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# **A RHEOLOGICAL STUDY OF AMMONIUM PHOSPHATE SLURRIES**

Thesis Submitted by  
Graeme Robert CAMPBELL  
In August 2007

For the Degree of Doctor of Philosophy  
In the School of Engineering  
James Cook University

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Date

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## PUBLICATIONS

The following publications have been produced during the course of this work:

Campbell G.R., Leong Y.K. and Yeow Y.L., “Obtaining The Shear Stress Shear Rate Relationship and Yield Stress of Liquid Foods from Parallel Disk Data.” *J. Food Sci.* **70** (2005) E50-55.

Campbell G.R., Leong Y.K., Berndt C.C. and Liow J.L., “Ammonium Phosphate Slurry Rheology and Particle Properties - The influence of Fe(III) and Al(III) impurities, solid concentration and degree of neutralization”, *Chem Eng Sci*, **61** (2006) 5856-5866.

Leong YK, Sganzerla M, Berndt CC and Campbell GR, “Metal ions Solubility in Plant Phosphoric acid – degree of ammonia neutralization and temperature effects”, *Ind. Eng. Chem. Res.* (2008) – in press.

## ABSTRACT

Phosphate Hill is a mine site located in North West Queensland. At the site, mined phosphoric rock is reacted with sulphuric acid to produce phosphoric acid. The phosphoric acid is combined with ammonia in a reactor known as the pre-neutraliser. The reaction forms a very hot and viscous slurry which is later further ammoniated in a cylindrical vessel known as a granulator, to produce solid fertiliser granules of mono-ammonium phosphate (MAP) or di-ammonium phosphate (DAP). Two important parameters used in the processing of ammonium phosphate slurries are the nitrogen to phosphorous mole ratio (MR) and the specific gravity (SG). Both of these parameters can affect the rheology of the slurry produced inside the reactor. The impurities carried over in the phosphoric acid from the reaction with the phosphate rock can also have significant effects on the rheology of the slurry. The objective of this study was to examine the rheological characteristics of the ammonium phosphate slurries formed in the pre-neutraliser (PN) and determine how the viscosity changes with mole ratio, impurity composition and specific gravity.

There is a lot of variability in the literature on the rheology of ammonium phosphate slurries. Previous work did not take into account the non-Newtonian nature of the slurry, whilst also basing their findings on plant based measurements, where proper control of the slurry properties would have been difficult. A bulk quantity of phosphoric acid was collected from Phosphate Hill and used as a baseline for testing the effect of adding impurities. Laboratory grade  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and  $\text{Mg}_3(\text{PO}_4)_2$  were added to the plant acid to form acids of varying impurity content. Further to the viscosity experiments, work was conducted to determine the slurry particle size, chemical composition (by XRD/XRF analysis), solubility of precipitates and physical characteristics, in an attempt to explain the mechanisms behind the observed viscosity changes. Testing the viscosity of ammonium phosphate slurry was found to be very time consuming and problematic. The experimental work was complicated by a multitude of factors, including high temperatures, slow reaction and evaporation times, the precipitation of impurities and the solidification of the slurry.

The trend in the viscosity with mole ratio for the as-received acid was similar to that seen in the literature. The addition of both aluminium and iron caused an increase in the viscosity around the MAP minimum solubility point of 0.9 MR. In both cases, the formation of hydrolysis products were shown to have reduced the particle size of the precipitating ammonium phosphate crystals, thus increasing the viscosity. As the mole ratio is increased, mono-ammonium phosphate combines with the additional ammonia to form di-ammonium phosphate. The hydrolysis products for iron also changed at the same time and the resultant slurry formed particles with high interparticle attractive forces which in turn formed a flocculated suspension. Increasing the iron content not only increased the viscosity in this region, but also lowered the mole ratio whereby the increase in viscosity is seen to occur. An increase in the aluminium content had no effect on the viscosity at higher mole ratios. Based on the findings, it is recommended that slurries containing high iron be preferentially processed to make mono-ammonium phosphate and slurries with high aluminium be preferentially processed to make di-ammonium phosphate.

Computational Fluid Dynamics (CFD) modelling was conducted on the mixing dynamics of the PN vessel. The CFD model showed that the upper region of the vessel was the least well mixed. The potential for stagnation of the flow field and subsequent solidification increases when the viscosity of the slurry also increases. To counteract this threat, the volume of slurry in the reactor must be decreased, or the agitation speed increased. The most effective method to ensure proper mixing dynamics in the vessel was to lower the viscosity, by preferentially processing each slurry by its impurity content as mentioned above.

## SUMMARY

Phosphate Hill is a mine site located 180km south-east of Mt Isa in a remote area of North West Queensland. Situated on a large deposit of high quality phosphate rock, the mine combines ammonia, which it produces from natural gas, with phosphoric acid to produce ammonium phosphate fertiliser. The ammonium and the phosphoric acid are first mixed together in a vessel known as the pre-neutraliser (PN). Neutralisation is the term used to describe when enough ammonia is reacted with the phosphoric acid to produce and solidify out mono-ammonium phosphate (MAP) or di-ammonium phosphate (DAP), the two main fertiliser products of the mine. This study is concerned with characterising the rheological properties of the slurry produced within the PN, so as to determine methods to enhance the mixing dynamics of the vessel and increase product throughput.

The literature survey revealed that phosphoric acid impurities such as iron, aluminium, magnesium and fluorine were primarily thought to be responsible for changes in the pre-neutraliser slurry viscosity. Ando and Akiyama (1972) claimed that high F:R<sub>2</sub>O<sub>3</sub> (where R is Al or Fe) ratios led to the formation of small colloidal crystals that increased the viscosity. However, Achorn et al. (1980) claimed that crystals formed in a slurry with high F:R<sub>2</sub>O<sub>3</sub> ratio were coarser than those with lower levels of fluorine. Handley (1984) stated that fluorine was beneficial to lowering slurry viscosity, but did not compare his results to the R<sub>2</sub>O<sub>3</sub> content. All three had differing opinions in respect to the extent that iron, aluminium and magnesium had in altering the slurry viscosity. Other literature focused on single viscosity measures using plant, or pilot plant based experiments, where accurately determining specific gravity and mole ratio would have been difficult. Leong (2002) demonstrated that large changes in the viscosity could occur with small changes in specific gravity or temperature. Making conclusions about the effects of impurities on viscosity is difficult without controlled and documented conditions. In order to properly characterise the rheological behaviour of ammonium phosphate slurries, comprehensive laboratory controlled experiments are required.

Laboratory testing of the viscosity of ammonium phosphate slurry appears to be a straight forward process. However, it has been found to be very time consuming and problematic as there was no previously established procedure for conducting such a test. The experimental work was complicated by a multitude of factors. These included high temperatures, slow reaction and evaporation times, the precipitation of impurities and the solidification of the slurry, as well as delays in determining the mole ratio of the slurry.

The phosphoric acid used was collected from the 40% acid tanks at the plant and contained some suspended solids. The as-received acid was designated DAP1 and all samples were collected at the same time from the same sample location in the plant.  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and  $\text{Mg}_3(\text{PO}_4)_2$  were dissolved in DAP1 to produce acids with different impurity contents. The DAP1 acid was used as a baseline to compare the changes in viscosity with varying impurity content.

Ammonia gas was bubbled through a continuously stirred solution of phosphoric acid in an 800 ml beaker until the desired mole ratio is reached. A sub-sample was then poured into a test tube, which was weighed to determine the specific gravity. The slurry was heated on a hot plate with stirring to evaporate water, increasing the specific gravity. The specific gravity of slurry is directly related to the free moisture content in the slurry at given mole ratio. Sub-samples were taken from the beaker periodically in clean test tubes until the slurry became too viscous to pour into the test tube. The reaction was highly exothermic, so the ammonia addition rate was controlled to ensure that the reaction stayed close to the boiling point of the liquid (110-120°C). Sub-samples were placed in a hot oil bath for several minutes, until the temperature was maintained at 110°C, ensuring that the viscosity was always measured at the same temperature. The rheology of the slurry was measured with a Brookfield LVDV-II+ viscometer using a concentric cylinder geometry with the cylindrical test-tube being the outer cylinder.

At low specific gravity (1.4), the flow behaviour was observed to be Newtonian in the range of shear rate characterised (10-100  $\text{s}^{-1}$ ). The slurry displayed non-Newtonian shear thinning behaviour at higher specific gravity (1.6). This was reflected by a

decreasing viscosity with increasing shear rate. The viscosity versus shear rate plot on a log-log scale was found to be linear, so the flow behaviour was reasonably well represented by a power law model. The viscosity was found to increase exponentially with increasing slurry specific gravity (or decreasing water content of the slurry).

The DAP1 plant acid slurry viscosity versus mole ratio trend compared favourably to the literature. Both Ando and Akiyama (1972) and Tang et al. (2004) showed trends with a peak in the viscosity occurring at 0.8-0.9 MR as with the DAP1 data. This was unexpected because the minimum solubility point of MAP occurs at 1.0 MR. Maximum solids content should coincide with the maximum viscosity. Compared to DAP1, the slurries containing additional iron showed increases in the maximum viscosity of the peak occurring at 0.9 MR and also increased viscosity above 1.2 MR. It was concluded that iron has a more significant effect on the viscosity during the production of di-ammonium phosphate, where the mole ratio in the pre-neutraliser is typically 1.55-1.60. During production of mono-ammonium phosphate, where the slurry mole ratio is typically 0.65-0.7, the iron content does appear to have an influence on the viscosity; however the measured viscosity was around an order of magnitude lower for the same specific gravity and shear rate, compared to that during di-ammonium phosphate production. In conclusion, ore with high iron content can be more effectively processed under MAP conditions than under DAP conditions.

The slurries containing additional aluminium showed an increase in the measured viscosity across all mole ratios below 1.3 MR. Above 1.4 MR the viscosity shows no significant change and may in fact decrease with increased aluminium content. This observation would lead us to believe that slurries containing high aluminium content should not be processed under MAP conditions. Under DAP conditions the aluminium content appears to have no effect on the viscosity. The measured viscosity of slurries containing the additional magnesium was irregular and trends were inconclusive with respect to viscosity and mole ratio.

Interestingly, the shape of the viscosity versus mole ratio curves were different for aluminium and iron. In the literature, aluminium and iron are commonly referred to together as  $R_2O_3$ , where R can be either Fe or Al. Therefore, it was assumed that the

effect of altering the concentration of either would be similar. Instead, the effects of these impurities were found to be significantly different. Iron increased the peak of the viscosity at 0.9 MR, while aluminium had a significant affect on broadening the peak, particularly above 0.9 MR. Iron increased the viscosity in the higher mole ratio range, above 1.4 MR, whilst aluminium had no real effect in this range. This suggests that combined high iron and high aluminium ores will be problematic to process at any mole ratio.

The titration method used to determine the mole ratio was found to be erroneous. The sulphate content of the acid affects the titration calculation, reporting a lower N:P mole ratio. The titration method was found to return the N:(P + 2S) mole ratio below 1.0 MR and the N:(P + S) mole ratio at higher mole ratios. Therefore, the peak in the viscosity that was observed at 0.8-0.9 MR instead occurred at closer to 1.0 N:P MR. The viscosity increase results from the precipitation of mono-ammonium phosphate.

The precipitation of ammonium phosphate solids, for slurries made from pure phosphoric acid with added metal ions, began at MR ~0.6 (pH ~2) for Fe(III), 0.85 (pH~3.5) for Al (III) and 1.3 (pH~7) for Mg(II). At the same mole ratio, the respective metal ions also formed hydrolysis products (Baes and Mesmer 1986), indicating that hydrolysis products are required to initiate solids formation. The hydrolysis products formed very small particles that act as nucleation sites for crystallization and have been shown to hinder crystal size growth. Aluminium based slurries had the smallest particle size, followed by iron and magnesium. Ammonium phosphate slurry made from pure phosphoric acid had large soluble particles (1-2 mm in size). Aluminium and iron based slurries did not have any of these large inter-dispersed ammonium phosphate crystals, whilst magnesium slurries did. However, magnesium did not form hydrolysis products below 1.25 MR and so large ammonium phosphate crystals were able to form.

Adsorbed hydrolysis products may give rise to a range of interparticle forces in slurry such as bridging, charged patch and enhanced van der Waals attraction (Leong 2005). These forces will have a significant effect on slurry rheology. Slurries containing iron were observed to form strong interparticle forces above 1.4 MR, at the same time as

the viscosity increased. The interparticle forces are demonstrated by adding 30 ml of the slurry to 500 ml of water. Slurries below 1.4 MR settled to the base of the beaker. Slurries above 1.4 MR formed a flocculated suspension that occupied almost all of the 500 ml solution. Ammonium phosphate slurries were generally white in colour. The increased interparticle forces for slurries with high iron content above 1.4 MR corresponded to a change in the slurry colour to yellow. The principle iron hydrolysis products in solution change between 1.3-1.5 MR, indicating that the viscosity increase is related to the hydrolysis products.

Computational Fluid Dynamics (CFD) modelling was conducted on the mixing dynamics of the PN vessel. The CFD model was validated by injecting a LiCl tracer into the PN vessel and comparing the residence time distribution of the simulated and experimental results. The focus of the research was on the rheological characterisation rather than the optimisation of the reactor geometry and as such, the modelling and model validation appears in the appendix only. Validation of the model was inhibited as the level in the PN vessel at the time of testing was unable to be determined. The CFD model showed that the upper region of the vessel was the least well mixed. The potential for stagnation of the flow field and subsequent solidification increases when the viscosity of the slurry also increases. To counteract this threat, the volume of slurry in the reactor must be decreased, or the agitation speed increased. The most effective method to ensure proper mixing dynamics in the vessel was to lower the viscosity, by preferentially processing each slurry by its impurity content.

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