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## Production of Potassium Monobasic Phosphate Using a Molten Salt Technique

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A molten salt technique has been developed for production of  $\text{KH}_2\text{PO}_4$  and  $\text{HCl}$  from  $\text{KCl}$  and  $\text{H}_3\text{PO}_4$ . A molten mixture of  $\text{KH}_2\text{PO}_4$  and  $\text{KCl}$  is contacted with  $\text{H}_3\text{PO}_4$  at about 250–320 °C and at a sufficient pressure to minimize thermal decomposition of  $\text{KH}_2\text{PO}_4$  (to  $\text{KPO}_3$  and steam). A small amount of sulfuric acid catalyzes the reaction. A flowsheet employing steam to strip  $\text{HCl}$  from the melt is proposed for production of  $\text{KH}_2\text{PO}_4$ .

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Potassium phosphates are highly desired as fertilizers since they contain two major crop nutrients, namely potassium and phosphate groups. They offer three major advantages as compared to potassium chloride commonly used as a potassium source and as compared to super phosphate fertilizers employed to furnish available phosphates. First, since they are highly concentrated, handling and shipping costs are relatively low. Second, no chloride ions are present; continued use of  $\text{KCl}$  may result in decreased yields of certain crops because of a large chloride buildup in some soils (Drechsel, 1976). Chloride ions are recognized as secondary nutrients and small amounts may, however, be desirable in fertilizers. Third, during the production of potassium phosphates from potassium chloride, the chlorine can be recovered and sold as either elemental chlorine or hydrogen chloride. Such sales reduce the cost of potassium phosphates. In addition when potassium monobasic phosphate ( $\text{KH}_2\text{PO}_4$ ) is ammoniated, the resulting product is a relatively well-balanced fertilizer since it also contains available nitrogen as a crop nutrient. Phosphate salts in addition also find uses in heavy-duty liquid detergents and as sequestering agents.

Several processes have been proposed for production of  $\text{KH}_2\text{PO}_4$ . In a process reported by Sawhill (1962),  $\text{KCl}$  is reacted with sodium monobasic phosphate ( $\text{NaH}_2\text{PO}_4$ ); the resulting  $\text{KH}_2\text{PO}_4$  and  $\text{NaCl}$  are separated by crystalli-

zation. Processes in which  $\text{KCl}$  is reacted with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) have also been reported by Ross and Merz (1932), Turrentine (1938), Madorsky and Clark (1940), Blumberg et al. (1968), Curless (1971), Worthington et al. (1973), and Moore (1974). In some processes, solid  $\text{KCl}$  is contacted with concentrated or glacial phosphoric acid; three phases including a solid, liquid, and gaseous ( $\text{HCl}$ ) phase are present during at least a portion of the reaction. Material handling problems tend to occur during such processes. For the remaining processes mentioned above, a solvent such as either water or methanol is employed in at least one step of the process in order to solubilize the reactants or products. The resulting solution must eventually be separated and  $\text{KH}_2\text{PO}_4$ , solvent, and  $\text{HCl}$  must be recovered; the separation is not easy nor really cheap. Recently Drechsel et al. (1972, 1976) have reported a process in which  $\text{KCl}$ , phosphate rock, and sulfuric acid are reacted to form  $\text{KH}_2\text{PO}_4$ ,  $\text{Ca}_2\text{SO}_4$ , and  $\text{HCl}$ . A solvent is employed, and  $\text{KHSO}_4$  is an intermediate.

In order to obtain rapid reactions between  $\text{KCl}$  and phosphoric acid, high temperatures are preferred. In such cases, relatively high pressures are sometimes used in order to prevent excessive evaporation of solvent or of water, formed by the thermal decomposition of  $\text{KH}_2\text{PO}_4$  or  $\text{H}_3\text{PO}_4$ . Kiehl and Wallace (1927), Tomkova et al. (1960), and Boros and Larant (1963) have presented information on such decomposition reactions. At especially higher temperatures and lower pressures,  $\text{KH}_2\text{PO}_4$  forms potassium metaphosphate ( $\text{KPO}_3$ ) and pyrophosphates that often cake resulting in serious handling problems. Metaphosphoric acid is also not as reactive as orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ). Removing (or stripping)  $\text{HCl}$  from the

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reaction mixture is a problem especially at lower temperatures. Stripping with steam (Askenasy and Nesslar, 1930), solvent, or inert gas has been found to be effective. Corrosion and environmental problems likely occur for at least some, if not all, of the above-mentioned processes.

Chin (1965) obtained preliminary information for reacting KCl dissolved in a melt of  $\text{KH}_2\text{PO}_4$  with  $\text{H}_3\text{PO}_4$ . When  $\text{H}_3\text{PO}_4$  was added to the melt, a portion of KCl reacted to form additional  $\text{KH}_2\text{PO}_4$  and there was the evolution of some HCl and steam.  $\text{KH}_2\text{PO}_4$  and/or  $\text{H}_3\text{PO}_4$  were obviously decomposing to at least some extent, and the melts eventually became too viscous to handle readily. For the molten salt method, there is still the need to determine if complete conversions of KCl can be obtained and to develop techniques to maintain low viscosity melts. If high partial pressures of steam are maintained over the melts, decomposition of both  $\text{KH}_2\text{PO}_4$  and phosphoric acid can probably be prevented or reversed (Halt and Myers, 1911). A  $\text{KH}_2\text{PO}_4$  process involving molten salts would appear to offer several key advantages as compared to processes involving solid-liquid slurries or employing solvents. Such a process would be similar in many respects to processes for production of alkali metal nitrates (Haug and Albright, 1965) and of alkali metal sulfates (Chin, 1969; Chin and Albright, 1971) using molten salts as reaction media.

In the present investigation, additional information has been obtained for the production of  $\text{KH}_2\text{PO}_4$  using a molten salt technique. A flow diagram is proposed.

#### EXPERIMENTAL DETAILS

The batch reactor used was similar to ones employed earlier by Chin (1965, 1969) and Chin and Albright (1971). Details of the equipment are reported by Lee (1970). A glass tube closed at the bottom was used to hold the reactants; it had an internal diameter of 4.45 cm and a length of 15.9 cm. This tube was placed inside a 300-mL stirred autoclave (Model ABE-305) manufactured by Autoclave Engineers. The tube was supported on the bottom by a steel spring that held the top of the tube firmly against the top cover of the autoclave. A Teflon impeller of 3.3 cm diameter was positioned inside the glass tube. Teflon tape was wrapped around the impeller shaft, an internal cooling coil, and the thermocouple wells positioned inside the glass tube. Corrosion of the steel was minimized by the use of the Teflon tape and the glass tube inside the stirred autoclave.

Pressures inside the reactor were measured using a stainless steel pressure gauge that could be read within 5 psig at pressures up to 1000 psig. The Bourdon tube of the pressure gauge and the lines to the pressure gauge were filled with oil to prevent water condensation in the tube or lines. Electrical heaters were used to maintain the desired temperatures of the molten salt. Thermocouples were employed, and the temperature of the molten salt was generally 10–15 °C higher than that of the gas phase.

Measured amounts of  $\text{KH}_2\text{PO}_4$ , water, and possibly one reactant were added to the reactor at the start of a run. This initial mixture was then heated until a pressure of several atmospheres occurred; the reactor was then vented for a short time to exhaust the air plus a small amount of steam. Next the liquid mixture was heated to the desired temperature, and additional reactants and/or water were added from thick-walled glass tubes. A pressure of about 400 psig nitrogen was employed to force the reactants into the reactor. KCl was introduced as a saturated water solution and concentrated phosphoric acid was used. The thick-walled tubes were calibrated so the amounts of liquid added could be measured to within 0.05 mL for volumes

Table I. Production of  $\text{KH}_2\text{PO}_4$  from KCl and  $\text{H}_3\text{PO}_4$  at 250–320 °C

run	6	7	8
initial melt			
$\text{KH}_2\text{PO}_4$ , g	96.3	136	136
mol	0.71	1.0	1.0
$\text{H}_3\text{PO}_4$ , g	13.7	14.7	14.7
mol	0.14	0.15	0.15
$\text{H}_2\text{O}$ , mL	50	50	50
increments of KCl added	5	6	5
total KCl added, g	3.7	4.5	4.5
mol	0.05	0.06	0.06
pressure before adding KCl increment, psig	380	300	300
temp. while adding KCl, °C	250-270	300-320	300-310
KCl conversion (%) based on HCl recovery during KCl additions	<1	2	2
increments of $\text{H}_2\text{O}$ added	3	3	5
volume of $\text{H}_2\text{O}$ increment, mL	2.7	2.7	3.0 to 6.0
pressure before adding $\text{H}_2\text{O}$ increment, psi	380	300	100
temp. while adding water, °C	268-278	300-350	305-350
water content of melt during additions, wt %	10-17	0.6-1.4	6-13
KCl conversion (%) based on HCl recovered	28	4	49

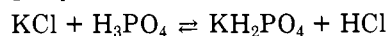
up to about 50 mL. During the run, temperatures and pressures were recorded at frequent intervals. When any gas was vented from the reactor, it was passed to a gas absorber. The amount of condensed water obtained was volumetrically measured.

Analytical methods used (Furman, 1962) include a silver chromate technique to measure the chloride (or HCl) content of the absorber solution and a gravimetric technique with magnesium chloride, ammonium chloride, and ammonia to measure the phosphate contents of the salts or absorber solutions.

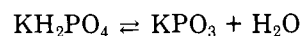
The amounts of reactants and the range of conditions investigated were as follows: amount  $\text{KH}_2\text{PO}_4$  used, 96 to 138 g (0.7 to 1.01 g mol); amount KCl used, 3 to 7.5 g (0.04 to 0.1 g mol); concentration of  $\text{H}_3\text{PO}_4$ , 75 to 86%; moles of  $\text{H}_3\text{PO}_4$  added, 0.10 to 0.15; molar ratio of  $\text{H}_3\text{PO}_4$  to KCl, 1.0 to 3.0; temperature, 250 to 350 °C; pressures, up to 400 psig. Vigorous agitation (700 rpm) was employed in all cases.

#### RESULTS

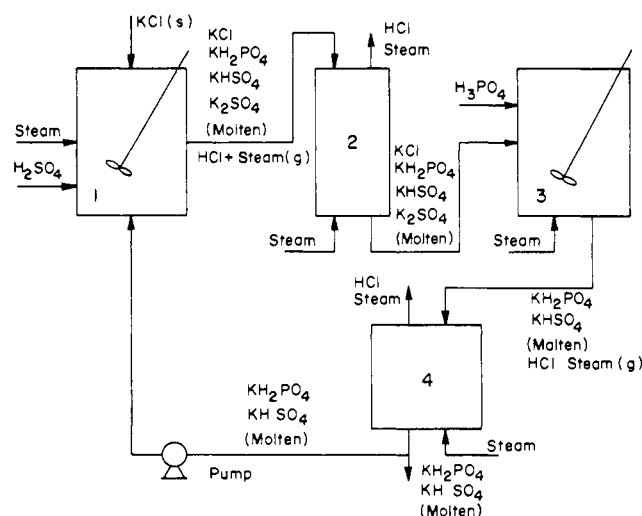
High temperatures, at least 320 °C, and substantial partial pressures of steam were found in the present investigation to be desirable for the following reaction in a molten  $\text{KH}_2\text{PO}_4$  media:



and simultaneously to suppress the following undesired reaction:



Three runs (runs 6, 7, and 8) were made at temperatures varying from 260 to 320 °C using  $\text{KH}_2\text{PO}_4$  melts that contained small amounts of  $\text{H}_3\text{PO}_4$  and water. Table I summarizes the results of these three runs. Saturated KCl



**Figure 1.** Proposed flowsheet for a continuous process producing potassium monobasic phosphate.

solution was added to a melt containing  $\text{KH}_2\text{PO}_4$ ,  $\text{H}_3\text{PO}_4$ , and water in the following manner. Three to six milliliters of solution was added causing a pressure rise of 15–100 psi depending on the amount of solution added and on the water content of the melt. About 15–20 min was required to obtain a steady-state pressure. After a steady-state pressure was obtained, the reactor was vented for about 5–10 min until the pressure had decreased to the initial pressure. Immediately, another increment of KCl solution was added. (If the melt had been allowed several minutes to reach steady state, the pressure would have been higher by about 10–30 psi). The above procedure was repeated several times. KCl conversions of about 2% occurred during the KCl additions for runs 7 and 8 made at about 300–320 °C as indicated by Table I. A conversion of <1% occurred, however, during the KCl additions for run 6 made at a much lower temperature, 250–270 °C.

The following technique was found to be effective as shown in Table I for flushing HCl from the reaction mixture. A small volume (3 or 6 mL) or water was added to the reaction mixture. Then controlling venting of steam was provided for about 5–10 min. This technique that stimulates steam stripping of the melt was repeated several times. While the technique was very effective for removing HCl in run 8, it was less so in run 7. The increased effectiveness in run 8 is thought to have been caused by the much higher water content of the melt and by the lower pressures used during venting. The higher water content of the melt in run 8 apparently acted to maintain higher concentrations of  $\text{H}_3\text{PO}_4$ . In run 7, more phosphoric acid had probably been dehydrated to form either meta or pyro forms of phosphoric acid; such forms are less reactive with KCl than the ortho form.

The technique of water addition such as used in run 8 was also found to be effective in run 6 for removing HCl from the melt. The water content of the melt in run 6 was also quite high. The lower KCl conversions of run 6 as compared to those of run 8 are thought to be caused by lower temperatures, fewer steam strippings, and higher pressures at the end of the venting period.

The earlier evidence (Halt and Myers, 1911) concerning the reversibility of  $\text{KH}_2\text{PO}_4$  decomposition to  $\text{KPO}_3$  and steam was confirmed by the following test. A series of runs were made in which mixtures of  $\text{KH}_2\text{PO}_4$  and small amounts of water were heated to produce melts. The mixture, after deaeration, was heated to a desired temperature in the 200 to 400 °C range. In all cases at a given temperature, the pressure (or vapor pressure) of the

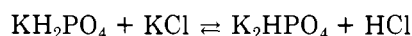
mixture reached a steady-state value within 5–10 min. When the vent valve was cracked to vent some of the gases (essentially just steam) from the reactor, a new and lower vapor pressure resulted. When an identical amount of water was added back to the mixture, the resulting vapor pressure was identical, after 10–15 min, to the initial vapor pressure before the steam had been vented. Furthermore, no changes were ever noted in the appearance or viscosity of the melts before or after venting (followed by water addition).

When a small amount of  $\text{H}_3\text{PO}_4$  was added to the  $\text{KH}_2\text{PO}_4$ – $\text{H}_2\text{O}$  mixture (or melt), the gases vented contained a trace of acid; the resulting condensate had a pH of 3–4. Titration of the condensate indicated trace amounts of phosphate ions.

In run 9, a total of 0.105 mol of  $\text{H}_3\text{PO}_4$  was added in three equal increments to a melt containing 1.0 mol of  $\text{KH}_2\text{PO}_4$ , 0.04 mole of KCl, and 25  $\text{cm}^3$   $\text{H}_2\text{O}$ . The reaction mixture during these additions was maintained at 295–310 °C. After each addition of phosphoric acid, the system was vented to reduce the pressure back to 300 psig. The KCl conversion during the addition of phosphoric acid was 38% (based on the moles of HCl recovered). Subsequent addition of two increments of water (totaling 12 mL) and venting to atmospheric pressure, resulted in a significant removal of additional HCl from the melt. The total KCl conversion for run 9 based on HCl recovered was 81%.

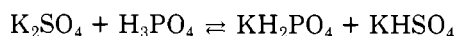
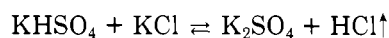
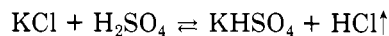
In run 9, the water content of the melt was relatively low, being in general in the 4 to 5% range. Nevertheless, the dehydration of  $\text{H}_3\text{PO}_4$  was probably slow and hence relatively unimportant. A comparison of the KCl conversions for runs 8 and 9 would seem to indicate that some dehydration of  $\text{H}_3\text{PO}_4$  had occurred in run 8 even though the water content of the melt was reasonably high.

Run 10 indicated that with steam stripping and high temperatures the following reaction occurred to at least a small extent:



A molten salt mixture of  $\text{KH}_2\text{PO}_4$ , KCl, and  $\text{H}_2\text{O}$  that was identical in composition to that of run 9 was heated first to 320 °C. Two water additions followed by venting resulted in KCl conversions based on the HCl removal of <1%. As the temperature was raised to 420 °C and with five further additions of water (followed by venting), a total conversion of 6% occurred.

One of the key findings of the present investigation is that small amounts of sulfuric acid promote or catalyze the production of  $\text{KH}_2\text{PO}_4$ . The following reactions probably occurred in the  $\text{KH}_2\text{PO}_4$  melts investigated in this investigation:



As will be discussed later, the second reaction above is thought to be the rate controlling one of the three. In run 11, a molten mixture of 1.1 mol of  $\text{KH}_2\text{PO}_4$ , 0.1 mol of KCl, 0.02 mol of  $\text{H}_2\text{SO}_4$ , and 1.89 mol (34 mL) of water was heated first to 250 °C and later to temperatures as high as 350 °C. Water was added in several increments as reported in Table II. After each addition of water, venting resulted in considerable evolution of HCl from the reaction mixture. Five additions of water and five ventings resulted in a KCl conversion of 33% based on the amount of HCl evolved. Only a 20% conversion can be accounted for by the first reaction above, and clearly some  $\text{K}_2\text{SO}_4$  had also been produced. This finding would also have been pre-

Table II. Chloride Ion Recovered at Each Venting in Run 11

no. of addition	material added, cm <sup>3</sup>	temp, °C	pressure before addition, psig	pressure at equilibrium, psig	wt % water in melt at equilibrium	final pressure for venting, psig	wt % water in melt after venting	total % Cl <sup>-</sup> recovery for KCl used
1	H <sub>2</sub> O, 3.0	250	115	295	19.7	200	14.3	2.4
2	H <sub>2</sub> O, 3.0	250-305	200	385	15.8	200	9.8	6.9
3	H <sub>2</sub> O, 6.0	290-330	200	440	13.0	200	8.1	15
4	H <sub>2</sub> O, 7.5	290-350	200	360	12.0	100	3.6	23
5	H <sub>2</sub> O, 9.0	290-330	100	220	9.0	0	7.3	33
6	H <sub>3</sub> PO <sub>4</sub> , 4.5	290-320	0	225	11.3	100	7.8	52
7	H <sub>2</sub> O, 6.0	290-330	100	275	11.3	0	2.1	83

dicted based on the results of Chin and Albright (1971). Furthermore, run 1-5 of the present investigation have shown that NaHSO<sub>4</sub> reacts readily with NaCl in a salt melt at temperatures as low as 250 °C.

As a continuation of run 11, 4.5 cm<sup>3</sup> (0.05 mol) of H<sub>3</sub>PO<sub>4</sub> was added to the melt maintained at 290-320 °C. Venting, a water addition, and another venting resulted in a total KCl conversion of 83% (see Table II). This conversion indicates that at least 86% of the H<sub>3</sub>PO<sub>4</sub> reacted to form KH<sub>2</sub>PO<sub>4</sub>. This latter conclusion was determined as follows: if all 0.02 mol of H<sub>2</sub>SO<sub>4</sub> reacted to form K<sub>2</sub>SO<sub>4</sub>, then 0.04 mol of HCl would simultaneously have been formed. Since 0.083 mol of HCl was evolved, then at least 0.043 mol of HCl was produced as a result of reactions with 0.05 mol of H<sub>3</sub>PO<sub>4</sub> to form KH<sub>2</sub>PO<sub>4</sub>. Hence, at least 86% of the H<sub>3</sub>PO<sub>4</sub> had reacted.

The temperature was found to have an important effect on reactions of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> in molten salt mixtures. For run 12 with a mixture containing 1.0 mol of KH<sub>2</sub>PO<sub>4</sub>, 0.1 mol of KCl, 0.02 mol of H<sub>2</sub>SO<sub>4</sub>, and 34 cm<sup>3</sup> H<sub>2</sub>O, KCl conversions at 240-280 °C were only 18%. If all H<sub>2</sub>SO<sub>4</sub> had reacted with KCl to form KHSO<sub>4</sub>, a conversion of 20% would have resulted. Apparently at the relatively low temperatures of this run, little or no K<sub>2</sub>SO<sub>4</sub> (or KH<sub>2</sub>PO<sub>4</sub>) was produced. It is thought that KH<sub>2</sub>PO<sub>4</sub> is produced primarily by reactions of H<sub>3</sub>PO<sub>4</sub> with K<sub>2</sub>SO<sub>4</sub>.

One run (run 14) was made in which 0.1 mol of KCl, 0.1 mol of H<sub>3</sub>PO<sub>4</sub>, and 0.02 mol of H<sub>2</sub>SO<sub>4</sub> were reacted in a KH<sub>2</sub>PO<sub>4</sub> melt at 350-390 °C. Pressures in this run were relatively low, atmospheric pressure before each addition of water. At such low pressures, the water content of the melt was low and some H<sub>3</sub>PO<sub>4</sub> was probably decomposed to HPO<sub>3</sub>. A total KCl conversion of 74% was obtained in this run; such a conversion was substantially higher than in comparable runs without the use of H<sub>2</sub>SO<sub>4</sub> but not as high as the conversion obtained for run 11. Loss of H<sub>3</sub>PO<sub>4</sub> by vaporization may also have been more of a factor in run 14.

In one run, nitric acid was added in small amounts to a KH<sub>2</sub>PO<sub>4</sub> melt containing KCl and H<sub>3</sub>PO<sub>4</sub>. The purpose of this run was to determine if nitric acid was a catalyst such as H<sub>2</sub>SO<sub>4</sub>. A slight increase was noted in the KCl conversion of this run, but the nitric acid was quite unstable and resulted primarily in the formation of nitrogen oxides.

#### SUGGESTED PROCESS FOR PRODUCTION OF KH<sub>2</sub>PO<sub>4</sub>

Based on the findings of this investigation, the flowsheet shown in Figure 1 is proposed for a continuous-flow process for production of KH<sub>2</sub>PO<sub>4</sub> from KCl and H<sub>3</sub>PO<sub>4</sub>. Operating variables to consider are as follows.

**A. Method of Adding Potassium Chloride and Phosphoric Acid.** The potassium chloride can be fed into the first reactor (unit no. 1) as either a solid salt or as an aqueous solution. An additional vessel would be required to prepare such a solution; and preheating of the aqueous solution to minimize the heat load in the reactor would

probably be desired. Based on energy requirements and on equipment costs, solid potassium chloride might be preferred, but more agitation would probably be needed in the first reactor in such a case. In order to minimize the vaporization or decomposition of H<sub>3</sub>PO<sub>4</sub>, this acid should be mixed rapidly with the melts in the second reaction (unit no. 3). H<sub>3</sub>PO<sub>4</sub> reacts in this reactor with K<sub>2</sub>SO<sub>4</sub> and residual KCl.

**B. Reaction Temperature.** Results of the experimental work indicated the temperature maintained in the first reactor should be somewhat higher than 320 °C. No information is available for the reaction at temperature above 350 °C, and a study of the reaction at 400 °C is recommended. Higher pressures would, however, be required at such temperatures. Similar temperatures are probably also needed for the second reactor.

**C. Reaction Pressures.** Pressures of at least 200 psi are probably needed in order to minimize decomposition reactions. More information is, however, needed to determine optimum pressures.

**D. Molar Ratio of H<sub>2</sub>SO<sub>4</sub> to H<sub>3</sub>PO<sub>4</sub>.** H<sub>2</sub>SO<sub>4</sub> has been found to promote the production of KH<sub>2</sub>PO<sub>4</sub>. If it is used, however, the KH<sub>2</sub>PO<sub>4</sub> product will contain some KHSO<sub>4</sub> or K<sub>2</sub>SO<sub>4</sub>. As little H<sub>2</sub>SO<sub>4</sub> should be used as is consistent with the overall economy. Lower ratios of H<sub>2</sub>SO<sub>4</sub> to H<sub>3</sub>PO<sub>4</sub> will likely be feasible as the reaction temperatures (and as a result reaction pressures) are increased. Perhaps if a sufficiently high temperature is used, there will be no need to use H<sub>2</sub>SO<sub>4</sub>.

**E. Separation of HCl.** About 40 to 100 psi is recommended for separation of HCl and steam from the melts in separators (units 2 and 4). It is thought that relative little KH<sub>2</sub>PO<sub>4</sub> will thermally decompose at such pressures. More experimental information is, however, needed to confirm this fact.

The process proposed in this investigation offers several advantages as compared to previous processes. First, and probably foremost, it is essentially one with liquid reactants; transfer of liquids throughout the unit should be reasonably easy. Processing and recovery of the products including KH<sub>2</sub>PO<sub>4</sub> and HCl should be quite simple and with a minimum of environmental problems. Handling molten KH<sub>2</sub>PO<sub>4</sub> offers potential benefits if this stream is to be decomposed to produce KPO<sub>3</sub>, if it is to be reacted with ammonia, or if it is to be pelletized or prilled. A problem that has not yet been solved is to find suitable materials of construction to minimize corrosion. Suitable metals can probably be found, however, and it is recommended that the next step in developing the process would be to make such a search.

#### CONCLUSION

The results of this investigation have provided important information relative to a process using molten salts for production of KH<sub>2</sub>PO<sub>4</sub>. Although the technique was not tested for production of other alkali metal phosphates, it would seem to be applicable for other phosphates such as

$\text{NaH}_2\text{PO}_4$  and  $\text{LiH}_2\text{PO}_4$ . Commercial production of  $\text{K}_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , etc. may also be possible if higher temperatures and pressures are employed; higher pressures are probably required to minimize thermal decomposition of the phosphates.

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## Elemental Content of Tissues of Sheep Fed Rations Containing Coal Fly Ash

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Sheep were fed up to 7.5% by weight of fly ash in complete pelleted rations for 124 days. Among 34 elements determined in rations and animal tissues, selenium increased slightly in specific tissues and blood as a function of the percentage of fly ash in the ration. Selenium concentration in blood increased slowly as the time of feeding progressed. There was no significant effect from the inclusion of fly ash in the ration on quantity of feed consumed, animal weight gain, or in vivo ration digestibility.

Whereas high concentrations of dietary selenium are known to be toxic to farm animals (Rosenfield and Beath, 1964), traces of the element are essential. Glutathione peroxidase isolated from bovine erythrocytes has recently been shown to contain four selenium atoms per molecule of the enzyme (Hoekstra, 1975). This enzyme is believed to destroy  $\text{H}_2\text{O}_2$  and other organic hydroperoxides which may produce oxidative damage in living cells. Decreases in glutathione peroxidase correlate with lesions caused by selenium deficiency.

Between 0.03 and 0.1 ppm of selenium in the diet appears to satisfy the essential requirements of the element for animals (Allaway et al., 1967). Since soils in many areas of the world are deficient in selenium available for plants,

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Table I. Composition of the Complete Pelleted Sheep Rations

constituent	% dry wt	% dry wt	% dry wt	% dry wt	% dry wt
fly ash	0 <sup>a</sup>	1	2.5	5	7.5
alfalfa meal	45	44	41.5	38	34.5
oats (crushed)	10	10	10	10	10
corn (ground)	13	13	13	13	13
wheat (middlings)	5	5	5	5	5
soybean meal	11.5	11.5	12.5	13.5	14.5
molasses	15	15	15	15	15
salt (without minerals)	0.45	0.45	0.45	0.45	0.45
vitamin supplement (A, D, and E)	0.05	0.05	0.05	0.05	0.05

<sup>a</sup> Control ration.

supplementation of the diets of farm animals with selenium has become common (Perry et al., 1976; Frost, 1973; Kuchel and Buckley, 1969; Handrick and Godwin, 1970). Recent studies here have shown that fly ashes produced in soft coal-burning electric power generating plants contain appreciable quantities of selenium which is readily available to plants grown in it (Gutenmann et al., 1976; Furr et al., 1975, 1976a) or to aquatic organisms when fly ash contaminates their water (Gutenmann et al., 1976). It