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Metal Ions Solubility in Plant Phosphoric Acid—Degree of Ammonia Neutralization and Temperature Effects

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The solubility of Fe(III), Al(III), Mg(II), Ca(II), and S in plant phosphoric acid was determined as a function of mole ratio of ammonia to phosphate (MR) and at temperatures of 25, 60, and 90 °C. For each metal ion, there is a unique MR characterizing the onset of a sharp decline in solubility and another characterizing the transition from sharp decline to a more gradual change. At any given temperature, these characteristic MR values generally increase with the following order: Ca(II) = Mg(II) > Al(III) > Fe(III). The temperature effects on the solubility behavior of these metal ions and S and the most likely cause(s) of such behavior were presented and discussed.

1. Introduction

Monoammonium phosphate (MAP; $\text{NH}_4\text{H}_2\text{PO}_4$) and diammonium phosphate [DAP; $(\text{NH}_4)_2\text{HPO}_4$] are important commercial fertilizers produced from concentrated slurries formed from the reaction between concentrated plant phosphoric acid and ammonia in a continuously stirred tank reactor. The phosphoric acid solution may contain a relatively high level of metal ion impurities depending upon the grade or quality of the phosphate rocks used in the reaction with concentrated sulfuric acid. The main impurities are Fe(III), Al(III), Mg(II), Ca(II), S, and F. The metal ion impurities at high concentration have a very profound effect on the rheology and processability of the slurries produced during ammoniation.^{1–4} These slurries typically displayed plastic flow behavior and formed a high yield stress gel in the reactor. Often the impeller and pump in the reactor, not designed to handle this type of flow behavior, failed and caused the plant to shutdown. A great deal of research effort has focused on methods to remove metal ions and also on developing strategies for mitigating the effects of these metal ions on slurry rheology. One such strategy is to blend “dirty” phosphate rock with high-grade rock in mines, provided that this high grade rock is available in the deposits. The resultant phosphoric acid produced from such a blend will have a moderate level of metal ions impurities and the slurry produced will have a relatively low viscosity and negligible yield stress, allowing it to be easily pumped and further processed in a granulator.

Ammonium phosphate slurries are produced in the reactor at 110 °C. These slurries solidify as it cools, so its rheological measurements have been a challenge. All earlier reports on viscosity behavior were based on single point viscosity measurements valid only for Newtonian fluids.^{1–3} Flow behavior was not characterized until recently.^{4,5} Ammonium phosphate slurries are usually non-Newtonian; hence, the single point viscosity data are not useful for process equipment design. However, the trend of viscosity variation with slurry properties such as solid content, degree of neutralization, and metal ion

composition and content are still valid. Campbell et al.⁴ related the rheological behavior of ammonium phosphate slurry to the formation of hydrolysis products of Fe(III) and Al(II) ions. In the presence of these metal ions, the particle size of the slurry is much finer. It was proposed that the hydrolysis products formed by these metal ions act as crystal nucleation sites that are present in relatively high concentration.

Another solution to mitigate the formation of unfavorable rheological behavior of slurries produced from impure phosphoric acid is to dilute the acid significantly prior to ammoniation.⁶ This strategy will incur additional cost as a large amount of additional energy is required to evaporate the excess water in the slurries during granulation. Metal ion removal via ion exchange resins and solvent extraction processes is also not cost-effective because of the large volume of phosphoric acid that needs to be treated in any given plant. A different approach is needed. Knowing and understanding the solubility behavior of metal ions in the phosphoric acid, in particular with respect to the degree of neutralization, may generate new process idea that may be cost-effective for removing specific metal ions. Recently, we developed a new method of determining the metal ion solubility at different degrees of neutralization.⁴ This method is quite complex, as some of the steps employed are quite innovative. It was employed to collect solubility data at room temperature.⁴ In this study, solubility data and trend at higher temperature were collected and are presented. It is, however, not possible to determine the solubility at the slurry formation temperature of 110 °C. This study will investigate how the solubility of various metal ions is affected by temperature, and the trend obtained may allow us to generalize the findings to temperatures greater than 100 °C.

Most metal ions form hydrolysis products, but the pH at which a significant amount of hydrolysis product begin to form is dependent upon the nature of the metal ions and, to a lesser extent, its concentration and solution ionic strength.⁷ For example, the onset of hydrolysis product formation begins at pH 2.5 at a concentration of 0.1 *m* (molality) Al(III) and pH 7 at 0.1 *m* Ni(II). The total ionic strength in these metal ions solutions was 1.0 *m*. However, at 10^{-5} *m* Ni(II) this pH is shifted slightly to a higher pH of 8.0 in solution with the same total

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Table 1. The Elemental Composition of Diluted Plant Phosphoric Acid

element	concentration, mg/kg or ppm		
	acid 1 (25 °C)	acid 2 (25 °C)	acid 3 (60 and 90 °C)
Al	3150	1850	1950
Ca	NA	117	147
Fe	19900	12400	13700
Mg	1190	834	917
P	136000	113000	124000
S	6430	4800	5640

ionic strength. In contrast, this pH did not change perceptibly in solution with 10^{-5} M Al(III) and 1.0 M total ionic strength. The presence of suspended colloidal particles can induce the hydrolysis product to form significantly at a slightly lower pH.⁸ Hydrolysis products are known to adsorb readily^{8,9} and to affect slurry rheology,^{9,10} electrokinetic properties,^{8,11} coagulation rate,^{12,13} and flotation recovery.¹⁴ In this study, the role of hydrolysis products on metal ion solubility is also examined.

2. Materials and Experimental Methods

The phosphoric acid used in this study was produced from the WMC (now Southern Cross) fertilizer plant located within its phosphate rock mine site at Phosphate Hill in Northwest Queensland, Australia. The fertilizer industry normally characterizes the phosphoric acid concentration in terms of its P_2O_5 content. Here, the acid used has a P_2O_5 content of about 40%. The elemental composition and concentration of impurities in the phosphoric acid were determined using ICPAES (inductively coupled plasma atomic emission spectroscopy). However, in solubility determination, a diluted sample of the acid was used and the degree of dilution employed was not more than 3 times. See Table 1 for the elemental concentration of the impurities in the diluted phosphoric acids used in this study.

For solubility determination, the diluted plant phosphoric acid solution was placed in an 800 mL beaker that was stirred by an overhead mechanical stirrer. Ammonia gas was bubbled through the solution over time to effect a progressive change in the degree of neutralization as measured by the mole ratio of ammonia to phosphoric acid. At the end of each bubbling time period, the ammonia gas supply was turned off and a sample was taken for a mole ratio determination. Two other samples of known weight were also taken, one for solid concentration determination and the other for elemental content determination of soluble ions. The one for solid content determination was washed repeatedly with ethanol to remove any unreacted phosphoric acid and soluble ammonium phosphate. Ethanol was added and mixed with the slurry, which was then allowed to settle, and the clear liquid layer that formed rapidly above the sediment was decanted. This procedure was repeated a few times. After washing, the slurry was dried in an oven set at 105 °C for at least 3 h. The second sample was diluted with approximately an equal mass of distilled water (mass added was measured), and this slurry was allowed to settle overnight in a constant temperature bath set at 60 and 90 °C. The supernatant was collected and filtered using a syringe connected to a 0.45 μ m micropore membrane filter. The filtered supernatant was then sent for ICPAES concentration determination of Fe(III), Al(III), Mg(II), Ca(II), and S. The actual metal ion concentration in the supernatant was corrected for dilution and solids formation. However, water evaporation during the neutralization reaction was not taken into account. The reaction between phosphoric acid and ammonia is highly exothermic and the

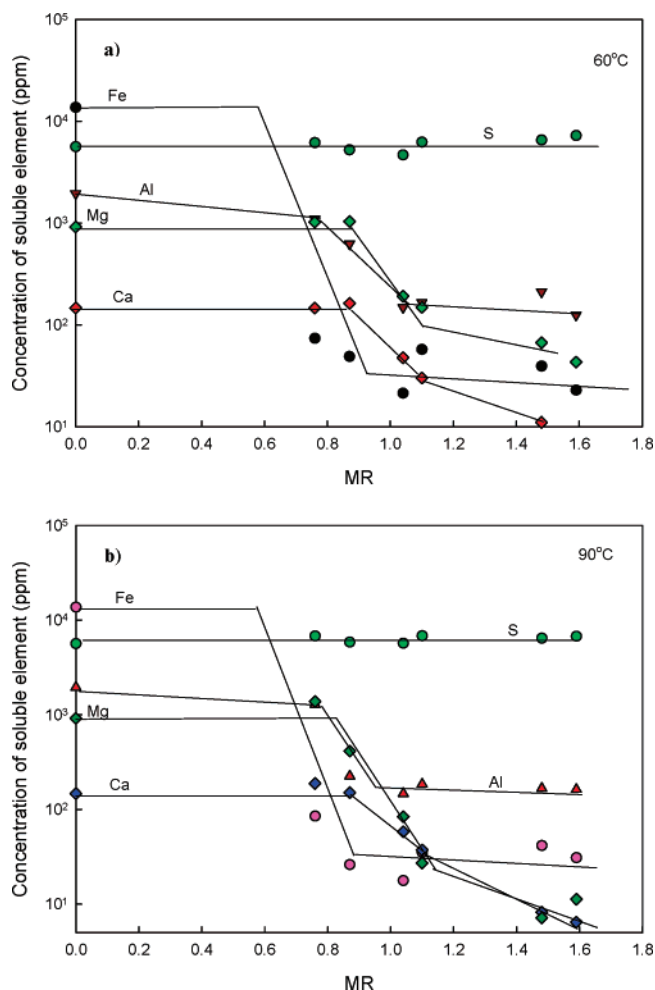


Figure 1. The concentration of elements in phosphoric acid determined as a function of mole ratio of ammonia to phosphoric acid at temperatures (a) 60 °C and (b) 90 °C. The concentration has been corrected for the concentration of solids and the water dilution effect. The initial concentration of the metal ions in the phosphoric acid is listed under acid 3 in Table 1.

slurry reached a temperature of 110–120 °C. A new method for taking this into account is discussed here.

The mole ratio (MR) of ammonia to phosphoric acid is obtained by titrating a sample of diluted ammonium phosphate slurry with standard 1 M NaOH and 1 M HCl solutions. The slurry was diluted approximately 10 times with distilled water. NaOH was added to bring the pH to 8.0 and then followed by HCl to bring the pH to 4.0. The amount of HCl and NaOH added was used to calculate the mole ratio [$MR = 2 - (\text{volume of NaOH})/(\text{volume of HCl})$]. The pH of a DAP slurry is 8.0 while that of MAP is 4.0. The (volume of NaOH)/(volume of HCl) is the ratio of the number of moles of hydroxide ions required to bring the test slurry to DAP to the number of moles of acid required bring the slurry back to MAP.

3. Results and Discussion

At MR greater than 0.5, precipitates were observed to form in the phosphoric acid. These precipitates were allowed to settle, and the clear supernatant was filtered and collected for concentration determination of soluble Fe(III), Al(III), Mg(II), Ca(II), and S. The plots of the concentration of these soluble ions in log scale versus mole ratio (MR) at 60 and 90 °C are shown in Figure 1a,b. The composition of the phosphoric acid used is tabulated in Table 1 as acid 3. The concentrations presented in these figures were corrected for solids formation

and the further dilution with distilled water required in the step leading to supernatant collection for ICPAES measurements.

At MR below 0.5, all four metal ions appeared to be almost completely soluble. For each metal ion, there is a critical MR value above which its solubility decreased sharply. This critical MR is ~ 0.6 for Fe(III), ~ 0.8 for Al(III), and ~ 0.9 for both Mg(II) and Ca(II). With Fe(III), the extent of solubility decrease is very large, as much as 3 orders of magnitude. For Al(III), Mg(II), and Ca(II), the decrease is between 1 and 2 orders of magnitude. This difference is due to the larger initial Fe(III) concentration in the acid. In terms of molality, Fe(III) is approximately 4 times more concentrated than Al(III), ~ 7 times larger than Mg(II), and ~ 68 times that of Ca(II). At the end of the sharp decline is a region of low solubility where the metal ions concentration is typically on the order of 10–100 ppm. In this region, the constituent metal ion concentration remained either approximately constant or trended slightly upward or downward with MR. The low values made these concentration data highly susceptible to experimental error. Water vaporization during the neutralization process, if not taken into account, can significantly enhance the concentration value in the low solubility region.

As with S, its concentration increases slightly with increasing MR. The change in S concentration is very small compared with the order of magnitude change displayed by the metal ions. The source of this sulfur is from the sulfuric acid used to convert the phosphate rock to phosphoric acid, yielding gypsum (calcium sulfate) as the main byproduct. In the absence of dilution with water, the product of the concentrations of sulfate and calcium present in the acid must be equal to the solubility product of gypsum. The use of diluted phosphoric acid in this study ensured that the concentrations of calcium and sulfate are well below the values needed to exceed its solubility product.

Campbell et al.⁴ showed that the solubility of metal ions, in particular Mg(II), in phosphoric acid at MR less than 1.0 is more than 100%. The reason being that water evaporation during the neutralization reaction at 110 °C has not been taken into account. It is very difficult to measure accurately the amount of water evaporated. Here an attempt is made to correct the concentration of the metal ions for water evaporation. We assumed that S in the form of sulfate remained soluble in the range of the MR investigated. The solubility data shown in Figure 1a,b appears to support this assumption. A plot of the percentage or relative solubility of S (S concentration at a particular MR divided by its concentration at MR = 0 multiplied by 100) in slurry supernatant kept at 25 °C versus MR is shown in the inset of Figure 2. It shows that the percentage solubility increases linearly with MR. Not one datum has a value less than a 100%. This must be due to water evaporation during the neutralization reaction. With these data we can estimate the amount of water evaporated at each MR that can be used for concentration correction of the metal ions in solution. We convert the S data to 100% solubility at each MR. The factor used in this conversion is the correction factor and is a function of MR. The appropriate value was applied to correct the solubility data of the metal ions. Figure 2 shows the plot of relative concentration in percent of metal ions versus MR after correction for evaporation. Note that the solubility of S is 100% at all MR. In this plot, the sharp drop in solubility is very pronounced. Also the MR region showing the sharp drop in solubility is separated to a higher degree for the different metal ions. Two sets of solubility data for Fe(III) were presented. One set was obtained from acid 1 (see Table 1) with an initial Fe(III) concentration of 19 900 ppm and the other from acid 2

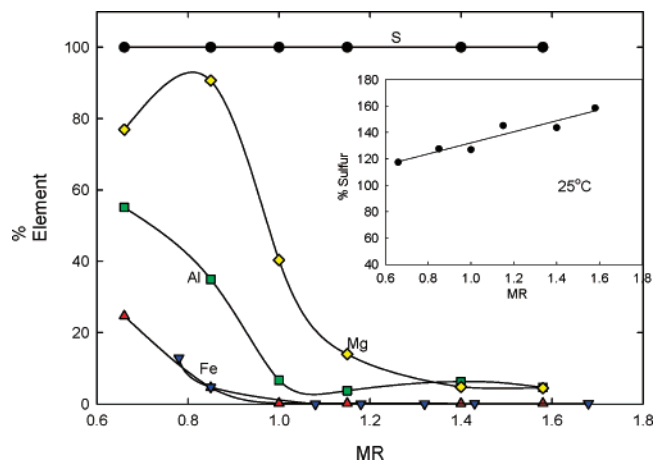


Figure 2. The solubility of Fe(III), Al(III), and Mg(II) in phosphoric acid solution as a function of mole ratio corrected for water evaporation using sulfur data (see inset). The initial concentration of Fe(III), Al(III), and Mg(II) in the phosphoric acid (Acid 1 in Table 1) is 19 900, 3150 and 1190 ppm, respectively. Below MR 0.5, the solution remains clear; thus, it was assumed that none of these metal ions formed hydrolysis product. The solubility data of Fe(II) obtained from another batch of phosphoric acid solution (Acid 2 in Table 1) with Fe(II) concentration of 12 400 ppm were also included in the plot. The inset is a plot of percent sulfur versus MR. The percent sulfur is more than 100%, and these data were used to correct the metal ions concentration data for water evaporation.

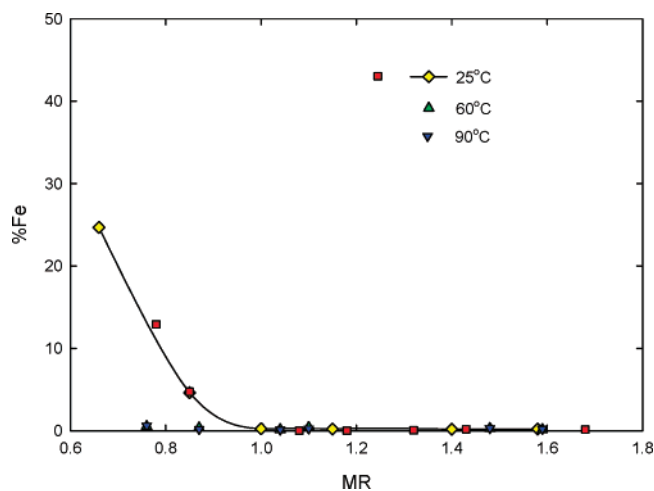


Figure 3. The solubility of Fe(III) ions showing the effects of MR and temperature.

with an initial Fe(III) concentration of 12 400 ppm. The excellent reproducibility of these sets of data provides strong support that the method and procedure employed in solubility characterization are relatively accurate and correct. At these initial Fe(III) concentrations, the pH at the onset of hydrolysis product formation should be the same.

The plots of the percentage relative solubility of Fe(III) ions at three different temperatures versus MR are shown in Figure 3. The data for 25 °C showed that the solubility decreased from about 30% at MR ~ 0.7 to almost 0% at MR ~ 1.0 . However, at the higher temperatures of 60 and 90 °C, the solubility is already close to 0% at MR ~ 0.75 . The variation of solubility with MR is almost identical at 60 and 90 °C. There is a 3 order of magnitude reduction in Fe(III) concentration in solution at 25 °C as MR was increased from 0 to 1.0. In fact, this decrease occurred over a much narrower MR range of between ~ 0.6 and 1.0. The decrease was from 19900 to 66 ppm at MR of 1.0. At the higher temperatures of 60 and 90 °C, the sharp decrease in Fe(II) solubility appeared to occur over an even

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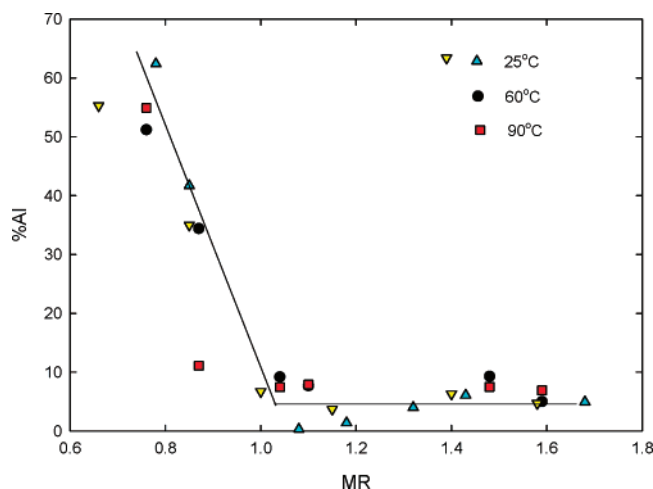


Figure 4. The solubility of Al(III) ions showing the effects of MR and temperature.

narrower MR range. At MR of 0.76, the concentration is already very low, 25.7 and 28.6 ppm.

Temperature appears to affect the formation or equilibrium constant of hydrolysis products in a manner that seems to explain the temperature effect on the solubility behavior of Fe(III). The amount formed of a given hydrolysis product can be gauged from its formation constant. Fe(III) formed a number of hydrolysis products and these products are generally represented by $\text{Fe}_x(\text{OH})_y^{(3x-y)}$. The formation constant of $\text{Fe}_x(\text{OH})_y^{(3x-y)}$ is given by:

$$K_{xy} = \frac{[\text{Fe}_x(\text{OH})_y^{(3x-y)}][\text{H}^+]^y}{[\text{Fe}^{3+}]^x}$$

When $x = 1$ and $y = 1$, the hydrolysis product is $\text{Fe}(\text{OH})^{2+}$. The formation constants of three hydrolysis products, $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^{+}$, and $\text{Fe}_2(\text{OH})_2^{4+}$, as a function of temperature are given in the work by Baes and Mesmer.⁷ Only one temperature formation constant was available for $\text{Fe}(\text{OH})^{2+}$. For both $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}_2(\text{OH})_2^{4+}$, the formation constants become larger at higher temperature. For example, the value of $\log K_{xy}$ for $\text{Fe}(\text{OH})^{2+}$ increased from -2.96 at 18°C to -2.61 at 32°C . Similarly, the value for $\text{Fe}_2(\text{OH})_2^{4+}$ increased from -2.92 to -2.65 for the same temperature increase. This means that the concentration of these hydrolysis products is larger and that less Fe(III) is in solution at higher temperature.

The effect of temperature on the solubility behavior of Al(III) metal ions with MR is shown in Figure 4. Within experimental error, it can be said that temperature did not have a significant effect on the solubility behavior and its trend with MR. The largest difference in solubility appears to occur at MR ~ 0.85 . The solubility is $\sim 39\%$ at 25°C , 34% at 60°C , and 11% at 90°C . It appears that at a temperature of 90°C , Al(III) reached minimum solubility at a lower MR like Fe(III). The difference is only 0.1 of an MR unit. The onset of low solubility behavior occurred at MR ~ 1.1 .

The amount of Al(III) ions hydrolyzed at pH below 2.0 is negligible.⁷ Between pH 2.6 and 5.0, four hydrolysis products, $\text{Al}(\text{OH})^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_3\text{O}_4(\text{OH})_{24}^{7+}$, are formed. Of these species, $\text{Al}_3\text{O}_4(\text{OH})_{24}^{7+}$ is most important and stable in solution. Between pH 5.0 and 8.0, $\text{Al}_3\text{O}_4(\text{OH})_{24}^{7+}$ is the only species present. Above pH 8.0, $\text{Al}_3\text{O}_4(\text{OH})_{24}^{7+}$ will undergo further hydrolysis to form $\text{Al}(\text{OH})_4^-$. In comparison, Fe(III) formed hydrolysis product in significant quantities at a much lower pH of 1.0.⁷ This certainly explains the sharp decline in solubility occurring at a lower MR value for Fe(III).

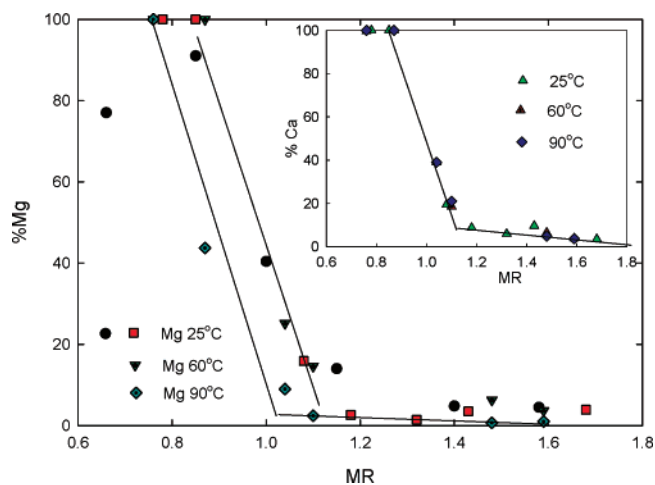


Figure 5. The solubility of Mg(II) ions in phosphoric acid solution showing the effect of MR and temperature. The inset is the solubility curve of Ca(II) as a function MR and temperature.

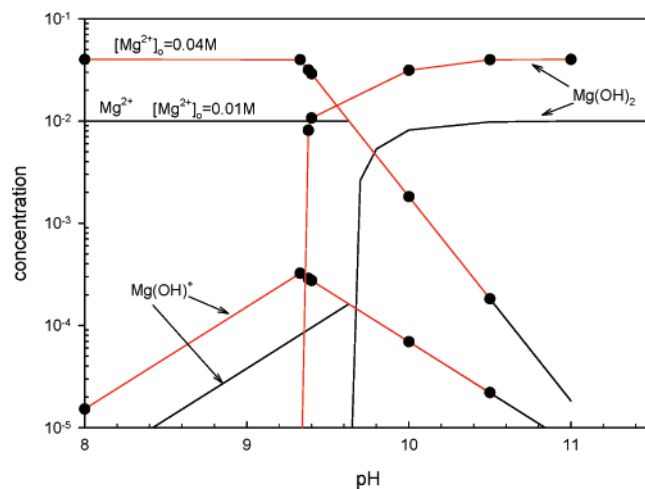


Figure 6. The nature and concentration of Mg(II) species as a function of pH.

The concentration of Mg(II) in the diluted phosphoric acid solution is $\sim 4 \times 10^{-2}$ M (~ 1000 ppm). Figure 5 shows its solubility as a function of MR at 25, 60, and 90°C . The solubility curves at 25 and 60°C are almost identical. At these two temperatures, complete solubility was observed at MR as high as 0.9. However, a sharp decline in solubility was observed at MR between 0.9 and 1.2. Beyond MR 1.2, the solubility is less than 10% and the solubility curve is relatively flat or shows a very gradual decrease with MR. However, at 90°C , the solubility data showed the onset of a sharp decline occurring at a lower MR of 0.8. Also, the transition from sharp to gradual decline in solubility was observed to occur at a slightly lower MR of 1.1. This result is consistent with that displayed by Fe(III) and Al(III) at the same temperature. At MR larger than 1.2, there is no significant difference in solubility at all three temperatures.

At 25°C , MR of 1.0 corresponded to a pH of 4.0. Between MR of 0.9 and 1.2, a sharp decline in Mg(II) solubility occurred corresponded to the pH range of between 3.5 and 5.0. On the basis of the hydrolysis species curve of 10^{-2} M Mg(II) shown in Figure 6 calculated using equilibrium constant data reported in the literature,¹⁵⁻¹⁷ the amount of hydrolysis product formed is negligible at pH 5.0. The concentration of $\text{Mg}(\text{OH})^+$ is less than 10^{-7} M. At pH 8.4, it is still only 10^{-5} M. A maximum concentration of 10^{-4} M formed at pH 9.63 is still very small, as it is about 2 orders of magnitude smaller than the initial Mg-

(II) concentration. The pH at which the concentration of $\text{Mg}(\text{OH})^+$ is maximum and when $\text{Mg}(\text{OH})_2$ comes out is a function of the initial $\text{Mg}(\text{II})$ concentration. At 0.04 M $\text{Mg}(\text{II})$, the maximum is located at a lower pH of 9.33, but its concentration is again 2 orders of magnitude smaller than the initial $\text{Mg}(\text{II})$ concentration. Similarly, $\text{Mg}(\text{OH})_2$ precipitate is formed significantly at 0.3 of a pH unit lower. It is unlikely that the presence of other particles in solution could induce hydrolysis product to form significantly at 3 pH units lower. The disappearance of $\text{Mg}(\text{II})$ from solution via the hydrolysis route is thus not probable.

Brown et al.¹⁸ studied the hydrolysis of $\text{Mg}(\text{II})$ at elevated temperatures in the range of 60–200 °C and at two ionic strengths of 0.1 and 1.0 mol kg^{-1} NaCl. They found that the concentration of $\text{Mg}(\text{OH})^+$ hydrolysis product is negligible prior to the formation of $\text{Mg}(\text{OH})_2$ solids, and this fact is consistent with the hydrolysis species curve presented in Figure 6. Yet $\text{Mg}(\text{OH})^+$ is the only hydrolysis product species formed apart from $\text{Mg}(\text{OH})_2$ precipitate. The formation constant of $\text{Mg}(\text{OH})_2$ was found to increase significantly with temperature but showed only slight dependence on ionic strength. At 60 °C, the formation constant is $10^{-15.52}$ and increased to $10^{-13.64}$ at 100 °C at 1 mol kg^{-1} of NaCl. Lowering the NaCl ionic strength to 0.1 mol kg^{-1} brought only a small reduction in the value to $10^{-15.29}$. At 60 °C, the solubility product, K_{sp} , of $\text{Mg}(\text{OH})_2$ at 1 mol kg^{-1} of NaCl was calculated to be 5.248×10^{-11} [$\beta_{1,2} = (K_w^2)/(K_{\text{sp}})$ with $\beta_{1,2} = 10^{-15.52}$ and dissociation constant of water, $K_w = 10^{-12.9}$].¹⁸ For the hydroxyl concentration to exceed the solubility product of $\text{Mg}(\text{OH})_2$ at this temperature, the pH has to be greater than 9.6 for 0.04 M $\text{Mg}(\text{II})$ initial concentration. At 100 °C, the pH required must be larger than 9.6. Thus, $\text{Mg}(\text{OH})_2$ does account for the large drop in $\text{Mg}(\text{II})$ solubility at pH 5.0 at the elevated temperature of 60 and 90 °C.

Also $\text{Mg}(\text{II})$ is known to react with ammonium and phosphate ions to form struvite or magnesium ammonium phosphate solids. Zhong et al.⁶ analyzed the composition of scale deposits with XRD from dilute phosphoric acid ammoniated to pH 5 and greater and found that it contained several compounds. Among them are $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite) and $\text{Mg}_3(\text{PO}_4)_2$. The solubility product of MgNH_4PO_4 at 25 °C is 2.5×10^{-13} . At pH 5.0, the concentration of $\text{Mg}(\text{II})$ is ~ 0.04 M and that of NH_4^+ is ~ 4 M. This requires the PO_4^{3-} concentration to be 1.6×10^{-12} M for MgNH_4PO_4 to precipitate or crystallize out. The concentration of PO_4^{3-} calculated using the dissociation constants of phosphoric acid is 1×10^{-9} M at pH 5. This concentration greatly exceeded the critical concentration for precipitation. So after precipitation, the amount of $\text{Mg}(\text{II})$ left in solution is only $\sim 5 \times 10^{-5}$ M, representing a loss of 99.8% to precipitation. Also, $\text{Mg}_3(\text{PO}_4)_2$ is another insoluble product. This compound has a solubility product of 1×10^{-25} . For it to precipitate at pH 5.0, PO_4^{3-} needs to exceed 3.9×10^{-11} M, a concentration higher than that required for MgNH_4PO_4 precipitation. In summary, the most likely cause for the diminished solubility of $\text{Mg}(\text{II})$ at pH 5.0 is due to the formation of struvite and magnesium phosphate precipitates.

Temperature appears not to affect the solubility behavior of $\text{Ca}(\text{II})$ with MR. See the inset of Figure 5. The concentration of $\text{Ca}(\text{II})$ in the phosphoric acid is only $\sim 10^{-3}$ M, much lower than that of the other metal ions. It is an order of magnitude lower than that of $\text{Mg}(\text{II})$. $\text{Ca}(\text{II})$ is completely soluble at MR < 0.9 and displayed a sharp decline in solubility at MR above 0.9. The transition from the sharp to gradual decline or the onset of the low solubility region occurred at MR ~ 1.1 , where its relative solubility is about 15%. The variation of solubility with

MR for both $\text{Ca}(\text{II})$ and $\text{Mg}(\text{II})$ ions is almost identical at temperatures of 25 and 60 °C, despite $\text{Mg}(\text{II})$ being an order of magnitude more concentrated.

On the basis of the hydrolysis species curve of 10^{-3} M $\text{Ca}(\text{II})$,^{15,16} the concentration of $\text{Ca}(\text{OH})^+$ is only 10^{-6} M at pH 9.0. $\text{Ca}(\text{OH})^+$ attains a maximum concentration of $\sim 10^{-3}$ M at pH 13.0. In phosphoric acid, $\text{Ca}(\text{II})$ concentration, however, decreased by 2 orders of magnitude as the pH increased from 3.5 to 5.0 or MR increased from 0.9 to 1.1. At pH 5.0, the amount of $\text{Ca}(\text{OH})^+$ formed is negligible. Experimental data appeared to show a small amount of $\text{Ca}(\text{II})$ adsorption at pH as low as 3.0 on silica.¹⁹ However, a sharp increase in $\text{Ca}(\text{II})$ adsorption was only observed at a pH between 9.0 and 11.0. The adsorbed $\text{Ca}(\text{II})$ species that was induced to form in significant concentration by silica at this pH range is $\text{Ca}(\text{OH})^+$.¹⁹ It is unlikely that the near complete disappearance of $\text{Ca}(\text{II})$ from phosphoric acid solution at pH 5.0 is due to the formation of hydrolysis product. The formation of other insoluble $\text{Ca}(\text{II})$ compounds is the likely cause. The most likely candidate is CaHPO_4 .

At 25 °C the solubility product of CaHPO_4 is 10^{-7} . This dissociation reaction of phosphoric acid is given below with their respective $\text{p}K_{\text{a}}$ values:¹⁷



The concentration of the initial diluted phosphoric acid is ~ 4 M. At pH 5.0, the concentration of H_2PO_4^- and HPO_4^{2-} calculated with the dissociation constants is ~ 4 and 0.025 M, respectively. With $\text{Ca}(\text{II})$ concentration being 0.001 M, the product of $\text{Ca}(\text{II})$ and HPO_4^{2-} concentrations is $\sim 10^{-4}$, well in excess of the solubility product value of 10^{-7} . Thus, CaHPO_4 precipitation is the likely cause for the near complete loss of $\text{Ca}(\text{II})$ solubility at pH 5.

4. Conclusion

For each metal ion, there is a unique MR characterizing the onset of a sharp decline in solubility and another characterizing the transition from sharp decline to a more gradual change. At any given temperature, these characteristics MR values generally increase with the following order: $\text{Ca}(\text{II}) = \text{Mg}(\text{II}) > \text{Al}(\text{III}) > \text{Fe}(\text{III})$.

At 60 and 90 °C, $\text{Fe}(\text{III})$ is almost completely insoluble at MR of 0.76. In contrast, 15% of $\text{Fe}(\text{III})$ still remained in solution at 25 °C. The solubility curves of both $\text{Al}(\text{III})$ and $\text{Ca}(\text{II})$ ions appeared to be only a function of MR and not temperature. However, with $\text{Mg}(\text{II})$, the solubility curve at 90 °C appeared to be shifted slightly to a lower MR value or pH when compared with that at 25 and 60 °C.

The low solubility of $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$ at pH ~ 5.0 is due to formation of insoluble compounds other than hydrolysis product compounds. Magnesium ammonium phosphate and calcium hydrogen phosphate are the likely insoluble compounds responsible for their disappearance.

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(with a top-up from WMC) derived from an ARC-linkage grant with WMC Fertilizers, LP0202026, working on the Rheology and CFD modeling of Ammonium Phosphate slurries in Pre-Neutraliser reactor. WMC Fertilizers (now Southern Cross Fertilizers) provided extra funding for this project on metal ions solubility. M.S. did the solubility measurements at elevated temperature. We wish to thank the contributions of the referees for making this a better paper.

Nomenclature

$K_{x,y}$ = equilibrium constant of hydrolysis product formation
 K_w = dissociation constant of water
 K_{sp} = solubility product of an insoluble compound
 $\beta_{1,2} = K_{1,2}$ where $x = 1$ and $y = 2$
 pK_a = the negative log of dissociation constant of phosphoric acid

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