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CHEMISTRY OF GYPSUM POND SYSTEMS

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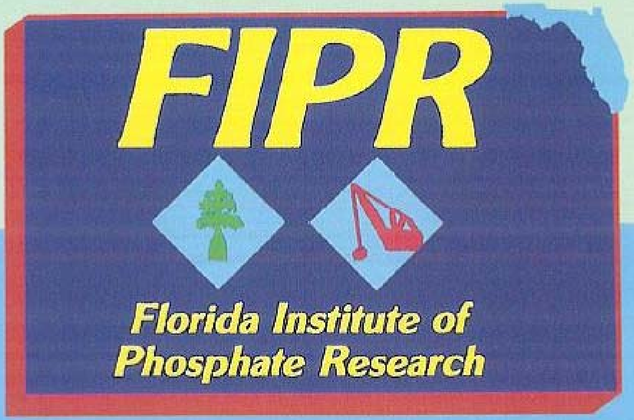

Florida Institute of
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AUGUST 1992

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CHEMISTRY OF GYPSUM POND SYSTEMS

(FIPR Contract No. 85-05-025R)

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CHEMISTRY OF GYPSUM POND SYSTEMS

(FIPR No. 85-05-025R)

EXECUTIVE SUMMARY

Previous studies on management of phosphoric acid gypsum ponds included attempts to describe chemical species and processes that influenced distributions of phosphorus, fluorine, and other elements in these systems. A lack of qualitative and quantitative information about the pertinent chemistry frustrated those efforts. The Florida Institute of Phosphate Research (FIPR) and the Tennessee Valley Authority (TVA) sponsored an investigation to gain information that will assist in better understanding the chemistry of gypsum pond systems.

Samples of gypsum pond return, discharge, and slurry waters were collected from operating Florida phosphoric acid producing plants in May 1988 and in December 1989. Densities, pH's, and concentrations of P_2O_5, F, SO_4-S, Si, Al, Ca, Fe, K, Mg, Na, NH_4-N, and Cl were determined on filtered aliquots of the samples. Results showed a wide variance in pond compositions. For example, approximate ranges of measured pH's were 1.4 to 1.9, $\%P_2O_5$ ranged 0.5 to 2.7, %F from 0.3 to 1.3, $\%SO_4$-S from 0.12 to about 0.3, and %Si from 0.1 to 0.3.

Inspections of sample data indicated that the operating characteristics of individual acid plants strongly influenced pond water compositions. Results from correlation and factor analyses point to feed rock source, free sulfuric acid, and the presence or absence of ancillary ammoniated phosphate production as typical influential characteristics. Sample type (return, discharge, or slurry waters) had negligible influence on variations in mean sample compositions. The only significant seasonal effects detected for samples collected in this study were the mean density and F, Si, and K concentrations were higher for the samples collected in May 1988 than for samples collected in December 1989. No large, universal variations were observed in compositions of pond water samples collected at different seasons.

Solids suspended in collected samples and sediments produced during storage contained gypsum; the alkali fluosilicates, Na_2SiF_6 and $NaKSiF_6$; chukhrovite, $Ca_4SO_4SiAlF_{13}\cdot nH_2O$; and a complex iron phosphate, $Fe_3(NH_4,K,H)H_8(PO_4)_6\cdot 6H_2O$. Data evaluations suggested the latter compound was mostly, but not exclusively, present in the ammonium form.

Sample aliquots were evaporated to increase concentrations and force precipitation of the principal saturating solid phases. Phases consistently detected in solids collected after the evaporations were gypsum and the alkali fluosilicates. Attempts to induce chukhrovite precipitation by addition of Al before evaporations were not successful. Results from mass balance experiments, conducted to check for inadvertent material losses that could have influenced distribution among the solution and solid phases, showed that the amounts of P, Si, and F in solutions and solids recovered after evaporations at 60°C equaled the amounts contained in the starting solutions within experimental error.

Pond water samples were treated with a variety of Ca and Al compounds to attempt removal of F by induced precipitation of F-containing solids. As expected, common neutralizing agents such as $Ca(OH)_2$ and a clay-sized fraction from a dolomitic phosphate ore were most effective agents for reducing soluble F levels. Reactions of pond water with Al powder and $AlPO_4$ also reduced soluble F concentrations. Treatments with the clay-sized fraction from a nondolomitic ore, an attapulgite clay, and $Al(OH)_3$ did not cause reductions in soluble F concentrations.

Results from computations with the chemical equilibrium modeling program PHREEQE were in good qualitative agreement with other investigations. The P species with highest computed concentrations in pond water samples were H_3PO_4 and $H_2PO_4^-$, consistent with the known dissociation reactions of phosphoric acid and expected distribution of species at low pH's. The dominant F species predicted by the model computations was SiF_6^{-2}; this was the only F-containing species detected by NMR spectroscopy. Saturation indices computed by PHREEQE predicted gypsum and sodium fluosilicate to be the important saturating phases, and these were the most prevalent compounds found in sediments collected from pond water samples. There was good agreement between ion activity products of saturated species and solubility product constant values obtained from other sources.

Solubility product constants were estimated for complex compounds about which no information was available in the literature. Log K is estimated to be -78.77 for chukhrovite dissolution by the reaction

$$Ca_4SO_4AlSiF_{13}\cdot 10H_2O = 4Ca^{+2} + Al^{+3} + 4H^+ + H_4SiO_4 + 6H_2O + SO_4^{-2} + 13F^-.$$

Estimated Log K_{sp} values for the ammonium and potassium forms of $Fe_3(NH_4,K)H_8(PO_4)_6\cdot 6H_2O$ are -140.9 and -141.6, respectively.

SECTION 1

INTRODUCTION

BACKGROUND

A wet-process phosphoric acid plant is typically operated in a closed loop with a system of drainage ditches and one or more diked ponds which serve to store and evaporatively cool the large quantity of water needed in the acid manufacturing operations. Although separate ponds might be maintained for various purposes, the overall water handling system is referred to as the gypsum pond for convenience. Since pond water is repeatedly used for scrubbing fumes generated during phosphoric acid production and for sluicing gypsum to the disposal pile, it becomes acidic and contaminated with phosphate, sulfate, fluosilicate, and other chemical species. The complex compositions of gypsum ponds and the natural variations in pond. compositions that occur at different sites and at different seasons of the year make it difficult to describe and predict chemical reactions that affect subsequent interactions of the pond with the chemical plant and the environment.

Considerable attention has been given to possible interactions of gypsum ponds with the environment. Much of this has been focused on problems related to the effects of unintentional movements of pond water constituents into the environment, such as evaporation of volatile compounds from pond surfaces or seepage of pond water into ground water. These concerns have stimulated numerous research programs to assess the impacts of gypsum ponds on the environment.

In the 1960s and 1970s emphasis was placed on determining the potential for movement of volatile fluorine compounds from gypsum ponds into the atmosphere, and several studies were conducted to measure fluorine emissions from pond surfaces. Linero and Barker [1] reviewed the field investigations of fluorine emissions that were reported by Cross and Ross [2] and by King and Farrell [3], and laboratory investigations made with pond water with added HF and H_2SiF_6 by Tatera [4]. Lehr [5] compared the fluoride vapor pressures measured by Tatera for gypsum pond water samples with added H_2SiF_6 with data from laboratory studies on reagent chemicals by Smirnova [6] and Baur [7]. The data correlated well and provided an estimate of a Henry's Law constant which related vapor pressure to the total %F in solution.

Potential movements of pond water constituents into the soil and ground water environments received less attention. Lehr inferred from past research on reactions of fertilizers with solids that pond water constituents such as phosphate, sulfate, and fluoride would be immobilized by reactions with clays and carbonates in the soil. This inference was supported by results of experimental studies by Wissa [8], Cochrane [9], and Murray [10] who found that solution phase concentrations of these species were reduced when gypsum pond waters reacted with soil minerals. Wissa and Cochrane both detected evidence of cementation in reaction zones, but the identity of the product from the cementation reaction was uncertain. The X-ray diffraction pattern reported by Cochrane and the description of the crystalline compound detected by Wissa suggest an important product may be a high fluorine-content compound, chukhrovite, which has been detected in laboratory studies on phosphoric acid systems [11].

There is relatively little information in the literature about the solubility status of gypsum ponds and the speciations of soluble species that likely influence interactions of the ponds with the environment. The emission parameters and Henry's Law constants that were estimated in studies on fluorine volatilizations described the available data assuming other solution composition variables were constant or had negligible effects. Attempts by Linero and Baker and by Lehr to describe how changes in pond chemistry might affect elemental distributions among soluble and insoluble phases were frustrated by a lack of information about the identities of important species and their equilibrium constants. They and Boscak [12] recommended further research to obtain better information about chemical species and reactions which will determine the behaviors of pond water constituents.

Murray and Lewis [13] applied a computerized aqueous chemical equilibrium model, GEOCHEM, to evaluate chemical species in pond water samples which had been reacted with various soil minerals. They found that computerized chemical modelingwas helpful in predictingbehaviors of ions, but models showed deviations from experimentally observed behaviors. Difficulties arose from problems in correcting for ionic strength effects and the lack of thermodynamic constants in the computerized chemical model data base. Based on the species they discussed in their report, it appears that the fluosilicate ion was not included in GEOCHEM model. Thus, the results of the model computations failed to account for a major chemical constituent of the pond systems.

OBJECTIVES

The current investigation was undertaken to acquire information which will provide a better understanding of the chemistry of gypsum pond systems. Specific attention was given to solution and solid phase identities and compositions to acquire information about pond system solubilities.

Objectives were to

- identify the major solid and soluble complex species that exist in a gypsum pond system,
- determine how changes in system compositions affect distributions of elements in the system,
- explore means for modifying natural distributions to remove some elements as low-solubility compounds, and
- determine whether existing computer software for modeling chemical equilibria provide useful information about gypsum pond systems.

SCOPE OF WORK

Samples were collected from gypsum pond systems at several operating phosphoric acid plants and analyzed to obtain information about their compositions. Statistical tests were applied to determine how sampling conditions influenced composition variations. Solids that were suspended in collected samples or were precipitated from samples during storage were analyzed and characterized to identify compounds that influenced the solubility status of gypsum ponds.

Solution phases of collected samples were evaporated to increase concentrations and force precipitation of saturating solids. Solution and solid phases were analyzed and data evaluated to investigate possible modes of elemental redistribution in pond systems. Selected samples were treated with additional amounts of key elements to investigate how variations in their concentrations affected precipitation patterns.

Exploratory experiments were conducted to examine possible ways to control pond chemistry by treating pond waters with relatively inexpensive reagents (e.g., clays, phosphate slimes, dolomite).

A computerized chemical modeling program which had been developed to calculate speciation distributions and solubility status of aqueous geochemical systems was tested with gypsum pond composition data.

Concentrations of soluble complex speciations were computed to obtain information about important species that are equilibrated with saturated solutions. Results from the computations and experimental studies were used to estimate solubility product constants of compounds for which no values were found in the literature.

SECTION 2

COLLECTION AND ANALYSES OF GYPSUM POND WATER SAMPLES

SAMPLING LOCATIONS AND DATES

After discussions with FIPR personnel and Dr. Ken Parks, consultant on the project, it was decided that analytical data would be needed for three types of water samples within the chemical plant-gypsum pond systems at a variety of operating phosphoric acid production sites. It also was decided that collections at different seasons of the year would be desired to obtain information about variations in compositions that might occur with variations in climate. A number of phosphoric acid producers in Florida were contacted to request their participation in the project. Seven companies participated; most requested anonymity, so sample identifications were coded.

In May 1988 samples of pond-to-plant return water, plant-to-pond discharge water, and gypsum slurry decant or filtrate water were collected from each of six phosphoric acid producers. In December 1989 additional samples of return waters and slurry waters were collected and sent to TVA so that a comparison could be made between compositions in warm weather and cool weather conditions. Collections made for this latter group included five of the initial sites sampled in May 1988. Samples were transported to TVA's laboratories in Muscle Shoals, Alabama, for analyses and experimental research.

CHEMICAL ANALYSES

An aliquot was taken from each sample and filtered for analyses and subsequent experimentation. Densities and pH's of the aliquots were determined at ambient room temperature (25°C ± 2°C). Filtrates were analyzed for P, S (sulfate), N (ammonium), F, Cl, Na, K, Ca, Mg, Al, Fe, and Si. At several times during the course of experimental studies, additional aliquots were taken from the samples and analyzed. Analytical methods used included specific ion electrode methods (most ammonium-N and F determinations), ion chromatography (some ammonium-N, F, sulfate-S, Na, and K determinations), and inductively coupled plasma spectroscopy (P, S, and cation determinations). Average compositions for the samples are given in Table 1. Detailed results from replicate determinations performed on the samples are in Appendix A.

OTHER INVESTIGATIONS

Aliquots of the pond water samples collected in May 1988 were examined by nuclear magnetic resonance (NMR) spectroscopy. The ^{19}F spectra were recorded at ambient temperature (about 26°C) with a JEOL FX-90Q instrument operated at 84.26 MHz. The external standard was trichlorofluoromethane. Each pond water sample gave a single ^{19}F NMR peak at -129 ppm which is assigned to the SiF_6^{-2} ion. This supports the assumption that the major F-containing species is fluosilicate. An attempt to quantitate F in the samples by NMR was not successful. Areas of the ^{19}F peaks did not show good linear correlation with sample F concentrations. The normalized areas (peak area divided by % F) were negatively correlated with the F concentration, indicating that the relative NMR response to F decreased with increasing F concentration.

Table 1. Gypsum Pond Water Sample Mean Compositions

	Density		<-------------					Weight %						--------------->	Mole ratio
ID[a]	g/mL	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl	F:Si
D1-1	1.032	1.58	2.02	1.06	0.299	0.269	0.0303	0.124	0.0195	0.038	0.033	0.214	0.196	0.030	5.8
D2-1	1.031	1.64	2.35	0.81	0.129	0.204	0.0134	0.161	0.0304	0.041	0.026	0.239	0.083	0.130	5.9
D3-1	1.008	1.94	0.47	0.38	0.132	0.105	0.0074	0.086	0.0080	0.017	0.008	0.117	0.064	0.010	5.4
D4-1	1.033	1.56	2.16	1.14	0.151	0.286	0.0305	0.148	0.0479	0.037	0.043	0.191	0.048	0.013	5.9
D5-1	1.016	1.81	0.96	0.64	0.127	0.178	0.0202	0.111	0.0179	0.019	0.013	0.137	0.065	0.010	5.3
D6-1	1.017	1.76	1.05	0.73	0.141	0.191	0.0063	0.123	0.0114	0.035	0.022	0.211	0.003	0.009	5.7
R1-1	1.034	1.63	2.02	1.07	0.274	0.271	0.0303	0.117	0.0220	0.042	0.034	0.216	0.169	0.012	5.8
R2-1	1.032	1.60	2.50	0.74	0.145	0.209	0.0130	0.167	0.0300	0.040	0.033	0.228	0.051	0.136	5.2
R3-1	1.009	1.88	0.48	0.41	0.139	0.108	0.0081	0.091	0.0082	0.011	0.012	0.125	0.061	0.010	5.6
R4-1	1.034	1.57	2.18	1.03	0.159	0.278	0.0176	0.127	0.0412	0.037	0.051	0.199	0.060	0.013	5.5
R5-1	1.017	1.78	0.98	0.65	0.131	0.173	0.0213	0.121	0.0173	0.019	0.013	0.157	0.056	0.007	5.6
R6-1	1.018	1.68	1.12	0.72	0.138	0.199	0.0119	0.132	0.0116	0.035	0.027	0.208	0.004	0.007	5.3
R1-2	1.030	1.68	2.31	0.99	0.259	0.235	0.0272	0.125	0.0188	0.031	0.038	0.220	0.198	0.014	6.2
R3-2	1.003	1.93	0.46	0.32	0.137	0.086	0.0069	0.088	0.0076	0.011	0.010	0.114	0.049	0.012	5.5
R4-2	1.023	1.60	2.04	1.02	0.177	0.230	0.0256	0.135	0.0324	0.030	0.041	0.192	0.048	0.003	6.6
R5-2	1.009	1.66	1.17	0.55	0.170	0.132	0.0202	0.116	0.0153	0.013	0.018	0.136	0.048	0.003	6.2
R6-2	1.016	1.69	1.40	0.64	0.162	0.167	0.0120	0.129	0.0143	0.030	0.027	0.217	0.002	0.004	5.7
R7-2	1.027	1.36	2.13	1.34	0.214	0.345	0.0292	0.185	0.0364	0.030	0.032	0.190	0.008	0.013	5.7
S1-1	1.034	1.64	2.17	1.06	0.290	0.266	0.0341	0.120	0.0258	0.044	0.033	0.217	0.227	0.010	5.9
S2-1	1.030	1.74	2.25	0.71	0.128	0.191	0.0095	0.162	0.0331	0.041	0.028	0.235	0.038	0.113	5.5
S3-1	1.009	1.88	0.53	0.58	0.150	0.137	0.0084	0.084	0.0101	0.018	0.007	0.199	0.061	0.010	6.3
S4-1	1.041	1.58	2.74	1.10	0.176	0.280	0.0223	0.144	0.0562	0.040	0.052	0.212	0.059	0.012	5.8
S5-1	1.021	1.75	1.16	0.88	0.157	0.201	0.0226	0.108	0.0207	0.030	0.015	0.215	0.132	0.007	6.5
S6-1	1.016	1.87	1.25	0.47	0.140	0.118	0.0086	0.103	0.0089	0.038	0.022	0.218	0.004	0.007	5.9
S1-2	1.033	1.66	2.57	1.04	0.241	0.223	0.0430	0.133	0.0276	0.025	0.049	0.224	0.205	0.012	6.9
S3-2	1.007	1.94	0.51	0.42	0.128	0.117	0.0056	0.095	0.0076	0.018	0.009	0.178	0.050	0.012	5.3
S4-2	1.022	1.60	1.89	1.03	0.179	0.250	0.0308	0.155	0.0312	0.020	0.039	0.185	0.049	0.001	6.1
S5-2	1.020	1.75	1.48	0.72	0.152	0.160	0.0195	0.141	0.0187	0.014	0.023	0.222	0.050	0.004	6.7
S6-2	1.017	1.77	1.60	0.62	0.121	0.154	0.0136	0.144	0.0221	0.024	0.034	0.237	0.001	0.004	6.0
S7-2	1.032	1.37	2.29	1.35	0.201	0.322	0.0382	0.187	0.0431	0.033	0.036	0.195	0.008	0.014	6.2

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[a] Sample ID code = "AB-C", where

A = Sample type: R = Return from pond, D = Discharge to pond, S = Slurry decant or filtrate;
B = Collection site number, 1 through 7; and
C = Collection group: 1 = May 1988 and 2 = December 1989.

Pond water aliquots also were examined by Fourier transform infrared (FTIR) spectroscopy. Spectra were recorded at ambient temperature with a Nicolet 60SX instrument operated at 4 cm^{-1} resolution. Samples were contained in a Spectrotech CIRCLE cell; a cell containing deionized water was the background reference. All spectra had absorbance bands in the region from 1320 to 845 cm^{-1} which are assigned to vibrations of orthophosphate species. The summed area of absorbance peaks in the region from 1320 to 845 cm^{-1} correlated reasonably well with total P_2O_5 concentration; however there was a moderate amount of scatter that increased with increasing P_2O_5 concentrations. The absorbance band at 1000 cm^{-1}, which is assigned to a P-O stretch, showed less variation from sample to sample than did other bands, and the area of the 1000 cm^{-1} peak showed better correlation with concentration than did the area of the total IR absorbing region.

COLLECTION SITE EFFECTS

Inspections of the compositions in Table 1 show relatively large variations among compositions of samples collected at different acid plants. This is attributed to differences in operating practices involving fluosilicate recovery or co-production of ammonium phosphate fertilizers that occurred at the different plants. These practices obviously influence the quantities of materials passed into the pond systems and the resultant compositions of the pond water samples.

EFFECTS OF SAMPLE TYPES

The sample collection scheme included two pond inputs (gypsum slurry and plant discharge waters) and one output (return water) to provide data for investigating whether significant changes in composition could be detected at opposing ends of the material flow through the pond system. The composition data were grouped according to sample type and means and variances for the groups were calculated. Evaluations with the Student t Test for means and the F Test for variances were made to test hypotheses that the means and variances for the data pairs return-discharge, return-slurry, and discharge-slurry were equal. Results from these tests are tallied in Table 2.

Calculated F and t values were compared with values in standard tables of the F statistic and the t statistic to determine whether values from the gypsum pond samples showed significant deviations from values that would be expected from random variations in a normally distributed data set. All comparisons except two gave t and F values that were within ranges that would be expected for groups with equal means and variances. The two deviant comparisons both involved Na concentrations in slurry water samples. Therefore, except for Na, the hypothesis that compositions of the discharge, return, and slurry water samples are equal is retained.

Table 2. Gypsum Pond Water Sample F- and t-Tests by Types (D, R, S)[a]

					Sample Group Comparisons					
					D to R		D to S		R to S	
Variable		No. Cases	Mean	Standard Deviation	F value	t value	F value	t value	F value	t value
Density	Type = D	6	1.023	0.011	1.02	0.35	1.00	-0.13	1.02	-0.58
	Type = R	12	1.021	0.011						
	Type = S	12	1.024	0.011						
pH	Type = D	6	1.715	0.148	1.00	0.58	1.11	0.03	1.10	-0.66
	Type = R	12	1.672	0.148						
	Type = S	12	1.713	0.156						
P_2O_5	Type = D	6	1.502	0.772	1.16	-0.17	1.08	-0.54	1.07	-0.46
	Type = R	12	1.566	0.719						
	Type = S	12	1.703	0.744						
F	Type = D	6	0.793	0.279	1.17	0.02	1.06	-0.27	1.10	-0.35
	Type = R	12	0.790	0.302						
	Type = S	12	0.832	0.288						
SO_4S	Type = D	6	0.163	0.067	1.92	-0.45	1.76	-0.31	1.09	0.17
	Type = R	12	0.175	0.048						
	Type = S	12	0.172	0.051						
Si	Type = D	6	0.206	0.066	1.31	0.08	1.05	0.12	1.24	0.04
	Type = R	12	0.203	0.075						
	Type = S	12	0.202	0.067						
Al	Type = D	6	0.018	0.011	1.71	-0.13	1.40	-0.55	2.39	-0.63
	Type = R	12	0.019	0.008						
	Type = S	12	0.021	0.013						
Ca	Type = D	6	0.126	0.027	1.04	-0.17	1.29	-0.40	1.24	-0.31
	Type = R	12	0.128	0.027						
	Type = S	12	0.131	0.030						
Fe	Type = D	6	0.023	0.015	1.70	0.20	1.04	-0.40	1.63	-0.79
	Type = R	12	0.021	0.011						
	Type = S	12	0.025	0.014						

Table 2 (continued)

				Comparisons:	D to R		D to S		R to S	
Variable		No. Cases	Mean	Standard Deviation	F value	t value	F value	t value	F value	t value
K	Type = D	6	0.031	0.010	1.15	0.69	1.01	0.47	1.17	-0.30
	Type = R	12	0.027	0.011						
	Type = S	12	0.029	0.010						
Mg	Type = D	6	0.024	0.013	1.02	-0.60	1.26	-0.68	1.28	-0.17
	Type = R	12	0.028	0.013						
	Type = S	12	0.029	0.014						
Na	Type = D	6	0.185	0.048	1.42	0.06	6.59	-1.72	4.64	-2.19
	Type = R	12	0.184	0.040						
	Type = S	12	0.211	0.019						
NH_4N	Type = D	6	0.077	0.065	1.13	0.44	1.35	0.08	1.53	-0.39
	Type = R	12	0.063	0.061						
	Type = S	12	0.074	0.075						
Cl	Type = D	6	0.034	0.048	1.68	0.70	2.47	0.90	1.47	0.17
	Type = R	12	0.020	0.037						
	Type = S	12	0.017	0.030						

Critical values:	D to R	D to S	R to S
$t_{0.025}$	2.12	2.12	2.07
$t_{0.050}$	1.75	1.75	1.72
$F_{0.05}$	3.00	3.00	2.69

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[a] Types: D = Discharge plant-to-pond
R = Return pond-to-plant
S = Slurry filtrate or decant

In considering the Na concentrations, the t test results indicated that the mean Na concentration for the discharge samples exceeded that for the slurry sample group at the 90% significance level, and the mean Na concentration for the return water samples exceeded that for the slurry water samples at the 95% significance level. Results from the F tests showed that variances in Na data for D-S and R-S pairings exceeded statistically expected values at the 95% confidence level. The mean Na concentration in the group of slurry water samples was about 0.21%, and mean concentrations for the return and discharge water samples were each about 0.18%. The standard deviation for the slurry water data (about 0.02) was about one-half that of either of the other two groups (about 0.04). These differences are relatively small when compared with the variations in data for other groupings of composition-sample type data. Thus, the "significant" differences in Na concentration data may be due more to a happenstance of relatively low scatter in analytical data than to a chemical phenomenon.

EFFECTS OF SAMPLE COLLECTION DATE

Evaluations to detect whether sample compositions varied according to the time of collection were made with data for which the same type sample had been collected from the same plant sites in May 1988 and in December 1989. These ten pairs, listed in Table 3, were evaluated with the Paired t Test method to determine whether mean differencesbetween data for the May 1988 samples (Group 1) and the December 1989 samples (Group 2) showed significant deviations from zero. Calculated t statistics for differences are given at the bottom of Table 3. The critical t values which are shown are the extreme values that would be expected at several levels of significance if collection time had no influence on the variables and differences in means were solely due to random variations.

Calculated t values for differences in means of Si and K concentrations between the groups exceeded the value expected for a normal distribution at the 99% significance level. Sample densities and Ca concentrations also were influenced by collection time; the calculated t values were outside the expected range at the 95% significance level. Similarly, the t value for the mean difference in F concentrations exceeded the critical value at the 90% significance level. Therefore, the hypothesis that there is no significant difference in means for these variables is rejected. The mean density and the mean F, Si, and K concentrations were higher for samples collected in May 1988 than for samples collected in December 1989, and the mean Ca concentration was lower for the May 1988 samples than for the December 1989 samples.

CORRELATIONS AMONG SAMPLE VARIABLES

Sample composition data were subjected to analyses with the correlation procedure of the SPSS/PC+ software package to examine relationships among the pond water composition variables. Correlation coefficients computed for pairs of variables Density, pH, P_2O_5, F, etc. are listed in Table 4. Coefficients marked with "*" and "**" are highly significant; the probabilities are less than 0.01 and 0.001, respectively, that coefficients with these values would be found by random selection from uncorrelated data. Inspection of Table 4 shows significant correlations among several variables. Chloride is conspicuous by its absence of significant correlation with any other variable. Correlation of F with Si is very high, consistent with the assumption that F in gypsum ponds exists mostly in a fluosilicate complex. All significant correlations with pH are negative, which is understandable since the more acid solutions (i.e., low pH's) would contain higher levels of phosphoric acid and dissolved ions.

Table 3. Paired t-Tests for Gypsum Pond Water Sample Collection Groups 1 and 2

Mean Compositions For Sample Pairings

			<---------------				Weight %					-------------->		
ID	Density	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl
R1-1	1.034	1.63	2.02	1.07	0.274	0.271	0.0303	0.117	0.0220	0.042	0.034	0.216	0.169	0.012
R1-2	1.030	1.68	2.31	0.99	0.259	0.235	0.0272	0.125	0.0188	0.031	0.038	0.220	0.198	0.014
R3-1	1.009	1.88	0.48	0.41	0.139	0.108	0.0081	0.091	0.0082	0.011	0.012	0.125	0.061	0.010
R3-2	1.003	1.93	0.46	0.32	0.137	0.086	0.0069	0.088	0.0076	0.011	0.010	0.114	0.049	0.012
R4-1	1.034	1.57	2.18	1.03	0.159	0.278	0.0176	0.127	0.0412	0.037	0.051	0.199	0.060	0.013
R4-2	1.023	1.60	2.04	1.02	0.177	0.230	0.0256	0.135	0.0324	0.030	0.041	0.192	0.048	0.003
R5-1	1.017	1.78	0.98	0.65	0.131	0.173	0.0213	0.121	0.0173	0.019	0.013	0.157	0.056	0.007
R5-2	1.009	1.66	1.17	0.55	0.170	0.132	0.0202	0.116	0.0153	0.013	0.018	0.136	0.048	0.003
R6-1	1.018	1.68	1.12	0.72	0.138	0.199	0.0119	0.132	0.0116	0.035	0.027	0.208	0.004	0.007
R6-2	1.016	1.69	1.40	0.64	0.162	0.167	0.0120	0.129	0.0143	0.030	0.027	0.217	0.002	0.004
S1-1	1.034	1.64	2.17	1.06	0.290	0.266	0.0341	0.120	0.0258	0.044	0.033	0.217	0.227	0.010
S1-2	1.033	1.66	2.57	1.04	0.241	0.223	0.0430	0.133	0.0276	0.025	0.049	0.224	0.205	0.012
S3-1	1.009	1.88	0.53	0.58	0.150	0.137	0.0084	0.084	0.0101	0.018	0.007	0.199	0.061	0.010
S3-2	1.007	1.94	0.51	0.42	0.128	0.117	0.0056	0.095	0.0076	0.018	0.009	0.178	0.050	0.012
S4-1	1.041	1.58	2.74	1.10	0.176	0.280	0.0223	0.144	0.0562	0.040	0.052	0.212	0.059	0.012
S4-2	1.022	1.60	1.89	1.03	0.179	0.250	0.0308	0.155	0.0312	0.020	0.039	0.185	0.049	0.001
S5-1	1.021	1.75	1.16	0.88	0.157	0.201	0.0226	0.108	0.0207	0.030	0.015	0.215	0.132	0.007
S5-2	1.020	1.75	1.48	0.72	0.152	0.160	0.0195	0.141	0.0187	0.014	0.023	0.222	0.050	0.004
S6-1	1.016	1.87	1.25	0.47	0.140	0.118	0.0086	0.103	0.0089	0.038	0.022	0.218	0.004	0.007
S6-2	1.017	1.77	1.60	0.62	0.121	0.154	0.0136	0.144	0.0221	0.024	0.034	0.237	0.001	0.004

Comparisons For Differences (Group 1 - Group 2):

	Density	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl
Mean diff.	0.005	-0.002	-0.08	0.06	0.003	0.028	-0.0019	-0.011	0.0026	0.010	-0.002	0.004	0.013	0.003
t values	2.78	-0.10	-0.68	2.20	0.35	3.63	-1.19	-2.39	0.86	4.23	-0.77	0.84	1.52	1.69

Critical values for 9 degrees of freedom: t = 1.83 (P = 0.10) t = 2.26 (P = 0.05) t = 3.25 (P = 0.01)

Table 4. Correlation Coefficient Matrix for Pond Water Sample Composition Variables[a]

	Density	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K
Density	1.000									
pH	-0.757^{**}	1.000								
P_2O_5	0.943^{**}	-0.797^{**}	1.000							
F	0.838^{**}	-0.911^{**}	0.805^{**}	1.000						
SO_4S	0.554^{*}	-0.496^{*}	0.506^{*}	0.640^{**}	1.000					
Si	0.851^{**}	-0.920^{**}	0.795^{**}	0.980^{**}	0.596^{**}	1.000				
Al	0.655^{**}	-0.712^{**}	0.650^{**}	0.836^{**}	0.742^{**}	0.759^{**}	1.000			
Ca	0.656^{**}	-0.828^{**}	0.767^{**}	0.686^{**}	0.131	0.704^{**}	0.453	1.000		
Fe	0.814^{**}	-0.779^{**}	0.824^{**}	0.787^{**}	0.204	0.800^{**}	0.562^{*}	0.736^{**}	1.000	
K	0.795^{**}	-0.537^{*}	0.711^{**}	0.573^{**}	0.375	0.634^{**}	0.261	0.475^{*}	0.528^{*}	1.000
Mg	0.843^{**}	-0.741^{**}	0.892^{**}	0.778^{**}	0.464^{*}	0.764^{**}	0.630^{**}	0.621^{**}	0.799^{**}	0.598^{**}
Na	0.641^{**}	-0.391	0.656^{**}	0.452	0.275	0.429	0.222	0.511^{*}	0.361	0.716^{**}
NH_4N	0.416	-0.068	0.315	0.310	0.772^{**}	0.251	0.545^{*}	-0.201	0.015	0.215
Cl	0.337	-0.125	0.389	-0.016	-0.165	0.049	0.203	0.422	0.225	0.429

	Mg	Na	NH_4N	Cl
Mg	1.000			
Na	0.545^{*}	1.000		
NH_4N	0.219	0.177	1.000	
Cl	0.062	0.365	0.008	1.000

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[a] Probability levels that coefficients differ from zero: * = 0.99 ** = 0.999

Because of the extensive intercorrelation among the pond water composition variables, the data were subjected to factor analysis using the Factor procedure of the SPSS/PC+ statistical software package. Factor analysis is a multivariate statistical analysis technique that has been developed for simplifying a data set by analyzing inter-correlations within a set of variables and determining whether a smaller number of "derived" variables (i.e. factors) can adequately describe the observations. Details of factor analysis methods and examples of applications are given by Darryl G. Howery in "Factor analyzing the multifactor data of chemistry" (American Laboratory, pp. 14-25, February 1976) and Paul H. Weiner in "Solve problems via factor analysis" (Chemtech, pp. 321-328, May 1977).

Although factor analysis can be used to construct quantitative models, it is particularly useful for interpreting the qualitative features of a complex data set. Since the purpose of this analysis was to obtain a qualitative description, the variables representing the sample collection site, the type of sample, and the collection date group were numerically coded and included with the composition variables for the factor analysis, which are given in Table 5. Assigned values for the qualitative variables correspond to the identification codes described in the footnote to Table 1. Site and Group are the collection site numbers 1 through 7 and the collection date groups 1 and 2, respectively. Values for the variable Type are 1,2, and 3 for the R (return water), D (discharge water), and S (slurry water) samples, respectively.

The first section of the Table 5 shows results from a principal components extraction procedure, in which abstract factors are related to the variance in the raw data matrix. Eigenvalues and variance distribution data for 10 factors are given. An eigenvalue is an approximate measure of the number of experimental variables that are explained by a derived factor. For example, factor number one with an eigenvalue of 8.4733 accounts for about the same variance in the initial data set as do 8.5 experimental variables, factor two is approximately equivalent to 2.5 variables, etc. With default conditions which limit significant factors to those with eigenvalues of 1.0 or greater, the principal components step indicated that four factors were sufficient to describe the input data matrix. These four factors cumulatively explain about 86% of the variance in the data. This variance is attributed to an "effect" of the factors, and the remaining variance is attributed to sampling and analytical scatter.

After the initial factor extraction step, data were further simplified by the Varimax rotation method, which attempts to minimize the number of variables that have high degrees of association with each factor. After rotation, the procedure generated a matrix of factor loadings that show the relationships between factors and variables. Bach factor loading is a measure of the correlation between a variable and a factor.

The matrix in Table 5 is sorted by the loading magnitudes to better illustrate relationships between the variables and factors. For example, one can see that the first factor is more strongly correlated with pH, Si, F, Fe, P_2O_5, Density, Mg Ca, and Al than with other variables. The second factor is correlated with NH_4, SO_4-S, and the sampling site; the third with Cl, K, and Na; and the fourth with the sample type and collection group. A qualitative interpretation of the rotated factor matrix is given below.

Factor 1 apparently relates to the primary inputs to the gypsum pond system by way of the wet-process phosphoric acid production plant. A negative loading by pH reflects a positive correlation with total acidity in the pond. Density is included in this factor since density correlates positively with the amounts of dissolved acids and salts in the solution. The other significant contributors (Si, F, Fe, P_2O_5, Mg, Ca, and Al) are common constituents in phosphate rock. They have a common mode of entry to the pond via residual acid, undissolved rock, precipitated impurities, and phosphogypsum in the filter cake slurry. The variables SO_4, K, and Na which also would enter the pond via the slurry have moderate, positive loadings on Factor 1. However, they are more important contributors to other factors.

Table 5. Factor Analysis of Gypsum Pond Water Data

Initial statistics

Factor	Eigenvalue	% of Var	Cum %
1	8.47330	49.8	49.8
2	2.50917	14.8	64.6
3	2.23220	13.1	77.7
4	1.31860	7.8	85.5
5	.89144	5.2	90.7
6	.59465	3.5	94.2
7	.42252	2.5	96.7
8	.20110	1.2	97.9
9	.11795	.7	98.6
10	.08213	.5	99.1

Factor Loadings by Variables

(after principal components extraction and varimax rotation)

Variable	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
pH	-.96335	.04104	.01603	.01093
Si	.95722	.15150	.01183	-.08398
F	.95435	.20624	-.05409	.02445
Fe	.86248	-.09284	.20157	.02683
P_2O_5	.85167	.21958	.38048	.16938
Density	.83779	.32190	.40084	-.00093
Mg	.83675	.16229	.15743	.18687
Ca	.81141	-.32468	.26781	.17320
Al	.76038	.44776	-.31993	.12503
NH_4	.11269	.97158	.01061	-.01524
Site	.11196	-.83426	-.34889	.06229
SO_4	.49115	.77260	-.18939	.05957
Cl	.06250	-.04227	.84767	-.11481
K	.58620	.17962	.63235	-.13232
Na	.43519	.12882	.61837	.42155
Type	-.00120	.02738	.02271	.88723
Group	.11958	-.13958	-.51005	.62979

(See text for explanation of Site, Type, and Group variables.)

Factor 2 is related to operating conditions at the different sampling sites. The Site variable has high loading (the negative value is a result of an arbitrary choice of site numbers). The SO_4 contribution is assumed to arise from variations in free sulfuric acid content in the gypsum slurry and process acid introduced to ponds at different sites. The NH_4 variable is correlated with the "site" factor since the practice of using pond water to scrub ammonia from fertilizer production effluents is a site dependent variable. The F content is not as strongly associated with these variables as it is with the primary input factor.

Factor 3 has high loadings by Cl, K, and Na. It is interpreted as a factor that reflects the introduction of these contaminants into the pond water. Since K and Na also have moderate loadings on Factor 1, their contribution to Factor 3 may arise from a source that is independent of K and Na in phosphate rock feeds.

Factor 4 has high loadings by the Type and Group variables. Therefore, this factor is related to variance in the data due to the collection of different sample types and collection of two sample groups at different times of the year. It is interesting to note that contributions of these two variables were sufficient to generate only one factor and not two.

CONCLUSIONS FROM SAMPLE COLLECTIONS AND ANALYSES

Compositions of gypsum pond water samples collected for this project appear to have relatively few independent constituents. Simple inspection of data showed that operating characteristics of the acid plant from which samples were collected had strong influence on compositions. Concentrations of most individual pond water constituents are strongly correlated which suggests a common influence. Factor analyses isolated a factor which contained many of the chemical constituents and appeared to be related to the input of materials to the pond. Such a factor would be dependent on the specific composition of the pond input streams, which again points to plant operating characteristics as the strong influence on pond composition. Differences in compositions of return, discharge, and slurry water compositions were very small to none, as were differences in compositions of samples collected at different seasons. Hence, chemical reactions which might change compositions with residence time in the pond or aging during the year may not be as influential as are those characteristics which determine initial inputs to the pond systems.

SECTION 3

IDENTIFICATIONS OF SOLIDS CONTAINED IN POND WATER SEDIMENTS

SOLIDS IN COLLECTED SAMPLES

When the May 1988 group of collected pond water samples were delivered to the TVA laboratories, approximately two-liter aliquots were taken from each of the 18 samples and filtered to remove suspended solids. These solids were rinsed with a methanol-water solution then with methanol, dried, and submitted for materials characterizations; there were not sufficient amounts of the solids to obtain chemical analyses. Results of materials characterizations by polarized light microscopy (PLM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) that were conducted on the solids in June 1988 are given in Table 6.

A majority of the solids filtered from pond water samples in June 1988 contained gypsum, Na_2SiF_6, and chukhrovite. Several samples contained amorphous unknowns, one with a refractive index in the range 1.53 to 1.55, and another with a refractive index of 1.430. XRD patterns for several samples had unidentified peaks at d spacings about 7.12 to 7.20. Based on information from more extensive examinations of a later group of samples (discussed below), the unknown material with a refractive index near 1.55 and XRD peak near 7.18 is probably a compound with the general formula $Fe_3XH_8(PO_4)_6{\cdot}6H_2O$, where X could be H, K, and/or NH_4. Information from other sample examinations suggests that the unknown with a refractive index about 1.43 is probably silica gel.

SEDIMENTS REMOVED NOVEMBER 1988

After the 2-liter aliquots were removed, the remaining samples were stored at room temperature (22°C - 26°C) in the plastic bottles used for their collection and transport. Examinations made several months later showed that some of the stored samples contained larger amounts of sediment than when they were first stored. Sediments were collected from samples D6-1, R4-1, S2-1, and S4-1 in November 1988. Solid phases were filtered from the mother liquor, washed with methanol, and dried overnight at 60°C. The dry solids were submitted for materials characterizations; there were not sufficient amounts collected at that time for chemical analyses. Table 7 contains results of these characterizations.

The initial characterizations of the four sediments collected in November 1988 showed that gypsum, Na_2SiF_6, chukhrovite were present. PLM examinations showed that the sediments also contained an amorphous unknown material with a refractive index about 1.42 and another unknown material comprised of hexagonal crystals with refractive index in the range from 1.56 to 1.57. After accounting for contributions due to gypsum, Na_2SiF_6, and chukhrovite, there were several unidentified peaks in the XRD pattern at d spacings 7.18, 4.58, 3.58, 3.10, and 2.89. Samples were subsequently examined with scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX) to identify the unknowns.

Table 6. Characterizations of Solids Filtered from Gypsum Pond Samples June 1988

Sample ID	PLM	est %	XRD	FTIR[a]
D1-1	$CaSO_4 \cdot 2H_2O$	30	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Na_2SiF_6	60-70	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.550)	5-10	UI[b] 7.19, 5.78	
D2-1	$CaSO_4 \cdot 2H_2O$	10-20	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	10	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.310)	80	$NaKSiF_6$	
			Chukhrovite	
D3-1	$CaSO_4 \cdot 2H_2O$	90-95	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	5	Na_2SiF_6 (t)	Na_2SiF_6
D4-1	$CaSO_4 \cdot 2H_2O$	10	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	20	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.430)	70	Chukhrovite	
			UI[b] 7.20	
D5-1	$CaSO_4 \cdot 2H_2O$	90-95	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	5	Na_2SiF_6 (t)	Na_2SiF_6
			Chukhrovite	
D6-1	$CaSO_4 \cdot 2H_2O$	80	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	<5	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.430)	10		
R1-1	$CaSO_4 \cdot 2H_2O$	40-50	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Na_2SiF_6	40-50	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI = 1.532 - 1.550)	<5	$NaKSiF_6$	
			UI[b] 7.18	
R2-1	CaSO4	10-20	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	$NaKSiF_6$	80	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.550)	<5	$NaKSiF_6$	
			UI[b] 7.12 & 4.58	
R3-1	$CaSO_4 \cdot 2H_2O$ (t)	100	Insufficient sample	$CaSO_4 \cdot 2H_2O$
				Na_2SiF_6
R4-1	$CaSO_4 \cdot 2H_2O$	50	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	20-30	Na_2SiF_6 (t)	Na_2SiF_6
	Amorphous (RI=1.430)	20-30	Chukhrovite	
			UI[b] 7.14, 5.75 & 3.06	

Table 6 (continued)

Sample Number	PLM	est %	XRD	FTIR
R5-1	$CaSO_4 \cdot 2H_2O$ (t)	90-95	Insufficient sample	
	Chukhrovite (t)	<5		
R6-1	$CaSO_4 \cdot 2H_2O$	60-70	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	10-20	Na_2SiF_6	Na_2SiF_6
	Amorphous (RI=1.430)	20	Chukhrovite	
S1-1	$CaSO_4 \cdot 2H_2O$	20	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Na_2SiF_6	80	Na_2SiF_6	Na_2SiF_6
S2-1	$CaSO_4 \cdot 2H_2O$	60	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Amorphous (RI=1.430)	40	Na_2SiF_6	Na_2SiF_6
			$NaKSiF_6$ (t)	
			Chukhrovite (t)	
S3-1	$CaSO_4 \cdot 2H_2O$	80-90	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	10-20	Na_2SiF_6 (t)	Na_2SiF_6
			Chukhrovite (t)	
S4-1	$CaSO_4 \cdot 2H_2O$	50-60	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Na_2SiF_6	10-20	Na_2SiF_6	Na_2SiF_6
	Chukhrovite	5-10	Chukhrovite	
	Amorphous (RI=1.430)	20-30	UI[b] 7.12	
S5-1	$CaSO_4 \cdot 2H_2O$	20	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$ (t)
	Na_2SiF_6	50	Na_2SiF_6	Na_2SiF_6
	Chukhrovite	30	Chukhrovite	Chukhrovite
S6-1		Insufficient sample		

Chukhrovite = $Ca_4AlSi(SO_4)F_{13} \cdot 12H_2O$

(t) = tentative identifications

[a] Cannot differentiate between Na_2SiF_6 and $NaKSiF_6$ from FTIR spectra, therefore SiF_6^{-2} compounds are reported as Na_2SiF_6.

[b] Unidentified peaks (d spacings) in XRD pattern; see text for possible identification.

Table 7. Characterizations of Solids Collected from Gypsum Pond Samples Nov. 1988

ID Number	PLM	est %	XRD	FTIR[a]
D6-1	$CaSO_4 \cdot 2H_2O$	80	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Chukhrovite	20	Chukhrovite	Chukhrovite
R4-1	Chukhrovite	60-70	Chukhrovite	Chukhrovite
	Amorphous	20-30	$Fe_3KH_8(PO_4)_6 \cdot 6H_2O$	
	Hexagonal unknown	10		
S2-1	$CaSO_4 \cdot 2H_2O$	30-40	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 2H_2O$
	Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6
	Chukhrovite	30-40	Chukhrovite	Chukhrovite
S4-1	Na_2SiF_6	60	Na_2SiF_6	Na_2SiF_6
	Chukhrovite	10-20	Chukhrovite	Chukhrovite
	Amorphous	<5	$Fe_3KH_8(PO_4)_6 \cdot 6H_2O$	
	Hexagonal unknown	10-20		

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[a] Cannot differentiate between Na_2SiF_6 and $NaKSiF_6$ from FTIR spectra, therefore SiF_6^{-2} compounds are reported as Na_2SiF_6.

SEM examinations confirmed the presence of gypsum and Na_2SiF_6. EDX spectra of cubic and bipyramidal octahedral crystals showed they contained Ca, S, Si, Al, and F. This is consistent with the elemental composition expected for chukhrovite, and thereby confirmed the identity of the octahedral crystal phase as chukhrovite. EDX spectra of the hexagonal crystals, most of which were coated with fine particles of other materials, showed strong peaks due to Si, P, and Fe and smaller peaks due to S, K, and Ca. Reevaluation of the XRD data, as discussed below, assigned the group of previously unidentified peaks to the compound $Fe_3(X)H_8(PO_4)_6 \cdot 6H_2O$, and the hexagonal crystals were identified as an iron phosphate compound. The amorphous unknown with refractive index about 1.42 was identified as silica gel, which can have a refractive index in the range 1.40 to 1.47. In addition, very fine particles of gypsum were detected on the surfaces of other crystals.

SEDIMENTS REMOVED FEBRUARY AND JUNE 1989

In February 1989 sediments were taken from samples D2-1, D4-1, Rl-1, R4-1 and S4-1. Sediments also were collected from Dl-1, D3-1, D5-1, R2-l, R4-1, S1-1, and S2-1 in June 1989. The solids were separated from mother liquor by centrifugation, washed twice with 1:1 methanol:water and once with 100% methanol, and dried at 60°C. Sufficient amounts were collected to obtain chemical analyses and materials characterizations. Results of characterizations by XRD are in Table 8 for sediments collected in February 1989 and in Table 9 for sediments collected in June 1989; chemical compositions are given in Table 10.

The XRD characterizations of the sediments detected gypsum, Na_2SiF_6, chukhrovite, and an iron phosphate compound, identified as $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$. Although the latter three compounds were found in a majority of samples, sediment compositions were variable. Comparisons of the qualitative determinations with mole ratios, calculated from the analytical data, helped with the interpretation of the data.

Sediments from Dl-1, D3-1, Rl-1, and Sl-1 had definite XRD patterns for gypsum, and mole ratios Ca:S for these four samples were close to the expected value of one. Mole ratios Ca:S for the other eight sediment samples, all of which contained chukhrovite according to XRD, ranged from 3.8 to 4.8. Ratios Ca:Al for these eight samples ranged from 3.0 to 4.0. Although reported stoichiometries of compounds regarded as “chukhrovite” vary, a formula that has been used for the material seen in phosphoric acid systems is $Ca_4SO_4SiAlF_{13} \cdot 10H_2O$. This stoichiometry predicts the ratios Ca:S and Ca:Al both equal to 4.0. Other ratios (e.g., F:Si and Al:Si) varied from values predicted by this formula, probably because of contributions from relatively larger amounts of Na_2SiF_6 and an occasional occurrence of XRD-undetectable, amorphous F-, Al-, and Si-containing materials. Thus, there is relatively good agreement between findings from XRD examinations and chemical compositions for the Ca, S, and Al constituents.

All sediment samples except those from D3-1 and D5-1 contained a compound which was identified by XRD as $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$. Mole ratios P:Fe calculated from chemical analyses of samples that contained the iron phosphate compound ranged from 2.0 to 2.3, which are consistent with the stoichiometry of this compound. The observed mole ratios Fe:K varied considerably from the expected value of 3.0, and most samples contained higher concentrations of ammonium-N than they did K. So, there is uncertainty about the exact nature of this iron phosphate material.

Table 8. XRD Characterizations of Solids Collected from Samples Feb. 1989

ID Number	Constituents
D2-1	Chukhrovite $Fe_3KH_8(PO_4)_6\cdot 6H_2O$ Na_2SiF_6
D4-1	Chukhrovite $Fe_3KH_8(PO_4)_6\cdot 6H_2O$
R1-1	$CaSO_4\cdot 2H_2O$ $CaSO_4\cdot 0.5H_2O$ $Fe_3KH_8(PO_4)_6\cdot 6H_2O$ Na_2SiF_6 Chukhrovite (tentative)
R4-1	Chukhrovite $Fe_3KH_8(PO_4)_6\cdot 6H_2O$
S4-1	Chukhrovite $Fe_3KH_8(PO_4)_6\cdot 6H_2O$ Na_2SiF_6 $NaKSiF_6$

Table 9. XRD Characterizations of Solids Collected from Samples June 1989

ID Number	Constituents
D1-1	$CaSO_4 \cdot 2H_2O$ Na_2SiF_6 Chukhrovite $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$
D3-1	$CaSO_4 \cdot 2H_2O$ Chukhrovite
D5-1	Chukhrovite
R2-1	Na_2SiF_6 Chukhrovite $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$
R4-1	Chukhrovite $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$ Unidentified material
S1-1	$CaSO_4 \cdot 2H_2O$ Na_2SiF_6 $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$
S2-1	Na_2SiF_6 Chukhrovite $Fe_3KH_8(PO_4)_6 \cdot 6H_2O$

Table 10. Gypsum Pond Water Sample Sediment Compositions

ID		<------					Weight percent					------>
Number	Date	P	F	SO_4-S	Si	Al	Ca	Fe	K	Mg	Na	NH_4-N
D1-1	6/89	5.35	13.6	6.22	6.95	0.45	9.72	4.83	0.441	0.004	6.16	0.3115
D2-1	2/89	1.98	36.7	2.10	7.99	1.68	9.86	1.76	0.13	0.0036	6.44	0.292
D3-1	6/89	0.15	1.3	17.20	0.82	0.22	23.10	0.089	0.061	0.005	0.11	0.0256
D4-1	2/89	1.34	24.5	3.12	6.78	2.74	15.10	1.18	0.07	0.0078	0.33	0.210
D5-1	6/89	0.05	27.9	3.67	5.53	4.19	18.80	0.021	0.029	0.011	0.94	0.0112
R1-1	2/89	4.19	22.1	7.23	5.73	0.21	9.71	3.74	0.09	0.0048	7.63	0.486
R2-1	6/89	2.05	24.9	1.64	8.55	1.49	8.65	1.69	0.608	0.070	8.45	0.0965
R4-1	2/89	2.93	25.2	2.94	6.19	2.65	14.40	2.60	0.14	0.0061	0.34	0.307
R4-1	6/89	6.43	10.7	1.51	10.40	1.56	9.05	5.86	0.282	0.028	0.51	0.3207
S1-1	6/89	1.69	22.3	7.05	7.71	0.03	9.09	1.34	0.388	0.006	12.50	0.0866
S2-1	6/89	1.83	29.7	1.81	8.98	1.63	9.19	1.50	0.493	0.013	10.60	0.0624
S4-1	2/89	2.91	32.7	2.36	7.14	2.17	11.10	2.52	0.57	0.0059	4.65	0.237

Mole Ratios

ID Number	Date	Ca:S	Ca:Al	F:Si	F:Na	P:Fe	Fe:K	Fe:N
D1-1	6/89	1.3	14.5	2.9	2.7	2.0	7.7	3.9
D2-1	2/89	3.8	4.0	6.8	6.9	2.0	9.5	1.5
D3-1	6/89	1.1	71.7	2.4	14.5	3.0	1.0	0.88
D4-1	2/89	3.9	3.7	5.3	89.8	2.0	11.9	1.4
D5-1	6/89	4.1	3.0	7.5	35.9	4.3	0.5	0.47
R1-1	2/89	1.1	31.1	5.7	3.5	2.0	29.3	1.9
R2-1	6/89	4.2	3.9	4.3	3.6	2.2	2.0	4.4
R4-1	2/89	3.9	3.7	6.0	89.7	2.0	13.1	2.1
R4-1	6/89	4.8	3.9	1.5	25.4	2.0	14.6	4.6
S1-1	6/89	1.0	211.0	4.3	2.2	2.3	2.4	3.9
S2-1	6/89	4.1	3.8	4.9	3.4	2.2	2.1	6.1
S4-1	2/89	3.8	3.4	6.8	8.5	2.1	3.1	2.7

Past research on iron phosphate compounds in wet-process phosphoric acid systems detected similar compounds with an ammonium ion or proton substituted for the potassium ion. Reference patterns from the XRD data files used at TVA for identifications of compounds $Fe_3XH_8(PO_4)_6{\cdot}6H_2O$, where X is H, K, or NH_4, are given in Table 11. Inspection of these patterns show strong qualitative similarities. All three compounds have major peaks at d spacings about 7.10 - 7.20, 5.70 - 5.80, 4.50 - 4.60, 3.00 - 3.10, and 2.80 - 2.90. Thus, a pattern generated by a mixture of the H-, K-, and NH_4-containing compounds will be difficult to resolve. The chemical and X-ray data on the sample sediments suggest that these solids contained such a mixture rather than only the Fe-K-PO_4 compound. Since mole ratios Fe:N were less than 3 for several sediments, it's possible that part of the ammonium nitrogen is present in a phase other than the Fe-containing material.

CORRELATION AND FACTOR ANALYSES OF SEDIMENT DATA

The sediment chemical composition data were evaluated with correlation and factor analyses methods to determine whether these methods provided additional information about the identities of sediment compounds. In addition to chemical variables, the variable Age (number of months between the collection of a pond water sample and the removal of the sediment from it) was included in the data set to look for effects of storage time.

Correlation coefficients for sediment concentration variable pairs are listed in Table 12. The significant correlations with the sediment phosphorus concentrations were positive correlationsbetween P and Fe and between P and NH_4-N; the correlation between P and Fe was nearly equal to one. The Fe concentration in the sediments had a positive, significant correlation with the NH_4-N concentration. Other significant correlations were those between SO_4-S and F, between SO_4-S and Si and between Si and Ca; all three of these relationships had negative correlation coefficients.

Application of factor analysis methods showed that the sediment composition data could be explained by four factors. Results from principal components extraction and varimax rotation are given in Table 13.

Examination of the factor matrix after the varimax rotation shows that one factor is heavily loaded by the Fe, P, and NH_4-N variables (all positive loadings). There appears to be very little contribution by the K variable. This factor is assigned to the $Fe_3(H,K,NH_4)H_8(PO_4)_6{\cdot}6H_2O$ compound, and it is obvious that NH_4-N is a more important constituent than is K. The factor loadings show evidence of some influence by the Ca (negative) and Si (positive) variables.

Strong positive loadings by F, Al, and Si in the second factor suggest that it could relate to the chukhrovite content of the sediments. Negative loadings by SO_4-S and Ca are confusing since one would expect positive loadings because of the Ca and SO_4 in chukhrovite. However, the negative contributions could mean that the dilution effect by gypsum overshadows the expected positive correlations with Ca and SO_4.

A third factor has a high positive loading by Na and a moderate loading by K, which suggest that it is related to Na_2SiF_6 and $NaKSiF_6$. However, the Si and F variable loadings are small. Because of the positive Na and K loadings and the moderate negative loadings by Ca and Al, this factor seems to be related more to the overall cation content in the sediments than to a specific compound.

Table 11. XRD Reference Patterns for $Fe_3(K,NH_4,H)H_8(PO4)_6 \cdot 6H_2O$ Compounds

$Fe_3KH_8(PO4)_6 \cdot 6H_2O$		$Fe_3NH_4H_8(PO4)_6 \cdot 6H_2O$		$Fe_3H_9(PO4)_6 \cdot 6H_2O$	
d	I/I_o	d	I/I_o	d	I/I_o
8.33	17	8.33	16	7.940	32
7.85	45	7.85	40	7.180	80
7.10	75	7.10	100	5.780	30
5.73	50	5.73	51	4.580	100
4.54	75	4.54	44	4.210	2
4.19	7	4.19	7	4.024	12
3.99	12	3.99	13	3.972	25
3.94	8	3.70	9	3.867	3
3.70	12	3.56	24	3.723	4
3.56	30	3.21	44	3.591	26
3.21	45	3.08	90	3.242	42
3.08	100	2.98	7	3.100	53
2.98	12	2.93	18	3.001	16
2.93	30	2.87	31	2.954	34
2.87	40	2.80	27	2.888	19
2.80	40	2.63	9	2.827	55
2.63	15	2.60	13	2.646	14
2.60	20	2.43	11	2.613	31
2.43	14	2.28	5	2.440	16
2.28	11	2.04	9	2.289	21
2.23	7			2.238	2
2.20	9			2.209	9
2.17	8			2.181	15
2.12	7			2.129	8
2.10	6			2.080	3
2.07	5			2.047	14
2.04	8			2.010	2

Table 12. Gypsum Pond Water Sample Sediments--Correlation Coefficients for Composition Variable Pairs

	P	F	SO_4-S	Si	Al	Ca
P	1.0000					
F	-.2193	1.0000				
SO_4-S	-.2956	-.7145*	1.0000			
Si	.5179	.4452	-.8599**	1.0000		
Al	-.3109	.4945	-.5534	.1303	1.0000	
Ca	-.6201	-.3930	.6267	-.8516**	.2909	1.0000
Fe	.9993**	-.2299	-.2884	.5039	-.2965	-.5978
K	.2807	.1818	-.3614	.5377	-.2382	-.6395
Mg	.0684	-.0160	-.3348	.3945	.0536	-.2976
Na	.0299	.3458	-.1420	.3938	-.5107	-.6877
NH_4-N	.7586*	.0571	-.2169	.2330	-.2180	-.4505
Age	-.0897	-.4453	.1965	.0827	-.1748	.0520

	Fe	K	Mg	Na	NH_4-N	Age
Fe	1.0000					
K	.2518	1.0000				
Mg	.0557	.4868	1.0000			
Na	-.0007	.5961	.1507	1.0000		
NH_4-N	.7642*	-.1322	-.2224	-.0616	1.0000	
Age	-.0948	.3439	.3732	.1963	-.6663	1.0000

Probabilities for Significance of Coefficients: * P = .99 ** P = .999

Table 13. Gypsum Pond Water Sample Sediments--Factor Analysis of Chemical Composition Variables

Factor Matrix After Principal Components Extraction (4 factors)

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
Ca	-.96382	-.06727	-.09899	.21411
Si	.88993	.28318	-.09289	.17208
P	.73961	-.60807	.08328	.24783
Fe	.72194	-.62363	.06786	.26432
SO_4-	-.71871	-.41182	.50857	-.21758
K	.63152	.39268	.45669	-.03030
NH_4-N	.52404	-.73536	-.35981	-.13022
Age	-.08377	.35159	.75976	.37899
Al	-.14857	.44858	-.73387	.44777
F	.35333	.55873	-.62894	-.38574
Na	.49111	.34717	.42893	-.64765
Mg	.34074	.44810	.31845	.47759

Factor Matrix After Varimax Rotation

Fe	.98892	.00321	.06358	.05067
P	.98622	.00807	.09463	.05900
NH_4-N	.81280	.08493	.02301	-.54167
SO_4-S	-.27252	-.94402	-.08611	-.13884
F	-.24672	.85284	.30404	-.31740
Al	-.28682	.71503	-.60662	.02884
Si	.46871	.67462	.35830	.32746
Na	-.07063	.06598	.97506	.07119
Ca	-.55893	-.41952	-.69942	-.10734
K	.16775	.21444	.63782	.53063
Age	-.17875	-.31474	.11240	.84134
Mg	.07060	.25414	.08687	.75451

The fourth factor has higher loadings by Age and Mg (both positive), a moderate positive loading by K, and a moderate negative loading by NH_4-N. Since sediment Mg concentrations were all very low, and Age did not have a particularly strong correlation with any of the chemical variables, this factor seems to be a miscellaneous factor which accounts for variance in the data that was not included in other factors.

CONCLUSIONS FROM SEDIMENT CHARACTERIZATIONS AND ANALYSES

The important compounds in solid materials suspended in gypsum pond water samples collected from several Florida phosphate producers and solids that settled from stored samples are gypsum, Na_2SiF_6, chukhrovite, $NaKSiF_6$, and $Fe_3(H,K,NH_4)H_8(PO_4)\cdot 6H_2O$. The ammonium form of the latter compound appears to be the more prevalent form. In addition, sediments contained varied amounts of amorphous materials, much of which appeared to be silica gel. The sediment analytical data were in good agreement with the qualitative findings.

SECTION 4

EVAPORATIONS OF POND WATER SAMPLES

Aliquots of the gypsum pond water samples collected from Florida phosphate producers in May 1988 were evaporated to increase solution concentrations and force the precipitation of low solubility compounds. The precipitated materials were analyzed and characterized to obtain additional information about conditions that influence on the distributions of F, P, S, and other elements in gypsum pond systems.

INITIAL EVAPORATIONS (Runs A - R2)

Initially, aliquots from all 18 samples were evaporated at a relatively fast rate. Six runs were replicated to check results and train a technician who was new to the project.

Weighed 500 mL aliquots were placed in tared 1 liter wide-mouth high density polyethylene bottles. The bottles were placed in a constant temperature (60°C) shaker bath and the solutions were allowed to evaporate until their volumes were reduced to about 25% of the initial volumes. The times needed to evaporate samples to the target volumes ranged from about 37 hours to about 50 hours.

When evaporations were completed, the bottles were capped and the samples were cooled and weighed. The evaporated samples were filtered tocollect theconcentrated solutionsand precipitated solids. The solids were washed with methanol and dried at about 75°C. Solution and solid phases were submitted for analyses and solids were submitted for materials characterizations.

Compositions of the solution phases filtered from evaporated samples are listed in Table 14. Inspection of the solution phase concentration data show that sample evaporations caused increases in acidity; pH's decreased by about 0.3 to 0.4 unit. In most cases the element concentrations in the solutions increased; Ca, Na, and ammonium-N concentrations showed decreases for several runs.

If sample evaporation produced no losses of materials from the solution phases by either precipitation or volatilization, the solution phase concentration of a given element would equal its starting concentration corrected for the loss of water. The ratio of an element's concentration in the recovered solution to that in the starting solution would equal the ratio of sample weight changes produced by the evaporation. Concentration ratios (recovered/initial), evaporation ratios [100/(100 - % evaporated)], and values for the quotients (concentration ratio/evaporation ratio) are listed in Table 15. Mean values of the quotients for Al and Fe both equal one, and the mean quotient for P is near to one. Therefore, essentially all of these three elements remained in the solution phase during evaporations. Most other elements had mean quotients distinctly less than one, indicating significant losses from solution. The high values for Mg and low values for N are believed to be due to analytical error.

Results from characterizations of precipitated solids made by PLM, XRD, and FTIR are in Table 16. Compositions of the solids are in Table 17 (weight % basis) and Table 18 (molar basis). Table 18 also gives values of selected mole fractions that were calculated to assist in the identification of compounds contained in the solids.

Table 14. Gypsum Pond Water Evaporations A-R2--Recovered Compositions

Run	ID	%				SO_4								NH_4
No.	No.	evapd	pH	% P	% F	% S	% Si	% Al	% Ca	% Fe	% K	% Mg	% Na	% N
A	R1-1	71.8	1.29	3.08	2.26	0.81	0.53	0.112	0.10	0.097	0.04	0.12	0.19	0.044
A2	R1-1	75.4	1.31	3.38	2.51	0.92	0.62	0.133	0.11	0.115	0.04	0.12	0.19	0.663
B	R2-1	81.5	1.01	6.42	1.50	0.27	0.34	0.107	0.29	0.214	0.04	0.18	0.16	0.011
C	D1-1	73.2	1.20	3.13	2.42	0.87	0.56	0.113	0.09	0.098	0.04	0.11	0.19	0.045
D	R3-1	75.5	1.47	0.70	1.07	0.35	0.25	0.031	0.07	0.034	0.05	0.02	0.27	0.017
E	R4-1	67.2	1.22	2.82	2.42	0.26	0.57	0.123	0.27	0.167	0.06	0.14	0.19	0.010
E2	R4-1	71.8	1.26	3.19	2.76	0.35	0.65	0.148	0.24	0.206	0.05	0.16	0.17	0.157
F	S5-1	73.4	1.28	1.66	1.78	0.34	0.42	0.104	0.14	0.092	0.05	0.05	0.21	0.013
G	S3-1	84.4	1.55	1.44	1.20	0.73	0.29	0.074	0.06	0.071	0.06	0.04	0.26	0.018
G2	S3-1	71.1	1.59	0.58	0.94	0.37	0.26	0.041	0.07	0.039	0.06	0.02	0.27	0.206
H	R6-1	82.8	1.32	2.85	1.58	0.48	0.37	0.079	0.12	0.077	0.04	0.13	0.18	0.003
I	S1-1	78.0	1.30	4.29	2.77	1.11	0.64	0.153	0.09	0.136	0.04	0.14	0.18	0.059
J	D4-1	70.6	1.32	3.14	2.91	0.31	0.65	0.126	0.03	0.171	0.04	0.13	0.17	0.014
K	D2-1	76.9	1.21	4.34	1.27	trace	0.29	0.075	0.20	0.152	0.05	0.14	0.17	0.011
K2	D2-1	69.5	1.33	3.11	1.13	trace	0.29	0.058	0.21	0.122	0.05	0.07	0.21	0.142
L	S4-1	72.1	1.22	4.46	2.91	0.28	0.61	0.212	0.27	0.290	0.04	0.19	0.13	0.010
M	D5-1	73.4	1.44	1.12	1.67	0.33	0.43	0.078	0.15	0.063	0.05	0.04	0.22	0.012
N	S6-1	75.4	1.51	2.00	0.51	0.38	0.12	0.035	0.09	0.035	0.06	0.09	0.38	0.000
O	R5-1	76.1	1.45	1.66	1.73	0.40	0.40	0.087	0.13	0.069	0.05	0.05	0.23	0.013
P	D3-1	73.2	1.63	0.44	1.03	0.36	0.28	0.029	0.08	0.032	0.05	0.02	0.27	0.014
Q	D6-1	71.7	1.46	1.20	1.29	0.29	0.31	0.043	0.14	0.042	0.05	0.06	0.27	0.001
Q2	D6-1	77.6	1.39	1.83	1.40	0.33	0.35	0.056	0.11	0.054	0.05	0.07	0.20	<0.003
R	S2-1	75.8	1.30	3.94	1.18	0.24	0.28	0.080	0.26	0.161	0.04	0.10	0.20	0.008
R2	S2-1	68.6	1.37	2.78	1.06	trace	0.25	0.062	0.34	0.123	0.05	0.06	0.21	0.116

Table 15. Evaporations A-R2--Comparisons of Concentration[a] and Evaporation[b] Ratios

Run No.	ID No.	Evapn[b] ratio	P	F	SO4 S	Si	Al	Ca	Fe	K	Mg	Na	NH4 N
			<--------		Concentration ratios/Evaporation ratios								-------->
A	R1-1	3.55	0.98	0.58	0.85	0.56	1.03	0.24	1.06	0.28	1.13	0.26	0.07
A2	R1-1	4.07	0.94	0.57	0.84	0.56	1.06	0.23	1.09	0.25	0.98	0.22	0.98
B	R2-1	5.41	1.06	0.34	0.36	0.28	1.12	0.28	1.12	0.19	1.11	0.12	0.04
C	D1-1	3.73	0.98	0.59	0.87	0.55	0.96	0.19	0.98	0.27	0.98	0.23	0.06
D	R3-1	4.08	0.82	0.67	0.80	0.58	0.91	0.19	0.98	1.22	1.63	0.55	0.07
E	R4-1	3.05	1.08	0.76	0.77	0.62	1.00	0.47	1.00	0.49	0.92	0.31	0.04
E2	R4-1	3.55	1.05	0.75	0.89	0.61	1.03	0.36	1.06	0.35	0.90	0.24	0.56
F	S5-1	3.76	0.89	0.53	0.69	0.51	1.06	0.29	1.07	0.44	1.33	0.27	0.00
G	S3-1	6.41	0.99	0.34	1.02	0.32	1.10	0.10	1.14	0.47	2.08	0.20	0.00
G2	S3-1	3.46	0.73	0.49	0.96	0.52	1.13	0.22	1.16	0.87	1.93	0.39	0.10
H	R6-1	5.81	1.04	0.37	0.72	0.32	1.09	0.15	1.15	0.17	1.12	0.15	-
I	S1-1	4.55	1.02	0.56	0.91	0.52	0.96	0.16	0.98	0.18	1.03	0.17	0.05
J	D4-1	3.40	0.99	0.73	0.69	0.63	0.95	0.05	0.96	0.29	0.96	0.26	0.08
K	D2-1	4.33	0.99	0.36	-	0.31	0.96	0.26	1.01	0.29	1.62	0.16	0.02
K2	D2-1	3.28	0.93	0.43	-	0.41	0.99	0.36	1.07	0.38	1.07	0.27	0.32
L	S4-1	3.58	1.01	0.67	0.52	0.56	1.14	0.38	1.12	0.28	1.06	0.17	0.03
M	D5-1	3.76	0.71	0.64	0.85	0.63	0.88	0.36	0.85	0.66	1.52	0.42	0.06
N	S6-1	4.07	1.05	0.30	1.28	0.24	0.89	0.22	0.91	0.37	1.11	0.42	-
O	R5-1	4.18	0.94	0.64	0.96	0.57	0.90	0.26	0.88	0.60	1.33	0.37	0.06
P	D3-1	3.73	0.57	0.69	0.89	0.72	1.02	0.24	1.09	0.67	1.34	2.41	0.07
Q	D6-1	3.53	0.75	0.49	0.74	0.46	0.91	0.28	0.95	0.35	0.85	0.35	-
Q2	D6-1	4.46	0.90	0.42	0.66	0.40	0.93	0.18	0.97	0.28	0.78	0.20	-
R	S2-1	4.13	0.96	0.37	0.58	0.34	0.97	0.33	1.04	0.24	1.21	0.20	0.05
R2	S2-1	3.18	0.88	0.43	-	0.40	0.97	0.56	1.03	0.39	0.94	0.27	0.89
Means			0.93	0.53	0.70	0.48	1.00	0.26	1.03	0.42	1.21	0.36	0.15
Std. Devn.			0.13	0.14	0.33	0.13	0.08	0.11	0.09	0.24	0.34	0.45	0.27
C.V.'s			14	27	46	27	8	43	8	59	28	125	183

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[a] $$\text{Concentration ratio} = \frac{\text{Recovered solution concentration}}{\text{Starting solution concentration}}$$

[b] Evaporation (Evapn) ratio = 100/(100 - % evaporated)

Table 16. Characterizations of Precipitated Solids from Evaporations A-R2

		<----- PLM ----->		<-- XRD -->	<----- FTIR ------>	
Run No.	ID No.	Identity	Estd %	Identity	Identity^a	Estd %
A	R1-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	30	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10-20	$NaKSiF_6$		
B	R2-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10-20	$NaKSiF_6$		
C	D1-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10-20	$NaKSiF_6$		
D	R3-1	Gypsum	50-60	Gypsum	Gypsum	50-70
		Na_2SiF_6	40-50	Na_2SiF_6	Na_2SiF_6	30-50
E	R4-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10-20	$NaKSiF_6$		
F	S5-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10-20	$NaKSiF_6$		
G	S3-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10	$NaKSiF_6$		
H	R6-1	Gypsum	60-70	Gypsum	Gypsum	50-70
		Na_2SiF_6	20	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10	$NaKSiF_6$		
I	S1-1	Gypsum	40-50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10	$NaKSiF_6$		
J	D4-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	10	$NaKSiF_6$		
K	D2-1	Gypsum	50-60	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		

Table 16 (continued)

Run No.	ID No.	PLM		XRD	FTIR	
		Identity	Estd %	Identity	Identity[a]	Estd %
L	S4-1	Gypsum	60-70	Gypsum	Gypsum	50-70
		Na_2SiF_6	30	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
M	D5-1	Gypsum	50-60	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
N	S6-1	Gypsum	40-50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40-50	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
				$CaSO_4 \cdot 0.5H_2O$		
O	R5-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40-50	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
P	D3-1	Gypsum	50	Gypsum	Gypsum	50-70
		Na_2SiF_6	40-50	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
Q	D6-1	Gypsum	60	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		
R	S2-1	Gypsum	60	Gypsum	Gypsum	50-70
		Na_2SiF_6	30-40	Na_2SiF_6	Na_2SiF_6	30-50
		$NaKSiF_6$	<10	$NaKSiF_6$		

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[a] FTIR characterizations did not distinguish between Na and K fluosilicates, so all fluosilicates detected are reported as Na_2SiF_6.

Table 17. Precipitated Solids Compositions from Evaporations A-R2

Run No.	ID No.	% evapd	%P	%F	SO_4 %S	%Si	%Ca	%K	%Na
A	R1-1	71.8	0.27	38.7	5.82	7.79	7.24	2.26	13.9
A2	R1-1	75.4	0.17	39.4	6.61	5.47	8.20	1.63	13.5
B	R2-1	81.5	0.38	36.0	6.99	8.01	8.97	1.67	13.2
C	D1-1	73.2	0.22	38.6	6.28	8.60	7.68	1.80	14.5
D	R3-1	75.5	0.11	29.2	10.50	6.29	12.60	0.08	11.3
E	R4-1	67.2	0.33	36.6	6.40	8.88	8.27	1.94	13.0
E2	R4-1	71.8	0.21	35.0	7.16	6.60	9.15	2.56	15.5
F	S5-1	73.4	0.18	39.4	6.74	8.25	8.22	1.95	14.4
G	S3-1	84.4	0.29	36.5	6.39	6.39	7.81	0.76	15.5
G2	S3-1	71.1	0.11	36.5	6.55	4.31	8.26	0.04	14.1
H	R6-1	82.8	0.17	37.3	7.17	7.17	8.86	1.66	14.0
I	S1-1	78.0	0.22	38.1	6.48	6.48	7.93	1.76	14.4
J	D4-1	70.6	0.25	33.2	7.15	7.15	8.98	1.79	12.7
K	D2-1	76.9	0.37	35.5	6.63	6.63	8.34	1.98	13.4
K2	D2-1	69.5	0.31	35.1	6.56	5.42	8.38	1.37	13.7
L	S4-1	72.1	0.36	33.9	7.19	7.19	9.22	1.65	12.7
M	D5-1	73.4	0.17	33.2	8.04	7.48	10.00	10.50	13.1
N	S6-1	75.4	0.64	38.4	6.59	7.54	8.04	2.12	14.1
O	R5-1	76.1	0.29	33.4	8.43	7.27	10.10	10.60	12.2
P	D3-1	73.2	0.10	24.7	8.74	5.29	10.70	0.05	13.0
Q	D6-1	71.7	0.13	36.3	6.83	8.36	8.34	1.70	14.3
Q2	D6-1	77.6	0.10	35.6	6.70	5.00	8.75	1.95	12.7
R	S2-1	75.8	0.37	35.4	6.71	8.00	8.52	1.88	13.2
R2	S2-1	68.6	0.68	33.4	6.73	4.72	8.89	1.92	13.6

Table 18. Precipitated Solids Molar Compositions from Evaporations A-R2

		<------------ moles/100 g						------------->	<------- mole ratios				------->
Run No.	ID No.	P	F	SO4 S	Si	Ca	K	Na	F:Si	Ca:S	F:Na	F: (Na+K)	(Na+K) :Si
A	R1-1	0.009	2.04	0.182	0.277	0.181	0.0577	0.605	7.34	1.00	3.37	3.08	2.39
A2	R1-1	0.005	2.07	0.206	0.195	0.205	0.0416	0.587	10.65	0.99	3.53	3.30	3.23
B	R2-1	0.012	1.89	0.218	0.285	0.224	0.0427	0.574	6.64	1.03	3.30	3.07	2.16
C	D1-1	0.007	2.03	0.196	0.306	0.192	0.0460	0.631	6.64	0.98	3.22	3.00	2.21
D	R3-1	0.004	1.54	0.327	0.224	0.314	0.0020	0.492	6.86	0.96	3.13	3.11	2.20
E	R4-1	0.011	1.93	0.200	0.316	0.206	0.0496	0.565	6.09	1.03	3.41	3.13	1.95
E2	R4-1	0.007	1.84	0.223	0.235	0.228	0.0654	0.674	7.84	1.02	2.73	2.49	3.15
F	S5-1	0.006	2.07	0.210	0.294	0.205	0.0498	0.626	7.06	0.98	3.31	3.07	2.30
G	S3-1	0.009	1.92	0.199	0.228	0.195	0.0194	0.674	8.44	0.98	2.85	2.77	3.05
G2	S3-1	0.004	1.92	0.204	0.153	0.206	0.0010	0.613	12.52	1.01	3.13	3.13	4.00
H	R6-1	0.005	1.96	0.224	0.255	0.221	0.0424	0.609	7.69	0.99	3.22	3.01	2.55
I	S1-1	0.007	2.01	0.202	0.231	0.198	0.0450	0.626	8.69	0.98	3.20	2.99	2.91
J	D4-1	0.008	1.75	0.223	0.255	0.224	0.0457	0.552	6.86	1.00	3.16	2.92	2.35
K	D2-1	0.012	1.87	0.207	0.236	0.208	0.0506	0.583	7.92	1.01	3.21	2.95	2.68
K2	D2-1	0.010	1.85	0.205	0.193	0.209	0.0350	0.596	9.57	1.02	3.10	2.93	3.27
L	S4-1	0.012	1.78	0.224	0.256	0.230	0.0421	0.552	6.97	1.03	3.23	3.00	2.32
M	D5-1	0.005	1.75	0.251	0.266	0.250	0.2685	0.570	6.56	1.00	3.07	2.08	3.15
N	S6-1	0.021	2.02	0.206	0.268	0.201	0.0542	0.613	7.53	0.98	3.30	3.03	2.49
O	R5-1	0.009	1.76	0.263	0.259	0.252	0.2710	0.531	6.79	0.96	3.31	2.19	3.10
P	D3-1	0.003	1.30	0.273	0.188	0.267	0.0012	0.565	6.90	0.98	2.30	2.29	3.01
Q	D6-1	0.004	1.91	0.213	0.298	0.208	0.0434	0.622	6.42	0.98	3.07	2.87	2.24
Q2	D6-1	0.003	1.87	0.209	0.178	0.218	0.0498	0.552	10.53	1.04	3.39	3.11	3.38
R	S2-1	0.012	1.86	0.209	0.285	0.213	0.0480	0.572	6.54	1.02	3.26	3.01	2.18
R2	S2-1	0.022	1.76	0.210	0.168	0.222	0.0491	0.592	10.46	1.06	2.97	2.74	3.81
							Averages		7.90	1.00	3.16	2.89	2.75
							Std. Devn.		1.68	0.03	0.25	0.31	0.56
							C.V.'s		21	3	8	11	20

Results of material characterizations showed that the predominant compounds precipitated when the solutions were concentrated by evaporation were gypsum and Na_2SiF_6. The only other crystalline compound detected with any frequency was $NaKSiF_6$. Quantitative estimates made by PLM and FTIR agreed that gypsum contents were higher than those of the fluosilicate compounds. Usually, gypsum content was estimated to be slightly over 50%, Na_2SiF_6 content was slightly under 50%, and any difference was accounted for by $NaKSiF_6$. A typical ratio of gypsum to fluosilicate for the group of solid precipitated from the 18 pond water samples would be 60:40.

Data in Table 18 show that the average observed mole ratio Ca:S equaled one as would be expected for gypsum. The average ratio F:Si (= 7.9) is higher than that expected for fluosilicate compounds, the ratios F:Na and F:(Na+K) bracket the expected value of 3.0, and the ratio (Na+K):Si is higher than expected (2.75 versus 2.0). Assuming that all Ca and S in the solids was present in the form of gypsum, values for the weight percent gypsum were calculated from %Ca and %S contents. The calculated gypsum contents ranged from 31.1% to 54.1% (Ca basis) and from 31.3% to 56.4% (S basis). Means were 37.8% and 37.9%, and standard deviations were 4.87% and 5.32% based on Ca and S, respectively. Similar calculations of sodium fluosilicate contents were made based on %Na, % Si, and %F. The respective ranges observed were 46.2% to 63.4%, 28.9% to 59.5%, and 40.8% to 65.0%. Averages and standard deviations, in parentheses, were 55.5% (3.96%), 45.8% (8.60%), and 58.4% (5.45%) based on Na, Si, and F, respectively.

The sample compositions calculated from chemical analyses gave a slightly different distribution of gypsum and fluosilicate compounds than that estimated by materials characterizations methods. Rather than a ratio gypsum:fluosilicate of 60:40, the analytical data suggest a composition approximately 40% gypsum, 50-55% fluosilicate, and 5-10% unaccounted material. Considering that the materials characterizations techniques are primarily qualitative rather than quantitative methods, compositions estimated by the two approaches are in reasonable agreement.

EVAPORATIONS AT 40°C

Since solids precipitated during the initial evaporation experiments did not contain chukhrovite, which had been detected in sediments from unevaporated samples, additional tests were conducted to determine whether slower evaporations and more gradual formation of precipitating phases might induce chukhrovite formation. These tests were run on the six samples which had been collected at chemical plant water intakes, e.g., the pond-to-plant return water samples.

Evaporations were conducted in the same manner as those described above, except the bath temperature was set at 40°C, and the heater was turned off at the end of each workday. For these conditions, total times needed to evaporate samples to the target volumes ranged from about 90 to 98 hours.

Starting solutions were reanalyzed prior to beginning the evaporation runs; compositions are given in Table 19. Compositions of solutions recovered after the evaporation runs are given in Table 20. The evaporation ratios and comparisons of concentration and evaporation ratios, which were calculated as describe above, are listed in Table 21. Results from materials characterizations by PLM and XRD of solids collected from the evaporated samples are in Table 22. Table 23 contains the analytical data on the solids and mole ratios which were calculated to assist in evaluating the characterization data.

Table 19. Gypsum Pond Water 40°C Evaporation Experiments

Starting Solution Compositions

Run No.	ID No.	pH	% P	% F	ppm SO_4-S	ppm Si	ppm Al	ppm Ca	ppm Fe	ppm K	ppm Mg	ppm Na	ppm NH_4-N
1	R1-1	1.64	0.882	1.05	2801	2713	297	1142	180	425	381	2212	1713
2	R2-1	1.61	1.051	0.72	1515	2094	134	1614	326	383	356	2250	400
3	R3-1	1.89	0.210	0.42	1690	1112	78	905	79	118	202	1288	566
4	R4-1	1.56	1.005	1.02	1746	2776	232	1104	415	340	542	2001	464
5	R6-1	1.67	0.501	0.71	1602	2017	113	1242	117	304	334	2155	<10
6	R5-1	1.76	0.433	0.64	1613	1767	194	1224	157	178	156	1634	555

Recovered Solution Compositions

Run No.	% evapd	pH	% P	% F	ppm SO_4-S	ppm Si	ppm Al	ppm Ca	ppm Fe	ppm K	ppm Mg	ppm Na	ppm NH_4-N
1	72.4	0.76	3.22	2.41	8091	5911	1143	1155	707	393	1278	1879	6460
2	68.5	0.79	3.45	1.02	2533	2707	412	2017	1032	418	1042	2100	1465
3	74.5	1.23	0.82	1.02	4646	2684	312	992	326	447	355	2664	2477
4	71.6	0.61	3.63	2.19	4650	5766	798	1634	1399	363	1769	1650	1603
5	75.0	0.81	2.02	1.22	3762	3458	463	1388	505	458	971	2042	20
6	77.0	0.93	1.91	1.70	4154	4479	881	1479	722	428	708	2014	2430

Table 20. Comparisons of Concentration[a] and Evaporation Ratios[b] for 40°C Evaporations

			<---------- Concentration ratio/Evaporation ratio ---------->										
Run No.	ID No.	Evapn[b] ratio	P	F	SO_4 S	Si	Al	Ca	Fe	K	Mg	Na	NH_4 N
1	R1-1	3.62	1.01	0.63	0.80	0.60	1.06	0.28	1.08	0.26	0.93	0.23	1.04
2	R2-1	3.17	1.03	0.45	0.53	0.41	0.97	0.39	1.00	0.34	0.92	0.29	1.15
3	R3-1	3.92	1.00	0.62	0.70	0.62	1.02	0.28	1.05	0.97	0.45	0.53	1.12
4	R4-1	3.52	1.03	0.61	0.76	0.59	0.98	0.42	0.96	0.30	0.93	0.23	0.98
5	R6-1	4.01	1.00	0.43	0.59	0.43	1.02	0.28	1.08	0.38	0.73	0.24	-
6	R5-1	4.35	1.01	0.61	0.59	0.58	1.04	0.28	1.06	0.55	1.04	0.28	1.01
	Average		1.01	0.56	0.66	0.54	1.02	0.32	1.04	0.47	0.83	0.30	1.06
	Std. Devn.		0.013	0.094	0.11	0.093	0.036	0.066	0.049	0.26	0.21	0.11	0.073
	C.V.		1	17	16	17	4	21	5	57	26	38	7

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[a] Concentration ratio = $\dfrac{\text{Recovered solution concentration}}{\text{Starting solution concentration}}$

[b] Evaporation (Evapn) ratio = 100/(100 - % evaporated)

Table 21. Compositions of Solids from Pond Water Evaporations at 40°C

		Weight %						
Run	ID No.	P	F	SO_4-S	Si	Ca	K	Na
1	R1-1	0.46	38.0	5.52	8.74	6.77	1.90	14.4
2	R2-1	0.27	39.1	6.30	9.71	8.13	2.11	13.8
3	R3-1	0.13	24.1	10.30	5.68	12.80	0.13	10.0
4	R4-1	0.23	36.6	5.75	8.89	7.21	1.87	15.9
5	R6-1	0.22	40.2	4.29	9.62	5.39	2.55	16.6
6	R5-1	0.23	30.1	8.29	8.50	11.00	0.77	11.8

		Moles/100 g						
Run	ID No.	P	F	SO_4-S	Si	Ca	K	Na
1	R1-1	0.015	2.00	0.17	0.31	0.17	0.049	0.63
2	R2-1	0.009	2.06	0.20	0.35	0.20	0.054	0.60
3	R3-1	0.004	1.27	0.32	0.20	0.32	0.003	0.43
4	R4-1	0.007	1.93	0.18	0.32	0.18	0.048	0.69
5	R6-1	0.007	2.12	0.13	0.34	0.13	0.065	0.72
6	R5-1	0.007	1.58	0.26	0.30	0.27	0.020	0.51

		Mole ratios					
Run	ID No.	Ca:S	F:Si	F:Na	Na:Si	F: (Na+K)	(Na+K) Si
1	R1-1	0.98	6.43	3.19	2.01	2.96	2.17
2	R2-1	1.03	5.95	3.43	1.74	3.15	1.89
3	R3-1	0.99	6.27	2.92	2.15	2.89	2.17
4	R4-1	1.00	6.09	2.79	2.18	2.61	2.34
5	R6-1	1.01	6.18	2.93	2.11	2.69	2.30
6	R5-1	1.06	5.24	3.09	1.70	2.97	1.76
Average		1.01	6.03	3.06	1.98	2.88	2.10
Std. Devn.		0.029	0.42	0.23	0.21	0.20	0.23
C.V.		3	7	8	11	7	11

Table 22. Characterizations of Solids from Pond Water Evaporations at 40°C

		<------- PLM ------->		<-- XRD -->
Run No.	ID No.	Identity	Estd %	Identity
1	R1-1	Gypsum	30-40	Gypsum
		Na_2SiF_6	60-70	Na_2SiF_6
				$NaKSiF_6$
2	R2-1	Gypsum	40-50	Gypsum
		Na_2SiF_6	50-60	Na_2SiF_6
				$NaKSiF_6$
3	R3-1	Gypsum	70-80	Gypsum
		Na_2SiF_6	20-30	Na_2SiF_6
4	R4-1	Gypsum	30-40	Gypsum
		Na_2SiF_6	60-70	Na_2SiF_6
				$NaKSiF_6$
5	R6-1	Gypsum	50	Gypsum
		Na_2SiF_6	50	Na_2SiF_6
				$NaKSiF_6$
				$CaSO_4 \cdot 0.5H_2O$
6	R5-1	Gypsum	50	Gypsum
		Na_2SiF_6	50	Na_2SiF_6

Table 23. Gypsum Pond Water Evaporations with Added Metal Ions--Experimental Design and Solution Compositions

Run No.	Coded Factor Levels[a] Na	K	Al	Fe	Starting Solutions % P	% F	mg/Kg Na	K	Al	Fe
1	-1	-1	-1	-1	0.66	0.76	1995	276	172	217
2	+1	-1	-1	+1	0.71	0.70	2660	278	173	1080
3	-1	+1	-1	+1	0.72	0.71	2000	546	171	1030
4	+1	+1	-1	-1	0.68	0.62	2620	626	171	208
5	-1	-1	+1	+1	0.67	0.74	1930	270	1000	1020
6	+1	-1	+1	-1	0.68	0.75	2920	273	1020	208
7	-1	+1	+1	-1	0.68	0.75	1940	939	1030	218
8	+1	+1	+1	+1	0.67	0.77	2955	1083	1010	1085

[a] Factor Levels: "-1" = no addition
"+1" = Na & K added as chlorides; Al & Fe added as nitrates

Evaporated solutions

Run No.	% evapd	% P	% F	mg/kg Na	K	Al	Fe
1	72.6	2.51	1.53	2177	384	642	826
2	71.0	2.49	0.80	2855	497	641	3420
3	70.9	2.41	1.15	2225	364	622	3621
4	74.1	2.58	0.77	3962	748	661	822
5	75.0	3.00	1.66	2229	500	4480	4580
6	73.0	2.71	0.95	3377	655	4108	886
7	73.0	2.75	1.28	2642	509	4118	877
8	72.7	2.35	0.88	4423	805	3675	3603

Data in Table 21 helped reduce some of the uncertainties about element distribution behaviors that was present in the data from the initial evaporation experiments. Average values of the quotient (concentration ratio:evaporation ratio) for P, Al, Fe, and NH_4-N all equaled 1.0, and the standard deviations are 7% or less of the means. The data indicate that there were essentially no losses of these elements from the solution phases by precipitation or volatilization during the evaporations. The average quotient calculated for Mg is 0.83, but 4 of the 6 runs gave values that were 0.9 or higher. Since results from the previous set of evaporations indicated, albeit with high scatter, no Mg losses from solution, it is reasonable to assume that is the case with the latter 6 runs. Changes in solution phase concentrations for F, SO_4-S, Si, Ca, K, and Na indicate all of these were removed from solution during the evaporations,

Materials characterizations results showed that the principal constituents of solids precipitated during the lower temperature evaporations were gypsum, Na_2SiF_6, and $NaKSiF_6$. The mole ratios Ca:S, F:Si, F:Na, Na:Si, F:(Na+K), and (Na+K):Si were in good agreement with results that would be expected for a mixture of gypsum, Na_2SiF_6, and $NaKSiF_6$. The average for Ca:S was 1.01, which indicates no chukhrovite (Ca:S = 4.0) was present. Averages for F:Si (6.03), F:Na and F:(Na+K) (both about 3.0), and Na:Si and (Na+K):Si (about 2.0) all are consistent with Na_2SiF_6 containing traces of $NaKSiF_6$.

MASS BALANCE EXPERIMENTS

In the evaporation experiments described above there were minor losses of material during operations to separate and collect the solution and solid phases and to wash the solids. Therefore, it was not possible to obtain a precise measurement of the balance between starting and recovered materials. An additional experiment was conducted to determine whether significant volatilizations of F, Si, and other elements might have occurred.

The pond water solution used for the material balance experiments was a composite prepared from equal volumes of the 18 collected samples. Its pH was 1.55 and the composition was 0.66% P, 0.76% F, 1695ppm SO_4-S, 1995ppm Na, 276ppm K, 172ppm Al, 1155ppm Ca, 216ppm Fe, 286ppm Mg, 1910ppm Si, and 592ppm NH_4-N.

Weighed aliquots (150 grams each) of the composite solution were evaporated at 60°C until weights were reduced to approximately 25%, 50%, and 75% of the initial weights. After evaporations, no separations of solution and solid phases were made. HCl was added to each sample to solubilize any precipitated material, and the total sample was analyzed. The amounts of recovered P, F, Si, etc. were calculated and compared with the amounts present in the initial sample aliquots. Up to about 75% sample evaporation, the recovered amounts of solution components equaled the input amounts within experiment error.

Since volatilization of F was of particular interest, data for this element were subjected to regression analyses to evaluate how F composition behaved with changing degree of evaporation. The analysis showed that the fraction F recovered (i.e., F recovered/F input) was not dependent on the % sample evaporated. The regression equation for the data is:

$$\text{Fraction F recovered} = 0.982 - 0.0004(\text{\% evaporated})$$

The standard error in the constant term was 0.030, and the standard error in the coefficient of the (% evaporated) term was 0.0005. With a confidence range of plus or minus one standard error, the regression equation predicts that the fraction of F recovered in the nonvolatile fraction was 1.0, regardless of the percent of the sample that was evaporated. The regression correlation coefficient was low ($R^2 = 0.20$), which also indicates F recovery had little or no dependence on the percent evaporated.

Based on these results it is reasonable to assume that when the gypsum pond water samples were evaporated to remove water and concentrate them to saturation, the principal redistribution of solution constituents was by precipitation. No measurable volatilization of F, Si, or other elements occurred as long as the degree of sample evaporation was less than about 75%.

EVAPORATIONS WITH ADDED CATIONS

Since neither chukhrovite nor the ferric phosphate, which had been detected in pond water sediments, were detected during evaporations of pond water samples, additional experiments were conducted to determine if formations of either of these compounds could be induced. Samples were prepared by adding Al, Fe, Na, and K to a composite solution of several pond water samples. The levels of additives were chosen according to an experimental design, listed in Table 23. Aliquots of the treated solutions were evaporated to remove about 70% of the starting aliquot weight. Solution and solid phases were separated, solids were washed with methanol, and dried. The solutions were analyzed, and the solids were characterized by XRD. Compositions of starting solutions and of the solutions recovered after evaporations also are listed in Table 23.

Concentrations in the starting and final solutions were compared to evaluate the effects of the additives by calculating the concentrations that would have resulted if no changes occurred other than increases due to removal of water. The final concentrations actually observed were compared with the calculated concentrations. Examinations of ratios of observed to calculated concentrations given in Table 24 show that, within experimental error, concentrations of P, Al, and Fe were equal to the values that would occur if there were no losses of these elements from solution. Concentrations of F, Na, and K were lower than would be expected if the elements remained in solution. This indicates these latter three elements were removed from the solution phases during the treatments. Comparisons of mean ratio values for P and F at high and low levels of the treatment factors (Table 24) show that an addition of either Na or K caused a removal of F from solution. Additions of Al or Fe did not cause this effect.

XRD characterizations of solids collected from samples after evaporations (Table 25) detected gypsum, Na_2SiF_6, and $NaKSiF_6$ in all precipitated phases. The ferric (K,NH_4,H) phosphate compound was detected in five cases, however amounts of this material were very low and identifications from X-ray diffraction patterns were tentative. There is no evidence that additions of Fe caused a substantial increase in the precipitation of the ferric phosphate compound. Neither did the addition of Al cause precipitation of chukhrovite.

Table 24. Gypsum Pond Water Evaporations with Added Metal Ions--Effects of Additives

Concentration ratios: observed to calculated

Run		P	F	Na	K	Al	Fe
1		1.04	0.55	0.30	0.38	1.02	1.04
2		1.02	0.33	0.31	0.52	1.07	0.92
3		0.97	0.47	0.32	0.19	1.06	1.02
4		0.98	0.32	0.39	0.31	1.00	1.02
5		1.12	0.56	0.29	0.46	1.12	1.12
6		1.08	0.34	0.31	0.65	1.09	1.15
7		1.09	0.46	0.37	0.15	1.08	1.09
8		0.97	0.31	0.41	0.20	0.99	0.91
	Mean	1.03	0.42	0.34	0.36	1.05	1.03
	Std devn	0.06	0.10	0.05	0.18	0.04	0.09

Calculated concentration = (Initial concentration)/(1-fraction evaporated)

Mean Ratios at High (+1) and Low (-1) Levels

	P	F		P	F
Hi Na	1.01	0.32	Hi Al	1.06	0.42
Lo Na	1.05	0.50	Lo Al	1.00	0.42
Hi K	1.00	0.39	Hi Fe	1.02	0.42
Lo K	1.06	0.44	Lo Fe	1.05	0.42

Table 25. Gypsum Pond Water Evaporations with Added Metal Ions--Solids Recovered After Evaporations

	Phases detected by XRD					
Run	A	B	C	D	E	F
1	+	+	+			
2	+	+	+		(+)	
3	+	+	+		(+)	
4	+	+	+	(+)		(+)
5	(+)	+	+		(+)	+
6	(+)	+	+			+
7	+	+	+		(+)	
8	+	+	+		(+)	

"+" = Positive identification
"(+)" = Tentative identification

Phases: A = $CaSO_4 \cdot 2H_2O$
B = Na_2SiF_6
C = $NaKSiF_6$
D = K_2SiF_6
E = $Fe_3(K,NH_4,H)H_8(PO_4)_6 \cdot 6H_2O$
F = $CaSO_4 \cdot 0.5H_2O$

SECTION 5

TREATMENTS OF GYPSUM POND WATER SAMPLES

A number of experiments were conducted to explore the potential for reducing the soluble F content of gypsum pond water samples by treatments with materials which might cause the precipitation of F compounds such as chukhrovite or fluosilicates. In most cases, materials were added in excess and it was impractical to detect small quantities of reaction products in the solid phases separated from the reaction mixtures. Changes in solution phase compositions were used to determine whether significant removal of elements of interest had occurred.

TREATMENTS WITH Al AND Ca COMPOUNDS

These were exploratory experiments to investigate whether increased concentrations of Al and Ca selectively removed F and/or P from the solutions. The starting solution used in each test was a composite of collected pond water samples. Analysis of the composite showed that it contained 6720 mg/Kg P, 7195 mg/Kg F, 1780 mg/Kg SO_4-S, and 874 mg/Kg Si. The added materials were gypsum, aluminum hydroxide, aluminum powder, aluminum phosphate, kaolin, and calcium hydroxide. All were commercial reagent chemicals. The amount of each reagent added (given in Table 26) supplied 1.0 gram Ca or Al to 100 grams of solution.

Material additions were made according to the scouting experimental design listed in Table 26. Materials were added to solution phases contained in plastic conical flasks. The reaction mixtures were shaken on an oscillatory shaker platform. Aliquots of the mixtures were collected after they had reacted for 2 days and again after they had reacted for 9 days. Samples were withdrawn and filtered through membrane filters (0.65-micron pore size), and the filtrates were analyzed to determine solution phase compositions.

Compositions of the filtrates and mean responses calculated for the two levels of the treatment factors are given in Table 27. Treatment effects are judged by inspecting differences between mean responses at high and low levels. A negative value for the difference between the mean concentration of a constituent at the +1 level and the mean concentration at the -1 level indicates that the treatment reduced the concentration of that constituent.

Inspection of data in Table 27 shows that relatively large drops in F concentrations occurred when $Ca(OH)_2$, $AlPO_4$, kaolin, and Al powder were added, but not when gypsum and $Al(OH)_3$ were added. Phosphate and Si concentrations in the first group of filtrates appear to have been affected more by additions of Al powder and $Ca(OH)_2$ than by the other treatment factors. After reaction for 9 days, P concentrations appear to have been reduced by treatments with all compounds except gypsum.

NEUTRALIZATIONS WITH PHOSPHATE ORE FRACTIONS

It is known that neutralization of gypsum pond water with limestone reduces F and P concentrations by precipitating insoluble fluoride and phosphate compounds. Therefore, neutralizing pond water with waste products from higher carbonate content phosphate ores might be a lower cost way to reduce soluble F levels in gypsum ponds.

Table 26. Treatments of Gypsum Pond Water with Ca and Al Compounds

Experimental design

	<------------ Factor Levels ------------>					
Run #	X1	X2	X3	X4	X5	X6
14625-1	-1	-1	-1	1	-1	1
14625-2	1	-1	-1	-1	1	1
14625-3	-1	1	-1	-1	-1	-1
14625-4	1	1	-1	1	1	-1
14625-5	-1	-1	1	1	1	-1
14625-6	1	-1	1	-1	-1	-1
14625-7	-1	1	1	-1	1	1
14625-8	1	1	1	1	-1	1

Material added at levels = +1; not added at levels = -1

Factors and amounts added to 100 grams pond water:

X1 = Gypsum, 5.0 grams
X2 = $Al(OH)_3$, 3.0 grams
X3 = Al powder, 1.0 gram
X4 = $AlPO_4$, 5.0 grams
X5 = Kaolin, 5.0 grams
X6 = $Ca(OH)_2$, 2.0 grams

Initial concentrations in gypsum pond water sample composite:

P = 6720 mg/Kg, F = 7195 mg/Kg, SO_4S = 1780 mg/Kg, Si = 874 mg/Kg.

Table 27. Treatments of Gypsum Pond Water with Al and Ca Compounds-- Concentrations in Flitrates and Treatment Effects

	<--- first filtrate group --->				<-- second filtrate group -->			
Run	mg/Kg P	mg/Kg F	mg/Kg SO_4-S	mg/Kg Si	mg/Kg P	mg/Kg F	mg/Kg SO_4-S	mg/Kg Si
14625-1	4040	67	1985	340	3390	60	1960	1520
14625-2	5050	1040	790	480	5000	90	820	1015
14625-3	6767	7430	1850	901	6552	7070	1790	345
14625-4	8050	2820	2580	440	4300	700	2460	710
14625-5	4100	329	2470	380	3480	240	2760	2170
14625-6	7120	5600	2060	250	6550	5780	2380	440
14625-7	2560	91	1630	87	1300	100	1810	93
14625-8	1940	108	2500	160	1310	60	3105	97
Means of all runs	4953	2186	1983	380	3985	1763	2136	799
Means at indicated factor levels								
X1 = +1	5540	2392	1983	333	4290	1658	2191	566
X1 = -1	4367	1979	1984	427	3681	1868	2080	1032
Diff.	1173	413	-1	-94	609	-210	111	-466
X2 = +1	4829	2612	2140	397	3366	1983	2291	311
X2 = -1	5078	1759	1826	363	4605	1543	1980	1286
Diff.	-249	853	314	34	-1239	440	311	-975
X3 = +1	3930	1532	2165	219	3160	1545	2514	700
X3 = -1	5977	2839	1801	540	4811	1980	1758	898
Diff.	-2047	-1307	364	-321	-1651	-435	756	-198
X4 = +1	4533	831	2384	330	3120	265	2571	1124
X4 = -1	5374	3540	1583	430	4851	3260	1700	473
Diff.	-841	-2709	801	-100	-1731	-2995	871	651
X5 = +1	4940	1070	1868	347	3520	283	1963	997
X5 = -1	4967	3301	2099	413	4451	3243	2309	601
Diff.	-27	-2231	-231	-66	-931	-2960	-346	396
X6 = +1	3398	327	1726	267	2750	78	1924	681
X6 = -1	6509	4045	2240	493	5221	3448	2348	916
Diff.	-3111	-3718	-514	-226	-2471	-3370	-424	-235

X1 = Gypsum, X2 = $Al(OH)_3$, X3 = Al powder,

X4 = $AlPO_4$, X5 = Kaolin, X6 = $Ca(OH)_2$

Clay-sized fractions (material passing through a 150-mesh sieve) of three phosphate ores, which had been collected from Florida for research on phosphate beneficiation, were used to test this concept. Experiments were conducted according to the experimental design listed in Table 28. The pond water solution used in the experiments was a composite prepared from several of the samples collected in Florida. Three clay fractions from ores of varying carbonate content (BL-17, BL-20, and BL-9) were used as neutralizing agents; compositions of these are given in Table 28. The design factors were clay reactant type (levels of Xl = 1, 2, and 3 in order of carbonate content), amount of agent added (levels of X2 = 1 and 2), reaction time (X3 = 1 or 2), and addition of excess gypsum (levels of X4 = 1 and 2). The latter factor was included to determine whether the presence of solid gypsum might promote the formation of chukhrovite to precipitate a relatively greater amount of F than would be precipitated by calcium fluoride alone.

For each experimental run, 100 mL of solution was placed in a 500 mL plastic conical flask, the designed amounts of clay reactant and reagent gypsum were added, and the mixture was reacted with shaking for the designed time. After reaction, mixtures were transferred to a plastic centrifuge bottle and centrifuged to separate solid and solution phases. Solution phases were analyzed, and the response data (pH's and concentrations of F and P) are in Table 28.

Evaluations of results are in Table 29. For simple comparisons, mean responses for each factor level were calculated. An inspection of these shows that solution pH's and F and P concentrations changed in proportion to the clay reactant'scarbonate content. The degree of neutralization decreased in the order BL-17 >BL-20 >BL-9. Effects of the amount of reactant clay added and reaction time also were consistent with this trend. Decreases in F and P concentrations and increases in pH's were higher with the larger amounts of reactants and longer reaction times. Comparisons of differences in mean responses show the higher responses to these factors occurred with the higher carbonate-content clays. Additions of gypsum had negligible effects.

These exploratory tests demonstrate that neutralizing pond water with minus 150-mesh slimes from a dolomitic phosphate ore might be used to reduce soluble F concentrations in gypsum ponds. Results from several samples were analyzed for Mg. Concentrations in solutions treated with the BL-17 and BL-20 materials ranged from about 1300 ppm Mg to about 2200 ppm Mg. Since neutralizing gypsum ponds at operating acid plants with dolomitic reactants could cause undesirable amounts of Mg to report back into the phosphoric acid products, this treatment may be practicable only for cases where gypsum pile/pond systems are retired from active operations.

TREATMENTS WITH ATTAPULGITE CLAY

This experiment was conducted to see whether a material which would be readily available to Florida phosphate producers could be used to remove F from gypsum ponds. Past research [14] has shown that several clay minerals react rapidly with acidic, F-containing solutions. One of the most reactive minerals was attapulgite which has been shown to be an important constituent of phosphate ore clay slimes. Therefore, treatment of gypsum ponds with phosphate clay slimes might introduce sufficient amounts of Al and excess Si into solution to precipitate chukhrovite or some other Al- or Si- fluoride thereby reducing soluble F levels in the ponds.

Table 28. Treatments of Composite Pond Water Sample with Phosphate Rock Clay Fractions

	Factor Levels				Responses		
Run No.	X1	X2	X3	X4	pH	ppm F	ppm P
0		No treatments			1.69	8339	6987
1	1	1	1	1	3.14	7736	6892
2	1	2	1	1	3.55	1142	5764
3	1	1	1	2	3.18	7770	6884
4	1	2	1	2	3.23	7254	6776
5	1	1	2	1	3.23	5682	6652
6	1	2	2	1	3.73	654	5650
7	1	1	2	2	2.88	4440	6436
8	1	2	2	2	4.02	200	5378
9	2	1	1	1	2.42	8310	7094
10	2	2	1	1	3.20	5556	6752
11	2	1	1	2	2.45	6538	5756
12	2	2	1	2	3.18	6178	6602
13	2	1	2	1	2.21	5610	7138
14	2	2	2	1	3.17	1798	6004
15	2	1	2	2	2.41	8634	7150
16	2	2	2	2	3.20	1644	5466
17	3	1	1	1	1.82	8692	7498
18	3	2	1	1	2.02	8020	7610
19	3	1	1	2	1.88	6656	6134
20	3	2	1	2	2.15	8590	7650
21	3	1	2	1	1.94	8600	7524
22	3	2	2	1	2.12	6846	7572
23	3	1	2	2	1.95	8688	7594
24	3	2	2	2	2.15	7730	7578

Factors ID's and Coded Levels:

X1 = Reactant ID "1" = BL-17 "2"=BL-20 "3" = BL-9
X2 = Grams reactant added "1" = 2 "2" = 5
X3 = Reaction time, hrs. "1" = 1 "2" = 3
X4 = Gypsum added "1" = No "2" = Yes

Reactant Compositions:

	% P	% F	% Ca	% Mg	% CO_3-C
BL-17	0.38	0.18	18.15	9.43	9.95
BL-20	1.51	0.41	12.00	6.06	4.86
BL-9	3.77	0.85	9.05	1.76	0.20

Table 29. Effects of Pond Water Treatments with Phosphate Rock Clay Fractions

Factor Contrasts

Treatment Levels	Reactant = BL-17 pH	ppm F	ppm P	Reactant = BL-20 pH	ppm F	ppm P	Reactant = BL-9 pH	ppm F	ppm P
Means for reactant	3.37	4360	6304	2.78	5534	6495	2.00	7978	7395
X2 = 1	3.11	6407	6716	2.37	7273	6785	1.90	8159	7188
X2 = 2	3.64	2313	5892	3.19	3794	6206	2.11	7797	7603
X3 = 1	3.28	5976	6579	2.81	6646	6551	1.97	7990	7223
X3 = 2	3.47	2744	6029	2.75	4422	6440	2.04	7966	7567
X4 = 1	3.42	3804	6240	2.75	5319	6747	1.98	8040	7551
X4 = 2	3.33	4916	6369	2.81	5749	6244	2.03	7916	7239

Regression Analyses for $Y = a + b \cdot X1 + c \cdot X2 + d \cdot X3 + e \cdot X4$

	Y = pH	Y = ppm F	Y = ppm P
R^2 of regression with data from 24 runs	0.915	0.637	0.445
Intercept "a"	3.19	8337	6636
Std error of "a"	0.21	1865	616
X1 Coefficient "b"	-0.684	1809	545
Std error of "b"	0.053	466	154
X2 Coefficient "c"	0.518	-2645	-329
Std error of "c"	0.086	761	252
X3 Coefficient "d"	0.067	-1826	-106
Std error of "d"	0.086	761	252
X4 Coefficient "e"	0.010	473	-229
Std error of "e"	0.086	761	252

Gypsum pond water samples with concentrations ranging 0.5% to 1.0% P and 0.4% to 0.7% F were treated with a commercial attapulgite clay to test this concept. Slurries of clay and pond water were reacted with shaking at ambient laboratory temperature for four days. Aliquots were removed and centrifuged to obtain solids for characterizations. The centrifugates were filtered through a 0.65-micron pore size membrane filter and sent for chemical analysis.

Solids recovered from the reaction mixtures were examined by PLM and XRD. These characterizations revealed mostly unreacted and partially decomposed clay particles. Other materials detected were gypsum, quartz, unidentified amorphous materials, and a few tentatively identified minor products. The minor products had properties that suggested they could be sodium potassium fluosilicate, calcium fluoride, and/or chukhrovite. None were consistently present in all samples or present in amounts sufficient to make positive identifications.

Analyses of the liquid phases showed no changes in F concentrations that were significantly greater than experimental error. Thus, treatments with the attapulgite did not cause measurable precipitation of chukhrovite or other F-containing compounds.

SECTION 6

APPLICATIONS OF CHEMICAL MODELING COMPUTER PROGRAMS

During the past two decades a number of chemical modeling computer programs have been developed to assist chemists, geologists, soil scientists, and others who have a need for information about equilibrium conditions in complex aquatic chemical systems [15,16]. These programs calculate distributions and activities of chemical species on the assumption than chemical equilibrium exists in the system. The computed species distributions can then be used to determine solubility status in the systems and evaluate cause and effect relationships which might change the systems.

Two of these computerized chemical modeling programs, WATEQ4F [17,18] and PHREEQE [19], were developed by the U.S. Geological Survey to model chemical reactions in surface and ground water hydrogeochemical systems. The programs calculate solution speciation and saturation states of the aqueous phase with respect to various mineral phases. An essential input for the computations is a chemical model of elements, soluble complexes, and solid phases, with appropriate formation or solubility product constants. These data and user supplied inputs for the analytical concentrations of the elements, pH, temperature, and pe are used to iteratively solve the appropriate mass and charge balance equations for the concentrations of the soluble chemical species and the saturation indices of the solid species that were included with the input model. (Note: pe is the negative logarithm of electron activity, and is a measure of oxidizing intensity in solution that is analogous to pH as a measure of solution acidity. pe is related to the experimentally determined redox potential, E_H, by $pe = E_H(F/2.3RT)$; at 25°C, $pe = 16.9E_H$). Copies of the programs were acquired and tested with gypsum pond water analytical data to gain information about probable distributions of F, P, and other elements among various species that might exist in pond water solutions and to compare computed solubility conditions with experimental observations.

WATEQ4F

Initial tests with WATEQ4F revealed a significant shortcoming. The set of mass and charge balance equations that the program uses for chemical equilibrium model calculations did not include an entry for undissociated phosphoric acid. Therefore, at low pH's where a significant fraction of the total phosphate exists as undissociated phosphoric acid, the calculated chemical model was incorrect. The model equations used by WATEQ4F are part of the program code, and modifications of the program to add H_3PO_4 and other species important in a gypsum pond system model would require considerable revisions in the source code. Since an alternative program was available, no further evaluations were made with WATEQ4F.

PHREEQE

With the program PHREEQE, the chemical model of elements, aqueous species, and mineral phases are contained in an exterior data file. This can be modified by the user to include any pertinent chemical equilibria for which species formation constants are available. Thus, PHREEQE was capable of handling the chemical system needed to describe gypsum pond systems. After making the needed modifications to the chemical model data, this program was used to compute distributions of aqueous species and to evaluate saturation indices for mineral phases which might be in equilibrium with the pond water solutions.

The chemical data library supplied with PHREEQE contained values for approximately 200 soluble complexes and solid compounds comprised of the elements H, O, Ca, Mg, Na, K, Fe, Mn, Al, Ba, Si, Si, Cl, C, S, N, B, P. F, Li, and Br. This was modified to fit the chemical system of gypsum ponds by excluding data for species of little importance or those involving elements for which no analytical data was obtained (e.g., Mn, Ba, Sr, ... Br). Table 30 contains a list of elements and soluble species contained in the model after the modifications.

Most equilibrium constants in Table 30 were taken from the PHREEQE and WATEQ4F data libraries [17-20]. Since neither of these contained an entry for $SiF_4(aq)$, a value for the formation constant of this species was estimated from values reported in the literature [21,22] using the Davies' equation to adjust reported values to values at zero ionic strength. The validity of this value for the constant is questionable since there is disagreement among several reported investigations of fluorine complexes with silicon about whether a stable $SiF_4(aq)$ species exits. Nevertheless, the derived value for $SiF_4(aq)$ formation was included in the PHREEQE model to obtain as much information as possible about species that could influence the distribution of F in gypsum pond solutions.

PHREEQE contains a procedure, called LOOK MIN, which computes ion activity products (IAP's) for solid compounds to test for saturation. The IAP for a given solid and the value of its solubility product constant (KT) at 25°C are used to compute the saturation index, SI=Log(IAP/KT). The program user must define the appropriate stoichiometries for dissolution reactions of interest. Those included in the gypsum pond chemical model are listed in Table 31. In most cases, solubility product constant values were taken from the thermodynamic data included with PHREEQE and WATEQ4F or from chemical reference data handbooks.

Solubility product constants for Na and K fluosilicates were not available in the reference literature, and values were calculated from data on the solubilities of these compounds in water [24]. Calculations were made assuming no hydrolysis of the fluosilicate ion and using the Davies equation to adjust values to conditions of zero ionic strength.

No data was found to permit similar calculations of solubility product constants for chukhrovite or the $Fe\text{-}(NH_4,K)\text{-}PO_4$ compounds. When these compounds were included in chemical models their LOG KT values were set to zero. The computations generated IAP values which, as discussed later, were used to obtain estimates of the solubility product constant values.

COMPUTATIONS WITH SOLUTION/SEDIMENT SAMPLE DATA

PHREEQE was evaluated with data on compositions of solutions that were separated from the sample sediments collected in February 1989 to determine how well the computed model description matched experimental observations. Results are given in Table 32. Molalities and activities of soluble species with concentrations above 0.00001 molal are given in the first section of the table; species with computed concentrations less than 0.00001 molal are tallied in the second section. Computed SI values for several solid phases that might occur in gypsum pond systems also are listed. The solid phases considered for these computations were limited to those contained in the initial database plus the alkali fluosilicates.

Table 30. Master Species and Complex Species in PHREEQE Chemical Model

NO.	MASTER SPECIES	NO.	SPECIES	Log K[a]	NO.	SPECIES	Log K[a]
1	H^+	31	OH^-	-14.00	119	$Fe(OH)_4^-$	-21.60
2	e^-	40	HSO_4^-	1.99	120	$Fe_2(OH)_2^{+4}$	-2.95
3	H_2O	50	$NH_3(aq)$	-9.24	121	$Fe_3(OH)_4^{+5}$	-6.30
4	Ca^{+2}	52	$NH_4SO_4^-$	1.11	122	$FeCl^{+2}$	1.48
5	Mg^{+2}	65	HPO_4^{-2}	12.35	123	$FeCl_2^+$	2.13
6	Na^+	66	$H_2PO_4^-$	19.55	124	$FeCl_3$	1.13
7	K^+	67	H_3PO_4	21.70	125	$FeSO_4^+$	3.92
10	Al^{+3}	69	$HF(aq)$	3.17	126	$Fe(SO_4)_2^-$	5.42
13	H_4SiO_4	70	HF_2^-	3.75	127	$FeHPO_4^+$	17.77
14	Cl^-	75	$CaOH^+$	-12.60	128	$FeH_2PO_4^{+2}$	24.98
16	SO_4^{-2}	78	$CaSO_4$	2.31	129	FeF^{+2}	6.20
19	PO_4^{-3}	79	$CaPO_4^-$	6.46	130	FeF_2^+	10.80
20	F^-	80	$CaHPO_4$	15.09	131	FeF_3	14.00
23	NH_4^+	81	$CaH_2PO_4^+$	20.96	150	$AlOH^{+2}$	-4.99
24	Fe^{+3}	82	CaF^+	0.94	151	$Al(OH)_2^+$	-10.10
		85	$MgOH^+$	-11.79	152	$Al(OH)_3$	-16.00
		88	$MgSO_4$	2.25	153	$Al(OH)_4^-$	-23.00
		89	$MgPO_4^-$	6.59	154	$AlSO_4^+$	3.02
		90	$MgHPO_4$	15.22	155	$Al(SO_4)_2^-$	4.92
		91	$MgH_2PO_4^+$	21.07	156	AlF^{+2}	7.01
		92	MgF^+	1.82	157	AlF_2^+	12.75
		97	$NaSO_4^-$	0.70	158	AlF_3	17.02
		98	$NaHPO_4^-$	12.64	159	AlF_4^-	19.72
		100	KSO_4^-	0.85	170	$H_3SiO_4^-$	-9.93
		101	$KHPO_4^-$	12.64	171	$H_2SiO_4^{-2}$	-21.62
		116	$FeOH^{+2}$	-2.19	172	SiF_6^{-2}	30.18
		117	$Fe(OH)_2^+$	-5.67	173	$SiF_4(aq)$	21.20
		118	$Fe(OH)_3$	-13.60			

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[a] Logarithm of formation constant expressed in terms of master species.

Example: $H_4SiO_4 + 4H^+ + 6F^- - 4H_2O \text{ --> } SiF_6^{-2}$, Log K = 30.18

Table 31. Stoichiometries for Ion Activity Product Computations by "LOOK MIN" Procedure

LOOK MIN Name	Reaction Stoichiometry
GYPSUM	$CaSO_4 \cdot 2H_2O = Ca^{+2} + SO_4^{-2} + 2\ H_2O$
ANHYDRITE	$CaSO_4 = Ca^{+2} + SO_4^{-2}$
NA2SIF6	$Na_2SiF_6 = 2\ Na^+ + H_4SiO_4 + 6\ F^- + 4\ H^+ - 4\ H_2O$
K2SIF6	$K_2SiF_6 = 2\ K^+ + H_4SiO_4 + 6\ F^- + 4\ H^+ - 4\ H_2O$
NAKSIF6	$NaKSiF_6 = Na^+ + K^+ + H_4SiO_4 + 6\ F^- + 4\ H^+ - 4\ H_2O$
FLUORITE	$CaF_2 = Ca^{+2} + 2\ F^-$
QUARTZ	$SiO_2 = H_4SiO_4 - 2\ H_2O$
SIO2 GEL	$SiO_2(amorph) = H_4SiO_4 - 2\ H_2O$
CHUKHROV	$Ca_4SO_4AlSiF_{13} \cdot 10H_2O =$ $4\ Ca^{+2} + Al^{+3} + 4\ H^+ + H_4SiO_4 + 6\ H_2O + SO_4^{-2} + 13\ F^-$
STRENGIT	$FePO_4 \cdot 2H_2O = Fe^{+3} + PO_4^{-3} + 2\ H_2O$
VARISCIT	$AlPO_4 \cdot H_2O = Al^{+3} + PO_4^{-3} + 2\ H_2O$
BRUSHITE	$CaHPO_4 \cdot H_2O = Ca^{+2} + HPO_4^{-2} + 2\ H_2O$
STRUVITE	$MgNH_4PO_4 \cdot 6H_2O = Mg^{+2} + NH_4^+ + PO_4^{-3} + 6\ H_2O$
N-FE-PO4	$Fe_3NH_4H_8(PO_4)_6 \cdot 6H_2O = Fe^{+3} + NH_4^+ + 8\ H^+ + 6\ PO_4^{-3} + 6\ H_2O$
K-FE-PO4	$Fe_3KH_8(PO_4)_6 \cdot 6H_2O = Fe^{+3} + K^+ + 8\ H^+ + 6\ PO_4^{-3} + 6\ H_2O$
FLUORAP	$Ca_5(PO_4)_3F = 5\ Ca^{+2} + 3\ HPO_4^{-2} + F^- - 3\ H^+$
HYDROXAP	$Ca_5(PO_4)_3OH = 5\ Ca^{+2} + 3\ HPO_4^{-2} + H_2O - 4\ H^+$

Table 32. Equilibria Calculations with PHREEQE

Species in Solutions Collected 2/89

		Sample D2-1		Sample D4-1		Sample R1-1		Sample R4-1		Sample S4-1	
No.	Species	Molality	Activity	Molality	Activity	Molality	Activity	Molality	Activity	Molality	Activity
4	Ca^{+2}	0.01859	0.00501	0.01587	0.00418	0.01478	0.00381	0.01547	0.00409	0.01429	0.00375
5	Mg^{+2}	0.00610	0.00183	0.00968	0.00285	0.00746	0.00217	0.01102	0.00325	0.00998	0.00293
6	Na^{+}	0.10750	0.07671	0.08531	0.06059	0.09774	0.06917	0.08986	0.06385	0.09480	0.06728
7	K^{+}	0.01072	0.00705	0.00865	0.00562	0.01111	0.00712	0.00891	0.00580	0.01028	0.00666
13	H_4SiO_4	0.00045	0.00050	0.00235	0.00262	0.01008	0.01136	0.01417	0.01573	0.00704	0.00785
16	SO_4^{-2}	0.02364	0.00526	0.02529	0.00538	0.04102	0.00827	0.02598	0.00554	0.02893	0.00608
20	F^{-}	0.00029	0.00021	0.00021	0.00015	0.00017	0.00013	0.00015	0.00011	0.00017	0.00013
23	NH_4^{+}	0.02261	0.01651	0.03041	0.02223	0.11720	0.08601	0.03252	0.02377	0.02475	0.01810
40	HSO_4^{-}	0.01601	0.01169	0.01965	0.01437	0.02623	0.01925	0.01980	0.01448	0.02122	0.01552
52	$NH_4SO_4^{-}$	0.00153	0.00112	0.00211	0.00154	0.01248	0.00916	0.00232	0.00170	0.00194	0.00142
66	$H_2PO_4^{-}$	0.10470	0.07641	0.08471	0.06193	0.08888	0.06524	0.09076	0.06634	0.11350	0.08304
67	H_3PO_4	0.22410	0.24610	0.21590	0.23980	0.19520	0.22000	0.22620	0.25110	0.27560	0.30710
69	HF(aq)	0.00655	0.00719	0.00550	0.00611	0.00402	0.00453	0.00400	0.00443	0.00445	0.00495
78	$CaSO_4$	0.00489	0.00537	0.00412	0.00458	0.00570	0.00642	0.00416	0.00461	0.00417	0.00464
81	$CaH_2PO_4^{+}$	0.01342	0.00980	0.00907	0.00663	0.00867	0.00636	0.00949	0.00694	0.01089	0.00797
88	$MgSO_4$	0.00155	0.00171	0.00246	0.00273	0.00283	0.00320	0.00289	0.00321	0.00285	0.00317
91	$MgH_2PO_4^{+}$	0.00622	0.00454	0.00788	0.00576	0.00629	0.00462	0.00962	0.00703	0.01085	0.00794
92	MgF^{+}	0.00004	0.00003	0.00004	0.00003	0.00003	0.00002	0.00003	0.00002	0.00003	0.00002
97	$NaSO_4^{-}$	0.00277	0.00202	0.00223	0.00163	0.00391	0.00287	0.00243	0.00177	0.00280	0.00205
100	KSO_4^{-}	0.00036	0.00026	0.00029	0.00021	0.00057	0.00042	0.00031	0.00023	0.00039	0.00029
128	$FeH_2PO_4^{+2}$	0.00453	0.00129	0.00780	0.00223	0.00331	0.00096	0.00769	0.00220	0.00767	0.00220
129	FeF^{+2}	0.00007	0.00002	0.00011	0.00003	0.00004	0.00001	0.00008	0.00002	0.00007	0.00002
130	FeF_2^{+}	0.00025	0.00018	0.00026	0.00019	0.00008	0.00006	0.00013	0.00010	0.00014	0.00010
131	FeF_3	0.00006	0.00006	0.00004	0.00005	0.00001	0.00001	0.00002	0.00002	0.00002	0.00002
156	AlF^{+2}	0.00002	0.00001	0.00009	0.00002	0.00015	0.00004	0.00015	0.00004	0.00016	0.00004
157	AlF_2^{+}	0.00084	0.00062	0.00280	0.00205	0.00427	0.00313	0.00361	0.00264	0.00429	0.00314
158	AlF_3	0.00222	0.00244	0.00516	0.00573	0.00662	0.00746	0.00494	0.00548	0.00670	0.00746
159	AlF_4^{-}	0.00036	0.00026	0.00059	0.00043	0.00065	0.00048	0.00042	0.00031	0.00065	0.00048
172	SiF_6^{-2}	0.07098	0.02017	0.09644	0.02755	0.09091	0.02638	0.08892	0.02538	0.09040	0.02589
173	SiF_4(aq)	0.00042	0.00047	0.00115	0.00128	0.00150	0.00169	0.00192	0.00213	0.00150	0.00167

Table 32 (continued)

Species with Concentrations Below 0.00001 Molal

10 Al^{+3}
19 PO_4^{-3}
24 Fe^{+3}
50 $NH_3(aq)$
65 HPO_4^{-2}
70 HF_2^-
75 $CaOH^+$
79 $CaPO_4^-$
80 $CaHPO_4$
82 CaF^+
85 $MgOH^+$
89 $MgPO_4^-$
90 $MgHPO_4$
98 $NaHPO_4^-$
101 $KHPO_4^-$
116 $FeOH^{+2}$
117 $Fe(OH)_2^+$
118 $Fe(OH)_3$
119 $Fe(OH)_4^-$
120 $Fe_2(OH)_2^{+4}$
121 $Fe_3(OH)_4^{+5}$
125 $FeSO_4^+$
126 $Fe(SO_4)_2^-$
127 $FeHPO_4^+$
150 $AlOH^{+2}$
151 $Al(OH)_2^+$
152 $Al(OH)_3$
153 $Al(OH)_4^-$
154 $AlSO_4^+$
155 $Al(SO_4)_2^-$
170 $H_3SiO_4^-$
171 $H_2SiO_4^{-2}$

Computed Solubility Indices

Phase	Log KT	Sample D2-1	Sample D4-1	Sample R1-1	Sample R4-1	Sample S4-1
$CaSO_4 \cdot 2H_2O$	-4.603	0.01	-0.06	0.09	-0.05	-0.05
$CaSO_4$	-4.384	-0.20	-0.26	-0.12	-0.26	-0.26
Na_2SiF_6	-34.300	0.19	0.13	0.22	0.13	0.19
K_2SiF_6	-36.170	-0.01	-0.07	0.12	-0.08	0.05
CaF_2	-10.960	1.32	0.94	0.76	0.67	0.75
Fluoroapatite	-17.600	-12.70	-14.00	-13.85	-14.03	-13.81
Hydroxyapatite	-3.421	-21.58	-22.80	-22.52	-22.69	-22.52
SiO_2 (quartz)	-4.006	0.71	1.43	2.07	2.21	1.91

According to the computed concentrations, undissociated phosphoric acid and the $H_2PO_4^-$ are the important P-containing species in solution. Most F is tied up as fluosilicate ions, but complexes with Al, particularly AlF_3, are important species that influence the distribution of F in solution. Estimated HF concentrations are two to three times higher than estimated SiF_4 concentrations.

The computed SI values show that the solutions were saturated with gypsum, as expected. The SI values also indicate that solutions were saturated with Na_2SiF_6. Only two solutions (Rl-1 and S4-1) had positive SI's for K_2SiF_6. Negative SI values for the two apatite compounds indicate undersaturation. Computed positive SI's for CaF_2 and quartz indicate the solutions are supersaturated with these two materials. Although amorphous silica was detected in some solids filtered from collected samples, CaF_2 was not found in solids taken shortly after sample collections or in solids that precipitated during storage of the samples.

In comparing results from the PHREEQE computations with the findings from sediment characterizations, one notes that the two samples (D4-1 and R4-1) in which Na_2SiF_6 was not detected had the lowest computed SI values for this compound. The sample R1-1 with a positive SI value for gypsum was the only sample for which there was a definite identification of gypsum by XRD characterization. Considering the relative insensitivity of the XRD method when examining a complex mixture of materials, there is the likelihood that undetected amounts of gypsum and sodium fluosilicate were present in all samples. Thus, for these compounds there is a qualitative agreement between the model and the observations. All five sediments contained chukhrovite. As mentioned above, no value for a solubility product constant was available in the PHREEQE database for this compound and no SI value was computed. Likewise, $Fe_3(H,NH_4,K)H_8(PO_4)_6 \cdot 6H_2O$ was detected in all five sediments, but no K_{sp} values were in the PHREEQE database and SI values were not computed.

Based on these cursory comparisons, the computed models agreed with the major characteristics of the sediments. Phosphate and fluoride distributions in solution were consistent with known chemical information, and the solubility computations indicated saturation with the expected solids. Lack of data to formulate a more extensive model formulation and low sensitivity of methods for analyzing mixed solids obstructed more rigorous comparisons.

COMPUTATIONS WITH COLLECTED SAMPLE DATA

Computations were made with the mean composition data for all 18 samples collected in May 1988 to obtain an overview of gypsum pond water sample speciations and solubility states. Outputs from computations on the six return water samples are given in Appendix B to illustrate the type information generated by PHREEQE. Each output lists the experimental conditions (concentrations, pH, temperature, and a mean value of pe determined from redox potentials measured with an Orion 96-78-00 electrode); information derived from these data (e.g., ionic strength, electrical ion balance); and the distribution of chemical species (computed concentrations, activities, and activity coefficients). Results for return water and slurry water samples were similar to those of the return water samples except for minor variations in species distributions because of the differences in compositions.

The list of solids to be considered with the LOOK MIN procedure was expanded for these computations by adding solubility product constants for several metal phosphate minerals. Stoichiometric expressions were included for cases in which values for solubility product constants were not available; values of LOG KT for these entries were arbitrarily set equal to zero). Information about saturation states generated with this procedure for 18 pond water samples is summarized in Appendix C.

Solution phase species activities for the six return water samples were averaged. These averages are listed in Table 33 to show the relative importances of the soluble complexes. Undissociated phosphoric acid and the $H_2PO_4^-$ ion account for about 95% of the total phosphate in the system. The remaining 5% is accounted for by complexes of $H_2PO_4^-$ with Ca^+ (3%), Mg^+ (1.5%), and Fe^{+3} (0.5%). Most fluorine is complexed with Si or Al-about 80% as SiF_6^{-2}, 8% as AlF_3, 6% as SiF_4, and 3% as AlF_2^-. HF(aq) accounts for an additional 2% of the total moles F in the solution.

ESTIMATES OF SOLUBILITY PRODUCT CONSTANTS

Inspections of the solubility data in Appendix C showed patterns similar to those found with solutions collected with sediment samples. Table 34 contains a statistical summary of these data. Inspections of SI values show that, on average, the pond water solutions are well under the saturation limits for the phosphate compounds hydroxyapatite, fluorapatite, struvite, brushite, and variscite. They are slightly under saturation limits for anhydrite and potassium fluosilicate. Mean SI's for strengite, fluorite and silica (expressed as amorphous silica gel) indicate that solution conditions exceed the saturation limits for these compounds. Solutions appear to be just at the saturation limits for gypsum and sodium fluosilicate.

The data were used to obtain estimates of the solubility products for compounds that were detected in sample sediments but for which no solubility constants could be found in the literature. Since chukhrovite, $NaKSiF_6$, Na_2SiF_6, and the (K,NH_4,H) ferric phosphate were detected in several solid phases collected from the pond water samples, it was assumed that the solutions were saturated with these compounds. Therefore, the SI values should equal zero and the computed LOG IAP values should equal the solubility product constants for the compounds. The two sets of LOG IAP data in Table 34 were obtained by different ways. The first was the mean of results from all 18 samples. This assumes all samples were in equilibrium with the compounds of interest and provides a mean based on the maximum available data. For the second set, mean LOG IAP's were computed only for samples in which the compound of interest had been definitely detected by materials characterizations. These values should be very close to the "true" values of the solubility products but are based on fewer data.

Comparisons of the results from the PHREEQE IAP computations with solubility product constants that were available in the literature provide a measure of reliability in the assumption that computed IAP's are estimators of solubility product constants for compounds detected in the sediments. Values of solubility constants estimated from sources other than the current experimentation are available for only two compounds detected in sediments, gypsum and Na_2SiF_6, and only the value for gypsum is based on a critical review of determinations reported in the literature. LOG IAP values for gypsum computed from all 18 samples and from samples in which positive identifications of gypsum were reported are -4.56 and -4.55, respectively. The standard deviation is approximately 0.05. The value for LOG KT of gypsum is -4.603. Clearly, experimental error and uncertainties in the methods used to make ionic strength corrections in ion activity coefficients can account for the difference of about 0.05 unit in the values for gypsum. Thus, the estimate from the PHREEQE computation is in good agreement with the literature value. LOG IAP values for Na_2SiF_6 are -34.34 and -34.21, and the mean of these is -34.27. This is to be compared with LOG(KT) = -34.30 estimated from reported solubility data. Again, considering experimental error and uncertainties introduced by ionic strength corrections the agreement is very good.

Table 33. PHREEQE Chemical Model--Average Species Activities in Return Water Samples

No.	Species	Activity	No.	Species	Activity	No.	Species	Activity
3	H_2O	9.89E-01	128	$FeH_2PO_4^{+2}$	1.14E-03	101	$KHPO_4^-$	1.50E-09
67	H_3PO_4	1.56E-01	100	KSO_4^-	2.13E-04	123	$FeCl_2^+$	1.33E-09
13	H_4SiO_4	6.08E-02	159	AlF_4^-	1.93E-04	50	NH_3 AQ	8.07E-10
6	Na^+	6.01E-02	20	F^-	1.04E-04	117	$Fe(OH)_2^+$	4.61E-10
66	$H_2PO_4^-$	4.88E-02	130	FeF_2^+	5.74E-05	170	$H_3SiO_4^-$	3.35E-10
23	NH_4^+	2.87E-02	156	AlF^{+2}	3.84E-05	150	$AlOH^{+2}$	1.76E-11
1	H^+	2.10E-02	129	FeF^{+2}	1.36E-05	2	e^-	3.98E-12
172	SiF_6^{-2}	1.92E-02	92	MgF^+	1.20E-05	124	$FeCl_3$	3.44E-12
40	HSO_4^-	1.16E-02	131	FeF_3	9.96E-06	31	OH^-	5.03E-13
81	$CaH_2PO_4^+$	6.50E-03	82	CaF^+	4.65E-06	85	$MgOH^+$	1.36E-13
14	Cl^-	6.04E-03	125	$FeSO_4^+$	3.92E-06	75	$CaOH^+$	6.48E-14
78	$CaSO_4$	5.85E-03	70	HF_2^-	1.21E-06	79	$CaPO_4^-$	4.50E-14
16	SO_4^{-2}	5.71E-03	126	$Fe(SO_4)_2^-$	7.23E-07	89	$MgPO_4^-$	2.07E-14
7	K^+	5.25E-03	80	$CaHPO_4$	3.95E-07	120	$Fe_2(OH)_2^{+4}$	2.04E-14
4	Ca^{+2}	5.17E-03	154	$AlSO_4^+$	2.50E-07	151	$AlOH_2^+$	6.26E-15
158	AlF_3	3.79E-03	90	$MgHPO_4$	1.97E-07	118	$FeOH_3$	3.06E-16
91	$MgH_2PO_4^+$	3.24E-03	65	HPO_4^{-2}	1.39E-07	19	PO_4^{-3}	3.04E-18
69	HF(aq)	3.09E-03	155	$Al(SO_4)_2^-$	1.29E-07	152	$AlOH_3$	3.79E-19
52	$NH_4SO_4^-$	2.40E-03	24	Fe^{+3}	8.44E-08	171	$H_2SiO_4^{-2}$	3.40E-20
173	SiF_4(aq)	2.17E-03	10	Al^{+3}	3.92E-08	121	$Fe_3(OH)_4^{+5}$	2.43E-21
157	AlF_2^+	2.05E-03	116	$FeOH^{+2}$	2.67E-08	119	$FeOH_4^-$	1.86E-22
88	$MgSO_4$	1.86E-03	98	$NaHPO_4^-$	1.68E-08	153	$AlOH_4^-$	1.92E-24
5	Mg^{+2}	1.86E-03	122	$FeCl^{+2}$	1.51E-08			
97	$NaSO_4^-$	1.72E-03	127	$FeHPO_4^+$	3.15E-09			

Table 34. Summary IAP's, SI's, and Solubility Product Estimates Computed from Mean Pond Water Sample Compositions

PHASE	LOG KT	Mean LOG IAP[a]	Std. Devn[a]	C.V.[a]	Mean LOG IAP[b]	Mean SI[a]
CHUKHROV	-	-78.781	0.189	0.2%	-78.757	-
K-Fe-PO$_4$	-	-142.008	1.117	0.8%	-141.10	-
N-Fe-PO$_4$	-	-141.413	1.260	0.9%	-140.43	-
NaKSiF$_6$	-	-35.408	0.382	1.1%	-35.121	-
Na$_2$SiF$_6$	-34.300	-34.335	0.307	0.9%	-34.213	-0.03
GYPSUM	-4.603	-4.562	0.053	1.2%	-4.552	0.04
ANHYDRIT	-4.384	-4.552	0.054	1.2%	-	-0.17
K$_2$SiF$_6$	-36.170	-36.480	0.467	1.3%	-	-0.31
FLUORITE	-10.960	-10.242	0.155	1.5%	-	0.72
SiO$_2$ GEL	-3.018	-1.256	0.162	12.9%	-	1.76
STRENGIT	-26.430	-24.552	0.147	0.6%	-	1.88
VARISCIT	-22.520	-25.035	0.374	1.5%	-	-2.52
BRUSHITE	-6.600	-9.134	0.147	1.6%	-	-2.53
STRUVITE	-13.150	-21.988	0.529	2.4%	-	-8.84
FLUORAP	-17.600	-30.810	0.525	1.7%	-	-13.21
HYDROXAP	-3.421	-25.133	0.545	2.2%	-	-21.71

Solubility Product Constants (T = 24° to 26°C) Estimated from LOG IAP's

PHASE	LOG KT
CHUKHROV	-78.77
K-FE-PO$_4$	-141.6
N-FE-PO$_4$	-140.9
NaKSiF$_6$	-35.26
Na$_2$SiF$_6$	-34.27

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[a] Computed from all 18 samples.

[b] Computed from samples with positive phase identifications only.

Since comparisons for gypsum and Na_2SiF_6 showed good agreement, the computed LOG IAP values for other compounds that had been detected in pond water sample sediments were used to estimate solubility products. These are given at the bottom of Table 34.

Log K values for chukhrovite estimated from means calculated from all 18 samples and from those in which positive identifications were made (-78.78 and -78.76, respectively) are in good agreement. Therefore, a value of -78.77 is taken as the best estimate for the solubility product constant of chukluovite at 25°C, according to the reaction stoichiometry given in Table 31. Values for the potassium and ammonium ferric phosphate compounds have poorer agreement, which is understandable considering uncertainties in the exact composition of the material detected in sediments. However, LOG IAP values provide "ballpark" estimates of -141.6 and -140.9 for LOG KT's of the potassium and ammonium forms, respectively. Agreement between the two computed LOG IAP's for $NaKSiF_6$ is moderately good, and the estimated LOG KT is -35.26.

CONCLUSIONS FROM COMPUTER MODELING STUDIES

As with any attempt to mathematically describe chemical equilibria, the reliability of the PHREEQE model depends on the reliabilities in the analytical data and the values of formation constants of various complex species included in the model. Criteria generated by PHREEQE to help judge the combined accuracies of the solution analytical data and the equilibrium constants of various soluble complexes in the model are the result of an ionic charge balance ("ELECTRICAL BALANCE" parameter in the outputs) and whether the computation converged in a finite number of iterations (default limit of PHREEQE is 200). In computations with the mean composition data of collected pond waters, results of the charge balance computations, which would be zero for an ideal situation, ranged from about -0.002 to about -0.08. Computations converged in less than 100 iterations, many in less than 50. Since ionic strengths computed by the model ranged from about 0.2 to about 0.5, a region where activity coefficients estimated by available mathematical approaches show significant deviations from experimental data, the quality with which the PHREEQE model fit the experimental data and estimated distributions of elements among the soluble complexes is relatively good. The distributions predicted by PHREEQE are consistent with the expectations that species most likely to be involved in gypsum pond equilibria are complexes of F with Si and Al.

The solubility states of the pond water solutions estimated by PHREEQE qualitatively agree with experimental observations. An exception was the prediction that strengite ($FePO_4{\cdot}2H_2O$) should be precipitated, but this phase was not detected by direct examinations of the solids. Instead, an iron potassium / ammonium phosphate was found. The model also predicted precipitation of silica gel and only traces were reported in the materials characterizations. This is understandable since the amorphous gel is difficult to determine by the methods used.

Potentially valuable results from tests with the computer modeling are the estimates of solubility product constants for several compounds found in gypsum pond sediments-chukhrovite, alkali fluosilicates, and the ferric (K, NH_4) phosphates. The estimated values are internally consistent in that the relative standard deviations were on the order of 1% of the calculated means, and the compounds were observed in numerous collected solid phases. Furthermore, agreements between values estimated by the PHREEQE computations and other sources of data for gypsum and sodium fluosilicate, add confidence in the estimates.

Compound stoichiometries for chukhrovite and the ferric phosphates are vague and these values should be considered as "ballpark" estimates only. Other research on chukhrovite has determined that its composition is variable, depending on the mole ratio of Al to Si (personal communication, J. J. Kohler and S. J. Meischen, TVA Chemical Research Department). The stoichiometry used to calculate IAP's is likely to exist only in limited circumstances. Uncertainties in the exact compositions of the ferric phosphate compound exist because of the observed variations in the K and N contents of the collected solids, and an inability to resolve XRD data to specifically identify discrete phases.

In summary, results from tests with the PHREEQE program have shown good agreement with experimental observations. The program or similar modeling programs can be useful for exploring chemical equilibria in complex aquatic systems, particularly in situations where time or financial constraints prohibit direct experimentation and qualitative information is sufficient. When combined with experimental data, the program can be used to extract working estimates of solubility parameters.

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Appendix A. REPLICATE DETERMINATIONS OF GYPSUM POND WATER SAMPLE COMPOSITIONS

	Sample	Detn	Density		<--------------					Weight %						--------------->
ID^a	Number	Date^b	g/mL	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl
DISCHARGE WATER SAMPLES																
D1-1	PW103	88/06	1.032	1.58	1.97	1.10	0.268	0.270	0.0315	0.130	0.0269	0.040	0.030	0.220	0.210	0.030
D1-1	PW103	89/06			2.06	1.01	0.330	0.268	0.0290	0.118	0.0120	0.036	0.035	0.207	0.182	
D2-1	PW111	88/06	1.031	1.64	2.33	0.81	0.104	0.217	0.0179	0.180	0.0349	0.040	0.020	0.240	0.134	0.160
D2-1	PW111	89/03			2.37	0.80	0.154	0.191	0.0088	0.141	0.0258	0.041	0.032	0.238	0.032	0.099
D3-1	PW116	88/06	1.008	1.94	0.47	0.40	0.108	0.104	0.0077	0.090	0.0079	0.020	0.004	0.120	0.050	0.010
D3-1	PW116	89/06			0.46	0.36	0.155	0.105	0.0070	0.082	0.0080	0.013	0.011	0.114	0.077	
D4-1	PW110	88/06	1.033	1.56	2.13	1.18	0.132	0.306	0.0390	0.190	0.0526	0.040	0.040	0.190	0.053	0.020
D4-1	PW110	89/03			2.18	1.10	0.170	0.265	0.0220	0.106	0.0431	0.033	0.046	0.191	0.043	0.006
D5-1	PW113	88/06	1.016	1.81	0.96	0.69	0.104	0.181	0.0234	0.110	0.0197	0.020	0.007	0.140	0.055	0.010
D5-1	PW113	89/06			0.96	0.59	0.150	0.174	0.0170	0.112	0.0160	0.018	0.018	0.134	0.075	
D6-1	PW117	88/06	1.017	1.76	1.04	0.74	0.112	0.191	0.0135	0.140	0.0125	0.040	0.020	0.220	0.004	0.010
D6-1	PW117	88/11			1.05	0.74	0.150	0.200	0.0098	0.110	0.0100		0.022	0.210	0.003	0.010
D6-1	PW117	88/12			1.10											
D6-1	PW117	89/01			0.96	0.76										
D6-1	PW117	89/03			1.10	0.68	0.162	0.181	0.0084	0.118	0.0118	0.030	0.023	0.202	0.001	0.006
RETURN WATER SAMPLES																
R1-1	PW101	88/06	1.034	1.62	2.02	1.09	0.268	0.270	0.0308	0.120	0.0259	0.040	0.030	0.210	0.167	0.010
R1-1	PW101	89/02		1.64	2.02	1.05	0.280	0.271	0.0297	0.114	0.0180	0.043	0.038	0.221	0.171	0.013
R2-1	PW102	88/06	1.032	1.58	2.56	0.82	0.136	0.218	0.0176	0.190	0.0354	0.040	0.030	0.240	0.057	0.180
R2-1	PW102	89/02		1.61	2.41	0.72	0.152	0.209	0.0134	0.161	0.0326	0.038	0.036	0.225	0.040	0.091
R2-1	PW102	89/06			2.54	0.69	0.148	0.201	0.0080	0.150	0.0220	0.041	0.034	0.219	0.056	
R3-1	PW104	88/06	1.009	1.87	0.48	0.39	0.108	0.105	0.0084	0.090	0.0085	0.010	0.003	0.120	0.064	0.010
R3-1	PW104	89/02		1.89	0.48	0.42	0.169	0.111	0.0078	0.091	0.0079	0.012	0.020	0.129	0.057	0.010
R4-1	PW105	88/06	1.034	1.57	1.96	1.04	0.112	0.299	0.0405	0.190	0.0547	0.040	0.050	0.200	0.079	0.020
R4-1	PW105	88/11			2.15	1.05	0.180	0.270	0.0211	0.100	0.0375		0.047	0.210	0.053	0.012
R4-1	PW105	88/12			2.22											
R4-1	PW105	89/01			2.11	1.09										
R4-1	PW105	89/02		1.56	2.30	1.02	0.175	0.278	0.0232	0.110	0.0415	0.034	0.054	0.200	0.046	0.006
R4-1	PW105	89/06			2.31	0.95	0.167	0.264	0.0210	0.106	0.0310	0.036	0.052	0.186	0.062	
R5-1	PW115	88/06	1.017	1.80	0.97	0.65	0.100	0.169	0.0231	0.120	0.0188	0.020	0.009	0.150	0.056	0.010
R5-1	PW115	89/02		1.76	0.99	0.64	0.161	0.177	0.0194	0.122	0.0157	0.018	0.016	0.163	0.056	0.004

Appendix A (continued)

	Sample	Detn	Density		<--------------					Weight %				---------------->		
ID[a]	Number	Date[b]	g/mL	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl
----	------	-----	-------	----	----	----	-----	-----	------	-----	------	-----	-----	-----	-----	-----
R6-1	PW108	88/06	1.018	1.69	1.08	0.73	0.116	0.196	0.0125	0.140	0.0115	0.040	0.020	0.200	0.006	0.009
R6-1	PW108	89/02		1.67	1.15	0.71	0.160	0.202	0.0113	0.124	0.0117	0.030	0.033	0.216	0.001	0.005
R1-2	PW201	90/01	1.030	1.68	2.19	0.98	0.260	0.233	0.0277	0.128	0.0217	0.022	0.038	0.215	0.207	0.014
R1-2	PW201	90/05			2.56	0.97	0.258	0.212	0.0266	0.117	0.0158	0.040	0.038	0.225	0.188	0.014
R1-2	PW201	90/08			2.29	1.01	0.262	0.247		0.127						
R1-2	PW201	90/08			2.22	1.00	0.256	0.247		0.126						
R3-2	PW212	90/01	1.003	1.93	0.46	0.32	0.139	0.084	0.0067	0.088	0.0076	0.011	0.008	0.114	0.052	0.011
R3-2	PW212	90/05			0.47	0.32	0.141	0.086	0.0071	0.086	0.0076	0.011	0.011	0.113	0.045	0.013
R3-2	PW212	90/07			0.46	0.32	0.132	0.088		0.090						
R4-2	PW207	90/01	1.023	1.60	1.95	1.05	0.185	0.231	0.0319	0.171	0.0332	0.027	0.041	0.197	0.048	0.001
R4-2	PW207	90/05			2.10	0.97	0.170	0.224	0.0193	0.112	0.0315	0.033	0.041	0.187	0.047	0.005
R4-2	PW207	90/07			2.08	1.02	0.175	0.234		0.121						
R5-2	PW204	90/01	1.009	1.66	1.20	0.55	0.172	0.129	0.0203	0.117	0.0163	0.011	0.018	0.138	0.051	0.002
R5-2	PW204	90/05			1.16	0.53	0.167	0.128	0.0200	0.111	0.0143	0.015	0.018	0.133	0.045	0.004
R5-2	PW204	90/07			1.20	0.52	0.174	0.136		0.119						
R5-2	PW204	90/08			1.17	0.57	0.170	0.135		0.116						
R5-2	PW204	90/08			1.13	0.57	0.169	0.133		0.117						
R6-2	PW210	90/01	1.016	1.69	1.36	0.66	0.171	0.155	0.0121	0.136	0.0145	0.024	0.027	0.220	0.001	0.003
R6-2	PW210	90/05			1.43	0.62	0.157	0.163	0.0118	0.119	0.0141	0.037	0.027	0.214	0.002	0.005
R6-2	PW210	90/07			1.41	0.65	0.159	0.182		0.133						
R6-2	PW210	90/07			1.39	0.64	0.160	0.167		0.130						
R7-2	PW206	90/01	1.027	1.36	2.14	1.37	0.217	0.361	0.0316	0.207	0.0391	0.025	0.033	0.195	0.008	0.015
R7-2	PW206	90/05			2.09	1.30	0.222	0.322	0.0267	0.159	0.0337	0.034	0.032	0.186	0.009	0.011
R7-2	PW206	90/08			2.19	1.36	0.211	0.353		0.194						
R7-2	PW206	90/08			2.10	1.32	0.207	0.343		0.179						
SLURRY WATER SAMPLES																
S1-1	PW109	88/06	1.034	1.64	2.12	1.09	0.268	0.269	0.0351	0.120	0.0306	0.050	0.030	0.230	0.263	0.010
S1-1	PW109	89/06			2.22	1.03	0.312	0.263	0.0330	0.119	0.0210	0.038	0.036	0.204	0.191	
S2-1	PW118	88/06	1.030	1.74	2.27	0.77	0.100	0.195	0.0201	0.190	0.0374	0.040	0.020	0.240	0.041	0.150
S2-1	PW118	88/11			2.25	0.77	0.140	0.200	0.0160	0.160	0.0340		0.032	0.240	0.042	0.082
S2-1	PW118	88/12			2.27											
S2-1	PW118	89/01			2.02	0.78										
S2-1	PW118	89/03			2.30	0.69	0.161	0.185	0.0116	0.153	0.0320	0.041	0.029	0.234	0.028	0.107
S2-1	PW118	89/06			2.36	0.54	0.109	0.184	0.0090	0.146	0.0290	0.042	0.031	0.224	0.041	
S3-1	PW107	88/06	1.009	1.88	0.52	0.55	0.112	0.145	0.0105	0.090	0.0097	0.020	0.003	0.200	0.061	0.010
S3-1	PW107	90/05			0.54	0.62	0.170	0.130	0.0062	0.079	0.0105	0.016	0.011	0.198	0.062	0.010
S3-1	PW107	90/08			0.54	0.56	0.168	0.137		0.083						

Appendix A (continued)

	Sample	Detn	Density		<-------------- Weight % ---------------->											
ID[a]	Number	Date[b]	g/mL	pH	P_2O_5	F	SO_4S	Si	Al	Ca	Fe	K	Mg	Na	NH_4N	Cl
S4-1	PW112	88/06	1.041	1.58	2.82	1.21	0.152	0.300	0.0519	0.200	0.0722	0.040	0.050	0.210	0.088	0.020
S4-1	PW112	88/11			2.77	1.06	0.190	0.280	0.0301	0.120	0.0550		0.053	0.220	0.054	0.011
S4-1	PW112	88/12			2.75											
S4-1	PW112	89/01			2.59	1.09										
S4-1	PW112	89/03			2.78	1.04	0.187	0.260	0.0297	0.111	0.0413	0.039	0.054	0.206	0.035	0.006
S5-1	PW106	88/06	1.021	1.75	1.14	0.90	0.132	0.220	0.0262	0.130	0.0229	0.030	0.010	0.210	0.071	0.010
S5-1	PW106	90/05			1.19	0.85	0.171	0.188	0.0190	0.093	0.0185	0.030	0.019	0.220	0.194	0.005
S5-1	PW106	90/08			1.15	0.89	0.168	0.194		0.100						
S6-1	PW114	88/06	1.016	1.87	1.07	0.42	0.072	0.124	0.0098	0.100	0.0095	0.040	0.020	0.220	0.006	0.010
S6-1	PW114	90/05			1.51	0.53	0.165	0.111	0.0073	0.096	0.0082	0.036	0.024	0.216	0.001	0.004
S6-1	PW114	90/07			1.22	0.46	0.160	0.120		0.110						
S6-1	PW114	90/07			1.21	0.46	0.161	0.119		0.107						
S1-2	PW203	90/01	1.033	1.66	2.57	1.04	0.241	0.223	0.0430	0.133	0.0276	0.025	0.049	0.224	0.205	0.012
S3-2	PW211	90/01	1.007	1.94	0.51	0.42	0.128	0.117	0.0056	0.095	0.0076	0.018	0.009	0.178	0.050	0.012
S4-2	PW208	90/01	1.022	1.60	1.89	1.03	0.179	0.250	0.0308	0.155	0.0312	0.020	0.039	0.185	0.049	0.001
S5-2	PW202	90/01	1.020	1.75	1.48	0.72	0.152	0.160	0.0195	0.141	0.0187	0.014	0.023	0.222	0.050	0.004
S6-2	PW209	90/01	1.017	1.77	1.60	0.62	0.121	0.154	0.0136	0.144	0.0221	0.024	0.034	0.237	0.001	0.004
S7-2	PW205	90/01	1.032	1.37	2.29	1.35	0.201	0.322	0.0382	0.187	0.0431	0.033	0.036	0.195	0.008	0.014

---

[a] Sample ID code = "AB-C", where

A = Sample type: R = Return from pond, D = Discharge to pond, S = Slurry decant or filtrate;

B = Collection site 1 through 7; and

C = Collection group: 1 = May 1988 and 2 = December 1989.

[b] Determination date = Year/Month of analyses.

Appendix B. PHREEQE Speciation Computations of Gypsum Pond-to-Plant Return Water Samples

Solution Compositions and Speciations for Sample R1-1

```
                    TOTAL MOLALITIES OF ELEMENTS

             ELEMENT          MOLALITY          LOG MOLALITY

             Ca              3.112521D-02          -1.5069
             Mg              1.491549D-02          -1.8264
             Na              1.001781D-01           -.9992
             K               1.145369D-02          -1.9411
             Al              1.197376D-02          -1.9218
             Si              1.645736D-01           -.7836
             Cl              3.608963D-03          -2.4426
             S               9.111750D-02          -1.0404
             P               3.034641D-01           -.5179
             F               6.005109D-01           -.2215
             NH4             1.286796D-01           -.8905
             FeIII           4.200267D-03          -2.3767

                    ----DESCRIPTION OF SOLUTION----

                               PH =   1.6300
                     ACTIVITY H2O =    .9854
                  IONIC STRENGTH =    .5321
                     TEMPERATURE =  25.0000
              ELECTRICAL BALANCE =  -8.0305D-02
                      ITERATIONS =  75

                      -----------------------
                      DISTRIBUTION OF SPECIES
                      -----------------------

 I  SPECIES      Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 1  H+          1.0  3.076E-02   -1.512   2.344E-02  -1.630  7.621E-01   -.118
 4  Ca+2        2.0  1.585E-02   -1.800   4.074E-03  -2.390  2.569E-01   -.590
 5  Mg+2        2.0  6.736E-03   -2.172   1.958E-03  -2.708  2.907E-01   -.536
 6  Na+         1.0  9.629E-02   -1.016   6.812E-02  -1.167  7.074E-01   -.150
 7  K+          1.0  1.089E-02   -1.963   6.958E-03  -2.158  6.388E-01   -.195
10  Al+3        3.0  8.884E-07   -6.051   7.700E-08  -7.114  8.667E-02  -1.062
13  H4SiO4       .0  6.919E-02   -1.160   7.821E-02  -1.107  1.130E+00    .053
14  Cl-        -1.0  3.609E-03   -2.443   2.305E-03  -2.637  6.388E-01   -.195
16  SO4-2      -2.0  4.186E-02   -1.378   8.367E-03  -2.077  1.999E-01   -.699
19  PO4-3      -3.0  1.688E-16  -15.773   3.275E-18 -17.485  1.941E-02  -1.712
20  F-         -1.0  1.507E-04   -3.822   9.448E-05  -4.025  6.272E-01   -.203
23  NH4+        1.0  1.185E-01    -.926   6.930E-02  -1.159  5.848E-01   -.233
24  Fe+3        3.0  8.011E-07   -6.096   6.943E-08  -7.158  8.667E-02  -1.062
31  OH-        -1.0  6.734E-13  -12.172   4.223E-13 -12.374  6.272E-01   -.203
40  HSO4-      -1.0  2.591E-02   -1.587   1.903E-02  -1.720  7.346E-01   -.134
50  NH3 AQ       .0  1.491E-09   -8.826   1.686E-09  -8.773  1.130E+00    .053
52  NH4SO4-    -1.0  1.017E-02   -1.993   7.470E-03  -2.127  7.346E-01   -.134
65  HPO4-2     -2.0  9.820E-07   -6.008   1.703E-07  -6.769  1.734E-01   -.761
66  H2PO4-     -1.0  9.716E-02   -1.013   6.430E-02  -1.192  6.618E-01   -.179
67  H3PO4        .0  1.875E-01    -.727   2.119E-01   -.674  1.130E+00    .053
```

Sample R1-1 Distribution of Species (continued).

```
  I SPECIES      Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 69 HF AQ       .0  2.892E-03   -2.539    3.269E-03  -2.486  1.130E+00    .053
 70 HF2-      -1.0  1.598E-06   -5.796    1.174E-06  -5.930  7.346E-01   -.134
 75 CaOH+      1.0  5.882E-14  -13.230    4.321E-14 -13.364  7.346E-01   -.134
 78 CaSO4       .0  6.143E-03   -2.212    6.943E-03  -2.158  1.130E+00    .053
 79 CaPO4-    -1.0  5.226E-14  -13.282    3.839E-14 -13.416  7.346E-01   -.134
 80 CaHPO4      .0  3.365E-07   -6.473    3.804E-07  -6.420  1.130E+00    .053
 81 CaH2PO4+   1.0  9.123E-03   -2.040    6.702E-03  -2.174  7.346E-01   -.134
 82 CaF+       1.0  4.563E-06   -5.341    3.352E-06  -5.475  7.346E-01   -.134
 85 MgOH+      1.0  1.801E-13  -12.745    1.323E-13 -12.878  7.346E-01   -.134
 88 MgSO4       .0  2.578E-03   -2.589    2.914E-03  -2.536  1.130E+00    .053
 89 MgPO4-    -1.0  3.389E-14  -13.470    2.489E-14 -13.604  7.346E-01   -.134
 90 MgHPO4      .0  2.187E-07   -6.660    2.472E-07  -6.607  1.130E+00    .053
 91 MgH2PO4+   1.0  5.585E-03   -2.253    4.103E-03  -2.387  7.346E-01   -.134
 92 MgF+       1.0  1.664E-05   -4.779    1.222E-05  -4.913  7.346E-01   -.134
 97 NaSO4-    -1.0  3.888E-03   -2.410    2.856E-03  -2.544  7.346E-01   -.134
 98 NaHPO4-   -1.0  3.079E-08   -7.512    2.262E-08  -7.646  7.346E-01   -.134
100 KSO4-     -1.0  5.610E-04   -3.251    4.121E-04  -3.385  7.346E-01   -.134
101 KHPO4-    -1.0  3.145E-09   -8.502    2.310E-09  -8.636  7.346E-01   -.134
116 FeOH+2     2.0  6.499E-08   -7.187    1.893E-08  -7.723  2.913E-01   -.536
117 FeOH2+     1.0  3.570E-10   -9.447    2.623E-10  -9.581  7.346E-01   -.134
118 FeOH3       .0  1.146E-16  -15.941    1.295E-16 -15.888  1.130E+00    .053
119 FeOH4-    -1.0  7.413E-23  -22.130    5.446E-23 -22.264  7.346E-01   -.134
120 Fe2OH2+4   4.0  1.328E-12  -11.877    9.557E-15 -14.020  7.197E-03  -2.143
121 Fe3OH4+5   5.0  1.168E-18  -17.933    5.238E-22 -21.281  4.486E-04  -3.348
122 FeCl+2     2.0  1.660E-08   -7.780    4.834E-09  -8.316  2.913E-01   -.536
123 FeCl2+     1.0  6.776E-11  -10.169    4.978E-11 -10.303  7.346E-01   -.134
124 FeCl3       .0  1.015E-14  -13.993    1.147E-14 -13.940  1.130E+00    .053
125 FeSO4+     1.0  6.577E-06   -5.182    4.832E-06  -5.316  7.346E-01   -.134
126 FeSO42-   -1.0  1.740E-06   -5.759    1.278E-06  -5.893  7.346E-01   -.134
127 FeHPO4+    1.0  4.272E-09   -8.369    3.139E-09  -8.503  7.346E-01   -.134
128 FeH2P+2    2.0  4.097E-03   -2.388    1.193E-03  -2.923  2.913E-01   -.536
129 FeF+2      2.0  3.569E-05   -4.447    1.040E-05  -4.983  2.913E-01   -.536
130 FeF2+      1.0  5.323E-05   -4.274    3.911E-05  -4.408  7.346E-01   -.134
131 FeF3        .0  5.181E-06   -5.286    5.856E-06  -5.232  1.130E+00    .053
150 AlOH+2     2.0  1.137E-10   -9.944    3.312E-11 -10.480  2.913E-01   -.536
151 AlOH2+     1.0  1.471E-14  -13.832    1.081E-14 -13.966  7.346E-01   -.134
152 AlOH3       .0  5.060E-19  -18.296    5.719E-19 -18.243  1.130E+00    .053
153 AlOH4-    -1.0  3.273E-24  -23.485    2.404E-24 -23.619  7.346E-01   -.134
154 AlSO4+     1.0  9.183E-07   -6.037    6.746E-07  -6.171  7.346E-01   -.134
155 AlSO42-   -1.0  6.103E-07   -6.214    4.483E-07  -6.348  7.346E-01   -.134
156 AlF+2      2.0  2.556E-04   -3.592    7.444E-05  -4.128  2.913E-01   -.536
157 AlF2+      1.0  5.261E-03   -2.279    3.865E-03  -2.413  7.346E-01   -.134
158 AlF3        .0  6.016E-03   -2.221    6.800E-03  -2.167  1.130E+00    .053
159 AlF4-     -1.0  4.383E-04   -3.358    3.220E-04  -3.492  7.346E-01   -.134
170 H3SiO4-   -1.0  5.348E-10   -9.272    3.929E-10  -9.406  7.346E-01   -.134
171 H2SiO4-2 -2.0  1.179E-19  -18.928    3.435E-20 -19.464  2.913E-01   -.536
172 SiF6-2    -2.0  9.259E-02   -1.033    2.697E-02  -1.569  2.913E-01   -.536
173 SiF4 aq     .0  2.799E-03   -2.553    3.163E-03  -2.500  1.130E+00    .053
```

Solution Compositions and Speciations for Sample R2-1

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                     TOTAL MOLALITIES OF ELEMENTS
                     ----- ---------- -- --------

               ELEMENT            MOLALITY          LOG MOLALITY

               Ca               4.430155D-02           -1.3536
               Mg               1.443605D-02           -1.8406
               Na               1.054459D-01            -.9770
               K                1.087758D-02           -1.9635
               Al               5.122800D-03           -2.2905
               Si               1.265600D-01            -.8977
               Cl               4.078646D-02           -1.3895
               S                4.808143D-02           -1.3180
               P                3.745177D-01            -.4265
               F                4.141377D-01            -.3829
               NH4              3.872511D-02           -1.4120
               FeIII            5.711518D-03           -2.2432



                     ----DESCRIPTION OF SOLUTION----

                                    PH =   1.6000
                          ACTIVITY H2O =    .9862
                        IONIC STRENGTH =    .4325
                           TEMPERATURE =  25.0000
                    ELECTRICAL BALANCE =  -6.4268D-02
                            ITERATIONS =  42


                       -----------------------
                       DISTRIBUTION OF SPECIES
                       -----------------------

 I  SPECIES      Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

  1 H+         1.0  3.266E-02   -1.486   2.512E-02  -1.600  7.690E-01   -.114
  4 Ca+2       2.0  2.308E-02   -1.637   6.147E-03  -2.211  2.664E-01   -.575
  5 Mg+2       2.0  6.546E-03   -2.184   1.943E-03  -2.712  2.968E-01   -.527
  6 Na+        1.0  1.031E-01    -.987   7.337E-02  -1.134  7.116E-01   -.148
  7 K+         1.0  1.057E-02   -1.976   6.905E-03  -2.161  6.534E-01   -.185
 10 Al+3       3.0  4.228E-07   -6.374   3.976E-08  -7.401  9.405E-02  -1.027
 13 H4SiO4      .0  5.947E-02   -1.226   6.570E-02  -1.182  1.105E+00    .043
 14 Cl-       -1.0  4.079E-02   -1.389   2.665E-02  -1.574  6.534E-01   -.185
 16 SO4-2     -2.0  2.138E-02   -1.670   4.644E-03  -2.333  2.172E-01   -.663
 19 PO4-3     -3.0  1.376E-16  -15.862   3.287E-18 -17.483  2.389E-02  -1.622
 20 F-        -1.0  1.355E-04   -3.868   8.724E-05  -4.059  6.438E-01   -.191
 23 NH4+       1.0  3.690E-02   -1.433   2.233E-02  -1.651  6.052E-01   -.218
 24 Fe+3       3.0  8.574E-07   -6.067   8.063E-08  -7.093  9.405E-02  -1.027
 31 OH-       -1.0  6.127E-13  -12.213   3.944E-13 -12.404  6.438E-01   -.191
 40 HSO4-     -1.0  1.550E-02   -1.810   1.132E-02  -1.946  7.305E-01   -.136
 50 NH3 AQ      .0  4.588E-10   -9.338   5.068E-10  -9.295  1.105E+00    .043
 52 NH4SO4-   -1.0  1.829E-03   -2.738   1.336E-03  -2.874  7.305E-01   -.136
 65 HPO4-2    -2.0  9.628E-07   -6.016   1.831E-07  -6.737  1.902E-01   -.721
 66 H2PO4-    -1.0  1.097E-01    -.960   7.409E-02  -1.130  6.756E-01   -.170
 67 H3PO4       .0  2.369E-01    -.625   2.617E-01   -.582  1.105E+00    .043
```

Sample R2-1 Distribution of Species (continued)

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  I  SPECIES     Z    MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 69 HF AQ       .0  2.927E-03   -2.534   3.234E-03  -2.490  1.105E+00    .043
 70 HF2-      -1.0  1.468E-06   -5.833   1.073E-06  -5.970  7.305E-01   -.136
 75 CaOH+      1.0  8.338E-14  -13.079   6.090E-14 -13.215  7.305E-01   -.136
 78 CaSO4       .0  5.264E-03   -2.279   5.815E-03  -2.235  1.105E+00    .043
 79 CaPO4-    -1.0  7.958E-14  -13.099   5.813E-14 -13.236  7.305E-01   -.136
 80 CaHPO4      .0  5.587E-07   -6.253   6.172E-07  -6.210  1.105E+00    .043
 81 CaH2PO4+   1.0  1.595E-02   -1.797   1.165E-02  -1.934  7.305E-01   -.136
 82 CaF+       1.0  6.394E-06   -5.194   4.671E-06  -5.331  7.305E-01   -.136
 85 MgOH+      1.0  1.678E-13  -12.775   1.226E-13 -12.912  7.305E-01   -.136
 88 MgSO4       .0  1.453E-03   -2.838   1.605E-03  -2.795  1.105E+00    .043
 89 MgPO4-    -1.0  3.393E-14  -13.469   2.479E-14 -13.606  7.305E-01   -.136
 90 MgHPO4      .0  2.388E-07   -6.622   2.638E-07  -6.579  1.105E+00    .043
 91 MgH2PO4+   1.0  6.422E-03   -2.192   4.691E-03  -2.329  7.305E-01   -.136
 92 MgF+       1.0  1.533E-05   -4.814   1.120E-05  -4.951  7.305E-01   -.136
 97 NaSO4-    -1.0  2.338E-03   -2.631   1.708E-03  -2.768  7.305E-01   -.136
 98 NaHPO4-   -1.0  3.587E-08   -7.445   2.620E-08  -7.582  7.305E-01   -.136
100 KSO4-     -1.0  3.108E-04   -3.508   2.270E-04  -3.644  7.305E-01   -.136
101 KHPO4-    -1.0  3.375E-09   -8.472   2.466E-09  -8.608  7.305E-01   -.136
116 FeOH+2     2.0  7.212E-08   -7.142   2.053E-08  -7.688  2.847E-01   -.546
117 FeOH2+     1.0  3.638E-10   -9.439   2.657E-10  -9.576  7.305E-01   -.136
118 FeOH3       .0  1.110E-16  -15.955   1.226E-16 -15.912  1.105E+00    .043
119 FeOH4-    -1.0  6.588E-23  -22.181   4.813E-23 -22.318  7.305E-01   -.136
120 Fe2OH2+4   4.0  1.711E-12  -11.767   1.125E-14 -13.949  6.572E-03  -2.182
121 Fe3OH4+5   5.0  1.604E-18  -17.795   6.243E-22 -21.205  3.892E-04  -3.410
122 FeCl+2     2.0  2.279E-07   -6.642   6.490E-08  -7.188  2.847E-01   -.546
123 FeCl2+     1.0  1.058E-08   -7.976   7.726E-09  -8.112  7.305E-01   -.136
124 FeCl3       .0  1.864E-11  -10.730   2.059E-11 -10.686  1.105E+00    .043
125 FeSO4+     1.0  4.264E-06   -5.370   3.115E-06  -5.507  7.305E-01   -.136
126 FeSO42-   -1.0  6.262E-07   -6.203   4.574E-07  -6.340  7.305E-01   -.136
127 FeHPO4+    1.0  5.366E-09   -8.270   3.920E-09  -8.407  7.305E-01   -.136
128 FeH2P+2    2.0  5.608E-03   -2.251   1.597E-03  -2.797  2.847E-01   -.546
129 FeF+2      2.0  3.916E-05   -4.407   1.115E-05  -4.953  2.847E-01   -.546
130 FeF2+      1.0  5.301E-05   -4.276   3.872E-05  -4.412  7.305E-01   -.136
131 FeF3        .0  4.846E-06   -5.315   5.354E-06  -5.271  1.105E+00    .043
150 AlOH+2     2.0  5.611E-11  -10.251   1.597E-11 -10.797  2.847E-01   -.546
151 AlOH2+     1.0  6.665E-15  -14.176   4.869E-15 -14.313  7.305E-01   -.136
152 AlOH3       .0  2.178E-19  -18.662   2.406E-19 -18.619  1.105E+00    .043
153 AlOH4-    -1.0  1.293E-24  -23.888   9.448E-25 -24.025  7.305E-01   -.136
154 AlSO4+     1.0  2.647E-07   -6.577   1.934E-07  -6.714  7.305E-01   -.136
155 AlSO42-   -1.0  9.765E-08   -7.010   7.133E-08  -7.147  7.305E-01   -.136
156 AlF+2      2.0  1.247E-04   -3.904   3.550E-05  -4.450  2.847E-01   -.546
157 AlF2+      1.0  2.330E-03   -2.633   1.702E-03  -2.769  7.305E-01   -.136
158 AlF3        .0  2.502E-03   -2.602   2.764E-03  -2.558  1.105E+00    .043
159 AlF4-     -1.0  1.655E-04   -3.781   1.209E-04  -3.918  7.305E-01   -.136
170 H3SiO4-   -1.0  4.216E-10   -9.375   3.080E-10  -9.511  7.305E-01   -.136
171 H2SiO4-2 -2.0  8.827E-20  -19.054   2.513E-20 -19.600  2.847E-01   -.546
172 SiF6-2    -2.0  6.479E-02   -1.188   1.845E-02  -1.734  2.847E-01   -.546
173 SiF4 aq     .0  2.298E-03   -2.639   2.538E-03  -2.595  1.105E+00    .043
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Solution Compositions and Speciations for Sample R3-1

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                        TOTAL MOLALITIES OF ELEMENTS
                        ----- ---------- -- --------

                ELEMENT            MOLALITY          LOG MOLALITY

                Ca               2.321110D-02           -1.6343
                Mg               5.047400D-03           -2.2969
                Na               5.558491D-02           -1.2550
                K                2.876186D-03           -2.5412
                Al               3.069029D-03           -2.5130
                Si               6.288587D-02           -1.2014
                Cl               2.883561D-03           -2.5401
                S                4.431495D-02           -1.3534
                P                6.913965D-02           -1.1603
                F                2.206221D-01            -.6564
                NH4              4.454529D-02           -1.3512
                FeIII            1.501053D-03           -2.8236


                        ----DESCRIPTION OF SOLUTION----

                                   PH =   1.8800
                         ACTIVITY H2O =    .9946
                       IONIC STRENGTH =    .2358
                          TEMPERATURE =  25.0000
                   ELECTRICAL BALANCE =  -2.4498D-03
                           ITERATIONS =  43


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                         DISTRIBUTION OF SPECIES
                         -----------------------

 I  SPECIES      Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

  1 H+         1.0  1.667E-02   -1.778   1.318E-02  -1.880  7.910E-01   -.102
  4 Ca+2       2.0  1.468E-02   -1.833   4.506E-03  -2.346  3.069E-01   -.513
  5 Mg+2       2.0  3.074E-03   -2.512   1.015E-03  -2.994  3.302E-01   -.481
  6 Na+        1.0  5.393E-02   -1.268   3.964E-02  -1.402  7.350E-01   -.134
  7 K+         1.0  2.762E-03   -2.559   1.930E-03  -2.714  6.988E-01   -.156
 10 Al+3       3.0  5.587E-08   -7.253   6.773E-09  -8.169  1.212E-01   -.916
 13 H4SiO4      .0  2.785E-02   -1.555   2.941E-02  -1.532  1.056E+00    .024
 14 Cl-       -1.0  2.884E-03   -2.540   2.015E-03  -2.696  6.988E-01   -.156
 16 SO4-2     -2.0  2.248E-02   -1.648   6.171E-03  -2.210  2.746E-01   -.561
 19 PO4-3     -3.0  7.518E-17  -16.124   3.261E-18 -17.487  4.338E-02  -1.363
 20 F-        -1.0  2.020E-04   -3.695   1.400E-04  -3.854  6.932E-01   -.159
 23 NH4+       1.0  4.158E-02   -1.381   2.764E-02  -1.558  6.648E-01   -.177
 24 Fe+3       3.0  5.946E-07   -6.226   7.208E-08  -7.142  1.212E-01   -.916
 31 OH-       -1.0  1.093E-12  -11.961   7.580E-13 -12.120  6.932E-01   -.159
 40 HSO4-     -1.0  1.067E-02   -1.972   7.895E-03  -2.103  7.399E-01   -.131
 50 NH3 AQ      .0  1.132E-09   -8.946   1.195E-09  -8.922  1.056E+00    .024
 52 NH4SO4-   -1.0  2.970E-03   -2.527   2.197E-03  -2.658  7.399E-01   -.131
 65 HPO4-2    -2.0  3.846E-07   -6.415   9.536E-08  -7.021  2.479E-01   -.606
 66 H2PO4-    -1.0  2.823E-02   -1.549   2.025E-02  -1.694  7.172E-01   -.144
 67 H3PO4       .0  3.555E-02   -1.449   3.753E-02  -1.426  1.056E+00    .024
```

Sample R3-1 Distribution of Species (continued)

I	SPECIES	Z	MOLALITY	LOG MOLAL	ACTIVITY	LOG ACT	GAMMA	LOG GAM
69	HF AQ	.0	2.579E-03	-2.588	2.723E-03	-2.565	1.056E+00	.024
70	HF2-	-1.0	1.959E-06	-5.708	1.450E-06	-5.839	7.399E-01	-.131
75	CaOH+	1.0	1.160E-13	-12.936	8.579E-14	-13.067	7.399E-01	-.131
78	CaSO4	.0	5.366E-03	-2.270	5.665E-03	-2.247	1.056E+00	.024
79	CaPO4-	-1.0	5.715E-14	-13.243	4.228E-14	-13.374	7.399E-01	-.131
80	CaHPO4	.0	2.231E-07	-6.651	2.356E-07	-6.628	1.056E+00	.024
81	CaH2PO4+	1.0	3.155E-03	-2.501	2.334E-03	-2.632	7.399E-01	-.131
82	CaF+	1.0	7.426E-06	-5.129	5.494E-06	-5.260	7.399E-01	-.131
85	MgOH+	1.0	1.663E-13	-12.779	1.231E-13	-12.910	7.399E-01	-.131
88	MgSO4	.0	1.055E-03	-2.977	1.114E-03	-2.953	1.056E+00	.024
89	MgPO4-	-1.0	1.737E-14	-13.760	1.285E-14	-13.891	7.399E-01	-.131
90	MgHPO4	.0	6.796E-08	-7.168	7.175E-08	-7.144	1.056E+00	.024
91	MgH2PO4+	1.0	9.051E-04	-3.043	6.696E-04	-3.174	7.399E-01	-.131
92	MgF+	1.0	1.269E-05	-4.897	9.389E-06	-5.027	7.399E-01	-.131
97	NaSO4-	-1.0	1.657E-03	-2.781	1.226E-03	-2.912	7.399E-01	-.131
98	NaHPO4-	-1.0	9.961E-09	-8.002	7.370E-09	-8.133	7.399E-01	-.131
100	KSO4-	-1.0	1.140E-04	-3.943	8.434E-05	-4.074	7.399E-01	-.131
101	KHPO4-	-1.0	4.851E-10	-9.314	3.589E-10	-9.445	7.399E-01	-.131
116	FeOH+2	2.0	1.177E-07	-6.929	3.527E-08	-7.453	2.996E-01	-.523
117	FeOH2+	1.0	1.186E-09	-8.926	8.772E-10	-9.057	7.399E-01	-.131
118	FeOH3	.0	7.365E-16	-15.133	7.776E-16	-15.109	1.056E+00	.024
119	FeOH4-	-1.0	7.929E-22	-21.101	5.866E-22	-21.232	7.399E-01	-.131
120	Fe2OH2+4	4.0	4.116E-12	-11.386	3.318E-14	-13.479	8.062E-03	-2.094
121	Fe3OH4+5	5.0	1.135E-17	-16.945	6.081E-21	-20.216	5.356E-04	-3.271
122	FeCl+2	2.0	1.464E-08	-7.835	4.386E-09	-8.358	2.996E-01	-.523
123	FeCl2+	1.0	5.336E-11	-10.273	3.948E-11	-10.404	7.399E-01	-.131
124	FeCl3	.0	7.535E-15	-14.123	7.956E-15	-14.099	1.056E+00	.024
125	FeSO4+	1.0	5.001E-06	-5.301	3.700E-06	-5.432	7.399E-01	-.131
126	FeSO42-	-1.0	9.759E-07	-6.011	7.221E-07	-6.141	7.399E-01	-.131
127	FeHPO4+	1.0	2.466E-09	-8.608	1.825E-09	-8.739	7.399E-01	-.131
128	FeH2P+2	2.0	1.302E-03	-2.885	3.901E-04	-3.409	2.996E-01	-.523
129	FeF+2	2.0	5.337E-05	-4.273	1.599E-05	-4.796	2.996E-01	-.523
130	FeF2+	1.0	1.205E-04	-3.919	8.913E-05	-4.050	7.399E-01	-.131
131	FeF3	.0	1.873E-05	-4.727	1.978E-05	-4.704	1.056E+00	.024
150	AlOH+2	2.0	1.745E-11	-10.758	5.229E-12	-11.282	2.996E-01	-.523
151	AlOH2+	1.0	4.139E-15	-14.383	3.062E-15	-14.514	7.399E-01	-.131
152	AlOH3	.0	2.755E-19	-18.560	2.909E-19	-18.536	1.056E+00	.024
153	AlOH4-	-1.0	2.966E-24	-23.528	2.195E-24	-23.659	7.399E-01	-.131
154	AlSO4+	1.0	5.916E-08	-7.228	4.377E-08	-7.359	7.399E-01	-.131
155	AlSO42-	-1.0	2.900E-08	-7.538	2.146E-08	-7.668	7.399E-01	-.131
156	AlF+2	2.0	3.238E-05	-4.490	9.703E-06	-5.013	2.996E-01	-.523
157	AlF2+	1.0	1.009E-03	-2.996	7.465E-04	-3.127	7.399E-01	-.131
158	AlF3	.0	1.843E-03	-2.734	1.946E-03	-2.711	1.056E+00	.024
159	AlF4-	-1.0	1.845E-04	-3.734	1.365E-04	-3.865	7.399E-01	-.131
170	H3SiO4-	-1.0	3.551E-10	-9.450	2.627E-10	-9.581	7.399E-01	-.131
171	H2SiO4-2	-2.0	1.363E-19	-18.866	4.084E-20	-19.389	2.996E-01	-.523
172	SiF6-2	-2.0	3.451E-02	-1.462	1.034E-02	-1.985	2.996E-01	-.523
173	SiF4 aq	.0	5.233E-04	-3.281	5.525E-04	-3.258	1.056E+00	.024

Solution Compositions and Speciations for Sample R4-1

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                    TOTAL MOLALITIES OF ELEMENTS
                    ----- ---------- -- --------

            ELEMENT           MOLALITY          LOG MOLALITY

            Ca              3.368692D-02           -1.4725
            Mg              2.230796D-02           -1.6515
            Na              9.202445D-02           -1.0361
            K               1.006072D-02           -1.9974
            Al              6.934768D-03           -2.1590
            Si              1.683224D-01            -.7739
            Cl              3.898304D-03           -2.4091
            S               5.272475D-02           -1.2780
            P               3.265456D-01            -.4861
            F               5.763755D-01            -.2393
            NH4             4.555772D-02           -1.3414
            FeIII           7.843009D-03           -2.1055



                    ----DESCRIPTION OF SOLUTION----

                                PH =   1.5700
                      ACTIVITY H2O =    .9869
                    IONIC STRENGTH =    .4617
                       TEMPERATURE =  25.0000
                ELECTRICAL BALANCE =  -6.9376D-02
                        ITERATIONS =  73


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                     DISTRIBUTION OF SPECIES
                     -----------------------

 I  SPECIES     Z   MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

  1 H+         1.0  3.510E-02   -1.455   2.692E-02  -1.570  7.668E-01   -.115
  4 Ca+2       2.0  1.869E-02   -1.728   4.919E-03  -2.308  2.631E-01   -.580
  5 Mg+2       2.0  1.094E-02   -1.961   3.223E-03  -2.492  2.946E-01   -.531
  6 Na+        1.0  8.986E-02   -1.046   6.381E-02  -1.195  7.100E-01   -.149
  7 K+         1.0  9.758E-03   -2.011   6.331E-03  -2.199  6.488E-01   -.188
 10 Al+3       3.0  6.336E-07   -6.198   5.805E-08  -7.236  9.162E-02  -1.038
 13 H4SiO4      .0  7.462E-02   -1.127   8.299E-02  -1.081  1.112E+00    .046
 14 Cl-       -1.0  3.898E-03   -2.409   2.529E-03  -2.597  6.488E-01   -.188
 16 SO4-2     -2.0  2.335E-02   -1.632   4.941E-03  -2.306  2.116E-01   -.674
 19 PO4-3     -3.0  1.057E-16  -15.976   2.365E-18 -17.626  2.238E-02  -1.650
 20 F-        -1.0  1.328E-04   -3.877   8.480E-05  -4.072  6.385E-01   -.195
 23 NH4+       1.0  4.330E-02   -1.364   2.593E-02  -1.586  5.987E-01   -.223
 24 Fe+3       3.0  1.464E-06   -5.834   1.342E-07  -6.872  9.162E-02  -1.038
 31 OH-       -1.0  5.769E-13  -12.239   3.684E-13 -12.434  6.385E-01   -.195
 40 HSO4-     -1.0  1.765E-02   -1.753   1.290E-02  -1.889  7.313E-01   -.136
 50 NH3 AQ      .0  4.938E-10   -9.306   5.492E-10  -9.260  1.112E+00    .046
 52 NH4SO4-   -1.0  2.257E-03   -2.647   1.650E-03  -2.782  7.313E-01   -.136
 65 HPO4-2    -2.0  7.644E-07   -6.117   1.412E-07  -6.850  1.848E-01   -.733
 66 H2PO4-    -1.0  9.121E-02   -1.040   6.122E-02  -1.213  6.712E-01   -.173
 67 H3PO4       .0  2.083E-01    -.681   2.317E-01   -.635  1.112E+00    .046
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Sample R4-1 Distribution of Species (continued)

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  I  SPECIES      Z    MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 69  HF AQ       .0   3.028E-03   -2.519    3.368E-03  -2.473  1.112E+00    .046
 70  HF2-      -1.0   1.485E-06   -5.828    1.086E-06  -5.964  7.313E-01   -.136
 75  CaOH+      1.0   6.224E-14  -13.206    4.551E-14 -13.342  7.313E-01   -.136
 78  CaSO4       .0   4.451E-03   -2.352    4.951E-03  -2.305  1.112E+00    .046
 79  CaPO4-    -1.0   4.578E-14  -13.339    3.348E-14 -13.475  7.313E-01   -.136
 80  CaHPO4      .0   3.425E-07   -6.465    3.809E-07  -6.419  1.112E+00    .046
 81  CaH2PO4+   1.0   1.054E-02   -1.977    7.705E-03  -2.113  7.313E-01   -.136
 82  CaF+       1.0   4.968E-06   -5.304    3.633E-06  -5.440  7.313E-01   -.136
 85  MgOH+      1.0   2.597E-13  -12.585    1.899E-13 -12.721  7.313E-01   -.136
 88  MgSO4       .0   2.547E-03   -2.594    2.832E-03  -2.548  1.112E+00    .046
 89  MgPO4-    -1.0   4.047E-14  -13.393    2.960E-14 -13.529  7.313E-01   -.136
 90  MgHPO4      .0   3.034E-07   -6.518    3.375E-07  -6.472  1.112E+00    .046
 91  MgH2PO4+   1.0   8.794E-03   -2.056    6.430E-03  -2.192  7.313E-01   -.136
 92  MgF+       1.0   2.470E-05   -4.607    1.806E-05  -4.743  7.313E-01   -.136
 97  NaSO4-    -1.0   2.161E-03   -2.665    1.580E-03  -2.801  7.313E-01   -.136
 98  NaHPO4-   -1.0   2.403E-08   -7.619    1.757E-08  -7.755  7.313E-01   -.136
100  KSO4-     -1.0   3.028E-04   -3.519    2.214E-04  -3.655  7.313E-01   -.136
101  KHPO4-    -1.0   2.384E-09   -8.623    1.743E-09  -8.759  7.313E-01   -.136
116  FeOH+2     2.0   1.116E-07   -6.952    3.191E-08  -7.496  2.860E-01   -.544
117  FeOH2+     1.0   5.275E-10   -9.278    3.857E-10  -9.414  7.313E-01   -.136
118  FeOH3       .0   1.494E-16  -15.826    1.662E-16 -15.779  1.112E+00    .046
119  FeOH4-    -1.0   8.332E-23  -22.079    6.093E-23 -22.215  7.313E-01   -.136
120  Fe2OH2+4   4.0   4.062E-12  -11.391    2.716E-14 -13.566  6.686E-03  -2.175
121  Fe3OH4+5   5.0   5.474E-18  -17.262    2.189E-21 -20.660  3.998E-04  -3.398
122  FeCl+2     2.0   3.584E-08   -7.446    1.025E-08  -7.989  2.860E-01   -.544
123  FeCl2+     1.0   1.583E-10   -9.800    1.158E-10  -9.936  7.313E-01   -.136
124  FeCl3       .0   2.633E-14  -13.580    2.928E-14 -13.533  1.112E+00    .046
125  FeSO4+     1.0   7.541E-06   -5.123    5.514E-06  -5.259  7.313E-01   -.136
126  FeSO42-   -1.0   1.178E-06   -5.929    8.615E-07  -6.065  7.313E-01   -.136
127  FeHPO4+    1.0   6.879E-09   -8.162    5.030E-09  -8.298  7.313E-01   -.136
128  FeH2P+2    2.0   7.679E-03   -2.115    2.196E-03  -2.658  2.860E-01   -.544
129  FeF+2      2.0   6.306E-05   -4.200    1.803E-05  -4.744  2.860E-01   -.544
130  FeF2+      1.0   8.325E-05   -4.080    6.087E-05  -4.216  7.313E-01   -.136
131  FeF3        .0   7.356E-06   -5.133    8.181E-06  -5.087  1.112E+00    .046
150  AlOH+2     2.0   7.617E-11  -10.118    2.178E-11 -10.662  2.860E-01   -.544
151  AlOH2+     1.0   8.478E-15  -14.072    6.200E-15 -14.208  7.313E-01   -.136
152  AlOH3       .0   2.573E-19  -18.590    2.862E-19 -18.543  1.112E+00    .046
153  AlOH4-    -1.0   1.435E-24  -23.843    1.049E-24 -23.979  7.313E-01   -.136
154  AlSO4+     1.0   4.107E-07   -6.386    3.003E-07  -6.522  7.313E-01   -.136
155  AlSO42-   -1.0   1.612E-07   -6.793    1.179E-07  -6.929  7.313E-01   -.136
156  AlF+2      2.0   1.761E-04   -3.754    5.037E-05  -4.298  2.860E-01   -.544
157  AlF2+      1.0   3.210E-03   -2.494    2.347E-03  -2.629  7.313E-01   -.136
158  AlF3        .0   3.332E-03   -2.477    3.706E-03  -2.431  1.112E+00    .046
159  AlF4-     -1.0   2.154E-04   -3.667    1.575E-04  -3.803  7.313E-01   -.136
170  H3SiO4-   -1.0   4.965E-10   -9.304    3.631E-10  -9.440  7.313E-01   -.136
171  H2SiO4-2  -2.0   9.669E-20  -19.015    2.765E-20 -19.558  2.860E-01   -.544
172  SiF6-2    -2.0   9.032E-02   -1.044    2.583E-02  -1.588  2.860E-01   -.544
173  SiF4 aq     .0   3.382E-03   -2.471    3.762E-03  -2.425  1.112E+00    .046
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Solution Compositions and Speciations for Sample R5-1

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                         TOTAL MOLALITIES OF ELEMENTS
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                  ELEMENT          MOLALITY         LOG MOLALITY

                  Ca             3.124362D-02          -1.5052
                  Mg             5.535431D-03          -2.2568
                  Na             7.067539D-02          -1.1507
                  K              5.029207D-03          -2.2985
                  Al             8.169910D-03          -2.0878
                  Si             1.019681D-01           -.9915
                  Cl             2.043378D-03          -2.6897
                  S              4.228641D-02          -1.3738
                  P              1.428937D-01           -.8450
                  F              3.540789D-01           -.4509
                  NH4            4.136530D-02          -1.3834
                  FeIII          3.205900D-03          -2.4940


                         ----DESCRIPTION OF SOLUTION----

                                     PH =   1.7800
                           ACTIVITY H2O =    .9922
                         IONIC STRENGTH =    .3084
                            TEMPERATURE =  25.0000
                     ELECTRICAL BALANCE =  -2.3419D-02
                             ITERATIONS =  46


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                          DISTRIBUTION OF SPECIES
                          -----------------------

 I  SPECIES     Z   MOLALITY  LOG MOLAL  ACTIVITY  LOG ACT   GAMMA    LOG GAM

  1 H+        1.0  2.125E-02   -1.673  1.660E-02  -1.780  7.810E-01   -.107
  4 Ca+2      2.0  1.900E-02   -1.721  5.448E-03  -2.264  2.868E-01   -.542
  5 Mg+2      2.0  3.116E-03   -2.506  9.750E-04  -3.011  3.129E-01   -.505
  6 Na+       1.0  6.893E-02   -1.162  4.983E-02  -1.302  7.230E-01   -.141
  7 K+        1.0  4.866E-03   -2.313  3.301E-03  -2.481  6.784E-01   -.168
 10 Al+3      3.0  2.683E-07   -6.571  2.900E-08  -7.538  1.081E-01   -.966
 13 H4SiO4     .0  4.672E-02   -1.331  5.015E-02  -1.300  1.074E+00    .031
 14 Cl-      -1.0  2.043E-03   -2.690  1.386E-03  -2.858  6.784E-01   -.168
 16 SO4-2    -2.0  2.070E-02   -1.684  5.132E-03  -2.290  2.479E-01   -.606
 19 PO4-3    -3.0  1.108E-16  -15.956  3.703E-18 -17.431  3.343E-02  -1.476
 20 F-       -1.0  1.750E-04   -3.757  1.175E-04  -3.930  6.713E-01   -.173
 23 NH4+      1.0  3.911E-02   -1.408  2.497E-02  -1.603  6.385E-01   -.195
 24 Fe+3      3.0  8.266E-07   -6.083  8.935E-08  -7.049  1.081E-01   -.966
 31 OH-      -1.0  8.948E-13  -12.048  6.006E-13 -12.221  6.713E-01   -.173
 40 HSO4-    -1.0  1.128E-02   -1.948  8.264E-03  -2.083  7.326E-01   -.135
 50 NH3 AQ     .0  7.992E-10   -9.097  8.580E-10  -9.067  1.074E+00    .031
 52 NH4SO4-  -1.0  2.254E-03   -2.647  1.651E-03  -2.782  7.326E-01   -.135
 65 HPO4-2   -2.0  6.173E-07   -6.210  1.363E-07  -6.865  2.208E-01   -.656
 66 H2PO4-   -1.0  5.216E-02   -1.283  3.644E-02  -1.438  6.986E-01   -.156
 67 H3PO4      .0  7.920E-02   -1.101  8.503E-02  -1.070  1.074E+00    .031
```

Sample R5-1 Distribution of Species (continued)

```
  I  SPECIES     Z    MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT     GAMMA    LOG GAM

 69 HF AQ       .0   2.679E-03   -2.572   2.876E-03   -2.541  1.074E+00     .031
 70 HF2-      -1.0   1.753E-06   -5.756   1.284E-06   -5.891  7.326E-01    -.135
 75 CaOH+      1.0   1.122E-13  -12.950   8.220E-14  -13.085  7.326E-01    -.135
 78 CaSO4       .0   5.305E-03   -2.275   5.695E-03   -2.244  1.074E+00     .031
 79 CaPO4-    -1.0   7.924E-14  -13.101   5.805E-14  -13.236  7.326E-01    -.135
 80 CaHPO4      .0   3.793E-07   -6.421   4.072E-07   -6.390  1.074E+00     .031
 81 CaH2PO4+   1.0   6.933E-03   -2.159   5.079E-03   -2.294  7.326E-01    -.135
 82 CaF+       1.0   7.608E-06   -5.119   5.573E-06   -5.254  7.326E-01    -.135
 85 MgOH+      1.0   1.279E-13  -12.893   9.367E-14  -13.028  7.326E-01    -.135
 88 MgSO4       .0   8.287E-04   -3.082   8.897E-04   -3.051  1.074E+00     .031
 89 MgPO4-    -1.0   1.913E-14  -13.718   1.401E-14  -13.853  7.326E-01    -.135
 90 MgHPO4      .0   9.177E-08   -7.037   9.852E-08   -7.006  1.074E+00     .031
 91 MgH2PO4+   1.0   1.580E-03   -2.801   1.158E-03   -2.936  7.326E-01    -.135
 92 MgF+       1.0   1.033E-05   -4.986   7.566E-06   -5.121  7.326E-01    -.135
 97 NaSO4-    -1.0   1.750E-03   -2.757   1.282E-03   -2.892  7.326E-01    -.135
 98 NaHPO4-   -1.0   1.808E-08   -7.743   1.325E-08   -7.878  7.326E-01    -.135
100 KSO4-     -1.0   1.637E-04   -3.786   1.199E-04   -3.921  7.326E-01    -.135
101 KHPO4-    -1.0   1.198E-09   -8.922   8.774E-10   -9.057  7.326E-01    -.135
116 FeOH+2     2.0   1.203E-07   -6.920   3.465E-08   -7.460  2.880E-01    -.541
117 FeOH2+     1.0   9.321E-10   -9.031   6.829E-10   -9.166  7.326E-01    -.135
118 FeOH3       .0   4.468E-16  -15.350   4.797E-16  -15.319  1.074E+00     .031
119 FeOH4-    -1.0   3.915E-22  -21.407   2.868E-22  -21.542  7.326E-01    -.135
120 Fe2OH2+4   4.0   4.652E-12  -11.332   3.202E-14  -13.495  6.883E-03   -2.162
121 Fe3OH4+5   5.0   1.092E-17  -16.962   4.568E-21  -20.340  4.183E-04   -3.378
122 FeCl+2     2.0   1.299E-08   -7.886   3.741E-09   -8.427  2.880E-01    -.541
123 FeCl2+     1.0   3.162E-11  -10.500   2.316E-11  -10.635  7.326E-01    -.135
124 FeCl3       .0   2.991E-15  -14.524   3.211E-15  -14.493  1.074E+00     .031
125 FeSO4+     1.0   5.206E-06   -5.283   3.814E-06   -5.419  7.326E-01    -.135
126 FeSO42-   -1.0   8.448E-07   -6.073   6.189E-07   -6.208  7.326E-01    -.135
127 FeHPO4+    1.0   4.414E-09   -8.355   3.233E-09   -8.490  7.326E-01    -.135
128 FeH2P+2    2.0   3.021E-03   -2.520   8.703E-04   -3.060  2.880E-01    -.541
129 FeF+2      2.0   5.775E-05   -4.238   1.663E-05   -4.779  2.880E-01    -.541
130 FeF2+      1.0   1.062E-04   -3.974   7.777E-05   -4.109  7.326E-01    -.135
131 FeF3        .0   1.349E-05   -4.870   1.448E-05   -4.839  1.074E+00     .031
150 AlOH+2     2.0   6.159E-11  -10.210   1.774E-11  -10.751  2.880E-01    -.541
151 AlOH2+     1.0   1.124E-14  -13.949   8.233E-15  -14.084  7.326E-01    -.135
152 AlOH3       .0   5.772E-19  -18.239   6.197E-19  -18.208  1.074E+00     .031
153 AlOH4-    -1.0   5.058E-24  -23.296   3.705E-24  -23.431  7.326E-01    -.135
154 AlSO4+     1.0   2.127E-07   -6.672   1.558E-07   -6.807  7.326E-01    -.135
155 AlSO42-   -1.0   8.670E-08   -7.062   6.351E-08   -7.197  7.326E-01    -.135
156 AlF+2      2.0   1.210E-04   -3.917   3.485E-05   -4.458  2.880E-01    -.541
157 AlF2+      1.0   3.071E-03   -2.513   2.249E-03   -2.648  7.326E-01    -.135
158 AlF3        .0   4.582E-03   -2.339   4.920E-03   -2.308  1.074E+00     .031
159 AlF4-     -1.0   3.953E-04   -3.403   2.896E-04   -3.538  7.326E-01    -.135
170 H3SiO4-   -1.0   4.858E-10   -9.314   3.559E-10   -9.449  7.326E-01    -.135
171 H2SiO4-2  -2.0   1.526E-19  -18.816   4.395E-20  -19.357  2.880E-01    -.541
172 SiF6-2    -2.0   5.415E-02   -1.266   1.560E-02   -1.807  2.880E-01    -.541
173 SiF4 aq     .0   1.103E-03   -2.958   1.184E-03   -2.927  1.074E+00     .031
```

Solution Compositions and Speciations for Sample R6-1

```
                         TOTAL MOLALITIES OF ELEMENTS
                         ----- ---------- -- --------

                  ELEMENT           MOLALITY          LOG MOLALITY

                  Ca              3.421756D-02           -1.4658
                  Mg              1.154173D-02           -1.9377
                  Na              9.400068D-02           -1.0269
                  K               9.300644D-03           -2.0315
                  Al              4.582302D-03           -2.3389
                  Si              1.177576D-01            -.9290
                  Cl              2.051389D-03           -2.6880
                  S               4.471269D-02           -1.3496
                  P               1.639550D-01            -.7853
                  F               3.937480D-01            -.4048
                  NH4             2.995045D-03           -2.5236
                  FeIII           2.158048D-03           -2.6659



                         ----DESCRIPTION OF SOLUTION----

                                      PH =   1.6800
                            ACTIVITY H2O =    .9916
                        IONIC STRENGTH =    .3325
                             TEMPERATURE =  25.0000
                      ELECTRICAL BALANCE =  -3.4044D-02
                              ITERATIONS =  48


                          -----------------------
                          DISTRIBUTION OF SPECIES
                          -----------------------

I  SPECIES     Z    MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT     GAMMA    LOG GAM

 1 H+         1.0  2.685E-02   -1.571   2.089E-02   -1.680  7.783E-01    -.109
 4 Ca+2       2.0  2.106E-02   -1.676   5.935E-03   -2.227  2.817E-01    -.550
 5 Mg+2       2.0  6.570E-03   -2.182   2.028E-03   -2.693  3.087E-01    -.510
 6 Na+        1.0  9.173E-02   -1.037   6.605E-02   -1.180  7.201E-01    -.143
 7 K+         1.0  9.007E-03   -2.045   6.060E-03   -2.218  6.728E-01    -.172
10 Al+3       3.0  2.351E-07   -6.629   2.462E-08   -7.609  1.047E-01    -.980
13 H4SiO4      .0  5.407E-02   -1.267   5.837E-02   -1.234  1.080E+00     .033
14 Cl-       -1.0  2.051E-03   -2.688   1.380E-03   -2.860  6.728E-01    -.172
16 SO4-2     -2.0  2.081E-02   -1.682   5.011E-03   -2.300  2.408E-01    -.618
19 PO4-3     -3.0  7.496E-17  -16.125   2.327E-18  -17.633  3.104E-02   -1.508
20 F-        -1.0  1.508E-04   -3.822   1.003E-04   -3.999  6.651E-01    -.177
23 NH4+       1.0  2.837E-03   -2.547   1.791E-03   -2.747  6.311E-01    -.200
24 Fe+3       3.0  5.804E-07   -6.236   6.079E-08   -7.216  1.047E-01    -.980
31 OH-       -1.0  7.169E-13  -12.145   4.768E-13  -12.322  6.651E-01    -.177
40 HSO4-     -1.0  1.389E-02   -1.857   1.016E-02   -1.993  7.313E-01    -.136
50 NH3 AQ      .0  4.526E-11  -10.344   4.886E-11  -10.311  1.080E+00     .033
52 NH4SO4-   -1.0  1.581E-04   -3.801   1.156E-04   -3.937  7.313E-01    -.136
65 HPO4-2    -2.0  5.047E-07   -6.297   1.078E-07   -6.967  2.137E-01    -.670
66 H2PO4-    -1.0  5.233E-02   -1.281   3.629E-02   -1.440  6.934E-01    -.159
67 H3PO4       .0  9.875E-02   -1.005   1.066E-01    -.972  1.080E+00     .033
```

Sample R6-1 Distribution of Species (continued)

```
  I  SPECIES      Z    MOLALITY  LOG MOLAL   ACTIVITY  LOG ACT    GAMMA    LOG GAM

 69 HF AQ        .0   2.865E-03   -2.543   3.092E-03   -2.510  1.080E+00    .033
 70 HF2-       -1.0   1.612E-06   -5.793   1.179E-06   -5.928  7.313E-01   -.136
 75 CaOH+       1.0   9.719E-14  -13.012   7.108E-14  -13.148  7.313E-01   -.136
 78 CaSO4        .0   5.612E-03   -2.251   6.058E-03   -2.218  1.080E+00    .033
 79 CaPO4-     -1.0   5.433E-14  -13.265   3.973E-14  -13.401  7.313E-01   -.136
 80 CaHPO4       .0   3.250E-07   -6.488   3.509E-07   -6.455  1.080E+00    .033
 81 CaH2PO4+    1.0   7.534E-03   -2.123   5.510E-03   -2.259  7.313E-01   -.136
 82 CaF+        1.0   7.089E-06   -5.149   5.184E-06   -5.285  7.313E-01   -.136
 85 MgOH+       1.0   2.115E-13  -12.675   1.547E-13  -12.811  7.313E-01   -.136
 88 MgSO4        .0   1.674E-03   -2.776   1.807E-03   -2.743  1.080E+00    .033
 89 MgPO4-     -1.0   2.505E-14  -13.601   1.832E-14  -13.737  7.313E-01   -.136
 90 MgHPO4       .0   1.502E-07   -6.823   1.621E-07   -6.790  1.080E+00    .033
 91 MgH2PO4+    1.0   3.279E-03   -2.484   2.398E-03   -2.620  7.313E-01   -.136
 92 MgF+        1.0   1.838E-05   -4.736   1.344E-05   -4.872  7.313E-01   -.136
 97 NaSO4-     -1.0   2.268E-03   -2.644   1.659E-03   -2.780  7.313E-01   -.136
 98 NaHPO4-    -1.0   1.899E-08   -7.721   1.389E-08   -7.857  7.313E-01   -.136
100 KSO4-      -1.0   2.939E-04   -3.532   2.150E-04   -3.668  7.313E-01   -.136
101 KHPO4-     -1.0   1.742E-09   -8.759   1.274E-09   -8.895  7.313E-01   -.136
116 FeOH+2      2.0   6.541E-08   -7.184   1.871E-08   -7.728  2.861E-01   -.544
117 FeOH2+      1.0   4.003E-10   -9.398   2.927E-10   -9.534  7.313E-01   -.136
118 FeOH3        .0   1.512E-16  -15.820   1.632E-16  -15.787  1.080E+00    .033
119 FeOH4-     -1.0   1.059E-22  -21.975   7.747E-23  -22.111  7.313E-01   -.136
120 Fe2OH2+4    4.0   1.394E-12  -11.856   9.339E-15  -14.030  6.697E-03  -2.174
121 Fe3OH4+5    5.0   1.425E-18  -17.846   5.712E-22  -21.243  4.008E-04  -3.397
122 FeCl+2      2.0   8.857E-09   -8.053   2.534E-09   -8.596  2.861E-01   -.544
123 FeCl2+      1.0   2.136E-11  -10.670   1.562E-11  -10.806  7.313E-01   -.136
124 FeCl3        .0   1.997E-15  -14.700   2.156E-15  -14.666  1.080E+00    .033
125 FeSO4+      1.0   3.464E-06   -5.460   2.534E-06   -5.596  7.313E-01   -.136
126 FeSO42-    -1.0   5.490E-07   -6.260   4.015E-07   -6.396  7.313E-01   -.136
127 FeHPO4+     1.0   2.379E-09   -8.624   1.740E-09   -8.759  7.313E-01   -.136
128 FeH2P+2     2.0   2.061E-03   -2.686   5.896E-04   -3.229  2.861E-01   -.544
129 FeF+2       2.0   3.378E-05   -4.471   9.663E-06   -5.015  2.861E-01   -.544
130 FeF2+       1.0   5.276E-05   -4.278   3.858E-05   -4.414  7.313E-01   -.136
131 FeF3         .0   5.682E-06   -5.246   6.134E-06   -5.212  1.080E+00    .033
150 AlOH+2      2.0   4.180E-11  -10.379   1.196E-11  -10.922  2.861E-01   -.544
151 AlOH2+      1.0   6.024E-15  -14.220   4.406E-15  -14.356  7.313E-01   -.136
152 AlOH3        .0   2.438E-19  -18.613   2.632E-19  -18.580  1.080E+00    .033
153 AlOH4-     -1.0   1.708E-24  -23.767   1.249E-24  -23.903  7.313E-01   -.136
154 AlSO4+      1.0   1.767E-07   -6.753   1.292E-07   -6.889  7.313E-01   -.136
155 AlSO42-    -1.0   7.032E-08   -7.153   5.143E-08   -7.289  7.313E-01   -.136
156 AlF+2       2.0   8.834E-05   -4.054   2.527E-05   -4.597  2.861E-01   -.544
157 AlF2+       1.0   1.905E-03   -2.720   1.393E-03   -2.856  7.313E-01   -.136
158 AlF3         .0   2.410E-03   -2.618   2.602E-03   -2.585  1.080E+00    .033
159 AlF4-      -1.0   1.788E-04   -3.748   1.308E-04   -3.883  7.313E-01   -.136
170 H3SiO4-    -1.0   4.499E-10   -9.347   3.290E-10   -9.483  7.313E-01   -.136
171 H2SiO4-2   -2.0   1.128E-19  -18.948   3.227E-20  -19.491  2.861E-01   -.544
172 SiF6-2     -2.0   6.198E-02   -1.208   1.773E-02   -1.751  2.861E-01   -.544
173 SiF4 aq      .0   1.709E-03   -2.767   1.845E-03   -2.734  1.080E+00    .033
```

Appendix C. PHREEQE Program Output-- Computed Saturation-States of Mean Pond Water Sample Compositions

```
                                 Sample D1-1            Sample D2-1            Sample D3-1

PHASE        LOG KT           LOG IAP       SI       LOG IAP       SI       LOG IAP       SI

GYPSUM        -4.603           -4.436     0.167       -4.618    -0.015       -4.585     0.018
ANHYDRIT      -4.384           -4.423    -0.039       -4.606    -0.222       -4.580    -0.196
NA2SIF6      -34.300          -34.094     0.206      -34.100     0.200      -35.054    -0.754
K2SIF6       -36.170          -36.157     0.013      -36.174    -0.004      -37.241    -1.071
NAKSIF6        0.000          -35.125   -35.125      -35.137   -35.137      -36.148   -36.148
FLUORITE     -10.960          -10.476     0.485      -10.250     0.710      -10.013     0.948
FLUORAP      -17.600          -31.661   -14.061      -30.304   -12.704      -30.665   -13.065
HYDROXAP      -3.421          -26.029   -22.608      -24.657   -21.236      -24.907   -21.486
SIO2 GEL      -3.018           -1.094     1.924       -1.244     1.774       -1.516     1.503
STRENGIT     -26.430          -24.806     1.624      -24.504     1.926      -24.526     1.904
VARISCIT     -22.520          -24.655    -2.135      -24.920    -2.400      -25.646    -3.126
BRUSHITE      -6.600           -9.222    -2.622       -8.933    -2.333       -9.312    -2.712
STRUVITE     -13.150          -21.465    -8.315      -21.692    -8.541      -22.063    -8.913
CHUKHROV       0.000          -78.752   -78.752      -78.806   -78.806      -78.955   -78.955
N-FE-PO4       0.000         -141.002  -141.002     -140.283  -140.283     -142.658  -142.658
K-FE-PO4       0.000         -142.107  -142.107     -140.994  -140.994     -143.646  -143.646


                                 Sample D4-1            Sample D5-1            Sample D6-1

PHASE        LOG KT           LOG IAP       SI       LOG IAP       SI       LOG IAP       SI

GYPSUM        -4.603           -4.579     0.023       -4.599     0.004       -4.535     0.068
ANHYDRIT      -4.384           -4.568    -0.184       -4.593    -0.209       -4.528    -0.144
NA2SIF6      -34.300          -34.154     0.146      -34.714    -0.414      -34.268     0.032
K2SIF6       -36.170          -36.127     0.043      -36.953    -0.783      -36.356    -0.186
NAKSIF6        0.000          -35.141   -35.141      -35.833   -35.833      -35.312   -35.312
FLUORITE     -10.960          -10.373     0.587      -10.134     0.826      -10.137     0.823
FLUORAP      -17.600          -31.181   -13.581      -30.475   -12.875      -30.597   -12.997
HYDROXAP      -3.421          -25.558   -22.137      -24.752   -21.331      -24.907   -21.486
SIO2 GEL      -3.018           -1.088     1.930       -1.261     1.757       -1.282     1.736
STRENGIT     -26.430          -24.463     1.967      -24.412     2.018      -24.709     1.721
VARISCIT     -22.520          -24.673    -2.153      -24.967    -2.447      -25.513    -2.993
BRUSHITE      -6.600           -9.119    -2.519       -9.135    -2.535       -9.142    -2.542
STRUVITE     -13.150          -21.934    -8.784      -21.932    -8.782      -23.142    -9.992
CHUKHROV       0.000          -78.545   -78.545      -78.535   -78.535      -78.881   -78.881
N-FE-PO4       0.000         -140.528  -140.528     -141.341  -141.341     -143.433  -143.433
K-FE-PO4       0.000         -141.043  -141.043     -142.285  -142.285     -142.778  -142.778
```

Appendix C (continued)

		Sample R1-1		Sample R2-1		Sample R3-1	
PHASE	LOG KT	LOG IAP	SI	LOG IAP	SI	LOG IAP	SI
GYPSUM	-4.603	-4.480	0.123	-4.557	0.046	-4.561	0.042
ANHYDRIT	-4.384	-4.467	-0.083	-4.544	-0.160	-4.556	-0.172
NA2SIF6	-34.300	-34.083	0.217	-34.183	0.117	-34.969	-0.669
K2SIF6	-36.170	-36.064	0.106	-36.236	-0.066	-37.594	-1.424
NAKSIF6	0.000	-35.073	-35.073	-35.209	-35.209	-36.282	-36.282
FLUORITE	-10.960	-10.439	0.521	-10.330	0.630	-10.054	0.906
FLUORAP	-17.600	-31.391	-13.791	-30.528	-12.928	-31.007	-13.407
HYDROXAP	-3.421	-25.743	-22.322	-24.874	-21.453	-25.275	-21.854
SIO2 GEL	-3.018	-1.094	1.924	-1.170	1.848	-1.527	1.491
STRENGIT	-26.430	-24.656	1.774	-24.589	1.841	-24.634	1.796
VARISCIT	-22.520	-24.611	-2.091	-24.896	-2.376	-25.661	-3.141
BRUSHITE	-6.600	-9.172	-2.572	-8.961	-2.361	-9.371	-2.772
STRUVITE	-13.150	-21.390	-8.240	-21.882	-8.732	-22.053	-8.903
CHUKHROV	0.000	-78.736	-78.736	-78.968	-78.968	-78.930	-78.930
N-FE-PO4	0.000	-140.622	-140.622	-140.667	-140.667	-142.959	-142.959
K-FE-PO4	0.000	-141.620	-141.620	-141.177	-141.177	-144.115	-144.115

		Sample R4-1		Sample R5-1		Sample R6-1	
PHASE	LOG KT	LOG IAP	SI	LOG IAP	SI	LOG IAP	SI
GYPSUM	-4.603	-4.626	-0.023	-4.560	0.043	-4.534	0.069
ANHYDRIT	-4.384	-4.614	-0.230	-4.554	-0.170	-4.527	-0.143
NA2SIF6	-34.300	-34.158	0.142	-34.592	-0.292	-34.292	0.009
K2SIF6	-36.170	-36.165	0.005	-36.950	-0.780	-36.366	-0.196
NAKSIF6	0.000	-35.162	-35.162	-35.771	-35.771	-35.329	-35.329
FLUORITE	-10.960	-10.451	0.509	-10.124	0.836	-10.224	0.736
FLUORAP	-17.600	-31.453	-13.853	-30.505	-12.905	-30.993	-13.393
HYDROXAP	-3.421	-25.817	-22.396	-24.799	-21.378	-25.318	-21.897
SIO2 GEL	-3.018	-1.070	1.948	-1.293	1.725	-1.227	1.792
STRENGIT	-26.430	-24.510	1.920	-24.487	1.943	-24.857	1.573
VARISCIT	-22.520	-24.874	-2.354	-24.976	-2.456	-25.249	-2.729
BRUSHITE	-6.600	-9.170	-2.570	-9.136	-2.536	-9.201	-2.601
STRUVITE	-13.150	-21.738	-8.588	-22.065	-8.915	-23.095	-9.945
CHUKHROV	0.000	-79.101	-79.101	-78.414	-78.414	-78.774	-78.774
N-FE-PO4	0.000	-140.554	-140.554	-141.598	-141.598	-143.657	-143.657
K-FE-PO4	0.000	-141.166	-141.166	-142.477	-142.477	-143.128	-143.128

Appendix C (continued)

		Sample S1-1		Sample S2-1		Sample S3-1	
PHASE	LOG KT	LOG IAP	SI	LOG IAP	SI	LOG IAP	SI
GYPSUM	-4.603	-4.474	0.129	-4.585	0.017	-4.599	0.003
ANHYDRIT	-4.384	-4.460	-0.076	-4.575	-0.191	-4.594	-0.210
NA2SIF6	-34.300	-34.078	0.222	-34.174	0.126	-34.428	-0.128
K2SIF6	-36.170	-36.028	0.142	-36.229	-0.059	-37.037	-0.867
NAKSIF6	0.000	-35.053	-35.053	-35.202	-35.202	-35.732	-35.732
FLUORITE	-10.960	-10.428	0.532	-10.151	0.809	-10.074	0.886
FLUORAP	-17.600	-31.216	-13.616	-29.609	-12.009	-31.130	-13.530
HYDROXAP	-3.421	-25.565	-22.144	-23.919	-20.498	-25.418	-21.997
SIO2 GEL	-3.018	-1.098	1.921	-1.242	1.776	-1.494	1.525
STRENGIT	-26.430	-24.561	1.869	-24.271	2.159	-24.553	1.877
VARISCIT	-22.520	-24.515	-1.995	-24.982	-2.462	-25.645	-3.125
BRUSHITE	-6.600	-9.125	-2.525	-8.809	-2.209	-9.382	-2.782
STRUVITE	-13.150	-21.237	-8.087	-21.778	-8.628	-22.274	-9.124
CHUKHROV	0.000	-78.656	-78.656	-78.773	-78.773	-78.899	-78.899
N-FE-PO4	0.000	-140.112	-140.112	-140.007	-140.007	-142.584	-142.584
K-FE-PO4	0.000	-141.216	-141.216	-140.379	-140.379	-143.522	-143.522

		Sample S4-1		Sample S5-1		Sample S6-1	
PHASE	LOG KT	LOG IAP	SI	LOG IAP	SI	LOG IAP	SI
GYPSUM	-4.603	-4.570	0.033	-4.616	-0.013	-4.599	0.004
ANHYDRIT	-4.384	-4.557	-0.173	-4.607	-0.223	-4.592	-0.208
NA2SIF6	-34.300	-34.063	0.237	-34.188	0.112	-34.431	-0.131
K2SIF6	-36.170	-36.064	0.106	-36.436	-0.266	-36.470	-0.300
NAKSIF6	0.000	-35.064	-35.064	-35.312	-35.312	-35.451	-35.451
FLUORITE	-10.960	-10.409	0.551	-10.190	0.770	-10.095	0.865
FLUORAP	-17.600	-30.980	-13.380	-30.884	-13.284	-30.006	-12.406
HYDROXAP	-3.421	-25.350	-21.929	-25.216	-21.795	-24.284	-20.863
SIO2 GEL	-3.018	-1.086	1.932	-1.319	1.699	-1.508	1.511
STRENGIT	-26.430	-24.346	2.084	-24.471	1.960	-24.590	1.840
VARISCIT	-22.520	-24.672	-2.152	-24.958	-2.438	-25.228	-2.708
BRUSHITE	-6.600	-9.037	-2.437	-9.184	-2.584	-9.004	-2.404
STRUVITE	-13.150	-21.664	-8.514	-21.677	-8.527	-22.697	-9.547
CHUKHROV	0.000	-78.801	-78.801	-78.516	-78.516	-79.010	-79.010
N-FE-PO4	0.000	-139.759	-139.759	-140.940	-140.940	-142.738	-142.738
K-FE-PO4	0.000	-140.327	-140.327	-141.987	-141.987	-142.173	-142.173