UNIVERSITY OF CAPE TOWN

DEPARTMENT OF CIVIL ENGINEERING

Report to the

WATER RESEARCH COMMISSION

on

THE APPLICATION OF CHEMICAL EQUILIBRIUM TO THE CONTROL OF STRUVITE AND CALCITE PRECIPITATION IN WASTE WATER TREATMENT

by

R E Loewenthal

WRC Report No. 602/1/97
ISBN 1 86845 320 0

PRETORIA

EXECUTIVE SUMMARY

Precipitation of struvite ($MgNH_4PO_4$) is a common phenomenon in anaerobic treatment of both wine distillery and piggery waste waters, and also sludge waste derived from excess biological phosphate removal systems. The reason for this is that these wastes contain higher than usual concentrations of dissolved orthophosphates, free and saline ammonia and magnesium ions and these species form the components of the mineral struvite.

Struvite precipitation in anaerobic fermentation systems occurs mainly in two areas. First, within the pipe network transporting the treated effluent, particularly where pressure changes occur, for example, at bends and inlets to pumps. Second, on surfaces close to the inlet and outlet of the secondary settler effecting separation of the treated effluent. The mass of precipitant formed can be so extensive that it may lead to blockages and ultimately operational failure.

In both of the above instances of struvite precipitation fouling, it would appear that the trigger mechanism is a reduction of the partial pressure of carbon dioxide, $\bar{p}CO_2$. Reduction of $\bar{p}CO_2$ may cause expulsion of CO_2 from the aqueous phase and a concomitant increase in pH, giving rise to a state of supersaturation with respect to struvite that is sufficiently high so as to cause precipitation of this mineral.

For the purposes of process control, clearly it would be useful to be able to (1) predict the conditions under which struvite precipitation fouling problems are likely to arise, (2) determine the potential mass of struvite which can precipitate, and (3) formulate chemical dosing strategies so that precipitation will be negligible in critical areas of the system. These problems are complex but an approach to their resolution can be developed via equilibrium chemistry.

The objectives of this research contract were as follows:

a. Identify and evaluate the causes of struvite/calcite precipitation and fouling in waste water treatment processes.

b. Develop strategies to either control (prevent) or effect struvite/calcite precipitation using chemical equilibrium modelling.

These objectives were met sequentially. First, a review is presented on the utilization of equilibrium chemistry to explain the establishment of pH in anaerobic digesters where a number of weak acid systems (acetate, carbonate, phosphate and ammonia systems) are all present simultaneously in solution, i.e. a single aqueous phase scenario. This was then extended to include a gas phase, with carbon dioxide at some specified partial pressure. Algorithms were developed to predict changes in state (i.e. the changes in pH) which arise as a result of the perturbations (i) a change in pressure, this occurs in practice either at inlet to pumps transporting the waste water, or in sedimentation basins designed to effect liquids-solids separation, and (ii) addition or removal of strong acids and bases specifically applied to adjust pH of the system.

Secondly, algorithms were developed to predict the masses of struvite and/or calcite which may precipitate (or dissolve) as a result of the perturbations outlined above (i.e. a three phase equilibrium scenario involving aqueous, gaseous and solid species).

The equilibrium algorithms described above were evaluated experimentally in the laboratory. It was found that the models correctly predicted the masses of struvite and calcite precipitated due to the various perturbations (i.e. due to change in the partial pressure of carbon dioxide and/or addition of strong acids or bases).

A user friendly computer program ("STRUVITE") has been developed so that controllers of waste water treatment plants can easily predict both the potential for mineral fouling, and chemical dosing strategies to prevent such fouling. It is felt that the contract objectives have been successfully achieved through the development of this computer program, in that it both successfully predicts the propensity of a waste water to cause mineral fouling, and provides waste water plant personnel with quantitative chemical treatment options to prevent such fouling. A remaining factor would be the successful distribution of the program to industry. That is, that the relevant authorities be made aware of the existence of this report and the appended computer program. At present we are writing a paper for submission to WATER SA as a first attempt to effect technological transfer. This would be further expedited if the existence of the program "STRUVITE" be advertised in WATER BULLETIN.

With regard to future research, the work presented here describes only the physical chemistry arising in a bio-reactor (i.e. anaerobic bio-treatment of waste waters). That is, concentrations of weak acids, various cation species and pH form the input to the models developed, and in practice are measured routinely. However, the values established for these parameters arise from biological reactions (for example acidogenesis and methanogenesis). It is felt that a kinetic model (and an associated user friendly computer program) that integrates the biological with the physico-chemical aspects (described in this report) could form an invaluable tool for the control of anaerobic bio-digesters.

ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission and entitled :

"The Application of Chemical Equilibrium to the Control of Struvite and Calcite Precipitation in Waste Water Treatment".

The Selecting Committee responsible for this project, consisted of the following persons:

Dr T C Erasmus	Water Research Commission (Chairman)
Mr F P Marais	Water Research Commission (Secretary)
Prof C A Buckley	University of Natal
Prof P P Coetzee	RAU
Mr I R Morrison	City of Cape Town
Mr A R Pitman	GJTMC

Financing of the project by the Water Research Committees and the contribution of members of the Steering Committee are acknowledged with gratitude.

TABLE OF CONTENTS

LIST OF FIGURES

Page No

CHAPTER 1

INTRODUCTION

Precipitation of struvite ($MgNH_4PO_4$) is a common phenomenon in anaerobic treatment of both wine distillery and piggery waste waters, and also sludge waste derived from excess biological phosphate removal systems. The reason for this is that these wastes contain higher than usual concentrations of dissolved orthophosphates, free and saline ammonia and magnesium ions and these species form the components of the mineral struvite.

Struvite precipitation in anaerobic fermentation systems occurs mainly in two areas. First, within the pipe network transporting the treated effluent, particularly where pressure changes occur, for example, at bends and inlets to pumps. Second, on surfaces close to the inlet and outlet of the secondary settler effecting separation of the treated effluent. The mass of precipitant formed can be so extensive that it may lead to operational failure.

In both of the above instances of struvite precipitation fouling, it would appear that the trigger mechanism is a reduction of the partial pressure of carbon dioxide, $\bar{p}CO_2$. Reduction of $\bar{p}CO_2$ may cause expulsion of CO_2 from the aqueous phase and a concomitant increase in pH, giving rise to a state of supersaturation with respect to struvite that is sufficiently high so as to cause precipitation of this mineral.

For the purposes of process control, clearly it would be useful to be able to (1) predict the conditions under which struvite precipitation fouling problems are likely to arise, (2) determine the potential mass of struvite which can precipitate, and (3) formulate chemical dosing strategies so that precipitation will be negligible in critical areas of the system. These problems are complex but an approach to their resolution can be developed via equilibrium chemistry.

Equilibrium chemistry has been utilised by both Stumm and Morgan (1970) and Snoeyink and Jenkins (1980) to address struvite precipitation problems. They formulated a "conditional solubility product" equation for struvite in terms of the total species concentrations in solution of magnesium, free and saline ammonia (N_T) and orthophosphate (P_T). At saturation this total species product equals a pH dependent solubility product constant, termed the conditional solubility product. The struvite saturation state is then determined by comparing the total species product with the conditional solubility product constant (determined for the measured solution pH value). Where the total species product exceeds the pH dependent conditional solubility product a state of super saturation exists with respect to struvite, and *vice versa* for under saturation.

Although the approach above forms a useful basis for assessing struvite saturation state, its usefulness is limited by exactly the same factors limiting the Langelier Saturation Index for scale control in distribution of municipal water supplies. That is, it neither gives a measure of the mass of mineral which potentially can precipitate from solution, nor does it lead to a predictive approach for estimating change in precipitation potential with chemical dosing, either prescribed (eg. acid dosing) or inadvertent (eg. CO_2 loss from solution). In this report these problems will be addressed. Equilibrium chemistry will be used to develop both algorithms and a user friendly computer program for practical, quantitative solutions.

Formulation of algorithms (using equilibrium chemistry) to address chemical dosing and mineral precipitation problems in mixed weak acid systems requires addressing a number of factors considered below.

Firstly, a thorough review of aqueous solutions comprising a mixture of weak acid systems needs to be effected. This will lead naturally to the problem of characterising such systems from some set of observations which can be carried out relatively simply in practice.

The term characterisation implies that system equations can be used, together with a set of observations, to determine any of the weak acid species concentrations in solution. With regard to characterisation, particular emphasis is given to the carbonate weak acid sub-system, because often no direct practical measurement (eg. the total inorganic carbon content via an inorganic carbon analyser) is possible. In this regard, system alkalinities and acidities will be introduced and utilised for practical measurement via strong acid titration procedures.

Having dealt with characterisation of solutions containing more than one weak acid system, the next important aspect is that of chemical conditioning of such solutions. That is, either determining the new state for a prescribed type and mass of chemical dosing, or determining the mass of a prescribed chemical dose to adjust a solution to a specified final state.

Chemical conditioning is necessary in a wide spectrum of aqueous weak acid problems. Examples of such problems, characterised according to the phases with which the dissolved weak acid species interact, ie. aqueous, solid and gaseous, are as follows :

1. **Single aqueous phase problems.** These include adjustment of solutions by addition of weak or strong acids and bases or salts of these; assessment of intermediate solution states during which precipitation/dissolution or gas exchange takes place.

2. **Two phase (aqueous/gas) equilibrium problems.** This would include determining the final state a water attains either on reaching equilibrium between dissolved and gaseous species (at some prescribed partial pressure), or in moving between two equilibrium states, each described by a different partial pressure of the gas phase.

3. **Two phase (aqueous/solid) equilibrium problems.** Typically this would involve determining the final state water would attain on reaching equilibrium between species in the dissolved and solid phases. This would automatically quantify the mass of mineral which would dissolve or precipitate to attain two phase equilibrium.

4. **Three phase (aqueous/solid/gas) equilibrium problems.** Typical of these would be either precipitation of $CaCO_3$ or Mg NH_4PO_4 (struvite) in anaerobic digesters in which the aqueous phase is also in equilibrium with a gas phase (CO_2) (with some partial pressure) established by the micro-organisms in the process.

With regard to the practical application of (3) and (4) above, the environment of interest in this report is in biosystems where dissolved organic substances are present. These dissolved organics may have a profound effect on mineral dissolution/precipitation. It has been observed that the solubility of many minerals is increased appreciably due to the presence of dissolved organics; this change cannot be quantified in terms of equilibrium chemistry (Stumm & Morgan, 1972, and Wiechers, 1978). From a practical point of view it is common practice to replace the thermodynamic solubility product by an experimentally determined value for a particular aqueous medium. Consequently, solubility products for $CaCO_3$ and $Mg\ NH_4\ PO_4$ need to be quantified in a typical waste water environment.

The report will present the factors discussed above using the following format :

Chapter 2 deals with basic mixed weak acid equilibrium chemistry in environments where the carbonate, phosphate, ammonia and acetate systems are all present simultaneously in solution. In addition, both characterisation of these systems and the fundamentals of change in state due to chemical dosing will be considered.

Chapter 3 deals with algorithms for a quantitative solution to the problems listed in (1) and (4) above. Measurements of solubility products for $CaCO_3$ and $Mg\ NH_4\ PO_4$ in tertiary effluents will be presented.

Appended are the directions for use of a user-friendly program "STRUVITE" to address the problems above.

CHAPTER 2

MIXED WEAK ACID SYSTEMS - EQUILIBRIUM CHEMISTRY

Introduction

In the aqueous environment, weak acids and their dissociated species play an important role in establishing the pH and damping pH changes (i.e. buffering the solution). In terrestrial waters the carbonate system is the dominating one, to such a degree that other weak acid systems are usually neglected. In waste waters, however, in addition to the carbonate system, the phosphate and ammonia systems are present, and in anaerobic waste treatment processes, sulphide and short-chain fatty acid systems (e.g. acetate and proprionate) are generated. All these systems may be present in such large concentrations relative to the carbonate system, that they exert a significant influence on the pH established.

In working with these weak acid systems one is confronted with a number of problems, viz:

- estimation of the concentrations of the species of each of the weak acid systems from a set of observations, called <u>characterization</u>
- estimation of chemicals to be added to change the pH and species concentrations to desired values, called dosing estimation; and
- estimation of the potential mass concentration of a mineral to be precipitated or dissolved to attain saturation, called determination of precipitation potential.

In this chapter characterisation is considered.

pH in Mixed Weak Acid Systems

pH in anaerobic systems is controlled by weak acid chemistry involving a number of weak acid sub-systems simultaneously present in solution, typically the carbonate, phosphate, ammonia, acetate and water sub-systems. The influence of pH on each of these sub-systems is described by a set of aqueous Equilibrium equations (aqueous phase):

$(H^+)[HCO_3^-]/[H_2CO_3^*] = K_{c1}/f_m = K_{c1}'$ } Carbonate sub-system (1)
$(H^+)[CO_3^{2-}]/[HCO_3^-] = K_{c2}\, f_m/f_d = K_{c2}'$ } (2)

$(H^+)[H_2PO_4^-]/[H_3PO_4] = K_{p1}/f_m = K_{p1}'$ } (3)
$(H^+)[HPO_4^{2-}]/[H_2PO_4^-] = K_{p2}\, f_m/f_d = K_{p2}'$ } Phosphate sub-system (4)
$(H^+)[PO_4^{3-}]/[HPO_4^{2-}] = K_{p3}\, f_d/f_t = K_{p3}$ } (5)

$(H^+)[NH_3]/[NH_4^+] = K_n\, f_m = K_n'$ } Ammonia sub-system (6)

$(H^+)[Ac^-]/[HAc] = K_a/f_m = K_a'$ } Acetate sub-system (7)

Values for these equilibrium constants with temperature are given in Table 1.

In addition to the above equations, one can formulate mass balance equations for each of the weak acid sub-systems present in solution :

$$C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (8)$$
$$P_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] \quad (9)$$
$$N_T = [NH_4^+] + [NH_3] \quad (10)$$
$$A_T = [HAc] + [Ac^-] \quad (11)$$

where

(X) = activity of species X in mol/ℓ
$[X]$ = molarity of species X in mol/ℓ
f = activity coefficient, subscripts m and d refer to mono- and di-protic states
K_x = thermodynamic equilibrium constant of species X
K_x' = thermodynamic equilibrium constant of species X, adjusted for Debye-Hückel effects.

The parameters C_T, P_T, N_T and A_T are the total species concentrations for the carbonate, phosphate, ammonia and acetate sub-systems respectively.

TABLE 1

WEAK ACID DISSOCIATION CONSTANTS AND STRUVITE SOLUBILITY PRODUCT AND THEIR TEMPERATURE DEPENDANCY.

pK = (A/T) - B + C.T WHERE IT IS IN DEGREES KELVIN. (TRUESDELL and JONES, 1973)

		pK25° C	A	B	C
Water	pK_w	14.000			
Carbonate	pK_{c1}	6.352	3404.7	14.8435	0.03279
	pK_{c2}	10.329	2902.4	6.4980	0.02379
Henry's constant	pK_H	1.47	-1760.0	-9.619	-0.00753
Phosphate	pK_{p1}	2.148	799.3	4.5535	0.01349
	pK_{p2}	7.198	1979.5	5.3541	0.01984
	pK_{p3}	12.023		not given	
Acetate	pK_a	4.756	1170.5	3.165	0.0134
Ammonium	pK_n	9.245	2835.8	0.6322	0.00123
Struvite solubility product	pK_{spm}	12.60			

Considering water and its species H^+ and OH^- as a separate weak acid sub-system, equilibrium chemistry gives the activity product equilibrium equation :

$$(H^+)\ [OH^-] = K_w/f_m = K_w' \qquad (12)$$

Examination of the above set of equations (i.e. equations 1 - 12) for the five weak acid systems present (the water sub-system making up the fifth), indicates twelve equations with seventeen unknowns (i.e. $[H_2CO_3^*]$, $[HCO_3^-]$, $[CO_3^{2-}]$, ... $[H^+]$, $[OH^-]$, C_T ..... A_T). Thus, in order to speciate the solution (i.e. determine each of the weak acid species concentrations), a value for a parameter for each of the sub-systems must be known (Loewenthal et al, 1989).

That is, some selected set of measurements needs to be made (at least five independent measurements) to characterise the system.

For example, if total weak acid species concentrations, C_T, P_T, N_T and A_T. constitute the measured characterisation parameters for the carbonate, phosphate, ammonia and acetate sub-systems respectively, and pH the measured parameter for the water sub-system, then each of the weak acid species concentrations can be calculated using Equations (1 - 12).

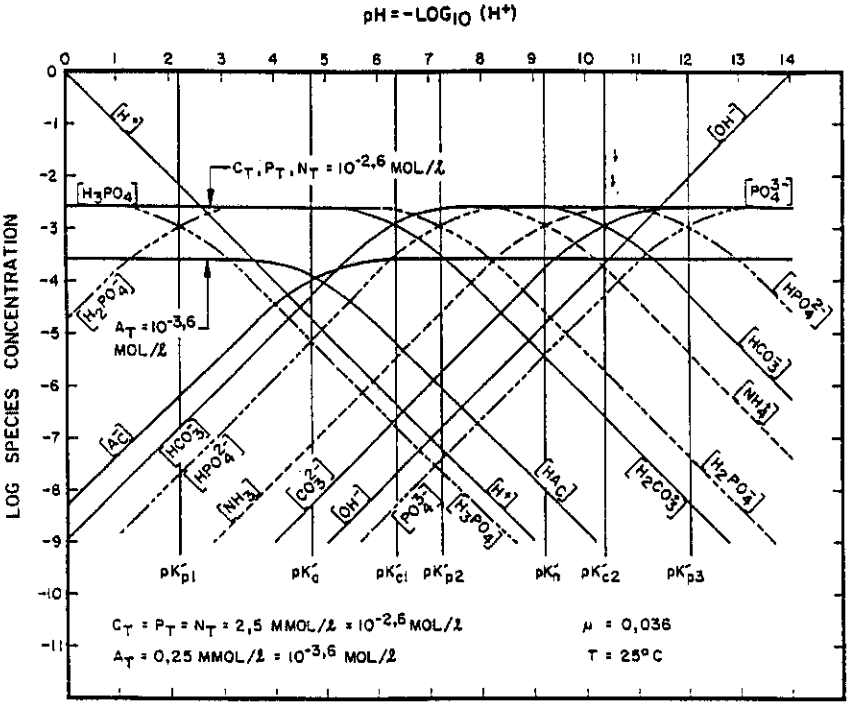

Figure 1: Typical log[species] - pH plot for C_T , P_T and N_T each $10^{-2,6}$ mol/ℓ and A_T = $10^{-3,6}$ mol/ℓ.

Assuming pH is unknown, it is possible to develop a general solution for each of the species concentrations as a function of pH. This is depicted in the log (species) -pH plot shown in Figure 1.

The log (species) -pH plot shown in Figure 1 illustrates clearly that speciation is possible provided pH and total species concentrations for each weak acid sub-system are known. Furthermore, it provides an excellent visual description of the set of system equations, (equations 1 - 12). However, in practice this set of equations is not the most useful for a number of reasons. Firstly, from a characterisation point of view, although pH, P_T, N_T and A_T can be easily measured in the laboratory, C_T can only be measured directly using an inorganic carbon analyser, an instrument rarely available.

Secondly, the set of equations does not form a convenient basis for dealing with problems involving determination of change of state due to some chemical perturbation. In this regard Loewenthal et al (1991), showed that capacity parameters are useful. There are two types of proton accepting/donating capacity parameters :

1. Sub-system Proton accepting/donating/capacity parameters with selected reference species for each of the weak acid sub-systems in the solution termed the sub-system alkalinities/acidities, and

2. solution proton accepting/donating capacity parameters relative to a set of reference species for each of the weak acid sub-systems, termed solution alkalinities/acidities. The solution alkalinities/acidities being equal to the sum of the sub-system alkalinities/acidities.

The solution alkalinities/acidities have a central role in both characterisation of mixed weak acid systems and in solving problems associated with change in state, for two reasons. Firstly, certain of these parameters are amenable to measurement in the laboratory via relatively simple acidimetric/alkalimetric titration. Secondly, these parameters change in a simple stoichometric fashion with chemical dosing.

Before dealing with these two aspects, it is necessary to review briefly the nomenclature that will be used for the various sub-system and solution alkalinities and acidities, and indicate how these parameters are inter-related.

Sub-system and Solution Alkalinities and Acidities

Alkalinity of a sub-system is defined as the proton accepting capacity of weak acid species (belonging to that sub-system) relative to a selected reference species. For example, considering the carbonate system, there is a sub-system alkalinity parameter and equation for each of the three species $H_2CO_3^*$, HCO_3^- and CO_3^{2-} . Using the nomenclature Alk H_2CO_3 to denote the proton accepting capacity of the carbonate sub-system with reference species H_2CO_3 :

$$\text{Alk } H_2CO_3^* = 2\,[CO_3^{2-}] + [HCO_3^-] \tag{13}$$

and similarly selecting each of HCO_3^- and CO_3^{2-} as reference species,

$$\text{Alk } HCO_3^- = [CO_3^{2-}] - [H_2CO_3^*] \tag{14}$$

$$\text{Alk } CO_3^{2-} = -\,[HCO_3^-] - 2\,[H_2CO_3^*] \tag{15}$$

Similar sub-system alkalinity equations can be formulated for each of the weak acid sub-systems with selected reference species.

Acidity of a sub-system is defined as the proton donating capacity (of weak acid species belonging to that sub-system) relative to a selected reference species. Again, considering the carbonate system and using a similar nomenclature to that applied to the alkalinity parameters,

$$\text{Acidity } H_2CO_3^* = -[HCO_3^-] - 2[CO_3^{2-}] \tag{16}$$

$$\text{Acidity } HCO_3^- = [H_2CO_3^*] - [CO_3^{2-}] \tag{17}$$

$$\text{Acidity } CO_3^{2-} = 2[H_2CO_3^*] + [HCO_3^-] \tag{18}$$

For each sub-system the various alkalinities, acidities and total species concentration are interdependant. Two forms of interdependance exist. Firstly, for a particular reference species, alkalinity is simply the negative acidity (see equations 13 and 16, equations 14 and 17 and equations 15 and 18). Secondly, the sum of alkalinities and acidities with reference species one proton apart, equals total species concentration; for reference species two protons apart, the sum is twice the total species concentration, etc. This is illustrated by adding equations 13 and 17, i.e. :

$$\text{Alkalinity } H_2CO_3^* + \text{Acidity } HCO_3^- = C_T \tag{19}$$

and from equations 13 and 18

$$\text{Alkalinity } H_2CO_3^* + \text{Acidity } CO_3^{2-} = 2\,C_T \tag{20}$$

pH and Sub-system Alkalinities and Acidities

The log (species) - pH plot (see Figure 1) illustrates that for any weak acid system in solution, if total species concentration and pH (i.e. (H^+)) are known, then the concentrations of all species for that sub-system can be determined via equilibrium equations. Knowing the species concentrations, the various sub-system alkalinities and acidities can be calculated from the respective equations (i.e. substituting the species concentrations into the relevant alkalinity/acidity equation). Alternatively if pH and a sub-system alkalinity (or acidity) are known, each of the species concentrations, total species concentration and acidity (or alkalinity) for the sub-system can be determined. The same situation applies for each sub-system in the mixture. This is illustrated for the ammonia monoprotic weak acid sub-system below.

(i) If pH and Alk NH_4 are known :

$$\text{Acidity } NH_3 = \{ (H^+)/K_a' \}. \text{ Alk } NH_4 \tag{21}$$

(ii) If pH and N_T are known :

$$\text{Alk } NH_4 = N_T/\{1 + (H^+)/K_a'\} \tag{22}$$

Graphical exposition of the relationships linking pH, total species concentration, alkalinity and acidity for a monoprotic weak acid system (the ammonia system) is easily effected with Alk NH_4 and Acidity NH_3 as coordinates (Loewenthal et al, 1991). Lines representing pH are plotted using Equation (21) and for N_T , using the earlier observation :

$$\text{Alk } NH_4 + \text{Acidity } NH_3 = N_T \quad .$$

Similar plots can be effected for each of the weak acid sub-systems in solution.

pH and Solution Alkalinities and Acidities

Solution alkalinities/acidities equal the sum of all the sub-system alkalinities/acidities. From a nomenclature standpoint, the reference species to a solution alkalinity/acidity are simply the references species for each of the component sub-system values. For example, for an aqueous solution containing the carbonate, phosphate, ammonia and acetate sub-systems, the solution alkalinity with reference species for each sub-system being the most protonated species (termed total Alkalinity, T.Alk)

$$H_2CO_3^*/H_3PO_4/NH_4^+/HAc \text{ alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } H_3PO_4 + \text{Alk } NH_4^+ + \text{Alk HAc} + \text{Alk } H_20$$

$$\begin{aligned} &= \left(2[CO_3^{2-}] + [HCO_3^-]\right) + \left(3[PO_4^{3-}] + 2[H_4PO_4^{2-}] + [H_2PO_4^-]\right) \\ &\quad + \left([NH_3]\right) + \left([OH^-] - [H^+]\right) \qquad (23) \\ &= \text{T.Alk} \end{aligned}$$

Similarly, for solution acidity with reference species for each sub-system being the least protonated species (i.e. total Acidity or T.Acidity) :

$$CO_3^{2-}/PO_4^{3-}/NH_3/Ac^- \text{acidity} = \text{Acid } CO_3^{2-} + \text{Acid } PO_4^{3-} + \text{Acid } NH_3 + \text{Acid } Ac^- + \text{Acid } H_20$$

$$\begin{aligned} &= \left(2[H_2CO_3^*] + [HCO_3^-]\right) + \left(3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{2-}]\right) \qquad (24) \\ &\quad + \left([NH_4^+]\right) + \left([HAc]\right) + \left([H^+] - [OH^-]\right) \\ &= \text{T.Acidity} \end{aligned}$$

Clearly the reference species selected for each weak acid sub-system are arbitrary and selection is made from a point of convenience. This will be clarified later in the report when dealing with chemical dosing problems.

Changes in Solution Capacity Parameters with Dosing

Solution capacity parameters (for example T.Alk and T.Acidity) are extremely useful in aqueous chemistry principally for two reasons. Firstly, certain of these parameters are amenable to measurement thereby aiding in the characterisation of weak acid systems in solution. For example, measurement of T.Alk using a modified Gran titration (see later). Secondly, the values of these parameters change in a simple stoichiometric fashion with chemical dosing. These two observations form the basis to the formulation of algorithms in water and waste water treatment.

With respect to the effects of chemical dosing on the solution capacity parameters, two important points are to be recognised :

(i) addition of a dosing type that constitutes one of the reference species to the solution capacity parameter, has zero effect on that solution capacity parameter, and

(ii) addition/removal of X moles/ℓ of a weak acid dosing type other than a reference species, will increase/decrease a solution alkalinity/acidity by nX moles/ℓ. Where n is the proton deficiency/excess of the dosing chemical relative to the reference species.

These statements are best clarified by examples.

As a first example, consider a solution with T.Alk (i.e. $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alk) equal to X moles/ℓ and T.Acidity (i.e. $CO_3^{2-}/PO_4^{3-}/NH_3/Ac^-$ acidity) equal to Y moles/ℓ. If A moles/ℓ CO_2 (i.e. $H_2CO_3^*$), B moles/ℓ H_3PO_4, C moles/ℓ NH_4^+ and D moles/ℓ HAc are added to the solution, then

$$\Delta\ \text{T.Alk} = 0$$

This arises because all the dosing chemicals are reference species for T.Alk, and

$$\Delta\ \text{T.Acid} = 2\,A + 3\,B + C + D$$

This arises because H_2CO_3 species has a proton excess of 2 relative to reference species CO_3^{2-} ; H_3PO_4 an excess of 3 relative to PO_4^{3-}, and NH_4^+ and HAc each have excesses of 1 relative to the respective reference species NH_3 and Ac^-. The values for T.Alk and T.Acidity after dosing are simply the initial value plus the change(s), i.e.

$$\text{T.Acid (final)} = \text{T.Acid (initial)} + \Delta\ \text{T.Acid}$$

As a second example, consider a solution again with T.Alk equal to X moles/ℓ and T.Acidity equal to Y moles/ℓ. The affects on these parameters of addition of A moles/ℓ CO_3^{2-} (e.g. addition of $Na_2\,CO_3$), B moles/ℓ PO_4^{3-}, C moles/ℓ of NH_3 and D moles/ℓ of Ac^- to the solution are :

$$\Delta \text{ T.Alk} = 2\,A + 3\,B + C + D$$

That is, CO_3^{2-} species has a proton deficiency of 2 relative to the reference species H_2CO_3 ; PO_4^{3-} a deficiency of 3 relative to H_3PO_4 (the reference species for T.Alk), and NH_3 and Ac^- each a deficiency of 1 relative to the reference species NH_4^+ and HAc, respectively.

For the change(s) in T.Acidity, the species added constitute reference species, i.e.

$$\Delta \text{ T.Acidity} = 0$$

Again, the final values for T.Alk and T.Acidity will be the initial values plus the changes (i.e. Δ T.Alk and Δ T.Acidity).

As a third example, consider addition of either a strong acid or a strong base to a solution. The changes in T.Alk and T.Acidity follow directly from the definitions of these parameters, that is,

$$\Delta \text{ T.Alk} = \text{moles}/\ell \text{ of } OH^- \text{ added} - \text{moles}/\ell \text{ of } H^+ \text{ added}$$

and

$$\Delta \text{ T.Acidity} = \text{moles}/\ell \text{ of } H^+ \text{ added} - \text{moles}/\ell \text{ of } OH^- \text{ added.}$$

Summarising the affects on T.Alk (i.e. $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alk) and T.Acididty (i.e. $CO_3/PO_4/NH_3/Ac$ acidity) of addition of various chemical dosing types,

$$\begin{aligned}\Delta \text{T.Alk} = {} & (2[CO_3]_a + [HCO_3]_a) + (3[PO_4]_a + 2[HPO_4]_a + [H_2PO_4]_a) \\ & + ([NH_3]_a) + ([Ac]_a) + ([OH]_a - [H]_a)\end{aligned} \tag{25}$$

$$\begin{aligned}\Delta \text{T.Acidity} = {} & (2\,[H_2CO_3]_a + [HCO_3]_a) + (3\,[H_3PO_4]_a + 2\,[H_2PO_4]_a + [HPO_4]_a) \\ & + ([NH_4]_a) + (\,[HAc]_a) + (\,[H]_a - [OH]_a)\end{aligned} \tag{26}$$

Where :

$[\,X\,]_a$ = moles/ℓ of dosing species X added to the solution.

Characterisation of Mixed Weak Acid Systems

It has been stated repeatedly in this report that characterisation requires knowing (measuring) values for one parameter for each weak acid sub-system present. Earlier it was shown that if total species concentrations for each weak acid sub-system are known, and pH for the water sub-system, then the solution is completely characterised. In practice, the total species concentrations for the phosphate, ammonia, and acetate sub-systems are easily measured following procedures set out in Standard Methods (1983). Further, pH is commonly and easily measured. The remaining problem regarding measurement of a parameter for the carbonate sub-system is considered below.

Three parameters would appear to be convenient for direct measurement to characterise the carbonate sub-system. Firstly the partial pressure of CO_2 ($\bar{p}\ CO_2$), and secondly, the total dissolved inorganic carbon (C_T). Alternatively, an indirect method of characterising the carbonate system is available via measurement of solution alkalinity. As stated earlier, C_T requires using an inorganic carbon analyzer which is expensive and only rarely available in conventional laboratories. Measurement of the partial pressure of CO_2 is practical using an appropriate electrode.

Characterisation of the Carbonate Sub-system via $\bar{p}\ CO_2$ Measurement

Where a carbon dioxide sensitive probe is available, the partial pressure of CO_2 in solution, $\bar{p}\ CO_2$, can be measured directly. This measurement can then be used to quantify the dissolved carbonate species via equilibrium chemistry as set out below :

The sum of molecularly dissolved CO_2 and carbonic acid, $H_2CO_3^*$, is determined via Henry's Law, i.e. :

$$[H_2CO_3^*] = K_H \,.\, \bar{p}\,CO_2 \qquad (27)$$

where K_H = Henry's Constant.

In a mixed weak acid system where the water sub-system has been characterised by pH measurement, the bicarbonate concentration is then determined via equilibrium chemistry as :

$$[HCO_3^-] = K_1'.K_H.\bar{p}CO_2/(H^+)$$

and the carbonate concentration as :

$$[CO_3^{2-}] = K_2'.K_1'.K_H.\bar{p}CO_2/(H^+)^2$$

The total dissolved inorganic carbon species concentration is then given by the sum of the three species above.

Characterisation of the Carbonate Sub-system via Solution Alkalinity (T.Alk) Measurement

In essence the method constitutes an extension of the Gran method for determining Total alkalinity ($H_2CO_3^*$ alkalinity) in waters where the carbonate system is the only weak acid sub-system in solution. Gran, (1952), developed a method for determining any of the alkalinities and acidities relative to respective equivalent solutions, without requiring knowledge of the respective equivalence points; **the method was formulated for waters containing only one weak acid sub-system in solution.** Up to the present, Gran's method has found application principally for determining $H_2CO_3^*$ alkalinity, in this report this determination is extended to determine a total alkalinity in solutions where a number of weak acid sub-systems are simultaneously present in solution. In developing the method, first the Gran determination of $H_2CO_3^*$ alkalinity will be reviewed and thereafter extended to mixed systems.

Consider an aqueous solution in which only the carbonate sub-system is present. Assume a strong acid titration has been performed on the solution to well below the $H_2CO_3^*$ equivalence point (i.e. $pH \leq 4{,}5$), and that pH titration data is available in this region (i.e. $3{,}3 \leq pH \leq 3{,}8$). Assume also, that V_E is the **unknown** volume of strong acid to reach the $H_2CO_3^*$ equivalence point, which is to be determined, i.e.

$$H_2CO_3^* \text{ alkalinity} = V_e \cdot C_a / V_s \tag{28}$$

Where C_a = H^+ molarity of standard acid
V_s = volume of sample (mℓ)

Now, after adding V_x mℓ of standard acid, two equations can be formulated for the $H_2CO_3^*$ alkalinity (after addition of acid). First, in terms of weak acid species concentrations :

$$H_2CO_3^* \text{ alk.}_x = 2[CO_3^{2-}]_x + [HCO_3^-]_x + [OH^-]_x - [H^+]_x \tag{29}$$

Where subscript 'x' = value of parameter after addition of V_x mℓ strong acid.

In the pH region under consideration (i.e. pH well below the $H_2CO_3^*$ equivalence point ($3{,}8 \geq pH_x \geq 3{,}3$), Equation (29) above approximates to :

$$H_2CO_3^* \text{ alk.}_x \approx -[H^+]_x \tag{30}$$

Second, an equation in terms of V_E and V_x , the volumes of acid to the $H_2CO_3^*$ equivalence point and that actually added respectively, i.e.

$$H_2CO_3^* \text{ alk}_x = \frac{V_e \bar{c}_a}{V_s + V_x} - \frac{V_x \bar{c}_a}{V_s + V_x} \tag{31}$$

Equating Equations (30 and 31) and simplifying, gives the first Gran Function value (F_{1x}) after addition of V_x mℓ strong acid, i.e.

$$\bar{c}_a\ (V_e - V_x) = -10^{-pH_x}\ (V_s + V_x) = F_{1x} \tag{32}$$

Values for F_{1x} in the pH region under consideration are determined by substituting V_x and corresponding pH_x into the middle term in Equation (32) above. Furthermore a plot of V_x versus F_{1x} will be linear ($\delta F_{1x} / \delta V_x = -\bar{C}_a$, from the first term in Equation 32), and linear extrapolation to $F_{1x} = 0$ gives $V_e = V_x$. This value determined for V_e is then used to calculate $H_2CO_3^*$ alkalinity.

The approach above can be extended to solutions comprising a mixture of carbonate and other weak acid systems, provided total species concentrations are known for these extra weak acid sub-systems.

Proceeding in the same way as for the carbonate system alone in solution, assume that V_E is the unknown volume of strong acid needed to adjust the solution to an equivalent $H_2CO_3^*$ / $H_2PO_4^-$ / HA / NH_4^+ solution, i.e.

$$H_2CO_3^*/H_2PO_4^-/HA/NH_4^+ \text{ alkalinity} = V_E.\bar{c}_a/V_s \tag{33}$$

$$= \text{T.Alk} \tag{33a}$$

After addition of V_x mℓ of standard acid, two equations can be formulated for T Alk_x (T Alk after addition of V_x mℓ acid).

First, in terms of weak acid species concentrations of the various sub-systems present in solution. In our case the carbonate, phosphate, ammonia and acetate sub-systems are present. Selecting the most protonated species as reference species for each sub-system and H_2PO_4 for the phosphate sub-system,

$$\begin{aligned} H_2CO_3^*/H_2PO_4^-/NH_4^+/HA \text{ alk} &= \left(2\,[CO_3^{2-}]_x + [HCO_3^-]_x\right) \\ &+ \left(2\,[PO_4^{3-}] + [HPO_4^-]_x - [H_3PO_4]_x\right) + \ldots\ldots\left([OH]_x - [H^+]_x\right) \end{aligned} \tag{34}$$

$$= \text{Alk}_x \tag{34a}$$

where subscript 'x' = value of parameter after addition of V_x mℓ standard acid (H^+).

The reason for utilising $H_2PO_4^-$ as the reference species for the phosphate sub-system, is one of convenience in formulating a Gran function (see below).

In the pH region where the Gran function is to be formulated (i.e. where CO_3^{2-} and HCO_3^- species concentrations are negligible, pH $\leq$ 3,8) Equation (34) above approximates to :

$$\text{Alk}_x = -[H_3PO_4]_x + [A^-]_x - [H^+]_x \tag{35}$$

Second, an equation for T Alk_x in terms of V_E and V_x , i.e.

$$\text{TAlk}_x = \frac{V_E\,\bar{c}_a}{V_s + V_x} - \frac{V_x\,\bar{c}_a}{V_s + V_x} \tag{36}$$

Equating Equations (35) and (36) and simplifying :

$$\left(-[H^+]_x - [H_3PO_4]_x + [A\bar{c}]_x\right).(V_s + V_x) = \bar{C}_a\,(V_e - V_x) \tag{37}$$

For this function to be useful in constructing a Gran plot from pH_x and V_x measurements, the $[H^+]_x$ term needs to be expressed in terms of pH_x , and the terms $[H_3PO_4]_x$ and $[A\bar{c}]_x$ need to be expressed in terms of pH_x and the respective measured total species concentrations, P_T and A_T , i.e.

$$[H^+]_x = 10^{-pH_x}/f_m \tag{38}$$

$$[H_3PO_4]_x = \frac{10^{-pH_x}}{10^{-pH_x} + 10^{-pK'_{p1}}} \cdot \frac{P_T\ V_s}{V_s + V_x} \tag{39}$$

and

$$[A\bar{c}]_x = \frac{10^{-pK'_a}}{10^{-pH_x} + 10^{-pK'_a}} \cdot \frac{A_T\ V_s}{V_s + V_x} \tag{40}$$

where K'_a and K'_{p1} = acetate and first phosphate apparent weak acid dissociation constants respectively.

Substituting Equations (38) to (40), into Equation (37), and simplifying, gives a useful form for the Gran function, F_{1x} for a mixed weak acid system, comprising the carbonate, phosphate, acetate and ammonia sub-systems with $H_2CO_3^*$ / $H_2PO'_4$ / HAc / NH^+_4 reference species :

$$F_{1x} = f_m\ \bar{c}_a\ (V_e - V_x) \tag{41a}$$

$$= O_x + Q_x + R_x \tag{41b}$$

$$\text{where } O_x = (10^{-pH_x}) \cdot (V_s + V_x) \tag{42a}$$

$$Q_x = \frac{f_m . P_T . 10^{-pH_x}}{10^{-pH_x} + 10^{-pK'_{p1}}} . V_s \qquad (42b)$$

$$R_x = \frac{f_m \; A_T \; 10^{-pK''_a}}{10^{-pH_x} + 10^{-pK'_a}} . V_s \qquad (42c)$$

To obtain the Gran plot, F_{1x} values are calculated for a set of pH_x and V_x values (using Equation 41b and Equations 42a to 42c) and plotted against V_x. In the region $pH_x \leq 3,8$ the plot will be linear; if extrapolated to intersect the V_x axis, i.e. where $F_{1x} = 0$, the point of intersection defines the value of V_E. Substituting V_E into Equation 33, gives T Alk (i.e. $H_2CO_3^*$ / $H_2PO^-_4$ / HAc / NH^+_4 alkalinity) of the sample.

To characterise the carbonate sub-system from the T Alk value determined using the Gran plot, we note that T Alk is the sum of the sub-system alkalinities, i.e.

$$\begin{aligned} H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+alk &= AlkH_2CO_3^* + AlkH_2PO_4^- + AlkHAc \\ &+ AlkNH_4^+ + AlkH_2O \end{aligned} \qquad (43)$$

Each of the sub-system alkalinities (except for alk $H_2CO_3^*$) are determined from the measured total species concentration and initial pH of the solution, e.g. the initial pH is in the region pH ~ 7, then the terms $[H_3\,PO_4]$ and $[PO^{3-}{}_4]$ are negligible, and alk $H_2PO^-_4 \approx [HPO^-_4]$

$$\approx P_T \, . \, K'_{2p}/\left[\, (H^+) + K'_{2p} \right] \qquad (44)$$

The Alk NH^+_4 and Alk HAc values are determined as set out in Equation (22). Alk $H_2CO^*_3$ is then given by

$$AlkH_2CO_3^* = H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+alk - AlkH_2PO_4^- - AlkHAc - AlkNH_4^+ \quad (45)$$

Once Alk $H_2CO^*_3$ has been determined, C_T can be calculated from equilibrium equations and the measured pH, i.e.

$$\begin{aligned} C_T &= AlkH_2CO_3^*/(2K'_{cz}.Z/(H^+) + Z) \\ \text{where } Z &= (H^+)/K'_{c1} + 1 + K'_{c2}/(H^+) \end{aligned} \quad (46)$$

K'_{c1} and K'_{c2} = apparent first and second dissociation constants for the carbonate system.

CHAPTER 3

ALGORITHMS FOR CONTROL OF pH AND MINERAL PRECIPITATION

For an aqueous solution containing weak acid-base systems in solution, first these systems need to be characterised via a set of measurements (see Chapter 2), thereafter a number of water treatment tasks can be addressed. Those of importance to this report include (a) estimating the dosage of a specified chemical to adjust the water to some desired final pH; (b) determining the potential of a mineral to either precipitate or dissolve (quantitatively and qualitatively) in the solution; and (c) determining changes in the mineral precipitation potential arising from some external perturbation (for example, loss of CO_2 from solution to the air). All these types of problems can be solved using algorithms based on equilibrium chemistry.

In this chapter a number of algorithms are presented. These include (a) estimating strong acid or base to adjust pH to a desired value, (b) estimating struvite and calcite precipitation potential, (c) estimating change in state with carbon dioxide uptake or release, and (d) estimating the change in mineral precipitation/dissolution potential resulting from (a) and (c).

These algorithms are set out in some detail below. Recognising that the work reported here is relevant to waste waters with high concentrations of Ca^{2+}, Mg^{2+}, P_T, N_T and C_T, and that these solutions arise principally in either anaerobic digesters or treatment of bio-sludges, two treatment scenarios need to be addressed. Firstly, the situation within an anaerobic digester where the aqueous solution remains in equilibrium with a gaseous phase (CO_2) with a partial pressure established by the micro-organisms. In this scenario one may wish either to predict change in state (pH) caused by a change in partial pressure of CO_2, or a change in state arising from chemical dosing to the system. In both cases, equilibrium between species in the aqueous and gaseous phases (i.e. two phase equilibrium) is maintained. Secondly, the situation outside an anaerobic digester where CO_2 exchange with a gas phase may not necessarily occur (depending on physical conditions), in which event one is dealing with a chemical dosing problem involving single aqueous phase equilibrium. In both the scenarious set out above one may also wish to determine the propensity of the solution to precipitate/dissolve a particular mineral (for example struvite). Here the precipitating/dissolving mineral is considered to be the dosing chemical, and depending on the physical conditions, the carbonate system is characterised either via the carbon dioxide partial pressure (aqueous-gas phase scenario), or via the initial total dissolved inorganic carbon concentration (aqueous phase scenario, i.e. no CO_2 exchange with the gas phase).

Algorithm 1 : pH Adjustment with Addition of Strong Acid/Base

Step 1 : Input data required includes a known value for each of the weak acid sub-systems present, i.e. A_T, N_T and P_T for the acetate, ammonia and phosphate sub-systems, respectively, and pH for the water sub-system. For the carbonate sub-system, either $\bar{p}CO_2$ or T.Alk, constitute the measured parameters (see characterisation in Chapter 2). In addition, to calculate the apparent equilibrium constants, the temperature and ionic strength (TDS) need to be known.

Step 2 : Obtain thermodynamic equilibrium constants for each of the weak acid systems present (using relevant data listed in Table 1). Determine activity coefficients from the Debye-Hückel equation and adjust the equilibrium constants to obtain apparent values (valid for TDS $\leq$ 1 000 mg/ℓ.

Step 3 : Speciate the initial solution. For each of the weak acid sub-systems in the solution (except for the carbonate sub-system) determine individual weak acid species concentrations from the known total species concentration and intial pH. For the carbonate sub-system, each of the species concentrations is determined depending on how this sub-system is characterised. If characterisation is via pH and $\bar{p}CO_2$, then $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ are determined as set out in Chapter 2. However, if characterisation is via T.Alk and pH, then each of the sub-system akalinities, Alk NH_4, Alk H_3PO_4 Alk H_2O are determined from the relevant species concentrations calculated above, and Alk $H_2CO_3^*$ as :

$$\mathrm{AlkH_2CO_3^*} \;=\; \mathrm{T.Alk} - (\mathrm{AlkNH_4} + \mathrm{AlkH_3PO_4} + \mathrm{AlkH_2O})$$

The individual carbonate species concentrations are then determined from pH and Alk $H_2CO_3^*$.

Step 4 : Speciate the solution at the final pH (after strong acid/base dosing). For each of the weak acid sub-systems (except for the carbonate system) species concentrations and sub-system alkalinities are determined as in Step 3 above. For the carbonate sub-system, if equilibrium is maintained with the gas phase (i.e. within an anaerobic digester) then each of the carbonate species concentrations is determined from pH and pCO_2. If no CO_2 exchange occurs with the gas phase, C_T is known from Step 3 and each of the species concentrations is determined for the new pH.

Step 5 : Determine the solution alkalinity, i.e. T.Alk after dosing.

Each of the sub-system alkalinities is determined from the species concentrations determined in Step 4.

$$\text{T.Alk (final)} = \Sigma \text{ sub-system alk (final)}.$$

Step 6 : Determine strong acid/base dosage.

$$\text{Dosage} = \text{T.Alk (final)} - \text{T.Alk (initial)}.$$

If dosage is positive, a strong base is to be added; if negative, a strong acid.

Struvite Saturation State

Struvite ($MgNH_4PO_4$) will either precipitate or dissolve into solution (provided the mineral is present) until an equilibrium situation occurs between magnesium, ammonium and phosphate species in the aqueous and solid phases, i.e. at equilibrium,

$$(MgNH_4PO_4)_{SOLID} \rightleftharpoons Mg^{2+} + NH_4^{+} + PO_4^{3-} \qquad (47)$$

with the thermodynamic solubility product equation

$$[Mg^{2+}]\ [NH_4^{+}]\ [PO_4^{3-}] = K_{spm}' \qquad (48)$$

where :

K_{spm}' = thermodynamic solubility product for struvite adjusted for Debye-Hückel effects.

When the product of the species concentrations on the left hand side of equation (48) exceeds K_{spm}' the solution is supersaturated with respect to struvite and the mineral will precipitate from solution, and when the product is less than K_{spm}' the mineral will tend to dissolve into solution.

To assess the saturation state of a solution, concentrations in solution of Mg^{2+}, NH_4^{+} and PO_4^{3-} need to be determined. For Mg^{2+} this is effected by direct measurement (Standard Methods 1985). For NH_4^{+} and PO_4^{3-}, these would be determined from speciation as set out above. The product of species concentrations is compared with K_{spm}' yielding a qualitative description of the saturation state. As the mineral is composed of weak acid species (NH_4^{+}, PO_4^{3-}), the concentrations of which are affected by both the precipitation/dissolution phenomenon and the resultant pH change, this technique cannot reflect the mass concentration of mineral that can precipitate out of solution. In this regard, from a practical point of view the struvite precipitation potential is of fundamental importance.

Struvite Precipitation Potential

The precipitation potential of a mineral is the mass concentration of the mineral that will precipitate from solution to establish an equilibrium state between species in the aqueous and solid phases. Loewenthal *et al* (1976, 1986) showed that where the carbonate and water sub-systems are the only weak acid sub-systems in solution, the precipitation potential for carbonate minerals can be determined relatively easily from the initial characterised state (initial pH, Alkalinity and calcium concentrations). Their algorithm is based on two fundamentals. First, if an aqueous calcium carbonate solution is known to be saturated with respect to calcite, values for only two parameters need to be known at saturation to characterise the solution. In this regard Total acidity and Total alkalinity minus twice calcium molarity (AM2C), are parameters that remain unchanged with calcite precipitation, so that the values for these parameters at saturation equals the initial known values. Second, for a fixed Total acidity, the Total alkalinity increases or decreases with increase or decrease in pH respectively. This latter observation allows for a rapid successive approximation technique to determine the saturation state. Unfortunately an analogous algorithm cannot be applied to determine the struvite precipitation potential because this mineral is composed of both proton donating and accepting species (NH_4^+ and PO_4^{3-}) so that the solubility of the mineral does not necessarily vary monotonically with pH.

An approach to determine the struvite precipitation is one of successive approximation applied directly to the precipitation potential. In this approach a dosage of struvite is applied to (or removed from) the solution and the solution characterised in the new state allowing determination of the new species product ($[Mg^{2+}]$ $[NH_4^+]$ $[PO_4^{3-}]$). The dosage is then adjusted, the solution characterised and the species product recalculated. This is repeated until the species product equals the appropriate solubility product K_{spm}'.

In this regard the crux of the problem is to characterise the new state of a solution for a known applied dose of struvite.

This in essence is a single aqueous phase conditioning problem, the solution of which can be obtained using principles, for chemical conditioning of solutions comprised of mixtures of weak acid sub-systems, Loewenthal *et al* (1991).

Formulation of an algorithm for precipitation potential will be done in a piece-meal fashion. First, an algorithm will be formulated to determine change in state with addition/removal of a specific molar mass of struvite. Second, this will be extended to determine the dosage to obtain saturation with respect to struvite. Finally the algorithm will be extended to determine the change in struvite precipitation potential arising from some external perturbation applied to the system either by change in $\bar{p}CO_2$ or generation/abstraction of volatile fatty acids (i.e. acetic acid).

Algorithm 2 : Change in State with Addition/Removal of Struvite

An algorithm to determine the state of a solution after dosing centres around the criteria discussed earlier for characterisation. That is, the state after dosing can be determined provided a value is known for a parameter for each sub-system *after* dosing. Where the dosing type is struvite (i.e. $MgNH_4PO_4$) the final total species concentrations for the ammonium and phosphate sub-systems can be determined stoichiometrically, as the original concentration minus (plus) the molar mass of struvite removed (added). For the carbonate sub-system, the parameter used depends on whether the aqueous solution is isolated from, or in equilibrium with, the gas phase. If the solution is isolated, then the total carbonate species concentration (C_T) is unaffected by the struvite dosage and the final value for C_T equals the initial value; if the solution is in equilibrium with the gas phase then $\bar{p}CO_2$ (which is known) is used. For the water sub-system, however, a problem arises as pH (final) is unknown and is to be calculated. To overcome the problem of not knowing the pH (final) for the water sub-system, an alternative parameter has to be selected. In this regard, the parameter selected is a solution alkalinity with *all* the reference species either in the most protonated form (i.e. $H_2CO_3^*$, NH_4^+, H_3PO_4 , HAc alkalinity) or in the least protonated form (i.e. CO_3^{2-} , NH_3 , PO_4^{3-} , Ac^- alkalinity). The reason for this selection is that it is only with these two sets of reference species that the corresponding alkalinity value will vary monotonically with pH for dosing with NH_4^+ and PO_4^{3-} species simultaneously (i.e. $MgNH_4PO_4$ addition or removal). Such monotonic behaviour is necessary because the final state (i.e. final pH) is determined by a method of successive approximation.

For an assumed pH value, and known $\bar{p}CO_2$ (or solution alkalinity) and total species concentration for each weak acid sub-system (except for the carbonate sub-system), the solution alkalinity is determined and compared with the known value; pH is adjusted until the calculated and known solution alkalinities agree to within some prescribed limit. Clearly, for the algorithm to converge, the calculated solution alkalinity must either increase or decrease monotonically with pH. The only two solution alkalinities that fulfil this requirement are those with reference species all either in the most or least protonated form.

The various steps in an algorithm to determine change in state due to precipitation of X mol/ℓ of struvite from an aqueous solution with known pH before dosing, in equilibrium with a gas phase with carbon dioxide partial pressure $\bar{p}CO_2$ and containing the phosphate, ammonium and acetate weak acid systems each with total species concentrations P_T, N_T and A_T (all on the molar scale) respectively, are as follows :

Step 1 : Obtain thermodynamic equilibrium constants for each of the weak acid system present (using relevant data listed in Table 1). Determine activity coefficients from the Debye-Hückel equation and adjust the equilibrium constants to obtain apparent values.

Step 2 : Speciate the solution : For each of the weak acid systems in the solution (except for the carbonate system) determine the individual weak acid species concentrations from the known total species concentration and pH. For example, for the acetate system

$$[Ac^-] = A_T \,.\, K_a' \,/\, \{K_a' + (H^+)\} \tag{49a}$$

$$[HAc] = A_T \,.\, (H^+) \,/\, \{K_a' + (H^+)\} \tag{49b}$$

For the carbonate solution, each of the species concentrations is determined from $\bar{p}CO_2$ and pH as set out in Chapter 2.

Step 3 : Determine solution alkalinity (with reference species in the most protonated form) by substituting the relevant species concentration determined in (2) above into the equation for this parameter.

Step 4 : Determine values for the total species concentrations for each of the weak acid subsystems (except for the carbonate system) and X moles/ℓ of struvite has precipitated, i.e.

$$N_T \text{ (final)} = N_T \text{ (initial)} - X \quad (50a)$$

$$P_T \text{ (final)} = P_T \text{ (initial)} - X \quad (50b)$$

$$A_T \text{ (final)} = A_T \text{ (initial)} \quad (50c)$$

Step 5 : Determine the new solution alkalinity (with reference species $H_2CO_3^*$, H_3PO_4, NH_4^+ and HA_c) for the state after precipitation of X mol/ℓ of struvite as;

$$H_2CO_3^*, H_3PO_4, NH_4^+, HAc \text{ alk (final)} = H_2CO_3^*, H_3PO_4, NH_4^+, HA_c \text{ alk (initial)} - 3X \quad (51)$$

Step 6 : Determine pH after dosing (i.e. after precipitation of X mol/ℓ of struvite) using an iterative method of successive approximation as follows: Select a pH value and determine *a calculated* solution alkalinity (with respect to the most protonated reference weak acid species) following steps (2) and (3) above with the specified $\bar{p}CO_2$ and total weak acid species concentration determined in (4) above. The calculated solution alkalinity now is compared with the known value determined in (5) above after removal of X moles/ℓ of struvite. If the calculated value exceeds the known value pH is decreased, and *vice versa* if the calculated value is less than the known value. This procedure is repeated until the calculated and known solution alkalinities are equal (within prescribed limits).

Algorithm 3 : Determination of Struvite Precipitation Potential

The algorithm above is extended easily to determine the struvite precipitation potential. Briefly, this is effected by assuming initially a dosage of struvite instead of using a prescribed dosage as in Algorithm 2. The solution pH then is determined for this assumed dosage (following Steps (4) to (6) above), and the individual weak acid species concentrations (in particular NH_4^+ and PO_4^{3-}) determined from the calculated pH and adjusted total weak acid species concentrations as outlined in Step 2 above. The molar product of the species Mg^{2+}, NH_4^+ and PO_4^{3-} then is calculated and compared with the apparent solubility product K_{spm}'. If the calculated species product value exceeds K_{spm}' the assumed value for X is decreased, and if the molar product value is less than K_{spm}' the assumed value for X is increased. This procedure is repeated until the species product and K_{spm}' are equal (within the prescribed limits).

The struvite precipitation potential (on the molar scale) is then determined either as the change in Mg_T or N_T or P_T between the initial and final states, or as three times the change in the solution alkalinity (with reference species in the most protonated form).

Algorithm 4 : Change in Struvite Precipitation Potential with (change in) $\bar{p}CO_2$

This algorithm models a situation often arising in anaerobic biotreatment processes where the mixed liquor in the bioreactor is in equilibrium with CO_2 in the gas phase at some $\bar{p}CO_2$ value and the solution is either undersaturated, or not excessively supersaturated with respect to struvite, but in transporting the treated liquor, pressure reductions (i.e. a decrease in $\bar{p}CO_2$) may cause gross supersaturation and associated struvite precipitation fouling problems. An algorithm to model this situation involves a simple extension to Algorithm 3. That is, for a particular set of input data (including pH, $\bar{p}CO_2$ and total species concentrations for each of the weak acid sub-systems in the solution except for the carbonate system), Algorithm 3 is used to determine, *inter alia*, the struvite precipitation potential and solution alkalinity at the initial $\bar{p}CO_2$ value. Thence an extra step is introduced to determine the new characteristics of the solution (including the new pH) corresponding to the prescribed new $\bar{p}CO_2$ value. Algorithm 3 is then reused to determine the new struvite precipitation potential at the new pH and $\bar{p}CO_2$ values.

Determination of the new characteristics (i.e. the new pH and individual weak acid species concentrations) corresponding to a prescribed new $\bar{p}CO_2$ value is in essence a chemical conditioning problem involving "dosing" with carbon dioxide. As such solution is effected using principles set out by Loewenthal *et al* (1991). They showed that the state of a water after chemical dosing can be determined using equilibrium chemistry provided that a value is known in the final state for each of the weak acid sub-systems (including water as a separate sub-system). In this regard, the prescribed final $\bar{p}CO_2$ suffices for the carbonate sub-system and the input (original) total weak acid species concentrations suffice for all the other weak acid sub-systems (except for the water sub-system). For the water sub-system no obvious system parameter appears available (in this example final pH is unknown and to be determined), however, recognizing that the 'dosing chemical' is CO_2, any **solution** alkalinity or acidity with $H_2CO_3^*$ as reference species remains unchanged between initial and final state.

Consequently, the **initial** solution alkalinity (with reference species in the most protonated form) which is determined from the input data to determine the initial struvite precipitation potential (i.e. step 4 of Algorithm 3) equals the final solution alkalinity after the change in $\bar{p}CO_2$ and constitutes the required system parameter for the water sub-system. Final pH is determined then by a method of successive approximation.

Experimental Verification

The algorithms presented above were assessed using observed data from laboratory-scale investigations. Solutions were prepared by adding measured molar masses of $NH_4C\ell$, K_2HPO_4 and $MgC\ell_2.6H_2O$ to distilled water; carbonate species were introduced into solution by continuous sparging with CO_2 of known partial pressure. Measurement of free and saline ammonia (N_T) and dissolved orthophosphate concentration (P_T) were effected following Standard Methods (1985), and magnesium concentration via atomic adsorption spectrophotometry.

Two aspects of the algorithms presented above were investigated. First, an aqueous/gaseous phase equilibrium situation where known molar masses of phosphate and ammonia species were added to solution (establishing a known P_T, N_T and solution total alkalinity) and $\bar{p}CO_2$ concentration established by sparging with CO_2 of known partial pressure (i.e. a solution undersaturated with respect to $MgNH_4PO_4$ - because no Mg^{2+} was added). The pH of the solution was measured and compared with pH predicted using Algorithm 2. Second, an aqueous/gaseous/solid ($MgNH_4PO_4$) phase equilibrium situation where a known molar mass of Mg^{2+} was added to the solution above causing struvite to precipitate. The three phase equilibrium condition was assumed once pH attained a constant value. Hereafter, the solution was filtered and concentrations in solution of Mg^{2+}, N_T and P_T measured. The struvite precipitated was determined from the average molar changes in these three parameters and compared with the value predicted using Algorithm 4. Results for two solutions, one with zero carbonate species and a second for a solution sparged with air ($\bar{p}CO_2$ = 0.00037 Atm.) are shown in Tables 2 and 3 respectively.

Struvite fouling problems in anaerobic digesters usually arise in situations where reduction in $\bar{p}CO_2$ occurs, for example at inlet to pumps and in sedimentation units which are open to the atmosphere. This is illustrated in Figure 2, in which is shown the effect of change in $\bar{p}CO_2$ on pH and struvite precipitation potential (predicted using algorithm 3) for a water with the *initial* characteristics $\bar{p}CO_2$ = 0.5 Atm, pH = 7.0, Mg_T = 150 mg/ℓ, N_T = 135 mg/ℓ, P_T = 140 mg/ℓ, Ca = 100 mgCaCO$_3$/ℓ and temperature 20° C. Referring to Figure 2, initially the water has a propensity to **dissolve** 140 mg/ℓ of struvite; with **decrease** in $\bar{p}CO_2$ both pH and struvite precipitation potential **increase** to the eventual state shown in the plot where $\bar{p}CO_2$ is 0,05 Atm. giving a pH = 7.99 and a struvite precipitation potential of 378 mg/ℓ. The model clearly predicts that for relatively small decreases in pressure large increases may arise in struvite precipitation potential. This in turn could give rise to acute mineral precipitation fouling problems.

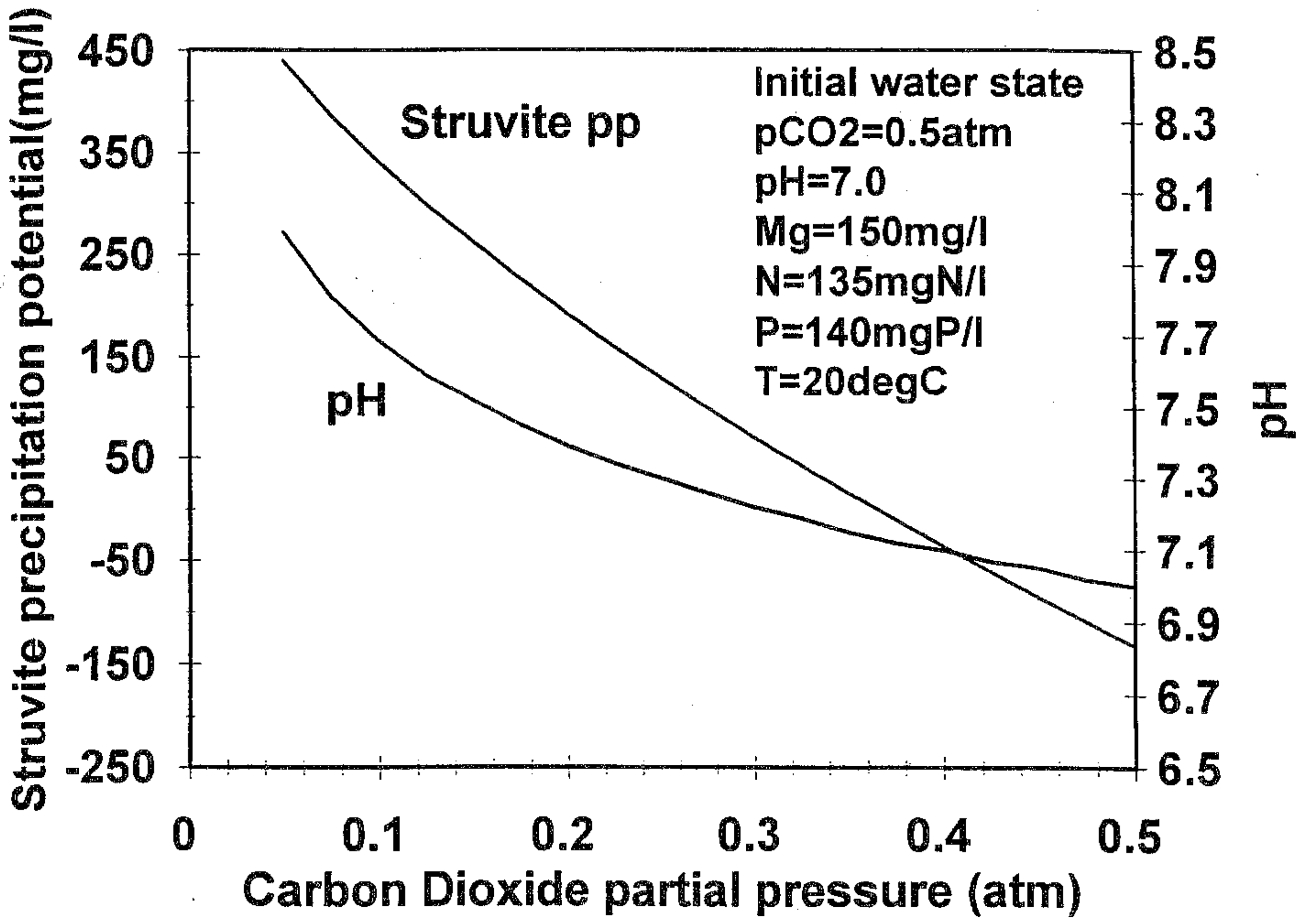

Figure 2 : A plot of $\bar{p}CO_2$ versus both Struvite precipitation potential, and pH after reaching equilibrium with CO_2 in the gas phase but before struvite precipitation

TABLE 2

PREDICTED AND OBSERVED pH AND STRUVITE PRECIPITATION POTENTIAL FOR A SOLUTION INITIALLY WITH C_T = 0.0 mg/ℓ, N_T = 300 mg/ℓ, P_T = 400 mg/ℓ (solution Total alk. = 1 276 mg/ℓ as $CaCO_3$ and temperature 20°C, TDS = 1000 mg/ℓ)

		pH		Struvite precipitated	
	Mg^{2+} mg/ℓ Observed	Predicted	Observed	Predicted mg/ℓ	Observed mg/ℓ
Before addition of Mg^{2+}	0	8,05	7,99	-	-
After addition of 200 mg Mg^{2+}/ℓ and subsequent struvite precipitation	94	6,92	6,80	603	601*

* Determined from the mean of the measured molar changes in Mg_T N_T and P_T between initial and final states

TABLE 3

PREDICTED AND OBSERVED pH AND STRUVITE PRECIPITATION POTENTIAL FOR A SOLUTION IN EQUILIBRIUM WITH CO_2 IN AIR, AND INITIAL VALUES N_T = 250 mg/ℓ, P_T = 300 mg/ℓ (solution Total alk. = 968 mg/ℓ as $CaCO_3$, TDS = 1000 mg/ℓ)

		pH		Struvite precipitated	
	Mg^{2+} mg/ℓ Observed	Predicted	Observed	Predicted mg/ℓ	Observed mg/ℓ
Before addition of Mg^{2+}	0	7,92	7,91	-	-
After addition of 200 mg Mg^{2+}/ℓ and subsequent struvite precipitation	135	6,97	6,90	448	428*

* Determined from the mean of the measured molar changes in Mg_T N_T and P_T between initial and final states

With regard to the verification of the algorithms, good agreement is obtained between experimental observation and theoretical prediction using the algorithms (see Tables 2 and 3). Referring to these tables, for the aqueous/gaseous phase equilibrium situation, the predicted and observed pH values are within 0.05 pH units. For the aqueous/gaseous/solid phase equilibrium situation, the predicted and observed struvite precipitated is within one percent. However, for both waters (i.e. with and without carbonate species), the pH established at three phase equilibrium is about 0.1 units below the predicted value. This deviation may arise from ion pairing effects between Mg^{2+} and the various anionic species in solution, an effect which is not taken into account in the theoretical model. One final point, the work presented here is for water without dissolved organic species, this does not reflect the situation in an anaerobic digester. Occurrence of organic species is known to inhibit (or reduce) precipitation of many minerals, Stumm and Morgan (1970). If such organic inhibition occurs for struvite mineralisation, the precipitation potential could be significantly less in biological anaerobic systems than values predicted using the algorithms presented in this paper.

Solubility Product for Struvite and Calcite in Tertiary Effluents

The poisoning effects of dissolved organics on mineral precipitation has been widely acknowledged, (Stumm and Morgan, 1971). Recognizing that this study involves mineral fouling from tertiary (and other) effluents, principally in anaerobic digestion, the solubility products for struvite and calcite in effluents from activated sludge plants were measured.

For struvite, the experimental procedure involved using both distilled water and effluent derived from an activated sludge plant and adding known molar masses of magnesium (via addition of $MgC\ell_2$), ammonia species (via addition of $NH_4C\ell$) and phosphate species (via addition of Na_2HPO_4). For both the distilled water and effluent three sets of concentrations of Mg^{2+}, N_T and P_T were established such that all were supersaturated with respect to struvite. The solution temperature and ionic strength were measured (see Table 4). The solutions were mixed for approximately 12 hours after which saturation was assumed to have been attained (pH remained unchanged within ½ hour after chemical addition) occur. The pH and Mg^{2+}, N_T, P_T concentrations and ionic strength of the solutions were then measured. For each of the three concentration sets, experiments were repeated four times and the mean data for each was used to determine the corresponding solubility product as follows :

i) Activity coefficients were determined from ionic strength measurement.

ii) Molarities of NH^+_4 and PO^{3-}_4 were determined from known apparent weak acid equilibrium constants, measured pH and total weak acid species concentrations N_T and P_T respectively.

iii) The product of molarities of Mg^{2+}, NH^+_4 and PO^{3-}_4 was then adjusted using relevant activity coefficients to obtain the activity product and hence the thermodynamic equilibrium solubility product. (See Table 3).

TABLE 4

EXPERIMENTAL DETERMINATION OF THERMODYNAMIC SOLUBILITY PRODUCT OF STRUVITE IN DISTILLED WATER AND IN ACTIVATED SLUDGE EFFLUENT AT 20° C

Background electroylte	Addition of :			μ	pH	pK_{sp}
	P_T mg/ℓ	N_T mg/ℓ	Mg^{2+} mg/ℓ			
Distilled water	400	300	300	0.088	6.725	12.82
Distilled water	500	300	300	0.091	6.768	12.83
Distilled water	500	300	400	0.100	6.653	12.85
Activated sludge effluent	500	500	500	0.137	6.495	12.97
Activated sludge effluent	500	500	400	0.121	6.653	12.88
Activated sludge effluent	500	300	300	0.102	6.773	12.92

Referring to the experimental results listed in Table 4, there is no significant difference in the values determined for the thermodynamic product for struvite with background solutions distilled water and activated sluge effluent.

Thermodynamic solubility product value for struvite quoted in the literature is pK 12,6 at 25° C, the values determined here at 20° C agree favourably with the literature value.

For calcium carbonate precipitation from effluents Wiechers, 1978, in an investigation into High Lime Water reclamation, noted that the solubility of this mineral apparently increases compared with terrestrial waters, i.e. pK_{sp} apparently decreases. It would appear that this arises due to adsorption of dissolved organic species at crystal growth sites. However, because Wiechers' investigation was for a single effluent derived from Daspoort water treatment plant, it was considered judicious to effect an investigation on other tertiary effluents, in particular those from a laboratory-scale activated sludge treatment process.

Batches of effluent and diluted effluent were adjusted to a state of supersaturation with respect to calcium carbonate and seeded with excess mineral calcite. The batches were stirred for 24 hours, after which filtered samples were analysed. Due precaution was taken to avoid errors likely to arise due to CO_2 exchange with the atmosphere during sampling and analysis. Analyses included pH, P_T, N_T, TDS, T alk and calcium. Equilibrium chemistry was then applied to speciate the solutions and the activities of Ca^{2+} and CO_3^{2-} determined. In Figure 3 are shown plotted the measured activity products (i.e. K_{sp}) versus total dissolved organic carbon for the various tests effected.

Referring to Figure 3, the activity product for calcium carbonate for the effluent (after 24 hours mixing, normally well in excess of sufficient time to attain saturation for a seeded sample) gives a value of 2 x 10^{-7} moles^2 i.e. an apparent pK_{sp} value of 6.7 for calcium carbonate. This value is exactly the same as that determined by Wiechers for calcium carbonate solubility product in the effluent from Daspoort. Consequently, the program developed under this contract will utilize this apparent solubility product value for calcium carbonate in assessing the possibility of mineral fouling in tertiary effluents.

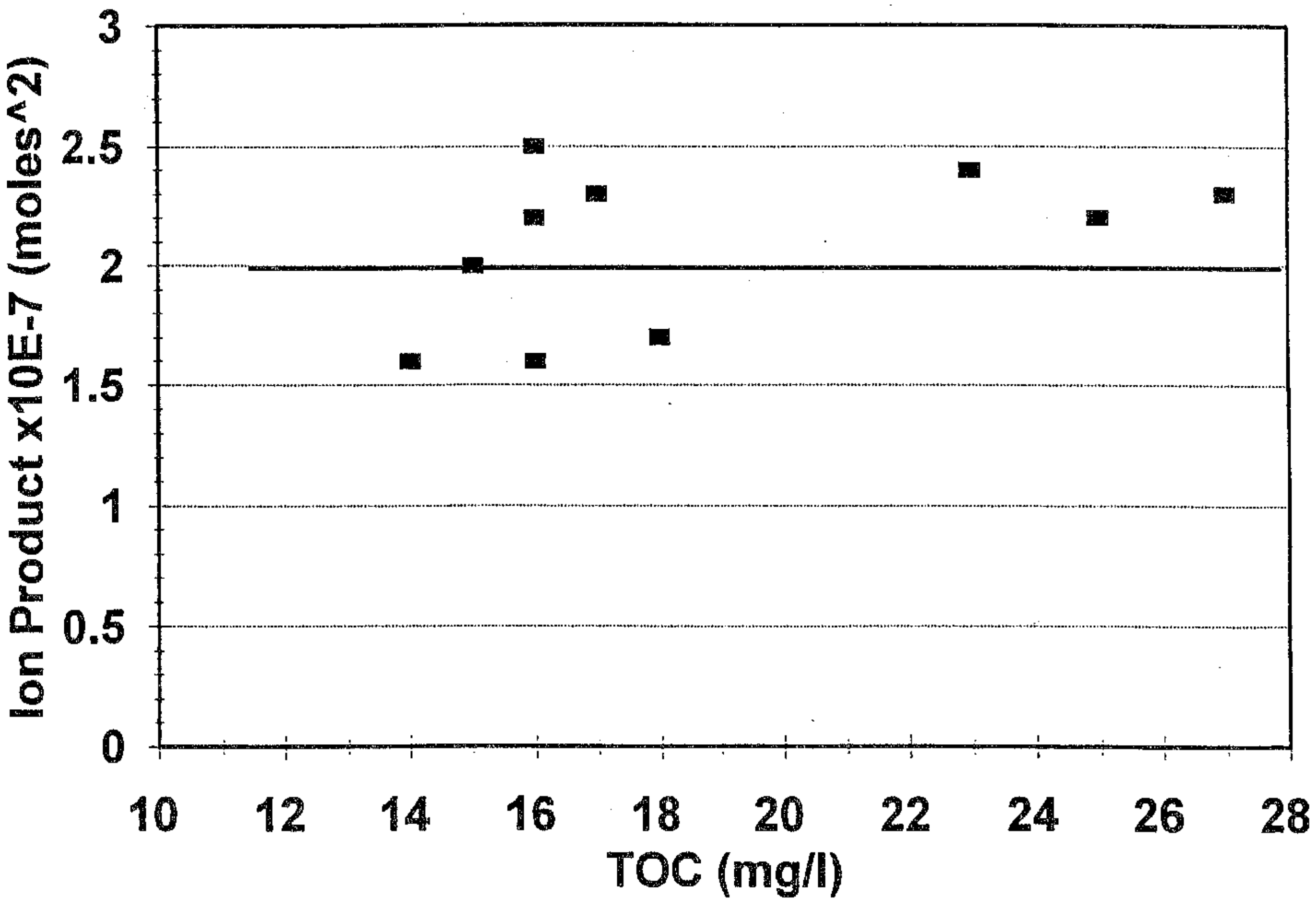

Figure 3 : Ion product for calcium carbonate versus organic C (after 24 hours)

REFERENCES

APHA, AWWA, WPCF (1985) *Standard Methods for the Examination of Water and Wastewater.* American Public Health Assication, 1015 Fifteenth Street NW, Washington, DC 20005.

LOEWENTHAL, R.E., EKAMA, G.A. and MARAIS, GvR. (1989) Mixed Weak Acid/Base Systems, Part 1 - Mixture Characterisation. *Water SA* vol. 15(1) pp 3-24.

LOEWENTHAL, R.E. and MARAIS GvR. (1976) *Carbonate Chemistry of Aquatic Systems: Theory and Application.* Anne Arbor Science Publ., P O Box 1425, Anne Arbor, Michigan 48106.

LOEWENTHAL, R.E., WENTZEL, M.C., EKAMA G.A.and MARAIS GvR. (1991) Mixed Weak Acid/Base Systems, Part II - Dosing Estimation, Aqueous Phase. *Water SA* Vol 15(2) pp 107-122.

LOEWENTHAL, R.E., WIECHERS, H.N.S. and MARAIS, GvR. (1986) *Softening and Stabilisation of Municipal Waters.* Water Research Commission, P O Box 824, Pretoria 0001, South Africa.

SNOEYINK V.L. and JENKINS D. (1980) *Water Chemistry.* John Wiley & Sons, New York.

STUMM W. and MORGAN J.J. (1970) *Aquatic Chemistry.* John Wiley & Sons, New York.

TRUESDELL A.H. and JONES B.J. (1973) *WATEQ. a computer program for calculating chemical equilibria of natural waters.* NTIS, report No. PB-220646.

APPENDIX

COMPUTER PROGRAM : STRUVITE Version 2.10 (September 1996)

A. OBJECTIVE:

This program performs analyses on a water with specified chemical characteristics. It determines the struvite and calcite precipitation potentials and effects calculations for both change in CO_2 partial pressure and dosage calculations for pH adjustment. It also performs calculations for pH dosing and changing CO_2 partial pressure to a prescribed value.

Data is displayed on screen and can be printed to a file.

The program and user manual were developed for the Water Research Commission by RE Loewenthal, Department of Civil Engineering, University of Cape Town and I Morrison, private consultant.

B. PROGRAM DEVELOPMENT

Address: Department of Civil Engineering
University of Cape Town
Private Bag
Rondebosch, 7700
South Africa

Telephone: (021) 650-2584
Fax: (021) 689-7471
E-mail: dick@engfac.uct.ac.za

Program written in True Basic (version 3.04)

C. SYSTEM REQUIREMENTS

This program runs under DOS 3.30 or later releases. It should also run under any version of Windows that supports DOS software.

D. SOFTWARE INSTALLATION AND USAGE:

The software is supplied on a single diskette and contains the following file:

STRUVITE.EXE executable version of the program

The software is installed by copying the STRUVITE.EXE files to the desired location. The program is started by entering STRUVITE at the DOS prompt.

E. ASSUMPTIONS AND LIMITATIONS:

The program has been written particularly for control of anaerobic fermentation processes. The following assumptions and limitations are pertinent :

1. The water is well mixed and in equilibrium with the surrounding gas - usually the case in anaerobic digestion. Note, however, that pH measurements on the digester liquor should be made as it emerges from the digester or carbon dioxide will be lost to the atmosphere, upsetting the equilibrium condition.

2. The precipitation potentials determined within the program should be regarded only as the maximum propensity of the water to effect such precipitation/dissolution. In practice the mass of mineral precipitated is governed by kinetics in the process and this maximum is only rarely attained.

3. The precipitation potentials determined for calcite are <u>not</u> based on thermodynamic data because where organics are present, experimental work has indicated that this mineral is very much more soluble than in their absence. Because this work is for use with anaerobic digestion, the program has been arranged to calculate the maximum expected calcite precipitation in the presence of organic materials resulting from waste water treatment.

F. USER MANUAL:

1. Input Screen

The program is menu driven. A header display is followed by an input/output screen on which the raw water characteristics may be entered and the results displayed.

This screen has three columns of numbers:

Firstly, one headed **ORIGINAL**, in which the raw water characteristics are displayed and entered.

Secondly, a column headed **TREATED**, which reflects the treated water composition, should a treatment be applied.

Thirdly, a column headed **STRUVITE EQM** which gives the state of the water once equilibrium (saturation) with the solid phase struvite (magnesium ammonium phosphate) has been attained. Alternatively, the user can choose to view the result of equilibrium with calcite (calcium carbonate) by pressing F8.

The struvite or calcite precipitation potentials of each of these waters appears in the bottom row.

Any change made in water composition results in the immediate recalculation and display of the new characteristics.

2. Entering Data

All the fields start off with default values.

Use the ↑ and ↓ arrow keys to move between fields. The current field will be highlighted in red, with a green cursor.

Key in the desired value and press either **Enter** or one of the arrow keys. Recalculation will result.

Change all fields necessary to give the desired raw water characteristics.

Further changes can be made at any time. Experiment with the composition to get an idea of the sensitivity of the system to changes in composition.

Note particularly that only two of the parameters: Total Alkalinity, pH and Partial Pressure of CO_2 are needed for the third to be calculated and displayed automatically. The two most recently entered are used in the calculation and the calculated value is marked with a star.

3. Precipitation Potentials

Precipitation potentials for each water are displayed on the bottom row and the resultant saturated state is reflected in the last column.

To toggle between struvite and calcite equilibrium, press **F8.**

4. Treatments

These treatment actions are available:

- Change to a given CO_2 partial pressure - Press **F5**.
- Change to a given pH by adding strong acid or base - Press **F6**.
- Clear treatment - Press **F7**.

When you press **F5 or F6** the cursor moves to the CO_2 partial pressure or the pH field, respectively, in the treated water column. Enter the desired value.

The treated and equilibrated water columns will now represent the treated condition and the resultant equilibrium composition and the heading will give the dosage required to achieve it.

The chosen treatment will remain in place until cleared or changed to another treatment. If you change the raw water composition the treatment applies to the new conditions. Struvite or calcite equilibria can be selected.

The effect of other changes in conditions, such as discharging the liquor into a pond and allowing it to cool down, can be estimated by changing the conditions of the original water to approximate the new ones.

5. Creating a File and Printing

The contents of the screen can be sent to a text file, which in turn can be sent to a printer by one of the usual DOS or Windows methods or incorporated in a word processing document.

When you press F4, you will be prompted for a file name, to which the screen contents will then be sent. If you use the same file name more than once, the new data will be added on to the end of that previously sent. The usual DOS rules for file names apply, i.e. 1 to 8 characters, optionally followed by a full stop and up to three more characters.

6. Editing Fields

The first character you enter into a field will cause the previous content to be cleared. This is usually what is wanted. However, when dealing with a sample name, which might be quite long, you might only wish to alter one or two characters of the previously used name without having to enter everything again.

To do this, first press **Delete** or **Backspace** and then proceed to make the desired changes. Pressing **Insert** will cause subsequent characters to be inserted instead of overwriting existing text. You can turn this off by pressing **Insert** a second time.

7. Help - Press **F1**

8. Quitting the Program - Press **F10**

9. Partial Pressure of CO_2

The partial pressure of CO_2 in the gas space above the digester liquor is calculated by multiplying the total gas pressure, in atmospheres, by the volume percentage of CO_2 in the gas. Digesters usually run at slightly above atmospheric pressure, with a CO_2 content of about 30%, resulting in a partial pressure of about 0.3 atmospheres. However, check your own figures.

When the liquor is pumped out, the overall pressure on the suction side of the pump will be lower than in the digester, possibly causing conditions suitable for precipitation of struvite - the program will reveal such conditions.

10. Error Conditions

The program will happily accept conditions well outside the range of those likely to be encountered in practice and will calculate the resultant equilibria. These are not necessarily in error but use some discretion in making use of them.

However, some combinations of input values will produce an error message because they represent an impossible chemical condition. In such cases the program will restore the original value of the parameter being altered and invite you to make some changes.

This condition only occurs when pH and alkalinity have been entered and the partial pressure of CO_2 is being calculated. It may then happen that the alkalinity is lower than expected given the entered values for the components that make up total alkalinity. Contributions to the latter from acetate, phosphate and ammonia - the latter only at high pH values - are fixed by their concentrations and the pH. If these contributions add up to more than the entered alkalinity a negative contribution from the carbonic species, and therefore a negative partial pressure for CO_2, would have to be assumed to balance the equation - an impossible chemical condition. One or more of these values will be in error and in need of change.