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SYNTHESIS OF ADVANCED CHEMICALLY BONDED CERAMICS FOR SOLIDIFICATION OF RADIOACTIVE WASTES

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ABSTRACT

This paper presents the results of a preliminary study on the synthesis of advanced chemically bounded ceramics for use to immobilize radioactive wastes. A monolithic, crystalline, ceramic-like material, in the form of $MgKPO_4.6H_2O$, is obtained by reaction of magnesium oxide with potassium monophosphate, at room temperature. The thermodynamics of the reaction indicates the need of a previous treatment of the MgO above 1200 ºC to avoid the formation of magnesium phosphate salts, as revealed by thermogravimetric analysis and X-ray diffraction. The different crystalline phases and microstructure of reaction products are analyzed by X-ray diffraction and scanning electron microscopy, indicating that the material has the characteristics of a matrix for immobilization of radioactive waste. Results obtained thus far indicate the possibility of using this material to replace Portland cement in waste immobilization, offsetting the higher cost of raw material input with a larger fraction of waste in the waste form. More research on characterization of the waste form with mechanical strength tests of specimens incorporating varying waste compositions, and on the leaching potential of the material for a series of radioactive as well hazardous industrial wastes is being planned.

1. INTRODUCTION

The class of hydraulic cements and ceramics do not cover fully the structural inorganic solid materials used for immobilization of radioactive wastes, which has been developed in recent decades. Ceramics are prepared by compaction of solids at high temperatures. Hydraulic cements are prepared by mixing anhydrous cement compounds with water, forming chemical bonds at room temperature. The main difference between structures of ceramics and hydraulic cement is that ceramics have ionic and covalent bonding, while hydraulic cement structure are maintained by Van deer Waals forces.

A new class of material, known as chemically bonded ceramic (CBC), was added to fill the gap. This class is considered a ceramic because its structure is formed by ionic and covalent bonds at room temperature. This class includes the ceramics based on magnesium phosphate ions. In the studies of Kingery [1], various inorganic oxides react with phosphoric acid solutions resulting in hydrophosphate products. Wagh and Jeong [2] using these materials have produced ceramic-based chemically bonded phosphates (CBPC), intended for use to solidifying radioactive waste. The $MgKPO_4.6H_2O$ (MKP) is a promising candidate of these compounds as a solidification matrix.

The formation of the MKP has been studied by several authors [1-3], and its formation involves the following steps:

a) Dissolution of oxide: $MgO + H_2O \rightarrow Mg^{2+}(aq) + 2\,OH^{-}(aq)$

b) Formation of aquosols: $Mg^{2+}(aq) + \,:O<^{H}_{H} \rightarrow [Mg \leftarrow O^{\rightarrow H}_{\rightarrow H}]^{2+}(aq)$

c) Acid-base reaction
and condensation: $:Mg(OH_2)^{2+} + HPO_4^{2-} + 5\,H_2O \rightarrow MgHPO_4.6H_2O$

d) Percolation and gel formation, and, finally, saturation and crystallization.

The Institute of Energy and Nuclear Research (IPEN-CNEN/SP) conducts studies for the immobilization of low- and medium-activity wastes with cement and, to expand the forms of treatment created a group of R&D to study the new possibilities of using CBPC to immobilize wastes. In this context, this paper presents and briefly discusses the preliminary results of synthesis for the formation of CBPC.

2. MATERIALS AND METHODS

2.1 Raw-Material

Magnesium oxide (MgO) from Magnesita Co., and potassium dihydrogen phosphate (KH_2PO_4 or KDP), from Fosmix Co. have the chemical compositions presented in Tables 1 and 2. Both materials are in the form of powder with particle size ≤ 50 mesh.

Thermogravimetric analyses were done with 6.0 mg of MgO and 31 mg of KDP samples in aluminum capsules with 70 µL using the Mettler-Toledo TGA/SDTA 851 with analysis software version 4.20, heating program in an atmosphere of N_2, temperature ranging from 25 to 1400 °C, heating rate of 10 ^{o}C min^{-1} and total heating time of 140 min.

Diffractograms were obtained with the X-ray diffractometer MINIFLEX II - Rigaku with source CuKα - 1.54056 Å, 30 kV, 15 mA, integrated software Power X-ray Diffraction PDXL - Rigaku version 1.5.0, step width 0.05 ° s^{-1}, 2Θ values between 5^{o} and 80^{o}.

Table 1. Chemical analysis of MgO (by EDX) [4]

Chemical species	Mg	MgO	Fe_2O_3	Al_2O_3	SiO_2	MnO	CaO
%	59	98.3	0.4	0.1	0.3	0.1	0.8

Table 2. Chemical analysis of KH_2PO_4 (by EDX) [5]

Chemical species	KH_2PO_4	F^-	As	Pb
%	98.5			
µg g^{-1}		10	3	3

2.2 Synthesis of Potassium Magnesium Phosphate Hexahydrate

$KMgPO_4.6H_2O$ (MKP) is obtained by mixing MgO with water and vigorously stirring the mixture for 5 minutes in a borosilicate glass beaker. KDP is then added and the mixture stirred during approximately 25 minutes to homogenize. Immediately thereafter, the mixture is poured in polyurethane moulds (8 cm^3) and left to complete the reactions for 48 hours.

Exploratory tests with different reactant mass ratios were performed. The MgO:KDP:H_2O molar ratio 1:1:6 is the stoichiometric composition and the following ratios were tested: 1:1:4, 1:1:5, 1:1:6, 2:1:6, 4:1:6, and 6:1:6.

2.2.1- Characterization of the MKP ceramics

After curing, the MKP ceramic samples are removed from the moulds, dried in oven at 40 °C for 24 hours, and then the crystalline phases are characterized by X-ray diffraction analysis and the microstructure by scanning electron microscopy of fractured surfaces of samples.

3. RESULTS AND DISCUSSIONS

Results of TGA samples of the raw materials are presented in Fig.1 and Fig. 2. From the ‘MgO’ TGA curve, a steady weight loss is observed until the sample temperature reaches a value above 1200 ^oC, followed by a pronounced weight loss step from 1200 to 1400 ^oC. In both temperature ranges, the lost material is unidentified.

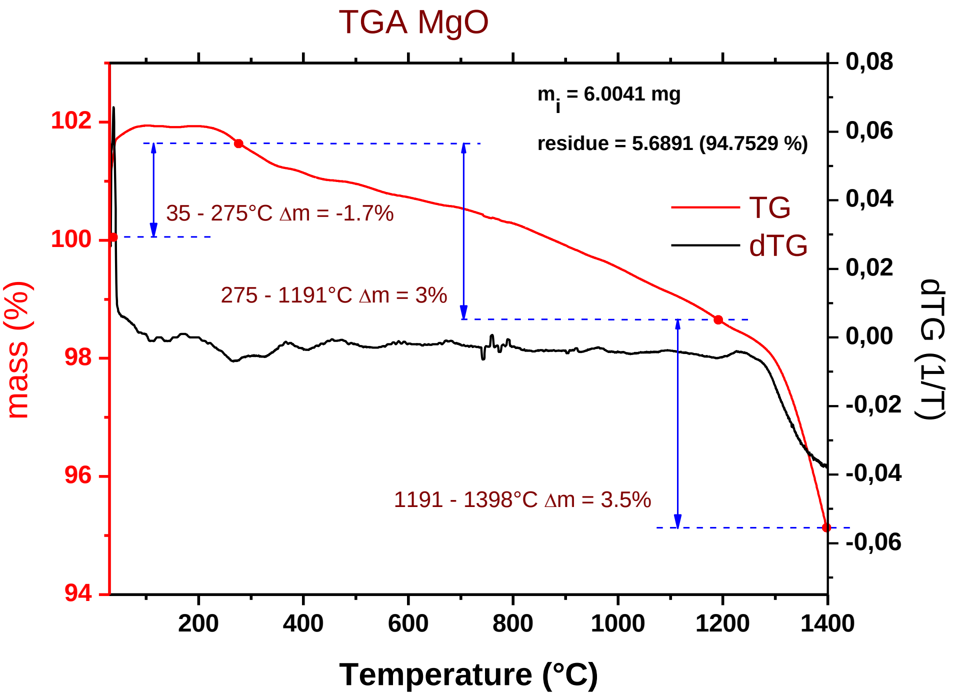


Figure 1. Thermograms MgO (25-1400^{o}C).

In the ‘KDP’ TGA curve, three well-defined endothermic peaks are observed between 201 °C and 386 °C corresponding to the decomposition of KH_2PO_4 hydrates to form KPO_3 [6].

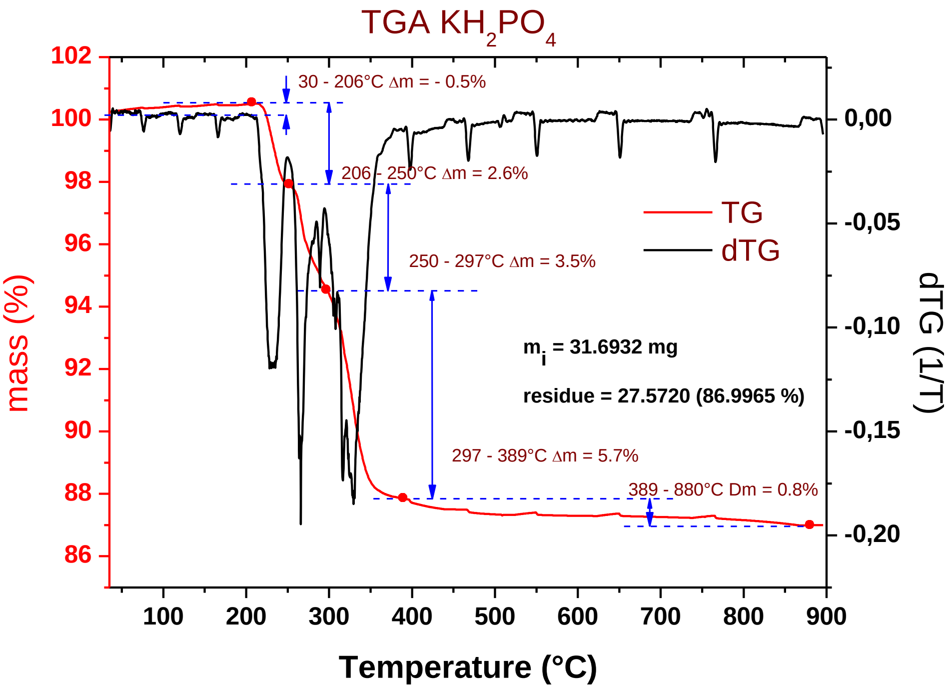


Figure 2. Thermograms KH_2PO_4 (25-900°C).

The thermodynamic conditions necessary for the formation of phosphate ceramics require a low reactivity MgO that is obtained calcining the raw compound to above 1200 °C in two steps heating. Fig. 3 shows the X-ray diffraction peaks and Table 3 shows the change of the specific surface area as a function of the calcination temperature. The surface area was reduced from 26.1 m^2g^{-1} for the raw material to 1.3 m^2g^{-1} when calcined at 1200 °C for 2 hours. This lower reactivity of MgO provides the conditions for the formation of the MKP hydrate.

The XRD patterns of the raw material MgO, shown in Fig. 3, shows that the diffraction peaks can be indexed as those from the known periclase structure (ICDD File No. 00-001-1235). Characteristic peaks from impurities are not detected.

Table 3. Specific surface area of MgO, by the BET method

Compound	MgO (as received)	MgO 900 °C	MgO 1200 °C
Specific surface area (m^2 g^{-1})	26.1	8.8	1.3

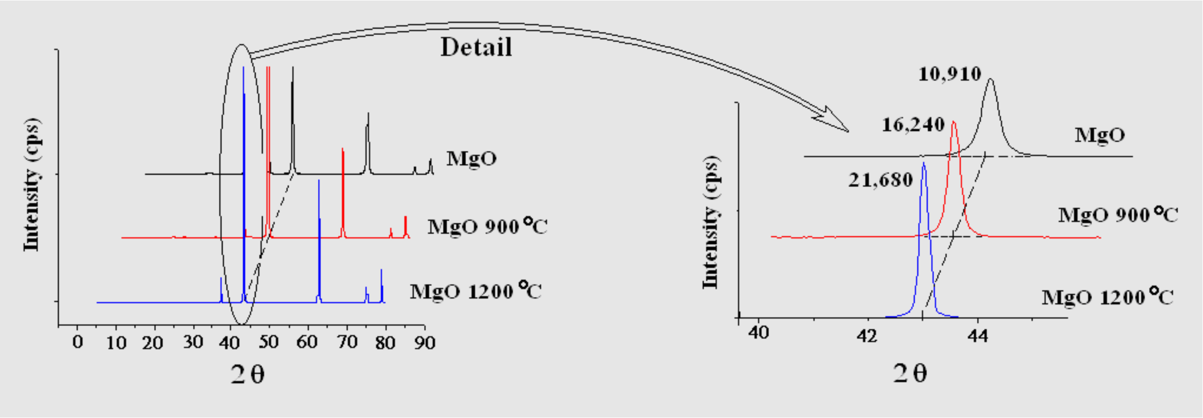


Figure 3. XRD of MgO (25-1200°C).

Fig. 4 shows the XRD patterns of MKP obtained by the reaction of MgO calcined at 900 and 1200 °C. The XRD patterns show that the periclase peaks are absent in MgO calcined at 900 °C and present in MgO calcined at 1200 °C. The reason of this behavior, is that below some point between 900 and 1200 °C, the high specific surface area of MgO powder forms the double magnesium-potassium phosphate salt and prevents the formation of the MKP hydrate ceramic-like product, which is the phase that we seek to form. The rapid dissolution of raw highly reactive magnesium oxide is evidenced by a highly exothermic acid-base reaction.

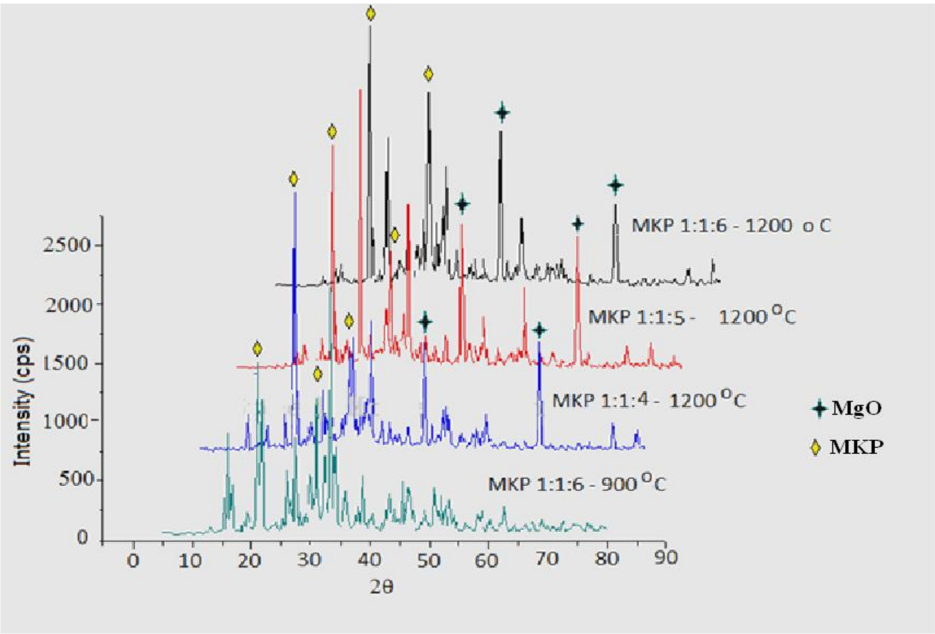
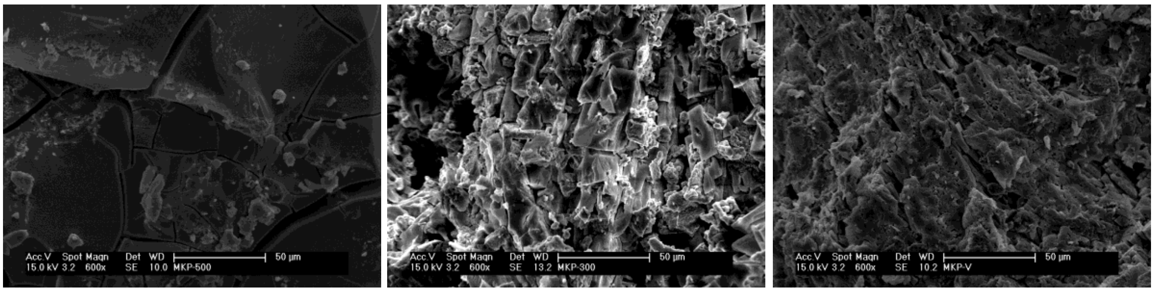


Figure 4. Effect of the calcination temperature of MgO in the synthesis of the MKP.

The Fig. 5 shows the microstructure of fractured surfaces of the MKP samples obtained with calcined MgO, molar ratio 2:1:6, 4:1:6, and 6:1:6 or with excess ratios of the 100 (MKP 100), 300 (MKP 300) and 500 (MKP 500) % above the stoichiometric ratio. Fig. 6 presents the X-ray diffraction pattern of these samples. The micrographs and XRD patterns indicate that the sample obtained with 100% excess MgO has a high content of unreacted KDP (the high peak at 2θ = 24°), while the other samples show a typical grained structure in the MKP, which is confirmed by the peaks of this phase in X-ray diffractograms (ICDD File No. 00-035-0812) to MKP 300 and MKP 500, and (ICDD File No. 01-075-1076) to MKP 100.



a b c

Figure 5. Microstructure of the MKP obtained with (a) 100%, (b) 300% and (c) 500% excess calcined MgO.

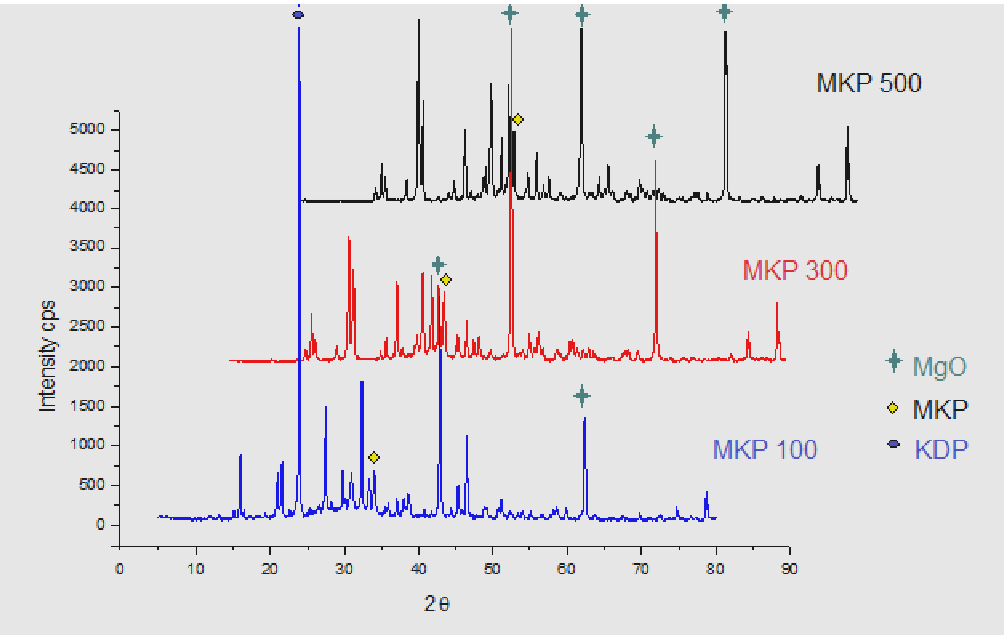


Figure 6. XRD of the MKP obtained with (a) 100%, (b) 300% and (c) 500% excess calcined MgO.

4. CONCLUSIONS

The large exothermic heat generated during the reaction of raw MgO indicates that it is necessary to retard the reaction rate. A calcination pretreatment of MgO significantly reduces the specific surface area of the reactant, allowing the formation of the ceramic-like product MKP hydrate.

Molar ratios of MgO higher than 300 % above the stoichiometric ratio, improve the microstructural characteristics of the ceramic. An optimization of the molar ratio will be the object of future work.

This process may be applied to other oxides besides MgO to form relatively inexpensive ceramics to immobilize radioactive as well other hazardous wastes.

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