New glass-ceramic fertilizer based on K_2O-CaO-MgO-P_2O_5

Martin Maryska, Zdenka Patockova
ICT Prague, Department Glass and Ceramics, Technicka 5, 166 28 Praha 6 - Dejvice

A new glass-ceramic material was prepared, which can be used as slowly soluble fertilizer for different type of plants. This material is based on K_2O-CaO-MgO-P_2O_5 system and was made by glass technology. This one created three crystallographic modifications, which differs in solubility in water solutions. Temperature and pH dependence of solubility of crystallographic phases in aqueous mediums were studied. Samples for static tests were grains with diameter in range 0.16 – 0.315 mm. The pH value was changed between 6.06 and 9.2, temperature of solution was 4, 37 and 220°C and time of dissolution was 72 hours, ratio S/V = 0.1 cm^{-1}. Chemical changes in solution were determined by colorimetry, flame spectrometry and atomic absorption spectrometry. Chemical changes on the surface of sample were determined by x-ray microanalysis (EDS method) and structural changes by optical and electron microscope. From results it can be concluded:
Gama phase is most dissoluble in water solution.
Dissolution of phases is congruent.
$Ca_3(PO_4)_2$, $K_2MgP_2O_7$, $K_5Mg_3P_5O_{18}$ and K_3PO_4 crystallize from this solution.
In solutions it was found periodical changes of concentrations of monitored elements.

New Glass

Introduction

The environment protection is very important in an industrial world. Using of fertilizers in agriculture can be very useful for a food production, but on the other side it may be very dangerous for environment. Therefore only necessary amount of fertilizers can be used for successful vegetation. It means that we must use fertilizers, which dissolved just quickly as is nutrient requirement of plants. In this case it is not a contamination hazard for environment. The aim of this study was development of such fertilizer.
The main elements for successful plant vegetation are K, Ca, Mg, P and N. Many types of fertilizers supply these elements, but the velocity of dissolution of fertilizers in an agricultural land is greater than requirements of plants.

Experimental

Preparation and identification of $K_2CaMg(PO_4)_2$

From literature[1,2] is known, that it is possible to use some types of silica-phosphate glass as fertilizers. We felt a preparation of same type of material without silica but with important elements for the plants ($K_2CaMg(PO_4)_2$). The ceramic material was prepared by the glass technology (the melting of batch), which the chemical composition is shown in the Table 1.

These methods were used for identification of the prepared material: differential thermal analysis (DTA) and x-ray diffraction[3]. It was identified, that the material is created from the crystals where may be in 3 crystallographic modifications (α, β, γ). DTA diagram shows Fig. 1.

Table 1 Chemical composition of the material

Components	Weight %
PO_4^{3-}	57.12
K^+	23.52
Ca^{2+}	12.05
Mg^{2+}	7.31

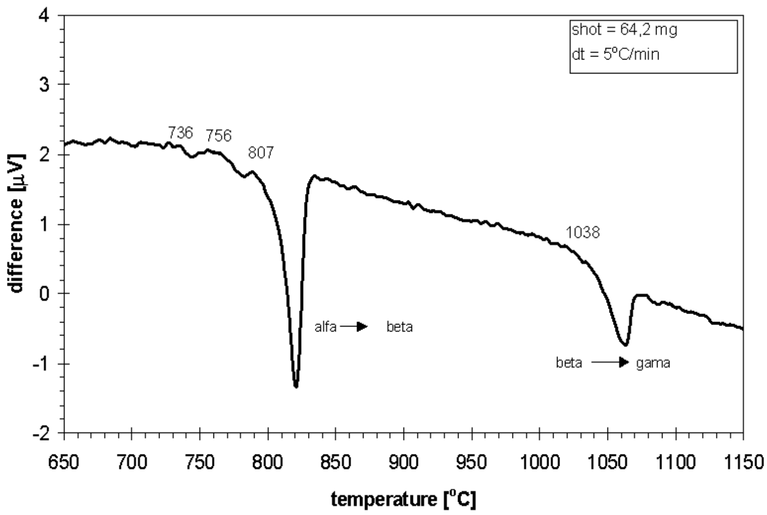

Fig. 1 DTA curve of prepared $K_2CaMg(PO_4)_2$

The separate crystallographic phases were prepared from the original material by tempering of this at the temperature of phase change; the temperatures of phase transitions from α to β and from β to γ are 820 and 1060°C, respectively and time of the tempering was 2 hours. The samples were quickly quenched in liquid nitrogen after this operation. The rtg. diffractograms are shown below (Fig. 2).

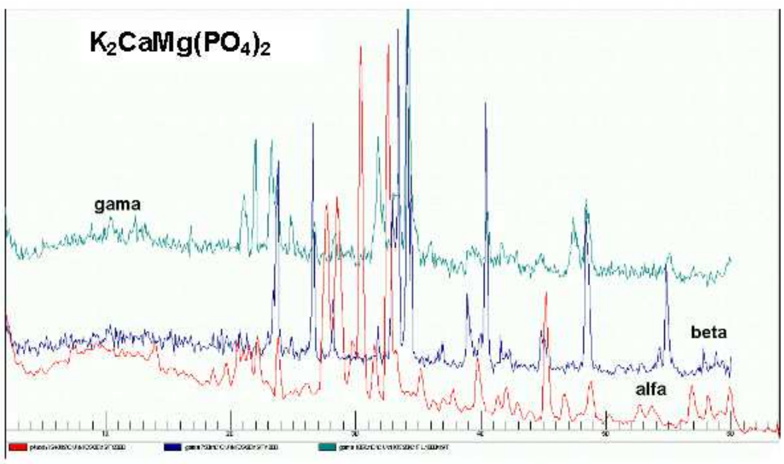

Fig. 2 The rtg. diffractograms of $K_2CaMg(PO_4)_2$ crystallographic phases

Dissolution of crystallographic phases

The samples used for static tests were the grains with diameter in range 0.16 -0.315 mm. Each sample was cleaned by ultrasonic cleaner (the cleaning solution was acetone). The start value of pH of distilled water using for experiments was 6.06. The temperatures of experiments were 4, 37 and 220°C (autoclave) and the time of the dissolution of material was from 2 to 72 hours. The ratio S/V=0.1cm^{-1} (Surface of sample/Volume of solution); it was the shot 0.0833 g of the sample into 80 ml of distilled water. The chemical changes in solution were determined using colorimetry (PO_4^{3-}), flame spectrometry (K^+, Ca^{2+}) and atomic absorption spectrometry (Mg^{2+}).

The results of dissolution tests

Next figures (Fig. **3**, Fig. 4) show some results of chemical analysis of solutions after leaching of the γ samples by the temperature 220°C. The dissolution of materials is congruent and therefore are not all results presented. Other results were published in [3].

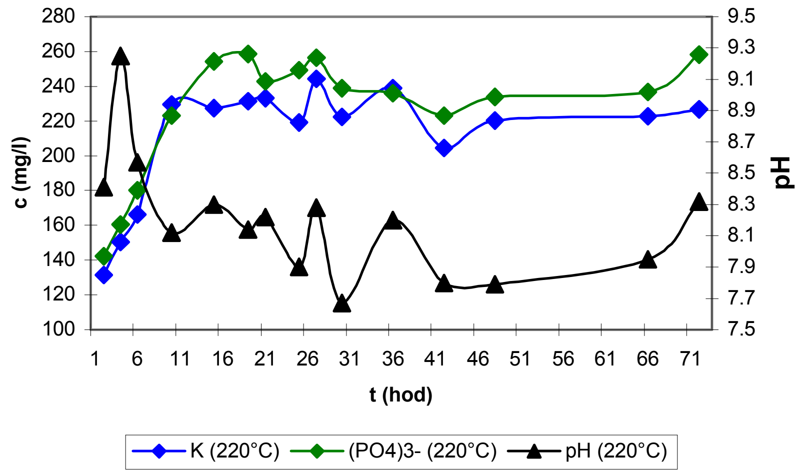

Fig. 3 Dependence of concentrations of K^+ and PO_4^{3-} and pH in the solution on the time at the temperature 220°C

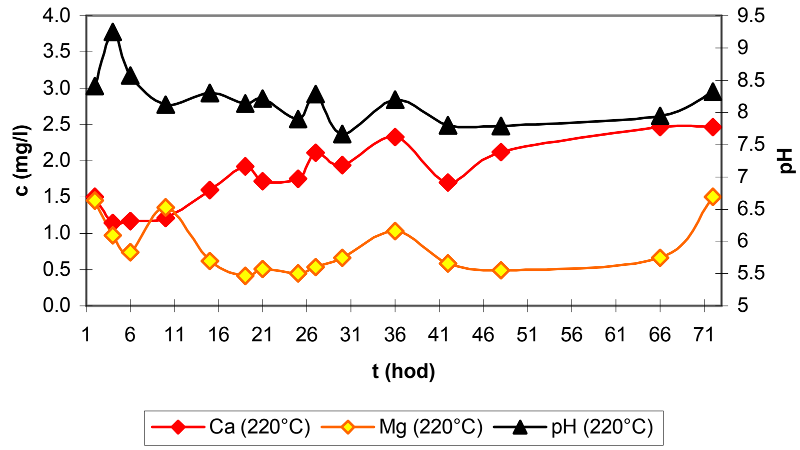

Fig. 4 Dependence of concentrations of Ca^{2+} and Mg^{2+} and pH in the solution on the time at the temperature 220°C

Analysis of solid state after 72 hours of leaching of γ phase at the temperature 220°C

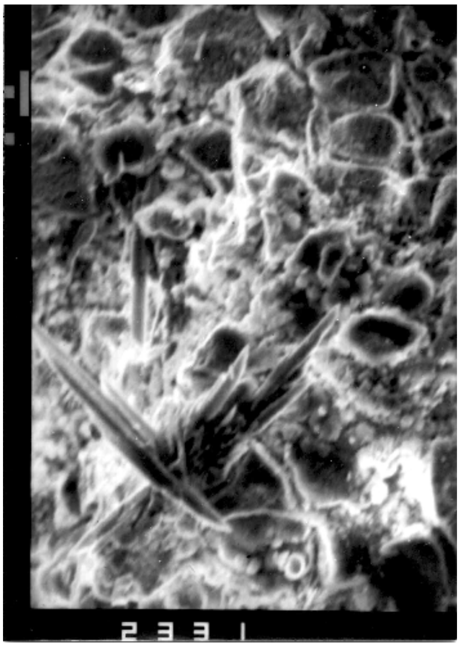

Fig. 5 Crystal phases after 72 hours of leaching

Table 2 Composition of crystal phases after 72 hours of leaching

oxide	Weight % of oxides		
	Time of exposition 72 h		
	Lamella	Lamella	Skewer
K_2O	0.3	0.1	0.1
CaO	79.4	54.2	2.3
MgO	0.3	1.7	34.3
P_2O_5	20.0	44.0	63.4

Conclusions

- The material can be prepared in 3 crystallographic modifications with different solubility.
- By selection of modification and/or grain size may be control of velocity of dissolution. The gama phase is most dissoluble in water solutions.
- It seems, that dissolution of phases is congruent.

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[1] C.F. Drake, Vitreous controlled release fertilizer composition, U.K. Patent no. 1512637.10C

[2] C.F. Drake, M. Trip, Glass composition, U.K. Patent no. 2037735 B

[3] M. Maryska, Rivista della Staz. Sper. del Vetro, **6**, p. 151-154 (2000)