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Contents

Modelling C* - 2003

Vol 64 n° 1

page

- "The effect of hardening by heat treatment for gray cast iron on corrosion rate in H₂SO₄ solutions" S. H. El-Nekhai, Abd Allah A. Mohamed (Egypt) 1
- "Mathematical modelling of weathering process on soil water ions concentration" J. O. Odigire, O. D. Adeniyi (Nigeria) 9
- "Prediction of geoelectric anisotropy over precambrian basement complex: A case study of Iferra area around Ilesa, Osun state SW Nigeria" A. O. Adelus (Nigeria) 21
- "A¹ Dehydrogenation of cortisol by immobilized pseudomonas fluorescens cells entrapped in calcium alginate or polyacrylamide gels" N. Z. Adham, A. A. El-Hady, N. Naim (Egypt) 31
- "Chemical evaluation of annona squamosa seed oil" Elham A. A. Yousel (Egypt) 59

Vol 64 n° 2

page

- "A mathematical model of blood flow through permeable tube" Modh Abdul Rahim, T. R. Ranganatha, M. V. Ramana Murthy (India) 1
- "Application of the three-lump model for the simulation of a fluid catalytic cracking riser reactor" Essio O. Obobo (Nigeria) 17
- "Evaluation of different methods of estimating potential evapotranspiration at samaru northern guinea savannah zone, Zaria-Nigeria" R. N. Edoga, J. J. Owonubi, V. O. Chude, M. O. Edoga (Nigeria) 29
- "Effect of anti-browning and anti-microbial constituents of some spices on the quality and safety of apple juice" Hesham A. Issa, Abd-Elaziz S. Nadir, Kamal I. Hamad (Egypt) 43
- "Chemical analysis of coke from enugu coals and it's suitability for Nigeria's iron and steel industry" Ubaczie Ugochukwu Egerconu (Nigeria) 59

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Mathematical Modelling of Weathering Process On Soil Water Ions Concentration

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Abstract

Weathering and fertilizer applications are two factors responsible for the contribution of minerals to soil water. As a result of chemical reactions within the soil and in the presence of excess water, most of these minerals could be ionized in aqueous solutions, and leached/ transferred to other area. This paper proposes a mathematical model based on the rate of reaction that can be used to predict the extent of soil saturation as a result of weathering of parent rock. The basic principles of chemical thermodynamics of soil have been applied in the development of the model.

Keywords

Mathematical modeling, weathering, fertilizer, soil water ions concentration.

1.0 Introduction

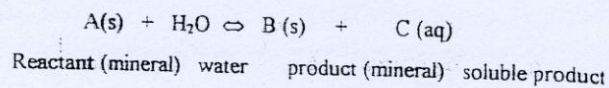
Water on entering the soil becomes acidic due to dissolution of carbon dioxide, carbonic acid and humid compounds. To a large extent water becomes acidic chiefly because of the carbonic acid (H_2CO_3) from the decomposition of organic matter. In the lower parts of the soils strata, and deeper in the ground, the dissolved compounds in water consist mostly of carbonate, sulphate, calcium, magnesium, sodium and potassium ions, with (usually) small amounts of chloride, iron and silica. Common dissolved gases include carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), methane (CH_4), and hydrogen sulphide (H_2S) [Petersen et-al, 1996; Ugolini et-al, 1996; Egharevba, 1999; Adeniyi, 2001].

A major contributor to the presence of ions in soil water is the chemical weathering process. Weathering produces a wide range of changes, minerals are dissolved and the components carried away in solution. This process and its effectiveness vary greatly depending on the environment. The major objective of this research is to develop a mathematical model that could give the concentration of cation and consequently the extent of soil saturation as a result of weathering.

1.1 Chemical thermodynamics of soil reactions

Chemical thermodynamics can be used to calculate the reaction equilibrium, and to determine the stability of minerals in a given environmental condition. The most useful tool for predicting whether or not a soil reaction will occur is to compare the values of Gibbs free energy of formation, ΔG_f° (in kJmol^{-1}) for reactants and products, to obtain a ΔG_r° for the soil reaction.

Consider the reaction:



Then

$$\Delta G_r^\circ = \sum \Delta G_f^\circ [\text{B,C}] - \sum \Delta G_f^\circ [\text{A,H}_2\text{O}]$$

where ΔG_r° = change in Gibbs free energy for the reaction

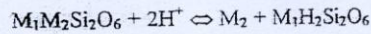
$\sum \Delta G_f^\circ [\text{B,C}]$ = Sum of Gibbs free energies for all the products in their standard states. $\sum \Delta G_f^\circ [\text{A,H}_2\text{O}]$ = Sum of Gibbs free energies for all the reactants in their standard state.

When values of ΔG_f° are negative, then ΔG_f° (reactants) > ΔG_f° (products) and the mineral A in this case, is unstable and the reaction is likely to take place in the forward direction. The driving force of a chemical reaction is the tendency of the free energy of the system to decline until, at equilibrium, the sum of the free energies of the products equals that of the remaining reactants (Ponnamperuma, 1972; Curtis, 1975; Bohn et-al, 1985; Smith et-al, 1996).

1.2 Exchange reactions

Chemisorption is accompanied by a substitution of Ca^{2+} , Na^+ , K^+ cations whose attraction with respect to the oxygen of the crystalline structure is weaker because of their large diameter (Touray, 1980; Scheidegger and Sparks, 1996; Perry, 1997). Following Lasaga (1981) and taking

as an example the weathering of pyroxene, Schott and Berner (1985) proposed (chemisorption and substitution) the following expression for this surface reaction.



The progressive rate of the reaction can be set as:

$$r^- = dn_{M_2} / dt = k_+ x_{m_2} \theta_H^2 \dots\dots\dots 1$$

With θ_H expressed in Langmuir isotherm:

$$K = \theta_H / (m_H - \theta_H) \dots\dots\dots 2$$

$$x_{m_2} = 1 - x_H \dots\dots\dots 3$$

Where θ_H = fraction of the adsorption site occupied by H^+

θ_E = fraction of the adsorption site that is vacant

x_{m_2} = fraction of surface of M_2 sites occupied by M_2 cations

K = equilibrium constant for adsorption

M_H = concentration of H^+ in the solution

x_{m_2} and x_H can be expressed as a function of the number of moles of M_2 cations (n_{M_2px}) and of hydrogen (n_{Hpx}) contained in the M_2 sites of the surface of the pyroxene that is:

$$n_{px} = n_{M_2px} + n_{Hpx} \dots\dots\dots 4$$

Assuming that the number of moles of pyroxenes protonated at the surface is given by:

$$n_{Hpx} = n_{M_2s} - n_{M_1s} \dots\dots\dots 5$$

Where n_{M_2} and n_{M_1} are the number of moles of cations released in solution from sites M_1 and M_2 , Schott and Berner (1985) reached the following expression:

$$r^+ = k_+ K^2 \theta_E^2 m_H^2 - k_- K^2 \theta_E^2 m_H^2 \frac{(n_{m_2s} - n_{m_1s})}{n_{px}} \dots\dots\dots 6$$

For a constant pH, equation 6 implies a linear relationship between the rate of reaction and moles of pyroxenes protonated at the surface. From equation 6:

$$r^+ = k_+ \{ K^2 \theta_E^2 m_H^2 - K^2 \theta_E^2 m_H^2 \frac{(n_{m_2s} - n_{m_1s})}{n_{px}} \} \dots\dots\dots 7$$

Substituting equations 1 into 7 we obtain:

$$k_+ x_{m_2} \theta_H^2 = k_+ \{ K^2 \theta_E^2 m_H^2 - K^2 \theta_E^2 m_H^2 \frac{(n_{m_2s} - n_{m_1s})}{n_{px}} \} \dots\dots\dots 8$$

$$x_{m2}\theta_H^2 = K^2\theta_E^2m_H^2 - K^2\theta_E^2m_H^2 \frac{(n_{m2s} - n_{m1s})}{n_{px}} \dots\dots\dots 9$$

For soil sample such as clay, which can absorb water molecules and thus leave negligible site as vacant (saturated), θ_E becomes negligible (equation 2), consequently,

$$K = \theta_H / m_H \dots\dots\dots 10$$

$$\text{Or } \theta_H = Km_H \dots\dots\dots 11$$

Rearranging equation 9, we have

$$x_{m2} = \frac{K^2\theta_E^2m_H^2}{\theta_H^2} - \frac{K^2\theta_E^2m_H^2}{\theta_H^2n_{px}}(n_{m2s} - n_{m1s}) \dots\dots\dots 12$$

Substituting equation 11 into equation 12 becomes:

$$x_{m2} = \frac{K^2\theta_E^2m_H^2}{K^2m_H^2} - \frac{K^2\theta_E^2m_H^2}{K^2m_H^2n_{px}}(n_{m2s} - n_{m1s}) \dots\dots\dots 13$$

$$x_{m2} = \theta_E^2 - \frac{\theta_E^2}{n_{px}}(n_{m2s} - n_{m1s}) \dots\dots\dots 14$$

From equation 9

$$x_{m2}\theta_H^2 = m_H^2 \left\{ K^2\theta_E^2 - \frac{K^2\theta_E^2}{n_{px}}(n_{m2s} - n_{m1s}) \right\} \dots\dots\dots 15$$

$$\frac{1}{m_H^2} = \frac{K^2\theta_E^2 - \frac{K^2\theta_E^2}{n_{px}}(n_{m2s} - n_{m1s})}{x_{m2}\theta_H^2} \dots\dots\dots 16$$

$$\frac{1}{m_H^2} = \frac{K^2\theta_E^2 \left(1 - \frac{n_{m1s}}{n_{px}} \right)}{x_{m2}\theta_H^2} \dots\dots\dots 17$$

$$\frac{1}{m_H} = \sqrt{\frac{K^2\theta_E^2 \left(1 - \frac{n_{m1s}}{n_{px}} \right)}{x_{m2}\theta_H^2}} \dots\dots\dots 18$$

$$\frac{1}{m_H} = \frac{K \theta_E \sqrt{\left(1 - \frac{n_{H^+}}{n_{H^+}}\right)}}{x_{m2}^{1/2} \theta_H} \dots\dots\dots 19$$

Equation 19 is a reflection of the concentration of any ion in soil relative to H⁺, this is the extent of soil saturation, and it is proportional to the inverse of the hydrogen ion concentration, thus M_H=1/m_H

$$M_H = \frac{K \theta_E \sqrt{\left(1 - \frac{n_{H^+}}{n_{H^+}}\right)}}{x_{m2}^{1/2} \theta_H} \dots\dots\dots 20$$

The equilibrium constant K for a given reaction can be evaluated using

$$\Delta G_r^\circ = -RT \ln K \dots\dots\dots 21$$

$$\Delta G_r^\circ = -2.3026 RT \log K \dots\dots\dots 22$$

Using R= 8.314 x 10⁻³ kJmol⁻¹, T= 298 K

$$\Delta G_r^\circ = - 5.705 \log K$$

$$\log K = - \Delta G_r^\circ / 5.705 \dots\dots\dots 23$$

The values of ΔG_r[°] and ΔG_r[°] for three types of clay soil are presented in table 1 (Ross, 1989):

Table 1: Gibb's free energy

Soil type	ΔG _r [°] (KJ/mol)	ΔG _r [°] (KJ/mol)
1. Albite (NaAlSi ₃ O ₈)	-3708.32	43.555
2. Anorthite (CaAl ₂ Si ₂ O ₈)	-3992.79	47.614
3. Kaolinite [Al ₂ Si ₂ O ₅ (OH) ₄]	-3789.07	-

Therefore the K values for some clay can be calculated

For Albite:

$$\log K = -\Delta G_r^\circ / 5.705 = -43.555/5.705 = -7.635$$

$$K = 2.32 \times 10^{-8}$$

And for anorthite:

$$\log k = -47.614/5.705 = -8.346$$

$$K = 4.51 \times 10^{-9}$$

At a constant pH, equation 7 implies a linear relationship between the rate of the exchange reaction and the number of moles of pyroxene protonated at the surface.

1.3 Dissolution reaction and pH

The rate of reaction depends on the pH, or the activity of H⁺ ions or H₃O⁺, designated respectively a_{H⁺} or a_{H₃O⁺}. In the case of the congruent dissolution of mineral θ, the rate of dissolution can be written in the form (Lasaga, 1981, 1984):

$$dC_i/dt(\text{dissolution}) = (A_\theta/V) \cdot v_i \cdot K_\theta \dots\dots\dots 24$$

In which, v_i is the stoichiometric content of 'i' in mineral θ and K_θ the overall dissolution rate of mineral θ; A_θ is the surface area of mineral θ; V is the volume of solution in contact with mineral θ; the ratio dC_i/dt expresses the change of concentration of element i due only to mineral θ (Schott and Petit, 1987).

2.0 Results

Equation 20 was simulated using experimental data obtained from irrigational sites in Kerawa small earth dam between 1991 and 1995, Niger State, Nigeria. Three cations were considered and the results are presented in the tables 2-7:

Table 2: Simulated concentration and pH using Phosphorus (P³⁺)[1991/92]

n _{Hpx} /n _{px}	θ _H =0.20		θ _H =0.25		θ _H =0.30		Experimental	
	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	PH	M _H (mg/L)	pH
0.000126	1.45x10 ⁻⁷	6.84	1.09x10 ⁻⁷	6.96	8.47x10 ⁻⁸	7.07	7.94x10 ⁻⁸	7.10
0.100126	1.37x10 ⁻⁷	6.86	1.03x10 ⁻⁷	6.98	8.00x10 ⁻⁸	7.10		
0.200126	1.30x10 ⁻⁷	6.89	9.71x10 ⁻⁸	7.01	7.58x10 ⁻⁸	7.12		
0.300126	1.21x10 ⁻⁷	6.92	9.09x10 ⁻⁸	7.04	7.04x10 ⁻⁸	7.15		
0.400126	1.12x10 ⁻⁷	6.95	8.40x10 ⁻⁸	7.07	6.54x10 ⁻⁸	7.18		
0.500126	1.02x10 ⁻⁷	6.99	7.69x10 ⁻⁸	7.11	5.99x10 ⁻⁸	7.22		
0.600126	9.17x10 ⁻⁸	7.04	6.85x10 ⁻⁸	7.16	5.35x10 ⁻⁸	7.27		
0.700126	7.94x10 ⁻⁸	7.10	5.95x10 ⁻⁸	7.23	4.63x10 ⁻⁸	7.33		
0.800126	6.49x10 ⁻⁸	7.19	4.85x10 ⁻⁸	7.31	3.77x10 ⁻⁸	7.42		
0.900126	4.59x10 ⁻⁸	7.34	3.44x10 ⁻⁸	7.46	2.67x10 ⁻⁸	7.57		

Table 3: Simulated concentration and pH using Nitrogen (N⁻)[1991/92]

$\theta_{H_2O}/\theta_{max}$	$\theta_H=0.20$		$\theta_H=0.25$		$\theta_H=0.30$		Experimental	
	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH
0.00000198	1.45x10 ⁻⁷	6.84	1.09x10 ⁻⁷	6.96	8.47x10 ⁻⁸	7.07	7.94x10 ⁻⁸	7.10
0.10000198	1.37x10 ⁻⁷	6.86	1.03x10 ⁻⁷	6.98	8.00x10 ⁻⁸	7.10		
0.20000198	1.30x10 ⁻⁷	6.89	9.71x10 ⁻⁸	7.01	7.58x10 ⁻⁸	7.12		
0.30000198	1.21x10 ⁻⁷	6.92	9.09x10 ⁻⁸	7.04	7.04x10 ⁻⁸	7.15		
0.40000198	1.12x10 ⁻⁷	6.95	8.40x10 ⁻⁸	7.07	6.54x10 ⁻⁸	7.18		
0.50000198	1.02x10 ⁻⁷	6.99	7.69x10 ⁻⁸	7.11	5.99x10 ⁻⁸	7.22		
0.60000198	9.17x10 ⁻⁸	7.04	6.85x10 ⁻⁸	7.16	5.35x10 ⁻⁸	7.27		
0.70000198	7.94x10 ⁻⁸	7.10	5.95x10 ⁻⁸	7.23	4.63x10 ⁻⁸	7.33		
0.80000198	6.49x10 ⁻⁸	7.19	4.85x10 ⁻⁸	7.31	3.77x10 ⁻⁸	7.42		
0.90000198	4.59x10 ⁻⁸	7.34	3.44x10 ⁻⁸	7.46	2.67x10 ⁻⁸	7.57		

Table 4: Simulated concentration and pH using Potassium (K⁺)[1991/92]

$\theta_{H_2O}/\theta_{max}$	$\theta_H=0.20$		$\theta_H=0.25$		$\theta_H=0.30$		Experimental	
	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH
0.00000836	1.45x10 ⁻⁷	6.84	1.09x10 ⁻⁷	6.96	8.47x10 ⁻⁸	7.07	7.94x10 ⁻⁸	7.10
0.10000836	1.37x10 ⁻⁷	6.86	1.03x10 ⁻⁷	6.98	8.00x10 ⁻⁸	7.10		
0.20000836	1.30x10 ⁻⁷	6.89	9.71x10 ⁻⁸	7.01	7.58x10 ⁻⁸	7.12		
0.30000836	1.21x10 ⁻⁷	6.92	9.09x10 ⁻⁸	7.04	7.04x10 ⁻⁸	7.15		
0.40000836	1.12x10 ⁻⁷	6.95	8.40x10 ⁻⁸	7.07	6.54x10 ⁻⁸	7.18		
0.50000836	1.02x10 ⁻⁷	6.99	7.69x10 ⁻⁸	7.11	5.99x10 ⁻⁸	7.22		
0.60000836	9.17x10 ⁻⁸	7.04	6.85x10 ⁻⁸	7.16	5.35x10 ⁻⁸	7.27		
0.70000836	7.94x10 ⁻⁸	7.10	5.95x10 ⁻⁸	7.23	4.63x10 ⁻⁸	7.33		
0.80000836	6.49x10 ⁻⁸	7.19	4.85x10 ⁻⁸	7.31	3.77x10 ⁻⁸	7.42		
0.90000836	4.59x10 ⁻⁸	7.34	3.44x10 ⁻⁸	7.46	2.67x10 ⁻⁸	7.57		

Table 5: Simulated concentration and pH using Phosphorus (P³⁺)[1991/95]

$\theta_{H_2O}/\theta_{max}$	$\theta_H=0.20$		$\theta_H=0.25$		$\theta_H=0.30$		Experimental	
	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH	M _H (mg/L)	pH
0.000141	1.45x10 ⁻⁷	6.84	1.09x10 ⁻⁷	6.96	8.47x10 ⁻⁸	7.07	8.91x10 ⁻⁸	7.05
0.100141	1.37x10 ⁻⁷	6.86	1.03x10 ⁻⁷	6.98	8.00x10 ⁻⁸	7.10		
0.200141	1.30x10 ⁻⁷	6.89	9.71x10 ⁻⁸	7.01	7.58x10 ⁻⁸	7.12		
0.300141	1.21x10 ⁻⁷	6.92	9.09x10 ⁻⁸	7.04	7.04x10 ⁻⁸	7.15		
0.400141	1.12x10 ⁻⁷	6.95	8.40x10 ⁻⁸	7.07	6.54x10 ⁻⁸	7.18		
0.500141	1.02x10 ⁻⁷	6.99	7.69x10 ⁻⁸	7.11	5.99x10 ⁻⁸	7.22		
0.600141	9.17x10 ⁻⁸	7.04	6.85x10 ⁻⁸	7.16	5.35x10 ⁻⁸	7.27		
0.700141	7.94x10 ⁻⁸	7.10	5.95x10 ⁻⁸	7.23	4.63x10 ⁻⁸	7.33		
0.800141	6.49x10 ⁻⁸	7.19	4.85x10 ⁻⁸	7.31	3.77x10 ⁻⁸	7.42		
0.900141	4.59x10 ⁻⁸	7.34	3.44x10 ⁻⁸	7.46	2.67x10 ⁻⁸	7.57		

Table 6: Simulated concentration and pH using Nitrogen (N⁺)[1991/95]

n_{Hpx}/n_{px}	$\theta_H=0.20$		$\theta_H=0.25$		$\theta_H=0.30$		Experimental	
	M_H (mg/L)	pH	M_H (mg/L)	pH	M_H (mg/L)	pH	M_H (mg/L)	pH
0.00000213	1.45×10^{-7}	6.84	1.09×10^{-7}	6.96	8.47×10^{-8}	7.07	8.91×10^{-8}	7.05
0.10000213	1.37×10^{-7}	6.86	1.03×10^{-7}	6.98	8.00×10^{-8}	7.10		
0.20000213	1.30×10^{-7}	6.89	9.71×10^{-8}	7.01	7.58×10^{-8}	7.12		
0.30000213	1.21×10^{-7}	6.92	9.09×10^{-8}	7.04	7.04×10^{-8}	7.15		
0.40000213	1.12×10^{-7}	6.95	8.40×10^{-8}	7.07	6.54×10^{-8}	7.18		
0.50000213	1.02×10^{-7}	6.99	7.69×10^{-8}	7.11	5.99×10^{-8}	7.22		
0.60000213	9.17×10^{-8}	7.04	6.85×10^{-8}	7.16	5.35×10^{-8}	7.27		
0.70000213	7.94×10^{-8}	7.10	5.95×10^{-8}	7.23	4.63×10^{-8}	7.33		
0.80000213	6.49×10^{-8}	7.19	4.85×10^{-8}	7.31	3.77×10^{-8}	7.42		
0.90000213	4.59×10^{-8}	7.34	3.44×10^{-8}	7.46	2.67×10^{-8}	7.57		

Table 7: Simulated concentration and pH using Potassium (K⁺)[1991/95]

n_{Hpx}/n_{px}	$\theta_H=0.20$		$\theta_H=0.25$		$\theta_H=0.30$		Experimental	
	M_H (mg/L)	pH	M_H (mg/L)	pH	M_H (mg/L)	pH	M_H (mg/L)	pH
0.00000484	1.45×10^{-7}	6.84	1.09×10^{-7}	6.96	8.47×10^{-8}	7.07	8.91×10^{-8}	7.05
0.10000484	1.37×10^{-7}	6.86	1.03×10^{-7}	6.98	8.00×10^{-8}	7.10		
0.20000484	1.30×10^{-7}	6.89	9.71×10^{-8}	7.01	7.58×10^{-8}	7.12		
0.30000484	1.21×10^{-7}	6.92	9.09×10^{-8}	7.04	7.04×10^{-8}	7.15		
0.40000484	1.12×10^{-7}	6.95	8.40×10^{-8}	7.07	6.54×10^{-8}	7.18		
0.50000484	1.02×10^{-7}	6.99	7.69×10^{-8}	7.11	5.99×10^{-8}	7.22		
0.60000484	9.17×10^{-8}	7.04	6.85×10^{-8}	7.16	5.35×10^{-8}	7.27		
0.70000484	7.94×10^{-8}	7.10	5.95×10^{-8}	7.23	4.63×10^{-8}	7.33		
0.80000484	6.49×10^{-8}	7.19	4.85×10^{-8}	7.31	3.77×10^{-8}	7.42		
0.90000484	4.59×10^{-8}	7.34	3.44×10^{-8}	7.46	2.67×10^{-8}	7.57		

3.0 Discussion of result

Three different fractions (θ_H , extent of soil saturation) of the site occupied by H^+ were considered under this model (based on equation 20); thus giving three different pH and M_H (concentration of H^+) simulated values, as presented in tables 2 to 7. The fraction (x_{m2}) of the cation was kept constant for different extent of saturation (Adeniyi, 2001).

Comparative analysis of possible change in the retentive ability of the soil for various cations between the year 1992 and 1991 at Kerawa dam for different n_{Hpx}/n_{px} , are presented in table 2 to 4. Likewise the relative change in concentration for three cations between the year 1995 and

1991 for the same Kerawa dam are presented in table 5 to 7. Simulated results for the site shows the same patterns of concentration change (M_H) and pH for the years under review.

Table 2 shows the simulated soil water pH values in Kerawa dam (1991/92) for various extent of soil saturation using phosphorus (P^{3+}). The n_{pHx}/n_{px} fractions used for simulation were varied from 0.000126 to 1.0. Results in table 2 showed that the optimum extent of soil saturation that best fit the experimental pH value was 0.25 and the corresponding n_{pHx}/n_{px} value was between 0.4 - 0.5. Fractions higher than this lead to higher pH values. The optimum M_H value was between 8.40×10^{-8} to 7.69×10^{-8} mg/L.

The results reveal that the higher the fraction of n_{pHx}/n_{px} , the higher the M_H and pH values. Full saturation can be achieved at $\theta_H = 1.0$ and the corresponding M_H and pH will then be zero. For the year 1991/92 the optimum value of saturation that gave the H^+ concentration close to an experimental pH value of 7.10, assuming extent of soil saturation of 0.3 was at 0.100126. Between 1991/95 the value was 0.100141, this gives a difference of 0.000015 for n_{pHx}/n_{px} . This difference remains relatively the same for other pH and extent of soil saturation values considered.

The similarity in simulated and experimental values within the saturation limit θ_H as presented in the tables can be attributed to the fact that the rate of dissolution of these minerals from the bedrock mineral to the soil is very slow (Nahon, 1991; Petersen et-al, 1996; ugolini et-al, 1996). The dissolution constant (k_d) calculated for Kerawa in 1991/92 and 1991/95 was 2.32×10^{-8} . Consequently the time (t) required to dissolve a unit crystal of the parent rock is 4.32×10^7 years using equation 24. The rate of dissolution of the parent mineral is therefore very slow; consequently within the time considered in this work (1991 to 1995), the expected changes are highly negligible. It therefore follows that observed changes in cations concentration in irrigated farmland is insignificantly influenced by the weathering of the parent rock. Cations concentration change is therefore mainly as a result of external influences.

4.0 Conclusion

From this work, the following conclusions can be deduced; the depletion of ions in soil is greatly dependent on the type of soil, pH of the soil water, interaction among the cations present in soil and removal by leaching, plants and living organisms. It is almost independent on the rate of weathering of the parent rock and dependent on external factors. The developed mathematical model, to a good extent showed the contribution of weathering process to the soil cation concentration at a given extent of soil saturation.

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