PHOSPHORUS REMOVAL IN THE MODIFIED ACTIVATED SLUDGE PROCESS

by

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DECLARATION BY CANDIDATE

I, Rainer Hoffmann, hereby declare that this thesis is my own work and that it has not been submitted for a degree at another university.

Signed by candidate

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SYNOPSIS

The principle objective of this investigation was to enquire in what measure calcium phosphate precipitation and luxury biological uptake contributes to excess removal of phosphorus in activated sludge systems, i.e. removal in excess of the basic biological requirement for metabolic purposes. This objective was pursued by imposing conditions in which one or the other of the two mechanisms had negligible influence.

From the series of batch and continuous activated sludge experiments the following conclusions are made regarding excess phosphorus removal.

Phosphate Precipitation Removal

Precipitation of calcium phosphate is a function of the calcium, phosphorus, pH organic content and seed crystals in the sludge.

The form of the precipitated crystal was not identified but it appears that a crystal with a Ca/P (in mg/l) of about 4:1 is formed. For pH $\geq$ 7,0 Ca^{++} = 40 mg/l and P = 10 mg/l, approximately 1,0 to 1,5 mg/l phosphorus can be expected to be removed. The contribution to phosphorus removal is therefore quite small. At pH < 7,0 precipitation decreases and at about pH = 6,5 and below the precipitate that has formed can redissolve.

By batch precipitation and dissolution studies it was established that in the ranges pH 6,5 to 7,5 the disappearance of soluble calcium is always associated with the disappearance of phosphorus in the ratio mentioned above. Therefore in this pH range the precipitate of calcium as calcium carbonate ($CaCO_3$) did not take place.

The removal of phosphorus by precipitation is independent

of whether the condition is anoxic, anaerobic or aerobic, provided the pH $\geq$ about 6,8.

Carbon dioxide has an effect on precipitation only in possibly reducing the pH and thereby causing dissolution of some form of calcium phosphate.

Excess (Luxury) Biological Uptake

The exact conditions for triggering off the biological removal mechanism are not yet established. There is conclusive evidence that the organism must be placed in a form of anoxic stress but the condition under which the anoxic stress is created is not yet defined. The two current hypotheses were tested to determine which is valid.

One hypothesis suggested (Barnard, 1975) is creating the anoxic stress by using a primary anoxic reactor. It receives the recycle sludge from the settling tank together with the influent waste stream. These flows are retained in the primary anoxic reactor until a nett release of phosphorus is observed (i.e. the effluent soluble phosphorus concentration is greater than the average concentration in the influent due to the total phosphorus in the influent waste stream plus the soluble phosphorus in the recycle stream. The release of phosphorus (as defined above) is considered a necessary condition for phosphorus removal and will occur only when no nitrates are present.

The second hypothesis is that based on the works of Fuhs and Min Chen (1975) as implemented by Osborn and Nicholls (1977). The basic element in this hypothesis is that the organism must be stressed under anoxic condition with no nutrients and nitrates present.

Experimental plants operating in accordance with the conditions required by each of the two hypotheses has given inconclusive results.

It is concluded that there are other factors that must be satisfied in addition to the requirement for anoxic state, and phosphorus release for optimum removal. It is suggested that a possible additional requirement is that the return sludge to the primary anoxic reactor must be completely depleted of stored COD before entering the anoxic zone for phosphorus removal to be optimised. The nitrate concentration and presence in the anoxic zone also appears to be important, but quantitative description of their effects is not yet possible.

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CONTENTS

CHAPTER 1

INTRODUCTION

It is a well attested observation that in certain activated sludge plants very efficient phosphorus removal has been attained without the addition of chemicals. Because of the increasing importance of phosphorus removal in the control of eutrophication problems and because biological phosphorus removal without the addition of chemicals has major economic implications, a concerted research effort into identifying the mechanism and the conditions for optimum operation is being undertaken in South Africa.

Two mechanisms have been proposed to account for the excess removal of phosphorus. The first is the biological luxury uptake hypothesis, the second the calcium phosphate precipitation hypothesis.

Barnard (1975a, 1975b, 1975c), on observing high phosphorus removal in nitrification-denitrification activated sludge plants has put forward a biological excess uptake hypothesis with regard to the mechanism of phosphorus removal. He proposes that to obtain excess phosphorus removal two conditions must be fulfilled. First the organisms must be put into a state of anoxic stress in the presence of a high nutrient supply. Second, the anoxic stress condition must be such that the organism is deprived of any source of oxygen, either dissolved or chemical bound in the form of nitrates. The second condition will induce a biological release of phosphorus and trigger off a mechanism which induces the organisms to take up both the released and excess phosphorus when subsequently placed under aerobic conditions. Barnard's experimental investigation appears to support his hypothesis.

A biological excess uptake hypothesis slightly different from that of Barnard has been proposed by Fuhs and Min Chen (1975). They propose that the organisms must be stressed anoxically in the absence of nutrient in order to induce the uptake of excess phosphorus. During the anoxic state phosphorus is released and when the sludge is subsequently aerated in the presence of high nutrient concentrations excess phosphorus is shunted into storage to bring about phosphorus removal. Experimental plant investigations based on this storage mechanism has been undertaken principally by research workers in the Johannesburg City Council and their results appear to support it (Osborn and Nicholls, 1977).

Martin and Marais (1975), following the hypothesis of Barnard, endeavoured to identify more precisely the conditions necessary to induce phosphorus removal and to establish kinetic relationships for the removal. Their work supports Barnard's hypothesis that removal is biological and is induced by a state of anoxic stress of organisms in the presence of nutrient. They find that anoxic conditions in the absence of nutrient apparently does not initiate excess biological uptake. They differed from Barnard in that they do not find it necessary that the anoxic condition must be free of nitrates or that release of phosphorus is necessary. They developed a biological kinetic theory by means of which it is possible to calculate the phosphorus removal to be expected under these conditions. This work was extended by Marsden and Marais (1977) who attempted to establish the conditions in the primary anoxic zone which would lead to optimum removal of phosphorus. They found that the actual anoxic retention time is quite critical; too long or too short retention times leading to reduced phosphorus removal.

In contrast to some of the results above, McLaren and Wood (1976) found that long primary anoxic retention times are necessary, that there must be phosphorus release in the anoxic zone for excess phosphorus removal and that the

nitrates must be zero in the primary anoxic zone.

From the investigations reviewed above, it appears that plants designed to operate on one or the other of these two hypotheses have given both good and bad results. This appears to indicate one of three possibilities:

1. In plants giving good phosphorus removal, although the plants may have been designed to conform specifically to the requirement of one hypothesis, the conditions for the other has in fact also been fulfilled.

2. In plants giving poor removal the conditions in one or the other hypothesis has not been fully satisfied due to a lack of knowledge of the precise conditions necessary.

3. A different hypothesis is operative.

These contradictory results indicate that the condition for biological excess uptake is not yet precisely understood.

The hypothesis on the physical-chemical removal of phosphorus finds its chief support from research workers in America (Menar and Jenkins, 1970; Ferguson and McCarty, 1969). They endeavoured to explain phosphorus removal by precipitation of a form of calcium phosphate. The magnitude of precipitation depends on the chemical constitution of the liquid, i.e. calcium, magnesium, carbonate and phosphorus concentration, and pH.

The problem with the chemical precipitation theory is that the type of phosphate crystal that precipitates has not been positively identified so that the models proposed by the proponents of this theory are not reliable. Furthermore, their experimental results appear contradictory and does not definitely support their models, so that it is not possible to state categorically that their hypothesis

is solely responsible for excess phosphorus removal.

When one examines the physical-chemical and the biological uptake approaches it would appear that there is a likelihood that both mechanisms, biological and chemical precipitation may be responsible for phosphorus removal, but that the conditions conducive to optimum removal and the extent each contributes to phosphorus removal may be different. Up to the present time, no specific attempt has been made to determine whether both mechanisms contribute to phosphorus removal or not. Furthermore, despite the considerable research effort it is not yet clear exactly what conditions must be imposed on the system for optimum removal of phosphorus, both biological and physical chemical. This, in part, is probably due to the fact that the mechanism/s responsible for phosphorus removal have not been completely identified, so that it is not possible to evaluate the mechanism performance or establish the conditions for optimum removal.

With these considerations in mind it was decided to investigate the contribution of the two mechanisms, i.e. calcium phosphate precipitation and biological luxury uptake to excess phosphorus removal in activated sludge plants.

Chapter 2 deals with a critical review of literature of the biological uptake and the chemical precipitation mechanism. In Chapter 3 a theoretical model for calcium phosphate precipitation is presented. In Chapter 4 the experimental investigation undertaken to identify the calcium phosphate precipitation mechanism is reported. In Chapter 5 consideration is given to the biological luxury uptake mechanism.

CHAPTER 2

LITERATURE REVIEW

INTRODUCTION

The normal requirement of phosphorus for microorganisms to metabolize the organic matter in the activated sludge is expressed as a P/VSS ratio where both P and VSS is in (mg/l). This ratio has been reported to range from 0,02 to 0,03. However, data has been reported from a number of activated sludge systems in which the ratio is in excess of these quoted figures. Hypotheses proposed to account for the excess concentration of phosphorus in the sludge can be divided into two categories:

1. A physical-chemical precipitation mechanism whereby a solid species of calcium phosphate is precipitated out of solution, and

2. A biological mechanism whereby excess phosphorus is incorporated by the active fraction of the sludge, the so called "luxury uptake".

Both hypotheses have found support from a number of investigators but from the literature it is not possible to definitely conclude which mechanism is operative or if, in fact, both mechanisms contribute to the excess phosphorus in the sludge. The two hypotheses will now be briefly reviewed.

PHYSICAL CHEMICAL PRECIPITATION OF PHOSPHORUS

Menar and Jenkins (1970, 1972), Ferguson and McCarty (1969, 1971), Ferguson, Jenkins and Eastman (1973), Ferguson,

Jenkins and Stumm (1970), and Morgan and Fruh (1972), have conducted extensive work on the physical-chemical precipitation phenomena in waste water systems. From their work it appears that theoretically the forms of calcium phosphate most likely to precipitate in waste waters are (i) dicalcium phosphate ($CaHPO_4$); (ii) hydroxyapatite ($Ca_5OH\ (PO_4)_3$) and (iii) beta tricalcium phosphate ($Ca_3(PO_4)_2$). Apparently the formation of a particular calcium phosphate mineral is affected by the pH, carbonic Alkalinity, magnesium concentration and the presence of organic material in the system. These factors can influence the kinetics of removal of phosphorus, inhibit the formation of a particular calcium phosphate mineral or cause a mineral to precipitate different from the three listed above.

For activated sludge systems, Menar and Jenkins (1970) postulated that phosphorus removal in excess of that predicted by biological growth requirement (2 - 3 percent of MLVSS) is caused by chemical precipitation. The phosphate precipitate is physically entrapped in the matrix of the activated sludge floc and is removed via the wasted sludge. According to them the pH of the mixed liquor is governed by an equilibrium set up between the metabolically produced carbon dioxide and the alkalinity of the system. The pH of the system must be high enough to exceed the calcium phosphate solubility of the precipitating mineral so that precipitation can take place. The mass of phosphorus removed depends on the initial concentration of calcium, phosphorus, alkalinity and pH and the form of calcium phosphate precipitated. Laboratory batch tests, pilot plant and full scale plant studies by them seem to show that enhanced phosphate removal by activated sludge in hard water sewage can be explained by calcium phosphate precipitation. The work of Menar and Jenkins is particularly comprehensive and will now be considered.

Menar and Jenkins (1970) conducted three batch tests on

identical activated sludge samples to test the precipitation hypothesis. One sample was aerated with air, the second sample was aerated with air plus 0,5 percent CO_2 and the third sample was aerated with air plus 5 percent CO_2 for three hours. The [Ca]/[P] molar ratios of ΔCa and ΔP taken up or released are given in Table 2.1.

TABLE 2.1 : Release and uptake of phosphorus from activated sludge

pH	[ΔCa] mM	[ΔP] mM	[ΔCa]/[ΔP]	Condition
8,17				Initial
8,43	+ 0,13	+ 0,08	1,63	Aeration with Air
7,60	- 0,23	- 0,18	1,28	Aeration with Air + ,5% CO_2
6,85	- 0,96	- 0,71	1,35	Aeration with Air + 5% CO_2

\+ Uptake of P or Ca by the sludge

\- Release of P or Ca by the sludge

The average [Ca]/[P] ratio obtained from the three experiments is 1,42. From their results there appears to be a constant relationship between the soluble calcium and phosphorus increase and decrease. The mineral having this ratio of [Ca]/[P] is either beta tricalcium phosphate with [Ca]/[P] = 1,5 or hydroxyapatite with [Ca]/[P] = 1,67, or, some unknown form.

Menar and Jenkins (1970) then conducted a continuous pilot plant experiment to determine whether the pH of the incoming sewage can be raised by preaeration to such a degree that phosphate precipitation will take place in the activated sludge aeration basin. The operating conditions and relevant results are shown in Table 2.2.

TABLE 2.2 : Operating condition and results of pre-aeration experiment at pilot scale level.

Parameter	Influent	Preaeration Basin	Activated Sludge
pH	7,7	8,3	8,3
COD mg/l	217	78,0	41,0
P mg/l	15,3	11,0	10,1
Ca mg/l	64,4	62,0	58,8
MLVSS mg/l	-		589
	R_s = 2,3 days		R = 0,36 day

It is apparent that there is a reduction in calcium between the total influent and effluent concentrations. This reduction in all probability can be attributed to the precipitation of some insoluble form of calcium phosphate.

With regard to the change in concentration of the phosphorus this can be ascribed to two causes; (1) the requirement for metabolism, and (2) that for precipitation of a calcium phosphate mineral. Assuming that luxury uptake did not take place (due to the fact that the whole system was aerobic), the metabolic requirements can be evaluated as follows.

Assume the metabolic phosphorus requirement is 0,025 with respect to the MLVSS.

$$P_{met} = \frac{2,5 \cdot X_v . R}{100\ R_s}$$

where X_v = total volatile solids concentration (mg/l)

R = hydraulic retention time (day)

R_s = sludge age (day)

P_{met} = change in influent phosphorus due to normal metabolic requirements (mg/l)

$$P_{met} = \frac{2,5}{100} \cdot \frac{589}{2,3} \cdot \frac{8,7}{24} \quad mg/l$$

$$= 2,3 \quad mg/l$$

The total overall removal of phosphorus from the system is (15, 3-10, 1) = 5,2 mg/l as P. Subtracting the phosphorus requirement for metabolism from this value gives (5,2 - 2,3) = 2,9 mg/l as P. Provided there is no biological luxury uptake of phosphorus it can now be considered that the excess uptake of phosphorus (i.e. 2,9 mg/l as P) is due to calcium phosphate precipitation. The change in calcium concentration is (64,4 - 58,8) = 5,6 mg/l as Ca. Consequently the [Ca]/[P] molar ratio for precipitation is (5,6/40)/(2,9/31) = 1,50. This value compares favourably with the Ca / P molar ratios obtained for the batch experiments.

There is some doubt as to the values of the parameters reported by Menar and Jenkins. For example, they report the influent COD = 217 mg/l, MLVSS = 589 mg/l and sludge age = 2,3 days, hydraulic retention time = 0,36 days. These values indicate that the equivalent COD in the wasted sludge and effluent should be

$$\text{Equivalent COD} = \text{COD in wasted sludge and effluent COD}$$

$$= \frac{R}{R_s} \cdot (\text{MLVSS}) \cdot 1,42 + 41 \text{ mg/l}$$

$$= 172 \text{ mg/l}$$

where $\frac{COD}{VSS} = 1,42$.

The COD for normal energy requirement, i.e. (217-172) = 45 mg/l is only 21 percent of the total influent COD. Normally the total COD equivalent, i.e. the wasted sludge and effluent should be at least 50 percent of the influent COD. It would seem that either the sludge age was longer, or, the MLVSS value was too high. This incompatability in the data is apparent in all the pilot and full scale studies reported by Menar and Jenkins.

They do not report how the sludge age was controlled and hence the reliability of their data cannot be assessed. Later in this chapter this matter is considered further.

Menar and Jenkins also conducted a comparative study on a pilot plant and full scale plant (VCSD). The operating conditions and results relevant to this analysis are shown in Table 2.3.

TABLE 2.3 : Operating condition and results for comparative study

Parameter	Pilot plant		VCSD Plant	
	Influent	Effluent	Influent	Effluent
pH	7,7	8,3	7,7	7,2
COD mg/l	267	30	264	23
MLVSS mg/l	-	2196	-	2500
P mg/l	16,6	11,8	16,8	14,1
Ca mg/l	69,6	56,0	68,0	58,0
	R_s = 12,6 days R = 0,33 day		R_s = 12,9 days R = 0,38 day	

Applying the same method of analysis to the results from the two plants as for the pilot plant study considered previously, gives the values reported in Table 2.4.

TABLE 2.4 : [Ca]/[P] uptake ratios in pilot and full scale plants

Plant	P_{met}	[Ca] / [P]
Pilot Plant	1,4 mg/l	3,1
VCSD Plant	1,84 mg/l	9,0

[ ] indicates molar concentration

The [Ca]/[P] uptake molar ratio obtained in this comparative study (Table 2.4) is significantly different to that listed in Table 2.1. The results definitely indicate that more calcium is taken up than predicted by any of the calcium phosphate minerals. The concurrent removal of calcium and phosphorus again indicates that a calcium phosphate mineral is being precipitated.

Two additional pilot plant experiments were then conducted at long and short sludge ages respectively, to give a high MLVSS concentration (i.e. 3727 mg/l) and a low MLVSS concentration (i.e. 1343 mg/l) respectively. The operating conditions and results relevant to the analysis are reported in Table 2.5.

TABLE 2.5 : Operating conditions and results of pilot scale study at long and short sludge ages respectively

Parameter	Long sludge age		Short sludge age	
	Influent	Effluent	Influent	Effluent
pH	7,5	8,1	7,7	8,1
COD mg/l	273	33	232	36
MLVSS mg/l	-	3272	-	1343
P mg/l	17,7	11,1	15,8	10,4
Ca mg/l	64,3	55,5	62,8	56,0
	R_s = 14,5 days R = 0,28 day		R_s = 4,0 days R = 0,25 day	

Again the total phosphorus removed can be subdivided into two fractions, for (1) normal metabolic requirement of 2,5 percent of MLVSS and (2) phosphorus precipitation. Analysing the two experiments the results are given in Table 2.6.

TABLE 2.6 : [Ca]/[P] uptake ratios for the two pilot experiments at long and short sludge ages

Plant	P_{met}	[Ca]/ [P]
Long sludge age	1,6 mg/l	1,36
Short sludge age	2,1 mg/l	1,60

[ ] indicates molar concentration

These results are very similar to the [Ca]/[P] ratios obtained for the batch experiments on activated sludge. Considering all pilot and full scale plant results the [Ca]/[P] molar ratios show such a wide variation that no conclusion can be drawn as to the form of calcium phosphate mineral precipitating. One problem is that in the analysis the removal of calcium was assumed to be due solely to the formation of a calcium phosphate mineral, whereas the possibility of some other cation precipitating with phosphorus is also possible.

It is difficult to assess the value of the results calculated from the analysis of the data obtained by Menar and Jenkins. The principle uncertainty arises from their reported values of the MLVSS, which appears to be incompatible with their reported values for the sludge age. Accepting their values for the sludge age, calculation of MLVSS from the activated sludge theory as given by Marais and Ekama (1976) indicate that the MLVSS reported are far too high. Mass balances of the COD in and out of the systems tend to support the conclusion that there is some error in the parameters reported. This can be illustrated as follows.

Accepting the measured parameters for COD and MLVSS, the actual sludge age value can be calculated from the activated sludge theory as given by Marais and Ekama (1976).

Using primary effluent (Menar and Jenkins)

$$X_v = \frac{Y\ (\Delta S)}{H\ bR_s} \quad \frac{R_s}{R} \quad (1 + 0,2 \cdot bR_s)$$

where X_v = total volatile solids concentration (mg/l)
Y = growth yield coefficient
b = endogenous mass loss rate constant (mg VAS/mg VAS/day)
R_s = sludge age (day)
R = hydraulic retention time (day)

Substituting in this equation the values for the constants at 20°C, i.e. Y = 0,43 and b = 0,24 and the values of the measured parameters of the pilot plant, i.e. COD = 176 mg/l and MLVSS = 589 mg/l, gives a sludge age of 5 days. This value is considerably higher than the value reported by Menar and Jenkins, i.e. 2,3 days. Accepting the value of R_s = 5 days and assuming that 2,5 percent of the MLVSS is the metabolic requirement of phosphorus, the phosphorus removed can again be calculated as follows:

$$P_{met} = \frac{2,5\ X_v.R}{100\ R_s} \quad \text{mg/l}$$

$$= \frac{2,5}{100} \cdot \frac{589}{5} \cdot 0,36 \quad \text{mg/l}$$

$$= 1,1 \text{ mg/l}$$

Now from Table 2.2 the total overall removal of phosphorus is 5,2 mg/l as P. Subtracting the phosphorus requirement for metabolism from this leaves (5,2 - 1,1) = 4,1 mg/l as P. Accepting that this value (i.e. 4,1 mg/l as P) is due to calcium phosphate precipitation the [Ca]/[P] molar ratio is (5,6/40)/(4,1/31) = 1,06, this molar ratio is significantly lower than the molar ratio obtained by accepting R_s = 2,3 day, i.e. 1,06 versus 1,50 (see Table 2.7).

This anomaly is apparent in all pilot and full scale plant

investigations reported by Menar and Jenkins. The comparison between the reported sludge ages and calculated sludge ages with the relevant results are shown in Table 2.7.

TABLE 2.7 : Comparison of analyses for reported and calculated sludge ages

Analyses from reported R_s			Analyses from calculated R_s		
R_s (days)	P_{syn} (mg/l)	$[\Delta P]/[\Delta Ca]$	R_s	P_{syn}	$[\Delta P]/[\Delta Ca]$
2,3	2,30	1,50	5,0	1,1	1,06
12,6	1,40	3,10	20,0	0,9	2,70
12,9	1,84	9,00	33,0	0,7	3,88
14,5	1,60	1,36	30,0	0,8	1,18
4,0	2,10	1,60	8,5	1,0	1,20

[ ] indicates molar concentration

Due to the uncertainty in connection with the reported data no conclusions can be made regarding the type of precipitant. The only conclusion possible is that some calcium phosphate did precipitate.

Ferguson, Jenkins and Eastman (1973) investigated the precipitation of calcium phosphate from chemically defined solutions, containing only $CaCl_2$, NaH_2PO_4 and $NaHCO_3$. They conducted steady state experiments with an influent containing phosphorus of 0,3mM, calcium of 2,0mM and HCO_3 of 1,1mM. Keeping phosphorus and calcium concentrations constant for the next four experiments, the bicarbonate concentration was increased incrementally up to 7,0mM.

The results are given in Table 2.8.

The uptake [Ca]/[P] molar ratios of the first three experiments are very similar but at the high bicarbonate concen-

TABLE 2.8 : [Ca]/[P] uptake molar ratios for batch experiments at different bicarbonate concentrations

R(hrs)	pH	HCO_3 mM	[ΔCa] (mM)	[ΔP] (mM)	[ΔCa]/[ΔP]
7,5	7,2	1,1	0,27	0,2	1,32
6,0	7,78	1,2	0,36	0,24	1,51
6,8	8,08	1,3	0,34	0,25	1,38
5,9	7,95	7,0	0,39	0,20	1,94

tration more calcium was removed, indicating that maybe some calcite is formed. X-ray diffraction patterns for the precipitate showed decreasing calcium phosphate crystallinity with increasing bicarbonate concentrations. Some calcite formation at the high bicarbonate concentration was identified.

The [Ca]/[P] molar ratios for the three sets of results can now be compared in Table 2.9.

TABLE 2.9 : Comparison of [Ca]/[P] ratios for the three systems analysed

Pure System (CSTR)		Batch Activated Sludge Experiments		Pilot and full scale** Plant Results	
pH	[Ca]/[P]	pH	[Ca]/[P]	pH	[Ca]/[P]
7,2	1,32	8,43	1,63*	8,3	1,45
7,78	1,51	7,60	1,28*	8,3	3,00
8,08	1,38	6,85	1,38*	7,2	8,30
7,95	1,94			8,1	1,30
				8,1	1,55

* Release of Ca and P by the sludge

** Our analysis using the reported values of VSS, etc. See Table 2.7.

From the analysis it is still not clear which mineral will precipitate. In chemically defined solutions at pH values between 7,5 and 8,5 a number of investigators seem to support the precipitation of hydroxyapatite (Ferguson, Jenkins and Eastman, 1973) and others beta tricalcium phosphate (Menar and Jenkins, 1972; De Boice and Thomas, 1975). The occurrence of a particular calcium phosphate crystal in waste water has not been identified due to the influence of many organic and inorganic species which may directly affect the calcium phosphate precipitation process. In continuous flow activated sludge systems, to determine which mineral precipitates, it is essential to consider the metabolic activities of the organisms since they alter the concentrations of the free species (e.g. PO_4^{3-}).

Ferguson, Jenkins and Stumm (1970) also noted the complexity of a waste water system and were not able to identify the mineral precipitating from activated sludge systems.

Stumm and Morgan (1970) suggested the formation of a replaced apatite, i.e. $Ca_{11}(PO_4CO_3)_4F_2$, in areas of high organic productivity and in eutrophic lakes. It is possible that the formation of a replaced apatite takes place in high bicarbonate concentration systems and in activated sludge systems, giving a [Ca]/[P] molar ratio of about 11/4 = 2,75.

From all the investigations conducted on chemical precipitation, it can be summarized that calcium is shown to be capable of precipitating phosphorus in the pH range and concentration of calcium and phosphorus encountered in waste waters. It is also apparent that predicting the precipitation of calcium phosphate in activated sludge is a complex problem. There are a number of parameters (i.e. pH, Mg, Alkalinity, phosphorus and organic material) that can significantly affect the solubility of the calcium phosphate mineral. However, it can be concluded that a physical-chemical mechanism is in all probability partly

responsible for the excess uptake of phosphorus in activated sludge systems.

From the work conducted on chemical precipitation of phosphorus with a [Ca]/[P] molar ratio of about 1,5, it would appear that the mineral precipitating from chemical defined solutions is either beta-tricalcium phosphate or hydroxyapatite.

The results above indicate that it would be worth while to investigate the possible removal of phosphorus by precipitation in activated sludge plants, as the contribution to phosphorus removal could be significant in the many high calcium and alkalinity waste waters encountered in South Africa.

BIOLOGICAL REMOVAL OF PHOSPHORUS

Martin and Marais (1975) have exhaustively reviewed the literature pertaining to the biological luxury uptake of phosphorus and it is felt that there is little merit in repeating their review. However, one may summarise the earlier work as follows:

Investigations conducted prior to Barnard's (1975a, 1975b, 1975c) work on biological phosphorus removal indicated that little quantitative work has been accomplished to establish a predictive model. Many investigators were primarily concerned in emperically establishing the factors influencing, and the conditions necessary, for phosphorus removal. Factors influencing the uptake of phosphorus in the activated sludge process were reported to include dissolved oxygen, length of aeration time, mixed liquor solids, pH, nitrogen concentration and substrate concentration. The principle experimental methods employed were to aerate return sludge in a flask under the various conditions. Although the results from these batch tests often indicated

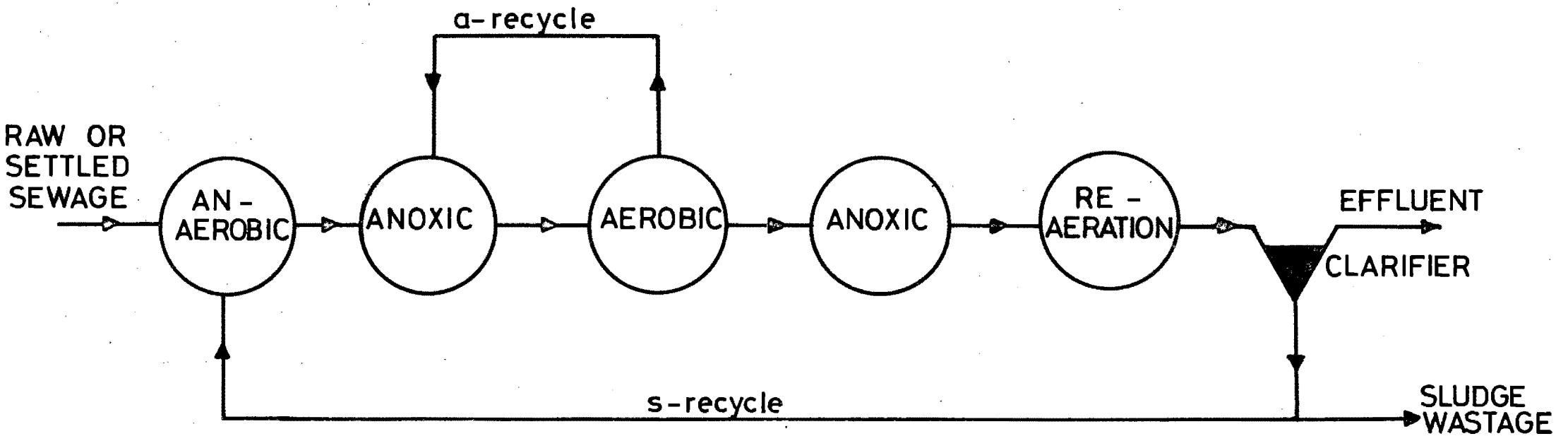


Figure 2.1 *The Bardenpho Process for denitrification and phosphorus removal.*

very good phosphorus removal, their relationship with respect to continuous process removal was difficult to establish. Continuous flow systems showing good removal of phosphorus usually served as the source of sludge for batch tests. When the batch tests also showed good removals, conclusions were made regarding the mechanism of phosphorus removal. However, reporting is often not clear as to the exact conditions existing within the activated sludge plant. Furthermore, the pre-handling of the sludge in the batch test differed from the conditions it is subjected to in the main plant; as a consequence the behaviour under batch test conditions is different and therefore it is impossible to relate it to the behaviour under continuous flow condition.

The justification for the conclusion above can be found by examining the work of Barnard. Barnard found that a factor of major importance effecting the removal of phosphorus is the presence of an anoxic zone somewhere in the plant. This zone forms an essential part in his system of denitrification and is therefore built into the plant. See Figure 2.1. In the reporting of full scale plants by other investigators, it is never clear whether such anoxic zones were not perhaps inadvertently formed in some part of the plant, particularly at the head end of the aeration chamber operating under more or less plug flow conditions. This could in fact create the condition for biological phosphorus removal as hypothesized by Barnard. With regard to the batch tests of these earlier investigators the sludge collected often underwent a period of anoxia or anaerobiasis prior to conducting the test, thus creating the required condition for triggering off the biological luxury uptake mechanism in accordance with the Barnard hypothesis. For these reasons it is usually impossible to pin-point from the earlier investigations the causes for excess phosphorus removal.

Barnard not only proposed an anoxic state but a <u>particular</u>

anoxic state which he termed a 'deep' anoxic condition. This condition, he maintains, is obtained when no nitrates are present in the anoxic reactor. He also maintains that there must be a release of phosphorus to stimulate phosphorus uptake in the aerobic reactor. Now Levin and Shapiro (1965) and Levin, Tapol, Tarnay and Samworth (1972) have also been interested in phosphorus release by allowing an 'anaerobic' condition in a side recycle stream. Their objective is to enrich the supernatant by means of the phosphorus release and then separate the sludge from the supernatant by settling. The densified sludge is returned to the plant and the supernatant treated with lime to precipitate the phosphorus. They consider it important to deplete phosphorus in the sludge so that the depleted sludge will more readily take up excess phosphorus in the reactor. In contrast Barnard considers release of phosphorus as an important prerequisite to stimulate excess uptake of phosphorus in the aerobic reactor, the phosphorus thus taken up by the sludge is removed from the system in the sludge wasted daily from the plant. Whereas the Levin and Shapiro system requires chemical addition to precipitate the enriched supernatant phosphorus, the Barnard system requires no addition.

In one aspect the two systems may in fact not be so different. By inducing the sludge to go anaerobic, Levin and Shapiro may in fact create the condition necessary for excess uptake in the main reactor. From this point of view the conditions for uptake is specifically recognized as such by Barnard but occurs 'fortuitously' in the Levin and Shapiro system - they do not appear to have recognized the triggering-off function of the anaerobic state. It would seem that they ascribe the phosphorus uptake phenomenon to the fact that phosphorus in the sludge is depleted when it enters the aerobic reactor from the secondary settler. As Barnard found that the phosphorus adsorbed onto the organism mass is not significantly released (if aerobic conditions are maintained before the sludge passes through to the secondary settling tank),

the physical-chemical precipitation unit process in the Levin and Shapiro system may in fact not be required. This does not, of course, reject the possibility that by depleting the phosphorus under anaerobic conditions, superior uptake of excess phosphorus subsequently will not take place in the Levin and Shapiro system.

Martin and Marais (1975) and Marsden and Marais (1977) accepted a biological mechanism and carried out a series of experiments first to establish the conditions for induction of optimum phosphorus removal and secondly to establish a biological theory to model the removal. From their work the following conclusions were drawn:

1. Luxury uptake of phosphorus is induced by the presence of a primary anoxic zone, i.e. anoxic conditions in the presence of high nutrients. The secondary anoxic zone was found to have little influence on the induction of phosphorus removal; this observation, however, may have been valid only because the actual retention time in the secondary anoxic zone was not long enough and did not fulfil Barnard's contention that phosphorus must be released to trigger-off phosphorus removal. However, in one experiment they obtained release in the secondary anoxic zone (with NO_3-N still present) but this did not improve overall phosphorus reduction from the system. Here again in accordance with the Barnard hypothesis phosphorus removal may have been inhibited because nitrates were still present.

2. There is an optimum actual retention time in the primary anoxic reactor for maximum removal. At shorter and longer retention times the removal of phosphorus by the system decreases. The optimum value appears to coincide with the condition where there is no net release of phosphorus in the anoxic zone. Marsden and Marais (1977) observed optimum phosphorus removal at an actual anoxic retention time of 30 minutes.

3. Increasing the influent ammonia-nitrogen and hence the reactor nitrate concentration enhances phosphorus removal. This conclusion is in direct opposition to Barnard's conclusion, for as the nitrate concentration increases the possibility of "anaerobic" conditions decreases.

4. An increase in aeration reactor pH to between pH 7 - 8 enhances phosphorus removal. The increase was not substantial and possibly can be accounted for by some precipitation mechanism.

5. The mechanism of phosphorus removal does not appear to be precipitation. Although an increase in pH through the anoxic reactor was observed due to denitrification, phosphorus was released into solution. This conclusion does not necessarily follow from their work when one considers it in the light of the precipitation removal mechanism reviewed in the first part of this report. If biological removal takes place conjointly with precipitation removal then in the anoxic zone where the biological removal of phosphorus is again released, the mass released may be in excess of the mass precipitated giving an observed apparent biological release only.

6. The degree of phosphorus removal appears to be independent of the influent phosphorus concentration. This will be true if the removal is only biological. If precipitation can take place then the mass of phosphorus removed will increase as the concentration of phosphorus increases in order to satisfy the chemical equilibrium equation. However, chemical precipitation will only be evident if the pH is 7,0 and above. It will not be so evident in waste water plants in Cape Town as the average pH in denitrifying plants ranges from 6,8 to 7,2, so that the phosphorus precipitation will tend to be of a minor nature. Plants operating

on the Reef, where the pH tends to be between 7,5 and 8,0, may very likely show increased phosphorus removal due to precipitation as the influent phosphorus increases.

7. Anoxic stripping of phosphorus is not a prerequisite for luxury uptake of phosphorus as implied by Levin and Shapiro (1965) and Barnard (1975). This conclusion of Martin and Marais (1975) and Marsden and Marais (1977) is probably the most contentious. The results obtained by different investigators are frankly contradictory. This aspect will be discussed later.

8. The concentration of phosphorus removed is a function of the COD utilized. The ratio of phosphorus removed to the COD utilized is constant at a particular sludge age, so that as the concentration of COD utilized increases, the concentration of phosphorus removed increases. If the removal is biological this conclusion is not unreasonable.

9. The concentration of phosphorus removed is a function of the sludge age. For a fixed biodegradable influent COD, the longer the sludge age, the less phosphorus is removed. This conclusion also follows rationally from the biological uptake hypothesis.

In a configuration where the actual anoxic retention time is fixed, the concentration of phosphorus removed from the effluent may be described by the equation:

$$P = \frac{Y(S_i - S)}{1 + bR_s} \left(\alpha + 0{,}03.0{,}2\ bR_s \right) + 0{,}0027 \frac{(S_i - S)}{0{,}82}$$

where P = reduction in phosphorus in the influent total PO_4-P, i.e. $(P_{influent} - P_{effluent})$

S_i = biodegradable influent COD (mg/l)

S = unmetabolized biodegradable COD in effluent (mg/l)

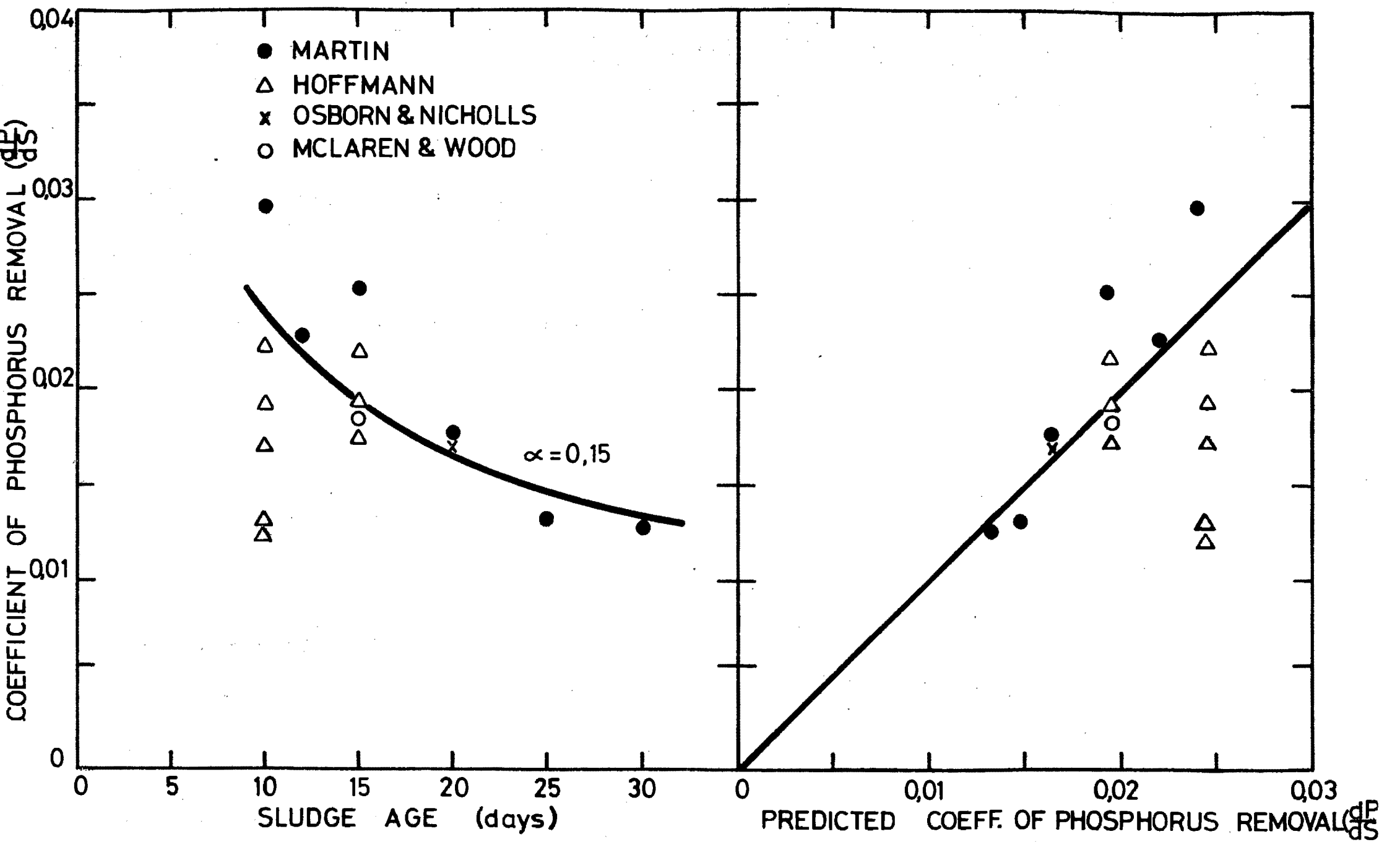


Figure 2.2 Mean values of the coefficient of phosphorus removal $(\frac{dP}{dS})$ *for systems operated at different sludge ages*

R_s = sludge age (day) defined by mass of sludge in reactor/mass of sludge wasted/d

Y = growth yield coefficient - mass of organisms synthesized per mass of COD utilized (mg/l)

b = endogenous mass loss rate constant (mg VAS/mg VAS/day)

α = the fraction of phosphorus relative to the mixed liquor volatile active suspended solids (MLVASS)

Martin and Marais found that the value of α is approximately 0,15 for conditions where the removal is apparently optimal in their system at 20°C. This value for α has been obtained a number of times with different configurations and for sludge ages ranging from 10 - 30 days at 20°C. However, the system of Martin and Marais does not appear to be stable. Some series of experiments give a value for α very much less than 0,15. The value of α = 0,15 appears to be a optimum value. Values obtained for α from many series of tests are all shown plotted in Figure 2.2.

Fuhs and Min Chen (1975), in a very comprehensive review of phosphorus removal in the activated sludge process, claim that luxury uptake of phosphorus is essentially due to a single organism (acinetobacter) or several closely related forms, which differ from other bacteria in their ability to store large quantities of polyphosphates. Requirements for optimal performance appears to be that the MLVSS must be exposed to an anaerobic condition where no nutrients are present thus releasing phosphorus. Bacteria that have been subjected to this condition are then capable of taking up excess amounts subsequently in the aerobic zone. Liss and Langen (1962) referred to this phenomena as 'polyphosphate overplus' or as generally known, 'luxury uptake'. Harold (1966) and many other researchers have investigated the transportation of phosphorus within the bacterial cell, but the precise mechanism does not appear to be fully

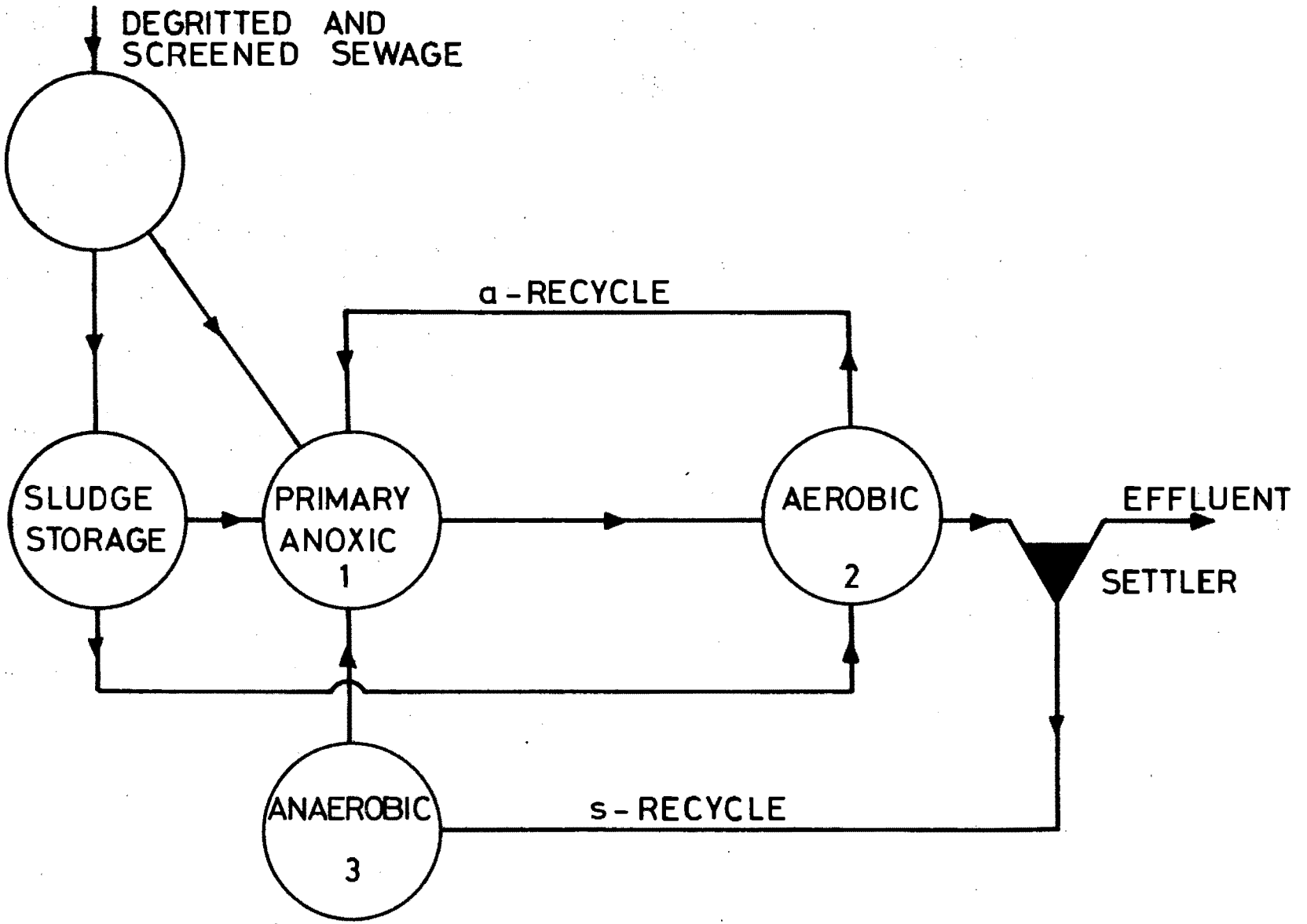


Figure 2.3 Configuration proposed by Osborn and Nicholls for biological removal of phosphorus

understood. Evidently, the requirements stipulated by Fuhs and Min Chen (1975) that no nutrients must be present in the anoxic phase is not supported by the work of Martin and Marais (1975) who concluded that optimum removal is obtained by having a primary anoxic reactor, receiving the influent flow energy. As Barnard requires only that there must be an anaerobic condition somewhere in the system his results will be contradictory to Fuhs and Min Chen if high removals are obtained where his secondary anoxic zone does not lead to a release of phosphorus.

Research workers in the Johannesburg City Council (Osborn and Nicholls, 1977) are at present investigating the 'overplus' mechanism and the results obtained from pilot plant and batch studies tend to support this hypothesis. They suggest that a primary requirement is to establish a process which will induce the excess uptake of phosphorus by polyphosphate storing bacteria. They propose the configuration in Figure 2.3 for optimal phosphorus removal. This system is principally based on the Bardenpho process except that the second anoxic reactor is separated from the system and serves the function of a 'deep' anaerobic zone. According to Osborn and Nicholls the deep anaerobic zone (Reactor 3, Figure 2.3) is the region devoid of nutrient and nitrates which serves to starve the bacteria, thus releasing phosphorus. On coming into contact with nutrients and nitrates in the primary anoxic zone (which receives the high nitrate recycle from the main aeration tank) the organisms can rapidly adsorb soluble phosphorus according to the 'overplus' mechanism. Their hypothesis therefore implies that (NO_3-N) oxygen serves the same function as O_2 oxygen in the Fuhs and Min Chen proposal.

Osborn and Nicholls' hypothesis deviates from that of Fuhs and Min Chen in that the latter hypothesis removal only takes place in the aerobic zone whereas the former accepts phosphorus removal in both the 'anoxic' and the aerobic zone. Osborn and Nicholls also do not appear to support

Fuhs and Chen who claim that acetic acid only is the nutrient necessary for stimulating the growth of the acinetobacter. The investigations of Osborn and Nicholls indicate that other organisms besides acinetobacter are capable of storing excess amounts of phosphorus.

The theory of Fuhs and Chen implicitly requires that the acinetobacter be established, i.e. removal of phosphorus will develop as the organism accumulates. This is not in conformity with observations where plants have been changed from pure aerobic to anoxic-aerobic an immediate increase in removal has been observed (Martin and Marais, 1975; Davelaar, Davies and Wiechers, 1977).

Comparing the optimal results obtained by Osborn and Nicholls (1977) with the predicted values from the kinetic theory of Martin and Marais (1975) the results are almost identical.

For example, run (d) of pilot plant investigation (Table 2) by Osborn and Nicholls.

where S_o = 823 mg COD/l

S_{xii} = 0,09.1,42.823 mg COD/l

= 105,2 mg COD/l

S_{eff} = 40 (say) mg COD/l

$(S_i - S)$ = (823 - 105 - 40)

= 678 mg COD/l

$$P = \frac{Y(S_i - S)}{1 + bR_s} (\alpha + 0,03.0,2.bR_s) + \frac{0,0027\ (S_i - S)}{0,82}$$

where R_s = 20 days, α = 0,15, b = 0,24 and Y = 0,43

$$P = \frac{0,43.678}{1 + 0,24.20} (0,15 + 0,03.0,2.0,24.20) + \frac{0,0027\ (678)}{0,82}$$

= (8,99 + 2,33)

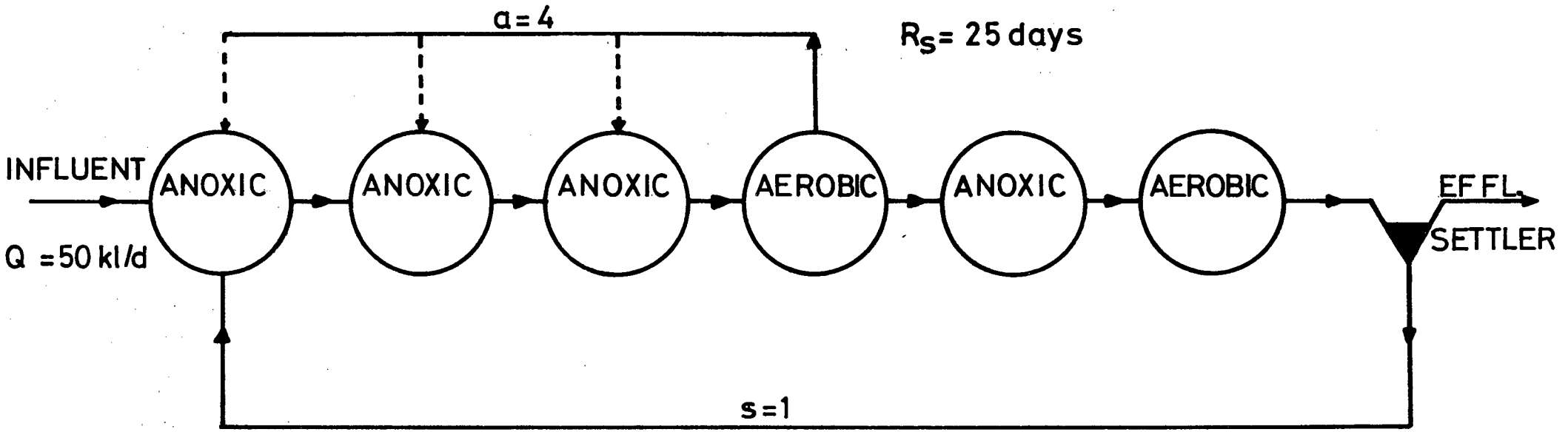


Figure 2.4 Pilot Plant configuration (i.e. Standard Barnard Process) used by McLaren and Wood to study the effect of the primary anoxic zone on phosphorus removal

= 11,22 mg/l as PO_4-P

The removal obtained by Osborn and Nicholls is 11,3 mg/l as PO_4-P.

Osborn and Nicholls also state that if release of phosphorus is too excessive in the anaerobic zone then the removal in the aerobic zone is reduced.

McLaren and Wood also investigated the effect of phosphorus release on subsequent excess phosphorus uptake. Their pilot scale plant is shown in Figure 2.4. This is a standard Bardenpho process except that the primary anoxic zone was a series system of tanks. The recycle from the settling tank was always to the first anoxic reactor, but the internal recycle from aerobic zone could be directed into the first, second or third primary anoxic tank. They found that directing the flow into the first anoxic tank gave poor phosphorus removal with little improvement when directed into the second anoxic tank, but good results when directing the flow into the third anoxic reactor. They found that the rate of phosphorus removal coincided with observed release of phosphorus in the second primary anoxic tank and concluded that phosphorus release was a prerequisite for excess uptake. Although anaerobic conditions, i.e. absence of nitrates, was found to be a prerequisite for phosphorus release, it was not a sufficient condition, for when anaerobic conditions were established with no phosphorus release was observed, the removal of phosphorus was poor.

Their results are contradictory to the hypothesis of Fuhs and Min Chen (and hence contradictory to the system of Osborn and Nicholls) since Fuhs and Min Chen maintain that release of phosphorus must take place under no nutrient condition. The results of McLaren and Wood show that good phosphorus removal can be maintained with release of phosphorus in the presence of nutrients.

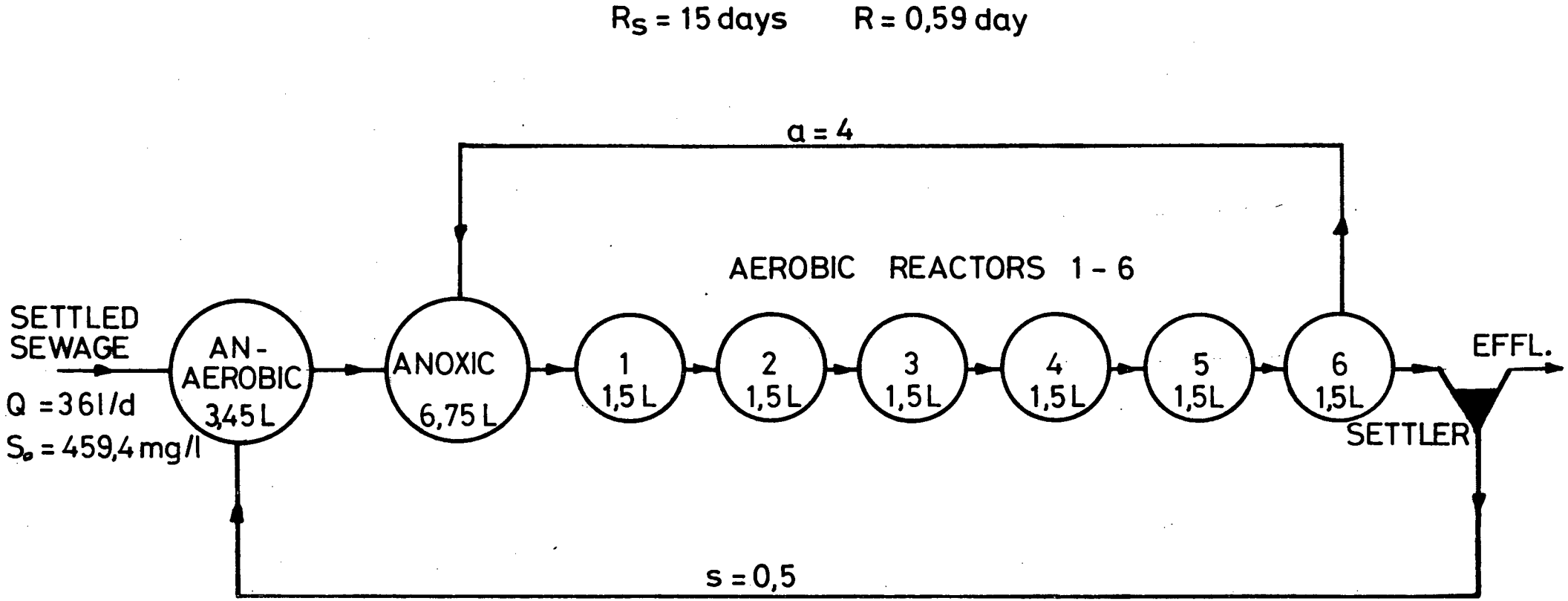


Figure 2.5 Laboratory unit used to study phosphorus removal (McLaren and Wood)

McLaren and Wood repeated their tests on a laboratory scale plant in which the secondary anoxic zone was omitted but the aeration zone was subdivided into six compartments, (see Figure 2.5). Considerable release, i.e. 8,66 mg/l of phosphorus occurred in the anaerobic zone, a small uptake in the anoxic zone and massive uptake in the aeration zone. The system removal was 7,84 mg/l, i.e. α of 0,15. This work further establishes that good phosphorus removal can be obtained while not conforming to Fuhs and Min Chen's requirement, i.e. anoxic stress in the absence of nutrients.

With regard to the data presented by McLaren and Wood, it should be noted that differences in concentration between the different reactors give completely misleading descriptions of the removal of phosphorus, because the internal and external recycles cause dilutions so that the apparent removal often is completely different with the actual removal in the units. The only rational method for determining the behaviour of the system is to evaluate the systems removal or release of phosphorus in each reactor, i.e. removal obtained by doing a mass balance on a particular reactor.

As an example, the calculation of the system's release and uptake of the laboratory unit is presented below: (McLaren and Wood)

Release in anaerobic reactor

$$\Delta P_{AN} = (11,4.1,5 - (8,24.1 + 0,4.0,5))$$

$$= 8,66 \text{ mg/l as } PO_4\text{-P}$$

Uptake in anoxic zone

$$\Delta P_{AX} = (11,4.1,5 + 0,1.4,0 - 3,1.5,5)$$

$$= 0,45 \text{ mg/l as } PO_4\text{-P}$$

Uptake in aerobic reactors

Reactor 1 - $\Delta P_1 = (3,1 - 2,0).5,5 = 6,05$ mg/l as PO_4-P

Reactor 2 - $\Delta P_2 = (2,0 - 1,3).5,5 = 3,85$ " "

Reactor 3 - $\Delta P_3 = (1,3 - 0,8).5,5 = 2,75$ " "

Reactor 4 - $\Delta P_4 = (0,8 - 0,3).5,5 = 2,75$ " "

Reactor 5 - $\Delta P_5 = (0,3 - 0,3).5,5 = 0,00$ " "

Reactor 6 - $\Delta P_6 = (0,3 - 0,1).5,5 = 1,10$ " "

$\therefore$ Total uptake of phosphorus

$$\Delta P_{TU} = \Delta P_{AX} + \Delta P_1 + \Delta P_2 + \Delta P_3 + \Delta P_4 + \Delta P_5 + \Delta P_6$$

$$= 16,95 \text{ mg/l as } PO_4\text{-P}$$

Release in settler

$$\Delta P_S = 1,5.0,4 - 0,1.1,5$$

$$= 0,45 \text{ mg/l as } PO_4\text{-P}$$

Doing a balance between influent and effluent including the settler

$$P_{EFF} = (P_I + P_{EFF}.0,5 + \Delta P_{AN} + \Delta P_S - \Delta P_{TU} - P_{EFF}.0,5)$$

$$= (8,24 + 0,2 + 8,66 + 0,45 - 16,95 - 0,2)$$

$$= 0,4 \text{ mg/l as } PO_4\text{-P}$$

OR

$$\text{Overall removal} = P_I - P_{EFF}$$

$$= \text{(Total system uptake - Total system release)}$$

$$= (16,95 - 0,45 - 8,66)$$

$$= 7,84 \text{ mg/l as } PO_4\text{-P}.$$

Evidently the anoxic reactor gave very little uptake whereas the aerobic reactor gave enormous uptake.

If one compares the concentrations only a mistake can easily be made by crediting most of the removal to the anoxic zone and minor removal to the aeration zone. For example, the uptake of phosphorus in the anoxic reactor is reported as 8,3 mg/l, whereas the system uptake is 0,45 mg/l.

In McLaren and Wood's paper it is also difficult to assess whether any calcium phosphate precipitation took place in the laboratory scale units as the soluble calcium values are not reported for each reactor. There also appears to be some doubt as to the influent calcium reported, i.e. 34,9 mg/l as Ca. This value seems to be an inordinately low value for Reef sewage and is possibly due to the method of measurement. Appreciable calcium in the precipitated form is on the volatile solids in the influent and in testing it, it is necessary to acidify the sample to solubilize the calcium ions.

Taking an overview of the results from the systems examined above, the following observations can be made:

(a) The presence of an anoxic zone in the system is crucial to the removal of the phosphorus in the system.

(b) Good phosphorus removal has been reported for systems with an anoxic zone in the presence or absence of nutrients.

(c) Very good and very poor systems removal of phosphorus has been attained with high nitrates, low nitrates and zero nitrates in the primary anoxic zone receiving the influent waste water.

(d) Very good removals have been obtained with phosphorus uptake, no phosphorus uptake and phosphorus release in the primary anoxic zone.

(e) Very good and very poor release of phosphorus has been reported with short and long actual primary anoxic retention times.

Considering the different hypotheses that have been presented in this review, the one positive conclusion that can be made is that there is as yet no certainty as to precisely what are the conditions that lead to optimum biological removal of phosphorus. Only one conclusion appears to be well substantiated, that an anoxic state in the system is necessary to induce excess phosphorus removal. The evidence as to the characteristics of this state (NO_3-N present or not, length of anoxic retention time, release of phosphorus in the anoxic state as against uptake of phosphorus in the anoxic zone and anoxic state in the presence or absence of nutrients) are contradictory and confusing.

OBJECTIVES

It is clear from the literature review that no general conclusion can be drawn to specifically identify the mechanism(s) responsible for the excess uptake of phosphorus in activated sludge systems. From the investigations of

Barnard and Martin and Marais, it appears that the conditions imposed by them on the activated sludge system enhanced the biological removal of phosphorus, whereas investigations of Menar and Jenkins tend to indicate that a physical-chemical mechanism is also possible. In both fields of investigations the authors were primarily concerned with one particular excess removal mechanism and no attempt was made to enquire whether a combination of the two mechanisms is in fact responsible for excess uptake of phosphorus. The work of Menar and Jenkins definitely indicates that the physical-chemical mechanism can be partly responsible for excess uptake of phosphorus and may account for some of the removal observed by Barnard and Martin and Marais.

Menar and Jenkins did not impose anaerobic conditions on their plants whereas Barnard and Martin, Marsden and Marais did. If Menar and Jenkins' hypothesis is sustained, then phosphorus removal by precipitation could also take place in the biological removal system as the physical-chemical removal can take place in anoxic conditions if the pH, Alkalinity and calcium values are favourable.

It is, therefore, necessary to investigate whether a biological cum chemical mechanism is in fact responsible for the excess removal of phosphorus. To observe this phenomenon it is proposed that firstly the physical-chemical mechanism is identified by removing the biological luxury uptake mechanism and, secondly, to identify the biological luxury uptake mechanism by removing the physical-chemical mechanism.

The first part of the investigation constitutes the theoretical development of calcium phosphate precipitation from pure systems. Two phase conditioning diagrams for the various calcium phosphate minerals were developed so that they can be subsequently applied to experimental work to identify the form of calcium phosphate mineral

precipitated. Due to the complex inter-relationships of the various parameters within the activated sludge system it was impracticable to develop a good predictive model, but a theoretical model could perhaps indicate new lines of approach in this and other investigations.

The second part of the investigation entails the experimental work into the chemical precipitation of phosphorus from biologically treated wastewaters. It is desirable to identify the precipitation of a calcium phosphate mineral in batch experiments and to obtain the condition required for precipitation to take place in activated sludge systems.

The third part of the investigation is concerned with the conditions required for optimum phosphorus removal and the mechanism(s) responsible for this removal. It is desired to first identify the two mechanisms separately under conditions that would allow only one excess removal mechanism to operate at a time. Having identified the two mechanisms it is then possible to operate the systems configuration in accordance with Barnard and Martin and Marais' proposal and thereby induce optimum phosphorus removal due to the combined mechanisms, i.e. biological cum chemical mechanism.

CHAPTER 3

PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION - THEORETICAL CONSIDERATIONS

INTRODUCTION

In the literature survey it was shown that phosphorus precipitates in three forms in natural waters, as (i) beta tricalcium phosphate $Ca_3(PO_4)_2$, (ii) hydroxyapatite $Ca_5(OH)(PO_4)_3$, and (iii) dicalcium phosphate $CaHPO_4$.

For pH values greater than about 7,0 hydroxyapatite (pK_s = 55,6) is thermodynamically the least soluble of these minerals followed by tricalcium phosphate (pK_s = 25,46) and then by dicalcium phosphate (pK_s = 7,0). However, the least soluble mineral need not necessarily precipitate as the presence of foreign ions, notably Mg, may significantly alter the stabilities of the solids and cause the precipitation of a more soluble phase (Ferguson, Jenkins and Stumm, 1970). From their observations, it appears that hydroxyapatite is a mineral whose growth sites are poisoned in wastewater when the magnesium concentration is high (i.e. for Ca/Mg ratio less than 5). This inhibits precipitation of a apatite crystal.

The presence of the carbonic weak acid system may cause a co-precipitation problem by the formation of $CaCO_3$ or some other calcium salt. Also PO_4^{3-} can be adsorbed onto the charged $CaCO_3$ surface; this will result in the poisoning or reduction of growth sites. The degree of adsorption of PO_4^{3-} depends on the phosphorus concentration in solution.

From these remarks it is evident that to predict the form and existence of calcium phosphate crystals in a particular

water is a complex problem. To find some solution, an approach is first to investigate pure system precipitation phenomena. The investigation is then extended by replacing the pure liquid by treated effluent. Thereafter, to utilize the activated sludge mixed liquor.

APPROACH TO THEORETICAL SOLUTION

The $Ca^{++} - PO_4^{3-} - HPO_4^{=} - H_2PO_4^{-} - H_3PO_4$ is a complex one involving a number of ionic equilibrium equations which are subject to restriction by the solubility equations of beta - tricalcium phosphate, dicalcium phosphate and hydroxyapatite where supersaturated conditions exist.

Numerical methods of solution involving the ionic phase only, or, the ionic and solid phases are not for general use due to the complex inter-relationship between the variables defining the equilibrium conditions. However, practical methods of solution are possible, using graphical plots called conditioning diagrams which link the equilibria inter-relationship in terms of certain basic variables (i.e. P-Alkalinity, P-Acidity and P_T). This approach has been extensively investigated for the $Ca^{++} - CO_3^{=} - HCO_3^{-} - H_2CO_3$ system by Loewenthal and Marais (1976). It can be extended quite readily to the phosphoric system. The application to the phosphoric system will closely follow the concepts of Loewenthal and Marais (1976).

Loewenthal and Marais (1976) set out in detail the development of the basic concepts utilized in the development of their conditioning diagrams. It is, therefore, not necessary to give extensive exposition of their basic ideas as these can be found in their monograph.

In our development we shall presume that the definitions of the basic parameters are understood. Consideration will be given to the basic definitions only where these

require adaption to our particular system. The following equilibrium diagrams will be developed.

1. Single aqueous phase equilibrium between phosphoric acid species and water species, and

2. Two phase equilibrium between solid calcium phosphate and aqueous species.

Equilibrium of Orthophosphate in Pure Water

All natural waters are governed by the carbonic weak acid system. However, the presence of dissolved orthophosphate results in the formation of another weak acid system.

As for the carbonic system, the single phase equilibrium conditions for the phosphoric species will be considered in pure water (i.e. presence of dissolved orthophosphate species only).

The pH in a water containing only phosphoric species and associated ions is governed by equilibria reaction between the phosphoric species (H_3PO_4, $H_2PO_4^-$, $HPO_4^=$ and PO_4^{3-}) and water species (H^+ and OH^-).

The equilibrium equations for the orthophosphate species are:

$$[H^+][H_2PO_4^-]/[H_3PO_4] = K_1' \quad \ldots\ldots\ldots\ldots \quad (3.1)$$

$$[H^+][HPO_4^=]/[H_2PO_4^-] = K_2' \quad \ldots\ldots\ldots\ldots \quad (3.2)$$

$$[H^+][PO_4^{3-}]/[HPO_4^=] = K_3' \quad \ldots\ldots\ldots\ldots \quad (3.3)$$

$$[H^+][OH^-] = K_w' \quad \ldots\ldots\ldots\ldots \quad (3.4)$$

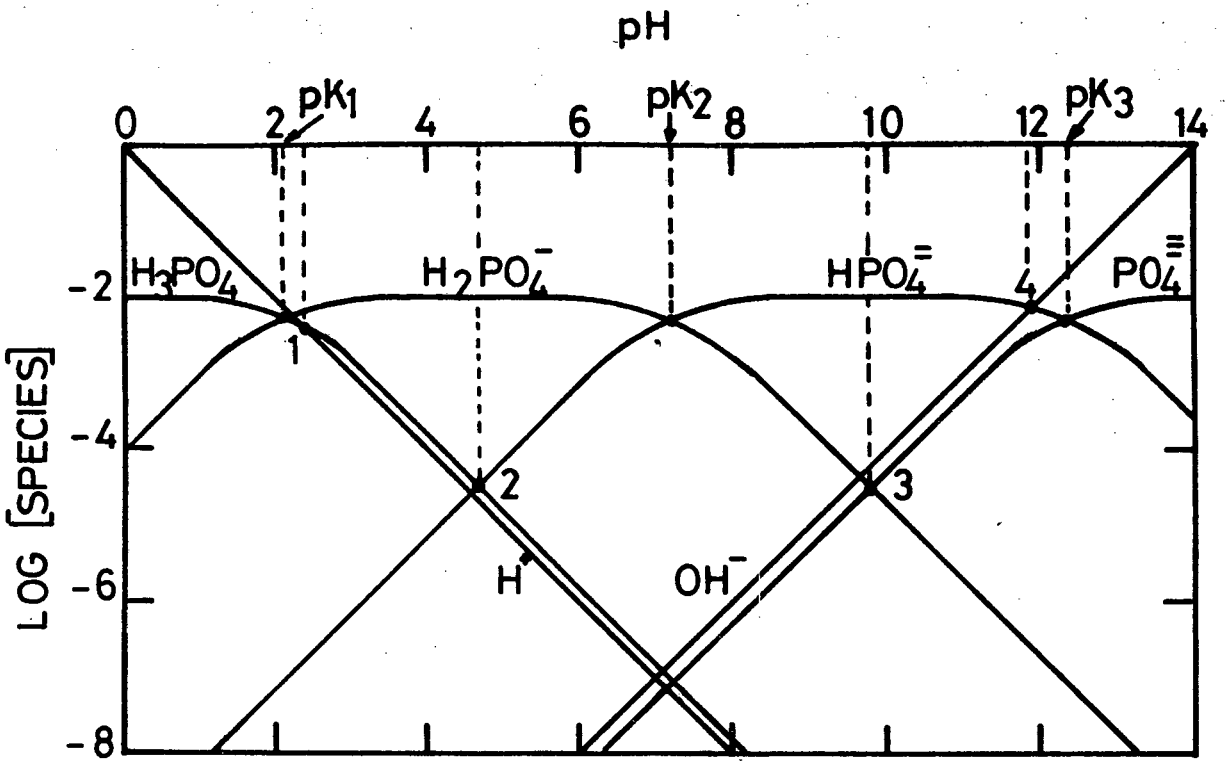


Figure 3.1 *Distribution of phosphoric species with* $P_T = 10^{-2}$ M

where [ ] indicates molar concentration

K' indicates an equilibrium constant which has been adjusted for ionic strength effects.

The total phosphoric concentration (P_T) must equal the sum of the concentration of its ionized species in solution.

i.e. $$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{=}] + [PO_4^{3-}] \quad \ldots\ldots \quad (3.5)$$

For a value of P_T the logarithim of each of the orthophosphate species concentrations are plotted against pH (see Figure 3.1).

The pH values of the equivalence points for H_3PO_4, $H_2PO_4^-$, $HPO_4^{=}$ and PO_4^{3-} solutions are marked 1, 2, 3 and 4 respectively on the log species pH diagram.

Alkalinity and Acidity

The alkalinity of a solution implies the concentration of H^+ ions which must be added to water to change the pH from an initial value to some selected lower final value. The acidity implies the concentration of OH^- ions which must be added to change the pH of a water from some initial value to some higher final value.

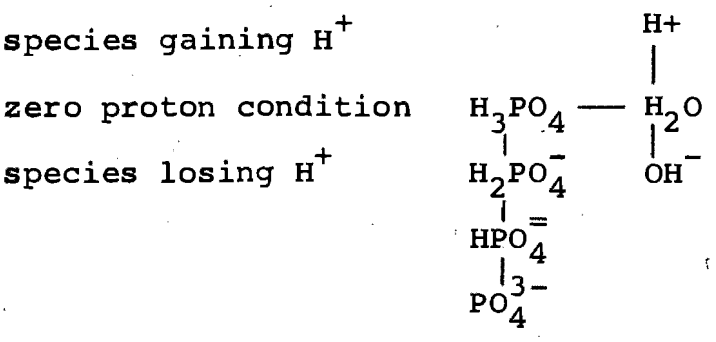
Phosphoric Alkalinity

Alkalinity for a particular equivalent solution (say H_3PO_4) is best explained by an example.

If, say, P_T mole/ℓ of H_3PO_4 is added to pure water an equivalent H_3PO_4 solution is obtained and the pH is defined by the equivalence point of H_3PO_4.

Using the concept of proton balance the H_3PO_4 equivalent

solution is derived as follows:



Sum of species formed by gaining H^+ = sum of species formed by losing H^+ .

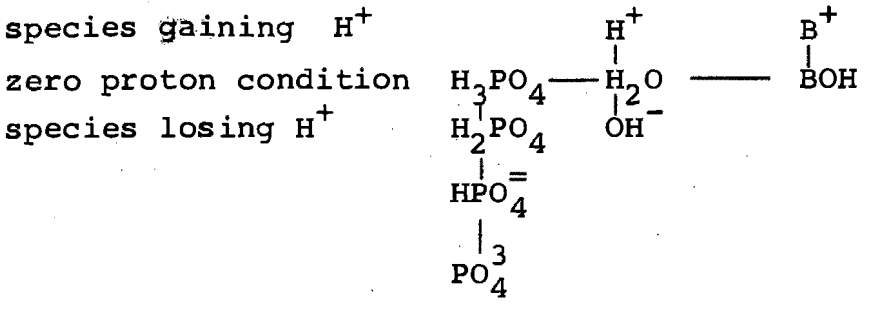
i.e. $[H^+] = [H_2PO_4^-] + 2[HPO_4^=] + 3[PO_4^{3-}] + [OH^-]$.

Referring to Figure (3.1) the intersection of the $H_3PO_4^-$ and H^+ line (i.e. pt. 1) defines the pH of an equivalent phosphoric acid solution and hence the above equations reduces to $[H^+] = [H_2PO_4^-]$.

Note: Other species negligible.

It is now possible to derive a definition for the total Alkalinity in terms of the species of the phosphoric acid system.

Supposing P_B moles/ℓ of nett strong base (BOH) is added to the solution, a relationship linking the nett strong base to the weak acid species can be developed from the concept of proton balance.



The sum of the proton charges must equal sum of the negative charges.

$$[B^+] + [H^+] = [H_2PO_4^-] + 2[HPO_4^{=}] + 3[PO_4^{3-}] + [OH^-]$$

$$\text{i.e.} \quad [B^+] = [H_2PO_4^-] + 2[HPO_4^{=}] + 3[PO_4^{3-}] + [OH^-] - [H^+]$$

$$\text{but} \quad P_B = [B^+] = [OH^-] \text{ added}$$

Titrating the solution using a strong acid to the H_3PO_4 equivalence point one must supply H^+ ions to balance the OH^- ions added from the alkalinity definition. This concentration of H^+ is expressed as the total P-Alkalinity, hence

$$\text{Total P-Alkalinity} = [H_2PO_4^-] + 2[HPO_4^{=}] + 3[PO_4^{3-}] + [OH^-] - [H^+] \quad \ldots\ldots (3.6)$$

Using similar methods of solution as above, the equation for the $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-} Alkalinities can be developed giving:

$$H_2PO_4^- \text{ Alk} = 2[PO_4^{3-}] + [HPO_4^{=}] + [OH^-] - [H_3PO_4] + [H^+] \quad .. (3.7)$$

$$HPO_4^{=} \text{ Alk} = [PO_4^{3-}] + [OH^-] + [H^+] - [H_2PO_4^-] - 2[H_3PO_4] .. (3.8)$$

$$PO_4^{3-} \text{ Alk} = [OH^-] - [H^+] - [HPO_4^{=}] - 2[H_2PO_4^-] - 3[H_3PO_4] \ldots (3.9)$$

Phosphoric Acidity

Equations for total Acidity, $HPO_4^{=}$ Acidity, $H_2PO_4^-$ Acidity and H_3PO_4 Acidity are derived by a similar method as that used in developing the alkalinity equations giving:

$$\text{Total Acidity} = 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{=}] + [H^+] - [OH^-] \quad \ldots\ldots (3.10)$$

$$HPO_4^{=} \text{ Acidity} = 2[H_3PO_4] + [H_2PO_4] - [PO_4^{3-}] - [OH^-] + [H^+] \quad \ldots\ldots (3.11)$$

$$H_2PO_4 \text{ Acidity} = [H_3PO_4] + [H^+] - 2[PO_4^{3-}] + [HPO_4^{=}] + [OH^-] \quad \ldots\ldots (3.12)$$

$$H_3PO_4 \text{ Acidity} = [H^+] - [H_2PO_4^-] - 2[HPO_4^{=}] - 3[PO_4^{3-}] - [OH^-]$$

DEVELOPMENT OF SINGLE PHASE MODEL

The single phase model assumes that no calcium phosphate precipitation occurs from the water and that no CO_2 exchange occurs between the water and the air in contact with the water. It considers only changes in equilibrium between the dissolved orthophosphate species in aqueous phase due to chemical conditioning.

This model is based on the Loewenthal and Marais (1976) single phase model for the carbonic system, where the behaviour of the system is described in terms of the parameter Alkalinity, Acidity and pH.

Equations governing the single phase model are as follows:

The equilibria equation for the phosphoric systems are:

$$[H^+]\,[H_2PO_4^-]/[H_3PO_4] = K_1' \quad \ldots\ldots (3.14)$$

$$[H^+]\,[HPO_4^{=}]/[H_2PO_4^{=}] = K_2' \quad \ldots\ldots (3.15)$$

$$[H^+]\,[PO_4^{3-}]/[HPO_4^{=}] = K_3' \quad \ldots\ldots (3.16)$$

$$[H^+]\,[OH^-] = K_w' \quad \ldots\ldots (3.17)$$

where [ ] indicates molar concentrations

K_1', K_2', K_3' and K_w' = equilibrium constants which have been adjusted for ionic strength effects.

Equations (3.14 to 3.17) are a set of 4 independent equations with 6 unknown, i.e. H^+, OH^-, H_3PO_4, $H_2PO_4^-$, $HPO_4^=$ and PO_4^{3-}. To define the initial ionic state of the water completely, it is necessary to obtain experimental values of at least two parameters. It is not possible to determine separately any of the phosphate species. However, H^+ can be calculated by measuring pH and including Equation (3.18), i.e.:

$$pH = -\log (f_m [H^+]) \quad \ldots\ldots\ldots\ldots \quad (3.18)$$

in the system. Hence one more parameter needs to be determined. The mass parameters, P_T, P-Alkalinity and P-Acidity are in terms of the basic parameters and if it is possible to measure one of them, the system will be completely defined.

$$\text{i.e.} \quad P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^{3-}] \quad \ldots\ldots\ldots \quad (3.19)$$

$$\text{P-Alkalinity} = 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-] + [OH^-] - [H^+] \quad (3.20)$$

$$\text{P-Acidity} = 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^=] + [H^+] - [OH^-] \ldots \quad (3.21)$$

where

P_T = sum of concentration of its ionized species in solution

P-Alkalinity = moles of H^+ to change the pH of a water to that of a phosphoric acid solution.

P-Acidity = moles of OH^- to change the pH of a water to that of a phosphoric solution.

In practice it is difficult to obtain P-Alkalinity and P-Acidity experimentally because of the low concentration present. However, P_T can be measured experimentally very accurately.

Hence Eq. (3.19) is included in the system. This increases the number of independent equations to six and the number of

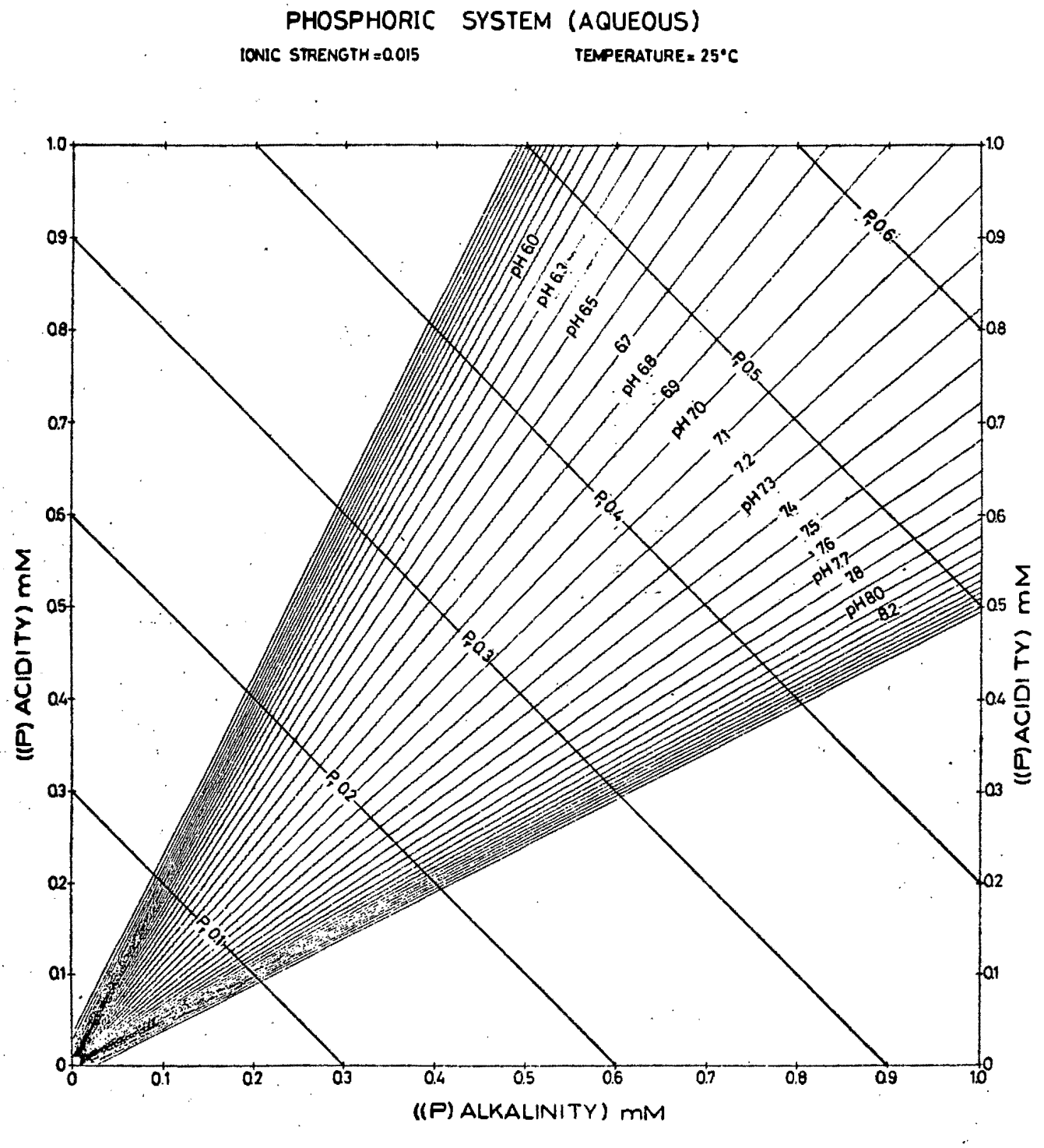


Figure 3.2 *P-Alkalinity - P-Acidity - pH equilibrium diagram*

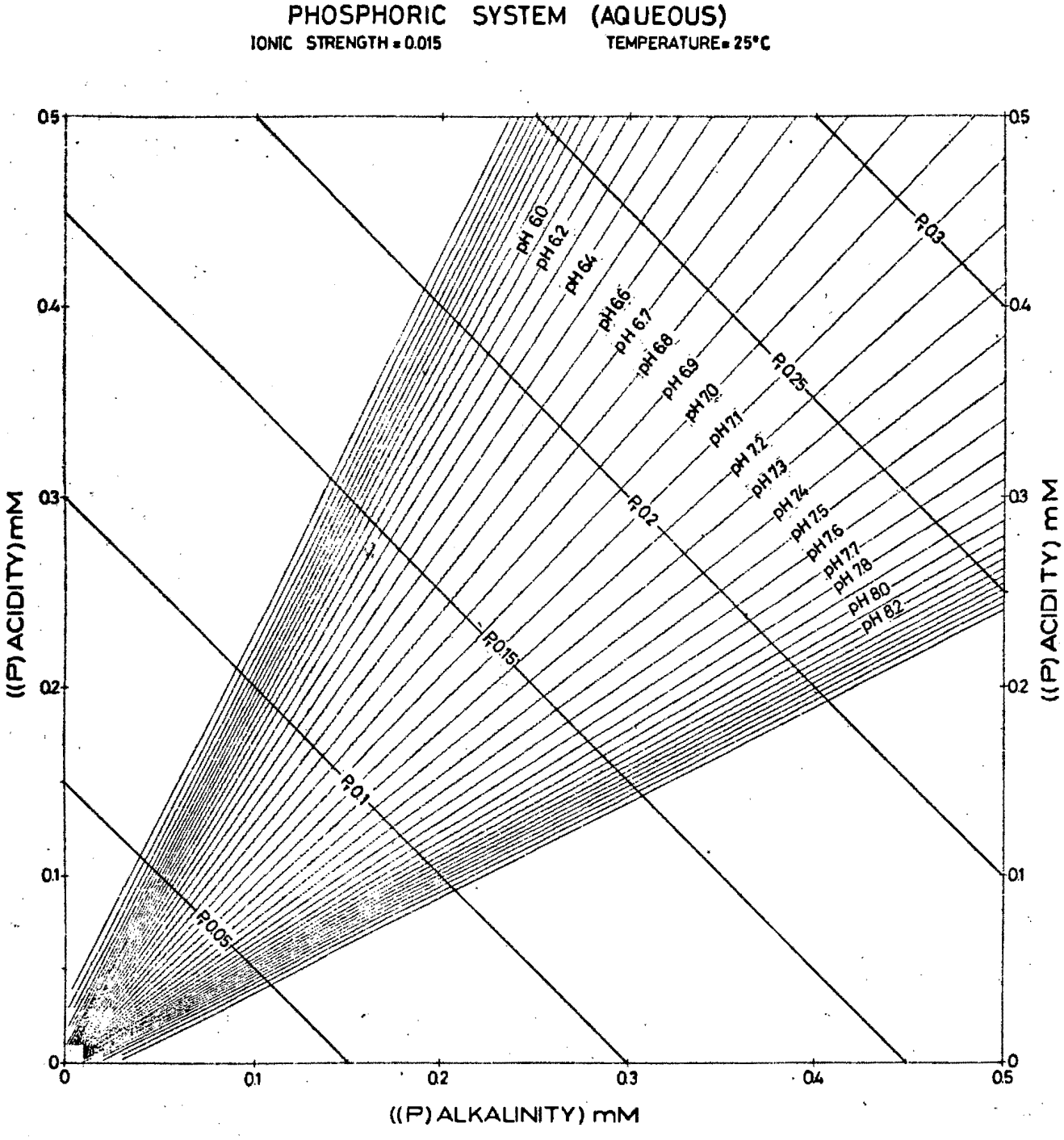


Figure 3.3 *P-Alkalinity - P-Acidity - pH equilibrium diagram*

unknowns to 8, but the parameters pH and P_T can be measured, hence the remaining six unknowns were found by solving the Equations (3.14 to 3.19).

In conformity to Loewenthal and Marais (1976) the single phase conditioning diagram makes use of the parameters P-Alkalinity and P-Acidity. As the system is completely defined, these parameters can be calculated from Eq. (3.20) and Eq. (3.21) respectively.

In water conditioning the only practical method of solution is by using graphical aids which comprise graphical plots linking Alkalinity, Acidity and pH. Choosing Alkalinity and Acidity as cartesian co-ordinates, pH can be written in terms of these parameters (by applying equilibria relationships) and plotted as a series of constant pH lines in the co-ordinate diagram (see Fig. 3.2). This plot constitutes an ionic equilibrium or single phase diagram for the phosphoric system.

A family of straight lines representing constant values of P_T can also be plotted in the single phase diagram using the relationship between the mass parameters P_T, P-Alkalinity and P-Acidity as follows:

$$\text{P-Alkalinity} + \text{P-Acidity} = 3P_T$$

This equation indicates a linear relationship between the three mass parameters so that a particular value for P_T plots as a straight line in the diagram and intersects both P-Acidity and P-Alkalinity axes at the values $P_T/3$ (see Fig. 3.2).

The theoretical relationship between Alkalinity, Acidity and pH for plotting the single phase diagram for the phosphoric system is developed as follows:

From Eq. (3.15)

$$H_2PO_4^- = \frac{[H^+][HPO_4^=]}{K_2'} \quad \ldots\ldots\ldots\ldots (3.22)$$

Substitute Eq. (3.22) into Eq. (3.20)

$$\text{P-Alkalinity} = 3[PO_4^{3-}] + 2[HPO_4^=] + \frac{[H^+][HPO_4^=]}{K_2'} + [OH^-] - [H^+] \quad \ldots (3.23)$$

From Eq. (3.16)

$$[PO_4^{3-}] = \frac{K_3'[HPO_4^=]}{[H^+]} \quad \ldots\ldots\ldots\ldots (3.24)$$

Substituting Eq. (3.24) and Eq. (3.17) into Eq. (3.23)

$$\therefore \text{P-Alkalinity} = \frac{[HPO_4^=]K_3'}{[H^+]} + 2[HPO_4^=] + \frac{[H^+][HPO_4^=]}{K_2'} + \frac{K_w'}{[H^+]} - [H^+] \quad \ldots\ldots\ldots (3.25)$$

Solving for $[HPO_4^=]$: i.e.

$$HPO_4^= = \frac{\text{P-Alkalinity} - \frac{K_w'}{[H^+]} + [H^+]}{\frac{K_3'}{[H^+]} + 2 + \frac{[H^+]}{2}} \quad \ldots\ldots (3.26)$$

From Eq. (3.14)

$$[H_3PO_4] = \frac{[H^+][H_2PO_4^-]}{K_1'} \quad \ldots\ldots\ldots\ldots (3.27)$$

Substituting Eq. (3.22) into Eq. (3.27)

$$[H_3PO_4] = \frac{[H^+][H^+][HPO_4^=]}{K_1' * K_2'} \quad \text{..... (3.28)}$$

Substituting Equations (3.17), (3.22) and (3.28) into Eq. (3.21)

$$\text{Acidity} = \frac{2[H^+][HPO_4^=]}{K_2'} + [HPO_4^=] + \frac{3[H^+]^2[HPO_4^=]}{K_1' * K_2'}$$

$$+ [H^+] - K_w'/[H^+]$$

Solving for $[HPO_4^=]$

$$[HPO_4^=] = \frac{(\text{Acidity} - [H^+] + K_w'/[H^+])}{(\frac{2[H^+]}{K_2'} + 1 + \frac{3[H^+]^2}{K_1' * K_2'})} \quad \text{..... (3.29)}$$

Equating Eq. (3.26) and Eq. (3.29) the general equilibrium equation in terms of Alkalinity, Acidity and H^+, is obtained:

$$\text{Alkalinity} - \frac{K_w'}{[H^+]} + [H^+] \quad \frac{2[H^+]}{K_2'} + 1 + \frac{3[H^+]^2}{K_1' * K_2'}$$

$$= \text{Acidity} - [H^+] + \frac{K_w'}{[H^+]} \quad \frac{K_3'}{[H^+]} + 2 + \frac{[H^+]}{2} \quad \text{.. (3.30)}$$

A graphical plot of Eq. (3.30) with Alkalinity and Acidity as co-ordinate axis can now be determined using a high speed digital computer (see Appendix D for computer programme).

For some chosen fixed value of pH (and hence some fixed value of H^+) there is a linear relationship between Alkalinity and Acidity (see Figs. 3.2 and 3.3).

EQUILIBRIUM CONDITIONING DIAGRAM FOR THE TWO PHASE MODEL

Introduction

In the two phase equilibrium model the objective is to describe the inter relationships between the equilibria ionic phases and the equilibria solid phase. Three solid phases can be in equilibrium with the ionic phase (i.e. beta tricalcium phosphate, dicalcium phosphate and hydroxyapatite).

After various attempts to develop a diagram including all three solid phases, it was decided that the simplest approach is to develop the two phase diagram for each of the solid phases separately. By joint utilization of all three diagrams it is possible to readily determine which is the significant precipitation phase applicable under the particular conditions existing or imposed on the solution.

It should be noted that besides the calcium phosphate system a number of other cations (Mg^{2+}, Fe^{3+} and Na^{+}) can form precipitants and complexes with the ortho-phosphate ion. However, the cation of major importance is calcium due to its higher concentration in terrestrial waters. Therefore consideration was restricted to the calcium phosphate system only.

The forms of calcium phosphate precipitants in an aquatic environment in order of decreasing solubility are:

(i) mono calcium phosphate - $Ca(H_2PO_4)$

(ii) dicalcium phosphate - $Ca\ HPO_4$

(iii) beta tricalcium phosphate - $Ca_3(PO_4)_2$, and

(iv) hydroxyapatite - $Ca_5(OH)(PO_4)_3$

Mono calcium phosphate is unlikely to precipitate from natural terrestrial waters as the conditions for precipitation

are low pH (pH < 6) and high calcium and phosphorus concentrations. For this reason a conditioning diagram including this mineral was not developed.

Development of Two Phase Model

In order to develop a two phase conditioning diagram for a particular calcium phosphate mineral it is assumed that the concentration of the species in solution is governed by that calcium phosphate crystal and the acqueous species.

The model is based on the weak acid-base parameters similar to those used in the three phase model for the calcium carbonate system (Loewenthal and Marais, 1976). Their model describes the behaviour of the system in terms of the parameters Alkalinity, Acidity and pH.

Equations governing the phosphoric system are:

(1) The equilibrium equation for the ortho-phosphate species

$$[H^+][H_2PO_4^-]/[H_3PO_4] = K_1' \quad \ldots\ldots\ldots (3.31)$$

$$[H^+][HPO_4^=]/[H_2PO_4^-] = K_2' \quad \ldots\ldots\ldots (3.32)$$

$$[H^+][PO_4^{3-}]/[HPO_4^=] = K_3' \quad \ldots\ldots\ldots (3.33)$$

$$[H^+][OH^-] = K_w' \quad \ldots\ldots\ldots (3.34)$$

(2) The equations defining the saturated state for the particular calcium phosphate mineral, i.e. one of the following:

$$Ca_3(PO_4)_2 \text{ mineral } K_{s1}' = [Ca^{++}]^3[PO_4^{3-}]^2 \quad \ldots\ldots (3.35)$$

$$CaHPO_4 \text{ mineral } K_{s2}' = [Ca^{++}]\frac{[H^+][PO_4^{3-}]}{K_3'} \quad \ldots\ldots (3.36)$$

$$\text{or} \quad Ca_5(OH)(PO_4)_3 \text{ mineral } K_{s3}' = \frac{[Ca^{++}]^5 [PO_4^{3-}]^3}{[H^+]} K_w' \quad \ldots (3.37)$$

where K_{s1}', K_{s2}' and K_{s3}' = the solubility products of the three calcium phosphate minerals, adjusted for ionic strength effects;

K_1', K_2', K_3' and K_w' = thermodynamic equilibrium constants adjusted for ionic strength effects.

[ ] indicates molar concentration.

For equilibrium, Eqs. (3.31 to 3.34) and one of the Eqs. (3.35), (3.36) or (3.37) must be simultaneously satisfied.

These equations constitute a set of 4 independent equations containing 7 unknown parameters, i.e. H^+, OH^-, $H_3PO_4^-$, $HPO_4^=$, PO_4^{3-} and Ca^{++}.

The parameters Ca^{++} can be found by experimental determination of Ca_T. If there is no significant ion pairing $Ca_T = Ca^{++}$. This leaves two more unknown parameters to be determined. It is not possible to determine separately any of the phosphate species. However, H^+ can be determined by measuring pH and including Eq. (3.38), i.e.

$$pH = -\log f_m[H^+] \quad \ldots\ldots\ldots\ldots\ldots (3.38)$$

in the system.

Hence one more parameter needs to be determined. The only possibility that remains, is to investigate if one of the mass parameters P-Alk, P-Acid or total phosphoric species can be experimentally found. The mass parameters are in terms of the basic parameters and hence if it is possible to measure one of them, the system will be completely defined.

i.e. $P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^{3-}]$ ..... (3.39)

P-Alkalinity $= 3[PO_4^{3-}] + 2[HPO_4^=] + [H_2PO_4^-] + [OH^-] - [H^+]$ .. (3.40)

P-Acidity $= 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^=] + [H^+] - [OH^-]$ ... (3.41)

where

P_T = sum of concentration of its ionized species in solution.

P-Alkalinity = is defined as moles of H^+ to change the pH of a water to that of a phosphoric acid solution.

P-Acidity = is defined as moles of OH^- to change the pH of a water to that of a phosphoric acid solution.

In practice, it is difficult to obtain P-Alkalinity and P-Acidity experimentally because of the low concentration present. However, P_T can be measured experimentally very accurately. Hence Eq. (3.39) is included in the system. This increases the number of independent equations to six and the number of unknowns to nine, but the parameters pH, P_T and Ca_T can be measured, hence the remaining six unknowns were found by solving the set of Eqs. (3.31 to 3.34) and Eq. (3.38) and (3.39). This set will be valid whether the water is undersaturated, saturated or supersaturated with respect to one of the calcium phosphate minerals provided neither dissolution nor precipitation of the calcium phosphate mineral occurs.

In conformity to Loewenthal and Marais (1976) the conditioning diagrams make use of the parameters P-Alkalinity and P-Acidity. As the system is completely defined these can be calculated from Eq. (3.40) and Eq. (3.41) respectively.

Loewenthal and Marais (1976) proposed an additional mass parameter for the carbonic weak acid base system (i.e. Ca-Alk)

and used as the basic co-ordinate system (Ca-Alk) and Acidity. They then transformed the systems of equations to solve pH, Alk and Ca in terms of the basic co-ordinates (Ca-Alk) and Acidity:

$$pH = f_1 \ (Ca\text{-}Alk \ , \ Acidity)$$
$$Alk = f_2 \ (\ " \ \ \ " \ )$$
$$Ca = f_3 \ (\ " \ \ \ " \ )$$

The definitions of the mean parameters Alkalinity and Acidity are applicable to any weak acid base system (Loewenthal and Marais). The mass parameters Alkalinity and Acidity for the particular phosphoric acid base system are listed in Eqs.(3.40) and (3.41) respectively. These parameters are expressed in moles/litre which gives a different algebraic expression than when expressed as equivalent or as ppm $CaCO_3$.

The conditioning diagram for the phosphoric weak acid system graphically presents equilibria inter-relationships between Alkalinity, Acidity, pH and calcium in a plot with the parameters Acidity and (Alk-2Ca) as co-ordinates.

The co-ordinate system selected for the two phase condition diagram is shown in Fig. (3.4).

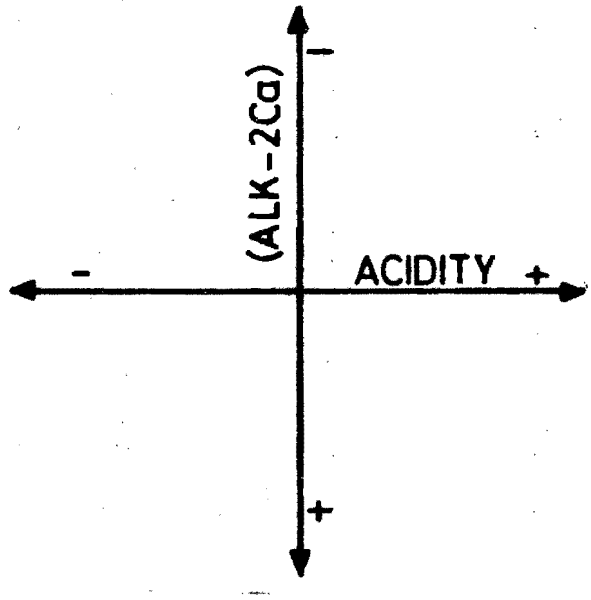


Figure 3.4 *Co-ordinate system for the two phase conditioning diagram*

Note (Alk - 2Ca) increases in the positive X direction and acidity increases in the negative Y direction.

$$X = -\text{Acidity}$$

$$\text{i.e.} \quad X = [OH^-] - [H^+] - 3[H_3PO_4] - 2[H_2PO_4^-] - [HPO_3^{=}]$$

$$\text{and} \quad Y = (\text{Alk} - 2\text{Ca})$$

To represent saturated calcium equilibrium values for each of the parameters Alkalinity, calcium and pH the solubility and ionic equilibria relationships are used to derive equilibria equations for each of the three parameters in terms of the co-ordinate parameter (Alk-2Ca) and (Acidity).

$$\text{i.e.} \quad \text{pH} = f_1 \ (\text{Alk-2Ca} \ , \ \text{Acidity})$$

$$\text{Alk} = f_2 \ (\ " \ \ " \ )$$

$$\text{Ca} = f_3 \ (\ " \ \ " \ )$$

To plot the particular parameter in the diagram, say pH, in terms of (Alk-2Ca) a fixed value is given to the pH and assuming values for (Alk-2Ca), the Acidity is calculated. By this means, the constant pH line is plotted on the diagram. The method of solution for constant Alkalinity and calcium lines are similar.

The mathematical development for calculating the above relationships are set out in Appendix B and the corresponding computer programme is listed in Appendix E.

The two phase conditioning diagram for beta-tricalcium phosphate is shown in Fig. (3.5) for dicalcium phosphate in Fig. (3.6) and for hydroxyapatite in Fig. (3.7).

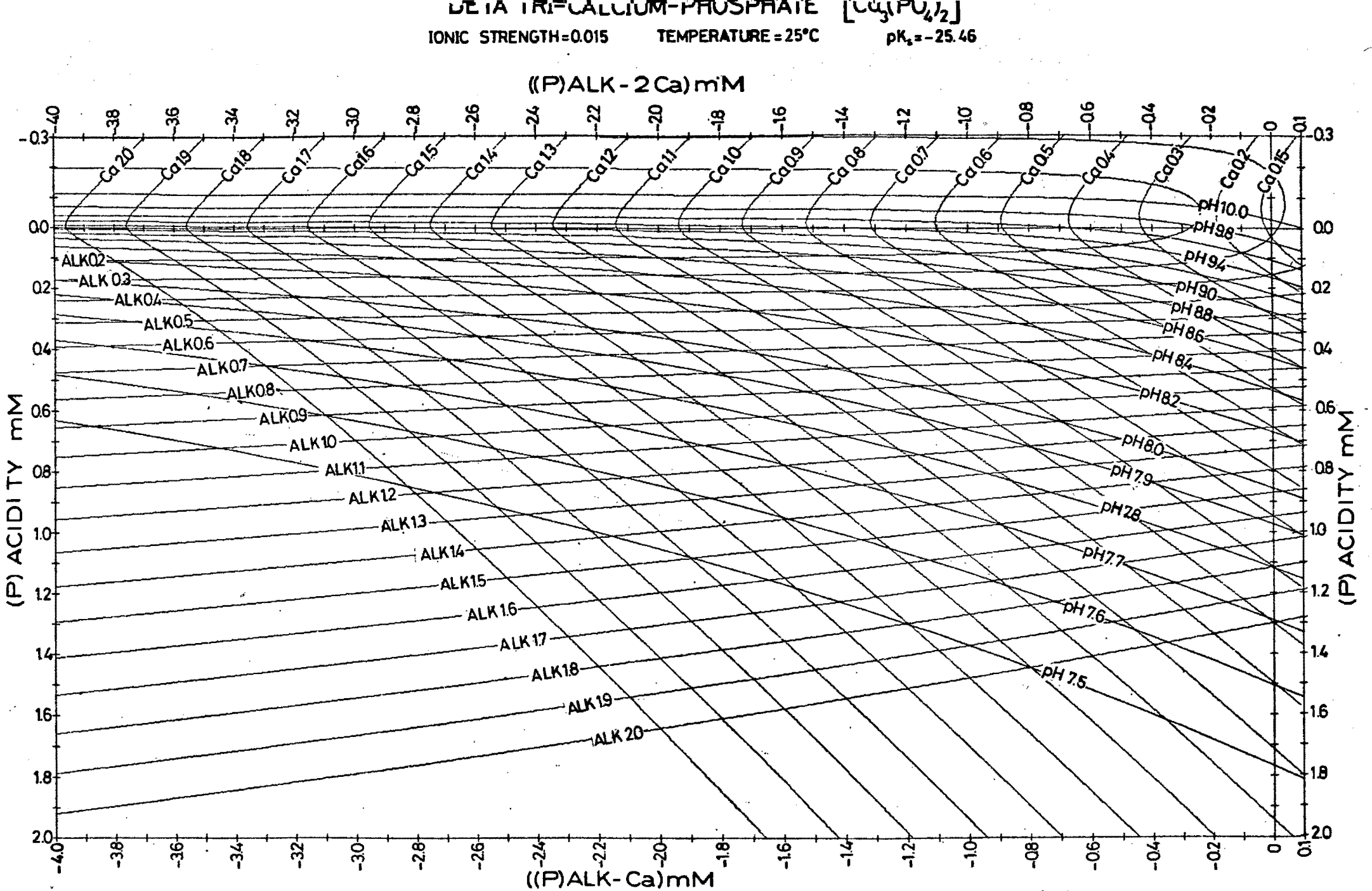


Figure 3.5 *Two phase conditioning diagram for beta-tricalcium phosphate*

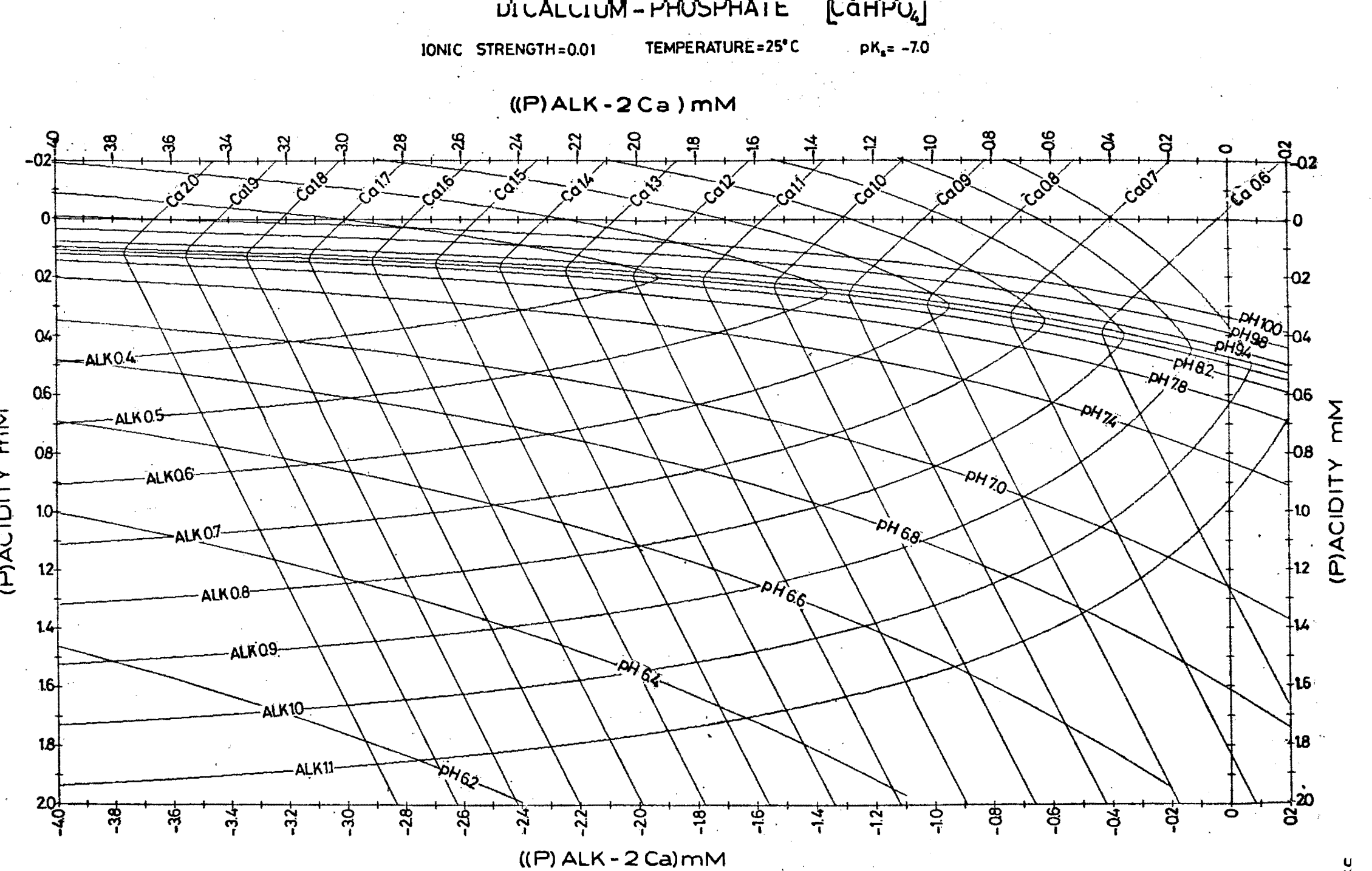


Figure 3.6 Two phase conditioning diagram for dicalcium phosphate

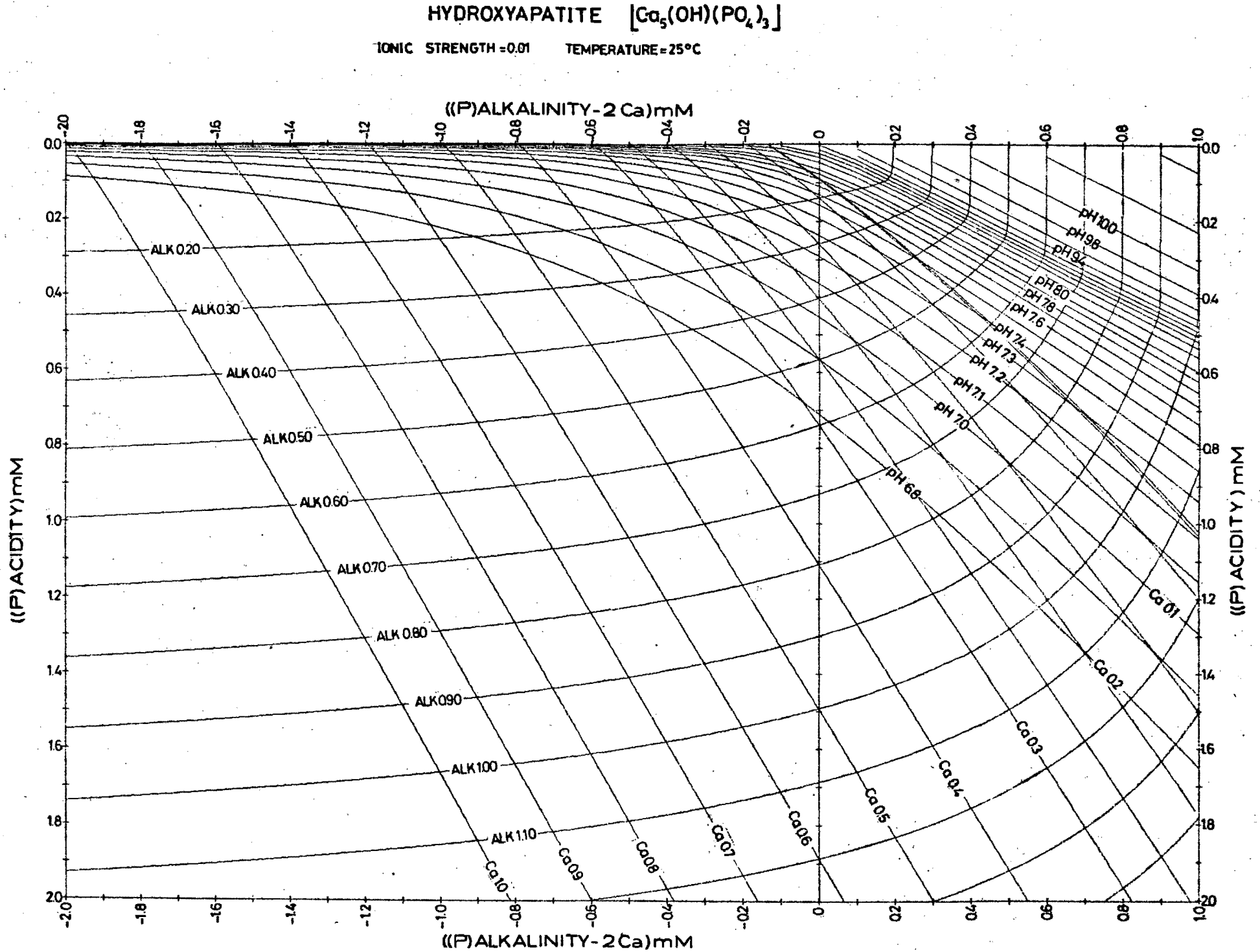


Figure 3.7 Two phase conditioning diagram for hydroxyapatite

APPLICATION OF SINGLE AND TWO PHASE CONDITIONING DIAGRAMS

The two phase conditioning diagram developed for the three calcium phosphate minerals are used for estimating:

1. The initial state of a water with respect to one of the calcium phosphate minerals with and without species of the carbonic system present. This problem is the usual one and must be solved before any further calculations can be made. The calculation will give the initial ionic state of the water with respect to the phosphoric system.

2. Dosage to effect a certain phosphorus removal, again with and without species of carbonic system present. This calculation follows subsequently to (1) above.

1. Initial State

(i) Without the presence of carbonic species

Depicting the initial condition of the water on a two phase diagram is done as follows:

Assume you have a pure solution (i.e. no carbonic species present) with Ca^{++} and PO_4^{3-} ions and it is desired to estimate whether the solution is undersaturated, saturated or supersaturated with respect to the minerals $Ca_3(PO_4)_2$, $Ca\,HPO_4$ and $Ca_5(OH)(PO_4)_3$. The initial state on the 2-phase diagram is obtained by the intersection of the pH and P-Alkalinity lines. P-Alkalinity is difficult to measure experimentally because of its low concentration. However, parameters P_T, Ca_T and pH can be measured experimentally very accurately.

To obtain P-Acidity and P-Alkalinity the single phase diagram is used. Plot the P_T and pH lines on the diagram and the intersection of these lines given the initial P-Acidity and P-Alkalinity of the solution.

Accepting the P-Alkalinity (or P-Acidity) value, plot these parameter values versus pH on the two phase diagram. The intersection of the P-Alkalinity and pH lines gives the ionic state of the water. To determine if the solution is undersaturated, saturated or supersaturated compare the experimental value Ca_{exp} with the theoretical value Ca_{th} (found from the Ca intersection at the ionic point). If $Ca_{exp} > Ca_{th}$ the solution is supersaturated, if $Ca_{exp} = Ca_{th}$, the solution is saturated and if $Ca_{exp} < Ca_{th}$ then the solution is undersaturated with respect to one of the three calcium phosphate minerals.

The procedure described above is best illustrated by solving the following example:

Example 3.1: Consider a solution with only phosphoric species present where the following parameters are measured;

i.e. pH = 7,0, P_T = 0,3 m mole and Ca = 1,0 m moles. Plot pH and P_T on single phase diagram as shown in Fig.(3.8).

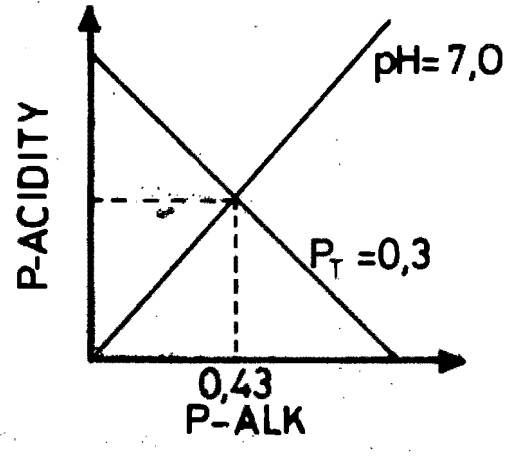


Figure 3.8 *Estimation of initial P-Alkalinity from single phase diagram*

From Fig. (3.8) P-Alkalinity = 0,43 m moles.

Plot P-Alkalinity and pH on three phase diagram shown in Fig. (3.9). Consider the $Ca_5(OH)(PO_4)_3$ two phase diagram.

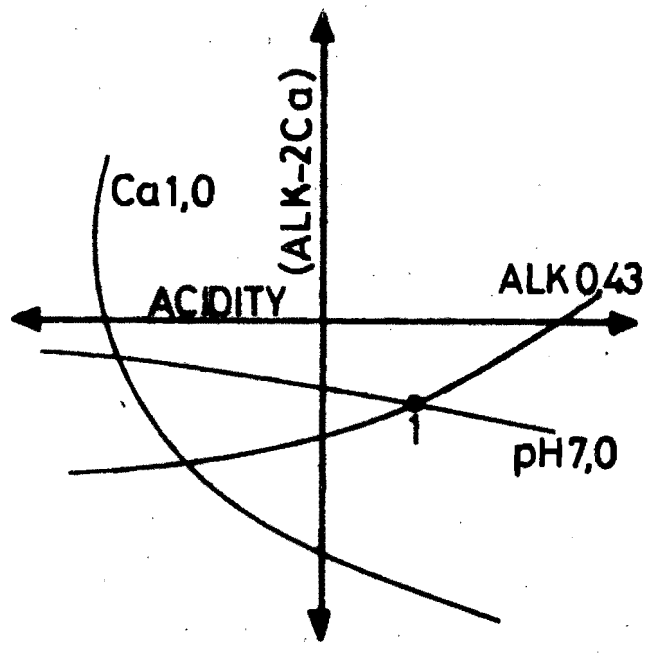


Figure 3.9 *Initial state of water in the* $Ca_5(OH)(PO_3)_3$ *diagram*

Point 1 gives initial ionic state. Ca line passing through this point gives Ca_{th} = 0,27.

But Ca_{exp} = 1,0 m moles.

The solution, therefore, is supersaturated with respect to the $Ca_5(OH)(PO_4)_3$ mineral.

(ii) <u>The presence of carbonic species</u>:

The difficulties of obtaining the initial state of the phosphoric system is increased when species of the carbonic system are present as the solution now contains two weak acid-base systems. However, a practical method

of solution is by jointly using the single phase conditioning diagrams for the phosphoric and carbonic systems. The procedure for determining the initial carbonic and phosphoric Alkalinity is best explained by an example.

Example 3.2: Analysis of a water gives total phosphoric acid species concentration, P_T, of 0,4 m moles/ℓ and pH 7,8. The pH of the water is adjusted to pH 7,0 by addition of 0,6 m moles/ ℓ of strong acid.

Referring to single phase phosphoric system diagram the values of P_T = 7,8, and pH 7,0 are plotted in Fig. (3.10).

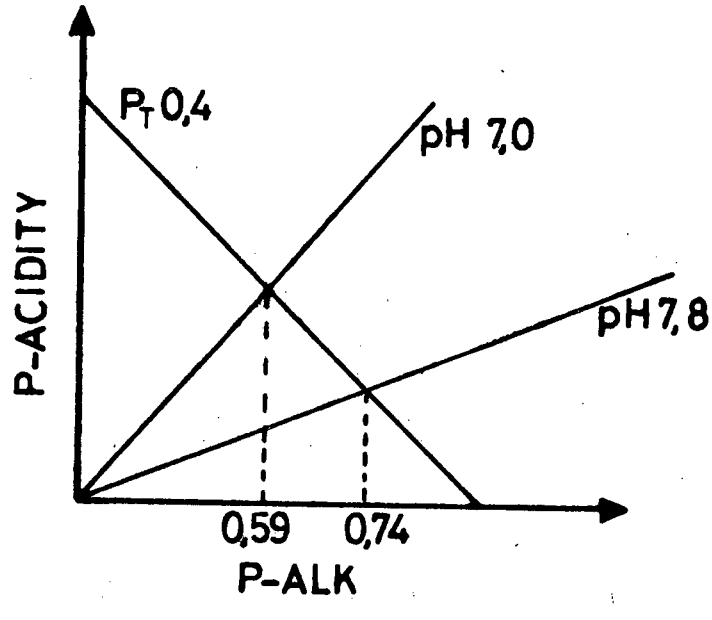


Figure 3.10 *Estimation of initial and final P-Alkalinity*

The difference in Alkalinity between the intersection of the pH lines and the constant P_T line is the fraction of acid taken up by the phosphoric acid system.

From Fig. (3.10) the fraction of phosphoric acid

= 0,74 - 0,59

= 0,15 m mole.

The fraction of acid taken up by the carbonic acid system is hence (0,6 - 0,15) = 0,45 m moles.

Plot pH 7,0 and pH 7,8 on the single phase carbonic diagram. The vector of 0,45 m moles is then moved between the pH lines until nose and tail just touch, the pH 7,0 and pH 7,8 lines respectively. The initial carbonic Alkalinity is given by the intersection of the vector tail and the pH 7,8 line (see Fig. (3.11)).

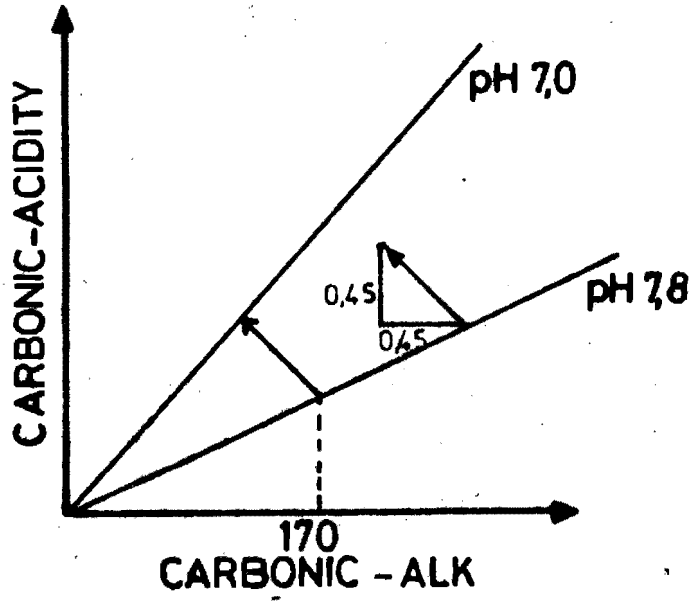


Figure 3.11 *Estimation of initial carbonic Alkalinity*

From Fig. (3.11) the initial carbonic –Alkalinity is 170 ppm as $CaCO_3$ = 3,4 m moles. Referring to the single phase phosphoric diagram (Fig. 3.10) the intersection of pH = 7,8 and P_T = 0,4 gives the initial P-Alkalinity. Plot, as before, this value versus pH on the two phase phosphoric system diagram and obtain the state of the water (i.e. undersaturated, saturated or supersaturated).

2. Chemical Conditioning

(i) No carbonic species present:

If an undersaturated solution of $Ca_5(OH)(PO_4)_3$ is seeded with calcium phosphate crystals no precipitation will occur, but dissolution of the calcium phosphate seed occurs until a saturated state is obtained.

Example 3.3: Analysis of water gives total phosphoric acid species, P_T = 0,3 m moles/ℓ pH = 7,0 and Ca = 0,15 m moles/ℓ.

Considering the $Ca_5(OH)(PO_4)_3$ mineral, the initial ionic state plots at pt. 1 on the two phase conditioning diagram (Fig. 3.9).

The solution is undersaturated and dissolution of calcium phosphate results. When dissolution occurs the P-Acidity remains constant and pt. 1 moves horizontally to, say, point 2 (see Fig. 3.12). The intersection of the horizontal co-ordinate (Acidity) and vertical co-ordinate (Alk-2Ca) defines the final saturated condition.

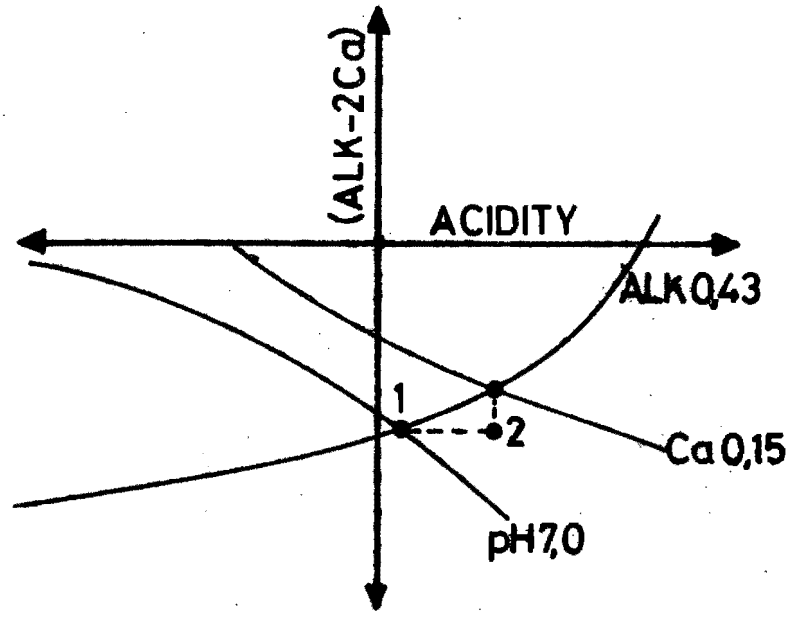


Figure 3.12 *Estimation of final saturated condition*

From Fig. (3.12) the saturated state gives:

New Alkalinity = Alki + Δ Alk
= 0,43 + 0,05
= 0,48 m moles/ℓ

New Calcium = Ca_i + ΔCa
= 0,15 + 0,025
= 0,175 m moles/ ℓ

and New pH = 7,10

Note that 2 Δ Ca = $Ca_5(OH)(PO_4)_3$ dissolved.

Accepting that the solution is saturated and it is required to reduce the P_T concentration by 0,05 m moles/ℓ no precipitation will occur unless it is chemically conditioned. Depending on the type and mass of chemical added, the point will move in a direction of the vector shown in Fig. (3.13).

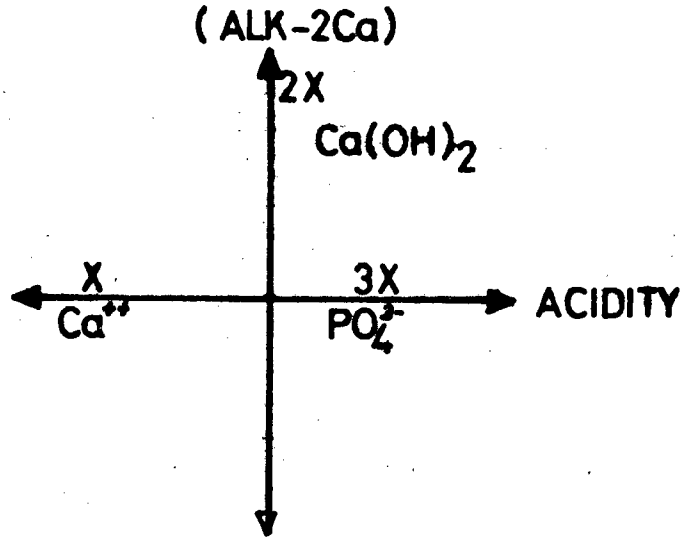


Figure 3.13 *Direction format diagram*

In this example line, $Ca(OH)_2$ is used to reduce P_T, of 0,3 m moles/ ℓ to 0,25 m moles/ℓ

At saturation

$$(Alk-2Ca) = 0,14 \text{ m moles/litre}$$

This value stays constant since the vector moves vertically.

The equivalent mass of calcium removed when $Ca_5(OH)(PO_4)_3$ precipitates is 0,05.(5/3) m moles/l. = 0,083 m moles/l.

Hence new calcium value

$$= (Ca_i - \Delta Ca)$$
$$= (0,175 - 0,083)$$
$$= 0,09 \text{ m moles/l.}$$

New Alk

$$= (Alk_i - 2Ca)$$
$$= (0,48 - 0,166)$$
$$= 0,314 \text{ m moles/l.}$$

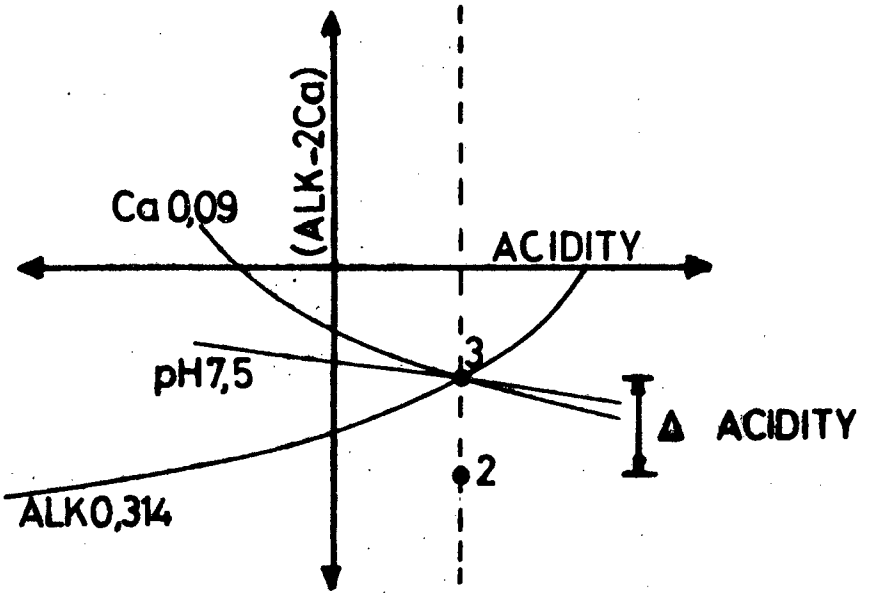


Figure 3.14 *Mass of lime required (i.e.* 0,11 mM/ℓ)

The intersection of the new Alkalinity value and the vertical co-ordinate (Alk-2Ca), point 3, defines the final saturated state of the water. The Acidity difference between point 2 and point 3 gives the mass of lime required to effect the desired phosphorus removal. See Figure 3.14.

$$\text{lime required} = \frac{\text{Acidity}}{2}$$

$$= \frac{0,21}{2} = 0,11 \text{ m moles/litre.}$$

From Fig. (3.14) final saturated pH = 7,5.

(ii) Carbonic species present:

Example 3.4: Considering that carbonic acid species are also present in the above phosphoric system and we require to reduce P_T by the desired amount of 0,05 mm/l assuming no $CaCO_3$ precipitation, the procedure is the same as in the example above to give a final pH and hence dosage of lime, as far as the phosphoric system is concerned.

For the carbonic acid system, C_T stays constant provided no $CaCO_3$ precipitation or CO_2 is lost. Assume that C_T is 2 m moles/litre. C_T can also be obtained from Example 3.2. Referring to the carbonic two phase diagram pH = 7,1, pH = 7,5 and C_T = 2 mm/litre are plotted in Fig. (3.15).

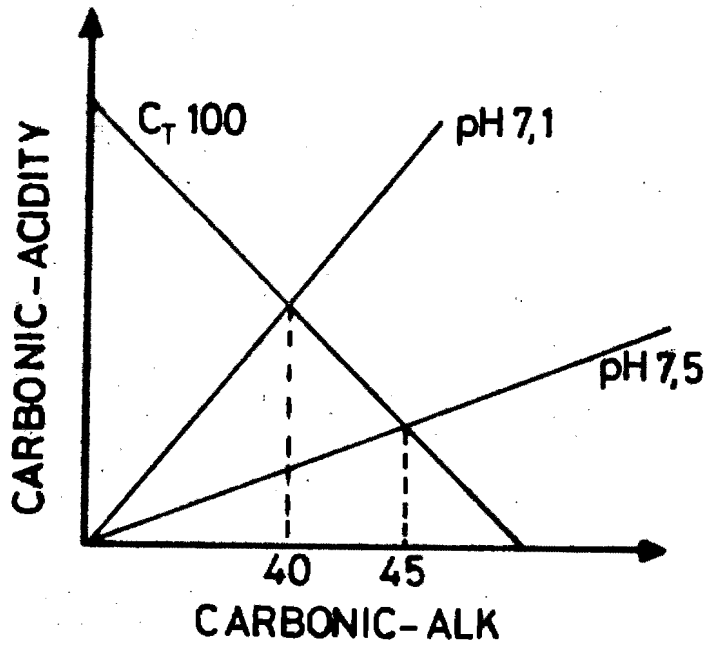


Figure 3.15 *Initial and final carbonic Alkalinity*

Initial carbonic Alkalinity = $\frac{40}{50}$ m moles/litre

Final carbonic Alkalinity = $\frac{45}{50}$ m moles/litre

$\therefore$ change in Alkalinity = 0,1 m moles/litre

$\therefore$ lime dosage for carbonic system = $\frac{0,1}{2}$ m moles/litre

Total dosage of lime required is the sum of the separate dosages for the phosphoric system and the carbonic system.

i.e. $Ca(OH)_2$ dosage = $0,11 + \frac{0,1}{2}$

= <u>0,16 m moles/litre</u>

The method of application and the solutions are the same for the other two calcium phosphate minerals, i.e. beta tricalcium phosphate and dicalcium phosphate.

CHAPTER 4

PHOSPHORUS REMOVAL BY CHEMICAL PRECIPITATION - EXPERIMENTAL INVESTIGATIONS

PHOSPHORUS PRECIPITATION FROM TREATED WASTE WATER

In the previous chapter the theoretical behaviour of a pure system in two phase equilibrium was analysed. In order to investigate if this system does in fact apply to solutions made up with treated waste waters, it was necessary to inaugurate experimental precipitation tests.

To induce precipitation of calcium phosphate minerals, a series of batch tests on a filtered effluent were conducted. The phosphorus and calcium concentrations in the effluent were those normally encountered in domestic raw sewage at Cape Town, i.e. P = 5-10 mg/litre and Ca = 40 mg/litre. The objectives of these tests were to :

1. Obtain the solubility product for the particular calcium phosphate mineral in order to compare these values to those noted for the pure system.

2. Define the conditions necessary for calcium phosphate precipitation.

The range of pH over which the precipitation was measured was selected such that $CaCO_3$ precipitation was not theoretically possible when based on pure $CaCO_3$ solubility product. This product forms the lower concentration bound to Ca^{++} and $CO_3^{=}$ for $CaCO_3$ precipitation; with P in the solution the solubility product usually increases, i.e. the $CaCO_3$ becomes more soluble and less likely to precipitate.

The batch precipitation tests were conducted on the filtered effluent samples from an activated sludge unit in the following sequence:

1. Calcium phosphate seed is prepared as follows: an unknown quantity of sodium bicarbonate ($NaHCO_3$) followed by calcium chloride ($CaCl_2$) and then disodium hydrogen phosphate ($NaHPO_4$) is added to a continuously stirred effluent sample in a flask and allowed to mix for 8 hours. Phosphorus precipitation commences. This procedure is repeated using the same sample until a slurry is formed. The sample is then centrifuged, the supernatant discarded and the precipitate washed with distilled water. The concentrated slurry is then dried at 100°C and crushed into a powdered form.

2. A sample from the activated sludge effluent (Total P = 3 mg/litre) is aerated to establish equilibrium between CO_2 in the air and molecularly dissolved CO_2. This is necessary to assure the same conditions from test to test.

3. The calcium and phosphorus concentrations in the sample are increased to values representative of waste water (i.e. Ca = 80 mg/litre as Ca and P = 10-15 mg/litre as P).

4. Alkalinity (in the form of $NaHCO_3$) is added to the sample, then alkalinity is added incrementally increasing with each test from 50 to 300 mg/litre as $CaCO_3$.

5. Calcium phosphate seed is added - 200 mg/litre.

6. The sample is vigorously aerated and continuously stirred until the pH attains a steady value (after approximately 5 hours). The mixture is then filtered and the following parameters, pH, calcium and total

soluble phosphorus, are measured experimentally on the filtrate (see Appendix A for procedures and test methods employed).

Twelve tests in all were conducted. In Table (4.1) the final saturated conditions attained for each test are listed. In Table (4.2) the soluble calcium and phosphorus removed in each test are listed.

Table 4.1: Final saturated [Ca] and [P] values in calcium phosphorus batch precipitation tests using treated sewage

pH	Ca_T M	P_T M	pK_{s1}	pK_{s2}
8,280	$0,150 * 10^{-2}$	$0,337 * 10^{-3}$	-29,62	-6,785
8,380	$0,183 * 10^{-2}$	$0,330 * 10^{-3}$	-29,20	-6,735
8,440	$0,140 * 10^{-2}$	$0,333 * 10^{-3}$	-29,15	-6,805
8,480	$0,162 * 10^{-2}$	$0,280 * 10^{-3}$	-29,14	-6,812
8,690	$0,151 * 10^{-2}$	$0,230 * 10^{-3}$	-29,04	-6,987
8,690	$0,135 * 10^{-2}$	$0,248 * 10^{-3}$	-29,11	-6,987
8,699	$0,154 * 10^{-2}$	$0,210 * 10^{-3}$	-29,06	-7,038
8,720	$0,156 * 10^{-2}$	$0,200 * 10^{-3}$	-29,02	-7,073
8,750	$0,135 * 10^{-2}$	$0,231 * 10^{-3}$	-29,00	-7,057
8,770	$0,130 * 10^{-2}$	$0,213 * 10^{-3}$	-29,10	-7,085
8,880	$0,163 * 10^{-2}$	$0,195 * 10^{-3}$	-28,77	-7,107
8,945	$0,131 * 10^{-2}$	$0,206 * 10^{-3}$	-28,73	-7,133

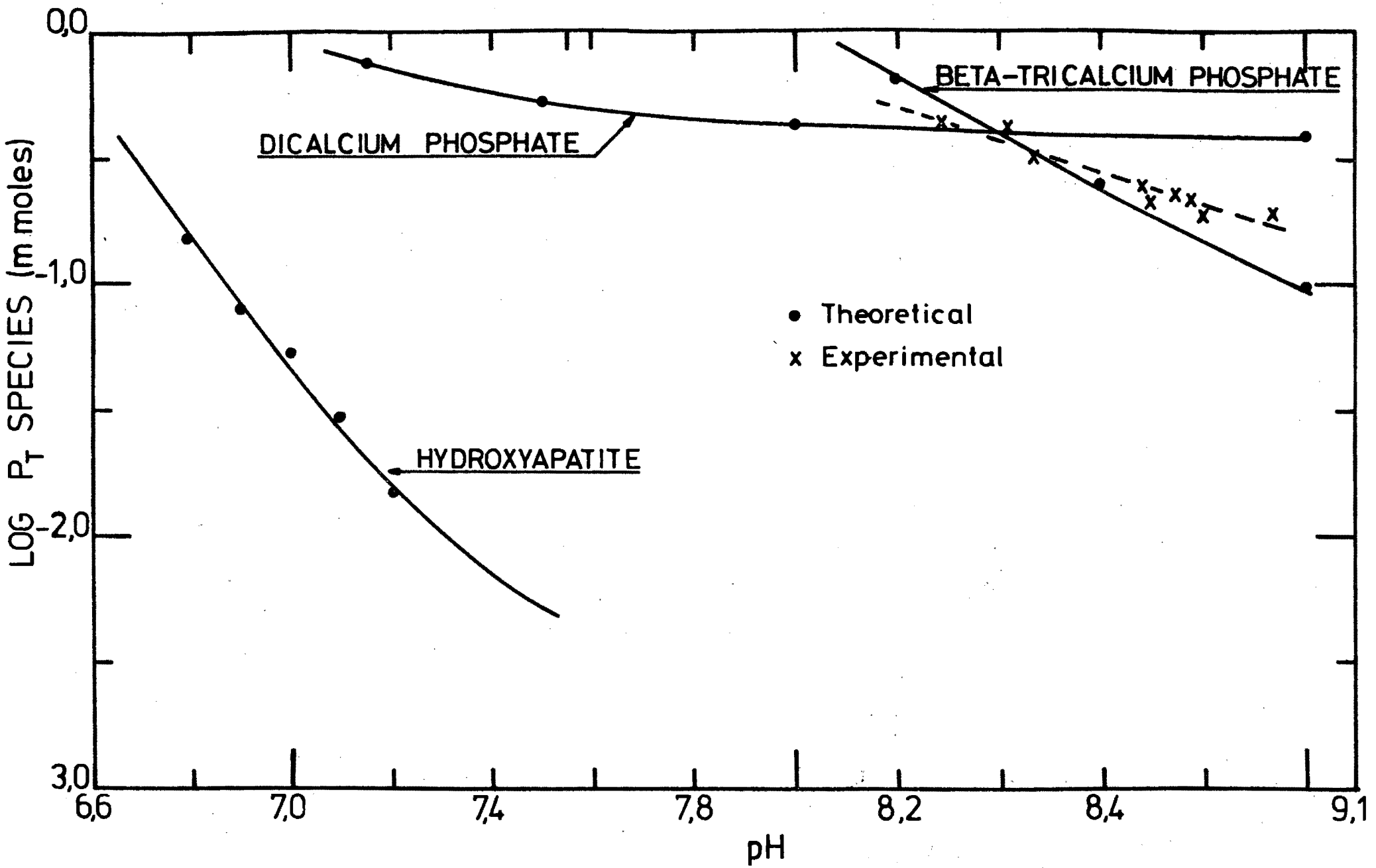


Figure 4.1 *P-concentration and pH values of solutions saturated with respect to the various calcium phosphates in systems that contain only calcium and phosphate ions in water*

Table 4.2: Experimental [ΔCa] and [ΔP] molar removals

$[Ca_i]$ mM	$[Ca_f]$ mM	[ΔCa] mM	$[P_i]$ mM	$[P_f]$ mM	[ΔP] mM	[ΔCa]/[ΔP]
1,72	1,50	0,22	0,48	0,337	0,143	1,54
1,95	1,83	0,12	0,41	0,330	0,080	1,50
1,64	1,40	0,24	0,51	0,333	0,177	1,36
1,76	1,62	0,14	0,38	0,280	0,10	1,40
1,69	1,52	0,17	0,34	0,230	0,11	1,55
1,68	1,35	0,33	0,45	0,248	0,20	1,65
1,78	1,54	0,24	0,33	0,210	0,12	2,0
1,75	1,56	0,19	0,31	0,200	0,11	1,73
1,66	1,35	0,31	0,44	0,231	0,21	1,48
1,69	1,30	0,39	0,49	0,213	0,27	1,44
1,89	1,63	0,26	0,33	0,195	0,135	1,93
1,68	1,31	0,37	0,47	0,206	0,26	1,42

The first problem to resolve is to find which mineral of the three possible forms actually precipitates. This was done by theoretically calculating the final P_T concentration versus pH values for each of the minerals over the pH range 6,6 to 9,0, then compare these with the experimental P_T versus pH data. The comparison is made by plotting the theoretical and experimental data in Fig. (4.1). It is evident that the mineral which precipitated was either beta-tricalcium phosphate or dicalcium phosphate but the data

allows no clear identification.

It was considered that possibly a positive decision on the mineral precipitated could be obtained from the experimental solubility products assuming either beta-tricalcium phosphate or dicalcium phosphate. This was done as follows:

Using Ca_T, P_T and pH values of the final saturated state the parameters Ca^{++}, $HPO_4^{=}$ and PO_4^{3-} were calculated from the equilibrium relationship for the system (see Appendix C), by means of a computer. These values were used to determine pK_{s1} for beta-tricalcium phosphate and pK_{s2} for dicalcium phosphate. The values are listed in Table 4.1. It is evident that the pK_s values are pH dependent, pK_{s1} decreasing and pK_{s2} increasing with pH. As a preliminary comparison the averages were compared with the theoretical values (see Table 4.3).

Table 4.3: Comparison of theoretical and average experimental solubility products for $Ca_3(PO_4)_2$ and $CaHPO_4$.

Mineral	Theoretical (pK_s)	Experimental (pK_s)
$Ca_3(PO_4)_2$	- 25,46	- 29,08
$CaHPO_4$	- 7,00	- 6,97

Clearly the experimental pK_{s1} is 4 orders of magnitude greater than the theoretical, whereas pK_{s2} is approximately the same as the theoretical value. This would support the conclusion that the pK_{s2} for dicalcium phosphate is the correct one. However, if one calculates the experimental

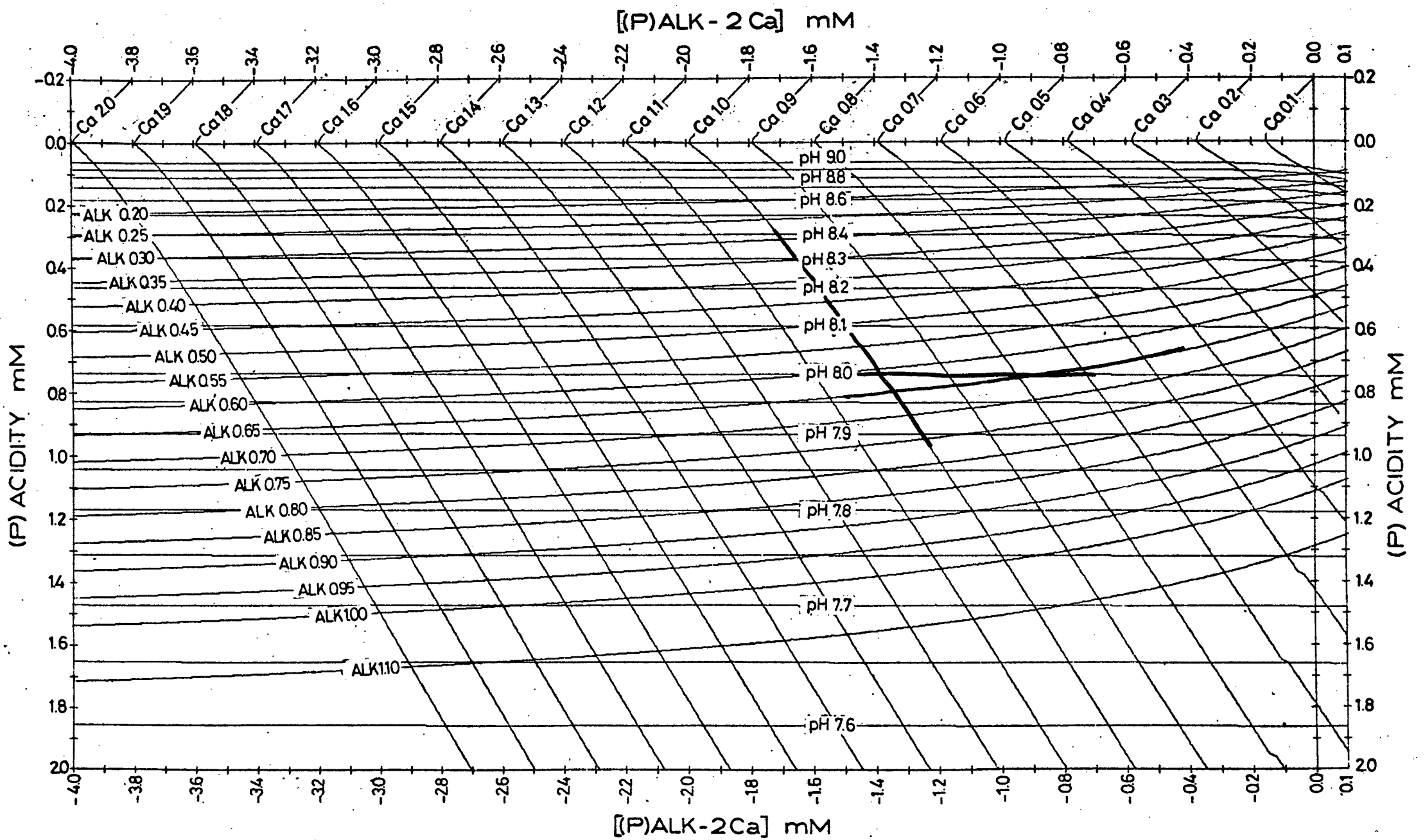


Figure 4.2 Two phase conditioning diagram for beta-tricalcium phosphate

DICALCIUM - PHOSPHATE [$CaHPO_4$]

IONIC STRENGTH = 0.01 TEMPERATURE = 25°C pK_s = -7.0

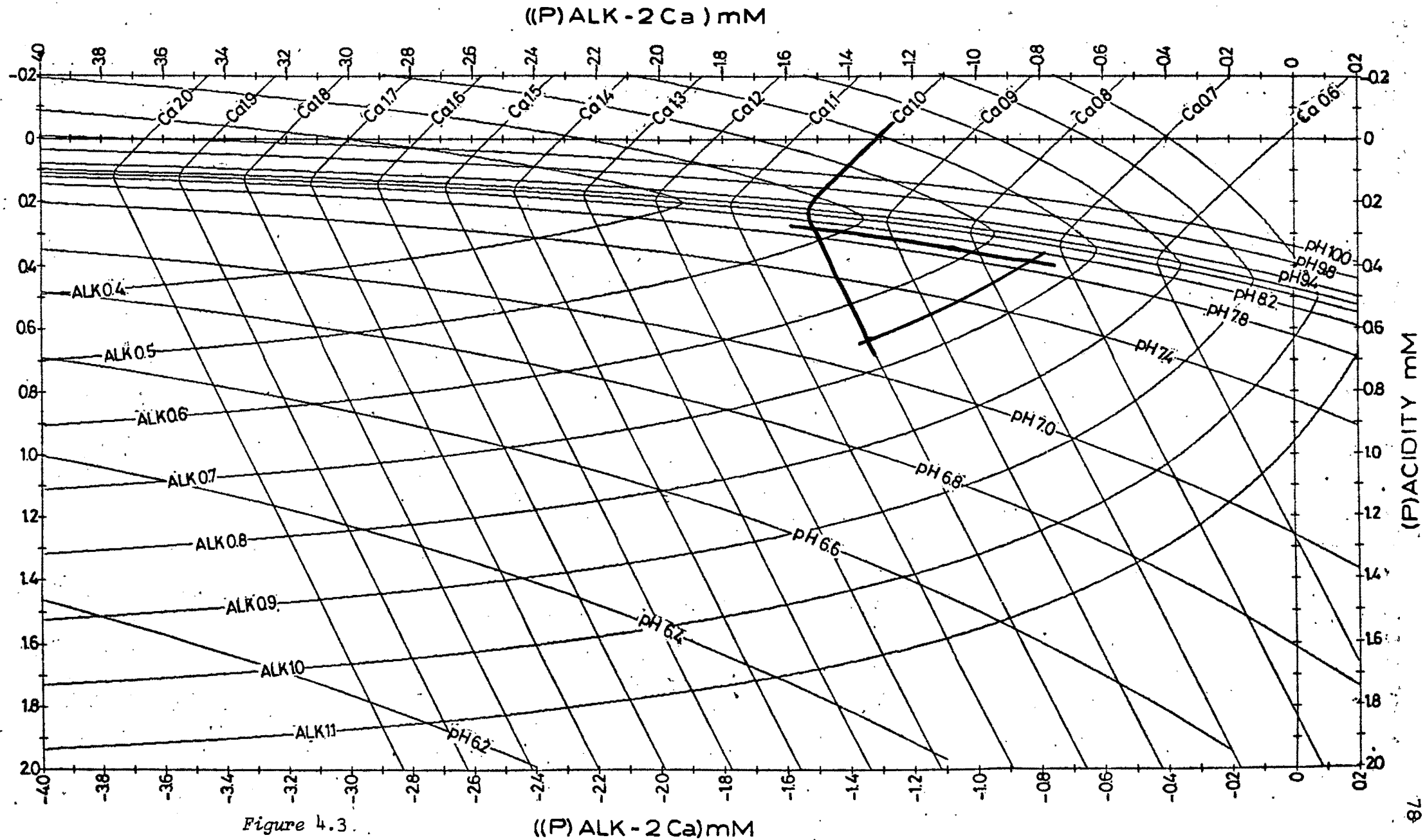


Figure 4.3

$\Delta P_T / \Delta Ca_T$ ratios from Table 4.2 and compare these with the theoretical values (see Table 4.4), it seems that beta tricalcium phosphate is the potential precipitant.

Table 4.4: Comparison of theoretical and average experimental [Ca]/[P] ratios for $Ca_3(PO_4)_2$ and $CaHPO_4$.

Mineral	Theoretical	Experimental
$Ca_3(PO_4)_2$	1,5 : 1,0	1,58 : 1,0
$CaHPO_4$	1,0 : 1,0	1,58 : 1,0

From the observations above it is clear that no definite conclusion can be drawn as to which mineral:beta-tricalcium phosphate or dicalcium phosphate was precipitated. However, the data *in toto* does appear to indicate that hydroxyapatite does not precipitate even though it is thermodynamically the most likely crystal to form, probably being inhibited by some substance in the waste water. For our purpose, a definite answer as to the type of mineral precipitated was not of vital concern as it was more important to establish that precipitation did, in fact, take place and the ratio of Ca^{++} to PO_4^{3-} in the precipitate.

With regard to the condition necessary for precipitation this can be roughly evaluated from the conditioning diagram using pK_s = 29,08 and pK_s = 7,00 in Fig. (4.2) and Fig. (4.3) respectively. By inserting the final values for pH and P_T it is clear for say P_T = 10 mg/litre and pH = 8,0 that no precipitation can occur if Ca_T is less than 40 mg/litre as Ca^{++}. This prediction is supported by the batch tests.

Analysis of the batch tests results forms a basis for judging whether precipitation can possibly occur in the mixed liquor. It is probably quite reasonable to assume that hydroxyapatite cannot precipitate. Further, the precipitation behaviour of the other two minerals is so similar for the pH ranges usual in an activated sludge process that it is immaterial which actually precipitates. Furthermore, if one assumes that the precipitation behaviour is the same in both the activated sludge process and the batch test condition described above, any excess phosphorus removal can be partitioned and attributed to chemical precipitation and some other phosphorus removal mechanism.

Effect of Sludge

Experiment 4.1: Sludge and distilled water + PO_4^{3-} + Ca^{++}

The batch precipitation systems in the previous section contained no sludge. In order to investigate the effect of sludge it was decided to make standard solutions with distilled water, sludge, calcium and phosphorus and operate the system at a specified pH. To determine whether phosphorus is adsorbed in the free form (or luxury uptake) or whether a calcium phosphate precipitate is indeed formed, two systems were monitored concurrently:

to (1) calcium ($CaCl_2$) and phosphorus (Na_2HPO_4) was added and

to (2) only phosphorus was added (Na_2HPO_4).

To ensure a uniform constitution of the samples, two batches were prepared from one sample. Two litres of mixed liquor were centrifuged, the supernatant discarded and replaced with the same volume of distilled water. The sample was then thoroughly mixed and two 1-litre samples were prepared.

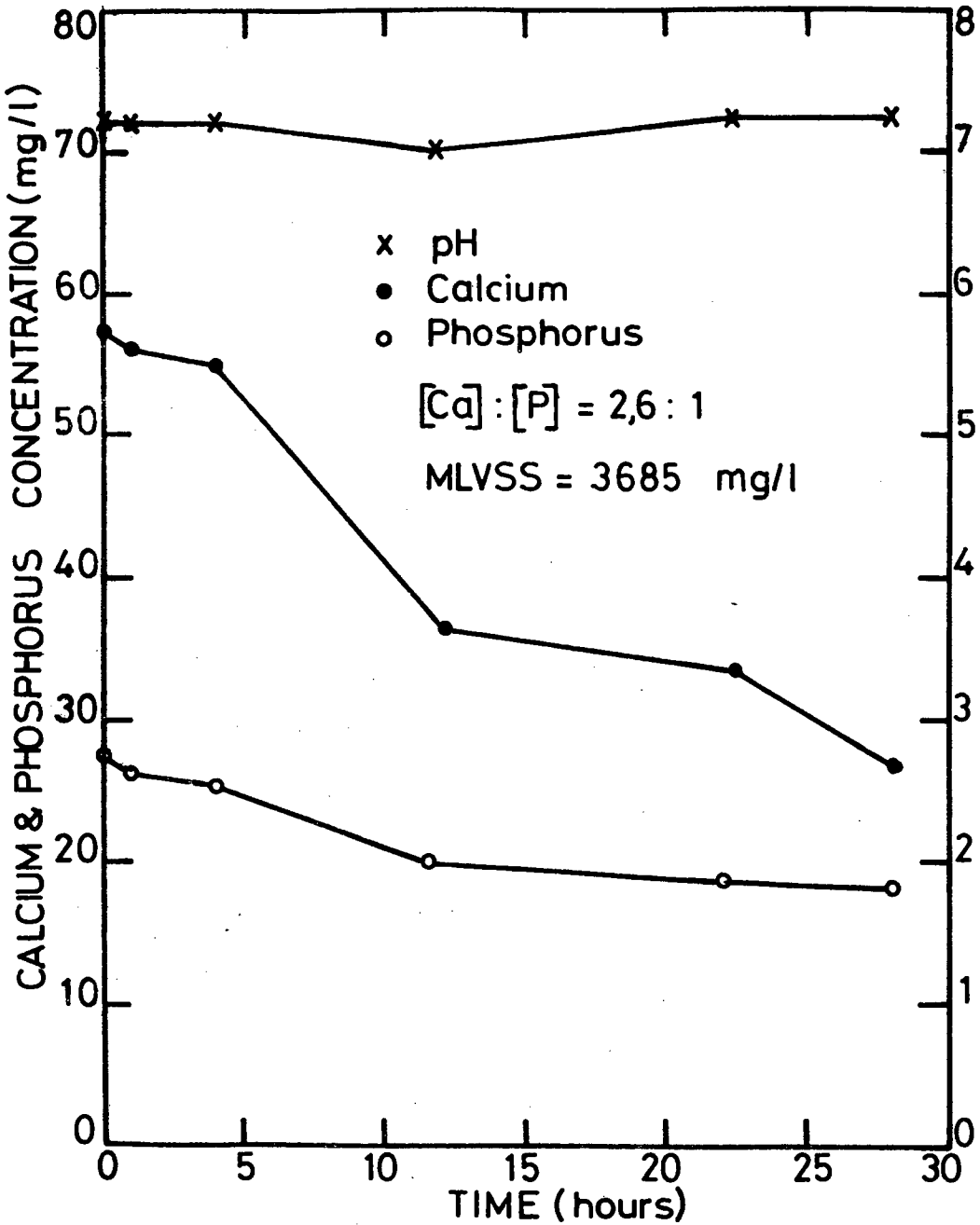


Figure 4.4a Behaviour of soluble calcium and phosphorus at constant pH in the presence of sludge

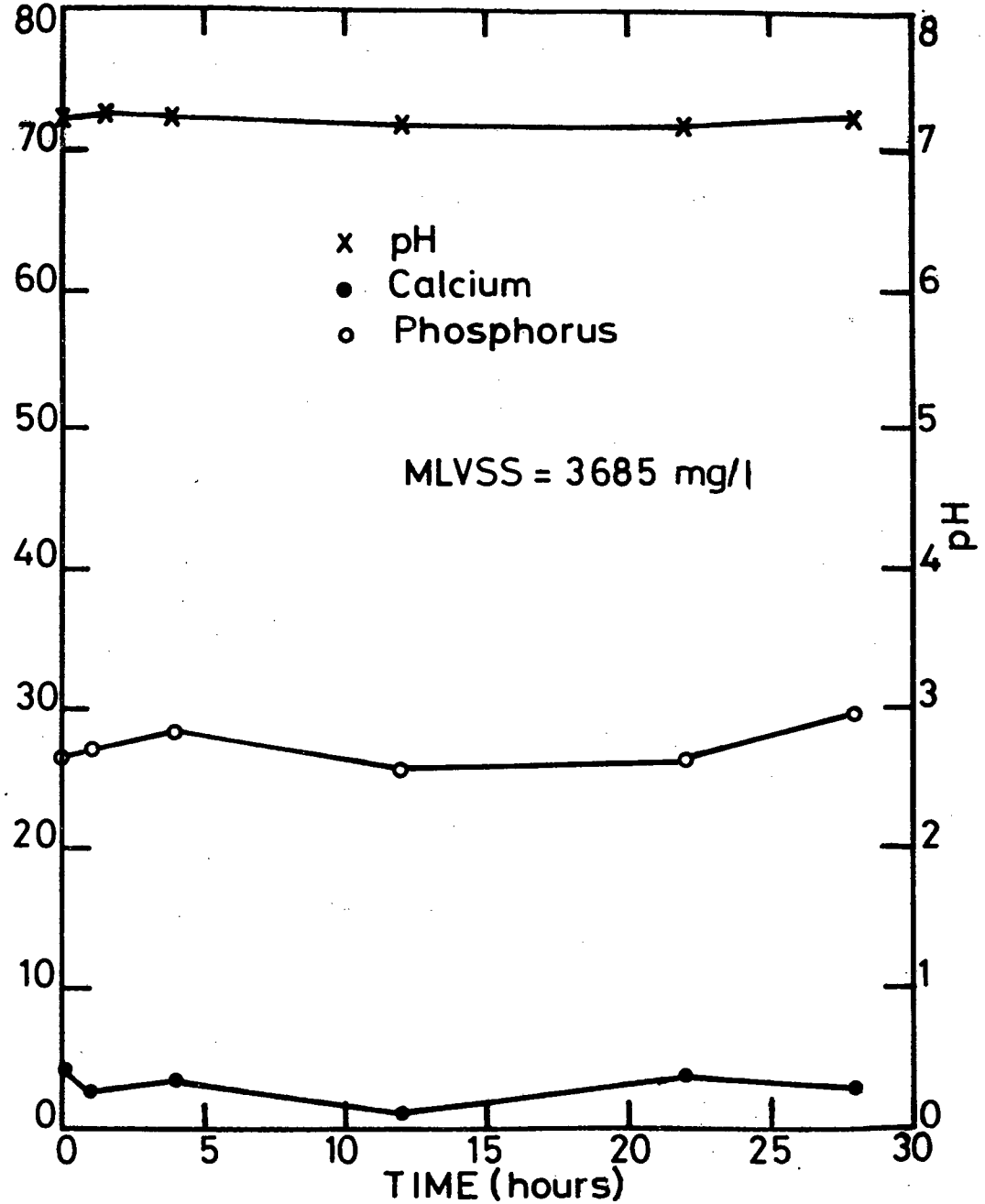


Figure 4.4b Behaviour of soluble phosphorus at constant pH in the presence of sludge

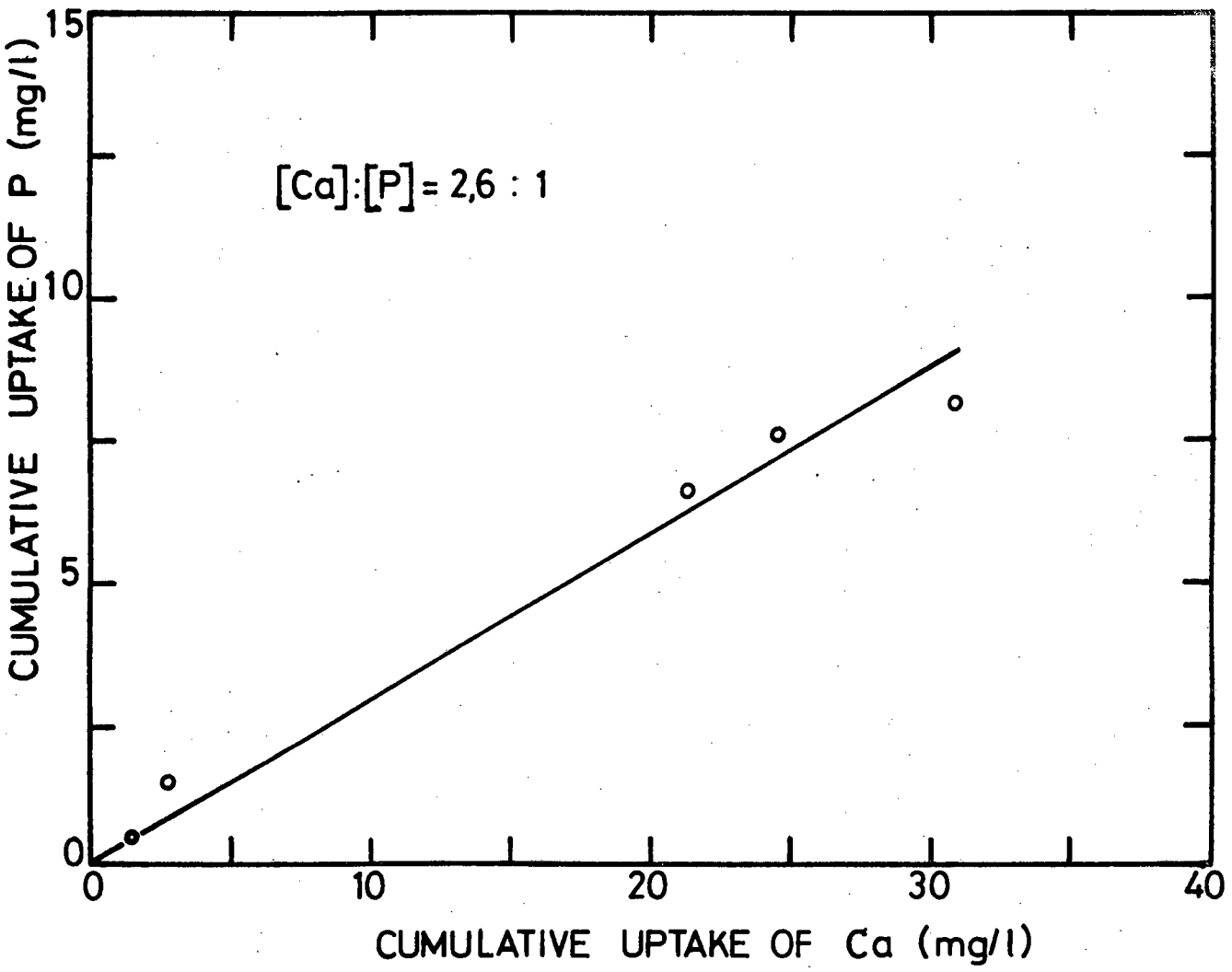


Figure 4.5 *Observed constant ratio in calcium and phosphorus reduction from the supernatant*

In the first sample about 25 mg/litre of Na_2HPO_4 (as P) and 50 mg/litre $CaCl_2$ (as Ca) and to the second sample 25 mg/litre Na_2HPO_4 (as P) only was added. Both batches were aerated with air and continuously mixed by means of a magnetic stirrer. The pH of the liquid was kept constant at pH 7,2 by adding $NaHCO_3$.

The experiments were carried out over a period of 28 hours and samples were taken at intervals, filtered and tested for dissolved phosphorus and calcium. The results of this investigation are plotted in Fig. (4.4a) and Fig. (4.4b). For the system where phosphorus and calcium were added, calcium and phosphorus removals from the supernatant were observed in the molar ratio of [Ca]/[P] = 2,6 (see Fig. (4.5). In the system with only P present a nett release occurred, i.e. phosphorus release exceeded any phosphorus uptake which may have occurred (see Fig. 4.4b). Although no Ca^{++} was present in the latter system, the presence of the Na^+ cation assured the possibility of free PO_4^{3-} being adsorbed if the action was biological. The fact that the Ca^{++} disappeared concurrently with the P, whereas no P disappeared with the Na^+, seems to indicate that the removal of soluble P is due to a precipitation phenomenon and not due to biological adsorption.

In system (1) the [Ca]/[P] uptake rate of 2,6 exceeds the value determined in the previous section (i.e. 1,58). This observation indicates that the calcium phosphate precipitate in the presence of sludge apparently is not one of the three calcium phosphate minerals suggested. However, it can be concluded that the mechanism of removal is not adsorption (or luxury uptake) but some form of calcium phosphate precipitation.

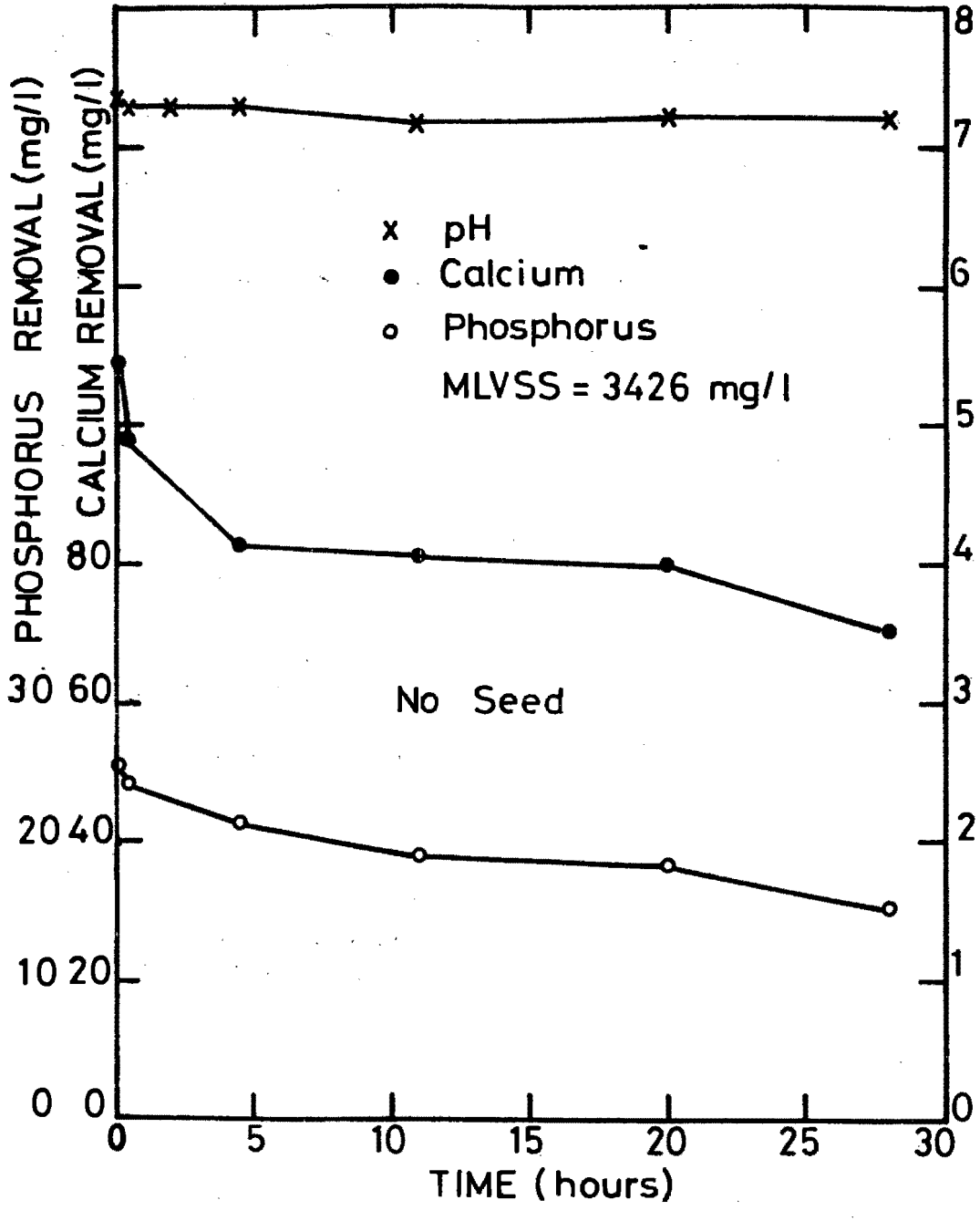


Figure 4.6a Soluble calcium and phosphorus behaviour with no calcium phosphate seed

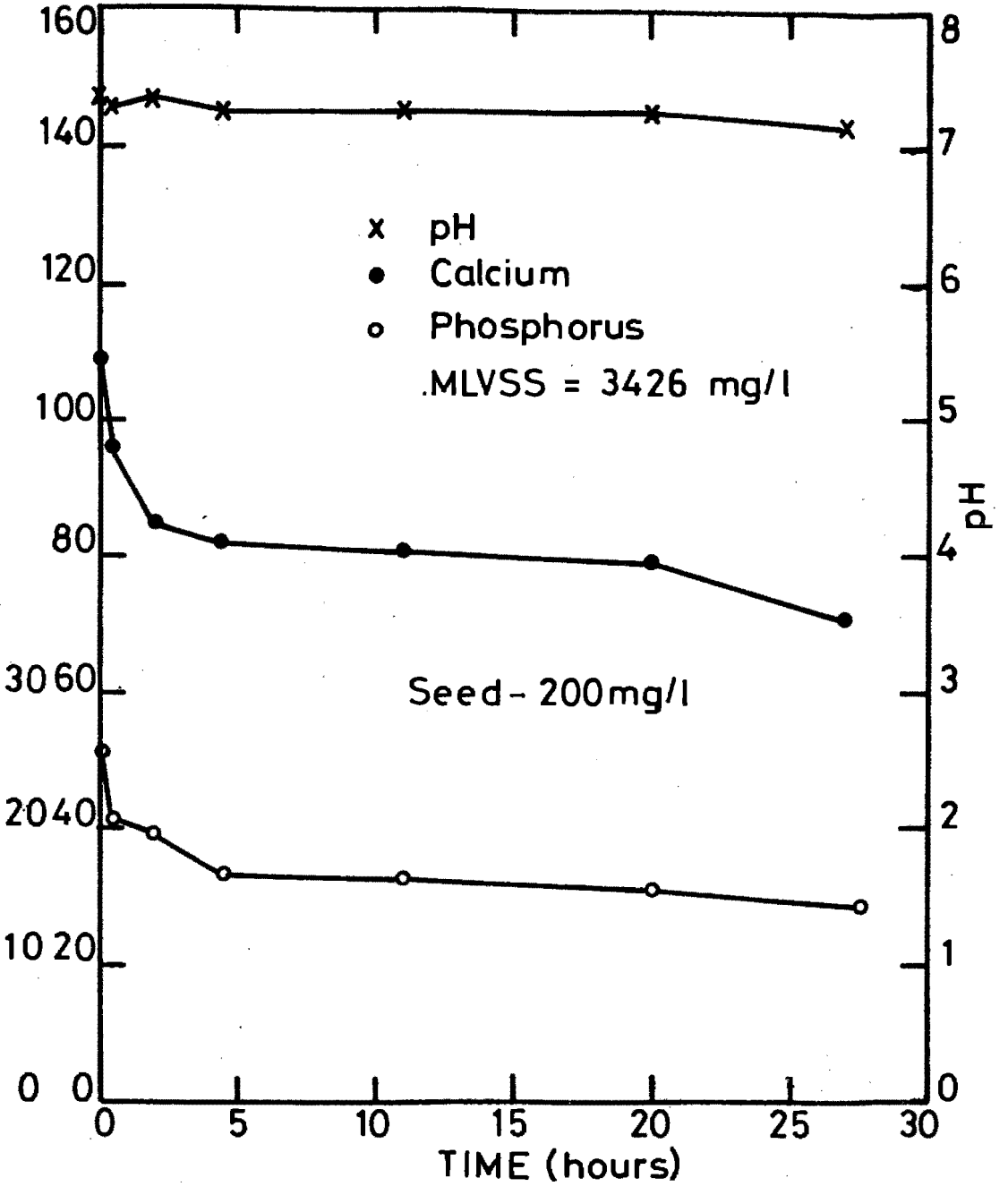


Figure 4.6b Soluble calcium and phosphorus behaviour with calcium phosphate seed present

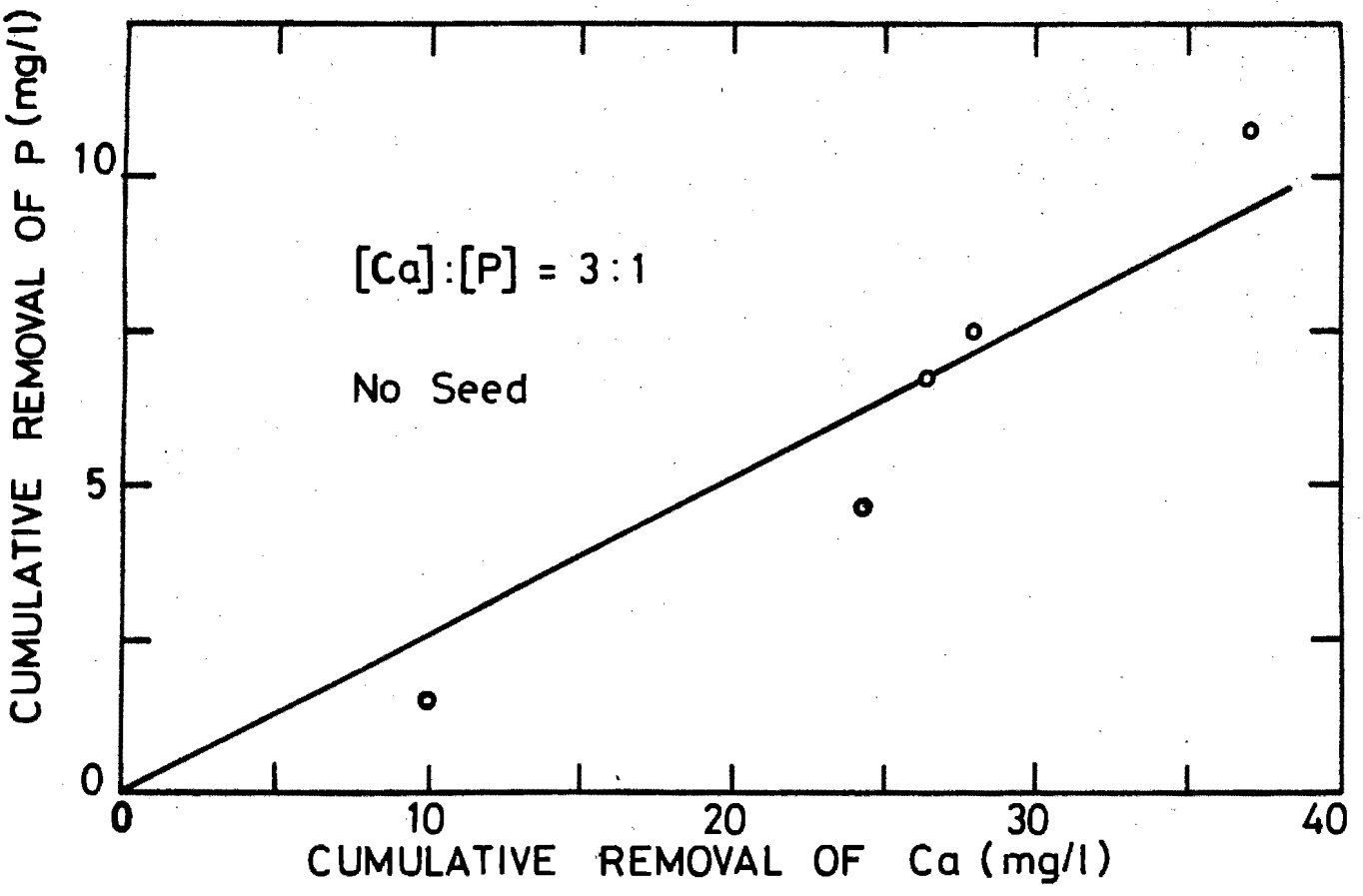


Figure 4.7 Cumulative removal of soluble calcium and phosphorus onto the sludge

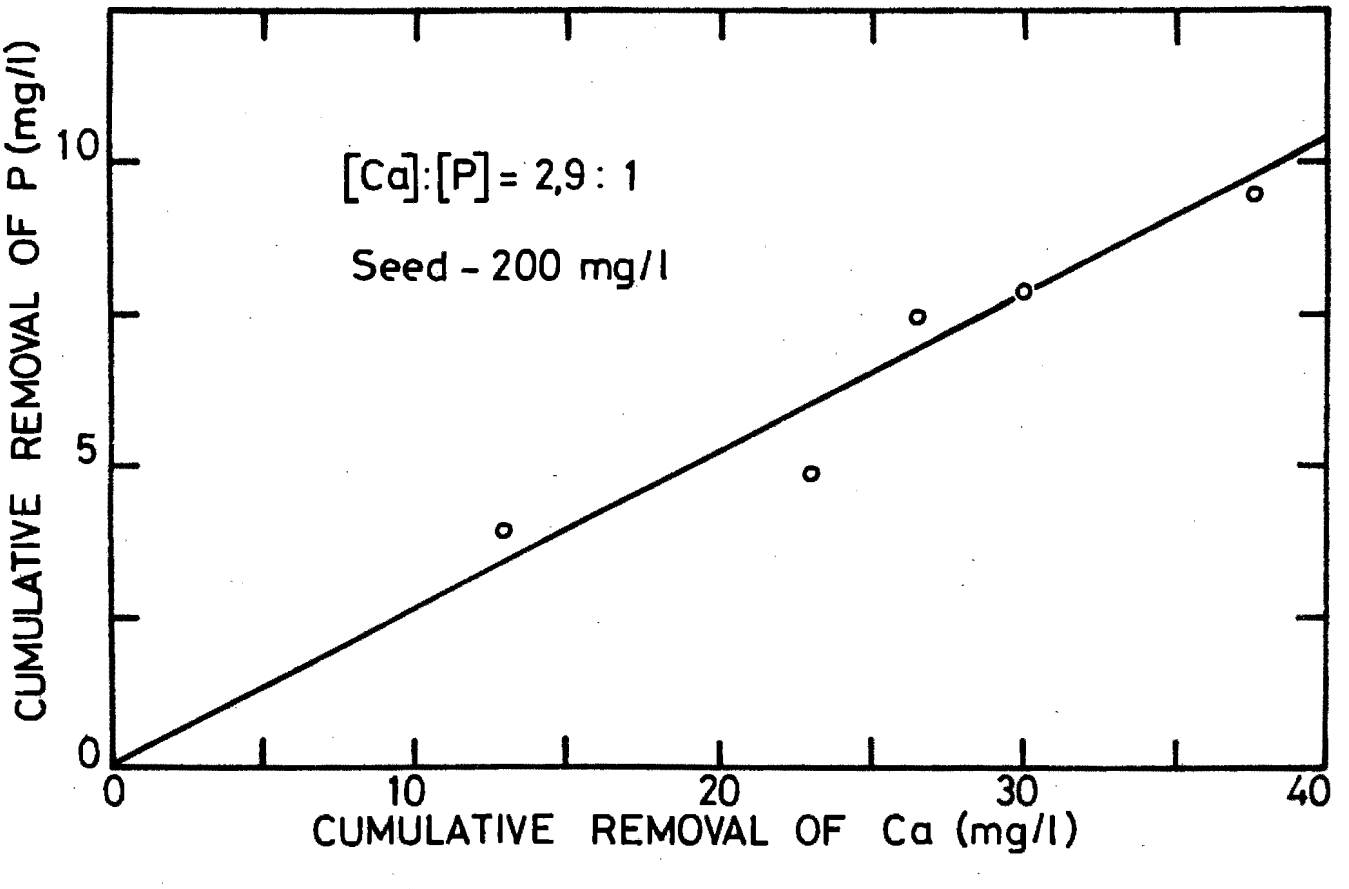


Figure 4.8 Cumulative removal of soluble calcium and phosphorus onto the sludge

Effect of Calcium Phosphate Seed

Experiment 4.2: Sludge and distilled water + PO_4^{3-} + Ca^{++} + calcium phosphate seed

In the previous investigations no seed was added to the samples prepared with sludge present. It was now of interest to investigate whether, if seed is added to such a sample, it would influence the magnitude of precipitation or change the [Ca]/[P] ratio.

To obtain two identical samples, one original sample was prepared and divided. As in the previous section, two litres of mixed liquor were centrifuged; the supernatant discarded and replaced with the same volume of distilled water. To this sample about 25 mg/litre of Na_2HPO_4 (as P) and 100 mg/litre $CaCl_2$ (as Ca^{++}) were added. The sample was thoroughly mixed, by means of a magnetic stirrer, to obtain a uniform solution. The sample was then divided into two parts to obtain two identical solutions. The one sample (sample 1) was seeded with 200 mg/litre of calcium phosphate seed (see previous section for preparation of seed). The other sample (sample 2) served as a control. The mixed liquor was kept constant at pH 7,2, maintained by adding $NaHCO_3$. Both samples were aerated with air and continuously stirred.

The duration of the batch precipitation experiments was 28 hours and samples were taken concurrently, filtered and tested for dissolved phosphorus and calcium. The results of this investigation are plotted in Fig. (4.6a) and Fig. (4.6b).

In the system without the cultured seed, calcium and phosphorus removal from the supernatant was observed in the molar ratio of [Ca]/[P] = 3,0 (see Fig. 4.7). In the system where seed was added the calcium and phosphorus

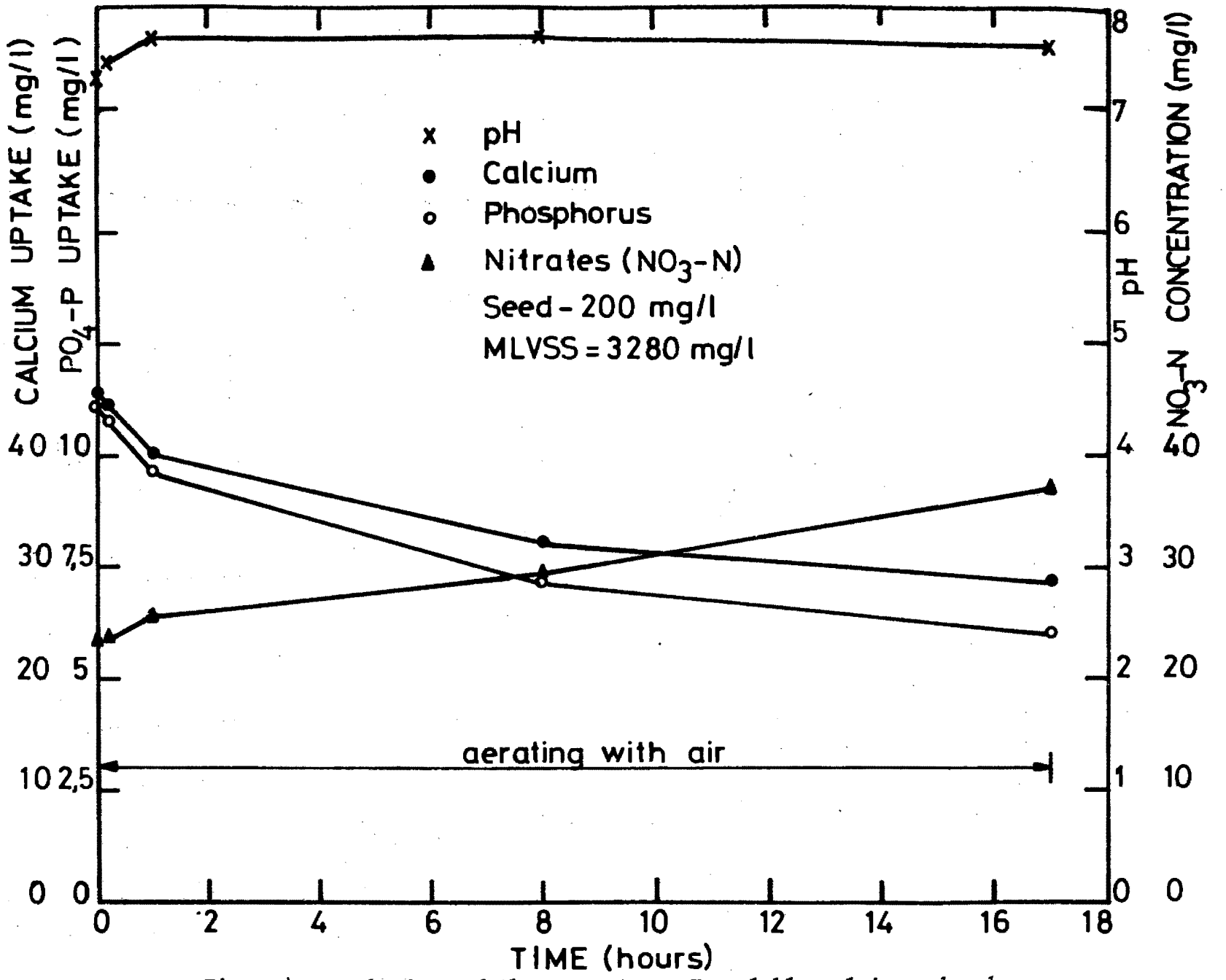


Figure 4.9 Behaviour of the parameters pH, soluble calcium, phosphorus and nitrates in a solution of mixed liquor plus PO_4^{-3} plus Ca^{++} plus calcium phosphate seed

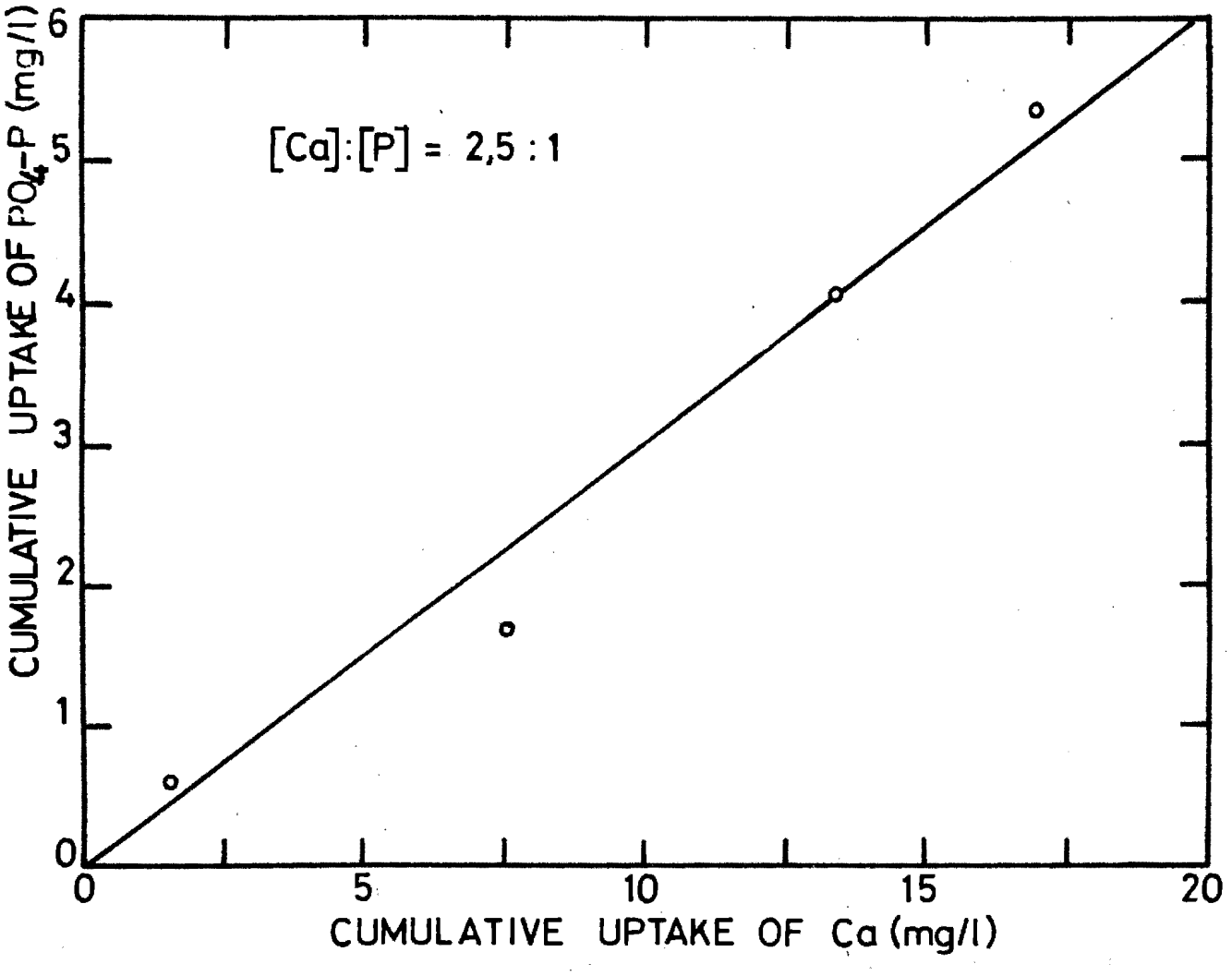


Figure 4.10 *Cumulative experimental removal of soluble calcium and phosphorus onto the sludge*

removal resulted in a molar ratio of [Ca]/[P] = 2,9 (see Fig. 4.8). If the disappearance of calcium and phosphorus was due to precipitation onto the calcium phosphate seed then a molar ratio of 1,58 should have been observed. However, both systems indicated the same calcium and phosphorus removal trend. It appears that the growth sites in the crystal were poisoned by the presence of the sludge.

In samples 1 and 2 the inordinately high [Ca]/[P]ratios of 3,0 and 2,9 respectively exceeds the value determined for treated waste water (i.e. 1,58). Again, this value indicates that the calcium phosphate precipitates in the presence of sludge apparently is not one of the three potential calcium phosphate minerals suggested.

Experiment 4.3: Mixed liquor + PO_4^{3-} + Ca^{++} + Seed

The previous tests utilize distilled water to which concentrated sludge was added. It was now necessary to examine the precipitation phenomenon when the mixed liquor was taken directly from the reactor.

The procedure described in Experiment 4.2 was repeated for a mixed liquor sample. The sample was spiked with $CaCl_2$, Na_2HPO_4 and $NaHCO_3$ to give a supersaturated solution. Seed (approximately 200 mg/litre) was then added to the sample which was aerated with air and continuously stirred. The behaviour of the parameters calcium, phosphorus, pH and nitrates are plotted in Fig. (4.9). The observed [Ca]/[P] molar removal rate is plotted in Fig. (4.10) and a value of 2,5 is obtained. This value is very similar to the values obtained for the standard solutions of sludge and distilled water. Again it appears that the seed exerts no significant effect on the removal of soluble calcium and phosphorus.

From the above observations (i.e. Exp. 4.2 and Exp. 4.3),

it can be concluded that when conditions are favourable for precipitation in a sample of mixed liquor, (1) the organisms act as growth sites for a calcium phosphate precipitate; (2) if cultured seed is added to the solution it is either poisoned or captured in the sludge floc such that the surface area is not exposed to the solution so that the seed does not appear to have any influence on the precipitation; (3) the precipitant that forms is not one of the standard calcium phosphates but a calcium phosphate that has a [Ca]/[P] ratio of about 3,0.

Effect of pH

Thus far the batch experiments were conducted at a specified pH. However, in practice different values of pH may be expected and it is therefore necessary to investigate the effect of pH on soluble calcium and phosphorus removal. It was considered that by aerating the sample with CO_2 or air (i.e. by inducting or stripping CO_2) a stable control of pH could be achieved. Furthermore, for the pH range of 5 to 8 in which the batch tests were conducted, the bacterial kinetics of the system remained virtually unaffected (for example, endogeneous respiration remained constant). The objectives of the tests were to determine the behaviour of calcium and phosphorus in:

1. a solution containing sludge and distilled water; and

2. mixed liquor.

The samples were initially sparged with 92 percent CO_2 to reduce the pH and subsequently aerated with air, to strip excess CO_2.

Experiment 4.4: Solution containing sludge + distilled water

A two-litre mixed liquor sample was centrifuged for a few

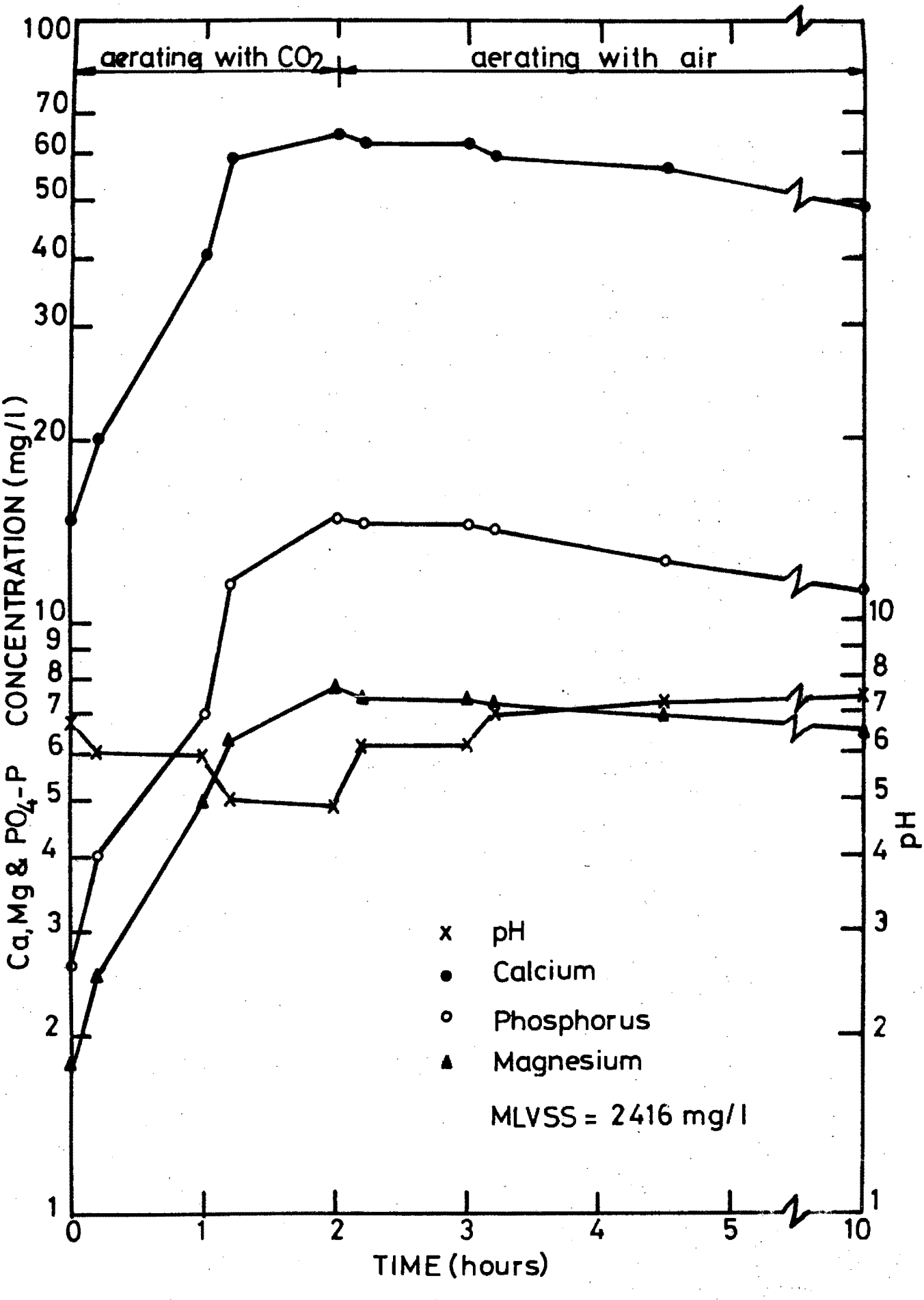


Figure 4.11 *Behaviour of the parameters soluble-calcium, magnesium and phosphorus and pH when aerating a solution (sludge + distilled water) first with 92 per cent* CO_2 *and then with air*

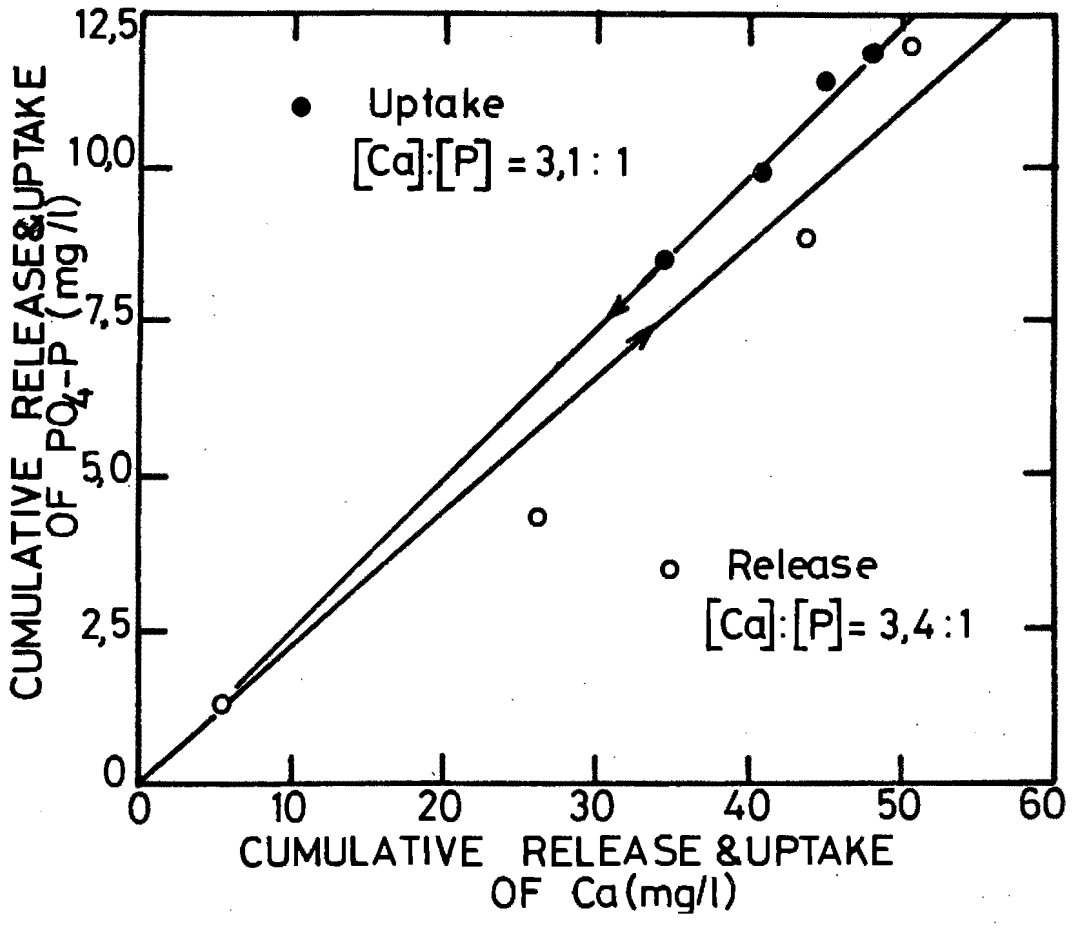


Figure 4.12 *Release and uptake rates of calcium and phosphorus by the sludge*

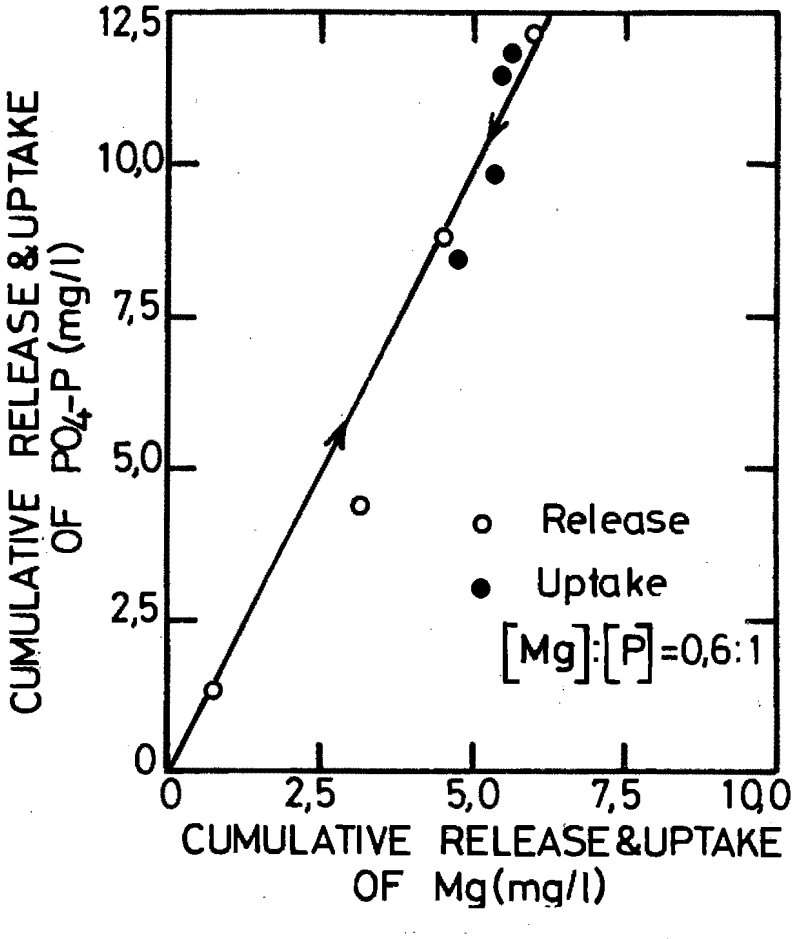


Figure 4.13 *Release and uptake rates of magnesium and phosphorus by the sludge*

minutes, the supernatant discarded and replaced with the same volume of distilled.water. The sample was continuously stirred, aerated with 92 percent CO_2 for the first two hours and subsequently aerated with air for 8 hours. Samples were taken at intervals, filtered and tested for dissolved phosphorus, calcium and magnesium. The behaviour of the measured parameters are plotted in Fig. (4.11).

Aerating the sample with 92 percent CO_2 caused a pH decrease from about 7,0 to 5,0 due to the increase of carbonic acidity. A corresponding increase in dissolved phosphate, calcium and magnesium took place, indicating that the sludge contained some calcium, magnesium and phosphorus that could be solubilized at pH values below 7,0. The release rates of Ca and P, and Mg and P are plotted in Fig. (4.12) and Fig.(4.13)respectively. The molar ratio of [Ca]/[P] is 3,4 whereas the [Mg]/[P]ratio is 0,6. Again the dissolution of calcium and phosphorus did not conform to the expected molar ratio of 1,58 as observed in the treated waste water system.

The sample was then aerated with air to strip the excess dissolved CO_2, thereby causing an increase in the mixed liquor pH to 7,4. A decrease in dissolved calcium, magnesium and phosphorus was observed indicating the formation of insoluble forms of calcium phosphate and magnesium phosphate, see Figs. (4.12) and (4.13). The disappearance of calcium and phosphorus resulted in the molar ratio of [Ca]/[P] = 3,1. That is, the [Ca]/[P] disappearance conformed to the values obtained for the standard batch experiments in the presence of sludge. In the present experiment the final Ca, Mg and P concentrations were higher than the initial concentrations. This can possibly be attributed to the long nucleation period required for the formation of the particular calcium phosphate mineral.

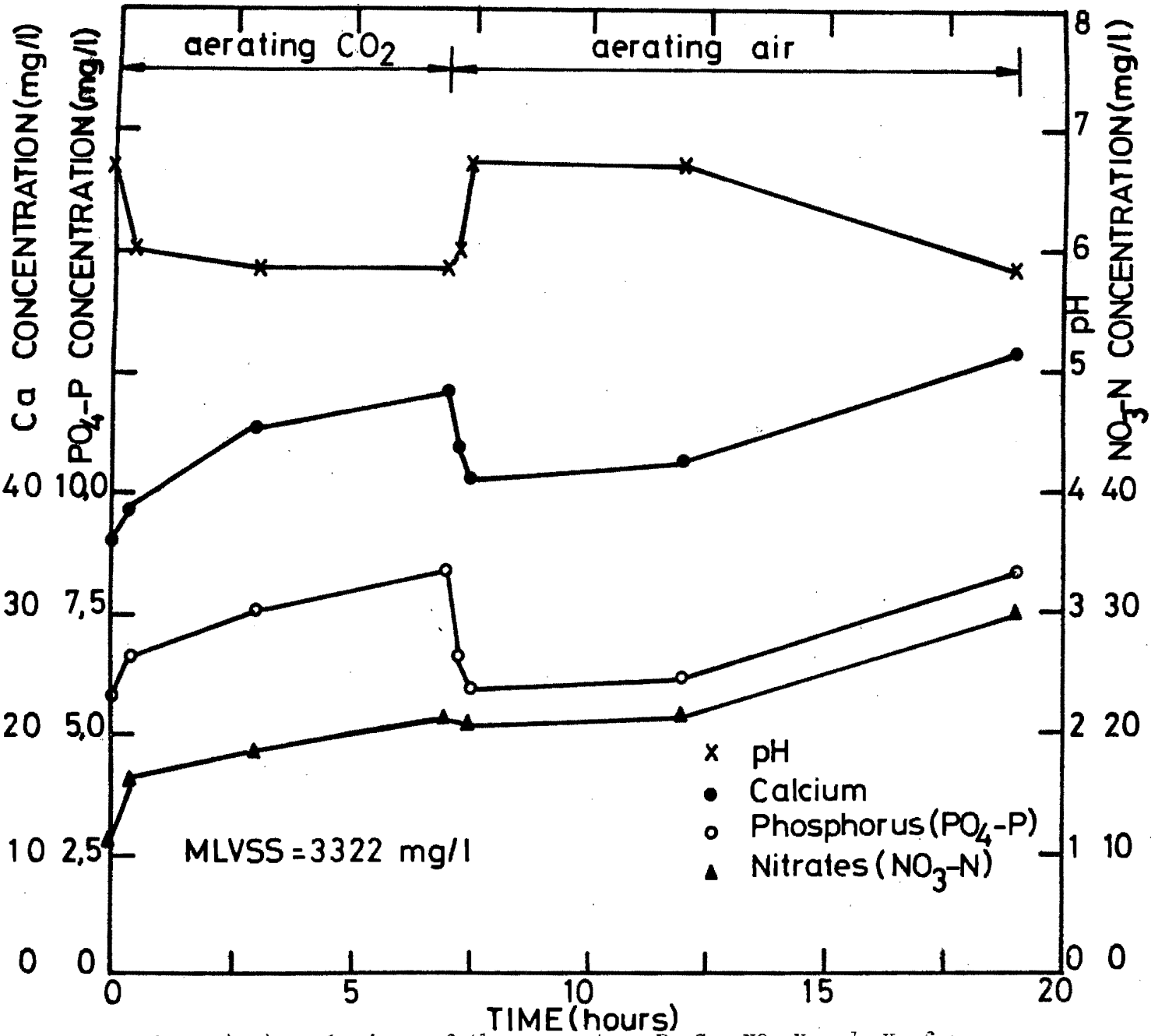


Figure 4.14 *Behaviour of the parameters* P, Ca, NO_3-N *and* pH *of a mixed liquor sample aerated for* 7 *hours first with* 92 *per cent* CO_2 *and then with air for* 12 *hours*

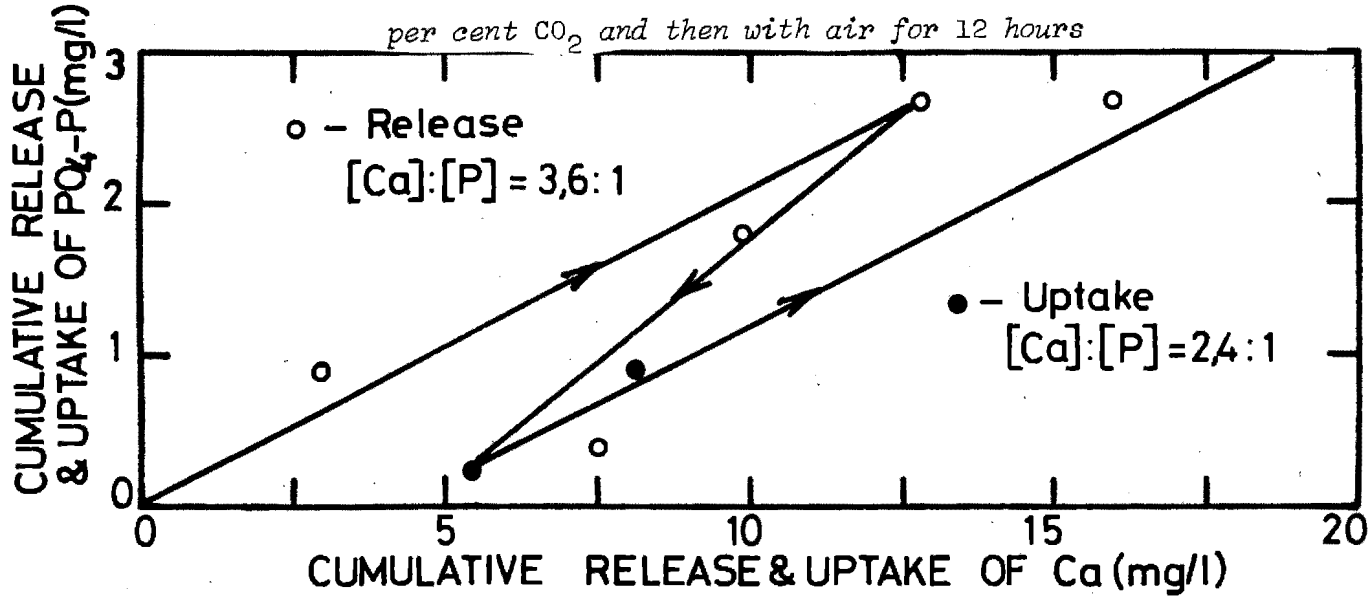


Figure 4.15 *Release and uptake rates of phosphorus and calcium by the sludge*

Experiment 4.5: Mixed liquor

A two-litre mixed liquor sample (MLVSS = 3322 mg/litre) was aerated for 7 hours with 92 percent CO_2 and subsequently aerated with air for 12 hours. Continuous mixing ensured a uniform constitution throughout the experiment. Filtered samples were tested for dissolved P, Ca and NO_3-N. The behaviour of the measured parameter is plotted in Fig. (4.14).

The first stage of this experiment was the aeration of CO_2 gas for 7 hours. A decrease in pH from 6,7 to 5,8 was observed which resulted in the dissolution of insoluble calcium and phosphorus in the molar ratio of [Ca]/[P] = 3,6 (see Fig. 4.15). Aerating the sample with air and stripping excess CO_2 the observed pH rise resulted in a rapid disappearance of soluble calcium and phosphorus. The [Ca]/[P]molar ratio of 2,4 was, however, less than that for the release ratio (see Fig. (4.I5).

After 4 hours aeration with air the pH commenced to decrease gradually from 6,7 to 5,8. Resolubilization of the calcium phosphate mineral was observed in the [Ca]/[P] molar ratio of 3,6, (see Fig. 4.15). The pH drop from 6,7 to 5,8 was a result of nitrification because the nitrate concentration increased from 2,15 to 30 mg/litre as N (see Fig. 4.14).

Experiments (4.4) and (4.5) showed very similar calcium and phosphorus release and uptake ratios. These ratios again indicate that the mineral or minerals precipitating are of some unknown form. However, it can be concluded that the major cation in phosphorus precipitation is calcium. Due to the inability to isolate this precipitant in the sludge the results can only be inferred.

From the above data it can be reasoned that :

1. On lowering the pH resolubilization of some calcium phosphate and magnesium phosphate minerals took place;

2. On increasing the pH of the same sample, recrystallization of these minerals took place; and

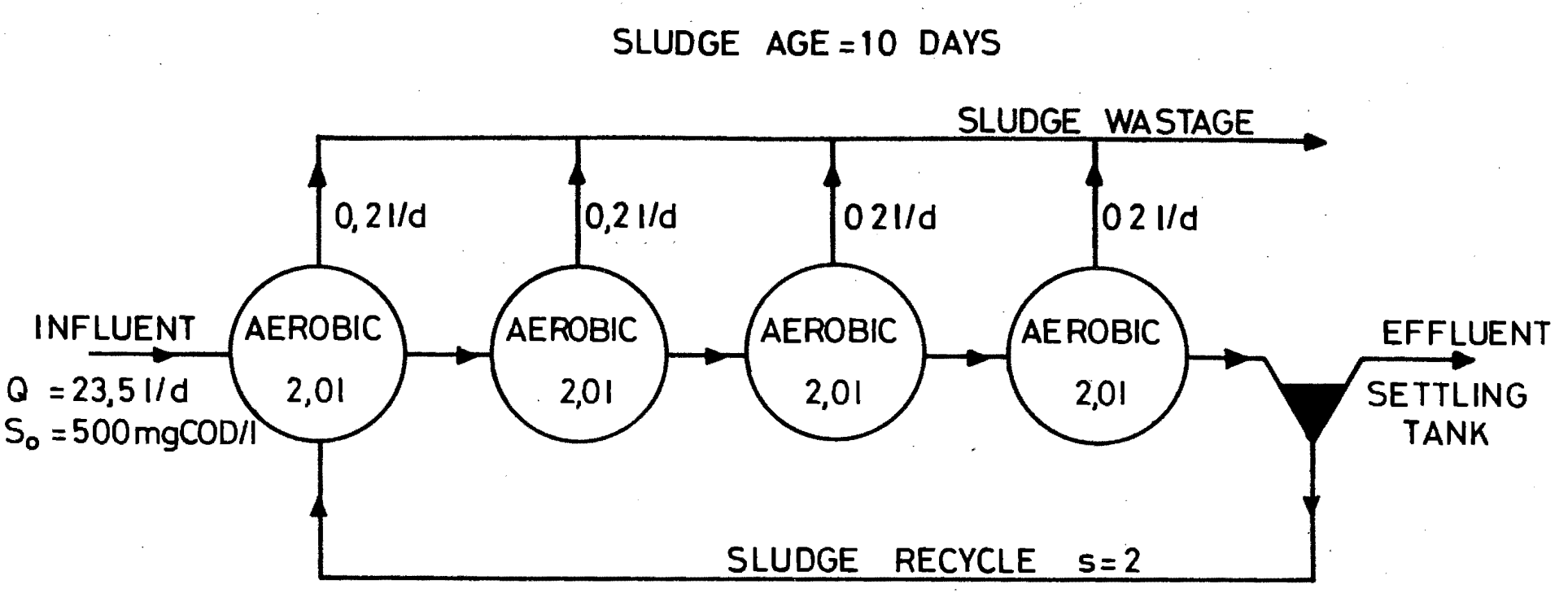
3. The [Ca]/[P] molar ratios in precipitation and resolubilization was constant at about 3,0.

PRELIMINARY INVESTIGATION ON CONTINUOUS FLOW SYSTEMS

In the previous section batch test results on mixed liquor showed a definite relationship between the removal of soluble calcium and phosphorus. It is now necessary to investigate this phenomena in continuous flow systems. With this objective a series of phosphorus removal experiments in semi-plug flow activated sludge systems were initiated.

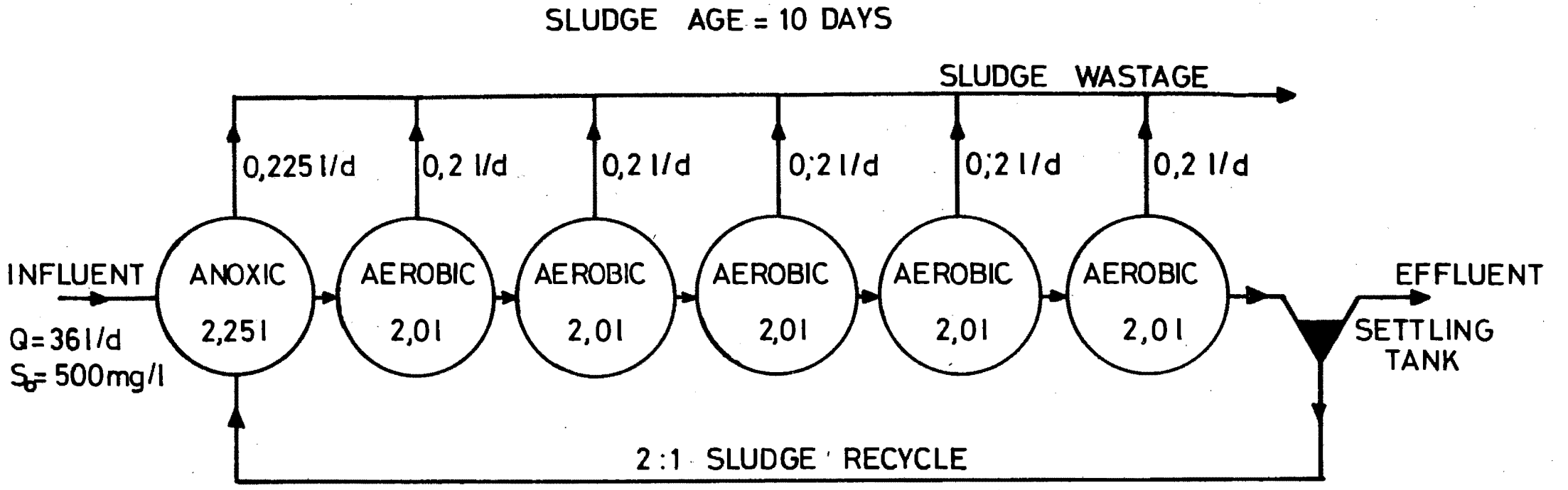
To investigate the precipitation phenomena in continuous flow systems, using sewage from Cape Town, it was found necessary to spike the mixed liquor with alkalinity, calcium, and phosphorus as the mixed liquor apparently was undersaturated with respect to a particular calcium phosphate mineral. The laboratory scale plants, procedures and test methods are outlined in Appendix A.

Two semi-plug flow activated sludge units were operated at the same design parameters (Table 4.5). The aerobic unit (Fig. 4.16), with 4 aeration tanks in series, served as a control to the anoxic-aerobic unit (Fig. 4.17) with 1 anoxic tank and 5 aeration tanks in series. Initially the units were run with high oxygen concentrations to strip excess CO_2 to increase the mixed liquor pH. The high aeration rates had a detrimental effect on the settling characteristics of the sludge in the settler. This problem was solved by controlling the aeration rate in the last aeration reactor to give an oxygen concentration of between 1 and 3 mg/litre.



Reactors	Nominal Retention Time (hrs)	Actual Retention Time (mins).
1 aeration	2,04	41,0
Total aeration	8,16	164,0

Figure 4.16 *A diagrammatic representation of the 4-tank series activated sludge process, with hydraulic control of sludge age and sludge recycle*



Reactors	Nominal Retention Times (hrs)	Actual Retention Time (mins).
Anoxic	1,5	30,0
aeration	1,35	27,0
Total aeration	6,7	135,0

Figure 4.17 *A diagrammatic representation of the 6-tank series activated sludge process, with hydraulic control of sludge age and sludge recycle*

An initial condition was established by operating the units without the addition of chemicals. The results are given in Tablve (4.6). The removal of P for the aerobic system was slightly less than the removal of P for the anoxic-aerobic unit. At this stage of the investigation (which actually preceded the batch tests) calcium was unfortunately not yet measured so it was not possible to state categorically that any removal observed was due to phosphate precipitation.

Table 4.5: Design parameters for laboratory scale semi-plug flow activated sludge units

Parameter	Aerobic Unit	Anoxic-aerobic Unit
Configuration	Series	Series
Number of tanks	4	6
Total volume of reactors (l)	8,10	12,25
Sludge age (days)	10	10
Influent COD (mg/OD/l	500	500
Volume of feed (l/d)	23,5	36,0
Wastage (l/d)	0,8	1,225

Table 4.6: Steady state results of the aerobic-aerobic and anoxic-aerobic system without the addition of chemicals

Parameters (Mean value)	Aerobic	Anoxic-aerobic
COD influent mg/l	473	473
COD effluent mg/l	21	19,2
TKN influent mg/l	25,7	25,7
TKN effluent mg/l	1,9	2,4
MLVSS last aeration reactor mg/l	3240	3534
(NO_3-N) reactor 1 mg/l	13,0	5,6
(NO_3-N) effluent mg/l	16,4	12,6
O_2 uptake rate last reactor mg/l/hr	-	22,8
pH first reactor	6,8	6,94
pH effluent	6,7	6,95
(PO_4-P) influent mg/l	8,1	8,1
reactor 1 mg/l	3,6	2,7
effluent mg/l	3,4	2,6
removed mg/l	4,70	5,5

Table 4.7: Steady state results of the aerobic system and anoxic-aerobic system with alkalinity addition of 100 mg/l as $CaCO_3$

Parameters (Mean values)	aerobic	anoxic-aerobic
COD influent mg/l	491,0	491,0
COD effluent mg/l	19,0	25,0
TKN influent mg/l	32,3	32,3
TKN effluent mg/l	1,0	2,2
MLVSS ceration reactor mg/l	3240	3545
(NO_3-N) reactor 1 mg/l	18,1	3,8
(NO_3-N) effluent mg/l	19,7	11,7
O_2 uptake rate in last reactor mg/l/hr	21,9	22,1
pH first reactor	7,5	7,40
pH effluent	7,7	7,51
Ca filtered influent mg/l	22,0	22,0
Ca effluent mg/l	22,8	23,3
(PO_4-P) influent mg/l	10,3	10,3
reactor 1 mg/l	3,6	5,1
effluent mg/l	3,4	4,6
removed mg/l	6,9	5,7

Table 4.8: Steady state results of the aerobic unit and anoxic-aerobic unit with alkalinity (100 mg/l as $CaCO_3$) and calcium (50 mg/l as CA^{++}) addition

Parameters (Mean values)	aerobic	anoxic-aerobic
COD influent mg/l	476	476
COD effluent mg/l	26,2	20,7
TKN influent mg/l	40,7	40,7
TKN effluent mg/l	2,0	1,9
MLVSS last aeration reactor mg/l	2875	3075
(NO_3-N) reactor 1 mg/l	20,9	9,7
(NO_3-N) effluent mg/l	26,2	20,7
O_2 uptake rate mg/l/hr	20,7	21,8
pH first reactor	7,30	7,20
pH effluent	7,30	7,35
Ca filtered influent mg/l	88,5	88,5
Ca effluent mg/l	91,4	88,5
(PO_4-P) influent mg/l	10,3	10,3
reactor 1 mg/l	5,8	5,7
effluent mg/l	5,4	5,2
removed mg/l	4,9	5,1

In the next stage of the experimental investigations, the alkalinity of the mixed liquor activated sludge in both units was increased by 100 ppm as $CaCO_3$ with $NaHCO_3$ addition. This caused the mixed liquor pH to increase appreciably. In this series (and the ones following) the Ca was measured but only on filtered influent and effluent. The results are listed in Table 4.7. It is apparent that the pH in the aerobic system is now higher than in the anoxic-aerobic system. The greater removal in the aerobic system would appear to be due to the high pH in this system and it was concluded that if a chemical mechanism is responsible for the excess uptake, it is pH dependent. Comparing these results to the first set of data (Table 4.6), it is evident also that P removal increased on the addition of alkalinity. This was probably due to the high pH effect.

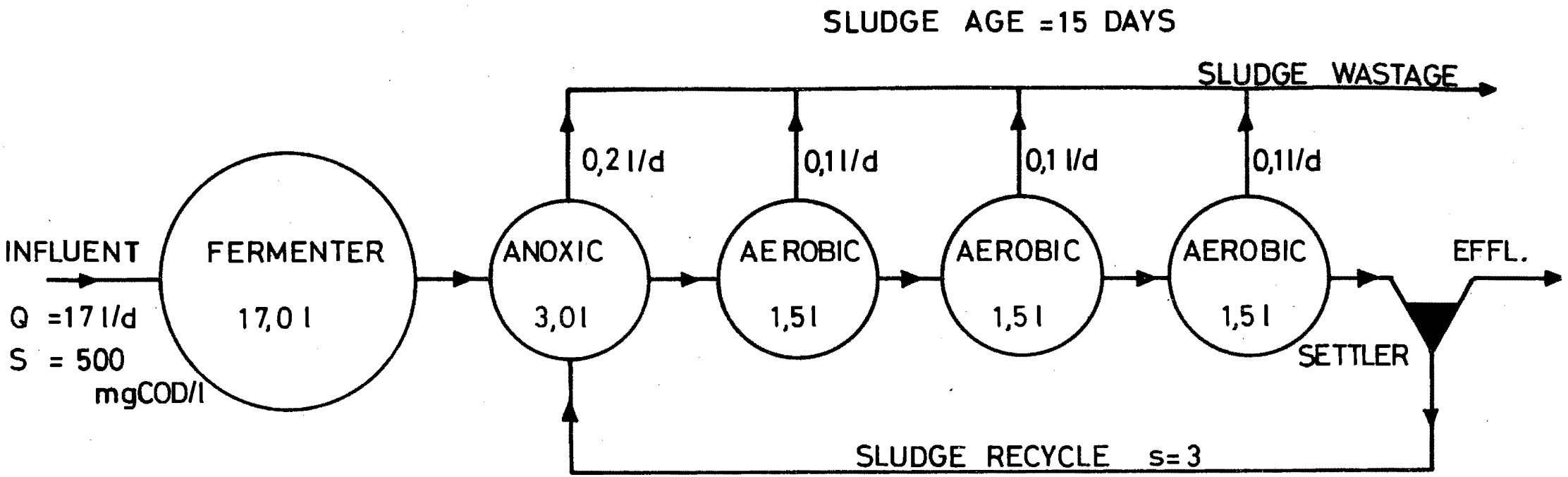
Calcium concentrations on the influent supernatant were very low (i.e. $\pm$ 25 mg/l as Ca) and it was therefore decided to increase the influent calcium concentration by 50 mg/litre as Ca^{++} using $CaCl_2$. Alkalinity dosage of 100 ppm as $CaCO_3$ was continued for both units. Results are given in Table 4.8.

The pH values for both units were nearly the same and the same phosphorus removals were observed. Comparing these results to the previous test indicates that pH values were slightly less and so also the removal of phosphorus. It would appear from this comparison that the pH has a dominating effect compared to the Ca^{++} concentration on the amount of P removed.

Since no significant improvement in the uptake of soluble phosphorus was observed it was decided to spike the influent sewage with 5 mg/litre of P, using Na_2HPO_4. The addition of alkalinity and calcium to the aerobic system was continued but the nitrification-denitrification system

Table 4.9: Steady state results of aerobic system and anoxic-aerobic system with the addition of 5 mg/l as PO_4-P to the influent

Parameters (Mean values)	Aerobic	Anoxic-aerobic
COD influent mg/l	463	463
COD effluent mg/l	25,5	18,3
TKN influent mg/l	26,9	26,9
TKN effluent mg/l	3,3	2,1
MLVSS last aeration reactor mg/l	2604	2770
(NO_3-N) reactor 1 mg/l	11,5	3,6
(NO_3-N) effluent mg/l	13,6	9,6
O_2 uptake rate last reactor mg/l/hr	17,9	23,1
pH first reactor	7,8	7,2
pH effluent	7,9	7,1
Ca filtered influent mg/l	73,3	26,1
Ca effluent mg/l	72,0	26,9
(PO_4-P) influent mg/l	15,42	15,42
reactor 1 mg/l	8,1	9,1
effluent mg/l	7,05	8,2
removed mg/l	8,37	7,20



Reactors	Nominal Retention Time (hrs)	Actual Retention (Time (mins).
Influent storage tank		24 * 60
Anoxic	4,24	62,5
aeration 1	2,12	31,2
total	10,9	156

Figure 4.18 *A diagrammatic representation of the 4-tank series activated sludge process with a fermenter*

was operated without extra alkalinity and calcium. The results of this investigation are shown in Table 4.9. A significant increase of soluble P removal in both systems was evident. The pH in the aerobic system was higher, resulting in a greater phosphorus removal. However, the effluent phosphorus concentration was unsatisfactory indicating the inefficiency of this removal mechanism.

The experimental series were unsatisfactory as calcium measurements were not correctly done: calcium values were determined only on the filtered influent and effluent. Subsequently, it was found that a major portion of the calcium removed was on the volatile material of the influent. Ignoring this fraction made it impossible to obtain a calcium balance. It was, therefore, decided that in the future experiments, both soluble and particulate calcium and phosphorus fractions should be measured. In consequence it was decided to repeat the experiments. However, at about this time research workers at the Municipality of Johannesburg were of the opinion that phosphorus removal was solely a biological luxury uptake phenomena and that this was promoted if fatty acids were available for the bacteria which biologically incorporated excess phosphorus. They conceded, however, that for biological assimilation, phosphates probably require the presence of some cation - for example, calcium.

To stimulate the production of fatty acids the influent raw sewage to the 4 series tank unit was passed through a stirred anaerobic reactor (called a fermenter) with a one day hydraulic retention time, before entering the CMAS series unit comprising 1 anoxic tank and 3 aeration tanks in series (see Fig. 4.18). The other control unit consisted of 2 anoxic and 4 aeration tanks in series. Both units were operated on the same influent raw sewage.

Influent samples were taken for both units separately. The sample for the 4-series tank unit was taken from the

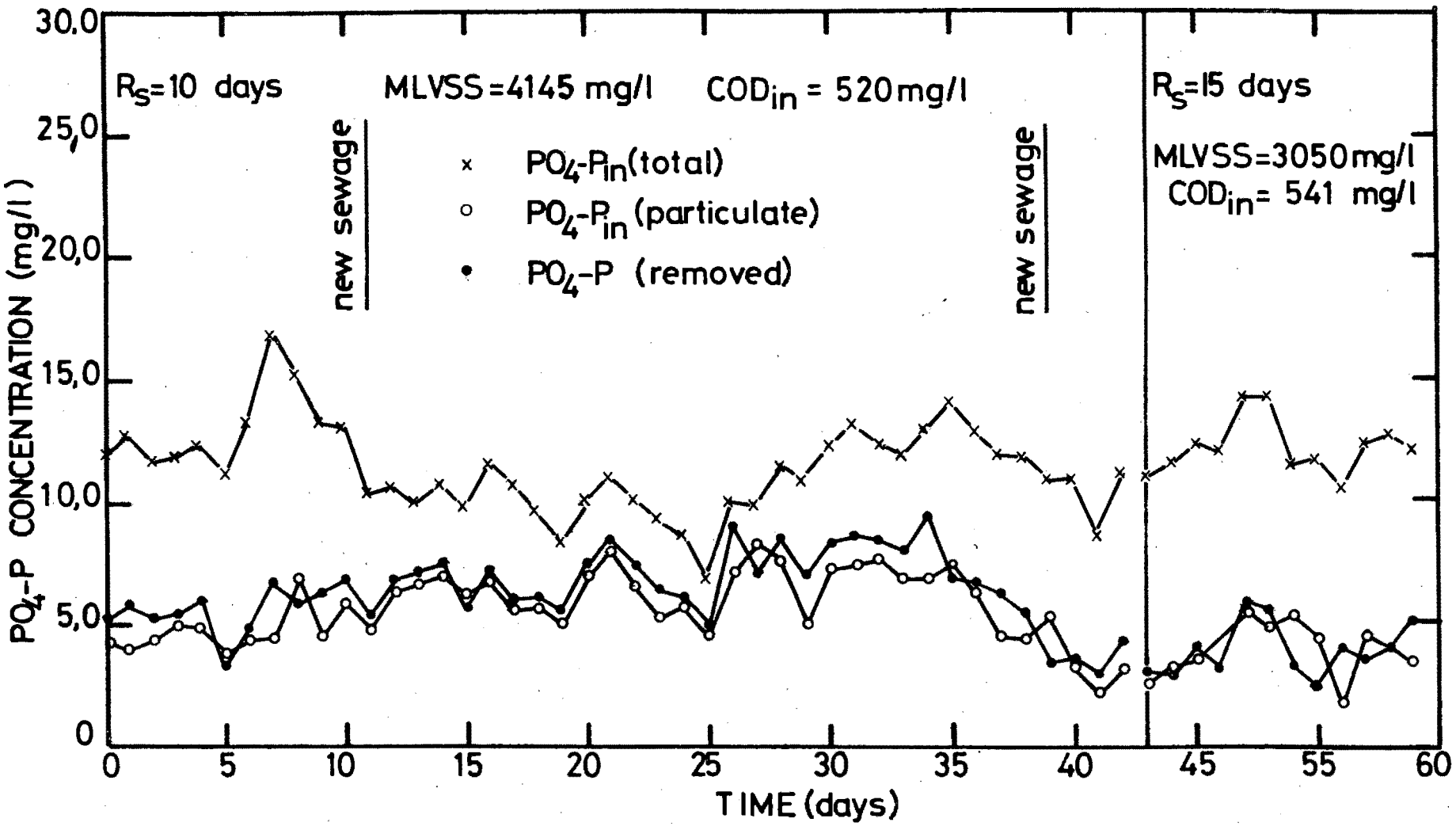


Figure 4.19 *Phosphorus removal corresponds to phosphorus concentration bound to particulate fraction in the influent in an activated sludge system preceded by a fermenter*

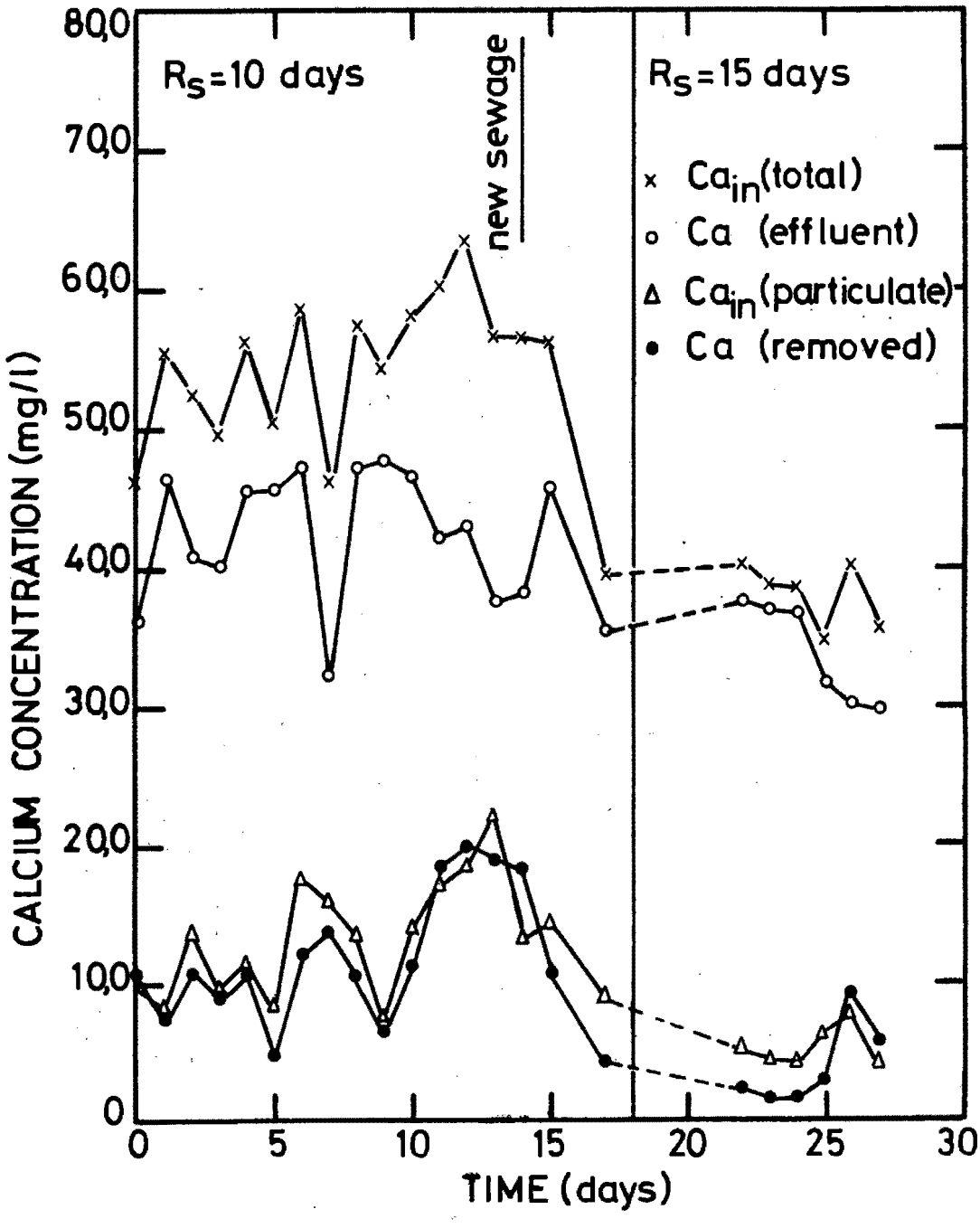


Figure 4.20 *Calcium removal and particulate calcium follow a similar trend as phosphorus in Figure* 4.19

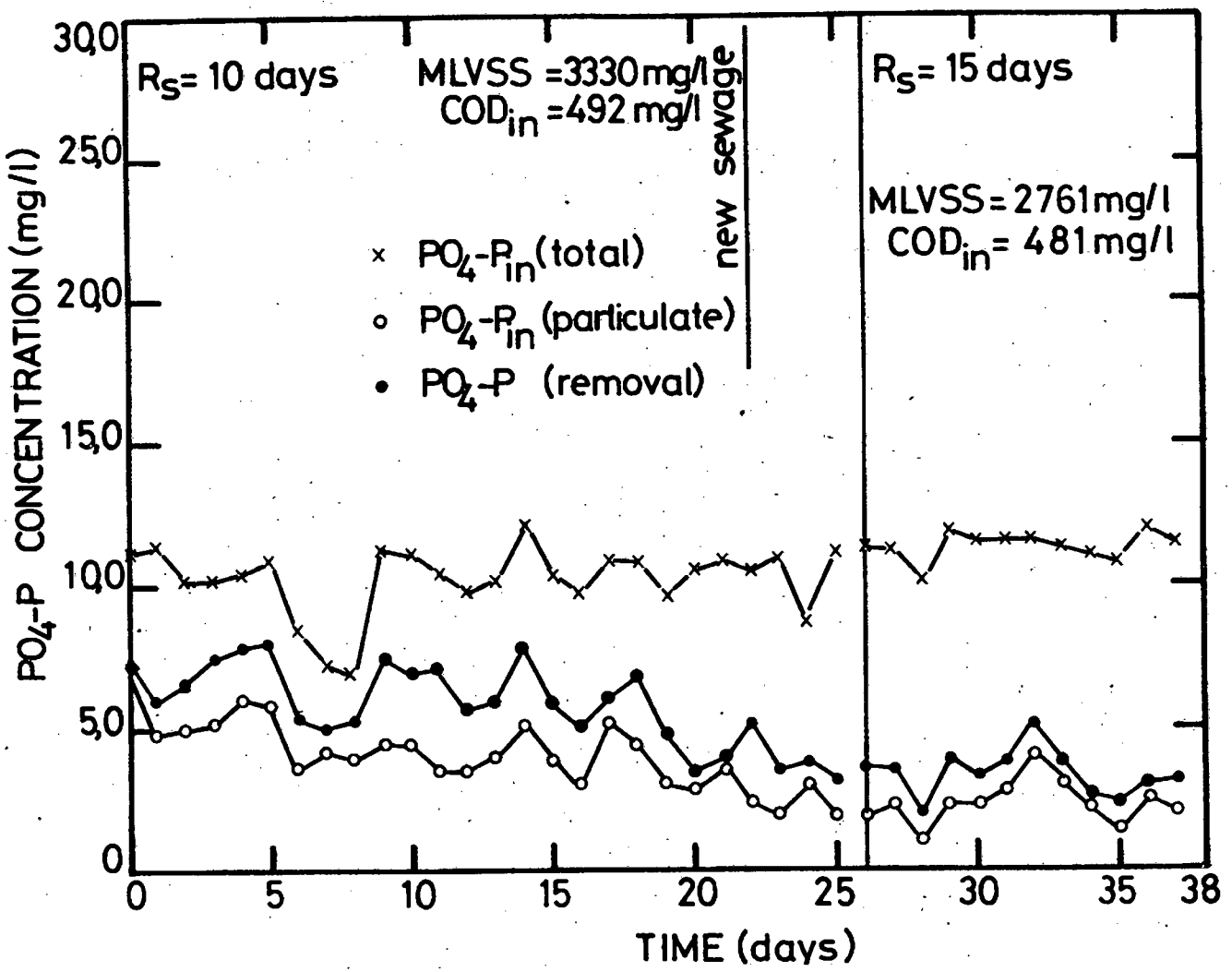


Figure 4.21 *Phosphorus removal follows the same pattern as the influent particulate bound phosphorus in a nitrification-denitrification activated sludge system without a fermenter*

fermenter 1 hour prior to taking samples from the system to ensure a reasonable assessment of the overall process behaviour at the same point in time. The total (i.e. supernatant and particulate) and filtered influent sewage to both units were tested for phosphorus and calcium concentrations. The results are plotted in Fig.(4.19) and Fig. (4.20) for the 4 series tank system and in Fig. (4.21) and Fig. (4.22) for the 6 series tank system.

The phosphorus removal of the 6 series tank nitrification-denitrification (anoxic-aerobic) control system followed the same pattern as the concentration of phosphorus on the influent solid phase (see Fig. 4.21). The particulate phosphorus was, however, less than the total removal of phosphorus in the process. In the same way, the calcium removal followed a similar trend tothe concentration of calcium on the influent particulate (see Fig. 4.22), both calcium concentrations being almost identical. Furthermore, the removal of calcium and phosphorus was observed to take place in the anoxic tank (see Fig. 4.23).

The four series tank system, which included a fermentation tank behaved slightly differently to the other system. It was observed that after one week's operation the pH stabilized at about 7,4 in the fermenter. The pH of the raw sewage before entering the fermenter was about 7,25. The increase in pH was due to the production of methane thereby increasing the alkalinity. Measurements of phosphorus on the solid fraction and filtrate of the fermentation liquid surprisingly showed that some of the soluble phosphorus in the raw influent supernatant had disappeared either by precipitation or adsorption onto the solid fraction. Compare Fig. (4.19) to Fig.(4.21).

The phosphorus removal again followed an identical pattern to the phosphorus concentration on the influent volatile solid material. It is noted that the concentration of

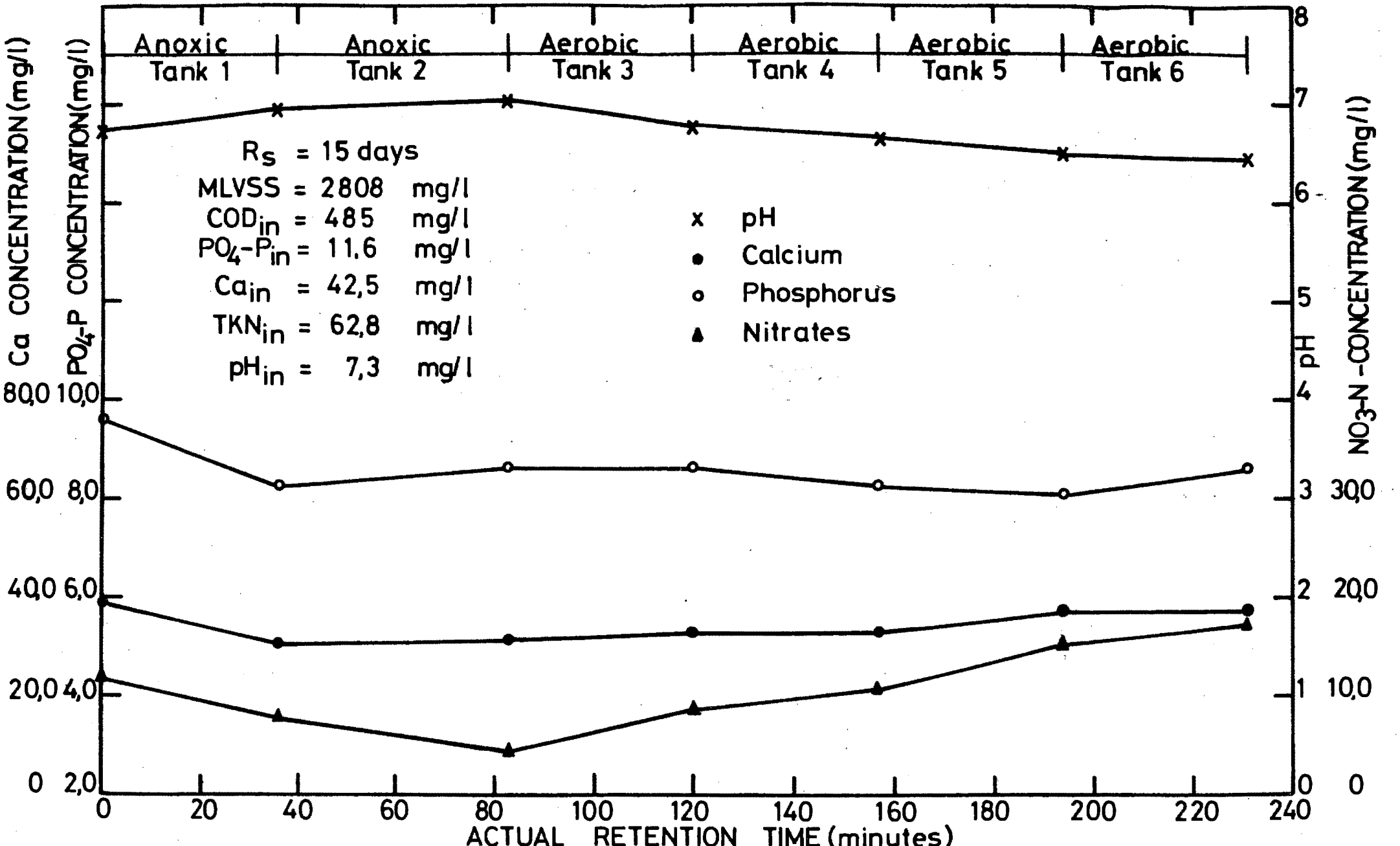


Figure 4.23 Filtrate calcium and phosphorus values follow identical trends during passage through intermediate plug flow (six series reactors) system with two primary anoxic reactors.

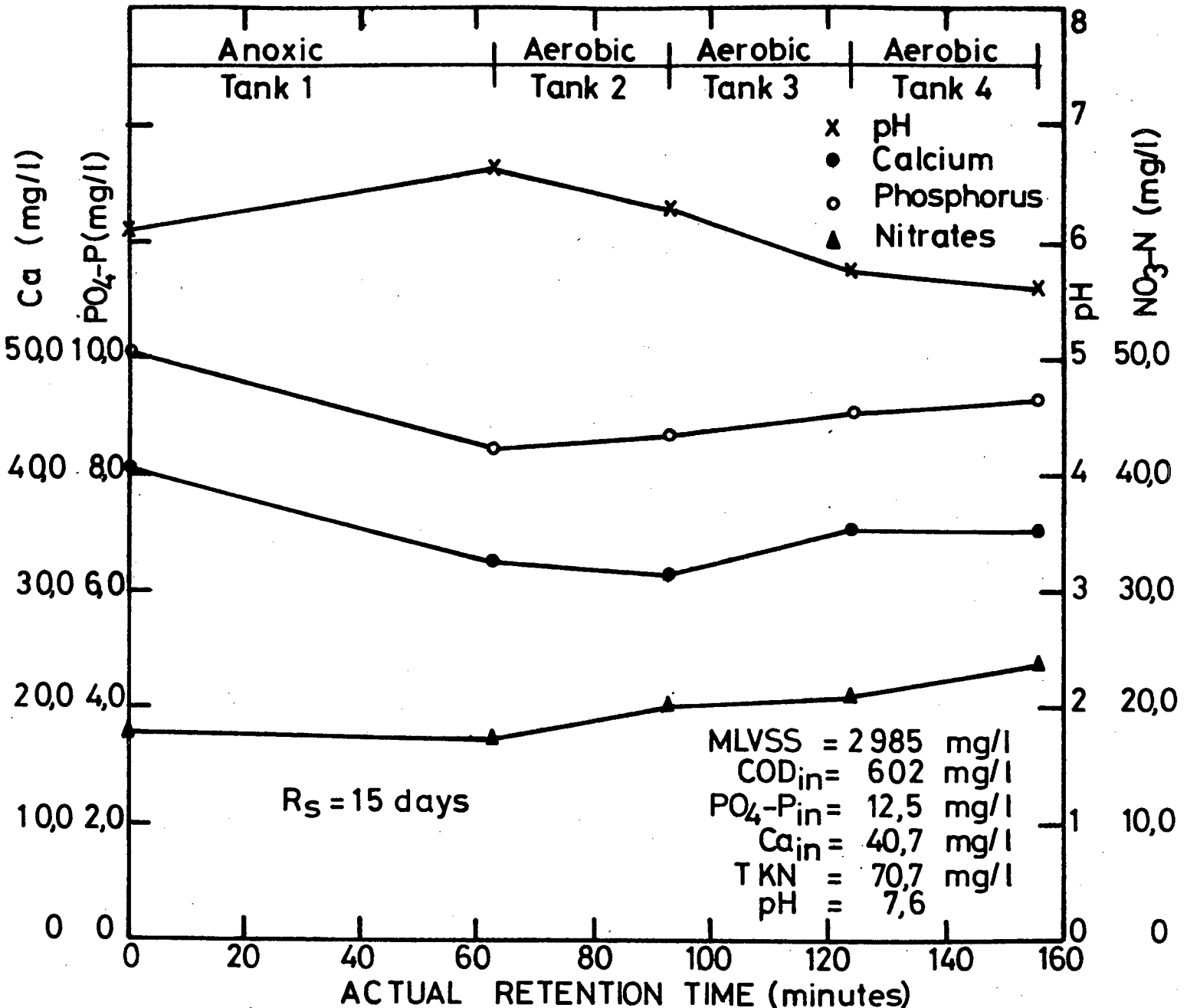


Figure 4.24 Filtrate calcium and phosphorus values follow identical pattern through intermediate plug flow (four series reactor) system with one primary anoxic reactor

particulate phosphorus were identical throughout the investigation. The concentrations of phosphorus removed, moreover, were the same as that for the 6-series tank system. The calcium removal also followed a pattern similar to that described for the phosphorus (see Fig. 4.22). Again the removal of soluble calcium and phosphorus was observed to take place in the anoxic tank. See Fig. (4.24).

The removal of soluble phosphorus onto the solid phase in the fermenter could not have been due to the action of an aerobic obligate (e.g. acinetobacter) as suggested by Fuhs and Chen (1975) and corroborated by researchers in Johannesburg. The observed pH rise indicates a precipitation phenomenon, although it is difficult to detect this in the calcium measurements of the particulate material.

It was shown earlier from batch tests on sludge that an average $[\Delta Ca]/[\Delta P]$ molar ratio of about 3,0 was observed, (see exps. 4.1 to 4.5). Accepting this ratio for this investigation, then the removal of P corresponding to the average Ca removal of 10 mg/litre, is 2,5 mg/litre as P. Adding this value to the phosphorus requirement for synthesis (3,0 mg/litre as P) and subtracting this from the total average removal, gives 0,5 - 1,5 mg/litre as P which can be attributed to excess biological removal by luxury uptake. From this calculation it would seem that biological cum chemical removal is responsible for the removal of the phosphorus in excess of the basic biological requirement.

It was also noted that during the latter stages of this investigation the constitution of the raw sewage significantly effected the amount of phosphorus removed. This is evident from Fig. (4.19) and Fig. (4.21) where the concentration of the phosphorus on the particulate material decreased by between 2 and 3 mg/litre as P. The sewage had a high influent TKN of between 50 and 60 mg/litre as N,

resulting in high nitrates and hence low pH values. This very likely affected the precipitation removal mechanism.

PRELIMINARY CONCLUSIONS

From the series of batch and continuous activated sludge process experiments the following preliminary conclusions are made regarding excess phosphorus removal, i.e. removal in excess of the basic biological requirement for systhesis:

Excess phosphorus removal is due to two phenomena:

1. Calcium phosphate precipitation removes phosphorus and calcium simultaneously in the molar ratio of [Ca]/[P] of approximately 3,0. The solubility product for this precipitant is not known and at present cannot be calculated as the mineral composition is not available. However, the solubility product is very pH sensitive so that as the pH drops, removal of phosphorus and calcium is sharply decreased. For reasonable removal of phosphorus the pH in the system must be 7,0 or higher and the calcium concentration must exceed about 40 mg/litre as Ca. If these conditions are fulfilled the concentration of phosphorus removed will be dependent upon the influent phosphorus concentration. The higher the phosphorus concentration the greater the removal of phosphorus. However, as the influent phosphorus increases, even though the removal of phosphorus increases, the effluent phosphorus also increases. The chemical removal of phosphorus by auto-precipitation with calcium appears to be independent of aerobic or anaerobic conditions. In fact, it is readily taken up under anaerobic conditions, even in the influent itself, if Ca and pH conditions are favourable.

2. Biological removal by luxury uptake appears to account for additional removal of phosphorus. Although this aspect at present has not yet been dealt with experimentally, the expected behavioural pattern should be different from that for physical chemical removal of phosphorus. From the work of Martin and Marais (1975) luxury uptake is induced by having a primary anoxic zone which receives the influent and the recycle flow from the main reactor. The removal now appears no longer to be dependent on the calcium concentration nor to so specifically the pH value (these points will be clarified later). Also, the removal is no longer considered dependent on the initial phosphorus concentration.

It is evident from this investigation that compared to excess phosphorus removal obtained in plants, the contribution by precipitation is small. Removal by biological luxury uptake can be very effective and reduces the phosphorus to low values; in fact to such low values that precipitation of calcium phosphate cannot take place as the phosphorus concentration is too low. If the luxury uptake rate is very much higher than the precipitation rate it appears unlikely that the precipitation of calcium phosphate would have a significant effect on the phosphorus removal. It is concluded that where luxury uptake is operational a physical-chemical precipitation mechanism will be of minor importance.

In the series of experiments above, one may ask "Why did luxury uptake not play a more prominent part in the phosphorus removal, particularly when the conditions imposed on the system are such that luxury uptake should have been promoted?" It is not possible to give an explicit answer to this question. It would seem that it is due to some effect in the influent itself. The period of low phosphorus removal by luxury uptake coincides with a period of

high rainfall in Cape Town so that the influent sewage was greatly diluted. During this period poor phosphorus removals were observed in every one of the five investigations undertaken in the laboratory, by the writer and other research students. It is perhaps fortunate that this occurred as it allowed identification of both mechanisms of removal.

CHAPTER 5

BIOLOGICAL EXCESS PHOSPHORUS REMOVAL - EXPERIMENTAL INVESTIGATION

INTRODUCTION

Up to this stage of the investigation the experimental work on excess phosphorus uptake has been focussed on the calcium phosphate precipitation mechanism. It is evident from the work reported in the precious chapter that the condition for calcium phosphate precipitation is rather specific and, in particular, if the pH is below 7,0, this method of phosphorus removal will not be very efficient. Research by Barnard (1975), Martin and Marais (1975) and Marsden and Marais (1977) has shown that biological luxury uptake can result in very high phosphorus removals. Their work has indicated a set of conditions which results in luxury uptake and they have optimised their configurations and operations procedures. However, their results do not specifically identify luxury uptake as the only mechanism. The conditions obtained in their experiments were such that precipitation could also have made a contribution.

Although it was concluded in the previous chapter that, if luxury uptake is dominant, the calcium-phosphate precipitation mechanism will probably be suppressed, no experimental data was presented to support this conclusion. Now that the conditions for calcium phosphate precipitation is better understood it is desirable to examine again the luxury uptake phenomena to, firstly, verify if the preconditions they proposed for luxury uptake are valid and, secondly, enquire if it is possible to obtain luxury uptake under conditions where calcium phosphate precipitation cannot possibly be expected to occur.

CONDITIONS FOR LUXURY UPTAKE

Martin and Marais (1975) formed the hypothesis that a primary anoxic zone preceding an aeration zone is a necessary prerequisite for the luxury uptake mechanism. They tested this hypothesis by running a process configuration with an anoxic reactor followed by an aerobic reactor and comparing the results with those from the same configuration, but with both reactors aerobic. Although their results supported the hypothesis, the results were not positively conclusive because of their mode of conducting the experiments: they used one set of reactors and ran the plant first anoxic-aerobic, then aerobic-aerobic and then anoxic-aerobic again. This would have been satisfactory if they had not fed a new batch of sewage every time the system was changed. By doing this they introduced two changes simultaneously thereby causing some uncertainty in their conclusions.

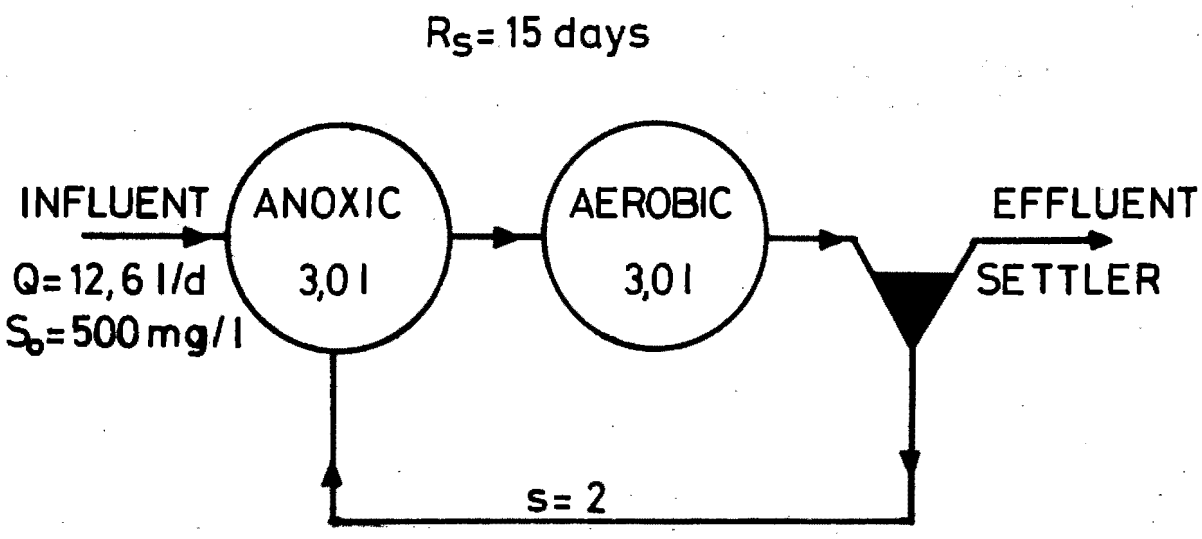
The importance and implication of Martin and Marais' hypothesis is such that it should be tested conclusively. This section deals with the various phases of the experimental work to test the hypothesis that a primary anoxic reactor is a prerequisite to luxury uptake.

The laboratory scale plants, procedures and test methods are outlined in Appendix A.

First Phase Investigation

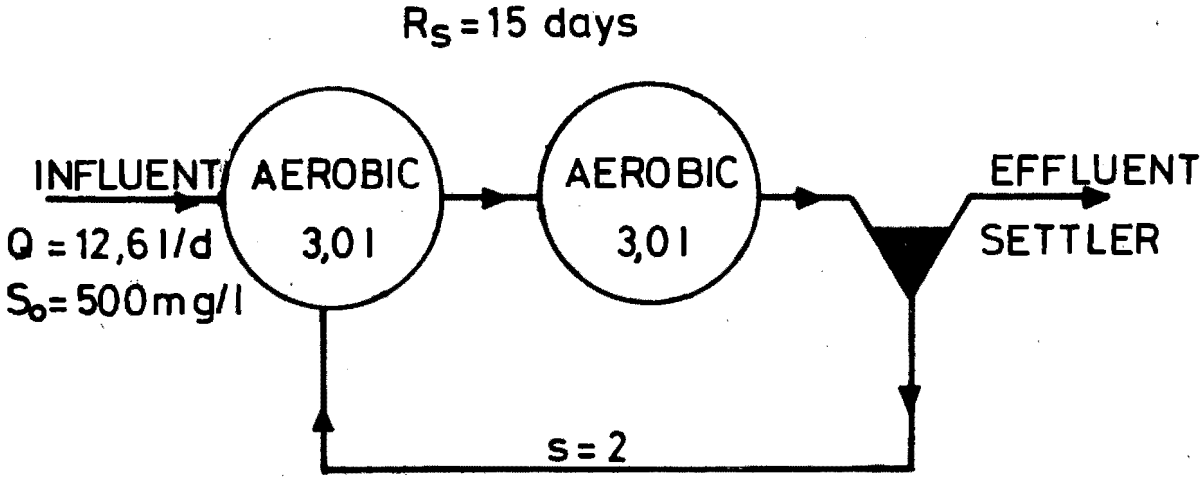
Experiment 5.1: Aerobic-aerobic and anoxic-aerobic systems compared

In the first phase of the investigation, two systems were run simultaneously, receiving the identical flows of sewage. The one system was run anoxic-aerobic (Fig. 5.1) with 50 percent hydraulic anoxic retention time and the other aerobic-



Reactors	Nominal Retention Time (hrs)	Actual Retention Time (Mins)
Anoxic	5,71	114
aeration	5,71	114
total	11,42	228

Figure 5.1 Configuration and process data of anoxic-aerobic system



Reactors	Nominal Retention Time (hrs.)	Actual Retention Time (mins).
Aeration 1	5,72	114
Aeration 2	5,71	114
Total	11,42	228

Figure 5.2 Configuration and process data of aerobic-aerobic system

aerobic (Fig. 5.2). Both units were operated with the same design parameters (Table 5.1). To ensure that the mixed liquor condition was identical initially, the investigation was commenced with mixed liquor from the same source. The units were run for about two weeks to obtain steady state conditions. No chemicals were added to modify the pH.

Table 5.1: Design parameters for laboratory scale semi-plug flow activated sludge units

Parameter	Aerobic-aerobic Unit	Anoxic-aerobic Unit
Configuration	Series	Series
No. of tanks	2	2 or 3
Total volume of reactors (l)	6,0	6,0 or 4,5
Sludge age (days)	15,0	15,0
Influent COD (mgCOD/l)	500	500
Volume of feed (l/d)	12,6	12,6
Wasteage (l/d)	0,4	0,4 or 0,3

The results for this investigation are given in Table (5.2) for the anoxic-aerobic system, and for the aerobic-aerobic system. The aerobic-aerobic system had a lower pH value (i.e. pH 6,13) than the anoxic-aerobic system (pH = 7,2). This difference is attributable to the higher nitrates in the aerobic-aerobic system. The higher pH in the anoxic aerobic system is due to denitrification, i.e. recovery of alkalinity by denitrification in the anoxic zone.

In the aerobic-aerobic system, the total influent calcium concentration was identical to the effluent calcium concentration. This would indicate that any removal of

Table 5.2: Steady state results of the anoxic-aerobic system and aerobic-aerobic system (Exp. 5.1)

Parameters (Mean Values)	Anoxic-aerobic	Aerobic-aerobic
COD influent mg/l	506	506
COD effluent mg/l	27,8	27,2
TKN influent mg/l	45,9	45,9
TKN effluent mg/l	20,8	1,0
MLVSS aeration reactor mg/l	3740	3536
O_2 uptake rate reactor 2 mg/l/hr	40,0	33,9
Alkalinity effluent mg/l (as $CaCO_3$)	100,0	50,0
pH influent	7,19	7,19
reactor 1	7,07	6,30
reactor 2	7,17	6,13
(NO_3-N) reactor 1 mg/l	0,6	25,3
reactor 2 mg/l	0,5	27,8
Ca influent mg/l	31,5	31,5
influent particulate mg/l	8,6	8,6
sludge mg/l	89,2	96,0
reactor 1 mg/l	28,6	31,8
reactor 2 mg/l	27,6	31,6
(PO_4-P) influent mg/l	10,63	10,63
influent particulate mg/l	4,32	4,32
sludge mg/l	165,0	142,2
reactor 1 mg/l	6,4	5,7
reactor 2 mg/l	1,6	5,7
removed mg/l	9,03	4,93

phosphorus must be due to biological action. Now accepting that 2,5 percent of the MLVSS is the normal metabolic requirement of phosphorus, then the phosphorus removal due to metabolism is 3,0 mg/l as P. However, the total phosphorus removal in the system was 4,93 mg/l as P which exceeds the metabolic phosphorus requirements. It is therefore concluded that a luxury biological uptake of phosphorus of 1,9 mg/l took place in the aerobic-aerobic system at the pH of 6,1.

In the anoxic-aerobic system, a reduction in calcium of 3,9 mg/l as Ca was observed between the total influent and effluent concentration. The removal of calcium occurred in the anoxic zone even though a release of P was observed in this reactor. The uptake of calcium would indicate that some of the soluble phosphorus was removed as calcium phosphate. Due to the higher pH, it is likely that the calcium removed is the result of a precipitation phenomenon. Accepting the molar ratio [Ca]/[P] of 3,0 obtained experimentally on MLVSS batch tests reported in Chapter 4, the corresponding phosphorus removal can be calculated to give 1 mg/l removed as P. As there was a nett release of phosphorus in the anoxic reactor it would appear that two mechanisms were operating simultaneously - (1) a removal of P by precipitation and (2) a release of P, possibly biological.

The system removal of phosphorus was 9,0 mg/l. To establish if excess biological removal had taken place, both the phosphorus concentration for metabolism and that due to precipitation must be subtracted from the total phosphorus removed. This gives 5 mg/l phosphorus removal due to biological luxury uptake.

Comparing the aerobic-aerobic system and the anoxic-aerobic system, it is evident that:

1. The excess biological uptake of phosphorus in the aerobic-aerobic and the anoxic-aerobic was in the ratio

of 2:5 mg/l respectively, i.e. the anoxic-aerobic system does appear to promote luxury biological uptake of phosphorus.

2. Whereas phosphorus removed in the aerobic-aerobic system at the low pH 6,1 appears to be due only to biological uptake, the results of the anoxic-aerobic system tend to indicate that the excess uptake of phosphorus was a biological cum chemical mechanism.

The investigations above tend to support the results of the batch tests that pH has a significant effect on the results, particularly on the calcium phosphate removal mechanism. Perhaps the luxury biological uptake is also affected, but this is not yet clear. It is evident, however, that more explicit information will only be obtained if the pH in both reactors are controlled to the same value.

Second Phase Investigation

Experiment 5.2: High pH in both systems

In the previous section and earlier work on batch tests, it was verified that pH seems to play a significant role in the chemical removal of phosphorus. In order to identify the effect of pH, the two systems were run under identical pH conditions by first raising the mixed liquor pH of the aerobic-aerobic (i.e. pH 6,1) system to the value of the anoxic-aerobic (i.e. pH 7,2) and thereafter lowering the pH of the anoxic-aerobic (i.e. pH 7,2) to that of the aerobic-aerobic system (i.e. pH 6,1).

To raise the pH in the aerobic-aerobic system, the influent sewage pH to the aerobic-aerobic system was increased from pH 7,2 to pH 7,6 by adding alkalinity, using $NaHCO_3$. The units were run for about two weeks under identical conditions.

Table 5.3: Results of anoxic-aerobic unit and aerobic-aerobic unit operated at the same high pH (Exp. 5.2)

Parameters (Mean values)	Anoxic-Aerobic	Aerobic-aerobic
COD influent mg/l	513	513
COD effluent mg/l	20,6	24,4
TKN influent mg/l	39,3	39,3
TKN effluent mg/l	6,7	2,5
MLVSS aeration reactor mg/l/hr	3900	3640
O_2 uptake rate in reactor 1 mg/l/hr		35,3
O_2 uptake rate in reactor 2 mg/l/hr	41,7	30,5
Alkalinity effluent mg/l as $CaCO_3$	79,0	140,0
pH influent	7,19	7,63
reactor 1	7,02	6,97
reactor 2	6,97	6,90
(NO_3-N) reactor 1 mg/l	0,4	20,9
reactor 2 mg/l	4,4	20,3
Ca influent mg/l	36,9	36,9
influent particulate mg/l	11,3	11,3
sludge mg/l	177,1	114,5
reactor 1 mg/l	31,6	32,3
reactor 2 mg/l	31,6	32,3
(PO_4-P) influent mg/l	10,34	10,34
influent particulate mg/l	4,5	4,5
sludge mg/l	192,0	146,4
reactor 1 mg/l	4,7	4,4
reactor 2 mg/l	0,8	4,2
removed mg/l	9,54	5,96

The results of the two systems are given in Table 5.3 for the anoxic-aerobic and aerobic-aerobic systems respectively.

The results show that the pH values for the two systems were identical, although the carbonic alkalinity for the aerobic-aerobic system (140 ppm as $CaCO_3$) was higher by about 60 ppm as $CaCO_3$ than the alkalinity in the anoxic-aerobic system (79 ppm as $CaCO_3$). In the aerobic-aerobic system the higher pH value resulted in the removal of calcium and phosphorus simultaneously. This is in contrast to the previous behaviour where at pH 6,1 no calcium was removed. The removal can in all probability be attributed to the precipitation of a calcium phosphate mineral. Comparing Table 5.2 and Table 5.3 for the aerobic-aerobic system, the removal of phosphorus also increased from 4,9 to 6,0 mg/l as P. This increased phosphorus removal (of 1,1 mg/l) corresponds favourably to the calcium removal of 4,6 mg/l as Ca, giving a [Ca]/[P] molar ratio of 3,0. Accepting that precipitation had taken place, the removal of phosphorus in the aerobic-aerobic system can now be broken down into the following categories;

(i)	Calcium phosphate precipitation	=	1,1 mg/l as P
(ii)	metabolic requirement	=	3,0 mg/l as P
			4,1 mg/l as P

As the removal of phosphorus is 6,0 mg/l as P, luxury uptake of phosphorus is estimated at (6,0 - 4,1) mg/l = 1,9 mg/l. This value for the luxury uptake, 1,9 mg/l as P, is approximately the same as 2,0 mg/l as P obtained for luxury uptake in the aerobic-aerobic system at the lower pH (see Exp. 5.1).

In the anoxic-aerobic system, the results (Table 5.3) remained the same as before, i.e. 9,5 mg/l versus 9,0 mg/l removed as P. This is to be expected as no pH changes had taken place in the anoxic-aerobic system. The pH

maintained a value of 7,1 for both phases of the investigation. The calcium removal was 5,3 mg/l corresponding to a phosphorus removal of 1,3 mg/l. The removal of phosphorus for the anoxic-aerobic system can also be broken down as follows:

For	(i)	Calcium phosphate precipitation	=	1,3 mg/l as P
	(ii)	Metabolic requirement	=	3,0 mg/l as P
				4,3 mg/l as P

Total removal of phosphorus is 9,5 mg/l as P. Hence luxury uptake is (9,5 - 4,3) = 5,2 mg/l as P. Previously the value estimated for luxury uptake was 5,0 mg/l as P, so that the behaviour remained consistent.

Comparing the luxury uptake for the two systems in both the anoxic-aerobic and aerobic-aerobic system the removal maintained the same ratio of phosphorus for luxury uptake as in the first phase, i.e. aerobic-aerobic versus anoxic-aerobic is 2 : 5 mg/l. This could point to the following conclusion: The increase in pH of the aerobic-aerobic system had a positive effect on the chemical precipitation mechanism. In contrast, the biological mechanism was not affected.

The evidence so far indicates the following general conclusion: At pH 7,2 a biological-cum-chemical mechanism is responsible for some excess uptake of phosphorus in both an aerobic-aerobic and anoxic-aerobic system. The greater biological excess uptake in the anoxic-aerobic system depends primarily on the presence of an anoxic zone.

Experiment 5.3: Low pH in both systems

To investigate the effect of low pH, the pH in the aerobic-aerobic system was lowered from 7,2 to 6,0 by omitting the alkalinity addition. Acidity was added to the anoxic-aerobic system to bring the pH down to the same level as

that of the aerobic-aerobic system (i.e. pH 6,0) (see Table 5.4). In the anoxic-aerobic system the increase in acidity resulted in an appreciable decrease in total carbonic alkalinity from 79,0 to 17,0 ppm as $CaCO_3$. Initially a release of calcium (10 mg/l as Ca) was observed in the anoxic-aerobic system which in time reduced to zero, i.e. initially the effluent calcium concentration was higher than the total influent concentration, probably due to dissolution of calcium phosphate that had precipitated in the previous experiment. The average removal of phosphorus compared with previous investigation, decreased from 9,5 mg/l to 7,6 mg/l as P. The decrease of 1,9 mg/l, P, can be attributed to two effects:

1. the redissolution of some calcium phosphate mineral, and

2. the fact that at the pH 5,8 to 6,0 no calcium phosphate precipitation can occur.

Accepting that the phosphorus removal is solely due to a biological mechanism the removal of phosphorus can again be broken down as follows:

(i)	Metabolic requirement	=	3,0 mg/l as P
(ii)	Luxury uptake	=	(7,6 - 3,0)
		=	4,6 mg/l as P

The luxury uptake still remained unaffected. The results of the phosphorus removals at low and high pH values are compared in Table 5.5 for the anoxic-aerobic and aerobic-aerobic systems.

Comparing the data in Table 5.5 it is concluded that the lower pH (i.e. pH 6) has no significant effect on the functioning of the luxury uptake mechanism. The lower removal of phosphorus observed appears to be due to the dissolution of some calcium phosphate already precipitated

Table 5.5: Phosphorus removal fractions at the various pH values for the anoxic-aerobic system and aerobic-aerobic system

	Low pH					High pH				
	(PO_4-P) Concentration mg/l					(PO_4-P) concentration mg/l				
	pH	Synthe-sis	Ca-P precipi-tation	Luxury uptake	Total remo-val	pH	Synthe sis	Ca-P precipi-tation	Luxury uptake	Total remo-val
Anoxic-aerobic:	5,81	3,0	-	4,6	7,6	6,97	3,0	1,3	5,2	9,5
Aerobic-aerobic:	6,13	3,0	-	1,9	4,9	6,90	3,0	1,1	1,9	6,0

and the fact that calcium phosphate does not precipitate at low pH values.

The two phases of this investigation point to the following conclusions:

1. Phosphorus removal by calcium phosphate precipitation is primarily influenced by pH. If a reasonable concentration of calcium, about 40 mg/l as Ca^{++} or more is available an influent phosphorus of 10 mg/l as P or more and pH > 7,0 phosphorus will be removed by calcium phosphate precipitation in the ratio of [Ca]/[P] = 3/1. This removal is independent of anoxic, anaerobic or aerobic condition in the system.

2. Luxury biological uptake is promoted by having a primary anoxic zone, although luxury uptake can also take place to a minor degree in aerobic conditions.

3. Luxury uptake is not significantly affected in the pH range 5,8 to 7,3.

The above experiments have been primarily concerned with establishing the type of phosphorus removal mechanism and the importance of the primary anoxic zone. The next stage of the investigation will deal with the condition within the anoxic zone for optimum removal.

ANOXIC CONDITIONS FOR LUXURY UPTAKE

In the previous investigation a qualitative condition for excess biological uptake was identified, i.e. a primary anoxic zone preceding an aeration zone. This configuration, however, can be brought about using different reactor configurations and reactor volumes. Therefore, it is necessary to investigate the configurations and conditions of operation for maximum excess biological uptake of phosphorus.

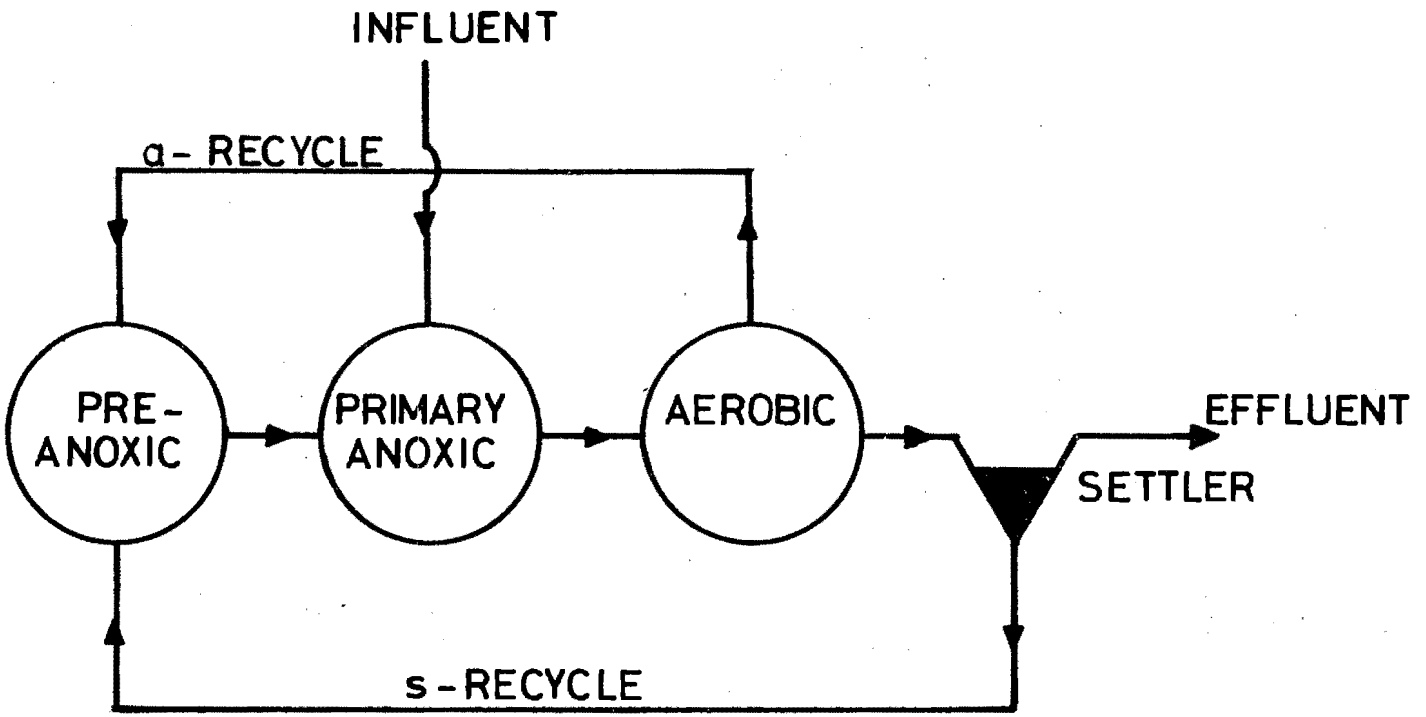


Figure 5.3 *Modified Barnard configuration as proposed by Martin and Marais* (1975)

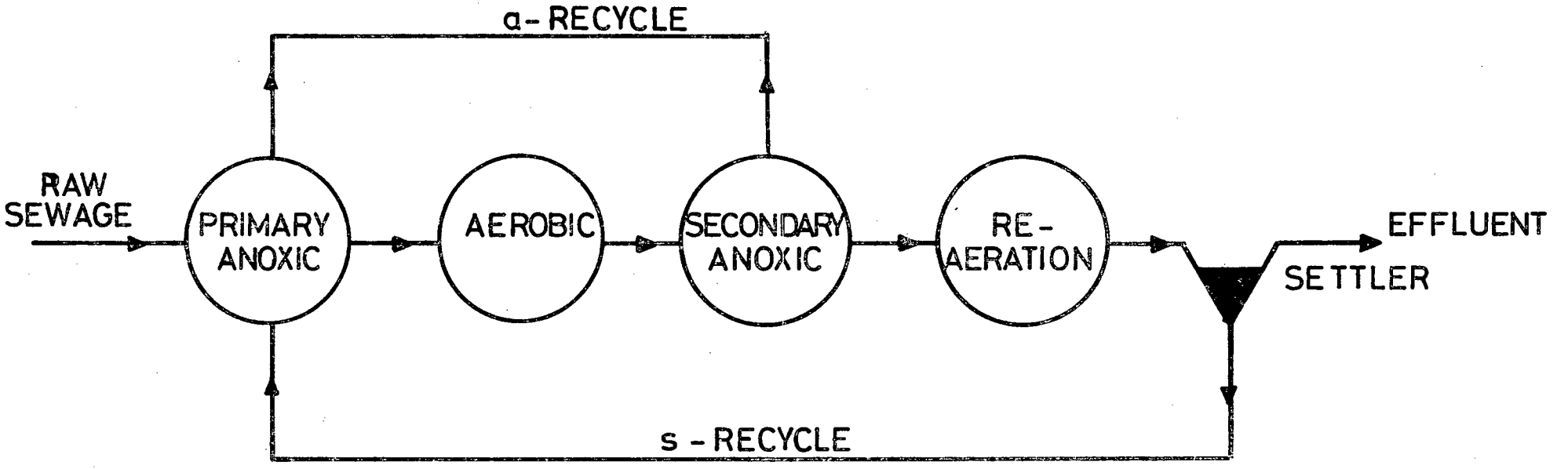
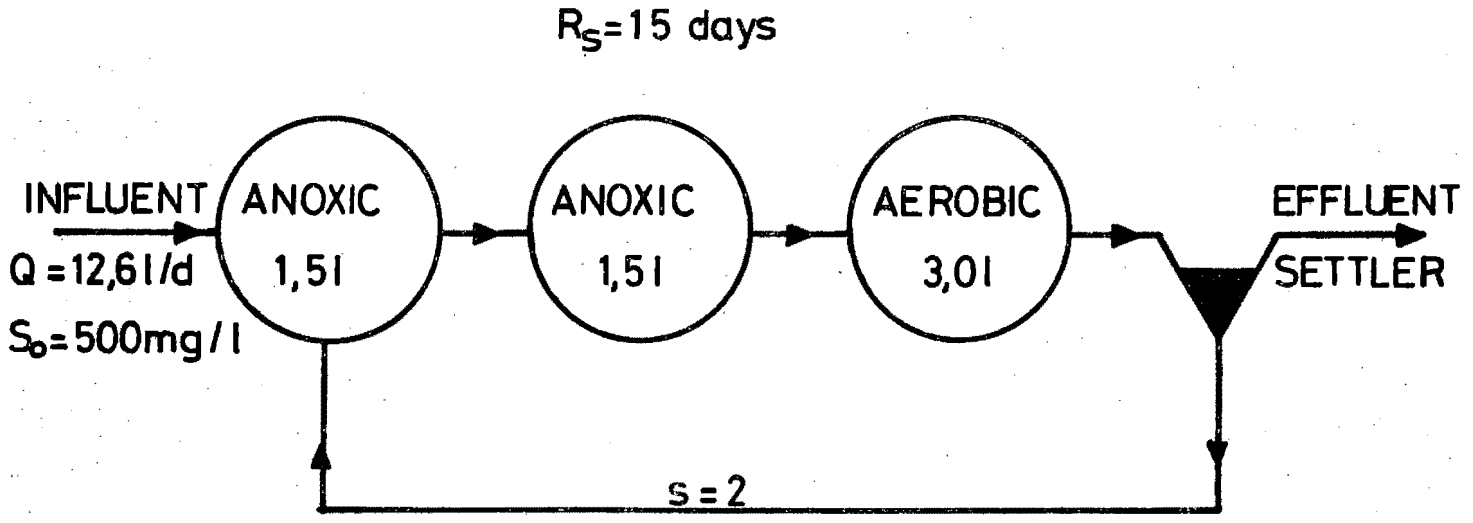


Figure 5.4 Modified Barnard configuration as proposed by Stern and Marais (1973)

The Barnard process includes anaerobic-anoxic zones and could serve as the basis towards establishing the most effective configuration.

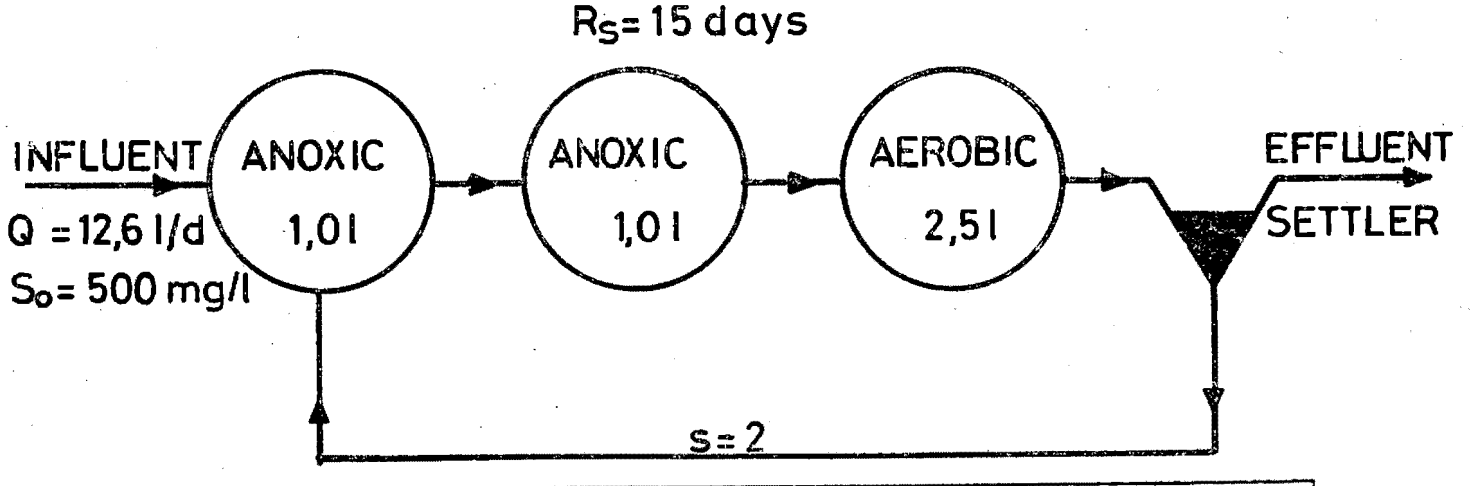
Barnard hypothesized that the organism mass must pass through an anaerobic phase somewhere in the system cycle for optimum phosphorus removal to be attained. He defined an anaerobic condition as one in which no nitrates are present. He proposed to bring about this condition by having two primary anoxic zones in series preceding the aerobic zone. (See Fig. 2.1). The recycle from the settling tank discharges into the first anoxic (or 'anaerobic') zone which also receives the influent waste flow. The recycle contains very low nitrates concentration which is rapidly depleted when the raw sewage mixes with the recycle in the first anoxic zone to bring about an 'anaerobic' condition. Nitrate reduction is achieved by recycling from the aerobic tank into the second anoxic reactor which also receives the discharge from the first anoxic reactor. Martin and Marais attempted a somewhat similar configuration by recycling from the aerobic zone and settling tank to a pre-anoxic tank, however, they did not discharge the sewage into the first reactor but into the second anoxic reactor (see Fig. 5.3). The objective was simply to remove the nitrates before they entered the main anoxic reactor. No attempt was made to create a 'deep anaerobic' zone.

Stern and Marais (1973), to ensure the absence of oxygen in the primary anoxic zone, proposed recycling from the second anoxic reactor into a single primary anoxic zone as this effluent would already have a low nitrate level. See Fig.(5.4). However, the large recycle through the second anoxic reactor caused that appreciable oxygen entered the secondary anoxic reactor and the reduction in nitrates in this reactor became insignificantly small. Nitrates were still carried back into the primary anoxic reactor.



Reactors	Nominal Retention Time (hrs)	Actual Retention Time (mins)
Anoxic 1	2,86	57
Anoxic 2	2,86	57
aeration	5,71	114
Total	11,42	228

Figure 5.5 Configuration and process data of unit with two anoxic tanks in series



Reactors	Nominal Retention Time (hrs)	Actual Retention Time (Min)
Anoxic 1	1,90	38,1
Anoxic 2	1,90	38,1
Aeration	4,76	95,2
Total	8,57	171,4

Figure 5.6 Configuration and process data of unit with high MLVSS

The configuration of Barnard (1975), Fig. (2.1) is different from the two procedures of Martin and Marais (1975) and Stern and Marais (1973) and it was therefore desirable to test if the Barnard configuration leads to superior phosphorus removals.

Basically the experimental objective was to determine if, as suggested by Barnard, release of phosphorus in the anoxic zone had any effect on the phosphorus removal. A number of configurations were tested each sequential configuration approach further along the way toward the Barnard process.

Experiment 5.4: Initial condition established

The first configuration together with the process data are shown in Fig. 5.5. The unit was operated with the design parameters shown in Table 5.1. In order to obtain the anoxic/anaerobic condition it was necessary to operate the system at a long hydraulic anoxic retention time (2 hours). The unit was monitored for about 2 weeks to ensure steady state condition.

The results are given in Table 5.6 for the anoxic-aerobic system.

The total removal of phosphorus was 8,5 mg/l as P. The removal concentration compares favourably with the results obtained for Experiment 5.1 and Experiment 5.2, i.e. 9,0 and 9,5 mg/l respectively for the anoxic-aerobic system, where the anoxic and aerobic volumes were the same as in this unit, except that there was only one anoxic reactor, instead of two as in this unit. The calcium decrease of 3,7 mg/l between the total influent and effluent concentration indicated that the calcium removal was due to the formation of some calcium phosphate mineral. Accepting the [Ca]/[P] molar ratio of 3,0 obtained from batch experiments, the corresponding phosphorus removal gives 0,9 mg/l. The concentration

Table 5.6: Steady state results for anoxic-aerobic system

Parameters (Mean values)	Exp. 5.4	Exp. 5.5	Exp. 5.6
COD influent mg/l	518	500	486
COD effluent mg/l	20,4	20,8	25,1
TKN influent mg/l	34,2	34,1	35,9
TKN effluent mg/l	1,9	0,0	0,5
MLVSS aeration reactor mg/l	4160	5340	4350
O_2 uptake rate mg/l/hr	46,5	46,7	55,4
Alkalinity effluent mg/l as $CaCO_3$	62,0	-	-
pH influent	7,20	7,22	7,13
anoxic reactor 1	6,96	6,80	6,93
anoxic reactor 2	7,00	6,83	6,93
aeration reactor	6,80	6,72	6,84
(NO_3-N) anoxic reactor 1 mg/l	0,7	0,7	0,4
anoxic reactor 2 mg/l	0,8	0,4	0,5
aeration reactor mg/l	7,9	6,4	4,4
Ca influent mg/l	33,3	31,0	35,2
influent particulate mg/l	9,9	7,3	7,6
sludge mg/l	124,2	140,0	117,0
anoxic reactor 1 mg/l	28,4	27,1	30,0
anoxic reactor 2 mg/l	30,7	27,9	30,4
aeration reactor mg/l	29,6	28,5	30,7
(PO_4-P) influent mg/l	10,3	10,2	10,46
influent particulate mg/l	4,1	4,08	2,86
sludge mg/l	179,2	233,0	208,8
anoxic reactor 1 mg/l	4,7	5,13	14,2
anoxic reactor 2 mg/l	4,8	5,37	3,3
aeration reactor mg/l	1,8	1,8	1,56
removed mg/l	8,5	8,4	8,9

of phosphorus for normal metabolic requirement gives 3,1 mg/l as P, and subtracting it from the total removal of phosphorus, the luxury uptake of phosphorus is thus obtained, 4,5 mg/l.

In both the previous tests (i.e. Exps. 5.1 and 5.2) and this system there was a slight release of phosphorus in the anoxic zone, accompanied by an uptake of 3 mg/l of Ca, in the reactor. This behaviour pattern is in contrast to behaviour in continuous tests (Chapter 4) where calcium and phosphorus always decreased together in the anoxic zone. It would indicate that in this configuration there was a release of luxury phosphorus and an uptake of P by precipitation. The two phenomena occur simultaneously, but the luxury release being more than the precipitation removal to give a nett release.

Experiment 5.5: Increased VSS

Barnard, in his investigation, operated the systems at high mixed liquor activated sludge concentration and it was then decided to increase the MLVSS from 4000 to 5200 mg/l to test if increased MLVSS improved the phosphorus removal. This was achieved by decreasing the total mixed liquor volume from 6,0 to 4,5 litres, by reducing the volume in each reactor by 0,5 litres. The configuration and process data are shown in Fig. 5.6. The flow of sewage per day was kept the same as in the previous investigation, but the hydraulic retention times for each reactor were decreased considerably.

After two weeks' operation, the results of this experiment are given in Table 5.5.

From Table 5.6 the total removal of phosphorus is 8,4 mg/l, which is no improvement to the removal of 8,5 mg/l obtained in the first experiment. It is also noted that the calcium removal was slightly less than the removal obtained in Exp. 5.4 (i.e. 2,5 versus 3,7 mg/l). Hence calculating the

phosphorus removal due to calcium phosphate precipitation gives 0,6 mg/l as P. Again, the fractions of phosphorus removed can be sub-divided as follows:

For (i) Calcium phosphate precipitation = 0,6 mg/l as P
(ii) Metabolic requirement = 3,0
3,6

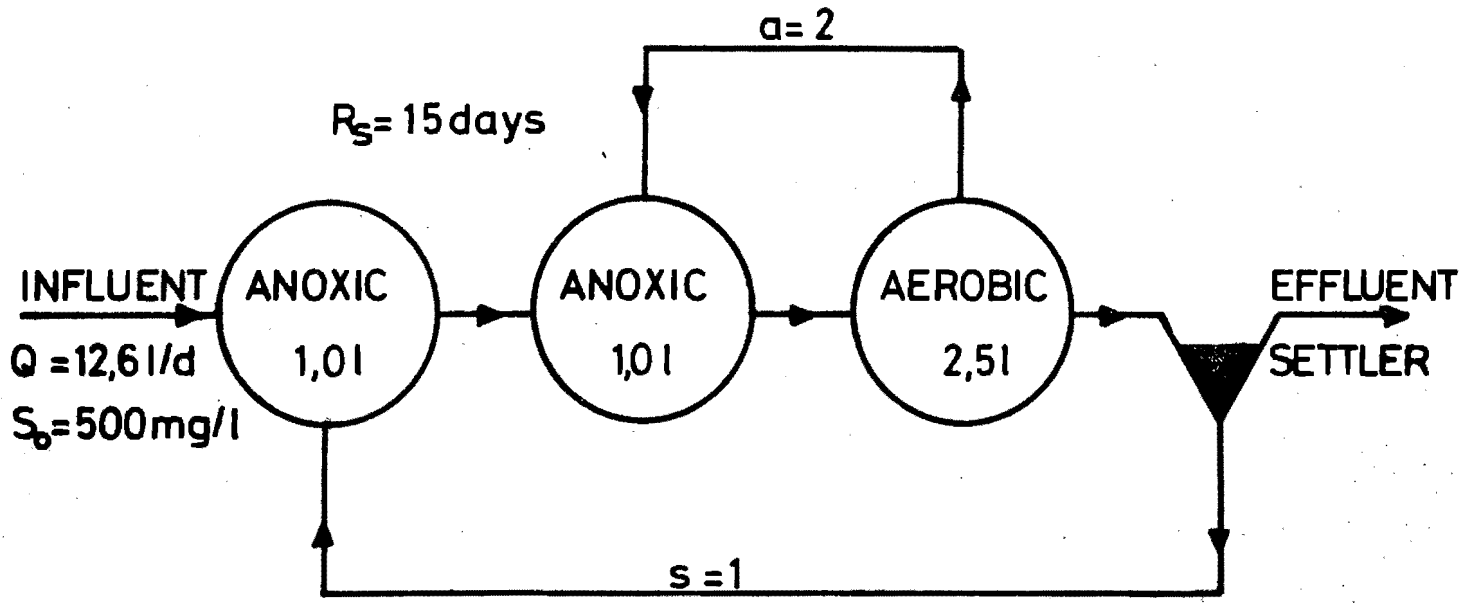
Subtracting this value, 3,6 mg/l, from the total removal of 8,4 mg/l gives the concentration for luxury uptake of 4,8 mg/l. Previously the value estimated for luxury uptake was 4,5 mg/l, so that the behaviour remained consistent.

In this experiment a release of 0,5 mg/l of phosphorus took place in the first anoxic tank and a further release 0,2 mg/l in the second anoxic reactor. Calcium remained virtually unaffected, in fact, a slight release occurred between the second anoxic reactor and the aeration zone, which in all probability is due to the decrease in pH from 6,83 to 6,77.

With regard to the above results, it again appears that in this configuration there was a biological release in the anoxic zone. However, the release is not significant enough to be able to identify this mechanism. Since Barnard proposed that an anaerobic zone is essential for luxury uptake, a release of phosphorus in the anaerobic zone, according to him, is desirable.

Experiment 5.6: Presence of nitrates

In Experiment 5.5, the nitrate concentration in the first anoxic zone was very near zero and zero in the second anoxic reactor. Therefore, if the recycle is increased the total reduction of nitrates can be further accomplished. The following modification was done to the previous configuration:



Reactors	Nominal Retention Time (hrs)	Actual Retention Time (mins)
Anoxic 1	1,90	57,1
Anoxic 2	1,90	28,6
Aeration	4,76	72,0
Total	8,57	158,0

Figure 5.7 Modified Barnard process with process data.

An internal recycle a = 2 from the aerobic zone to the second anoxic reactor was introduced and the sludge recycle, S, from the settler was reduced to S = 1, from S = 2. The objective of the internal recycle was to reduce the nitrates in the aerobic zone such that complete depletion of nitrates was obtained in the first anoxic zone, hence resulting in the 'anaerobic' condition proposed by Barnard. The configuration together with the process data is shown in Fig. (5.7).

The unit was run for about two weeks to ensure steady state condition. The average results of the measured parameters are given also in Table 5.6.

The nitrates in the effluent decreased from 6,4 mg/l to 4,4 mg/l and the nitrates were always zero in the first anoxic reactor. The phosphorus removed was 8,9 mg/l as against 8,4 mg/l in Experiment 5.5. This difference is not significant and cannot be ascribed to increased luxury uptake because the calcium removed also increased from 2,5 to 4,5 mg/l. Calculating that phosphorus removal due to calcium phosphorus precipitation gives 1,1 mg/l. Subdividing the phosphorus removal as follows:

For (i) Calcium phosphate precipitation = 1,1 mg/l
(ii) Biological metabolic requirement = 3,0 mg/l
hence (iii) Luxury uptake = 8,9 - 4,1
= 4,8 mg/l

The fractions of phosphorus for Experiments 5.4, 5.5 and 5,6 are shown in Table 5.7.

In Experiment 5,6, it can be noted that significant more phosphorus was released in the first anoxic zone, than in the previous experiments, indicating that an anaerobic condition was established (see Table 5.8). The released phosphorus was subsequently removed in the second anoxic zone. Calcium concentration between the first and second

Table 5.7: Comparison of phosphorus fractions for the three experiments

	(PO_4-P Concentration mg/l			
Experiment	Metabolic Requirement	Ca-P precipitation	Luxury Uptake	Total PO_4-P removed
5,4	3,1	0,9	4,5	8,5
5,5	3,0	0,6	4,8	8,4
5,6	3,0	1,1	4,8	8,9

Table 5. 8: Systems release and uptake of phosphorus by the sludge

	(PO_4-P) in mg/l			
Experiment	Anoxic 1	Anoxic 2	Aerobic	Overall removal
5,4	- 0,20	- 0,30	+ 9,00	8,5
5,5	- 1,59	- 0,72	+10,72	8,4
5,6	-16,38	-18,32	+ 6,96	8,9

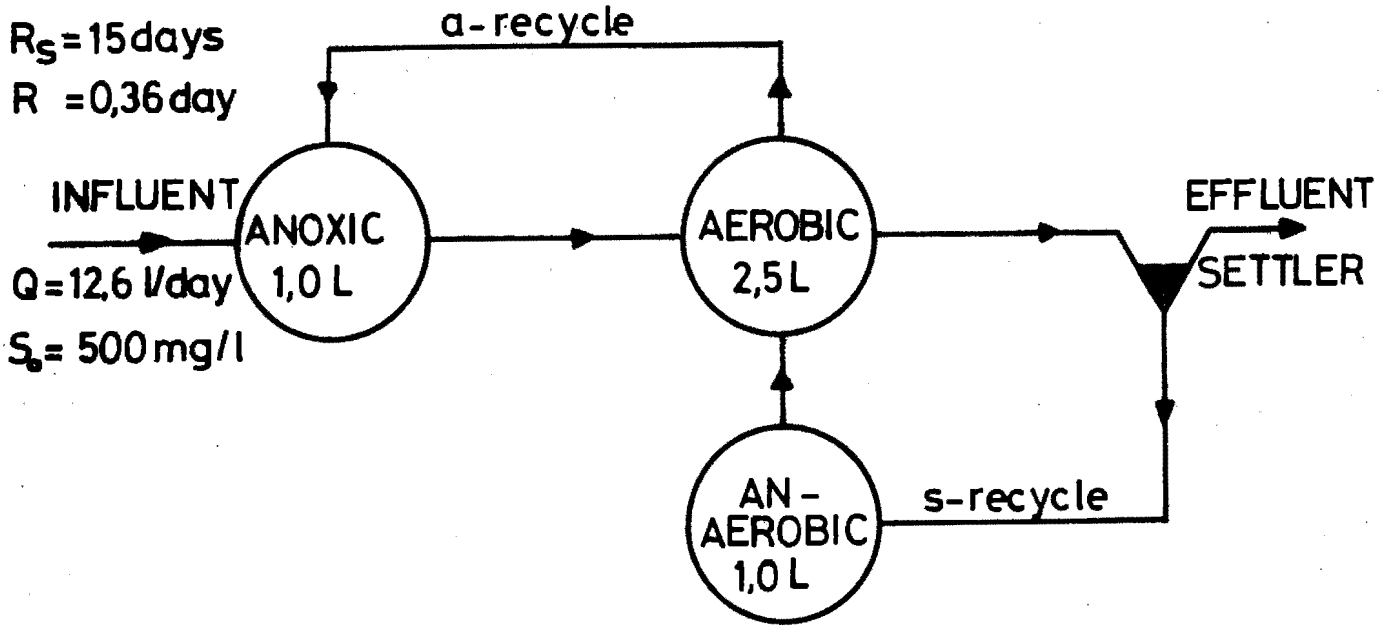
anoxic tank remained the same, indicating that the release of phosphorus in the first anoxic reactor and the uptake of phosphorus in the second anoxic reactor was due to a biological mechanism only.

Although a significant concentration of phosphorus was released in the primary anoxic zone in Experiment 5.6, a subsequent exceptionally high excess uptake of phosphorus was not observed, in fact, the removal was about the same as in previous experiments. This observation tends to indicate that the degree of nett phosphorus release in the

anoxic zone is not a major factor in subsequent excess uptake.

The excess release of phosphorus can be attributed to the low nitrate concentration entering the anoxic zone. It would appear feasible that the reasons for release of phosphorus in the anoxic zone is that the organism requires an energy source both for adsorption and metabolism. If nitrate is present, then it can serve as an electron acceptor to provide energy for the organism and in this way relieve the organism of the need to seek an alternative energy source, i.e. from the conversion of polyphosphate to orthophosphate. The degree to which the organism will be relieved will be proportional to the mass of nitrate actually reduced. (The mass of nitrate reduced is a function of the concentration of active material, the influent COD concentration and the actual anoxic retention time).

From the above experiments it appears that a nett release of phosphorus occurs where the nitrates are less than 1,0 mg/l. However, in plug flow experiments Marsden and Marais (1977) observed that initially there is a sharp disappearance of phosphorus and nitrates in the primary anoxic zone immediately followed by phosphorus release in the presence of nitrates. If the actual anoxic retention time is sufficiently long this eventually manifests itself in the effluent of the plug flow anoxic zone as a nett release of phosphorus with respect to the influent. It can be concluded that the presence of nitrates reduces the pressure on the organisms to release phosphorus for energy. If the nitrates entering the anoxic zone are large it would mean that long actual retention times are necessary for all the organisms to be stressed sufficiently to release phosphorus and trigger off the mechanism for subsequent excess uptake in the aerobic zone. Therefore, the presence of nitrates <u>per se</u> is not the only factor to be taken into account in estimating the stress impact on the organism, but also the actual anoxic retention time.



s = 1 a = 2

Reactors	Nominal Retention Time (hrs)	Actual Retention Time (mins)
Primary Anoxic	1,92	38,0
Secondary Anoxic	1,92	114,0
Aeration	4,76	72,0

s = 1 a = 1

Primary Anoxic	1,92	57,1
Secondary Anoxic	1,92	114,0
Aeration	4,76	95,2

Figure 5.8 *Modified Osborn and Nicholls' configuration with process data*

These remarks tend to go contrary to the direct application of Fuhs and Min Chen's (1975) ideas in that release must be obtained under conditions of no nutrients present and that uptake will take place in the presence of oxygen and high nutrients. In our investigation release was under condition of high nutrient present and uptake took place (in part) under anoxic conditions (Exp. 5.6).

Osborn and Nicholls System

Osborn and Nicholls (1977) propose a system where release of phosphorus is obtained in an anaerobic zone under conditions of no nutrient. They showed that in batch tests phosphorus is released more readily when no nitrates and nutrients are present.

The configuration of Osborn and Nicholls (Fig. 2.3) is different from the Barnard process and it is therefore desirable to test if this configuration also leads to good phosphorus removal when operated with the same sewage and sludge as the previous investigations. The basic experimental objective was to determine if, as suggested by Osborn and Nicholls, release of phosphorus in the anaerobic zone (no nutrients present) has any effect on the phosphorus removal. A configuration similar to the one suggested by Osborn and Nicholls was proposed to investigate the hypothesis that an anaerobic zone with no nutrients present is a prerequisite for biological luxury uptake.

Experiment 5.7:

The configuration together with the process data is shown in Fig. (5.8). This unit was operated with the same design parameters as the unit in Experiment 5.6 except that the configuration was different. In order to obtain the desired anaerobic condition it was necessary to have a long actual retention time in the anaerobic zone (i.e. 2 hours).

Table 5.9: The experimental results for the modified Osborn and Nicholls system

Parameters (Mean values)	Experiment 5.7	Experiment 5.8
COD influent mg/l	521	474
COD effluent mg/l	25,7	26,0
TKN influent mg/l	34,3	34,9
TKN effluent mg/l	0,0	0,0
MLVSS anoxic reactor mg/l	2887	2242
anaerobic reactor mg/l	7414	7695
aerobic reactor mg/l	3964	4008
(NO_3-N) anoxic reactor mg/l	1,3	0,2
anaerobic reactor mg/l	0,9	0,1
pH influent	7,28	7,30
anoxic reactor	7,28	7,32
anaerobic reactor	6,95	6,98
aerobic reactor	7,15	7,13
Ca influent mg/l	41,4	37,5
influent particulate mg/l	9,5	5,9
anoxic reactor mg/l	30,0	29,3
anaerobic reactor mg/l	34,4	33,4
aerobic reactor mg/l	34,4	32,1
(PO_4-P) influent	10,14	9,98
influent particulate mg/l	2,11	2,1
anoxic reactor mg/l	4,21	5,62
anaerobic reactor mg/l	4,92	4,31
aerobic reactor mg/l	3,00	2,93
removed	7,14	7,05
O_2 uptake rate mg/l/hr	50,2	42,7
(NO_3-N aerobic reactor mg/l	6,0	7,8

The unit was operated for about 2 weeks to ensure steady state condition.

The results are given in Table 5.9.

The total removal of phosphorus was 7,14 mg/l, which is about 1,8 mg/l as P less than observed in the other experiments. A system's release of phosphorus occurred in the anaerobic zone of 1,92 mg/l, but an uptake of phosphorus of 3,51 mg/l was observed in the primary anoxic zone. The release of phosphorus in the anaerobic zone can be attributed to the depletion of nitrates and hence the long anoxic retention time, whereas the uptake of phosphorus in the anoxic zone is to be expected as nitrates were still present (i.e. 1,3 mg/l as N).

According to Osborn and Nicholls the release of phosphorus in the anaerobic zone is desirable to trigger off the mechanism for subsequent excess uptake in the aerobic zone. Although this condition prevailed in this experiment the overall removal of phosphorus was less than observed in the modified Barnard process. If the primary anoxic zone, i.e. reactor receiving the influent waste and recycle from the aerobic zone, is the factor influencing the uptake of phosphorus then a larger anoxic retention time is required.

Experiment 5.8:

With regard to the above remarks the process configuration in Experiment 5.7 was continued but the internal recycle was reduced to increase the actual anoxic retention time (see Fig. 5.8). The unit was again operated for about two weeks.

The results are shown in Table 5.9.

No improvement was observed in the total removal of phosphorus,

i.e. 7,05 mg/l. Again a release of phosphorus occurred in the anaerobic zone of 1,38, mg/l, and an uptake of phosphorus in the primary anoxic zone of 1,67 mg/l. In both, the anoxic and aerobic reactor the nitrate concentration was less than 1 mg/l as N. Although the nitrates were less than 1 mg/l in the anoxic zone no release was observed indicating that the organisms need to be longer under stress.

The phosphorus removal in Experiment 5.7 and Experiment 5.8 can also be subdivided as before and compared to the fractions removed in Experiment 5.6 (see Table 5.10).

Table 5.10: Comparison of experimental phosphorus fractions for the modified Barnard and Osborn and Nicholls systems

	(PO_4-P) concentration mg/l			
Experiment	Synthesis	Ca-P Precipitation	Luxury Uptake	Total PO_4-P Removed
5,6	3,0	1,1	4,8	8,9
5,7	2,7	1,8	2,6	7,1
5,8	2,7	1,4	2,9	7,0

A significant decrease in biological luxury uptake was observed which in all probability can be attributed to the high mass of nitrates entering the anoxic zone and also the low active mass present to utilize this as an energy source. It appears that a slightly longer anoxic retention time would have resulted in a biological nett release of phosphorus.

From the results obtained for the Osborn and Nicholls system it would appear that the anaerobic zone (without the

Table 5.11: Steady state results for the modified Barnard process

Parameters (mean values)	Exp. 5.9	Exp. 5.10
COD influent mg/l	479	534
COD effluent mg/l	30,0	31,0
TKN influent mg/l	56,7	43,3
TKN effluent mg/l	6,0	3,1
O_2 uptake rate mg/l/hr	49,3	56,5
MLVSS mg/l	3654	3539
pH influent	7,95	7,61
anoxic reactor 1	7,21	7,38
anoxic reactor 2	7,24	7,38
anoxic reactor 3	7,06	7,28
(NO_3-N) anoxic reactor 1 mg/l	9,9	0,30
anoxic reactor 2 mg/l	8,73	0,30
anoxic reactor 3 mg/l	10,0	0,26
aerobic reactor 4 mg/l	19,5	7,42
Ca influent mg/l	-	-
anoxic reactor 1 mg/l	37,8	27,0
anoxic reactor 2 mg/l	36,6	27,3
aerobic reactor mg/l	31,0	27,6
(PO_4-P) influent mg/l	12,91	8,48
influent particulate mg/l	3,45	3,45
anoxic reactor 1 mg/l	7,48	4,60
anoxic reactor 2 mg/l	7,12	4,92
anoxic reactor 3 mg/l	6,40	5,26
aerobic reactor mg/l	7,31	4,54
removal mg/l	5,60	3,94

presence of nutrients) has no discernible effect on the removal of phosphorus, in fact a decrease in biological luxury uptake was observed. The reason for this behaviour is as yet unknown and needs further experimental investigation to either reject or support the Osborn and Nicholls proposed system.

EFFECT OF NITRATES IN ANOXIC ZONE

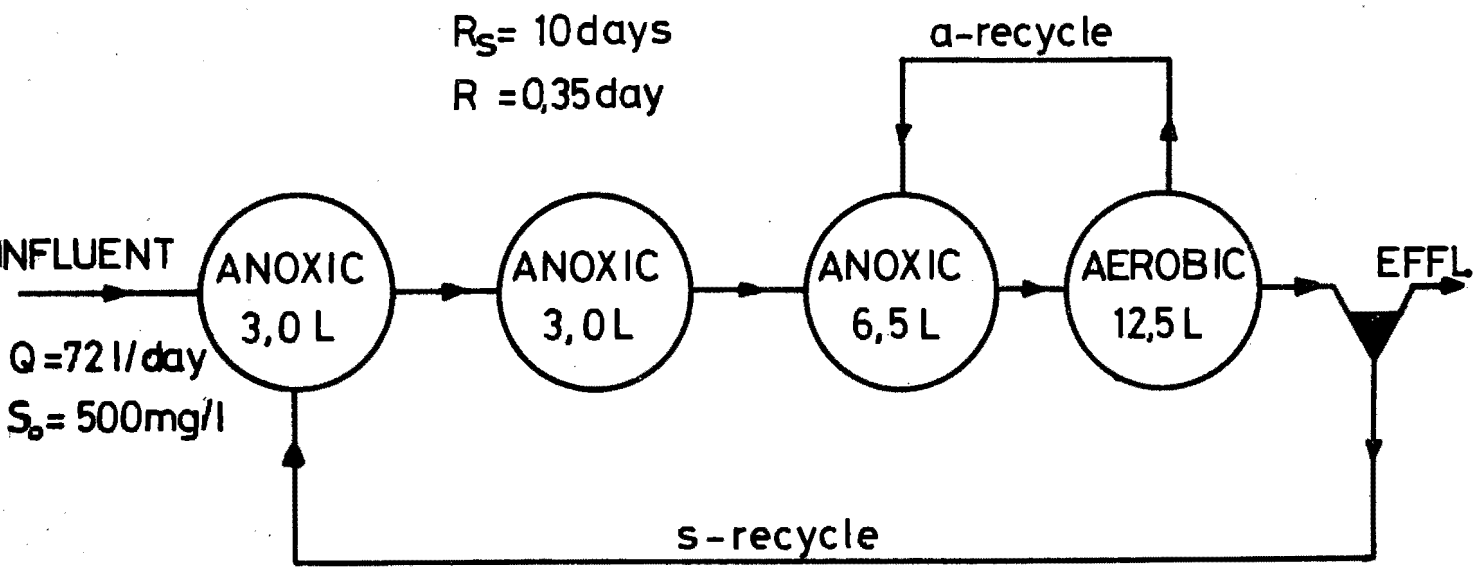
A further series of experiments was subsequently conducted on the modified Barnard process to investigate the effect of nitrates in the anoxic zone. The configuration and process data is shown in Fig. 5.9. A significant variable different from the previous test is the sludge age which was reduced from 15 to 10 days.

For one experiment the unit was run with nitrates present in the anoxic zone and in the second experiment the recycle was changed such that zero nitrates were present in the anoxic zone. The results are shown in Table 5.11.

The results for these experiments are contrary to what has been observed previously. Experiment 5.10 with zero nitrates in the anoxic zone showed poor removal, i.e. 3,94 mg/l, whereas Exp. 5.9 with nitrates present removed more phosphorus (i.e. 5,60 mg/l) than in Experiment 5.10.

The results of Experiments 5.9 and 5.10 indicate that the luxury uptake mechanism does not always work and that the parameters which control the onset and the efficiency of phosphorus removal may not be correctly identified.

The system release and uptake of phosphorus for all the experiments with anoxic/aerobic zones is shown in Table 5.12.



a = 2 s = 2

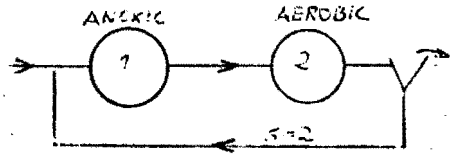
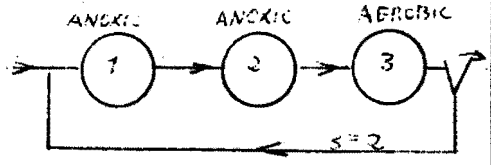
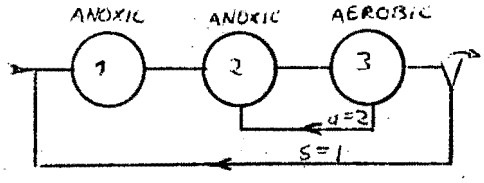
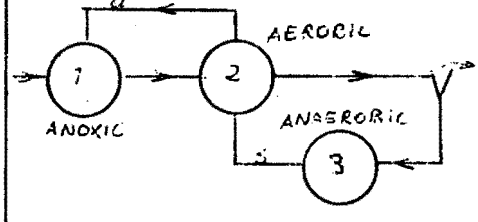
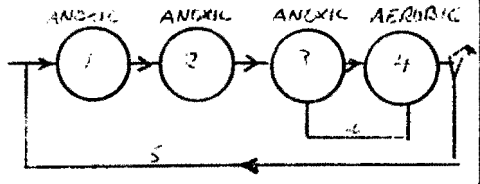
Reactors	Nominal Retention Times (hrs)	Actual Retention Time (mins)
Anoxic 1	1,0	30,0
Anoxic 2	1,0	30,0
Anoxic 3	2,2	32,5
Aerobic	4,2	62,5
TOTAL	8,4	155,0

a = 2 s = 0,5

Reactors	Nominal Retention Time (hrs)	Actual Retention Time (mins)
Anoxic 1	1,0	40,0
Anoxic 2	1,0	40,0
Anoxic 3	2,2	37,0
Aerobic	4,2	71,4
Total	8,4	188,4

Figure 5.9 Configuration and process data of modified Barnard process with nitrates and no nitrates present in the primary anoxic zone

Table 5.12: System's release and uptake of phosphorus by the sludge

Experiment	Reactor 1	Reactor 2	Reactor 3	Reactor 4	Configuration
	PO_4-P mg/l	PO_4-P mg/l	PO_4-P mg/l	PO_4-P mg/l	
5,1	- 5,37	+14,40			
5.2	- 2,16	+11,70			"
5.3	+ 4,26	+ 3,30			"
5.4	- 0,20	- 0,30	+ 9,00		
5.5	- 1,59	- 0,72	+10,72		"
5.6	-16,38	+18,32	+ 6,96		
5.7	+ 3,51	+ 5,55	- 1,92		
5.8	+ 1,61	+ 6,76	- 1,38		
5.9	+ 5,09	+ 1,08	+ 3,98	- 4,55	
5.10	+ 3,85	- 0,48	- 1,95	+ 2,52	

\+ uptake of P by the sludge

\- release of P by the sludge

Previous experiments (i.e. Exps. 5.1 to 5.6) with release of phosphorus in the anoxic zone, showed good overall phosphorus removal. However, Exp. 5.10 with no nitrates present in the anoxic zone and a release of phosphorus in Reactors 2 and 3 showed poor overall removal of phosphorus. This removal of phosphorus was due to (1) the metabolic requirement of the sludge and (2) precipitation of phosphorus; indicating that no excess biological uptake of phosphorus occurred. It appears that either the anoxic retention time is still too short to trigger off the mechanism or that the phosphate storing bacteria are not present to effect subsequent luxury uptake in the aerobic zone.

An explanation for the reduction in excess phosphorus may be that the sludge age of 10 days was too short. Martin and Marais (1975) did report that when they reduced the sludge age to below 10 days the excess biological uptake mechanism suddenly ceased to operate. Perhaps 10 days sludge age is in a region where the process may show signs of instability. If this is indeed correct then Exps. 5.9 and 5.10 were of great importance in contributing to the knowledge regarding limitations to be imposed on the process.

CHAPTER 6

CONCLUSIONS

From the series of batch and continuous activated sludge process experiments conducted in this investigation the following conclusions are made regarding excess phosphorus removal, i.e. removal in excess of the basic biological requirement for metabolic purposes.

Excess phosphorus removal is due to two distinctly definable mechanisms:

1. Precipitation of some form of calcium phosphate;
2. Excess (luxury) biological uptake.

1. Phosphate Precipitation Removal

(a) Precipitation of calcium phosphate is a function of the calcium, phosphorus, pH, organic content and seed crystals in the sludge.

(b) The form of the precipitated crystal has not been identified but it appears that a crystal with a [Ca]/[P] molar ratio of about 3:1, i.e. Ca/P (in mg/l) is 4,1, is formed.

(c) The pH value for precipitation is critical. For pH $\geq$ 7, Ca^{++} = 40 mg/l and P = 10 mg/l, approximately 1,0 to 1,5 mg/l phosphorus can be expected to be removed by precipitation from the influent at pH < 7 precipitation decreases and at about pH = 6,5 and below, the precipitate that has formed will redissolve.

(d) In an activated sludge plant the phosphorus uptake and removal by precipitation can be monitored by measuring the change in Ca^{++} between the total Ca^{++} in the influent and the soluble Ca^{++} in the effluent. The total Ca^{++} in the influent is measured by acidifying the influent sample, filtering it and then measuring the dissolved Ca^{++} in the filtrate. The phosphorus removal, P, is given by -

$$\Delta P = \tfrac{1}{4} \Delta Ca^{++}$$

where ΔP, ΔCa^{++} are the changes in phosphorus and calcium respectively in mg/l.

(e) The fact that precipitation of a calcium mineral takes place at pH = 7,0 further supports the contention that the mineral must be calcium phosphate, since calcium carbonate precipitation only takes place at pH > 9,0.

(f) In the reactors, phosphorus removal or uptake by precipitation is monitored by the removal or uptake of soluble Ca^{++}.

(g) Removal of phosphorus by precipitation is independent of whether the condition is anoxic, anaerobic aerobic, provided the pH $\geq$ about 6,8.

(h) Carbon dioxide has an effect on precipitation only in possibly reducing the pH and thereby causing dissolution of calcium phosphate.

2. Excess (Luxury) Phosphorus Removal

The exact conditions for triggering off the biological removal mechanism is not yet established. There is conclusive evidence that the organism must be placed

in a form of anoxic stress but the condition under which the anoxic stress is created is not yet defined.

(a) Barnard's Hypothesis

One hypothesis is creating the anoxic stress by using a primary anoxic reactor. It receives the recycle sludge from the settling tank together with the influent waste stream. These flows are retained in the primary anoxic reactor, until a net release of phosphorus is observed, i.e. the effluent soluble phosphorus concentration is greater than the average concentration in the influent, due to the total phosphorus in the influent waste stream plus the soluble phosphorus in the recycle stream. The release of phosphorus thus defined is considered a necessary condition (Barnard's Hypothesis) which occurs when no nitrates are present.

(i) With regard to the release in terms of the Barnard Hypothesis, the influent waste stream containing an appreciable percentage of phosphorus in the particulate form which is filtered out when testing for phosphorus. The effluent phosphorus of the anoxic reactor is always tested for soluble phosphorus only. From the work of Marsden and Marais (1977) and Vogelzang and Marais (1977) the soluble phosphorus concentration commences to increase (i.e. phosphorus is released), virtually from the moment the recycle and influent waste enters the anoxic plug flow reactor, so that phosphorus is released to a significant degree long before the condition is satisfied as defined by Barnard.

If release of phosphorus is a necessary requirement then this requirement is virtually always satisfied at actual anoxic retention times greater than about

15 minutes. In terms of Barnard's definition of phosphorus release, at short anoxic retention times, the phosphorus change in the anoxic zone would have been observed as a net uptake of phosphorus whereas in fact considerable release had taken place. This confusion has arisen because of the omission to identify the phosphorus in the particulate matter.

By separating the particulate phosphorus from the soluble phosphorus it is now evident that phosphorus release is always attained in the anoxic reactor and Barnards hypothesis of release becomes irrelevant. It is of course possible that the triggering-off mechanism only operates after a certain concentration of phosphorus release has taken place but not necessarily to the degree required by Barnard. This point of view may have validity as high systems removal of phosphorus has been observed with a short anoxic retention time.

Because the phosphorus removal in the anoxic zone is measured as the difference between a phosphorus concentration containing particulate matter and a soluble phosphorus concentration it is not clear what happens to the particulate phosphorus. From the work of Vogelzang and Marais (1977) it appears that with the short anoxic retention times the particulate phosphorus in the aerobic zone does not solubilise but apparently is retained in some form on or in the sludge. It is evident that somewhere in the system, probably the aerobic zone, it must enter into some metabolic reaction as the particulate stored COD containing the phosphorus is metabolised in the aerobic zone.

(ii) With regard to the requirement that no nitrates must be present in the primary anoxic zone (a postulation of Barnard), although this investigation was

not specifically concerned with nitrate removal it is a most relevant question when attempting to determine the underlying mechanism(s) for phosphorus removal. The evidence on this point is most contradictory as both good and bad systems removal has been observed with nitrates present or no nitrates in the anoxic reactor.

(b) Osborn and Nicholls' Hypothesis

The second hypothesis as to the mechanism of removal of phosphorus is that based on Fuhs and Min Chen's (1975) works and as implemented by Osborn and Nicholls (1977). The basic element in this hypothesis is that the organism must be stressed under anoxic condition with no nutrients and nitrates present. Here again contradictory evidence can be produced.

When the condition triggering off the mechanism is not known, it is difficult to judge why one process removes phosphorus and another apparently similar does not, for it may be in the apparently unimportant dissimilarities that the necessary ingredient for the solution is to be found. The only path open, at this stage of our knowledge, is to consider all the aspects of similarity and dissimilarities between the plants showing good and bad removal and attempt to isolate some factor that may be the vital one.

3. Proposed Hypothesis

The following hypothesis would in a certain measure explain the favourable results obtained by Barnard (1975) and Osborn and Nicholls (1977). In both Barnard's and Osborn and Nicholls' reactor configurations, semi plug flow conditions are established. In Barnard's configuration the reaeration reactor receiving a relatively low recycle is likely to

utilize all the stored COD in the organism, a situation not dissimilar to the condition established in the configuration tested by Osborn and Nichills (1977). Subsequently in both systems the sludges which are virtually in the endogeneous phase are stressed anoxically. In Barnard's configuration this is done in the presence of waste flow nutrients whereas in Osborn and Nicholls' configuration this is done in the absence of influent nutrients. However, it may be that the presence of the influent waste nutrient in the anoxic phase is irrelevant, for, with the long anoxic retention time in the Osborn and Nicholls' system considerable energy is released due to endogenous mass loss; in this fashion equalising in some degree the presence of energy in both systems. Perhaps it is the establishment of the sludge while under aerobic condition in a true endogenous phase before stressing it anoxically (i.e. stressing the organisms aerobically before stressing them anoxically) that triggers off the phosphorus removal mechanism to the maximum degree.

With regard to the nitrates, it seems that zero nitrates are a necessary condition in the primary anoxic zone (or anaerobic zone) as it can serve as an electron acceptor to provide energy for the organism. If the nitrates entering the anoxic zone is large it would mean that long actual retention times are necessary for all the organisms to be stressed sufficiently. The mass of nitrate reduced in the anoxic zone is a function of the concentration of active material in the sludge. The influent COD concentration, COD available due to endogenous mass loss and the actual anoxic retention time.

It would seem that a series of tests to prove or disprove the hypothesis set out above would be worthwhile. No rational hypothesis should be discarded without testing. At present the approach used in design is purely phenomological. Whereas such an approach is most valuable in circumstances where little is known of the mechanism of behaviour it always contains the uncertainty that the plant may not work when the conditions of operation are changed.

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APPENDIX A

EXPERIMENTAL PROCEDURES

This section describes the apparatus, procedures and test methods employed during the experimental studies of both batch and completely mixed continuous flow activated sludge units.

APPARATUS

General layout of an anoxic-aerobic reactor system is shown in Fig. (A.1).

Anoxic reactor

The anoxic reactor was constructed from perspex in accordance with the detailed design in Fig. (A.2). Points to note are the following: Ingress of air and oxygen was prevented by having a sealed cover on the reactor. This was achieved by providing a sealed bearing on the paddle stirrer and an O-ring between the cover and reactor body. The paddle stirrer was driven by a small D.C. brush motor at about 100 rpm. The paddle was simply 2 flat plates on a bush attached to the paddle driving rod by screws. The paddle was located near the bottom of the reactor. The size of the paddle was found by trial and error as it was effected by the speed of rotation. In general it was desirable to have good mixing without too intense turbulence. Mixing was assisted by a mixing vane, half inch in depth glued vertically along the side of the reactor. The vane minimizes vortex formation and improves vertical mixing. The volume of the mixed liquor was regulated by setting

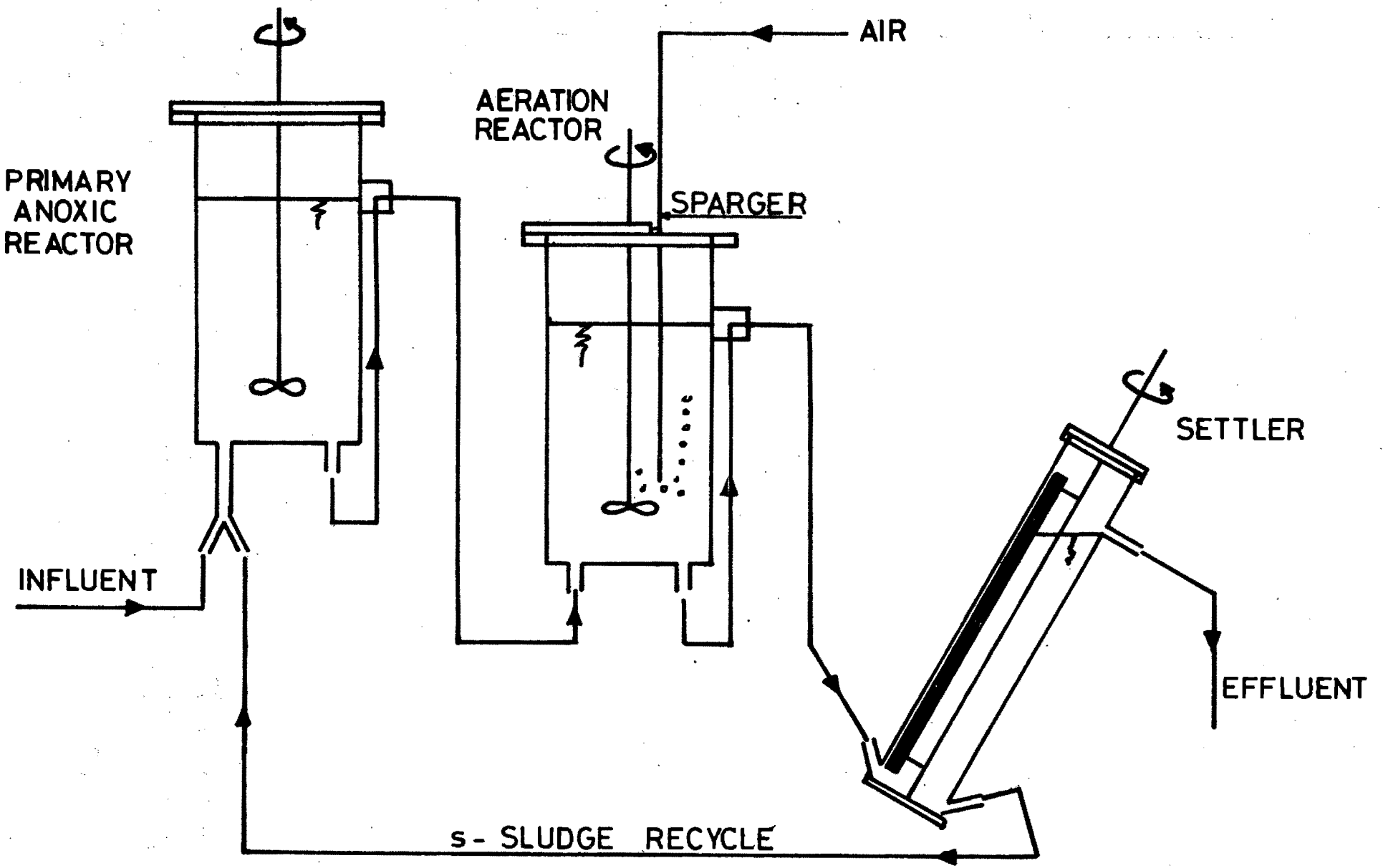

Figure A.1 *General layout of reactor system*

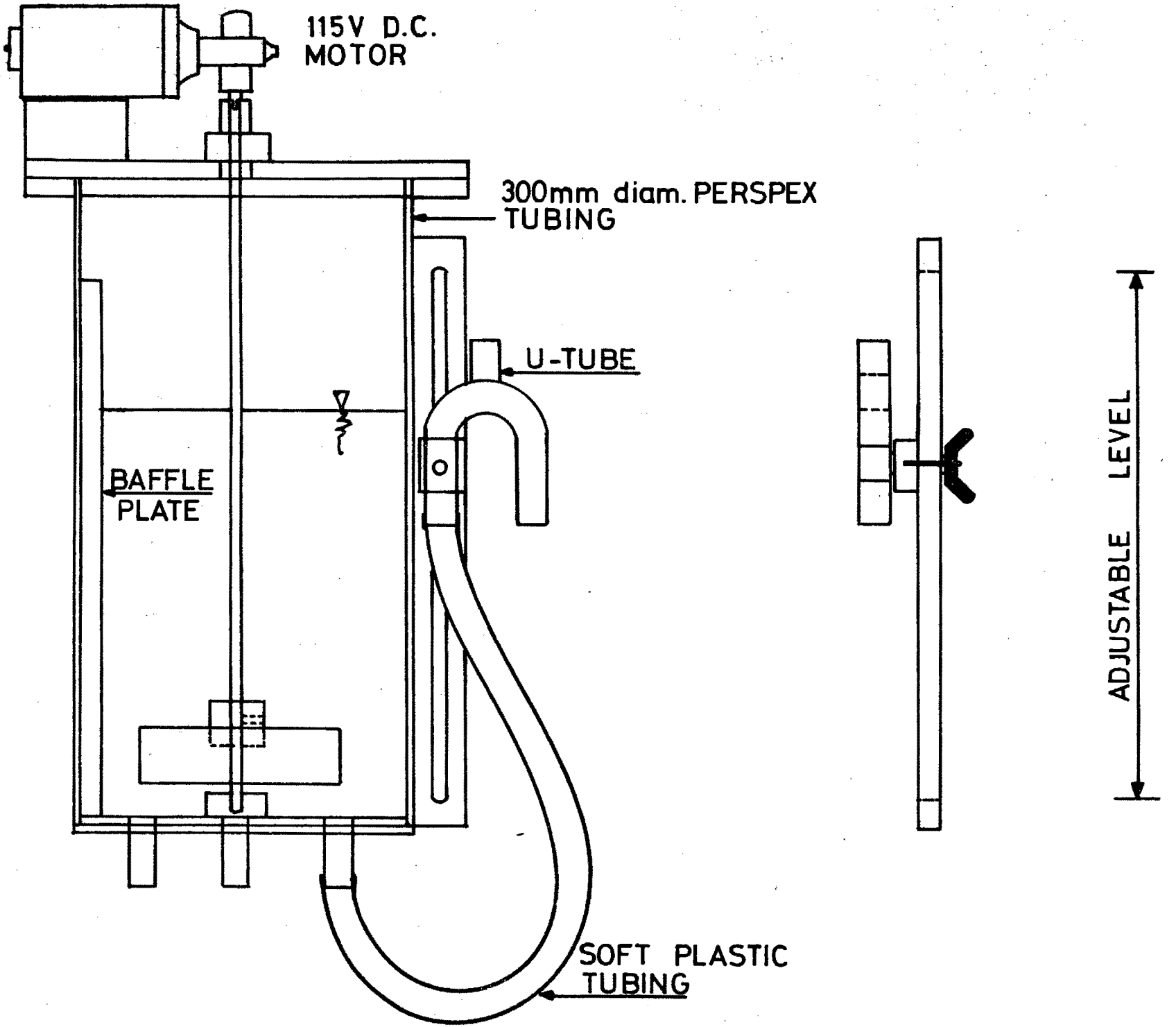

Figure A.2 Design details of activated sludge laboratory scale reactor

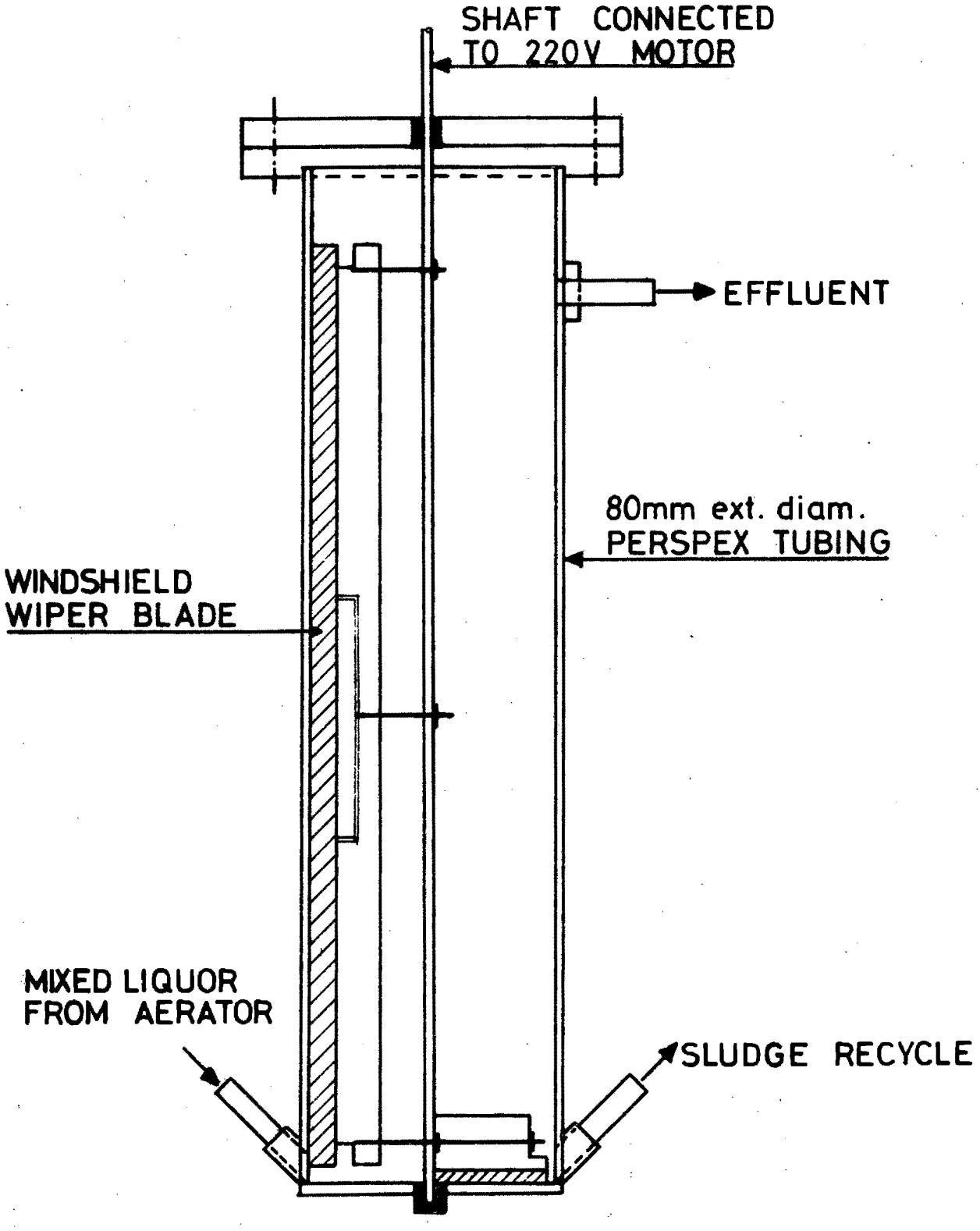

Figure A.3 *Design details of laboratory scale settling tank*

the upper level of the water. This was done by means of an overflow inverted U-tube, which can be set at any level. In the cover an access port was provided for taking samples and pH measurements. The port was sealed by means of a rubber stopper.

Aerobic reactor

The aerobic reactor was of the same basic construction as the anoxic reactor, except that the cover only extends over half the reactor to allow free communication between the liquid and the atmosphere (see Fig. A.2). Aeration was provided by means of a glass fritter attached to a glass tubing clipped to the cover. The fritter could be set at any liquid depth. The air supply was passed through a tank filled with water to humidify the air before it flows to a manifold. The flow was regulated from the manifold to the aeration tube by means of a valve. The flow of air to a reactor was controlled by means of a rotameter.

Settling tank

The design of the settling tank is shown in Fig. (A.3). The settling tank constructed of perspex tubing, inclined at 60^{o} to the horizontal to facilitate solid-liquid separation. The mixed liquor was both introduced and withdrawn at the bottom of the tank. A rubber wiper connected to a motor driven shaft revolved very slowly, preventing sludge adhering to the sides of the tank. The motor was connected to a timer so that every 5 minutes the wiper would operate for 20 seconds.

Tubing and pumps

Soft, transparent plastic tubing was used for all pipelines. The lengths of these lines were kept as short as possible to reduce the residence time. Also the diameters of these

pipelines were chosen such that a high flow velocity was achieved, thereby minimizing biological growth mass in the pipes.

Variable speed peristaltic pumps, manufactured by Scientific Manufacturing Company of Cape Town, were used to regulate the flow rates of the influent feed and the recycles. These pumps were very sensitive to voltage fluctuation and daily adjustment of the flow rates was necessary to ensure a reasonably accurate flow.

OPERATION

The investigation and all the experiments were conducted in an air-conditioned laboratory at $20^{o}C \pm 1^{o}C$.

Unsettled municipal sewage was used as influent to the units throughout the investigation. The sewage was collected in a 1000 l tank at Zeekoevlei Sewage Works. The tank's contents were passed through a macerator and stored at $4^{o}C$ in 200 litre stainless steel tanks. The tanks were filled in pairs by discharging into each tank alternatively to ensure a uniform composition of the sewage in both.

To obtain the strength of the raw sewage, COD tests were conducted on five different samples from the same tank. The COD of the raw sewage generally ranged from 600 - 1200 mg/l. During the winter months the COD was usually of a lower strength $\pm$ 450 mg/l.

Before removing the daily required quantity of sewage from the storage tank, the contents of the tank was thoroughly mixed. The daily influent feed volume to the units (usually two) was prepared from the known COD of the raw sewage by suitably diluting with tap water to the required concentration, usually 500 mg/l. The total volume of

influent feed prepared was equal to the feed requirements plus 500 ml. After thorough mixing of the diluted contents, a 500 ml sample was taken and stored at $4^{o}C$. The remaining volume was then distributed to the influent feed containers, i.e. each unit receiving its required feed volume per day. The influent containers were kept at about $5^{o}C$ to reduce degradation prior to feeding and the contents was continuously stirred by means of a slowly revolving paddle. To prevent aeration, a styreen cover floated on the feed surface.

The feed pumps were calibrated to constantly deliver the required volume of sewage per day. If a pump breakdown occurred during the night, the influent flow was increased in the morning to deliver the required volume per day. If, however, the sewage had a lower COD than desired, the influent volume was increased to deliver the required mass of COD per day. This was achieved by increasing the flow rate.

The units were operated at either 10 days or 15 days sludge age. This was ensured by wasting one-tenth or one-fifteenth of the total mixed liquor volume per day. Sludge was wasted before feeding and for the series tank configuration this was done by drawing off equal amounts from each reactor.

The dissolved oxygen concentrations were kept between 1 - 3 ppm, except where otherwise mentioned, measured and controlled by means of a Yellow Springs oxygen probe.

TEST METHOD

The parameters measured daily on the unfiltered influent, filtered influent, centrifuged samples and the sludge are shown in Table A.1.

Table A.1: Daily tests conducted on the units

Parameter	Unfiltered Influent	Filtered Influent	Sludge	Anoxic Reactor	Aerobic Reactors
PO_4-P mg/l	X	X	X	X	X
Ca mg/l	X	X	X	X	X
pH	X			X	X
COD	X				X
TKN	X				X
NO_3				X	X
NO_2				X	X
MLVSS					X
O_2					X

The test methods for the COD, TKN and MLVSS were in accordance with the methods described in "Standard Methods for the Examination of Water and Wastewater" (1971). The nitrate (NO_3-N) and nitrite (NO_2-N) concentration were measured by the auto-analyzer automated method. The testing procedures followed are given in "Technicon Auto-Analyzer Methodology". The pH was measured with a pH meter, Radiometer Type 29, to an accuracy of 0,05 pH unit.

Total phosphorus concentration was measured using the technique described in the latter part of this Appendix. The concentration of phosphorus in the sludge is very high and

must be reduced to a value between 0 - 25 mg/l in order to fall within the working range of the test. To measure the phosphorus in the sludge the following procedure was followed: a 100 ml mixed liquor sample from the process was centrifuged for 20 minutes at 3000 rpm. The supernatant was discarded and replaced with 1 litre distilled water. The diluted sludge was macerated in a blender for a few minutes, to obtain a uniform sludge concentration, and then tested for total PO_4-P.

Calcium concentration was measured with an Automatic Atomic Adsorption Spectrophotometer manufactured by Varian Tectron (Model 1200). The procedure is outlined in the manufacturer's manual. The instrument is very sensitive to volatile solids in the sample and it was necessary to ensure that the sample was free of particulate matter. To measure the unfiltered sewage and sludge sample for calcium, it was initially thought impossible, but during the latter stages of the experimental investigation the following technique was applied: A few drops of 1N HCl was added to the influent and sludge samples until the pH attained a value of about 2,5. This dissolved any precipitated calcium. The samples were vacuum filtered using a Buchner funnel and diluted with distilled water in the ratio of 1 sample : distilled water as 1 : 50.

At one stage during the investigation the total carbonic alkalinity was measured using a titration method. A 100 ml effluent sample was stirred and titrated against an acid of known normality. Simultaneously to adding the acid the pH was monitored. Noting the volume of acid required to reduce the pH to about 4,3, the total carbonic alkalinity was then calculated.

The oxygen consumption rates were measured using a Yellow Springs Oxygen Probe as follows: The oxygen concentration in the aerobic reactor was raised from the normal operating level of 1 to 3 mg/l to 6 to 8 mg/l by measuring the aeration

rate. Aeration was stopped, and the change in dissolved oxygen concentration against time was recorded for about 6 minutes, while the aeration tank was still being fed and well stirred. The total oxygen consumption rate was given by the slope of line (usually linear) of the dissolved oxygen concentration versus time plot.

PHOSPHORUS BALANCE

As mentioned in the previous section, phosphorus tests were conducted on unfiltered influent, sludge and effluent samples. With these concentrations it was possible to verify the accuracy of the phosphorus determination technique as follows:

$$MP_{in} = MP_{eff} + MP_{sludge}/R_s \qquad \text{mg/day}$$

where

MP_{in} = mass of total influent phosphorus per day, i.e. $P_{in}.Q$

MP_{eff} = mass of total effluent phosphorus per day, i.e. $P_{eff}.Q$

$(MP_{sludge})/R_s$ = mass of total sludge phosphorus in the reactor divided by sludge age to give sludge wastage per day, i.e. $(V.P_{sludge})/R_s$

Figures (A.4) and (A.5) present representative results illustrating the excellent phosphorus balances obtained on the process by the phosphorus determination technique described in this Appendix. Virtually all the phosphorus in the influent is accounted for (99%). These good results were obtained when the total removal of phosphorus in the system was between 3 and 5 mg/l. See Tables (A.1) to (A.4). However, when phosphorus removals were high, $\pm$ 9 mg/l, the

mass per day into the process was greater than the mass out of the process. The discrepancy seems to be in the sludge phosphorus measurement where no significant improvement in the concentration was observed (see Figs. A.6 and A.7). Only 60 - 70% of the total influent phosphorus was accounted for. It is hence of major importance that in the future an investigation is undertaken into the testing procedure for the sludge phosphorus concentration, since the results tend to indicate that the observed anomaly in the phosphorus balance is due to the phosphorus measurement on the sludge.

DETERMINATION OF TOTAL PHOSPHATE PHOSPHORUS USING COLORIMETRIC MOLYBDATE-VANDATE TECHNIQUE

PRINCIPLE OF THE METHOD

In the presence of vanadates, phosphates react with molybdates to form yellow phosphovanadomolybdate. The intensity of this yellow colour, which is proportional to the amount of phosphate present is determined by absorbance using the spectrophotometer. This system obeys BEER'S LAW at a wavelength of 470 u to a concentration of 300 mg/l.

If the sample is coloured by the presence of organic matter, this is removed by the addition of Anhydrous Sodium Carbonate and ashing.

REAGENTS

1. Anhydrous sodium carbonate: (Check the bottle as to the percentage impurity. That for phosphate should not exceed 0,001%. This quantity is negligible).

2. Vanadomolybdate reagent

   Solution A: 20 g of ammonium molybdate tetrahydrate dissolved in 250 ml distilled water

   Solution B: 1 g ammonium metavanadate dissolved in 40 ml nitric acid (conc.) and 200 ml distilled water

   Mix solutions A and B, add 100 ml nitric acid and dilute to 1 000 ml with water (stable for ± 12 months).

3. Solution C: 1 HNO_3 solution

TECHNIQUE

1. The sample is centrifuged or filtered using a Buchner funnel.

2. 25 ml of the sample is measured into a platinum bowl and boiled to dryness (see diagram for method of setting up apparatus). Takes ± 45 minutes.

3. Add ± 1g Anhydrous Sodium Carbonate into the platinum bowl. Heat the Na_2CO_3 in the bowl strongly over a Meaker Bunsen for ± 10 - 15 minutes.* The Na_2CO_3 melts. Using tongs, turn the bowl while heating in the flame to ensure that the Na_2CO_3 comes into contact with all the dried sample. Remove from flame, cool, wash bowl with 1 - 2 ml distilled water, pouring contents into a 25 ml volumetric flask.

4. Add Solution C dropwise to the platinum bowl till effervescence ceases. Transfer this solution to the 25 ml volumetric flask by rinsing bowl with distilled water. Add more HNO_3 to the platinum bowl to ensure complete dissolution of the PO_4-P into the HNO_3 solution and rinse again into the 25 ml volumetric flask. This procedure of adding HNO_3 solution and rinsing with distilled water should be repeated 3 times. No more than 10 mls HNO_3 is usually required.

5. Make up volume to 25 ml.

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* Experience has shown that this time of ± 10 minutes applies more appropriately only when soluble phosphorus is measured. However, when particulate matter is present in the sample the bowls should only be heated for 2 to 3 minutes. It has been observed that too excessive heating reduces the actual phosphorus content of the sample.

6. Into a test tube add 5 ml treated sample and 5 ml Vanadomolybdate reagent. Stand for 10 minutes for colour to develop and read at $\lambda = 470\mu$

(Note: It was found by experiment that colour did not fade even after standing for 24 hours).

A blank is done using 5 ml distilled water plus 5 ml Vanadomolybdate reagent.

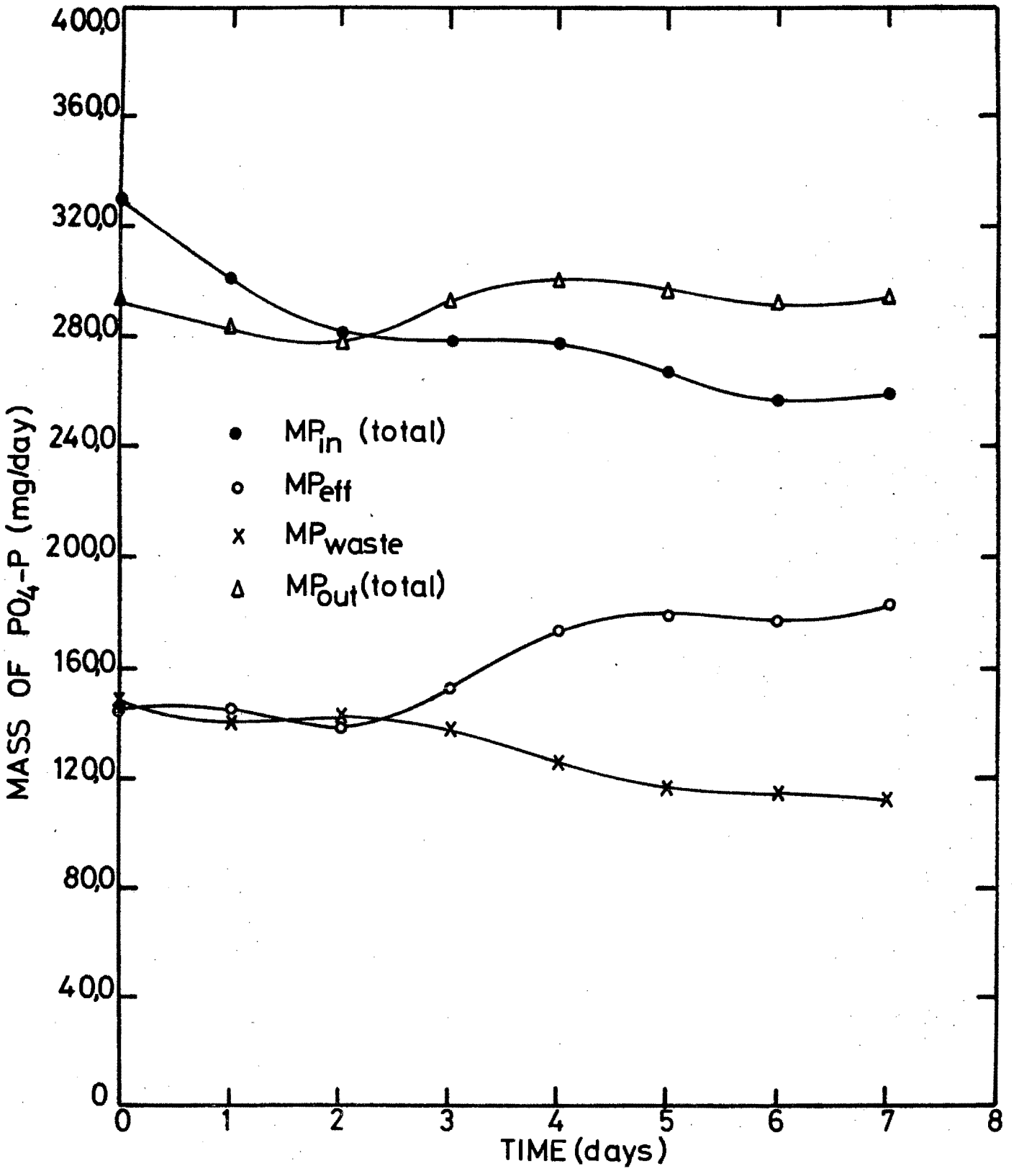

Figure A.5 *As Figure* A.4 *all phosphorus is balanced*

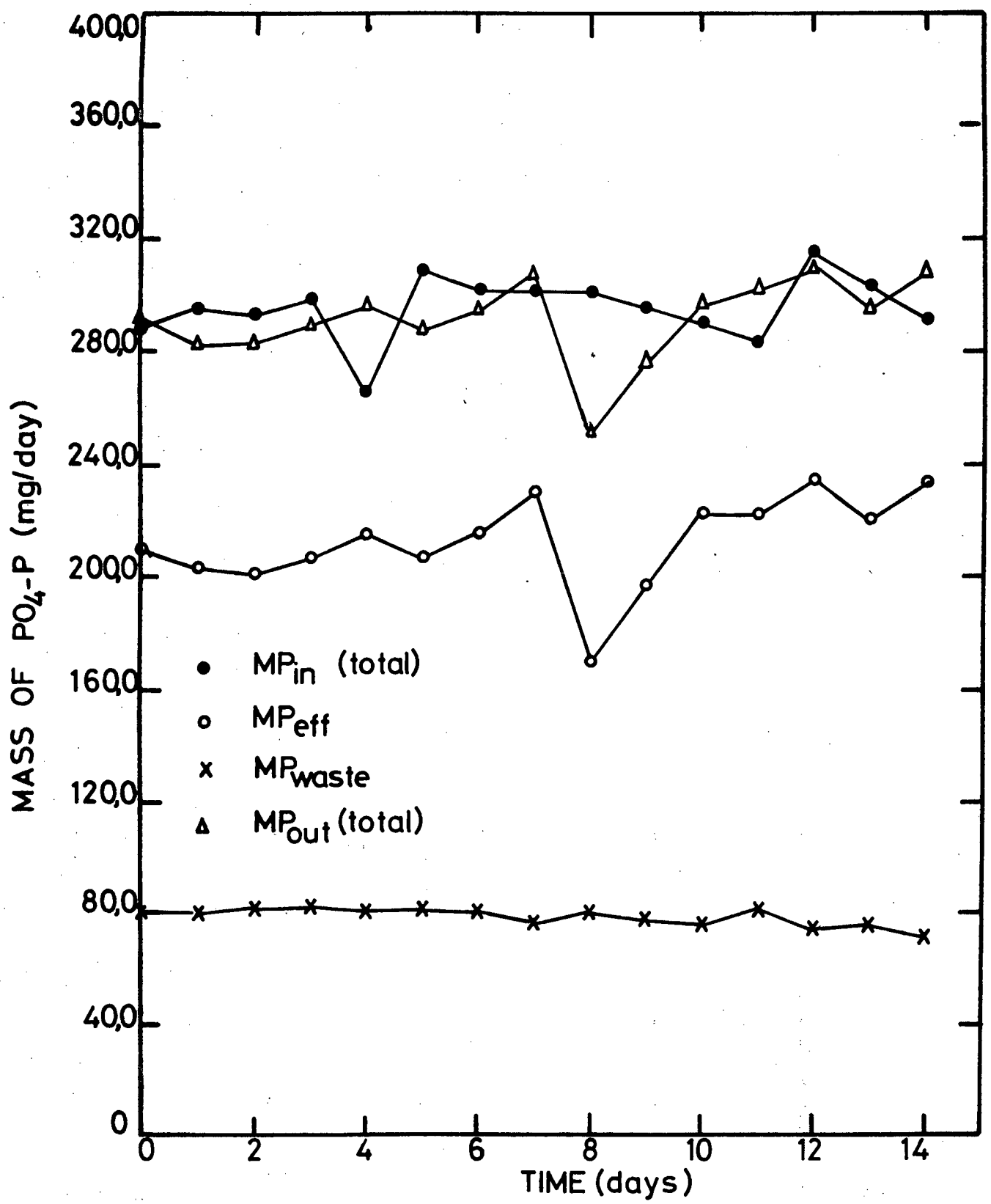

Figure A.4 *Virtually all influent phosphorus is balanced by measuring phosphorus in the waste sludge/day and in effluent*

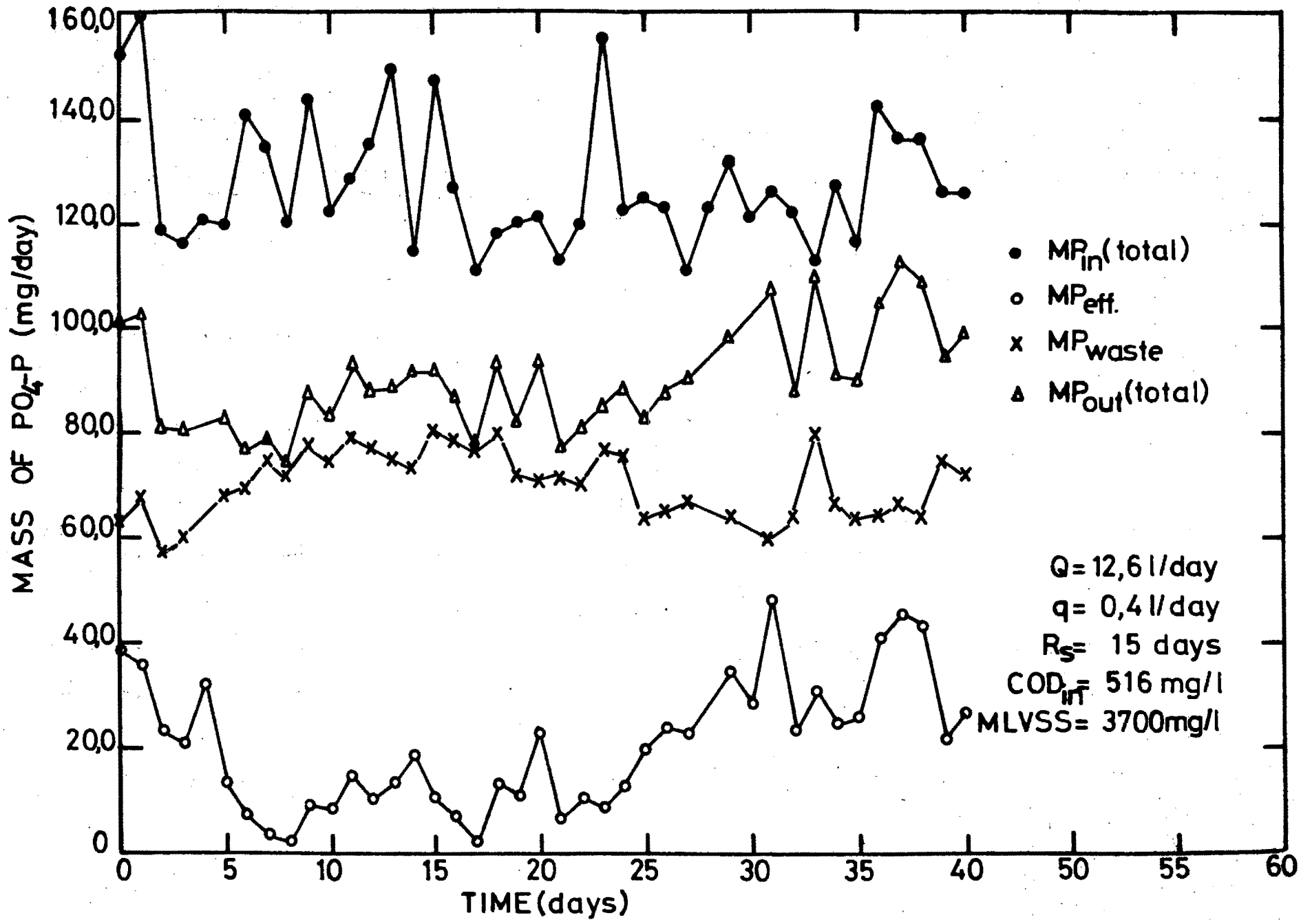

Figure A.6 Only 60 to 70 per cent recovery of total influent phosphorus

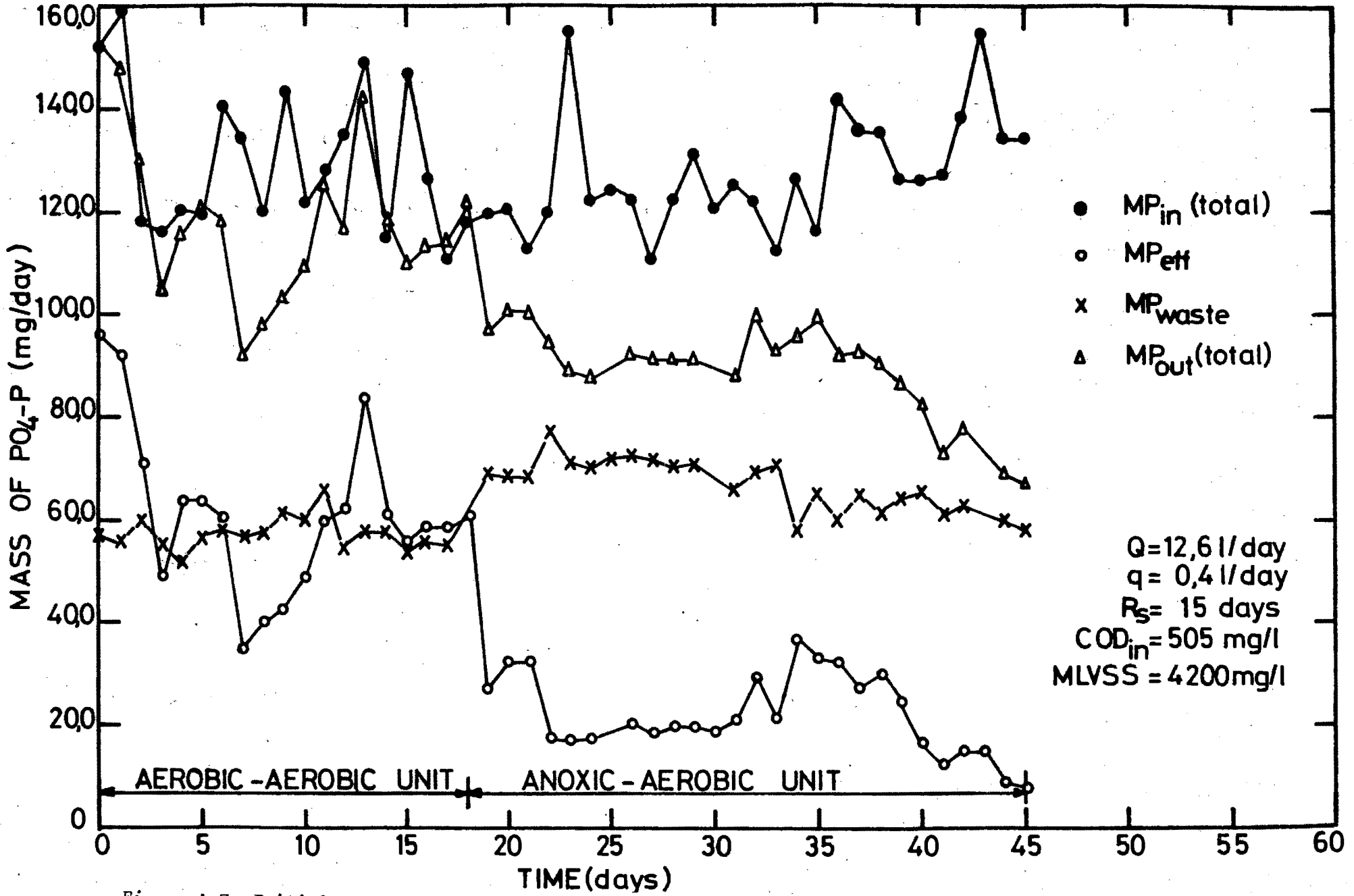

Figure A.7 Initial good phosphorus balance but when system was changed to anoxic-aerobic only 60 to 70 per cent recovery of total influent phosphorus

Table A.1:

	(PO_4-P concentrations in mg/l			
	Total Influent	Effluent	Removal	Sludge
	10,88	4,00	6,88	135,4
	9,66	4,77	4,89	139,9
	10,66	7,22	3,44	122,1
	10,88	7,10	3,78	121,0
	10,55	5,44	5,11	108,8
	10,93	7,44	3,49	113,2
	8,70	5,00	3,70	117,0
	9,10	6,55	2,55	105,5
Average:	10,17	5,94	4,23	120,4

Sludge age = 10 days

Influent flow Q = 36 l/day

sludge wastage = 1,25 litres/day

MLVSS = 3170 mg/l

average (PO_4-P) balance on system:

total MP_{in} = total MP_{out} = (MP_{wasted} + $MP_{effluent}$) mg

MP_{in} = 10,17 * 36 = 366,1 mg/day

$MP_{effluent}$ = 5,94 * 36 = 213,8 mg/day

MP_{waste} = 120,4 * 1,25 = 150,5 mg/day

$\therefore$ MP_{out} = 364,3 mg/day

$\therefore$ $\frac{MP_{out}}{MP_{in}}\%$ = $\frac{364,3}{366,1} * 100$ = 99,4%

Table A.2:

	(PO_4-P) concentrations in mg/l			
	Total Influent	Effluent	Removal	Sludge
	14,1	6,22	7,89	197,6
	12,8	6,22	6,58	185,4
	11,99	5,88	6,11	189,8
	11,88	6,55	5,33	186,4
	11,88	7,44	4,44	167,6
	11,44	7,66	3,78	158,0
	10,99	7,55	3,44	155,4
	11,10	7,77	3,33	152,0
Average:	12,02	6,91	5,11	174,0

sludge age = 10 days

Influent flow Q = 23,5 litres/day

Sludge wastage = 0,75 litres/day

MLVSS = 3840 mg/l

Average (PO_4-P) balance on system:

$$\text{Total } MP_{in} = \text{Total } MP_{out} = (MP_{wasted} + MP_{effluent}) \text{ mg/day}$$

MP_{in} = 12,02 * 23,5 = 282,5 mg/day

MP_{effl} = 6,91 * 23,5 = 162,4 mg/day

MP_{wasted} = 174 * 10,75 = 130,5 mg/day

$\therefore MP_{out} = (162,4 + 130,5) = 292,9$ mg/day

$$\therefore \frac{MP_{out}}{MP_{in}} \% = \frac{292,9}{282,5} * 100 = 103,2\%$$

Table A.3:

	$(PO_4$-P) concentrations in mg/l			
	Total Influent	Effluent	Removal	Sludge
	11,15	8,10	3,05	98,0
	11,40	7,82	3,58	96,5
	11,29	7,75	3,54	99,0
	11,50	7,98	3,52	100,0
	10,15	8,32	1,83	97,2
	11,90	7,98	3,92	97,0
	11,63	8,32	3,31	96,9
	11,63	8,89	2,74	92,8
	11,63	6,50	5,13	97,2
	11,40	7,64	3,76	94,6
	11,17	8,55	2,62	92,3
	10,90	8,53	2,37	98,3
	12,10	9,07	3,03	89,6
	11,66	8,50	3,16	91,8
	11,23	9,07	2,16	88,5
Average:	11,38	8,20	3,18	95,10

Sludge age = 15 days

Influent flow Q = 26 litres/day

Sludge wastage = 0,83 litres day

MLVSS = 2700 mg/l

Average $(PO_4$-P) balance on system

Total MP_{in} = Total MP_{out} = $(MP_{wasted} + MP_{effl})$ mg/day

MP_{in} = (11,38 * 26) = 295,9 mg/day

MP_{eff} = (8,20 * 26) = 213,2 mg/day

$MP_{wastage}$ = (95,1 * 0,83 = 78,9 mg/day

MP_{out} = 292,1 mg/day

$$\frac{MP_{out}}{MP_{in}} \% = \frac{292,1}{295,9} * 100 = 99\%$$

Table A.4:

	(PO_4-P) concentrations in mg/l			
	Total Influent	Effluent	Removal	Sludge
	11,06	8,44	2,62	126,5
	11,51	8,44	3,07	135,6
	12,31	8,66	3,65	130,4
	12,00	7,98	4,02	127,3
	11,86	8,78	3,08	120,6
	12,25	8,55	3,70	115,6
	14,25	9,35	4,90	101,5
	11,4	6,16	5,24	87,8
	11,63	7,41	4,22	109,4
	10,49	8,89	1,60	100,3
	12,31	7,87	4,44	103,7
	12,64	8,64	4,00	106,9
	11,91	8,64	3,27	109,1
	12,0	9,61	2,39	102,6
	11,56	9,40	2,10	105,3
Average:	11,90	8,50	3,49	112,1

Sludge age = 15 days

Influent flow Q = 17 litres/day

Sludge wastage = 0,5 litres/day

MLVSS = 2950 mg/l

Average (PO_4-P) balance on system

$$\text{Total } MP_{in} = \text{Total } MP_{out} = (MP_{wasted} + MP_{eff}) \text{ mg/day}$$

$MP_{in} = (11,9 * 17) = 202,3$ mg/day

$MP_{eff} = (8,5 * 17) = 144,5$ mg/day

$MP_{wasted} = (112,1 * 0,5) = 56,1$ mg/day

$MP_{out} = 200,6$ mg/day

$$\frac{MP_{out}}{MP_{in}} \% = \frac{200,6}{202,3} * 100 = 99,2\%$$

APPENDIX B

Theoretical relationships are developed for plotting the parameters, Alkalinity, pH and calcium for each of the three calcium phosphate minerals (i.e. beta-tricalcium phosphate ($Ca_3(PO_4)_2$), dicalcium phosphate ($CaHPO_4$) and hydroxyapatite ($Ca_5(OH)(PO_4)_3$).

1. Beta Tricalcium Phosphate

Equilibria equation relating each of the parameters Alkalinity, pH and calcium to the co-ordinates X and Y are derived from basic equilibria equations as follows:

Equations for pH lines

$$Y = (Alk - 2Ca) \tag{B.1}$$

From Eq. (3.6)

$$Alk = 3[PO_4^{3-}] + 2[HPO_4^{=}] + [H_2PO_4^{-}] + [OH^{-}] - [H^{+}] \tag{B.2}$$

Substituting (B.2) into (B.1)

$$Y = 3[PO_4^{3-}] + 2[HPO_4^{=}] + [H_2PO_4^{-}] + [OH^{-}] - [H^{+}] - 2[Ca^{++}] \tag{B.3}$$

and $[Ca^{++}]^3 [PO_4^{3-}]^2 = K'_{S1}$

where K'_{S1} is the solubility product for $Ca_3(PO_4)_2$ adjusted for ionic strength effect.

$$[Ca^{++}] = \left(\frac{K'_{S1}}{[PO_4^{3-}]^2} \right)^{\frac{1}{3}} \tag{B.4}$$

From Eq. (A.3)

$$[HPO_4^{=}] = \frac{[H^{+}] [PO_4^{3-}]}{K'_3} \tag{B.5}$$

From Eq. (A.2)

$$[H_2PO_4^-] = \frac{[H^+][HPO_4^=]}{K_2'} \qquad (B.6)$$

Substituting Eq. (B.5) into Eq. (B.6) gives

$$[H_2PO_4^-] = \frac{[H^+]^2[PO_4^{3-}]}{K_3' * K_2'} \qquad (B.7)$$

and from Eq. (A.5)

$$[OH^-] = \frac{K_w'}{[H^+]} \qquad (B.8)$$

Substituting Equations (B.4), (B.5), (B.7) and (B.8) into Eq. (B.3)

$$Y = 3[PO_4^{3-}] + \frac{2[H^+][PO_4^{3-}]}{K_3'} + \frac{[H^+]^2[PO_4^{3-}]}{K_2' * K_3'} + \frac{K_w'}{[H^+]} - [H^+] - 2\left(\frac{K_{S1}'}{[PO_4^{3-}]^2}\right)^{\frac{1}{3}} \qquad (B.9)$$

Also

X = Acidity

i.e. $X = -3[H_3PO_4] - 2[H_2PO_4^=] - [HPO_4^-] + [OH^-] - [H^+]$ (B.10)

From Eq. (A.1)

$$[H_3PO_4] = \frac{[H^+][H_2PO_4^-]}{K_1'} \qquad (B.11)$$

Substituting Eq. (B.7) into Eq. (B.11)

$$[H_3PO_4] = \frac{[H^+]^3[PO_4^{3-}]}{K_1' * K_2' * K_3'} \qquad (B.12)$$

Substituting Eqations (B.5), (B.7), (B.8) and (B.12) into Eq. (B.10)

$$X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+]^3 [PO_4^{3-}]}{K'_1 * K'_2 * K'_3} - \frac{2 * [H^+]^2 [PO_4^{3-}]}{K'_2 * K'_3} - \frac{[H^+][PO_4^{3-}]}{K'_3} \quad (B.13)$$

For a chosen fixed $[H^+]$ (i.e. pH) and a range of values for $[PO_4^{3-}]$ the equation (B.9) in Y has only one real root which can be calculated by an interative method of trial and error. Substituting the value $[PO_4^{3-}]$ obtained in Eq. (B.9) into Eq. (B.13) gives X value corresponding to each Y value.

Plotting these corresponding values of X and Y in Fig. 3.5 traces a line for the selected pH in the equilibrium diagram.

Equations for Calcium Lines

From Eq. (B.4)

$$[PO_4^{3-}] = \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} \quad (B.14)$$

Substituting Eq. (B.14) into (B.9)

$$Y = 3\left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} + \frac{2[H^+]}{K'_3} \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} + \frac{[H^+]^2}{K'_2 * K'_3} \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} + \frac{K'_w}{[H^+]} - [H^+] - 2[Ca^{++}] \quad (B.15$$

and substituting Eq. (B.14) into (B.13)

$$X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+]^3}{K'_1 * K'_2 * K'_3} \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} - \frac{2[H^+]^2}{K'_2 * K'_3} \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} - \frac{[H^+]}{K'_3} \left(\frac{K'_{S1}}{[Ca^{++}]^3} \right)^{\frac{1}{2}} \quad (B.16)$$

For a fixed value of $[Ca^{++}]$ and a range of values for $[H^+]$ Eq. (B.16) has only one real root and can be calculated by an iterative method of trial and error. Substituting $[H^+]$ in Eq. (B.16) into (B.15) gives the corresponding Y values to each X value.

Plotting the corresponding X and Y values traces a line for calcium in the equilibrium diagram.

Equations for Alkalinity Lines

Alkalinity lines plot in the beta tricalcium phosphate diagram with two horizontal sections upper and lower part, joined by a vertical section. The method of solution for the horizontal and vertical section is different and will therefore be considered separately.

(a) Equations for Horizontal Section of Alkalinity Line

From Eq. (B.1)

$$[Ca^{++}] = \frac{(Alk - Y)}{2} \tag{B.17}$$

Substituting Eq. (B.17) into Eq. (B.14)

$$[PO_4^{3-}] = K'_{S1} \frac{2^3}{(Alk - Y)}^{\frac{1}{2}} \tag{B.18}$$

Substituting Eq. (B.18) into (B.13)

$$X = \frac{K'_w}{[H^+]} - \frac{2 * [H^+]^2 K'^{\frac{1}{2}}_{S1}}{K'_2 * K'_3} \left(\frac{2}{(Alk - Y)}\right)^{\frac{1}{6}} - \frac{[H^+] K'^{\frac{1}{2}}_{S1}}{K'_3}$$

$$\left(\frac{2}{(Alk - Y)}\right)^{\frac{1}{6}} - \frac{3 * [H^+] K'^{\frac{1}{2}}_{S1}}{K'_1 * K'_2 * K'_3} \left(\frac{2}{(Alk - Y)}\right)^{\frac{1}{6}} - [H^+] \tag{B.19}$$

From Eq. (B.1)

$$Alk = Y + 2[Ca^{++}]$$

$$= 3[PO_4^{3-}] + \frac{2[H^+][PO_4^{3-}]}{K_3'} + \frac{[H^+]^2[PO_4^{3-}]}{K_2' * K_3'} + \frac{K_w'}{[H^+]} - [H^+] \qquad (B.20)$$

Substituting Eq. (B.18) into (B.20)

$$Alk = 3 * K_{S1}'^{\frac{1}{2}} \left(\frac{2}{(Alk - Y)}\right)^{\frac{1}{6}} + \frac{2[H^+]K_{S1}'^{\frac{1}{2}}}{K_3'} \left(\frac{2}{(Alk - Y)}\right)^{\frac{1}{6}}$$

$$+ \frac{[H^+]^2 K_{S1}'^{\frac{1}{2}}}{K_2' * K_3'} \left(\frac{2}{(Alk-Y)}\right)^{\frac{1}{6}} + \frac{K_w'}{[H^+]} - [H^+] \qquad (B.21)$$

For a fixed value of Alkalinity and a range of values for $[H^+]$, using an iterative trial and error method, Y in Eq. (B.21) can be solved. The value of $[H^+]$ and Y values can then be substituted into Eq. (B.19) to give the X value corresponding to the Y value.

Plotting the corresponding X and Y values traces the horizontal section of the Alkalinity line.

(b) Equations for the Vertical Section of the Alkalinity Curve

From Eq. (B.20)

$$[PO_4^{3-}] = \frac{Alk - \frac{K_w'}{[H^+]} + [H^+]}{3 + \frac{2[H^+]}{K_3'} + \frac{[H^+]^2}{K_2' * K_3'}} \qquad (B.22)$$

From Eq. (B.13)

$$-X = [PO_4^{3-}]\left(\frac{2 * [H^+]^2}{K_2' * K_3'} + \frac{[H^+]}{K_3'} + \frac{3 * [H^+]^3}{K_1' * K_2' * K_3'}\right) + [H^+] - \frac{K_w'}{[H^+]} \quad (B.23)$$

Substituting Eq. (B.22) into (B.23)

$$-X = \left(\left(Alk - \frac{K_w'}{[H^+]} + [H^+]\right)\left(\frac{2[H^+]}{K_2'} + 1 + \frac{3[H^+]^2}{K_1' * K_2'}\right)\Big/ \left(\frac{3 * K_3'}{[H^+]} + \frac{[H^+]}{K_2'} + 2\right)\right) + [H^+] - \frac{K_w'}{[H^+]} \quad (B.24)$$

From Eq. (B.1)

$$Y = Alk - 2[Ca^{++}] \quad (B.25)$$

Substitute (B.5) into (B.25)

$$Y = Alk - 2\left(\frac{K_{S1}'}{[PO_4^{3-}]}\right)^{\frac{1}{3}} \quad (B.26)$$

Substitute Eq. (B.22) into (B.26)

$$Y = Alk - 2.\left(K_{S1}'\left(\left(3 + \frac{2[H^+]}{K_3'} + \frac{[H^+]^2}{K_2' * K_3'}\right)\Big/\left(Alk - \frac{K_w'}{[H^+]} + [H^+]\right)\right)^2\right)^{\frac{1}{3}} \quad (B.27)$$

Eq. (B.24) is in terms of $[H^+]$ Alkalinity and X. For some chosen Alkalinity and a range of values for $[H^+]$, X can be calculated by an iterative method of trial and error. The

corresponding Y value to each X value is calculated from Eq. (B.27) using the $[H^+]$ obtained in the iterative method.

Plotting the corresponding X and Y values the vertical section of the Alkalinity line is thus defined.

The complete Alkalinity line for some fixed Alkalinity value is obtained as follows: the lower horizontal limit of the Alkalinity line is plotted at first using Eqs. (B.19) and (B.21) until the slope of line is greater than 45^o. Eqs. (B.24) and (B.27) are then solved to plot the vertical section of the Alkalinity line until the slope of the line is less than 45^o. The equation defining the lower limit of the Alkalinity line is then used again to plot the upper horizontal section of the Alkalinity line.

Fig. (3.5) shows the complete two phase diagram for the beta tricalcium phosphate mineral.

(2) Dicalcium Phosphate

Equilibria equation relating each of the parameters Alkalinity, pH and calcium to the co-ordinates X and Y are derived from basic equilibria equations as before. The development of equations is very similar to the previous section and only the relevant equations will therefore be given.

Equations for pH lines

$$K'_{S2} = [Ca^{++}]\,[HPO_4^{2-}]$$

$$K'_{S2} = \frac{[Ca^{++}]\,[H^+][PO_4^{3-}]}{K'_3}$$

$$\therefore \quad [Ca^{++}] = \frac{K'_{S2} * K'_{S3}}{[H^+]\,[PO_4^{3-}]} \qquad \text{(B.28)}$$

Note:

K'_{S2} is the solubility product for $CaHPO_4$ adjusted for ionic strength effect.

Substituting Eq. (B.28) into Eq. (B.3)

$$Y = 3[PO_4^{3-}] + \frac{2[H^+][PO_4^{3-}]}{K'_3} + \frac{[H^+]^2[PO_4^{3-}]}{K'_2 * K'_3} + \frac{K'_w}{[H^+]} - [H^+] - \frac{2 * K'_{S2} * K'_3}{[H^+][PO_4^{3-}]} \quad (B.29)$$

$$\text{and } X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+][PO_4^{3-}]}{K'_1 * K'_2 * K'_3} - \frac{2 * [H^+][PO_4^{3-}]}{K'_2 * K'_3} - \frac{[H^+][PO_4^{3-}]}{K'_2} \quad (B.30)$$

For a chosen fixed $[H^+]$ (i.e. pH) and a range of values for $[PO_4^{3-}]$ the equation (B.29) in Y has only one real root which can be calculated by an interative method of trial and error. Substituting the value PO_4^{3-} obtained in Eq. (B.29) into Eq. (B.30) gives X value corresponding to each Y value.

Plotting these corresponding values of X and Y in Fig. 3.6 traces a line for the selected pH in the two phase diagram.

Equations for Calcium Lines

From Eq. (B.28)

$$[PO_4^{3-}] = \frac{K'_{S2} * K'_3}{[Ca^{++}][H^+]} \quad (B.31)$$

Substituting Eq. (B.31) into Eq. (B.29)

$$Y = \frac{3 * K'_{S2} * K'_3}{[Ca^{++}][H^+]} + \frac{2[H^+] K'_{S2}}{[Ca^{++}]} + \frac{H^+ K'_{S2}}{K'_2 [Ca^{++}]} \quad \frac{K'_w}{[H^+]}$$

$$- [H^+] - 2 * [Ca^{++}] \qquad \text{(B.32)}$$

and substituting Eq. (B.31) into Eq. (B.30)

$$X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+]^2 K'_{S2}}{K'_1 * K'_2 [Ca^{++}]} - \frac{2 * [H^+] K'_{S2}}{K'_2 [Ca^{++}]} - \frac{K'_{S2}}{[Ca^{++}]} \qquad \text{(B.33)}$$

For a fixed value of $[Ca^{++}]$ and a range of values for $[H^+]$ Eq. (B.33) has only one real root and can be calculated by an iterative method of trial and error. Substituting $[H^+]$ in Eq. (B.33) into Eq. (B.32) gives the corresponding Y values for each X value.

Plotting the X and Y values in Fig. (3.6) traces a line for Calcium in the Equilibria diagram.

Equations for Alkalinity Lines

Alkalinity lines plot in the dicalcium phosphate diagram with two horizontal sections, upper and lower part, joined by a vertical section.

(a) Equations for Horizontal Section of Alkalinity Line

From Equation (B.1)

$$[Ca^{++}] = \frac{(Alk - Y)}{2} \qquad \text{(B.34)}$$

Substituting Eq. (B.34) into (B.31)

$$[HPO_4^{=}] = \frac{K'_{S2} * 2}{(Alk-Y)} \qquad (B.35)$$

But

$$Alk = 3[PO_4^{3-}] + 2[HPO_4^{=}] + [H_2 PO_4^{-}] + [OH^-] - [H^+] \qquad (B.36)$$

From Eq. (B.5)

$$[PO_4^{3-}] = \frac{[HPO_4^{=}] * K'_3}{[H^+]} \qquad (B.37)$$

From Eq. (B.6)

$$[H_2PO_4^-] = \frac{[H^+][HPO_4^{=}]}{K'_2} \qquad (B.38)$$

Substituting Eqs. (B.36) and (B.37) into Eq. (B.35)

$$Alk = \frac{3 * K'_3 * [HPO_4^{=}]}{[H^+]} + 2[HPO_4^{=}] + \frac{[H^+][HPO_4^{=}]}{K'_2}$$

$$+ [OH^-] - [H^+] \qquad (B.39$$

Substituting Eq. (B.35) into (B.39)

$$Alk = \frac{6 * K'_3 * K'_{S2}}{[H^+]\ (Alk-Y)} + \frac{4 * K'_{S2}}{(Alk-Y)} + \frac{[H^+]\ K'_{S2} * 2}{K'_2\ (Alk-Y)}$$

$$+ \frac{K'_w}{[H^+]} - [H^+]$$

Multiplying both sides by $[H^+]$ and Equating to zero.

$$[H^+]^2\left(\frac{K'_{S2} * 2}{K'_2\ (Alk-Y)} - 1\right) + [H^+]\left(\frac{4 * K'_{S2}}{(Alk-Y)} - Alk\right) + \left(K'_w + \frac{6 * K'_3 * K'_{S2}}{(Alk-Y)}\right) = 0 \qquad (B.40)$$

Also from Eq. (B.10)

$$X = -\frac{3 * [H^+][H^+]\ HPO_4^=}{K'_1 * K'_2} - 2\,[H^+][HPO_4^=] - [HPO_4^=] + \frac{K'_w}{[H^+]} - [H^+] \qquad (B.41)$$

For a chosen value of Alkalinity and assuming a range of values for Y, $[H^+]$ has only one real root in Equation (B.40). Substituting the $[H^+]$ value obtained into Eq. (B.41) gives X value corresponding to Y value.

Plotting the corresponding X and Y values traces the horizontal section of the Alkalinity line.

(b) Equations for the Vertical Section of the Alkalinity Curve

From Eq. (B.24)

$$-X = \left(\left(Alk - \frac{K'_w}{[H^+]} + H^+\right)\left(\frac{2[H^+]}{K'_2} + 1 + \frac{3[H^+]^2}{K'_1 * K'_2}\right)\Big/ \left(\frac{3 * K'_3}{[H^+]} + \frac{[H^+]}{K'_2} + 2\right)\right) + [H^+] - \frac{K'_w}{[H^+]} \qquad (B.42)$$

Substituting Eq. (B.22) into (B.28)

$$[Ca^{++}] = \frac{K'_{S2} * K'_3}{[H^+]}\left(\frac{3 + \frac{2[H^+]}{K'_3} + \frac{[H^+]^2}{K'_2 * K'_3}}{Alk - \frac{K'_w}{[H^+]} + [H^+]}\right) \qquad (B.43)$$

But $Y = Alk - 2Ca$ (B.44)

Substituting Eq. (B.43) into Eq. (B.44)

$$Y = Alk - \frac{2 * K'_{S2} * K'_3}{[H^+]} \left(3 + \frac{2[H^+]}{K'_3} + \frac{[H^+]^2}{K'_2 * K'_3} \right) \Bigg/ \left(Alk - \frac{K'_w}{[H^+]} + [H^+] \right) \quad \text{(B.45)}$$

For some chosen Alkalinity and a range of values for $[H^+]$ X in Eq. (B.42) can be calculated by an iterative method of trial and error. The corresponding Y to each X value is calculated from Eq. (B.45) using the $[H^+]$ obtained in the interative method.

Plotting the corresponding X and Y values, the vertical section of the Alkalinity line is thus defined.

The complete Alkalinity line for some fixed Alkalinity value is obtained as follows: The lower horizontal limit of the Alkalinity line is plotted at first using Eqs. (B.40) and (B.41) until the slope of line is greater than 45^o. Eqs. (B.42) and (B.45) are then solved to plot the vertical section of the Alkalinity line until the slope of the line is less than 45^o. Eqs. (B.40) and (B.41) are then used again to plot the upper horizontal section of the Alkalinity line.

Fig. 3.6 shows the complete two phase diagram for the dicalcium phosphate mineral.

(3) Hydroxyapatite

The equilibria equations relating each of the parameters Alkalinity, pH and calcium to the co-ordinates X and Y are as follows:

Equations for pH lines

$$K^*_{S3} = [Ca^{++}]^5 * [OH^-] * [PO_4^{3-}]^3 \qquad (B.46)$$

where K'_{S3} is the solubility product for hydroxyapatite ($Ca(OH)(PO_4)_3$) adjusted for ionic strength effect.

From Eq. (B.46)

$$[Ca^{++}] = \left(\frac{K'_{S3}\ [H^+]}{K'_w\ [PO_4^{3-}]^3} \right)^{\frac{1}{5}} \qquad (B.47)$$

Substituting Eq. (B.47) into Eq. (B.3)

$$Y = 3[PO_4^{3-}] + \frac{2[H^+]\ [PO_4^{3-}]}{K'_3} + \frac{3[H^+]\ [PO_4^{3-}]}{K'_2 * K'_3} + \frac{K'_w}{[H^+]}$$

$$+ [H^+] - 2 * \left(\frac{K'_{S3}\ [H^+]}{K'_w\ [PO_4^{3-}]^3} \right)^{\frac{1}{5}} \qquad (B48)$$

From Eq. (B.30)

$$X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+]^3 [PO_4^{3-}]}{K'_1 * K'_2 * K'_3} - \frac{2 * [H^+]^2 [PO]_4^{3-}}{K'_2 * K'_3}$$

$$- \frac{[H^+][PO_4^{3-}]}{K'_3} \qquad (B.49)$$

For a chosen fixed $[H^+]$ (i.e. pH) value and a range of Y values, using a trial and error iterative method, Equation (B.48) in $[PO_4^{3-}]$ has only one real root. Substituting the $[PO_4^{3-}]$ value into Equation (B.49) gives X value corresponding to each Y value.

Plotting these corresponding values of X and Y in Fig. traces a line for the selected pH in the equilibrium diagram.

Equations for Plotting Calcium Lines

From Eq. (B.47)

$$[PO_4^{3-}] = \left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}} \qquad \text{(B.50)}$$

Substituting Eq. (B.50) into Eq. (B.49)

$$X = \frac{K'_w}{[H^+]} - [H^+] - \frac{3 * [H^+]^3}{K'_1 * K'_2 * K'_3} \left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}}$$

$$- \frac{2 * [H^+]^2}{K'_2 * K'_3} \left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}} - \frac{[H^+]}{K'_3} \left(\frac{K'_{S3}\,[H^+]}{K'_w [Ca^{++}]^5} \right)^{\frac{1}{3}} \qquad \text{(B.51)}$$

and substituting Eq. (B.50) into Eq. (B.48)

$$Y = 3\left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}} + \frac{2[H^+]}{K'_3} \left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}}$$

$$+ \frac{3[H^+]^2}{K'_2 * K'_3} \left(\frac{K'_{S3}\,[H^+]}{K'_w\,[Ca^{++}]^5} \right)^{\frac{1}{3}} + \frac{K'_w}{[H^+]} - [H^+] - 2[Ca^{++}] \qquad \text{(B.52)}$$

For a chosen fixed value of $[Ca^{++}]$ and a range of values for X, Eq. (B.51) in $[H^+]$ has only one real root which can be calculated using an iterative method of trial and error. Substituting the $[H^+]$ value into equation (B.52) gives Y value corresponding to each X value.

Plotting these corresponding values of X and Y in Fig. 3.7 traces a line for the selected $[Ca^{++}]$ in the two phase equilibrium diagram.

Equations for Alkalinity Lines

Alkalinity curves plot in the hydroxyapatite diagram with two horizontal sections upper and lower part, joined by a vertical section.

(a) Equations for Horizontal Section of Alkalinity Line

From Eq. (B.1)

$$[Ca^{++}] = \frac{Alk - Y}{2} \tag{B.53}$$

Substituting Eq. (B.53) into Eq. (B.50)

$$[PO_4^{3-}] = \left(\frac{K'_{S3}\,[H^+]}{K'_w \left(\frac{Alk-Y}{2}\right)^5} \right)^{\frac{1}{3}} \tag{B.54}$$

Substituting Eq. (B.54) into Eq. (B.20)

$$Alk = 3\left(\frac{K'_{S3}\,[H^+]}{K'_w \left(\frac{Alk-Y}{2}\right)^5} \right)^{\frac{1}{3}} + \frac{2[H^+]}{K'_3}\left(\frac{K'_{S3}[H^+]}{K'_w \left(\frac{Alk-Y}{2}\right)^5} \right)^{\frac{1}{3}}$$

$$+ \frac{[H^+]^2}{K'_2 * K'_3}\left(\frac{K'_{S3}\,[H^+]}{K'_w \left(\frac{Alk-Y}{2}\right)^5} \right)^{\frac{1}{3}} + \frac{K'_w}{[H^+]} - [H^+] \tag{B.55}$$

From Eq. (B.49)

$$-X = [PO_4^{3-}]\left(\frac{2 * [H^+]^2}{K_2' * K_3'} + \frac{[H^+]}{K_3'} + \frac{3[H^+]^3}{K_1' * K_2' * K_3'}\right) + [H^+] - \frac{K_w'}{[H^+]} \quad \text{(B.56)}$$

Substituting Eq. (B.54) into Eq. (B.56)

$$-X = \left(\frac{K_{S3}' [H^+]}{K_w' \left(\frac{Alk-Y}{2}\right)^5}\right)^{\frac{1}{3}} \left(\frac{2 * [H^+]^2}{K_2' * K_3'} + \frac{[H^+]}{K_3'} + \frac{3 [H^+]^3}{K_1' * K_2' * K_3'}\right)$$

$$+ [H^+] - \frac{K_w'}{[H^+]} \quad \text{(B.57)}$$

For a chosen Alkalinity value and a series of $[H^+]$ values, Eq. (B.55) in Y has one real root. The Y and $[H^+]$ values obtained in Eq. (B.55) can then be substituted into Eq. (B.57) to calculate the corresponding X value. Plotting the corresponding X and Y values gives a trace of the horizontal sections of the Alkalinity line in the diagram.

(b) Equations for Plotting the Vertical Section of the Alkalinity Line

From Eq. (B.24)

$$-X = \left(\left(Alk - \frac{K_w'}{[H^+]} + [H^+]\right)\left(\frac{2[H^+]}{K_2'} + 1 + \frac{3[H^+]^2}{K_1' * K_2'}\right) \Big/ \left(\frac{3 * K_3'}{[H^+]} + \frac{[H^+]}{K_2'} + 2\right)\right) + [H^+] - \frac{K_w'}{[H^+]} \quad \text{(B.58)}$$

Substituting Eq. (B.47) into Eq. (B.53) and re-arranging:

$$Y = Alk - 2\left(\frac{K'_{S3}}{K'_w}\,\frac{[H^+]}{[PO_4^{3-}]^3}\right)^{\frac{1}{5}} \qquad (B.59)$$

Substituting Eq. (B.22) into Eq. (B.59)

$$Y = Alk - 2\left(\frac{K'_{S3}[H^+]}{K'_w}\left(\frac{3 + \frac{2[H^+]}{K'_3} + \frac{[H^+]^2}{K'_2 * K'_3}}{Alk - \frac{K'_w}{[H^+]} + [H^+]}\right)^3\right)^{\frac{1}{5}} \qquad (B.60)$$

For a fixed chosen value of Alkalinity, X is solved for series of values $[H^+]$ in Eq. (B.58). The Y value corresponding to each X value is calculated from Eq. (B.60). Plotting the corresponding X and Y values traces the vertical section of an Alkalinity line in the hydroxyapatite diagram.

The complete Alkalinity line for some fixed Alkalinity value is plotted in the diagram as follows: the lower horizontal limb is plotted at first using Eqs. (B.5)) and (B.57) until the slope of the line is less than 45^o. Eqs. (B.58) and (B.60) are then solved to plot the vertical section of the Alkalinity line until the slope of the line is less than 45^o. The equation for the horizontal section of the Alkalinity line is then again used to trace the upper horizontal limb of the Alkalinity line.

Fig. (3.7) shows the complete two phase equilibrium diagram for the hydroxyapatite mineral.

APPENDIX C

DETERMINATION OF SOLUBILITY PRODUCT FOR A CALCIUM PHOSPHATE MINERAL

Considering single aquous phase equilibrium between phosphoric acid species, the following equilibrium and mass balance equations must be satisfied:

Equilibrium Equations

$$[H^+][H_2PO_4^-] / [H_3PO_4] = K_1' \quad (C.1)$$

$$[H^+][HPO_4^{=}] / [H_2PO_4^-] = K_2' \quad (C.2)$$

$$[H^+][PO_4^{3-}] / [HPO_4^{=}] = K_3' \quad (C.3)$$

$$[Ca^{++}]_F[HPO_4^{=}]/[CaHPO_4^{o}] = K_4' \quad (C.4)$$

$$[H^+][OH^-] = K_w' \quad (C.5)$$

Mass Balance Equation

$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{=}] + [PO_4^{3-}] + [CaHPO_4] \quad (C.6)$$

$$Ca_T = [Ca^{++}]_F + [CaHPO_4^{o}] \quad (c.7)$$

and if pH measured

$$pH = - \log_{10} (H^+) \quad (C.8)$$

Subscripts 'T' and 'F' refer to total and free ion species concentrations respectively

[ ] indicates molar concentration.
( ) indicates activities.
K' indicates an equilibrium constant which has been adjusted for ionic strength effects.

Equations (C.1) to (C.8) are eight equations with eight unknowns ($[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^=]$, $[PO_4^{3-}]$, $[Ca^{++}]_F$, $[CaHPO_4^o]$, $[H^+]$ and $[OH^-]$), the parameters pH, Ca_T and P_T can be measured. These eight equations are solved by numerical iteration using a digital computer. The values determined for $[Ca^{++}]_F$, $[PO_4^{3-}]$ and $[HPO_4^=]$ are then used together with the measured values for ionic strength, to calculate the solubility products for $Ca_3(PO_4)_2$ and $CaHPO_4$, i.e.

$$(f_d\ [Ca^{++}])^3\ (f_t\ [PO_4^{3-}])^2 = K_{s1}$$

$$(f_d\ [Ca^{++}])\ (f_d\ [HPO_4^=]) = K_{s2}$$

where f_d and f_t are di and trivalent activity coefficients.

APPENDIX D

PROGRAMME FOR SINGLE PHASE PHOSPHORIC SYSTEM

```
C*********************************************************
C PROGRAM PLOTS SINGLE PHASE
C PHOSPHORIC-SYSTEM DIAGRAM
C*********************************************************
      REAL K1,K2,K3,KW
      DIMENSION ACID(500),ALK(500),PH(50)
C*********************************************************
C FIRST DATA CARD:DIAGRAM LIMITS
      READ(5,10)ALKMAX,ALKMIN,ACIMAX,ACIMIN
   10 FORMAT()
C WHERE:ALKMAX:MAX(ALKALINITY)
C       ALKMIN:MIN(ALKALINITY)
C       ACIMAX:MAX(ACIDITY)
C       ACIMIN:MIN(ACIDITY)
C*********************************************************
C SECOND DATA CARD:NO.OF PH VALUES
      READ(5,15)NPH
   15 FORMAT(I2)
C*********************************************************
C THIRD DATA CARD:IONIC STRENGTH=U;TEMP(DEGC)=T
      READ(5,20)U,T
   20 FORMAT(2F10.4)
C*********************************************************
C DATA CARDS FOR PH VALUES
      DO 30 I=1,NPH
      READ(5,25)PH(I)
   25 FORMAT(F10.4)
   30 CONTINUE
C*********************************************************
C EQUILIBRIUM CONSTANTS
      PK1=2.14
      PK2=7.20
      PK3=12.35
      PKW=14.0
C*********************************************************
C CALCULATING MONO,DI+TRI VALENT ACTIVITY FACTORS
C USING DAVIES EQUATION
      U1=U**0.5
      A=(U1/(1+U1))-0.2*U
      FM=0.5*A
      FM=1./(10.**FM)
      FD=2.*A
      FD=1./(10.**FD)
      FT=4.5*A
      FT=1./(10.**FT)
C*********************************************************
C CONVERT PK VALUES TO K VALUES
      K1=(1./(10.**PK1))*1000.
      K2=(1./(10.**PK2))*1000.
      K3=(1./(10.**PK3))*1000.
      KW=(1./(10.**PKW))*10.**6.
C*********************************************************
C CONVERT K VALUES TO ACCOUNT FOR ACTIVITY
      K1=K1/(FM**2.)
      K2=K2/FD
      K3=K3*FD/(FM*FT)
C*********************************************************
C PLOT DIAGRAM OUTLINE
      SC=24.
```

```
      CALL SCALF(SC,SC,-0.5,-0.75)
      NTMX=(ACIMAX-ACIMIN)/0.1
      NTMY=(ALKMAX-ALKMIN)/0.1
      CALL FGRID(0,ACIMIN,-ALKMAX,0.1,NTMX)
      CALL FGRID(1,ACIMAX,-ALKMAX,0.1,NTMY)
      CALL FGRID(2,ACIMAX,-ALKMIN,0.1,NTMX)
      CALL FGRID(3,ACIMIN,-ALKMIN,0.1,NTMY)
C     ******************************************************
C     CALCULATES PH LINES AND PLOTS THEM
      CALL PLTIME (25)
      LL=0
      DO 200 I=1,NPH
      PHH=PH(I)
      H=((1./(10.**PHH))/FM)*1000.
      OH=KW/H
      JJ=1
      IF(LL-1)40,110,110
40    ACID(1)=ACIMAX
      DO 80 J=1,500
      ALK(J)=(ACID(J)-H+OH)*(3.*K3/H+2.+H/K2)/((3.*H**2.)/(K1*K2)+2.*H/K
     .2+1.)+OH-H
      IF(ALK(J)-ALKMAX)50,50,110
50    IF(ALK(J)-ALKMIN)90,90,60
60    IF(ACID(J)-ACIMIN)90,90,70
70    ACID(J+1)=ACID(J)-0.01
      JJ=JJ+1
80    CONTINUE
90    CALL FPLOT(3,ACID(1),-ALK(1))
      JJ=JJ-1
      DO 100 J=1,JJ
      CALL FPLOT(2,ACID(J),-ALK(J))
100   CONTINUE
      GO TO 200
110   ALK(1)=ALKMAX
      LL=1
      DO 190 J=1,500
      ACID(J)=(ALK(J)-OH+H)*((3.*H**2.)/(K1*K2)+(2.*H/K2)+1.)/(3.*K3/H+2.+H/K2
     .+H/K2)+H-OH
      IF(ACID(J)-ACIMIN)191,191,120
120   IF(ALK(J)-ALKMIN)191,191,180
180   JJ=JJ+1
      ALK(J+1)=ALK(J)-0.01
190   CONTINUE
191   CALL FPLOT(3,ACID(1),-ALK(1))
      JJ=JJ-1
      DO 193 J=1,JJ
      CALL FPLOT(2,ACID(J),-ALK(J))
193   CONTINUE
200   CONTINUE
      CALL PEND(2.5,-2.5)
      STOP
      END
```

APPENDIX E

PROGRAMMES FOR PLOTTING THE THREE CALCIUM PHOSPHATE MINERALS

1. Beta tricalcium phosphate
2. Hydroxyapatite
3. Dicalcium phosphate

```
C     ******************************************************
C     PROGRAM PLOTS THE DIAGRAM FOR
C     BETA-TRI CALCIUM PHOPHATE-(CA)3(PO4)2
C     ******************************************************
      REAL KW,K1,K2,K3,KS,MAXAMC,MINAMC,MAXACD,MINACD
      DOUBLE PRECISION PO4,FRACT,H,Y,C,A,AL
      DIMENSION PH(50),ALK(50),CAA(50),ACID(3000),AMC(3000)
C     ******************************************************
C     FIRST DATA CARD:DIAGRAM LIMITS
      READ(8,7)MAXACD,MINACD,MAXAMC,MINAMC
    7 FORMAT(4F10.3)
C     WHERE:MAXACD=POSITIVE(ACIDITY)
C           MINACD=NEGATIVE(ACIDITY)
C           MAXAMC=MAX(ALK-2CA)
C           MINAMC=MIN(ALK-2CA)
C     ******************************************************
C     SECOND DATA CARD:NO.OF PH,ALK AND CA VALUES
      READ(8,4)NPH,NA,NC
    4 FORMAT(3I2)
C     ******************************************************
C     THIRD DATA CARD:IONIC STRENGTH
      READ(8,6)U
    6 FORMAT(F10.4)
C     ******************************************************
C     DATA CARDS FOR PH VALUES
      DO 10 I=1,NPH
      READ(8,9)PH(I)
    9 FORMAT(F10.4)
   10 CONTINUE
C     ******************************************************
C     DATA CARDS FOR ALK. VALUES
C     IN ASCENDING ORDER
      DO 20 I=1,NA
      READ(8,15)ALK(I)
   15 FORMAT(F10.4)
   20 CONTINUE
C     ******************************************************
C     DATA CARDS FOR CA VALUES
C     IN ASCENDING ORDER
      DO 30 I=1,NC
      READ(8,25)CAA(I)
   25  FORMAT(F10.4)
   30 CONTINUE
C     ******************************************************
C     CALCULATING MONO,DI+TRI VALENT ACTIVITY FACTORS
C     USING DAVIES EQUATION
      U1=U**0.5
      FT=4.5*((U1/(1+U1))-0.2*U)
      FT=1./(10.**FT)
      FD=2.*((U1/(1+U1))-0.2*U)
      FD=1./(10.**FD)
      FM=0.5*((U1/(1+U1))-0.2*U)
      FM=1./(10.**FM)
C     ******************************************************
C     EQUILIBRIUM CONSTANTS
      PK1=2.14
      PK2=7.20
      PK3=12.35
      PKS=25.46
```

```
      PKW=14.00
      ************************************************************
      CONVERT PK VALUES TO K VALUES
      KS=(1./(10.**PKS))*10.**15.
      K1=(1./(10.**PK1))*1000.
      K2=(1./(10.**PK2))*1000.
      K3=(1./(10.**PK3))*1000.
      KW=(1./(10.**PKW))*10.**6.
      ************************************************************
      CONVERT K VALUES TO ACCOUNT FOR ACTIVITY
      K1=K1/(FM**2.)
      K2=K2/FD
      K3=K3*FD/(FM*FT)
      KW=KW/(FM**2.)
      KS=KS/((FD**3.)*(FT**2.))
      ************************************************************
      PLOT DIAGRAM OUTLINE
      SC=4.0
      CALL SCALF(SC,SC,-2.5,-1.0)
      NTMX=(MAXACD-MINACD)/0.1
      NTMY=(MAXAMC-MINAMC)/0.1
      CALL FGRID(0,-MAXACD,-MAXAMC,0.1,NTMX)
      CALL FGRID(1,-MINACD,-MAXAMC,0.1,NTMY)
      CALL FGRID(2,-MINACD,-MINAMC,0.1,NTMX)
      CALL FGRID(3,-MAXACD,-MINAMC,0.1,NTMY)
      CALL FGRID(0,-MAXACD,0.,0.1,NTMX)
      CALL FGRID(1,0.,-MAXAMC,0.1,NTMY)
      ************************************************************
      CALCULATIONS TO PLOT PH LINES
      CALL PLTIME(25)
      CAHPO4=0.0
      DO 400 I=1,NPH
      AMC(I)=MINAMC
      NN=1
      PHH=PH(I)
       H=((1./(10.**PHH))/FM)*1000.
      OH=KW/H
      II=1
      JJ=1
      PO4=100.
      DO 390 J=1,1000
      NN=1
      PO4=100.
      C=AMC(J)
0     Y=(3.*PO4+2.*H*PO4/K3+2.*CAHPO4+(H**2.)*PO4/(K2*K3)+KW/H-H)-2.*(KS
     1/(PO4)**2.)**0.333
      IF(Y-C)330,370,325
25    PO4=0.1*PO4
      GO TO 320
30    FRACT=PO4
      PO4=PO4+FRACT
5     Y=(3.*PO4+2.*H*PO4/K3+2.*CAHPO4+(H**2.)*PO4/(K2*K3)+KW/H-H)-2.*(KS
     1/(PO4)**2.)**0.333
      IF(Y-C)340,370,350
40    PO4=PO4+FRACT
      GO TO 335
50    PO4=PO4-FRACT
      FRACT=FRACT*0.1
      PO4=PO4+FRACT
      IF(NN-5)360,360,370
```

```
 360  NN=NN+1
      GO TO 335
 370  HPO4=H*PO4/K3
      H2PO4=H*HPO4/K2
      H3PO4=H*H2PO4/K1
      ACID(J)=3.*H3PO4+2.*H2PO4+HPO4+H-OH+CAHPO4
      AMC(J+1)=AMC(J)+0.1
      IF(ACID(J)-MINACD)371,371,372
 371  JJ=JJ+1
 372  IF(ACID(J)-MAXACD)373,391,391
 373  IF(AMC(J)-MAXAMC)374,391,391
 374  II=II+1
 390  CONTINUE
C     ********************************************************
C     PLOT PH LINES
 391  CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      II=II-1
      DO 392 J=JJ,II
      CALL FPLOT(2,-ACID(J),-AMC(J))
 392  CONTINUE
      WRITE(5,21) PHH
 21   FORMAT(10X,E10.4)
 400  CONTINUE
      CALL FPLOT(3,0.,0.)
C     ********************************************************
C     CALCULATIONS TO PLOT ALKALINITY LINES
      AMC(1)=MINAMC
      LOC=1
      DO 499 J=1,NA
C     ********************************************************
C     CALCULATIONS TO PLOT LOWER HORIZONTAL
C     LIMB OF ALKALINITY LINE
      LL=0
      AL=ALK(J)
      JJ=1
      II=1
      IF(LOC-1)402,402,401
 401  ACID(1)=MAXACD
      LL=1
 402  DO 490 I=1,3000
      JJ=JJ+1
      NN=1
      IF(LL-1)403,417,470
 403  CA=(AL-AMC(I))/2.
      PO4=(KS/(CA**3.))**0.5
      H=1./(10.**4.)
 404  OH=KW/H
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3)+OH-H+2.*CAHPO4
      IF(Y-AL)406,409,405
 405  H=0.1*H
      GO TO 404
 406  FRACT=H
 407  H=H+FRACT
      OH=KW/H
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3)+OH-H+2.*CAHPO4
      IF(Y-AL)407,409,408
 408  H=H-FRACT
      NN=NN+1
      FRACT=0.1*FRACT
      IF(NN-6)407,407,409
```

```
409   ACID(I)=(3.*PO4*H**3.)/(K1*K2*K3)+(2.*PO4*H**2.)/(K2*K3)+(H*PO4)/
     .K3+H-KW/H+CAHPO4
      IF(ACID(I)-MAXACD)411,411,410
410   LOC=2
      ACID(1)=MAXACD
      GO TO 417
411   IF(II-1)412,412,413
412   X=ACID(1)
      Y=AMC(I)
413   IF(AMC(I)-MAXAMC)414,500,500
414   IF(II-1)416,416,415
415   II=II+1
      IF(ACID(I-1)-ACID(I)-0.005)416,417,417
416   AMC(I+1)=AMC(I)+0.01
      II=II+1
      GO TO 490
C     ************************************************
C     CALCULATIONS TO PLOT VERTICAL LIMB
C     OF ALKALINITY LINE
417   LL=1
      NN=1
      A=ACID(1)
      H=1./(10.**3.)
418   Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     1+H-KW/H+CAHPO4(
      IF(Y-A)420,460,419
419   H=0.95*H
      GO TO 418
420   FRACT=H
425   H=H+FRACT
430   Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     1+H-KW/H+CAHPO4
      IF(Y-A)425,460,440
440   H=H-FRACT
      FRACT=0.1*FRACT
      H=H+FRACT
      OH=KW/H
      IF(NN-4)450,450,460
450   NN=NN+1
      GO TO 430
460   PO4=(AL-KW/H+H)/(3.+2.*H/K3+(H**2.)/(K2*K3))
      CA=(KS/(PO4**2.))**0.3333
      AMC(1)=AL-2.*CA
      IF(AMC(1)-MAXAMC)461,500,500
461   IF(A-MINACD)500,500,462
462   IF(II-1)463,463,464
463   II=II+1
      X=ACID(I)
      Y=AMC(I)
      GO TO 465
464   IF(AMC(I-1)-AMC(I)-0.005)465,470,470
465   ACID(I+1)=ACID(I)-0.01
      GO TO 490
      ************************************************
      CALCULATIONS TO PLOT UPPER HORIZONTAL
      LIMB OF ALKALINITY LINE
470   LL=2
      CA=(AL-AMC(I))/2.
      PO4=(KS/(CA**3.))**0.5
      B=(AL-3.*PO4)
```

```
      CON=4.*(2.*PO4/K3-1.)*Kw
      D=B**2.-CON
      DD=D**0.5
      DDD=B-DD
      H=DDD/(2.*(2.*PO4/K3-1.))
      ACID(I)=(3.*PO4*H**3.)/(K1*K2*K3)+(2.*PO4*H**2.)/(K2*K3)+(H*PO4)/K
     .3+H-Kw/H+CAHPO4
      IF(AMC(I)-MINAMC)500,500,475
475   AMC(I+1)=AMC(I)-0.02
490   CONTINUE
      **********************************************************
      PLOT ALKALINITY CURVE
500   CALL FPLOT(3,-ACID(1),-AMC(1))
      JJ=JJ-1
      DO 491 I=1,JJ
      CALL FPLOT(2,-ACID(I),-AMC(I))
491   CONTINUE
      LL=0
      WRITE(5,22) AL
2     FORMAT(10X,E10.4)
499   CONTINUE
      CALL FPLOT(3,0.,0.)
      **********************************************************
      CALCULATIONS FOR CALCIUM LINES
      II=1
      JJ=1
      DO 600 I=1,NC
      ACID(1)=MINACD
      CAL=CAA(I)
      FCA=CAL
      WRITE(5,23) FCA
3     FORMAT(10X,E10.4)
      DO 590 J=1,500
      NN=1
      A=ACID(J)
      PO4 =(KS/(FCA**3.))**0.5
      H=1.
510   Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     .-KW/H+CAHPO4
      IF(Y-A) 530,555,520
520   H=0.1*H
      GO TO 510
530   FRACT=H
535   H=H+FRACT
      Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     .-KW/H+CAHPO4
      IF(Y-A) 535,555,540
540   H=H-FRACT
      FRACT=0.1*FRACT
      IF(NN-4) 550,550,555
550   NN=NN+1
      GO TO 535
555   ALK=3.*PO4+2.*H*PO4/K3+(H**2.)*PO4/(K2*K3)
     .+KW/H-H+2.*CAHPO4
      AMC(J)=ALK-2.*CAL
      IF(AMC(J)-MINAMC)595,595,560
560   IF(AMC(J)-MAXAMC)563,563,561
561   NABZ=-MINACD*10.
      IF(II-NABZ)562,562,595
562   JJ=JJ+1
```

```
563   IF(ACID(J)-MAXACD)564,595,595
564   ACID(J+1)=ACID(J)+0.01
      II=II+1
590   CONTINUE
C     ************************************************
C     PLOT CALCIUM LINES
595   CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      II=II-1
      DO 599 J=JJ,II
      CALL FPLOT(2,-ACID(J),-AMC(J))
599   CONTINUE
      II=1
      JJ=1
600   CONTINUE
      CALL FPLOT(3,0.,0.)
      CALL PEND(3.,-3.)
      STOP
      END
```

```
C     ********************************************************
C     PROGRAM PLOTS THE DIAGRAM FOR
C     HYDROXYAPATITE-(CA)5(OH)(PO4)3
C     ********************************************************
      REAL KW,K1,K2,K3,KS,MAXAMC,MINAMC,MAXACD
      DOUBLE PRECISION PO4,FRACT,H,Y,C,OH
      DIMENSION PH(50),ALK(50),CA(50),ACID(3000),AMC(3000)
C     ********************************************************
C     FIRST DATA CARD:DIAGRAM LIMITS
      READ(8,7)MAXACD,MINACD,MAXAMC,MINAMC
    7 FORMAT(4F10.3)
C     WHERE:MAXACD=POSITIVE(ACIDITY)
C           MINACD=NEGATIVE(ACIDITY)
C           MAXAMC=MAX(ALK-2CA)
C           MINAMC=MIN(ALK-2CA)
C     ********************************************************
C     SECOND DATA CARD:NO.OF PH,ALK AND CA VALUES
      READ(8,4)NPH,NA,NC
    4 FORMAT(3I2)
C     ********************************************************
C     THIRD DATA CARD:IONIC STRENGTH
      READ(8,6)U
    6 FORMAT(F10.4)
C     ********************************************************
C     DATA CARDS FOR PH VALUES
      DO 10 I=1,NPH
      READ(8,9)PH(I)
    9 FORMAT(F10.4)
   10 CONTINUE
C     ********************************************************
C     DATA CARDS FOR ALK. VALUES
C     IN ASCENDING ORDER
      DO 20 I=1,NA
      READ(8,15)ALK(I)
   15 FORMAT(F10.4)
   20 CONTINUE
C     ********************************************************
C     DATA CARDS FOR CA VALUES
C     IN ASCENDING ORDER
      DO 30 I=1,NC
      READ(8,25)CA(I)
   25  FORMAT(F10.4)
   30 CONTINUE
C     ********************************************************
C     CALCULATING MONO,DI+TRI VALENT ACTIVITY FACTORS
C     USING DAVIES EQUATION
      U1=U**0.5
      FT=4.5*((U1/(1+U1))-0.2*U)
      FT=1./(10.**FT)
      FD=2.*((U1/(1+U1))-0.2*U)
      FD=1./(10.**FD)
      FM=0.5*((U1/(1+U1))-0.2*U)
      FM=1./(10.**FM)
C     ********************************************************
C     EQUILIBRIUM CONSTANTS
      PK1=2.14
      PK2=7.20
      PK3=12.35
      PKW=14.00
```

```
      PKS=27.41
      ************************************************************
      CONVERT PK VALUES TO K VALUES
      KS=(1./(10.**PKS))
      K1=(1./(10.**PK1))*1000.
      K2=(1./(10.**PK2))*1000.
      K3=(1./(10.**PK3))*1000.
      KW=(1./(10.**PKW))*10.**6.
      ************************************************************
      CONVERT K VALUES TO ACCOUNT FOR ACTIVITY
      K1=K1/(FM**2.)
      K2=K2/FD
      K3=K3*FD/(FM*FT)
      KW=KW/(FM**2.)
      KS=KS/((FD**5.)*(FT**3.)*(FM))
      ************************************************************
      PLOT DIAGRAM OUTLINE
      SC=0.6
      CALL SCALF(SC,SC,-2.5,-2.0)
      NTMX=(MAXACD-MINACD)/0.1
      NTMY=(MAXAMC-MINAMC)/0.1
      CALL FGRID(0,-MAXACD,-MAXAMC,0.1,NTMX)
      CALL FGRID(1,-MINACD,-MAXAMC,0.1,NTMY)
      CALL FGRID(2,-MINACD,-MINAMC,0.1,NTMX)
      CALL FGRID(3,-MAXACD,-MINAMC,0.1,NTMY)
      CALL FGRID(0,-MAXACD,0.,0.1,NTMX)
      CALL FGRID(1,0.,-MAXAMC,0.1,NTMY)
      ************************************************************
      CALCULATIONS TO PLOT PH LINES
      CALL PLTIME(25)
      DO 400 I=1,NPH
      AMC(1)=MINAMC
      NN=1
      PHH=PH(I)
       H=((1./(10.**PHH))/FM)*1000.
      OH=KW/H
      II=1
      JJ=1
      P04=100.
      DO 390 J=1,1000
      NN=1
      P04=100.
      C=AMC(J)
20    Y=(3.*P04+2.*H*P04/K3+(H**2.)*P04/(K2*K3)+KW/H-H)-2.*(KS/((P04**3.)
     .)*(OH)))**0.2
      IF(Y-C)330,370,325
25    P04=0.1*P04
      GO TO 320
30    FRACT=P04
      P04=P04+FRACT
335   Y=(3.*P04+2.*H*P04/K3+(H**2.)*P04/(K2*K3)+KW/H-H)-2.*(KS/((P04**3.)
     .)*(OH)))**0.2
      IF(Y-C)340,370,350
340   P04=P04+FRACT
      GO TO 335
350   P04=P04-FRACT
      FRACT=FRACT*0.1
      P04=P04+FRACT
      IF(NN-5)360,360,370
360   NN=NN+1
```

```
      GO TO 335
  370 HPO4=H*PO4/K3
      H2PO4=H*HPO4/K2
      H3PO4=H*H2PO4/K1
      ACID(J)=3.*H3PO4+2.*H2PO4+HPO4+H-OH
      AMC(J+1)=AMC(J)+0.1
      IF(ACID(J)-MINACD)371,371,372
  371 JJ=JJ+1
  372 IF(ACID(J)-MAXACD)373,391,391
  373 IF(AMC(J)-MAXAMC)374,391,391
  374 II=II+1
  390 CONTINUE
C     ************************************************************
C     PLOT PH LINES
  391 CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      II=II-1
      DO 392 J=JJ,II
      CALL FPLOT(2,-ACID(J),-AMC(J))
  392 CONTINUE
  400 CONTINUE
      CALL FPLOT(3,0.,0.)
C     ************************************************************
C     CALCULATIONS TO PLOT ALKALINITY LINES
      AMC(1)=MINAMC
      LOC=1
      DO 499 J=1,NA
C     ************************************************************
C     CALCULATIONS TO PLOT LOWER HORIZONTAL
C     LIMB OF ALKALINITY LINE
      LL=0
      AL=ALK(J)
      JJ=1
      II=1
      IF(LOC-1)402,402,401
  401 ACID(1)=MAXACD
      LL=1
  402 DO 490 I=1,3000
      JJ=JJ+1
      NN=1
      IF(LL-1)403,417,470
  403 CA=(AL-AMC(I))/2.
      H=1./(10.**4.)
  404 OH=KW/H
      PO4=(KS/((CA**5.)*OH))**0.333
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3)+OH-H
      IF(Y-AL)406,409,405
  405 H=0.1*H
      GO TO 404
  406 FRACT=H
  407 H=H+FRACT
      OH=KW/H
      PO4=(KS/((CA**5.)*OH))**0.333
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3)+OH-H
      IF(Y-AL)407,409,408
  408 H=H-FRACT
      NN=NN+1
      FRACT=0.1*FRACT
      IF(NN-6)407,407,409
  409 ACID(1)=(3.*PO4*H**3.)/(K1*K2*K3)+(2.*PO4*H**2.)/(K2*K3)+(H*PO4)/
     .K3+H-KW/H
```

```
      IF(ACID(I)-MAXACD)411,411,410
  410 LOC=2
      ACID(1)=MAXACD
      GO TO 417
  411 IF(II-1)412,412,413
  412 X=ACID(I)
      Y=AMC(I)
  413 IF(AMC(I)-MAXAMC)414,500,500
  414 IF(II-1)416,416,415
  415 II=II+1
      IF(ACID(I-1)-ACID(I)-0.005)416,417,417
  416 AMC(I+1)=AMC(I)+0.01
      II=II+1
      GO TO 490
C     ******************************************************
C     CALCULATIONS TO PLOT VERTICAL LIMB
C     OF ALKALINITY LINE
  417 LL=1
      NN=1
      A=ACID(I)
      H=1./(10.**3.)
  418 Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     .+H-KW/H
      IF(Y-A)420,460,419
  419 H=0.1*H
      GO TO 418
  420 FRACT=H
  425 H=H+FRACT
  430 Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     .+H-KW/H
      IF(Y-A)425,460,440
  440 H=H-FRACT
      FRACT=0.1*FRACT
      H=H+FRACT
      IF(NN-4)450,450,460
  450 NN=NN+1
      GO TO 450
  460 PO4=(AL-KW/H+H)/(3.+2.*H/K3+(H**2.)/(K2*K3))
      CA=(KS/((PO4**3.)*(KW/H)))**0.2
      AMC(I)=AL-2.*CA
      IF(AMC(I)-MAXAMC)461,500,500
  461 IF(A-MINACD)500,500,462
  462 IF(II-1)463,463,464
  463 II=II+1
      X=ACID(I)
      Y=AMC(I)
      GO TO 465
  464 IF(AMC(I-1)-AMC(I)-0.005)465,470,470
  465 ACID(I+1)=ACID(I)-0.01
      GO TO 490
C     ******************************************************
C     CALCULATIONS TO PLOT UPPER HORIZONTAL
C     LIMB OF ALKALINITY LINE
  470 LL=2
      CA=(AL-AMC(I))/2.
      NN=1
      OH=50.
  480 H=KW/H
      PO4=(KS/((CA**3.)*OH))**0.333
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3) +KW/H-H
```

```
      IF(Y-AL)472,476,471
  471 OH=OH*0.9
       GO TO 4700
  472 FRACT=OH
  473 OH=OH+FRACT
      H=KW/OH
      PO4=(KS/((CA**5.)*OH))**0.333
      Y=3.*PO4+2.*H*PO4/K3+(PO4*H**2.)/(K2*K3) +KW/H-H
      IF(Y-AL)473,476,474
  474 OH=OH-FRACT
      FRACT=0.1*FRACT
      NN=NN+1
      IF(NN-6)473,476,476
  476 CONTINUE
      ACID(I)=(3.*PO4*H**3.)/(K1*K2*K3)+(2.*PO4*H**2.)/(K2*K3)+(H*PO4)/K
     .3+H-KW/H
      IF(AMC(1)-MINAMC)500,500,475
  475 AMC(I+1)=AMC(I)-0.02
  490 CONTINUE
C     ************************************************
C     PLOT ALKALINITY CURVE
  500 CALL FPLOT(3,-ACID(1),-AMC(1))
      JJ=JJ-1
      DO 491 I=1,JJ
      CALL FPLOT(2,-ACID(I),-AMC(I))
  491 CONTINUE
      LL=0
  499 CONTINUE
      CALL FPLOT(3,0.,0.)
C     ************************************************
C     CALCULATIONS FOR CALCIUM LINES
      II=1
      JJ=1
      DO 600 I=1,NC
      ACID(1)=MINACD
      CAL=CA(I)
      DO 590 J=1,500
      NN=1
      A=ACID(J)
      H=1.
  510 PO4=(KS/((CAL**5.)*(KW/H)))**0.333
      Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     .-KW/H
      IF(Y-A)530,555,520
  520 H=0.1*H
      GO TO 510
  530 FRACT=H
  535 H=H+FRACT
      PO4=(KS/((CAL**5.)*(KW/H)))**0.333
      Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     .-KW/H
      IF(Y-A)535,555,540
  540 H=H-FRACT
      FRACT=0.1*FRACT
      IF(NN-4)550,550,555
  550 NN=NN+1
      GO TO 535
  555 ALK=3.*PO4+2.*H*PO4/K3+(H**2.)*PO4/(K2*K3)
     .+KW/H-H
      AMC(J)=ALK-2.*CAL
```

```
      IF(AMC(J)-MINAMC)595,595,560
  560 IF(AMC(J)-MAXAMC)563,563,561
  561 NABZ=-MINACD*10.
      IF(II-NABZ)562,562,595
  562 JJ=JJ+1
  563 IF(ACID(J)-MAXACD)564,595,595
  564 ACID(J+1)=ACID(J)+0.01
      II=II+1
  590 CONTINUE
C     ************************************************
C     PLOT CALCIUM LINES
  595 CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      II=II-1
      DO 599 J=JJ,II
      CALL FPLOT(2,-ACID(J),-AMC(J))
  599 CONTINUE
      II=1
      JJ=1
  600 CONTINUE
      CALL FPLOT(3,0.,0.)
      CALL PEND(3.,-3.)
      STOP
      END
```

```
C     ************************************************
C     PROGRAM PLOTS THE DIAGRAM FOR
C     DI-CALCIUM PHOSPHATE-CAHPO4
C     ************************************************
      REAL KW,K1,K2,K3,KS,MAXAMC,MINAMC,MAXACD,MINACD
      DOUBLE PRECISION PO4,FRACT,H,Y,C,OH
      DIMENSION PH(50),ALK(50),CAA(50),ACID(3000),AMC(3000)
C     ************************************************
C     FIRST DATA CARD:DIAGRAM LIMITS
      READ(6,7)MAXACD,MINACD,MAXAMC,MINAMC
    7 FORMAT(4F10.3)
C     WHERE:MAXACD=POSITIVE(ACIDITY)
C           MINACD=NEGATIVE(ACIDITY)
C           MAXAMC=MAX(ALK-2CA)
C           MINAMC=MIN(ALK-2CA)
C     ************************************************
C     SECOND DATA CARD:NO.OF PH,ALK AND CA VALUES
      READ(8,4)NPH,NA,NC
    4 FORMAT(3I2)
      ************************************************
      THIRD DATA CARD:IONIC STRENGTH
      READ(6,6)U
    6 FORMAT(F10.4)
      ************************************************
      DATA CARDS FOR PH VALUES
      DO 10 I=1,NPH
      READ(8,9)PH(I)
    9 FORMAT(F10.4)
   10 CONTINUE
      ************************************************
      DATA CARDS FOR ALK. VALUES
      IN ASCENDING ORDER
      DO 20 I=1,NA
      READ(8,15)ALK(I)
   15 FORMAT(F10.4)
   20 CONTINUE
      ************************************************
      DATA CARDS FOR CA VALUES
      IN ASCENDING ORDER
      DO 30 I=1,NC
      READ(8,25) CAA(I)
   25  FORMAT(F10.4)
   30 CONTINUE
      ************************************************
      CALCULATING MONO,DI+TRI VALENT ACTIVITY FACTORS
      USING DAVIES EQUATION
      U1=U**0.5
      F1=4.5*((U1/(1+U1))-0.2*U)
      FT=1./(10.**FT)
      FD=2.*((U1/(1+U1))-0.2*U)
      FD=1./(10.**FD)
      FM=0.5*((U1/(1+U1))-0.2*U)
      FM=1./(10.**FM)
      ************************************************
      EQUILIBRIUM CONSTANTS
      PK1=2.14
      PK2=7.20
      PK3=12.35
      PKS=7.0
```

```
      PKW=14.00
C     ********************************************************
C     CONVERT PK VALUES TO K VALUES
      KS=(1./(10.**PKS))*10.**6
      K1=(1./(10.**PK1))*1000.
      K2=(1./(10.**PK2))*1000.
      K3=(1./(10.**PK3))*1000.
      KW=(1./(10.**PKW))*10.**6.
C     ********************************************************
C     CONVERT K VALUES TO ACCOUNT FOR ACTIVITY
      K1=K1/(FM**2.)
      K2=K2/FD
      K3=K3*FD/(FM*FT)
      KW=KW/(FM**2.)
      KS=KS/(FD**2)
C     ********************************************************
C     PLOT DIAGRAM OUTLINE
      SC=4.0
      CALL SCALF(SC,SC,-2.5,-1.0)
      NTMX=(MAXACD-MINACD)/0.1
      NTMY=(MAXAMC-MINAMC)/0.1
      CALL FGRID(0,-MAXACD,-MAXAMC,0.1,NTMX)
      CALL FGRID(1,-MINACD,-MAXAMC,0.1,NTMY)
      CALL FGRID(2,-MINACD,-MINAMC,0.1,NTMX)
      CALL FGRID(3,-MAXACD,-MINAMC,0.1,NTMY)
      CALL FGRID(0,-MAXACD,0.,0.1,NTMX)
      CALL FGRID(1,0.,-MAXAMC,0.1,NTMY)
C     ********************************************************
C     CALCULATIONS TO PLOT PH LINES
      CALL PLTIME(25)
      DO 400 I=1,NPH
      AMC(I)=MINAMC
      NN=1
      PHH=PH(I)
      H=((1./(10.**PHH))/FM)*1000.
      OH=KW/H
      II=1
      JJ=1
      P04=100.
      DO 390 J=1,1000
      NN=1
      P04=100.
      C=AMC(J)
320   Y=(3.*P04+2.*H*P04/K3+(H**2.)*P04/(K2*K3)+KW/H-H)-2.*KS*K3/(H*P04)
      IF(Y-C)330,370,325
325   P04=0.1*P04
      GO TO 320
330   FRACT=P04
      P04=P04+FRACT
335   Y=(3.*P04+2.*H*P04/K3+(H**2.)*P04/(K2*K3)+KW/H-H)-2.*KS*K3/(H*P04)
      IF(Y-C)340,370,350
340   P04=P04+FRACT
      GO TO 335
350   P04=P04-FRACT
      FRACT=FRACT*0.1
      P04=P04+FRACT
      IF(NN-5)360,360,370
360   NN=NN+1
      GO TO 335
370   HP04=H*P04/K3
```

```
      H2P04=H*HP04/K2
      H3P04=H*H2P04/K1
      ACID(J)=3.*H3P04+2.*H2P04+HP04+H-OH
      AMC(J+1)=AMC(J)+0.1
      IF(ACID(J)-MINACD)371,371,372
-371  JJ=JJ+1
-372  IF(ACID(J)-MAXACD)373,391,391
-373  IF(AMC(J)-MAXAMC)374,391,391
-374  II=II+1
-390  CONTINUE
      **********************************************************
      PLOT PH LINES
-391  CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      I1=II-1
      DO 392 J=JJ,I1
      CALL FPLOT(2,-ACID(J),-AMC(J))
392   CONTINUE
      WRITE(5,21)PHH
      FORMAT(10X,E10.4)
400   CONTINUE
      CALL FPLOT(3,0.,0.)
      **********************************************************
      CALCULATIONS TO PLOT ALKALINITY LINES
      AMC(1)=MINAMC
      LOC=1
      DO 499 J=1,NA
      **********************************************************
      CALCULATIONS TO PLOT LOWER HORIZONTAL
      LIMB OF ALKALINITY LINE
      LL=0
      AL=ALK(J)
      JJ=1
      II=1
      IF(LOC-1)402,402,401
401   ACID(1)=MAXACD
      LL=1
402   DO 490 I=1,3000
      JJ=JJ+1
      NN=1
      IF(LL-1)403,417,470
403   CA=(AL-AMC(1))/2.
      HP04=KS/CA
      A=HP04/K2
      B=2.*HP04-AL
      C=3.*K3*HP04+KW
      H=(-B+(B**2.-4.*A*C)**0.5)/(2.*A)
      P04=K3*HP04/H
409   ACID(I)=(3.*P04*H**3.)/(K1*K2*K3)+(2.*P04*H**2.)/(K2*K3)+(H*P04)/
     .K3+H-KW/H
      IF(ACID(I)-MAXACD)411,411,410
410   LOC=2
      ACID(1)=MAXACD
      GO TO 417
411   IF(II-1)412,412,413
412   X=ACID(I)
      Y=AMC(I)
413   IF(AMC(I)-MAXAMC)414,500,500
414   IF(II-1)416,416,415
415   II=II+1
      IF(ACID(I-1)-ACID(I)-0.005)416,417,417
```

```
 416  AMC(I+1)=AMC(I)+0.01
      II=II+1
      GO TO 490
C     ********************************************************
C     CALCULATIONS TO PLOT VERTICAL LIMB
C     OF ALKALINITY LINE
 417  LL=1
      NN=1
      A=ACID(1)
      H=1./(10.**3.)
 418  Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     .+H-KW/H
      IF(Y-A)420,460,419
 419  H=0.95*H
      GO TO 418
 420  FRACT=H
 425  H=H+FRACT
 430  Y=(AL-KW/H+H)*((3.*(H**2.))/(K1*K2)+2.*H/K2+1.)/(3.*K3/H+2.+H/K2)
     .+H-KW/H
      IF(Y-A)425,460,440
 440  H=H-FRACT
      FRACT=0.1*FRACT
      H=H+FRACT
      IF(NN-4)450,450,460
 450  NN=NN+1
      GO TO 430
 460  PO4=(AL-KW/H+H)/(3.+2.*H/K3+(H**2.)/(K2*K3))
      CA=(KS*K3)/(PO4*H)
      AMC(I)=AL-2.*CA
      IF(AMC(I)-MAXAMC)461,500,500
 461  IF(A-MINACD)500,500,462
 462  IF(II-1)463,465,464
 463  II=II+1
      X=ACID(I)
      Y=AMC(I)
      GO TO 465
 464  IF(AMC(I-1)-AMC(I)-0.005)465,470,470
 465  ACID(I+1)=ACID(I)-0.01
      GO TO 490
      ********************************************************
      CALCULATIONS TO PLOT UPPER HORIZONTAL
      LIMB OF ALKALINITY LINE
 470  LL=2
      CA=(AL-AMC(I))/2.
      HPO4=KS/CA
      A=HPO4/K2
      B=2.*HPO4-AL
      C=3.*K3*HPO4+KW
      H=(-B-(B**2.-4.*A*C)**0.5)/(2.*A)
      PO4=(K3*HPO4)/H
      ACID(I)=(3.*PO4*H**3.)/(K1*K2*K3)+(2.*PO4*H**2.)/(K2*K3)+(H*PO4)/K
     .3+H-KW/H
      IF(ACID(I)-MINACD) 500,500,475
 475  IF(AMC(I)-MINAMC) 500,500,476
 476  AMC(I+1)=AMC(I)-0.02
 490  CONTINUE
      ********************************************************
      PLOT ALKALINITY CURVE
 500  CALL FPLOT(3,-ACID(1),-AMC(1))
      JJ=JJ-1
```

```
      DO 491 I=1,JJ
      CALL FPLOT(2,-ACID(I),-AMC(I))
 491  CONTINUE
      LL=0
      WRITE(5,22)AL
22    FORMAT(10X,E10.4)
 499  CONTINUE
      CALL FPLOT(3,0.,0.)
C     ************************************************************
C     CALCULATIONS FOR CALCIUM LINES
      II=1
      JJ=1
      DO 600 I=1,NC
      ACID(1)=MINACD
      CAL=CAA(I)
      WRITE(5,23)CAL
23    FORMAT(10X,E10.4)
      DO 590 J=1,500
      NN=1
      A=ACID(J)
      HPO4=KS/CAL
      H=1.
510   PO4=K3*HPO4/H
      Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     *-KW/H
      IF (Y-A) 530,555,520
520   H=0.1*H
      GO TO 510
530   FRACT=H
535   H=H+FRACT
      PO4=K3*HPO4/H
      Y=(3.*PO4*(H**3.))/(K1*K2*K3)+(2.*PO4*(H**2.))/(K2*K3)+H*PO4/K3+H
     *-KW/H
      IF (Y-A) 535,555,540
540   H=H-FRACT
      FRACT=0.1*FRACT
      IF(NN-4)550,550,555
550   NN=NN+1
      GO TO 535
555   ALK=3.*PO4+2.*H*PO4/K3+(H**2.)*PO4/(K2*K3)
     *+KW/H-H
      AMC(J)=ALK-2.*CAL
      IF(AMC(J)-MINAMC)595,595,560
560   IF(AMC(J)-MAXAMC)563,563,561
561   NABZ=-MINACD*10.
      IF(II-NABZ)562,562,595
562   JJ=JJ+1
563   IF(ACID(J)-MAXACD)564,595,595
564   ACID(J+1)=ACID(J)+0.01
      II=II+1
590   CONTINUE
      ************************************************************
      PLOT CALCIUM LINES
595   CALL FPLOT(3,-ACID(JJ),-AMC(JJ))
      II=II-1
      DO 599 J=JJ,II
      CALL FPLOT(2,-ACID(J),-AMC(J))
599   CONTINUE
      II=1
      JJ=1
```

```
600   CONTINUE
      CALL FPLOT(3.,0.,0.)
      CALL PEND(3.,-3.)
      STOP
      END
```

APPENDIX F

PROGRAMME FOR CALCULATING THE SOLUBILITY PRODUCT OF BETA TRICALCIUM PHOSPHATE AND DI-CALCIUM PHOSPHATE

```
C     ******************************************************
C     PROGRAM FOR DETERMINATION OF SOLUBILITY PRODUCT
C     ******************************************************
      REAL K1,K2,K3,K4,KSP1,KSP2,K11,K22,K33,K44,MGCA,MGALK,MGP,MGCAP
      DOUBLE PRECISION PO4,PT,PTC,H2PO4,HPO4,FRACT
      DIMENSION CA(100),PH(100),PT(100),MGCA(100),MGALK(100),MGP(100),
     1MGCAP(100),H(100)
      READ(8,10) N
 10   FORMAT()
      READ(8,5) (CA(I),PH(I),PT(I),MGP(I),MGCA(I),MGALK(I),MGCAP(I),
     2I=1,N)
 5    FORMAT(7F8.4)
      WRITE(5,20)
 20   FORMAT(1H ,10X,'PKSP1',10X,'PKSP2',10X,'U',10X,'CA(I)',10X,'PO4',
     310X,'HPO4',10X,'PH',10X,'PT')
      DO 50 I=1,N
C     ******************************************
C     EQUILIBRIUM CONSTANTS
      K1=7.1
      K2=0.063
      K3=4.7/(10.**10)
      K4=1.99/(10.**5)
C     ******************************************
C     CALCULATING TOTAL DISSOLVED INSOLUBLE SOLIDS
      TDIS=248.0
      TDIS=TDIS+MGALK(I)+MGCA(I)+MGP(I)-MGCAP(I)
C     ******************************************
C     CALCULATING IONIC STRENGTH
      U=(2.5/(10.**5))*TDIS
C     ******************************************
C     CALC. MONO,DI+TRI VALENT ACTIVITY FACTORS
      U1=U**0.5
      FT=4.5*((U1/(1+U1))-0.2*U)
      FT=1.0/(10.0**FT)
      FD=2.0*((U1/(1+U1))-0.2*U)
      FD=1.0/(10.0**FD)
      FM=0.5*((U1/(1+U1))-0.2*U)
      FM=1.0/(10.0**FM)
C     ******************************************
C     ADJUSTMENT OF K1,K2,K3&K4
      K11=K1/(FM**2)
      K22=K2/(FD**2)
      K33=K3/(FT**2)
      K44=K4/(FD**2)
C     ******************************************
C     CALC. H
      H(I)=(1.0/((10.**PH(I))*FM))*10.0**3
C     ******************************************
C     CALCULATING PO4
      PO4=PT(I)/(H(I)**3/(K11*K22*K33)+H(I)**2/(K22*K33)+H(I)/K33+1.0)
C     ******************************************
C     CONVERSION OF MMOLES TO-MOLES
      PT(I)=PT(I)/(10.**3)
      K11=K11/(10.**3)
      K22=K22/(10.**3)
      K33=K33/(10.**3)
      PO4=PO4/(10.**3)
      CA(I)=CA(I)/(10.**3)
C     ******************************************
```

```
      LL=1
100   HPO4=(H(I)*PO4)/K33
      H2PO4=(H(I)*HPO4)/K22
      CAHPO4=(CA(I)*HPO4)/K44
      PTC=PO4+HPO4+H2PO4+CAHPO4
      IF(PT(I)-PTC) 110,200,120
110   PO4=0.9*PO4
      GO TO 100
120   FRACT=PO4
130   PO4=PO4+FRACT
      HPO4=(H(I)*PO4)/K33
      H2PO4=(H(I)*HPO4)/K22
      CAHPO4=(CA(I)*HPO4)/K44
      PTC=PO4+HPO4+H2PO4+CAHPO4
      IF(PT(I)-PTC) 140,200,130
140   LL=LL+1
      IF(LL-5) 150,200,200
150   PO4=PO4-FRACT
      FRACT=0.1*FRACT
      GO TO 130
200   CONTINUE
C     ***********************************************
C     CALC. SOLUBILITY PRODUCT OF (CA)3(PO4)2
      KSP1=(CA(I)**3)*(PO4**2)
      KSP1=KSP1*(FD**3)*(FT**2)
      PKSP1=(-1.)*ALOG10(KSP1)
C     ***********************************************
C     CALC. SOLUBILITY PRODUCT FOR (CA)(HPO4)
      KSP2=CA(I)*HPO4
      KSP2=KSP2*(FD**2)
      PKSP2=(-1.)*ALOG10(KSP2)
      WRITE(6,21) PKSP1,PKSP2,0,CA(I),PO4,HPO4,PH(I),PT(I)
21    FORMAT(6X,E10.4,4X,E10.4,4X,E10.4,3X,E10.4,3X,E10.4,3X,E10.4,
     43X,E10.4,3X,E10.4)
50    CONTINUE
      STOP
      END
```

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