FORMATION OF CALCIUM AMMONIUM AND CALCIUM PYROPHOSPHATES DURING THERMAL TREATMENT IN THE $NH_4H_2PO_4$ – CAO SYSTEM

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Abstract. Phase transformations occurring during the heating of an $NH_4H_2PO_4$: CaO = 2 : 1 (molar ratio) mixture up to 800 °C were studied by thermogravimetric and X-ray diffraction analyses. The sequence of formation of calcium ammonium pyrophosphate, calcium dihydrogen pyrophosphate and calcium metaphosphate depending on the temperature range was established.

Keywords: calcium ammonium pyrophosphate, calcium pyrophosphate, calcium metaphosphate, thermogravimetric analysis, X-ray diffraction.

A number of fundamental and applied studies are being carried out on the production of concentrated phosphorus fertilizers [1]. Nevertheless, condensed phosphates, whose properties differ from those of orthophosphates, remain insufficiently studied. Condensed (poly-) phosphates are gradually assimilated by plants, reduce phosphorus retrogradation in soil and are valuable as slow-release fertilizers [2, 3]. Among them, polyphosphate-based compound fertilizers are the most widely used worldwide.

Condensed calcium phosphates are used both as fertilizers and as technical materials and biomaterials. Since their properties depend on the phase composition, identifying the phases formed during the thermal treatment of mixtures of monoammonium phosphate and calcium compounds makes it possible to select an appropriate process regime.

Thermal analysis of the $NH_4H_2PO_4$: CaO = 2 : 1 mixture was carried out on a LabSys Evo simultaneous thermal analyzer (Setaram, France) in air (heating rate 10 °C/min, temperature range 30–800 °C, sample weight 16 mg). The samples obtained at 210 and 250 °C were examined by X-ray diffraction.

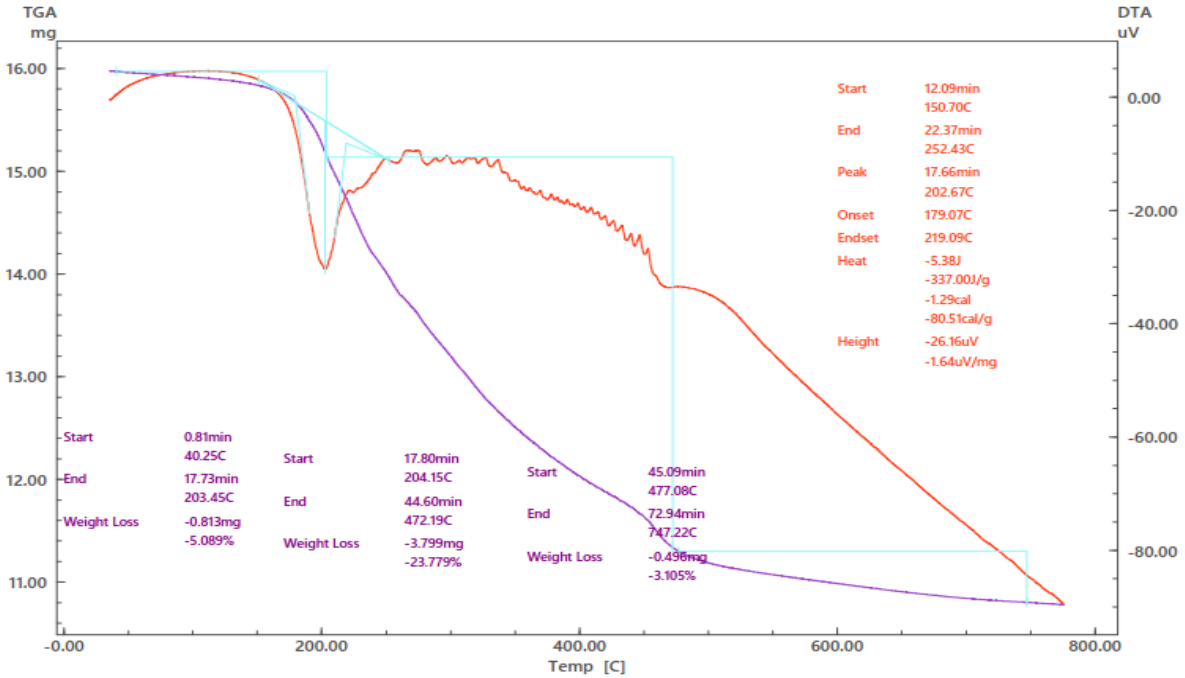


Fig. 1. Derivatogram of the $NH_4H_2PO_4$: CaO = 2 : 1 mixture

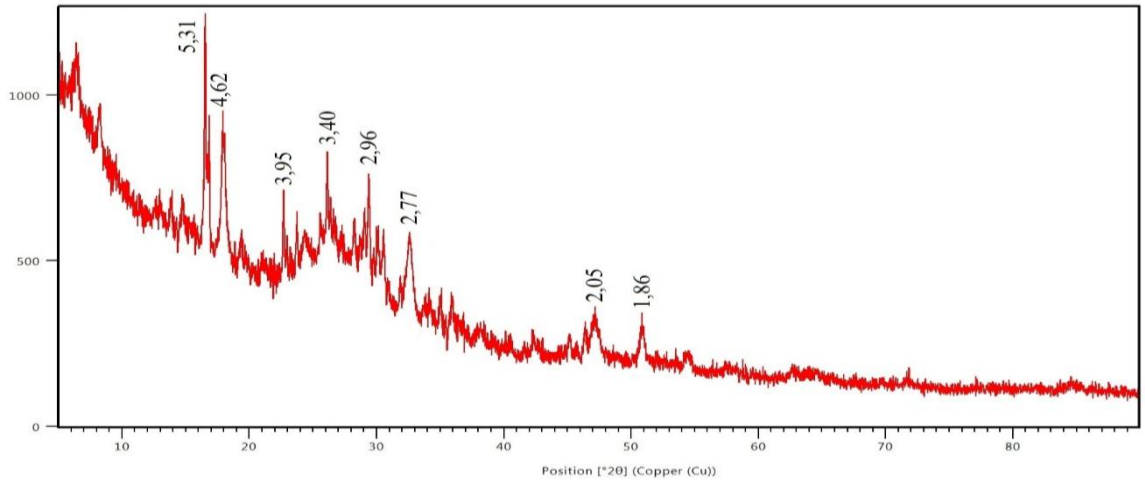
Upon heating to 800 °C, the total mass loss was 31%, and three main stages were distinguished: 40–203.45 °C (5.089%), 204.15–472.19 °C (23.779%) and 477.08–747.22 °C (3.105%). The endothermic effects below 203.45 °C correspond to the release of ammonia and water of crystallization, while the subsequent endo- and exothermic effects correspond to the decomposition of monoammonium phosphate and the interaction of free phosphorus oxide with CaO. Heating to 250–300 °C results in a mass loss of 18–20%. The processes can be described by the following reactions:

$$2NH_4H_2PO_4 + CaO \rightarrow Ca(NH_4)_2P_2O_7 + 2H_2O\uparrow \ (\approx 203\ ^\circ C) \quad (1)$$

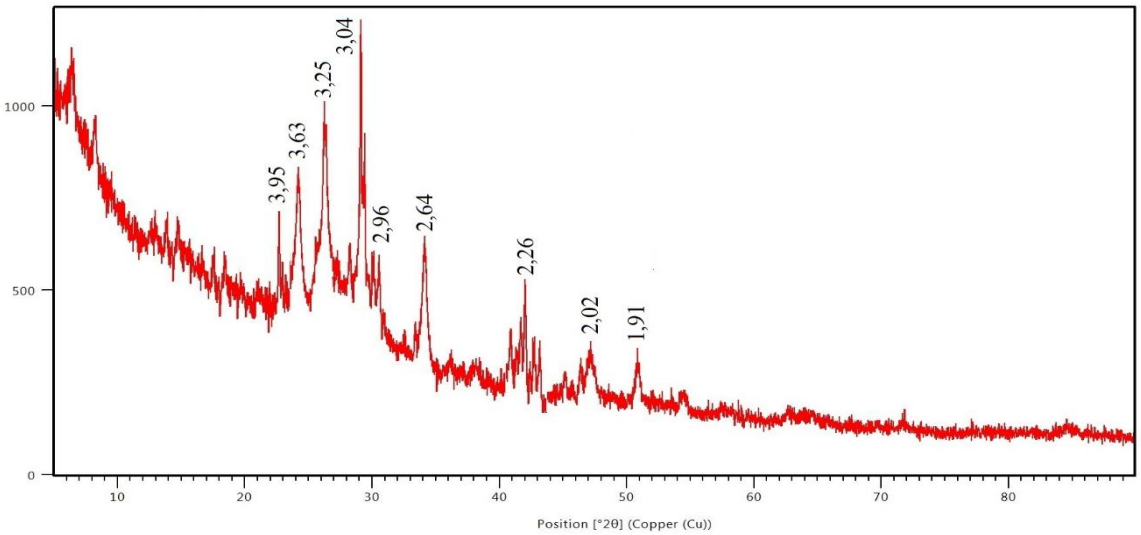
$$2NH_4H_2PO_4 + CaO \rightarrow CaNH_4HP_2O_7 + NH_3\uparrow + 2H_2O\uparrow \ (204–250\ ^\circ C) \quad (2)$$

$$2NH_4H_2PO_4 + CaO \rightarrow CaH_2P_2O_7 + 2NH_3\uparrow + 2H_2O\uparrow \ (250–450\ ^\circ C) \quad (3)$$

$$CaH_2P_2O_7 \rightarrow Ca(PO_3)_2 + H_2O\uparrow \ (470–500\ ^\circ C) \quad (4)$$



a)



b)

Fig. 2. X-ray diffraction patterns of calcium ammonium pyrophosphate and calcium pyrophosphate:

a – 210 °C, b – 250 °C

The X-ray diffraction pattern of the sample obtained at 210 °C shows intense peaks at d = 5.31, 4.62, 3.95, 3.40, 2.96, 2.77, 2.05 and 1.86 Å, characteristic of calcium ammonium pyrophosphate ($Ca(NH_4)_2P_2O_7$). At 250 °C, strong peaks at 3.25 and 3.04 Å and weaker peaks at 3.63, 2.64, 2.26, 2.02 and 1.91 Å indicate the formation of $CaH_2P_2O_7$, while the peaks at 3.95 and 2.96 Å confirm that a small

amount of undecomposed $Ca(NH_4)_2P_2O_7$ remains.

Conclusion. Thermal treatment of the $NH_4H_2PO_4$: CaO = 2 : 1 mixture leads to the formation of calcium ammonium pyrophosphate at 205–210 °C, calcium pyrophosphate at 250–270 °C and calcium metaphosphate at 450–470 °C. The obtained calcium ammonium and calcium pyrophosphates can be used as slow-release condensed fertilizers.

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