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Preparation and Dissolution Properties of the Trace Elements doped K_2O-CaO-P_2O_5 Glasses

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미량원소함유 K_2O-CaO-P_2O_5유리의 제조 및 용출 특성

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Abstract At the previous papers, we showed that K_2O-CaO-P_2O_5 glasses had a solubility in air so that they could be used for glass fertilizer. In this work, we fabricated the Eco-glass fertilizer containing trace elements of B, Mg, Zn, Fe, Cu, Co, Mo, the needed micronutrients for plants to grow, by a melt-quenching process. The dissolution properties in these glasses were investigated with a pH meter and an ICP analyzer. The trace elements doped glasses showed similar behavior in dissolutions and stability properties with the mother glass without containing trace elements. In addition, the dissolution amount of each trace elements depends on the mother glass composition and the quantity of each trace elements, which determine the dissolving velocity of chemical elements

요 약 앞선 논문에서 K_2O-CaO-P_2O_5유리의 용출 특성을 이용한 유리질 비료로서의 가능성을 보고한바 있으며, 본 연구에서는 K_2O-CaO-P_2O_5 조성에 식물의 성장에 필요한 미량원소인 B, Mg, Zn, Fe, Cu, Co, Mo을 첨가한 유리를 제조하였으며, 제조된 유리의 용출 특성을 pH와 ICP 분석을 통하여 관찰하였다. 미량원소가 첨가된 유리의 경우 첨가전의 pH값의 변화와 차이가 없었으며, 모유리의 안정화에 영향을 미치지 못함을 알 수 있었다. 첨가된 미량원소의 용출량은 모유리조성과 첨가된 함량에 비례하였으며, 이러한 원소들의 용출속도는 모유리 조성에 의하여 결정되었다.

Key Words : Environmentally conscious, Glass fertilizer, Dissolution, Phosphate glasses, Slowly-effective fertilizer

1. Introduction

Since conventional phosphate glass has hygroscopic property and poor chemical durability caused by the glass structure, its application was limited. Thus many efforts have been focused on to increase the chemical durability [1, 2] However, the new applications for phosphate glasses are lately emerging for environmental materials such as glass fertilizer, anti-bacterial, far-infrared radiation, dental, and bio-medical materials [3, 4] The usage for glass fertilizer is being focused nowadays for environment conscious inorganic fertilizer [5]. Presently, the dissolution properties of chemical fertilizers used widely in agriculture have immediate effect so that it offers excess nutrition than those plants needed or releases to the soil, resulting in not only the great waste of fertilizer but environmental problems due to the soil acidulation. Therefore, the controllable release glass fertilizer that offers the nutrients as much as the plants needed for months or years is studied by many researchers. Motohiro *et al.* showed the properties and cytotoxicity of water soluble Na_2O-CaO-P_2O_5 [6]. Bunker et al. reported the dissolution properties and mechanism of Na_2O-CaO-P_2O_5 and Li_2O-CaO-P_2O_5 glass systems [7]. Even though there are the many achievements in soluble phosphate glasses, the most of them are focusing on the not glass fertilizer but biomaterials. Thus we reported the paper concerned with glass fertilizer based on K_2O-CaO-P_2O_5 glasses to can supply nutrients (K^+, Ca^{2+}, P^{5+}) included in 5 elements of chemical fertilizer [8].

In this study, we prepared the trace elements needed for crops doped K_2O-CaO-P_2O_5 glasses by melt-quenching process and observed the dissolution

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behavior of the trace elements and mother glass with a pH meter and an ICP analyzer.

2. Experiment

Table 1 shows the chemical composition of this experiment. As inorganic fertilizer components, K_2O-CaO-P_2O_5 system [3] was selected and melting procedure was performed in 40 and 60 mole% P_2O_5 region for stable glass. In the present study, K_2CO_3 (Junsei, 99.5%), $CaCO_3$ (Junsei, 98.5%), H_3PO_4 (Duksan Chemical, 85%), B_2O_3 (Junsei, 99.0%), MgO (Duksan Chemical, 98%), Fe_2O_3 (Junsei, 98.5%), ZnO (Junei, 99.0%), CuO (Junsei, 99.0%), MnO (Duksan Chemical, 99.0%), MoO_3 (Aldrich, 99.0%) were used for batch mixing. The raw materials were mixed with distilled water for one hour and kept for 12 hours in dry oven at 120°C. Then the batch was melt in porcelain crucible at 1200°C for one hour and poured into water bath to prevent crystallization. And then glasses were dried in the dry oven at 120°C for several hours. For observation of dissolution properties, we used the 500-250 μm powder and placed them in plastic container full with distilled water of 25 ml and kept at room temperature. The pH and ICP-MS (Shimadzu Co., ICP 7500) measurements were used to observe dissolution behavior by time sequence.

3. Results and Discussion

3.1. pH changes

Table 1. Chemical Compositions of Glasses

Samples	KCP2 and KCP7 Glasses (93.92 wt%)	Trace Elements (6.08 wt%)	
KCP2M	30 mol%K_2O-30 mol%CaO -40 mol%P_2O_5	MgO	5.00%
		B_2O_3	0.322%
		Fe_2O_3	0.179%
		MnO	0.516%
KCP7M	10 mol%K_2O-30 mol%CaO -60 mol%P_2O_5	ZnO	0.0280%
		CuO	0.0188%
		MoO_3	0.0113%

The changes of pH values in the KCP2M (KCP2 glass containing trace elements) and KCP7M (KCP7 glass containing trace elements) is shown in Figs. 1 and 2. Dissolution mechanism in the phosphate glasses could be explained by the anti-branching rule [8]. By this rule, because PO_4 group in the phosphate glasses is unstable, it attracts water and develop the reaction of depolymerization to transfer to stable state when the value of MO (M_2O)/P_2O_5 (M = Ca, Mg, K, Na, etc.) is smaller than 1. Therefore, we can expect that the stability of the phosphate glasses depends on the quantity of alkali oxides or alkali earth oxides. In the case of KCP7M containing a large amount of 60 mol% P_2O_5, the pH values decrease to the acid range because the network of phosphate glass was broken by attracted water, and released phosphorus reacts with water

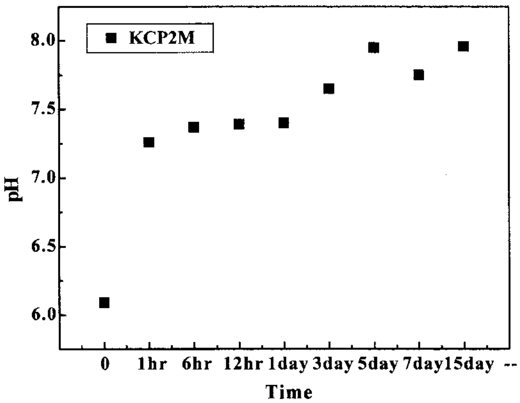

Fig. 1. pH changes of aqueous solution of the KCP2M glass according to time sequence.

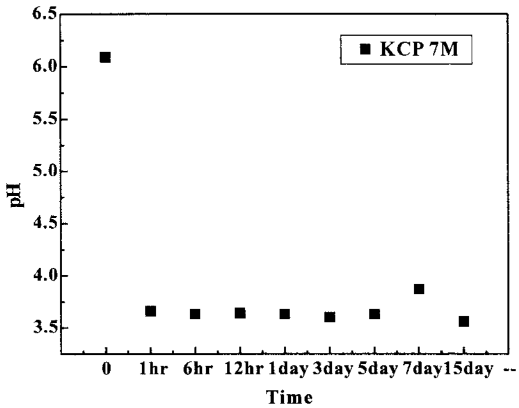

Fig. 2. pH changes of aqueous solution of the KCP7M glass according to time sequence.

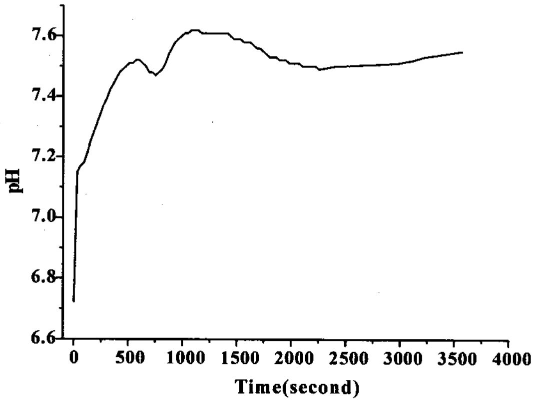

Fig. 3. pH changes of aqueous solution of the KCP2M glass during 1 hour. (measured by every 30 seconds)

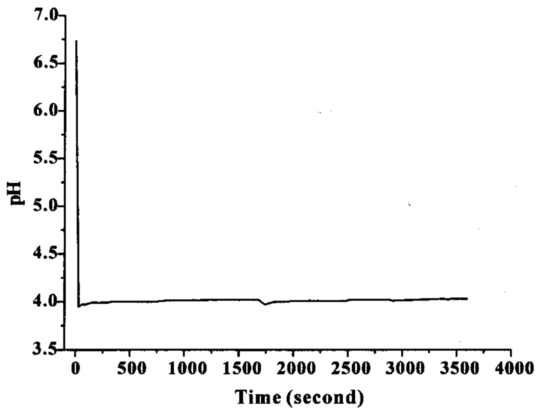

Fig. 4. pH changes of aqueous solution of the KCP7 glass during 1 hour. (measured by every 30 seconds)

and changes to HPO_3 resulting in decrease in pH value. Such change in pH value is similar with KCP7 without trace element, suggesting strongly that doped trace element (6.08 wt%) do not have effects on stability and pH value of the KCP7. In case of KCP2M, however, since this glass contains lots of amount of alkali oxide and less amount of P_2O_5 than KCP7M, the glass is stable and shows quite different result in pH value. This case could be considered by that the pH value depends on the dissolute alkali ion from glass as silicate glass [9, 10]. in the water bath. Consequently, the value increases to alkali range, and there is no significant effect by the trace elements. However, if we consider a long period, it can be expected that the value will finally move to acid range.

In Figs. 1 and 2, we found that the pH values were decided within 1hour so, we investigated pH value of both samples at 30 seconds intervals and shows in the Figs. 3 and 4. When we compared the Figs 1 and 2. and Fig. 3 and 4. we could find the little differences in the pH value at the same time. We assumed that the difference came from distilled water or experimental conditions of temperature and humidity. In case of KCP2M, the pH value increases rapidly at first 30 seconds and then it shows that the increase of tendency decreases according to increasing with time. In particular, this glass has two maximum points and minimum points at 600, 1500 second and 750, 2250 second, respectively. We assume that this phenomenon is caused by the amount of dissolving phosphorous during releasing the alkali ions. The change of KCP7M is finished within 30 secondsand then just shows little change according to time. This result supports that KCP7M easily releases the phosphorus and makes HPO_3 by reaction with H_2O.

3.2. Analysis of dissolution amount and elements

ICP-MS was used to analyze the dissolution amount and elements as shown in Figs. 5 and 6. It shows that the dissolution amount of KCP7M is about 250 times larger than KCP2M. Such a phenomenon indirectly proves why pH value of KCP7M rapidly decreases to acid range within 30 seconds. In the case of KCP7M, the dissolution amount of doped trace elements was in proportional to amount of doped oxides quantities and measured by the order as follow Mg > Mn > B > Fe > Zn > Cu > Mo. Even though KCP2M shows the similar tendency in the dissolution property, the amount of dissolved elements is much smaller than KCP7M. This cause would be explained with glass state as above-mentioned. As the composition of KCP2M contains lots of alkali oxides and less P_2O_5, it can be said that the glass is stable state and dissolution property is controlled by alkali ions as silicate glass in the water bath. Accordingly, the dissolution amount of the doped trace elements is small. In this case, the dissolution amount depends on the doped oxide quantities and checked by the order as Mg >

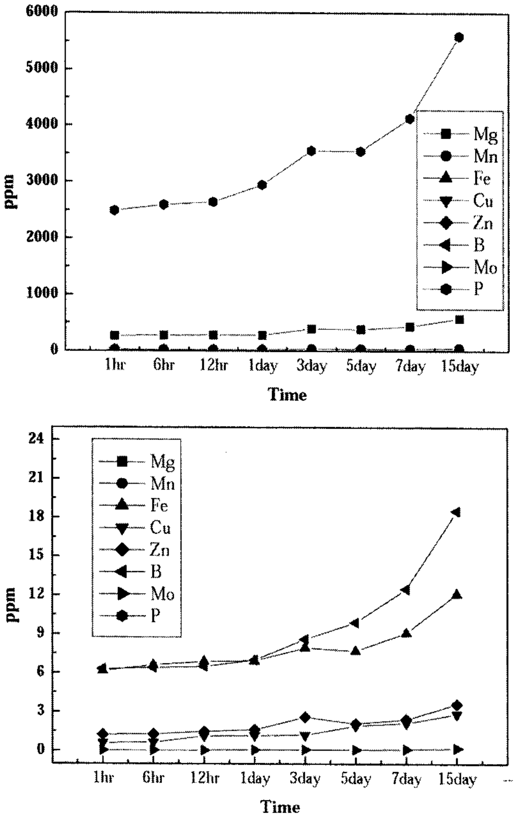

Fig. 5. Dissolved amount of chemical element contained in KCP7M glass in distilled water measured by ICP-MS. The lines are only guide for eyes.

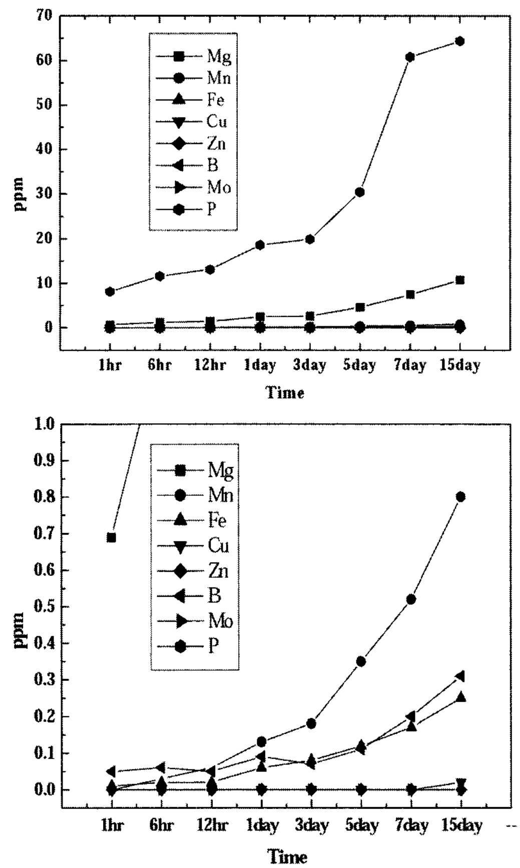

Fig. 6. Dissolved amount of chemical element contained in KCP2M glass in distilled water measured by ICP-MS. The lines are only guide for eyes.

Mn > B > Fe > Cu > Zn, Mo. Zn and Mo was not detected until 15 days

The dissolution mean velocity calculated with dissolution amount (ppm) and hour is shown in Table 2. This result indicates that KCP7 as well as trace elements have faster mean dissolution velocity compared to KCP2M and KCP2 and quietly agree with the result pH. Thus, the mother glasses determine the mean dissolution velocity of doped trace elements to increase or decrease.

Therefore, finally, we showed that it is possible to control the dissolution behavior by change the compositions of mother glasses due to its dependence on the properties of mother glasses.

Additionally, we expect that the needed nutrients will be supplied selectively and timely by changing the glass compositions.

4. Conclusion

We fabricated the K_2O-CaO-P_2O glasses containing trace elements and investigated the dissolution properties with pH meter and ICP analyzer. The

Table 2. Dissolution Velocity of Glasses

Glass Compositions	P	Mg	Mn	B	Fe	Zn	Cu	Mo
KCP2+trace elements (ppm/h)	0.1788	0.0299	0.0022	0.0009	0.0007	0	0	0
KCP7+trace elements (ppm/h)	15.5361	1.6058	0.1416	0.0514	0.0333	0.0100	0.0078	0.0005

doped trace elements do not have significant effect on the KCP2M, KCP7M, and the pH values of both samples were changed rapidly with 30 seconds and showed reciprocal results. The ICP analysis confirmed that the velocity of doped trace elements is proportional to the quantities of alkali oxides and could be controlled by mother glasses. Consequently, we think that the dissolution velocityand dissolution period would be controlled by composition change of mother glasses, and expect that it is possible to supply selectively and timely the needed nutrients by changing the glass compositions.

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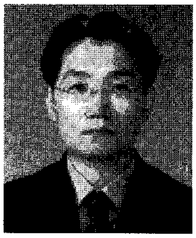

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<Research Interests>
Photonic Glass, Electronic Glass, Bio Glass

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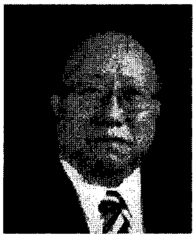

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