

# Magnesium Phosphate Cements to Solidify the Concrete Wastes from Decommissioning of the Nuclear Power Plants

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## 1. Introduction

Decommissioning of the nuclear power plants is important for the safe and economical disposal of the radioactive wastes. During the decommissioning of the nuclear power plants, large amount of radioactive wastes such as metals, concretes, combustible and non-combustible wastes is generated. The concrete wastes are expected to account for more than 80% of the total waste volume[1]. To reduce the volume of these concrete wastes, it is decontaminated by thermal crushing. During the decontamination process, most of radionuclides were easily separated from aggregate and exist mainly in the cement paste[2]. The cement paste wastes that we need to deal with are usually Portland cement mainly composed of  $\text{Ca}_3\text{SiO}_5$  and  $\text{Ca}_2\text{SiO}_4$ .

Magnesium potassium phosphate cement (MKPC) is used to solidify radioactive wastes because it has properties of rapid formation, chemical durability and low porosity[3,4]. MKPC is an acid-base reaction of cements when MgO and  $\text{KH}_2\text{PO}_4$  are dissolved and form  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ . Phosphate cement can use other cations such as CaO as well as MgO[5].

This study uses MKPC to solidify the Portland cement pastes generated from the concrete decontamination process. Effect of different cations such as  $\text{Ca}^{2+}$  on the synthesis and properties of the wastes are investigated.

## 2. Experimental Methods

### 2.1 Fabrication of simulated wastes

Ordinary Portland cement A (OPC) was used to make simulated wastes. Slurry with a water-to-solid ratio of 0.4 was mixed at 1000 rpm for 5 min with an overhead stirrer (DAIHAN Scientific). Then the slurry was poured into a plate mold and cured for 5 days at a room temperature of 50% humidity. The simulated waste was pulverized into powder, sieved to 150  $\mu\text{m}$  and then dried overnight at 90 °C.

### 2.2 Design of Mixing

The synthesis of magnesium phosphate cements in this study was based on the reaction of Dead Burnt Magnesia (DBM at 90% purity) and  $\text{KH}_2\text{PO}_4$  (Sigma-Aldrich). DBM is made by calcination of MgO at

temperature > 1500 °C, which is suitable for the synthesis of MKPC because of its low reactivity. The formulations of MKPC are shown in Table I. The MgO :  $\text{KH}_2\text{PO}_4$  molar ratios were selected as 2:1, 1:1, 1:2 to find the optimum composition. Waste (OPC paste) to MKPC (MgO +  $\text{KH}_2\text{PO}_4$  +  $\text{H}_2\text{O}$ ) weight ratio is 0.5 and a water-to-solids ratio used was 0.25. Since the acid-base reaction of MgO and  $\text{KH}_2\text{PO}_4$  is fast, 2 wt.% of boric acid ( $\text{H}_3\text{BO}_3$ , Sigma-Aldrich), known as a retarder, was added[6]. In addition, a specimen with a waste to MKPC ratio of 1 was also synthesized to determine compressive strengths when MKPC had high waste loading. The water-to-solid ratio increased to 0.28 due to workability when increasing the waste load.

The powders were initially mixed with a vortex mixer for 2 min. Afterwards, water was added to the powder and mixed at 1000 rpm for 5 min with an overhead stirrer (DAIHAN Scientific). Then the slurries were casted into a polypropylene mold and cured at room temperature.

Table I: Formulation of MKPC

Waste ratios	MgO:KH <sub>2</sub> PO <sub>4</sub> ratios	MgO (wt.%)	KH <sub>2</sub> PO <sub>4</sub> (wt.%)	Waste (wt.%)	H <sub>3</sub> BO <sub>3</sub> (wt.%)	H <sub>2</sub> O (wt.%)
0.5	2:1	17.13	28.92	32.89	1.32	19.74
	1:1	10.52	35.53			
	1:2	5.94	40.11			
1	2:1	10.36	17.49	49.51	0.99	21.66
	1:1	6.36	21.48			
	1:2	3.59	24.25			

### 2.3 Characterization

The analysis of phase structures was performed by X-ray diffraction (XRD, Rigaku). Diffraction patterns were collected between  $10^\circ < 2\theta < 60^\circ$  with a scan speed of 2°/min. The compressive strengths were determined from a cylinder shaped specimens after 7 days of curing time using a universal testing machine at a loading rate of 1 MPa/s.

### 2.4 Measurement of pH value and temperature

The values of pH and temperature were measured by pH electrode (InLab Expert Pro, Mettler Toledo) to analyze the effect of waste addition on synthesis reaction. The MgO :  $\text{KH}_2\text{PO}_4$  molar ratio was 2:1 and waste to MKPC weight ratios are 0, 0.25, 0.5 and 1. For each sample, a total weight of 50 g of batch in

centrifuge tube was mixed with a vortex mixer for 1 min at room temperature. The centrifuge tube was wrapped with insulating cotton to measure the temperature change well.

### 3. Results and Discussion

#### 3.1 X-ray diffraction patterns

X-ray diffraction (XRD) patterns of OPC before and after the curing reaction are shown in Fig. 1. The OPC mainly consists of  $\text{Ca}_3\text{SiO}_5$  and  $\text{Ca}_2\text{SiO}_4$ , with the formation of  $\text{Ca}(\text{OH})_2$  during water hardening. The XRD patterns of MKPC mixed with OPC paste are shown in Fig. 2. The specimens with  $\text{MgO} : \text{KH}_2\text{PO}_4$  ratios of 2:1 and 1:1 have a  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase together with  $\text{Ca}_3\text{SiO}_5$  and  $\text{MgO}$  that were not dissolved. As the amount of  $\text{MgO}$  decreased as in 1:2 specimen,  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase decreased and  $\text{KH}_2\text{PO}_4$  remained. It appeared that the amount of  $\text{Ca}(\text{OH})_2$  of OPC was not sufficient enough to form  $\text{CaKPO}_4$  during the MKPC synthesis. Therefore, the  $\text{MgO} : \text{KH}_2\text{PO}_4$  ratio should be at least 1:1 in order for the  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase to form during the synthesis. Fig. 3 shows the XRD patterns of the specimens with a waste rate of 1. In this case,  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase did not form but hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) peaks were present between  $30^\circ$  and  $45^\circ$  of  $2\theta$ . The hydroxyapatite phase was formed due to the increasing the amount of waste containing  $\text{Ca}(\text{OH})_2$ .

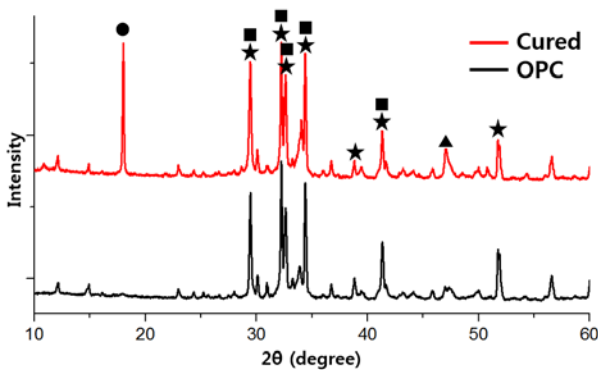


Fig. 1. X-ray diffraction patterns of OPC before and after curing; circles:  $\text{Ca}(\text{OH})_2$ , stars:  $\text{Ca}_3\text{SiO}_5$ , squares:  $\text{Ca}_2\text{SiO}_4$ , triangles:  $\text{Ca}_3\text{Al}_2\text{O}_6$

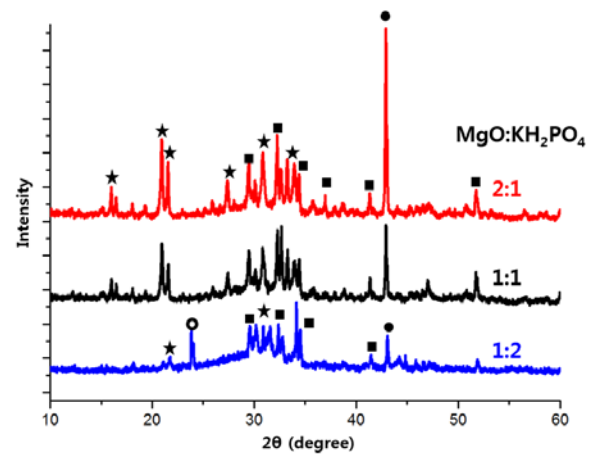


Fig. 2. XRD patterns of the specimens with a waste rate of 0.5 and different  $\text{MgO} : \text{KH}_2\text{PO}_4$  ratios; circles:  $\text{MgO}$ , stars:  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ , squares:  $\text{Ca}_3\text{SiO}_5$ , open circles:  $\text{KH}_2\text{PO}_4$ .

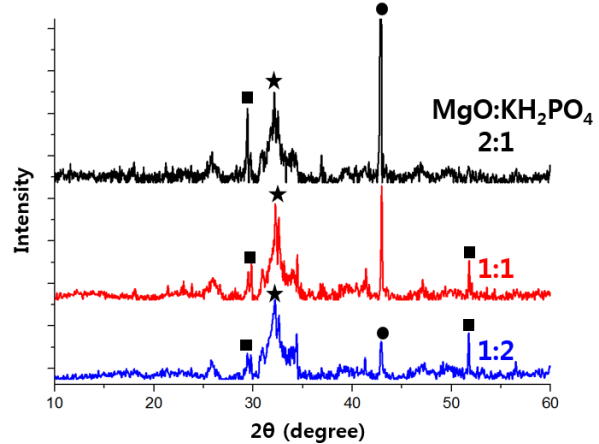


Fig. 3. XRD patterns of specimen with a waste rate of 1 and different  $\text{MgO} : \text{KH}_2\text{PO}_4$  ratios; circle:  $\text{MgO}$ , star:  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , square:  $\text{Ca}_3\text{SiO}_5$ .

#### 3.2 Compressive strengths

The compressive strengths of MKPC cured for 7 days are shown in Table II. All the specimens with a waste ratio of 0.5 achieved the regulatory standard of 3.45 MPa and the compressive strength increased as the amount of  $\text{MgO}$  increased. However, the samples with a waste ratio of 1 had a compressive strength of less than 3, which was not sufficiently solidified. The 2: 1 and 1: 1 samples of waste ratio 0.5 had high compressive strength because of the formation of the  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase as shown in the XRD results. The XRD results showed that  $\text{CaKPO}_4$  (or  $\text{MgKPO}_4$ ) crystals were hardly found in the 1: 2 sample, but a compressive strength of about 5 MPa means solidification by phase formation.

Table II: Compressive strength of MKPC

$\text{MgO}:\text{KH}_2\text{PO}_4$ ratios	Compressive strength (MPa)	
	Waste ratio 0.5	Waste ratio 1
2:1	$15.17 \pm 4.44$	$2.75 \pm 1.28$
1:1	$12.00 \pm 1.00$	$2.65 \pm 1.02$
1:2	$5.00 \pm 0.44$	$1.90 \pm 0.53$

### 3.3 Measurement of pH values and temperatures

The pH and temperature changes at the initial stage of the reaction are shown in Fig. 4. The synthesis of MKPC generates heat due to the exothermic acid-base reaction. Temperature increased to 63 °C during the synthesis of MKPC without the waste loading but the maximum temperature decreased to 40 °C with the addition of wastes. The reason for the decrease in the maximum temperature is because of the reduced amount of MgO and  $\text{KH}_2\text{PO}_4$  with waste loading. In addition, the dissolution of  $\text{Ca}(\text{OH})_2$  from waste increases pH of the slurry. At high pH, the solubility of MgO decreased and the reaction rate slowed down. A specimen with the waste ratio of 1 show a decrease in temperature after 15 minutes of curing. This indicates that the reaction is slow and the  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  does not form sufficiently that led to a low compressive strength. Therefore, waste ratio should be kept below 1 to realize the solid wasteforms with good mechanical strengths.

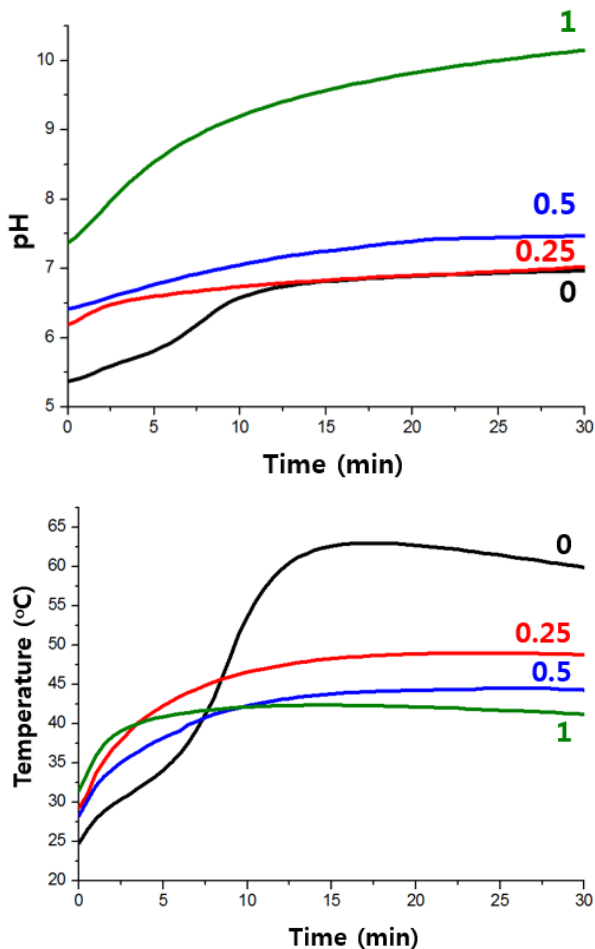


Fig. 4. Changes in pHs and temperatures during the initial reaction with increasing waste loading.

### 4. Conclusions

MKPCs were developed to solidify the OPC pastes from decontamination of radioactive concrete wastes. Specimens with a waste ratio of 0.5 and  $\text{MgO} : \text{KH}_2\text{PO}_4$  ratio of 2:1 and 1:1 were well formed with a  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  phase and a compressive strength of more than 10 MPa.  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$  was not synthesized when the waste ratio was increased to 1, and the compressive strength did not satisfy the regulation value of > 3.45 MPa. As the waste is added, the pH of the slurry increases and the reaction rate slows down because the waste contains  $\text{Ca}(\text{OH})_2$  which is more soluble than MgO.

### 4. Acknowledgements

This work was supported by the National Research Foundation (NRF) grant funded by the Ministry of Science & ICT (NRF-2017M2B2B1072405).

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