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COMPUTER SIMULATION OF TEMPERATURE-DEPENDENT EQUILIBRIUM PRECIPITATION

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ABSTRACT

The EQ3/EQ6 software package contains two computer codes (EQ3 and EQ6) and data files which form a useful tool in modeling precipitation from geothermal fluids caused by heating or cooling. The data files contain information on 140 aqueous species and nearly 150 minerals, and permit calculations over the temperature interval 0-350°C. Assumption of homogeneous thermodynamic equilibrium in aqueous solution permits calculation of the driving forces for precipitation as measured by the affinity (log Q/K) for each such reaction. Further assumption of precipitation and heterogeneous equilibrium for any mineral whose affinity would otherwise exceed a value of zero permits determination of the identity of the precipitates, their masses and volumes, and the temperature ranges in which they form.

We have used the EQ3/EQ6 capability to determine the effects of temperature increase on formation of precipitates form Salton Sea water.

EQ3 Software Package

EQ3 calculates a thermodynamic model of an aqueous solution given a set of values for analytical parameters (e.g., pH, Eh, and "total" concentrations of solutes). Temperature-dependent data are calculated from interpolating polynomials fit to data on a temperature grid. The program is very flexible in terms of the types and combinations of input analytical data. For example, the redox state can be defined alternatively to Eh by specifying pe^-, oxygen fugacity, or data on any redox couple. If redundant redox data are available, they can all be used by EQ3 to calculate a model in which complete redox equilibrium need not exist. The program is otherwise similar in function to the U.S.G.S. programs SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ (Truesdell and Jones, 1974). It can estimate precipitation affinities, but can not determine which of a set of supersaturated minerals would actually precipitate or what their volumes would be.

EQ6 Software Package

EQ6 is a reaction-progress code which can model precipitation starting with the fluid model calculated by EQ3. It is similar in function to the original reaction progress code PATHI (Helgeson, 1968; Helgeson et al., 1970), which was written to model isothermal, irreversible reaction between minerals and aqueous solution. One improvement of EQ6 over PATHI is that it can operate in a mode in which change in temperature is equivalenced to advancement of reaction progress. It operates numerically by a combination of the Newton Raphson method and finite-difference techniques, rather than integrating ordinary differential equations, as did PATHI. This eliminates "drift" errors while permitting high computational efficiency. EQ6 utilizes a set of semi-empirical algorithms to pick the correct set of precipitates from supersaturated solution, whereas PATHI could not handle such solutions.

SALTON SEA WATER REHEATING EXPERIMENT

An illustration of the application of EQ3/EQ6 codes is the calculation of species distribution of Salton Sea water (Table I), followed by a simulation of the consequences of heating the fluid from 25°C to 220°C in both a closed system and a flow-through system. This study was part of an LLL evaluation of Salton Sea water as a source of injection makeup water for the geothermal resources of California's Imperial Valley (Raber et al., 1979). In these examples, each possible precipitate is permitted to form. If in some application it is known a priori that one or more do not form for kinetic reasons, the user of EQ6 can suppress the calculation of precipitation of individual solids.

RESULTS

The distribution-of-species calculations performed by EQ3 at 25°C indicated super-saturation of 8 phases:

Mineral	Log (Q/K)
Magnetite (Fe_3O_4)	10.2
Hematite (Fe_2O_3)	18.8
Calcite ($CaCO_3$)	0.80
Aragonite ($CaCO_3$)	0.63
Huntite ($CaMg_3(CO_3)_4$)	0.68
Dolomite ($CaMg(CO_3)_2$)	2.96
Magnesite ($MgCO_3$)	0.54
Gypsum ($CaSO_4 \cdot 2H_2O$)	0.37
Anhydrite ($CaSO_4$)	-0.31

TABLE 1. SEAWATER, SALTON SEA, U.S. NAVY SALTON SEA BASE (T11SR11E-21P), SAMPLED JUNE 8, 1967.

Element	mg/ℓ (ppm)	% TDS
Na	10,500.	28.3
K	172.	0.46
Ca	954.	2.57
Mg	1,078.	2.90
Li	3.2	0.000086
Cl	15,000.	40.5
CO_3	0.	0.
HCO_3	203.	0.55
SO_4	8,146.	22.0
NO_3	14.	0.038
NH_4	-	-
B	9.20	0.025
F	3.2	0.0086
As	0.0	0.
Ba	1.	0.0027
Cd	0.005	0.000013
Co	0.0005	0.0000013
Cu	0.0050	0.000013
Fe	0.0100	0.000027
Hg	.2	0.00054
Mn	0.01	0.000027
Ni	0.003	0.0000081
Pb	0.002	0.0000054
Rb	-	-
Se	-	-
Sr	11.	0.03
Zn	0.062	0.00017
Total dissolved solids (TDS)	37,082.	
Specific mho/cm conductance, at 25C	42,100.	
Temperature, C	25.	
pH	7.7	

Calif. Dept. of Water Resources, Bulletin 143-7 (1970).

The solution is nearly saturated with respect to anhydrite. The supersaturations with respect to the iron oxides are probably fictive, because analyses of dissolved iron in natural waters are usually too high due to interference from colloidal ferric hydroxide. Supersaturations with respect to the carbonates are probably real, because these are well documented for surface ocean water. The small gypsum supersaturation may also be real.

Equilibrium precipitation at 25°C calculated by EQ6 yielded only 3 of the potential 8 phases: gypsum, dolomite, and hematite. Precipitation of these three solids modified the solution composition (including its pH) so that the precipitation affinities of all other solids were rendered negative. The consequences of heating to 220°C were then calculated for the case of a closed system and a flow-through system. The former can be visualized as a hydrothermal bomb containing fluid plus precipitates, the latter as fluid flowing through a pipe with a temperature gradient, in which the fluid advances but precipitates are physically left behind and can not later react with the packet of fluid which deposited them.

Precipitation in the closed system is depicted in Fig. 1. The mass of gypsum ($CaSO_4 \cdot 2H_2O$) initially increases, and is replaced by anhydrite ($CaSO_4$) near 95°C. Magnesite ($MgCO_3$) similarly replaces dolomite ($CaMg(CO_3)_2$) near 135°C. The calcium sulfate minerals make up most of the total volume of solids. The carbonates might in reality be kinetically inhibited from precipitating. An experiment on heating ocean water in closed system reported by Bischott and Seyfried (1978) produced neither dolomite nor magnesite, despite calculations based on analytical data which indicated moderate supersaturations. Salton Sea water is sufficiently similar chemically to ocean water that the same effect is quite likely. This points out the utility of combining experiment and theoretical calculations in modeling precipitations.

The results in precipitation modeling in a flow-through system are depicted in Fig. 2. The same solids occur in this particular case, but this time the gypsum and dolomite persist, as they would if left behind in cooler parts of the system. The temperatures at which anhydrite and magnesite appear are practically the same as in the closed system. This need not always be the case, however.

The total precipitate volumes for both closed and flow-through systems are shown in Fig. 3. The results are not grossly different. It is of interest, however, to note that from 25°C to 100°C, the total volume increases slightly in the flow-through system, whereas it decreases notably for the closed system due to dissolution of gypsum.

The capabilities of EQ3/EQ6 are described in more detail by Wolery (1979). EQ6 is capable of computing reaction progress models in which irreversible reaction with minerals occurs as well as change in temperature. Further examples of such calculations are given by Wolery (1978) for modeling hydrothermal sea water at mid-oceanic ridges and by Howard et al. (1979) for estimating the consequences of reinjecting fluids in the East Mesa KGRA, Imperial Valley, California. The code can handle sufficiently large variations in the redox state of modeled systems that it may also find utility in corrosion studies.

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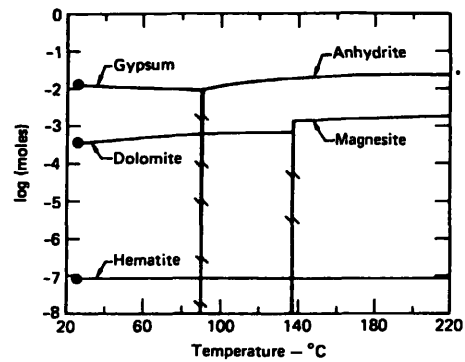
Figure 1. Masses of precipitates from Salton Sea water (relative to an initial 1000 g H_2O) produced by heating in a closed system. Pressure is 1.013 bars below 100°C and the steam saturation value at higher temperatures. Gypsum, dolomite, and hematite are initial precipitates from super-saturated solution.
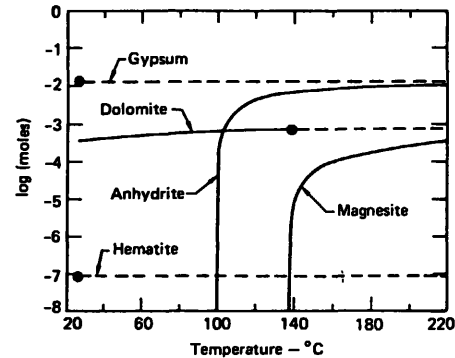

Figure 2. Cumulative masses of precipitates from Salton Sea water (relative to an initial 1000 g H_2O) produced by heating in a flow-through system. Pressure is 1.013 bars below 100°C and the steam saturation value at higher temperatures. The dashed lines indicate cessation of precipitation. Gypsum, dolomite, and hematite are initial precipitates from supersaturated solution.
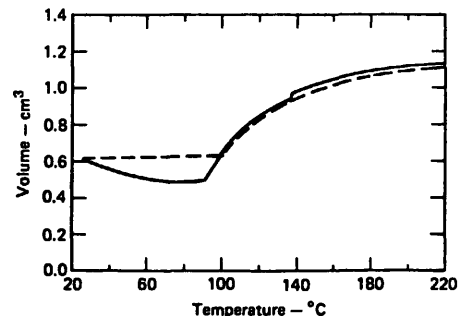

Figure 3. Total precipitate volume per 1000 g H_2O produced by heating Salton Sea water. The solid line represents the closed system and the dashed line the flow-through system.