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REACTIONS OF HEAVY METALS AND OTHER MINERAL WATER QUALITY CONSTITUENTS WITH SOIL MATERIALS IN RAPID INFILTRATION GROUNDWATER RECHARGE SYSTEMS USING RECLAIMED WASTEWATERS

by

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ABSTRACT

Solutions containing Ca, Mg, K, Na, Pb, Ni, Cd, Cr, Cu, Zn, NH_4, SO_4, Cl, HCO_3, PO_4 at concentrations that are typically encountered in wastewaters were allowed to percolate through soil columns 15 cm in diameter and 200 cm deep in two soils; San Emigdio and Superstition sands with known physical and chemical properties were used in these experiments. The analyses of the percolating waters indicated that the trace metal concentrations were attenuated to the extent of non-detectability by A.A. spectrometry. The San Emigdio soil showed greater attenuation of PO_4 and NH_4 in comparison with Superstition sand. Speciation calculations by using GEOCHEM indicated that the major fractions of the trace metals were in cationic form and therefore would be adsorbed by the soil exchange complex. Simulations that included the presence of dissolved organics indicated that a major fraction of Cu, Ni and Zn were complexed by the organic ligands. The speciation of Cd and Pb on the other hand were mainly influenced by the inorganic ligands.

JUSTIFICATION

As water development in California, in the USA, and elsewhere in the world becomes more difficult, increased attention is being placed on the use of reclaimed wastewaters. One of the methods for tertiary treatment of wastewaters to bring them to a quality where they might qualify for unrestricted agricultural, municipal, and industrial uses is to pass them through deep soil columns overlying storage aquifers. The soil columns serve as physical as well as chemical filters for many of the undesirable constituents in wastewaters.

The most effective method of putting large volumes of reclaimed water into ground water storage is by the use of rapid infiltration systems. These systems require sandy-gravelly soils and sediments having low quantities of colloids and thus low capacities for sorption of water quality constituents including those that are potentially toxic to biological systems. One of the deterrents to greater development of ground water recharge with reclaimed municipal wastewaters is the lack of information on the efficiency of the soil or sediment column in removing constituents that are important in drinking water quality considerations. These constituents include inorganic and organic substances as well as pathogenic organisms. Potential problems are greatest in rapid infiltration systems because of the inherent sandy and/or gravelly nature of the soil column and the short residence time of the water in the column.

The advantages of rapid infiltration systems as compared to slow infiltration systems include (1) small areas of land are required, (2) there is low evaporation during infiltration and consequently less concentration of constituents in the water, and (3) the recharged water accumulates in a smaller area where it can be more easily and quickly recovered for various uses. Because of these advantages, more information is needed on the disadvantage related to possible inefficiencies of the soil column as a filter.

A comprehensive review of the removal of chemical and biological contaminants by soil systems used for ground water recharge with reclaimed wastewaters was prepared by Pratt et al. (1975) for the Consulting Panel on Health Aspects of Wastewater Reclamation for Ground Water Recharge, which was organized by the Water Resources Control Board, the Department of Water Resources, and the Department of Health of the State of California. This review pointed out the need to determine the efficiency of removal of water quality constituents by soil infiltration systems, including the need for more information on (1) trace elements, (2) soil properties in relation to the effectiveness of the soil as a filter for trace elements, (3) organo-metal complexes, (4) biological contaminants, and (5) organic substances.

There have been numerous laboratory studies of the reactions of trace elements with soils. However, very few studies dealing with the retention of trace elements by soils and sediments used for rapid infiltration systems have been reported. Chang and Page (1978) in a review article indicated that, at that time, existing information did not permit a thorough review of the fate of toxic chemicals under land treatment options of irrigation, rapid infiltrations, and overland flow systems. They also indicated that trace elements could present a hazard during land treatment of wastewaters originating from industrial waste discharges.

Bouwer and Rice (1978) and Bouwer et al. (1974) reported that the trace element concentration of water that had been treated by rapid infiltration systems met the criteria for safe irrigation water, but that trace elements did migrate through the filter system. However, no information was presented on the effect of management factors on the migration of trace elements and on the effects of other water quality constituents. The reclaimed wastewater used by Bouwer and Rice and Bouwer et al. contained relatively low concentrations of trace elements and thus their work does not provide a satisfactory test for waters that might come from highly industrialized areas. The two volumes on land treatment of wastewater (McKim, 1978) contained no specific information on the retention of trace elements by rapid infiltration systems in relation to concentrations in the reclaimed water, transit time for water in the column; nature of the column, the concentration of other ions in the reclaimed water, and other management factors.

A multipurpose chemical equilibrium computer program, GEOCHEM, has been developed by Mattigod and Sposito (1979). GEOCHEM is an improved version of REDEQL2, developed at Cal Tech. This program is capable of simulating various types of chemical reactions that are generally encountered in soils and sediments viz acid-base equilibria, complex and ion pair formation with organic and inorganic ligands, dissolution-precipitation redox and adsorption-ion exchange equilibria. GEOCHEM is comprehensive and contains the largest collection of thermodynamic data among currently used chemical equilibrium computer programs (Nordstrom et al., 1979). The application of this program for computing trace metal speciation in soil solutions from soils amended with sewage sludge or subjected to accidental contamination of geothermal brines has been illustrated by Mattigod and Sposito (1979). Use of GEOCHEM will provide a better insight into the factors which control trace metal attenuation from percolating wastewaters.

REVIEW OF METHODOLOGY

Duplicate soil columns 15 cm in diameter and 200 cm deep were filled with two soils: San Emigdio soil and Superstition sand. The soil characterics such as particle size distribution, mineralogy, carbonate content, dithionite-citrate extractable iron, peroxide extractable Mn, cation exchange capacity, electrical conductivity and pH of the saturation pastes were determined.

To gain some understanding of the rate of adsorption reactions, adsorption isotherms for these soils were generated by equilibrating up to 48 hours, solutions containing 100 ppm Pb in 0.01 M $Ca(ClO_4)_2$.

Solutions containing Ca, Mg, K, Na, Pb, Ni, Cd, Cr, Cu, Zn, NH_4, SO_4, Cl, HCO_3, PO_4 were prepared with concentrations at levels typically encountered in wastewater. The synthetic wastewaters were allowed to percolate through the columns at rates of approximately 13 and 7 liters/day for San Emigdio and Superstition soil columns respectively. The solutions percolating through the columns were sampled from 10, 20 and 50 cm depths, and the chemical analyses of the solution were conducted.

Analyses of all cations were performed by atomic adsorption spectrometry. The concentrations of SO_4, Cl, HCO_3 and PO_4 were determined by turbidimetric, chloridometry, alkalimetric titrations and colorimetry respectively. The speciation calculations of input solutions were conducted by using GEOCHEM.

In order to gain some understanding of the partitioning of heavy metals between sludge and wastewater fractions, a sample of Los Angeles municipal sludge was subjected to size-density separation according to the method of Mattigod and Ervin (1983). The resulting heavier fraction was analyzed by energy dispersive X-ray analyses.

RESULTS AND DISCUSSION

The physical, chemical and mineralogical properties of the San Emigdio and the Superstition soils are listed in Tables 1 and 2. The particle size analysis (Table 1) shows that both the soils are sandy textured with sand content at 71 and 937 by weight respectively. Also, the San Emigdio soil contains more than three times the clay content of the Superstition soil. The chemical analyses (Table 2) indicated that the Superstition sand contains more extractable Ca, whereas the San Emigdio soil contains more extractable Fe, Mn, Al, and Si. Therefore, the San Emigdio soil has more Fe and Mn oxides and Al and Si amorphous oxide and hydroxides in comparison with more calcareous Superstition sand. The clay mineralogy indicates that the San Emigdio soil is smectite rich, whereas the Superstition soil is micaceous. The higher CEC of the San Emigdio soil reflects the higher oxide, hydroxide and smectite content of this soil.

The kinetic study indicated (Table 3) that bulk of Pb adsorption on the Superstition soil takes place within one hour. However, additional 47 hours of reaction increases adsorption by only 5%. This data indicates that Pb adsorption reactions occurs in two phases; viz early rapid reaction during which a major fraction of the total adsorption takes place, and followed by a slow reaction that extends over 2 days that accounts for a minor fraction of the total adsorption. This observation fits the two-step kinetics of metal adsorption onto soils that have been noted by Yates (1975). The early rapid step is attributed to adsorption onto highly accessible sites on the soil surface and the second slower step which may continue for days is characteristic of solid state diffusion.

The composition of influent water used for the percolation experiment is listed in Table 4. The anionic compositions of percolating waters are listed in Table 5. The concentrations of all trace metals in these waters were below the detection limits of AA spectrometry. At 10 cm depth, in the San Emigdio soil, the PO_4 was attenuated by 85% at the end of two days that decreased to 30% by the end of a week. During the same period of time, at 50 cm depth, the phosphate concentrations were 0.45 and 0.65 respectively. Therefore, at 50 cm depth, the PO_4 concentrations had decreased on average by 92%. In contrast, attenuation of PO_4 in the Superstition sand at the same depth was only 3% at the end of 7 days. Clearly, PO_4 is more mobile in this soil than in the San Emigdio soil. This significant difference in PO_4 attenuation can be explained by the differences in mineralogy of these soils. The San Emigdio soil has more extractable oxides and hydroxides of Mn, Fe, Al, Si with smectite as the dominant clay mineral, and thus has greater adsorption-precipitation potential for PO_4 than the Superstition sand.

Similar results were obtained for the attenuation of NH_4^+ in the percolating waters. The greater CEC of the San Emigdio soil explains the significant attenuation of NH_4^+ ions in the solution phase, whereas, no attenuation could be observed in the Superstition sand. In fact, a slight enhancement of NH_4^+ concentration in this soil even during the early part of the experiment indicates a release of this element from the soil matrix.

The concentration of NO_3-N was very low in all cases except at the end of the second day in the San Emigdio soil. High concentrations of NO_3 in the percolating waters during this period is likely due to the flushing of the accumulated nitrate in this soil. The low concentrations of NO_3-N in all subsequent samples are likely due to the nitrification reactions in these soils.

The concentration of all trace metals in the percolating waters were below detection limits at all times, indicating that these metals are immobilized in these soils by adsorption and/or precipitation phenomena.

To examine this phenomena in terms of elemental speciation in solution phase, calculations using GEOCHEM were performed. The input composition of wastewaters were the mean values obtained from the compilation of Chang and Page (1978). Nine cases were considered with pH, Cl and SO_4 content as variables. A second set of nine cases were also considered with organic ligands amounting to a total dissolved organic carbon of 25 mg/l. The mixture of organic ligands were based on the model proposed by Mattigod and Sposito (1979). The wastewater composition that was used in the calculations are listed in Table 6. The pH values were calculated for these compositions. Typical output from GEOCHEM computations are presented in Table 7. The computations show that bulk of the major cations (Ca, Mg, Na and K) exist as free and cationic species. In all cases, the solutions were supersaturated with respect to hydroxyapatite. Addition of organic ligands did not show any significant changes in the speciation of these major cations. However, the trace metals showed a dramatic shift in speciation in the presence of organic ligands. In the absence of organics, Cu, Cd, Zn and Ni were present mainly as cationic species. Major fraction of Pb and about 50% of Cd were predicted to be in solid forms. In the presence of organics, about 80% of Cu, 58% of Ni and 15.9% of Zn were predicted to be present as organic complexes. Only a minor fraction of Cd (1.9%) and Pb (0.5%) were bound with organics. These calculations show that the organic ligands have a major influence on the speciation of Cu, Ni and Zn and thus would affect the adsorption and precipitation reactions in the soils. In addition, the prediction of supersaturation for certain compounds indicate that the wastewater analyses include an unknown fraction of the colloids in addition to the metal in true solution phase. These predictions are also similar to trace metal speciation predicted in sewage sludge amended soils (Mattigod and Sposito, 1979).

These simulations predict that a major fraction of trace metal cations exist mainly as cationic species and in certain cases as solid phases and thus are likely to be immobilized in soils by adsorption and precipitation. Clearly, the tendency for a trace metal to be mobile in the soil would be dictated by the fraction of the metal that may be present as neutral and negatively charged complex species. Therefore, the relative immobility of all trace metals that was observed in the short-term column experiments can be explained by the speciation tendency of these metals in the wastewaters.

A sample of the Log Angeles municipal sludge that had Pb levels at 3065 ppm was subjected to sensity separation. Preliminary work on density fraction >2.9 gm/cm^3 using energy dispersive X-ray analysis revealed that Pb in the sludge fraction was associated mainly with Si with traces of Al. This preliminary data indicates that partitioning and speciation of trace metals in wastewaters is part of a complex web of interactions that needs further elucidation.

PRINCIPAL FINDINGS AND CONCLUSIONS

1. The kinetics of Pb adsorption conformed with two step kinetics observed for other trace metals.
2. The trace metals Cu and Zn were highly attenuated during percolation through soil columns. The mobility of PO_4 and NH_4 were related to the mineralogy of these soils.
3. Speciation computations indicate that speciation trace metals in wastewaters are significantly influenced by the presence of organic ligands. The metal forms in solution were predicted to be mainly cationic and thus would be expected to form part of the soil exchange complex.
4. The predicted formation of Cd and Pb solid phases in wastewaters indicate that the wastewater analyses are likely to reflect the presence of certain fraction of these metals in the colloidal form.

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Table 1. Particle Size Distribution

Particle fraction	San Emigdio	Superstition
	----------% by weight----------	
Very coarse sand	1.66	0.93
Coarse sand	7.71	3.56
Medium sand	19.72	10.63
Fine sand	30.06	49.05
Very fine sand	11.95	28.71
Coarse silt	9.06	2.75
Fine silt	6.64	0.77
Clay	13.18	3.59

Table 2. Chemical and Mineralogical Properties

Soil	Ca*	Mg*	Mn**	Fe***	Al_2O_3 (Clay Fraction)	SiO_2† (Clay Fraction)	CEC	EC
	ppm	ppm	ppm	ppm	ppm	ppm	meq/100 g	dS/m
San Emigdio	30109	483.4	32.05	2058.5	7539.1	38638.4	14.74	2.23
Superstition	15411	1199.2	3.00	1185.8	6337.7	20663.4	4.94	0.3

	pH	Mineralogy (clay fraction
San Emigdio	7.4	Smectite, quartz, muscovite, kaolinite
Superstition	8.8	Muscovite, kaolinite, mica-smectite interstratified, quartz, calcite

* 1 N NaOAc at pH 5.0 and H_2O_2 treatment.

** Hydrogen peroxide treatment.

*** Sodium dithionate-citrate treatment.

† KOH (0.5 N) treatment.

Table 3. Kinetics of Pb Adsorption on Superstition Sand.

Time (hrs)	Equilibrium Conc. (μg/ml)	Adsorbed (μg)	Adsorbed %
0.5	11.87	1633.4	87.3
1.0	5.52	1760.4	94.1
2.0	3.05	1809.8	96.7
4.0	1.59	1839.0	98.3
8.0	1.16	1847.6	98.8
24.0	0.85	1853.8	99.1
48.0	0.53	1860.2	99.4

Initial Pb concentration = 93.5 ppm

Background electrolyte: 0.01 N $Ca(ClO_4)_2$

Soil-solution ratio: 1:20

Table 4. Composition of influent water.

Constituent	Concentration (mg/l)
Na	294.4
K	23.0
Ca	50.0
Mg	53.0
Zn	0.15
Cu	0.15
Cd	0.22
Ni	0.60
Pb	0.50
Cr	0.30
NH_4	13.8
PO_4	7.0
Cl	477.5
HCO_3	330.9
SO_4	108.9

pH: 8.6

Table 5. Compositions of percolating water.

Soil	Time (Days)	Depth (cms)	pH	PO_4	NH_4	NO_3
				ppm	ppm	ppm
San Emigdio	2	10	8.0	1.05	1.40	314.75
		20		0.80	1.70	10.49
		50		0.45	3.70	39.34
	5	10	7.9	3.70	2.40	1.34
		20		3.55	5.30	0.78
		50		0.55	2.55	-
	7	10	8.0	4.90	7.25	0.61
		20		4.30	7.50	0.42
		50		0.65	2.40	0.06
Superstition	2	10	7.9	5.95	15.64	0.75
		20		5.45	13.82	0.85
		50		3.90	13.09	0.83
	5	10	8.0	6.25	14.18	0.29
		20		5.65	14.55	0.23
		50		5.65	15.65	0.30
	7	10	8.0	7.30	15.64	0.11
		20		7.15	15.64	0.12
		50		6.80	14.55	0.22

Concentrations of all trace metals were below detection limits of AA.

Table 6. Wastewater composition used for speciation calculation using GEOCHEM.

Component	pM*
Ca	3.00
Mg	2.71
K	3.23
Na	2.07
Cu	5.63
Cd	5.71
Zn	5.64
Ni	4.99
Pb	5.62
Cr	5.24
HCO_3	2.90
SO_4	3.00-2.96
Cl	1.91-1.87
N	2.85
P	3.49
Citric	4.34
Salicylic	4.47
Phtalic	4.17
Argimine	4.69
Ormithine	4.56
Lysine	4.56
Valine	4.56
Maleic	4.17
Benzine sulfonic	4.47

* Negative logarithm of molar concentration.

Table 7. Predicted speciation of metals in secondary waters.

Element	Total Concentration	Species (% total) Without Organics	 With Organics
Ca	3.00	Ca^{2+}(42.2), $Ca_5(PO_4)_3(OH)$ Solid (53.9) $CaSO_4^0$(2.4), $CaCl^+$(1.2), $CaHCO_3^+$(0.3)	Ca^{2+}(39.0), $Ca_5(PO_4)_3(OH)$(Solid)(53.9), $CaHCO_3^+$(0.4) $CaSO_4^0$(2.2), $CaCl^+$(1.1), Ca-org(3.4)
Mg	2.71	Mg^{2+}(93.3), $MgSO_4^0$(4.2), $MgCl^+$(2.0) $MgHCO_3^+$(0.5)	Mg^{2+}(92.6), $MgSO_4^0$(4.2), $MgCl^+$(2.0), $MgHCO_3^+$(0.6) Mg-org(0.3)
K	3.23	K^+(99.1), KSO_4^-(0.4), KCl^0(0.5)	K^+(99.1), KSO_4^-(0.6), KCl^0(0.5)
Na	2.07	Na^+(98.6), $NaSO_4^-$(0.6), $NaCl^0$(0.8)	Na^+(98.5), $NaSO_4^-$(0.6), $NaCl^+$(0.8)
Cu	5.63	Cu^{2+}(0.2), $CuHCO_3^+$(1.4), $CuNH_3^{2+}$(98.4)	$CuHCO_3^+$(0.3), $CuNH_3^{2+}$(19.9), Cu-org(79.8)
Cd	5.71	Cd^{2+}(25.7), $CdHCO_3^+$(1.8), $CdCO_3$(Solid) (50.1), $CdSO_4^0$(2.3), $CdCl^+$(17.8), $CdCl_2^0$(0.6), $CdNH_3^{2+}$(1.3), $CdOH^+$(0.2)	Cd^{2+}(17.2), $CdHCO_3^+$(1.6), $CdCO_3$(Solid) (64.0) $CdSO_4^0$(1.6), $CdCl^+$(12.3), $CdNH_3^{2+}$(1.2), $CdOH^+$(0.2) Cd-org(1.9)
Zn	5.64	Zn^{2+}(59.8), $ZnHCO_3^+$(20.7), $ZnSO_4^0$(4.3) $ZnCl^+$(0.7), $ZnNH_3^{2+}$(1.4), $ZnOH^+$(13.1)	Zn^{2+}(44.8), $ZnHCO_3^+$(20.6), $ZnSO_4^0$(3.2), $ZnCl^+$(0.6) $ZnNH_3^{2+}$(1.3), $ZnOH^+$(13.6), Zn-org(15.9)
Ni	4.99	Ni^{2+}(35.1), $NiHCO_3^+$(59.6), $NiSO_4^0$(2.0) $NiCl^+$(0.2), $NiNH_3^{2+}$(2.6), $NiOH^+$(0.4)	Ni^{2+}(11.8), $NiHCO_3^+$(28.7), $NiSO_4^0$(0.7), $NiNH_3^{2+}$(1.1) $NiOH^+$(0.2), Ni-org(57.5)
Pb	5.62	Pb^{2+}(0.6), $PbHCO_3^+$(13.2), $PbCO_3$(Solid) (84.9), $PbCl^+$(0.2), $PbOH^+$(1.1)	Pb^{2+}(0.4), $PbHCO_3^+$(13.2), $PbCO_3$(Solid)(84.9) $PbCl^+$(0.1), $PbOH^+$(0.9), Pb-org(0.5)
Cr	5.24	$Cr(CO_3)_3^{3-}$(100.0)	$Cr(CO_3)_3^{3-}$(100.0)
		Computed pH: 8.09	Computed pH: 8.17

APPENDIX

DESCRIPTION OF GEOCHEM PROGRAM

The following description of GEOCHEM is
abstracted from the manual entitled:
"GEOCHEM: A computer program for the
calculation of chemical equilibria in
soil solutions and other natural
water systems" by G. Sposito and S. V. Mattigod
Kearney Foundation of Soil Science
University of California, Riverside 1980

DEVELOPMENT OF THE PROGRAM

GEOCHEM is a multipurpose computer program for calculating the equilibrium speciation of the chemical elements in a soil solution. The method of calculation employed in the program is based on chemical thermodynamics. For each component of a soil solution, a mole balance equation is set up, and thermodynamic equilibrium constants corrected for ionic strength are incorporated into the various terms of this equation according to the law of mass action. The solution of the set of nonlinear algebraic equations that results from mole balance applied to all the components simultaneously ultimately provides the concentration of each dissolved, solid, and adsorbed species in the soil system under consideration. Some typical applications of GEOCHEM would include: (1) prediction of the concentrations of inorganic and organic complexes of a metal cation in a soil solution, (2) calculation of the concentration of a particular chemical form of a nutrient element in a solution bathing plant roots so as to correlate that form with nutrient uptake, (3) prediction of the fate of a pollutant metal added to a soil solution of known characteristics, and (4) estimation of the effect of changing pH, ionic strength, redox potential, water content, or the concentration of some element on the solubility of a chosen chemical element in a soil solution.

GEOCHEM is a modified version of the computer program REDEQL2, which was developed at the California Institute of Technology by F.M.M. Morel, R. E. McDuff, and J. J. Morgan. The detailed structure of REDEQL2 has been described in several published articles (Morel and Morgan, 1972; Morel et al., 1973; Morel and Yeasted, 1977) and in two reports (McDuff and Morel, 1973; Ingle et al., 1978). The methods of numerical analysis employed in the program are discussed by Morel and Morgan (1972) and are compared with the methods used in other computer programs by Leggett (1977). The potential user of GEOCHEM would be well advised to study these articles, and especially the two reports, for more than a casual understanding of the development of the program. GEOCHEM differs from REDEQL2 principally in the following ways: (1) It contains more than twice as many thermodynamic data, (2) it utilizes thermodynamic data that have been critically selected especially for soil systems, (3) it contains a method for describing cation exchange, and (4) it employs a different subroutine for correcting thermodynamic equilibrium constants for the effect of nonzero ionic strength.

GENERAL FEATURES OF THE PROGRAM

GEOCHEM is written in IBM 370 FORTRAN IV and requires about 200K of core. For any soil solution data to be analyzed by the program, the chemical components are identified as metals and unprotonated ligands. The principal variables considered by the program are the free ionic concentrations of the metals and ligands. Thus, e.g., the mole balance equation for a metal M, in the absence of precipitation-dissolution phenomena, is written in the form:

$$M_T = [M^{n+}] + \Sigma\, \alpha\, {}^{c}K_{\alpha\gamma\beta}\, [M^{n+}]^{\alpha}\, [H^{+}]^{\gamma}\, [L^{p-}]^{\beta} \tag{1}$$

where M_T is the total molar concentration of the metal, [ ] refers to a molar concentration, ${}^{c}K_{\alpha\gamma\beta}$ is the conditional stability constant for the complex, $M_{\alpha}H_{\gamma}L_{\beta}$, H refers to the proton, and L refers to a ligand. The conditional stability constants ${}^{c}K_{\alpha\gamma\beta}$ are discussed in section 2, as is the notation employed for a complex. The point to be made here is that Eq. (1) and the analogous expression for the total molar concentration of a ligand, L_T, are nonlinear algebraic equations in the free ionic concentrations. The numerical analysis problem solved by GEOCHEM is to calculate the set of free ionic concentrations that satisfies a given set of mole balance equations (one equation for each metal and each ligand in the system being investigated), subject to input values of the M_T and L_T and the values of the thermodynamic equilibrium constants $K_{\alpha\gamma\beta}$ which are stored in the program. During the computation, the ionic strength is calculated using the current values of the concentrations of all charged species that are possible and the ${}^{c}K_{\alpha\gamma\beta}$ are computed in the usual way from the values of the $K_{\alpha\gamma\beta}$ with the help of single-ion activity coefficients (see, e.g., Stumm and Morgan, 1970). Thus the computer calculation is done self-consistently, with the total analytical concentrations and the thermodynamic equilibrium constants corrected for ionic strength related through mole balance.

GEOCHEM currently stores thermodynamic data for 36 metals and 69 ligands. These metals and ligands are listed as follows, along with their code numbers (also called "INMAT numbers") and code symbols.

Metals

1. Ca^{2+}
2. Mg^{2+}
3. Sr^{2+}
4. K^{+}
5. Na^{+}
6. Fe^{3+}
7. Fe^{2+}
8. Mn^{2+}
9. Cu^{2+}
10. Ba^{2+}
11. Cd^{2+}
12. Zn^{2+}
13. Ni^{2+}
14. Hg^{2+}
15. Pb^{2+}
16. Co^{2+}
17. Co^{3+}
18. Ag^{+}
19. Cr^{3+}
20. Al^{3+}
21. Cs^{+}
22. Li^{+}
23. Be^{2+}
24. Sc^{3+}
25. TiO^{2+}
26. Sn^{2+}
27. Sn^{4+}
28. La^{3+}
29. Ce^{3+}
30. Au^{+}
31. Th^{4+}
32. UO_2^{2+}
33. Cu^{+}
34. $\mathrm{CH_3Hg}^{+}$
35. Rb^{+}
50. H^{+}

Ligands*

1. CO_3^{2-}
2. SO_4^{2-}
3. Cl^{-}
4. F^{-}
5. Br^{-}
6. I^{-}
7. NH_3^{0}
8. S^{2-}
9. PO_4^{3-}
10. $\mathrm{P_2O}_7^{4-}$
11. $\mathrm{P_3O}_{10}^{5-}$
12. $\mathrm{SiO_2(OH)}_2^{2-}$
13. $\mathrm{S_2O}_3^{2-}$
14. CN^{-}
15. AC^{-}
16. ACAC^{-}
17. CIT^{3-}
18. OX^{2-}
19. SAL^{2-}
20. TART^{2-}
21. EN^{0}
22. DIP^{0}
23. SUSAL^{3-}
24. GLY^{-}
25. GLUT^{2-}
26. PIC^{-}
27. NTA^{3-}
28. EDTA^{4-}
29. DCTA^{4-}
30. CYST^{2-}
31. NOC^{3-}
32. PHTH^{2-}
33. ARG^{-}
34. ORN^{-}
35. LYS^{-}
36. HIS^{-}

37. ASP$^-$
38. SER$^-$
39. ALA$^-$
40. TYR^{2-}
41. MET$^-$
42. VAL$^-$
43. THR$^-$
44. PHE$^-$
45. ISO$^-$
46. LEU$^-$
47. PRO$^-$
48. B(OH)$_4^-$

49. SO$_3^{2-}$
50. SCN$^-$
51. NH$_2$OH
52. MoO$_4^{2-}$
53. WO$_4^{2-}$
54. AsO$_4^{3-}$
55. HVO$_4^{2-}$
56. SeO$_3^{2-}$
57. NO$_3^-$
58. DTPA^{5-}
59. SeO$_4^{2-}$
60. MAL^{2-}

61. BES$^-$
62. ClO$_4^-$
63. CBER$^-$
64. CHAM$^-$
65. FOR$^-$
66. FUL1$^-$
67. FUL2$^-$
68. EDHG^{4-}
90. ADS1
91. ADS2
92. ADS3
93. ADS4

94. ADS5
99. OH$^-$

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* AC = acetate
ACAC = acetylacetate
CIT = citrate
OX = oxalate
SAL = salicylate
TART = tartrate
EN = ethylenediamine
DIP = dipyridyl
SUSAL = sulfosalicylate
GLY = glycine
GLUT = glutamate
PIC = picolinate
NTA = nitrilotriacetate
EDTA = ethylenediaminetetraacetate
DCTA = 1,2-diaminocyclohexanetetracetate
CYST = cysteine
NOC = nocardamine (desferriferrioxamine)
PHTH = phthalate
ARG = arginine
ORN = ornithine
LYS = lysine
HIS = histidine
DTPA = diethylenetriaminepentaacetate
ASP = aspartate
SER = serine
ALA = alanine
TYR = tyrosine
MET = methionine
VAL = valine
THR = threonine
PHE = phenylalanine
ISO = isoleucine
LEU = leucine
PRO = proline
MAL = maleate
BES = benzylsulfonate
CBER = Camp Berteau montmorillonite
CHAM = Chambers bentonite
FOR = formate
FUL1 = fulvic acid ligand
FUL2 = fulvic acid ligand
EDHG = EDDHA = ethylene dihydroxyphenyl glycine
ADS1-ADS5 = adsorption surfaces

For a given metal-ligand combination, up to six soluble complexes and up to three solids can be considered by the program. In addition to the three solids per metal-ligand combination, mixed solids containing more than one metal or ligand are included in the program as indicated in Table 1. Formation constants for up to 20 mixed solids may be incorporated into GEOCHEM; at present there are 18 included.

GEOCHEM can describe soil solution equilibria in which the partial pressures of N_2, O_2, and CO_2 are permitted to vary (see section 6). The variation in O_2 pressure is treated as an oxidation-reduction phenomenon through the inclusion of 24 redox equations in the program. These redox equations are listed in Table 2. A full discussion of redox equilibria is given in section 4 of this report.

There are several specific characteristics of GEOCHEM that should be kept in mind as the description of how to use the program is read. These characteristics are most conveniently emphasized by the following list:

(1) The data bank of GEOCHEM consists of thermodynamic data at 25°C and 1 atmosphere. Therefore, all equilibrium calculations are performed at this fixed temperature and pressure. It is possible for a user to run equilibrium computations on GEOCHEM at temperatures and pressures other than 25°C and 1 atmosphere provided that a separate data bank is compiled by the user for the temperature and pressure of interest.

(2) An accounting for metastable species and species that are not favored kinetically can be incorporated into the computation by methods which are described in sections 2 through 6. It is not necessary to assume complete thermodynamic equilibrium in order to do a calculation.

(3) The condition of electroneutrality is not imposed during a computation performed by GEOCHEM. The only constraint imposed is that of mole balance (i.e., mass conservation), as discussed above. The fact that charge conservation is not considered by the program has the advantage that analytical data in which, for reasons of experimental error or omission, the equivalents of metals do not equal the equivalents of ligands may still be analyzed for speciation. On the other hand, there is no guarantee that the weighted sum of positively-charged species will equal the weighted sum of negatively-charged species according to the electroneutrality principle. This condition may be useful when examining the speciation results for a complete and accurate set of analytical data to see if the computer results are self-consistent. If electrical neutrality is violated, the thermodynamic data that were used may need revision or augmentation.

(4) Ionic strength corrections are made in the program through the use of single-ion or single-molecule activity coefficients. The equation employed to compute the activity coefficients (at 25°C) is:

$$\log \gamma = -\frac{AZ^2\sqrt{I}}{1+aB\sqrt{I}} + B^{o}I \tag{2}$$

where $A = 0.5116$ liter^{½}/mol^{½}, $B = 0.3292 \times 10^{8}$ liter^{½}/cm mol^{½}, Z is the valence of the chemical species, and I is the true ionic strength in mol/liter. The values of the parameters a and B^{o} in turn depend on the value of I:

(a) If $I \leq 0.5$ mol/liter, $a = 1/B$ and $B^{o} = 0.3AZ^{2}$. Thus Eq. (1.2) reduces to the Davies equation.

(b) If $I > 0.5$ mol/liter, $B^{o} = 0.041$ liter/mol and $a = 4 \times 10^{-8}$ cm, 5×10^{-8} cm, and 6×10^{-8} cm for monovalent, bivalent, and trivalent ions, respectively. In this case, Eq. (2) becomes the Helgeson (1969) equation as modified by Truesdell and Jones (1973).

(c) For neutral species, at all values of I, $B^{o} = 0.1$ liter/mole (see, e.g., Helgeson, 1969). Since $Z = 0$ in this case, the first term in Eq. (2) does not contribute to the calculation of .

INPUT DATA REQUIRED BY THE PROGRAM

To some extent the data which must be input to GEOCHEM in order for the program to do a speciation analysis depend on the type of problem to be considered. The general requirements are as follows:

(1) Total molar concentrations of each metal and each ligand.

(2) The pH value or the total net proton concentration in mol/liter. If the pH value is available, it should be used (see section 2).

(3) If solids are to be considered, a choice must be made as to which solid phases will be permitted to precipitate during the computation.

(4) If the soil solution is to be regarded as open with respect to CO_2, the partial pressure of this gas must be imposed.

(5) If redox equilibria are important, a choice of which redox half-reactions to allow must be made and the partial pressure of N_2 must be specified if NO_3^- is one of the ligands considered.

(6) The nature of adsorbing surfaces (PZC and other properties) must be specified if "specific adsorption" of metals is to be considered (see section 5).

TABLE 1. MIXED SOLIDS CONSIDERED BY GEOCHEM

Code No.	Code Name*	Code No.	Code Name*
1	CHLORITE	10	FECACARB
2	ILLITE	11	FECOCARB
3	MICCLINE	12	FEMNCARB
4	NA-MONT	13	FECUCARB
5	PBPO4CL	14	MUSCOVIT
6	FAPATITE	15	K-MONT
7	CDZNCARB	16	CA-MONT
8	CD3ZNCARB	17	MG-MONT
9	FENICARB	18	VERM

* CHLORITE = $Mg_5Al_2Si_3O_{10}(OH)_8$

MICCLINE = microcline

NA-MONT = $Na_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

PBPO4CL = $Pb_5(PO_4)_3Cl$

FAPATITE = fluorapatite

CDZNCARB = $CdZn(CO_3)_2$

CD3ZNCARB = $Cd_3Zn(CO_3)_4$

FENICARB = $Fe_9Ni(CO_3)_{10}$

FECACARB = $Fe_9Ca(CO_3)_{10}$

FECOCARB = $Fe_9Co(CO_3)_{10}$

FEMNCARB = $Fe_4Mn(CO_3)_5$

FECUCARB = $Fe_4Cu(CO_3)_5$

MUSCOVIT = muscovite

K-MONT = $K_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

CA-MONT = $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

MG-MONT = $Mg_{0.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$

VERM = Mg-vermiculite

TABLE 2. REDOX REACTIONS AND REDOX PARAMETERS IN GEOCHEM

Reaction No.	Reaction Type	M	L	CM	CL	NE*	NH†	Redox Reaction	log K	Reaction Name
1	-10	6	7	0	0	-1	0	$Fe^{3+} + e- \text{—>} Fe^{2+}$	13.0	FE2/FE3
2	-2	8	99	1	0	2	-4	$Mn^{2+} + 2H_2O \text{—>} MnO_2(s) + 4H^+ + 2e-$	41.4	MNO2
3	-2	14	99	1	0	-2	0	$Hg^{2+} + 2e- \text{—>} Hg(liq)$	29.0	HG(LIQ)
4	3	14	99	2	0	-2	0	$2Hg^{2+} + 2e- \text{—>} Hg_2^{2+}\ (aq)$	31.1	HG2+2
5	-2	15	99	1	0	2	-4	$Pb^{2+} + 2H_2O \text{—>} PbO_2(s) + 4H^+ + 2e-$	-49.2	PBO2
6	-10	16	17	0	0	1	0	$Co^{2+} \text{—>} Co^{3+} + e-$	-30.9	CO2/CO3
7	3	50	1	0	1	-4	0	$CO_3^{2-} + 6H^+ + 4e- \text{—>} CH_2O(aq) + 2H_2O$	13.3	CH2O
8	10	2	8	0	0	-8	8	$SO_4^{2-} + 8H^+ + 8e- \text{—>} S^{2-} + 4H_2O$	20.2	SO4/S-2
9	10	7	57	0	0	8	-9	$NH_3(aq) + 3H_2O \text{—>} NO_3^- + 9H^+ + 8e-$	-88.1	NH3/NO3
10	1	50	99	0	0	2	-2	$2H_2O \text{—>} H_2O_2 + 2H^+ + 2e-$	-60.0	H2O2
11	-10	26	27	0	0	2	0	$Sn^{2+} \text{—>} Sn^{4+} + 2e-$	-5.1	SN2/SN4
12	-2	7	8	1	2	2	0	$Fe^{2+} + 2S^{2-} \text{—>} FeS_2(s) + 2e-$	45.3	FES2

Continued.

TABLE 2. (Continued)

Reaction No.	Reaction Type	M	L	CM	CL	NE	NH	Redox Reaction	log K	Reaction Name
13	-2	6	99	3	0	-1	-8	$3Fe^{3+} + 4H_2O + e^- \rightarrow Fe_3O_4(s) + 8H^+$	18.3	FE3O4
14	-3	8	99	3	0	2	-8	$3Mn^{2+} + 4H_2O \rightarrow Mn_3O_4(s) + 8H^+ + 2e^-$	-61.7	MN3O4
15	-1	8	99	1	0	1	-3	$Mn^{2+} + 2H_2O \rightarrow MnO(OH)(s) + 3H^+ + e^-$	-22.9	MnOOH
16	4	19	99	2	0	6	-14	$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$	-125.0	CR2O7
17	5	19	99	1	0	3	-7	$Cr^{3+} + 4H_2O \rightarrow HCrO_4^{2-} + 7H^+ + 3e^-$	-68.5	HCRO4
18	6	19	99	1	0	3	-8	$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^-$	-74.9	CRO4
19	-1	50	8	0	1	2	0	$S^{2-} \rightarrow S(s) + 2e^-$	16.1	1S(S)
20	3	50	8	0	4	6	0	$4S^{2-} \rightarrow S_4^{2-} + 6e^-$	156.7	4S4-2
21	4	50	8	0	5	8	0	$5S^{2-} \rightarrow S_5^{2-} + 8e^-$	276.0	5S5-2
22	-10	33	9	0	0	1	0	$Cu^+ \rightarrow Cu^{2+} + e^-$	-2.6	CU1/CU2
23	-1	33	99	1	0	-1	0	$Cu^+ + e^- \rightarrow Cu(s)$	8.8	CU(S)
24	-1	50	57	0	1	-10	12	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O$	210.6	N2(G)

[*] NE = number of electrons produced in the reaction.

[+] NH = number of protons consumed in the reaction.