THE COMPUTER SIMULATION OF PHOSPHATE REMOVAL FROM WASTEWATER USING LIME

THE COMPUTER SIMULATION OF PHOSPHATE REMOVAL FROM WASTEWATER USING LIME

by

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ABSTRACT

A simplistic equilibrium, computer model was devised to simulate the removal of orthophosphates from wastewater. The components of the model were calcium, magnesium, carbonate and orthophosphate present as simple hydrated ions, ligands, acid-base dissociation products, ion pairs, ion pair complexes, ion complexes and precipitates. Data from laboratory experiments were tested in the model to determine the apparent activity products of calcite, hydroxyapatite, tricalcium phosphate and brucite. The results indicated a degree of supersaturation of hydroxyapatite between 15 to 20 orders of magnitude dependent on the aqueous species included in the calculations. The apparent pK_{sp} values for different sets of data showed the mean ranging from 95 to 102.5 with standard deviations 2 to 5. The inclusion of the aqueous ion complexes $Ca_2.HPO_4.CO_3^0$ and $Ca_2.PO_4.CO_3^-$ when calculating the apparent activity products results in a pK_{sp} of 102.5 which varies little with pH or the presence of magnesium. The solubility of tricalcium phosphate varies more with pH than hydroxyapatite, a mean pK_{sp} of 26.8 was calculated which compares favourably with the pK_{sp} of 27.0 quoted in the literature. The apparent activity product of brucite was strongly dependent on pH while that of calcite was extremely variable. When hydroxyapatite precipitated, there was a minimum residual phosphate between pH 8.5 - 9.0, followed by an increase of phosphates in solution due to calcium being removed by the precipitation of calcite. Beyond pH 10, the phosphate concentration in solution decreased rapidly as there was an increase in the precipitation of hydroxyapatite coupled with a decrease of calcite. Under identical initial conditions, the precipitation of tricalcium phosphate compared to hydroxyapatite resulted in similar orthophosphate residuals. The use of the apparent activity products compared to literature solubility products results in 2 to 3 orders of magnitude greater phosphate residuals in solution.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont'd)

I. INTRODUCTION

The problem of wastewater treatment becomes more critical every year. Development, particularly around major waterways, leads to a subsequent increase in human wastewater. The discharge of inadequately treated wastewater changes the environment of the receiving bodies of water. There is increased difficulty in the treatment of water to make it fit for human consumption, and the recreational use of the water is lost due to the deteriorating qualities. With the increasing demand for fresh water and faltering water conditions, the treatment of wastewater becomes important. If we cannot find new economical sources of water, we must begin making those available more fit for human use. The preservation of existing clean water and the improvement of polluted waters will ease the difficulty of supplying future needs of fresh water.

The importance of wastewater treatment is directly related to the removal of those elements, phosphorus and nitrogen, which cause damage to the aquatic environment. Phosphorus and nitrogen, which are usually limiting nutrients for aquatic photosynthetic organisms, are dispersed throughout the receiving body of water in concentrations high enough to stimulate excessive algal and benthic plant growth. The approximate uptake of these nutrients by algae can be represented by the equation:

$$106CO_2 + 16NO_3^- + HPO_4^{-2} + 122H_2O + 18H^+ + \text{(trace elements; energy)} = C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

(Stumm and Morgan 1970) (1)

The carbon in equation 1 is usually supplied through the solution of CO_2 and calcareous minerals. As a major part of the earth's crust is covered by calcareous rocks, carbon is present in most bodies of water in excess of nitrogen and phosphorus. It is the availability of nitrogen and phosphorus which limits the algal population; any increase of these nutrients will cause a subsequent increase in the population. If present water quality is to be maintained or improved, nitrogen and/or phosphorus must be removed from wastewater prior to release into lakes and rivers. The disadvantage of limiting nitrogen to control the algal population lies in the fact that partial replenishment of nitrogen can be carried out by nitrogen fixation. A deficiency of nitrogen in solution while other nutrients are in excess of demand would promote the growth of those organisms, such as blue-green algae, which can fix nitrogen from the atmosphere. Phosphorus has no volatile component and is usually present in natural waters in low concentrations ($\leq 10\ \mu g\ P/l$). As phosphorus is mainly present on earth as apatites, its availability to photosynthetic organisms may be controlled by the dissolution of apatites. This restricts the concentration of phosphorus in water as apatite is quite insoluble. Due to these natural controls on phosphorus, its removal from wastewater will have the greatest effect on decreasing the populations of photosynthetic organisms.

Domestic wastewater, which is the primary source of phosphorus, contains an average of 10 mg P/l. The phosphates are principally from human waste and synthetic detergents. Phosphorus in human waste is mainly orthophosphate (PO_4^{-3}) and a small amount of organically bound phosphorus. In synthetic detergents, it is in the form of condensed phosphates, that is, pyrophosphate ($P_2O_7^{-4}$) and tripolyphosphate ($P_3O_{10}^{-5}$). Table 1 lists the relative concentrations of each form of phosphorus.

Table 1. Approximate Concentrations of Phosphate Forms in a Typical Raw Domestic Sewage

Phosphate Form	Concentration mg P l^{-1}	Molarity (g mol. l^{-1})
Total	10	3.2×10^{-4}
Ortho	5	1.6×10^{-4}
Tripoly	3	3.2×10^{-5}
Pyro	1	1.6×10^{-5}
Organic	$<$ 1	$< 3.2 \times 10^{-5}$

after (Jenkins, Ferguson, and Menar 197

When domestic wastewater enters a typical wastewater treatment plant, it undergoes two major phases of treatment. The primary treatment consists of the removal of the majority of solid material through the use of screens and the sedimentation of suspended material. The secondary treatment is usually a biological treatment, the most commonly used is an activated sludge system. Here a mixture of sewage and a special bacteriologically active sludge is kept in suspension by turbulence and supplied with oxygen. When the biological oxygen demand has decreased sixty to eighty-five per cent, the suspension is allowed to settle, the effluent is released into a body of water while the sludge is withdrawn (Bolton and Klein 1971). Part of the sludge is reconditioned for use again while the rest is removed for disposal. Figure 1 schematically shows a typical aerobic wastewater treatment plant.

Biological treatment removes P through the use by bacteria in growth which also reduces the oxygen demand of the wastewater. If wastewater is treated biologically, only 20 to 30 per cent of the P is removed from solution (Menar and Jenkins 1972) as organic carbon is the limiting nutrient while P and N are present in excess of demand (Stumm and Morgan 1970). If a chemical treatment is combined with the biological treatment, the phosphates may be reduced to an acceptible level through the precipitation of a phosphate compound. An acceptible level is one where the phosphate concentration in the effluent does not cause eutrophic conditions in the receiving body of water. Menar and Jenkins (1972) suggest 0.05 mg P/l or less as such a level. But the addition of chemicals to the biological treatment phase may

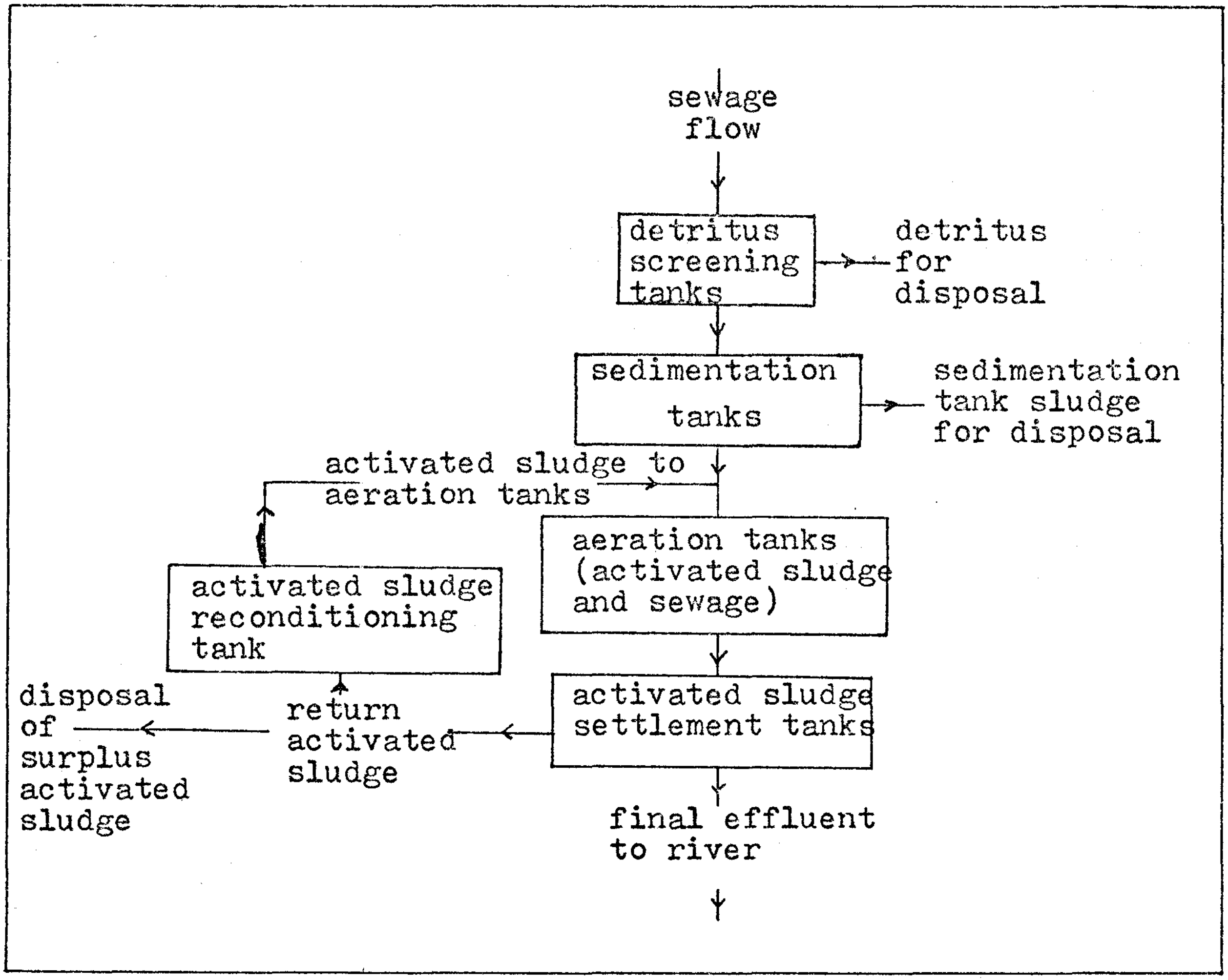

Figure 1 Schematic diagram of a typical wastewater treatment plant showing primary and secondary treatment. Adapted after Bolton and Klein (1971)

change the environment suitable for the growth of the bacteria. In addition, the reduction of P to an acceptible level may result in it becoming the limiting nutrient which would further hinder microbial growth (Buzzel and Sawyer 1967). Although the residual phosphate in the wastewater would be acceptible, the biological oxygen demand of the effluent would be too high. To avoid this, the chemical treatment to remove phosphorus must be separate and follow the biological treatment. This separate treatment requires a tertiary treatment where the phosphates are removed from the effluent by precipitation, adsorption, biological uptake or similar means. Precipitation using chemicals is the most common method of tertiary treatment.

To facilitate a high degree of phosphate removal, a cation, Al(3), Fe(3), La(3) or Ca^{+2}, interacts with the phosphate anion to form a precipitate. The cations are added as chemicals, $AlCl_3$, $FeCl_3$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$ or $Ca(OH)_2$, which readily dissolve in the wastewater. The chemical reactions which occur are represented by the equations:

$$X_2(SO_4)_3 + 2NaH_2PO_4 = 2XPO_4 + Na_2SO_4 + 2H_2SO_4 \qquad (2)$$

$$XCl_3 + NaH_2PO_4 = XPO_4 + NaCl + 2HCl \qquad (3)$$

$$X_2(SO_4)_3 + Na_2HPO_4 + 3H_2O = X(OH)_3 \cdot XPO_4 + Na_2SO_4 + 2H_2SO_4 \qquad (4)$$

or

$$10Ca(OH)_2 + 6NaH_2PO_4 = Ca_{10}(PO_4)_6(OH)_2 + 6NaOH + 12H_2O \qquad (5)$$

where X is Al(3), Fe(3) or La(3). The reactions of Al(3), Fe(3) and La(3) with phosphates are extremely rapid and not only precipitate orthophosphate but also condensed phosphates. When using Fe or Al, there must be an adjustment of the pH to a narrow range, around pH 5 for Fe and pH 5.8-6.4 for Al, to maximize phosphate removal. Lanthanum, which has only been used in pilot plant studies, is superior to Al and Fe as it is effective over a pH range 5.0 to 9.8; it totally removes P from the wastewater and no excess La need be added to the wastewater as the reaction with phosphates is stoichiometric (Cohen 1971). Figure 2 shows the concentrations of residual soluble phosphates obtained by Recht and Ghassemi (1970) using the above cations in laboratory experiments on P removal.

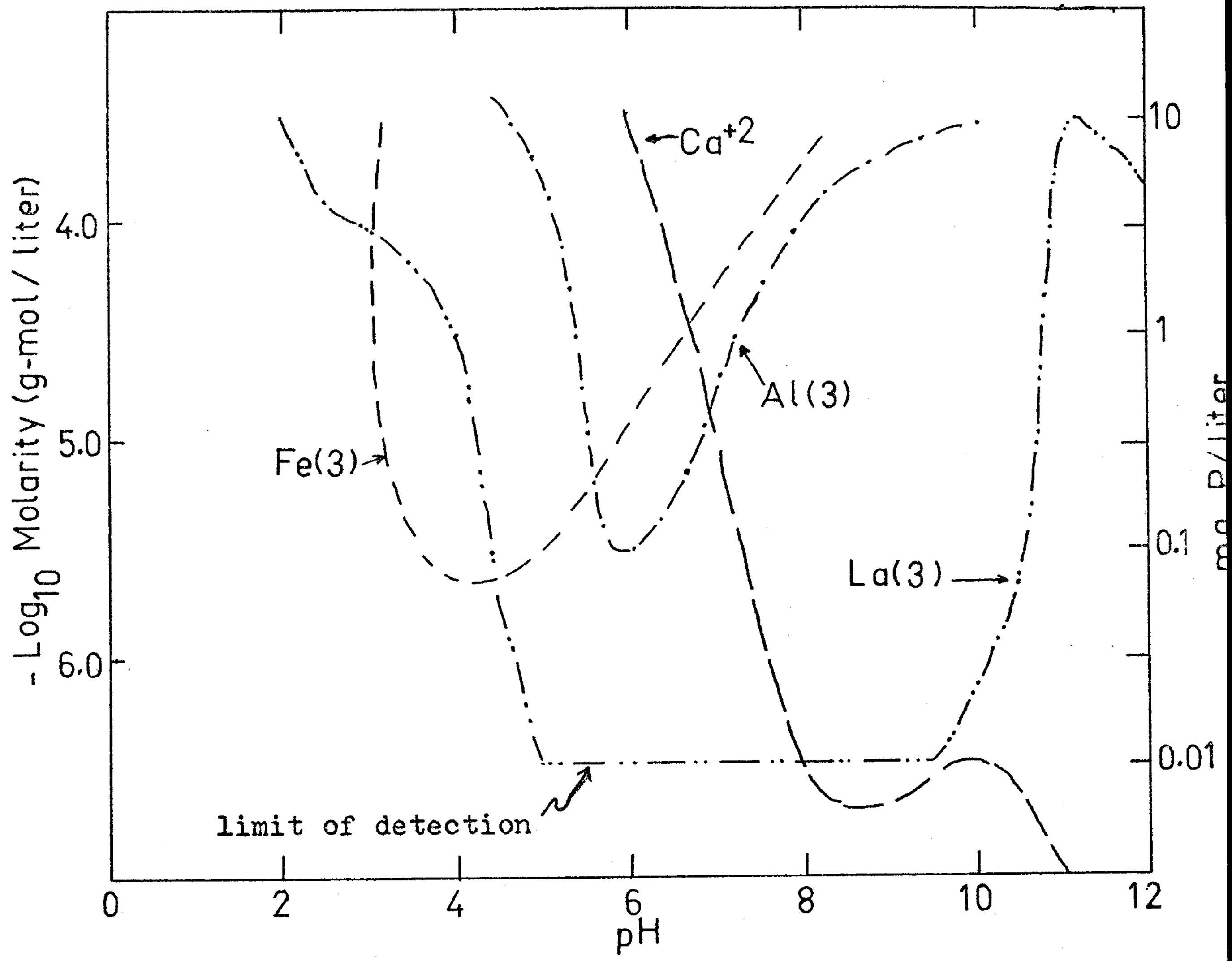

Figure 2 Residual orthophosphate remaining in solution after chemical precipitation. Fe, Al and Ca have a 2:1 cation to orthophosphate ratio while La has a 1:1 ratio. The residuals for Fe, Al and La are based on experiments by Recht and Ghassemi (1970). The residual for Ca from Jenkins et al (1971).

Equation 5 represents the use of lime to remove orthophosphates from wastewater through the precipitation of hydroxyapatite. Figure 2 illustrates that an increase in pH results in a decreased phosphate residual in solution. The pH does not have to be adjusted, as for Fe and Al, as the addition of lime causes an increase in pH. The greater the quantity of lime added to the wastewater, the higher the pH and the smaller the phosphate residual in solution. The use of lime does not introduce foreign ions, SO_4^{-2}, Cl^-, into the wastewater which cannot be removed. It is also the least expensive. Albertson and Sherwood (1969) list the cost of removing one mole of orthophosphate from solution as 1.32 cents for $Fe_2(SO_4)_3$, 5.03 cents for $FeCl_3$, 1.34 cents for $Al_2(SO_4)_3$ and 0.29 cents for $Ca(OH)_2$. This is based on a 2:1 ratio of cation to orthophosphate.

Lime has an added advantage as it can be recovered from the sludge. The sludge consists of calcite, a common precipitate when using lime, lime which didn't dissolve, brucite which forms when the pH is greater than 9.5 and a calcium phosphate compound. If the sludge is calcined, calcite and calcium hydroxide would be changed to lime. Upon slaking, the CaO would be recovered while the inert calcium phosphate compound would remain in the ash and be disposed of. Lime cannot precipitate condensed phosphates but this isn't critical when it is used in tertiary treatment. Condensed phosphates are readily hydrolyzed at a high pH or by enzymatic activity which is found in biological treatment (Cecil 1971). Normally less than ten per cent of the phosphates are condensed after effective secondary treatment (Seiden and Patel 1969). As a high degree of phosphate removal requires a high pH, the remaining condensed phosphates would be hydrolyzed to orthophosphate during tertiary treatment.

II. RATIONALE OF APPROACH

This study is concerned with lime treatment to remove orthophosphates from wastewater. Using geochemical techniques, a simplistic, equilibrium computer model was devised to simulate the chemical reactions which occur in wastewater upon the addition of lime. The objective is to use the model to accurately predict the minimum residual phosphate which can be attained in wastewater under varying initial conditions.

Simulation was used as all the major chemical reactions which occur in wastewater must be considered simultaneously and the use of the computer eases the handling of the large number of parameters. The parameters, concentration of dissolved components, various aqueous species, different precipitates, pH, ionic strength, can all be varied to simulate any wastewater under diverse conditions. The model initially attempts to duplicate existing data; as lime addition is both common and extensively used, there is considerable reliable data available. The parameters were modified, some were deleted while others were added until the model was verified on a broad spectrum of data. Having successfully reproduced existing data, the model can be used to probe assorted untested conditions some of which may be impractical, possibly expensive or impossible at present pilot sewage plants.

III THE SYSTEM

The model does not attempt to simulate every aspect of the treatment of wastewater using lime. It is only concerned with one individual process, the precipitation of insoluble Ca-PO_4 compounds to lower the soluble residual phosphates and the chemical factors which have an influence on this. It does not include the nature of the solids formed, the rates of reactions or the coagulation and flocculation of the precipitates. The system is closed, at standard temperature and pressure and has only liquids and solids; it does not allow for gases to be formed or dissolved in solution. Thermodynamic data in the form of equilibrium (stability) and solubility constants control respectively the concentration of aqueous species and the amount of precipitates.

The major soluble components which affect the phosphates in an average wastewater are calcium, magnesium and carbonate. These are present in solution as simple hydrated ions (Ca^{+2}, Mg^{+2}, H^{+}), ligands (CO_3^{-2}, PO_4^{-3}, OH^{-}), acid-base dissociation products, ion pairs, ion pair complexes and ion complexes ($Ca_2.HPO_4.CO_3^0$, $Ca_2.PO_4.CO_3^-$). Stumm and Morgan (1970) define an ion pair as a metal ion and a ligand separated by co-ordinated water molecule(s) while an ion pair complex has the ligand immediately adjacent to the metal. An ion complex is distinguished from an ion pair and an ion pair complex in that it has more than just one metal and one ligand. H_3PO_4, a polyprotic acid, and H_2CO_3, a diprotic acid, form the acid-base dissociation products; as both readily dissociate protons, the distribution of the products is strongly controlled by pH. As the system has no gases, H_2CO_3 is considered to be a nonvolatile acid. The predominant products at a low pH are $H_2PO_4^-$, H_3PO_4 and H_2CO_3; at a neutral pH, HPO_4^{-2}, $H_2PO_4^-$ and HCO_3^-; while at a high pH, HPO_4^{-2}, PO_4^{-3} and CO_3^{-2}. All the aqueous species used in the model are listed in table 2 along with the respective equilibrium constants. No distinction has been made between ion pairs and ion pair complexes as methods used to determine equilibrium constants do not allow a distinction to be drawn (Stumm and Morgan 1970). The ion pairs and ion pair complexes are represented by equations 6 to 11 and 15 to 18 in table 2. Table 2 does not list all the soluble species or components found in an average wastewater. Numerous minor and major components, such as NH_4^+, Cl^-, F^-, Na^+, K^+, SO_4^{-2} and organic molecules, are also present but are not included as they have negligible effects on the phosphates when compared to the major components.

The addition of lime to wastewater causes the precipitation of Ca-PO_4 compounds; the two principal precipitates thought to form are hydroxyapatite and beta tricalcium phosphate. Actual examination of the precipitates which form does not allow positive identification due to the amorphous character or poor crystallinity (Ferguson and McCarthy 1970). Rather than use only one of the precipitates, both are used in the

Table 2. Thermodynamic Data used in Calculations (constants are for 25°C and 1 atmosphere total pressure)

Equation	$-\mathrm{Log}_{10}$ of Equilibrium Constant	Reference
1. $H_2CO_3 = H^+ + HCO_3^-$	6.35	Sillen and Martell (1964)
2. $HCO_3^- = H^+ + CO_3^{-2}$	10.33	"
3. $H_3PO_4 = H^+ + H_2PO_4^-$	2.13	"
4. $H_2PO_4^- = H^+ + HPO_4^{-2}$	7.2	"
5. $HPO_4^{-2} = H + PO_4^{-3}$	12.32	"
6. $Ca^{+2} + CO_3^{-2} = CaCO_3(aq)$	-3.2	"
7. $Ca^{+2} + HCO_3^- = CaHCO_3^+$	-1.26	"
8. $Ca^{+2} + OH^- = CaOH^+$	-1.37	"
9. $Ca^{+2} + PO_4^{-3} = CaPO_4^-$	-6.46	"
10. $Ca^{+2} + HPO_4^{-2} = CaHPO_4(aq)$	-2.73	"
11. $Ca^{+2} + H_2PO_4^- = CaH_2PO_4^+$	-1.41	"
12. $H_2O = H^+ + OH^-$	14.00	"
13. $Ca_2.HPO_4.CO_3(aq) = 2Ca^{+2} + HPO_4^{-2} + CO_3^{-2}$	-1.33	Greenwald (1945)
14. $Ca_2.HPO_4.CO_3(aq) = H^+ + Ca_2.PO_4.CO_3^-$	-8.3	"
15. $Mg^{+2} + OH^- = MgOH^+$	-2.6	Sillen and Martell (1964)
16. $Mg^{+2} + CO_3^{-2} = MgCO_3(aq)$	-3.4	Garrels and Thompson (1962)
17. $Mg^{+2} + HCO_3^- = MgHCO_3^+$	-1.16	
18. $Mg^{+2} + HPO_4 = MgHPO_4(aq)$	-1.5	Greenwald (1940,1945)

Table 2 continued...

Equation	$-\text{Log}_{10}$ of Solubility Constant	Reference
1. $CaCO_3 = Ca^{+2} + CO_3^{-2}$	8.35	Sillen and Martell (1964)
2. $Ca_{10}\cdot(PO_4)_6\cdot OH_2 = 10Ca^{+2} + 6PO_4^{-3} + 2OH^-$	115.6	Clark (1950)
3. $Mg(OH)_2 = Mg^{+2} + 2OH^-$	11.6	Sillen and Martell (1964)
4. $(Ca_{0.94}Mg_{0.06})_3(PO_4)_2 = 2.82Ca^{+2} + 0.18Mg^{+2} + 2PO_4^{-3}$	27.0	Sillen and Martell (1964)
5. $Ca_XMg_{1-X}CO_3 = X\ Ca^{+2} + 1-X\ Mg^{+2}$		
where X is 0.97	8.0	Chave et al (1962)
0.89	6.6	"
0.8	6.3	"

Note: 1. is calcite

2. is hydroxyapatite

3. is brucite

4. is beta tricalcium phosphate

5. is varieties of Mg-calcite

model to predict residual soluble phosphates. Two other precipitates also form, the increase in calcium concentration due to the lime addition causes the precipitation of calcite and the increase in pH causes the simultaneous precipitation of magnesium hydroxide between pH 9.5 to 10.5. All precipitates used in the model are listed in table 2 along with their solubility constants.

IV THE MODEL

When devising an equilibrium model, the system is developed in two steps; first, the chemical methodology must be defined as completely as possible. This involves defining the theory to be used, formulating the chemical equations and specifying the values of constants. The second step is to develop a numerical method to facilitate the solution of chemical problems using algebraic equations which symbolize the chemical ones derived in step one.

Thermodynamic theory allows for equilibrium in closed systems to be calculated by two major techniques, one uses equilibrium constants while the other minimizes Gibb's free energy. Both methods should yield identical results; the only difference is the approach to the problem. Equilibrium models have been built using both techniques. White et al (1958) describe the theory used in formulating a minimum free energy model while Shapley and Cutler (1970) delineate the model and illustrates its use.

Equilibrium constant models preceded minimum free energy models, their initial use was in the geochemical interpretation of the composition of the oceans. Sillen (1961) pioneered in this approach with a model of seawater which was based on the chemical weathering of igneous rocks. The trapped volatiles and soluble components dissolved in water to form the present ocean. Garrels and Thompson (1962) continued this work by considering the eight most common soluble ions in seawater, Na^+, K^+, Mg^{+2}, Ca^{+2}, Cl^-, HCO_3^-, CO_3^{-2}, SO_4^{-2}, and from the predominant equilibrium interactions, they were able to show that the present composition of the ocean could be predicted as being in equilibrium with these ions and their precipitates. Kramer (1965) also developed an equilibrium model of an inorganic ocean; he approached the composition of the ocean by considering the equilibrium of solid phases, clay minerals, calcite, OH-apatite, CO_2-F-apatite, phillipsite, gypsum, strontianite, celestite and aragonite with water. Kramer (1967) later was able to model the Great Lakes using the same principle.

The model in this study uses the equilibrium constant technique, it approaches the problem in a manner similar as Garrels and Thompson (1962). It uses the soluble ions, Ca^{+2}, Mg^{+2}, CO_3^{-2}, PO_4^{-3}, in wastewater and through their equilibrium interactions determines the amount of possible precipitates which decrease the phosphates in solution.

Mass Law Equation

The model uses several types of chemical equations, the most basic being the equilibrium (mass law) equation. It has the form:

$$a(A) + b(B) = c(C) + d(D) \qquad (6)$$

where

$$\frac{(C)^c(D)^d}{(A)^a(B)^b} = K \qquad (7)$$

K is either an equilibrium or solubility constant and the parenthesis indicate concentrations*. When considering natural fresh water, the concentration of solutes are usually low enough so that the molar concentrations approximate the activities. As ionic strength increases, as in wastewater, this does not hold anymore, corrections must be made for the non-ideality of the system. The ion strength and the ion activity coefficients must be calculated. The ionic strength is calculated from:

$$I = \tfrac{1}{2}\sum_{i=1}^{n}(c_i z_i^2) \qquad (8)$$

where I is the ionic strength, c_i is the concentration of each aqueous species and z_i is the charge on the ion. Using the ionic strength, the ion activity coefficients can be calculated by the Debye-Huckel-Davies equation:

$$\log_{10}(f) = -Az^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right) \qquad (9)$$

where f is the ion activity coefficient and A has a value of approximately 0.5 for water at 25°C. Modifications are made to the equilibrium and solubility constants as activities are used rather than concentrations in all calculations. This allows the constants to be independent of the ionic strength. The equation for the relationship between activity and concentration is:

$$a_i = fx_i \qquad (10)$$

where a_i is the activity of species i which has a concentration

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* Concentration throughout this study is molarity (gram-moles/ liter) unless otherwise stated.

x_i and f is the ion activity coefficient for the charge present on species i. From equation 7, the concentrations are replaced by activities.

$$\frac{(a_c)^c(a_d)^d}{(a_a)^a(a_b)^b} = K \qquad (11)$$

The activities in equation 11 can be replaced by the concentration times the ion activity coefficient from equation 10. The resulting equation is:

$$\frac{(f_c x_c)^c(f_d x_d)^d}{(f_a x_a)^a(f_b x_b)^b} = K \qquad (12)$$

which can be modified to:

$$\frac{(x_c)^c(x_d)^d}{(x_a)^a(x_b)^b} = K\frac{(f_a)^a(f_b)^b}{(f_c)^c(f_d)^d} \qquad (13)$$

Using this equation, adjustments are made to the constants while concentrations are used in the calculations.

Mass Balance Equation

The second type of equation is the mass (mole) balance. One such equation exists for each component, calcium, magnesium, carbonate and orthophosphate in the system. The form of the equation is:

$$\text{Total X} = \sum x_a n_a + \sum x_p n_p \qquad (14)$$

where X is calcium, magnesium, carbonate or orthophosphate, x_a is each aqueous species containing X, n_a is the number of atoms of X in the aqueous species, and x_p and n_p refer to the possible precipitates. In the model, the left hand side of each mass balance equation is known, thereby forming the constraints for the mass law equations. The aqueous species for each mass balance equation can be found in table 2. The precipitates can only be included in the mass balance equations if they form; this isn't always known and has to be calculated.

Electroneutrality and Proton Equation

At this point each aqueous species is defined by a mass law equation and one mass balance equation exists for each component in the model. The only variable which isn't defined is the hydrogen ion concentration. In the model, pH can be specified or it can be determined using an equation based on the proton condition. When pH is known, the aqueous species and the precipitates are calculated at that pH for known concentrations of the four components. This usually results in a charge inbalance which is corrected using an equation for the **electroneutrality** condition. The form of this equation is:

$$\sum(x^+)(c) = \sum(x^-)(c) \begin{array}{l} + \text{ non-reacting base (NaOH) or} \\ - \text{ non-reacting acid (HCl)} \end{array} \qquad (15)$$

where x^+ represents the positive aqueous species, x^- the negative aqueous species and c the charge on the ion. If there is a surplus of negative charges, NaOH is added to balance the charge inbalance or if there is a surplus of positive charges, HCl is added. Otherwise the electroneutrality equation determines the amount of acid or base required to reach a specified pH based on the aqueous species in solution.

If pH isn't known, a proton equation is derived based on the proton condition; it can be considered a mass balance equation for the hydrogen ion concentration. Various chemicals, CO_2, $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, H_3PO_4, $Ca_{10}(PO_4)_6(OH)_2$, are dissolved in water and the resultant pH is calculated using the equation:

$$\sum \text{acids added} - \sum \text{bases added} = \sum(x^+)(c) - \sum(x^-)(c) \qquad (16)$$

where the species are both aqueous and precipitates and x^+ represents those containing H^+ while x^- represents those containing OH^-. Among the possible chemicals dissolved, the acids are CO_2 and H_3PO_4, the bases are $Mg(OH)_2$, $Ca(OH)_2$ and $Ca_{10}(PO_4)_6(OH)_2$ while $CaCO_3$ and $MgCO_3$ are neutral. CO_2 is considered to be an acid as the ligands used in the model are in the least protonated form while the metals are in the most protonated form. Morel and Morgan (1972) used this convention in the model they developed.

Method of computation

With the inclusion of the proton or electroneutrality equation, the system is completely defined; components, aqueous species, precipitates and the hydrogen ion concentration have equations assigned to them. If the total concentrations of the components are known, the equilibrium composition of the system can be determined.

This is facilitated by reducing the four mass balance equations and the proton equation, if required, to five variables, Ca^{+2}, Mg^{+2}, CO^{-2}, PO_4^{-3} and H^+. Each aqueous species in these five equations can be represented by the product of the equilibrium constant times one or more of the five variables. As an example, consider the species which are part of the mass balance equation for phosphate:

$$PO_4^{-3} + HPO_4^{-2} + H_2PO_4^- + H_3PO_4$$

The equilibrium constants for the species are:

$$\frac{(H_2PO_4^-)(H^+)}{(H_3PO_4)} = K_1 \quad \text{or} \quad \frac{(H_2PO_4^-)(H^+)}{K_1} = (H_3PO_4) \tag{17}$$

$$\frac{(HPO_4^{-2})(H^+)}{(H_2PO_4^-)} = K_2 \quad \text{or} \quad \frac{(HPO_4^{-2})(H^+)}{K_2} = (H_2PO_4^-) \tag{18}$$

$$\frac{(PO_4^{-3})(H^+)}{(HPO_4^{-2})} = K_3 \quad \text{or} \quad \frac{(PO_4^{-3})(H^+)}{K_3} = (HPO_4^{-2}) \tag{19}$$

Using the second form of the equations, HPO_4^{-2} in equation 18 can be replaced by equation 19; similarily, $H_2PO_4^{-2}$ in equation 17 can be replaced by equation 18. This reduces the species in the mass balance equation to:

$$(PO_4\ )\left[1 + \frac{(H^+)}{K_3} + \frac{(H^+)^2}{K_2K_3} + \frac{(H^+)^3}{K_1K_2K_3}\right]$$

where PO_4^{-3} and H^+ are the unknowns. If pH is defined in the model, the terms within the square parentheses are a constant. In a similar fashion, the proton and the mass balance equations can be reduced to five variables. The precipitates cannot be reduced; rather than including an equation for each of them in the calculations, they are eliminated by subtracting the appropriate mass balance and proton equations in which they appear. An example of the reduced mass balance and the proton equations plus the calculations carried out by the model are outlined in appendix 1.

Once the equations have been formulated equilibrium can be calculated to give the concentration of aqueous species and the amount of precipitate(s). Although the solubility products of the precipitates are known, the model cannot initally be used to determine if a precipitate will form. Therefore it assumes the maximum number of precipitates will form. This will be two or three depending on the presence of magnesium. For the case where two precipitates can possibily form, there are four combinations. Either both apatite and calcite will precipitate, or one of two will precipitate, or else neither of the two will precipitate. After the solution of the system of equations, the amounts of precipitates are determined. If a negative amount is arrived at for any precipitate, the model drops one precipitate and attempts the next case. This continues until either only positive amounts of precipitate(s) form or else no precipitates form at all.

The equations are solved using the Newton-Raphson method for non-linear equations; it was used as it is both common and efficient. The approach is an iterative one which uses trial and error to obtain a solution to a system of non-linear equations. Householder (1953) gives an extensive treatment of the Newton-Raphson and other methods used in solving non-linear equations. Other references which consider non-linear equations are Greenspan (1970), Moursund and Davis (1970), Nielson (1964), Pennington (1965), Freudenstein and Roth (1963) and Zeleznik (1968).

Capabilities of the Model

Table 3 outlines the constraints and various aspects of the model. The different aspects allows the model to calculate 16 different cases. Each case is based on the combination of four different aspects which are:

(1) Magnesium is or is not a component in the system.

(2) a. When magnesium is not a component, either the aqueous ion complexes are included or excluded from the model.

b. When magnesium is a component, either tricalcium phosphate or hydroxyapatite is the Ca-PO_4 precipitate.

(3) pH is specified or is calculated by the model.

(4) The initial concentration of all the components in the system is fixed for each increment of pH or chemical added , or the initial concentration of the components for each subsequent increment is decreased by the amount of each component precipitated in all previous increment(s).

Table 3. Principle Features of the Model

Constraints on the system	closed constant temperature of 25°C limited to solids and liquids one atmosphere total pressure
Components	Ca^{+2}, PO_4^{-3}, CO_3^{-2}, H_2O and/but not Mg^{+2}
Aqueous Species	hydrated metal ions, acid-base dissociation products, ion pairs, ion pair complexes and/but not ion complexes
Precipitates	(a) without Mg^{+2} as a component calcite and hydroxyapatite
	(b) with Mg^{+2} as a component (i) calcite, hydroxyapatite and brucite (ii) calcite, tricalcium phosphate and brucite

The 16 possible cases are schematically shown in figure 3.

Although the model does not consider kinetics, flocculation or the removal of the precipitates, it was generalized to simulate wastewater under different conditions. Using a theoretical approach the model attempts to duplicate existing data from laboratory studies. After the solution of a particular problem in which the aqueous species and precipitates have been determined, the model either increments pH by 0.5 units, if pH is articially fixed, or it increments specified chemicals before attempting the next step. This is illustrated in figure 3, features 4 and 7.

The model extensively used data provided by Ferguson and McCarthy (1969) in formulating the amount of precipitates

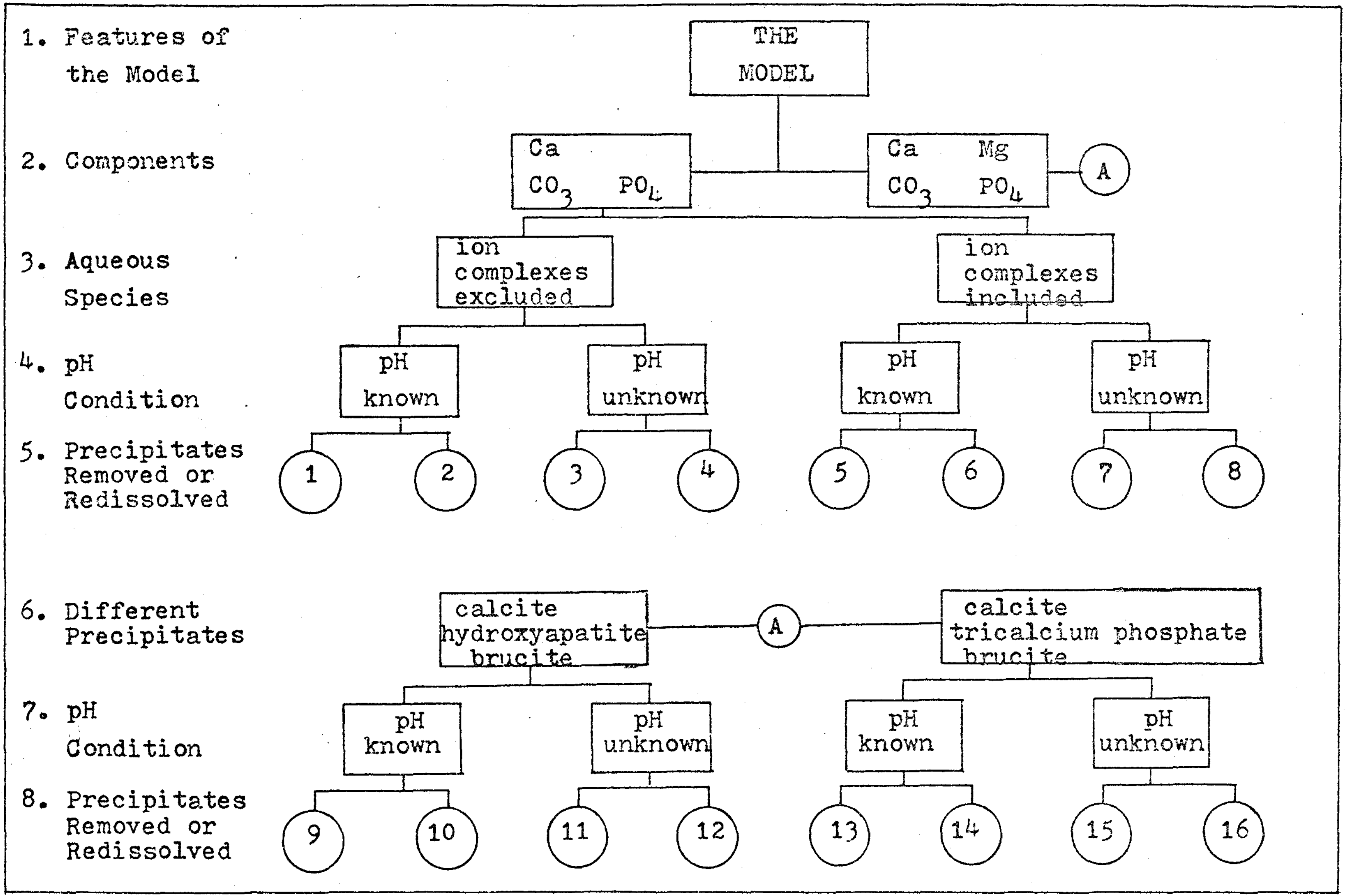


Figure 3. Schematic outline of the model. The even numbers indicate the precipitates are removed from solution while the odd numbers indicate the precipitates are redissolved on the next increment.

which would form under varying concentration of components. These data were divided into two major sets, one set including the components calcium, carbonate and orthophosphate while the other set included calcium, magnesium, carbonate and orthophosphate. A major part of the model was formulated for use of each of these sets of data. In figure 3, the magnesium free part of the model uses cases 1 to 8 while cases 9 to 16 are used when magnesium is a component in the system.

The section of the model which excluded magnesium as a component was further subdivided into two parts, feature 3, figure 3. The first was simply Ferguson and McCarthy's (1969) model, cases 1 to 4. The second part was similar to the first except that ion complexes, $Ca_2.HPO_4.CO_3^0$ and $Ca_2.PO_4.CO_3^-$, were included among the aqueous species, cases 5 to 8. In both parts, the precipitates were hydroxyapatite and calcite.

The section of the model which included magnesium among the components was also divided into two parts. Although the aqueous species were identical, the Ca-PO_4 precipitate was different for each. Ferguson and McCarthy (1969) noted that beta-tricalcium phosphate is a possible precipitate in wastewater; therefore one calculation included tricalcium phosphate,,calcite and brucite, cases 13 to 16, while the other section had the precipitates hydroxyapatite, calcite and brucite, cases 9 to 12.

The model was flexible in another respect, the hydrogen ion concentration can be determined or can be specified, features 4 and 7, figure 3. In not defining pH, various chemicals: H_2CO_3, $Ca(OH)_2$, $Mg(OH)_2$, $CaCO_3$, $MgCO_3$, $Ca_{10}(PO_4)_6OH_2$, H_3PO_4, can be dissolved in water and the resultant pH and the amount of precipitates are determined. The initial concentration of components is determined by the adding of known amounts of chemicals to solution. In doing this the concentration of components may be identical to that of a specified wastewater but the pH of the two may not correspond. This may be due to other ions in the wastewater which have an effect on pH and are not included in the model. This method is best applied to laboratory studies where the components present in solution can be effectively controlled. Also, pH can be artificially specified at some value and the amount of precipitates formed can be determined. This reflects a similar approach in the empirical model of Seiden and Patel (1970), but they used a regression technique while this model determines soluble residual orthophosphate theoretically.

The flexibility of the model was further enhanced by the choice of whether the initial conditions remained constant for all increments of pH or chemical added, or the initial conditions were allowed to change on each increment, features 5 and 8, figure 3. In the second situation, the precipitates which formed during an increment are removed from solution and the total starting concentration of components for the next increment would be decreased by the amount of each component present in the precipitates. The only other way the concentration of the components can be changed is in the situation where pH isn't known and one or more known chemicals added to solution are incremented on each successive step.

V RESULTS

During the study of the Ca-Mg-PO_4-CO_3-H_2O system, various areas were considered important. In the initial section of the results, the different aqueous species present in the five component system were examined. Here the model was run with and without the ion complexes, $Ca_2HPO_4CO_3(aq)$ and $Ca_2PO_4CO_3^-$. Differences in the results showed the effect of the ion complexes on the concentration of the other aqueous species.

In the second section, apparent activity products (solubility constants) were calculated for all the possible precipitates in the model. This step was necessary as the soluble residual orthophosphate and calcium calculated by the model did not match those found in laboratory experiments.

In the final section, the model was verified by predicting the soluble residual orthophosphate and calcium observed in laboratory experiments.

Aqueous Species

The magnesium free section of the model, cases 1-8, figure 3, calculates all aqueous species and precipitates for any concentration of total calcium, carbonate and orthophosphate and for any pH. The possible precipitates are hydroxyapatite and calcite while the possible aqueous species can be varied to test the influence of the ion complexes. Ion pairs, ion pair complexes and acid-base dissociation products use metals and ligands in their formation, thereby decreasing the concentrations of Ca^{+2}, CO_3^{-2} and PO_4^{-3} in solution. As one increases the number and concentration of aqueous species in the model, the amount of precipitate able to form will decrease. In one version of the Mg-free part of the model, cases 1-4, the aqueous species include metals, ligands, ion pairs, ion pair complexes and acid-base dissociation products; this version is basically Ferguson and McCarthy's (1969) model. The second version includes all the aqueous species of the first plus the ion complexes, cases 5-8, figure 3. The effect of these complexes on residual orthophosphates can be compared to cases where they are not included among the aqueous species.

The various aqueous species are shown in figures 4, 5, 6 and 7. As shown in figure 4, the principal carbonate are the dissociation products of carbonic acid. The aqueous species $CaHCO_3^+$ closely approximates the concentration curve of HCO_3^-, the only difference being the concentration which is 1 to 1.5 orders of magnitude less in solution. $CaCO_3(aq)$ closely approximates CO_3^{-2} from a pH of 4.5 to 7.0 but it does not increase significantly after pH 7.5; the concentration remains at approximately 3.41×10^{-5} moles/litre. This concentration is maintained **as calcite** and apatite are precipitating from solution.

The calcium species show the free hydrated metal, Ca^{+2}, being the predominant aqueous species from a pH of 3 to approximately 6.5. For a pH>6.5, $CaHCO_3^+$ is the predominant

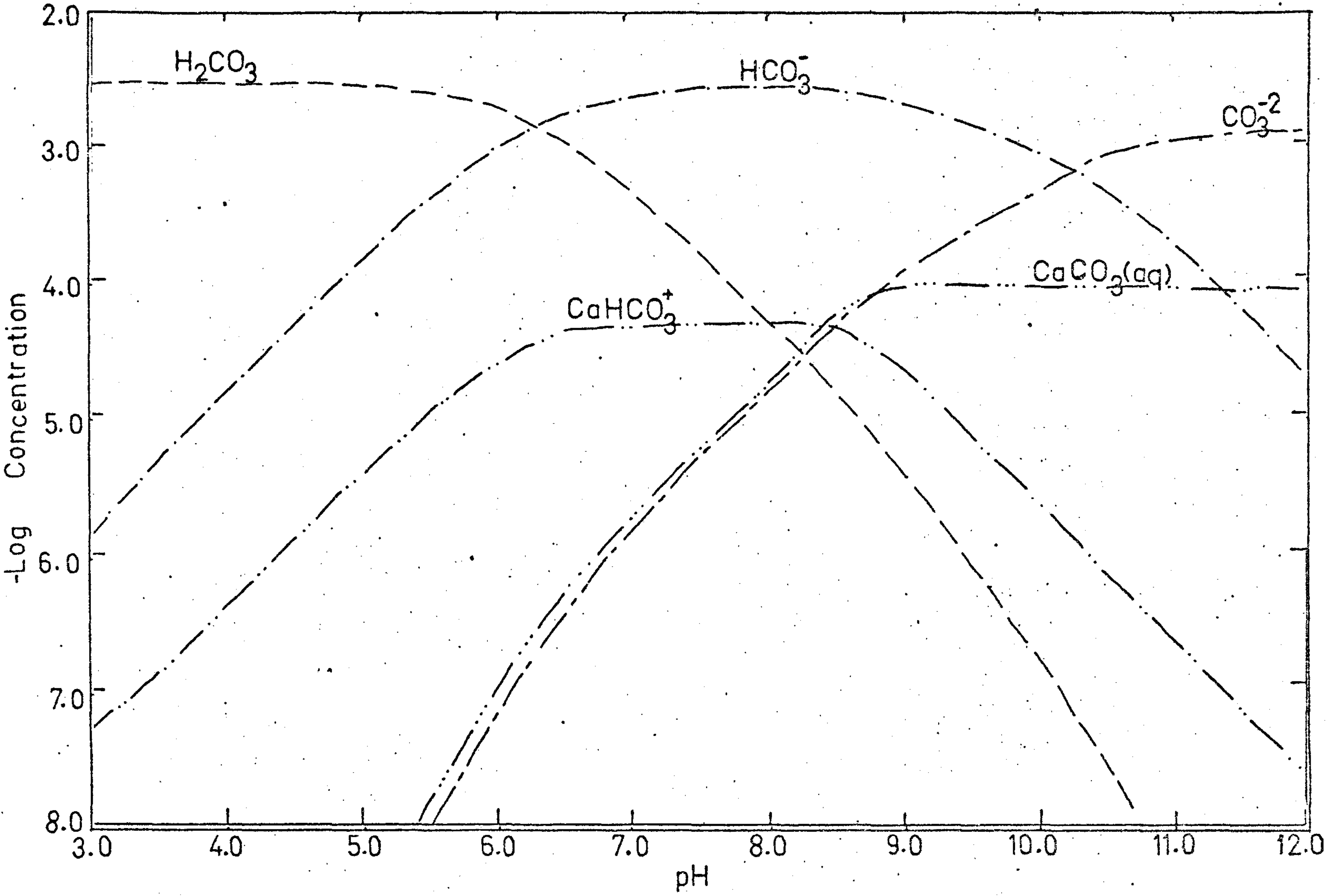


Figure 4. The concentration of the major carbonate species in a typical wastewater. The effect of adding the ion complexes, magnesium or having different precipitates does not change the distribution of the carbonate species significantly. The precipitation of calcite slightly decreases the carbonate concentration from pH 8.5 to 10.5.

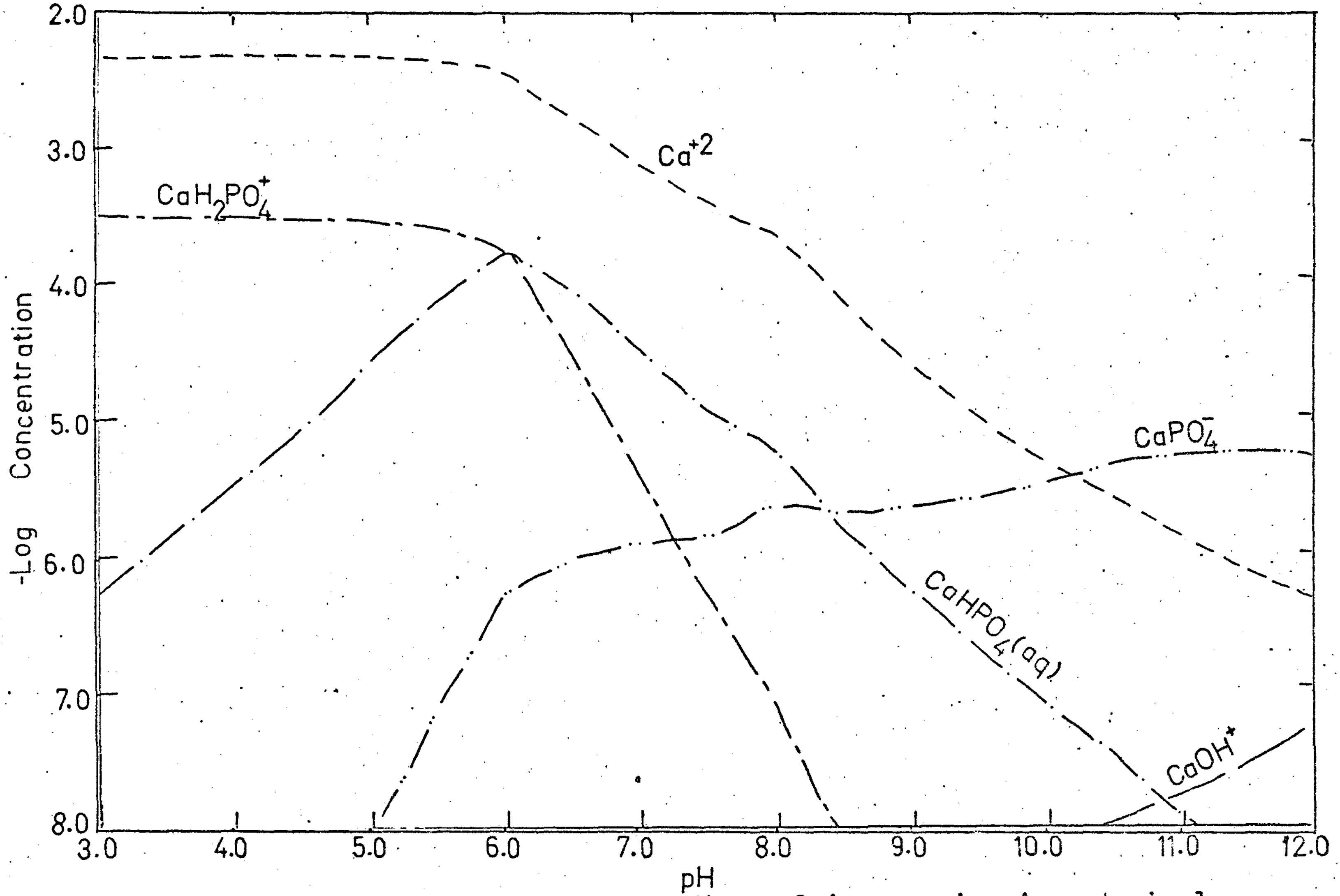


Figure 5. The concentration of the major calcium species in a typical wastewater. This figure can represent cases 5, 9 or 13. In case 1 where the ion complexes are not included, the concentration of the aqueous species $CaPO_4$ and $CaHPO_4$ would be higher. Calcium is being removed from solution through the precipitation of calcite and/or hydroxyapatite.

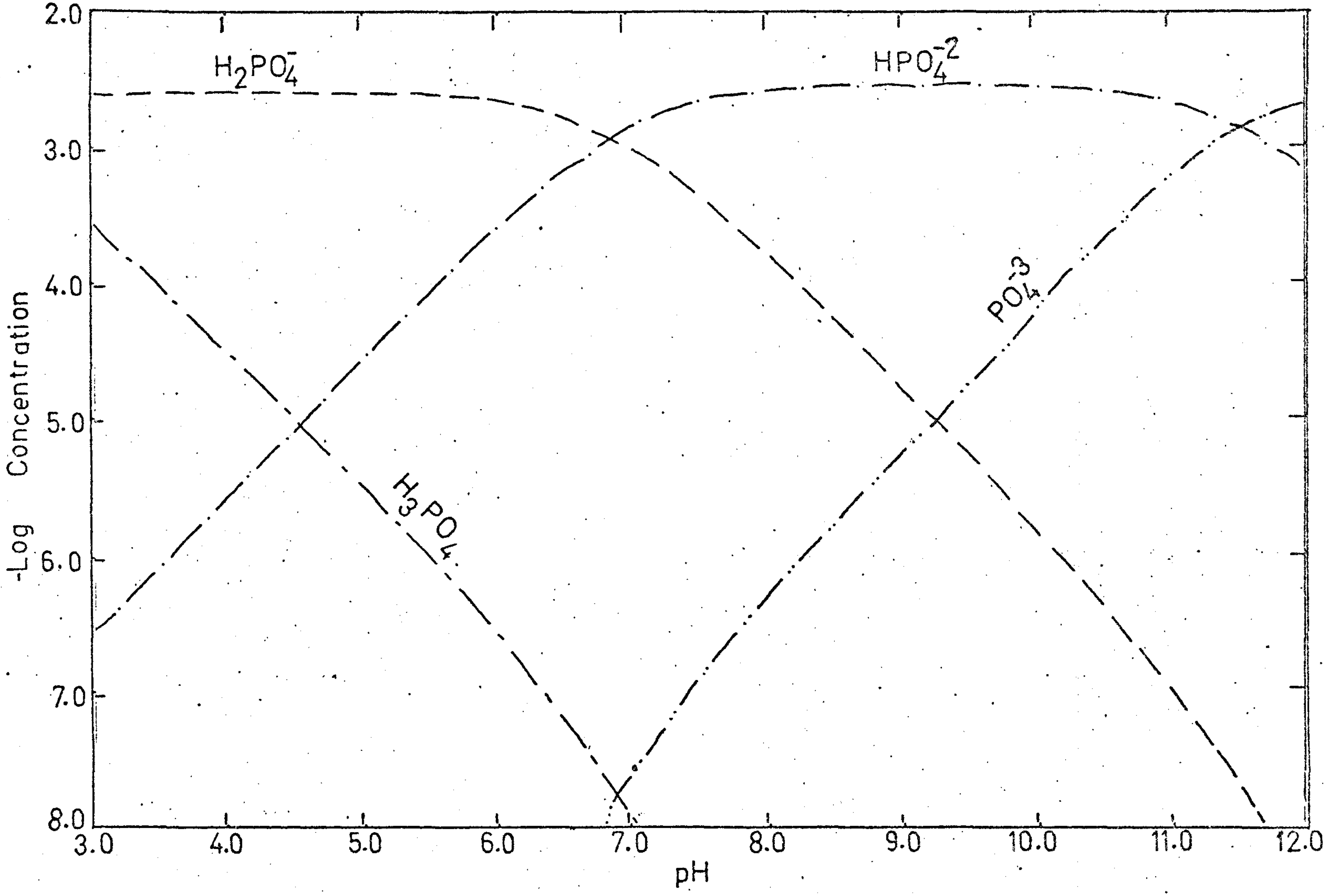


Figure 6. The concentration of the major orthophosphate species for case 1. The dissociation products of phosphoric acid are the predominant aqueous species. The ion pairs and ion pair complexes, $CaPO_4$, $CaHPO_4$(aq), CaH_2PO_4, are illustrated in figure 5. Orthophosphate is being removed from solution through the precipitation of hydroxyapatite.

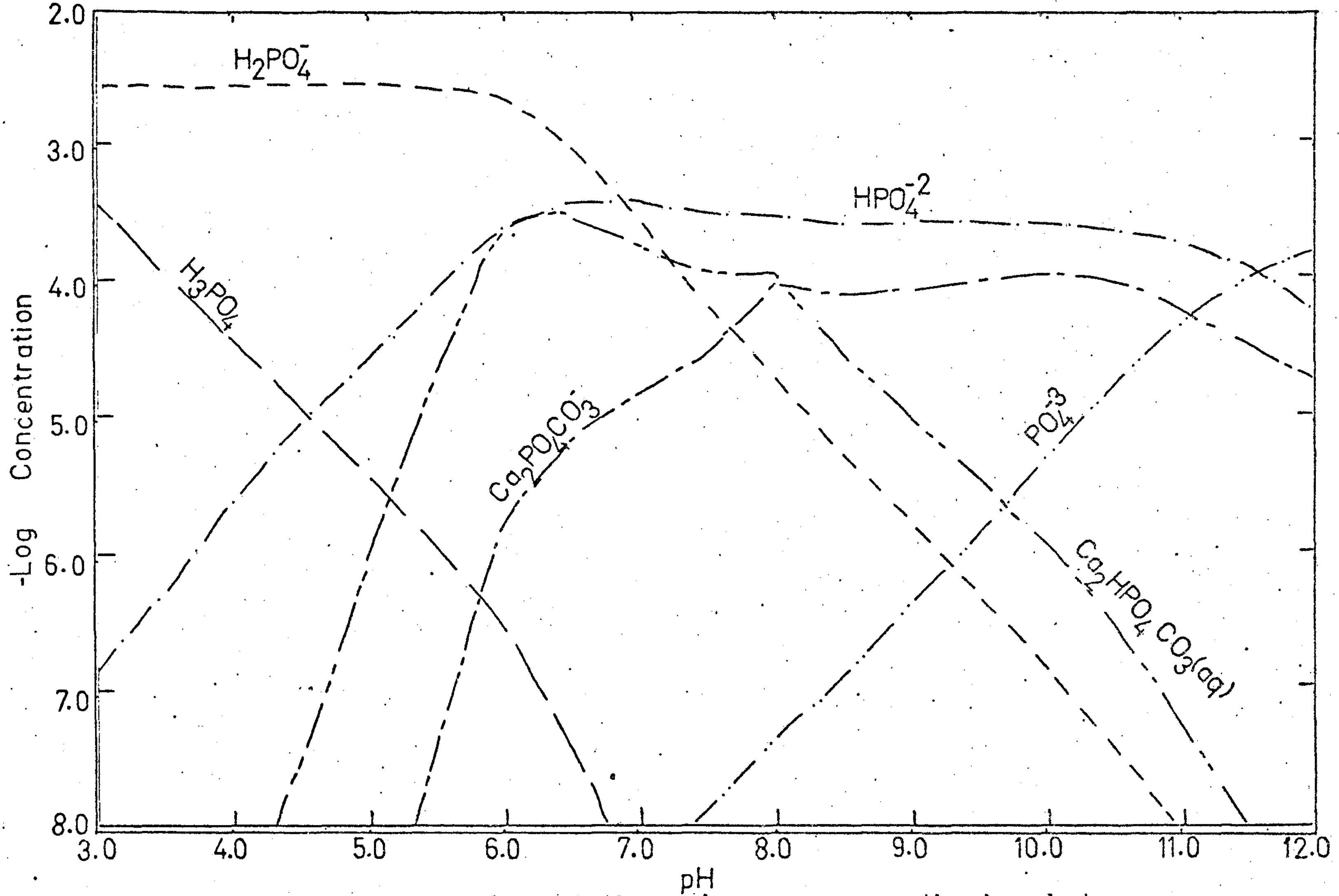


Figure 7. The concentration of the major aqueous orthophosphate species for cases 5, 9 or 13. This figure includes the ion complexes which were not among the aqueous species in case 1, figure 6. Orthophosphate is being removed from solution through the precipitation of hydroxyapatite.

aqueous species. In figure 5, the species $CaH_2PO_4^+$ and $CaHPO_4(aq)$ follow the concentration curves of the dissociation products of phosphoric acid. Again the only difference is the lower concentration of the aqueous species. When the $pH > 7$, this situation does not hold as calcite and hydroxyapatite precipitate and remove the components from solution.

The effect of the ion complexes is best illustrated in the aqueous phosphate species. Figure 6 shows the aqueous phosphate species when the ion complexes are not included while figure 7 displays them when the ion complexes are included. In figure 6, the dissociation products of phosphoric acid are the predominant aqueous species while in figure 7, $Ca_2PO_4CO_3^-$ becomes a predominant aqueous species at a pH of 7.

At a low pH, the ion complexes do not have an appreciable effect on the other aqueous species. Only when the $pH > 5$, the ion complexes begin to predominate and the other aqueous species decrease in concentration. From pH 5-7, the ion complex $Ca_2HPO_4CO_3(aq)$ is predominant, while for $pH > 7$, $Ca_2PO_4CO_3^-$ is the dominant aqueous phosphate species. As the pH increases, the ion complexes maintain a high concentration, thereby decreasing the amount of hydroxyapatite formed. Under identical conditions, cases 1-4 where the ion complexes are not included precipitate more hydroxyapatite and calcite than cases 5-8 where the complexes are included in the model.

In the section of the model which includes magnesium, cases 9-16, figure 3, five new aqueous species are added to the model. They are the metal Mg^{+2}, the ion pair and ion pair complexes $MgCO_3(aq)$, $MgHCO_3^+$, $MgHPO_4(aq)$ and $MgOH^+$. As the behaviour of magnesium parallels that of calcium, one would expect the aqueous species $MgPO_4^-$ and $MgH_2PO_4^+$ to be important. The concentration of magnesium in a typical wastewater is 0.25-1 mM while calcium is 0.5-5 mM (Jenkins et al 1971). Therefore the exclusion of these minor aqueous species would not greatly affect the removal of orthophosphate from solution. When magnesium is included in the model, all of the aqueous species listed in table 2 are considered.

The presence of magnesium does not radically change the distribution of aqueous species containing Ca^{+2}, CO_3^{-2} and PO_4^{-3}. Figures 4, 5 and 7 can also be considered to illustrate the behaviour of the aqueous species when hydroxyapatite or tricalcium phosphate, calcite and brucite precipitate. The only effect of the addition of the three new aqueous species, $MgCO_3(aq)$, $MgHCO_3$, $MgHPO_4(aq)$, is the slight lowering of the concentrations of all aqueous species containing CO_3^{-2} and PO_4^{-3}. Also at a pH$>$ 10, brucite precipitates which aids in the flocculation and removal of the orthophosphate precipitate (Menar and Jenkins 1972), this causes a slight lowering of all aqueous species containing CO_3^{-2} and PO_4^{-3}.

Figure 8 shows the distribution of the aqueous magnesium species with pH. The metal, Mg^{+2}, persists throughout the entire pH range; only at a pH$>$ 11, $MgOH^+$ is the predominant species. The sudden decrease in the aqueous

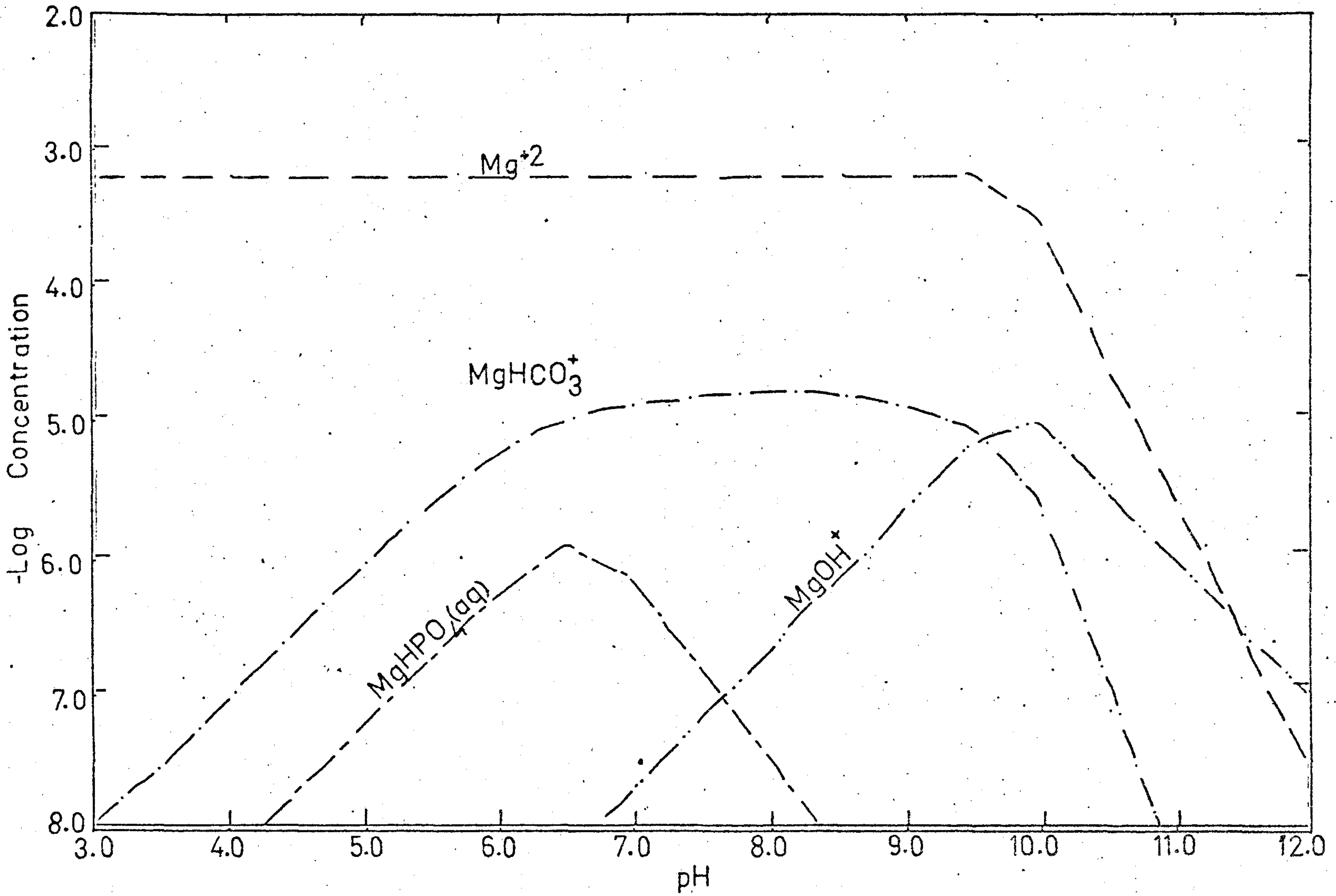


Figure 8. The concentration of the predominant aqueous magnesium species in a typical wastewater. The sudden decrease in the aqueous species at pH 10 is due to the precipitation of brucite.

magnesium species at pH of 10 is due to the precipitation of brucite. The concentration of the aqueous species $MgHCO_3^+$ and $MgHPO_4(aq)$ parallels the concentration of the acid dissociation products HCO_3^- and HPO_4^{-2}, respectively. The ion pair - ion pair complex $MgCO_3(aq)$ is not seen in figure 8 as its concentration is less than 10^{-8} moles/litre at any pH.

It must be realized that while the examples used depict average cases, a change in concentration of the components will result in different concentrations of aqueous species. The predominant species may change and the residuals in solution will be different. The examples used characterise the common components in wastewater at their respective concentrations outlined in table 1.

Apparent Activity Products

Literature values for the solubility products of the precipitates possible in the model are usually determined in a laboratory, in a solution limited to the ions forming the precipitate, at a stable pH and over a reasonably long period of time. But wastewater precipitates are not formed under the identical conditions, the solution contains numerous different aqueous species, organic and inorganic molecules plus colloidal material and the pH is varied to cause the rapid formation of precipitates to lower the residual phosphate. Literature values for the solubility constants for hydroxyapatite, calcite, beta tricalcium phosphate and brucite are 115.5, 8.35, 27.0 and 11.6 respectively. When these values were used in the model on actual sets of data, the predicted residual orthophosphate and calcium were always 1 to 3 orders of magnitude lower than the actual residuals observed in solution. This indicates that the solubility (activity) products used for the precipitates are not accurate or the precipitates assumed to form do not precipitate. Therefore, the apparent activity products for **hydroxyapatite** ($Ca_{10}(PO_4)_6OH_2$), beta tricalcium phosphate ($Ca_{2.82}Mg_{0.18}(PO_4)_2$), tricalcium phosphate ($Ca_3(PO_4)_2$), calcite ($CaCO_3$), Mg-calcites ($Ca_{0.97}Mg_{0.03}CO_3$, $Ca_{0.89}Mg_{0.11}CO_3$, $Ca_{0.8}Mg_{0.2}CO_3$) and brucite ($Mg(OH)_2$) were calculated.

The activity products were calculated using the chemical formulae listed above. The precipitates were not changed but new activity products were determined so phosphate residuals determined in laboratory experiments and the model would match. Ferguson and McCarthy (1969) did extensive laboratory experimentation on calcium phosphate precipitation under various conditions. They used a wide spectrum of calcium, magnesium, carbonate and orthophosphate concentrations and also varied the pH, temperature and time allowed for the settling of the precipitate. Two major sets of data resulted from their work, one being magnesium free while the other was not. Using the Mg-free data, the activity of calcite and hydroxyapatite were calculated by two different methods. Both included the metals Ca^{+2}, H^+, the ligands CO_3^{-2}, PO_4^{-3}, OH^-, the ion pairs, the ion pair complexes and acid-base dissociation products but the first excluded the ion complexes from the aqueous species, cases 1-4, figure 3. The results of calculating the apparent activity products for hydroxyapatite are shown in figures 9 and 10. Figure 9 represents cases 1-4 which do not include the ion complexes among the aqueous species while figure 10 does. Even though cases 1-4 and 5-8 were calculated on the same set of data, there is a marked difference in the apparent activity products. When the ion complexes are omitted from the model, the activity products are considerably greater, indicating a greater solubility for hydroxyapatite. Cases 1-4 are basically Ferguson and McCarthy's (1969) model and it duplicates their results. They found for a system with low magnesium and high carbonate, the apparent activity product for hydroxyapatite was 101 for $pH < 8$; for pH 8 to 11, the value was 90; and for $pH > 11$, the value was 96. Cases 5-8, which include the ion complexes, do not show this fluctuation of the apparent activity product but has a relatively uniform value of 102.5 for any pH. The least square line for cases 1-4 is:

$$pA(\text{hydroxyapatite}) = 106.39 - 1.12(pH) \qquad (20)$$

while the least square line for cases 5-8 is:

$$pA(\text{hydroxyapatite}) = 100.24 + 0.25(pH) \qquad (21)$$

From the equations of the least square lines, equation 21 is the least dependent on pH. This trend is also seen in figures 9 and 10 as the least square line in figure 9 has a significant negative slope while the least square line in

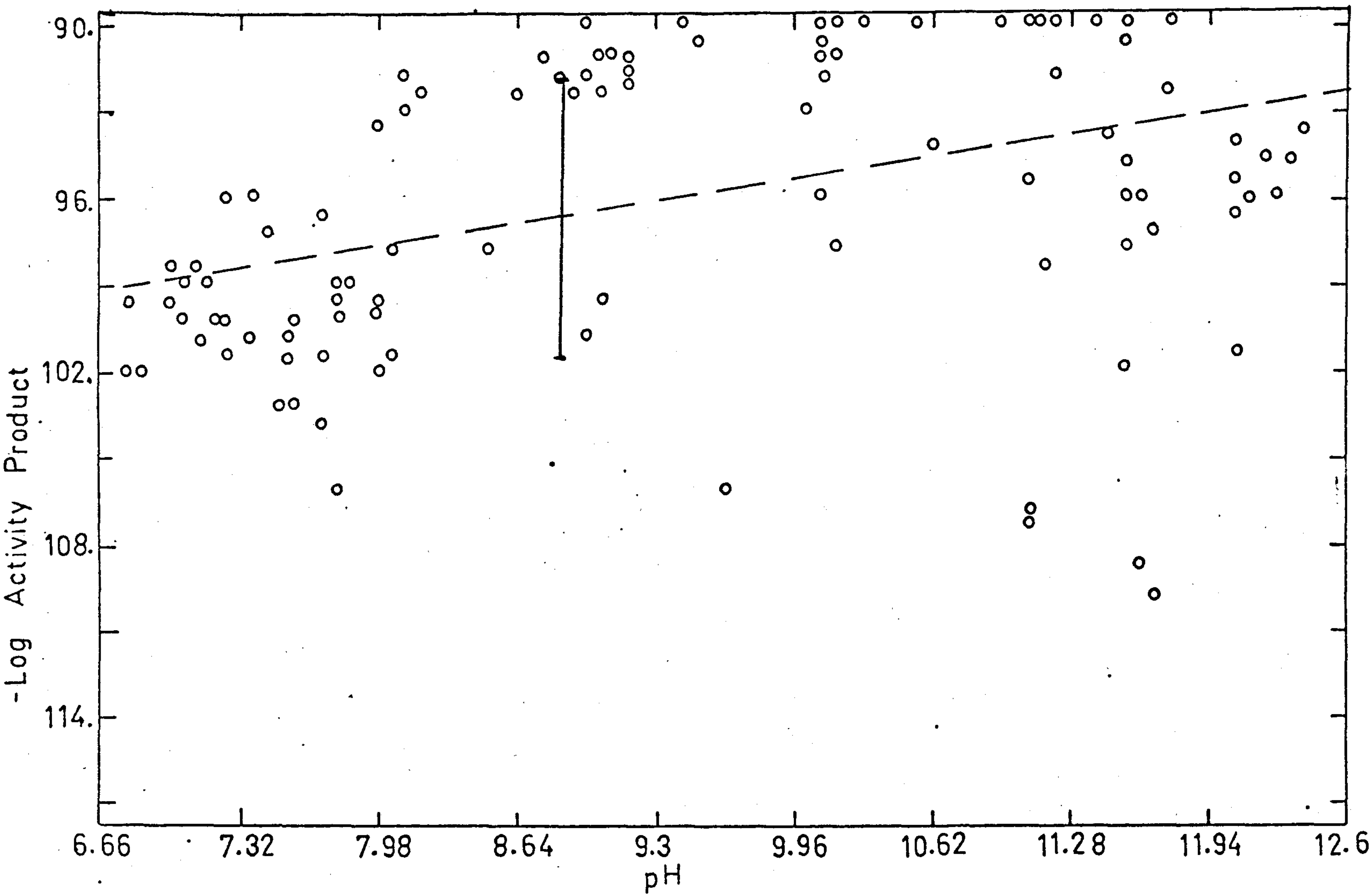


Figure 9. The apparent activity products for hydroxyapatite calculated using case 1. The components were limited to calcium, carbonate and orthophosphate. The line represents the least square equation. The bars represent a confidence limit of 95 per cent.

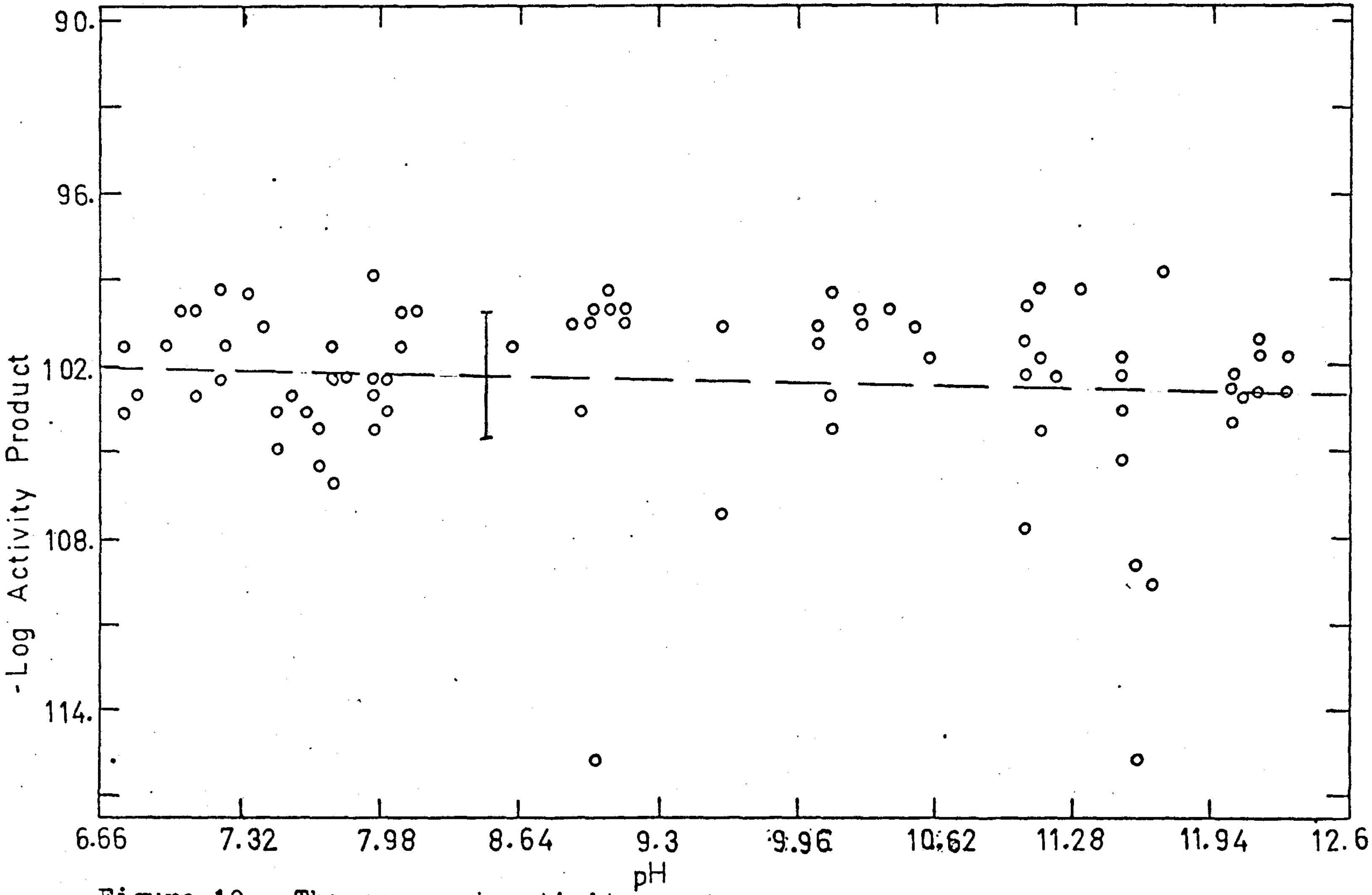


Figure 10. The apparent activity products for hydroxyapatite calculated using case 5. These values were determined on the same set of data as case 1; the only difference was the inclusion of the ion complexes among the aqueous species. The line represents the the least square equation. The bars represent a confidence limit of 95 per cent.

figure 10 has a slight positive slope. Table 4 compiles the statistics concerning the two methods. The ion complexes are shown to have a significant effect on the apparent activity products. Cases 1-4 have a larger mean, standard deviation and a greater range of values than cases 5-8.

Table 4. $-\mathrm{Log}_{10}$ Apparent Activity Products of Hydroxyapatite and Tricalcium Phosphate

Cases	Activity Product of	Mean	Standard Deviation	Maximum Value	Minimum Value	Activity Product of Calcite	Standard Deviation of Calcite
1-4	HAP	95.84	5.16	109.74	88.48	7.44	0.50
5-8	HAP	102.46	2.23	109.91	98.81	7.67	0.44
9-12	HAP	102.57	3.18	112.53	96.04	7.23	0.55
13-16	(a)TCP	26.87	1.35	31.25	24.20	6.49	0.62
	(b)TCP	29.87	1.60	33.32	26.63	7.23	0.62

For the set of data including magnesium, a variety of activity products were determined. The activity product of hydroxyapatite was calculated as Seiden and Patel (1970) felt it was the phosphate precipitate in wastewater. The activity products of beta tricalcium phosphate and tricalcium phosphate were calculated as Ferguson and McCarthy (1969) and Menar and Jenkins (1972) felt beta tricalcium phosphate is the major phosphate precipitate in wastewater containing a medium to high magnesium concentration; Ca:Mg ratio less than five. The activity products of calcite and various Mg-calcites were determined as the presence of magnesium in solution leads to its inclusion in the calcite lattice which decreases the solubility of calcite (Chave et al 1962). The activity product of brucite was computed as it forms at a pH of approximately 10 or greater. All of the above activity products are calculated with all the aqueous species listed in table 2 present in solution.

The activity of hydroxyapatite, beta tricalcium phosphate and tricalcium phosphate are shown in figures 11, 12 and 13 respectively. The least square lines for all the precipitates have a positive slope indicating a lower solubility as pH increases. The statistics for the different precipitates are tabulated in table 4 with cases 9 -12 representing the precipitation of hydroxyapatite, calcite and brucite; cases 13 - 16(a) representing the precipitation of beta tricalcium phosphate, Mg-calcite (3% magnesium in the calcite lattice) and brucite; while cases 13 - 16(b) represent the precipitation of tricalcium phosphate, calcite and brucite.

The mean value and range of values of the activity product for hydroxyapatite does not change significantly from cases 5 - 8 to cases 9 - 12 even though magnesium is present in cases 9 - 12 and the two results were calculated on two different sets of data. The standard deviation of cases 9 - 12 is slightly larger than cases 5 - 8 and this may be due to interference caused by the presence of magnesium. The precipitation of brucite may form a site for the nucleation of hydroxyapatite or help in producing a readily flocculating calcium-carbonate-phosphate precipitate (Menar and Jenkins 1972).

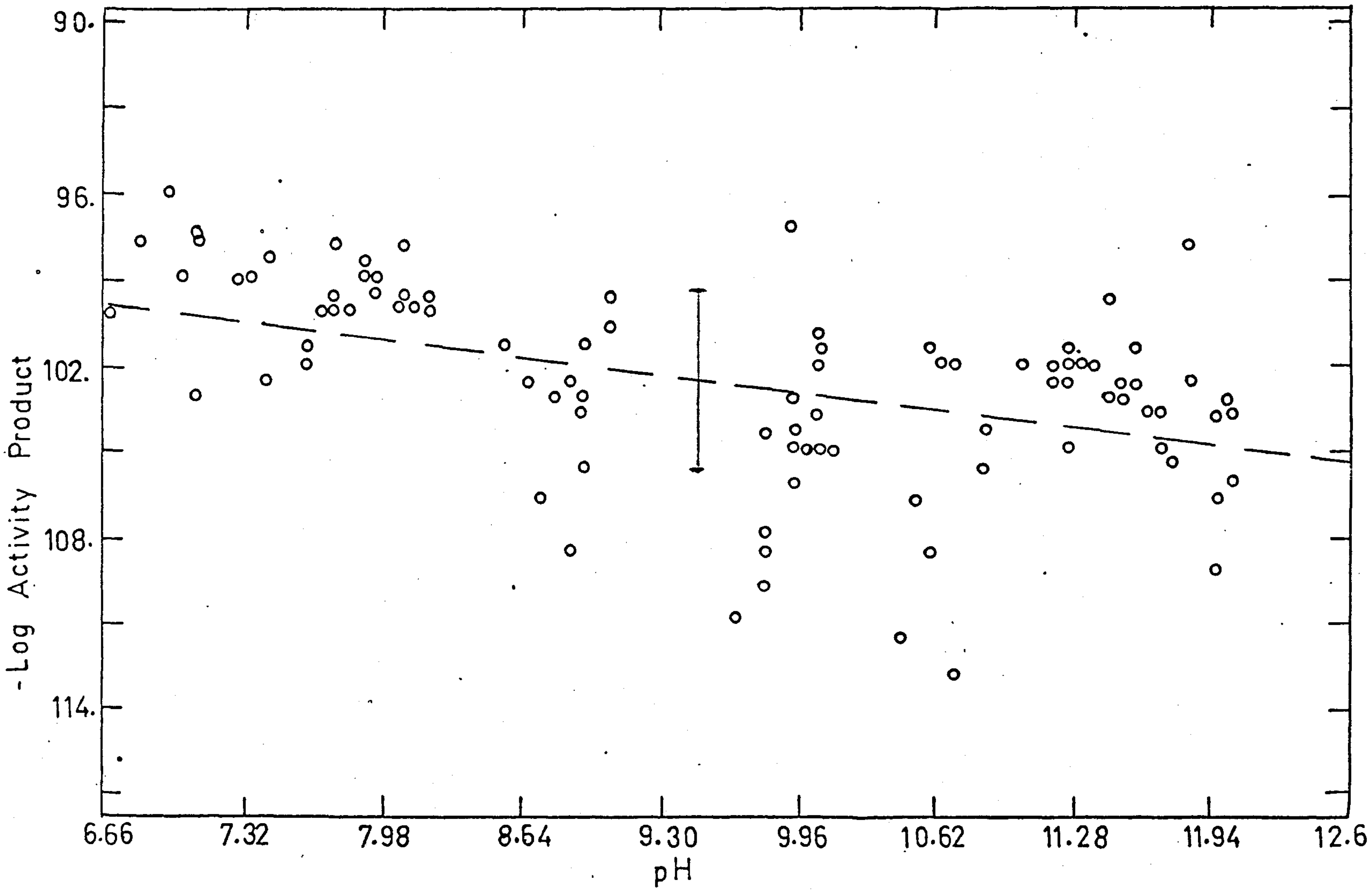


Figure 11. The apparent activity products for hydroxyapatite calculated using case 9. The components present in solution were calcium, magnesium, carbonate and orthophosphate. The line represents the equation of the least square line. The bars represent a confidence limit of 95 per cent.

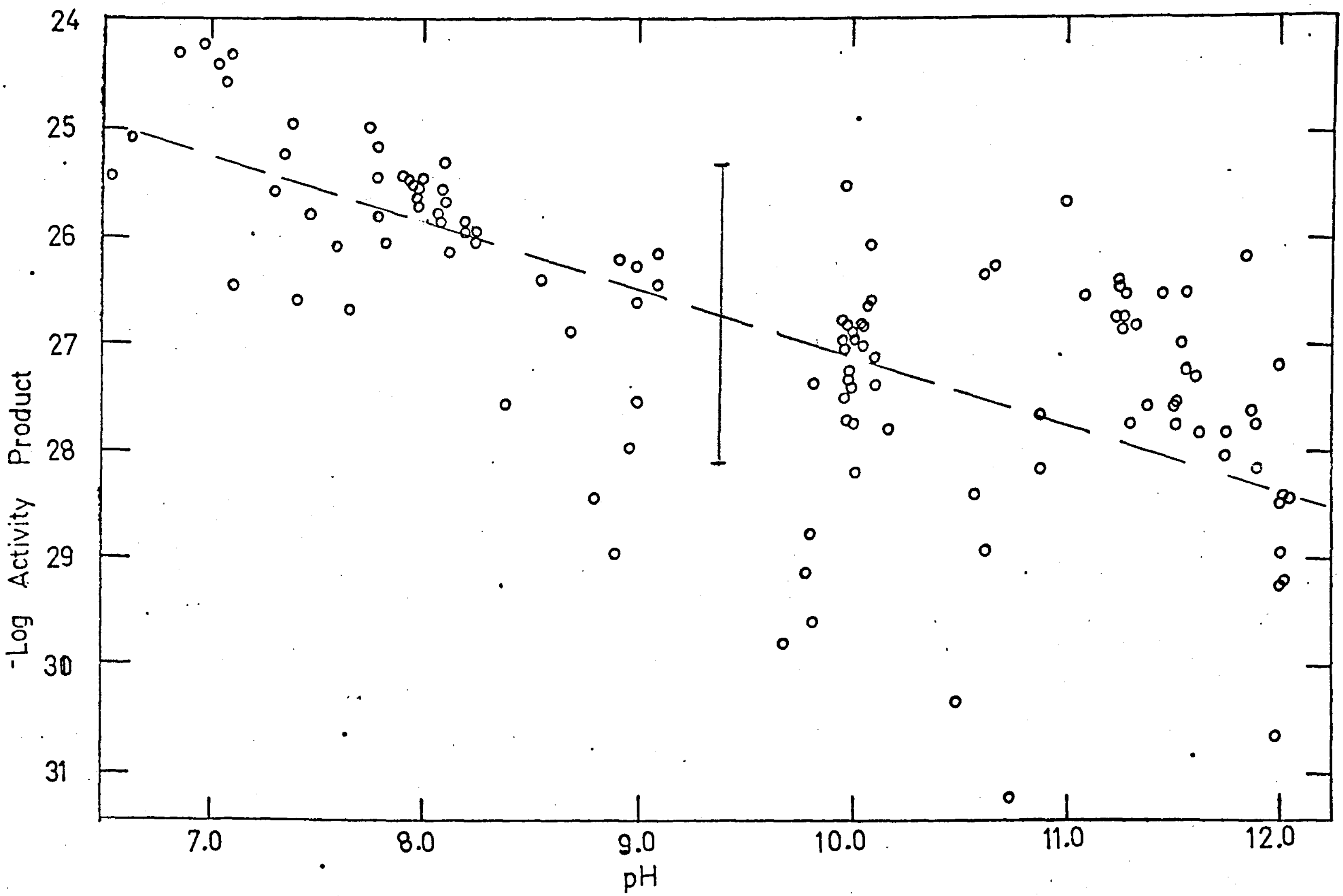


Figure 12. The apparent activity products for beta tricalcium phosphate (6 per cent magnesium in the lattice) calculated using case 13. The line represents the equation of the least square line. The data used were the same as those used in figure 11. The bars represent a confidence limit of 95 per cent.

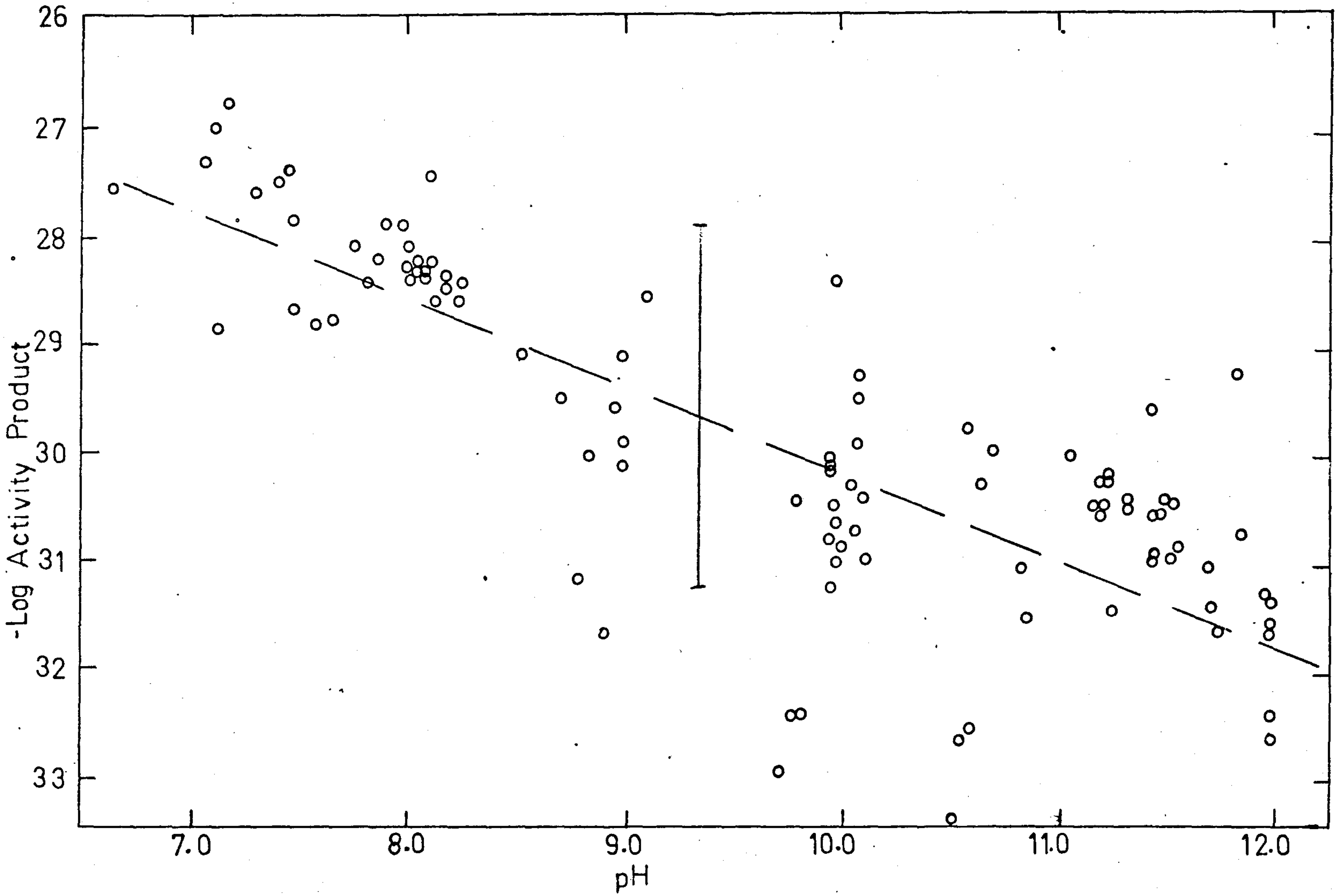


Figure 13. The apparent activity products for tricalcium phosphate calculated using case 13. There was no magnesium included in the lattice and the data were the same as those used in figures 11 and 12. The line represents the equation of the least square line. The bars represent a confidence limit of 95 per cent.

This is evidenced by the increased positive slope for hydroxyapatite from case 5 - 8 to cases 9 - 12. The equation for the least square line for cases 9 -12 is:

$$\text{pA(hydroxyapatite)} = 92.96 + 1.00(\text{pH}) \tag{22}$$

The mean values for beta tricalcium phosphate and tricalcium phosphate are 26.87 and 29.89 respectively. The first value is very close to the value of 27.0 quoted by Sillen and Martell (1964). The values for the activity product of tricalcium phosphate range from approximately 23.0 to 29.0 (Menar and Jenkins 1972), therefore the second value indicates a slightly lower solubility than the lower limit quoted. The standard deviation and the slope of the least square line for cases 13 -16(b) are slightly larger than cases 13 -16(a). The equations for the least square lines for cases 13 -16(a) and 13 -16(b) are respectively:

$$\text{pA(beta tricalcium phosphate)} = 20.73 + 0.64(\text{pH}) \tag{23}$$

$$\text{pA(tricalcium phosphate)} = 22.21 + 0.79(\text{pH}) \tag{24}$$

The least square lines and actual activity products determined are shown in figures 12 and 13.

The apparent activity products of calcite for the different cases were also calculated and are listed in table 4. There was no proof as to when or if calcite precipitated so the activity products were calculated over the entire pH range 6 to 12.6. The mean values for the apparent activity products are different for cases 1 -4 and 5 - 8 as the latter cases include the ion complexes among the aqueous species.

From cases 5 - 8 to cases 9 - 12, the apparent activity product increases 0.45 orders of magnitude; this occurs as magnesium tends to destabilize the formation of calcite (Chave et al 1962). Cases 13 - 16 calculate the apparent activity products with 3, 11 and 20 per cent magnesium being present in the calcite lattice. The values were 6.49, 6.46 and 6.42 respectively. The increased amount of magnesium in the calcite lattice did not alter the average apparent activity product to a great extent. Although cases 9 - 12 and 13 - 16 use the same set of data and have the same aqueous species, the average activity products have a difference of 0.75 orders of magnitude. In all cases, the apparent activity product of calcite does not show a linear behaviour similar to that of hydroxyapatite and tricalcium phosphate but assumes a parabolic one. The activity products of calcite indicate a low solubility at pH 6 but as pH increases, the solubility also increases. At pH 8 to 9, the solubility remains reasonably constant until pH 10 to 11 when the solubility decreases again. Seiden and Patel (1970) noted a similar behaviour for calcite in their model, they observed the same increase and levelling off of the solubility as the pH increased but they did not observe the decrease in solubility beyond pH 10. This may be due the fact that they did not carry their system to a pH of 10.8 or greater. Figures 15 (a) and (b) show typical values for the activity products of hydroxyapatite and calcite using constant concentrations of

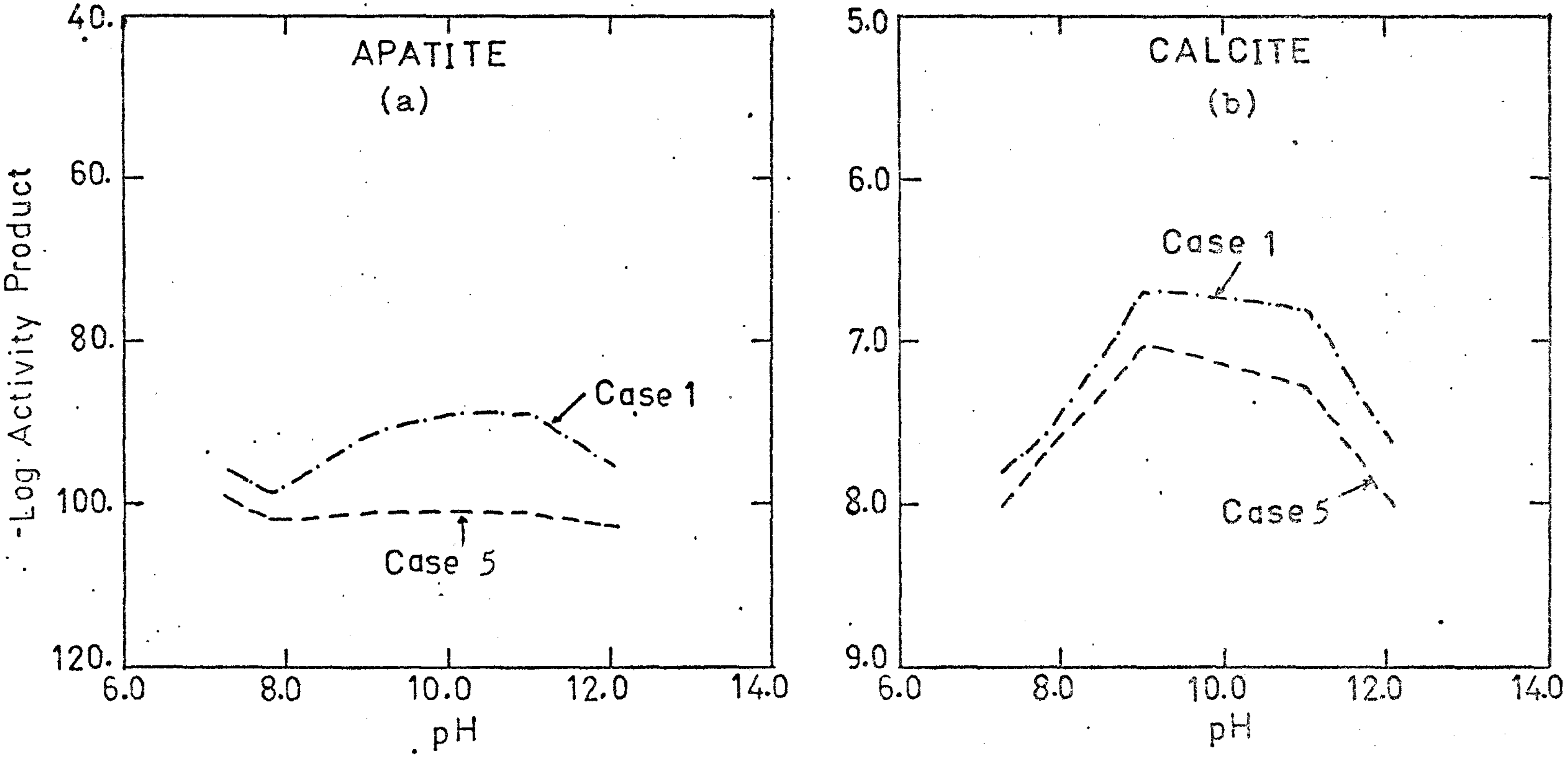


Figure 15. The apparent activity products of calcite and hydroxyapatite, these were calculated for components of concentration: Ca = 2.5 mM, CO_3 = 30 mM and PO_4 = 1.0 mM.

metals and ligands while varying pH. Ferguson and McCarthy (1969) note the pH range in which calcite precipitates in their laboratory experiments to range from pH 8.5 to 10.8. The values of the apparent activity products of calcite in this pH range are for cases 1 - 4, 7.05, cases 5 - 8, 7.35, cases 9 - 12, 6.85 and cases 13 - 16, 6.02. The use of these apparent activity products in the model will reflect more accurately the amount of calcite precipitation. Appendix 2 displays the remaining apparent activity products calculated using constant concentrations of the metals and ligands while varying pH.

The inclusion of different concentrations of magnesium in the calcite lattice did not lead to a marked difference in the activity product as was found in laboratory experiments by Chave et al (1962). Also, an increase or decrease of magnesium in the lattice of beta tricalcium phosphate did not have a significant effect on altering the computed activity products. This indicates that the inclusion of magnesium in the lattices of calcite and beta tricalcium phosphate cannot be explained through the calculation of apparent activity products. The results obtained for the Mg-calcites and beta tricalcium phosphate do not truly reflect the effect of magnesium which suppresses the formation of calcite and stabilizes the formation of beta tricalcium phosphate. Therefore for cases 13 - 16, the apparent activity product for calcite rather than Mg-calcite and tricalcium phosphate rather than beta tricalcium phosphate were used in the model. The apparent activity of calcite was obtained from cases 9 - 12 and the least square line, equation 24, was used for tricalcium phosphate. Hydroxyapatite in cases 1 - 4, 5 - 8 and 9 - 12 uses equations 20, 21 and 22 respectively, to represent the activity products in the model. The activity products for calcite were the mean of values between pH 8.3 to 10.8, each different case had its own value.

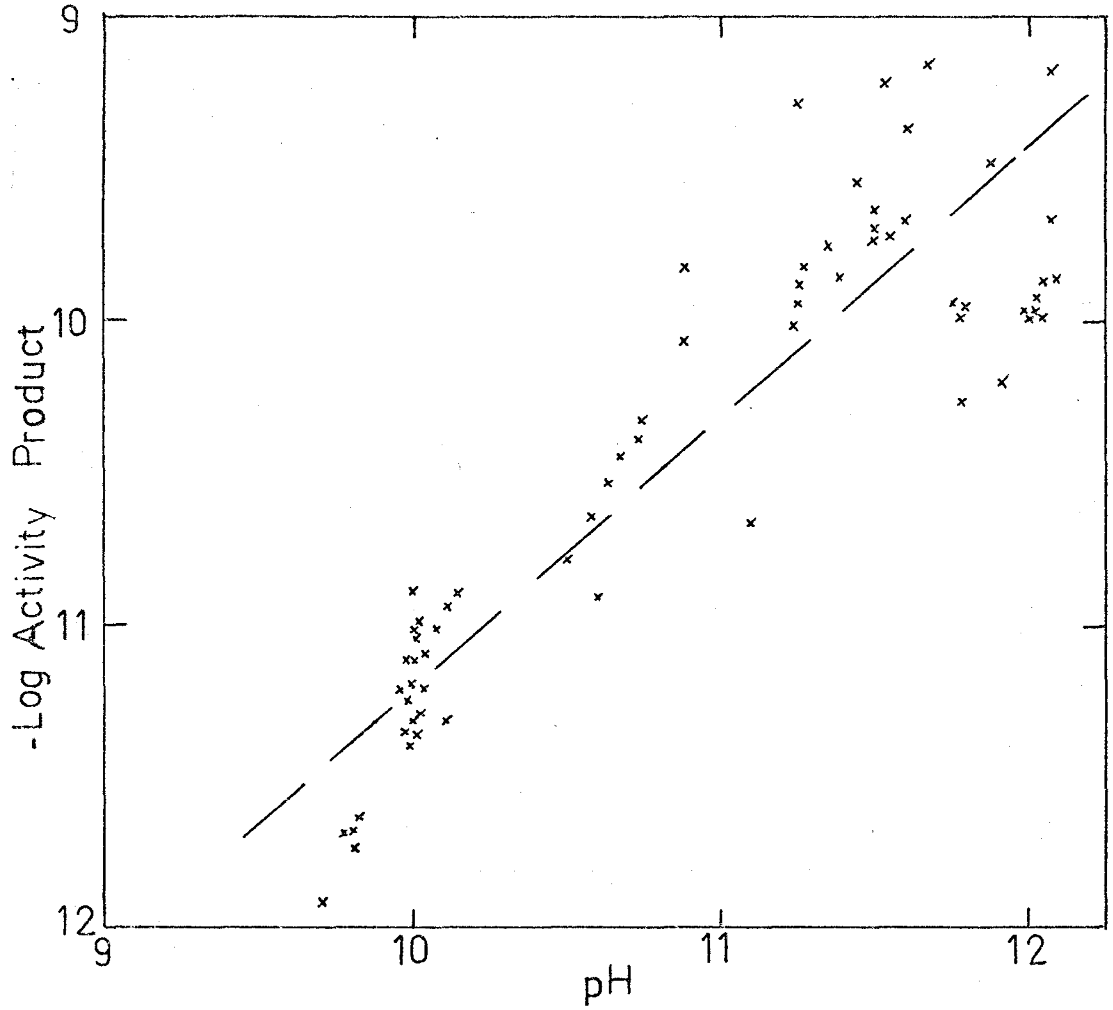


Figure 16. Apparent activity products of brucite calculated using cases 9 - 12 and 13 - 16. The line represents the least square equation.

The apparent activity product for brucite, $Mg(OH)_2$, was also determined; figure 16 shows the values obtained. The equation of the least square line is:

$$pA(\text{brucite}) = 20.13 - 0.89(pH) \qquad (25)$$

This equation indicates a strong dependence of brucite on pH; as pH increases so does the solubility of brucite. The equation for the least square line was used in cases 9 - 12 and 13 - 16 to describe the precipitation of brucite in the model.

Verification of the Model

In verifying the model, only cases 1, 5, 9 and 13, figure 3, were tested. In using these cases, the concentration of the components remained constant for each increment of pH. Upon incrementing the pH 0.5 units, the model calculates the concentration of the aqueous species, the amount of any precipitate formed in solution and the concentration of the components remaining in solution. The soluble residuals components illustrated in figures 17 to 33 are the result of subtracting the amount of the precipitate(s) formed at a specified pH from the initial concentration of components. The model uses the mean apparent activity product for the solubility of calcite and the least square lines of the apparent activity products for the solubility of hydroxyapatite, tricalcium phosphate and brucite.

(a) The Magnesium Free System

Two parts of the model were developed to simulate the magnesium free system; the initial one, case 1, is basically Ferguson and McCarthy's (1969) model while the second, case 5, is an extension of their model as it includes the ion complexes. The computed residual components vary between the two methods as figure 17 illustrates. Case 1 predicts a lower orthophosphate residual than case 5 by one order of magnitude. Case 1 does not always produce lower residuals than case 5, the activity products are only approximations and their use may lead to a degree of error in the results. In calculating the apparent activity product of hydroxyapatite, case 1 had a larger standard deviation than case 5 and is more likely to produce varying results. Both cases have a residual orthophosphate minimum between pH 8.7 and 9.0 followed by an increase in the orthophosphate residual. Calcite begins to precipitate between pH 8.5 and 9.5 which causes an increase in the residual orthophosphate due to the competition of both hydroxyapatite and calcite for the available free calcium ion. While calcite is precipitating, the residual orthophosphate remains relatively constant. When calcite ceases to precipitate, usually between pH 10.5 to 11.0, the residual orthophosphate decreases rapidly as calcium is used solely to precipitate hydroxyapatite. Rather than reproduce results obtained by Ferguson and McCarthy (1969), only case 5 will be considered while discussing the magnesium free system.

The three components in the magnesium free case are calcium, carbonate and orthophosphate. In solution, the

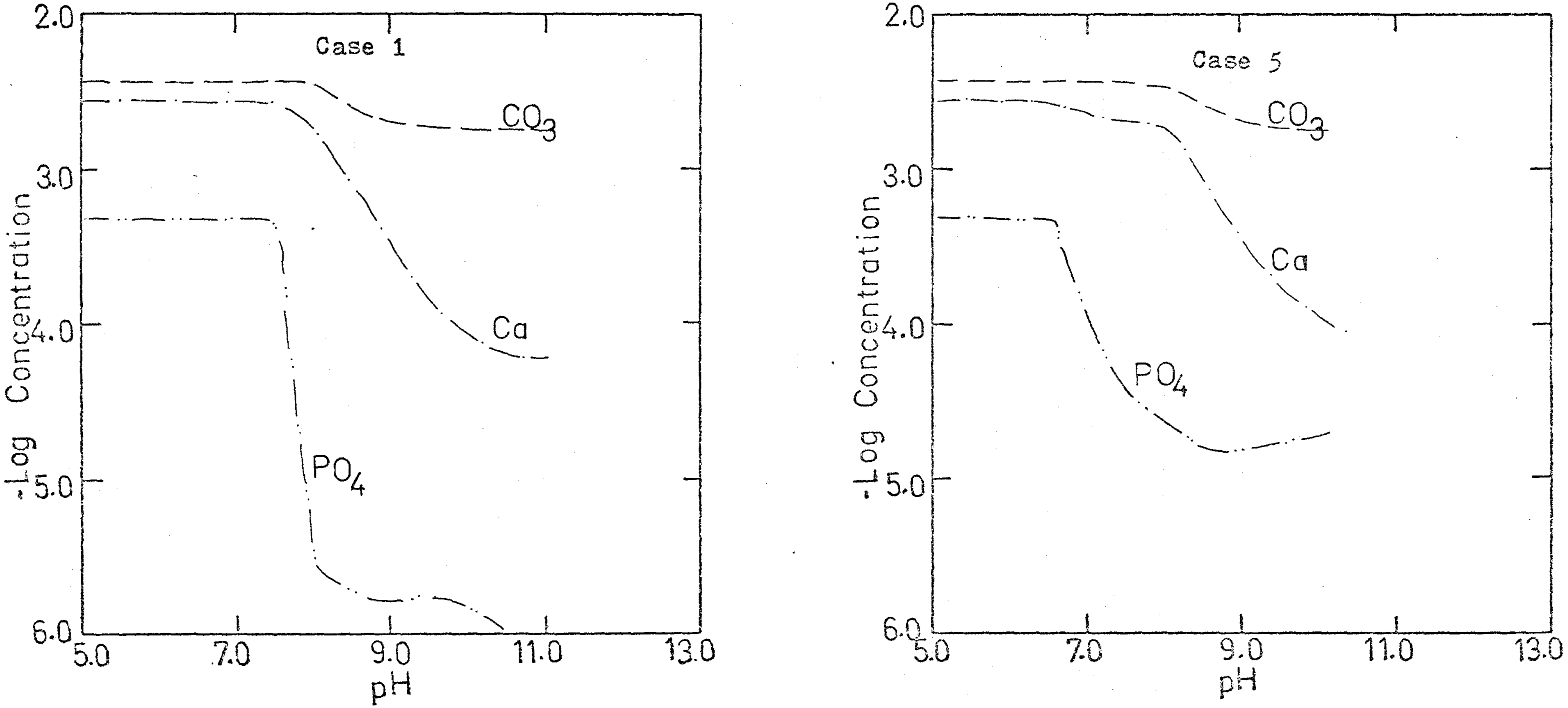


Figure 17. A comparison of the soluble residual components determined by Ferguson and McCarthy's (1969) model, case 1, and the model devised in this study, case 5. The effect of the ion complexes results in soluble orthophosphate residual. The initial concentration of the components, Ca = 0.003M, CO_3 = 0.004M and PO_4 = 0.005M, remained fixed while the pH was incremented 0.5 units.

concentration of one component affects the residual concentration of the other two. The concentration of calcium coupled with carbonate and orthophosphate determines, respectively, the amount of calcite and hydroxyapatite precipitated. As the calcium concentration increases in solution, the residual carbonate and orthophosphate will decrease due to the formation of the precipitates. As the concentration of carbonate increases, more calcite precipitates leaving less calcium to precipitate hydroxyapatite; subsequently, the residual orthophosphate increases in solution. The increase of carbonate also uses calcium through the increased concentration of the $Ca-CO_3$ aqueous species. In a similar but less significant manner, the increased concentration of orthophosphate leads to an increased precipitation of hydroxyapatite and a decreased precipitation of calcite.

I The Effect of Carbonate

Carbonate in a typical wastewater varies from 2 to 8 millimoles per litre (Ferguson 1970). In figure 18, the concentration of calcium and orthophosphate remained constant while the carbonate concentration was increased in steps from 0.1 mM to 5 mM. The initial low carbonate concentration allows for a linear decrease in residual orthophosphate as pH is increased. With an increased carbonate concentration, more calcite tends to precipitate thereby actively competing with orthophosphate for the free calcium ion. This results in an increased residual orthophosphate between pH 9.0 and 10.0

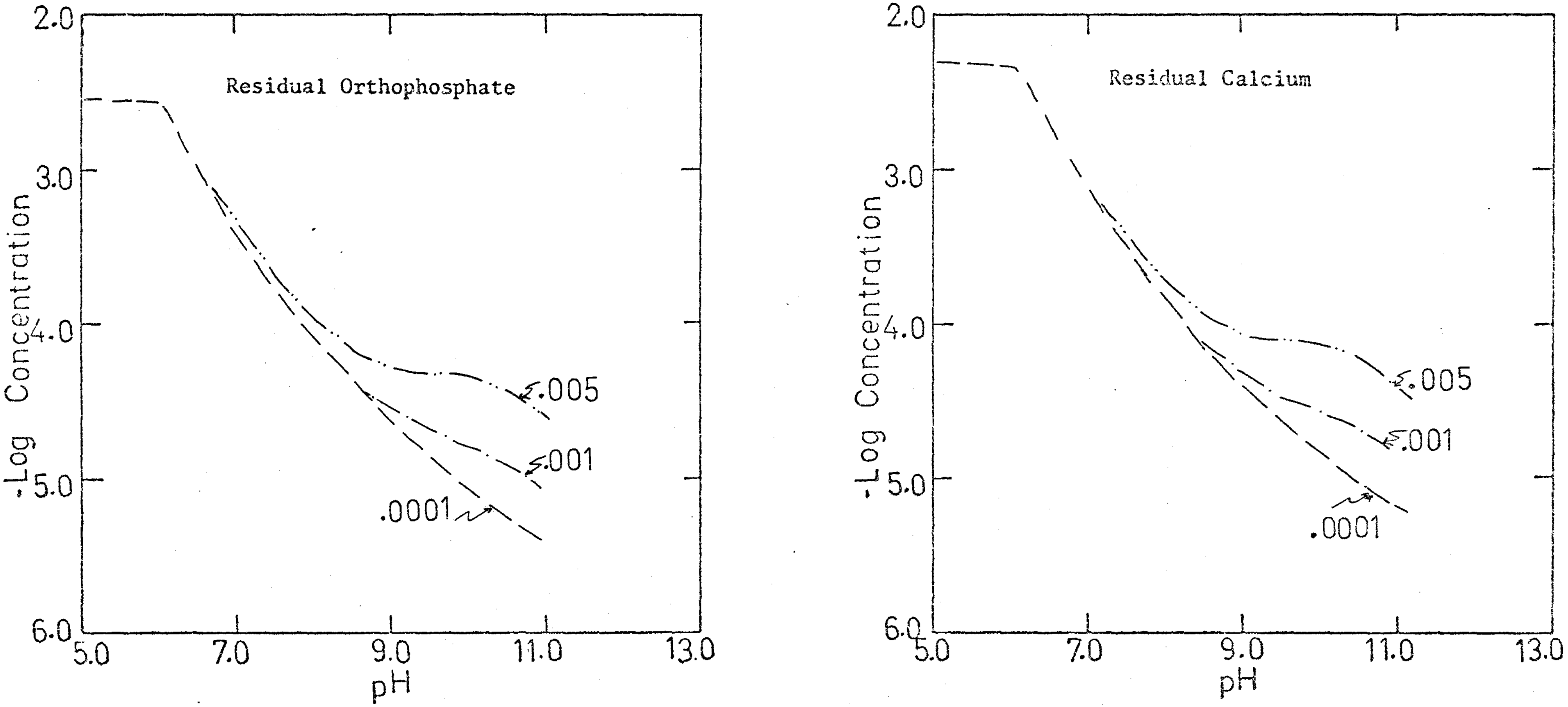


Figure 18. Soluble residual orthophosphate and calcium remaining in solution after the precipitation of calcite and/or hydroxyapatite at the specified pH. The total concentration of calcium and orthophosphate remained constant, Ca = 0.005 M, PO_4 = 0.003 M, while the carbonate concentration was changed, CO_3 = 0.005, 0.001 and 0.0001 M.

when calcite is precipitating. In figure 18, the ratio of calcium:orthophosphate is 1.67:1.0 which is the same as the stoichiometric ratio of calcium to orthophosphate in hydroxyapatite. As there was minimal calcite precipitation in these examples, the pattern of the residual calcium is similar to that of the residual orthophosphate. The residual calcium and orthophosphate increase as the carbonate concentration increases from 0.1mM to 5mM. This isn't due to the precipitation of calcite but is caused by the higher concentration of aqueous Ca-CO_3 species which decrease the available free calcium ion required to precipitate calcite and hydroxyapatite. .

Figure 19 illustrates a similar example in which the carbonate concentration is increased while the calcium and orthophosphate concentrations remain constant. In these examples the calcium:orthophosphate ratio is 2.64: 1.0. In these examples calcite is a major precipitate. When the carbonate concentration is 0.1 and 6 mM, calcite does not precipitate resulting in higher calcium residuals. In the former example, the low carbonate concentration restricts the precipitation of calcite while in the latter, limited calcite and hydroxyapatite precipitation occurs due to the high concentration of aqueous species. Figure 20 is a continuation of figure 19; in these examples the carbonate concentration has been increased to values rarely encountered in wastewater. The increased carbonate concentration influences the pH at which the precipitates form.

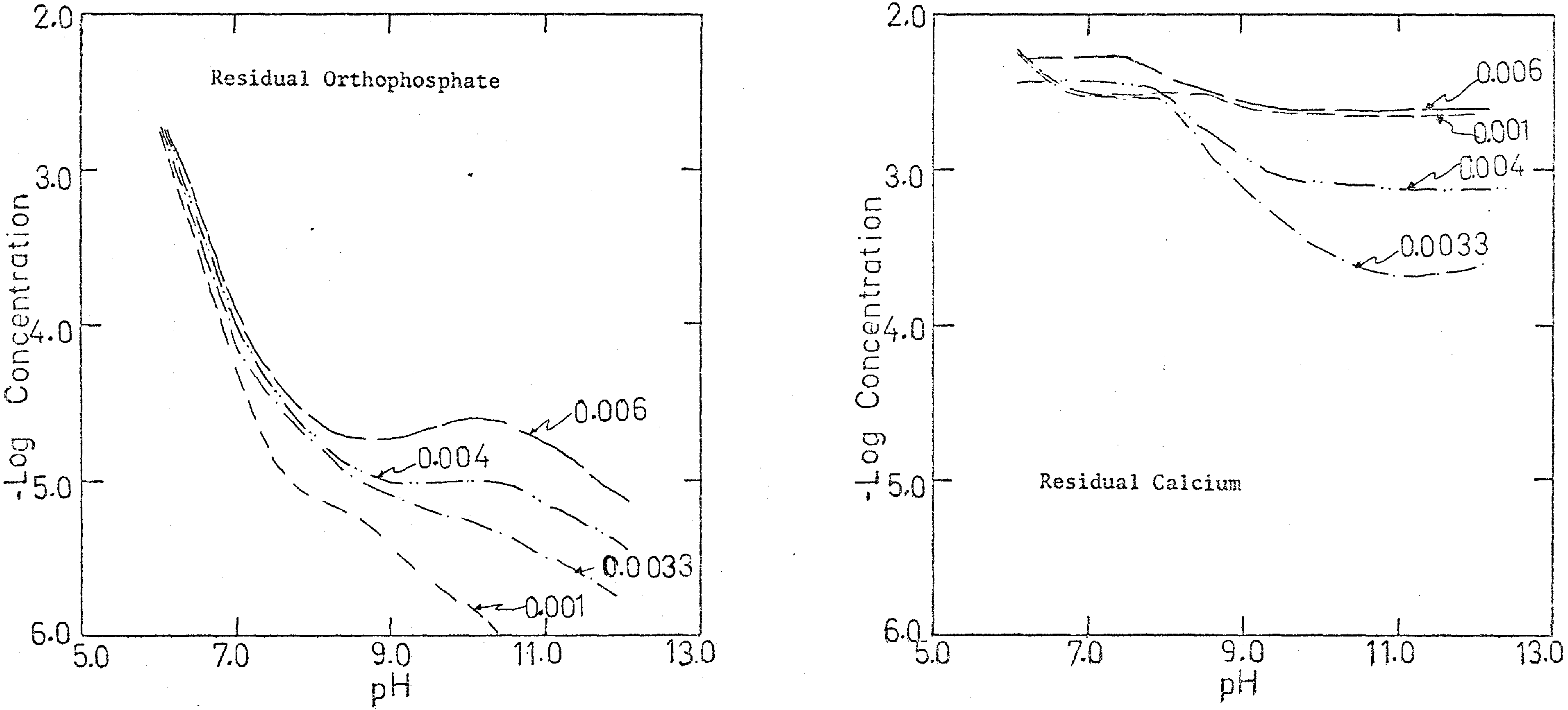


Figure 19. Residual orthophosphate and calcium remaining in solution. The total concentration of calcium and orthophosphate remained fixed, Ca = 0.00855 M, PO_4 = 0.00335 M, while the total carbonate was varied, CO_3 = 0.0033, 0.004, 0.001 and 0.006 M.

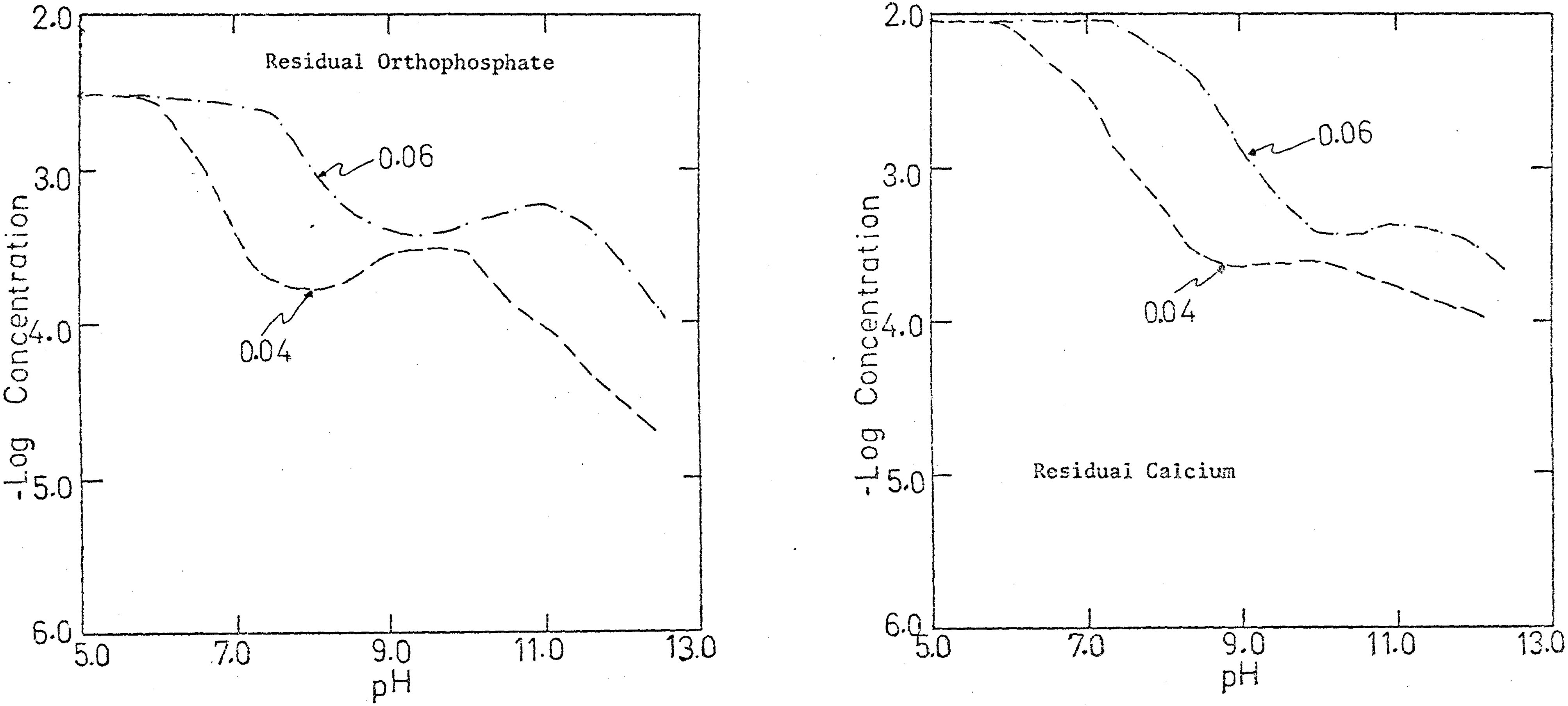


Figure 20. Residual calcium and orthophosphate remaining in solution after the removal of the precipitates. The total calcium and orthophosphate concentration remained constant, Ca = 0.00855 M, PO_4 = 0.00335 M, while the carbonate concentration was varied, CO_3 = 0.04, 0.06 M.

When the carbonate concentration is 40 mM, hydroxyapatite and calcite begin to precipitate at pH 6.5 and 7.5 respectively. With a carbonate concentration of 60 mM, the pH at which hydroxyapatite and calcite begin to precipitate is changed from 6.5 to 7.5 and from 7.5 to 8.5 respectively. The change in pH at which precipitation occurs also changes the pH at which a minimum orthophosphate residual occurs. With a carbonate concentration $\leq$ 40 mM, a minimum orthophosphate residual may exist from pH 8.0 to 9.0 but with a carbonate concentration $\geq$ 60 mM, a minimum residual orthophosphate occurs between pH 9.3 and 10.0.

Figure 21 shows Ferguson and McCarthy's (1969) laboratory results using the same concentrations of components as were used in figures 19 and 20. The model predicts the residual orthophosphate quite accurately but cannot predict the calcium residuals. The actual and the calculated orthophosphate residuals are within 0.5 orders of magnitude. Only when the carbonate concentration was $\geq$ 60 mM, a minimum orthophosphate occurs at a lower pH than that calculated by the model.

The model's inability to predict the residual calcium may be due to the inability in the earlier part of the study to calculate an apparent activity product for calcite which changed predictably with pH. The poor estimation of the solubility of calcite indirectly influences the residual orthophosphate as the model does not calculate an accurate amount of calcite. This poor estimation either increases or

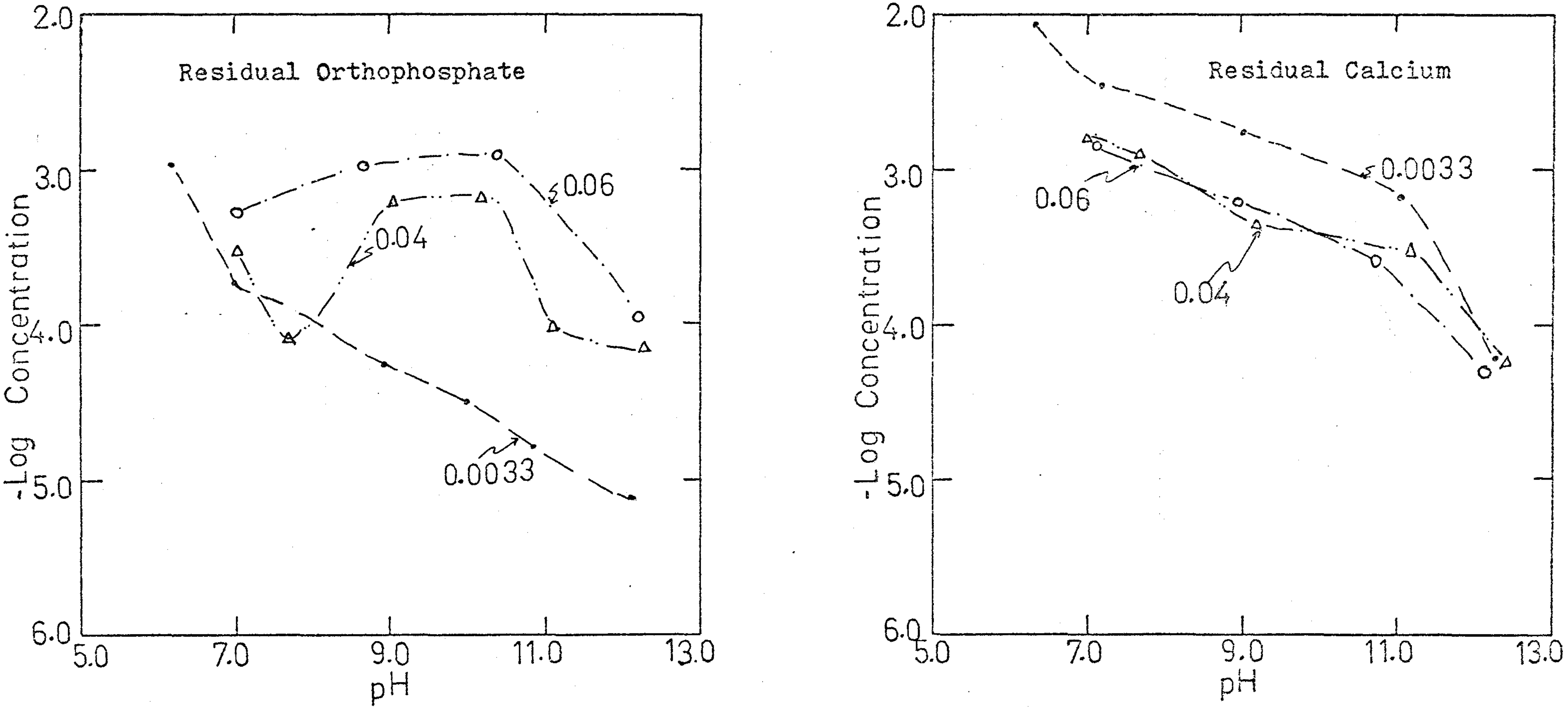


Figure 21. The residual orthophosphate and calcium remaining in solution as observed by Ferguson and McCarthy (1969) in laboratory experiments. The total calcium and orthophosphate concentrations remained constant, Ca = 0.00855 M, PO_4 = 0.00355 M, while the total carbonate concentration was varied, CO_3 = 0.06, 0.04 and 0.0033 M.

decreases the availability of calcium to precipitate orthophosphate.

II The Effect of Calcium

The increase of calcium in solution while the concentration of carbonate and orthophosphate is fixed, is comparable to the addition of lime to wastewater. The increased calcium addition causes increased precipitation of both calcite and hydroxyapatite. In figure 22, the concentration of calcium was increased from 3 to 11 mM. In the initial example, 3 mM calcium, calcium was not present in excess to meet the demands of both calcite and hydroxyapatite. The residual orthophosphate reaches a minimum concentration at approximately pH 9.0 due to the precipitation of hydroxyapatite but subsequently increases due to the active precipitation of calcite which uses the available free calcium ion. When the calcium concentration reaches 7 mM, the decrease in the orthophosphate residual is linear with increased pH. At this concentration, the calcium concentration is high enough to satisfy the needs of both calcite and hydroxyapatite.

Figure 23 compares actual laboratory residuals observed by Ferguson and McCarthy (1969) to calculated residual orthophosphate. The model does not predict the actual data with a great deal of accuracy; only in the low calcium example, 3.6 mM, does the model appoach the values determined in the laboratory. In the remaining examples, the model precipitates too much calcite. The removal of more calcium

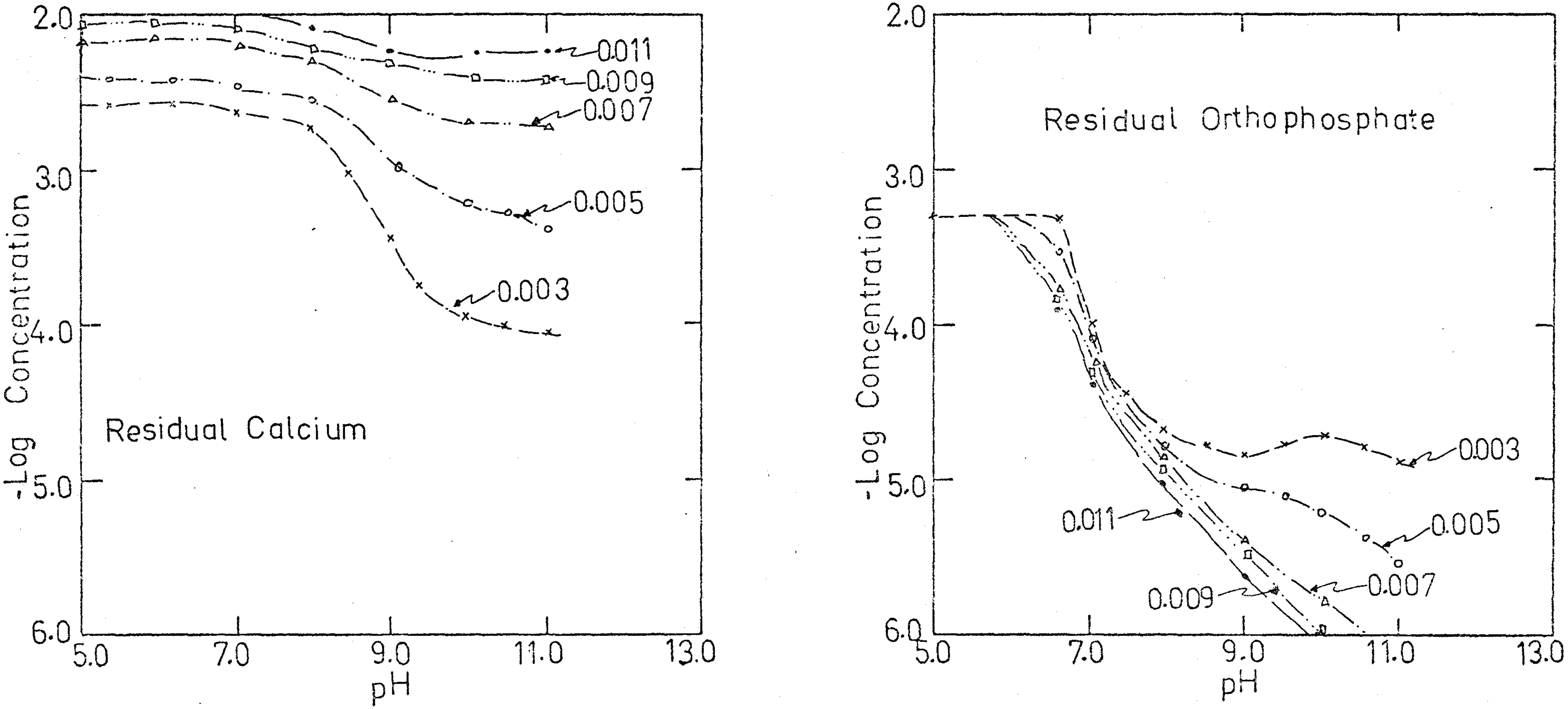


Figure 22. The effect of increasing the calcium concentration on the residual orthophosphate in solution. The concentration of total carbonate and orthophosphate remained constant, CO_3 = 0.004 M, PO_4 = 0.0005 M, while the concentration of the total calcium was increased, Ca = 0.003, 0.005, 0.007, 0.009 and 0.011 M.

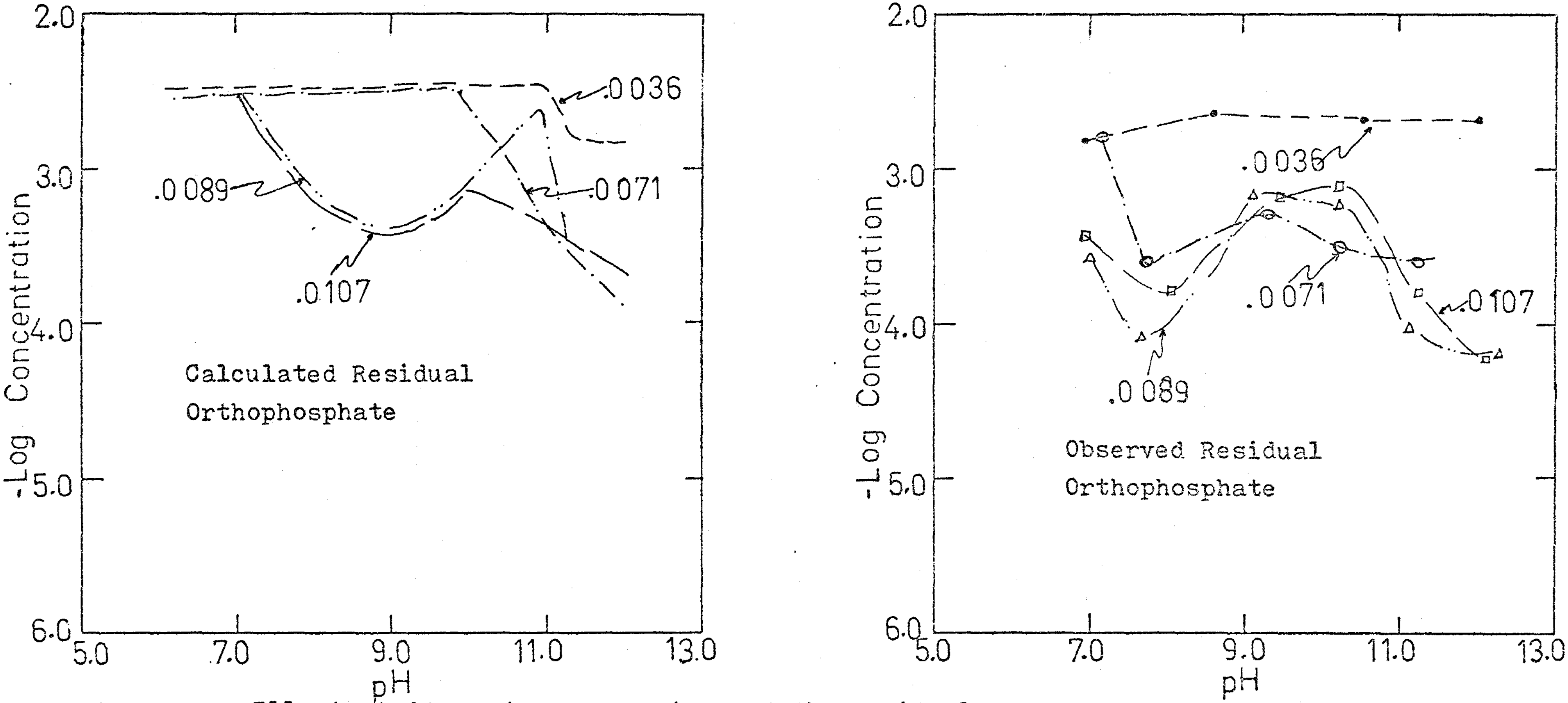


Figure 23. Illustrated here is a comparison of the residual orthophosphate observed by Ferguson and McCarthy (1969) and calculated by the model. The calcium concentration was varied, Ca = 0.0036, 0.0071, 0.0089 and 0.0107 M, while the carbonate and orthophosphate concentration remained constant, CO_3 = .028 M, PO_4 = 0.0036 M.

from solution through the excessive precipitation of calcite results in less hydroxyapatite precipitating. The probable cause of the excess calcite precipitation was the poor estimate of the activity product used in the model. For case 5, the mean value of the calculated activity product was 7.67 with a standard deviation of 0.44. A change in the activity product of calcite by ± 0.4 orders of magnitude can lead to an excessive or inadequate removal of calcium from solution. The inconsistency in the activity product of calcite indirectly affects the residual orthophosphate as the availability of the free calcium ion determines the amount of hydroxyapatite which will form.

(b) The System Including Magnesium

In adding magnesium to the system, one more metal was added to the system, four ion pair or ion pair complexes, $MgOH^+$, $MgCO_3(aq)$, $MgHCO_3^+$, $MgHPO_4(aq)$, and one precipitate $Mg(OH)_2$. The study also considered tricalcium phosphate as a possible phosphate precipitate using Morel and Morgan's (1972) model. The inclusion of magnesium in the lattices of tricalcium phosphate and calcite was not tested. It was felt that the inclusion of magnesium in the lattices was not controlled by equilibrium processes described in this study. From Ferguson and McCarthy's (1969) study, it was apparent that magnesium was included in the carbonate and phosphate precipitates but the model could not determine the concentration of magnesium in the lattices of each precipitate.

Therefore calcite and tricalcium phosphate were used instead of Mg-calcite and beta tricalcium phosphate.

The effect of different calcium and carbonate concentrations were the same for the cases including magnesium as they were for the cases without magnesium. The effect of changing these two components will be considered in the larger context of noting the effect of magnesium on the residual calcium and orthophosphate in solution.

In the initial examples, figures 24, 25 and 26, the concentration of magnesium was varied while the concentration of the other components remained constant. The pH was incremented 0.5 units and the residual calcium and orthophosphate in solution were calculated. The magnesium did not alter the calculated residual calcium and orthophosphate in solution, even though the concentration of magnesium was varied widely. The laboratory experiments by Ferguson and McCarthy (1969) showed a considerable change in the residual calcium and orthophosphate when the magnesium concentration was increased from 0.1 to 1 mM. The orthophosphate residual no longer has a minimum between pH 7.0 to 9.0, instead the residual decreases linearly with pH. The model continued to predict the minimum residual orthophosphate between pH 8.0 and 9.0 followed by an increase due to the precipitation of calcite. The use of Morel and Morgan's (1972) model, figure 26, results in a more pronounced orthophosphate residual than the case using hydroxyapatite. The high residuals may be due to the omission

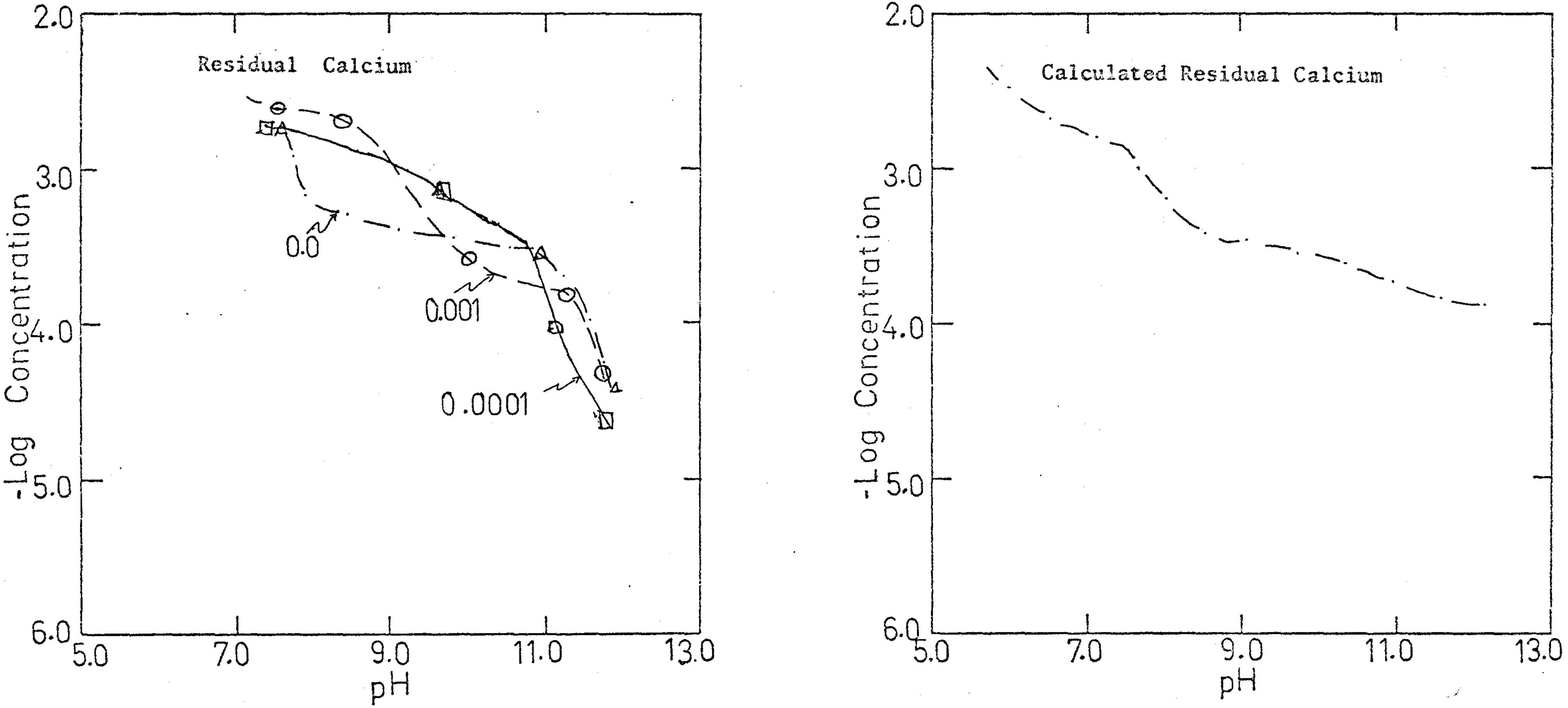


Figure 24. The effect of varying the magnesium concentration on the calcium residuals. The magnesium concentration was varied, Mg = 0.0, 0.001 and 0.0001 M, while the concentration of calcium, carbonate and orthophosphate remained constant, Ca = 0.005 M, CO_3 = 0.03 M, PO_4 = 0.002 M. Ferguson and McCarthy's (1969) laboratory data appears on the left while the model's calculations are on the right. There is only one set of data plotted for the model's calculations as the residuals do not vary with different magnesium concentrations. The possible precipitates are calcite, hydroxyapatite and brucite.

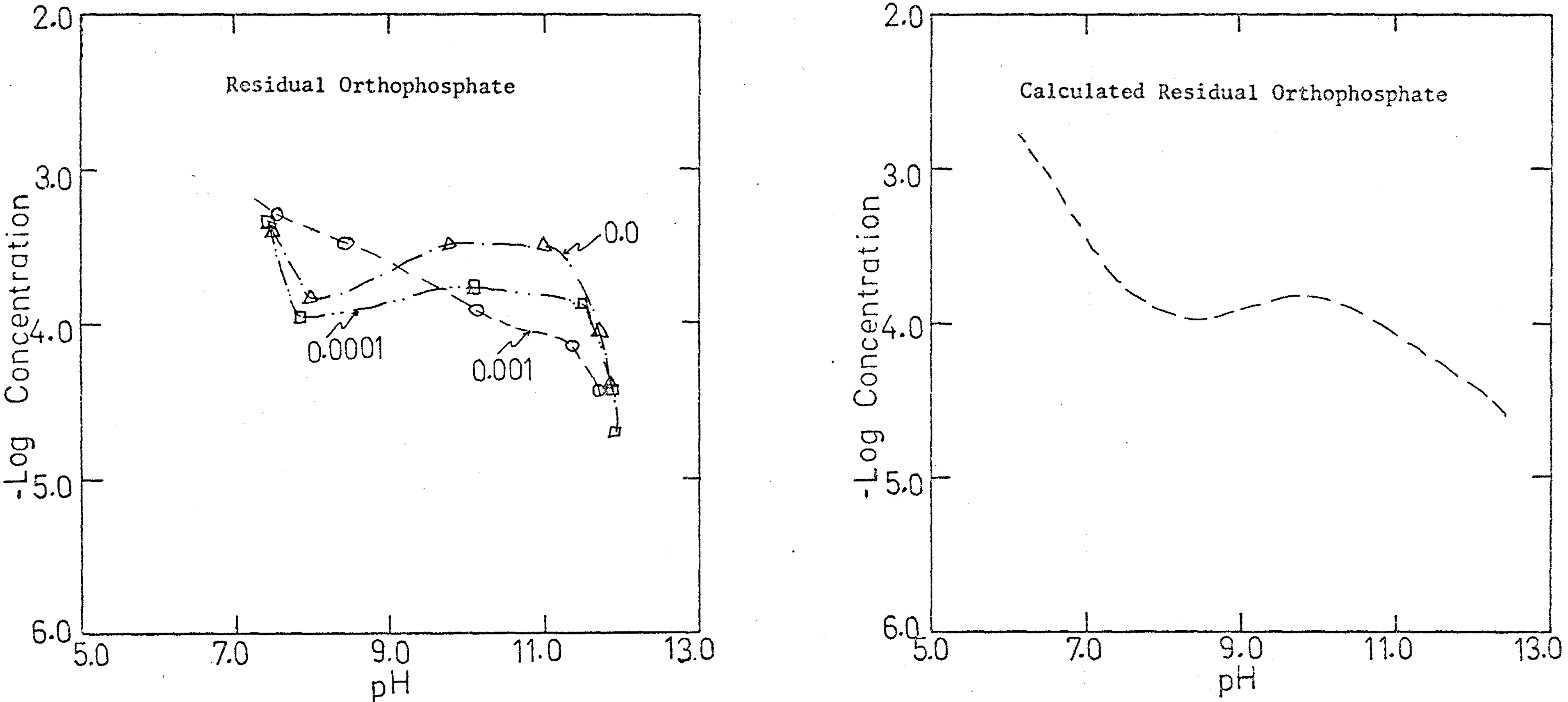


Figure 25. The effect of varying the magnesium concentration on the orthophosphate residuals. The magnesium concentration was varied, Mg = 0.0, 0.0001 and 0.001 M, while the concentration of calcium, carbonate and orthophosphate remained constant, Ca = 0.005 M, CO_3 = 0.03 M, PO_4 = 0.002 M. Ferguson and McCarthy's (1969) laboratory observations appear on the left while the model's calculations appear on the right. There is only one set of data plotted on the right as the residuals do not vary for the different magnesium concentrations. The possible precipitates were calcite, brucite and hydroxyapatite.

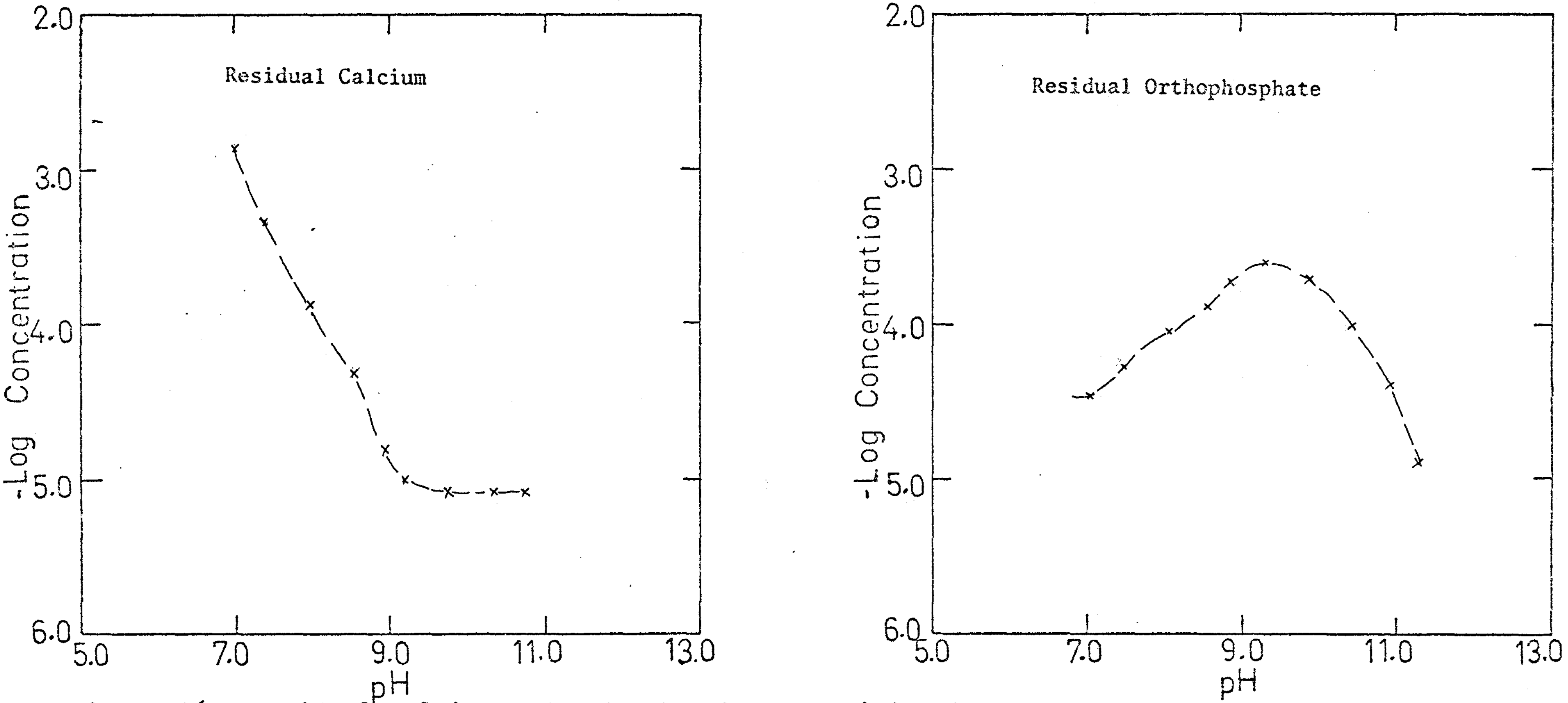


Figure 26. Residual calcium and orthophosphate remaining in solution. The conditions are the same as in the two previous figures except for the Ca-PO_4 precipitate which was changed from hydroxyapatite to tricalcium phosphate. Morel and Morgan's (1972) model was used to determine the residual calcium and orthophosphate.

of the ion complexes when calculating the equilibrium. Ferguson and McCarthy (1969) predicted the precipitation of tricalcium phosphate to result in a "gradually decreasing phosphate residual as the pH increases from 7 to 9, then further increases in pH decrease the phosphate residual only slightly". This behaviour was not noticed when using tricalcium phosphate as a precipitate. The residuals calculated were similar to those resulting from the use of hydroxyapatite as the phosphate precipitate. Minimum phosphate residuals were found at a neutral and high pH when using tricalcium phosphate as the phosphate precipitate. At a pH between the two minimums, the residual concentration of orthophosphate was higher.

Another aspect the model failed to reproduce was the rapid decrease in the calcium and orthophosphate residuals when the pH was greater than 10. Jenkins et al (1971) attributed this rapid decrease in the residuals to the precipitation of magnesium carbonate which may act as a flocculant for the suspended calcium phosphate precipitates.

Figures 27 and 28 illustrate two examples of actual laboratory residuals observed by Ferguson and McCarthy (1969) versus residuals calculated by the model. Again in figure 27 as in the previous three figures, the model predicts a residual orthophosphate minimum at pH 8 followed by an increase while the actual residual shows a linear decrease with pH. In figure 28, the magnesium residual remains constant until

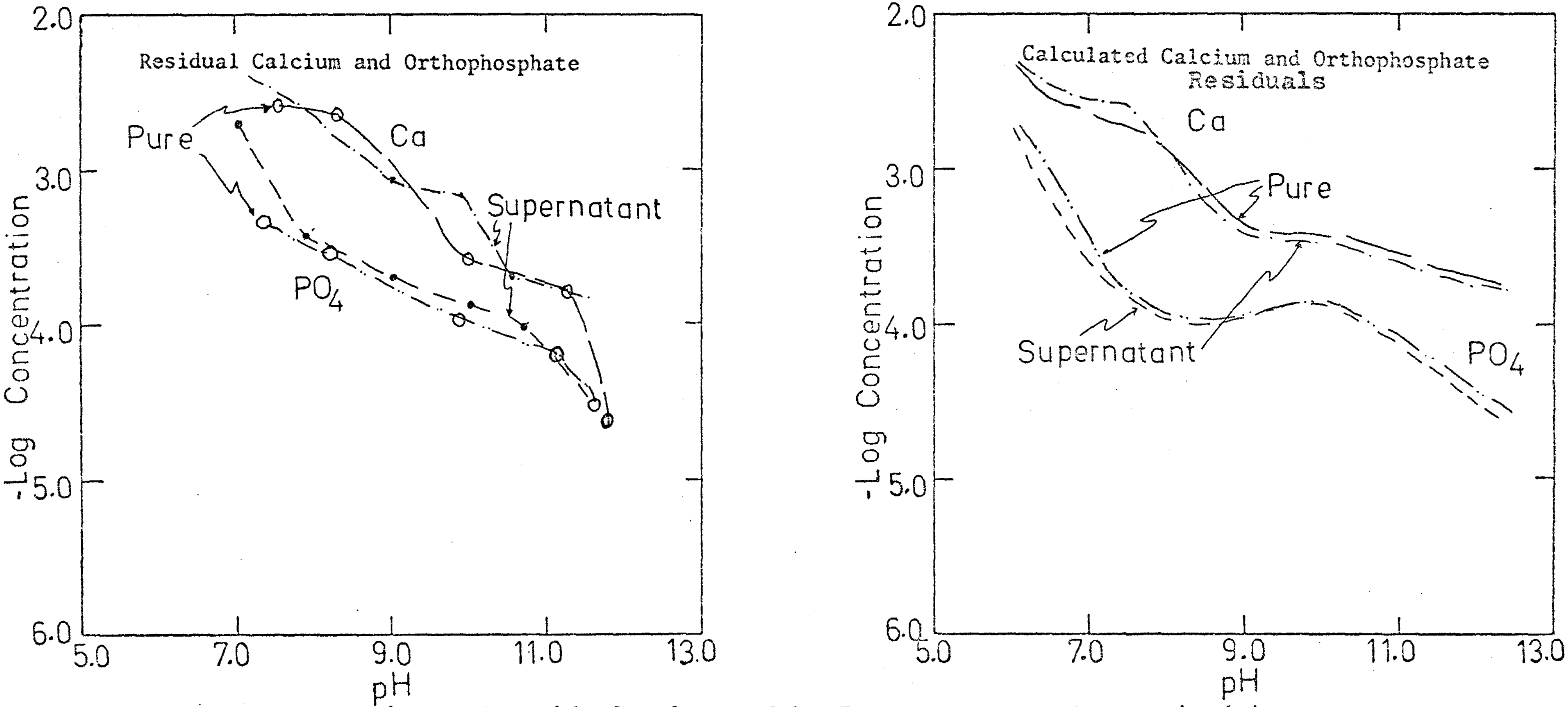


Figure 27. A comparison of residuals observed by Ferguson and McCarthy (1969) and calculated by the model. The supernatent from an anaeobic digestion system had components of concentration: Ca = 0.0059 M, Mg = 0.0018 M, CO_3 = 0.028 M, PO_4 = 0.0019 M while the pure liquid prepared in the laboratory has concentrations of: Ca = 0.005 M, Mg = 0.001, CO_3 = 0.03 M, PO_4 = 0.002 M. The observed residuals are on the left while the calculated ones are on the right.

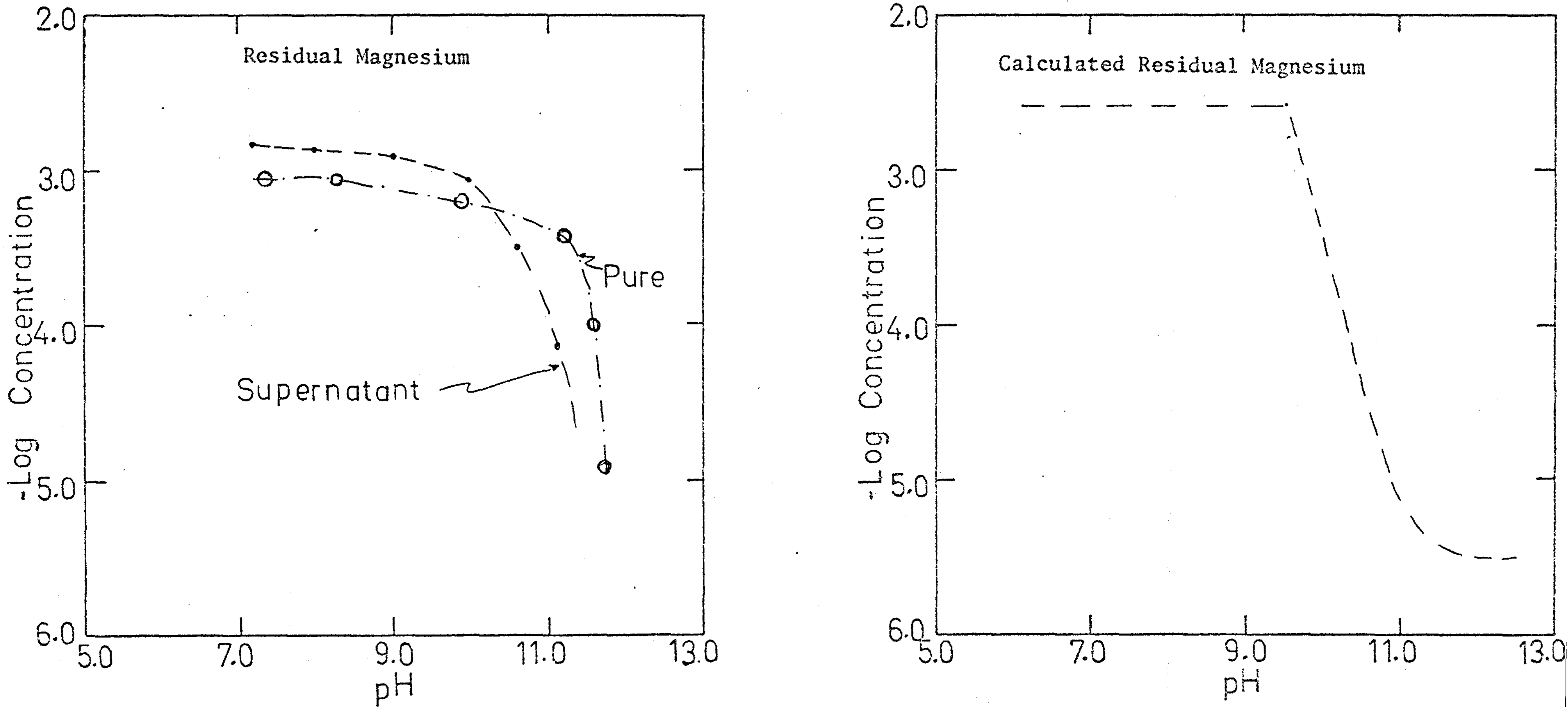


Figure 28. A comparison of magnesium residuals as observed by Ferguson and McCarthy (1969) and calculated by the model. The conditions are the same as in the previous diagram. The model calculated similar magnesium residuals for both examples.

brucite begins to precipitate at pH 9.5. In the actual laboratory experiments, the magnesium residual began to decrease when the first precipitate formed at pH 6.5. Both the model and the laboratory experiments have a rapid decrease in the magnesium residual between pH 9.5 and 10.5 when brucite forms.

Neither this model nor the model developed by Morel and Morgan (1972) could predict the residual orthophosphate in wastewater when magnesium was a major component. They both fail as they do not adequately explain the effect of magnesium on the solubility of calcite and the Ca-PO_4 precipitate(s). The modelling illustrated that the residual orthophosphate resulting from the use of either tricalcium phosphate or hydroxyapatite in a model was very similar. The advantage of using one precipitate over the other to explain the residual orthophosphate pattern was not found.

VI SUMMARY

A summary is presented in this chapter covering briefly the model and its use as a tool in analysing the complex equilibrium of orthophosphate precipitation in tertiary wastewater treatment. The model facilitates the determination of the effect of ion complexes on the concentration of aqueous species and on the amount of precipitates formed. It also allows the calculation of the apparent activity products using laboratory data and finally the verification of the model as a means of predicting the soluble phosphate residual in tertiary treated wastewater using lime.

The Model

The model is based on thermodynamic theory. It is simplistic in that it only includes five components, calcium, magnesium, carbonate, orthophosphate and water. These components are present as solids and aqueous species with the amounts and concentrations determined by equilibrium principles. Three basic equations were used to define the system, they were the mass action, mass balance and electroneutrality or proton equations. One mass action equation existed for each aqueous species and precipitate, a mass balance equation was formed for each component and an electroneutrality or proton equation balanced the charges in solution. As wastewater is usually a concentrated solution and the aqueous species behave in a non-ideal manner, it was necessary to calculate the ionic strength in solution and the activity coefficients using the Debye-Huckel-Davies theory. In the calculation of equilibrium, the model used activities instead of concentrations to compensate for the non-ideal behaviour of the aqueous species.

The model is general as pH may or may not be defined and it allows a limited variation of the aqueous species and precipitates. These variations are the inclusion in or omission from the model of the ion complexes $Ca_2.HPO_4.CO_3(aq)$ and $Ca_2.PO_4.CO_3^-$, the component magnesium along with the precipitate $Mg(OH)_2$ and magnesium aqueous species, and either hydroxyapatite or tricalcium phosphate precipitating in the wastewater. Figure 3 illustrates all the variations possible in the model.

Apparent Activity Products

After completion of the model building, testing revealed that simulated wastewater treatment by the model resulted in soluble phosphate residuals two to three orders of magnitude less than in actual laboratory experiments. To make the calcium, magnesium, orthophosphate and carbonate residuals calculated by the model match those observed in laboratory experiments, apparent activity products were calculated for calcite, Mg-calcite (3, 11 and 20 per cent magnesium in the calcite lattice), hydroxyapatite, beta tricalcium phosphate (6 per cent magnesium to stabilize its formation), tricalcium phosphate and brucite.

The apparent activity products were calculated using the data from two sets of laboratory experiments, one set excluded magnesium as a component while the other set included magnesium. For the data excluding magnesium, the apparent activity products of hydroxyapatite with the least variation were obtained when the ion complexes were included among the aqueous species. The equation of the least square line for the apparent activity products is:

pA (hydroxyapatite) = 100.24 + 0.25(pH)

For the data including magnesium, the equation of the least square lines for the apparent activity products of hydroxyapatite, beta tricalcium phosphate and tricalcium phosphate are respectively:

pA (hydroxyapatite) = 92.96 + 1.00(pH)

pA (beta tricalcium phosphate) = 20.73 + 0.64(pH)

pA (tricalcium phosphate) = 22.21 + 0.79(pH)

The apparent activity product for $Mg(OH)_2$ was also calculated for the data including magnesium, the least square line for the apparent activity products is:

pA (brucite) = 20.13 - 0.89(pH)

While the calculation of the apparent activity products for the calcium-phosphate precipitates and brucite resulted in linear relationships with pH, the activity products of calcite and Mg-calcite did not follow this trend. For both sets of laboratory data, the apparent activity products for the various types of calcite were extremely variable and showed no linear relationship with pH. A comparison of the mean apparent activity products for Mg-calcite and calcite showed the value for Mg-calcite approximately 0.75 orders of magnitude higher than calcite. This reflected literature values but increasing the concentration of magnesium in the calcite lattice from 3 to 20 per cent resulted in minimal changes in the apparent activity products. In actual laboratory experiments, the increase of magnesium in the calcite lattice resulted in an increase in solubility of 1.7 orders of magnitude. As the model could not predict this increase in solubility nor calculate the amount of magnesium present in the calcite lattice, only $CaCO_3$ was used in the verification of the model.

The mean values for calcite and the least square lines for calcium-phosphates and brucite were used in the model rather than the literature solubility products. Under identical initial conditions, this allows the model to approximate the soluble residuals of calcium and orthophosphate experienced in laboratory experiments.

Verification of the Model

The model was verified by simulating wastewater treatment for low carbonate to high carbonate water. The carbonate concentration was incremented while the concentration of calcium, orthophosphate and magnesium remained constant. In a similar manner the addition of lime was simulated by increasing the calcium concentration while the concentration of the other components remained constant. Upon defining the initial conditions for both of the above cases, the pH was incremented from 5.0 to 12.0 to determine the soluble residual calcium and orthophosphate and the amount of the precipitates calcite, brucite and/or calcium-phosphate. These two cases illustrated the increase in soluble residual orthophosphate with an increase in carbonate concentration and the decrease of both soluble residual carbonate and orthophosphate with increased calcium concentrations. The increase in the carbonate concentration resulted in additional calcite and less calcium-phosphate precipitating while the increase in the calcium concentration resulted in increased precipitation of both calcite and calcium-phosphate.

Using the apparent activity products in the model and having an orthophosphate concentration of 10 mg P/l, the hydroxyapatite or tricalcium phosphate would usually begin to precipitate between pH 7 to 8.5 followed by the precipitation of calcite between pH 8.5 to 10.5. Beyond pH 10.5, calcite commonly ceased to precipitate while brucite began at pH 10.0. When only the calcium-phosphate solid formed, the residual soluble orthophosphate decreased rapidly in solution but the precipitation of calcite in conjunction with the calcium-phosphate solid resulted in increased soluble residual orthophosphate due to the competition for the available free calcium ions. This resulted in minimum orthophosphate residuals between pH 7.0 to 8.5 and beyond pH 10.5. These minimum orthophosphate residuals existed whether tricalcium phosphate or hydroxyapatite was used as the calcium-phosphate precipitate. The model cannot determine whether hydroxyapatite or tricalcium phosphate precipitates nor can it show the effect of magnesium on the soluble residual orthophosphate; it is restricted to the precipitation of pure solids. The model functions best when simulating wastewater treatment with a low magnesium concentration.

Modelling does not replace analytical laboratory studies as a model can only be as good as the data it uses. The use of the model illustrates where the theory is lacking and where further laboratory studies are required. From this study, the two most lacking areas are the inconsistencies found in the solubility of calcite and the lack of a mathematical interpretation for the inclusion of foreign ions in the lattices of the precipitates.

VII CONCLUSIONS

This study researched several aspects of the chemical treatment of tertiary wastewater using lime. A model was designed and later used to better understand and explain the chemical equilibrium processes occurring in wastewater. The five major conclusions reached are:

1. The ion complexes, $Ca_2HPO_4CO_3$ and $Ca_2PO_4CO_3^-$, are important aqueous species when modelling aqueous systems which include calcium, carbonate and orthophosphate as components. This was demonstrated in calculating the apparent activity products for hydroxyapatite and tricalcium phosphate. Without the ion complexes, the activity products varied considerably with pH while their inclusion in the model resulted in apparent activity products which varied predictably with pH.
2. The apparent activity products of the four major precipitates in lime treated wastewater were calculated by the model from laboratory data. The apparent activity products of hydroxyapatite, tricalcium phosphate and magnesium hydroxide were dependent on pH and were represented by least-square equations for use in the model. The apparent activity products of calcite varied irregularly with pH and ionic strength. The model could not determine predictable activity products for data which included or excluded magnesium as a component. Mean values of the apparent activity products were used in the model.

3. The precipitates tricalcium phosphate and hydroxyapatite were both tested in the model under identical conditions. As the pH increased from 5 to 12, both precipitates usually formed at the same pH and had similar soluble residual orthophosphate concentrations. The model could not determine which precipitate forms in wastewater but it theoretically disproves the observation that the soluble residual orthophosphate concentration due to the precipitation of tricalcium phosphate is different from that of hydroxyapatite.
4. Standard equilibrium principles used in the model are not adequate to explain the effect of magnesium inclusion in the lattices of tricalcium phosphate and calcite. Apparent activity products of the precipitates were calculated with varying concentrations of magnesium present in the lattices. Although the inclusion of magnesium in the precipitates resulted in higher solubilities, the activity products were largely independent of the concentration of magnesium present in the lattice.
5. The model can simulate the lime treatment of wastewater with low magnesium concentrations and can predict within one order of magnitude the soluble residual orthophosphate obtained in laboratoy experiments. The model showed the feasibility of using lime for the chemical treatment of tertiary wastewater. In simulating low magnesium wastewater, the model predicts two minimums for soluble residual

orthophosphates, one between pH 8.0-9.0 and the other for pH 10.5. Inbetween the two minimums, the orthophosphates increased in solution due to the precipitation of calcite which actively competes with hydroxyapatite for the free calcium ion.

APPENDIX 1

EXAMPLE OF CALCULATIONS CARRIED OUT BY THE MODEL

Consider the case where hydroxyapatite ($Ca_{10}.(PO_4)_6.(OH)_2$) is assumed to precipitate and pH isn't known.

The mass balance equations are:

$$\begin{aligned}
\text{Total Calcium} = {} & Ca^{+2} + CaOH^{+} + CaHCO_3^{+} + CaCO_3(aq) + CaPO_4^{-} \\
& + CaHPO_4(aq) + CaH_2PO_4^{+} + 2Ca_2.HPO_4.CO_3(aq) \\
& + 2Ca_2.PO_4.CO_3^{-} + 10Ca_{10}.(PO_4)_6.(OH)_2 \qquad (1)
\end{aligned}$$

$$\begin{aligned}
\text{Total Magnesium} = {} & Mg^{+2} + MgOH^{+} + MgCO_3(aq) + MgHCO_3^{+} \\
& + MgHPO_4(aq) \qquad (2)
\end{aligned}$$

$$\begin{aligned}
\text{Total Carbonate} = {} & CO_3^{-2} + HCO_3^{-} + H_2CO_3 + CaCO_3(aq) + CaHCO_3^{+} \\
& + MgCO_3(aq) + MgHCO_3^{+} + Ca_2.HPO_4.CO_3(aq) \\
& + Ca_2.PO_4.CO_3^{-} \qquad (3)
\end{aligned}$$

$$\begin{aligned}
\text{Total Phosphate} = {} & PO_4^{-3} + HPO_4^{-2} + H_2PO_4^{-} + H_3PO_4 + CaPO_4^{-} \\
& + CaHPO_4(aq) + CaH_2PO_4^{+} + MgHPO_4(aq) \\
& + Ca_2.HPO_4.CO_3(aq) + Ca_2.PO_4.CO_3^{-} \\
& + 6Ca_{10}.(PO_4)_6.(OH)_2 \qquad (4)
\end{aligned}$$

and the proton equation is:

$$\begin{aligned}
\text{Total } H^{+} = {} & H^{+} - OH^{-} + HCO_3^{-} + 2H_2CO_3 + CaHCO_3^{+} + CaHPO_4(aq) \\
& + 2CaH_2PO_4^{+} + HPO_4^{-2} + 2H_2PO_4^{-} + 3H_3PO_4 \\
& - CaOH^{+} + Ca_2.HPO_4.CO_3(aq) + MgHCO_3^{+} \\
& + MgHPO_4(aq) - MgOH^{+} - 2Ca_{10}.(PO_4)_6.(OH)_2 \qquad (5)
\end{aligned}$$

The initial inputs to the model are the amounts of chemicals, H_2CO_3, $CaCO_3$, $MgCO_3$, $Ca(OH)_2$, $Mg(OH)_2$, H_3PO_4, and $Ca_{10}(PO_4)_6.(OH)_2$ which are assumed to **completely** dissolve in water. The quantities of chemicals are set by the user to simulate any condition. The left-hand sides of the five equations are calculated from the input as:

$$\text{Total Calcium} = CaCO_3 + Ca(OH)_2 + 10Ca_{10}.(PO_4)_6.(OH)_2$$

$$\text{Total Magnesium} = MgCO_3 + Mg(OH)_2$$

$$\text{Total Carbonate} = CO_2 + CaCO_3 + MgCO_3$$

$$\text{Total Phosphate} = H_3PO_4 + 6Ca_{10}.(PO_4)_6.(OH)_2$$

$$\text{Total } H^+ = 3H_3PO_4 + 2CO_2 - 2Ca(OH)_2 - 2Mg(OH)_2 - 2Ca_{10}.(PO_4)_6.(OH)_2$$

Before equilibrium can be calculated, the five equations must be reduced to five variables, Ca^{+2}, Mg^{+2}, CO_3^{-2}, PO_4^{-3}, H^+, and the precipitate, hydroxyapatite, must be eliminated from the equations it is found in. A convention which was adopted was to replace each OH^- by K_w/H^+; this eliminates one unknown from the equations. The other aqueous species which have one or more of the five variables in common are grouped and reduced as follows:

EXPRESSION

1. $Ca^{+2} + CaOH^+ = (Ca)\left[1.0 + K_{(CaOH)} \cdot K_w/H\right]$
2. $CaCO_3(aq) + CaHCO_3^+ = (Ca)(CO_3)\left[K_{(CaCO_3(aq))} + K_{(CaHCO_3)} \cdot H/K_{(HCO_3)}\right]$
3. $CaPO_4^- + CaHPO_4(aq) + CaH_2PO_4^+ = (Ca)(PO_4)\left[K_{(CaPO_4)} + K_{(CaHPO_4)} \cdot H/K_{(HPO_4)} + K_{(CaH_2PO_4)} \cdot H^2/(K_{(HPO_4)} \cdot K_{(H_2PO_4)})\right]$
4. $Ca_2.HPO_4.CO_3(aq) + Ca_2.PO_4.CO_3^- = (Ca)(PO_4)(CO_3)\left[H/(K_{(HCO_3)} \cdot K_{(HPO_4)} \cdot K_{(Ca_2.HPO_4.CO_3)}) + K_{(Ca_2.PO_4.CO_3)}/(K_{(HCO_3)} \cdot K_{(HPO_4)} \cdot K_{(Ca_2.HPO_4.CO_3)})\right]$
5. $Mg^{+2} + MgOH^+ = (Mg)\left[1.0 + K_{(MgOH)} \cdot K_w/H\right]$

6. $MgCO_3(aq) + MgHCO_3^+ = (Mg)(CO_3)\left[K_{(MgCO_3)} + K_{(MgHCO_3)} \cdot H/K_{(HCO_3)}\right]$

7. $MgHPO_4(aq) = (Mg)(PO_4)\left[K_{(MgHPO_4)} \cdot H/K_{(HPO_4)}\right]$

8. $CO_3^{-2} + HCO_3^- + H_2CO_3 = (CO_3)\left[1.0 + H/K_{(HCO_3)} + H^2/(K_{(HCO_3)} \cdot K_{(H_2CO_3)})\right]$

9. $PO_4^{-3} + HPO_4^{-2} + H_2PO_4^- + H_3PO_4 = (PO_4)\left[1.0 + H/K_{(HPO_4)} + H^2/(K_{(HPO_4)} \cdot K_{(H_2PO_4)}) + H^3/(K_{(HPO_4)} \cdot K_{(H_2PO_4)} \cdot K_{(H_3PO_4)})\right]$

Using this convention, the right hand sides of the mass balance equations are replaced by the above expressions:

Total Calcium = expressions 1, 2, 3, and 4 $+ 10Ca_{10} \cdot (PO_4)_6 \cdot (OH)_2$ (6)

Total Magnesium = expressions 5, 6, and 7 (7)

Total Carbonate = expressions 2, 4, 6, and 8 (8)

Total Phosphate = expressions 3, 4, 7, and 9 $+ 6Ca_{10}(PO_4)_6(OH)_2$ (9)

The precipitate is eliminated by multiplying and subtracting the equations in which it is found.

Total Calcium $- \frac{5}{3}$ (Total Phosphorus) = R.H.S.* equation 6 $-\frac{5}{3}$ (R.H.S. equation 9)

and

Total $H^+ + \frac{1}{3}$ (Total Phosphorus) = R.H.S. equation 5 $+ \frac{1}{3}$ (R.H.S. equation 9)

As hydroxyapatite is in equilibrium with the solution, the unknown component PO_4^{-3} can be eliminated from the equations by substituting:

$$PO_4^{-3} = \left(K_{(Ca_{10}(PO_4)_6(OH)_2)} \cdot H^2\right) \Big/ \left(Ca^{10} \cdot K_w^2\right)^{1/6} \qquad (10)$$

---

*R.H.S. = Right Hand Side

This results in four equations and four unknowns which can be solved using the Newton-Raphson method for two or more unknowns. Upon solution, PO_4 is calculated using equation 10 and the relative concentrations of the aqueous species are determined using the mass law equations. The amount of hydroxyapatite is calculated using equation 4:

$$Ca_{10}(PO_4)_6(OH)_2 = (\text{Total Phosphorus} - \text{aqueous species containing } PO_4)/6 \qquad (11)$$

In a similar manner, a $CaCO_3$ precipitate can be eliminated from the mass balance and proton equations by subtracting equation 8 from equation 6 while a $Mg(OH)_2$ precipitate is eliminated adding two times equation 7 to equation 5. For each precipitate that forms, one component and one equation are eliminated from use in the calculation of equilibrium in solution. If $CaCO_3$ precipitates, equation 8 is eliminated and CO_3 is replaced in all equations by:

$$CO_3 = \frac{K_{(CaCO_3)}}{Ca} \qquad (12)$$

If $Mg(OH)_2$ precipitates, equation 7 is eliminated and Mg is replaced by:

$$Mg = \frac{K_{(Mg(OH)_2)} \cdot H^2}{K_w^2} \qquad (13)$$

In using the model any of the listed chemicals can be incremented to simulate a changing composition of the components in solution; in particular $Ca(OH)_2$ may be incremented to simulate the case where lime is added to solution to remove orthophosphates.

If pH is defined by the user, there are several changes in the model. First, the proton equation is replaced by the electroneutrality equation; it is used to determine the charge imbalance after equilibrium has been calculated. Chemicals are no longer added to solution, instead, the total concentrations of calcium, magnesium, carbonate and orthophosphate are inputs by the user. Once defined, the total concentrations of components remained fixed while only pH is incremented. In expressions 1 to 9, the terms within the square parentheses become constants as pH is defined. There is a difficulty in eliminating $Mg(OH)_2$ from the mass balance equations; rather than assume a pure precipitate, the precipitate is $Mg_{0.999}Ca_{0.001}(OH)_2$. It is eliminated from the mass balance equations by:

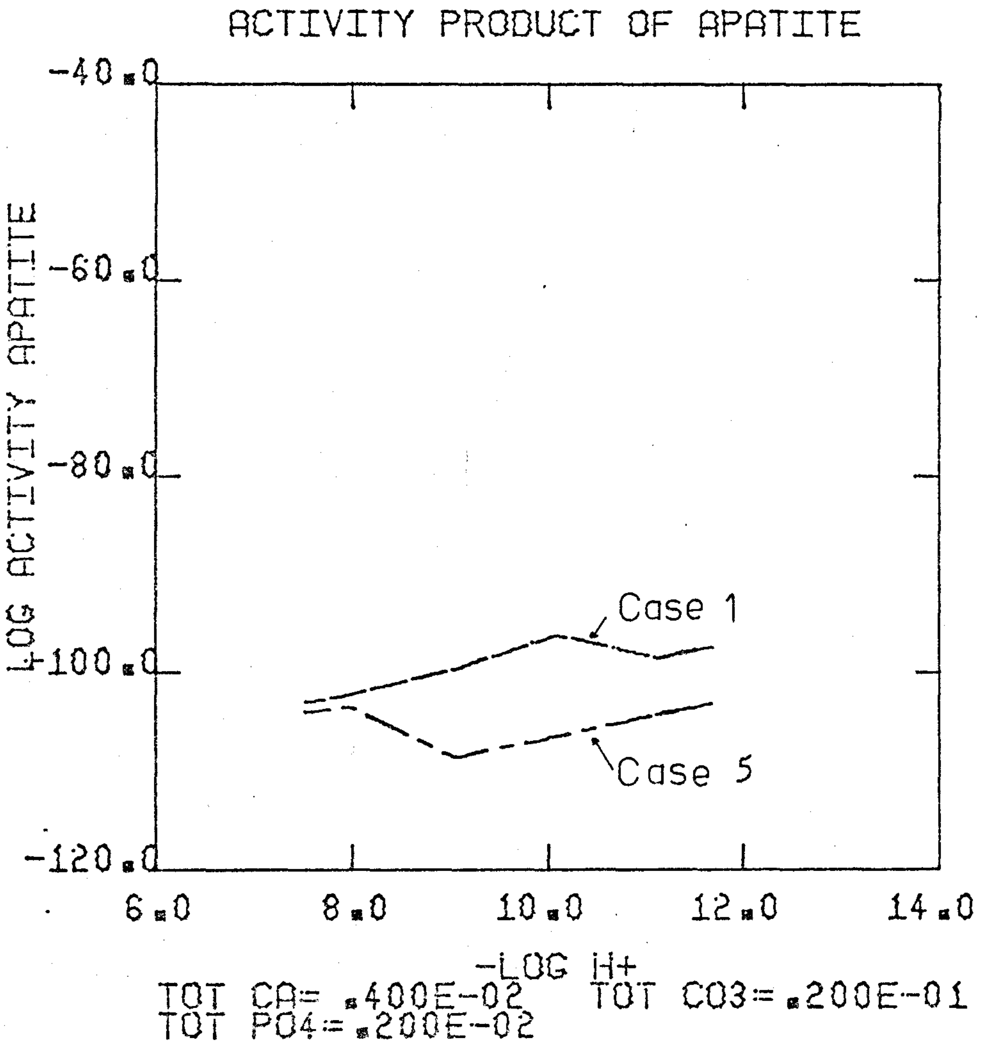
$$\text{Total Calcium} - \frac{0.001}{0.999}(\text{Total Magnesium}) = (\text{R.H.S. equation } 6) - \frac{0.001}{0.999}(\text{R.H.S. equation } 7) \quad (14)$$

After the model has completed the solution of all the steps desired, it can print a series of tables. These are: a table of equilibrium and solubility constants for each step which have been corrected using equation 13, page 19, a table of the aqueous ions and precipitates formed during each step, a table of the ionic strength and associated ion activity coeffients as determined by equation 9, page 18, and a table of the total calcium, magnesium, carbonate, and phosphate remaining in solution. Furthermore, graphs of the aqueous species and the totals remaining in solution can be plotted.

APPENDIX 2

The figures included in this appendix represent the apparent activity products of calcite, Mg-calcite (3 per cent Mg in the calcite lattice) and hydroxyapatite calculated at constant concentrations of the components Ca, Mg, CO_3 and PO_4. The initial sixteen pages, 90 to 106, represent cases one and five, where there isn't any magnesium present in solution. There are two different sets of computed results on each figure representing the apparent activity products of calcite and hydroxyapatite. The set of results with the higher solubility is case 1 while the set of results with the lower solubility is case 5.

The remaining pages, 106 to 115 inclusive, show the apparent activity products of calcite, Mg-calcite and hydroxyapatite when magnesium is a component in solution. The apparent activity product for hydroxyapatite and calcite are illustrated for case 9 while only Mg-calcite is shown for case 13. The set of results which represent Mg-calcite are always the line with the higher solubility.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-60.0
-80.0
-100.0
-120.0
LOG ACTIVITY APATITE
Case 1
Case 5
6.0
8.0
10.0
12.0
14.0
-LOG H+
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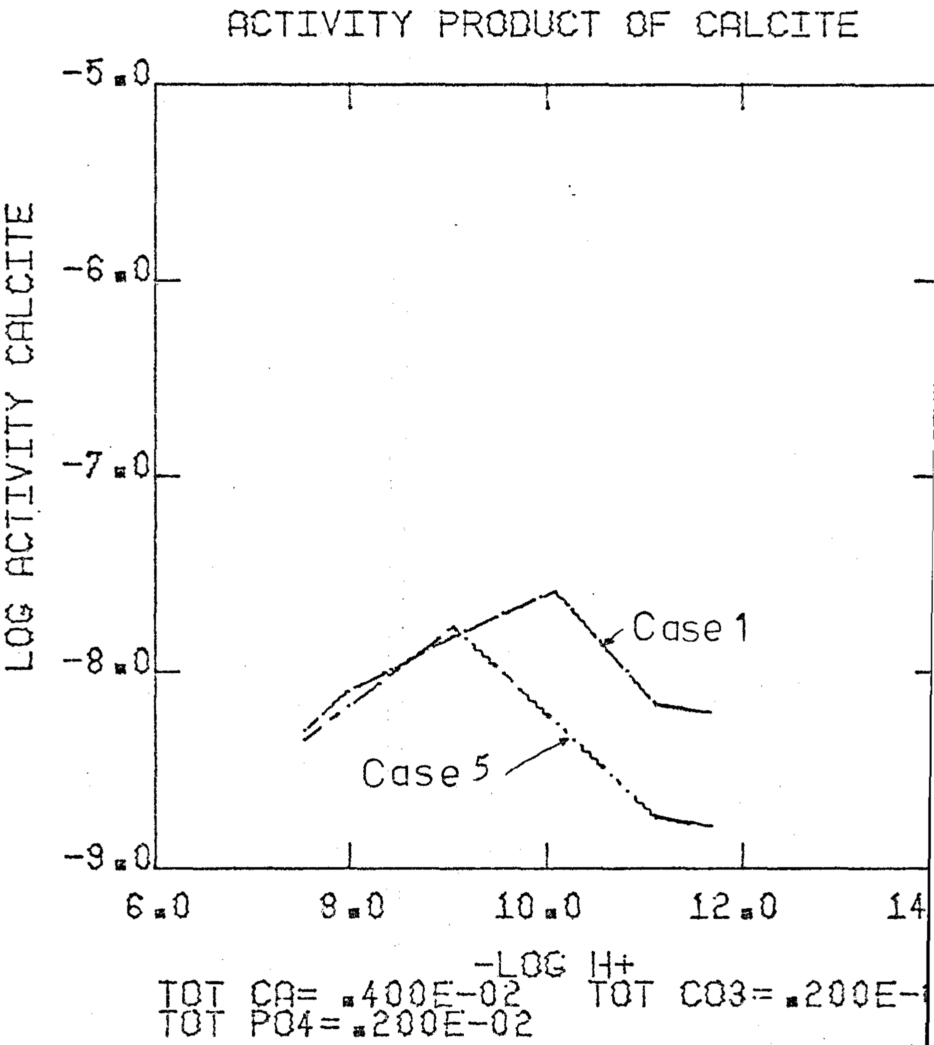
TOT PO4= .200E-02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LOG ACTIVITY CALCITE
Case 1
Case 5
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8.0
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12.0
14
-LOG H+
TOT CA= .400E-02   TOT CO3= .200E-
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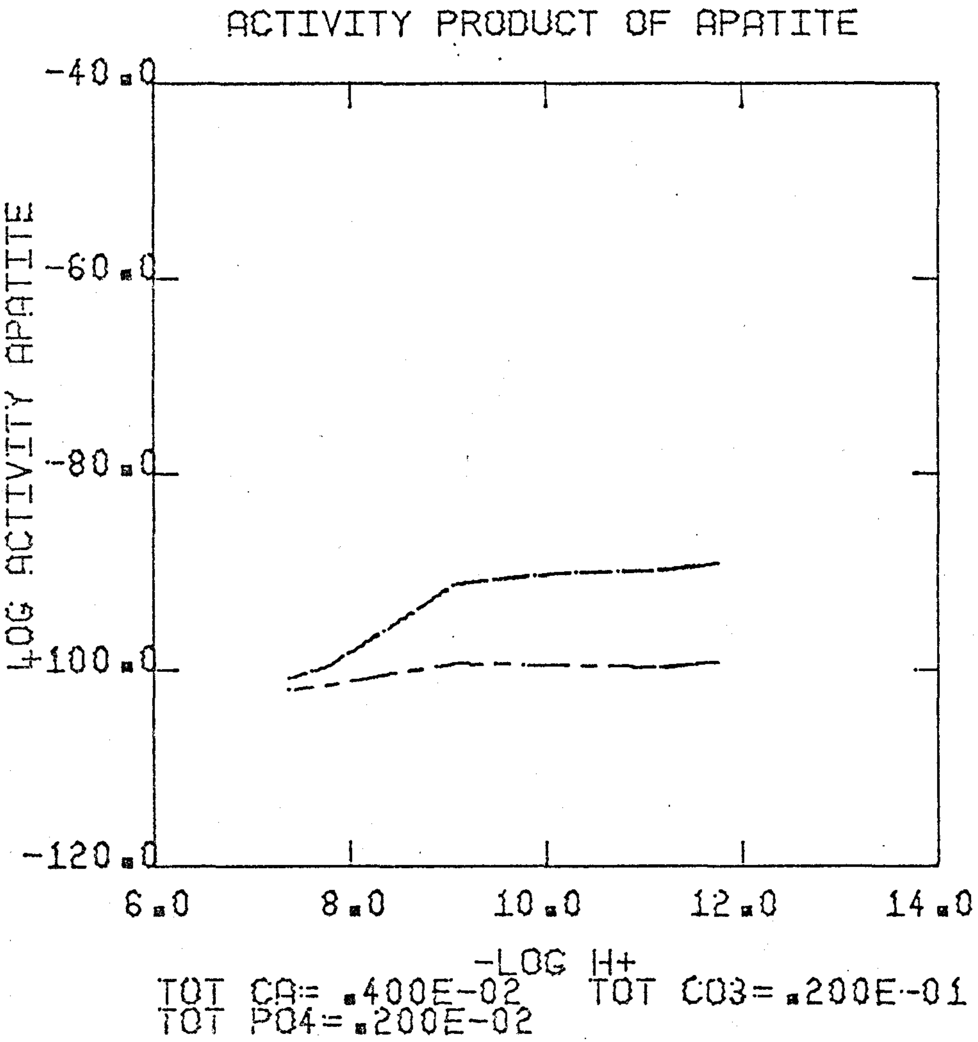
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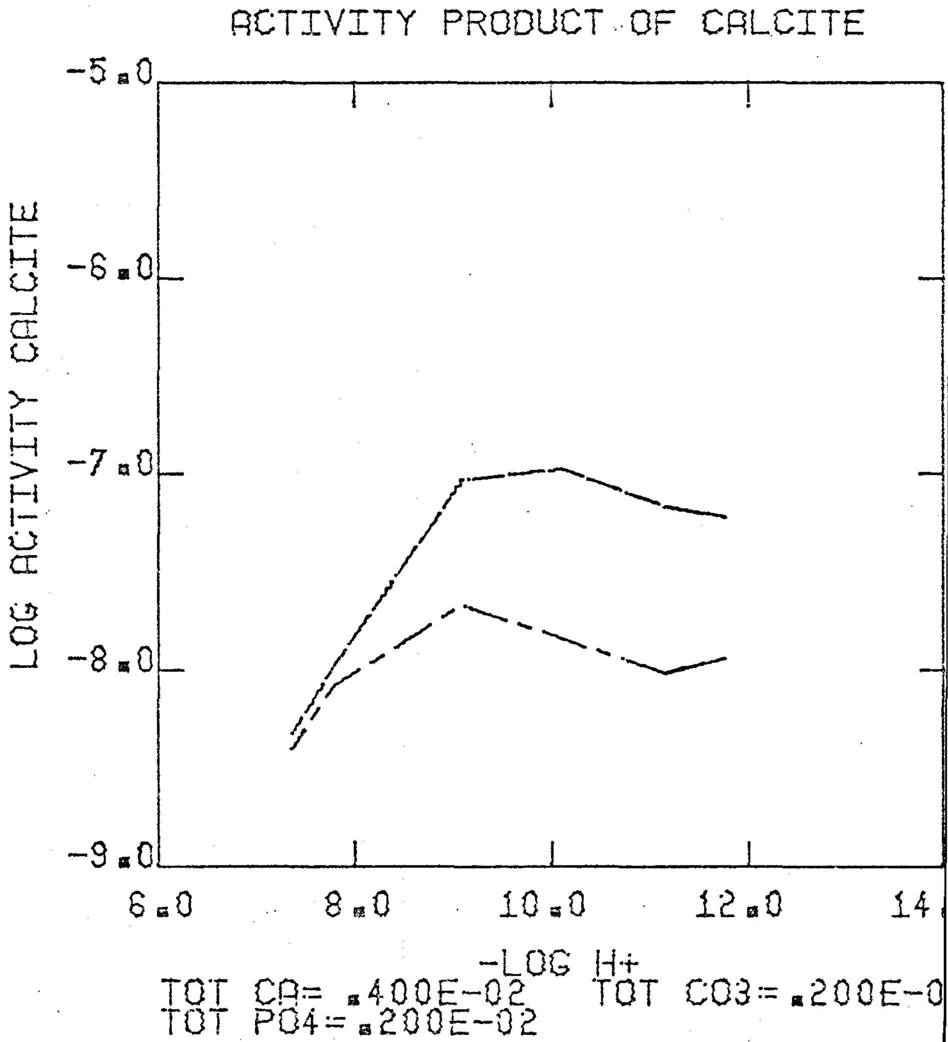
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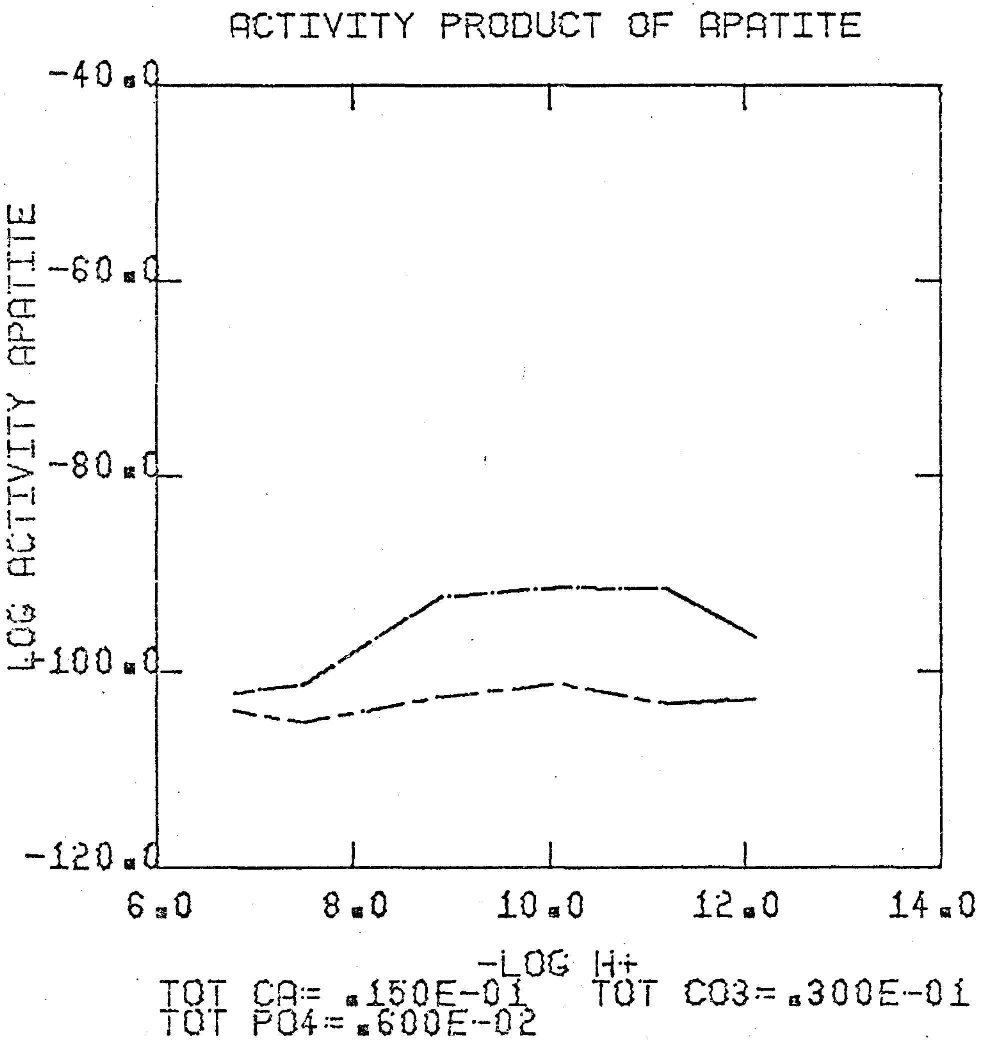
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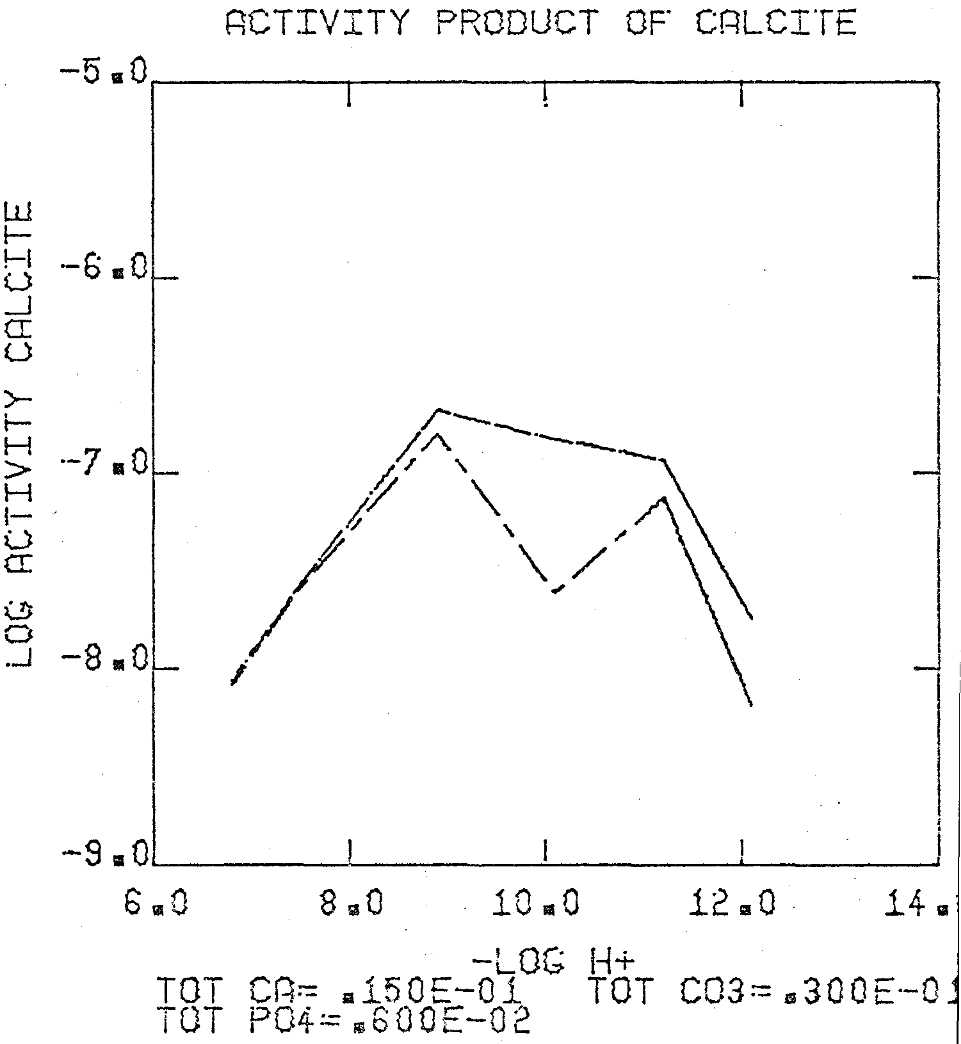
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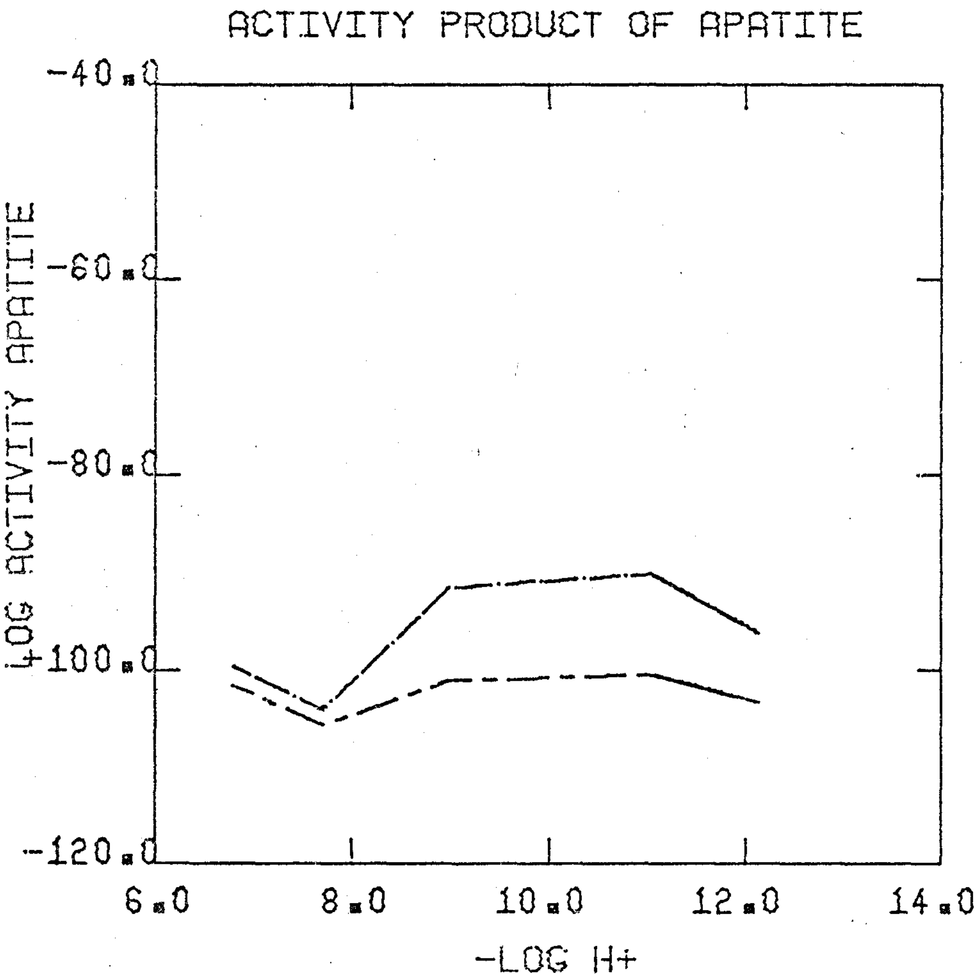

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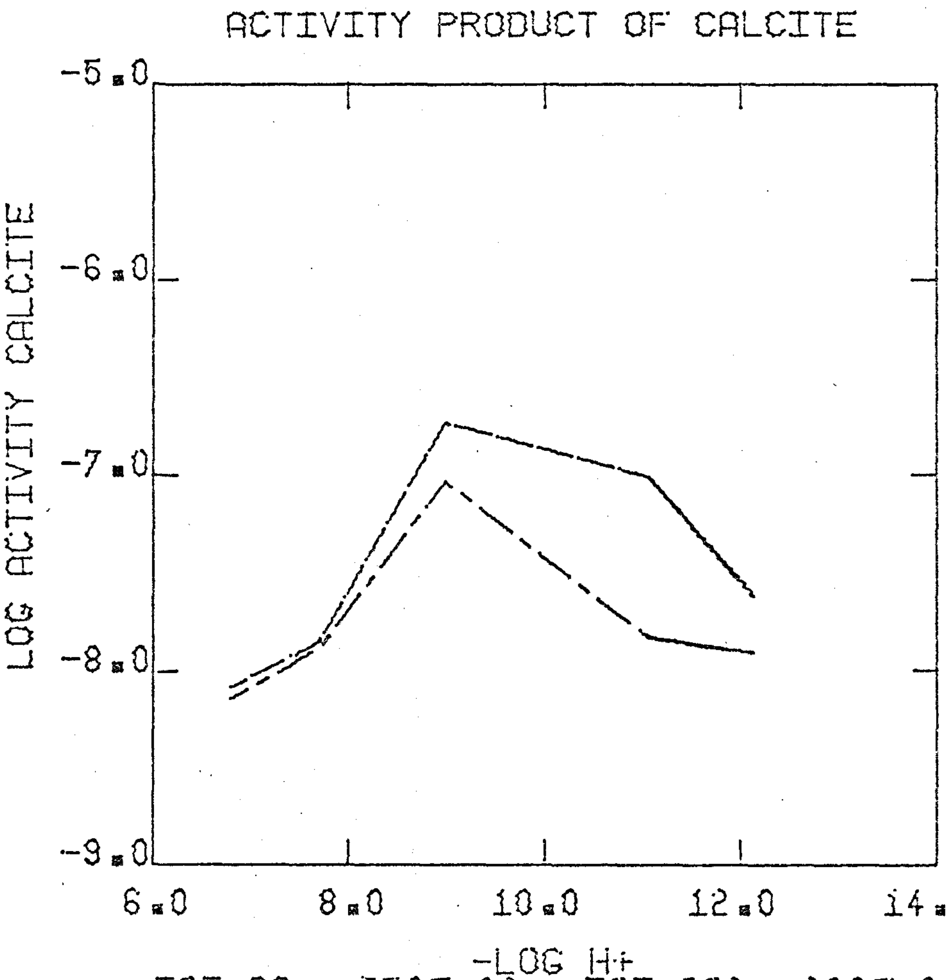

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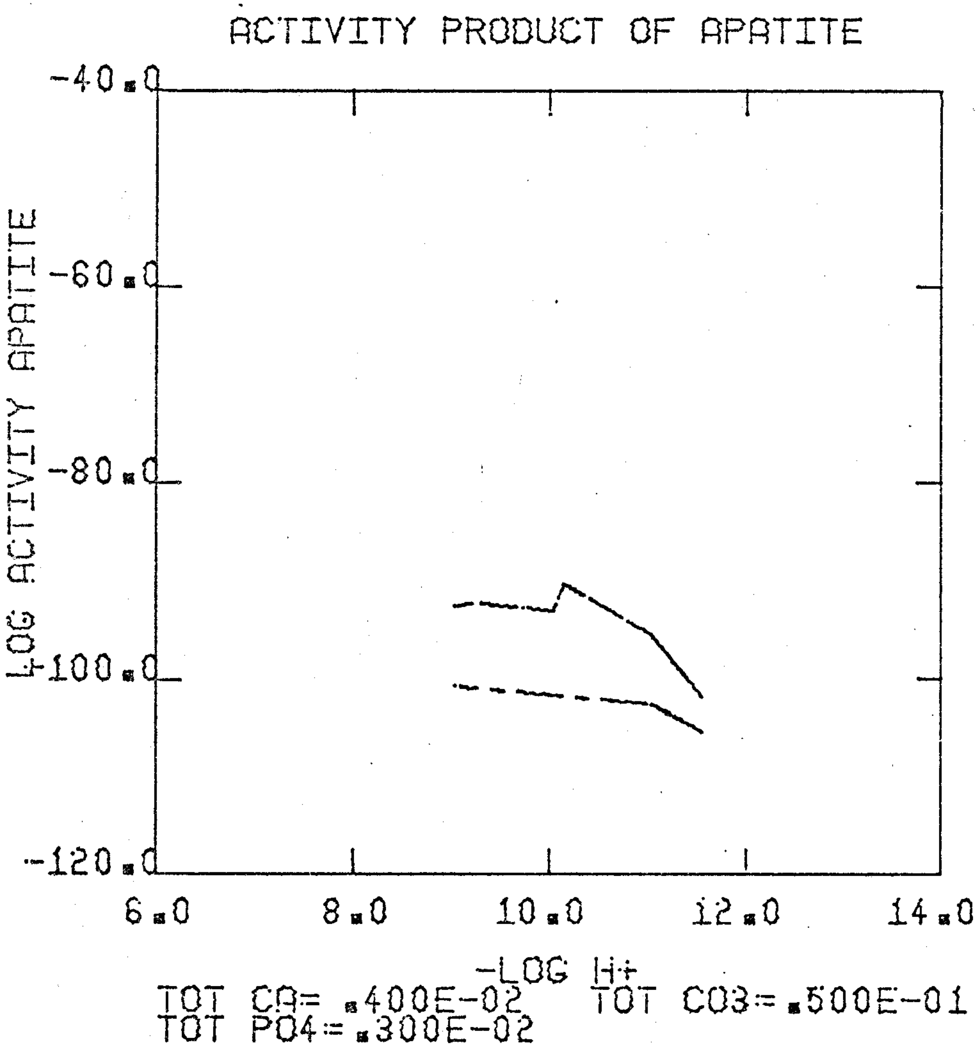
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-120.0
LOG ACTIVITY APATITE
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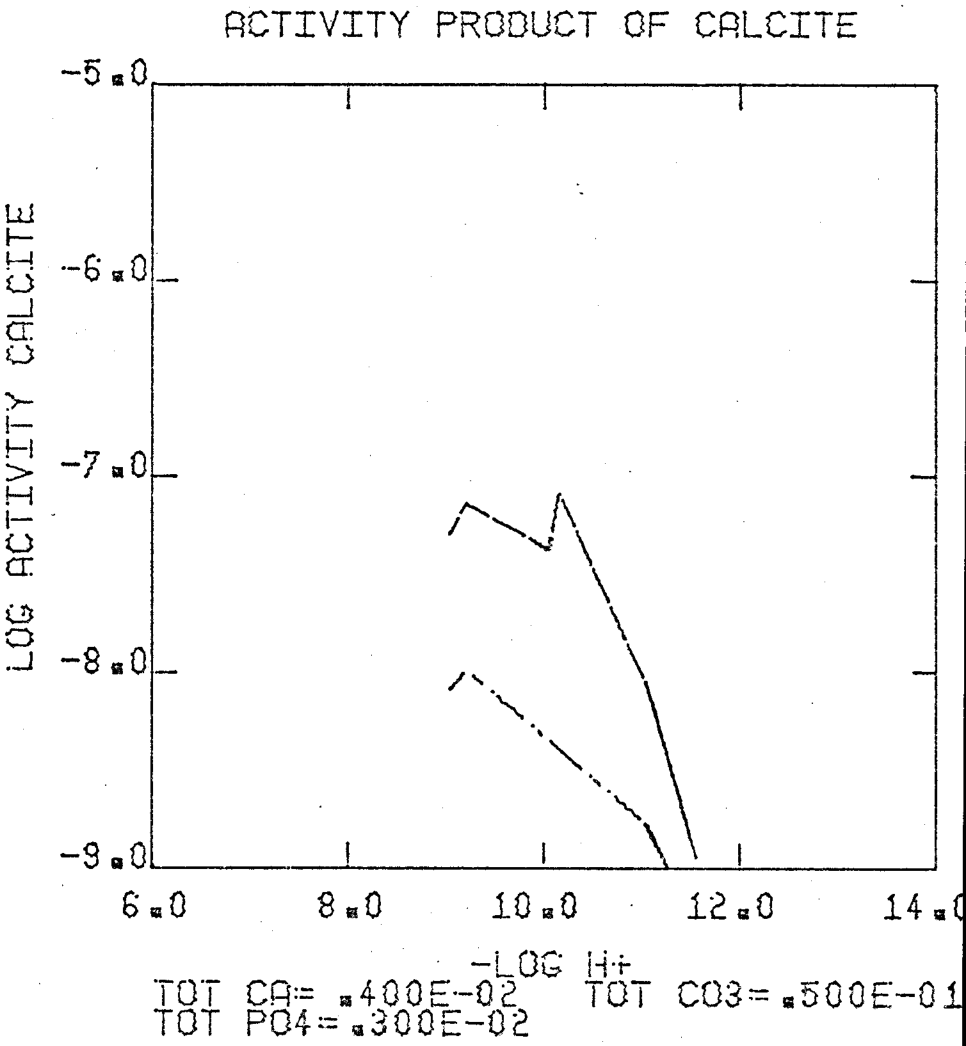
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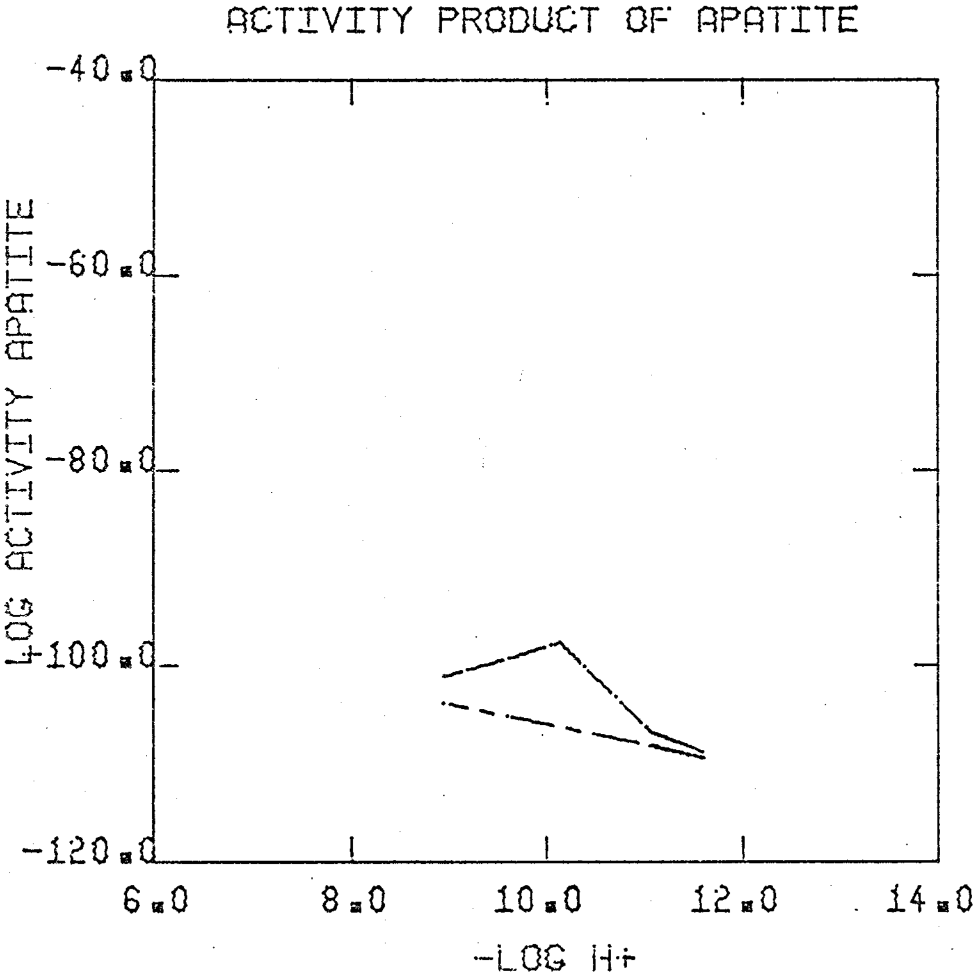
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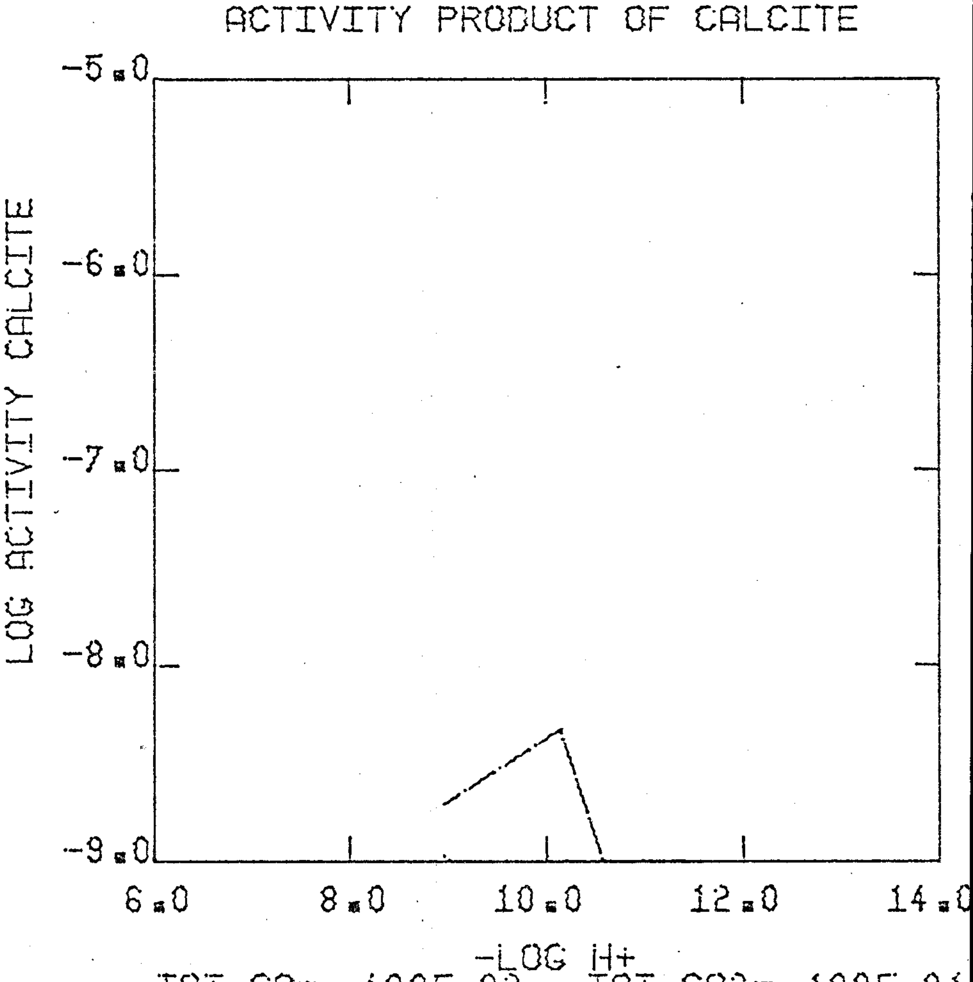
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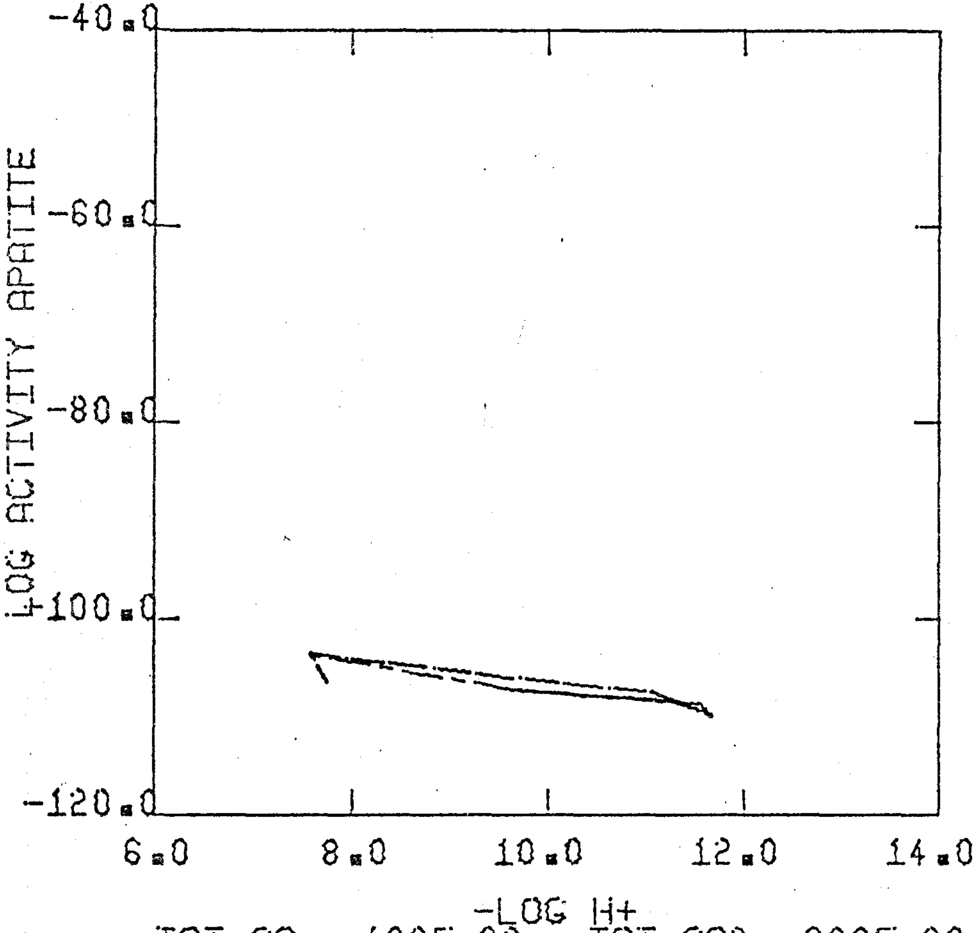

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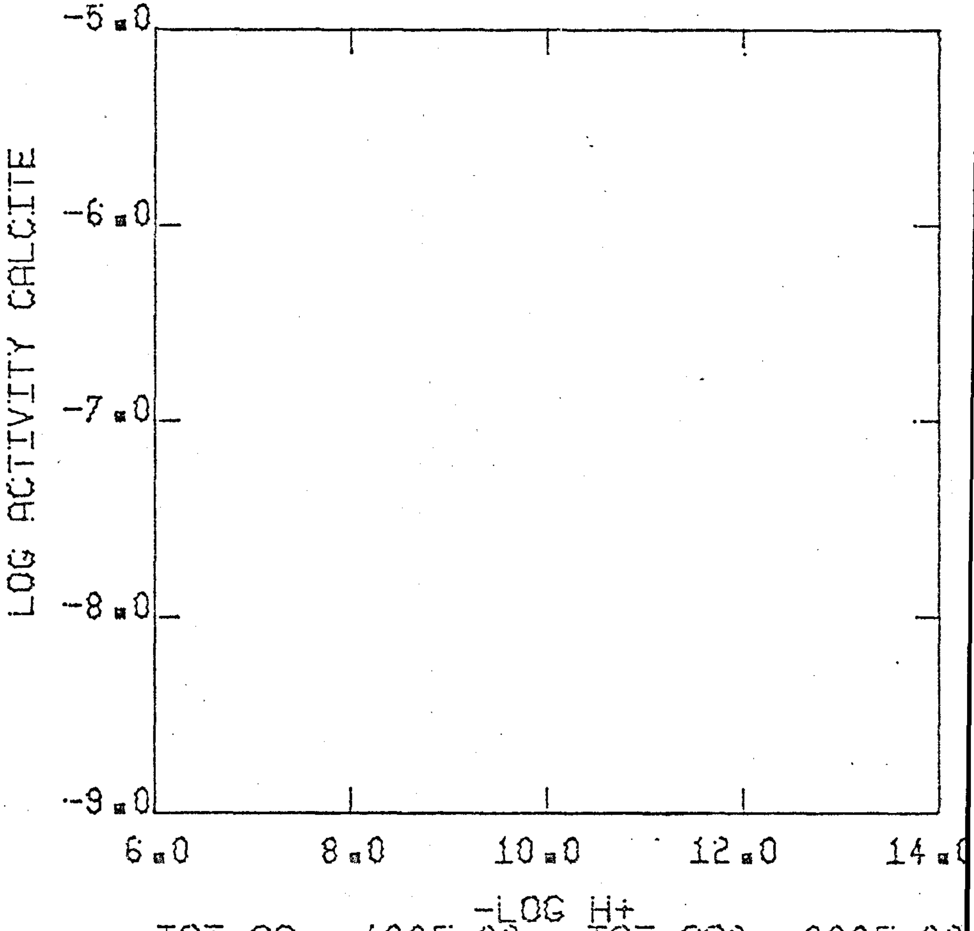

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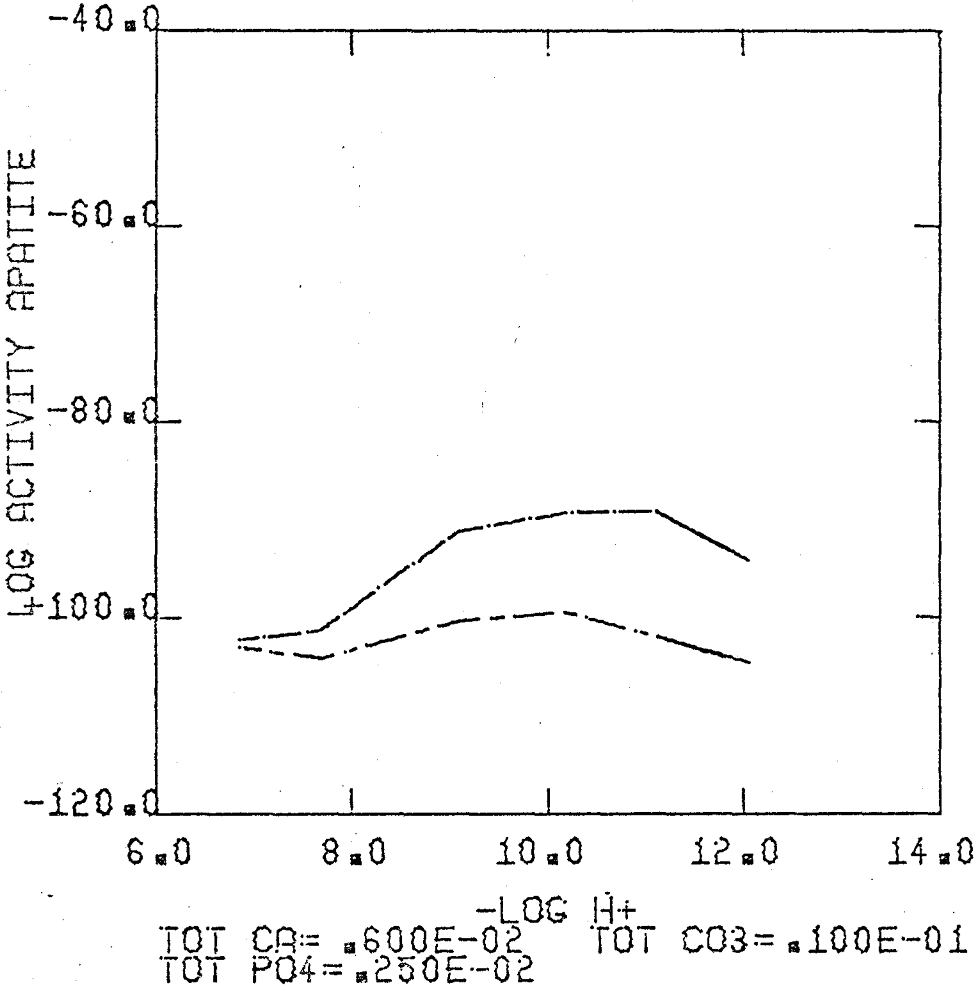

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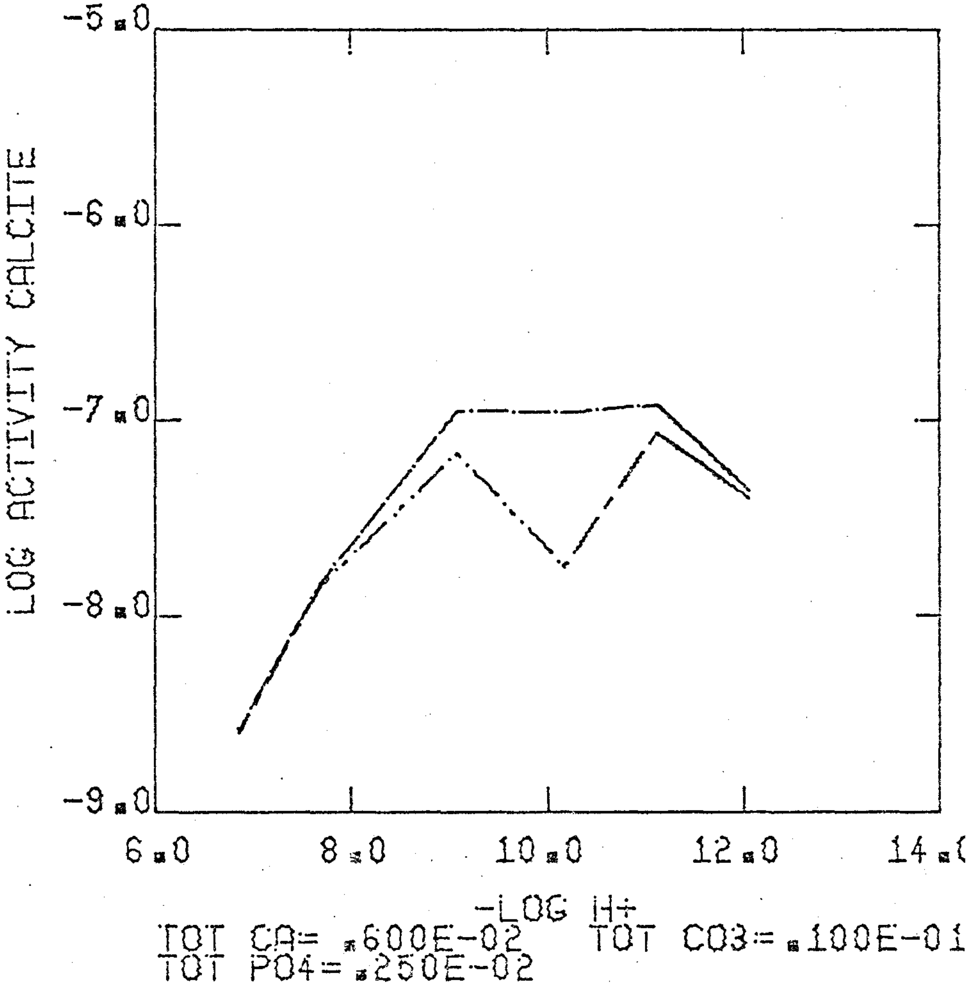

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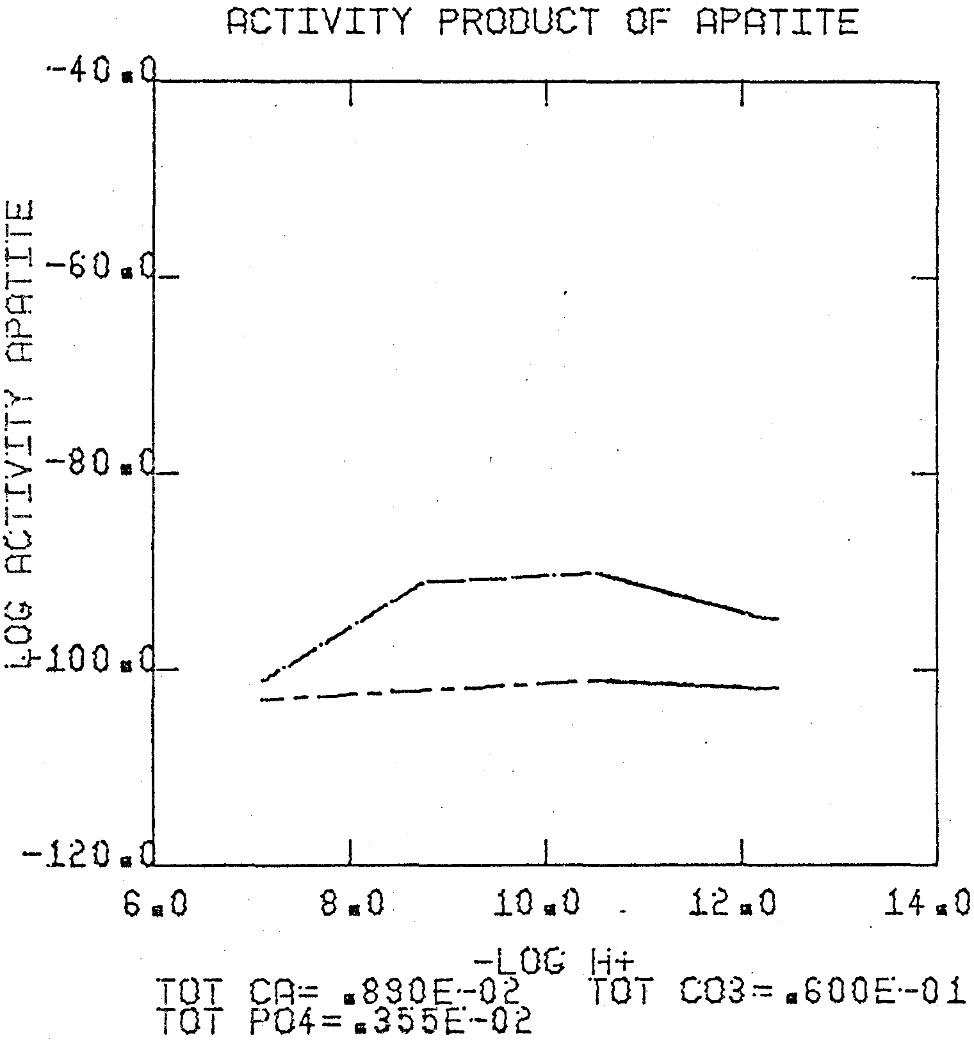
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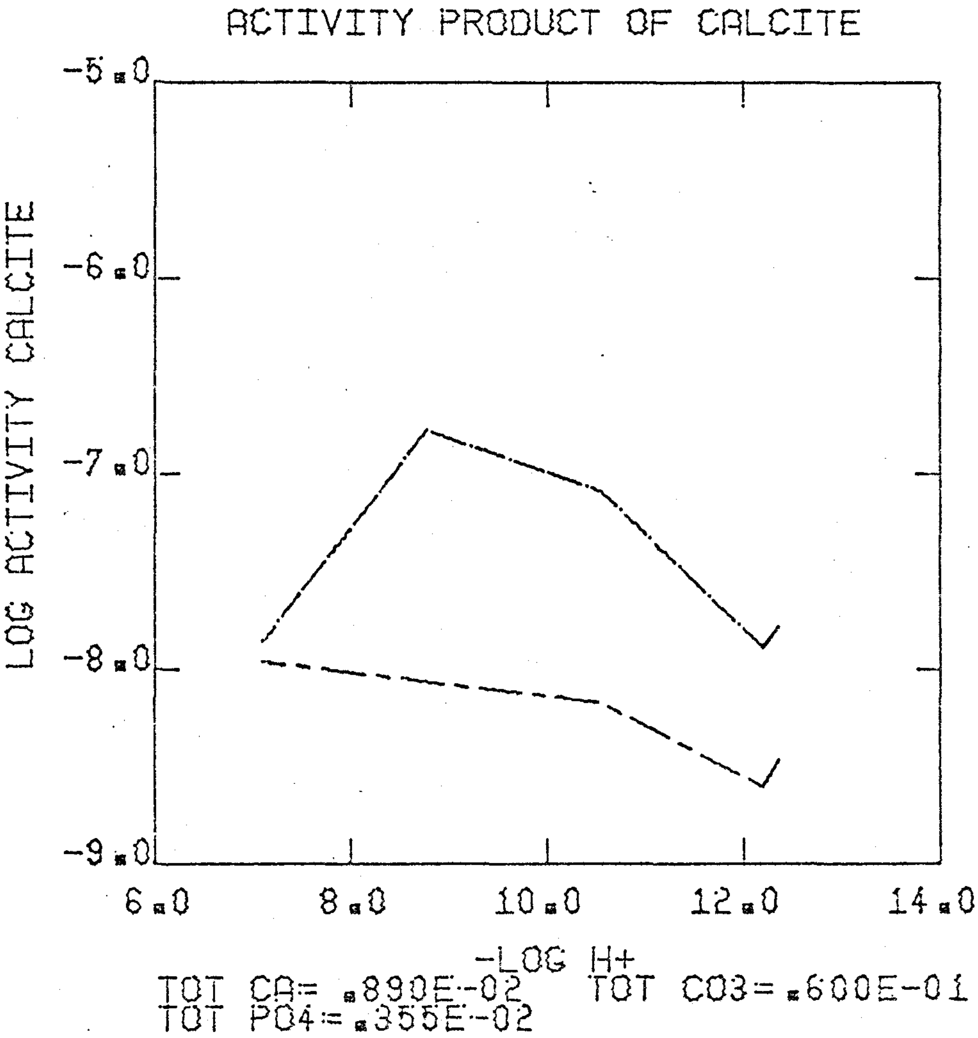
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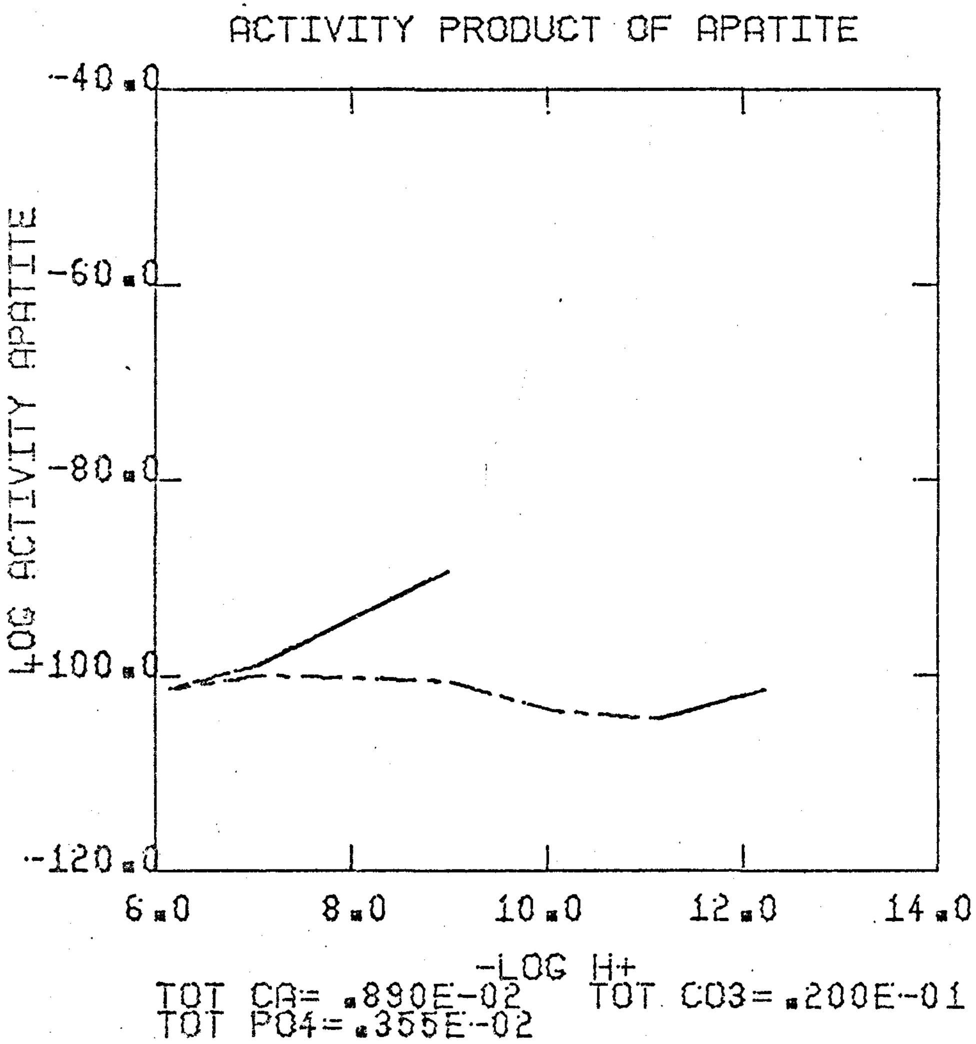
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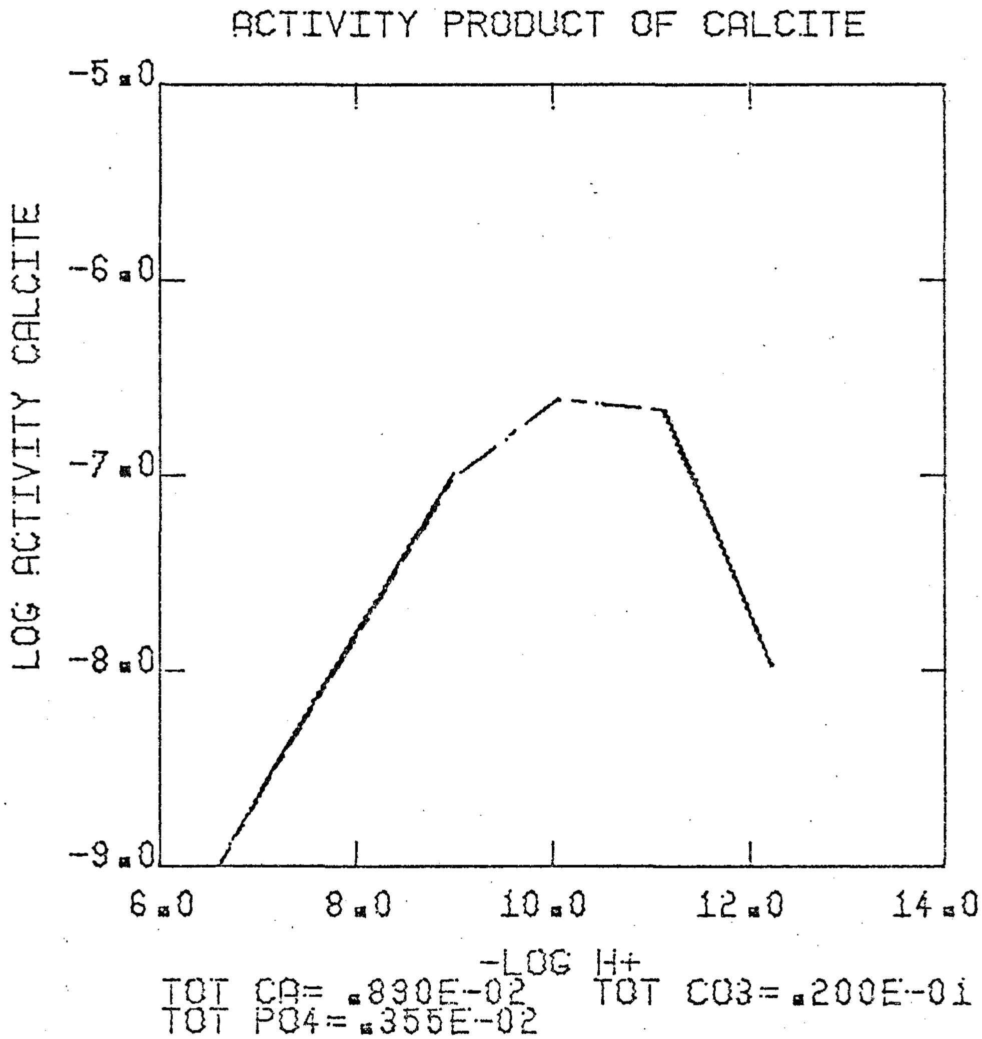
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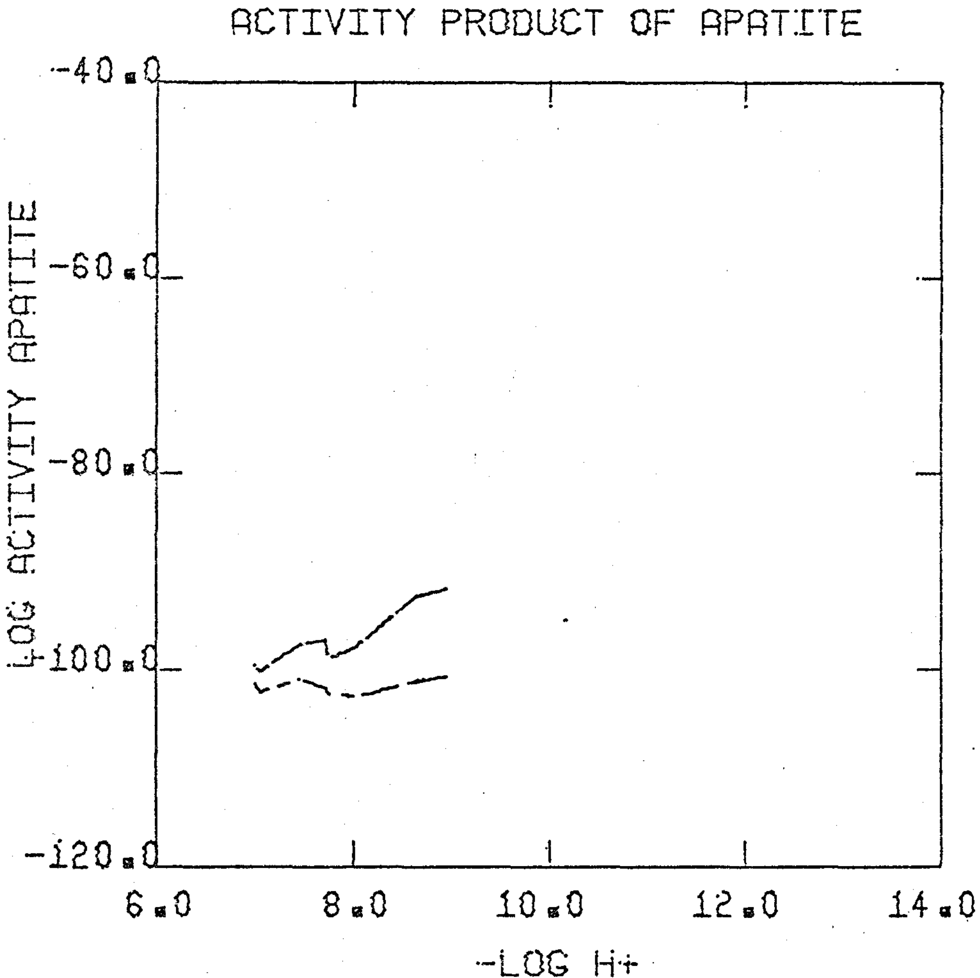

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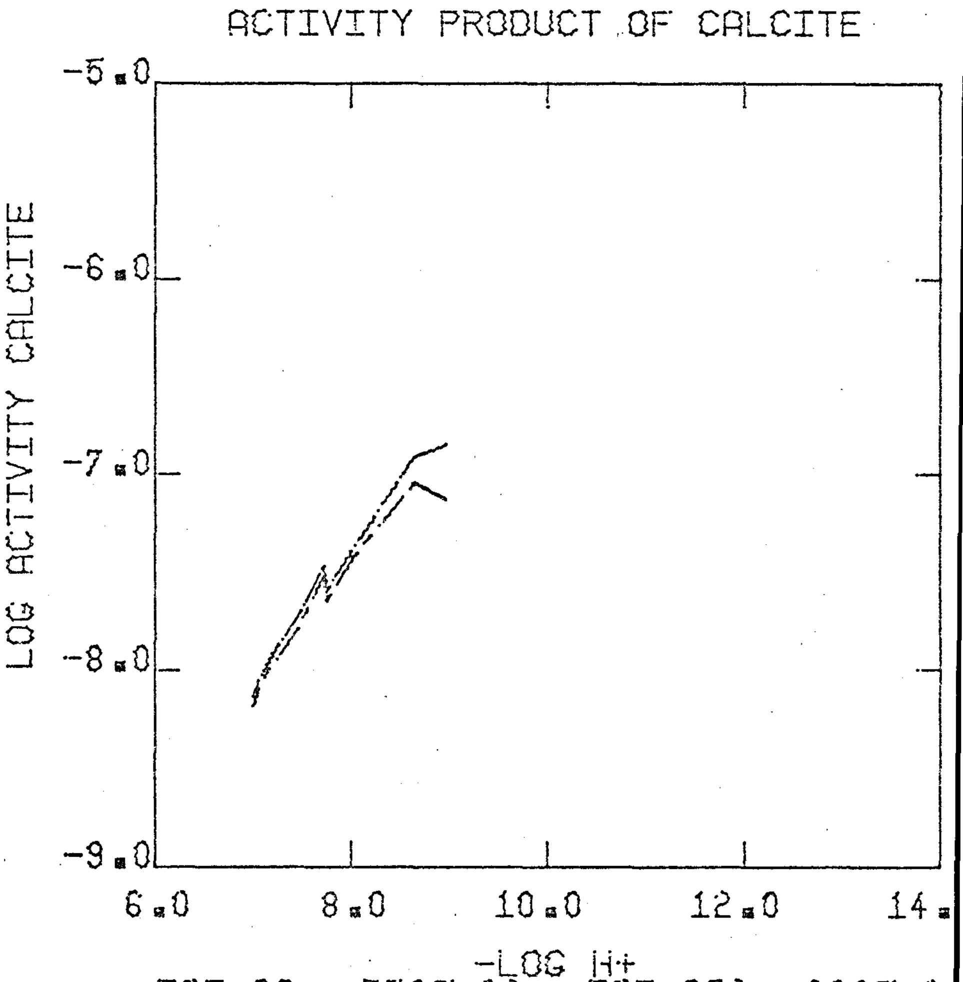

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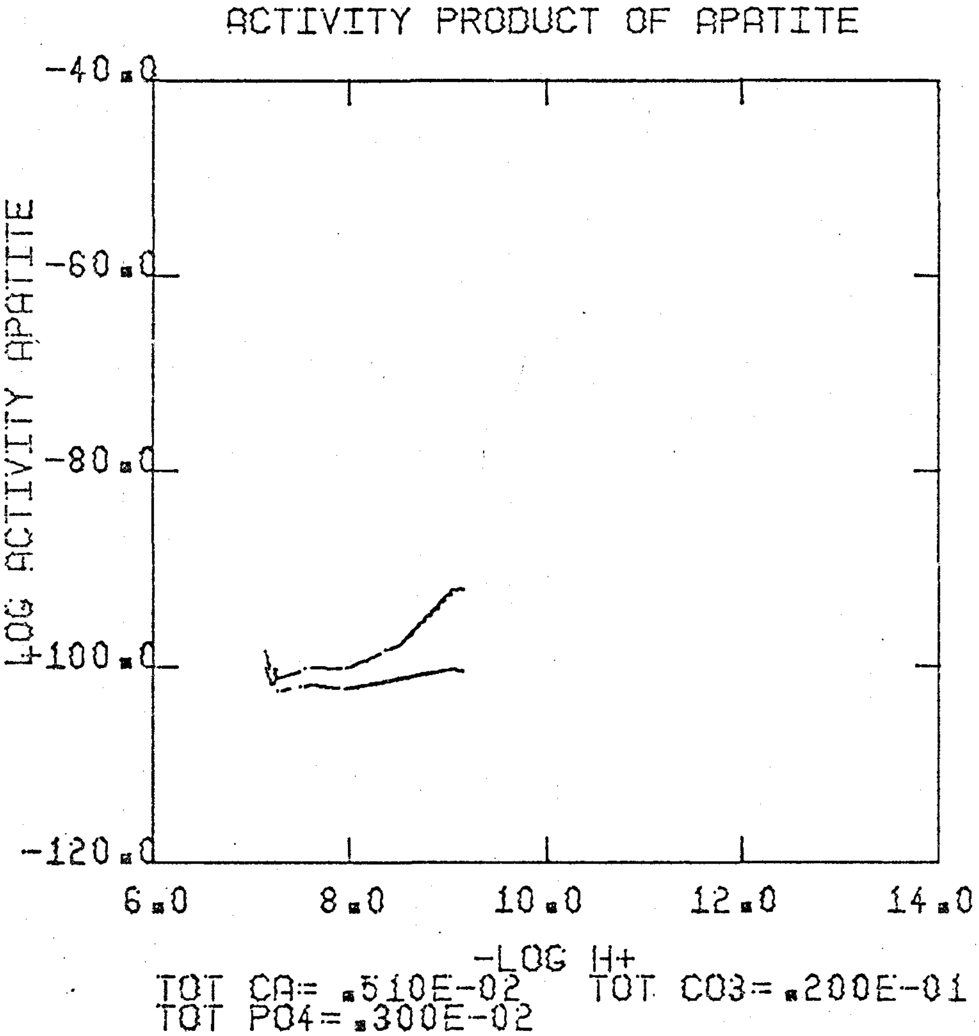
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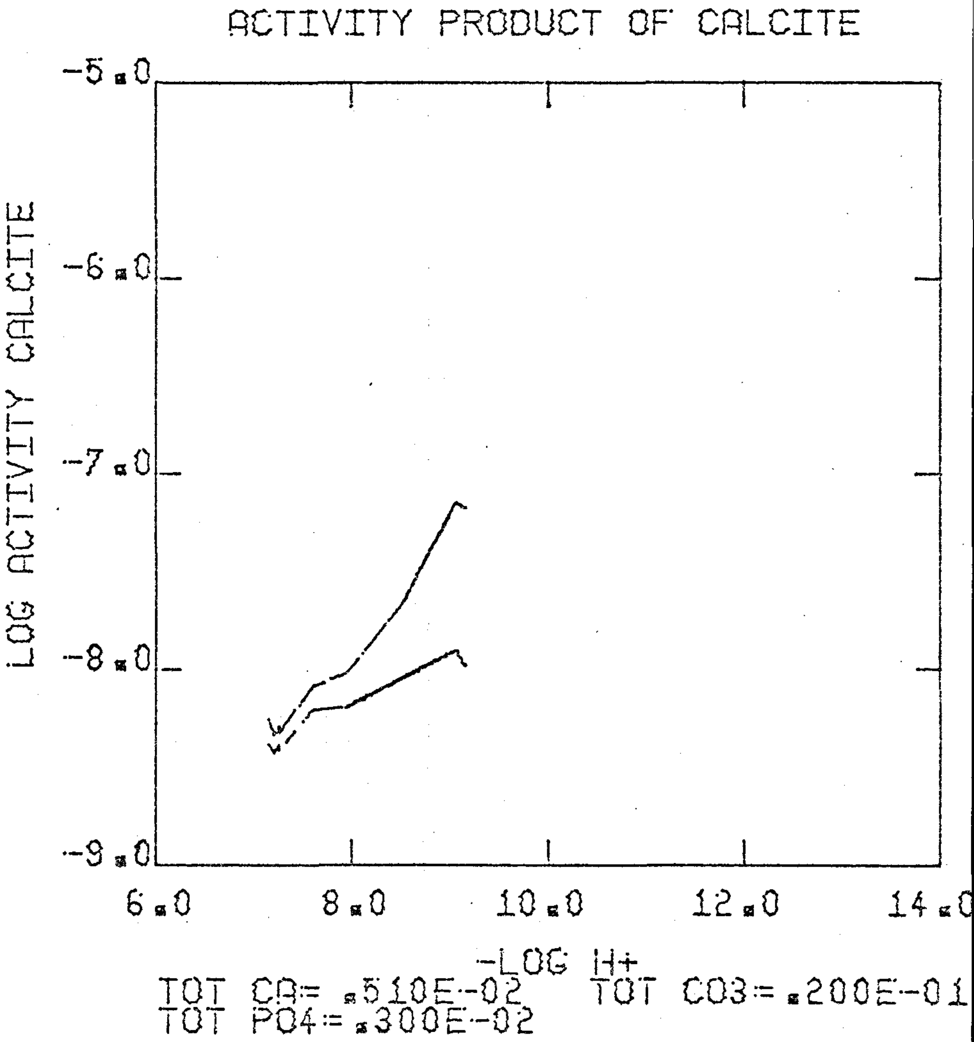
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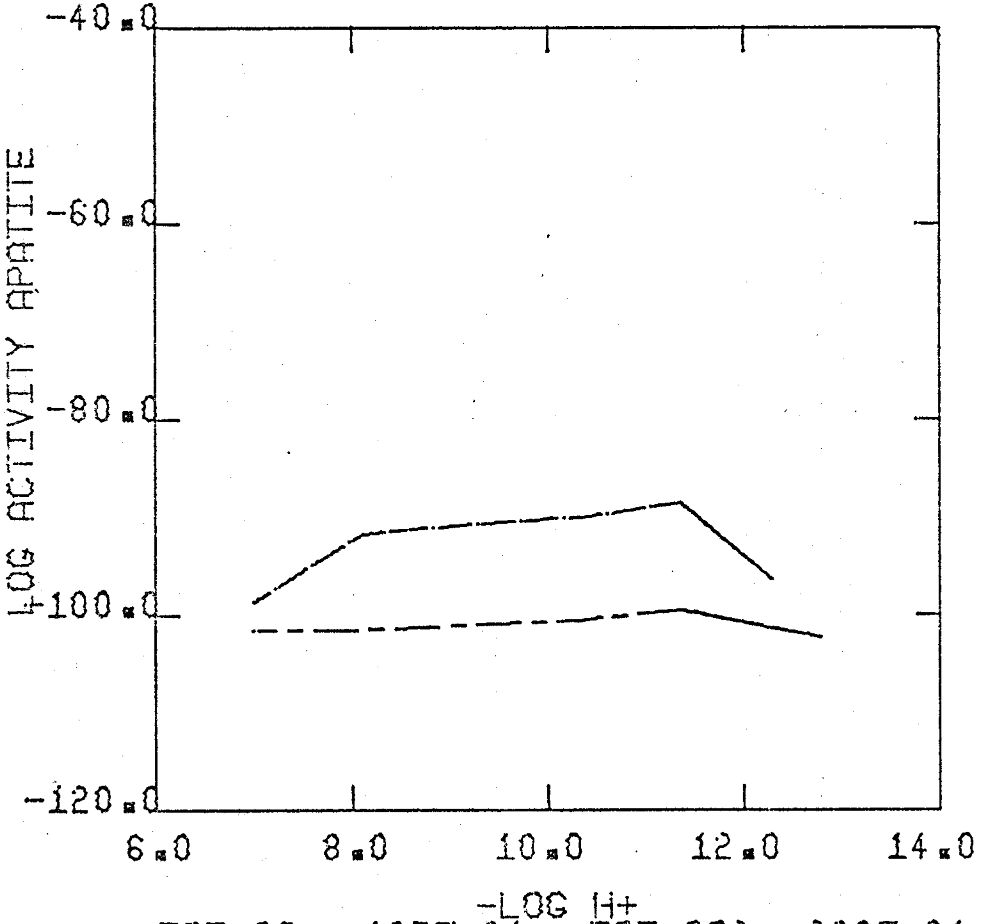

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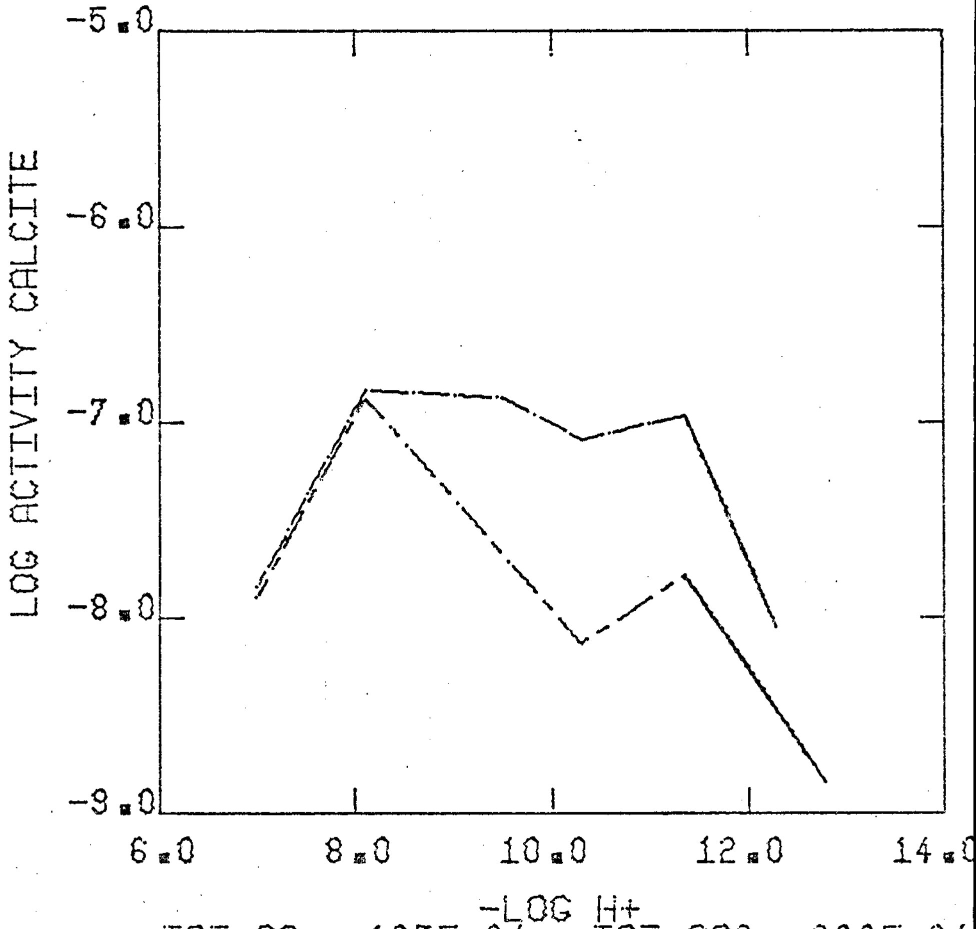

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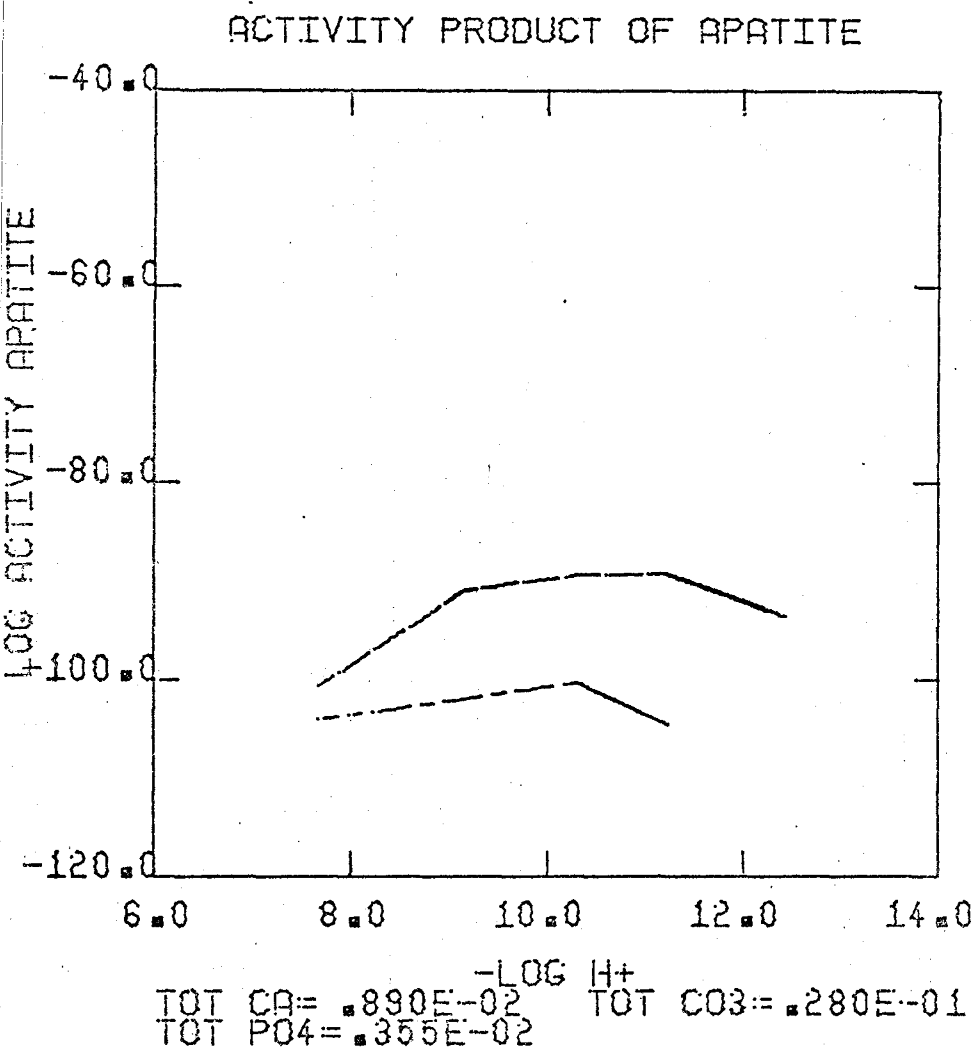
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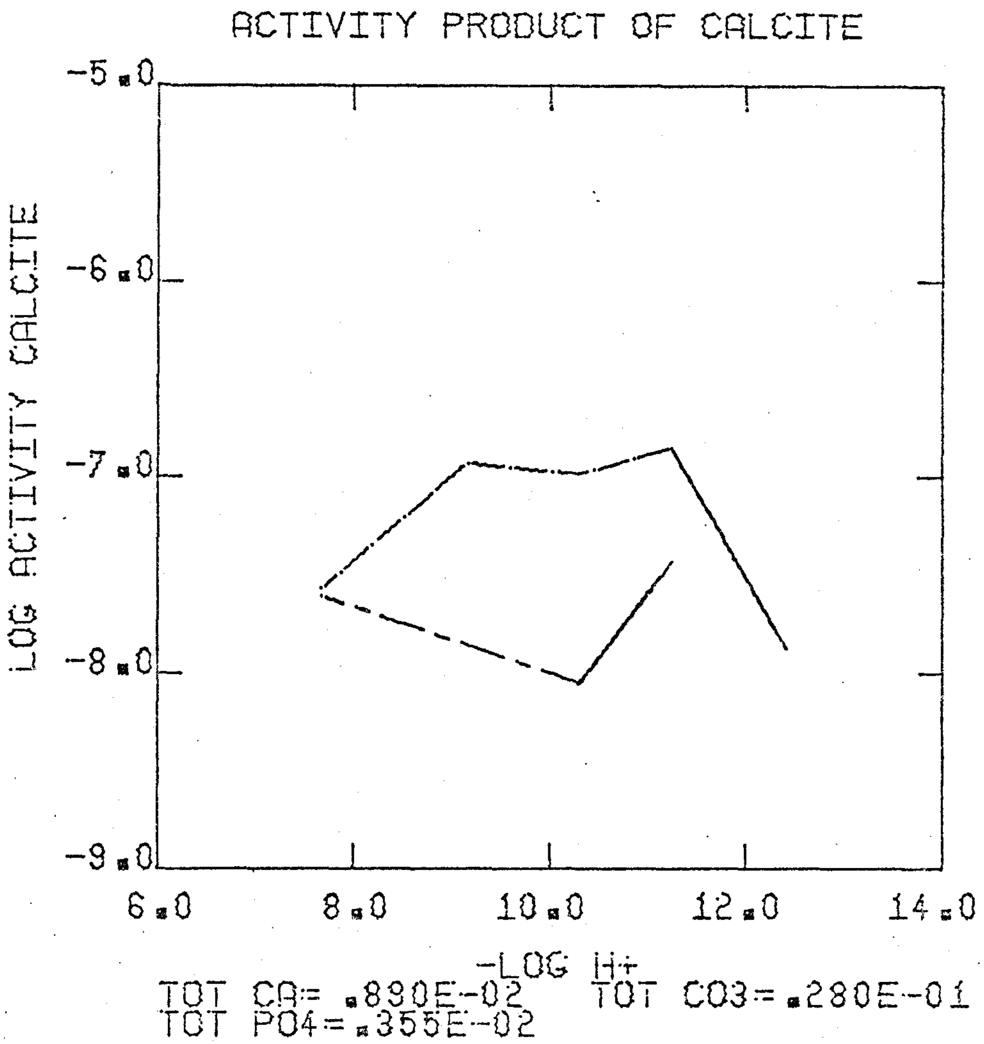
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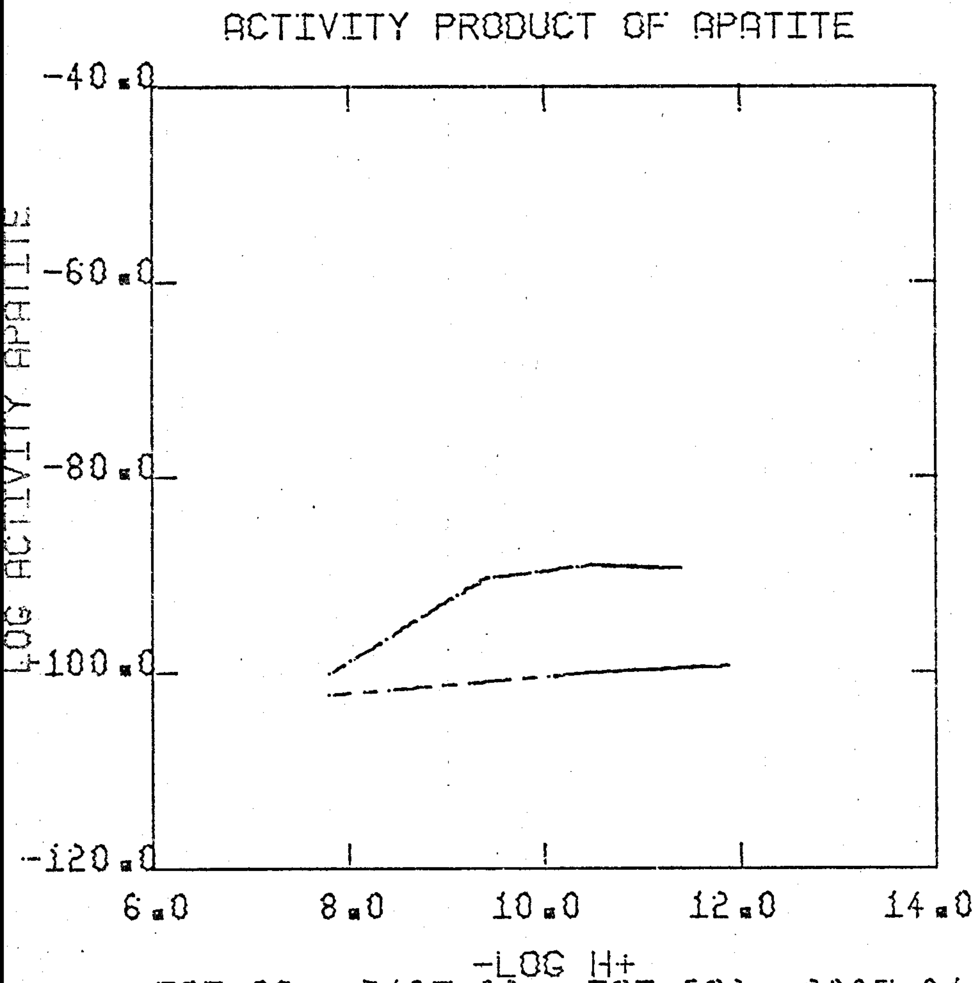

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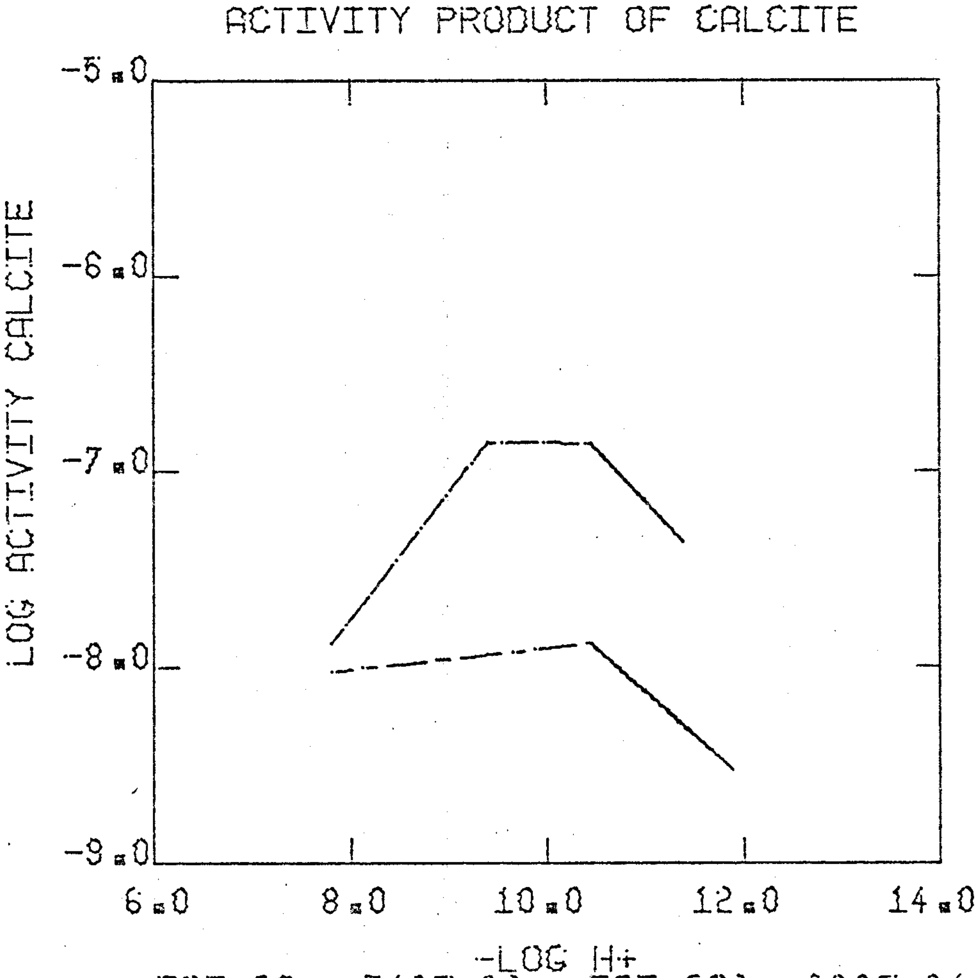

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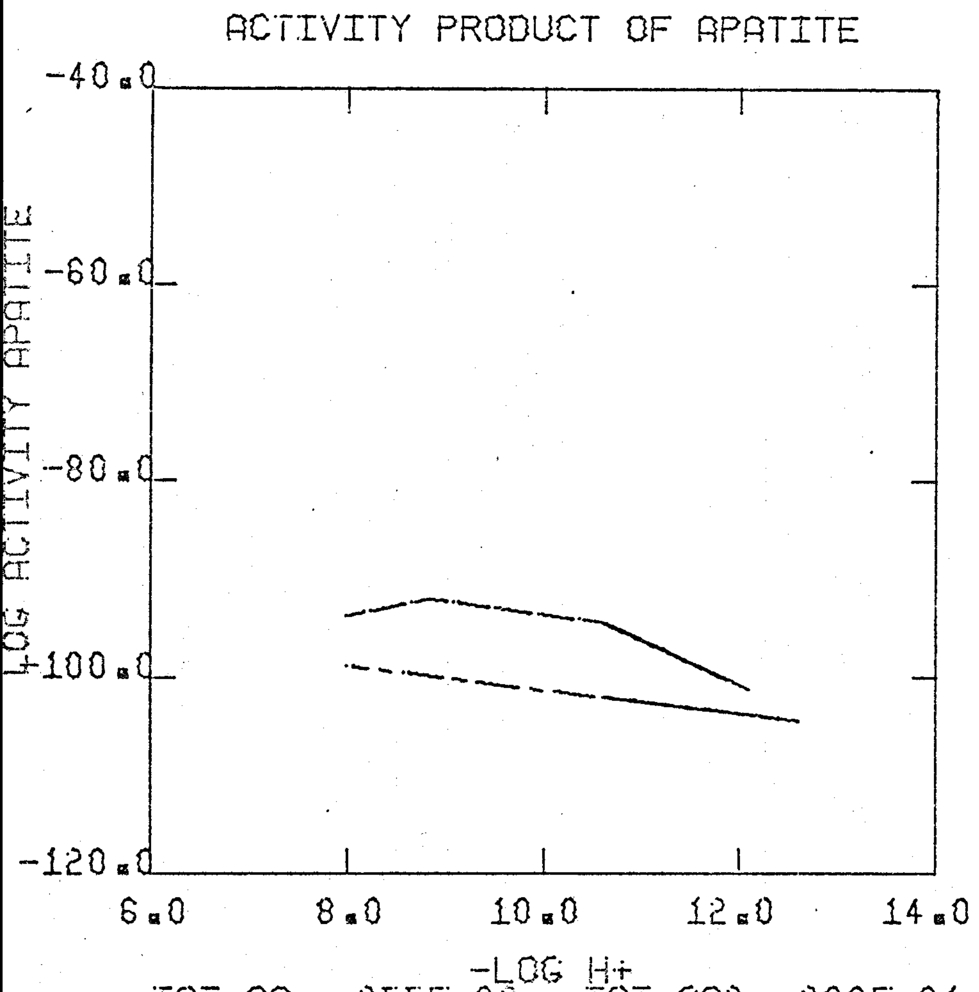

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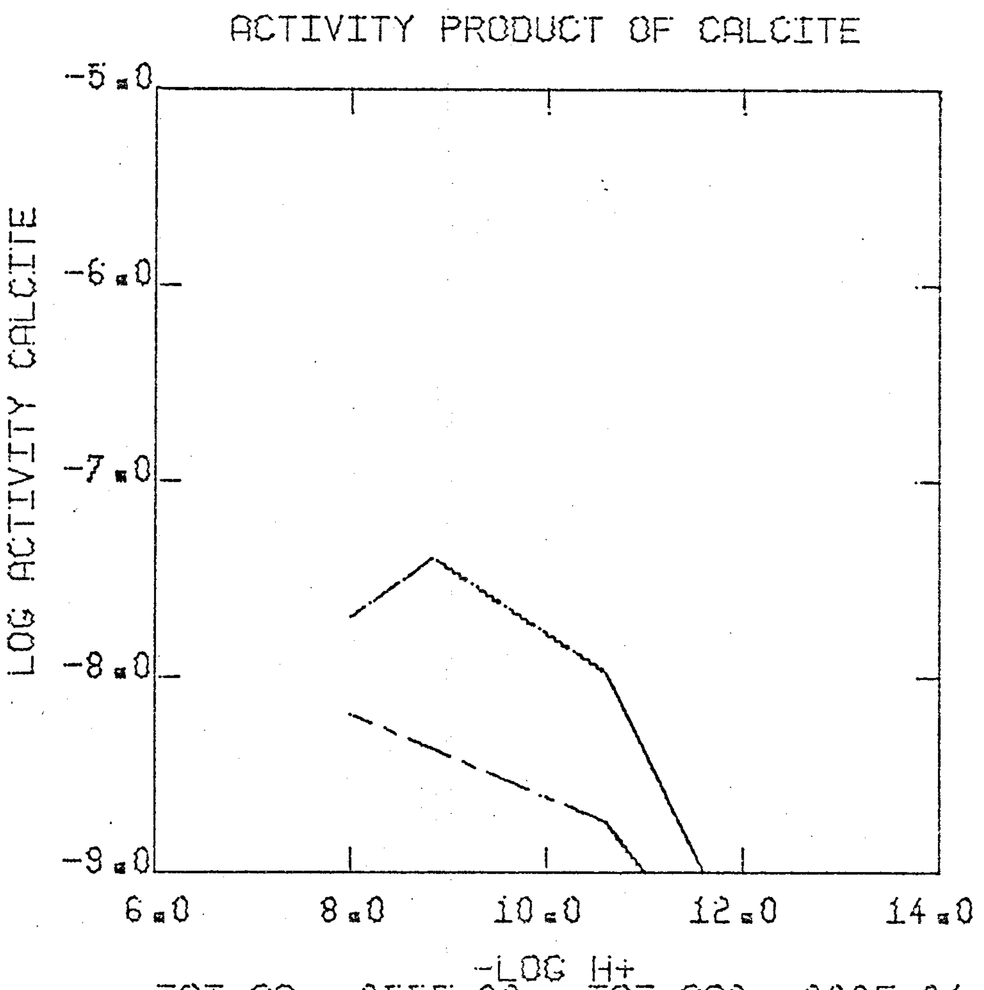

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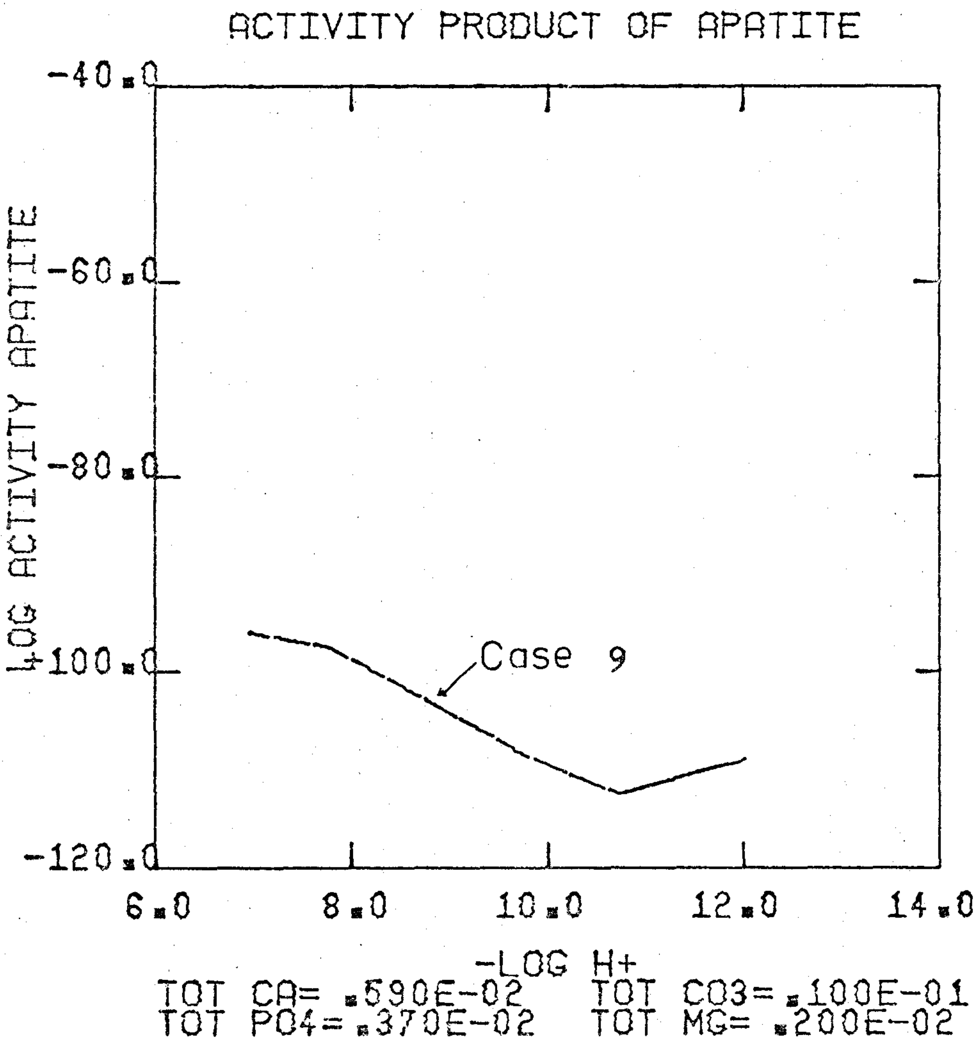
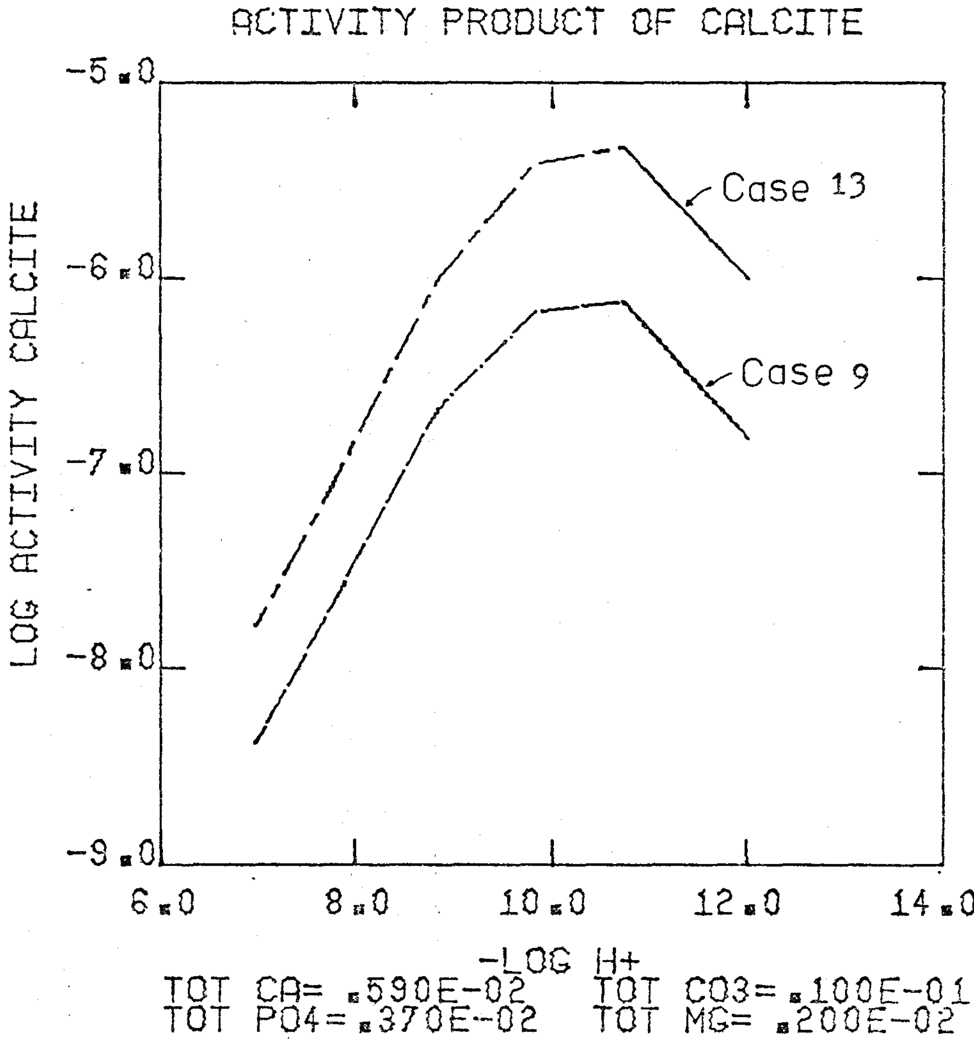

ACTIVITY PRODUCT OF APATITE
LOG ACTIVITY APATITE
-40.0
-60.0
-80.0
-100.0
-120.0
6.0
8.0
10.0
12.0
14.0
Case 9
-LOG H+
TOT CA= .590E-02
TOT CO3= .100E-01
TOT PO4= .370E-02
TOT MG= .200E-02


ACTIVITY PRODUCT OF CALCITE
LOG ACTIVITY CALCITE
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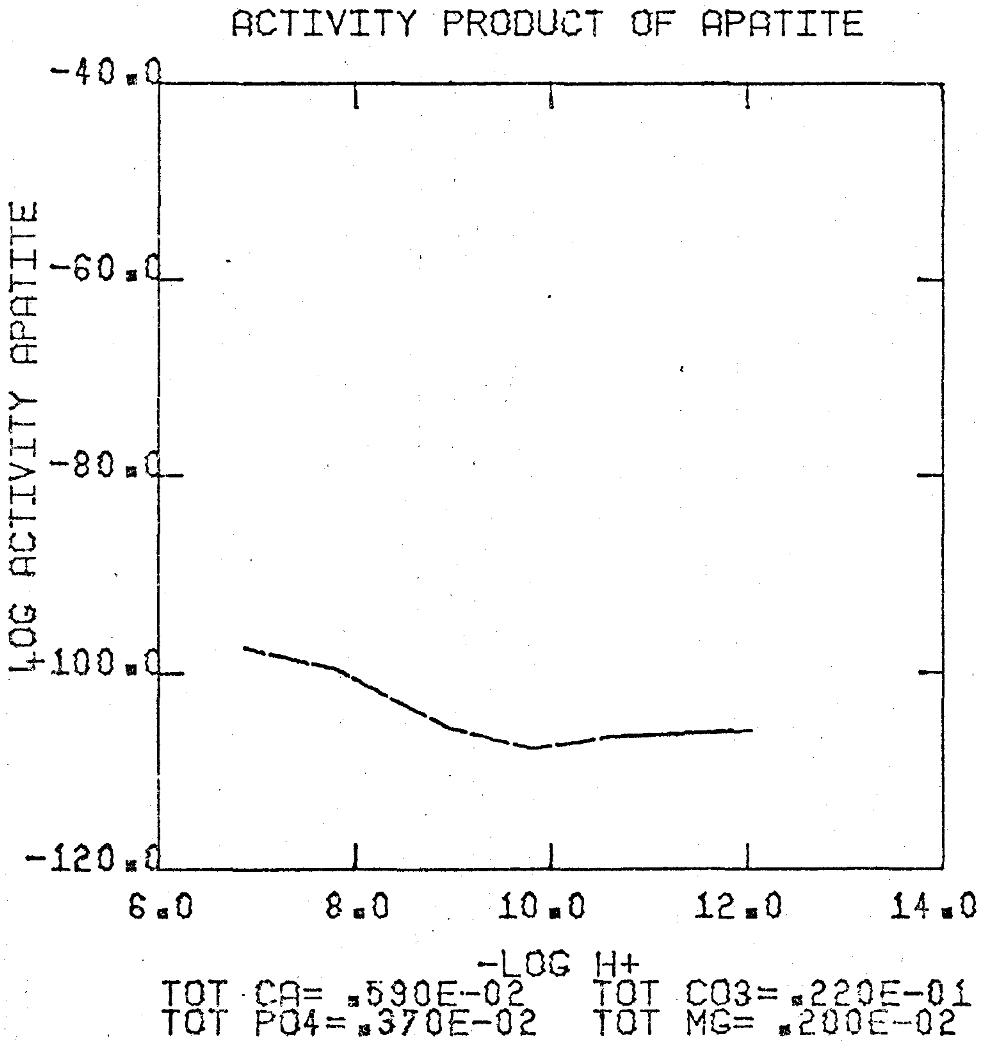
8.0
10.0
12.0
14.0
Case 13
Case 9
-LOG H+
TOT CA= .590E-02
TOT CO3= .100E-01
TOT PO4= .370E-02
TOT MG= .200E-02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LOG ACTIVITY APATITE
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-100.0
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6.0
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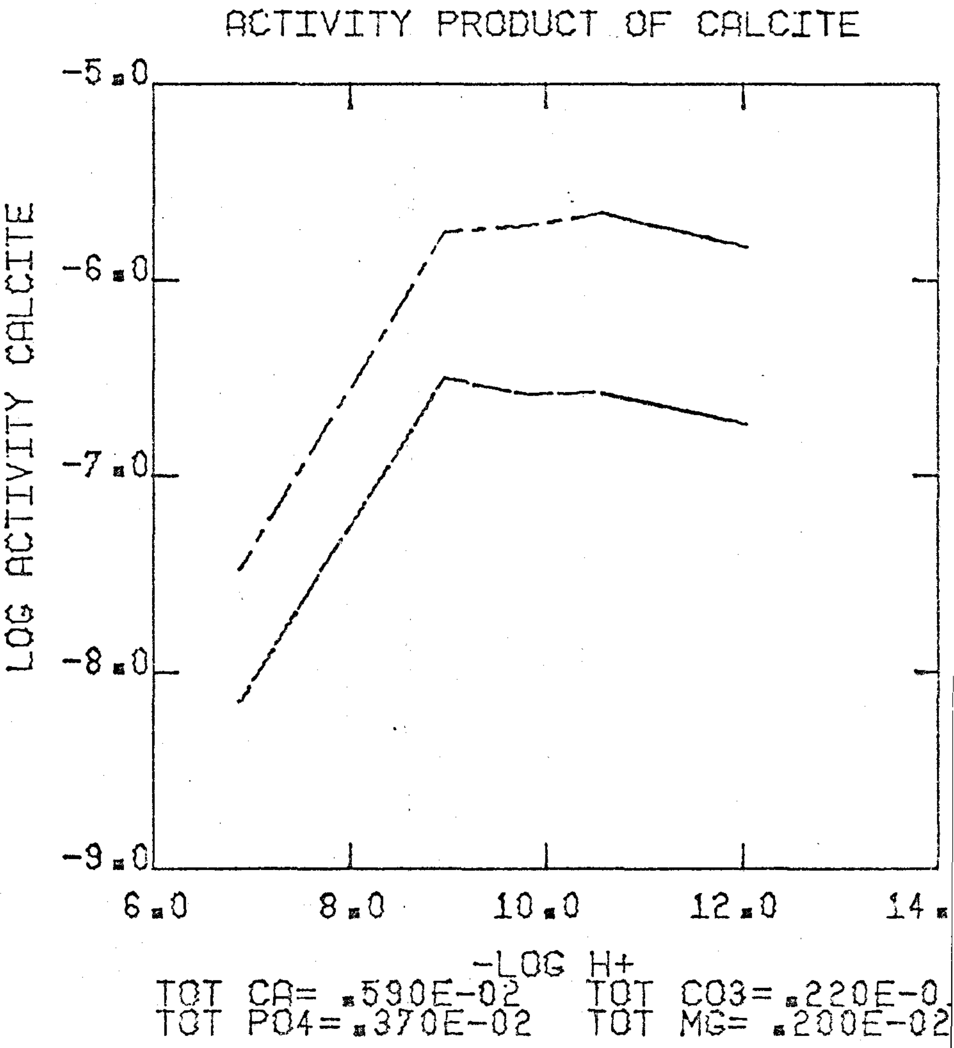
10.0
12.0
14.0
-LOG H+
TOT CA= .590E-02   TOT CO3= .220E-01
TOT PO4= .370E-02   TOT MG= .200E-02


ACTIVITY PRODUCT OF CALCITE
LOG ACTIVITY CALCITE
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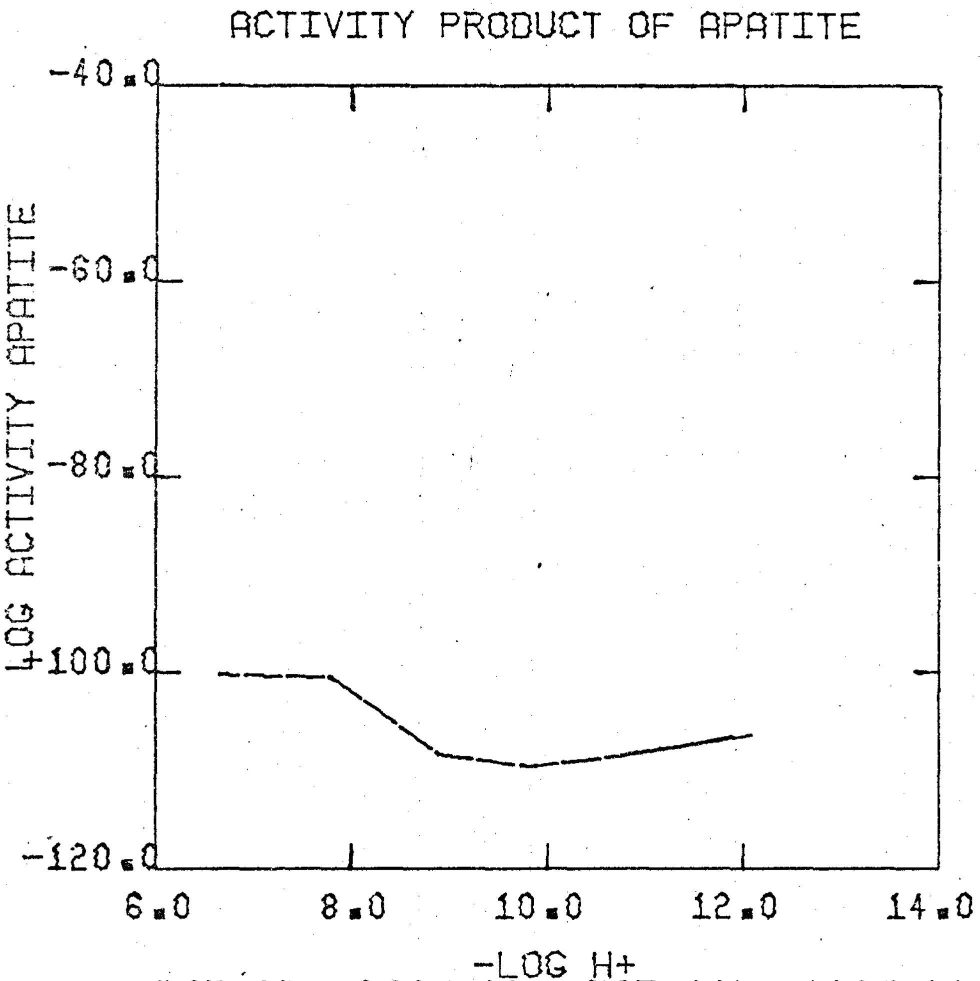
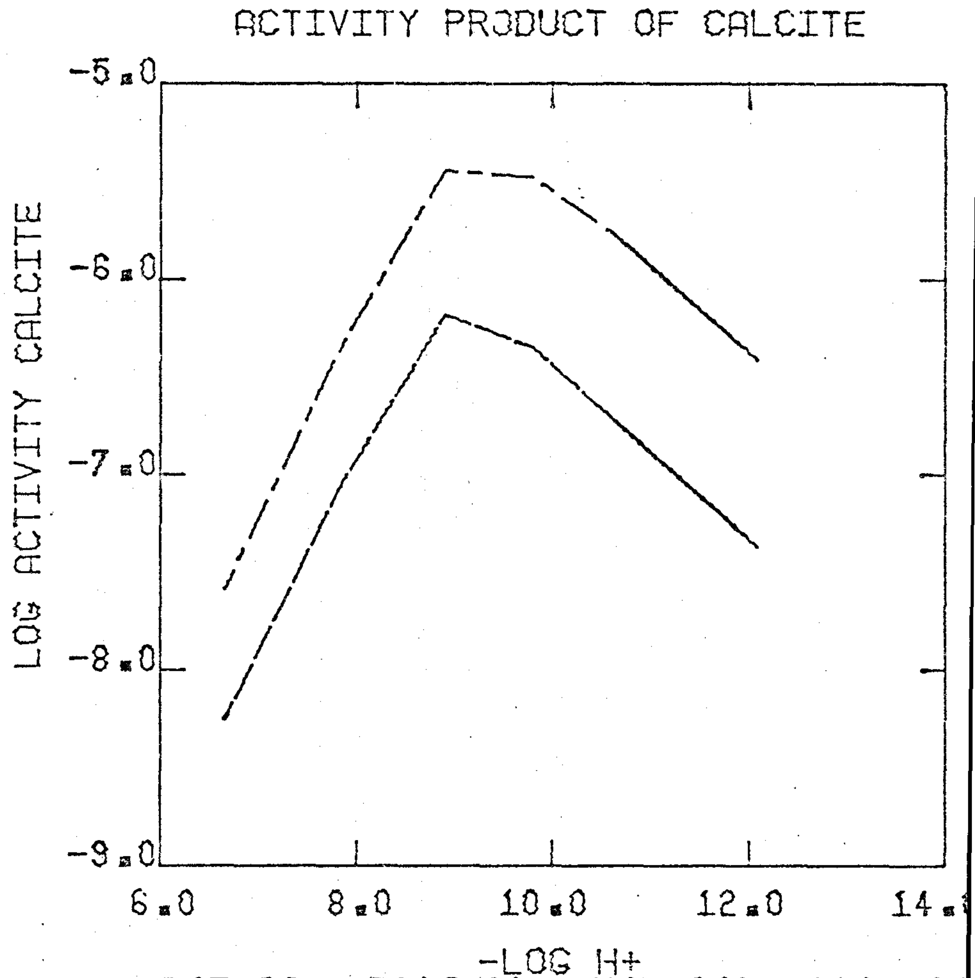
-8.0
-9.0
6.0
8.0
10.0
12.0
14.
-LOG H+
TOT CA= .590E-02   TOT CO3= .220E-0
TOT PO4= .370E-02   TOT MG= .200E-02



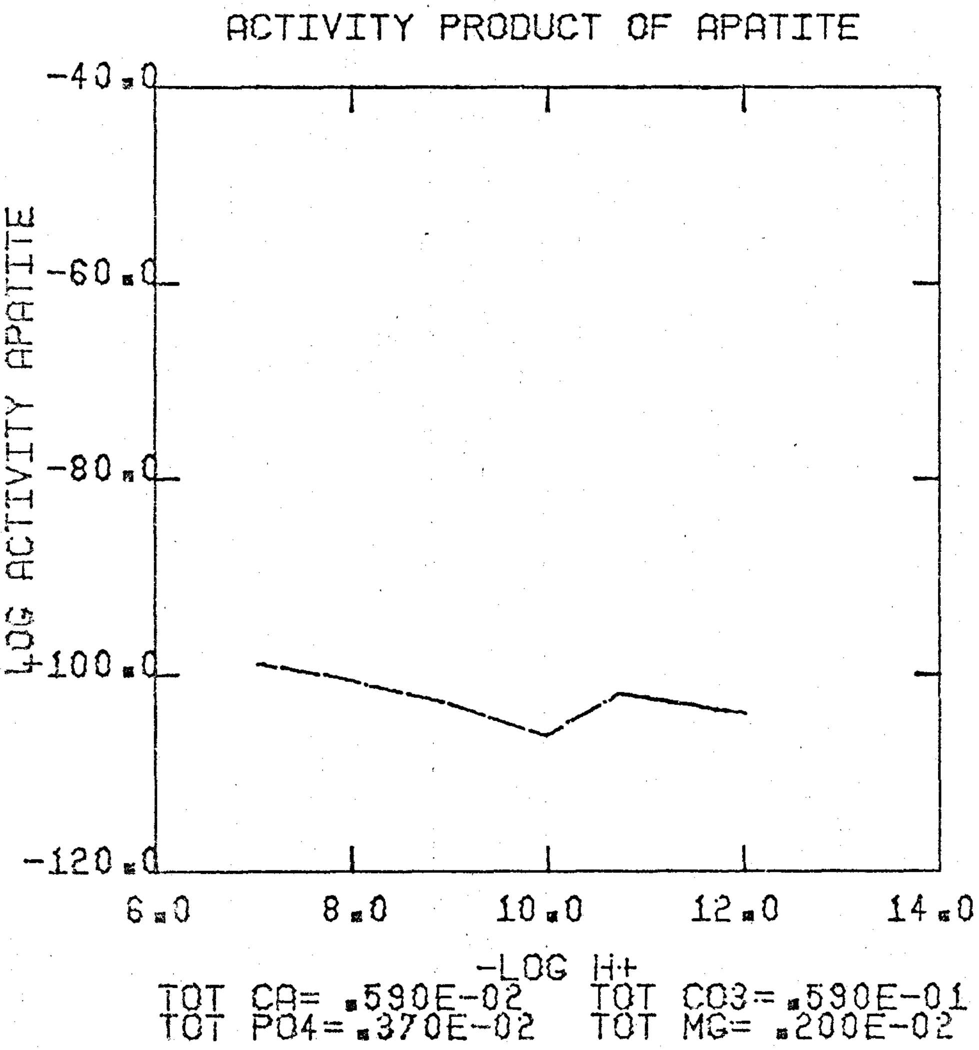
ACTIVITY PRODUCT OF APATITE

TOT CA= .790E-02 TOT CO3= .220E-01
TOT PO4= .370E-02 TOT MG= .200E-02



ACTIVITY PRODUCT OF CALCITE

TOT CA= .790E-02 TOT CO3= .220E-0
TOT PO4= .370E-02 TOT MG= .200E-02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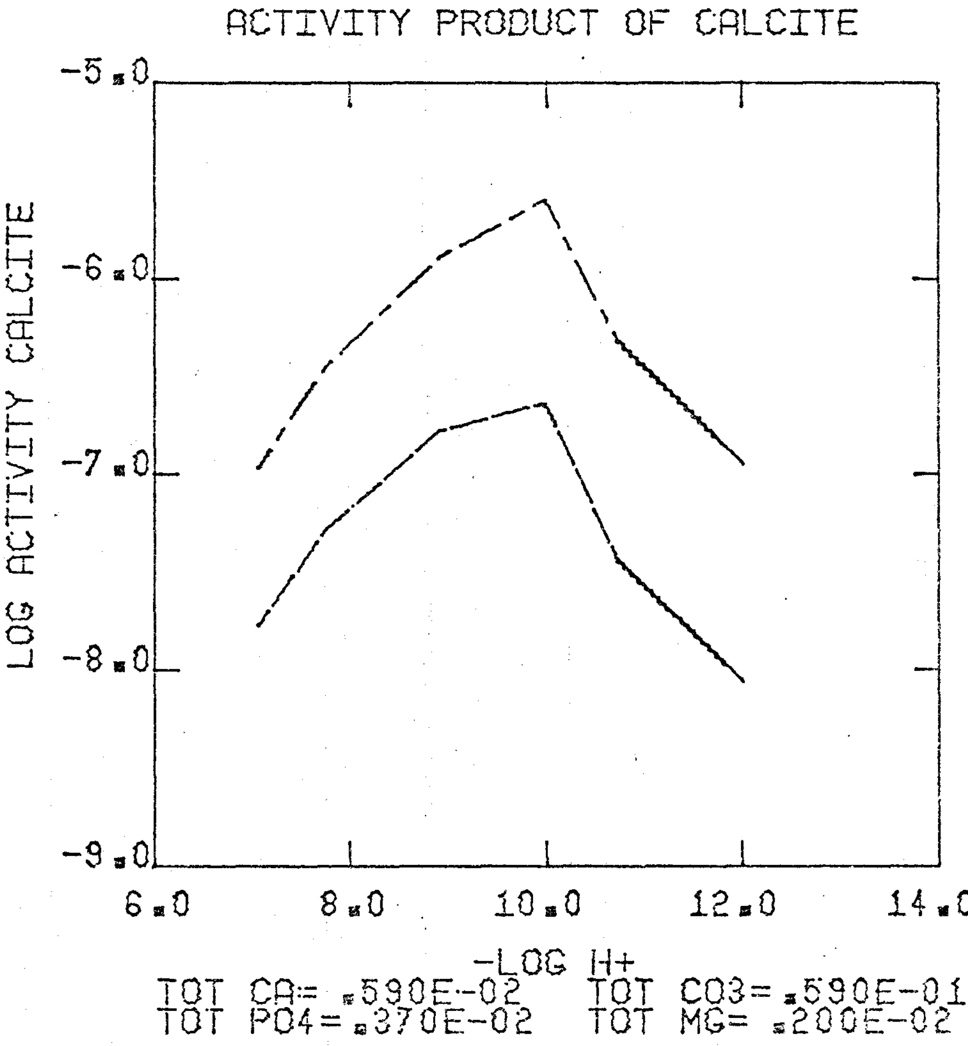
-LOG H+
TOT CA= .590E-02 TOT CO3= .590E-01
TOT PO4= .370E-02 TOT MG= .200E-02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LOG ACTIVITY CALCITE
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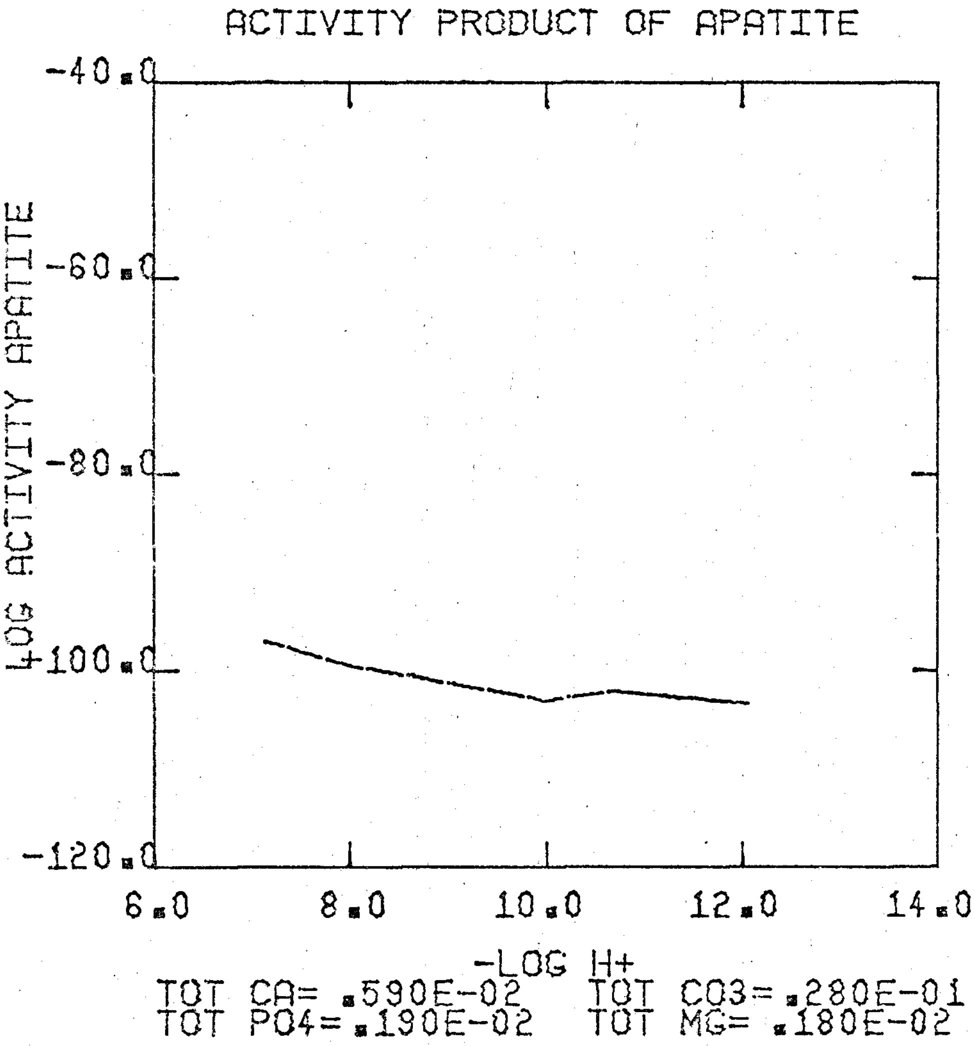
12.0
14.
-LOG H+
TOT CA= .590E-02 TOT CO3= .590E-01
TOT PO4= .370E-02 TOT MG= .200E-02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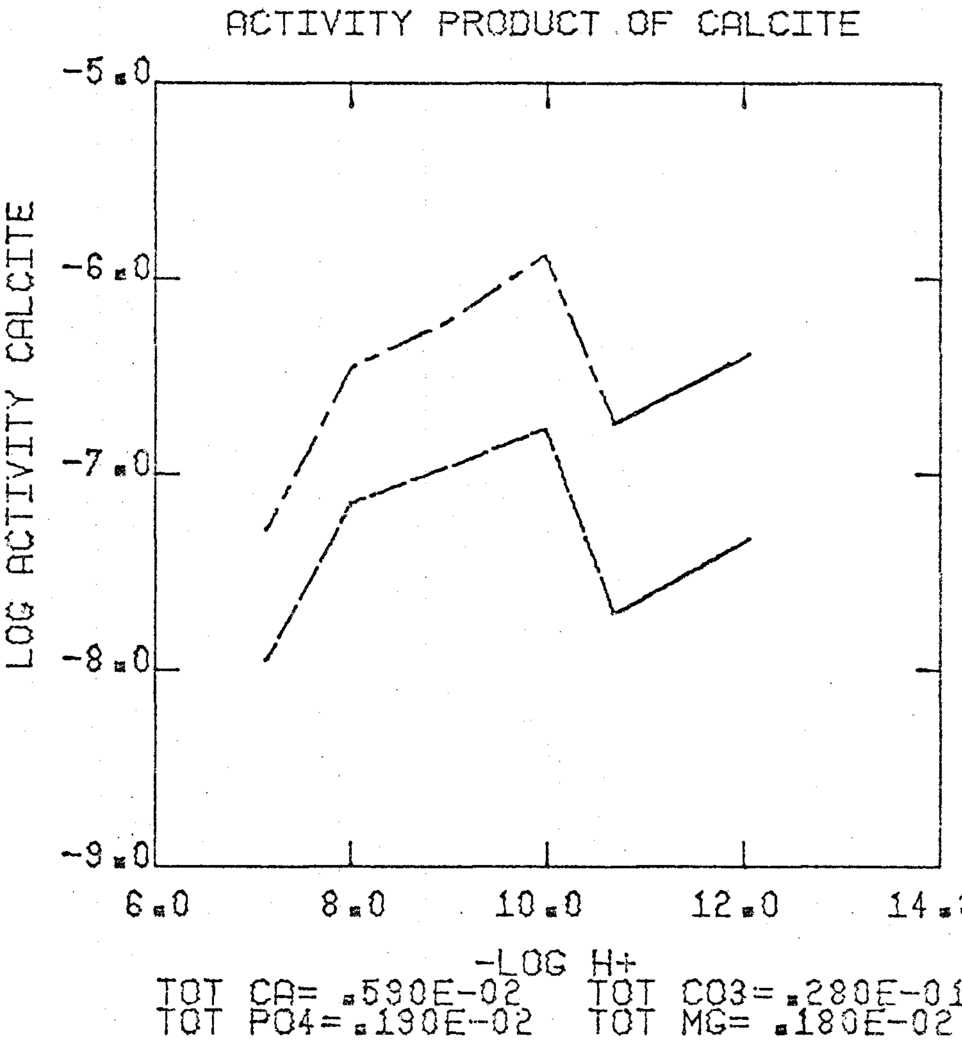
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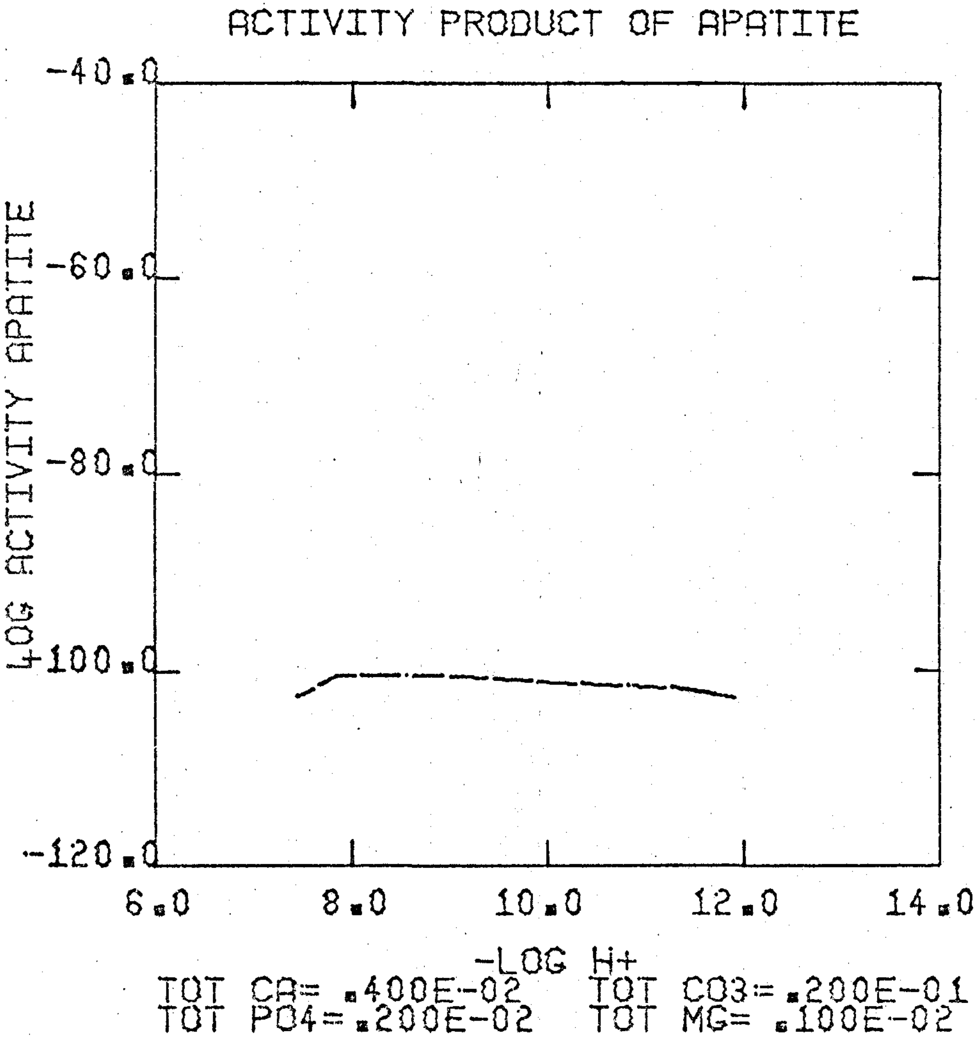
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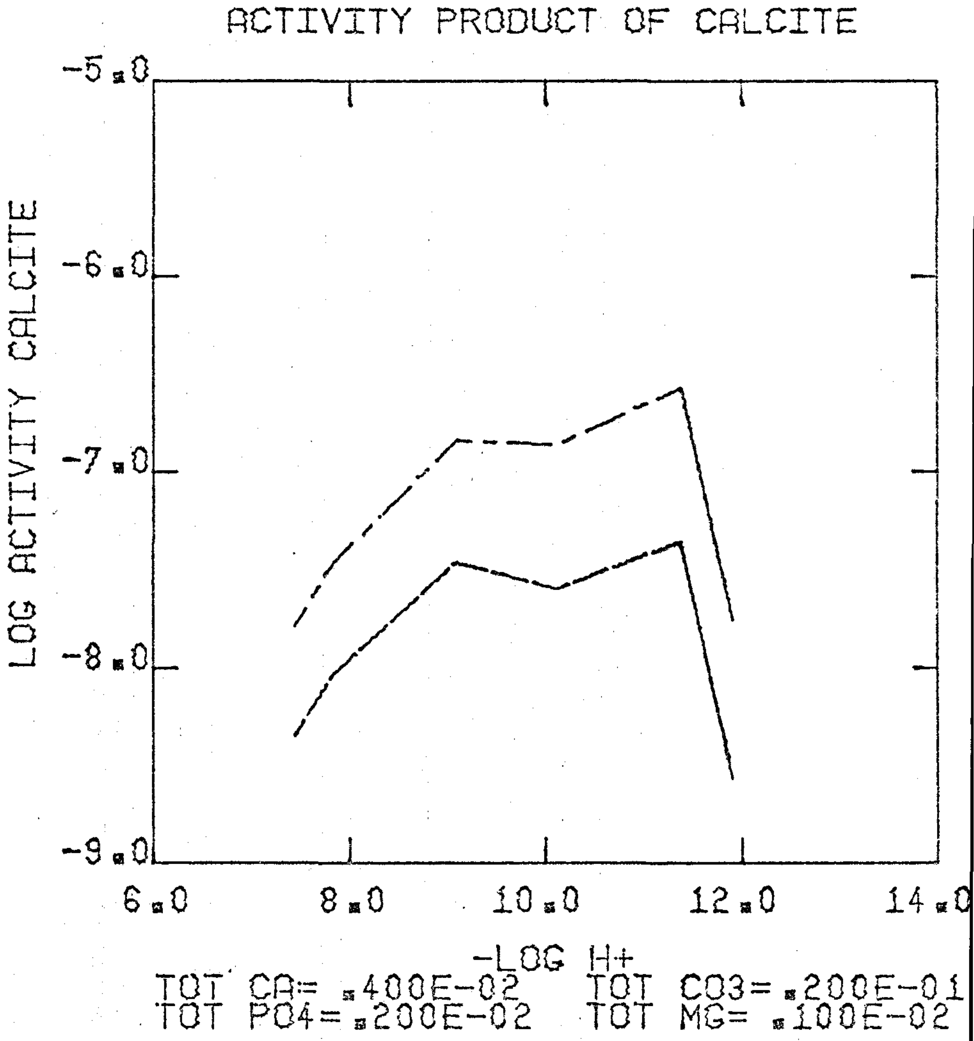
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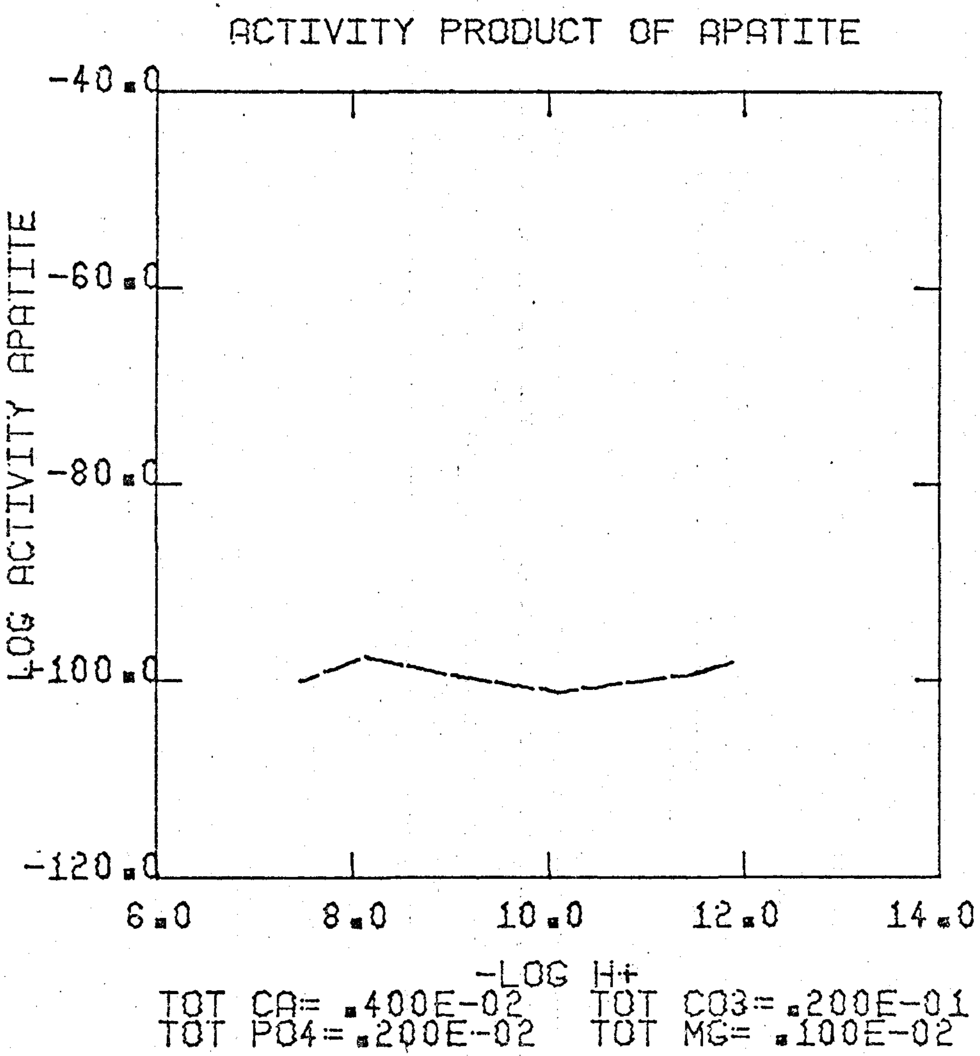
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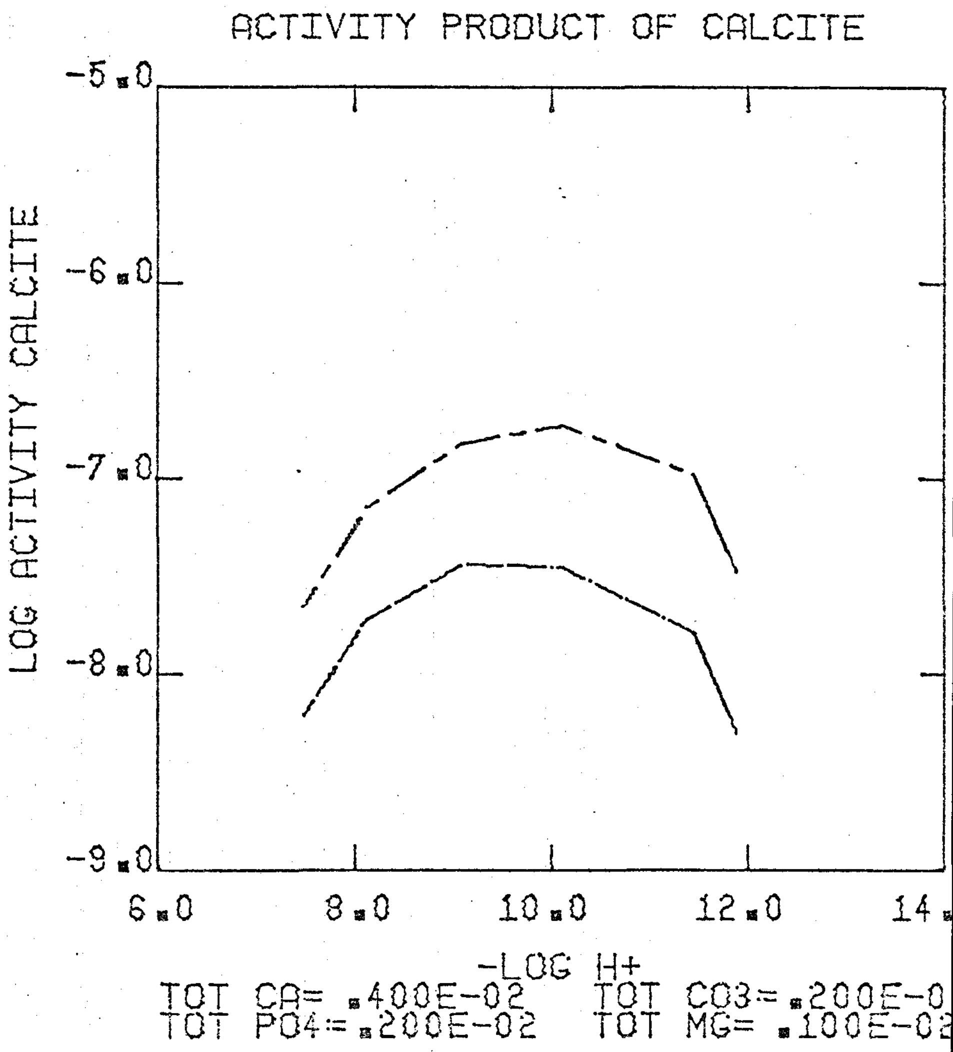
TOT CA= .400E-02 TOT CO3= .200E-01
TOT PO4= .200E-02 TOT MG= .100E-02


ACTIVITY PRODUCT OF CALCITE

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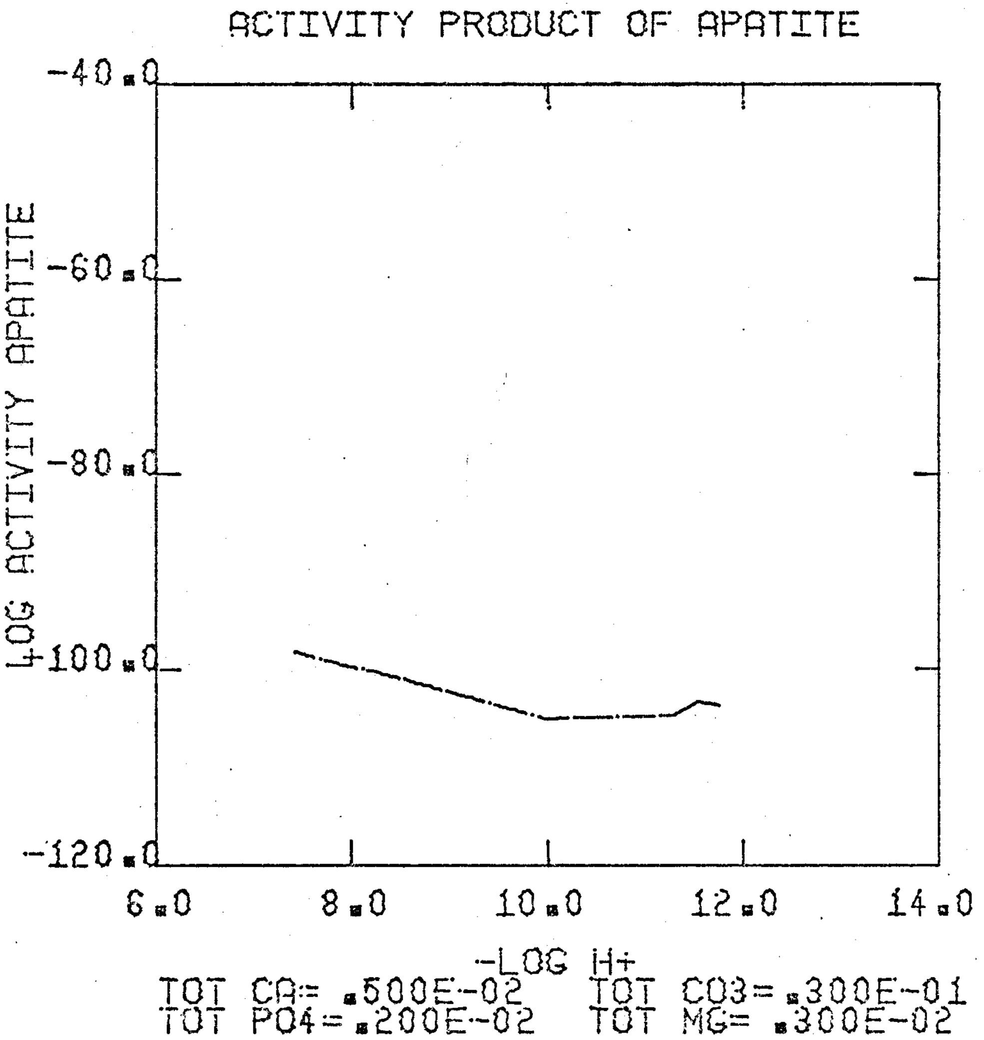
TOT PO4= .200E-02 TOT MG= .100E-0


ACTIVITY PRODUCT OF APATITE
LOG ACTIVITY APATITE
-40.0
-60.0
-80.0
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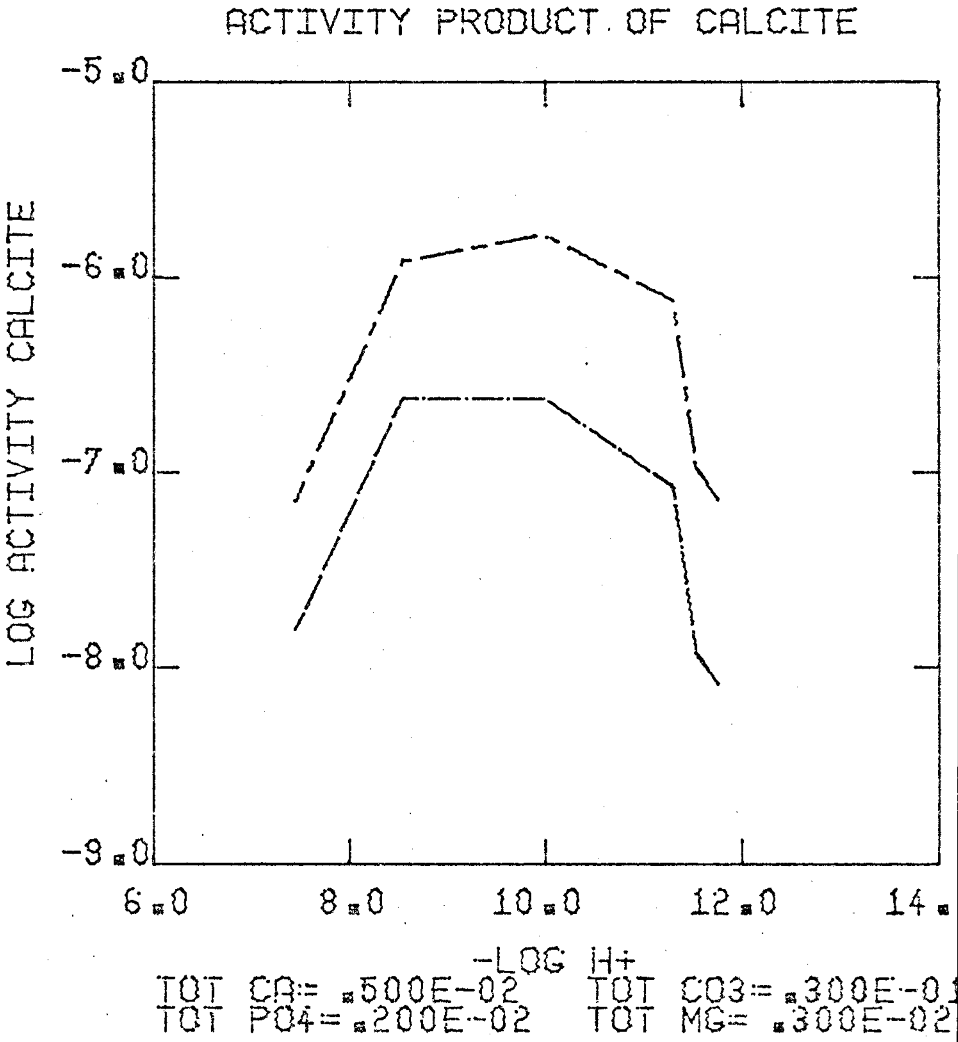
-120.0
6.0
8.0
10.0
12.0
14.0
-LOG H+
TOT CA= .500E-02 TOT CO3= .300E-01
TOT PO4= .200E-02 TOT MG= .300E-02


ACTIVITY PRODUCT OF CALCITE
LOG ACTIVITY CALCITE
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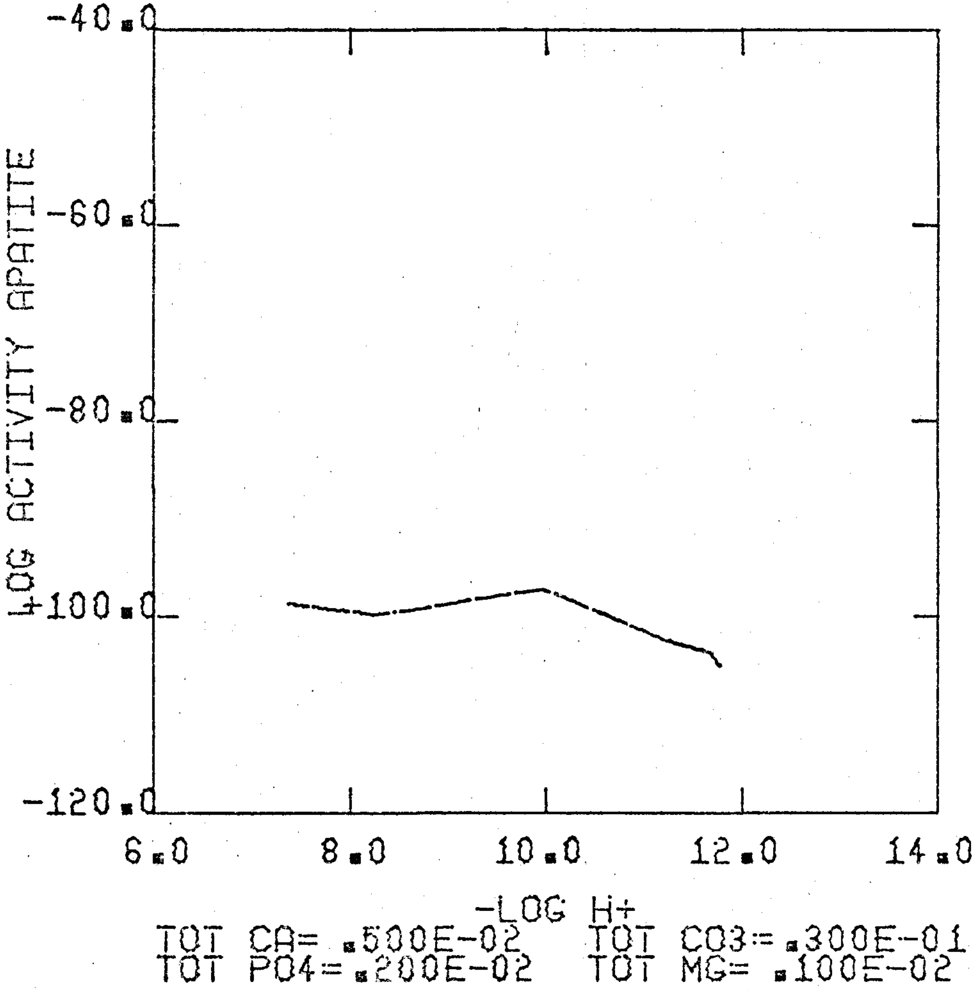
12.0
14.
-LOG H+
TOT CA= .500E-02 TOT CO3= .300E-0
TOT PO4= .200E-02 TOT MG= .300E-02

ACTIVITY PRODUCT OF APATITE



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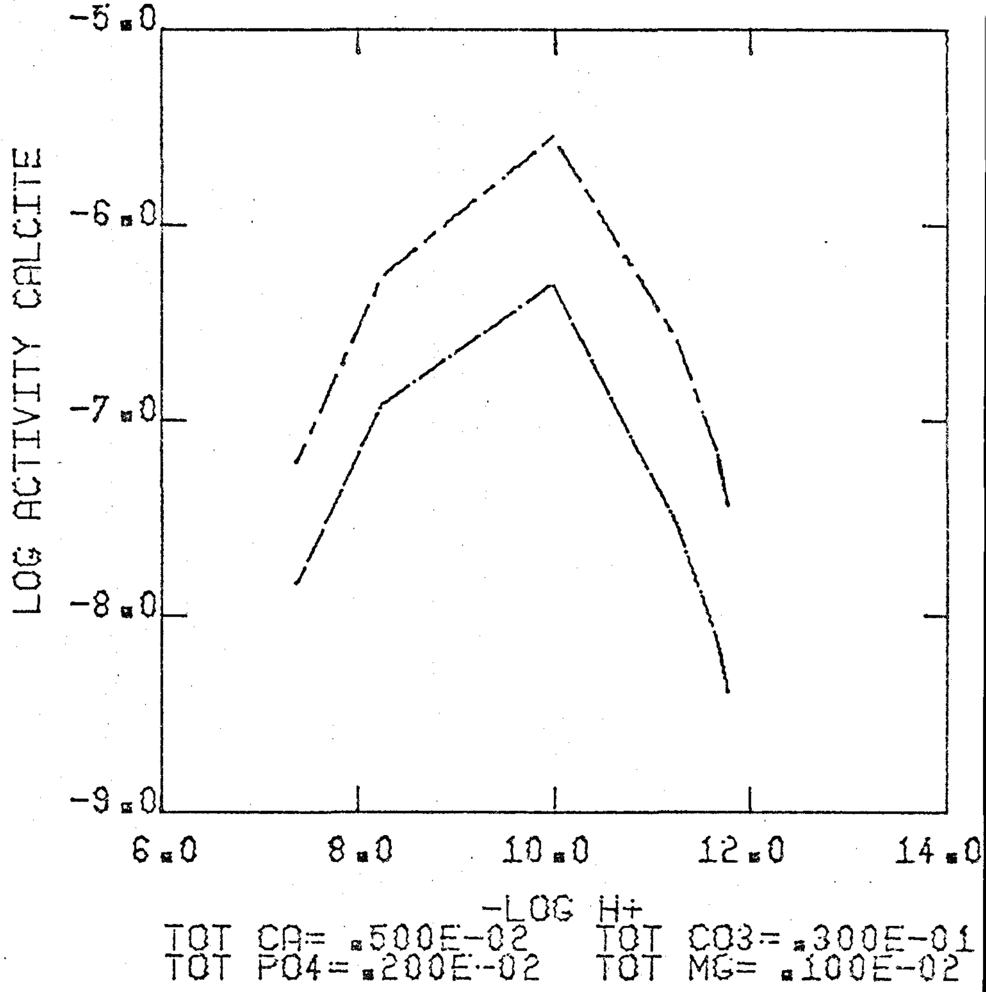

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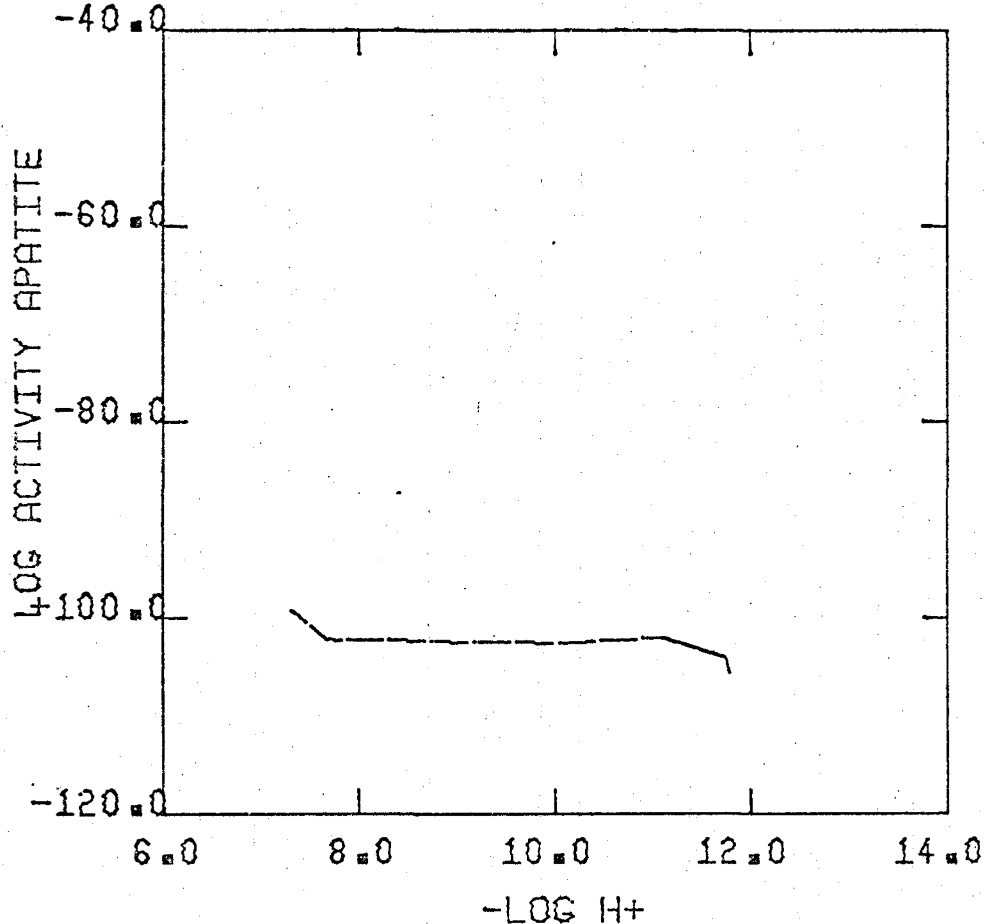
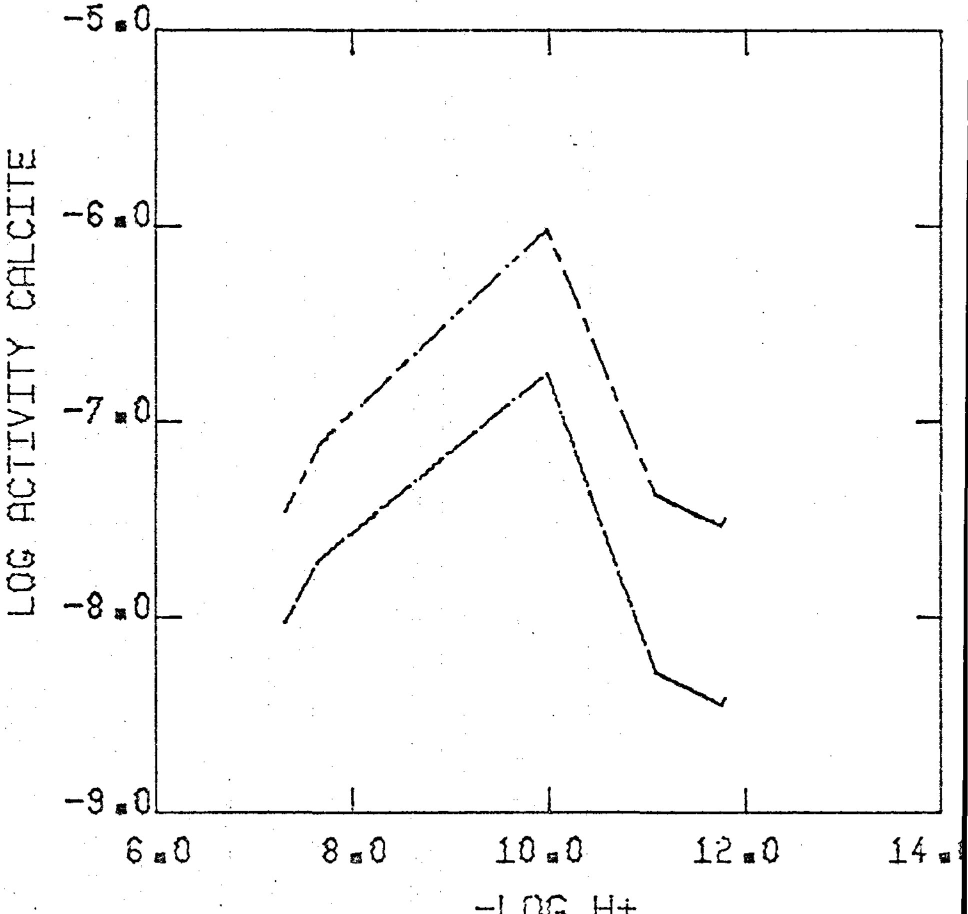


TOT CA= .500E-02 TOT CO3= .300E-01
TOT PO4= .200E-02 TOT MG= .100E-03

ACTIVITY PRODUCT OF CALCITE



TOT CA= .500E-02 TOT CO3= .300E-0
TOT PO4= .200E-02 TOT MG= .100E-03

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