Solutions to a combined problem of excessive hydrogen sulfide in biogas and struvite scaling

W. Charles*, R. Cord-Ruwisch*, G. Ho*, M. Costa** and P. Spencer**
*Centre for Organic Waste Management, Murdoch University, South Street, Murdoch, WA. 6150, Australia
(E-mail: _w.charles@murdoch.edu.au_)
**Water Corporation, 629 Newcastle Street, Leederville, 6007, WA, Australia.

Abstract
The Woodman Point Wastewater Treatment Plant (WWTP) at Western Australia has experienced two separate problems causing avoidable maintenance costs, the build-up of massive struvite ($MgNH_4PO_4 \cdot 6H_2O$) scaling downstream of the anaerobic digester and the formation of hydrogen sulfide (H_2S) levels in the digester gas to levels that compromised gas engine operation and caused high operating costs on the gas scrubber. As both problems hang together with a chemical imbalance in the anaerobic digester, we decided to investigate whether both problems could be (feasibly and economically) addressed by a common solution, (such as dosing of iron solutions to precipitate both sulfide and phosphate), or by using separate approaches.

Laboratory results showed that, the hydrogen sulfide emission in digesters could be effectively and economically controlled by the addition of iron dosing. Slightly higher than the theoretical value of 1.5 mol of $FeCl_3$ was required to precipitate 1 mol of dissolved sulfide inside the digester.

Due to the high concentration of PO_4^{3-} in the digested sludge liquor, significantly higher iron is required for struvite precipitation. Iron dosing did not appear an economic solution for struvite control via iron phosphate formation. By taking advantage of the natural tendency of struvite formation in the digester liquid, it is possible to reduce the risk of struvite precipitation in and around the sludge-dewatering centrifuge by increasing the pH to precipitate struvite out before passing through the centrifuge. However, as the Mg^{2+}/PO_4^{3-} molar ratio in digested sludge was low, by increasing the pH alone (using NaOH) the precipitation of PO_4^{3-} was limited by the amount of cations (Ca^{2+} and Mg^{2+}) available in the sludge. Although this would reduce struvite precipitation in the centrifuge, it could not significantly reduce PO_4^{3-} recycling back to the plant. For long-term operation, maximum PO_4^{3-} reduction should be the ultimate aim to minimise PO_4^{3-} accumulation in the plant. Magnesium hydroxide liquid (MHL) was found to be the most cost-effective chemical to achieve this goal. It enhanced struvite precipitation from both, digested sludge and centrate to the point where more than 95% PO_4^{3-} reduction in the digested sludge was achieved.
Keywords
Anaerobic digestion, hydrogen sulfide, struvite, wastewater, $FeCl_3$

INTRODUCTION
The Woodman Point Wastewater Treatment Plant in Perth, Western Australia, currently treats more than 115 million litres of wastewater daily. The treatment process consists of primary sedimentation followed by a sequencing batch reactor (SBR). The sludge from both steps are thickened, combined and then fed to anaerobic digesters. Digested sludge passes through a centrifuge where biosolids are discharged and the centrate recycled back to the beginning of the plant. The plant has been experiencing two significant problems, (1) a high concentration of hydrogen sulfide (H_2S) in the biogas extracted from the anaerobic digesters and (2) the formation of struvite in the centrifuge and downstream pipe work.

The generation and emission of H_2S gas from the anaerobic digestion of bio-solids in wastewater treatment processes is universal. H_2S is generated from the reduction of sulfate to sulfide by anaerobic sulfate-reducing bacteria (SRB). The total amount of sulfide produced by SRB is determined by the initial sulfate content of the wastewater but also by organic sulfur species (from proteinaceous materials), sulfonates (from household detergents) and inorganic sulfur (as sulfate) (Burgess _et al.,_ 2001).

H_2S is noxious, toxic and highly corrosive. When biogas produced by anaerobic digestion is to be utilised as a fuel source, H_2S needs to be removed to prevent corrosion of the power generation equipment and to reduce air pollution in the exhaust gas. At present, an iron-based chemical oxidant gas scrubber is used at Woodman Point WWTP. Apart from the high cost of this process, the H_2S removal is inadequate with associated high costs in engine maintenance. Moreover, it is theoretically likely that some oxidised sulfur from waste stream during the regeneration process is being recycled back to the digester.

Struvite is a white crystalline substance consisting of PO_4^{3-}, NH_4^+ and Mg^{2+} in equal molar concentrations. Struvite forms according to the general reaction shown below

$$PO_4^{3-} + NH_4^+ + Mg^{2+} + 6H2O \rightarrow MgNH_4PO_4.6H_2O.$$

However, this equation is a simplification of chemistry involved in struvite precipitation. The chemistry of struvite with regard to the wastewater industry is inexorably linked with solubility, for this reason struvite chemistry is discussed with solubility being the key issue (Doyle & Parsons, 2002).

Struvite precipitation occurs when the combined concentrations of PO_4^{3-}, NH_4^+ and Mg^{2+} exceed the struvite solubility limit. All three of the reacting ions exhibit complex equilibria in aqueous solution. The equilibrium is pH dependent, and this is the reason for the variation in the solubility of struvite with pH. Within the pH range expected in digested sludge, struvite solubility decreases as pH increases (6.0-8.0).

Since the commissioning of the sequencing batch reactor (SBR) at Woodman Point WWTP in 2002, a significant proportion of nitrogen and phosphorus is removed from the wastewater. However, during the anaerobic digestion of excess sludge from the SBR, PO_4^{3-}, NH_4^+ and Mg^{2+} are released as a result of solids degradation. Under certain conditions when PO_4^{3-}, NH_4^+ and Mg^{2+} concentrations exceed the struvite solubility limit, these dissolved constituents combine to form struvite in the digester or post-digestion processes. At Woodman Point WWTP, problems have been experienced with mineral precipitation in the centrifuges, and in the pipework leading from the centrifuges. Massive precipitation inside the centrifuges and within the pipe network caused pipe blockages and significant maintenance costs.

This study aimed to investigate the feasibility of practical solutions for these two problems preferably by using a common solution such as direct iron salt dosing to precipitate dissolved sulfide and phosphate in the digester. If iron dosing was found to be not economically viable for struvite control, alternative approaches via controlled struvite formation were investigated.

MATERIALS AND METHODS

Batch experiment to determine iron dosage

Digested sludge was sampled at Woodman Point WWTP to fill 17 Schott bottles (500 ml) with rubber inserted tops. Two series of experiments were performed:

- For the H_2S control experiment, eight bottles were immediately injected with ferric chloride solutions, through the rubber top, to give iron concentrations of 0.15, 0.30, 0.60, 0.90, 1.20, 1.50 and 3.00 mmol/l (1 mmol of Fe =55.85 mg).
- For the struvite control experiment, another 8 bottles were injected with ferric chloride solutions to give iron concentrations of 0.49, 0.70, 1.00, 1.42, 2.03, 2.90, 4.14 and 5.92mmol/l.

The last bottle was used as a control (no iron addition). After iron dosing, the bottles were vigorously shaken for 1 minute, then left for 30 minute for chemical reactions to complete. All bottles were then opened and analysed for pH, dissolved sulfide, PO_4^{3-}, NH_4^+, Mg^{2+}, Ca^{2+} and Fe.

Sulfide removal in continuous flow laboratory-scale reactor

To determine the possible effect of $FeCl_3$ dosing on the performance of anaerobic digester biomass, a continuous flow experiment using two computer-controlled 1 litre completely mixed anaerobic reactors were set up using digested sludge taken from Woodman Point WWTP. The system configuration simulated digester conditions at Woodman Point WWTP. A self designed program written in Labview (National Instruments) was used to control the reactors. The synthetic feed used is shown in Table 1. Nutrients and trace elements were omitted to minimise interference with sulfide precipitation (sufficient amounts of these should be present in the digested sludge).

Table 1 Stock solution used as feed

Compound	Concentration (mmol/l)
Lactic acid	272.11
Sodium sulfate	1.64
Sodium carbonate	0.1

Sulfide in the gas was measured by passing the biogas through a copper reagent (100 mmol/l HCl and 10 mmol/l $CuSO_4$) (Cord-Ruwisch, 1985).

Struvite precipitation by NaOH, lime and MHL addition

A series of titration experiments was performed on digested sludge and centrate sample from Woodman Point WWTP. NaOH, lime and MHL were used to increase the pH of the digested sludge and centrate to 7.5, 8, 8.5 and 9. After each pH was reached, 20 ml of sample was taken to determine for dissolved PO_4^{3-}, NH_4^+, Mg^{2+} and Ca^{2+}.

Chemical analysis

All chemical analyses were performed by the Marine and Freshwater Research Laboratory (NATA Accredited), Murdoch University.

RESULTS AND DISCUSSION

Iron salt dosing to precipitate H_2S

The characteristics of the anaerobic sludge used in the batch experiment were established (Table 2). Sulfide and phosphate concentrations are important, as both sulfide and phosphate are known to be precipitated with Fe^{3+}. The phosphate concentration was about an order of magnitude higher than the sulfide concentration confirming that substantially more Fe^{3+} was needed for phosphate precipitation than sulfide precipitation.

Table 2 Characteristics of anaerobic sludge used in the batch experiment.

Total solids (g/l)	51
Volatile solids (g/l)	39
pH	7.03
Sulfide (mmol/l)	0.497 (15.95 mg/l)
Phosphate (mmol/l)	7.23 (224 mg/l as P)

The results from the batch experiment (Figure 1) indicate that the dissolved sulfide concentration can be reduced to virtually zero with the addition of $FeCl_3$ at the ratio of approximately 1.5 mol of $FeCl_3$ per mol of dissolved sulfide. This is equivalent to 121 mg/l of $FeCl_3$ precipitating 16 mg/l of dissolved sulfide. Due to the small amount of $FeCl_3$ required relative to the large buffer capacity of the sludge, the pH of the mixed liquor was virtually unchanged, indicating that adverse effects to methanogenesis in the digester are not likely.

Since iron sulfide ($pK_{sp}=17.20$) has a much lower solubility than iron phosphate ($pK_{sp}=15.00$) or iron carbonate ($pK_{sp}=10.50$), the precipitation of iron sulfide is expected to occur preferentially. Excess iron was then precipitated by other available anions, such as phosphate (as shown in Figure 6) and carbonate. Note that in the absence of sulfide (where PO_4^{3-} and HCO_3^- are high), it is likely that phosphate will be precipitated as the less soluble vivianite $[Fe_3(PO_4)_2.8H_2O]$ to near completion before the onset of siderite ($FeCO_3$) precipitation (Zachara et al., 2001).
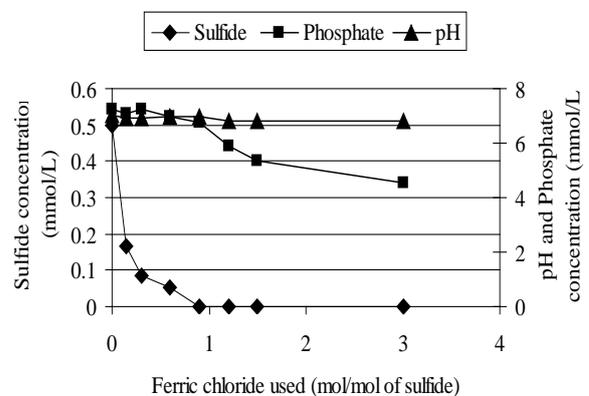
Fifure1 Effect of ferric chloride dosing on pH, sulfide and phosphate in anaerobic sludge

3

Effect of iron dosing on anaerobic digester performance

To test whether the promising results from the batch experiment were sustainable; a continuous flow experiment was set up (Table 3). Applying the results of the batch experiment, it was determined that 0.498 mmol/l (80.67 mg/l) $FeCl_3$ was required to precipitate all dissolved sulfide in the reactor. In practice, this could be achieved by slowly dosing the feed with $FeCl_3$ to reach this concentration over 1 HRT (20 days). Due to time constrains, accelerated dosing of $FeCl_3$ was used to complete the full dose within 2 days (0.249 mmol/l/day). Thereafter the dose was reduced to 0.123 mmol/l/day (equivalent to 1.5 times the rate of sulfur fed of the reactors).

Table 3 Characteristics of anaerobic sludge used in the continuous flow experiment

Total solids (g/l)	54.94
Volatile solids (g/l)	44.08
pH	7.16
Sulfide (mmol/l)	0.332 (10.65 mg/l)
Phosphate (mmol/l)	6.34 (196.3 mg/l as P)

Ferric chloride dosing had no significant effect on gas production (Figure 2). indicating that the oxidation power of ther ferric iron did not interfere with methanogenic bacteria. As dissolved sulfide precipitated, hydrogen sulfide in the off-gas gradually reduced to zero by the 5th day after $FeCl_3$ dosing, maintaining this level throughout the 30 days of the experiment (Figure 3).
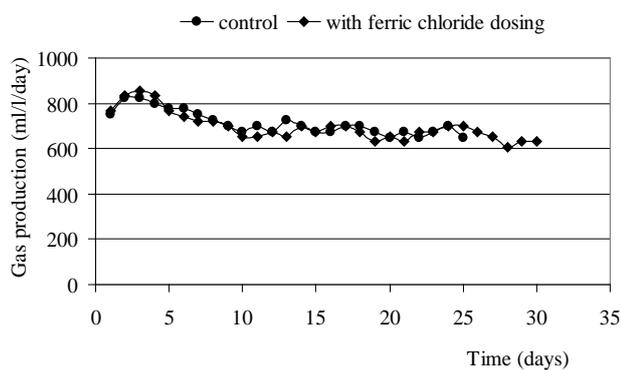

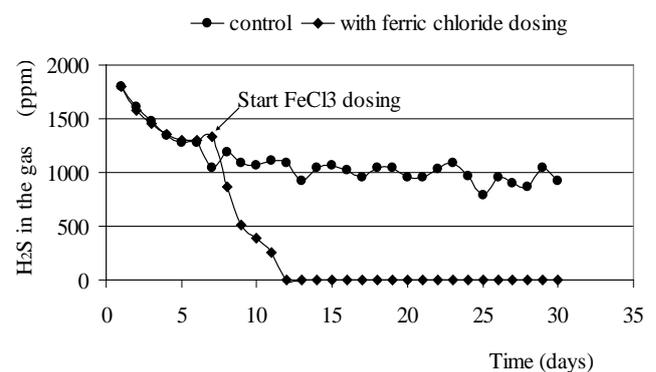**Figure 2** Gas production from two reactors (with and without ferric chloride dosing)

Figure 3 Hydrogen sulfide in biogas from the reactor dosed with $FeCl_3$ compared to the control reactor

Iron dosing to control struvite precipitation

Ferric iron can also be used to precipitate PO_4^{3-} as $Fe_3(PO_4)_2$, thus aiding to lower the concentration product of $[PO_4^{3-}][NH_4^+][Mg^{2+}]$ to less than the struvite solubility product. The first 0.7 mmol/l of $FeCl_3$ added did not cause phosphate precipitation due to its consumption for sulfide precipitation (figure 4, table 4). After this point PO_4^{3-} reduction was proportional to $FeCl_3$ used. Due to the high buffer capacity, pH of the sludge did not significantly change. As PO_4^{3-} gradually decreased while pH remained unchanged, pPs values (see Table for detail calculation) of $[PO_4^{3-}][NH_4^+][Mg^{2+}]$ shifted further towards the unsaturated zone (Figure 5). As a result, the possibility of struvite precipitation in the centrifuge was reduced.

Table 4 The effect of $FeCl_3$ used to concentration of $[PO_4^{3-}][NH_4^+][Mg^{2+}]$ and pH

$FeCl_3$ used		P		N		Mg		Ksp	pPs	pH
mmol/l	mg/l	mmol/l	mg/l	mmol/l	mg/l	mmol/l	mg/l			
0	0	6.41	198	48.9	685	1.48	36	4.638E-07	6.33	7.01
0.49	132	6.36	196	48.9	685	1.32	32	4.023E-07	6.40	6.97
0.70	188	6.25	194	48.5	679	1.312	32	3.956E-07	6.40	6.89
1.00	269	6.20	192	48.6	682	1.27	31	3.687E-07	6.43	6.9
1.42	384	5.94	184	48.7	683	0.25	6	7.385E-08	7.13	6.87
2.03	549	5.48	170	48.3	677	0.28	7	7.307E-08	7.14	6.9
2.90	784	4.93	153	49.0	687	0.31	8	7.452E-08	7.13	6.87
4.14	1120	4.42	137	49.0	687	0.34	8	7.303E-08	7.14	6.84
5.92	1600	2.63	82	48.5	680	0.41	10	5.253E-08	7.28	6.89

*Ksp = solubility product = $[PO_4^{3-}][NH_4^+][Mg^{2+}]$ **pPs = -log10(Ksp)

4
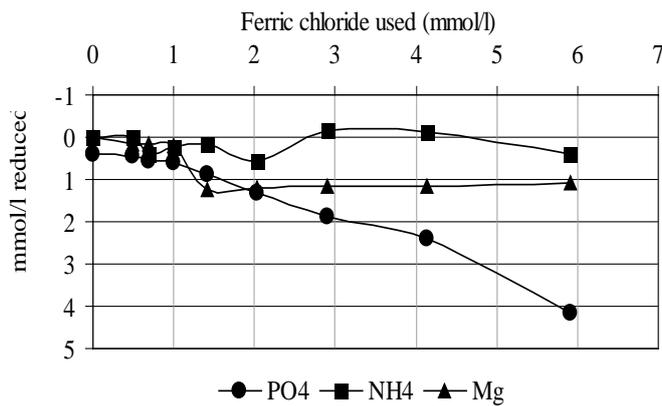
Figure 4 Effect of FeCl₃ dosing of PO_4^{3-}, NH_4^+ and Mg^{2+} concentration in digested sludge.
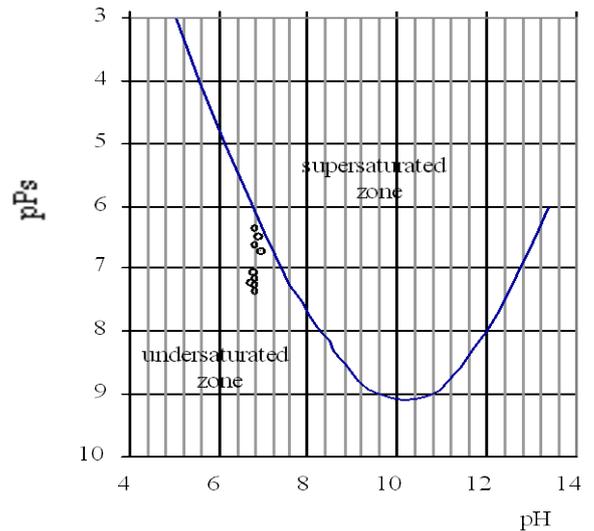

Figure 5 Predicted struvite precipitation potential of anaerobic sludge using different doses of FeCl₃.

The FeCl₃ requirement for PO_4^{3-} removal from the digested sludge was estimated to be 1.5 mol per mol of PO_4^{3-}. To increase pPs from 6.33 to 7.28 (Table 11), PO_4^{3-} should be reduced from 6.4 mmol/L to 2.6 mmol/L. This will require 5.7 mmol (924 mg) FeCl₃ per litre of digested sludge or 554 kg/day. The cost for FeCl₃ would be approximately $A 313,392 per year (FeCl₃ $A650 per ton-42% w/w solution).

Because of the costs iron dosing did not appear an economic solution for struvite control in the plant. By taking advantage of the natural tendency of struvite formation in the digested sludge, alternative ways were explored;

- Prevention of struvite precipitation in the centrifuge by increasing the pH of digested sludge to precipitate struvite before entering the centrifuge
- Harvesting struvite from the centrate to reduce P and N recycling back to the plant

By increasing the pH alone (using NaOH) the precipitation of PO_4^{3-} was limited to the amount of cations (Ca^{2+} and Mg^{2+}) available in the sludge (Figure 6). Although this would reduce struvite precipitation in the centrifuge, it will not significantly reduce PO_4^{3-} recycling back to the plant. The use of lime increased Ca^{2+} concentration and therefore significantly increased PO_4^{3-} precipitation (90% PO_4^{3-} reduction) in the form of apatite (not struvite) (Figure 7). Only MHL increased precipitation of PO_4^{3-} as struvite. MHL not only increased the pH, but also provided the Mg^{2+} necessary for struvite formation. This allows struvite precipitation also at a lower pH. As shown in Figure 8 most PO_4^{3-} was precipitated before pH 8. The addition of MHL beyond this point would not be required as it would only result in excess Mg^{2+} in the sludge as PO_4^{3-} becomes limiting for struvite precipitation.
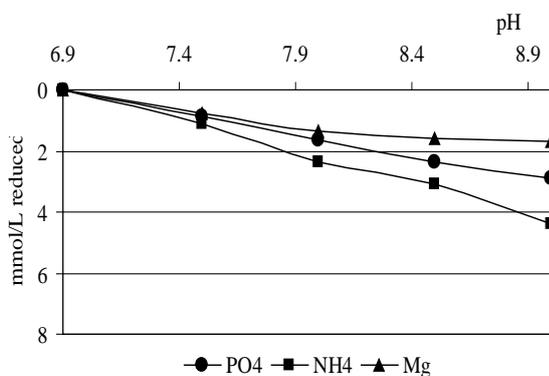

Figure 6 Effect of pH decrease by NaOH dosing on PO_4^{3-}, NH_4^+ and Mg^{2+} concentration in digested sludge.
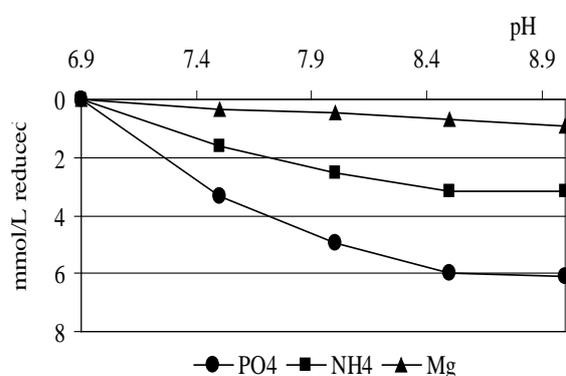
Figure 7 Effect of pH decrease by lime dosing on PO_4^{3-}, NH_4^+ and Mg^{2+} concentration in digested sludge.
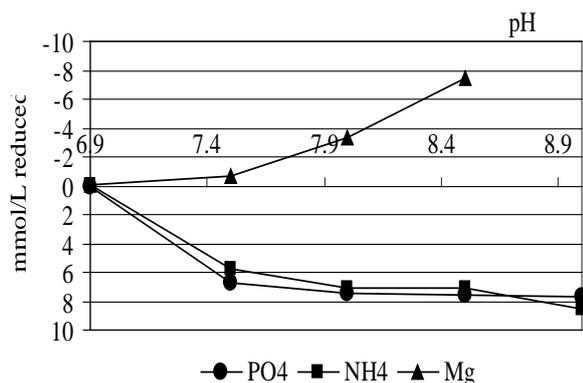
Figure 8 Effect of pH increases by MHL dosing on PO_4^{3-}, NH_4^+ and Mg^{2+} concentration in digested sludge.

Although a significant amount of struvite is currently precipitated out during centrifugation without chemical addition, the centrate from the centrifuge still contains high concentrations of PO_4^3 and NH_4^+. The pPs value of the centrate is still very close to supersaturated zone in regard to struvite precipitation (results not shown). This indicates the high potential for further struvite precipitation in the centrate. Our studies showed that 86% of PO_4^{3-} could be precipitated from the centrate as struvite by MHL dosing (Charles et al., 2003).

Harvesting struvite from the centrate could be beneficial for long-term operation. An obvious benefit would be the recovery of struvite as a slow release fertilizer. With regard to plant operation, struvite precipitation reduces P and N level recycled back to the plant, hence reducing P accumulation around the plant and reducing the cost for aeration at the SBR to reduce N from the final effluent.

From these studies, it is suggested that to prevent struvite precipitation in the centrifuge, MHL should be added in the digested sludge. Struvite can then be disposed of in the biosolids. Alternatively struvite harvesting could be attempted from the centrifuge centrate if the centrifuge was protected from struvite precipitation. Protecting the centrifuge by acid dosing has been determined to be uneconomic due to the high sludge buffer capacity. The centrifuge could also be protected by NaOH dosing. This would allow only a minor amount of phosphate to be removed as struvite and calcium phosphate limited by the Mg^{2+} and Ca^{2+} available in the sludge. After the sludge passes through the centrifuge, MHL can be added to recover the majority of phosphate in the form of struvite from the centrate.

CONCLUSIONS

$FeCl_3$ dosing to the anaerobic reactor was found to be an effective way of controlling H_2S emissions in the biogas. As only a small amount of $FeCl_3$ is required for H_2S precipitation in the digester, the effect to digester performance is likely to be minimal. A full-scale trial on one of the reactors is currently being planned.

Due to the high concentration of PO_4^{3-} in the digested sludge liquor, significantly higher iron is required for struvite precipitation. Iron dosing did not appear an economic solution for struvite control via iron phosphate formation. It is however possible to reduce the risk of struvite precipitation in and around the centrifuge by increasing the pH to precipitate struvite out before passing through the centrifuge, or recover struvite from the centrate to reduce P and N recycling back to the plant. MHL was shown to be the most cost-effective chemical to achieve these outcomes.

A significant proportion of the PO_4^{3-} released in the digester originates from polyphosphate-accumulating organisms that store PO_4^{3-} during the SBR operation. It seems reasonable to integrate the understanding of bacterial P-storage and to modify the SBR plant operation to control the bacterial phosphate release in the anaerobic digester.

ACKNOWLEDGEMENTS

REFERENCES
Burgess, J.E., Parsons, S.A. and Stuetz, R.M. (2001). Developments in odour control and waste gas treatment biotechnology: a review. *Biotechnology Advances,* Vol.19, 35-63.

Charles, W., Cord-Ruwisch, R., Ho, G. (2003). *A Research and Development Project to Control Hydrogen Sulfide and Struvite at Woodman Point WWTP*. Murdoch University, Perth.

Cord-Ruwisch, R. (1985). A quick method for the determination of dissolved and precipitated sulfides in cultures of sulfate-reducing bacteria. *Journal of Microbiological Methods*, Vol. 4, 33-36.

Doyle,J.D and Parsons, S.A. (2002). Struvite formation, control and recovery. Water Research, Vol. 36, 3925-3940.

Zachara, J.M., Fredrickson, J.K., Smith,S.C. and Gassman, P.L. (2001). Solubilization of Fe(III) oxide-bound trace metals by a dissimilatory Fe(III) reducing bacterium. *Geochimica et Cosmochimica Acta*, Vol. 65, No.1, 75-93.