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MEMORANDUM FOR: Malcolm R. Knapp, Chief
Geotechnical Branch
Division of Waste Management

Division of Waste Management Staff

FROM: Walton R. Kelly
Geochemistry Section
Geotechnical Branch
Division of Waste Management

SUBJECT: GEOCHEMICAL EQUILIBRIUM CODE WATEQF

WATEQF, the FORTRAN version of the geochemical equilibrium code WATEQ, is up and running on the BNL system and available to the WM staff. A description of the code and its capabilities is attached. Sample problems have been run for standard sea water and a river water by Walt Kelly and Bill Dam. The results agree with previous verifying calculations. The users guide is located in Room 456, and Walt Kelly and Bill Dam are available for questions regarding the use of WATEQF.

Walton R. Kelly
Geochemistry Section
Geotechnical Branch
Division of Waste Management

Enclosure:
As stated

WM Record File
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WM Project 1
Docket No.
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WATEQF

A GEOCHEMICAL CODE THAT CALCULATES CHEMICAL EQUILIBRIUM OF NATURAL WATERS

CODE CAPABILITIES:

WATEQF is the FORTRAN IV version of the computer code WATEQ developed by Truesdell and Jones (1973). WATEQF models the thermodynamic speciation of inorganic ions and complex species in solution for a given water analysis. With but a few exceptions, the thermochemical data, speciation, activity coefficients, and general calculation procedure is identical to WATEQ. WATEQF considers 114 aqueous species and 193 solids for 21 elements. For code verification, user's guides, and complete model assumptions and computational devices, the user is referred to Truesdell and Jones (1973, 1974) and Plummer, Jones and Truesdell (1976).

CODE INPUT AND CALCULATION:

Primary input is data for one or more water analyses. These data include total concentrations of predominant elements and species, solution temperature, pH, Eh, density, and dissolved oxygen content. The user has options concerning how alkalinity is to be treated, how pe and activity coefficients are to be calculated, and the number of species and minerals desired in the output. The code itself inputs the ΔH_r° and log K (at 25°C) of each aqueous species and the valence, Debye-Huckel $\mathring{a}$ parameter, and gram formula weight of the species for each solid. Ionic activity

coefficients are calculated using the Debye-Hückel equation (Robinson and Stokes, 1959) and the MacInnes assumption (MacInnes, 1939). Computation of solution species distribution is accomplished by means of a chemical model (Garrels and Thompson, 1962) using analytical concentrations, experimental solution equilibrium constants, mass balance equations, and the measured pH. Calculated values are iterated in the manner of Garrels and Thompson (1962) until the sums of all weak acids, complex ions and free ions for all anions agree with the analytical values within 0.5 percent.

INHERENT ASSUMPTIONS:

1. Equilibrium conditions are assumed to be attained simultaneously;

2. A linear dependence of log K with the reciprocal is assumed for temperatures not at $25^{o}C$, unless data is available to suggest otherwise;

3. Pressure effects are not considered; and

4. Measured Eh(or pe), dissolved oxygen, or $SO_4^{=}/S^{=}$ ratio is assumed to fix the redox state.

CODE OUTPUT:

The output of WATEQF consists of a table of data constants used in the caluclations (printed once). The output for each water analysis lists the title card and tabulates most of the input data. At the end of each iteration through the equilibria equations, the difference between the

computed and analytical anion species is tabulated so that convergence progress can be followed. When convergence on the aqueous model has been obtained, various parameters that describe the solution are printed. Some of these are ionic strength, activity of water, comparison of computed and analytical charge balance, pH, pe, temperature, P_{CO2}, P_{O2}, total dissolved solids, and others. The concentration of each aqueous species (value greater than zero) is printed as ppm, molality, activity, and log values, as well as ionic activity coefficients and their logs. Mole ratios and log activity ratios are computed and tabulated. The activity product of 101 minerals and their saturation indices, ΔG_r^o and log K are printed.

REFERENCES:

Garrels, R.M., and M. E. Thompson (1962). A chemical model for sea water at 25°C and one atmosphere total pressure: Am. Jour. Sci., v. 260, pp. 57-66.

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Robinson, R. A., and R. H. Stokes (1959). Electrolyte Solutions. London, Butterworths, 559 pp.

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