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Submitted in partial fulfilment of part of the requirements for the degree of Master of Engineering in the Faculty Engineering, the Built Environment and Information Technology, University of Pretoria, Pretoria

2003

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Degree: MEng (Chemical Engineering)

SYNOPSIS

Fedmis Pty (Ltd) situated in Palaborwa, South Africa produces phosphoric acid using the wet process production process. For this study, two main areas of concern in the wet process phosphoric acid production were investigated. The first area is the formation of sludge in the system due to impurities that reduces the grade of the acid produced, thereby lowering the selling price. The second area is the crystallisation of the gypsum that influences filtration and thereby affects plant productivity. These two aspects were investigated separately as they occur in different steps of the production process at different acid concentrations.

A major component of the acid sludge is known as x-compound, $((Fe,Al)_3KH_{14}(PO_4)_8.4H_2O)$. The purpose of the investigation of x-compound is to determine what effects different ionic impurities have on its precipitation and to determine if these effects could be used to decrease the amount of sludge formation. Due to the complexity of the system and the wide variety of impurities only the major impurities were considered in this study. These impurities included potassium (K^+), sodium (Na^+), magnesium (Mg^{2+}), aluminium (Al^{3+}) and iron (Fe^{3+}). For all the experiments investigating the effect of impurities, analytical reagents were used on laboratory scale. For the silica experiments, commercially available samples were used.

For the experiments investigating the impurity effects on the precipitation of x-compound it was found that:

- Agitation increases x-compound precipitation and can be used commercially to increase the precipitation rate to a point where sludge can be removed before transportation.

- Adding x-compound seeding crystals or magnesium ions also increases precipitation.

- Adding gypsum, sodium, hexafluorosilicates or fluorosilic acid reduces the precipitation, with sodium ions producing the lowest yield. This reduction is however not sufficient to be used commercially.

From the Raman study it became clear why x-compound precipitation is such a slow process.

- At low acid concentrations, more $H_2PO_4^-$ ions are present that form a complex with iron and aluminium.

- As the acid concentration increases the concentration of $H_2PO_4^-$ ions decrease as the degree of dissociation of phosphoric acid decreases. The ferric-$H_2PO_4^-$ and aluminium-$H_2PO_4^-$ complexes become less stable and ultimately precipitation of the x-compound is favoured above solvation.

- Addition of potassium impurities to the solutions had no visible effect on the Raman spectra and is suspected not to form a complex with the acid.

From the silica sources investigated namely Dicalite, Serina Kaolin, Foskor silica and Aerosil 200 it can be concluded that none of the sources will be useful for the removal of potassium through formation of potassium hexafluorosilicates.

For the determination of the concentration of impurities present in the production of phosphoric acid, the Fedmis monitoring program was initiated. It included the monitoring of Foskor rock analyses on a daily basis, and the monitoring of the 27%, 39% and 54% P_2O_5 phosphoric acid and precipitate, from these acid solutions on a weekly basis. From the investigation of the effect of these impurities on the solubility of potassium hexafluorosilicates, it was found that magnesium causes K_2SiF_6 to be the most soluble and fluoride the least. Unfortunately, the impurities did not help to reduce the potassium concentrations in the acid to below the required amount for sludge formation.

For the calcium sulphate dihydrate surfactant experiments, the purpose of the investigation was to determine whether higher crystallisation qualities could be obtained to improve plant productivity. The investigation was limited to using surfactants with sulphate or phosphate functionalities and experiments were done on laboratory scale using analytical reagents.

Atphos E3205, Atpol E3202 and Atpol E1231 are polyethoxylated alkyl phenol phosphate esters that had no visible effect on the crystal structure of the precipitated gypsum, but differences in the crystal sizes were observed. Smaller crystal structures with relatively equal masses compared to reference experiments are an indication of a growth inhibitor and a nucleation promoter as seen with Atphos E3205 and Atpol E3202. Increased crystal sizes were obtained using Atpol E1231.

The use of Calsoline Oil caused a wider crystal size distribution in the precipitated crystals as thin and broad crystals with approximately the same length are found. The crystal mass obtained is also approximately the same as that of the reference experiment. Thus, it can be concluded that the surfactant affects the growth of the crystals and not the nucleation.

Arlatone 1489, calcium gluconate monohydrate, Dowfax Hydrotrope and Tamol NN 8906 had no visible effect on the structure or size of the precipitated gypsum crystals.

With the use of Nansa SS30, drastic effects were seen on the crystallisation of the calcium sulphate as small hexagonal rods were found. With an increase in surfactant concentration, there is a clear decrease in the mass of crystals obtained as well as crystal size. An increase in the crystal size distribution and a decrease in crystal size reduced the filtration rate dramatically. Experiments carried out for 24 hours exhibited the same trends where there is a decrease in yield with an increase in surfactant concentration. Higher yields were however obtained proving that mass transfer barriers were overcome. The results from these experiments again indicate that the surfactant affects crystal growth and nucleation.

With the use of Dowfax 3B2 there is definite reduction in yield with an increase in surfactant concentration reaching a minimum at approximately 70% yield. Due to the presence of large

amounts of smaller crystals and the almost constant yield obtained compared to the reference experiment, it can be concluded that this surfactant is a growth and not a nucleation inhibitor.

As with Nansa SS30, experiments where Empicol LZ/D was used show a continuous decrease in the yield obtained with an increase in the surfactant concentration. At higher concentration of Empicol LZ/D, it seems as if this surfactant changed from a growth promoter to a growth inhibitor because although broad longer crystals are present, there are now also much smaller crystals formed. The crystal size distribution also broadens considerably.

Overall, very high yields were obtained using Empimin KSN70 and the observed crystal size distributions were very narrow. The only difference was that the crystals appeared to be more porous or fibrous compared to the reference experiment.

It is recommended that the experiments showing promise as crystal habit modifiers like Nansa SS30 and Empicol LZ/D be investigated in more detail as well as combinations of surfactants.

Both the areas of concern in the process were investigated successfully. For the sludge formation problem, it is now clear what effects the precipitation of x-compound as well as what affect the impurities and operating conditions have. For the crystallisation of gypsum using surfactants, it was proven that surfactants could be used to affect crystal growth, shape and distribution and in this way influence filtration.

KEY WORDS: crystallisation, crystal habit modifier, gypsum, x-compound, surfactant, wet-
              process phosphoric acid production

ACKNOWLEDGEMENTS

The author would like to thank:

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