

A COMPREHENSIVE STUDY ON AN IRON-PHOSPHATE REMOVAL SYSTEM

by

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EXECUTIVE SUMMARY

BACKGROUND AND MOTIVATION

The removal of phosphate from wastewater may be achieved by chemical or biological means. Chemical means involve precipitation by metal oxides (e.g. Ca, Mg or Na aluminate), or by addition of chlorides or sulphates of metal salts (e.g. Fe or Al).

Metal oxides are strongly alkaline thus demanding pH control in order not to interfere with the treatment process. Metallic salts are strongly acidic resulting in similar problems. Efficient control of chemical dosage or continuous operator attention is therefore a prerequisite for success. Efficient phosphate removal may require additional flocculation for which equipment such as clarifiers are needed to dispose of voluminous sludge produced. Ions remaining in solution further detract from the suitability of conventional process technologies.

Contact with elemental iron could enable the formation of insoluble iron phosphate compounds with little effect on the pH. Additional chemicals would not be required resulting in a less sophisticated treatment system. No soluble compounds would be introduced into the effluent. Preliminary investigations have indicated that the iron contactor system may be successful in the removal of phosphate from sewage wastewater. An extension of the studies should result in establishing the optimal performance criteria essential for the implementation of such a system. A major advantage in the application of the system resides in the use of relatively inexpensive raw material such as iron filings or scrap iron and minimal operator attention.

AIMS OF THE PROJECT

The primary objective of this study was to establish conditions for the continuous and optimal removal of phosphate from sewage works effluent by the contactor containing iron filings (Catphate system).

Individual aspects to be evaluated and reported on, as well as possible adjustments to the system, were as follows:

- The optimization of phosphate removal.
- The existing contactor would be modified to allow for pH control in the contactor and supplementation, viz. phosphate and heavy metals, in the holding tank ensuring homogeneous influent feed.
- The parameters which can influence the performance of the system would be varied to achieve phosphate removal to a level of maximally 1 mg P/l.
- Compilation of guidelines for the application of phosphate removal by an iron contactor in municipal wastewater treatment.

MAIN FINDINGS AND CONCLUSIONS

A trouble-free run of the plant with a minimum of supervision was experienced. The following parameters were addressed and the findings were as follows:

- **The extent of phosphate removal**

The Catphate system can efficiently and consistently remove in the order of 5 mg P/l.

- **pH range**

The pH ranged between 6,6 - 8,8. The pH level was dependant on the algal growth in the holding tank, which in turn was temperature dependant. The pH had no significant effect on the phosphate removal.

- **Temperature**

The temperature ranged between 12 and 28 °C., the highest temperatures occurring in January, at the beginning of the project, and the lowest in July, nearing the end of the project. There was no visible effect of temperature on the phosphate removal, thereby eliminating the possibility of climatic changes affecting the removal process.

- **Ions (calcium and magnesium)**

The effect of calcium ions was addressed first. There was no significant variation in calcium concentration throughout the process, and the phosphate removal did not seem to be affected by the presence of the calcium ions. On this basis it was decided that it was not necessary to address the effect of magnesium ions.

- **Heavy metals**

The most commonly found heavy metals in the sewage treatment works effluent are copper, chrome and nickel. These three metals were therefore selected for investigation. None of them had any negative influence of the phosphate removal. However, the system was able to reduce the concentration of the metals by a substantial amount, viz.

Chrome	-	1,03 mg/l
Copper	-	0,30 mg/l
Nickel	-	0,30 mg/l

This was regarded as a bonus to the potential of the system.

- **Retention time**

Retention time affected the performance of the system. The longer the retention time the higher the removal of phosphate.

RECOMMENDATIONS

The system would be appropriate for tertiary water treatment, where the required discharge phosphate concentration is below 1 mg P/l, or where phosphate concentrations of 5-6 mg P/l need be removed at an acceptable retention time of the order of 5 minutes. Future studies could involve the possible up-scaling of the Catphate system to full-scale application. This report should be distributed to interested parties, viz. consultants and municipalities.

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GLOSSARY

CATPHATE SYSTEM	:	Registered name derived from 'Catalytic phosphate removal'
IRON CONTACTOR	:	The central element of the system, operating in a rotary mill fashion. It consists of a hollow steel cylinder with an off-horizontal axis equipped with a variable speed drive capable of rotating the contactor at various speeds
IRON FILINGS	:	Scrap iron, prewashed with sulphuric acid and loaded into the contactor
HUMUS TANK EFFLUENT	:	The influent is humus tank effluent obtained by passing settled sewage through biofilters
INFLUENT	:	Humus tank effluent from the holding tank entering the contactor
EFFLUENT	:	The treated humus tank effluent leaving the contactor
DAILY AVERAGE	:	The average concentration of two or three samples taken at different times each day
DELTA PHOSPHATE OR IRON	:	The difference between the influent and final phosphate or iron concentrations. This reflects the actual phosphate removal or iron increase if any in each sample
SETTLED SEWAGE EFFLUENT	:	The supernatant from settled raw unscreened sewage
SUPER-PHOSPHATE	:	Commercialized calcium phosphate fertilizer added to the humus tank effluent to elevate the phosphate concentration in the first evaluation (1990)
<i>ortho</i>-PHOSPHORIC ACID	:	Added to the humus tank effluent to elevate the phosphate concentration in the second and third evaluation
RETENTION TIME	:	The contact time of the effluent with the iron filings
PUMP CYCLE	:	The time period between which the pump is switched on, viz. drawing effluent through the rotating contactor and out to waste thereby minimizing the contact time, and off, thus retaining the effluent in the rotating contactor thereby maximizing the contact time

- CYCLE CHANGE** : The adjustment to the time that the pump is on and off. viz. 1 min on and 8 min. off (8 min. retention time).
- FLOWRATE** : The rate at which the effluent is drawn through the contactor from the holding tank. This, with the pump cycle, is a determinant of retention time.
- BACKWASHED SYSTEM** : The pump action is reversed and the effluent, instead of being drawn through, is rather pumped back through the contactor into the holding tank

1. INTRODUCTION

1.1 Motivation

The removal of phosphate from wastewater may be achieved by chemical or biological means. Chemical methods involve precipitation by the addition of metal oxides (e.g. Ca, Mg or Na aluminate), or alternatively addition of chlorides or sulphates of metals such as Fe or Al. These chemicals can be applied at various stages of the treatment process, viz. during the primary sedimentation stage, within the secondary treatment system or after secondary clarification (Momborg, 1991a).

The disadvantages of the chemical methods have been well documented (Van Dijk & Braakensiek, 1985). The metal oxides are strongly alkaline resulting in an increase in pH which must be controlled so as not to interfere with the ensuing stages of the process. The metallic salts are strongly acidic and may cause similar pH problems. An effective distribution of the chemical dosage to the influent phosphate loading is necessary for the efficient utilization of the chemicals. This either necessitates automated control or continuous operator attention. In many cases effective phosphate removal requires the additional use of flocculants such as polyelectrolytes. This may require co-dosing with inorganic chemicals. When phosphate removal is applied to a tertiary stage, additional equipment, such as clarifiers or filters, may be required. The removal of phosphate by any of these methods results in additional sludge which must be disposed of. The voluminous precipitate produced when using metal salts is difficult to separate from the wastewater, demanding more costly equipment. A considerable portion of the supplied cation derived from the applied metal oxide may not be utilized in the reaction and remains in solution as a contaminant thereby reducing the value of the treated water for subsequent use. In the application of metal salts, the anion remains totally unused and is in solution with similar or even greater detrimental effects (Momborg, 1991a).

Aqueous contact of phosphates with elemental iron, such as employed by the Catphate system, could theoretically enable the formation of insoluble iron phosphate compounds having less effect on pH than that of metal salts or oxides. Such a system requires no additional chemicals for pH control therefore less sophisticated control equipment is required. Operator attention is minimal. Furthermore, no significant amounts of soluble constituents are introduced into the water (Momborg *et al.*, 1990). Preliminary investigations have indicated that the Catphate system is successful in the removal of phosphate from sewage wastewater (Momborg *et al.*, 1990; Momborg, 1991b). A major advantage of the Catphate system resides in the use of relatively inexpensive raw material such as iron filings or scrap iron for the efficient removal of phosphate to levels in the order of 1 mg P/l or less. The system is easy to maintain and operate, requiring minimal operator attention.

1.2 Background

1.2.1 International

Little research has been done on iron-phosphate removal using iron contactors. In 1991 Haruta *et al.* developed a process called the 'submerged iron contactor process'. Contactors made of rolled steel were submerged in effluent. Corrosion of the steel took place in two stages, firstly by the mechanism of aerobic corrosion using dissolved oxygen, and secondly by anaerobic corrosion caused by sulphate-reducing bacteria. The first stage occurs until

a biofilm has formed on the metal surface, producing anaerobic conditions as well as a nutrient source for the sulphate-reducing bacteria, thereby initiating the second stage. As the metal corrodes the iron bonds to the phosphate forming a precipitate which then settles to the bottom and can be removed from the tank. In practice this precipitate is usually removed with the sludge.

Although this process is not identical to the Catphate process, they both rely on the corrosion of the iron. Similar to biofilm formation on the steel contactor, biomass on the iron filings could cause constant corrosion. An advantage of the Catphate system is that the thickness of the biofilm layer is limited due to the revolving action of the contactor.

1.2.2 South Africa

Three separate evaluations of the iron contactor system were performed by the Division of Water Technology (Watertek), the first and third in collaboration with the WRC and the second an independent study by Watertek. In 1989 Watertek was approached by Mr D C van der Post to evaluate a pilot-scale iron-phosphate removal plant, a patented process called the 'Catphate system' (Annexure A), designed by himself (Momborg *et al.*, 1990). This was the first evaluation which was run between May - July 1990. While the initial results obtained over a 4 day period in May were encouraging, the system seemed to falter in the subsequent runs resulting in an erratic phosphate removal (Figure 1). It should be noted that the influent phosphate concentration was relatively constant. Although the pH fluctuated between 6,3 - 7,3, this did not appear to be the reason for the erratic phosphate removal.

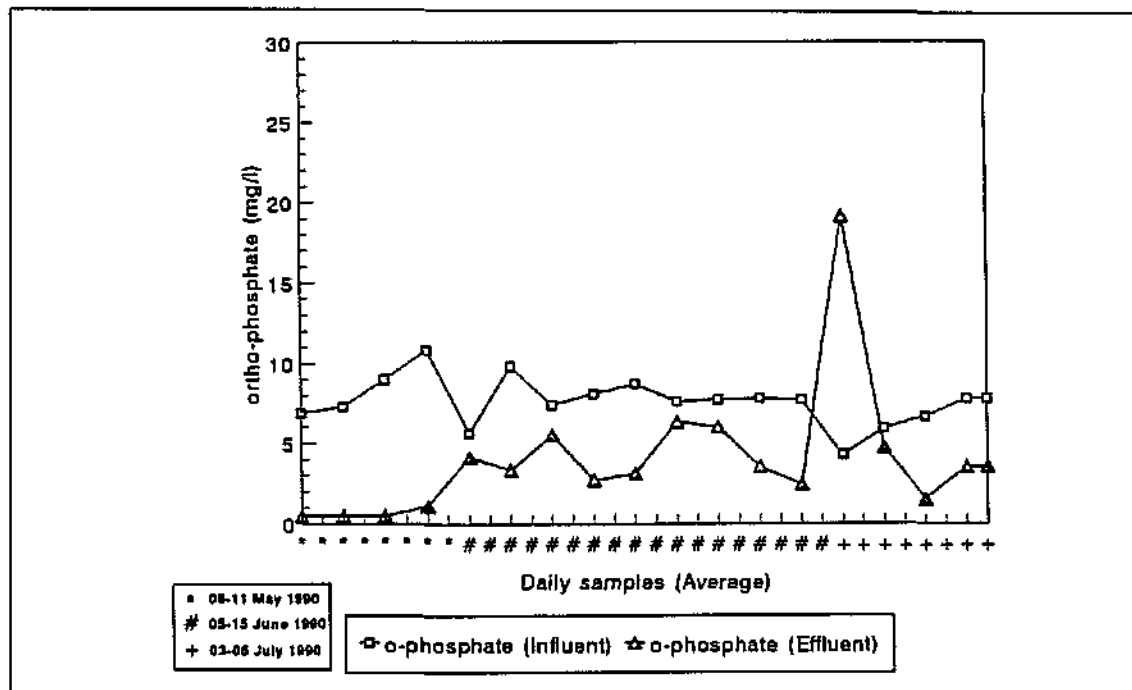


Figure 1. The daily average influent and effluent ortho-phosphate concentration in humus tank effluent during the first evaluation (8 May - 6 July 1990)

Figure 2 shows the actual phosphate removal and illustrates an increase in iron concentration, which was a point of concern as at times the level was well above the 0,3 mg/l required by the general standards (Government gazette, May 1984). Initially the phosphate removal was high, but as the evaluation progressed the removal decreased.

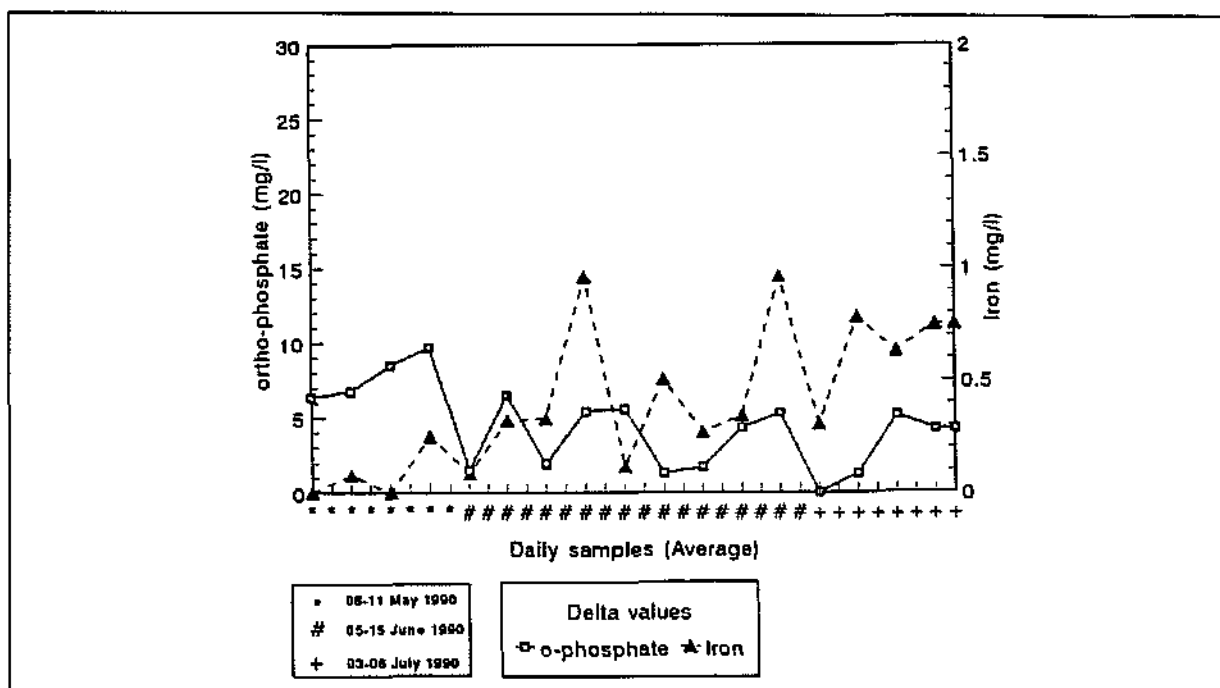


Figure 2. The daily average delta ortho-phosphate and iron concentration in humus tank effluent during the first evaluation (8 May - 6 July 1990)

The second evaluation was conducted in March 1991 (Momborg, 1991b). The phosphate removal was markedly less erratic, and the pattern of removal seemed to follow the influent phosphate concentration (Figure 3). The pH of the influent and effluent remained relatively constant, in the order of 7,1 throughout the run. Figure 4 illustrates that the actual phosphate removal was relatively constant, fluctuating between 5 - 8 mg P/l. The iron concentration remained below 0,5 mg/l which was an improvement on the first evaluation. The temperature fluctuated between 24 - 27 °C and, although the fluctuation was small, it appeared to have no detectable effect on the phosphate removal. Figure 5 shows analyses on unfiltered samples. The phosphate removal appeared to be slightly lower than with the filtered samples, but there was a substantial increase in the iron concentration. The samples were preacidified with concentrated HCl to determine the total iron concentration.

The third evaluation was conducted in the period January - September 1992 and will be discussed comprehensively in this report.

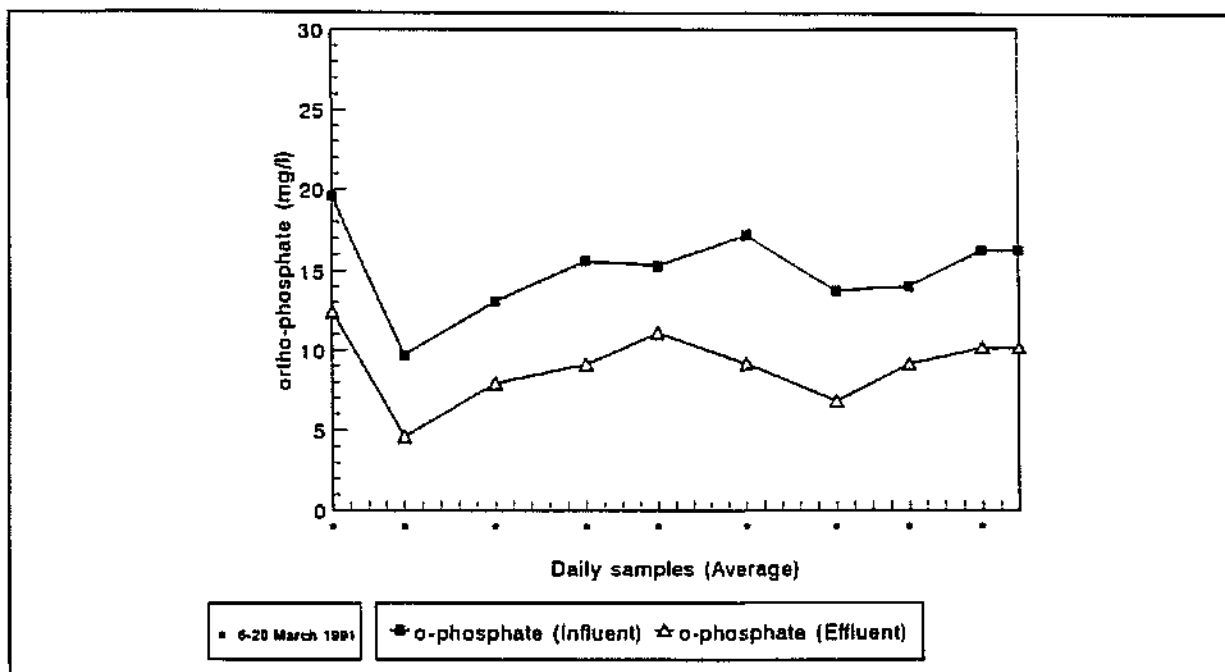


Figure 3. The daily average influent and effluent ortho-phosphate concentration in humus tank effluent filtered samples during the second evaluation (6 - 20 March 1991)

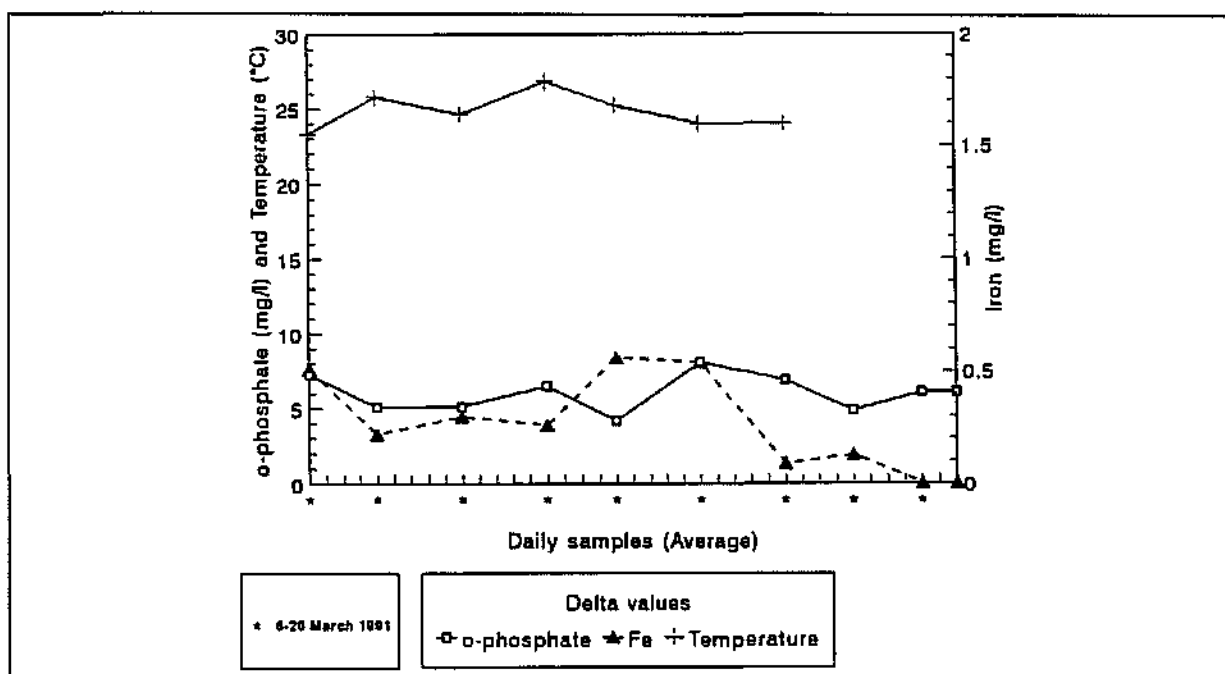


Figure 4. The daily average delta ortho-phosphate and iron concentrations and temperature of humus tank effluent filtered samples during the second evaluation (6 - 20 March 1991)

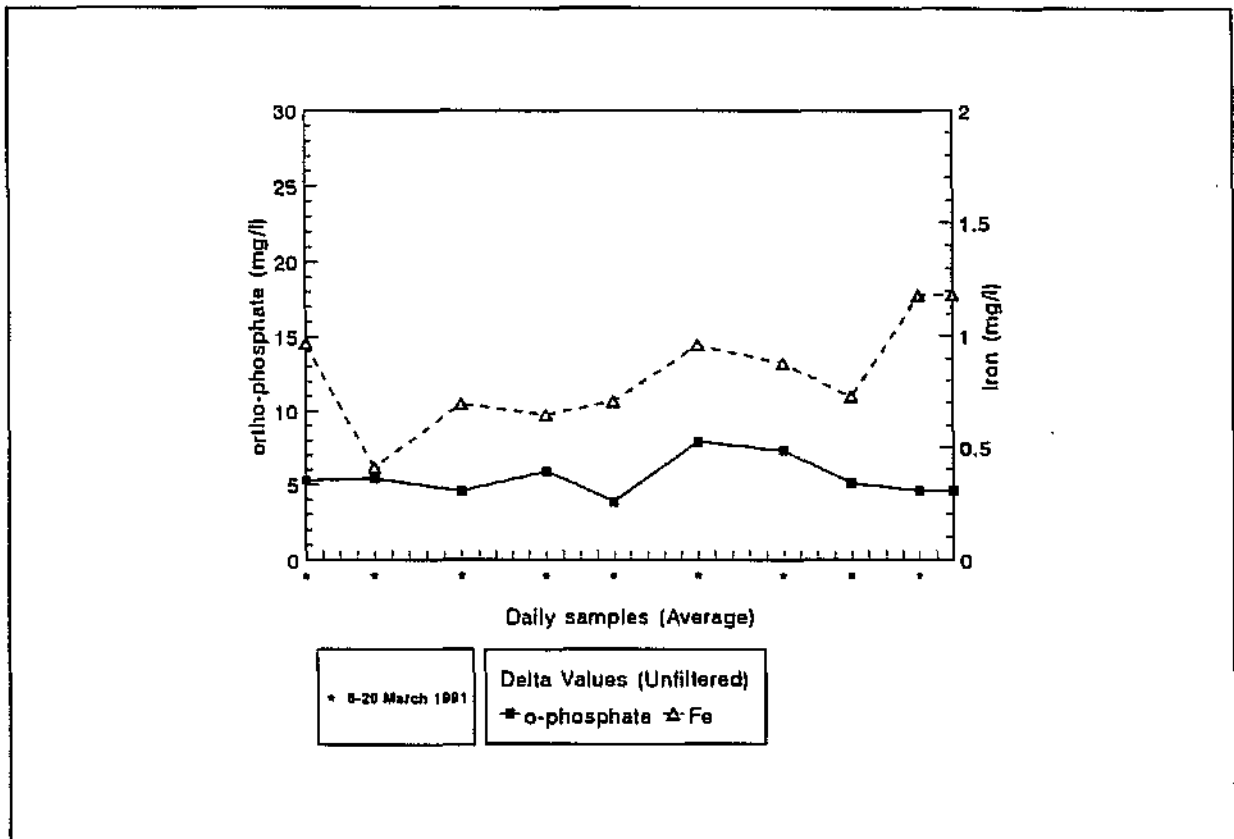


Figure 5. The daily average delta ortho-phosphate and iron concentrations in humus tank effluent unfiltered samples during the second evaluation (6 - 20 March 1991)

2. MATERIALS AND METHODS

2.1 Reactor configuration

The Catphate system is situated on the WATERTEK, CSIR site at the Daspoort Water Works (Figure 6). The central element of the system is an iron contactor, operating in a rotary mill fashion (Figure 7). The contactor consists of a hollow steel cylinder (1,005 m diameter by 3,080 m in length), with a near horizontal axis equipped with a variable speed drive. The 2m³ capacity cylinder was initially half-filled with iron filings, which had been precleaned with sulphuric acid. Two subsequent additions were made during the run of the project, with a final addition bringing the contactor load to three-quarters full. The scrap iron charge was retained in the drum by two end plates, containing fittings which allowed the humus tank effluent to respectively enter and leave the system under operational conditions. A hose pipe connected to the inlet of the contactor, allowed any gases formed in the contactor to be released into a drum filled with water. The system operated under a negative pressure within the contactor. A stainless steel sieve installed on the outlet of the contactor prevented the iron filings from being washed out. The system was designed to treat 1 M³/d. The iron contactor was fed from a 135 m³ holding tank containing humus tank effluent. The phosphate concentration in the holding tank was adjusted periodically to levels ranging from 10 - 20 mg P/l by appropriate phosphate supplementation.

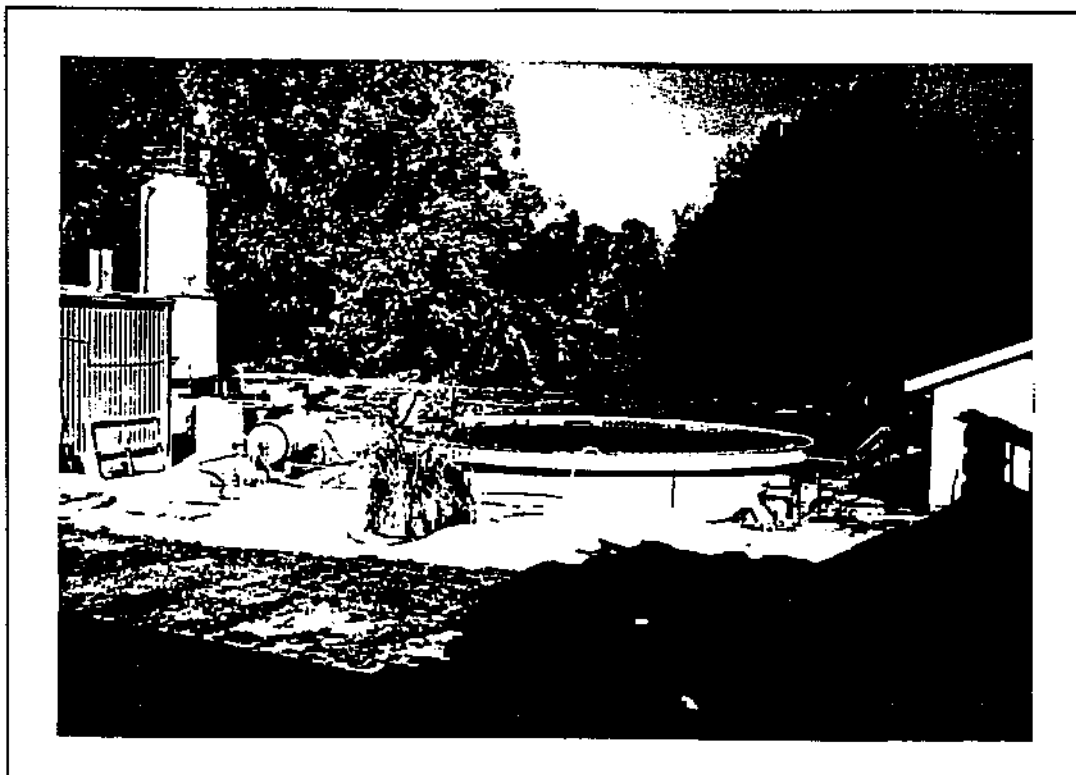


Figure 6. The Catphate iron-phosphate removal system at Daspoort Water Works (WATERTEK)

In order to eliminate the possibility of phosphate sedimentation, phosphoric acid, as opposed to super phosphate (added in the first evaluation), was used when supplementing the phosphate concentration in the holding tank. The phosphoric acid was diluted in a 1 m³ dosing tank and pumped at a steady rate simultaneously with the humus tank effluent into the holding tank. The flowrate of the dilute phosphoric acid was regulated to ensure that, when the holding tank was full all the dilute acid had been dosed, thereby obtaining a homogeneous phosphate/humus effluent mixture. This procedure took approximately 3½h. A mixing pump was also installed to circulate the effluent by drawing effluent from the bottom of the holding tank and pumping it out on the water fluid surface of the tank, ensuring a homogeneous mixture.

The system was operated from a 220V distribution box containing a control switch and timer. The control switch simply started and stopped the system, while the timer controlled the pump cycle, thereby controlling the flow of effluent through the contactor. While the contactor rotated continuously, the pump cycle consisted of two phases:

- i) The pump was switched on and the effluent flowed through the contactor
- ii) The pump was switched off and the effluent was retained in the contactor

The time span for each part of the cycle could be varied. Retention time was taken as the time that the effluent was retained in the contactor once the pump was switched off.

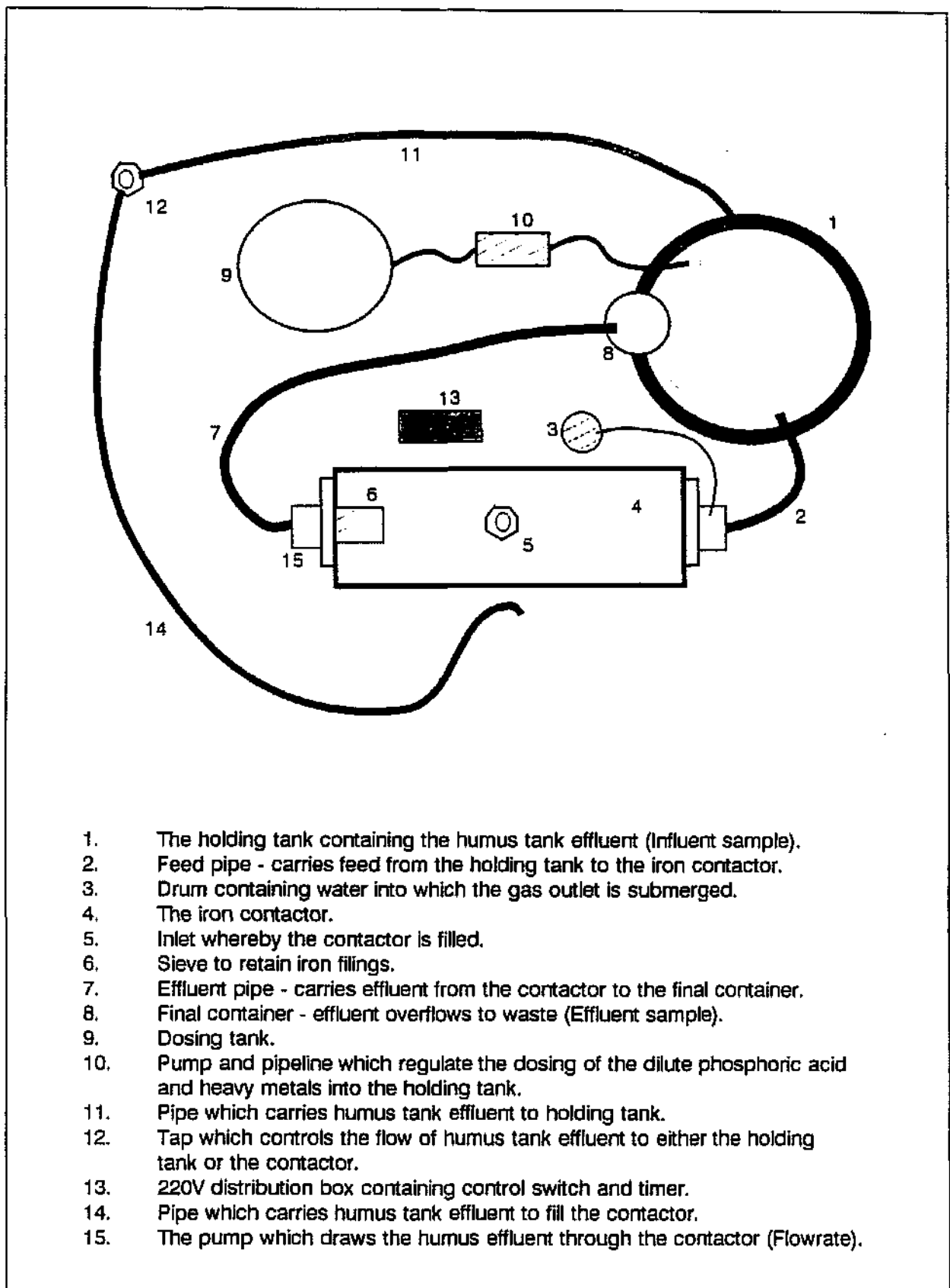


Figure 7a. A schematic diagram of the Catphate iron-phosphate removal system

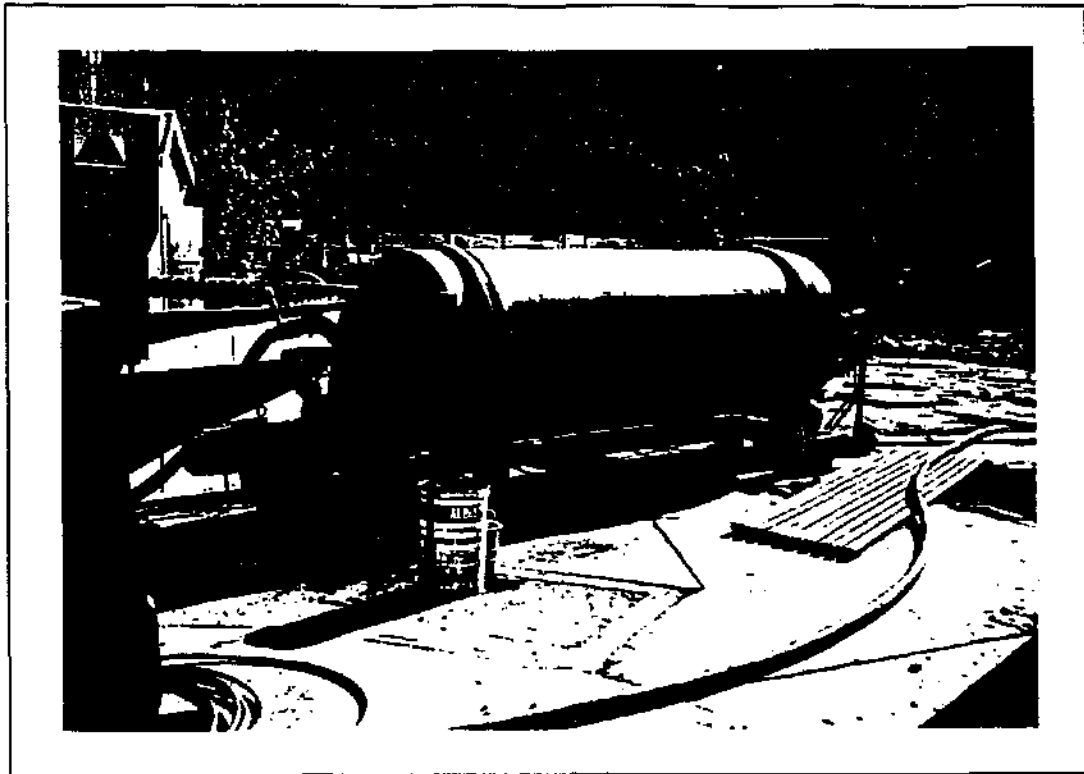


Figure 7b. A side view of the iron contactor with the pump (left), distribution box (far left) and holding tank (behind)

2.2 Sampling procedure

Two samples were taken three times daily. One sample was taken from the bottom of the holding tank and referred to as the 'influent sample', the other sample was taken from the outlet overflow and referred to as the 'effluent sample'. During January (15 -29) the samples were duplicated so that results could be obtained on filtered and unfiltered samples. The pH of the samples was determined and those samples to be filtered were vacuum filtered directly after sampling. A Whatman glass microfibre filter (GF/C, Cat. No. 1822047) was used. The samples were then analyzed by the Central Diagnostic Laboratories. The temperature of the humus tank effluent in the holding tank was recorded each time a sample was taken.

2.3 Analyses

The ortho-phosphate determinations were conducted according to the methods described in Standard Methods (Standard Methods, 1980) and Technikon Autoanalyser Methodology (Technikon Industrial Systems, 1975). The apparatus used was a Technikon Autoanalyser AA II.

The iron and calcium determinations were done on the Atomic Absorption Spectrophotometer.

One ml concentrated HCl was added to the unfiltered samples, to determine the total iron concentration, before the iron analyses were done on samples taken between 21 -29 January 1992.

2.4 Experimental procedure

The project was divided up into weekly, continuous, vacuum and settled sewage runs. The parameters remained the same for all the runs except no phosphoric acid was added to the settled sewage (Table 1). The holding tank was filled and the contactor switched on every day for the duration of the project, but sampling and the addition of phosphoric acid was only done during continuous and weekly runs.

2.4.1 *Continuous runs*

These runs took place over selected periods to provide information on the effect of climatic change on the phosphate removal, and the consistency of the removal on a daily basis.

2.4.2 *Weekly runs*

These took place once a week. The objective of the weekly run was to establish a continuity between continuous runs as the system could not be monitored on a daily basis. They help to provide a global picture, highlighting any problems that may occur were the system to run on a continuous basis, as will be expected when implemented as part of a water treatment works.

2.4.3 *Vacuum runs*

These runs were relatively short, and completed in one day. They were not combined with the weekly runs. The holding tank was filled to various levels for each specific run. The objective of the vacuum runs was to determine whether the volume in the holding tank, hence the vacuum pressure exerted on the effluent in the contactor, had any effect on the phosphate removal.

2.4.4 *Settled sewage*

This run was done over a period of three days. Instead of using humus tank feed, settled sewage was used and the experiment conducted under the same conditions as with humus tank effluent, except that no phosphoric acid was added to the feed. The objective of this run was to assess the performance of the Catphate system on different effluents

2.4.5 *Retention time*

This run was conducted to determine at which retention time the system could achieve a constant phosphate removal to below 1 mg P/l.

2.4.6 *Heavy metals*

To ascertain the effect of heavy metals, specifically, nickel, copper and chrome, on phosphate removal.

Table 1. The experimental procedure

	Time period	Run description	Average duration	Experiment commenced	Remark
P H A S E 1	07-08 Jan'92	Start-up	5h30	7h15	
	13-24 Jan'92	Continuous (1)	6h45	7h15	
	29 Jan'92	Weekly	6h15	7h15	
P H A S E 2	05 Feb'92	Vacuum (1)	5h00	7h30	
	08 Feb'92	Vacuum (2)	1h15	7h30	
	12 Feb'92	Vacuum (3)	6h00	7h30	
	13 Feb'92	Vacuum (4)	1h05	7h35	
	19 Feb-29 Apr'92	Weekly	6h15	7h30	28 Feb'92 - Iron loaded 25 Mar'92 - System blockage - system backwashed 23 Apr'92 - System backwashed
P H A S E 3	05-15 May'92	Continuous (2)	7h00	7h30	
	20 May - 08 Jul'92	Weekly	6h00	7h45	20 May'92 - Iron loaded - system backwashed 27 May'92 - Cycle change - 2 min. on - 2 min. off 11 Jun'92 - System backwashed 01 Jul'92 - Cycle change - 1 min. on - 1 min. off
	14-24 Jul'92	Continuous (3)	5h45	8h00	15 Jul'92 - Cycle change - 5 min. on - 1 min. off
	29-31 Jul'92	Sewage Continuous	7h30	7h45	
	05 Aug'92	Weekly	7h00	7h30	
P H A S E 4	01 Sept-16 Oct'92	Retention time	7h30	7h30	01-03 Sept'92 - 5,0 min. retention time 04-17 Sept'92 - 6,0 min. retention time 18 Sept'92 - 4,0 min. retention time 22 Sept'92 - 5,0 min. retention time 30 Sept-01 Oct'92 - 3,0 min. retention time 13-14 Oct'92 - 6,5 min. retention time 15-16 Oct'92 - 5,0 min. retention time
	18 - 19 Sept'92	Heavy metals	7h30	7h30	18 Oct'92 - additions: Copper CuSO ₄ (anhydrous) 1 kg Chrome Na ₂ Cr ₂ O ₇ 1 kg Nickel NiCl ₂ 1 kg

3. RESULTS AND DISCUSSION

The experimental part of the project ran from January to September 1992. For practical purposes the results and discussion will be divided into the following sections:

- *Phase 1 (7 - 29 January 1992)*

This was termed the 'Summer phase' during which the effect of temperature, in the order of 25 - 28 °C, and ions, such as calcium, on phosphate removal were monitored.

- *Phase 2 (5 February - 29 April 1992)*

The effect of vacuum was monitored in four one-day runs. Weekly runs monitored the effect of decreasing temperatures on the phosphate removal as the project moved into Autumn.

- *Phase 3 (5 May - 5 August 1992)*

This was termed the 'Winter phase' where the effect of low temperatures, between 12 - 19°C, on phosphate removal was monitored.

- *Phase 4 (1 September - 16 October 1992)*

In this phase the effect on phosphate removal was monitored by:

- Systematically increasing the retention time
- The addition of heavy metals, viz. copper, chrome and nickel
- Varying the influent flowrates

3.1 Phase 1 (7 - 29 January 1992)

The system was started up and checked over a period of two days (7 - 8 January). This was followed by a continuous run over a period of 9 days and ending with one weekly run (29 January). The temperature of the holding tank effluent was not formally monitored but was in the order of 25 - 28 °C. This temperature range was based on the atmospheric temperature experienced in January 1992.

Table 2. The daily average concentrations of the components analyzed in humus tank effluent during the first phase (7 - 29 January 1992)

Sample description	Filtered	Unfiltered
Average o-PO ₄ - Influent	15.78 mg/l	15.81 mg/l
Average o-PO ₄ - Effluent	10.11 mg/l	13.55 mg/l
Average Δ o-PO ₄	5.66 mg/l	2.26 mg/l
Average t-PO ₄ - Influent	16.58 mg/l	16.57 mg/l
Average t-PO ₄ - Effluent	10.90 mg/l	14.45 mg/l
Average Δ t-PO ₄	5.69 mg/l	2.12 mg/l
Average pH - Influent	7.31	6.96
Average pH - Effluent	7.42	7.00
Temperature	25 - 28 °C	
Average Ca - Influent	29.41 mg/l	29.00 mg/l
Average Ca - Effluent	27.37 mg/l	26.57 mg/l
Average Δ Ca	1.67 mg/l	1.33 mg/l
Average iron - Influent	0.02 mg/l	0.07 mg/l
Average iron - Effluent	0.80 mg/l	2.57 mg/l
Average Δ iron	0.777 mg/l	2.37 mg/l

3.1.1 Phosphate removal

Ortho-phosphate as well as total-phosphate were determined on filtered and unfiltered samples during this phase.

The ortho-phosphate concentration in the effluent closely mimicked that of the influent throughout the phase (Figure 8).

As illustrated in Figure 9, a relatively constant amount of ortho-phosphate was removed by the system fluctuating between 4 - 7 mg P/l. The removal shown in the unfiltered samples is lower. However, the initial removal was almost the same as in the filtered samples, being in the order of 5 mg P/l, but dropping sharply to between 1 - 2 mg P/l.

The total-phosphate removal in the filtered and unfiltered samples (Figure 10) is similar to that of the ortho-phosphate.

3.1.2 pH

The pH level remained relatively constant, ranging between 7 - 7.3, throughout the phase with a sharp increase towards the end, viz. the weekly run (Figure 11). This increase could have been due to the high climatic temperatures experienced over this period, which was conducive to algal growth in the holding tank. Figure 9 illustrates no change in ortho-phosphate removal despite the sudden increase in pH at the end of the phase as illustrated in Figure 11.

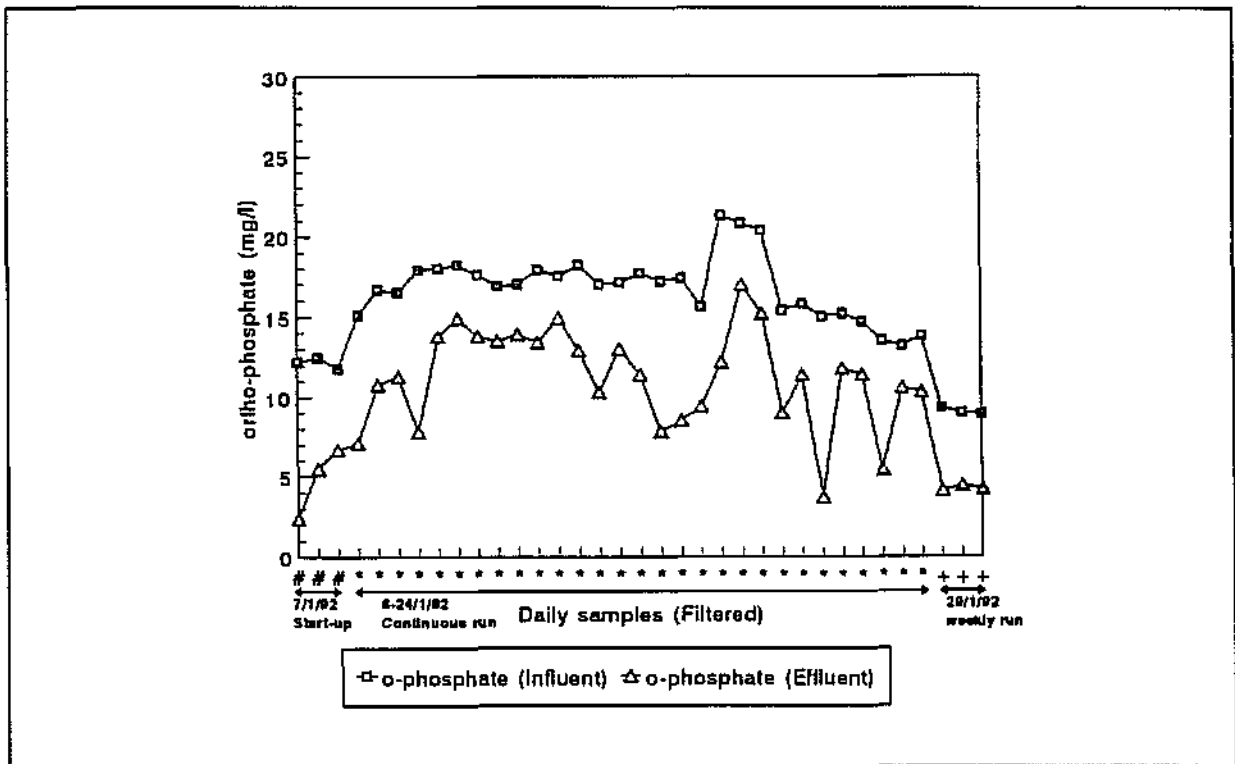


Figure 8. The daily average influent and effluent ortho-phosphate concentrations in humus tank effluent filtered samples during the first phase (7 - 29 January 1992)

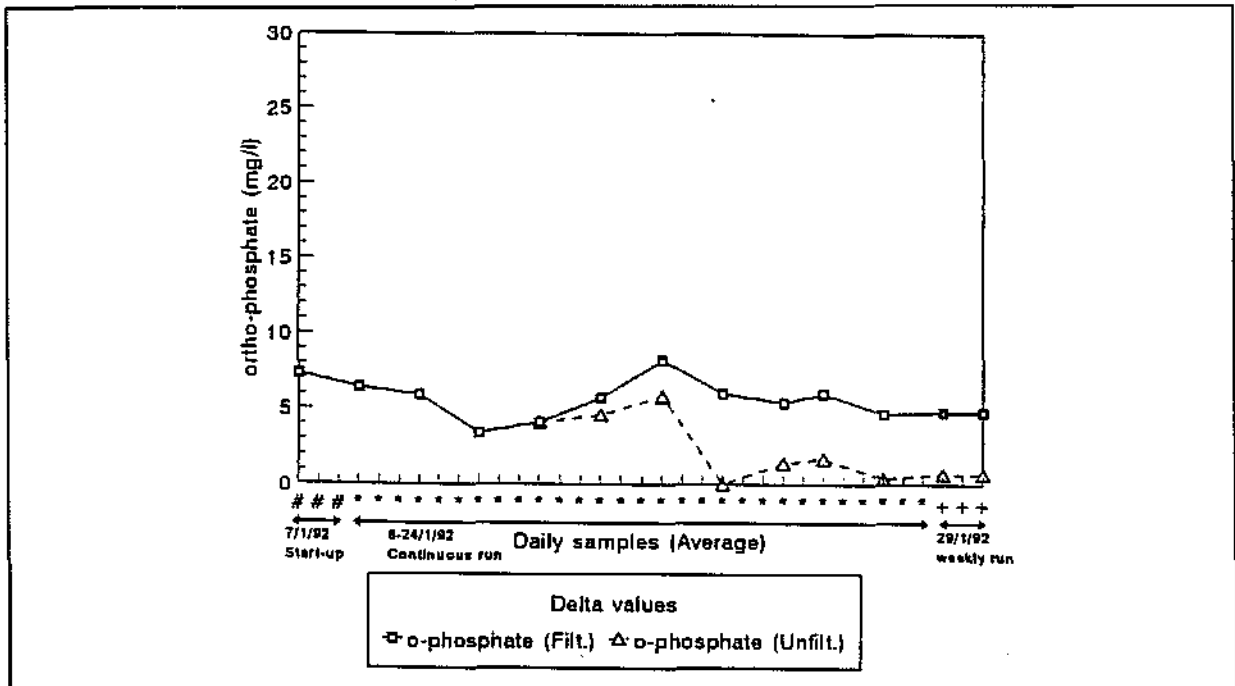


Figure 9. The daily average delta ortho-phosphate concentrations in humus tank effluent filtered and unfiltered samples during the first phase (7 - 29 January 1992)

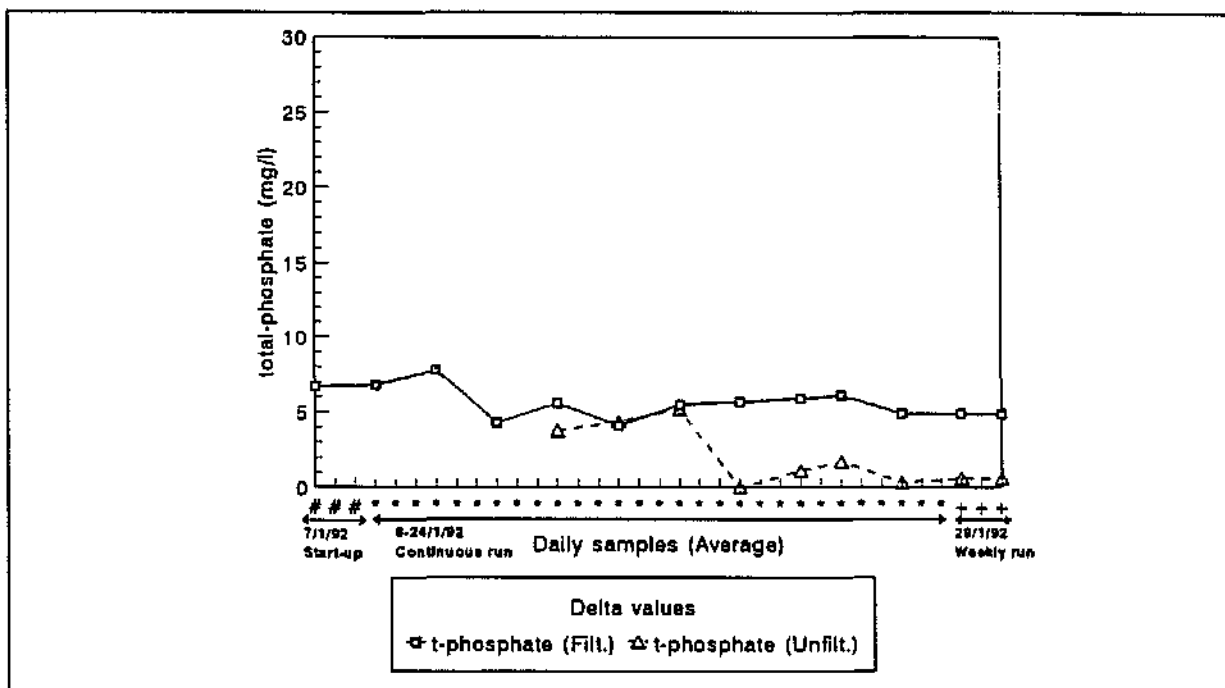


Figure 10. The daily average delta total-phosphate concentrations in humus tank effluent filtered and unfiltered samples during the first phase (7 - 29 January 1992)

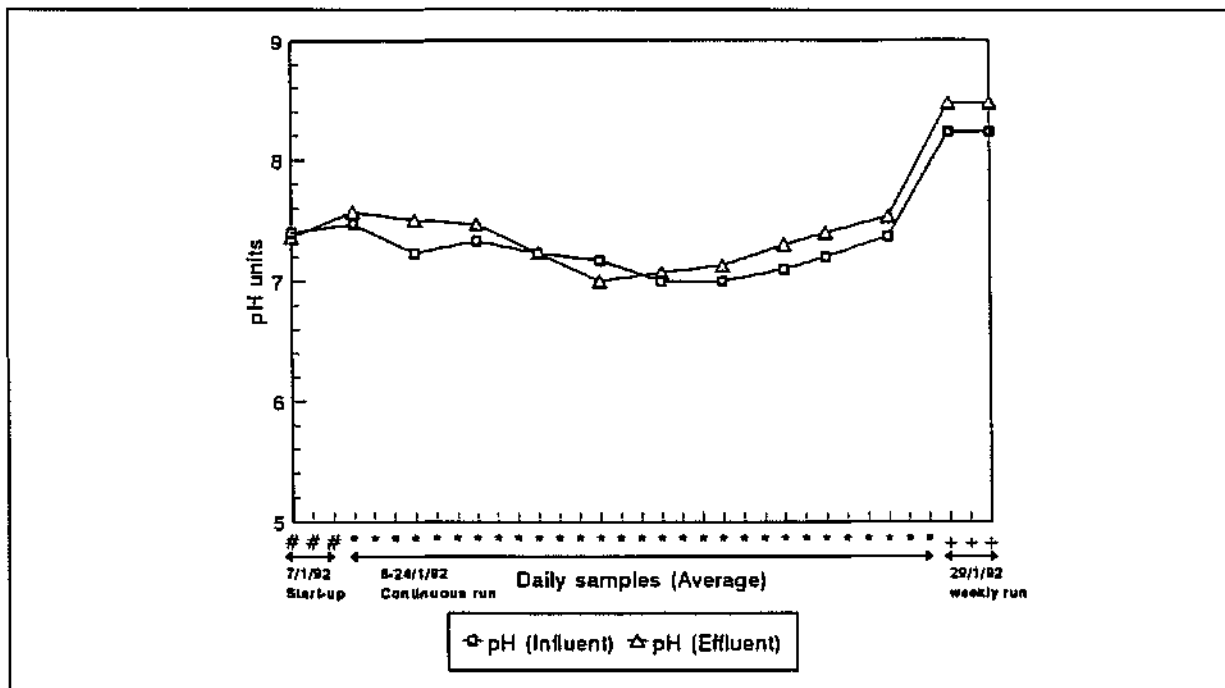


Figure 11. The daily average influent and effluent pH levels in humus tank effluent filtered samples during the first phase (7 - 29 January 1992)

3.1.3 Temperature

The temperature was not formally measured, was in the order of 25 - 28 °C throughout this phase, with the hottest part toward the end of the phase. Therefore taking the above into account, the high temperatures did not seem to have any significant effect on the phosphate removal.

3.1.4 Calcium

There was little difference between the influent and effluent calcium concentrations. The calcium did not seem to play any part in the phosphate removal process and the monitoring of the calcium was stopped after a few days.

3.1.5 Iron

In the previous evaluations it was found that when the system was started up, the iron concentration increased in the initial stages. The same tendency is illustrated in Figure 12. These high concentrations decreased after the system had run for a while, as is illustrated in the sharp drop in iron concentration at the end of the phase with the first weekly run.

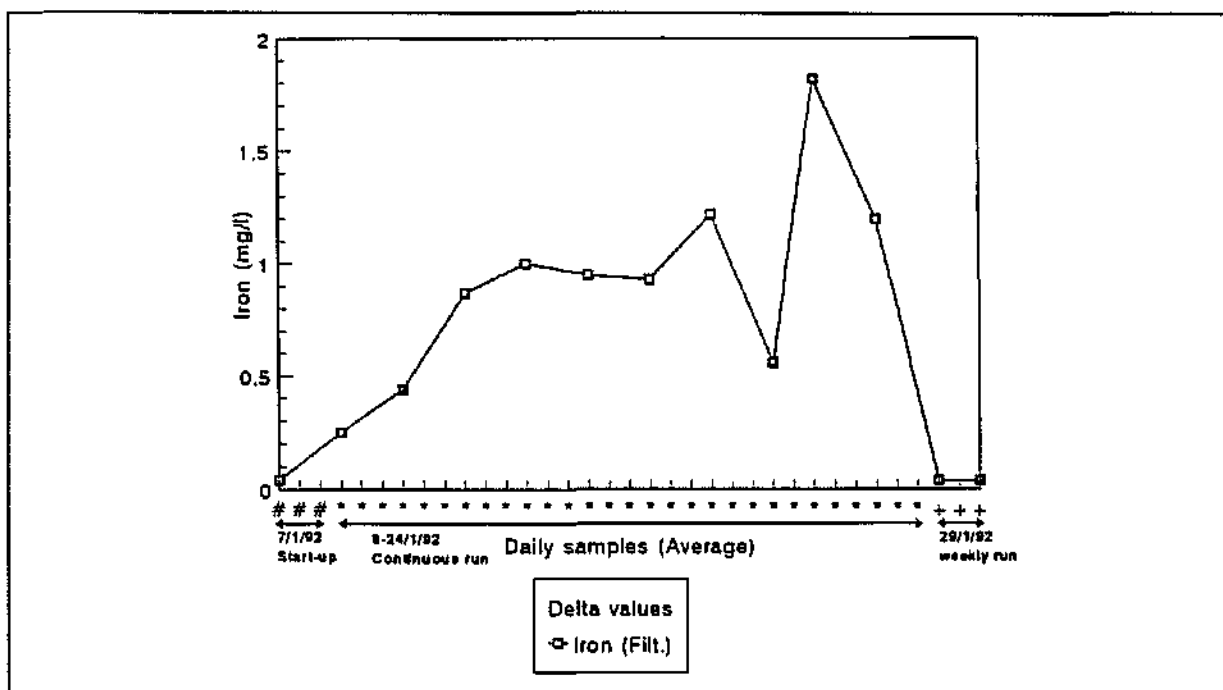


Figure 12. The daily average delta iron concentration in humus tank effluent filtered and unfiltered samples during the first phase (7 - 29 January 1992)

3.2 Phase 2 (5 February - 29 April 1992)

This phase started with four vacuum runs, followed by weekly runs up to the end of the phase. The system was backwashed three times and iron loaded once (Table 1). The temperature started to drop as the project moved into Autumn. All samples were filtered. The third backwash at the end of the phase was in preparation for the next phase and the second continuous run.

Table 3. The daily average concentrations of the components analyzed in humus tank effluent during the second phase (5 February - 29 April 1992)

Sample description	Filtered
Average o-PO ₄ - Influent	9.09 mg/l
Average o-PO ₄ - Effluent	5.05 mg/l
Average Δ o-PO ₄	4.04 mg/l
Average pH - Influent	7.38
Average pH - Effluent	7.83
Temperature	19-26°C
Average iron - Influent	0.05 mg/l
Average iron - Effluent	0.25 mg/l
Average Δ iron	0.20 mg/l

3.2.1 Phosphate removal

The ortho-phosphate effluent concentrations once again closely mimicked the influent (Figure 13), in the order of 3 - 5 mg P/l (Figure 14). An increase in phosphate removal is detectable in two places in this phase. The first was due to the loading of iron, where there was a slight improvement in removal, due to the increased contact time with the 'fresh' iron. The other was due to a blockage, resulting in an increased retention time, where there was a substantial improvement.

The improved phosphate removal due to iron loading and after backwashing, continued for the remainder of the day. However, the improvement due to the blockage was short lived, afterwards even dropping to slightly below that which was achieved at the beginning of the phase. This indicates that a correlation exists between increased phosphate removal and retention time.

3.2.2 pH and Temperature

As the project moved into autumn, the temperature decreased from 27 °C at the beginning of the phase to 19 °C at the end. The pH showed a similar decreasing tendency and thus could be linked to the fact that due to the lower temperatures, there was less algal growth in the holding tank. The decrease in both temperature and pH level had no significant detectable effect on the phosphate removal as the removal remained relatively constant throughout the phase (Figure 15).

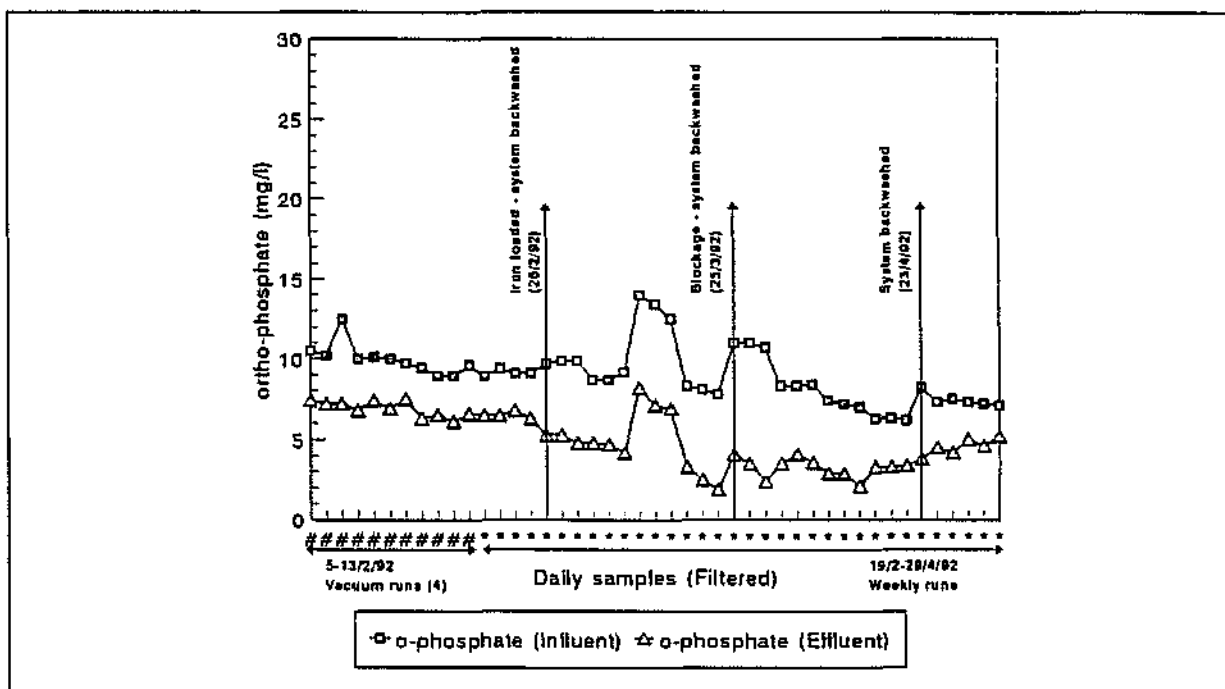


Figure 13. The daily average influent and effluent ortho-phosphate concentrations in humus tank effluent filtered samples during the second phase (5 February - 29 April 1992). Adjustments to the system are indicated

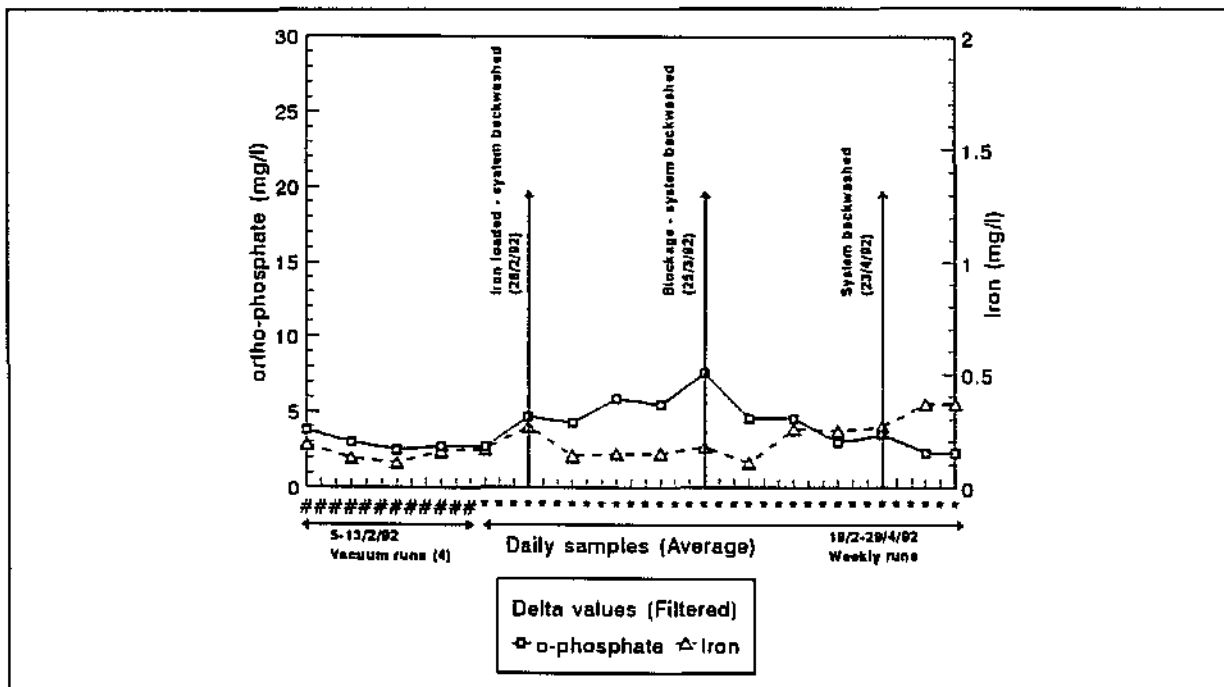


Figure 14. The daily average delta ortho-phosphate and iron concentrations in humus tank effluent filtered samples during the second phase (5 February - 29 April 1992). Adjustments to the system are indicated

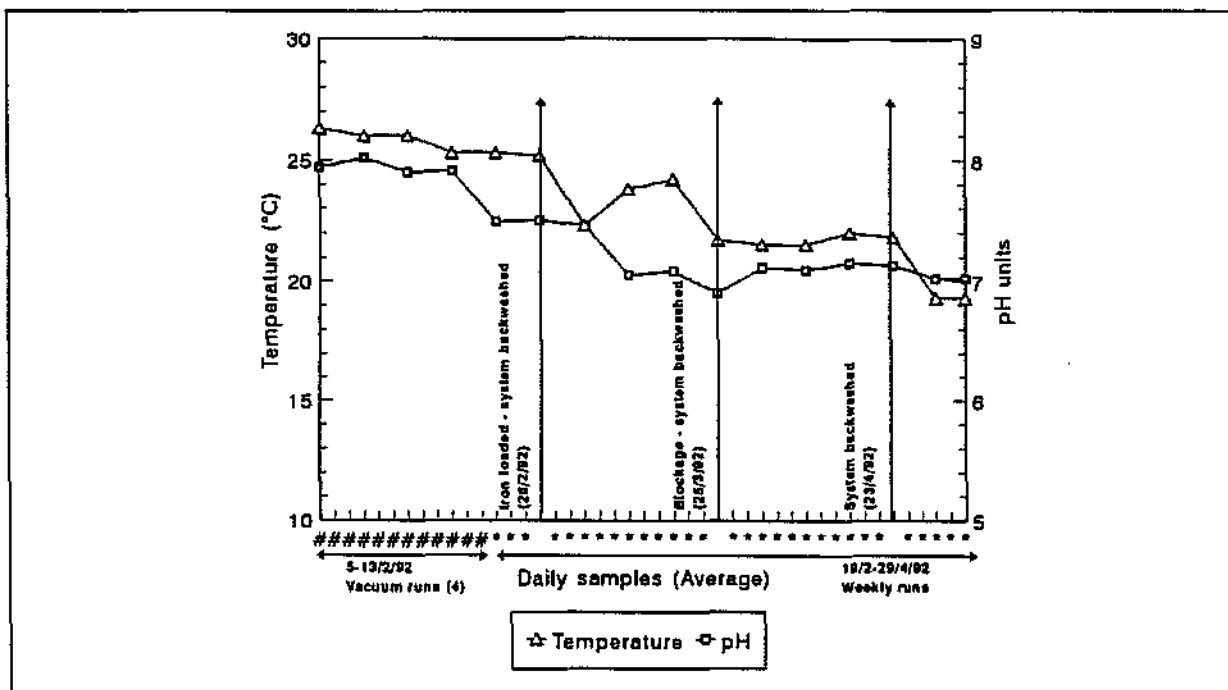


Figure 15. The daily average pH levels and temperature of humus tank effluent during the second phase of the third evaluation (5 February - 29 April 1992). Adjustments to the system are indicated

3.2.3 Iron

The lower iron concentration was an improvement on the first phase, although at times the final concentration still exceeded the requirements laid down by the water standard. However, the lower concentration corroborates the tendency that the longer the system runs, the iron concentration in the effluent decreases.

It is interesting to note that, in the initial stages of the phase, the delta phosphate and iron concentrations follow almost the same pattern. But towards the middle of the phase, as the phosphate removal increases the iron level drops. The opposite occurs towards the end of the phase (Figure 14).

3.3 Phase 3 (5 May - 5 August 1992)

This phase started off with a continuous run (8 days), followed by a weekly run and ended with another continuous run (9 days), a short three day settled sewage run and one weekly run. Iron was loaded once and the system was backwashed twice. The temperature decreased as the project moved into winter. During this phase the question of the effect of flowrate was investigated. The flowrate was recorded from about one quarter through the phase to the end of the second continuous run.

Table 4. The daily average concentrations of the components in humus tank effluent analyzed during the third phase (5 May - 5 August 1992)

Sample description	Filtered
Average o-PO ₄ - Influent	6.41 mg/l
Average o-PO ₄ - Effluent	4.51 mg/l
Average Δ o-PO ₄	3.90 mg/l
Average pH - Influent	6.89
Average pH - Effluent	7.05
Temperature	12 - 19°C
Average iron - Influent	0.13 mg/l
Average iron - Effluent	0.38 mg/l
Average Δ iron	0.25 mg/l

3.3.1 Phosphate removal

As in the previous phases the ortho-phosphate influent and effluent concentrations followed the same pattern, although at the end of May there was a noticeable decrease in the effluent concentration, to below 1 mg P/l (Figure 16).

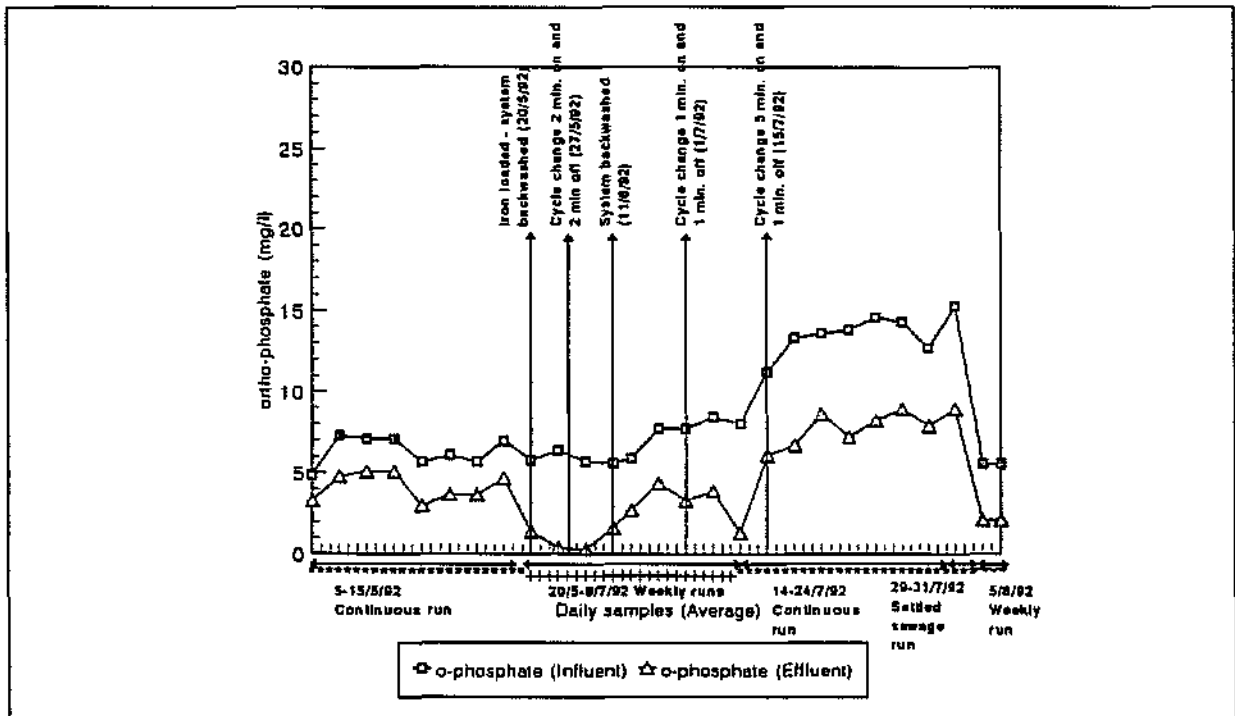


Figure 16. The daily average influent and effluent ortho-phosphate concentration in humus tank effluent during the third phase (5 May - 5 August 1992). Adjustments to the system are indicated

The results indicated an overall constant phosphate removal except for a sudden improvement on the 20th May (Figure 17). This could be due to the iron loading, thereby increasing the contact time, or a blockage causing the substantial drop in the flowrate (Figure 18), thereby increasing the retention time. An Increase in either the contact or retention will result in improved phosphate removal.

The subsequent decrease in phosphate removal supports the above theory. The system was backwashed and the removal improved. This tended to follow the same pattern as in the previous phase, where iron load was immediately followed by a backwash.

The changes in the pump cycle did not have a significant effect on the phosphate removal, and a constant removal pattern was maintained until the settled sewage run. Here the removal dropped sharply, with the same phosphate removal being obtained as in the August weekly run, where humus tank effluent was used once again. The maximum removal was obtained towards the end of the phase, but this could be due to a higher influent concentration. But, the average discharge phosphate concentration was in the order of 5 mg P/l. Although this did not meet with the required discharge phosphate removal level of ≤ 1 mg P/l, this was subsequently achieved and will be discussed in Phase 4.

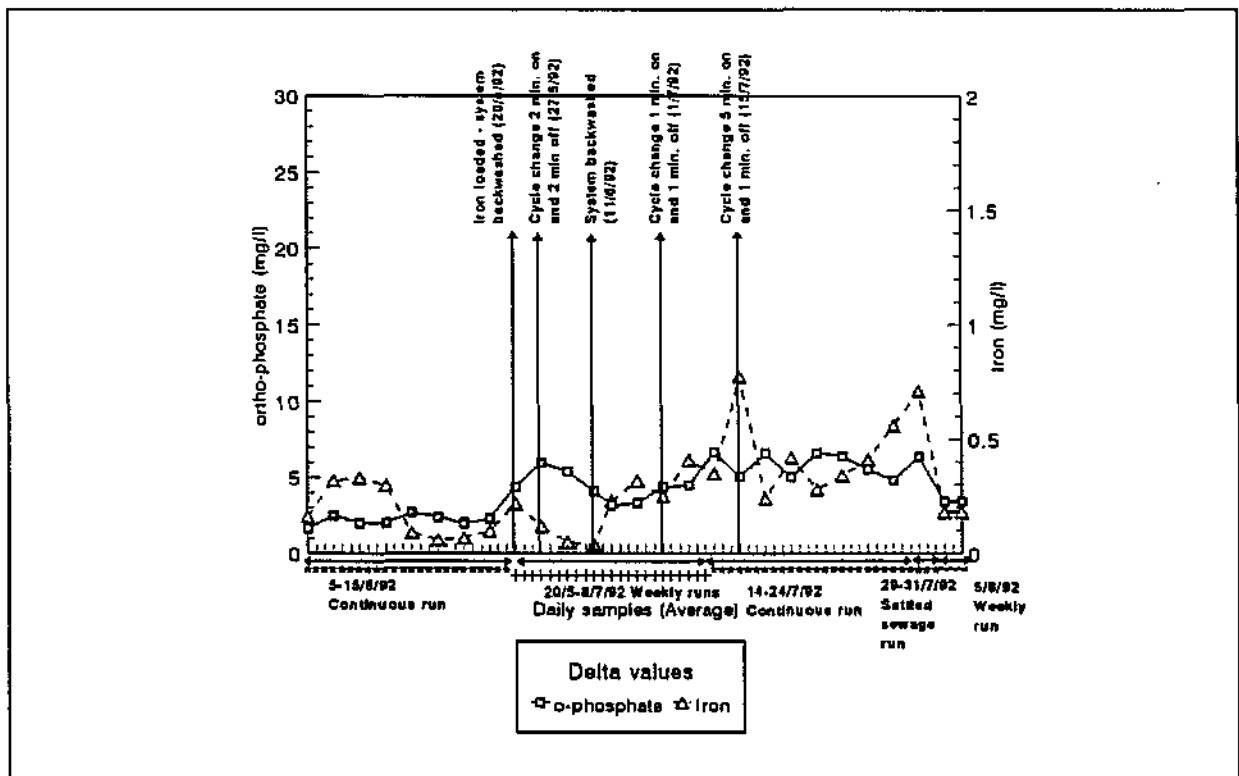


Figure 17. The daily average delta ortho-phosphate and iron concentrations in humus tank effluent during the third phase (5 May - 5 August 1992). Adjustments to the system are indicated

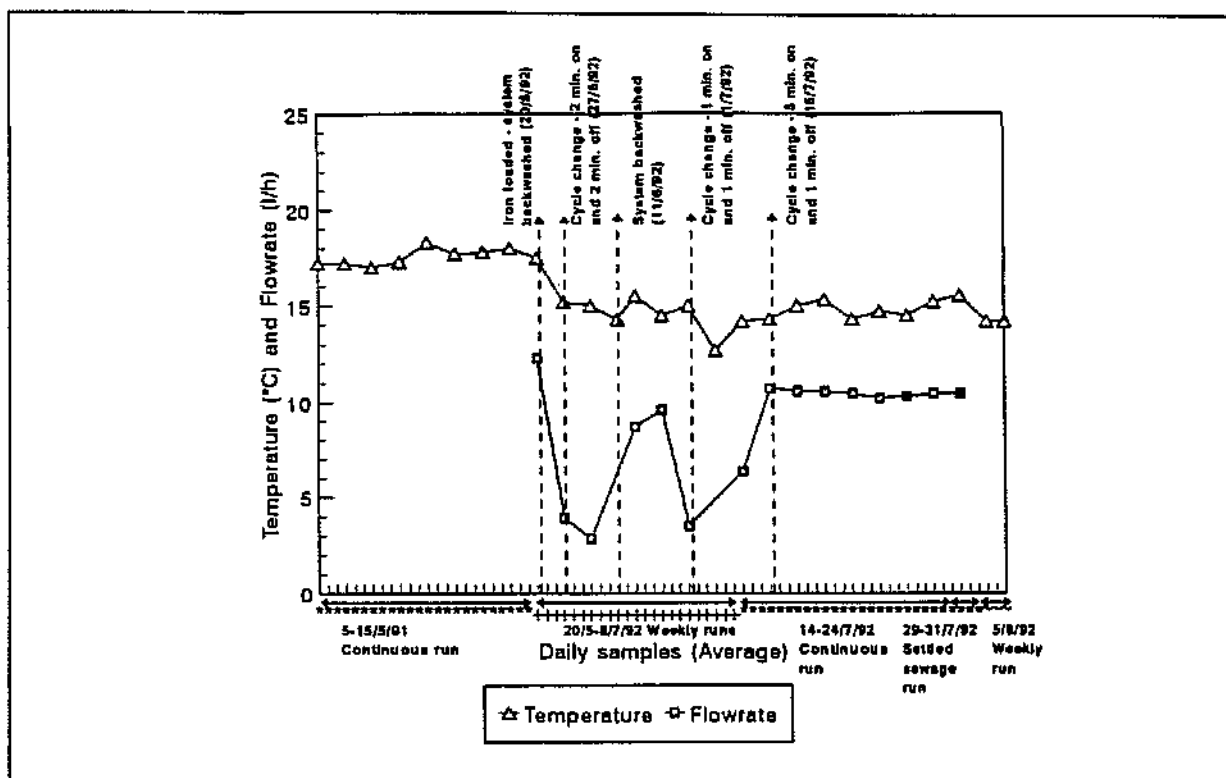


Figure 18. The daily average temperature of humus tank effluent and flowrate during the third phase (5 May -5 August 1992). Adjustments to the system are indicted

3.3.2 pH, temperature and flowrate

The pH remained relatively constant throughout the phase (Figure 19), fluctuating between 6,8 - 7,2. The decreasing temperature had no effect on the pH level, which supports the theory that the rise in pH was possibly linked to the algal growth and was not directly related to temperature. There was no significant effect of either the pH or the temperature on the phosphate removal. The flowrate showed an inverse correlation with the increase in phosphate removal as illustrated by a comparison of Figures 16 and 18.

3.3.3 Iron

The iron concentration generally seemed to follow a similar pattern as in the previous phase, with increased concentrations when the phosphate removal was low and vica-versa (Figure 17). The sudden increases possibly due to the decreased flowrate at those points, 20/5 and 15/7 (Figures 17 and 18). The sudden increase at the end of the phase was due to the high influent iron concentration of the settled sewage.

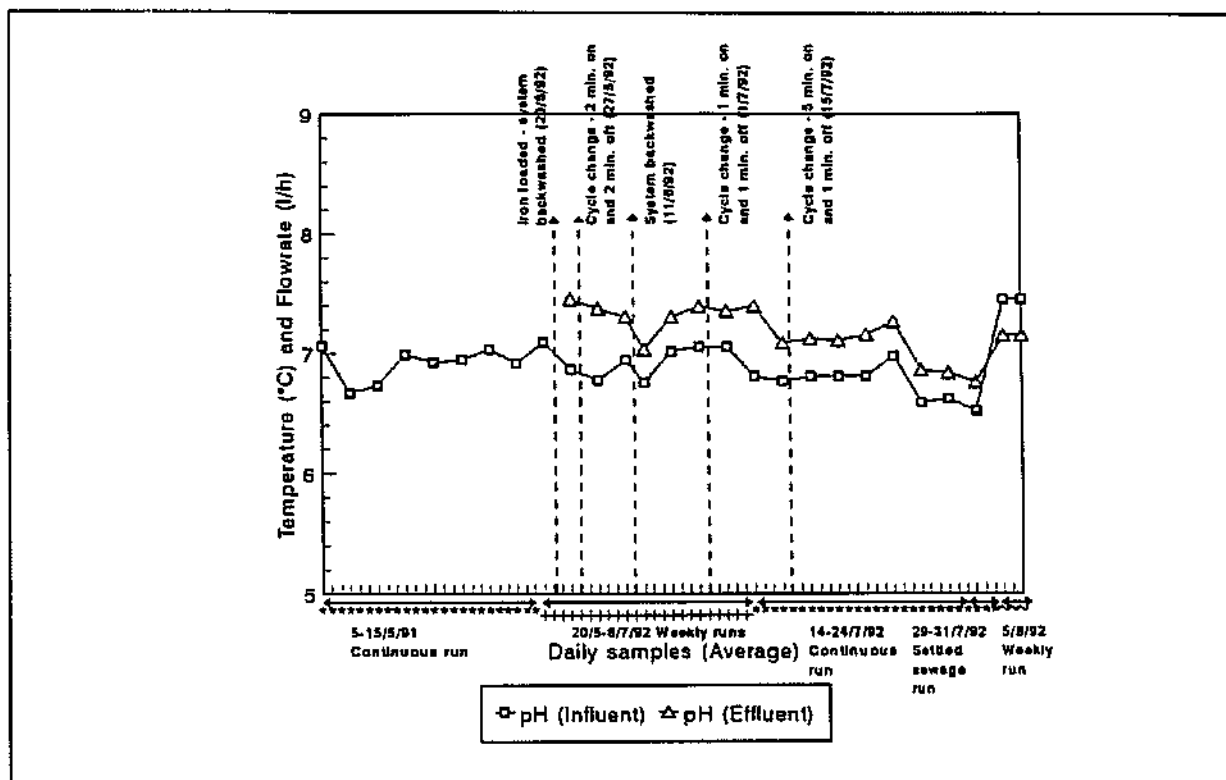


Figure 19. The daily average influent and effluent pH levels in the humus tank effluent during the third phase (5 May - 5 August 1992). Adjustment to the system are indicated

3.3.4 Settled sewage

Phosphate removal, using settled sewage over a period of three days in the Catphate system, was not successful. Figure 20 shows the ortho-phosphate influent and effluent concentrations to be practically the same, suggesting very little ortho-phosphate removal. The temperature remained relatively constant at 17°C with no visible effect on the phosphate removal, which fluctuated between 0 - 3 mg P/l (Figure 21).

As with the ortho-phosphate concentrations there was no significant difference between the influent and effluent iron concentration (Figure 22).

3.3.5 Phosphate load versus phosphate effluent concentration

An aspect of interest was to establish whether the phosphate load (influent phosphate concentration x flowrate) had a proportional effect on the phosphate removal. This was established by plotting the phosphate load against the effluent phosphate concentration. Figure 23 depicts a correlation, with a regression co-efficient of 0,88.

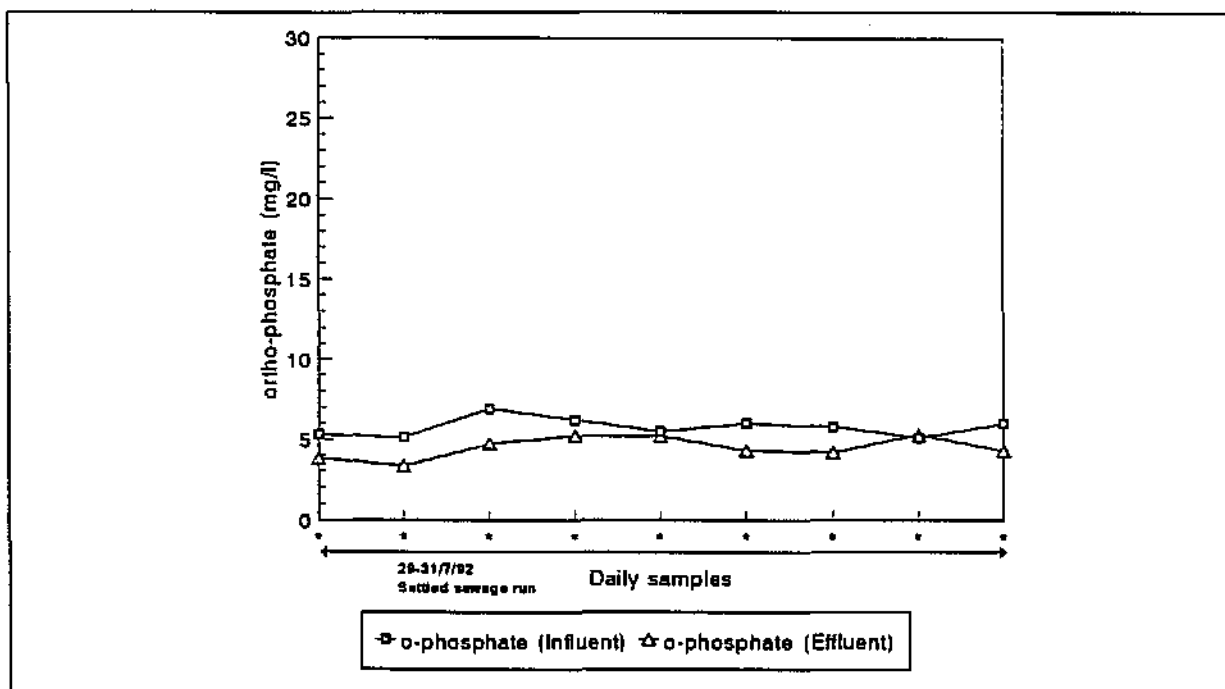


Figure 20. The influent and effluent ortho-phosphate concentrations in settled sewage during the third stage (5 May - 5 August 1992)

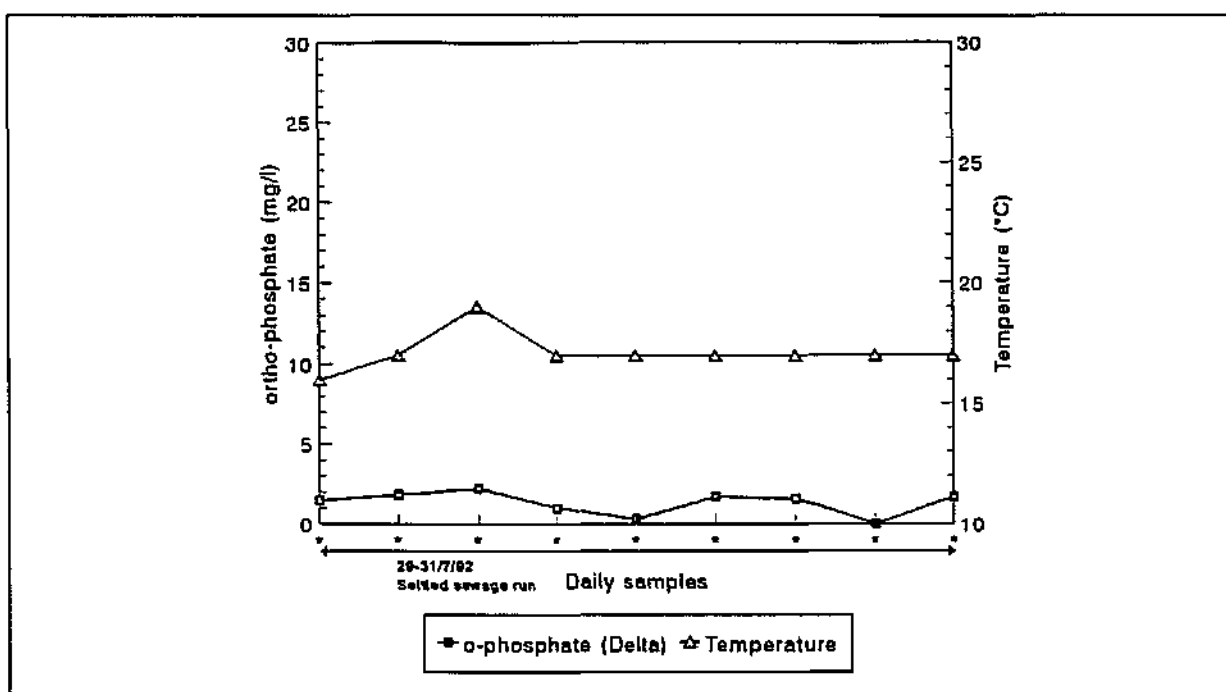


Figure 21. The delta ortho-phosphate concentration and the temperature of the settled sewage during the third phase (5 May - 5 August 1992)

3.4 Phase 4 (1 September - 16 October 1992)

In this phase, comprising a series of continuous runs (Table 5), the effect of retention time as well as that of heavy metals on phosphate removal was determined. The Catphate system, by adjusting the pump cycle times, was run at various retention times throughout the phase. On the 16 September 1992 three heavy metals were dissolved in water and pumped into the humus tank effluent in the holding tank. The system was then monitored for three days. The metals were added in the following forms:

Copper	-	CuSO ₄ (anhydrous)	(1 kg)
Chrome	-	Na ₂ Cr ₂ O ₇	(1 kg)
Nickel	-	NiCl ₂	(1 kg)

Table 5. The experimental procedure for phase 4 (1 September - 16 October 1992)

No.	Date of run	Retention time (minutes)	Pump cycle (minutes)	Flowrate (m ³ /h)	Additions
1.	01-03/09/92	5,0	1 on and 5 off	10,0	<i>ortho</i> -phosphoric acid
2.	04-17/09/92	8,0	1 on and 8 off	4,0	<i>ortho</i> -phosphoric acid Heavy metals (16/09/92)
3.	18/09/92	4,0	1 on and 4 off	12,0	<i>ortho</i> -phosphoric acid
4.	22/09/92	5,0	1 on and 5 off	10,0	
5.	30/9-01/10/92	3,0	1 on and 3 off	17,0	
6.	13-14/10/92	8,5	1 on and 8,5 off	3,5	No additions
7.	15-16/10/92	5,0	1 on and 5 off	10,0	

Table 6. The average concentrations of the components analyzed in humus tank effluent during the fourth phase (1 September - 16 October 1992)

Sample description	Filtered
Average o-PO ₄ - Influent	7,71 mg/t
Average o-PO ₄ - Effluent	2,61 mg/t
Average Δ o-PO ₄	5,10 mg/t
Average iron - Influent	0,07 mg/t
Average iron - Effluent	0,09 mg/t
Average Δ iron	0,02 mg/t
Average pH - Influent	7,70
Average pH - Effluent	8,12
Temperature	20 - 22° C

3.4.1 Phosphate removal and iron

a) Retention time

The results of this phase are depicted in Figures 24 and 25 with the phosphate removal shown in Table 7.

Table 7. The phosphate removal at the various retention times during the fourth phase (1 September - 16 October 1992)

Section no.	Date	Influent o-phosphate (mg/l)	Effluent o-phosphate (mg/l)	Delta o-phosphate (mg/l)	Delta o-phosphate (%)	Retention time (minutes)
1.	01/09/92	7,7	3,0	4,7	61,3	5,0
	02/09/92	9,7	5,6	4,6	47,3	
	03/09/92	10,5	4,2	4,9	46,6	
	Average	9,3	4,3	4,7	51,7	
2.	04/09/92	10,5	4,2	6,3	60,1	8,0
	07/09/92	10,2	3,8	6,4	63,1	
	08/09/92	9,9	5,1	4,8	48,8	
	09/09/92	12,9	4,9	8,0	61,6	
	11/09/92	10,7	5,3	5,5	51,1	
	14/09/92	9,6	3,7	5,9	61,8	
	15/09/92	10,6	2,5	8,1	75,7	
	16/09/92	7,9	2,0	5,8	74,1	
	17/09/92	7,6	1,8	5,8	76,8	
	Average	10,0	3,7	6,3	63,7	
3.	18/09/92	6,2	2,6	3,6	58,4	4,0
4.	22/09/92	4,1	0,1	4,0	97,6	5,0
5.	30/09/92	3,1	0,7	2,5	79,2	3,0
	01/10/92	1,7	0,3	1,4	83,2	
	Average	2,4	0,5	2,0	81,2	
6.	13/10/91	5,7	0,5	5,2	91,2	8,5
	14/10/92	5,6	0,4	5,2	93,4	
	Average	5,7	0,5	5,2	92,3	
7.	15/10/92	5,0	0,3	4,7	94,0	5,0
	16/10/92	5,0	0,3	4,7	94,0	
	Average	5,0	0,3	4,7	94,0	

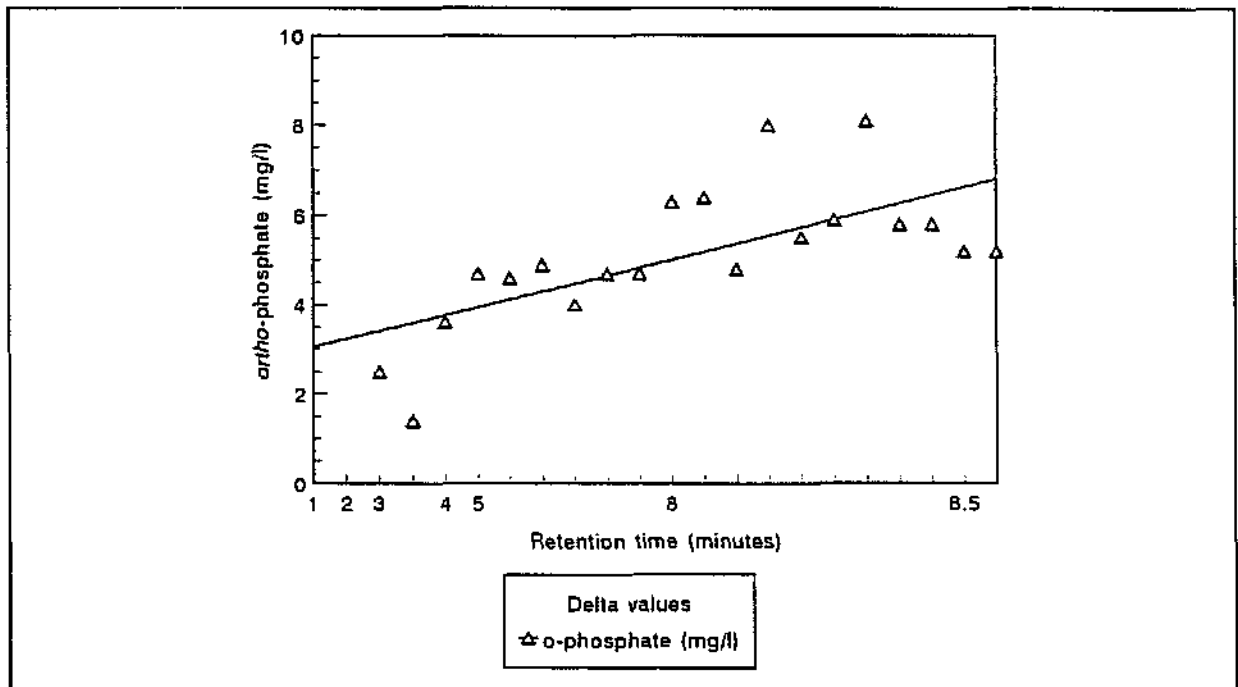


Figure 24. The effect of retention time on phosphate removal during the fourth phase (1 September - 16 October 1992)

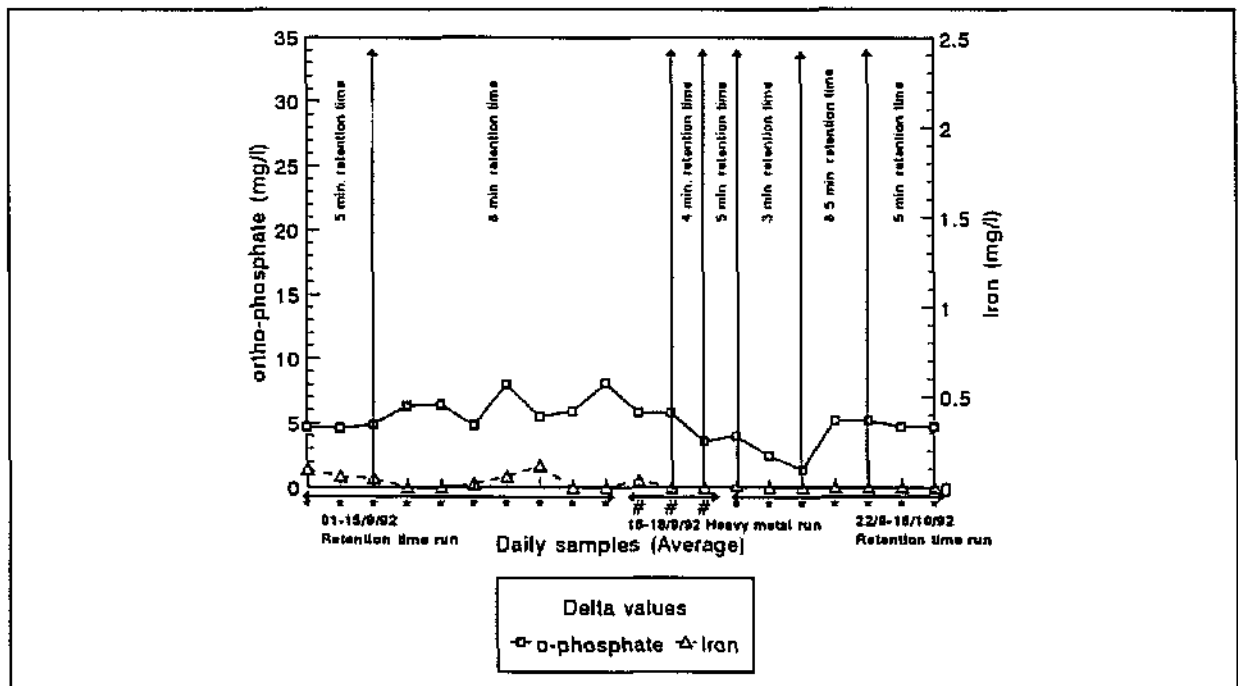


Figure 25. The daily average delta ortho-phosphate and iron concentrations during the fourth phase (1 September 1992 - 16 October 1992). Retention times are indicated

3.4.2 pH and temperature

The pH and temperature remained constant throughout the phase. This substantiated what has been the tendency throughout the study, that these two parameters do not influence the phosphate removal.

3.4.3 Phosphate loading versus effluent phosphate concentration

As in Figure 23, the phosphate load was compared to the phosphate removal (Figure 27). The correlation was substantially less than in the previous phase with a regression coefficient of 0,2. However this could be attributed to the erratic influent phosphate concentration of this phase, and the various adjustments made to the retention time, thereby affecting the flowrate. In phase three there is a steady increase in influent phosphate concentration with the flowrate remaining relatively constant throughout the phase.

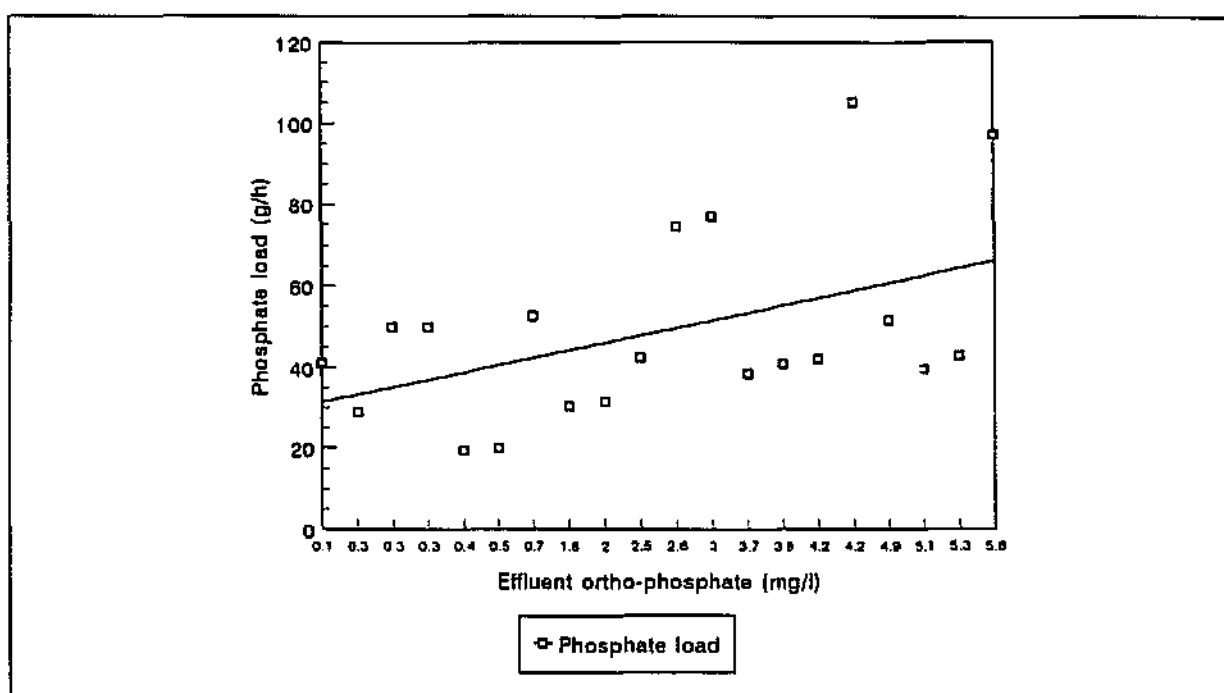


Figure 27. The regression curve of the phosphate load against the effluent phosphate concentration during the fourth phase (1 September - 16 October 1992). Flowrates are indicated

CONCLUSIONS

The system consistently removes in the order of 5-6 mg P/l at a retention time of approximately 5 minutes. It is capable of removing phosphate to below 1 mg P/l at suitable influent phosphate levels. The Catphate system is an example of clean technology. It requires the minimum supervision, and there is no waste.

The effects of the following parameters were examined in this evaluation and led to the following conclusions :

- **Phosphate removal**

The influent phosphate concentrations were erratic throughout the evaluation (Figure 28), but the average removal was in the order of 5-6 mg P/l (Figure 29). The factors that influenced the degree of phosphate removal were :

- The influent phosphate concentration. At influent phosphate levels > 10 mg P/l, removal in the order of 8 mg P/l was obtained. The required level 1 mg P/l can be achieved provided the influent phosphate level is not > 6 mg P/l. This is apparent on comparison of Figures 28 and 29.
- The retention time. The longer the contact time of the humus effluent with the iron filings, the higher the phosphate removal.

In phase three (Figure 23) it was established that there is a correlation between the phosphate load and the final effluent concentration, but it is dependant on retention time and illustrated in phase 4 (Figure 27).

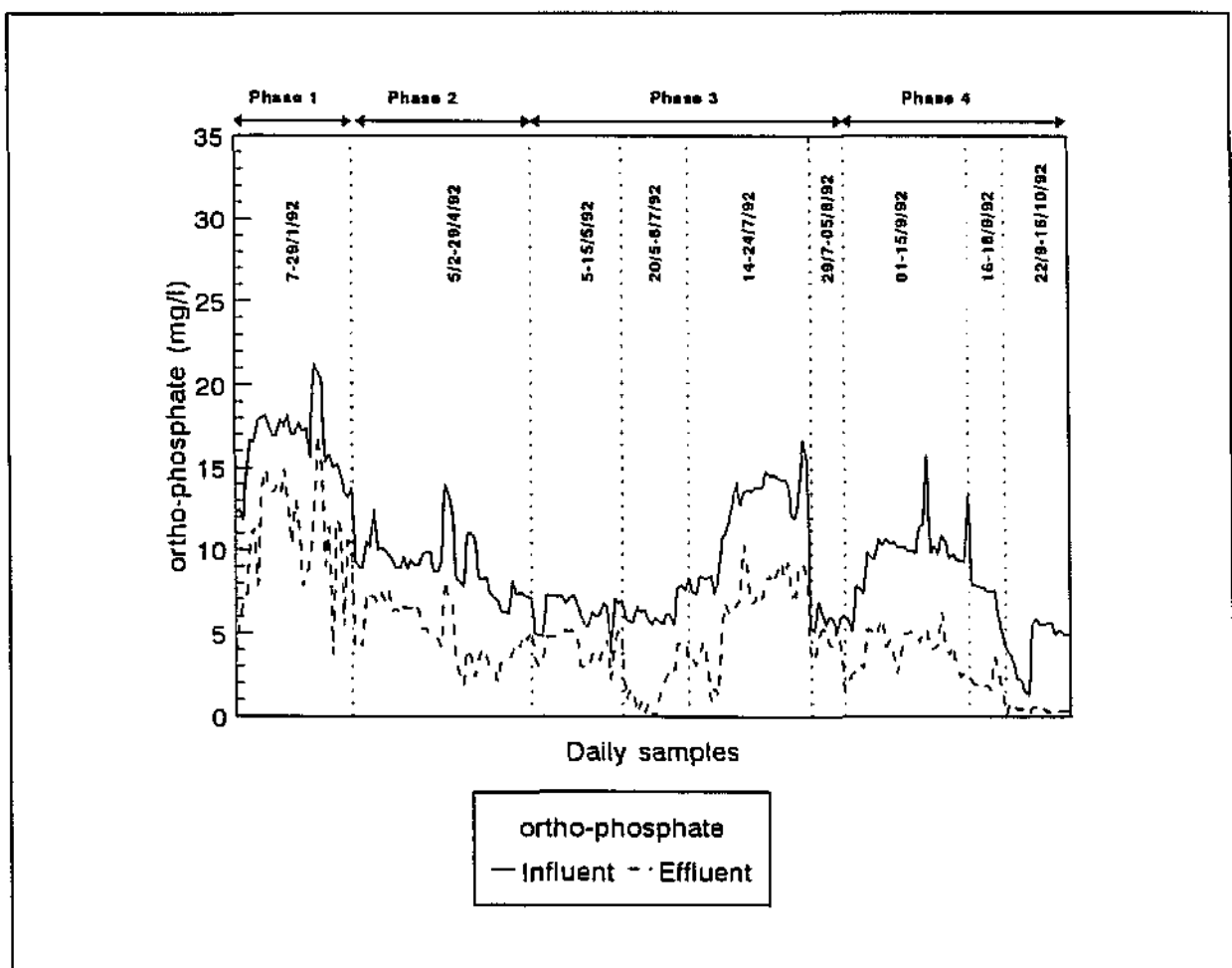


Figure 28. The influent and effluent ortho-phosphate concentration throughout the evaluation (7 January - 16 October 1992). Phases are indicated

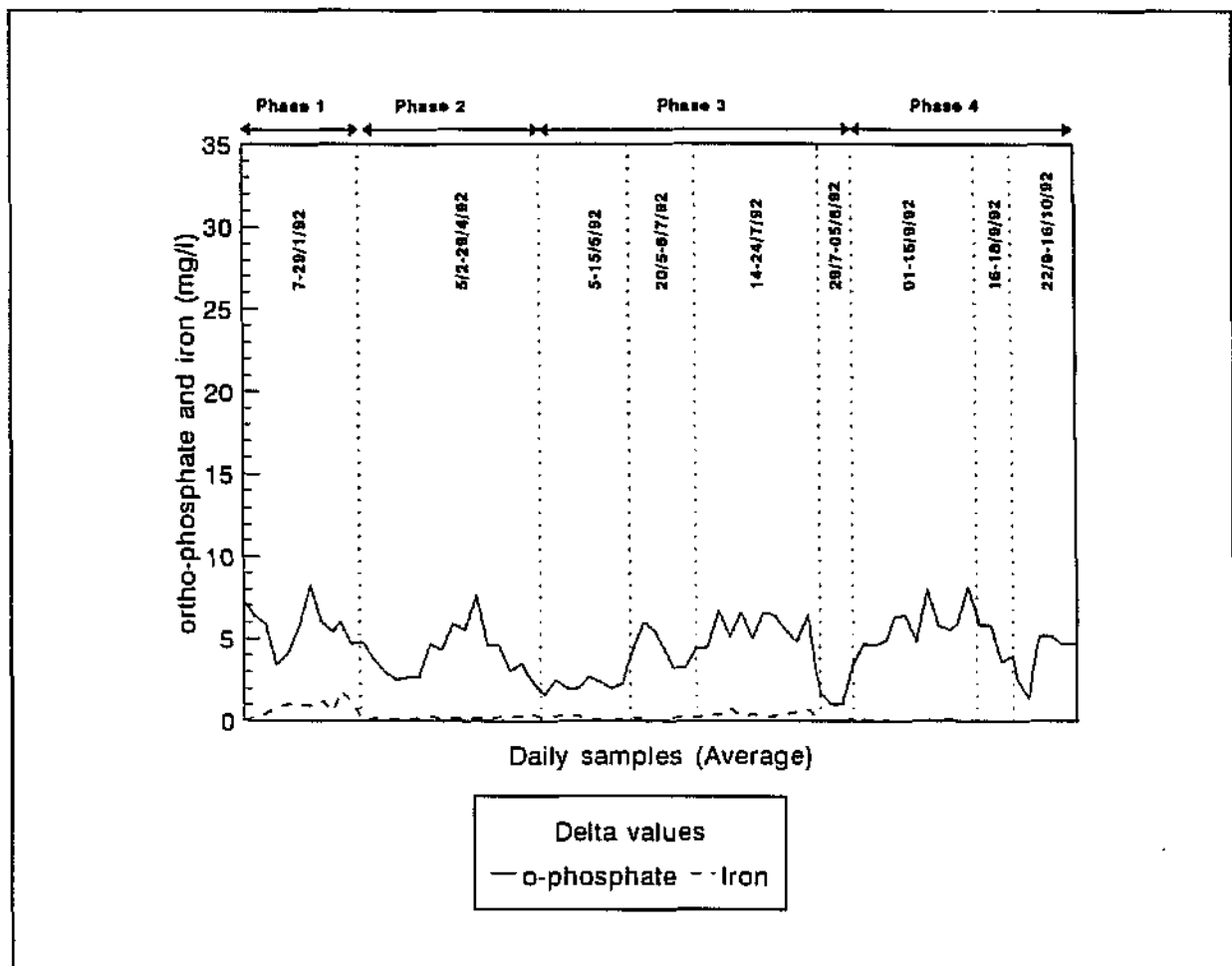


Figure 29. The daily average delta phosphate and iron concentration throughout the evaluation (7 January - 16 October 1992). Phases are indicated

- *Iron*

The iron concentration had no significant effect on the phosphate removal (Figure 29). Although the effluent iron concentration was high in phase 1, it stabilized in phase 2 and remained so for the remainder of the evaluation.

- *pH*

The pH ranged between 6.8-8.2 (Figure 30), and had no visible effect on phosphate removal throughout the evaluation. There are indications of the pH level being directly proportional to temperature. The pH level increased, probably due to algal growth, as the temperature rose, and decreased as the evaluation period moved into winter.

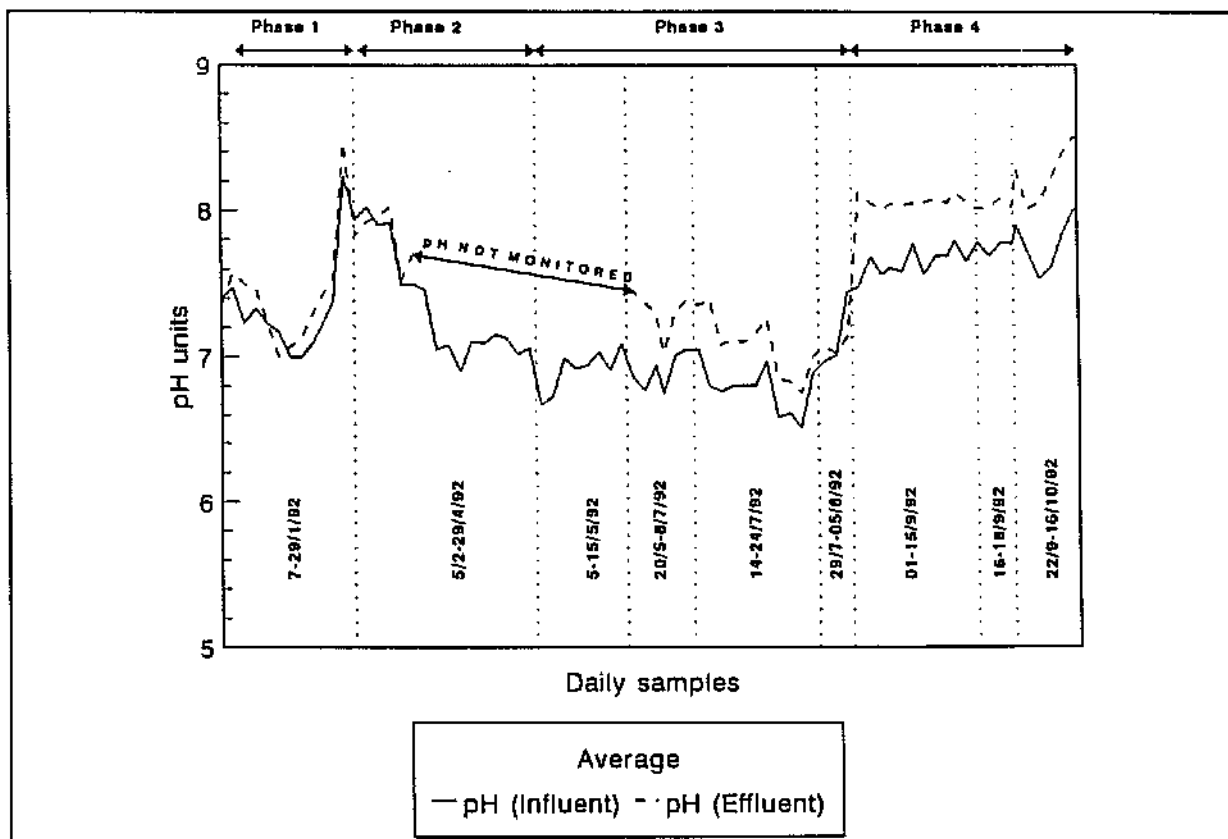


Figure 30. The daily influent and effluent pH levels throughout the evaluation (7 January - 16 October 1992). Phases are indicated

- *Temperature*

The temperature ranged between 12-28°C during the evaluation and had no significant effect on the phosphate removal (Figure 31).

- *Ions*

The effect of calcium was determined in phase 1, and no detectable effect on the phosphate removal was demonstrated.

- *Heavy metals*

There is no significant effect of the three heavy metals (copper, chrome and nickel) on phosphate removal. However, the system was able to significantly remove the metals, chrome removal being most efficient.

- *Retention time and flowrate*

The retention time was regulated by the pump cycle and flowrate. The flowrate and retention time are inversely proportional. Phase 4 demonstrated that the longer the retention time the higher the phosphate removal (Figure 32).

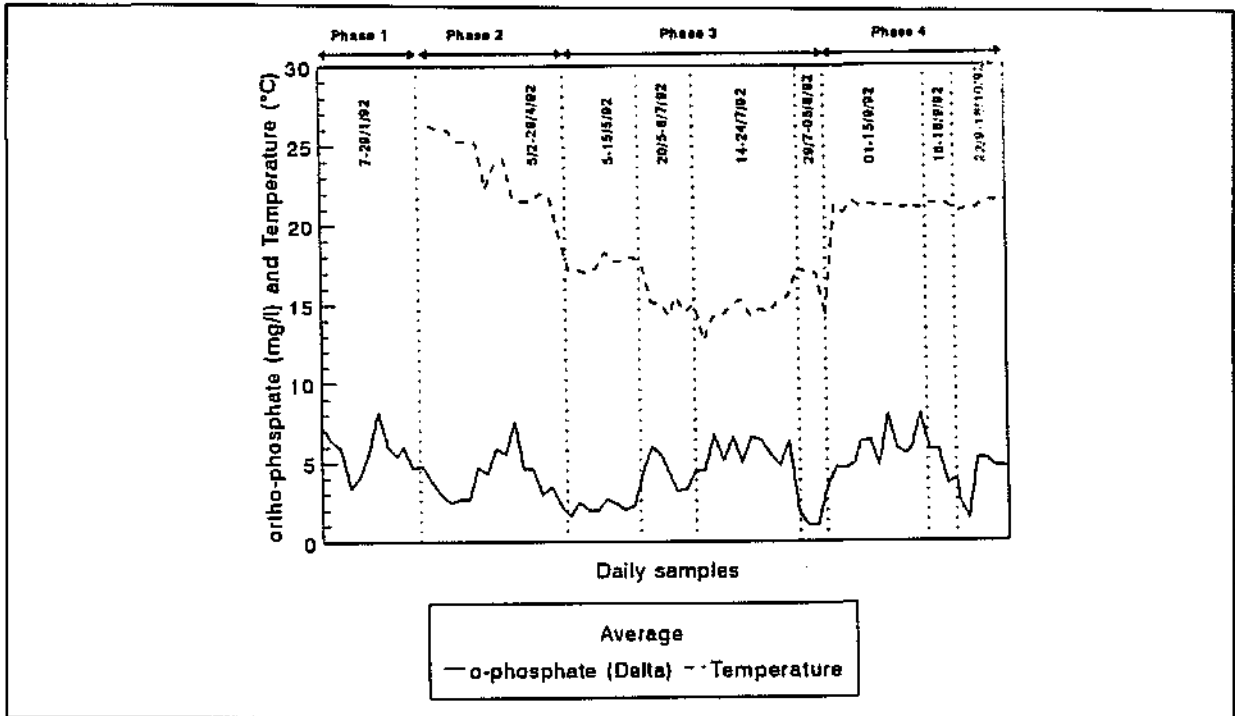


Figure 31. The daily average delta ortho-phosphate concentration and temperature throughout the evaluation (7 January - 16 October 1992). Phases are indicated

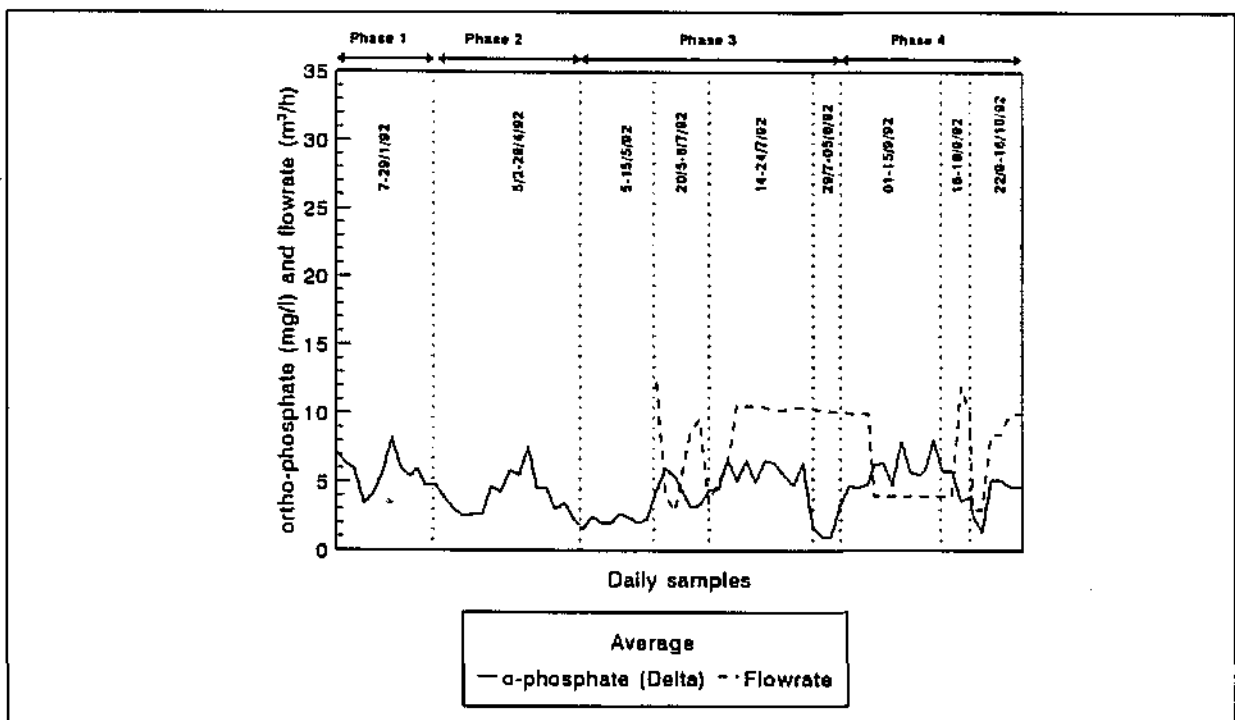


Figure 32. The daily average delta ortho-phosphate concentration and flowrate throughout the evaluation (7 January - 16 October 1992). Phases are indicated

- **Factors influencing the phosphate removal**

Table 8 displays simplified results obtained from a multiple regression. This regression was conducted by plotting the various independent variables against the dependant variable, viz. the effluent *ortho*-phosphate. All independent variables with a significant level percentage of 5 and less will influence or inhibit the phosphate removal.

Table 8. Multiple regression results indicating factors which influence the phosphate removal

No.	Independent variable	Significant level (%)	R-Sq.
1	o-Phosphate (ln) pH (ln) Fe (ln) Temperature Flow	0 4 5 7 2	0,90
2.	Calcium (ln)	30	0,01
3.	t-Phosphate (ln)	0	0,61
4.	Phosphate load	0	0,71

Components with a significant level of 5% and lower do influence the phosphate removal.

5. REFERENCES

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6. Annexure

ANNEXURE A

ADAMS & ADAMS
PATENT ATTORNEYS
BENSTRA BUILDING
PRETORIA

A. & A. Ref. No. 117061

FORM P7

REPUBLIC OF SOUTH AFRICA
Patents Act, 1978

COMPLETE SPECIFICATION

(Section 30 (1) — Regulation 28)

OFFICIAL APPLICATION NO.	
21	01 787700

LODGING DATE	
22	14th OCTOBER 1988

INTERNATIONAL CLASSIFICATION	
51	C02F

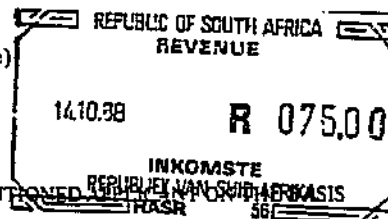
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FULL NAME(S) OF INVENTOR(S)	
72	DANIEL CORNELIUS VAN DER POST

TITLE OF INVENTION	
54	TREATMENT OF WATER

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
APPLICATION FOR A PATENT AND
ACKNOWLEDGEMENT OF RECEIPT
(Section 30(1) Regulation 22)

FORM P.1
(to be lodged in duplicate)



THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT(S) OF THE PRESENT APPLICATION FILED IN DUPLICATE.

PATENT APPLICATION NO.	
21	01 887700
71	FULL NAME(S) OF APPLICANT(S)

A & A REF: 117061

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Republic of South Africa

54 TITLE OF INVENTION

TREATMENT OF WATER

Only the items marked with an "X" in the blocks below are applicable.

- ☒ THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2
☐ THE APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO. 21 01
☐ THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON APPLICATION NO.

21 01

THIS APPLICATION IS ACCOMPANIED BY:

- ☒ 1. ~~Two copies of a complete specification of ... 20 ... pages~~
☒ 2. Drawings of ... 1 ... sheets.
☒ 3. Publication particulars and abstract (Form P.3 in duplicate) (for complete only).
☒ 4. A copy of Figure ... 1 ... of the drawings (if any) for the abstract (for complete only).
☐ 5. An assignment of invention.
☐ 6. Certified priority document(s) (State quantity) :
☐ 7. Translation of the priority document(s).
☐ 8. An assignment of priority rights.
☒ 9. A copy of the Form P.2 and the specification of S.A. Patent Application No. 21 01 87/7427
☒ 10. A Form P.2 in duplicate.
☒ 11. A declaration and power of attorney on Form P.3.
☐ 12. Request for ante-dating on Form P.4.
☐ 13. Request for classification on Form P.9.
☐ 14. Request for delay of acceptance on Form P.4.
☐ 15.

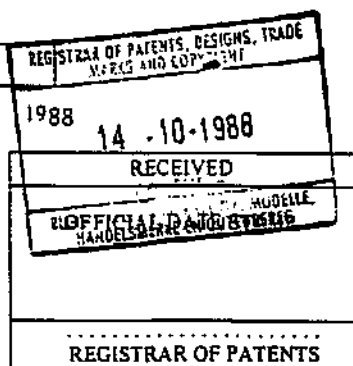
74 ADDRESS FOR SERVICE: Adams & Adams, Pretoria.

DATED THIS 14th DAY OF OCTOBER

ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

The duplicate will be returned to the applicant's
address for service as proof of lodging but is
not valid unless endorsed with official stamp.

A & A P.201



This invention relates to the treatment of water. It relates in particular to a process for treating water, and to water treatment apparatus.

According to a first aspect of the invention there is provided a process for treating water which includes

- feeding water retaining impurities into a treatment zone containing substantially water-insoluble iron-based particles;

- maintaining the treatment zone at sub-atmospheric pressure while affecting contact of the water and iron-based particles, thereby to convert impurities in the water to a form in which they are more readily separable from the water; and

- withdrawing treated water from the treatment zone while retaining a major proportion of the particles in the zone.

The pressure in the treatment zone may be maintained at at least 50 mm Hg vacuum, ie at at least 50 mm Hg below atmospheric pressure, and may be maintained at a pressure as low as 450 mm Hg vacuum.

The residence time in the treatment zone may be less than 5 minutes, eg between 0,5 and 2 minutes.

The treatment zone may be provided by a vessel, and the sub-atmospheric pressure or vacuum may be created by pump suction.

The process may also include periodically withdrawing accumulated gases from the vessel, to assist in maintaining said vacuum.

The impurities may comprise soluble impurities which are converted to insolubles. The soluble impurities may be, or include, orthophosphates and/or calcium compounds, with elemental iron in the particles catalyzing and/or forming part of the chemical reactions in which dissolved orthophosphates and/or calcium compounds are converted to insoluble phosphates and/or calcium compounds. The impurities may additionally, or instead, comprise difficult to separate insoluble impurities which form stable suspensions in the water and hence render it turbid. Such impurities will be converted into more readily separable form, eg in the form of flocs. Hence, only iron forming part of the chemical reactions will pass from the vessel with, as mentioned, the major proportion of the particles being retained in the vessel. The particles may be scrap metal particles such as filings, off-cuts, or the like.

The contacting may be affected by passing the water through the body of particles while moving the particles relative to the vessel. The relative movement of the particles to the vessel may be affected by rotating the vessel about an axis, and allowing the particles to move along at least a portion of its periphery as it rotates. The water may pass through the vessel in an axial direction. The degree of contact can be varied by varying the rotational speed of the vessel and/or by operating the vessel in intermittent fashion, ie periods of rotation followed by periods in which the vessel is stationary.

According to a second aspect of the invention, there is provided water treatment apparatus which includes

a vessel;

a water inlet leading into the vessel;

a water outlet leading from the vessel;

a bed of water-insoluble iron-based or iron-containing particles with which water in the vessel can be contacted, thereby to convert impurities in the water to a form in which they are more readily separable from the water, inside the vessel; and

vacuum-generating means for generating sub-atmospheric pressure or vacuum in the vessel.

As mentioned hereinbefore, the particles may be scrap metal particles such as metal filings, metal turnings, metal off-cuts, or the like. The particles may be of regular shape or configuration, eg rod-like, spherical, pellet-like, cylindrical, etc. or of irregular shape or configuration. The vessel may be of round cylindrical form, with the inlet and outlet being located axially at opposite ends of the vessel. The vessel may extend horizontally, and the apparatus may include drive means for driving the vessel to rotate about a horizontally extending axis, with the body of the particles being in the form of a bed in the vessel. The bed may extend up to at least the level of the rotational axis so that, its height will be at least 50% of the inner diameter of the vessel. Its height may be between 65% and 90% of the inner diameter, eg about 80%.

At least one baffle, protruding inwardly from the wall of the vessel, may be provided. The baffle may be of elongate form, and may extend parallel to the rotational axis. A plurality of the baffles, spaced circumferentially apart, may be provided.

The vacuum-generating means may include a pump operatively connected to the water outlet and being capable of generating or creating a vacuum of at least 50 mm Hg below atmospheric pressure, in the vessel.

The vacuum-generating means may also include gas-withdrawal means for withdrawing gases generated during treatment of the water, eg for withdrawing such gases periodically from the vessel. The gas-withdrawal means may comprise a conduit leading out of the vessel from a zone above the normal water level in the vessel, a venturi to which the conduit is connected, and pump means for pumping liquid through the venturi, thereby to create a vacuum in the conduit.

The invention will now be described by way of example, with reference to the accompanying diagrammatic drawings.

In the drawing

FIGURE 1 shows a side view of water treatment apparatus according to one embodiment of the second aspect of the invention;

FIGURE 2 shows a sectional view through II-II in Figure 1; and

FIGURE 3 shows a block diagram of water treatment apparatus according to another embodiment of the second aspect of the invention.

Referring to Figures 1 and 2, reference numeral **10** generally indicates water treatment apparatus according to a first embodiment of the second aspect of the invention.

The apparatus **10** includes a hollow cylindrical vessel **12**, the ends of which are closed off by means of annular end-pieces **14**, **16** respectively. A pair of circumferentially extending guide or rolling surfaces **18**, spaced apart in an axial direction, are provided around the vessel **12**. The vessel **12** is rotatably supported on rollers **20** rotatably mounted between cheek plates **22** protruding upwardly from a floor **24**. The guide surfaces **18** engage the rollers **20**. The vessel **12** can be of iron-containing material, eg steel.

One of the rollers **20** is connected, by means of a drive shaft **26**, to an electric motor **28**. Hence, the vessel **12** will be driven to rotate by the electric motor **28**, via the drive shaft **26** and its associated roller **20**. If necessary, the drive shaft **26** can be fitted with speed-reduction means such as a gear-box (not shown).

The apparatus **10** also includes a bed **30** of scrap iron particles. The scrap iron particles may comprise irregular-shaped metal turnings, filings, shavings, nuggets, or the like, and/or regular-shaped metal spheres or balls, pellets, rods, cylinders, plates, or the like. The sizes of the individual particles may vary from powder or granular size, from up to about $0,1 \text{ cm}^3$, to about 10 cm^3 , eg 1 cm^3 to 5 cm^3 . The bed **30** occupies about 80% or more of the volume of the vessel **12**, and its height H can be between 70% and 90%, eg about 80%, of the inner diameter of the vessel **12**.

For example, the particles can be scrap mild steel plates having a planar surface area of 1 to 5 cm², and a thickness of 1-2 mm. The bed will then typically have a bulk density of about 1 kg/l.

The axial opening of the end-piece 14 is provided with an outwardly protruding sleeve 32 to which is attached a water inlet conduit 34. The sleeve 32 is hence rotatable relative to the conduit 34, and suitable watertight seal means (not shown) is provided at the junction between the sleeve 32 and the conduit 34. An apertured plate 36 is spaced a small distance from the end-piece 14.

A sleeve 38 protrudes outwardly around the opening in the end-piece 16 and provides a water outlet. The sleeve is connected to the suction side (not shown) of a centrifugal pump 40 by means of a conduit 42, with a fluidtight connection (not shown) being provided between the sleeve 38 and the conduit 42, and with the sleeve 38 being rotatable relative to the conduit 42. The pump, by drawing water through the vessel 12, creates a sub-atmospheric pressure in the vessel. A conical sieve 39 protrudes inwardly from the opening in the end plate 16. A discharge conduit 44 leads from the pump 40.

The apparatus 10 also includes gas-withdrawal means, generally indicated by reference numeral 45. The gas-withdrawal means 45 includes a fixed conduit 46 leading from a zone 48 above the normal water level 50 in the vessel 12. The conduit 46 is connected at 52 to a conduit 54 extending along the axis of the vessel 12. Hence, the conduit 46 can rotate relative to the conduit 54 as the vessel 12 rotates. The conduit 54 passes through the wall of the sleeve 34 and leads into a venturi (not shown).

A pump (not shown) pumps liquid such as water through the venturi, thereby creating a zone of reduced pressure which is in communication with the conduits 54, 52. In this manner, gases accumulating in the zone 48 can be withdrawn. These gases would tend to retard the chemical reactions in the vessel 12 if allowed to accumulate, eg to the extent that a positive pressure is present in the vessel 12.

Radially inwardly protruding elongate baffles 56, extending parallel to the rotational axis and spaced apart equidistantly circumferentially, are provided on the inside of the vessel 12.

In use, the vessel 12 is driven to rotate by the electric motor 28, at a rotational speed of between 1 rpm and 5 rpm, typically about 2 rpm. As it rotates, the bed 30 of iron particles continually moves relative to the vessel 12. The water level is maintained at about the level 50, but can be varied, eg raised or lowered by 10-20%, if desired. This relative movement is enhanced by the baffles 56. This relative movement, which hence also causes the particles to move relative to one another, ensures a rubbing or scouring action between the iron particles, thereby removing deposits which may accumulate on the particles, and hence also continually exposing fresh surface to the water.

Water containing impurities such as dissolved orthophosphates and silanols, enters the vessel 12 via the inlet conduit 34. Treated water leaves the vessel via the outlet sleeve 38. Some deposition of the insoluble phosphates may take place inside the vessel, but the Applicant believes that this will be very little, if any.

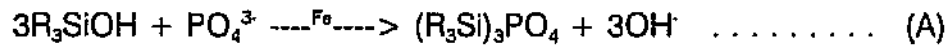
The capacity of the pump 40 is sufficient so that the water residence time of between 0,5 and 2 minutes, eg about 1 minute, is maintained in the vessel, and is also sufficient to create a vacuum or sub-atmospheric pressure of about 50 mm Hg below atmospheric pressure in the zone 48. Gases evolved during the action in the vessel 12, as described in more detail hereunder, accumulate in the zone 48, and it is thus necessary to withdraw these gases via the conduits 52, 54 periodically by operating the pump associated with the venturi intermittently, eg for about 5 minutes in one hour.

Most of the insoluble phosphates will pass out of the vessel in suspension with the water, and can then be routed to a solids removal stage (not shown). The solids removal stage may comprise conventional apparatus such as a flocculation unit, a gravity settler, a filter and/or a centrifuge, and water relatively free of orthophosphates recovered.

The iron-containing particles, it is believed, act as a catalyst for converting soluble orthophosphates to insoluble phosphate compounds. This is achieved by intimate contact of all the water entering the vessel with the iron particles, for a said contact or residence time.

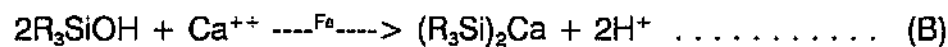
It is believed that the exact nature and form or configuration of the iron particles is not critical, and they can hence be of any available form or nature, provided that they are substantially water-soluble and can form a bed in the vessel. They may hence, as mentioned hereinbefore, comprise scrap iron or steel particles, or the like.

Without wishing to be bound by theory, the Applicant believes that the reactions taking place in the vessel 12 are as follows:



where R is methyl.

At the same time, elemental iron catalyses the reaction of calcium ions present in the water with silanols, as follows:

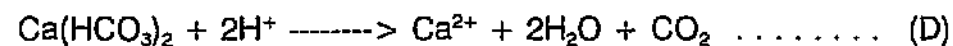


Reactions A and B take place simultaneously.

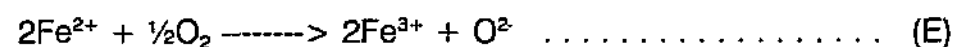
Secondly, the hydrogen ions formed in reaction (B) react with elemental iron, as follows:



The hydrogen ions also react with available alkalinity in the waste water, ie basic calcium compounds, as follows:



The dissolved iron ions formed in reaction (D) are oxidized from the ferrous to the ferric form by dissolved oxygen in the water, as follows:



The ferric ions of reaction (E) then react with the silane phosphate formed in reaction (A) to form ferric phosphate, as follows:



Finally, the silane ions of reaction (F) react with the hydroxyl ions of reaction (A) to reconstitute the silanols, as follows:



The silanols present in the water are thus believed to be involved in a cyclic reaction which will continue as long as there is elemental iron available as catalyst, and until all the dissolved orthophosphates are converted to insoluble ferric phosphates. However, some silanols will in fact be removed from the water in the form of the calcium compound form in reaction (B).

The iron particles will hence gradually be consumed and will require replenishment from time to time.

The insoluble phosphates which are formed and which are retained in suspension in the water can, for example, be removed by agitating or stirring the water very slowly for 10 to 15 minutes, to flocculate the suspended phosphates. Flocculation of the positively charged iron phosphate particles is assisted by the presence of the negatively charged silane ions which are formed during the reactions in the vessel. The resultant flocs readily settle.

It is envisaged that the apparatus 10 can be incorporated as a step or stage in a total water purification system, eg a sewage water purification system.

Tests were conducted on an apparatus 10 in which the vessel 12 had an internal diameter of 0,15 m and a length of 2 m, ie it had an internal volume of about 55 litres. The water level was maintained at approximately 90% of the inner diameter so that the effective volume was approximately 30 litres of water. Water throughput was maintained at 15-30 litres per minute to give a residence or contact time of 1-2 minutes. The vessel was filled to about 80% of its inner diameter with scrap mild steel plates, as described above, with a bulk or packed density of 0,5 kg/l. The plates were randomly orientated in the vessel.

It has also been found that by operating the vessel 12 under a vacuum of at least 50 mm mercury, a very high efficiency is obtained, eg up to 90% of the soluble phosphates present in the water entering the vessel is eventually deposited in a downstream settler, ie converted to insoluble phosphates. Typically, the dissolved phosphate levels in the water entering the vessel 12 was about 8,8 mg/l, while the water downstream of the settler contained only about 0,9 mg/l phosphates. These results were obtained consistently during a trial lasting for seven consecutive days. During this trial, there was no visible contamination, eg formation of an oily layer, on the iron particles, which hence remained clean and active for the full duration of the test. However, gases accumulated in the zone 48, and were withdrawn intermittently as hereinbefore described. The vessel 12 was operated to have a residence time of from 1 to 2 minutes, and, as mentioned hereinbefore, the iron particles remained clean, ie cleaning thereof, eg by means of an acid wash, was not required.

Naturally, the degree of vacuum in the vessel 12 can be regulated as desired. For example, it may be more than 50 mm mercury below atmospheric pressure, eg about 70-100 mm mercury below atmospheric pressure, with 450 mm vacuum, ie 450 mm below atmospheric pressure, or about 200-210 mm mercury absolute pressure, being considered a practical lower limit.

If desired, a non-return valve (not shown) can be fitted in the conduit 52 or the conduit 54, and a timer (not shown) can be fitted to the pump associated with venturi, to effect the intermittent operation thereof.

Naturally, water containing differing concentrations of orthophosphates can also be treated, and their concentrations can vary widely depending on the source of the water, eg between 5 and 10 mg/l, expressed as P, while achieving, it is believed, comparable results.

Apart from removal of dissolved phosphates, the apparatus 10 can also be used to remove turbidity and/or silanols from water, eg water not necessarily containing dissolved orthophosphates.

For silanol removal, only reaction (B) hereinbefore described, will be involved, ie the formation of $(R_3SiO)_2Ca$. For turbidity removal, the following reaction will primarily be involved:



The positively charged ions, ie R_3Si^+ , will tend to neutralize negatively charged particles which are normally present in stable suspensions of turbid water at a pH greater than 7.0, so that destabilization of the suspension and floc formation occurs.

The flocs can be removed by settling, or the like. In this fashion, silanols are also removed.

In a flocculation efficient test conducted on the apparatus 10, there was used surface water having a relatively high turbidity of 70 NTU's (ie turbidity units as measured by nephelometric analysis), and a chemical composition as follows:

pH	-	7,6
conductivity	-	254 micro mhos/cm
total hardness	-	105 mg/l as CaCO_3
calcium hardness	-	76 mg/l as CaCO_3
total alkalinity	-	102 mg/l as CaCO_3
chloride	-	14 mg/l as Cl
sodium	-	11 mg/l as Na

The residence time in the vessel 12 was 0,5 minutes, and a vacuum of 50 mm mercury below atmospheric pressure was maintained in the zone 48. The water leaving the vessel 12 was clarified, using 0,1 mg/l anionic floc aid to obtain a turbidity of less than 5 NTU's. As a control, the same water was treated with 0,1 mg/l of the anionic floc aid without passing it through the vessel 12, and substantially no improvement in the turbidity was observed. It was only after this water had also been treated with 7,5 mg/l cationic flocculant, ie in addition to the 0,1 mg/l anionic floc aid, that a turbidity of less than 5 NTU's was obtained. Hence, by using the vessel 12, the addition of the cationic flocculant can be dispensed with.

The process and apparatus of the invention can be used to treat any water containing dissolved impurities as described, including domestic sewage, industrial effluent, treated as well as raw surface waters, underground waters, drinking water, rain water, etc.

Referring to Figure 3, reference numeral **100** generally indicates a water treatment installation according to another embodiment of the second aspect of the invention.

Parts of the apparatus **100** which are the same or similar to those of the apparatus **10** hereinbefore described with reference to Figures **1 and 2**, are indicated with the same reference numerals.

The apparatus **100** comprises a cooling tower, generally indicated by reference numeral **102**, having a water collection zone **104**.

A conduit **106** leads from the zone **104** to the suction side of a pump **108**. A conduit **110** leads from the discharge of the pump **108** to a heating vessel **112** containing a heating coil **114**, with the conduit leading into the coil, and a conduit **116** leading from the other end of the coil. Hence, the water in the coil **114** is heated in the vessel **112**, which may hence be part of the chemical process (not shown). The conduit **116** passes through a coupon rack **118** containing corrosion coupons (not shown) for monitoring the corrositivity of the water in the conduit **116**. A conduit **120** leads from the coupon rack **118** back to the top of the cooling tower.

The conduit **34** extends down into the zone **104**, while the venturi of the gas-withdrawal system **45** is located in the conduit **44** leading from the pump **40**.

The venturi is numbered 122. A separate pump for the venturi 22 is thus not required. The mounting of the gas withdrawal system 45 is similar to that hereinabove described with reference to Figures 1 and 2, save that the gas withdrawal system is located at the downstream end of the vessel 10 rather than its upstream end. In use, a slipstream of the water from the zone 104, eg typically about 10% thereof, is routed via the vessel 12. The gases evolved in the vessel 12 are reintroduced into the water leaving the vessel 12, at the venturi 122.

The Applicant believes that these gases impart corrosion-resisting or inhibiting properties to iron components, eg the downstream conduits. Hence, by reintroducing this gaseous product into the water, corrosion protection of the downstream equipment is obtained.

In a test run conducted apparatus 100, a 10% side stream was withdrawn through vessel 12. The water was subjected to a maximum temperature rise of 10° in the vessel 112, ie from about 25° C to about 35° C. The water in the system was surface water having a chemical composition as set out above. Blow-down from the system was regulated to maintain approximately four cycles of concentration. A water velocity of approximately 1,2 m/sec was maintained through the coupon rack 118, and the effective retention time in the vessel 12 was about 0,5 minutes. An average corrosion, measured in the coupon rack 118, of 0,2 mm per year was measured. In a control run under similar conditions, but without the slipstream of water passing through the vessel 12, a corrosion rate of 1,19 mm per year was measured.

If desired, the vessel **12** can be adapted so that its rotational speed can be varied, eg by fitting it with a variable speed gearbox which is coupled to its drive motor. In this fashion, the degree of contact of the water with the iron particles can be varied. Instead, or additionally, the vessel drive motor can be adapted, eg by fitting a timing switch to it, such that it is activated/deactivated cyclically with the vessel, hence only rotating intermittently or at intervals and with the vessel rotational speed being constant during the periods of rotation.

Instead of, or in addition to, dissolved phosphates in the water, dissolved calcium compounds may be present. Such compounds can then also be removed from the water by means of the apparatus **10, 100**, thereby effecting softening of the water.

CLAIMS

1. A process for treating water, which includes

feeding water containing impurities into a treatment zone containing substantially water-insoluble iron-based particles;

maintaining the treatment zone at sub-atmospheric pressure while affecting contact of the water and the iron-based particles, thereby to convert impurities in the water to a form in which they are more readily separable from the water; and

withdrawing treated water from the treatment zone while retaining a major proportion of the particles in the zone.
2. A process as claimed in Claim 1, wherein the pressure in the treatment zone is maintained between 50 and 450 mm Hg vacuum.
3. A process as claimed in Claim 1 or Claim 2, wherein the water residence time in the treatment zone is less than 5 minutes.
4. A process as claimed in anyone of Claims 1 to 3 inclusive, wherein the treatment zone is provided by a vessel, with the sub-atmospheric pressure or vacuum being created by pump suction, and by periodically withdrawing accumulated gases from the vessel.
5. A process as claimed in any Claim 4, wherein the impurities comprise soluble orthophosphates and/or calcium compounds which are converted to insoluble phosphates and/or calcium compounds, with elemental iron in the particles catalyzing and/or forming part of the conversion reactions, and wherein the iron-based particles are scrap metal particles, with the contacting being effected by passing the water through a body of the particles in the vessel and moving the particles relative to the vessel.

6. A process as claimed in Claim 5, wherein the movement of the particles relative to the vessel is effected by rotating the vessel about an axis, and allowing the particles to move along at least a portion of its periphery as it rotates.
7. Water treatment apparatus which includes
 - a vessel;
 - a water inlet leading into the vessel;
 - a water outlet leading from the vessel;
 - a bed of water-insoluble iron-based or iron-containing particles with which water in the vessel can be contacted, thereby to convert impurities in the water to form in which they are more readily separable from the water, inside the vessel; and
 - vacuum-generating means for generating a sub-atmospheric pressure or vacuum in the vessel.
8. Apparatus according to Claim 7, wherein the particles are scrap metal particles.
9. Apparatus according to Claim 7 or Claim 8, wherein the vessel is of round cylindrical form with its axis extending horizontally, and with the inlet and outlet being located axially in opposite ends of the vessel, the apparatus also including drive means for driving the vessel to rotate about the axis.

10. Apparatus according to Claim 9, wherein the bed of particles extends up to at least the level of the axis.
11. Apparatus according to Claim 9 or Claim 10, wherein at least one baffle, protruding inwardly from the wall of the vessel, is provided.
12. Apparatus according to any one of Claims 7 to 11 inclusive, wherein the vacuum-generating means includes a pump operatively connected to the water outlet and being capable of generating or creating a vacuum of at least 50 mm Hg below atmospheric pressure, in the vessel.
13. Apparatus according to any one of Claims 7 to 12 inclusive, wherein the vacuum-generating means for withdrawing gases generated during the treatment of water from the vessel, the gas-withdrawal means comprising a conduit leading out of the vessel from a zone above the normal water level in the vessel, a venturi to which the conduit is connected, and a pump means for pumping liquid through the venturi, thereby to create a vacuum in the conduit.
14. A new method of treating water, substantially as described herein.
15. New water treatment apparatus, substantially as described and illustrated herein.

DATED THIS 14th DAY OF OCTOBER 1988.

ADAMS & ADAMS
APPLICANTS PATENT ATTORNEYS

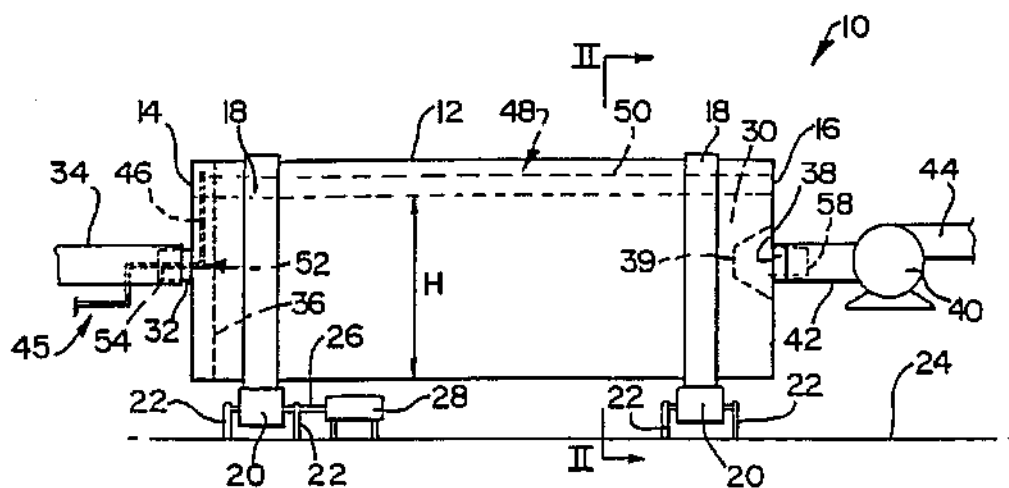


FIG 1

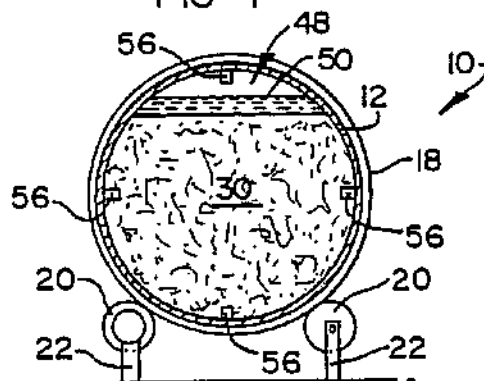


FIG 2

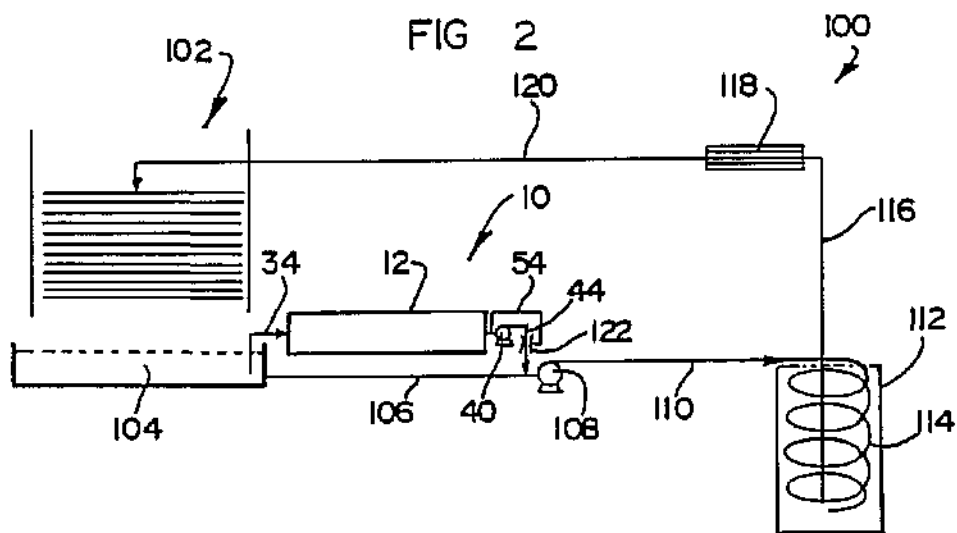


FIG 3

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