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THERMAL ANALYSIS AND X-RAY DIFFRACTION STUDIES ON CONTROLLED RELEASE FERTILIZERS PREPARED BY INCORPORATING NUTRIENTS INTO BLAST FURNACE SLAG

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ABSTRACT

Controlled release fertilizers, which release nutrients into the soil at slow rate, are prepared by melting mixtures of K_2CO_3, H_3PO_4 and blast furnace slag in various proportions. The present paper reports some thermal analysis and X-ray studies which throw light on the reactions that lead to formation of complex compounds in these mixtures. To ascertain the reaction paths, single, binary and ternary compositions in the system have been studied systematically by simultaneous TG and DTA. X-ray studies have also been carried out to identify the compounds formed during reactions indicated by DTA. Thermal analysis and X-ray studies have been used to explain the leaching behaviour of the nutrients, i.e. their rate of release in aqueous medium.

INTRODUCTION

The concept of controlled release of nutrients is a relatively new development in fertilizer technology. Controlled release fertilizer (CRF) are made by encapsulating nutrients or by incorporating them in a glassy matrix so that the nutrients are released slowly when the fertilizers come in contact with a leaching medium. This laboratory has previously reported some studies on the preparation of a blast furnace slag based CRF and the rate of nutrient release in various leaching media [1]. The release rate depends on the nature of compounds in the CRF and, therefore, it is important to study reactions that lead to the formation of such compounds. This paper presents a thermal analysis study on the reactions that take place during heating of K_2CO_3–H_3PO_4–slag mixtures. X-ray studies have been carried out to identify some compounds formed in the reaction mass. Some X-ray studies have also been done on residue left after exposure of CRF to leaching media, in order to identify the leachable compounds.

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The modified blast furnace slag is a mixture of a large number of complex silicates, phosphates and aluminates [2] which have been shown to release plant nutrients such as Ca, K, P in a complex manner. Compounds may dissolve fully or partially, quickly or over long periods. The rate of release of nutrients is, therefore, often non-uniform. Moreover, the release rate is also controlled by particle size, the pH of the leaching media, etc. However, the nature of compounds present in CRF is the most important factor and the present work was concerned with this aspect only.

EXPERIMENTAL PROCEDURE

For thermal analysis work blast furnace slag supplied by M/s Tata Iron and Steel Co. Ltd. Jamshedpur, India and K_2CO_3 were used as a fine powder (-149 μm) and H_3PO_4 as a solution of density 1.75 g ml^{-1} at 20°C. Their binaries and ternaries were prepared by simple mixing.

Preparation of samples involved melting down the ingredients taken in correct proportions at 1350°C for 2 h and subsequent cooling. For better homogeneity the mixture was remelted and cooled again. For leaching experiments, the mass so prepared was crushed to a fine powder ($-291+149$ μm). Further details are available elsewhere [1]. Thermal analysis work was also carried out on the residues which were left after previously prepared CRF samples were subjected to leaching experiments.

All thermal analysis work was done using a Stanton Redcroft simultaneous thermal analyser (model STA-781). To identify the compounds present, XRD powder patterns were taken on green and heated samples of different proportions, leached residues of different samples and residues of thermal analysis runs by an X-ray diffractometer (JEOL Model JDX-8P) with Ni filter and CuK_α radiation.

RESULTS AND DISCUSSION

Figure 1 shows the DTA plots for single components and some binaries. It can be seen that there are not many peaks for ordinary slag. One prominent exothermic peak at 925°C may be due to crystallization of Al_2O_3 or mullite as has been observed in some clays and synthetic slags [3]. This peak may also be due to oxidation of FeO (ca. 0.5 wt.%) in slag [4]. The TG plot shows a slight weight gain at this temperature as shown in a later figure.

The XRD pattern (Fig. 2) showed that ordinary granulated slag was an amorphous material. However, heating at 1000°C caused it to crystallize so that the XRD pattern of the heated slag indicated the presence of a number of phases including $2CaO \cdot Al_2O_3 \cdot SiO_2$, $Ca_2Al_2Si_3O_{10}(OH)_2$, $5CaO \cdot 6SiO_2 \cdot 0.5H_2O$, $Al_2O_3 \cdot 6SiO_2$, X-$CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2 \cdot 3H_2O$.

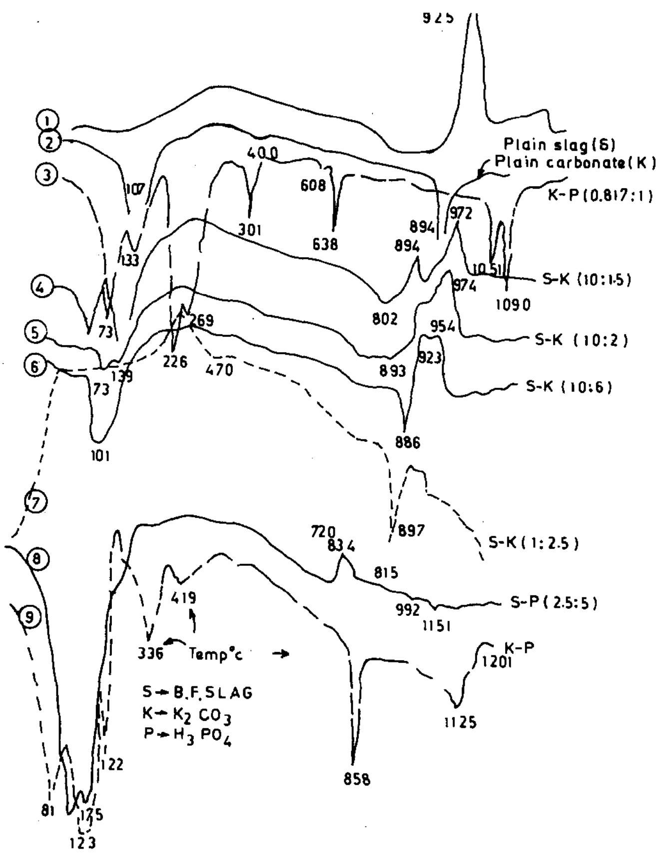

Fig. 1. DTA plots for single components and binaries.

The DTA plot of the ordinary carbonate indicates an initial endothermic peak and then another endotherm at around 894°C (Fig. 1). The latter, which is reversible on cooling presumably indicates melting of carbonate. There is no decomposition, as the TG plot shows no abrupt weight loss. No thermal analysis run was carried out using phosphoric acid because of possible chemical attack on the thermobalance hangdown system.

Figure 1 also shows the DTA plots for a number of binary systems. The slag–K_2CO_3 system, with varying proportions, shows newer peaks in addition to those for the pure components and thus, indicate chemical reaction near the melting point of the carbonate. Accordingly the TG plot (Fig. 3) shows considerable weight loss due to decomposition of carbonate. The characteristic peak of slag at 925°C gradually diminishes as the proportion of slag decreases. The heating of K_2CO_3–slag mixtures usually leads to formation of various potassium silicates which may be glassy and soluble (e.g. K_2SiO_5, $K_2Si_4O_9$) [5].

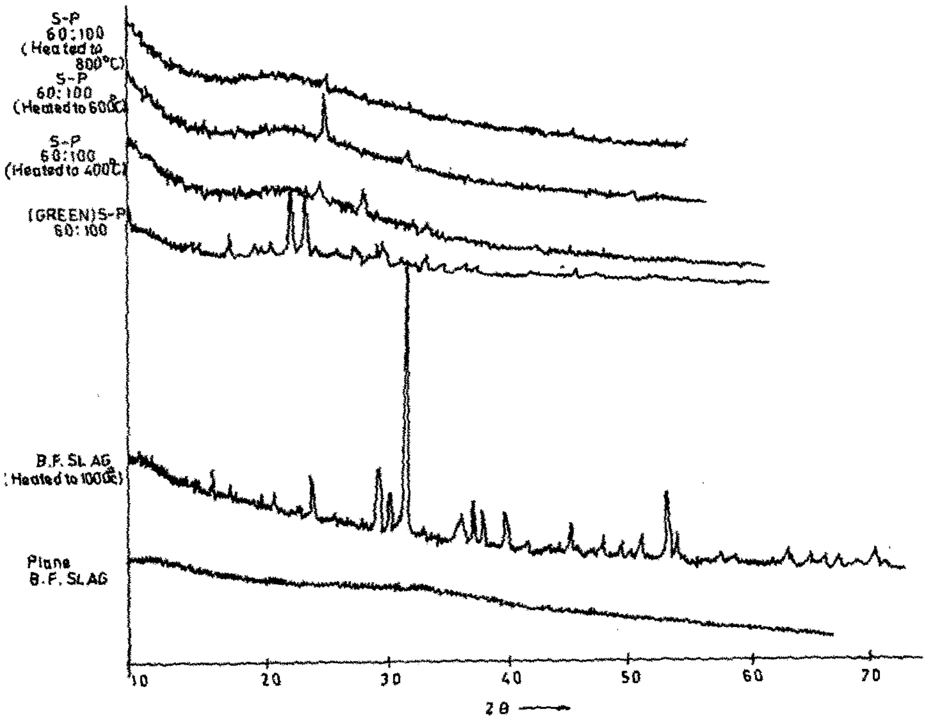

Fig. 2. XRD patterns of single and binary systems of BFS at different temperatures.

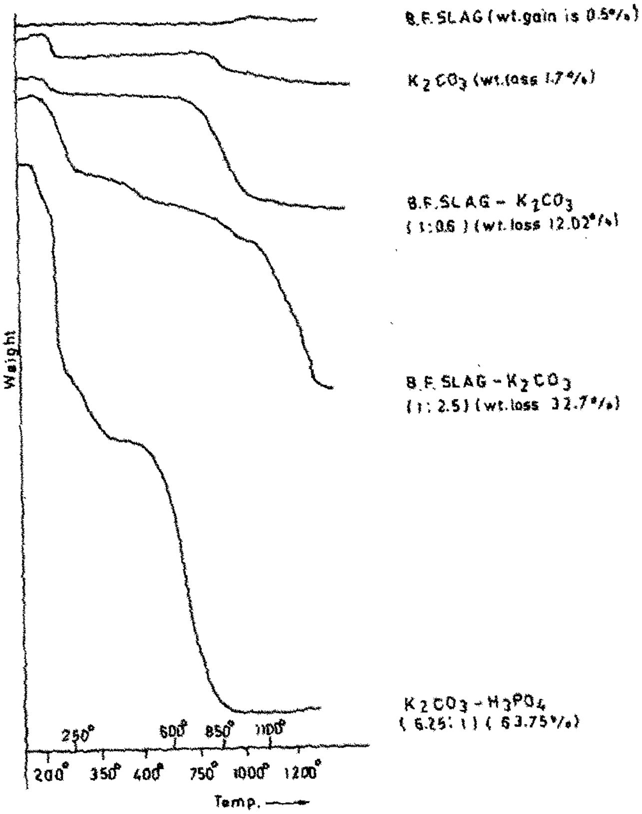

Fig. 3. TG plots for single components and binary systems.

Addition of H_3PO_4 to slag at room temperature generates a lot of heat and some hydrogen sulphide. The X-ray powder patterns on such mixture show the presence of a variety of phosphates e.g. CaP_2O_6, $Ca_3(PO_4)_2$, Ca_2SiO_4, $Ca_2SiO_4 \cdot Ca_3(PO_4)_2$, $Ca_3Si_2O_7$, $CaO \cdot 2SiO_2 \cdot 1/2H_2O$ etc. In addition, there may be formation of various calcium phosphate glasses [6].

The XRD pattern taken on the mixture of slag–phosphoric acid heated at different temperature, shows that the heated mass becomes less crystalline as shown in Fig. 2. Phosphate glasses are generally known to have poor chemical durability in comparison with silicate glasses. Unlike the silicate glasses, where the chemical durability is primarily controlled by the diffusion process, a breakdown of the phosphate network in the phosphate glasses occurs in aqueous solution [6].

The K_2CO_3–H_3PO_4 system showed a number of new peaks associated with weight losses (221, 336, 419 °C) as indicated in the TG plot. Some other peaks (269, 301, 608, 638 °C) indicate phase transformation only, which were reversible on cooling. This mixture leads to many reactions. There is also the possibility of formation of KPO_3 which reportedly, allows slow release of phosphorus [7].

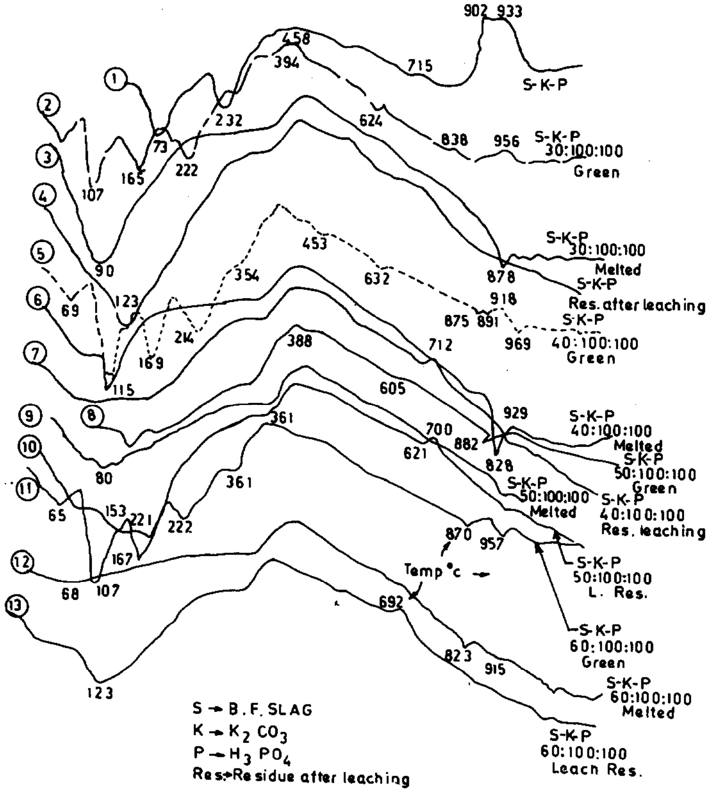

Fig. 4. DTA plots for ternary systems.

The DTA peaks for the ternary systems (Fig. 4) are generally combinations of the peaks found for the respective single components and their binaries. K_2CO_3–H_3PO_4 interactions are indicated by endo-peaks around 224 and 350°C and by exo-peaks at 450 and 624°C. Endo-peaks at high temperatures (870, 897, 960 and 990°C) indicate various phase transitions and complex reactions.

Ternary mixtures of slag, K_2CO_3 and H_3PO_4, after melting at 1350°C and cooling to room temperature, form a major glassy phase along with certain crystalline phases. It can be seen from Fig. 5 that the crystallinity increases with increase in slag content. Some compounds identified were $KH_3P_2O_7$, CaP_2O_6, $4CaO \cdot P_2O_5$, α-$KCaPO_4$ and $CaAl_2Si_2O_8$ [8]. These

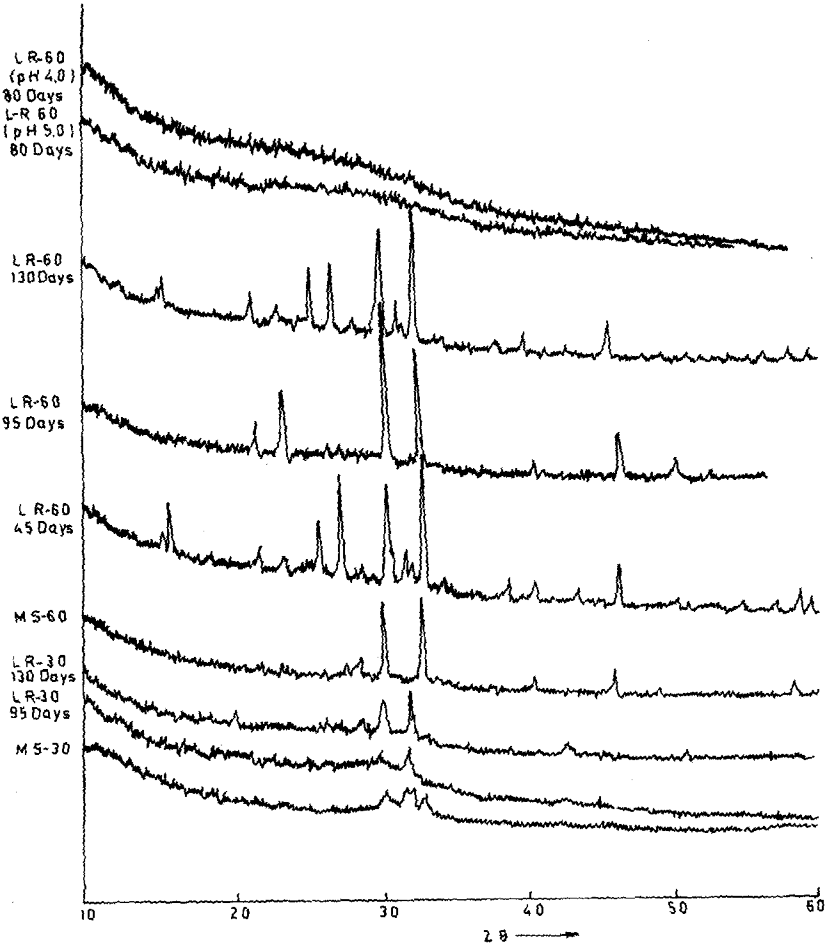

Fig. 5. XRD patterns for some leached and unleached samples.

phases have been reported to be of different solubility [9].

Leaching studies carried out on a typical sample have shown that nutrients are released in two stages [1]. This may be due to the difference in the solubility of various compounds formed during the preparation of the samples. The formation of such compounds has been confirmed by XRD and DTA studies [10].

In previous work, it was observed that the rate of release of nutrients from CRF increased with decrease in pH of aqueous solution. XRD studies were also carried out on leached residues of pH 4.0 and 5.0 to confirm this. In the case of pH 7.0, certain crystalline phases exist in the residue even after 80 days of leaching. These crystalline phases are identified to be hydroxy apatite $1/2[Ca(OH)_2 \cdot 3Ca_3(PO_4)_2]$, phosphates of calcium $Ca_3(PO_4)_2$, etc., which are soluble in aqueous media of lower pH [11]. However, the leach residue of the same sample at pH 4.0 and 5.0, after a similar period of leaching, showed complete absence of crystalline phases. This indicates that the crystalline phases are more soluble when the medium is more acidic.

CONCLUSIONS

It may be concluded that addition of K_2CO_3 and H_3PO_4 to molten blast furnace slag brings about many reactions which also change markedly the slag composition. Phosporic acid in particular, initiates several reactions, some even at low temperatures. The formation of new compounds and their dissolution behaviour during leaching, can be studied directly and indirectly by using thermal analysis and XRD. The silicates and phosphates thus formed on melting of mixtures make newer phases available for leaching in aqueous media. While some release the nutrients rapidly, some do it only slowly. The modified slag thus becomes an effective controlled release fertilizer.

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