

milk was 0.8–0.9 ng/mL at 1–3 h after dosing 30 mg of PGF<sub>2α</sub>. The concentration of PGF<sub>2α</sub> in milk declined to predose values (0.2 ng/mL) at 21 h after dosing. Thus for both cloprostenol and PGF<sub>2α</sub>, the clearance of the parent drug from milk follows a similar time course. For cloprostenol the clearance of the total drug derived residue is very rapid (Reeves, 1978). Similar data have not been reported for PGF<sub>2α</sub>.

#### ACKNOWLEDGMENT

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## Chlor-Phosphate Process for Production of Chlorine, Hydrogen, and Potassium Phosphates

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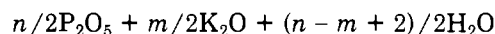
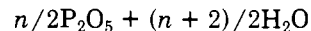
An electrolytic process for the production of chlorine, hydrogen, and potassium phosphates as solution, solid, or slurry was developed in a bench-scale continuous microplant. Potassium amalgam made by the decomposition of pure potassium chloride solution in a mercury-cathode electrolyzer was reacted with a solution of potassium phosphates to which controlled amounts of ortho- or polyphosphoric acid and water were supplied. Solutions were produced over a wide pH range. A 0–32–32 solution of pH 7.5 was prepared, but solutions with total plant food in excess of 70% are anticipated. The solution contained <100 ppm Cl and <0.01 ppm Hg. The polyphosphate levels of the products were slightly lower than those of the starting acids. Fertilizer grades of potassium chloride and wet-process phosphoric acid required special treatment to avoid operational problems.

Potassium chloride is the most abundant and least expensive source of potassium for fertilizer use. It contains 63% plant food as K<sub>2</sub>O and is an excellent low-cost fertilizer for most applications. Because potassium salts usually have high solubilities, it is perhaps surprising that at 0 °C a saturated aqueous solution of potassium chloride contains the equivalent of only 14% K<sub>2</sub>O (Noyes, 1966). For this reason the solubility of KCl is limiting for many solution fertilizers wherein high solubility is desirable. Furthermore, the chlorine associated with the potassium is not a nutrient and is toxic to some plants. The conversion of potassium chloride to other fertilizer materials, such as potassium phosphate, can be justified if the new potassium compound is a more desirable fertilizer and valuable coproducts are produced.

Nearly all processes for the production of potassium phosphates employ potassium chloride as the source of potassium. Potassium hydroxide, derived from the chloride, is usually regarded as too expensive for fertilizer use. Most of the processes produce monopotassium phosphate or a mixture of mono- and dipotassium phosphates as intermediates. Both solid and fluid fertilizers are produced.

The general expression for the phosphoric acids—ortho-, pyro-, tripoly-, tetrapoly-, etc.—which exist as an homologous series of chain phosphates is H<sub>n+1</sub>P<sub>n</sub>O<sub>3n+1</sub>. A similar but much more complex homologous series of potassium phosphates is described by the formula K<sub>m</sub>H<sub>n-m+2</sub>P<sub>n</sub>O<sub>3n+1</sub>. The respective corresponding oxide formulas for the above expressions more conveniently describe the materials in

terms of plant nutrients and water of constitution:



Although hydrated acids and salts also exist, water of hydration is not included in these formulas. Figure 1 shows some of the parent acid species and the many anhydrous salts that can be postulated by stoichiometry. These acids contain 72–84% plant nutrient as P<sub>2</sub>O<sub>5</sub>, and their salts contain 87–100% plant nutrients as K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>. Although only a few of the salts indicated exist as equilibrium solid phases, many hydrated forms of the potassium phosphates do exist, and double salts and others described by the inclusion of one or more moles of acid in some of the above salts have been reported (Van Wazer, 1958).

The potassium phosphates are very soluble in water, and the solubilities vary with the relative proportions of K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub> present. Potassium phosphates have maximum solubilities at 0 °C when the weight ratio K<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> is slightly greater than unity (Potts et al., 1961). At this temperature a solution with about 45% plant food is attainable with the ortho species (Van Wazer, 1958). Because mixtures of orthophosphates with polyphosphates are much more soluble than the orthophosphates alone (Farr and Williard, 1971; Frazier et al., 1972), it is understandable that solutions of even >70% plant food, crystal free at 0 °C, have been prepared. So in saturated potassium phosphate solutions there are P–K plant food concentrations that compare very favorably with those of solid fertilizers.

Potassium phosphates and their solutions are concentrated, chloride-free plant foods; they have low salt indices (Rader et al., 1943) and are especially suited to no-nitrogen and low-nitrogen applications. In spite of their higher

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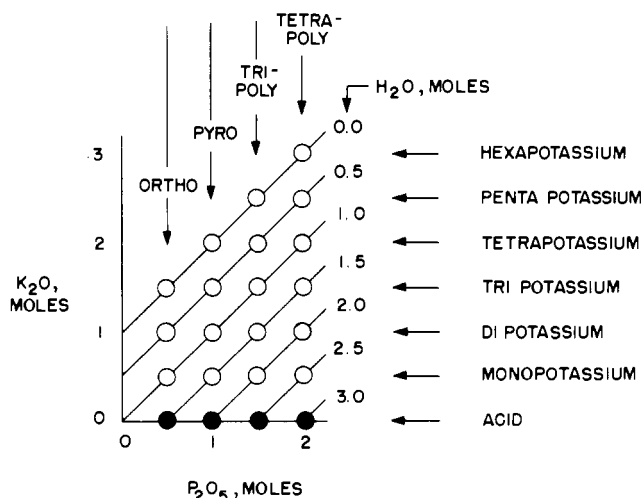


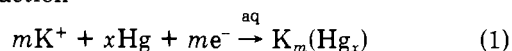
Figure 1. Compositions of phosphoric acids and potassium phosphates.

costs, they are of much interest to the fertilizer industry.

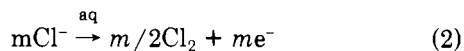
#### CHLOR-PHOSPHATE PROCESS

A new process has been developed which converts potassium chloride and phosphoric acid into chlorine, hydrogen, and potassium phosphates (Hignett and Smith, 1974). A flow diagram is shown in Figure 2. Potassium chloride solution is electrolyzed to produce potassium amalgam on a flowing mercury cathode and chlorine gas at the anode:

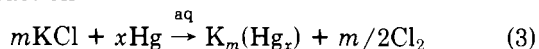
cathodic reaction



anodic reaction



overall reaction

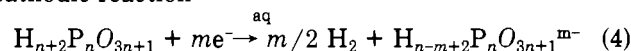


The amalgam flows into a decomposer unit where it reacts with phosphoric acid to produce hydrogen gas and, depending upon the pH that is maintained and the amount of water that is added, a solution of potassium phosphates

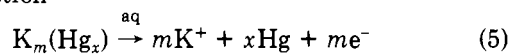
or a solution with precipitated potassium phosphate solids. The precipitated solids can be separated as product, or a mixture of solution and precipitated solids can be removed as product, or a liquid with no precipitated solids can be removed as product. Thus, solid, suspension, or liquid fertilizers may be produced.

The principal reactions taking place in the decomposer unit are

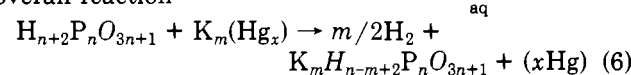
cathodic reaction



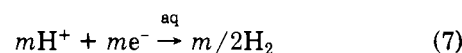
anodic reaction



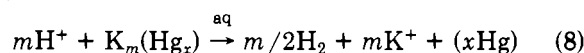
overall reaction



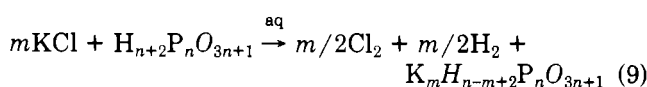
At low pH the cathodic reaction also can be described as



giving a net overall decomposer reaction:



The reaction rate is so high that it is unnecessary to use graphite or other short-circuiting packing in the decomposer to accelerate the reaction, as is the practice in the chlor-alkali industry (MacMullin, 1962), provided the pH of the liquor in the decomposer is <8. Thus, the exothermic reaction takes place at a convenient and controllable rate in acidic, neutralized, or overneutralized solution, permitting production of a fertilizer of desired pH simply by providing a suitably proportioned admixture of reactants. By control of the pH and specific gravity of the solution, particular crystalline species can be precipitated or precipitation of solids can be avoided. The overall reaction for the chlor-phosphate process is



Because there is no direct connection between the brine solution in the electrolyzer and the phosphate solution in

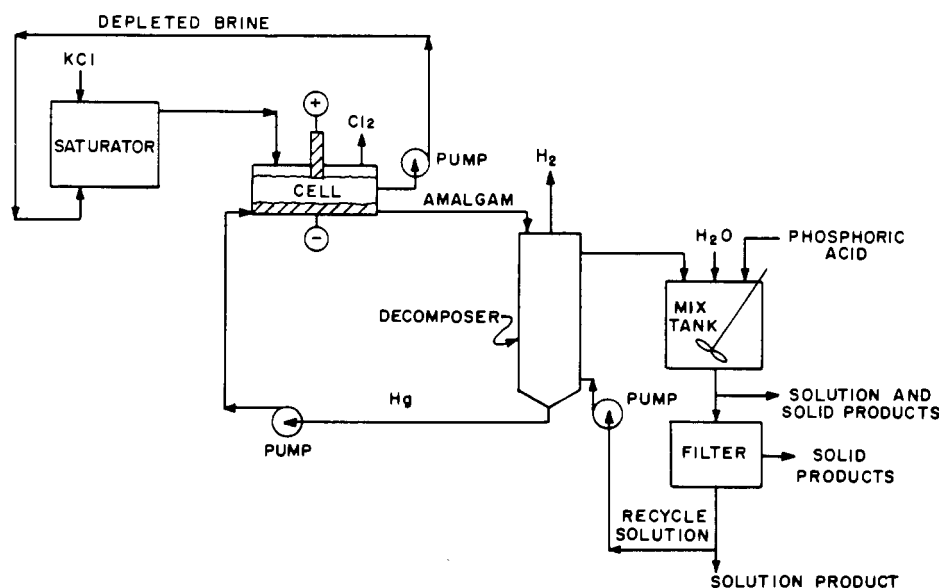


Figure 2. Chlor-phosphate process for reacting potassium amalgam, phosphoric acid, and water.

Table I. Compositions of Solid Potassium Chlorides<sup>a</sup>

component	composition, wt %		
	reagent grade	fertilizer grades	
		white	red
KCl	99.6	98.8	93-97
NaCl	0.008	0.9	1.8-3.5
Br	0.005	0.02	0.05
PO <sub>4</sub>	0.0003		
SO <sub>4</sub>		0.03	0.22
Al	Tr	<0.01	0.05
Ca	ND	0.01	0.02
Cr	ND	ND	ND
Cu	Tr	<0.01	<0.01
Fe	0.0001	ND	0.05-0.10
Mg	<0.001	0.05	0.2
Mn	<0.001	<0.01	<0.01
Ni	ND	ND	ND
Si	ND	ND	0.05
V	ND	<0.01	<0.01
other compounds	0.05	0.3	1.0
pH of satd soln at 25 °C	5.5	8.6	10.0

<sup>a</sup> Tr = trace; ND = not detected by spectrographic analysis.

the decomposer, the fertilizer produced is essentially free of chloride.

#### MATERIALS

Fertilizer grades of potassium chloride, which are less expensive than purer grades, range from 95% KCl (red) to 99% KCl (white). Most metallic impurities decrease the current efficiency of a mercury-cathode process by promoting the release of hydrogen from the cathode. The ideal raw material is a highly purified recrystallized salt; a purity of 99.99+% can be attained (MacMullin, 1962). Analyses of various grades of salt used in this study are given in Table I.

In conventional chlor-alkali plants using the purest commercially available KCl, a brine purification train is essential because, as new salt dissolves in the constantly recycled depleted brine, the levels of impurities eventually become intolerable. Also, the brine leaves the cell saturated with chlorine gas which, if not removed, will decrease the current efficiency. Brine purification ordinarily entails removal of dissolved chlorine as the gas, sulfate ion as the insoluble barium salt, and metallic impurities as the hydroxides (Gallone, 1964).

Reagent-grade orthophosphoric acid (62% P<sub>2</sub>O<sub>5</sub>), thermal polyphosphoric acid (80% P<sub>2</sub>O<sub>5</sub>), and wet-process orthophosphoric (54% P<sub>2</sub>O<sub>5</sub>) and polyphosphoric (71% P<sub>2</sub>O<sub>5</sub>) acids produced from North Carolina calcined rock were used. Analyses of thermal and wet-process polyphosphoric acids are given in Tables II and III, respectively.

Table II. Composition of Thermal Polyphosphoric Acid

composition, %			phosphate species distribution, %				metals present, ppm
P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> SO <sub>4</sub>	HF	ortho	pyro	tripoly	other	
79.7	0.006	<0.01	17.1	38.1	22.4	22.4	Al, Fe, Cr, Ni, Si, Pb <10

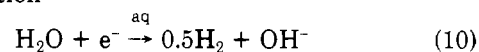
Table III. Composition of Wet-Process Polyphosphoric Acid from North Carolina Calcined Rock

composition, %			phosphate species distribution, %				metals present, ppm														
P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> SO <sub>4</sub>	HF	ortho	pyro	tripoly	other	Al	Ca	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Si	U	V	Zn
71.0	3.6	0.24	54.6	36.9	6.6	1.9	5000	<500	<0.3	300	1	6500	0.3	1700	50	70	27	600	127	96	490

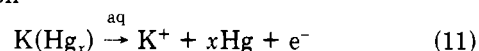
#### THE MICROPLANT

A continuously operable microplant, so named because it was capable of producing chlorine at about a millionth of the rate of a typical mercury-cell chloralkali plant, is shown in Figure 3. A constant-current dc power supply provided electrical energy to the cell, which was constructed of borosilicate glass. The anode of platinum was a vertical cylindrical screen, closed at the lower end with a horizontal screen that served as the principal anode surface. Connection to a mercury cathode was made with heavy tungsten wires sealed through the glass. Mercury and saturated KCl solution were pumped separately at 30 mL/min into the cell by peristaltic pumps. Electrode separation was approximately 3 mm. Chlorine produced at the anode was vented, and potassium amalgam produced on the flowing cathode was skimmed by overflowing into a well within the cell. The flow of amalgam from the well into a decomposer unit was controlled by throttling a stopcock, thereby preventing the flow of brine into the decomposer. Phosphoric acid and water were metered into the decomposer, an unpacked vertical glass vessel fitted with a magnetic agitator, at a rate indicated by the desired values of pH and specific gravity of the product solution being withdrawn. Measurements of pH were made with glass electrodes and of specific gravity with hydrometers. The current efficiency of the cell was calculated from the measured amount of charge and, after suitable corrections, from the volume of hydrogen collected over water at observed pressure and temperature. Mercury, stripped of potassium, was returned to the cell. Spent brine from the cell was stripped of dissolved chlorine, resaturated, treated to remove impurities, and after appropriate adjustment of pH, returned to the cell. The microplant was run intermittently for 500 h, with the cell operating at an average current of 15 A.

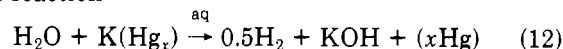
The reaction of amalgam with an excess of pure water produces hydrogen gas and potassium hydroxide solution:



anodic reaction



overall reaction



(Equation 12 equals eq 6 when the values  $m = 1$  and  $n = 0$  are used in the latter equation.) In the open-circuited decomposer, this reaction at 60 °C was very slow and virtually ceased when only a small volume of hydrogen, corresponding to the formation of enough KOH to raise

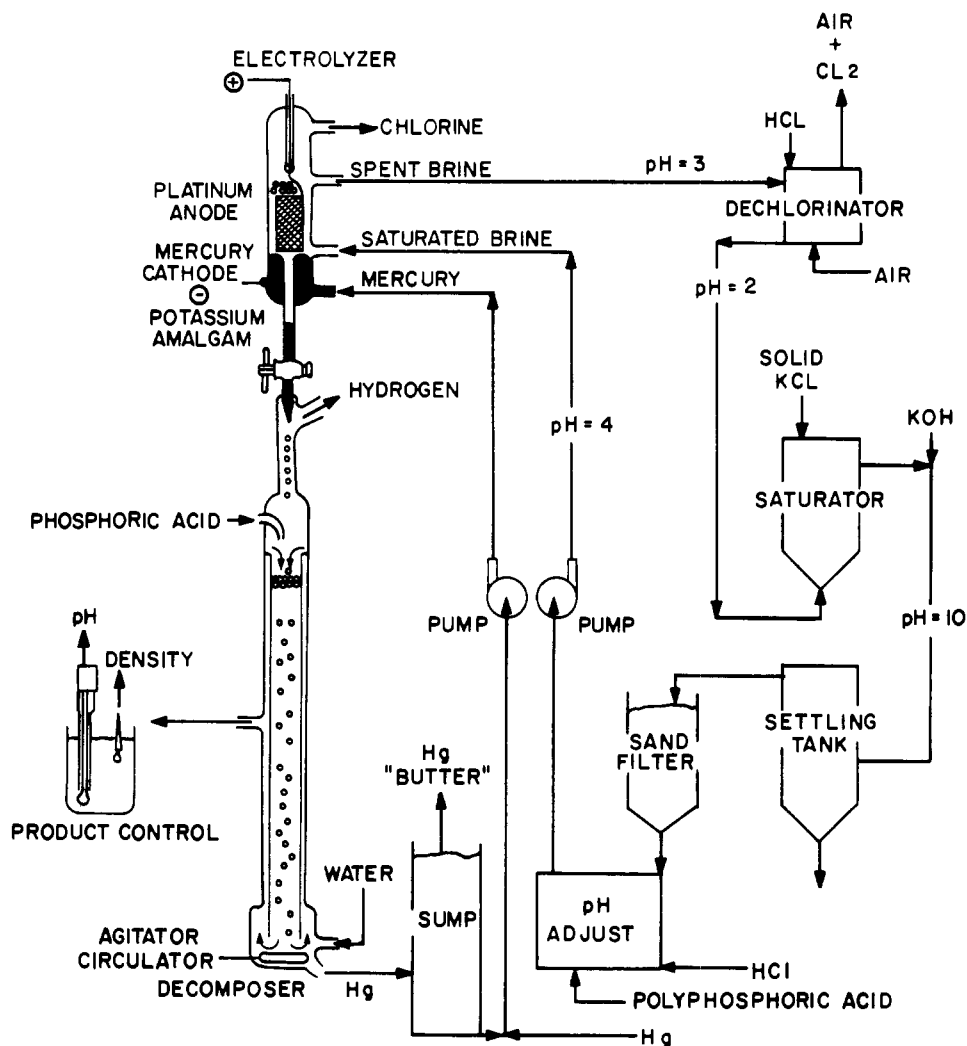


Figure 3. Chlor-phosphate microplant.

the pH to 11, had been formed. The decrease in the chemical free energy must equal the electrical energy produced:

$$-\Delta G = nFE \quad (13)$$

$n$  being the number of Faradays transferred per mole,  $F$ , the Faraday constant, and  $E$ , the electromotive force. Examination of the Nernst equation (MacMullin, 1962)

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{KOH}} a_{\text{H}_2}^{0.5}}{a_{\text{K}} a_{\text{H}_2\text{O}}} \quad (14)$$

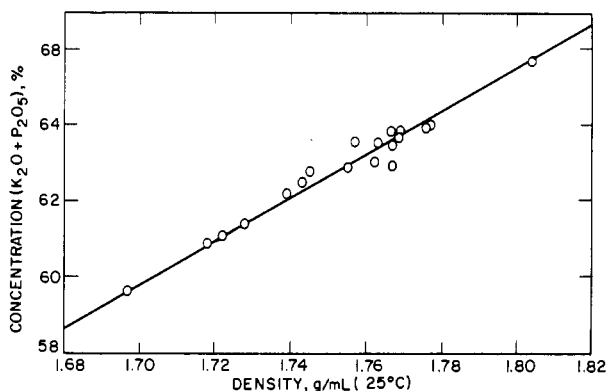
in which  $E^\circ$  is the emf when the reaction species are at unit activity,  $R$  is the gas constant, and  $T$  is the absolute temperature, shows that at constant temperature and hydrogen pressure the chemical potential increases with increase in the activities of potassium and water and decreases with increase in the activity of potassium hydroxide. A short-circuited decomposer, such as is used at chlor-alkali plants, accelerates the reaction because electrons from the amalgam are more readily transferred to the water through the large surface area of the graphite packing, and hydroxyl ions and hydrogen are formed at lower overvoltage than is required at the surface of the amalgam. The reaction takes place at a very high, essentially constant pH (>14). (When the decomposer was packed with 6-mm lengths of 6-mm diameter spectrograph-grade graphite rod it effected the rapid decomposition of amalgam at very high pH.) But in an open-circuited decomposer the reaction is so slow

that the magnitude of the negative free energy and the associated reaction rate is altered only by the logarithm of the activity of the potassium hydroxide produced. Thus, with a slow reaction the velocity is observably pH sensitive.

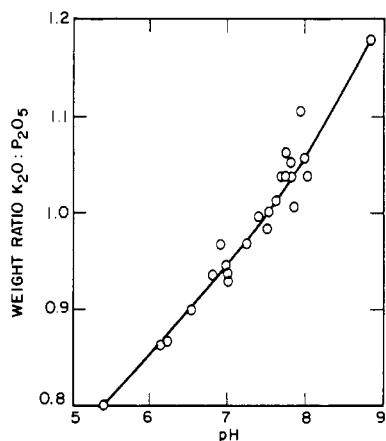
In an open-circuited decomposer, reaction of amalgam with thermal phosphoric acid at 60 °C was vigorous in the pH range 0 to 8, but slowed noticeably as the pH was increased and virtually ceased at pH 11. Application of the reaction (eq 8) to eq 14 shows that at constant temperature, the magnitude of the negative free energy decreases as the logarithm of the activity of the hydrogen ion decreases.

With reagent-grade KCl the electrolytic cell was operated at a current density of 0.07–3.2 A/cm<sup>2</sup> (1–22 A) and required as much as 10 V at the higher current densities. Commercial cells usually are operated at about 0.5 A/cm<sup>2</sup> and require about 4.3 V. Such cells expend about 1.5 kWh of dc electrical energy to produce a pound of chlorine (MacMullin, 1962). In a chlor-phosphate plant 0.028 lb of hydrogen gas also would be produced, and if the desired product were 0–30–30 potassium polyphosphate solution, 4.4 lbs would be produced. The current efficiency for the production of hydrogen was typically about 96% when pure acid, pure brine, and pure mercury were supplied to the cell, provided the brine was dechlorinated and appropriate adjustments of its pH were made.

When the decomposer was operated at pH <7, crystals of KH<sub>2</sub>PO<sub>4</sub> sometimes were produced. When total plant food (K<sub>2</sub>O + P<sub>2</sub>O<sub>5</sub>) of >60% was attained in hot solutions



**Figure 4.** Effect of density on total plant food of potassium polyphosphate solutions.



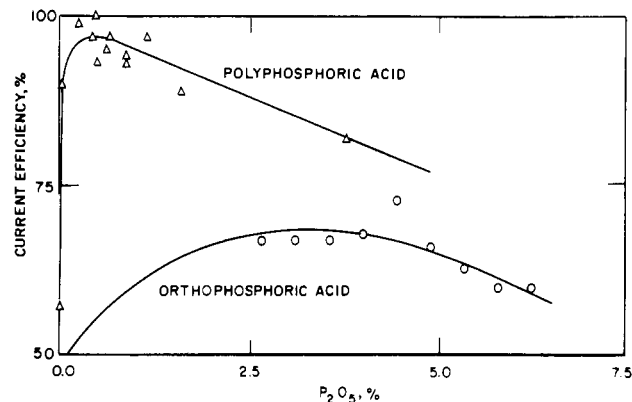
**Figure 5.** Effect of pH upon weight ratio  $K_2O/P_2O_5$  of potassium polyphosphate solutions.

of pH <7, upon cooling a white sol or thixotropic gel containing potassium polyphosphate microcrystalline rosettes and an occasional crystal of  $KH_2PO_4$  was produced. One such preparation (0-34.9-30.3) was unchanged after storage at room temperature for 3 years. Such material is potentially useful as a suspension fertilizer.

The most concentrated solutions were prepared from thermal acid (80%  $P_2O_5$ ), having a polyphosphate level of 83%. A 0-32-32 solution having a pH of 7.5 and a polyphosphate level of 71% was produced from this acid. The retention time of the polyphosphate in the decomposer was undesirably long (approximately 6 h). This long time at 60 °C was responsible for the observed degradation of the polyphosphate. Alteration of the decomposer to decrease retention time would decrease degradation and permit production of solutions of maximum concentration, perhaps in excess of 70% plant food. No solids formed upon storage of the 0-32-32 solution at room temperature for more than 90 days. In general, solutions were more stable when stored at 0 °C than at 25 °C because hydrolysis of the polyphosphates was retarded at the lower temperature. When crystals did form from concentrated solutions of pH 7.5-8.2, they were  $K_2HPO_4 \cdot 3H_2O$ .

Crystals usually did not form immediately when hot concentrated solutions were removed from the decomposer and cooled. The specific gravity and the pH of various cooled and supercooled solutions were measured. The relationship of total plant food to the density is shown in Figure 4 and that of the weight ratio  $K_2O:P_2O_5$  to the pH is shown in Figure 5.

When saturated brine was made from reagent-grade KCl it contained 17 ppm Hg; the thermal acid contained 8 ppm Hg. The potassium polyphosphate solutions made in the



**Figure 6.** Effect of phosphoric acids upon the current efficiencies for the electrolysis of impure brines.

**Table IV.** Impurities in Typical Treated Brine from Red KCl (ppm)

P	Al	Ca	Cr	Cu	Fe	Mg	Mo	Na	V
1500	13	80	0.4	0.9	17	143	<0.1	2000	<0.4

decomposer were filtered to remove entrained droplets of mercury and were found to contain only about 0.01 ppm Hg and <100 ppm Cl.

#### USE OF IMPURE KCL

When solutions of fertilizer grades of potassium chloride (Table I) were electrolyzed, the current efficiencies were extremely low (about 50%). Solids formed at the surface of the mercury, making its flow sluggish. When the cell was shaken, evolution of hydrogen from the cathode ceased temporarily, suggesting that addition of detergent to the brine might dislodge materials that act as sites for the evolution of hydrogen and might decrease the viscosity of the surface of the amalgam, thereby avoiding excessive concentration of potassium, which is known to promote hydrogen evolution at the cathode (Mantell, 1960). The effectiveness of minor concentrations of orthophosphoric and polyphosphoric acids as detergents was tested by adding these acids to the brine entering the cell. The results in Figure 6 show that the optimum concentration was 4%  $P_2O_5$  for reagent-grade orthophosphoric acid and 0.5%  $P_2O_5$  for thermal (80%  $P_2O_5$ ) polyphosphoric acid. Whereas, the optimum addition of orthophosphoric acid moderately improved the performance of the cell, the optimum addition of polyphosphoric acid virtually eliminated hydrogen evolution from the cathode. Impurities of a typical impure brine that permitted 97% current efficiency are shown in Table IV. The ability of phosphates and polyphosphates to improve the electrolysis of impure brine probably is associated primarily with the detergent capabilities of these materials which effectively dislodge solids and semisolids from the surface of the mercury cathode. Such solids are subsequently removed by sedimentation and filtration. Phosphates also have been used to retard the dissolution of impurities in solid alkali-metal salts (Roland, 1953; Burns, 1959). The rate of dissolution was not a factor in the operation of the microplant as dissolution occasionally totally depleted the salt bed of all solids without affecting the current efficiency.

#### USE OF IMPURE ACID

When wet-process acids from North Carolina calcined rock were used to decompose the amalgam, some of every metallic impurity present (Table III) was reduced in the decomposer and scavenged by the mercury. The rest of the impurities remained in the phosphate fluid. Part of

the impurities scavenged by the mercury was subsequently oxidized in the cell, transferred to the brine, and removed by the purification system. After a charge of a few hundred ampere hours was passed through the cell, the current efficiency decreased progressively to less than 80%. The rate of accumulation of the metals by the mercury was greater than the rate of transfer of these metals to the brine, causing loss of fluidity of the mercury and associated decrease of current efficiency. But when mercury "butter", rich in these impurities, was skimmed from the sump (Figure 3) and replaced with clean mercury, the current efficiencies were satisfactory.

The potassium phosphate solutions made from wet-process orthophosphoric acid (54%  $P_2O_5$ ) contained as much as 10% wet solids (primarily orthophosphates of iron, aluminum, potassium, and magnesium) but virtually no solids when made from wet-process polyphosphoric acid.

#### DISCUSSION

The chlor-phosphate process is capable of producing solids, solutions, or slurries of potassium phosphates along with coproducts of chlorine and hydrogen gases. The potential for production of a range of N-P-K solutions or slurries has not been studied. In one test a slurry of  $KH_2PO_4$  (pH 4.8) was ammoniated to produce a 2-25-19 solution (pH 6.7). It is undesirable to introduce fixed nitrogen compounds (e.g., ammonia, urea, and urea-phosphoric acid) into the decomposer because small quantities might be entrained with the mercury and subsequently be introduced into the cell where nitrogen trichloride (an explosive) would form and be concentrated in the chlorine (Nichols, 1969).

No economic evaluation of the chlor-phosphate process has been made, but many of the engineering problems match those of the chlor-alkali process, which is highly developed. Minimal operational problems are encountered when pure acid and pure salt are used; the use of impure

feeds is technically feasible, but the impact upon cost is unresolved. Although a mercury-cell chlor-alkali plant can treat and use almost any salt, the cost of handling brine is very dependent upon the quality of the salt. The extra cost of chlorine production will be as high as 10-20%, even when a process of selective solution is employed (Nichols, 1969). It is anticipated that the use of polyphosphoric acid as a detergent will preclude the need for selective dissolution of impure grades of KCl and will favor the economics of the use of impure materials. But the recovery of mercury from the "butter" will be a significant part of the cost of the use of impure materials.

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