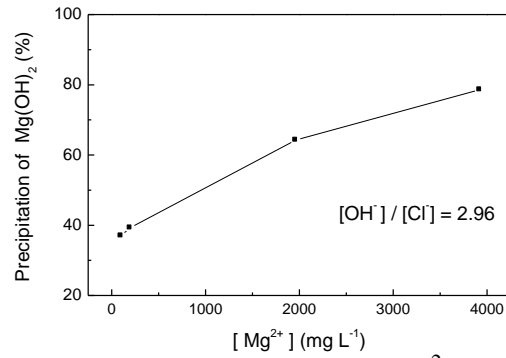


Figure 2. Precipitation of $\text{Mg}(\text{OH})_2$ as a function of Mg^{2+} concentration, $[\text{OH}^-]/[\text{Cl}^-] = 2.96$

Curves in Fig. 3 confirm this observation. Comparing the two curves in Fig.3, it is observed that the precipitation of $\text{Mg}(\text{OH})_2$, for a specific $[\text{OH}^-]/[\text{Cl}^-]$ value, is directly proportional to the concentration of Mg^{2+} . From those observations it can say that, higher the value of $[\text{OH}^-]/[\text{Cl}^-]$, lower is the Mg^{2+} concentration required to attain a specific precipitation yield, or vice-versa, higher the Mg^{2+} concentration, lower is the value of $[\text{OH}^-]/[\text{Cl}^-]$ required. Therefore, the optimum condition of $\text{Mg}(\text{OH})_2$ precipitation depends on the concentration of Mg^{2+} and molar ratio of $[\text{OH}^-]/[\text{Cl}^-]$. For Mg^{2+} concentration of 1960 mg L^{-1} the optimum value to $[\text{OH}^-]/[\text{Cl}^-]$ is 4 times 2.92, i. e., 11.68, determined from curve in Fig. 3. In this condition, ($[\text{Mg}^{2+}] = 1960 \text{ mg L}^{-1}$ and $[\text{OH}^-]/[\text{Cl}^-] = 11.68$), it is obtained the maximum precipitation yield with the maximum efficiency of the process.

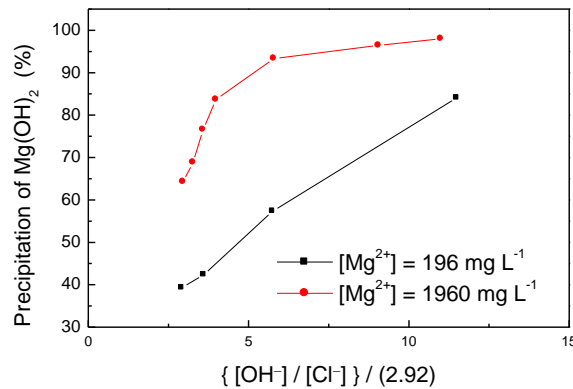


Figure 3. Precipitation of $\text{Mg}(\text{OH})_2$ as a function of $[\text{OH}^-]/[\text{Cl}^-]$, for two concentrations of Mg^{2+} , 196 mg L^{-1} and 1960 mg L^{-1} .

To co-precipitating zirconium hydroxide and $\text{Mg}(\text{OH})_2$, the value of $[\text{OH}^-]/[\text{Cl}^-]$ used was 4.4 times 2.92, 10% greater than above optimized value, to ensure the $\text{Mg}(\text{OH})_2$ precipitation. The results are shown in Table 1. Results in Tab.1 show that the precipitation of $\text{Mg}(\text{OH})_2$ reached in the range of 97.6 to 98.3 %. It is interesting to note that these results are higher than those (see Fig.3) obtained from precipitation of $\text{Mg}(\text{OH})_2$ without the presence of Zr^{4+} ion, indicating that the later facilitates the precipitation of Mg^{2+} .

Table 1. Co-precipitating of zirconium hydroxide and Mg(OH)₂ as a function of molar ratio of [MgO]/{[MgO]+[ZrO₂]} in the starting chloride solution (ZrOCl₂ and MgCl) with [OH⁻]/[Cl⁻] = 4,4 x2.92 and [Mg²⁺] = 392mg L⁻¹.

Sample	$\frac{[\text{MgO}]}{[\text{MgO}]+[\text{ZrO}_2]}$	Precipitation of Mg(OH) ₂ (%)
A	7.36	98,3
B	7.78	97,9
C	8.21	98,0
D	8.61	97.5
E	9.04	97,6

Sample A was chosen to characterize. In Fig.4 it is showed the micrograph of MgO-ZrO₂ powders of the sample A, dried at 100 °C for 1h, crushed in a mortar and pestle and calcined at 550 °C for 1h. It is observed particles of sub micron size.

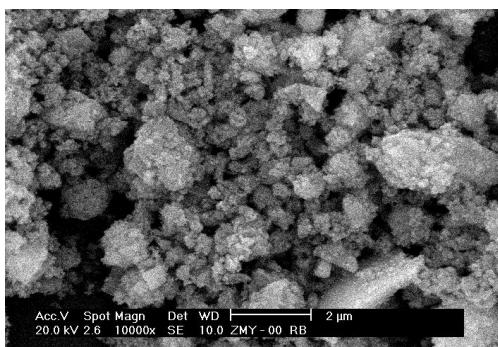


Figure 4. SEM micrograph of of MgO-ZrO₂ powders of the sample A, dried at 100 °C for 1h, crushed in a mortar and pestle and calcined at 550 °C for 1h.

In Fig. 5, the distribution of diameter particle size, determined by QELS technique, is shown. It is observed that the median diameter is about 40 nm, which is coherent to the respective surface area of 64.8 m² g⁻¹ determined by BET technique.

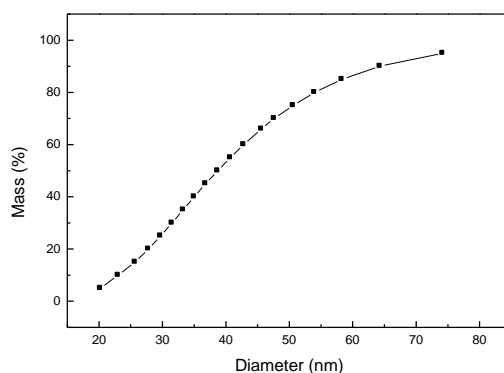


Figure 5. Distribution of diameter particles of MgO-ZrO₂ of A, dried at 100 °C for 1h, crushed in a mortar and pestle and calcined at 550 °C for 1h.

Fig. 6 shows XRD patterns of the powder. Cubic and monoclinic phase are present, being the cubic phase the main one.

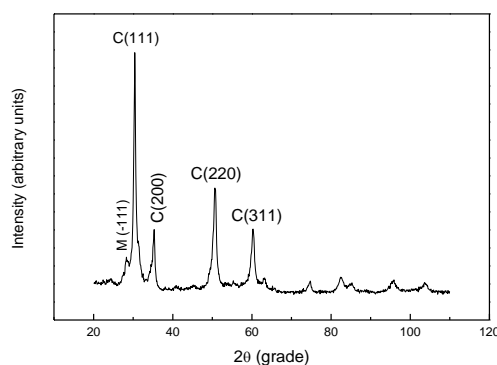


Figure 6. X-ray diffraction patterns of MgO-ZrO₂ sample A powder, dried at 100 °C for 1h, crushed in a mortar and pestle and calcined at 550 °C for 1h.

Conclusions

Precipitation of Mg(OH)₂, with NH₄OH, depends on the OH⁻, Cl⁻ and Mg²⁺ concentration. Higher the value of [OH⁻]/[Cl⁻], lower is the [Mg²⁺] required or vice-versa, i.e., higher the [Mg²⁺], lower value of [OH⁻]/[Cl⁻] is required. The main important conclusion is the pH measure, usually used to control others metal hydroxide precipitation, is not enough and decisive to control the Mg(OH)₂ precipitation with NH₄OH. The optimum condition of Mg(OH)₂ precipitation depends on the concentration of [Mg²⁺] and the value of [OH⁻]/[Cl⁻] molar ratio. Using [OH⁻]/[Cl⁻] the value of 4.4, in the process of co-precipitating zirconium and magnesium hydroxides, the precipitation of Mg(OH)₂ yielded in the range of 97.6 to 98.3 %. Powders of MgO-ZrO₂ prepared following the conditions of precipitation, settled in the present work, consisted of fine particles, with median diameter about 40 nm and surface area of 64.8 m² g⁻¹.

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