The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal Part 5: Experimental periods using a ferrous-ferric chloride blend

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Abstract

A blend of ferrous chloride and ferric chloride ($FeCl_2$-$FeCl_3$) was simultaneously dosed into an activated sludge system at pilot scale in order to test the effect on biological P removal. Additional removal due to chemical precipitation was measured as the difference in system P removal between parallel test and control systems. Both systems strongly exhibited biological excess P removal (BEPR). The extent of P release in the anaerobic reactors of the two systems was compared by mass balance, as one indicator of the relative "magnitude" of BEPR. Phosphorus fractionation of the mixed liquor also served as an indicator of the biological and chemical mechanisms. Evidence was found that the BEPR mechanism is partially inhibited by simultaneous $FeCl_2$-$FeCl_3$ addition, even in the absence of effluent phosphate limitation. However, the degree of inhibition was relatively low, ranging from 3 to 25% (approximately) for Fe doses in the range ca. 10 to 20 mg/ℓ as Fe, with an average system P removal of 14 to 18 mgP/ℓ in the control. $FeCl_2$-$FeCl_3$ dosing in this range was sufficient to produce additional P removal of the order of 1 to 8 mgP/ℓ over periods of one to seven sludge ages per experimental period, depending on the experimental conditions. Sustained operation of the BEPR mechanism in the presence of $FeCl_2$-$FeCl_3$ was possible over a continuous period of seven sludge ages, under conditions in which effluent phosphate was at least partially limiting. Under such conditions, the chemical and biological mechanisms appear to be "disadvantaged" to approximately the same extent, as evidenced by the apparent stoichiometry of Fe:P for the chemical precipitation and magnitude of the poly P containing fractions measured for the biological mechanism. This suggested that the biological mechanism is able to compete effectively with the chemical mechanism under conditions of low reactor phosphate concentrations (~1 mgP/ℓ orthoP) for sustained periods. However, the presence of simultaneous chemical precipitant significantly reduces the extent to which the biological P removal potential is utilised under P-limiting conditions. This could explain the difficulty sometimes reported in the control of full-scale activated sludge systems with simultaneous precipitant addition where a very low effluent P concentration (<1 mgP/ℓ) has to be achieved.

Nomenclature

D	Delta, meaning "difference in" or "change in" (e.g. DM,P_{rem} - see also below)
AE1 or 2	Aerobic zone or reactor
Fe~P~O	Ferric phosphate/ oxide precipitate (theoretical) after ashing of ferric hydroxy-phosphate
Fe~P~OH	Ferric hydroxy-phosphate
Alk.	Alkalinity (unless otherwise stated: *bicarbonate* alkalinity)
AN	Anaerobic zone or reactor
AX	Anoxic zone or reactor
Bicarb.	Bicarbonate (or sodium bicarbonate)
COD	Chemical oxygen demand
DSVI	Dilute sludge volume index
f	Filtered *(in italics)*
fP_t	Filtered total phosphate
$fP_{t,a}$	Filtered total phosphate, anaerobic zone or reactor
$fP_{t,b1\ or\ b2}$	Filtered total phosphate, first or second aerobic zone or reactor, respectively
$fP_{t,d}$	Filtered total phosphate, anoxic zone or reactor
ISS	Inorganic suspended solids
M,P_{rem}	Mass of phosphate removed (mgP/d)
M,P_{rel}	Mass of phosphate released (mgP/d)
N_{ae}	Concentration of ammonia in the effluent
N_{ai}	Concentration of ammonia in the influent
No_3	Concentration of nitrate
$No_{3,a}$	Concentration of nitrate in the anaerobic zone/ reactor
$No_{3,b1\ or\ b2}$	Concentration of nitrate in the first and second zone/ reactor, respectively
$No_{3,d}$	Concentration of nitrate in the anoxic zone/ reactor
$No_{3,e}$	Concentration of nitrate in the effluent
N_{te}	Effluent TKN concentration
N_{ti}	Influent TKN concentration
orthoP	Orthophosphate
O_t	Oxygen uptake rate (in mg/[ℓ·h])
PCA	Perchloric acid (fractionation studies)
poly P	Polyphosphate
$PO_{4,a}$	OrthoP concentration in the anaerobic zone
$PO_{4,b1}$ or $_{b2}$	OrthoP concentration in the first aerobic (b1) or second aerobic (b2) zone
$PO_{4,d}$	OrthoP concentration in the anoxic zone
$PO_{4,e}$	OrthoP concentration in the effluent
$PO_{4,i}$	OrthoP concentration in the influent
PSTs	Primary settling tanks (or primary sedimentation tanks)
P_{ti}	Influent total P concentration
P_{te}	Effluent total P concentration

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Received 14 November 2000.

P_{trem}	Total P concentration removed
P_{rel}	Total P concentration released (measured on filtered mixed liquor sample)
Q_i	Influent flow rate
Q_s	RAS (or s) recycle flow rate
rem	Removal/removed
RES	Residue (in fractionation studies)
SD	Sample standard deviation
S.G.	Specific gravity
S_{te}	Effluent (total) COD concentration
S_{ti}	Influent (total) COD concentration
SUP	Supernatant (in fractionation studies)
TKN	Total Kjeldahl nitrogen
TSS	Total suspended solids
VSS	Volatile suspended solids

Introduction

In Part 4 of this series of papers (De Haas et al., 2000a), the interaction between biological P removal and chemical P removal in an activated sludge system with simultaneous ferric chloride ($FeCl_3$) addition was examined. A major supplier of industrial chemicals for water and wastewater treatment in South Africa (*NCP Ultrafloc*) manufactures ferric (iron [III]) chloride by dissolving iron (including scrap iron) in hydrochloric acid to give a solution of mainly ferrous chloride, followed by oxidation of the ferrous ions to ferric ions using chlorine (Leopold, 1996). The option exists of removing a fraction of the (mainly) ferrous (iron [II]) chloride solution for commercial sale prior to the oxidation step. Work carried out by the Johannesburg City Council (Lötter, 1991) demonstrated the value of ferrous sulphate for simultaneous phosphate precipitation in nutrient removal plants, although the mechanism for the superior performance compared with ferric chloride could not be explained. Subsequently, many of the Johannesburg biological nutrient removal activated sludge plants were converted to ferrous chloride dosing (Leopold, 1996).

A review of the literature in Part 1 revealed that the oxidation of ferrous ions to ferric ions may be expected under aerobic conditions in an activated sludge plant (De Haas et al., 2000b). The theoretical oxygen demand for this reaction is small, namely 0.15 g O_2/ g Fe^{2+}. From the requisite supplementary P removal, the required iron dose would also be small (e.g. 5 to 10 mg/ℓ as Fe). This implies that the aeration requirement for iron oxidation would be negligible compared to that for carbonaceous removal and nitrification in a typical activated sludge plant. *[Yeoman et al. (1988) quoted an oxygen demand of 0.15 g O_2/ g Fe^{2+} from Singer (1970), stating that the oxygen demand is high and can cause operational problems. Taking the case of Darvill WWW in Pietermaritzburg (South Africa), with an average daily flow of 60 Mℓ/d, a typical maximum (dry weather) influent COD of 350 mgO_2/ℓ and TKN of 42 mgN/ℓ, at summer temperatures (ca. 22°C), the average total biological oxygen demand will not exceed approximately 21 400 kg O_2/d, excluding any oxygen "recovery" from denitrification (WRC, 1984). Assuming an additional 3 mgP/ℓ removal is required by dosing hypothetically pure ferrous chloride, and that a molar ratio of 2 mol Fe/mol P suffices, then the daily iron dose will be approx. 650 kg Fe/d. The oxygen demand for oxidation of the ferrous ions to ferric form will then be approx. 98 kg O_2/d, which is about 0.5% of the total biological oxygen demand in the system. This is a negligible contribution].*

In view of the above, and the potential for use of ferrous chloride in the full-scale plant at Darvill Wastewater Works (WWW) operated by Umgeni Water, it was decided to include in the study on simultaneous chemical P removal, a commercially available product comprising a blend of ferrous chloride and ferric chloride ($FeCl_2$/ $FeCl_3$). This product is manufactured by *NCP Ultrafloc* and typically contains approximately 90% of the total iron content in the ferrous form, with the remainder in the form of ferric chloride. Preliminary work with this product at pilot scale had indicated promise, giving not only good P removal, but also significantly better settling compared with ferric chloride (De Haas, 1998). The aim of this study was to test more fully the effect of this product on biological P removal initially at pilot scale, with a view to subsequent full-scale trials at Darvill WWW. This paper describes the results of the work at pilot scale. The full-scale trials were described by De Haas (1998).

Materials and methods

Pilot plant set-up

Two identical pilot-plant units (R1 as test and R2 as control) were set up and operated in the same manner as described in Part 3 (De Haas et al., 2000c). The only exception was that the units were operated at a sludge age of 10 d throughout for experimental periods using the $FeCl_2$-$FeCl_3$ blend.

Pilot-plant feed supplementation for enhanced cultures

The first period of dosing with $FeCl_2$-$FeCl_3$ blend followed on directly from a preceding period of $FeCl_3$ dosing (Period 3.3.6 described in Part 4 – De Haas et al., 2000a). An intervening operating period of 10 d (one sludge age) was allowed during which $FeCl_2$/ $FeCl_3$ was dosed, but no data were collected. Data collection started on 13/12/95 (Period 3.4.1).

For the $FeCl_2$/ $FeCl_3$ dosing periods, the influent supplements were not changed significantly from those used in the $FeCl_3$ dosing periods (Part 4). The acetate feed supplement was kept constant throughout at 150 mg/ℓ as COD except for periods with P limitation during which it was reduced to 20 mg/ℓ as COD (Table 1). Similarly, influent magnesium, potassium, and phosphate concentrations were held constant, except where P (and hence K) supplementation was withheld to create P-limiting conditions (Table 1). Influent alkalinity was supplemented in all periods (at 100 mg/ℓ $CaCO_3$) in the form of sodium bicarbonate. Hence, the main variations in influent composition were those due to the settled sewage sampled from the full-scale WWW. The main difference from $FeCl_3$ dosing periods was the lower influent acetate supplement for during times when influent P addition was withheld. *[The reason for this difference was that the P-limitation experiments with $FeCl_2$/ $FeCl_3$ blend were performed chronologically earlier than those with $FeCl_3$. Initially the aim was to reproduce the full-scale operation of Darvill WWW as closely as possible at pilot scale; 20 mg/ℓ COD as acetate (expressed on an influent flow basis) was fairly typical of what the side-stream fermentation system using primary sludge produced at this WWW. As will be shown here, the results of this study suggested that complete biological P removal could not be achieved at this low acetate dose for Darvill settled sewage. Hence, to achieve true P-limiting conditions, the acetate dose was increased in later experimental periods (with $FeCl_3$)].*

$FeCl_2$/$FeCl_3$ and acid dosing

$FeCl_2$/$FeCl_3$ chloride is supplied commercially by *NCP Ultrafloc* as a blend containing 12 to 14 % m/m total Fe, of which a *minimum* of 60% is guaranteed to be in the form of ferrous ions. In practice,

TABLE 1
Sewage supplement composition by experimental period
(Refer to Table 2 for relevant $FeCl_2$/ $FeCl_3$ and acid doses)

Period	Date range	No. of days	Na-acetate mg/ℓ as COD	K_2HPO_4 mgP/ℓ	$MgCl_2$ mg Mg/ℓ	K_2HPO_4 mg K/ℓ	$NaHCO_3$ mg/ℓ as $CaCO_3$
3.4.1	13/12/95 to 13/1/96	32	150	40	12.6	100	100
3.4.2	15/1/96 to 17/2/96	34	150	40	12.6	100	100
3.4.3	18/2/96 to 18/3/96	30	150	40	12.6	100	100
3.4.4	1/4/96 to 10/6/96	70	150	15	12.6	38	100
3.5.1	11/6/96 to 26/7/96	45	20	0	12.6	0	100
3.5.2	27/7/96 to 27/8/96	32	20	0	12.6	0	100

TABLE 2
Experimental periods of $FeCl_2$/$FeCl_3$ chloride and acid dosing to pilot plants
Target influent flow rate = 36 ℓ/d throughout. Sludge age = 10 d throughout.

Period name	Date range	No. of days	Zone with $FeCl_3$/ acid	$FeCl_2$/$FeCl_3$ dose to R1 (test) unit (mmol/d as Fe)	Acid (HCl) dose (mmol/d)
3.4.1 High Fe	13/12/95 to 13/1/96	32	AE1	12.4	10
3.4.2 Low Fe	15/1/96 to 17/2/96	34	AE1	6.2	10
3.4.3 Low Fe	18/2/96 to 18/3/96	30	AN	6.2	10
3.4.4 Low Fe Partial P limitation	1/4/96 to 10/6/96	70	AE1	6.2	0.5
3.5.1 Low Fe Partial P limitation	11/6/96 to 26/7/96	46	AE1	6.2	0.5
3.5.2 Low Fe Partial P limitation	27/7/96 to 27/8/96	32	AN	6.2	0.5

the product ranges from 85 to 95% Fe [II] (Reynolds, 1996). Like ferric chloride, the product contains approx. 0.5 to 1.0 % free HCl.

Two batches of $FeCl_2$/$FeCl_3$ chloride blend supplied by *NCP Ultrafloc* were used. *[The ferrous-ferric chloride blend could not be stored for extended periods (more than 4 months) because it was found that a precipitate formed in the concentrated stock solution. The composition of this precipitate was not determined, but its reddish-brown colour suggested that it was an oxide. By comparison, the ferric chloride solution was stable and did not give a precipitate, even after storage under identical conditions for over a year]*. Upon analysis by atomic absorption spectrometry, the first batch of $FeCl_2$/$FeCl_3$ chloride was found to contain 13.3 % m/m total Fe, and had an S.G. of 1.30 kg/ℓ, while the second contained 12.4 % m/m total Fe and had an S.G. of 1.32 kg/ℓ. A suitable stock solution (80 to 85 mℓ per ℓ) of this product was prepared using deionised water containing approximately 0.02M HCl. The HCl ensured that the solution remained acidic and the precipitation reaction was retarded. This stock solution lasted for approximately one month, with one aliquot of 25 mℓ/d supplying 6.2 mmol Fe/d and approx. 0.5 mmol/d as HCl to the pilot plant R1 (test unit). The daily aliquot (25 mℓ) was further diluted to 500 mℓ with tap water and dosed into the anaerobic (AN) or first aerobic (AE1) zone of the test unit. For consistency with earlier work (Parts 3 and 4), a small amount of acid was added to the Fe solution before dilution with tap water to preclude iron hydroxide precipitation. For this reason, 10 mmol/d of HCl was added to the diluted solution of $FeCl_2$/$FeCl_3$ dosed to R1, and the same amount of acid was fed with tap water only to R2, also at a rate of 500 mℓ/d. An acid dose of 10 mmol/d as HCl is equivalent to 14 mg/ℓ as HCl, based on an influent flow rate of 36 ℓ/d. This was considered to be small in relation to the influent alkalinity supplement of 100 mg/ℓ as $CaCO_3$. However, it was subsequently found that the supply of 0.02M HCl in the first dilution of $FeCl_2$/$FeCl_3$ blend (see above) was sufficient to prevent precipitation of iron hydroxide upon dilution to 500 mℓ with tap water. This lower acid dose was equivalent to 1 mmol/d (or 1.4 mg/ℓ as $CaCO_3$) - a negligible amount. Accordingly, the dosing of additional acid (10 mmol/d) to both test and control units was stopped in Period 3.4.4 (Table 2).

Table 2 gives the actual dosage rates applied for the respective experimental periods. Assuming a molar ratio of 0.5 mol $P_{removed}$/ mol Fe_{dosed} in the precipitation reaction, a dose of 6.2 mmol Fe/d or 12.4 mmol Fe/d translates into an expected additional P removal of 2.7 and 5.4 mgP/ℓ respectively at an influent flow rate of 36 l/d. As with alum and ferric chloride dosing (Parts 3 and 4), this appeared to be a reasonable target for "low" and "high" iron dosage rates on the basis of full-scale operating experience at Darvill WWW (De Haas et al., 2000a, c).

TABLE 3
Summary of P removal due to $FeCl_3$ measured in pilot plants
Pt_{rem} implies TP removal (Influent - Effluent). R1 : Fe dosed; R2 : Control.

Period	Data	Fe dose mmol/d	Zone	$P_{trem,R1}$ mgP/ℓ	$P_{trem,R2}$ mgP/ℓ	$P_{trem'R1} - P_{trem'R2}$ mgP/ℓ	DM($P_{trem,R1} - P_{trem'R2}$) mgP/d	Observed stoichiometry mol P_{rem}/ mol Fe_{dosed}
3.4.1	Average	12.4	AE1	25.6	17.8	7.8	289	0.75
	n			19	19	19	19	19
	SD			4.6	4.5	2.8	101	0.26
	95% CL, upper			-	-	-	338	0.88
	95% CL, lower			-	-	-	240	0.62
3.4.2	Average	6.2	AE1	20.8	17.0	4.2	144	0.75
	n			23	24	22	23	23
	SD			4.4	4.8	4.0	139	0.72
	95% CL, upper			-	-	-	205	1.06
	95% CL, lower			-	-	-	84	0.44
3.4.3	Average	6.2	AN	20.5	11.7	8.9	336	1.75
	n			20	19	19	19	19
	SD			4.0	3.8	2.0	64	0.33
	95% CL, upper			-	-	-	367	1.91
	95% CL, lower			-	-	-	306	1.59
3.4.4 Partially P limited	Average	6.2	AN	15.5	14.4	1.1	39	0.20
	n			42	42	40	40	40
	SD			2.9	2.9	1.3	52	0.27
	95% CL, upper			-	-	-	55	0.29
	95% CL, lower			-	-	-	22	0.11
3.5.1 Partially P limited	Average	6.2	AN	6.5	4.4	2.2	80	0.41
	n			25	25	21	21	21
	SD			3.3	3.7	0.9	33	0.17
	95% CL, upper			-	-	-	95	0.49
	95% CL, lower			-	-	-	64	0.34
3.5.2 Partially P limited	Average	6.2	AE1	8.2	7.0	0.8	31	0.16
	n			21	21	18	18	18
	SD			1.8	2.3	0.9	38	0.20
	95% CL, upper			-	-	-	49	0.26
	95% CL, lower			-	-	-	12	0.06

n: no. of observations; SD: Standard deviation; CL: Confidence limit

Parameters measured

All parameters were measured in the same manner as described in Part 3 of this series of papers (De Haas et al., 2000c).

Chemical fractionation of sludge samples

Fractionation and anaerobic batch P release tests were carried out according to the procedure described in Table 9 of Part 2 of this series of papers (De Haas et al., 2000d).

Results and discussion

Results for $FeCl_2/FeCl_3$ dosing with influent phosphate supplement

A summary of the results for the $FeCl_2/FeCl_3$ dosing periods is given in Table 3. A complete set of experimental results is given in Appendix A (Tables A1 to A4).

With few exceptions, total P removal was greater in R1 (iron dosed) than R2 (control), at both low and high $FeCl_2/FeCl_3$ doses. For Periods 3.4.1 to 3.4.3, where phosphate was never limiting (i.e. effluent contained well in excess of 1 mgP/ℓ soluble P), $FeCl_2/FeCl_3$ produced the largest improvement in P removal (Tables 3 and A4).

TABLE 4
Comparison of P release in anaerobic reactors (on mass basis) between test (R1) and control (R2) systems, expressed as a percentage (R1/R2)

Period	PO4e mgP/ℓ		MPrel(R1)/MPrel(R2) %				n
	Mean (SD) : R1	Mean (SD) : R2	Mean	SD	95% upper conf. limit	95% lower conf. limit	
3.4.1	16.57 (3.08)	23.12 (5.07)	131	156	235	26	11
3.4.2	22.69 (4.92)	25.61 (5.61)	91	9	114	86	13
3.4.3	21.25 (3.45)	29.55 (3.07)	108	8	114	102	9
3.4.4	1.14 (1.12)	2.10 (2.04)	81	5	84	79	23
3.5.1	3.07 (2.09)	5.15 (2.70)	97	142	172	21	16
3.5.2	1.29 (1.14)	2.31 (2.00)	58	9	64	51	10

SD: Standard deviation; n: no. of observations

As will be discussed below, where phosphate was "partially" limiting (i.e. effluent soluble P concentrations sometimes fell below 1mgP/ℓ), a smaller improvement in P removal was recorded.

A very noticeable drop in P removal performance in the unit R2 (control) occurred during Period 3.4.3. Whereas in Periods 3.4.1 and 3.4.2 P removal in the R2 averaged approximately 17 to 18 mgP/ℓ, during Period 3.4.3 P removal in R2 averaged less than 12 mgP/ℓ while that in R1 (the test unit) showed little change relative to the preceding period (Table 3). The reasons for weaker biological P removal performance in the control unit during this period were not immediately apparent during the experimental investigation. However, circumstantial evidence suggested that the underlying cause was the influent characteristics arising from the source of settled sewage. The sewage composition at Darvill WWW tends to be very variable in summer when rainfall in the catchment often leads to severe ingress of stormwater and/ or groundwater to the collection system. Late December 1995 and January 1996 were characterised by high rainfall in the catchment of Darvill WWW. It is normal operational practice at this WWW to divert surplus wet weather flows (ca. >3 x ADWF) to a storm dam. When the storm dam is full (as it was through most of January 1996 until the second week of February 1996), the excess sewage overflows from the storm dam to the adjacent river. When flow conditions and capacity permit, the storm dam contents are pumped back into the Works for treatment. For the period under review, this began in the first 10 days of February 1996 (i.e. during Period 3.4.2), but was interrupted again by heavy rain in the second and third week of February. The pumping of sewage back from the dam was accomplished mainly in March 1996 (i.e. during Period 3.4.3) as the summer rains came to an end. It is possible that pumping back septic sewage from the storm dam during February-March 1996 caused increased sulphide concentrations in the influent to the WWW, from which the feed to the pilot plants was derived. The sulphide content of the influent was not measured, but the black colour and septic smell (suspected sulphides) of the influent was noted on several occasions during the period in question. Sulphide (or H_2S) has been identified as a likely inhibitor of biological P removal (Comeau et al., 1986; Hartley et al., 1999). Dosing with $FeCl_2/FeCl_3$ appeared to ameliorate the negative effect on P removal. Assuming that influent sulphide was implicated in the observed decrease in P removal, it is likely that the formation of insoluble FeS in the mixed liquor would reduce the impact on the biological mechanism. This would have been particularly likely during Period 3.4.3 when ferrous ions were dosed directly to the anaerobic zone of R1 (test unit).

It is worth noting that the DSVI in R2 (control) also increased significantly during Period 3.4.3, relative to the preceding periods and to R1 (test unit) (Table A2). It therefore appeared that during this period poorer sludge settleability was linked with weakened biological P removal. Dosing with $FeCl_2/FeCl_3$ also appeared to ameliorate the negative effect on settleability. The positive effect of iron dosing on settleability (based on DSVI) was true for all the $FeCl_2/FeCl_3$ dosing periods (Table A2).

Mass balances

Overall mass balances for COD, N and P

The mass balances (Appendix A, Table A3) for COD and N removal were satisfactory (100% ± 15) for most periods (mean COD = 103% ±6; mean N = 95% ±10). However, for phosphorus the mass balances for Periods 3.4.1 through 3.4.3 and Period 3.5.1 were frequently greater than 100%, ranging from 101 to 196%. Confidence in the results for these periods is, therefore, somewhat reduced. The problem may have stemmed from a failure to achieve steady-state operation of the pilot plants during the experimental periods in question. For example, during Periods 3.4.1 to 3.4.3, each covering about three sludge ages, P removal performance was variable for reasons largely related to a variable source sewage composition (as discussed above). This was reflected also in the relatively large standard deviations for P content of the mixed liquor (see P/VSS in Table A3). The longest experimental period with the most stable plant operation (Period 3.4.4 spanning seven sludge ages) gave good P mass balances (Table A3).

P mass balance around the anaerobic reactor

From mass balance considerations around the anaerobic reactor it can be shown that:

$$M,P_{rel} = [(Q_i + Q_s).\, fP_{t,a}] - [Q_i.P_{ti} + Q_s.P_{te}] \qquad (1)$$

where M,P_{rel} is the mass of P released to the (filtered) supernatant in the anaerobic zone.

Using the measured data given in Tables A2 and A3 (Appendix A) and Eq 1 with $Q_i = Q_s$ (1:1 s-recycle ratio), P release in the anaerobic zone of the test unit (R1) could be calculated and

expressed as a percentage of that in the control unit. A result of 100% would indicate no inhibition of P release in the test unit relative to the control. The results are given in Table 4 and can be compared to effluent soluble orthophosphate concentrations (PO_4e).

The data in Table 4 show that large variances in the data were observed for some periods, as reflected in the wide range in 95% confidence intervals. This was particularly true for Periods 3.4.1 and 3.5.1. Since these periods also showed poor P mass balances, the results for these periods must be treated with caution. The results for Periods 3.4.2 and 3.4.3 show smaller variance with the 95% confidence interval for the mean ratio of P release (R1/R2) spanning 100%. This suggests that for these periods (without effluent P limitation), inhibition of P release in R1 in the presence of $FeCl_2/FeCl_3$ dosing (test unit) was minimal or absent. Alternatively, inhibition of the biological P removal mechanism in the control system due to extraneous factors such as influent characteristics (see above) could explain why the magnitude of P release in the anaerobic zone of the two systems in these periods was similar. By contrast, Periods 3.4.4 and 3.5.2 (during which effluent P limitation occurred at times), showed better P mass balances and smaller variances in the data. The results for these Periods suggest that inhibition of P release in the test unit was significant (approximately 20 to 40% inhibition) when P was at least partially limiting. The greatest degree of inhibition of P release was found for Period 3.5.2 after an extended operating period (nearly fifteen sludge ages) with sustained iron dosing and low effluent P concentrations. Interestingly, Period 3.5.2 also gave the lowest observed stoichiometry for $P_{removed}$:Fe_{dosed} (Table 3).

Molar ratios of P removed/ Fe dosed and point of dosing

Calculation of the average molar ratio of $P_{removal}$/ Fe_{dosed} in Table 3 is based on the assumption that the difference in system P removal between R1 (test) and R2 (control) is *only ascribable to chemical addition*. As discussed in Part 4 (De Haas et al., 2000a), the measured system P removal (Table 3) may not be a reliable indicator of precipitation stoichiometry. The difference in system P removal between R1 (test system) and R2 (control) is a measure of the *combined* chemical and biological removal. Hence, for example, at low effluent P concentrations (e.g. Periods 3.4.4 and 3.5.2), the apparent "precipitation efficiency" is greatly reduced, to the point that the system P removal in R1 (test system dosed with iron) approaches that of R2 (control). This may be partly due to inhibition of the biological mechanism, but partly also due to chemical precipitation being less efficient at low P concentrations. For this reason, fractionation of the mixed liquor was applied as an independent method of estimating the sizes of the chemical and biological phosphate "pools" (see below).

Alkalinity and pH considerations

The acidity of the $FeCl_2/FeCl_3$ blend (0.5 to 1% free acid as HCl in the product supplied) as well as alkalinity consumed in the precipitation process may be significant. In this study it was found that the effluent bicarbonate alkalinity in R1 (ferrous-ferric dosed) was consistently lower than in R2 (control), but the difference was small, in the range 8 to 22 mg/ℓ as $CaCO_3$ (Appendix A, Table A1). This difference was smaller than that obtained for ferric dosing (Part 4 – De Haas et al., 2000a), which may be significant for applications where a relatively low influent alkalinity requires lime dosing on a routine basis.

The oxidation of ferrous ions to ferric ions involves a *gain* in alkalinity (theoretically +0.89 mg as $CaCO_3$/ mg Fe, according to Loewenthal et al., 1986). The precipitation of ferric hydroxide involves a *loss* of alkalinity which theoretically is (-)0.92 mg as $CaCO_3$/ mg $FeCl_3$ (Loewenthal et al., 1986), or (-)2.67 mg as $CaCO_3$/ mg Fe. Assuming that typically 90% of the total Fe in the blend is in the ferrous form when dosed (Reynolds, 1996), and that all the ferrous ions are oxidised to ferric form, followed by precipitation as the hydroxide, the *net alkalinity loss* would be (-)1.87 mg as $CaCO_3$/mg Fe. From the information in **Materials and methods** and Table A1, it can be calculated that the observed mean alkalinity loss (R1 compared to R2) was 1.7 mg $CaCO_3$/ mg Fe for Periods 3.4.2 to 3.5.2 when the Fe dose was low (6.2 mmol/ d) and 1.0 mg $CaCO_3$/ mg Fe for Period 3.4.1 when the Fe dose was high (12.4 mmol/d). These data suggest that at the lower iron doses the alkalinity consumption was in broad agreement with the theoretical amount for iron hydroxide formation.

With the benefit of supplemented influent alkalinity to the pilot plants (Table 1), the data in Table A1 show that the pH in the anaerobic zone generally remained above 7.0, and there was little statistical difference between the behaviour of R1 compared to R2 in this respect, even when the anaerobic zone (of R1) was dosed with the ferrous-ferric blend. There was a slight tendency for the pH of the aerobic zones to be lower in R1 than R2 (Table A2), which may be expected since the ferrous-ferric dosing still produced a net alkalinity demand. However, this difference never exceeded 0.11 pH units on a median basis and was considered to be insignificant.

Accepting that ferrous (Fe[II]) ions dosed are oxidised in the activated sludge system to Fe[III] ions (De Haas et al., 2000b), empirical formulae for ferric hydroxy phosphate may be developed for the overall precipitation reaction. Luedecke et al. (1989) suggested the following general formula for ferric hydroxy-phosphate:

$$Fe_rPO_4\,(OH)_{3r-3}$$

From the experimental data discussed above, excluding any theoretical alkalinity recovery from the iron oxidation reaction, the iron precipitate which formed consumed approximately 1.8 to 2.5 mg as $CaCO_3$/mg Fe alkalinity (or 2 to 2.8 mol OH/mol Fe). The observed additional P removed as orthoP (from fractionation data for periods without P limitation - refer below and to Table 7) was in the order of 0.66 mol P/mol Fe dosed. From these observations, an alternative theoretical formula for ferric hydroxy phosphate may be proposed which includes X^{2+} as some unknown (possibly divalent) cation, such as calcium or magnesium:

$$Fe_r\,(X^{2+})\,PO_4\,(OH)_{3r-1}$$

Substituting a value of r = 1.33 to 1.66 (approximately) into this theoretical formula satisfies the observed alkalinity, Fe and P removal data for periods of dosing the ferrous-ferric chloride blend. The resultant formula is similar to that estimated for alum and ferric chloride dosing by the same means in Parts 3 and 4 respectively (De Haas et al., 2000a & c).

Fractionation studies

Periods without P limitation

The results of fractionation studies for Periods 3.4.1 through 3.4.3 are summarised in Table 5 and Fig. 1. These results show that $FeCl_2$-$FeCl_3$ increased the orthoP ("chemical precipitate") fraction of the sludge between two and six fold such that it came to represent between 19% and 39% of the combined "chemical" and "biological"

TABLE 5
Fractionation data for periods of $FeCl_2$-$FeCl_3$ dosing without P limitation. Percentages in parentheses are relative contributions to total P of mixed liquor solids (i.e. sum of extracts, including residue (RES) fraction but excluding supernatant (SUP) fraction)

Date, Unit	Period	Ferric dose, zone dosed Low = 9.6 mg/ℓ High = 19.2 mg/ℓ as Fe based on target influent flow = 36 ℓ/d see Table 2	PCA Complex P mgP/gVSS "Biological"	NaOH Complex P mgP/gVSS "Biological"	Sum of PCA and NaOH Complex P fractions mgP/gVSS Note 1 "Total Biological"	Sum of PCA and NaOH orthoP fractions mgP/gVSS Note 1 "Chemical"	VSS during fraction-ation g/ℓ	Inhibition (-) or stimulation (+) of biological fractions (PCA + NaOH) % (R1/R2) Note 2	Inhibition (-) or stimulation (+) of biological PCA fraction only % (R1/R2) Note 2
10/1/96, R1	3.4.1	High, AE1	4.45	175.99	**180.44** ***(56%)***	**143.578** ***(44%)***	**0.833**	**-13%**	**-98%**
10/1/96, R2		-	186.29	19.86	206.15 *(89%)*	24.834 *(11%)*	0.766	-	-
7/2/96, R1	3.4.2	Low, AE1	146.66	55.61	**202.27** ***(80%)***	**49.63** ***(20%)***	**0.907**	**-3%**	**-19%**
7/2/96, R2		-	180.86	27.40	208.27 *(90%)*	24.052 *(10%)*	0.866	-	-
18/2/96, R1	3.4.2/3	Low, AE1	148.83	34.96	**183.79** ***(81%)***	**44.22** ***(19%)***	**0.957**	**+10% ***	**+2% ***
18/2/96, R2		-	146.61	20.69	167.30 * *(91%)*	15.93 *(9%)*	0.888	-	-
18/3/96, R1	3.4.3	Low, AN	169.39	31.59	**200.98** ***(61%)***	**126.51** ***(39%)***	**0.906**	**+20% ***	**+14% ***
18/3/96, R2		-	148.44	17.66	166.1 * *(89%)*	21.48 *(11%)*	0.683		

* : Partial inhibition of biological P removal mechanism may have occurred during Period 3.4.3.
Note 1: (%) Percentages in parentheses refer to % of sum ("Total Biological" + "Chemical")
Note 2: Percentages, e.g. -5%, refer to percent inhibition of R1 fractions, relative to R2

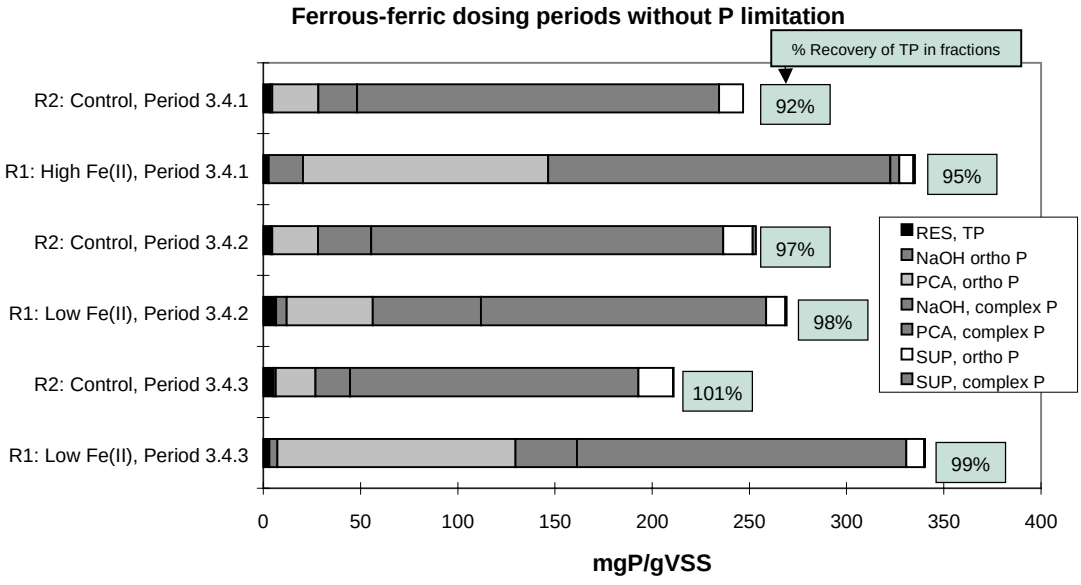

Figure 1
Fractionation data for periods of $FeCl_2$-$FeCl_3$ dosing without P limitation

P fractions in the sludge at the low ferric dose, and 44% on the same basis at the high ferric dose. In a similar manner to $FeCl_3$ (De Haas et al., 2000a), dosing with $FeCl_2$-$FeCl_3$ caused the acid extractable (PCA) complex P fraction to decrease in size (by 19% at low Fe dose and by up to 98% at high Fe dose). In the same manner as for $FeCl_3$, the corresponding alkaline-extractable complex P fraction increased (Table 5). The increased size of this fraction was particularly noticeable at a high Fe dose, when it predominated (Table 5). These observations are linked with the finding in Parts 2 and 4 of this series of papers (De Haas et al., 2000 a & d) that the speciation of complex P between the PCA and NaOH extracts is largely an artefact of the fractionation procedure itself. *[Batch P release tests performed on mixed liquor samples taken from $FeCl_2$-$FeCl_3$ dosing periods confirmed that both the PCA and NaOH complex P fractions are biologically active - data not shown]*. Therefore, the *sum* of these two complex P fractions should be taken as representing the magnitude of the biologically stored P. Table 5 suggests that the sum of the biological (complex P) fractions was not "inhibited" (depressed) by more than 13% in the R1 (test unit) relative to R2 (control).

The data in Table 5 also confirmed that during Period 3.4.3, inhibition of the biological (complex P) fractions was evident in R2 (the control), compared with R1 (the test system). Influent characteristics during this operational period appeared to be the cause, as discussed above. Accordingly, the results for Periods 3.4.2 and 3.4.3 should not be taken as being representative of typical P removal performance with $FeCl_2$-$FeCl_3$ addition. Nevertheless, these results do indicate that in the presence of $FeCl_2$-$FeCl_3$ addition, the biological P removal mechanism appeared to be "protected" to some extent from the apparent inhibitory effects seen in the control unit (e.g. precipitation of FeS preventing inhibition of the biological mechanism from aqueous sulphides).

Anaerobic batch P release tests in the presence of excess acetate (data not shown here) indicated that there was a tendency for $FeCl_2$-$FeCl_3$ dosing (particularly at high dose) to produce surplus chemical adsorption/ precipitation capacity for phosphate in the mixed liquor. This was evident from an increase in the orthoP fractions when comparing results before with those after the batch tests. The *net* P release to the *supernatant* in the batch tests for R1 (test unit) were slightly depressed (10 to 23%) relative to R2 (control) in two of the four experiments, while in the other two experiments, the release was equivalent (or slightly higher) in R1 than R2. The *net P change* (or sum of release and uptake) in the respective fractions implied that P release from R1 (test) was depressed by approximately 15 to 22% at most, compared with the control (R2). Taking account of the apparent uptake in the orthoP fractions by counting it as part of the total biological P release, the *total* release of P from the sludge was never depressed by more than 16%, relative to the control. On the same basis, one mixed liquor sample taken at high ferric dose from the test unit (15/8/95) showed significantly more *total* release of P (~16% more than the control). However, the apparent lack of steady state (poor mass balances) for most of these experimental periods suggest that caution in the acceptance of these results.

In summary, subject to the limitations of the data, it may be concluded that the fractionation results and batch P release test results are in agreement. In the absence of P limitation, the extent of inhibition of the biological P removal mechanism in the presence of $FeCl_2$-$FeCl_3$ dosing was probably less than 20%. Evidence was found of accumulation in the mixed liquor solids of surplus chemical binding capacity for phosphate (especially at high iron dose). Similarly, the bio P removal mechanism in the test system with iron dosing appeared to be more resilient to inhibition than in the control, apparently resulting from septic influent (e.g. aqueous sulphides).

Periods with P limitation

The results of fractionation studies for Periods 3.4.4 and 3.5.2 are summarised in Table 6 and Fig. 2. (For brevity, the results for Period 3.5.1 have been omitted, considering the fairly poor P mass balance for this period and the relatively high or variable effluent P concentrations - i.e. operating conditions which were usually not P limiting).

During Period 3.4.4 the influent to both units continued to be supplemented with sodium acetate (150 mg/ℓ as COD), but the added phosphate was limited to 15 mgP/ℓ. The effect was to produce an effluent with low P concentrations (Table A4) and hence to stimulate "competition" between the biological and chemical mechanisms for residual dissolved orthophosphate. Comparing Figs. 1 and 2 or Tables 5 and 6, it is clear that the P content of the mixed liquor (P/VSS) decreased in both units as a result of the partial P limitation. The R1 (test unit) almost always showed a higher P content (P/VSS basis) than R2 (control) during periods without P limitation (Fig. 1 and Table A3), whereas during periods with P limitation this was no longer true. The data for Periods 3.4.4 and 3.5.2 (Fig. 2 or Table A3) showed similar combined P removal in R1 (test unit) relative to R2 (control). The phosphate of the mixed liquor (P/VSS basis) in R1 was closely similar to (and sometimes slightly less than) that in R2 (control). The "biological" (PCA + NaOH complex P) fractions in R1 (test unit) relative to R2 (control) were "inhibited" to a slightly greater degree (18% to 25%), compared to periods without P limitation (Tables 5 and 6). Similarly, the fractionation data from batch tests showed that biological P release was depressed by between 5 and 28%, depending on whether apparent uptake in the minor fractions is counted as part of the biological release or not. Minor P uptake into one of the fractions (PCA orthoP) after the P release test was apparent in most cases, particularly for R1 (iron dosed). This suggests that orthoP may "migrate" between the biological and chemical P "pools" to some extent, especially where iron dosing results in spare adsorption/precipitation potential in the mixed liquor solids (e.g. in the form of iron hydroxide).

Seen as a whole, the fractionation data imply that the BEPR mechanism may have been depressed (or "inhibited") to a slightly greater extent when competing for available phosphate with the chemical mechanism, relative to periods without P limitation. Nevertheless, at the low Fe dose applied, the biological mechanism was still able to compete quite effectively against the chemical mechanism. This can be seen by comparing the relative sizes of the "biological" vs. "chemical" fractions overall. For periods with P limitation, the chemical fractions contributed between 19% and 29% of the combined biological and chemical fractions (Table 6), which is similar to values of 19% to 39% *[refer to earlier comments on poor BEPR performance during Period 3.4.3]* for periods without P limitation but the same Fe and acetate dose (Table 5). As would be expected, where the acetate dose was decreased but Fe dose left unchanged (Period 3.5.2), the system P removal in both test and control units decreased (Table A2) and the chemical fraction contributed *relatively* more to the combined chemical and biological P removal (45% in Table 6).

In summary, Table 6 shows that under low effluent P conditions, the BEPR component in the test unit with $FeCl_2$-$FeCl_3$ dosing appeared to be depressed to some extent compared to the control. However, the chemical P removal component in the test unit was also smaller under partially P limited conditions, compared to periods without P limitation at the same Fe dose. Therefore, the

TABLE 6
Fractionation data for periods of $FeCl_2$-$FeCl_3$ dosing with P limitation. Percentages in parentheses are relative contributions to total P of mixed liquor solids (i.e. sum of extracts, including residue (RES) fraction but *excluding supernatant (SUP) fraction)*

Date, Unit	Period	Ferric dose, zone dosed Low = 9.6 mg/ℓ High = 19.2 mg/ℓ as Fe based on target influent flow = 36 ℓ/d see Table 2	PCA Complex P mgP/gVSS "Biological"	NaOH Complex P mgP/gVSS "Biological"	Sum of PCA and NaOH Complex P fractions mgP/gVSS Note 1 "Total Biological"	Sum of PCA and NaOH orthoP fractions mgP/gVSS Note 1 "Chemical"	VSS during fraction-ation g/ℓ	Inhibition (-) or stimulation (+) of biological fractions (PCA + NaOH) % (R1/R2) Note 2	Inhibition (-) or stimulation (+) of biological PCA fraction only % (R1/R2) Note 2
28/5/96, R1	3.4.4	Low, AE1	55.49	47.99	**103.48 (71%)**	**41.56 (29%)**	**0.991**	**-18%**	**-52%**
28/5/96, R2		-	116.25	27.56	143.81 (92%)	11.98 (8%)	0.983	-	-
11/6/96, R1	3.4.4	Low, AN	42.75	48.07	**90.82 (81%)**	**21.34 (19%)**	**1.325**	**-25%**	**-57%**
11/6/96, R2		-	98.72	22.64	121.36 (96%)	4.62 (4%)	1.225	-	-
21/8/96, R1	3.5.2	Low, AN	0.59	36.56	**37.15 (55%)**	**30.23 (45%)**	**1.109**	**-22%**	**-98%**
21/8/96, R2		-	29.65	17.95	47.6 (82%)	10.27 (18%)	1.110		

Note 1: (%) Percentages in parentheses refer to % of sum ("Total Biological" + "Chemical")
Note 2: Percentages, e.g. -5%, refer to percent inhibition of R1 fractions, relative to R2

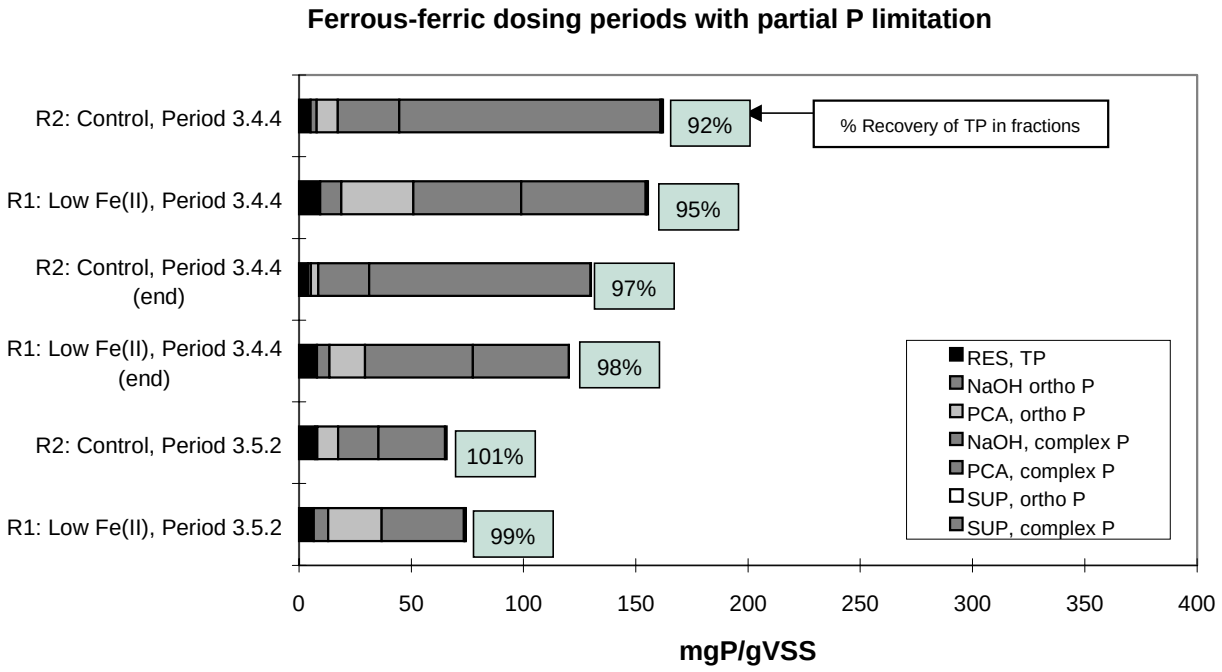

Figure 2
Fractionation data for periods of $FeCl_2$-$FeCl_3$ dosing with (partial) P limitation

TABLE 7
Estimation of molar ratio of additional P removed as chemical precipitate (PCA and NaOH extract orthoP fractions) versus iron dosed as $FeCl_2$-$FeCl_3$

UNIT/FERRIC	Date	PCA + NaOH orthoP fractions * mgP/gVSS	Ave. VSS for period g/ℓ	VSS wasted g/d	PCA + NaOH orthoP wasted mgP/d	Difference (R1-R2) PCA + NaOH orthoP wasted mgP/d	Fe dosed mmol/d	mol P /mol Fe (This table)	mol P /mol Fe (Table 3)
Without P limitation									
R1: High Fe: 3.4.1	1/6/95	143.57	1.332	4.262	611.97	523.92	12.4	1.36	0.75
R2: 3.4.1		24.83	1.108	3.546	88.05				
R1: Low Fe: 3.4.2	7/2/96	49.63	0.999	3.197	158.65	90.00	6.2	0.47	0.75
R2: 3.4.2		24.05	0.892	2.854	68.65				
R1: Low Fe: 3.4.2	18/2/96	44.22	0.999	3.197	141.36	95.89	6.2	0.50	0.75
R2: 3.4.2		15.93	0.892	2.854	45.47				
R1: Low Fe: 3.4.3	18/3/96	55.86	0.901	2.883	161.06	130.02	6.2	0.68	1.75
R2: 3.4.3		12.42	0.781	2.499	31.04				
With P limitation									
R1: Low Fe: 3.4.4	3/5/96	46.31	0.939	3.005	139.15	107.31	6.2	0.56	0.2
R2: 3.4.4		10.53	0.945	3.024	31.84				
R1: Low Fe: 3.4.4	28/5/96	41.56	0.939	3.005	124.88	88.65	6.2	0.46	0.2
R2: 3.4.4		11.98	0.945	3.024	36.23				
R1: Low Fe: 3.4.4	11/6/96	21.34	0.939	3.005	64.12	50.15	6.2	0.26	0.2
R2: 3.4.4		4.62	0.945	3.024	13.97				
R1: High Fe: 3.5.1	9/7/96	29.38	1.078	3.450	101.35	76.40	6.2	0.40	0.41
R2: 3.5.1		8.08	0.965	3.088	24.95				
R1: Low Fe: 3.5.2	21/8/96	30.23	1.061	3.395	102.64	70.27	6.2	0.37	0.16
R2: 3.5.2	08/21/96	10.27	0.985	3.152	32.37				

relative ratio of the biological and chemical mechanisms showed little change for equivalent dosing conditions with and without P limitation. Confirmation of the "efficiency" of the chemical mechanism can be obtained by examining the Fe:P stoichiometry calculated from the fractionation data.

Estimation of chemical precipitate stoichiometry from fractionation data

Table 7 compares the additional P removal as chemical precipitate with the metal dose on a molar basis, as estimated from the sludge orthoP fractionation data. The results from Table 7 may be compared with those found on the basis of the difference in system P removal between the two units (Table 3). Comparing the two sets of estimated precipitate stoichiometry (P/Fe ratio), it can be seen that there are discrepancies in the results for certain periods:

- In Period 3.4.1 the P/Fe molar ratio estimated using the fractionation data was much greater than that estimated from the system P removal (Table 7). This discrepancy probably arose from a failure of the test system to reach satisfactory steady-state after the change from the previous experimental period (Period 3.3.6 when $FeCl_3$ was dosed). The poor P mass balances (Table A3) and solids data (Table 8) for Period 3.4.1 substantiate this.
- In Periods 3.4.2 and 3.4.3 (at the lower Fe dose) the P/Fe stoichiometry estimated using fractionation data showed an increase with time from 0.47 to 0.68 (Table 7). Again this probably reflects slow equilibration of solids in the test system toward steady-state, as borne out by the relatively poor P mass balances. Nevertheless, for Period 3.4.2 it is interesting to note that the fractionation data P/Fe stochiometry accounted for 60 to 66% of that calculated from system P removal. This is a similar observation to that for $FeCl_3$ under equivalent acetate, P and Fe dosing conditions (Part 4 – De Haas et al., 2000a).
- In Period 3.4.3, as previously discussed, biological P removal in R2 (control) was weakened, probably due to influent characteristics stemming from the source sewage at the time. As expected, this affected the molar ratio estimate of the precipitate based on system P removal (Table 3), but not that based on fractionation data (Table 7).

For the remainder of the experimental periods, the data in Table 7 showed better agreement between the P/Fe stoichiometry estimated by the two methods. Both methods suggested that the precipitation efficiency is lower under conditions where low effluent P concentrations occur (i.e. as the system approaches P limitation). Under high effluent P conditions (ca. 20 mgP/ℓ), the P:Fe molar ratio appeared to be approximately 0.7 (based results for 18/3/96 at the end of Period 3.4.3 as being closest to steady state). For low effluent P concentrations (ca. 1 mgP/ℓ), the P:Fe molar ratio fell into the range ~0.2 to 0.4, based on the fractionation results at the end

of Period 3.4.4, as well as for Periods 3.5.1 and 3.5.2. Similar results were found from the system P removal data, based on the average results for these experimental periods (Table 3). *[Individual sub-periods of Period 3.4.4 showed more variation in the data based on differences in system P removal, which probably reflects limitations in accuracy of the vanadate-molybdate total P method at low concentrations (< 1 mgP/ℓ), as used at the time. In subsequent experimental periods (Periods 3.6.1. and 3.6.2, Part 4 - De Haas et al., 2000a), the more sensitive molybdate-ascorbic acid method was used].*

Sludge production

In terms of VSS production, the test (R1) and control (R2) units showed significant differences. During Period 3.4.1 (high Fe dose), VSS production was 20% greater in the test unit than the control (Table A2). At low Fe dose (Periods 3.4.2 and 3.4.3), additional VSS production in the test unit was not as large (12 to 15%). In Periods 3.5.1 and 3.5.2 (also at low Fe dose, but with a much smaller BEPR component due to the low acetate feed supplement), the additional VSS production in the test unit was again relatively small (7 to 12%).

These data suggest that iron (or iron hydroxide) forms complexes in the mixed liquor which involve increased adsorption/ enmeshment of colloidal organic material. It appears that this adsorbed/ enmeshed colloidal organic material is not available for biodegradation and hence contributes to the VSS. Effectively, this would be equivalent to an increase in the inert (unbiodegradable) particulate COD fraction of the influent, which contributes directly to the mixed liquor VSS. However, the observed differences in VSS need to be seen in their experimental context; in some cases, the differences may have been exaggerated, considering the following factors:

- The failure to closely reach steady-state operation of the units during Periods 3.4.1 through 3.4.3, as borne out by the P mass balances. These experimental periods were each about three sludge ages, which may not have been sufficient to allow steady state to be reached considering that the mixed liquor solids (concentration and composition) change relatively slowly;
- The apparent weakening of BEPR performance in the control unit during Periods 3.4.2 and 3.4.3 (particularly the latter, as previously discussed). It is well-known that BEPR results in increased VSS production, due to a lower death rate for poly P accumulating organisms (Wentzel et al., 1989). By contrast, during Period 3.4.4 (with good BEPR in the control but P-limited relative to the acetate dose), the difference in VSS production was negligible;
- Rather poor P mass balances for Period 3.5.1, again suggesting failure to approach steady state. The test and control systems may not have adapted to the change in operating conditions (feed characteristics) at exactly the same rate, which could account for some of the difference in observed VSS (12%). This difference was smaller for Period 3.5.2 (7%) after a longer operational period with the same feed characteristics.

In summary, it appears that an increase in VSS production not exceeding approximately 5 to 10% may be expected at a low $FeCl_2$-$FeCl_3$ dose of around 9 to 10 mg/ℓ Fe (based on influent flow) and a sludge age of 10 days. Higher VSS production may occur at higher iron doses, but this would need to be confirmed by further experimentation.

In terms of TSS (i.e. MLSS) the test unit showed a significant increase in sludge production compared with the control. TSS increases of 9 to 27% were observed for Periods 3.4.4 through 3.5.2 at low Fe dose and little or no P supplement to the feed; for Periods 3.4.2 and 3.4.3 at the same Fe dose but with P supplement to the feed, the TSS increases averaged between 19 and 36%. For Period 3.4.1, with a high Fe dose and feed P supplement, a large increase in TSS production (61%) occurred in the test unit, relative to the control. These results must be viewed in the context of additional P removal as a result of chemical precipitation, with the chemical precipitate contributing to the inorganic suspended solids (ISS).

From the measured mixed liquor VSS and TSS data, the difference in mixed liquor ISS (DISS) between the two units was calculated in the same manner as described in Parts 3 and 4 of this series of papers (De Haas et al., 2000a & c). The DISS values from observed data can be compared with DISS calculated on the basis of an estimated stoichiometry and theoretical formula for chemical precipitate formed. The results are shown in Table 8.

Table 8 indicates that the theoretical values of DISS calculated from stoichiometry show a fairly good agreement with the observed DISS. With the exception of Period 3.4.1, the recovery of estimated ISS was in the range 90 to 123% of the observed values. These results suggest that the increase in ISS due to chemical dosing may be estimated reasonably accurately (to within ~100 mg/ℓ or ~5% of the mixed liquor TSS) using the hypothetical chemical formulae given in Table 8 and the apparent stoichiometry. In cases where low effluent P concentrations limit P removal in the system, estimation of the precipitation stoichiometry by a technique such as fractionation of the mixed liquor solids described in this series of papers (De Haas et al., 2000 a & b) is advisable.

Considering the exception (Period 3.4.1) when the agreement between calculated and observed DISS values was poor (Table 8), it is most likely that failure to approach steady-state in this period was the cause of the discrepancy. Unlike the biological P removal processes, the TSS and VSS (and hence ISS) in the systems can be expected to take several sludge ages to reach steady state. During Period 3.4.1, a high iron dose (19 mg/ℓ as Fe) was administered. This experimental period lasted 32 days (three sludge ages) but followed directly from the last ferric chloride dosing period (Period 3.3.6), also at a high dose (20 mg/ℓ as Fe). It appears that Period 3.4.1 was too short to allow steady state to be approached. A significant change in mean ISS for R1 (420 mg/ℓ) and DISS (approx. +480 mg/ℓ) was noted when comparing Periods 3.3.6 and 3.4.1, possibly indicating that ferrous and ferric ions interact differently with the biomass (see comments above on VSS production). If the final TSS and VSS data set for Period 3.4.1 is taken (data not shown) and substituted for that in Table 8, the observed ISS value is closer to the predicted ISS, suggesting that the test system was closer to steady-state at the end of that period. Similarly, in Period 3.4.2, halving of the iron dose resulted in a large reduction in ISS in R1 (-1040 mg/ℓ on average) compared to Period 3.4.1. Period 3.4.2 may also have been too short to closely approximate steady state in the test unit in respect of solids.

Sludge settleability

Sludge settleability during all periods of $FeCl_2$-$FeCl_3$ dosing was better in the test unit, compared with the control. This was noted, firstly, from visual inspection of the clarifiers. The test unit clarifier normally contained less sludge (due to improved thickening) and showed better clarity compared to the control. The settling rate (unstirred zone settling velocity, ZSV) was measured over a one-month period during the transition from $FeCl_3$ to $FeCl_2$-$FeCl_3$ dosing (De Haas, 1998). The ZSV was usually slower in the test unit relative to the control when $FeCl_3$ was dosed, despite a lower

TABLE 8
Comparison of observed ISS and that predicted from chemical P removal for $FeCl_2$-$FeCl_3$ dosing periods
Fe~P~OH : hypothetical metal hydroxy-phosphate, $Fe_r PO_4 OH_{(3r-3)}$
Fe~P~O : hypothetical metal phosphate oxide, $Fe_r PO_4 O_{(1.5r - 1.5)}$

Period (Duration): $FeCl_2$-$FeCl_3$ dose	Stoichiometry Observed Tables 3 or 7	Estimate from Stoichiometry Observed	Estimated DISS from Stoichiometry Observed	D ISS Observed	Error (Estimate-Observed)
	mol P_{rem}: mol Fe_{dosed}	Fe~P~OH	Fe~P~O	mg/ℓ	% of MLSS in R1
Unit:	P:Fe	mg/ℓ	mg/ℓ	R1-R2	%
3.4.1 (32 d): High Fe, AE1	0.74	540	513	1082	-16%
3.4.2 (34 d): Low Fe, AE1	0.62	303	280	228	3%
3.4.3 (30 d): Low Fe, AN	(1.75) *	356	395	372	1%
3.4.4 (70 d): Low Fe, AE1	0.26 **	201	167	145	1%
3.5.1 (46 d): Low Fe, AE 1	0.41	242	211	232	-1%
3.5.2 (32 d): Low Fe, AN	0.16	308	247	218	2%

AN = Anaerobic zone; AE1 = First aerobic zone
* Inhibition of BEPR suspected in control system during Period 3.4.3.
** Stoichiometry from fractionation data in the case of Periods 3.4.4 due to P limitation on system P removal.

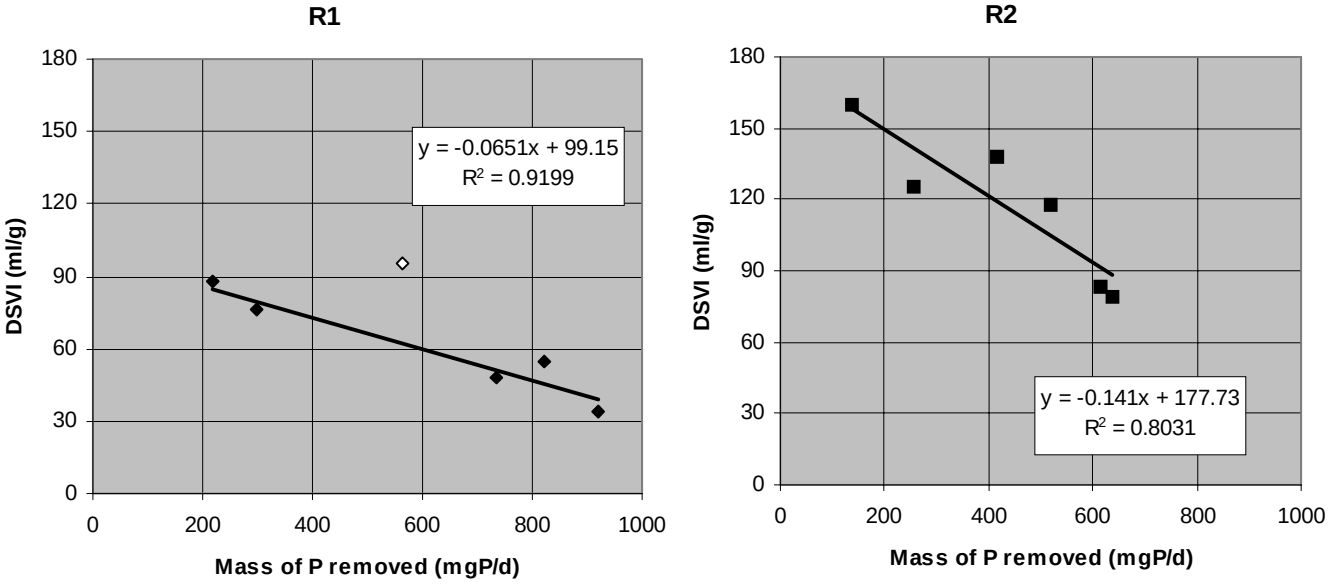

Figure 3
Relationship between DSVI and P removal for the test unit dosed with ferrous-ferric chloride (Fig. 3a) and the control unit (Fig. 3b). Data point with white symbol for Period 3.4.4 (R1) excluded from regression in Fig. 3a (refer to text)

DSVI in the test unit. After the change to $FeCl_2$-$FeCl_3$, similar ZSV values were observed in the test and control systems and the DSVI data (Table A2) indicated that settleability (or compactability) was generally better in R1 (test), compared with R2 (control). *[The only exception was a period in May 1996 (Period 3.4.4) when the DSVI in R1 underwent a sudden and transient increase, as opposed to the inverse in R2. During this period, imbalances in the microbial population may have occurred due to the high influent acetate concentration in relation to the low P concentration. Repeated problems were experienced with the units (particularly R1) with whitish clumps of organic matter clogging pipes in the system. Attempts (only partially successful) were made to remove this material from the unit by means of sieving. Microscopic inspection revealed the problem appeared to be caused by excessive growth of the protozoan Vorticella which produces a distinctive "stalk". This organism tends to grow in clumps (or "rosettes"). In large numbers, the stalks tended to get entwined to form dense lumps which attached to the walls of the reactors and tubing in the pilot plants].*

Figs. 3a and 3b indicate that there is a fairly strong correlation

between the mean daily mass of P removal and mean DSVI for the $FeCl_2$-$FeCl_3$ experimental periods. This applied to both units. In the case of the test unit (R1), the data for Period 3.4.4 was excluded from the regression in view of certain operational problems during this period. It is noteworthy that the slope and y-intercept of the regression line for the test unit with iron dosing (Fig. 3a) are lower than those of the control unit (Fig. 3b). From these data, it may be concluded that phosphate accumulation in the mixed liquor solids plays an important role in determining sludge DSVI. Iron dosing itself should produce an improvement in settleability, by virtue of the density of the iron complexed with the biomass. However, this improvement will not be as marked where the effluent residual phosphate concentrations are already fairly low (due to an active biological P removal mechanism) and iron addition can only bring about a small further increment in phosphate accumulated by the mixed liquor solids.

Conclusions

1. In the absence of phosphate limitation, negative interference in the biological P removal mechanism as a result of $FeCl_2$-$FeCl_3$ dosing is detectable, but not severe. Using pilot plants in which the effluent phosphate concentrations always exceeded approximately 10 mgP/ℓ, it was found that:
   - A net improvement in P removal was virtually always found in response to $FeCl_2$ $FeCl_3$ addition. Neglecting one experimental period when BEPR in the control unit appeared to be depressed due to extraneous factors, the additional system P removal averaged approximately 0.75 mol $P_{removed}$ per mol Fe $_{dosed}$. However, variance in the data reduced confidence in these results.
   - Partial "inhibition" of the biological P removal mechanism as a result of $FeCl_2$-$FeCl_3$ addition was found from fractionation studies and P release in the anaerobic zone of the test unit. However, in the absence of P limitation at the iron doses tested in this study, the biological mechanism was never inhibited by more than about ~20% on average, relative to the control.
2. In the presence of phosphate limitation (ie. low effluent P concentrations), "inhibition" or depression of the biological mechanism was slightly greater (18 to 25% from fractionation data). The P:Fe stoichiometry for chemical precipitate estimated from fractionation data was approximately 25 to 33% lower under P limiting conditions, compared with non-P-limiting conditions. It was concluded that the biological and chemical P removal mechanisms are "disadvantaged" to approximately the same degree under P-limiting conditions at the low iron dose studied here. However, the chemical precipitation mechanism does limit the extent to which the biological excess P removal (BEPR) *potential* can be utilised by removing part of the soluble phosphate fed to the system.
3. Although the main interaction between the biological and chemical P removal mechanisms appears to be competition for available phosphate, interaction between the two mechanisms in other ways cannot be ruled out. For example, some evidence was found from batch P release tests that a minor fraction of phosphate can "migrate" between biological storage and chemical adsorption/precipitation in the mixed liquor solids. Phosphate may be loosely bound in some chemical form (possibly an iron hydroxy-phosphate colloid) that could be extracted in cold perchloric acid using the fractionation procedure applied in this study. Alternatively, an association between such colloids and the biomass itself is possible (Brown and Lester, 1979; He et al., 1996), which could explain the occurrence of minor fractions of alkaline-extractable orthoP frequently found in this study.
4. The partial loss of BEPR potential in the presence of simultaneous addition chemical phosphate precipitants is expected to be most significant in plants operated at low (limiting) effluent P concentrations. Tertiary precipitation may be better in such plants. Considering that only minor inhibition of the BEPR mechanism was measured under conditions in which effluent P was not limiting (>1 mgP/ℓ), a sustained benefit from simultaneous metal dosing in modified activated sludge systems can nevertheless be achieved where very low effluent soluble P concentrations (say <1 mgP/ℓ) are not required.
5. Sludge production was greater in the test unit, with $FeCl_2$-$FeCl_3$ dosing. Minor increases in VSS production (ca. 7 to 15%) were noted, although confidence in the results was limited by the relatively short experimental periods. Considering the relatively low iron doses applied during this study, it may be tentatively concluded that iron (or iron hydroxide) significantly affects the coagulation of organic material with activated sludge and its biodegradation. Increases in observed TSS were significant, as expected, due to the additional ISS contributed by chemical precipitate. The observed increase in ISS could be estimated (to within ~100 mg/ℓ in the test unit) on the basis of a hypothetical general formula for the precipitate and the estimated stoichiometry. The stoichiometry could be determined from differences in system P removal between the test and control unit (where P was not limiting) or from fractionation data (where P was limiting).
6. Using the observed alkalinity changes and fractionation data an estimate of the average formula for precipitation *without P limitation* was in the approximate range:

$$Fe_{1.33}\,(X^{2+})\,PO_4\,(OH)_3 \text{ to } Fe_{1.66}\,(X^{2+})\,PO_4\,(OH)_4$$

where X^{2+} is some unknown (possibly divalent) cation (e.g. Mg^{2+} or Ca^{2+}) (Arvin, 1985). This is similar to the average formula found in Part 3 for alum (De Haas, 2000c) and corresponds reasonably well with the following general formula used by Luedecke et al. (1989) and Briggs (1996):

$$Fe_rPO_4\,(OH)_{(3r-3)}$$

The latter predicts less alkalinity loss per mol Fe. Nevertheless, Luedecke et al. (1989) reported values for r in the range approximately 1 to 2 mol Fe/mol P for residual phosphate concentrations of approx. 1 to 5 mgP/ℓ which are consistent with the stoichiometry observed in this study for non P-limiting conditions.

The average formula for ferric hydroxy-phosphate formed *under partially P limiting conditions* was found to lie in the following approximate range:

$$Fe_4\,(X^{2+})\,PO_4\,(OH)_{11} \text{ to } Fe_{2.5}\,(X^{2+})\,PO4\,(OH)_{6.5}$$

Acknowledgements

This work was conducted while the principal author was employed by Umgeni Water (South Africa). The financial assistance and support of Umgeni Water is gratefully acknowledged, as is the technical assistance provided by several persons, including Paul Gaydon, Gordon Borain, Emma Parkhouse, ZT Jikazi, Rose Smith and the staff of the Analytical Services department.

References

ARVIN E (1985) Biological removal of phosphorus from wastewater. *CRC Critical Reviews in Environmental Control* **15** 25 - 64.

BRIGGS TA (1996) Dynamic Modelling of Chemical Phosphorus Removal in the Activated Sludge Process. M. Eng. Thesis, School of Graduate Studies, McMaster Univ., Hamilton, Ontario, Canada.

BROWN MJ and LESTER JN (1979) Metal removal in activated sludge: The role of bacterial extracellular polymers. *Water Res.* **13** 817-837.

COMEAU Y, HALL KJ, HANCOCK REW and OLDHAM WK (1986) Biochemical model for enhanced biological phosphorus removal. *Water Res.* **20** (12) 1511-1521.

DE HAAS DW (1998) The Use of Simultaneous Chemical Precipitation in Modified Activated Sludge Systems Exhibiting Biological Enhanced Phosphate Removal. PhD Thesis, Dept. of Civil Eng., Univ. of Cape Town, Rondebosch, South Africa.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000a) The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 4: Experimental periods using ferric chloride. *Water SA* **26** (4) 485-504.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000b) The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 1: Literature review. *Water SA* **26** (4) 439-452.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000c) The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 3: Experimental periods using alum. *Water SA* **26** (4) 467-484.

DE HAAS DW, WENTZEL MC and EKAMA GA (2000d) The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological enhanced phosphate removal. Part 2: Method development for fractionation of phosphate compounds in activated sludge. *Water SA* **26** (4) 453-466.

HARTLEY K, HERTLE C, KOMAROWSKI S and WALPOLE R (1999) Operating experience with two activated primary tanks for sewage prefermentation. Paper presented at 18th AWWA Fed. Conv., April 1999, Adelaide, Australia.

HE QH, LEPPARD G, PAIGE CR and SNODGRASS WJ (1996) Transmission electron microscopy of a phosphate effect on the colloid structure of iron hydroxide. *Water Res.* **30** (6) 1345-1352.

LEOPOLD P (1996) Personal communication. *NCP Ultrafloc*, Johannesburg, South Africa.

LOEWENTHAL RE, WIECHERS HNS and MARAIS GvR (1986) Softening and Stabilization of Municipal waters. Water Research Commission, Pretoria, June 1986.

LÖTTER LH (1991) Combined chemical and biological removal in activated sludge plants. *Water Sci. Technol.* **23** (Kyoto) 611-621.

LUEDECKE C, HERMANOWICZ SH and JENKINS D (1989) Precipitation of ferric phosphate in activated sludge: A chemical model and its verification. *Water Sci. Technol.* **21** (Brighton) 325-327.

REYNOLDS T (1996) Personal communication. *NCP Ultrafloc*, Johannesburg, South Africa.

WENTZEL MC, EKAMA GA, LOWENTHAL RE, DOLD PL and MARAIS GvR (1989) Enhanced polyphosphate organism cultures in activated sludge systems. Part II: Experimental behaviour. *Water SA* **15** (2) 71-88.

WRC (1984) Theory, Design and Operation of Nutrient Removal Activated Sludge Processes. Editors: Ekama GA, Marais GvR, Siebritz IP, Pitman AR, Keay GFP, Buchan L, Gerber A and Smollen M. Water Research Commission, Pretoria.

YEOMAN S, STEPHENSON T, LESTER JN and PERRY R (1988) The removal of phosphorus during wastewater treatment: A review. *Environ. Pollution* **49** 183-233.

TABLE A1
Alkalinity and pH data for periods of ferrous-ferric chloride dosing

Period	Unit:	R1	R2	R1	R2	R1	R2	R1 H_2CO_3* Alk. mg/ℓ as $CaCO_3$	R2 H_2CO_3* Alk. mg/ℓ as $CaCO_3$
	Zone:	AN	AN	AE1	AE1	AE2	AE2	Effluent	Effluent
3.4.1	MEDIAN	7.16	7.00	7.35	7.34	7.55	7.62	258#	277#
	MIN.	6.93	6.93	7.11	7.15	7.33	7.46	230	232
	25%-ILE	7.11	6.97	7.28	7.25	7.49	7.57	-	-
	75%-ILE	7.22	7.07	7.38	7.41	7.59	7.67	-	-
	MAX.	7.30	7.21	7.65	7.46	7.99	7.78	290	315
3.4.2	MEDIAN	7.09	7.09	7.37	7.34	7.59	7.61	274#	287#
	MIN.	6.86	6.85	7.13	7.25	7.20	7.48	245	248
	25%-ILE	7.02	7.02	7.30	7.29	7.54	7.58	-	-
	75%-ILE	7.18	7.14	7.43	7.39	7.63	7.70	-	-
	MAX.	7.37	7.30	7.65	7.73	7.80	8.09	316	314
3.4.3	MEDIAN	7.05	7.01	7.44	7.33	7.68	7.62	271#	279#
	MIN.	7.01	6.94	7.21	7.23	7.40	7.46	250	257
	25%-ILE	7.02	6.98	7.39	7.31	7.62	7.59	-	-
	75%-ILE	7.07	7.03	7.48	7.37	7.73	7.68	-	-
	MAX.	7.16	7.18	7.82	7.73	8.16	8.15	284	290
3.4.4	MEDIAN	7.26	7.23	7.52	7.54	7.71	7.79	229#	251#
	MIN.	7.00	6.92	7.15	7.17	7.33	7.38	208	229
	25%-ILE	7.21	7.16	7.42	7.47	7.60	7.68	-	-
	75%-ILE	7.35	7.29	7.57	7.61	7.78	7.85	-	-
	MAX.	7.48	7.43	7.71	7.77	7.93	8.00	261	281
3.5.1	MEDIAN	7.50	7.53	7.21	7.26	7.32	7.37	109#	125#
	MIN.	7.27	7.29	7.09	7.11	7.21	7.27	82	102
	25%-ILE	7.45	7.44	7.14	7.18	7.27	7.34	-	-
	75%-ILE	7.56	7.59	7.33	7.34	7.47	7.52	-	-
	MAX.	7.67	7.72	7.55	7.59	7.81	7.90	148	153
3.5.2	MEDIAN	7.31	7.36	7.22	7.30	7.37	7.48	120#	142#
	MIN.	7.17	7.15	7.11	7.16	7.23	7.26	96	121
	25%-ILE	7.23	7.24	7.19	7.27	7.31	7.41	-	-
	75%-ILE	7.37	7.40	7.31	7.34	7.43	7.48	-	-
	MAX.	7.44	7.52	7.38	7.39	7.54	7.58	142	163

# denotes mean in place of median.
AN = Anaerobic zone; AE1 / AE2 = First / second aerobic zone respectively.

TABLE A2
Measured pilot plant results for periods of dosing ferrous-ferric chloride blend
Results are averages with sample standard deviations in parentheses. N.D. = Not determined. Refer to Nomenclature for definition of symbols.
The double horizontal line between experimental periods indicates a change in influent characteristics (refer to Table 1).

Period Unit	S_{ti} mgO/ℓ	S_{te} mgO/ℓ	N_{ti} mgN/ℓ	N_{te} mgN/ℓ	N_{ae} mgN/ℓ	$No_{3,e}$ mgN/ℓ	P_{ti} mgP/ℓ	P_{te} mgP/ℓ	P_{trem} mgP/ℓ	P/VSS mgP /gVSS	TSS mg/ℓ	VSS mg/ℓ	% VSS	DSVI mℓ/g	$fP_{t,a}$ mgP/ℓ	$fP_{t,d}$ mgP/ℓ	$fP_{t,b1}$ mgP/ℓ	$fP_{t,b2}$ mgP/ℓ
3.4.1	237	14	15.4	2.29	1.51	3.32	43.57	18.00	25.57	254.8	3475	1361	39.2	33	69.80	34.83	24.10	18.01
R1	(53)	(6)	(4.8)	(0.55)	(1.47)	(0.86)	(2.74)	(3.54)	(4.45)	(134.1)	(747)	(329)	(4.5)	(13)	(11.23)	(6.17)	(3.51)	(2.70)
3.4.1	237	16	15.4	2.14	1.12	2.78	43.57	25.80	17.77	248.83	2167	1135	52.1	76	78.77	45.83	33.55	26.83
R2	(53)	(8)	(4.8)	(0.38)	(1.13)	(0.79)	(2.74)	(3.58)	(4.39)	(132.4)	(598)	(349)	(5.5)	(23)	(17.75)	(8.80)	(4.85)	(4.52)
3.4.2	284	15	18.0	2.17	0.75	4.66	44.22	23.37	20.81	342.25	2070	999	48.5	48	82.30	42.44	30.52	22.64
R1	(59)	(5)	(5.0)	(0.58)	(0.57)	(2.19)	(2.99)	(3.59)	(4.26)	(99.03)	(260)	(163)	(6.2)	(9)	(10.37)	(5.42)	(3.70)	(3.54)
3.4.2	284	15	18.0	2.17	1.29	3.96	44.22	27.22	17.00	297.28	1735	892	51.5	83	88.46	45.50	33.98	25.82
R2	(59)	(4)	(5.0)	(0.60)	(3.14)	(1.98)	(2.99)	(5.30)	(4.73)	(49.33)	(138)	(75)	(3.6)	(18)	(12.45)	(6.55)	(6.03)	(5.10)
3.4.3	264	16	15.6	2.95	0.52	5.09	42.90	22.41	20.48	332.76	1855	901	48.6	55	80.46	41.93	29.82	22.63
R1	(69)	(2)	(3.5)	(1.80)	(0.11)	(0.85)	(2.98)	(3.32)	(3.89)	(34.72)	(117)	(54)	(2.2)	(8)	(10.17)	(5.36)	(4.14)	(4.09)
3.4.3	264	17	15.6	2.83	0.55	3.87	42.90	31.19	11.68	254.32	1363	781	57.4	138	82.01	47.93	39.24	31.33
R2	(69)	(2)	(3.5)	(1.75)	(0.16)	(1.00)	(2.98)	(3.09)	(3.70)	(87.36)	(91)	(43)	(2.8)	(13)	(10.41)	(5.56)	(4.14)	(4.28)
3.4.4	323	26	26.6	2.28	0.36	6.46	16.58	0.93	15.58	179.32	1642	939	57.2	92	49.67	16.68	4.96	0.77
R1	(71)	(31)	(5.9)	(0.71)	(0.67)	(1.66)	(3.00)	(0.68)	(2.85)	(33.20)	(214)	(139)	(3.2)	(29)	(10.99)	(3.56)	(2.83)	(0.65)
3.4.4	323	19	26.6	2.27	0.21	6.55	16.58	2.07	14.44	163.66	1503	945	63.0	118	63.22	20.34	8.40	4.17
R2	(71)	(4)	(5.9)	(0.57)	(0.25)	(1.75)	(3.00)	(1.66)	(2.86)	(20.90)	(184)	(108)	(3.3)	(24)	(23.05)	(4.36)	(3.87)	(4.32)
3.5.1	278	19	34.1	2.33	0.21	10.51	9.91	3.87	6.04	74.06	1627	1078	66.2	88	13.76	6.59	5.19	4.76
R1	(66)	(3)	(5.2)	(0.65)	(0.16)	(4.03)	(2.41)	(2.06)	(2.40)	(19.51)	(229)	(157)	(2.9)	(5)	(9.45)	(1.99)	(1.63)	(2.27)
3.5.1	278	19	34.1	2.28	0.26	9.89	9.91	6.06	3.85	62.90	1282	965	75.7	161	15.34	8.60	7.66	6.66
R2	(66)	(3)	(5.2)	(0.54)	(0.28)	(3.55)	(2.41)	(2.57)	(2.56)	(25.82)	(197)	(103)	(4.1)	(20)	(9.73)	(2.10)	(1.70)	(2.05)
3.5.2	341	20	35.7	3.74	0.25	8.86	10.77	2.68	8.15	68.97	1581	1061	67.1	76	12.77	6.39	3.84	2.88
R1	(59)	(2)	(5.6)	(1.71)	(0.08)	(3.09)	(1.96)	(1.46)	(1.79)	(7.54)	(106)	(70)	(1.5)	(4)	(4.10)	(1.94)	(1.60)	(1.52)
3.5.2	341	23	35.7	3.42	0.23	8.64	10.77	3.65	6.99	61.79	1287	985	76.7	125	17.20	9.06	6.06	4.29
R2	(59)	(2)	(5.6)	(1.51)	(0.07)	(3.03)	(1.96)	(2.21)	(2.24)	(10.38)	(127)	(84)	(2.5)	(15)	(4.76)	(2.56)	(2.48)	(2.47)

ISSN 0378-4738 = Water SA Vol. 27 No. 2 April 2001

TABLE A3

Mass balances for periods of dosing ferrous-ferric chloride blend.Results are averages with sample standard deviations in parentheses. Underlined results indicate estimates where spurious actual average values were recorded. The double horizontal line between experimental periods indicates a change in influent characteristics (refer to Table 1)

Period Unit	Flow Q, ℓ/d	VSS mg/ℓ	$No_{3,a}$ mgN/ℓ	$No_{3,d}$ mgN/ℓ	$No_{3,b2}$ mgN/ℓ	N_{te} mgN/ℓ	$No_{3,e}$ mgN/ℓ	N_{ti} mgN/ℓ	% N Bal.	Ot mgO/ℓ.h	S_{ti} mgO/ℓ	S_{te} mgO/ℓ	% COD Bal.	P_{trem} mgP/ℓ	Mixed liquorTP mgP/ℓ	% P Bal.
3.4.1	36.0	1361	0.08	1.97	3.29	2.29	3.32	15.4		7.88	237	14	**108**	25.57	296.1	**89**
R1		(329)	(0.05)	(0.61)	(0.92)	(0.55)	(0.86)	19.3	109	(1.97)	(53)	(6)		(4.45)	(99.8)	
3.4.1	35.8	1135	0.07	1.39	2.68	2.14	2.78	15.4		8.53	237	16	**98**	17.77	241.8	**125**
R2		(349)	(0.02)	(0.67)	(0.93)	(0.38)	(0.79)	19.3	**98**	(2.46)	(53)	(8)		(4.39)	(83.6)	
3.4.2	35.6	999	0.06	2.68	4.96	2.17	4.66	18.0		9.27	284	15	**99**	20.81	331.3	**150**
R1		(163)	(0.08)	(1.08)	(1.82)	(0.58)	(2.19)	22.5	**99**	(1.95)	(59)	(5)		(4.26)	(73.9)	
3.4.2	35.4	892	0.08	2.40	4.42	2.17	3.96	18.0		10.64	284	15	**97**	17.00	263.8	**155**
R2		(75)	(0.17)	(1.08)	(1.78)	(0.60)	(1.98)	22.5	**88**	(2.46)	(59)	(4)		(4.73)	(39.9)	
3.4.3	36.7	901	0.07	2.96	5.18	2.95	5.09	15.6		9.02	264	16	**104**	20.48	299.5	**142**
R1		(54)	(0.02)	(0.52)	(0.94)	(1.80)	(0.85)	19.5	**112**	(1.00)	(69)	(2)		(3.89)	(34.4)	
3.4.3	35.6	781	0.10	2.46	3.64	2.83	3.87	15.6		10.65	264	17	**99**	11.68	198.0	**196**
R2		(43)	(0.06)	(0.90)	(1.07)	(1.75)	(1.00)	19.5	**82**	(1.05)	(69)	(2)		(3.70)	(66.4)	
3.4.4	36.2	939	0.08	3.15	6.32	2.28	6.46	26.6	**100**	13.35	323	26	**97**	15.56	166.5	**102**
R1		(139)	(0.02)	(1.13)	(1.68)	(0.71)	(1.66)	(5.9)		(2.69)	(71)	(31)		(2.82)	(30.7)	
3.4.4	36.3	945	0.07	3.72	6.45	2.27	6.55	26.6	**92**	11.64	323	19	**110**	14.31	153.9	**100**
R2		(108)	(0.02)	(1.15)	(1.56)	(0.57)	(1.75)	(5.9)		(2.45)	(71)	(4)		(2.96)	(21.9)	
3.5.1	36.0	1063	0.57	6.85	10.74	2.33	10.51	34.1	**89**	11.91	278	19	**108**	6.04	83.2	**101**
R1		(152)	(0.92)	(3.00)	(4.04)	(0.65)	(3.93)	(5.2)		(1.60)	(67)	(3)		(2.40)	(26.6)	
3.5.1	36.0	965	0.64	6.79	10.56	2.28	9.89	34.1	**82**	11.98	278	20	**101**	3.85	63.8	**128**
R2		(98)	(0.87)	(2.60)	(4.09)	(0.54)	(3.49)	(5.2)		(1.64)	(67)	(3)		(2.56)	(24.5)	
3.5.2	36.4	1061	0.08	3.93	8.26	3.74	8.86	35.7	**99**	13.73	341	21	**98**	8.15	73.3	**80**
R1		(70)	(0.05)	(2.25)	(3.63)	(1.71)	(3.09)	(5.6)		(1.27)	(59)	(2)		(1.79)	(10.6)	
3.5.2	36.3	985	0.08	4.07	8.06	3.42	8.64	35.7	**95**	13.05	341	23	**108**	6.99	61.1	**93**
R2		(84)	(0.03)	(2.30)	(3.14)	(1.51)	(3.03)	(5.6)		(0.97)	(59)	(2)		(2.24)	(12.9)	
								Mean	**95**			Mean	**103**		Mean	**121**
								S.D.	**10**			S.D.	**6**		S.D.	**34**

TABLE A4
Effluent soluble orthophosphate concentrations for ferrous-ferric chloride dosing periods.
Results are averages with sample standard deviations in parentheses

Period Unit	$PO_{4,e}$, R1 mgP/ℓ	$PO_{4,e}$, R2 mgP/ℓ
3.4.1	16.57	23.12
	(3.08)	(5.07)
3.4.2	22.69	25.61
	(4.92)	(5.61)
3.4.3	21.25	29.55
	(3.45)	(3.07)
3.4.4	1.14	2.10
	(1.12)	(2.04)
3.5.1	3.07	5.15
	(2.09)	(2.70)
3.5.2	1.29	2.31
	(1.14)	(2.00)