

Purification of Phosphoric Acid with Methanol and Ammonia

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Purification of merchant-grade phosphoric acid with relatively small amounts of methanol and ammonia was tested. Regression equations were developed to show the effects of ammonia and methanol on precipitation of iron, aluminum, magnesium, fluorine, and P_2O_5 from the acid.

Metal impurities in wet-process phosphoric acid are undesirable because they lower both the quality of the acid and the quality of the subsequent fertilizer products produced from the acid. The presence of excessive iron, aluminum, and magnesium in wet-process acid will drastically increase the acid viscosity and cause formation of slow-settling, postprecipitated sludge (Slack, 1968). Metal impurities in ammoniated phosphoric acids cause the formation of insoluble metal ammonium phosphates, wherein both nitrogen and phosphorus are immobilized (Slack, 1968). The grade of diammonium phosphate produced from highly contaminated acid will generally be lower because iron and aluminum displace ammonia in the diammonium phosphate product (Slack, 1968). The presence of citrate-insoluble metal phosphates further lowers the quality of diammonium phosphate. Metallic impurities sometimes increase the stickiness of triple superphosphate (USDA-TVA, 1964). Other adverse effects have been noted (Slack, 1968).

A previous study (McCullough and Frederick, 1976) showed that addition of methanol and ammonia to wet-process acid precipitated most of the fluorine and metallic impurities from the acid. (This precipitate contained ~10% of the total P_2O_5 .) In this process the precipitate was filtered or centrifuged away from the methanol-acid liquor. Distillation of methanol from the liquor yielded a purified merchant-grade or superphosphoric acid. In that study 2.0-5.0 kg of methanol/kg of phosphoric acid and 0.05-0.20 g-atom of nitrogen/g-atom of phosphorus were used.

Where less purification is required, a lesser amount of methanol and ammonia may be desired for several reasons. Residual ammonia left in the purified phosphoric acid increases the viscosity of the acid (Slack, 1968), and less ammonia used in the purification would alleviate this problem. As noted, methanol is recovered from the purified acid by distillation. This distillation is one of the more expensive unit operations in the process and, therefore, use of less methanol would reduce purification costs. Finally, since metallic impurities precipitate mainly as metallic phosphates, the use of less methanol and ammonia would reduce the P_2O_5 loss to the precipitate.

For these reasons, further work is reported here in which lower amounts of methanol and ammonia were used in the purification. In the previous study (McCullough and Frederick, 1976) the ratio of magnesium to fluorine in the acid was one of the most important variables influencing magnesium purification. Because this variable was adequately delineated, it was not included in the present study.

EXPERIMENTAL SECTION

Batch purification tests were run on a partially clarified black wet-process acid. Solids which had formed and

settled during storage were resuspended before use. The composition of the acid, including solids, is as shown.

acid composition, wt %					
P_2O_5	Fe	Al	F	Mg	NH_4
50.7	0.97	1.2	1.8	0.38	0.06

The fluorine and aluminum concentrations were about twice that normally found in merchant-grade wet-process phosphoric acid while the iron and magnesium levels were similar to those normally found (Slack, 1968).

The following range of ammonia and methanol values was used in the acid purification tests.

	mini- mum	maxi- mum
atom ratio N:P (R_a)	0.0045	0.252
weight ratio $CH_3OH:H_3PO_4$ (R_w)	0.00	2.35

In all tests, 150 g (1.07 mol) of the 70.0% phosphoric acid (50.7% P_2O_5) was added to a three-necked, 500-mL flask, cooled to ~5 °C, and treated with a calculated amount of gaseous ammonia. The flask then was fitted with a reflux condenser, stirrer, and dropping funnel and heated to 100 °C for 30 min to dissolve solids. A calculated amount of methanol was added dropwise and the mixture digested for an additional 30 min at reflux temperatures (70-85 °C) to form a rapidly filtering slurry. The mixture was filtered hot and the solids were washed free of acid with methanol and then dried, weighed, and analyzed. Analyses were performed as in the previous study (McCullough and Frederick, 1976). The results are shown in Table I.

RESULTS AND DISCUSSION

The percent P_2O_5 precipitated from the acid and amounts of the different impurities remaining with the treated acid were correlated to R_a and R_w by linear regression analysis using the model

$$I_L = A_0 + A_1R_a + A_2R_w + A_{11}R_a^2 + A_{22}R_w^2 + A_{111}R_a^3 + A_{222}R_w^3 + A_{12}R_aR_w \quad (1)$$

where the A 's represent empirical constants and the response variable, I_L , is the percent P_2O_5 or the amounts of magnesium, iron, fluorine, etc., left in the treated acid expressed as grams of impurity per kilogram of P_2O_5 in the treated acid. The experimental values of I_L were calculated by difference from the composition of the untreated acid and the weight and composition of the precipitated solids. In the regression analysis, all combinations of the terms in the model were examined, and the combination of significant terms giving the lowest standard error was selected (Service, 1972). In the case of percent P_2O_5 , A_0 in the model was set equal to zero. The coefficients for the selected equations are shown in Table II. All terms shown are significant at the >97% confidence level. Coefficients for which no values are shown were not significant even at the 90% confidence level. There are significant interactions between R_a and R_w only with iron and magnesium

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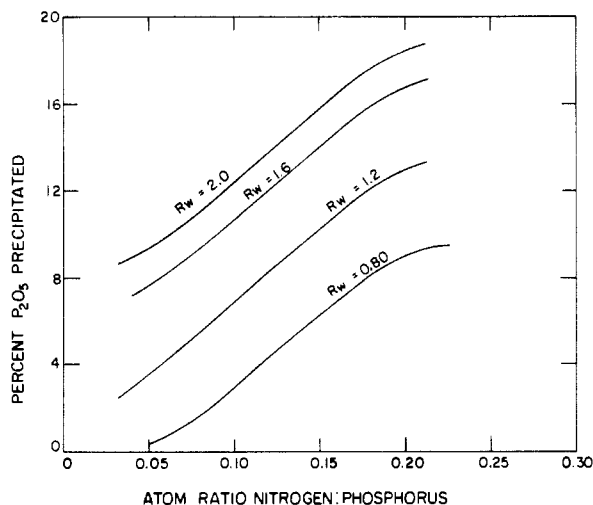


Figure 1. Effect of added ammonia on P_2O_5 precipitated at different weight ratios of methanol:phosphoric acid.

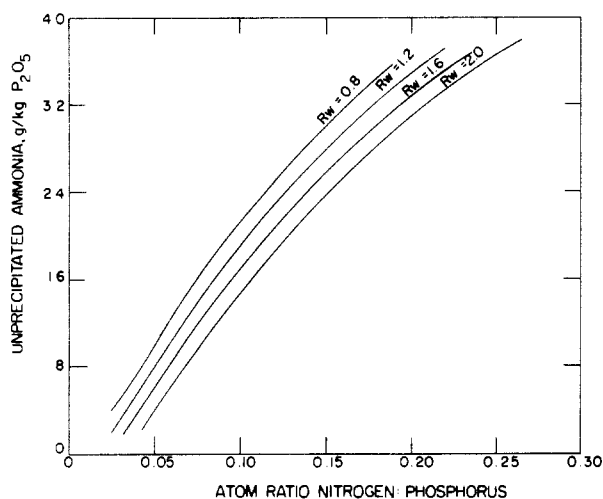


Figure 2. Effect of added ammonia on ammonia remaining in phosphoric acid at different weight ratios of methanol:phosphoric acid.

purification. Therefore, for other response variables, R_a and R_w act independently of each other, i.e., they are additive.

The regression equations may be used as in Figures 1–6 to show the effects of added ammonia on acid purification at several levels of methanol addition. The broken lines near the top of Figures 3–6 represent the impurity levels in the untreated acid. Although the regression equations could be used to calculate purification levels outside the region of experimentation such as those from the previous study, the results would be unreliable, particularly above an R_w value of 2.2.

Figure 1 shows the expected increase in P_2O_5 precipitated when either the amount of methanol or the amount of ammonia added to the acid is increased. Within the range of experimentation, the measured P_2O_5 precipitated ranged from almost nil up to ~17% at the highest levels of methanol and ammonia used.

Unprecipitated ammonia increased when the amount of ammonia used in the purification was increased (Figure 2). However, increased amounts of methanol slightly decreased the amount of ammonia left in the purified acid-methanol solution.

Iron, aluminum, and fluorine purification (Figures 3–5) increased with increased methanol and ammonia addition. At the higher levels of methanol and ammonia, these three

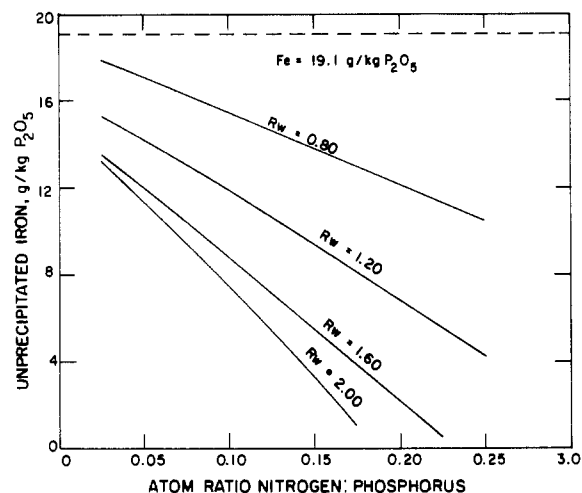


Figure 3. Effect of added ammonia on iron remaining in phosphoric acid at different weight ratios of methanol:phosphoric acid.

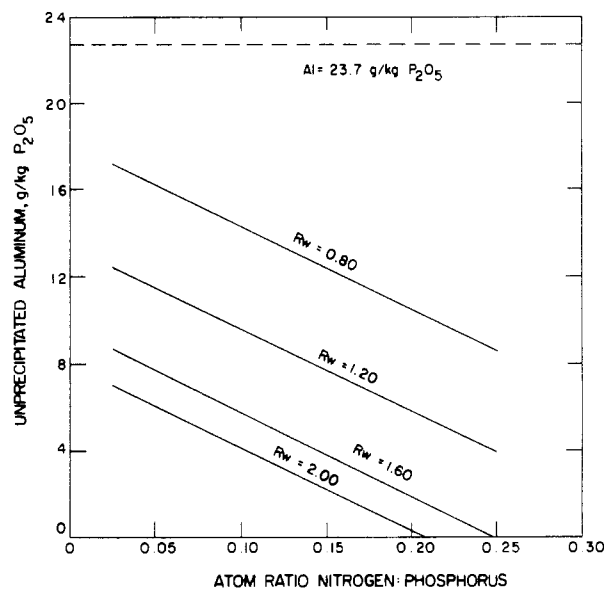


Figure 4. Effect of added ammonia on aluminum remaining in phosphoric acid at different weight ratios of methanol:phosphoric acid.

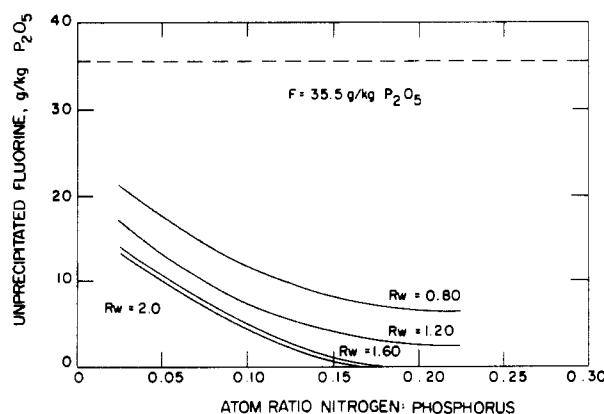


Figure 5. Effect of added ammonia on fluorine remaining in phosphoric acid at different weight ratios of methanol:phosphoric acid.

impurities were almost completely removed from the acid.

The effect of ammonia on magnesium purification (Figure 6) is particularly interesting. Addition of ammonia improves magnesium purification until the ratio nitro-

Table I. Chemical Composition of Precipitated Solids

observn	R_a	R_w	concn in pptd ^a solid, wt %						pptd solids, g/kg of input P_2O_5
			P_2O_5	Fe	Al	F	Mg	NH_3	
1	0.217	2.13	38.4	4.5	5.1	8.1	1.32	5.46	445.4
2	0.217	1.06	36.2	3.93	5.7	9.0	1.26	5.43	384.4
3	0.117	2.13	35.2	3.65	6.4	10.0	1.26	3.91	328.8
4	0.123	1.06	31.4	3.5	5.8	11.6	1.62	3.32	260.9
5	0.252	1.69	38.8	4.3	5.1	8.0	1.27	6.37	435.9
6	0.0946	1.60	34.6	4.1	5.6	10.5	1.42	2.90	304.3
7	0.165	2.35	38.7	4.6	5.3	8.2	1.26	4.72	407.7
8	0.165	0.84	27.8	2.6	6.0	13.2	1.90	3.50	199.0
9	0.170	1.60	39.4	4.0	5.0	8.1	1.24	4.24	421.1
10	0.169	1.60	38.6	4.5	5.5	8.6	1.34	4.37	393.9
11	0.167	1.60	37.3	4.6		8.8	1.32	4.18	380.5
12	0.0951	0.84	12.1	1.4	4.8	20.7	3.2	0.71	116.2
13	0.121	1.06	27.8	2.7	5.8	11.3	1.8	3.05	288.2
14	0.0424	0.40	4.7	0.16	3.3		2.0	0.32	101.4
15	0.0397	1.06	6.1	0.31		19.4	2.0	0.39	85.0
16	0.123	0.40	6.9	0.40	4.0	21.3	2.5	0.83	96.3
17	0.0045 ^b	0.0	4.6	0.12	3.5	13.6	2.2	0.01	49.9

^a pptd = precipitated. ^b Residual ammonia in parent acid.

Table II. Values of Empirical Constants for Iron, Aluminum, Fluorine, Magnesium, Ammonia, and P_2O_5 , Response Equations

	Fe	Al	F	Mg	NH_3	P_2O_5
A_0	21.4441	23.774	30.611	6.4782	1.7458	
A_1		-38.475	-182.97	-24.448	-271.22	
A_{11}			440.59	129.75	-365.69	582.535
A_{111}						-1646.87
A_2					-5.2396	-14.5384
A_{22}	-6.15411	-11.882	-10.966			20.8073
A_{222}	2.3363	3.9720	3.9055	0.29635		-5.77540
A_{12}	-40.9286			-17.849		
R	0.9623	0.9559	0.9717	0.9608	0.9881	0.9915
std error	2.31	2.57	2.32	0.408	1.75	1.73

gen:phosphorus reaches ~ 0.1 . But at progressively higher ammonia levels, especially above an R_a of 0.15, the response lines become almost parallel to the abscissa, indicating no further magnesium purification with added ammonia. Similarly, the crowding of the response lines at progressively higher methanol addition levels also indicates a lack of increased purification at progressively higher levels of methanol addition.

At the very lowest levels of ammonia addition ($R_a < 0.06$), magnesium purification is nearly independent of methanol addition. At higher ammonia levels, significant improvement in magnesium purification is possible by using more methanol. But there is a definite limit to the degree of magnesium purification possible, a limit beyond which further addition of methanol and ammonia produces no increased purification. For the acid tested, this limit is near 2 g of Mg/kg of P_2O_5 . Qualitatively similar responses for magnesium purification were seen in the previous work at the higher methanol levels used (McCullough and Frederick, 1976).

Examination of the data of Table I indicates that the amount of input ammonia and P_2O_5 lost to the cake at low R_a and R_w values is due to both the low concentration in the cake and the small amount of cake produced. The amounts of these materials lost to the cake is fairly high and constant until either or both R_a and R_w fall below about 0.1 or 1.0, respectively, suggesting a drastic change in the composition of the precipitated solid near R_a and R_w values of 0.1 and 1.0, respectively. Therefore, solids from observations 6 and 16, samples with either high or low P_2O_5 -iron-ammonia concentrations, were examined by X-ray and infrared spectroscopy.

Anhydrite, but no monoammonium phosphate, was observed in both samples as a major phase. Infrared showed

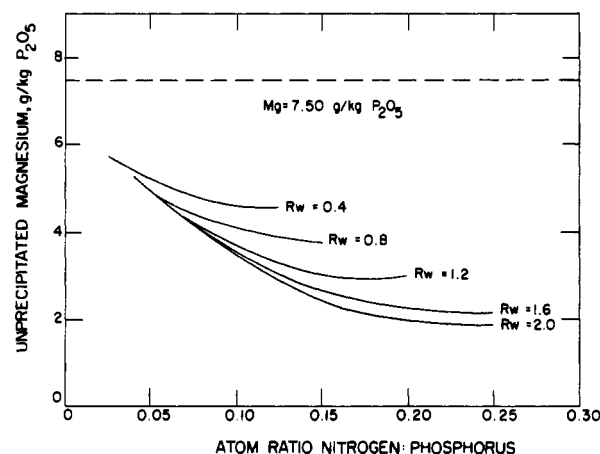


Figure 6. Effect of added ammonia on magnesium remaining in phosphoric acid at different weight ratios of methanol:phosphoric acid.

that sample 6 contained a trace of an unidentified hexafluorosilicate. In sample 16 the hexafluorosilicate was more abundant, although still minor, and was tentatively identified as the sodium salt by X-ray. In both samples there was a minor amount of the magnesium-sodium-aluminum-fluoride complex of the ralstonite type, $Na_xMg_xAl_{2-x}(F,OH)_6 \cdot H_2O$. This complex is most frequently formed in acids which are high in fluorine and contain significant amounts of magnesium, sodium, and aluminum (Slack, 1968); as noted, the acid tested in this study was particularly rich in aluminum and fluorine. The iron-rich solid, sample 6, also contained a major amount of $Fe_3NH_4H_{14}(PO_4)_8 \cdot 4H_2O$. The potassium analogue of this compound, $(Fe,Al)_3KH_{14}(PO_4)_8 \cdot 4H_2O$, is said to account

for the major fraction of most acid sludges (Slack, 1968).

Thus, the elevated concentrations of P_2O_5 , iron, and ammonia in solids which were precipitated with larger amounts of methanol and/or ammonia are probably due to the presence of the compound $Fe_3NH_4H_{14}(PO_4)_8 \cdot 4H_2O$. When lesser amounts of methanol and/or ammonia are used, this salt is absent, and the amounts of P_2O_5 , iron, and ammonia in the precipitates are correspondingly lower. Although aluminum is present in all samples, no aluminum-containing compound other than ralstonite was identified by X-ray.

The problem of removing magnesium from phosphoric acid is particularly important. Florida is the major domestic source of phosphate rock. Because sources of easily mined, high-quality rock in Florida are becoming depleted, fertilizer producers will increasingly turn to more abundant but lower quality phosphate ore. Dolomite is a principal impurity in this lower quality phosphate ore. Currently used beneficiation methods do not satisfactorily separate this magnesium-containing mineral from phosphate rock; therefore, it is likely that the magnesium concentration in phosphoric acid made from this rock will be higher.

If only magnesium purification is required, the lack of iron and aluminum purification at low methanol and ammonia addition levels may be advantageous. Since iron, and probably aluminum, precipitates in part as metal phosphates, use of low ammonia and methanol addition levels would minimize P_2O_5 losses to the solid phase and yield a solid composed largely of calcium sulfate, sodium hexafluorosilicate, and, in some cases, ralstonite.

As previously noted (McCullough and Frederick, 1976), one of the most important variables influencing magnesium removal is the ratio fluorine:magnesium, which suggests an additional method of improving magnesium removal by addition of fluorine to the acid. Solids precipitated at relatively low R_a and R_w levels may contain as much as 20% fluorine. A portion of this fluorine could be recovered from the solids for recycle as SiF_4 either by treating the solids with sulfuric acid or by thermally decomposing the solids at elevated temperature (Fugate and Banning, 1961; Koch and Blake, 1962). This would facilitate the recycle of fluorine back to the acid if necessary for improved magnesium purification.

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