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The simulation of geochemical reactions in the Heng-Chun limestone formation, Taiwan

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The potential for dissolution of the limestone formations in coastal freshwater-saltwater mixing zones can be analyzed by a geochemical transport model. Geochemical mixing theory suggests that mixing of sea water and calcite-saturated fresh groundwater can result in a solution that is undersaturated with respect to calcite and can lead to significant dissolution of carbonate rocks. The purpose of this study is to investigate the possible mechanisms of the limestone dissolution in Heng-Chun in southwestern Taiwan. The geochemical model EQ3NR / 6 and the geochemical transport model HYDROGEOCHEM are used to simulate a series of chemical reactions and solute transport. The input data for the simulation of groundwater quality and hydrogeological parameters were obtained from 24 wells around the Heng-Chun coastal area with reasonably simplified boundary conditions. Results of the simulation suggest that the dissolution process is not controlled by chemical reactions but strongly depends on the groundwater flow.

Keywords: simulation, geochemical reactions, limestone

1. Introduction

The coral limestone formation is an important geological formation in southwestern Taiwan. Because of the loose packing of the coral limestone, it is easy for rainwater to permeate. Only few surface streams are found in this formation. The water has dissolved part of the limestone, forming disappearing streams or sinkholes and creating the well-known karst formation. Evolution of the karst formation involves complicated rock/water interactions and solute transport. Dissolution of the limestone will form caverns.

Recently there was huge land subsidence in Florida resulting from the dissolution of the underground limestone formation, which caused serious damage to several building foundations. Therefore, understanding the possible mechanisms of the dissolution of limestone is of great interest to hydrogeochemists and engineering geologists. The study area, Heng-Chun, is located in southwestern Taiwan, as shown in *Figure 1*; a hill is located to the east, and a terrace is located to the west. Because of the shortage of surface water, the water resources are mainly from groundwater. The structures of this area consist of the Ti-Ping formation, the Shi-Tsi formation, the Heng-Chun limestone formation, and the Mar-Ain formation.

Tsao et al.[1] conducted a study to evaluate the groundwater resources in Heng-Chun, in which monitoring wells were constructed to provide the local hydrogeological and groundwater quality data. In addition to the original 10 monitoring wells, 14 new wells, E10–E24 as shown in *Figure 2*, were constructed. A series of tests, including pumping tests and the slug tests, was conducted. Groundwater from these 24 monitoring wells was sampled and analyzed monthly over a period of 1 year. The piper diagrams and ratios of the chloride concentrations to the carbonate concentrations were constructed to understand the extent of sea water intrusion in this area. Tsao et al.[1] concluded that sea water intrusion only occurred in the outlet of the freshwater stream to the sea. When the new monitoring wells were drilled, core records revealed some

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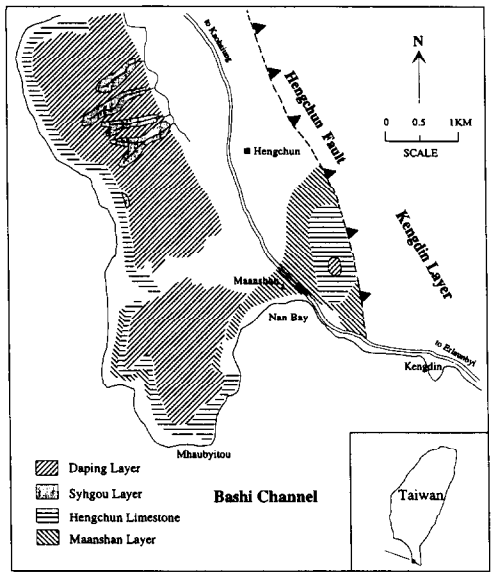

Figure 1. The geological formation diagram of Heng-Chun.[1]

limestone formations containing solution caverns, as shown in *Figure 3*. The local hydrogeological properties in Heng-Chun seem to be strongly influenced by these limestone formations.

The purpose of the current study was to investigate the possible mechanisms of formation of the limestone caverns. Since the creation of the limestone caverns involves complicated geochemical reactions and solute transport, it was decided to investigate the key formation process by

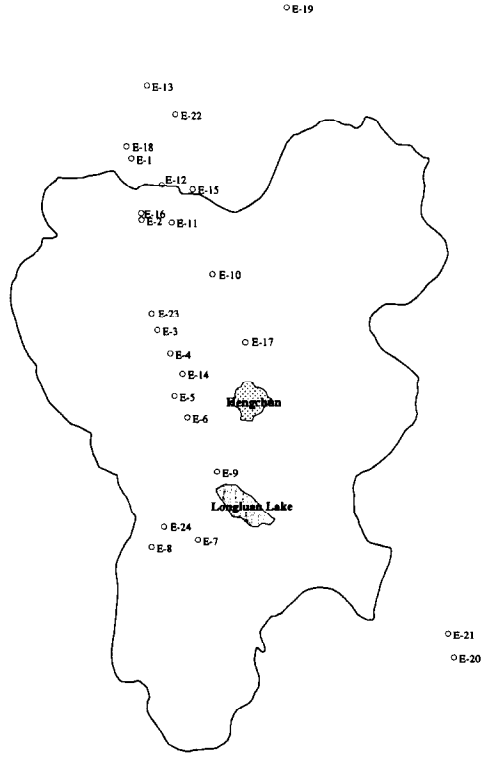

Figure 2. The location of monitoring wells.[1]

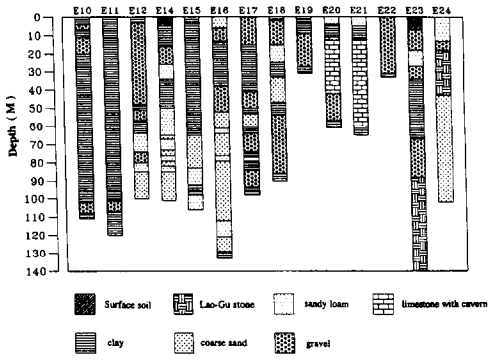

Figure 3. The core record of monitoring wells at Heng-Chun.[1]

starting from the modelling of the chemical reactions and solute transport. The geochemical model EQ3NR/6[2,3] and the geochemical transport model HYDROGEOCHEM[4] are applied to simulate geochemical interaction and solute transport. The simulation results are analyzed, and the possible formation process are discussed.

2. Literature review

The formation of a karst groundwater system involves a complicated reactive chemical transport process, and hydrogeochemists have been very interested in studying the interaction of dissolution/precipitation occurring within it. Cooper[5] and Kohout[6] studied the Biscayne aquifer in Florida and noted that some sea water was present in the water that discharged from the aquifer. They concluded that sea water also circulates in this aquifer, creating a "mixing zone" or "zone of dispersion" rather than a sharp interface (*Figure 4*). Henry[7] later demonstrated that the position and the width of the mixing zone are affected by other factors, such as tides, freshwater recharge, and groundwater withdrawal from wells.

The freshwater-saltwater mixing zone has been identified as the potential site of geochemical activities. Runnels[8] pointed out that when two liquids are mixed, the species concentrations in the mixed liquid are volume-weighted averages of the two end-member concentrations. However, the equilibrium equations for the ionic speciations and the relationship between the activity coefficients and the ionic strength are not linear; the two end-member solutions could be saturated with respect to a given mineral, but the mixed solution could be either undersaturated or supersaturated (*Figure 5*). This nonlinear ionic-strength effect on the calcite solubility has been demonstrated experimentally by Frear and Johnston.[9]

In coastal carbonate aquifers, the two end-member solutions are sea water and groundwater. When calcite-saturated groundwater combines in the mixing zone with sea water that is supersaturated with respect to calcite, the resulting mixture may be undersaturated with respect to calcite. Recently, extensive dissolution features have been observed in the freshwater-saltwater mixing zones in certain coastal carbonate rocks. Such features were described by Back et al.[10] in the carbonate rocks along the coast of the

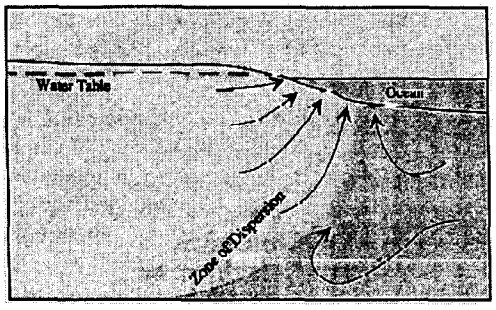

Figure 4. The mixing zone at Biscayne.[6]

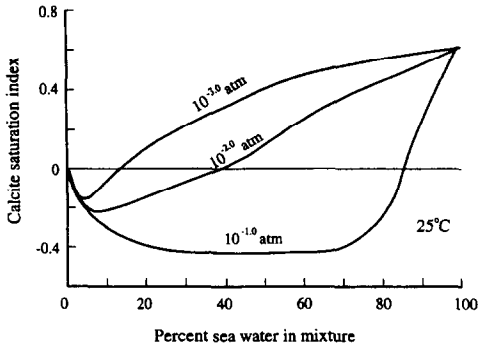

Figure 6. The quantitative illustration of the nonlinear effect of mixing.[11]

Yucatan Peninsula, Mexico. They noticed that the dissolution is most extensive where mixtures of freshwater and sea water are discharging along the coastline into the sea. They examined the geochemistry of the waters in 1979 and 1980. Sampling showed that unmixed groundwater is saturated with respect to calcite, while the sea water was supersaturated with respect to calcite. This phenomenon was believed to be responsible for creating the dissolution occurring in the Yucatan. Quantitative thermodynamic evidence for the nonlinear mixing effect was given by Plummer.[11] The saturation states of calcite for mixtures of seawater and freshwater at 25°C and three different CO_2 pressures ($10^{-3.0}$, $10^{-2.0}$, and $10^{-1.0}$ atm) of the freshwater end-member are shown in *Figure 6*. The results were obtained by using the aqueous speciation model WATEQ as documented by Truesdell and Jones.[12]

Plummer's other results show that not all mixing zones have the potential for creating undersaturated solutions. For example, when the freshwater is supersaturated with respect to calcite, the resulting mixtures with the sea water may be supersaturated. Mixed-water saturations also depend on the saturation state of the sea water. Compared with recent thermodynamic data, chemical analyses of the sea water reveal a supersaturation with respect to calcite. This appears reasonable given the calcium carbonate precipitation in the sea water and the inhibiting effect of ions such as magnesium. But Back et al.[13] studied the geochemical reactions and the reason for the form of the limestone formation. Palmer et al.[14] analyzed the effect of different sediment strata and the partial pressure on the dissolution of the limestone formation. Back et al.[10] interpreted the influence of the dissolution of the limestone on permeability and porosity of the stratum. They concluded that principles of geochemistry can determine the hydrogeological limit. This can be applied to other minerals. Sanford[15] combined the geochemical reaction model and the solute transport model to evaluate the dissolution of the limestone formation.

Questions should be asked, such as: Could the dissolution rate from geochemical reactions and solute transport of the limestone formation be important in creating porosity and permeability in freshwater-saltwater mixing through the geological time? Does such dissolution occur worldwide in carbonate mixing zones or only in some places? Studying the relationship among calcite dissoloution, solute transport, and groundwater flow could lead to further insights into these problems.

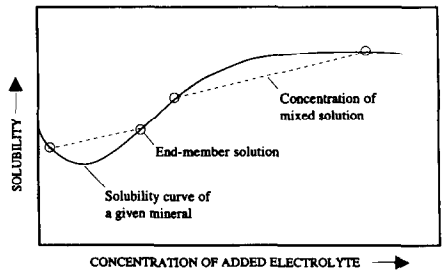

Figure 5. The schematical illustration of the nonlinear effect of mixing.[8]

3. Numerical models

In this study, to show if chemical reaction is the key mechanism in forming caverns, EQ3NR/6 is used to simulate the dissolution of the limestone under chemical equilibrium conditions. HYDROGEOCHEM is then used to evaluate the role of solute transport on the dissolution of the limestone.

3.1 EQ3NR/6

EQ3NR/6 is a geochemical aqueous species solubility and liquid/solid reaction path code.[2,3] It simulates reactions among solutions, liquid/solid, and mineral dissolution/precipitation in thermodynamic state. The model consists of four subprograms (EQ3NR, EQ6, MCRT, and EQTL) and three data sets (DATA0, DATA1, and DATA2). Their interrelations are shown in *Figure 7*. MCRT sets the thermodynamic data. EQTL establishes the database for EQ3NR/6. EQ3NR executes the calculation of the aqueous species product/solubility and makes the partial input file. Then EQ6 simulates the liquid/solid reaction path from the generated output data of EQ3NR. The output of EQ3NR/6 consists of the distribution of aqueous species, solvent concentration, and so on. The simulation is based on thermodynamic equilibrium conditions. These data are in the datafile DATA0.[3] DATA1 and DATA2 are gener-

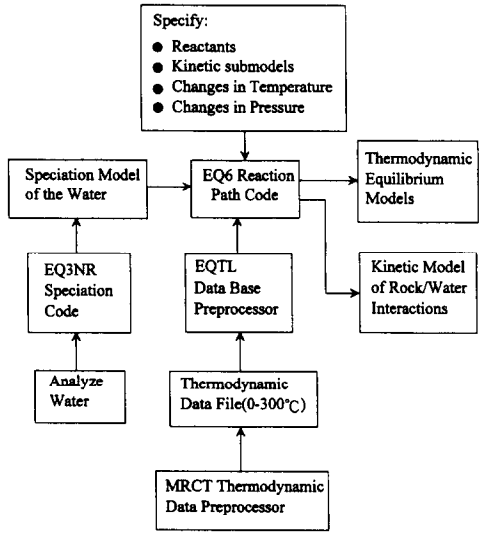

Figure 7. Flow of information between computer codes EQ3NR, EQ6, MCRT, and EQTL.

ated from DATA0. Only the thermodynamic data in DATA0 can be edited. The chemical equilibrium theory used in the simulation of EQ3NR/6 is similar to the reactive transport model HYDROGEOCHEM, as described below.

3.2 HYDROGEOCHEM

HYDROGEOCHEM, developed by Yeh and Tripathi,[4] is a reactive chemical transport model. The model is a two-dimensional finite-element code. It simulates the physical processes of advection and diffusion/dispersion and the chemical reactions of aqueous complexation, acid/base reaction, redox reaction, precipitation/dissolution, and adsorption. The flow equations, chemical transport equations, chemical equilibrium equations, initial boundary conditions, and numerical methods of the model are described as follows.

Flow equations. — The equations governing fluid flow through saturated and unsaturated media can be derived from these theories: (1) fluid continuity, (2) solid continuity, (3) fluid mobility, (4) media consolidation, and (5) fluid compressibility. Neglecting the compressibility of the media and fluid, flow equations can be described:

$$\frac{\partial\theta}{\partial t} = \frac{d\theta}{dh}\frac{\partial h}{\partial t} = \nabla\cdot(K\cdot\nabla H) + Q \qquad (1)$$

$$H = h + z \qquad (2)$$

$$V = -K\cdot\nabla H \qquad (3)$$

where θ = water content (L^3/L^3), h = pressure head (L), t = time (T), K = hydraulic conductivity tensor (L/T), H = total head (L), Q = sink/source [$(L^3/L^3)/t$], z = potential head (L), V = Darcy's velocity (L/T), and $d\theta/dh$ = water capacity (1/L).

The preprocessor, HYDROGEOFLOW, solves equations (1), (2), and (3) by the finite-element method. The output data from the HYDROGEOFLOW simulation will be used as the input data for HYDROGEOCHEM.

Chemical transport equations. — A system of N species can make M species and $M = M_a + M_s + M_p$, where M_a is the aqueous species, M_s is the sorption species, and M_p is the precipitated species. The sorption species, M_s, is the sum of the adsorbent component, N_s, the adsorbed species, M_y, and the ion-exchanged species, M_z. The aqueous species, M_a, is the sum of the aqueous component species, N_a, and the complex species, M_x. Assume that the aqueous species and the complex species are mobile and other species are immobile. From mass conservation, the solute transport equation of the aqueous species can be derived as

$$\frac{\partial\theta c_j}{\partial t} + \nabla\cdot(c_j V) - \nabla\cdot(\theta D\cdot\nabla c_j) = \theta(r_j^a - i_j^a) + m_j^a \qquad j = 1, 2, \ldots, N_a \qquad (4)$$

where c_j = the jth aqueous species concentration (M/L^3), r_j^a = the generation rate of the jth aqueous species in the unit volume from chemical reaction [$(M/L^3)/T$], m_j^a = the sink/source rate of the jth aqueous species [$(M/L^3)/T$], i_j^a = the decay rate of the jth aqueous species [$(M/L^3)/T$], N_a = the amounts of the aqueous species, and D = the bulk diffusion coefficient (L^2/T).

In equation (4), the first term is the mass accumulation, the second term is mass flux by advection, the third term is mass flux by dispersion and diffusion, the fourth term is mass flux by chemical reactions, and the last term is mass flux by pumping or injection. The solute transport equations of the complex species, the adsorbent species, the adsorbed species, and the precipitated species also can be presented by the same form.

Chemical equilibrium equations. — Two theories handle chemical equilibrium problems. One is the ion-association theory the other is mixed-electrolyte theory. Most programs use the ion-association theory. This theory can be solved by two different methods. One is the equilibrium-constant method the other is the Gibbs free-energy method. HYDROGEOCHEM uses the equilibrium-constant method. It solves the nonlinear equations of chemical equilibrium by the law of mass action.

The calcite precipitation/dissolution reaction and its equilibrium constant considered in the study are

$$C_aCO_3 = C_a^{2+} + CO_3^{2-},\ \log K = -8.46 \qquad (5)$$

Because of the relatively fast nature of calcite dissolution kinetics, the dissolution of calcite in the seawater/freshwater mixing zone is assumed to occur under chemical equilibrium conditions. Initially, sea water is supersaturated with respect to calcite, and the nonlinear mixing effect will cause the dissolution of calcite in the freshwater side of the mixing zone. As the groundwater flows through the mixing zone, the change of C_a^{2+} and CO_3^{2-} concentrations will enhance the calcite dissolution rate and cause the migration of the mixing zone further inland.

Initial and boundary conditions. — Assuming all component concentrations and the covalences of the ion-exchange site are known, the initial conditions can be described as

$$T_j = T_{j0} \qquad t = 0 \qquad j = 1, 2, 3, \ldots, N_a$$

$$W_j = W_{j0} \qquad t = 0 \qquad j = 1, 2, 2, \ldots, N_a$$

$$N_{eq} = N_{eq0} \qquad t = 0$$

where T_{j0} = the jth aqueous species initial concentration (M/L^3), W_{j0} = the jth adsorbent species initial concentration (M/L^3), and N_{eq0} = the ion-exchanged site covalences (M/L^3).

The boundary conditions in the solute transport model depend on the specific problems. Generally there are four kinds of boundary conditions:

at the boundary B_D $\quad T_j = T_{jD}$

$j = 1, 2, \ldots, N_a$

at the boundary B_N $\quad -\mathbf{n} \cdot \theta D \cdot \nabla C_j = q_{jN}$

$j = 1, 2, \ldots, N_a$

at the boundary B_c $\quad -n \cdot (VC_j - \theta D \cdot \nabla C_j) = q_{jC}$

$j = 1, 2, \ldots, N_a$

where T_{jD} = the initial concentration (M/L^3), q_{jN} = the Neumann flux (M/L^3), q_{jC} = the Cauchy flux (M/L^3), $\mathbf{n}$ = the unit normal vector, B_D = Dirichlet boundary, B_N = Neumann boundary, and B_C = Cauchy boundary. For the variable conditions, two situations can be applied:

at the boundary B_V $\quad -n \cdot \theta D \cdot \nabla C_j = q_{jV}$

if $V \cdot n > 0 j = 1, 2, \ldots, N_a$

at the boundary B_V $\quad -n \cdot (VC_j - \theta_D \cdot \nabla C_j) = q_{jV}$

if $V \cdot n < 0 j = 1, 2, \ldots, N_a$

where B_V = the variable boundary.

Numerical methods. — HYDROGEOCHEM uses a known flow field or a flow field calculated by HYDROGEOFLOW as the input advective flux. A two-step method is used to solve chemical transport equations and chemical equilibrium equations. After the solution for one time step has converged, the calculation continues to the next time step. Chemical transport equations are solved by the finite-element method, and chemical equilibrium equations are solved by the Newton–Raphson method.

Numerical simulation

4.1 The simulation of EQ3NR / 6

Since chemical reactions influence the dissolution of the limestone, one could find the mechanism of the creation of caverns by analyzing the effect of chemical reactions on the dissolution of carbonate rocks. Runnels' research[8] indi-

Table 1. The average ground water concentrations of 24 monitoring wells at Heng-chun.

Well no.	Temp (°C)	pH	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	NH_4^+ (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	K^+ (mg/l)	Na^+ (mg/l)	Fe^{2+} (mg/l)	Mn^{2+} (mg/l)
E1	28.0	7.25	260.4	79.1	232.3	0.07	113.9	44.4	2.74	117.2	0.03	0.01
E2	27.1	7.67	239.9	117.9	4.4	0.10	45.4	26.2	5.39	150.9	0.09	0.32
E3	26.7	7.47	270.0	54.3	38.7	0.04	95.7	23.6	1.87	64.2	0.07	0.06
E4	26.6	7.29	271.7	58.5	71.5	0.03	89.1	40.3	3.71	84.0	0.05	0.01
E5	27.0	7.40	238.0	25.0	9.5	0.06	86.8	5.9	0.66	41.1	0.04	0.02
E6	27.0	7.28	229.6	26.3	22.1	0.04	65.3	20.3	2.74	54.0	0.05	0.03
E7	26.4	7.35	252.8	37.9	34.5	0.04	110.1	12.6	1.75	49.9	0.03	0.02
E8	26.4	7.84	462.5	978.0	9.4	1.78	31.4	19.0	37.5	906.6	0.42	0.28
E9	25.0	7.54	4.86	30.2	17.5	0.76	55.5	12.8	0.8	133.0	1.00	0.11
E10	26.2	7.55	432.8	72.1	14.2	2.89	76.7	23.2	4.3	213.0	0.13	0.02
E11	26.5	7.37	206.5	30.6	140.2	0.11	68.4	23.6	2.7	51.7	0.05	0.01
E12	26.0	7.44	282.9	111.8	177.6	0.18	109.0	40.4	4.1	156.0	0.08	0.11
E13	25.8	7.45	369.0	166.5	217.4	1.03	118.3	48.9	6.8	239.2	0.30	0.17
E14	26.4	7.61	268.0	50.2	43.5	0.02	85.4	31.5	3.2	86.1	0.06	0.10
E15	26.6	7.70	389.4	82.2	41.9	0.97	63.2	21.6	3.6	213.2	0.08	0.57
E16	27.4	7.76	242.2	108.4	5.0	0.06	50.8	25.9	4.1	111.9	0.06	0.25
E17	27.0	7.57	211.0	42.28	62.8	0.33	62.3	21.9	2.9	59.7	0.03	0.22
E18	26.1	7.82	218.9	41.93	36.8	0.33	36.4	14.5	9.4	14.6	0.07	0.09
E19	26.5	6.99	141.0	18.17	21.0	0.07	43.8	15.0	1.1	33.5	0.04	0.02
E20	26.8	7.21	240.0	59.53	18.7	0.04	127.9	8.1	2.4	50.3	0.06	0.02
E21	26.0	7.47	181.4	33.22	10.1	0.11	85.2	4.4	3.1	38.8	0.04	0.02
E22	26.3	7.38	155.2	20.74	37.3	0.03	56.5	19.1	2.3	86.9	0.08	0.02
E23	27.3	7.43	255.5	33.03	23.8	0.18	58.9	19.5	6.1	75.6	0.05	0.11
E24	27.2	7.59	237.2	30.15	22.0	0.17	82.5	15.9	1.8	41.8	0.12	0.05

cated that when the two end-member solutions in the mixing process are seawater and fresh groundwater, calcite-saturated fresh groundwater combines in the mixing zone with sea water that is supersaturated with respect to calcite; the result is a mixture that is undersaturated with respect to calcite. The chemical equilibrium constant may be increasing nonlinearly, in turn increasing the dissolution rate of the limestone formation. Therefore, to evaluate the mixing effect, one can adjust the equilibrium constants of carbonate minerals until no carbonate minerals are precipitated. The adjusted numerical values of equilibrium constants will help us understand the influence of the nonlinear effect of the freshwater-saltwater mixing on the dissolution of the limestone.

The nonlinear increase of the equilibrium constants of the carbonate minerals to facilitate the amount of precipitation/dissolution are modeled by the geochemical code EQ3NR/6. By using the average groundwater concentrations of the Heng-Chun formation (*Table 1*) as input data, EQ3NR/6 simulates the amount of precipitation/dissolution caused by the increase of the equilibrium constants of the carbonate minerals. This will help to quantify the effect of the freshwater-saltwater mixing on the dissolution of carbonate rocks.

4.2 The simulation of HYDROGEOCHEM

Because the movement of groundwater may enhance the dissolution/precipitation of the limestone and change the rate of formation of limestone caverns, the geochemical transport model HYDROGEOCHEM is used to simulate the change of the solid-phase concentration of carbonate minerals caused by the groundwater flow.

The initial concentrations used are the average groundwater concentrations obtained from the 24 monitoring wells in the Heng-Chun formation.[1] The porosity is assumed to be 0.3. From Neuman's work[16] (*Figure 8*), the

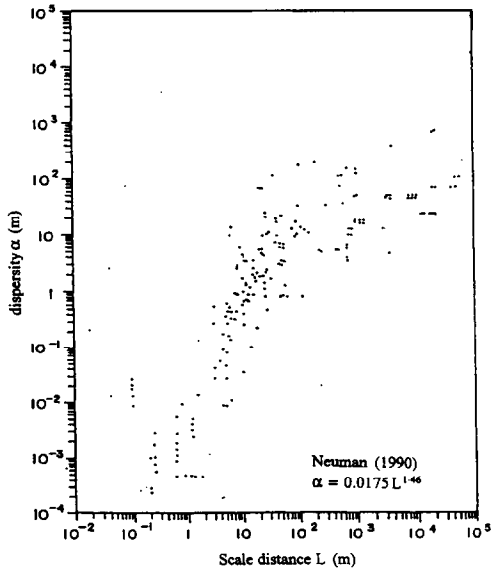

Figure 8. Apparent longitudinal dispersivities versus distance.[16]

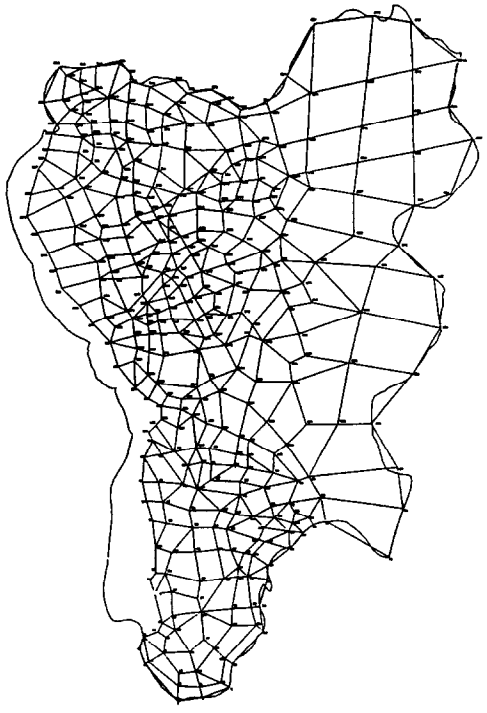

Figure 9. The numerical discretization of grids for HYDROGEOCHEM

longitudinal dispersivity may be approximated to be α_L = 1000 m for a 50 km distance. Because the ratio between the longitudinal dispersivity and the transverse dispersivity is generally 10:1, the transverse dispersivity is assumed to be α_T = 100 m. The density of the limestone is 2.5 g/cm^3. The boundary condition along the sea is the saltwater concentration, the upper boundary condition is the concentration of the river water, and the left and the right boundary conditions are the Neuman boundary conditions. This region is discretized using 364 nodes and 381 elements, as shown in *Figure 9*. The limestone formation is assumed to consist of 5% calcite. The distribution of velocity in this area is obtained from Gau,[17] who used the numerical model FEWA to simulate the groundwater flow field. HYDROGEOCHEM is then used to simulate the change of the calcite solid concentrations at the the initial time, after 8, 10, and 20 years.

5. Results and discussion

5.1 EQ3NR/6

The simulated amounts of the dissolved carbonate minerals caused by the increase of the equilibrium constant are not significant, as shown in *Table 2*. The maximum amount is 9.4×10^{-2} mg/l or 1.0×10^{-6} mol/l of dolomite. Comparing the distribution of the geological formation with the simulated result of EQ3NR/6, the amount of dissolved carbonate minerals and the change of the equilibrium constant do not exhibit the expected inverse relationship

with the distances from the monitoring wells to the sea. This seems to contradict the freshwater-saltwater mixing theory, which means that the closer the well to the sea, the greater the influence of sea water intrusion on the water quality of the well. Therefore, as the location of the well moves closer to the sea, the amounts of dissolved carbonate minerals should be more significant. However, this relationship is not found in the simulation result of EQ3NR/6. The reason may be that the distribution of the limestone formation is not homogeneous. For example, some wells near the sea might not have a well-developed limestone formation in their vicinity, so the mixing effect would not be observed. Since the changes of equilibrium constants of carbonate minerals are small, this also implies that the mixing effect may not have great influence on the dissolution/precipitation of carbonate minerals to speed up the dissolution of limestone rocks.

Garrel et al.[18] pointed out that carbonate minerals, except dolomite, can precipitate only when the pH of sea water is above 7 because of the structure of the minerals. For pH values less than 7, carbonate minerals will be supersaturated. This phenomenon is called the "carbonate fence." Generally dolomite does not precipitate except in the presence of high salinity. Since the results from EQ3NR/6 assumed chemical reaction is under thermodynamic equilibrium, the dolomite precipitation may not really occur. Comparing the core records of the 10 monitoring wells shown in *Figure 3*, limestone formations exist in the records of E20 and E21, so calcite mineral is expected to precipitate in these two wells. The simulation results (*Table 2*) show that groundwater samples in wells E20 and E21 are supersaturated with limestone and will

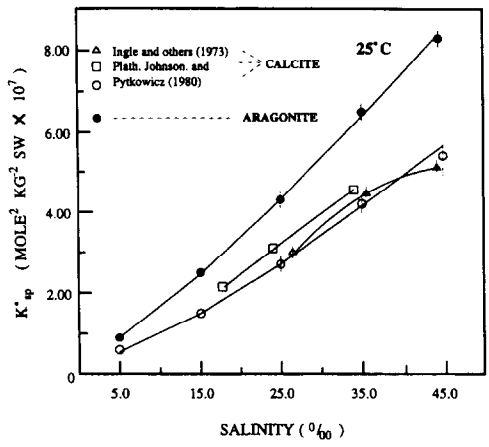

Figure 10. The equilibrium constants versus the percentage of freshwater-saltwater mixing.[19]

precipitate calcite mineral. The simulation's prediction of calcite mineral precipitation agrees with the lithological data from well drilling.

Mucci[19] reported that the equilibrium constant increases as the salinity increases, as shown in *Figure 10*. In the simulation, the equilibrium constant of limestone is adjusted so that no carbonate minerals are precipitated. After the adjustment, the largest value of K for calcite is 3.2×10^{-9}. The increase of the calcite equilibrium constant is relatively small and is close to its intrinsic value, 2.4×10^{-9}. This implies that the ratio of sea water in the mixing solution is insignificant. It also indicates that sea water intrusion may not be serious in the area being

Table 2. The simulated result of EQ3NR/6.

Well number	Supersaturated mineral	Amount of preprecipitation (mg/l) (use the intrinsic K)	Adjusted log K
E1	Dolomite	5.29×10^{-2}	−18.19
E2	Dolomite	3.87×10^{-2}	−18.18
E3	Dolomite	5.13×10^{-2}	−18.17
E4	Dolomite	5.55×10^{-2}	−18.17
E5	Calcite	2.16×10^{-2}	−8.58
	Dolomite	2.52×10^{-2}	−18.18
E6	Dolomite	2.85×10^{-2}	−18.18
E7	Dolomite	3.17×10^{-2}	−18.17
E8	Dolomite	6.00×10^{-2}	−18.17
E9	Dolomite	6.42×10^{-2}	−18.14
E10	Dolomite	8.88×10^{-2}	−18.16
E11	Dolomite	2.54×10^{-2}	−18.17
E12	Dolomite	6.13×10^{-2}	−18.16
E13	Dolomite	9.41×10^{-2}	−18.15
E14	Dolomite	5.85×10^{-2}	−18.17
E15	Dolomite	7.53×10^{-2}	−18.17
E16	Dolomite	4.43×10^{-2}	−18.18
E17	Dolomite	3.23×10^{-2}	−18.18
E18	Dolomite	2.61×10^{-2}	−18.16
E19	—	—	—
E20	Calcite	2.60×10^{-2}	−8.54
E21	Calcite	1.47×10^{-2}	−8.49
E22	Dolomite	1.18×10^{-2}	−18.16
E23	Dolomite	3.68×10^{-2}	−18.18
E24	Dolomite	3.84×10^{-2}	−18.18

* Intrinsic log $K_{Calcite} = -8.62$, log $K_{Dolomite} = -18.14$ (25°C).

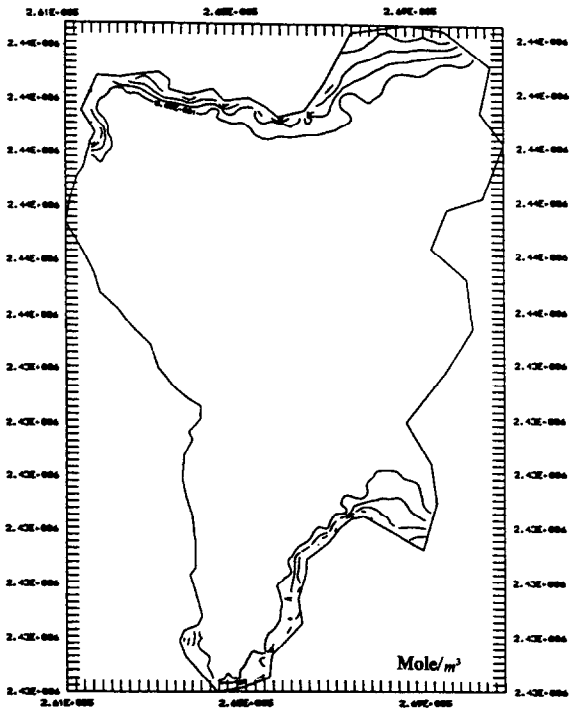

Figure 11. The initial calcite concentration distribution in the formation.

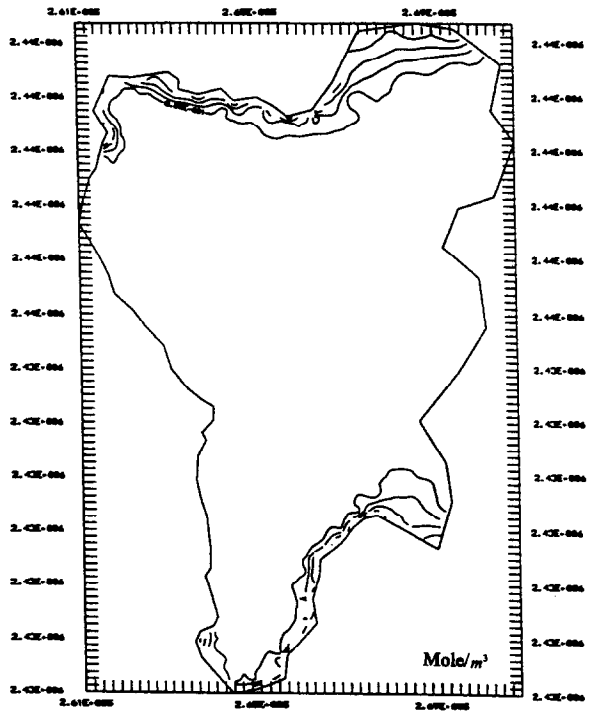

Figure 12. The calcite concentration distribution in the formation after 10 years of simulation.

simulated. The result agrees with the groundwater quality analysis of Tsao et al.,[1] which shows minor seawater intrusion in the Heng-Chun coastal area.

Since the amounts of the precipitates are small, it suggests that the geochemical equilibrium reactions may not cause a large amount of the limestone formation to dissolve to create the caverns. Therefore, the effect of groundwater flow on the dissolution of limestone is examined.

5.2 HYDROGEOCHEM

The simulated distribution of dissolved calcite concentrations at the initial time and after 10 and 20 years are shown in *Figures 11*, *12*, and *13*, respectively. It is found that the overall changes of calcite concentrations in the limestone formation are small. However, a significant change of dissolved calcite concentration appears along the coastal area. This is caused by the constant-concentration boundary condition of the sea. The calcite is supersaturated in the sea water and it is more concentrated in the sea water than it is inland. The concentration gradient across the constant-concentration boundary of sea water will make the diffusion occur toward the land, precipitating the calcite mineral to form the limestone formation. This explains why limestone formations may be frequently found in sea coastal areas.

From the distribution of the dissolved calcite concentration at the initial time and after 10 and 20 years, it is found that the solid-phase concentrations of calcite in the formation change slowly. To demonstrate the dissolution effects, the ratio of the dissolved calcite concentration difference is computed and plotted (*Figure 14*), which shows that the ratio of the difference in 20 years is about 1.4%. From *Figure 13* the average calcite dissolution rate in 20 years is 0.4 mol/m^3. It may be inferred that after 10,000 years, the amount of limestone dissolved is about 200 mol/m^3 or 0.2

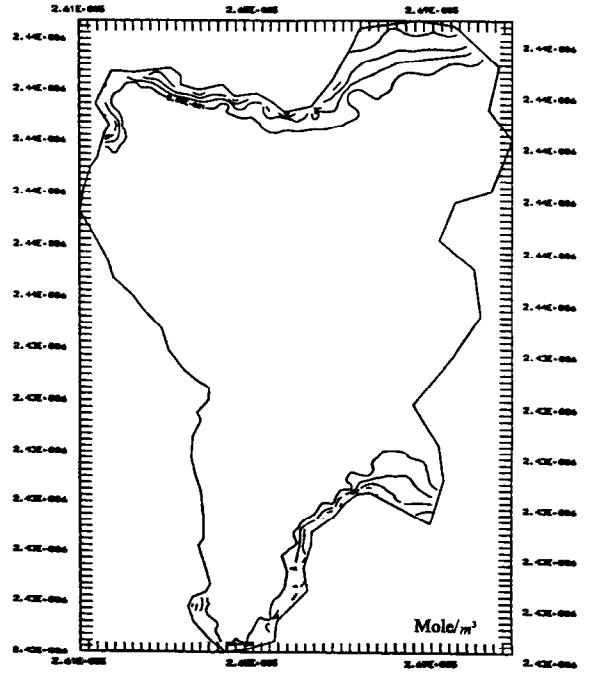

Figure 13. The calcite concentration distribution in the formation after 20 years of simulation.

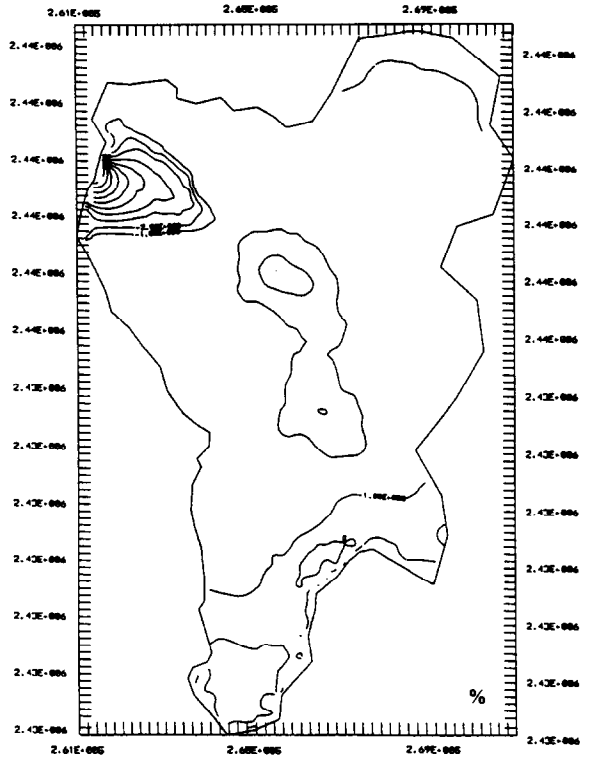

Figure 14. The change in percentage of the calcite concentration distribution in the formation after 20 years simulation.

mol/l, which is an increase of about 25% in the dissolved calcite concentration, as compared with that at time zero. Sanford[15] concluded that the porosity of the Yucatan limestone formation changes from 30–40% in 10,000 years. The increase of the porosity ratio is 33% after 10,000 years in his study. Both are in the same order of magnitude as the current findings. This suggests that solute transport resulting from groundwater flow has a major influence on the dissolution/precipitation of the limestone. Groundwater flow may be the key formation process creating the limestone caverns in Heng-Chun.

6. Conclusion and suggestions

6.1 Conclusion

In this study, the geochemical model EQ3NR/6 and the geochemical transport model HYDROGEOCHEM are used to analyze the mechanism of the dissolution of the Heng-Chun limestone formation. The EQ3NR/6 simulation includes hydrolysis, aqueous complexation, acid/base, and dissolution/precipitation geochemical reactions. The HYDROGEOCHEM simulation consists of the same geochemical reactions as used in EQ3NR/6, and advection and the diffusion/dispersion transport process are also included.

The conclusions from the EQ3NR/6 simulation are:

1. Because the simulated dissolution of the carbonate minerals is small, geochemical equilibrium may not cause a large amount of limestone to dissolve to create the caverns. Therefore, a coupled model of chemical reaction and solute transport should be considered.
2. From the variation of equilibrium constants, it can be inferred that the heterogeneity of the limestone formation may decrease the mixing effect of freshwater and saltwater.
3. Considering the small amount of calcite precipitation in the simulation, the seawater intrusion may not be serious in the Heng-Chun area.

The conclusions from the HYDROGEOCHEM simulation are:

1. From the initial change of calcite concentration in the limestone formation, the changes of the calcite concentrations were strongly influenced by the seawater boundary.
2. The effect of groundwater flow on the solid concentration of calcite suggests that solute transport may be the key formation process creating caverns in Heng-Chun limestone formation.

6.2 Suggestions

The purpose of this study was to find a possible mechanism of the dissolution of the limestone formation. In geochemical modelling, chemical reactions are considered under chemical equilibrium conditions, and the supersaturation resulting from the characteristic of the structure of the mineral were neglected. The chemical kinetics effect should be considered in future geochemical simulations. Also, it is suggested the other carbonate minerals should be included in future geochemical transport simulations. This study neglects the effect of the dissolution of the limestone on porosity, hydraulic conductivity, and equilibrium constant of the formation. The dissolution of carbonate rocks will increase the permeability and so will have a feedback effect on the groundwater flow and the solute transport processes. A coupled model of the geochemical mixing theory with the freshwater-saltwater flow theory needs to be developed to simulate the dissolution rate of the limestone formation in the future.

Nomenclature

θ	water content
h	pressure head
t	time
K	hydraulic conductivity tensor
H	total head
Q	sink/source
z	potential head
V	Darcy's velocity
$d\theta/dh$	water capacity
N	number of component species
M	number of species
M_a	the aqueous species
M_s	the sorption species
M_p	the precipitated species
N_s	the adsorption component

M_y the adsorbed species
M_z the ion-exchanged species
N_a the aqueous component species
M_x the complex species
T_{j0} the jth aqueous species initial concentration
c_j the jth aqueous species concentration
r_j the generation rate of the jth aqueous species in the unit volume from chemical reaction
m_j the sink/source rate of the jth aqueous species
i_j the decay rate of the jth aqueous species
N_a the amounts of the aqueous species
D the bulk diffusion coefficient
T_{j0} the jth aqueous species initial concentration
W_{j0} the jth absorbent species initial concentration
N_{eq0} the ion-exchange site covalences
q_{jN} the Newmann flux
q_{jC} the Cauchy flux
$\mathbf{h}$ the unit normal vector
B_D Dirichlet boundary
B_N Newmann boundary
B_C Cauchy boundary
B_V the variable boudnary
α_L the longitudinal dispersivity
α_T the transverse dispersivity

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