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Solubilities of Sideronatrite and Ferrinatrite in the System Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O

By C. M. Flynn, Jr., and J. A. Eisele

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
g	gram	mm	millimeter
g/cm^3	gram per cubic centimeter	mmol	millimol
h	hour	µm	micrometer
kg	kilogram	mol/L	mol per liter
kg/L	kilogram per liter	pct	percent
L	liter	pct/°C	percent per degree Celsius
M	gram mol per liter	vol pct	volume percent
mg	milligram		

SOLUBILITIES OF SIDERONATRITE AND FERRINATRITE IN THE SYSTEM NA$_2$SO$_4$-Fe$_2$O$_3$-H$_2$SO$_4$-H$_2$O

By C. M. Flynn, Jr.,[1] and J. A. Eisele[2]

ABSTRACT

The solubilities of sideronatrite [$Na_2Fe(OH)(SO_4)_2 \cdot 3H_2O$] and ferrinatrite [$Na_3Fe(SO_4)_3 \cdot 3H_2O$] were determined by the Bureau of Mines in the Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O system at 25°, 40°, 60°, and 90° C. The solution compositions investigated ranged from Na^+-Fe^{3+} mol ratios of 0.5 to >100 (Na_2SO_4 saturation) and H^+-SO_4^{2-} mol ratios of 0 to 1.0. The results are presented in the form of contour plots. The solubilities were determined by seeding supersaturated solutions of known composition with the specified solid phase to precipitate a substantial amount of solid. Water was then added in small portions to the solution until the last portion of the solid dissolved. Equilibration times at 25°, 40°, 60°, and 90° C were 2 days, 1 day, 8 to 16 h, and 2 to 4 h, respectively. The accuracy of the solubility data is estimated to be 1 to 2 pct. Low iron solubilities of <0.36 pct $Fe_2(SO_4)_3$, or 1 g Fe/kg solution, were obtained in solutions containing at least 8 pct Na_2SO_4 in the absence of H_2SO_4 or a total of at least 36 to 38 pct Na_2SO_4 + H_2SO_4 at high acidity. The filterability and density of sideronatrite and ferrinatrite in comparison with other iron compounds are reported. These compounds are suitable vehicles for iron removal in Na_2SO_4-rich solutions. Additional solubility data on the Na_2SO_4-H_2SO_4-H_2O system were also obtained.

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INTRODUCTION

Removal of iron impurities in hydromet-allurgical processes can be accomplished by precipitation and filtration. If the iron is precipitated as a voluminous and gelatinous hydrous oxide, the slurry is difficult to filter and dewater, and water is lost from the process. Precipitation of iron in a dense granular form would greatly facilitate liquid-solid separation. Requirements for filtration time, wash water, space for impoundment or further processing, and pollution control measures are substantially less when dense precipitates are formed rather than voluminous, gelatinous precipitates. An example is zinc electrolyte production, for which some iron removal processes have been developed (1-2).[3] These processes include iron precipitation as dense goethite or as ammonium or sodium jarosites.

Other iron compounds exist that can be precipitated from solution in dense form, but there is insufficient information on their formation and solubility. The Bureau of Mines conducted research to obtain solubility data on the dense iron sulfate compounds sideronatrite and ferrinatrite. A literature search indicated that data were available only on the properties of these solid compounds (3-8), aside from old solubility data on the $Na_2SO_4-H_2SO_4-H_2O$ and $Fe_2(SO_4)_3-H_2SO_4-H_2O$ systems compiled by Linke (9-10). The solubility data presented in this report extend over solution compositions ranging from mol ratio $Na^+-Fe^{3+} = 0.5$ to Na_2SO_4 saturation, where the saturating solid phases are mirabilite ($Na_2SO_4 \cdot 10H_2O$), thenardite (Na_2SO_4), or the sodium acid sulfate $Na_3H(SO_4)_2$. Another phase in the $Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O$ system is sodium jarosite [ideal formula $NaFe_3(OH)_6(SO_4)_2$], for which solubility data will be reported in another publication.

MATERIALS AND EQUIPMENT

All chemicals were of commercial reagent-grade and were used without purification. The iron(III) sulfate was either a very pale yellow powder, $Fe_2(SO_4)_3 \cdot xH_2O$ [typical manufacturer's assay, 73.2 pct $Fe_2(SO_4)_3$], or a mustard-yellow powder, which the Bureau's analyses indicated to be $Fe_2(SO_4)_{3-x}(OH)_{2x} \cdot yH_2O$, where typically $x \sim 0.20$ and $y \sim 5$ to 6. Both materials were amorphous to X-rays. Iron(III) sulfate solutions were prepared in deionized water from reagent-grade $Fe_2(SO_4)_3 \cdot xH_2O$ or $FeSO_4 \cdot 7H_2O$, H_2SO_4, and H_2O_2. The $Fe_2(SO_4)_3$, $Fe_4(OH)_2(SO_4)_5$, and H_2SO_4 solutions were standardized and used in the solubility determinations.

Temperature-controlled reciprocating shaker baths or baths equipped with controlled-temperature circulators and magnetic stirrers were used for solubility determinations. Bath liquids were water or glycerol-water mixtures. Temperature control precision was $\leq 1°$ C in the shaker baths and incubators, $\leq 0.5°$ C in the gly-cerol-water-filled circulator baths, and $\leq 0.2°$ C in the water-filled circulator baths. Thermometers were calibrated in freezing and boiling water and at temperatures near $25°$, $40°$, and $60°$ C against ASTM-standard thermometers.

EXPERIMENTAL PROCEDURES

ANALYSES

Solutions of H_2SO_4 were standardized against NaOH solutions which were standardized with potassium hydrogen

phthalate. Solutions of $Fe_2(SO_4)_3$ and $Fe_4(OH)_2(SO_4)_5$ were standardized with $K_2Cr_2O_7$ according to a standard procedure (11). Solid iron compounds were analyzed for iron by the same procedure after dissolution in $5M$ to $12M$ HCl. Sulfate analyses were conducted by dissolution in dilute HCl, reduction of Fe(III) to Fe(II) with aluminum, and precipitation as

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[3]Underlined numbers in parentheses refer to items in the references at the end of this report.

BaSO₄. Sodium analyses were performed on an atomic absorption spectrophotometer.

X-ray powder diffraction data were obtained on a diffractometer with solid state electronics.

Densities of H_2SO_4 solutions were obtained from tabulated data (12). Densities of $Fe_2(SO_4)_3$ and $Fe_4(OH)_2(SO_4)_5$ solutions were obtained by weighing known volumes of solution. Values obtained at 20° to 25° C were 1.016, 1.086, and 1.338 kg/L for 0.050, 0.250, and 1.000M $Fe_2(SO_4)_3$ solutions, respectively; and 1.151 and 1.305 kg/L for 0.250 and 0.500M $Fe_4(OH)_2(SO_4)_5$ solutions, respectively.

PREPARATIONS

Sideronatrite was prepared by dissolving $Fe_2(SO_4)_3 \cdot xH_2O$ and Na_2SO_4 in water, adding $NaHCO_3$, seeding with sideronatrite, and stirring at room temperature for 2 days until a viscous slurry resulted. For a typical preparation, the solution Na^+-Fe^{3+} mol ratio was 3.0, the $NaHCO_3$-Fe^{3+} mol ratio was 0.50, the initial iron concentration was 1.0M, and the amount of sideronatrite seed was equivalent to 0.2 pct of the iron in solution. The mixture was filtered on a Buchner funnel and washed with a volume of 0.5M Na_2SO_4 equal to the filter cake volume. The solid was repulped with 50 vol pct acetone made $10^{-2}M$ in H_2SO_4, refiltered, washed successively with 75 and 100 vol pct acetone, and air-dried at room temperature. Yields of the light orange-yellow powder exceeded 70 pct. Replicate analytical results were 12.5, 12.5, 12.7 pct Na and 15.20, 15.38, 15.24 pct Fe. Calculated values for $Na_2Fe(OH)(SO_4)_2 \cdot 3H_2O$ (formula weight 365.01) are 12.60 pct Na and 15.30 pct Fe. X-ray powder diffraction confirmed the identity as sideronatrite.

Ferrinatrite was prepared by dissolving $Fe_2(SO_4)_3 \cdot xH_2O$ and Na_2SO_4 in H_2SO_4 solution, heating almost to boiling, during which precipitation began, and cooling while stirring. For a typical preparation, the solution Na^+-Fe^{3+} mol ratio was 4.0, the H_2SO_4-Fe^{3+} mol ratio was 3.5, and the initial iron concentration was 1.2M. The solid was isolated in the same way as sideronatrite. Yields of the pale yellow powder exceeded 70 pct. Replicate analytical results were 14.5 and 14.6 pct Na, and 11.85 and 11.73 pct Fe. Calculated values for $Na_3Fe(SO_4)_3 \cdot 3H_2O$ (formula weight 467.05) are 14.77 pct Na and 11.96 pct Fe. X-ray powder diffraction confirmed the identity as ferrinatrite.

DETERMINATION OF SOLUBILITIES

The procedure employed avoided the labor of a large number of chemical analyses. Calculated quantities of Na_2SO_4, $Fe_2(SO_4)_3$ solution, H_2SO_4 solution, and water were weighed into glass containers, and the containers were stoppered. For determinations at 60° and 90° C, the stoppers were drilled with holes ∼0.5 mm in diameter to provide pressure relief without significant evaporation loss. Most compositions were prepared at selected Na^+-Fe^{3+} mol ratios of 0.50 to 100 and H^+-SO_4^{2-} mol ratios of 0 to 1.00. At 25° and 40° C, determinations were also made on solutions that contained base. Use of $NaHCO_3$ instead of $NaOH$ as base prevented formation of hydrous oxide. Solutions with low final iron concentrations (mol ratio Na^+-Fe^{3+} ≥40) were treated with $HgCl_2$ (final concentration, ∼5 ppm) to retard bacterial growth, which interfered with the solubility determinations.

The solutions were seeded with ∼1 mg of sideronatrite or ferrinatrite and agitated at temperature until a sufficient visible quantity of the respective solid phase precipitated. For sideronatrite in solutions with H^+-SO_4^{2-} ≥0.4, the acid was added after seeding and precipitation. For sideronatrite or ferrinatrite solutions with Na^+-Fe^{3+} ≥30, seeding and precipitation were accomplished first, after adding 5 to 10 mmol Na_2SO_4/mmol Fe^{3+}; then the H_2SO_4, the rest of the Na_2SO_4, and water were added. These procedural alterations increased the rate of precipitation after seeding.

Increments of water were added at intervals during agitation at temperature, and the mixtures were allowed to equilibrate after each addition. This water addition procedure was continued until

the last of the solid dissolved. The size of the water increments was initially as much as 5 pct of the weight of the solution and solid, and was decreased to 1 pct as the solid was progressively dissolved. Time intervals between water additions were 2 days at 25° C, 1 day at 40° C, 8 to 16 h at 60° C, and 1 to 2 h at 90° C. These times were established by observing dissolution in sets of solutions with constant amounts of reagents except for water, which was varied in increments corresponding to ~1-pct changes in total weight. The quantities of water bracketed the saturation composition. At completion of the water additions, the solutions were weighed. The solution compositions were calculated from the solution weights and the known amounts of input reagents. The accuracy of the solubility determinations is estimated as 1 to 2 pct and was determined by the weight of the final water increments (1 pct of the weight of the solution and solid) and the minimum visible concentration of solid phase.

For selected compositions, solubility determinations were conducted at temperatures of 30° to 90° C to characterize the temperature dependence. Because greater accuracy was desired, more time was required to complete the determinations, and the water increments added were smaller, 0.3 pct of the weight of the solution and solid. For temperatures ≥60° C, septum stoppers were used to prevent water loss by evaporation, and the water increments were added by syringe. The estimated accuracy of these determinations, done in duplicate, was 0.5 to 1 pct.

Prior to determining the solubilities of sideronatrite and ferrinatrite in solutions simultaneously saturated with sodium sulfate, solubilities were determined in the $Na_2SO_4-H_2SO_4-H_2O$ system at 25°, 40°, 60°, and 90° C, because published data in the region of interest (9) were incomplete. A circulator bath controlled to ±0.1° C was used at 25° C, because the solubility of $Na_2SO_4 \cdot 10H_2O$ varies by about 5 pct/°C at that temperature (9). The amount of water required was estimated from published data (9). Final water increments were 0.1 to 0.2 pct of total mixture weight and were added at intervals that varied from 4 to 16 h at 25° C to 1 to 2 h at 90° C. Accuracy based on replicate determinations was 0.2 to 0.5 pct.

The saturated Na_2SO_4 solutions, to which a trace (~1 mg) of Na_2SO_4 was added, were agitated with increments of sideronatrite or ferrinatrite and increments of water if necessary, until no more iron compound dissolved and all of the sodium sulfate phase dissolved. To insure saturation with the iron compound, agitation was continued after the last water addition for times varying from 5 days at 25° C to 4 h at 90° C. The solutions were weighed and returned to the temperature-controlled bath to permit settling of undissolved iron compound. Aliquots of solution were withdrawn, weighed, and analyzed for iron. From these data and the known amounts of Na_2SO_4 and H_2SO_4 present, the solution compositions were calculated.

CALCULATIONS

The sideronatrite and ferrinatrite solubility data for each temperature were calculated on a weight basis and plotted on a triangular diagram. Solubilities were plotted versus solution $H^+-SO_4^{2-}$ mol ratio at constant solution Na^+-Fe^{3+} mol ratio and versus solution Na^+-Fe^{3+} mol ratio at constant solution $H^+-SO_4^{2-}$ mol ratio. With the aid of these plots, the data on the triangular diagrams were converted to contour plots. The sideronatrite-ferrinatrite phase

boundary was obtained in a similar manner.

The input data consisted of millimols of Fe^{3+}, n_{Fe}; solution Na^+-Fe^{3+} mol ratio, r_M; solution $H^+-SO_4^{2-}$ mol ratio, r_A; and solution weight, w_T. The following relations hold, where millimols of Na^+, H^+, and SO_4^{2-} = n_{Na}, n_H, and n_S, respectively; mol ratio H^+-Fe^{3+} = r_H; weights of $Fe_2(SO_4)_3$, Na_2SO_4, and H_2SO_4 = W_{Fe}, W_{Na}, and W_H, respectively; and total weight of solutes = W_O:

By definition,

$$r_M = n_{Na}/n_{Fe}$$

$$r_A = n_H/n_S$$

$$r_H = n_H/n_{Fe}$$

Stoichiometry:

$$3n_{Fe} + n_{Na} + n_H = 2n_S$$

$$r_A = 2n_H/[(3 + r_M)n_{Fe} + n_H]$$

$$= 2r_H/(3 + r_M + r_H)$$

$$r_H = r_A(3 + r_M)/(2 - r_A)$$

Weights of solutes:

$$W_{Fe} = 0.19994 \, n_{Fe}$$

$$W_{Na} = 0.07102 \, n_{Na}$$

$$W_H = 0.04904 \, n_H$$

$$W_0 = W_{Fe} + W_{Na} + W_H$$

percent $Fe_2(SO_4)_3$ (dry basis) $= 100 \, W_{Fe}/W_0$

percent Na_2SO_4 (dry basis) $= 100 \, W_{Na}/W_0$

percent H_2SO_4 (dry basis) $= 100 \, W_H/W_0$

percent total solutes $= 100 \, W_0/W_T$

SOLUBILITIES OF SIDERONATRITE AND FERRINATRITE

METHOD OF DATA PRESENTATION AND EXPERIMENTAL LIMITATIONS

The Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O system, in which the solubilities of sideronatrite and ferrinatrite were determined, is a section of the quaternary Na_2O-Fe_2O_3-SO_3-H_2O system. Most of the data derived from this study are contained in the section Na_2SO_4-$Fe_2(SO_4)_3$-H_2SO_4-H_2O; solutions basic relative to Na_2SO_4 + $Fe_2(SO_4)_3$ are contained in the section Na_2SO_4-Fe_2O_3-$Fe_2(SO_4)_3$-H_2O.

The data are presented in a set of four triangular-prism-based diagrams showing equilibria at 25°, 40°, 60°, and 90° C (fig. 1). The triangular prism base of the diagrams contains the Na_2SO_4-$Fe_2(SO_4)_3$-H_2SO_4 coordinates. The H_2O coordinate, which corresponds to the prism altitude, is perpendicular to the plane of the paper. The water content is expressed in terms of contours of constant percent total solutes, denoted by the numbered curves. In figures 1A and 1B, data for solutions basic relative to Na_2SO_4 + $Fe_2(SO_4)_3$ are shown below the Na_2SO_4-$Fe_2(SO_4)_3$ triangle edge. This region corresponds to part of an adjoining triangular prism with Na_2SO_4-$Fe_2(SO_4)_3$-Fe_2O_3 coordinates on the triangular base and the H_2O coordinate along the prism altitude. The proportions of the individual solutes are indicated by the position of any point in the Na_2SO_4-$Fe_2(SO_4)_3$-H_2SO_4 triangle or Na_2SO_4-$Fe_2(SO_4)_3$-Fe_2O_3 triangle in the same way as on a ternary equilibrium diagram. Solution compositions are expressed in percent or in terms of the relative amounts of solutes in percent; the latter is referred to as dry basis. For example, the point $*$ on figure 1B corresponds to 16.8 pct total solutes. Relative to

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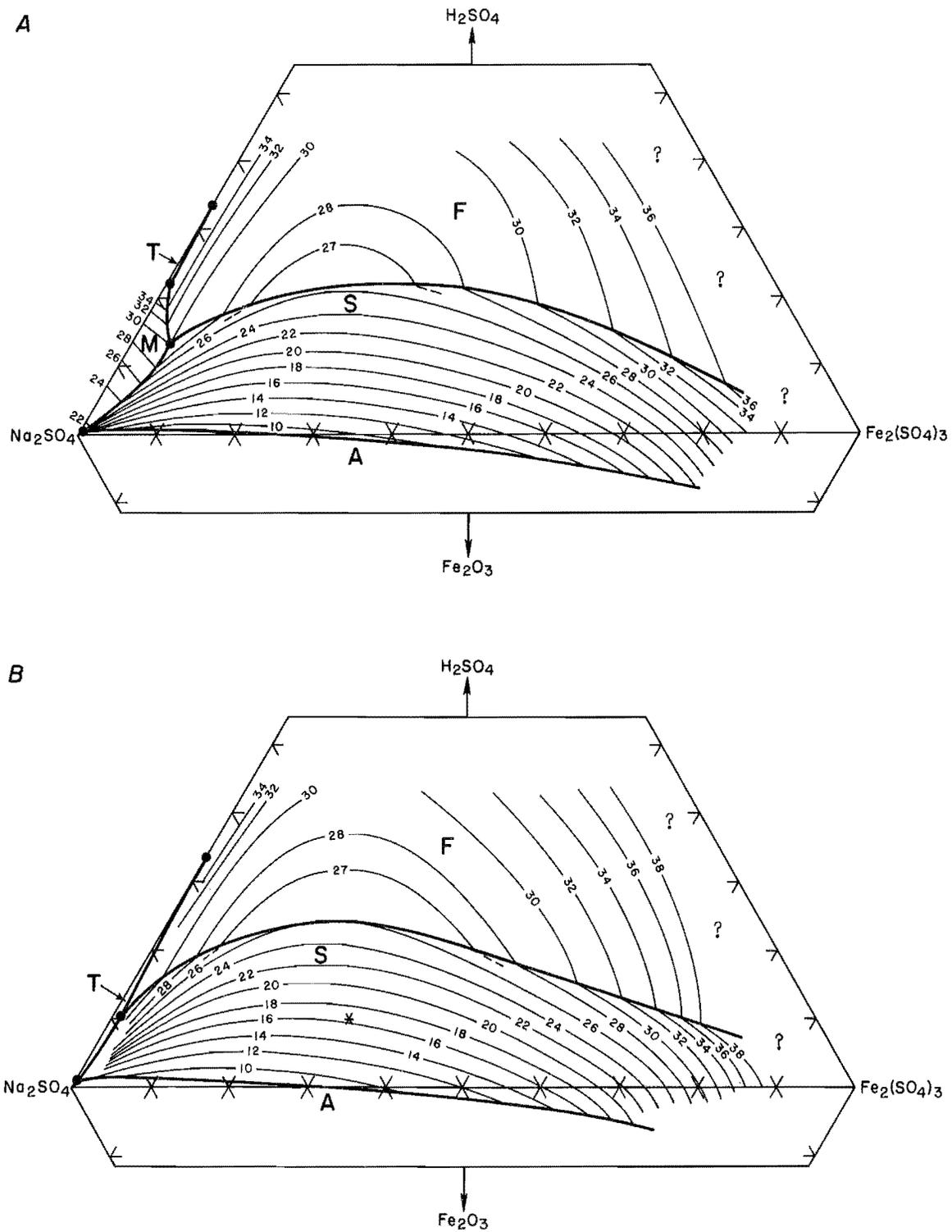
FIGURE 1.—Phase diagrams of Na₂SO₄-Fe₂(SO₄)₃-H₂SO₄-H₂O system. *A*, 25° C; *B*, 40° C; *C*, 60° C; *D*, 90° C. The lettered fields denote two-phase equilibria of solution and one solid phase: S = sideronatrite, F = ferrinatrite, A = amorphous basic iron sulfate, T = thenardite; M = mirabilite. The fields meet along the heavy curves, which correspond to equilibrium of solution with two solid phases. Near the left edge, the curves meet at points denoting equilibrium of solution with three solid phases. Numbers on contour lines indicate constant percent total solutes. Question marks indicate regions of undetermined solubilities.
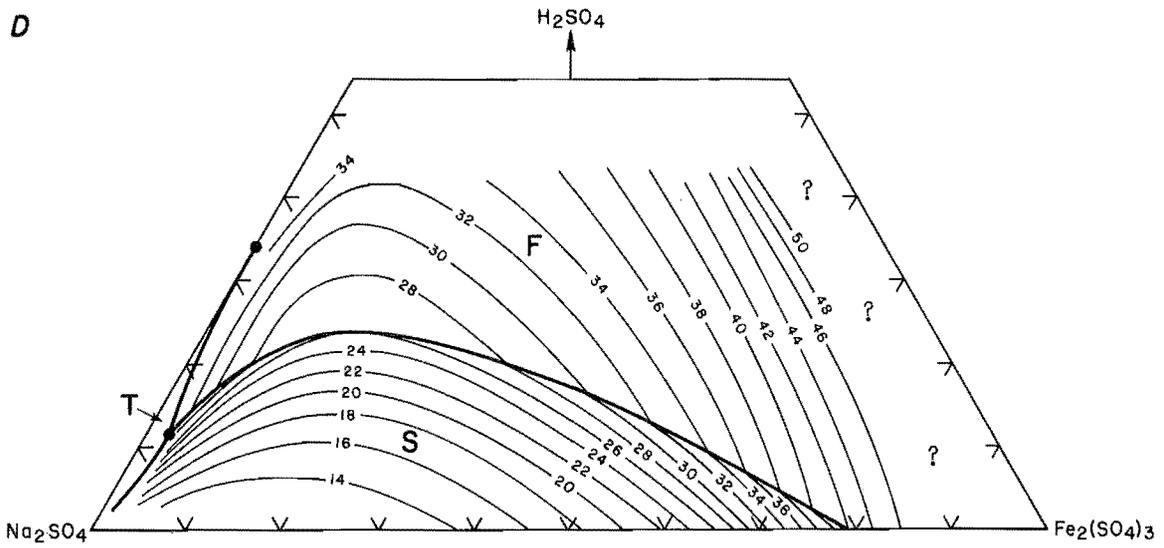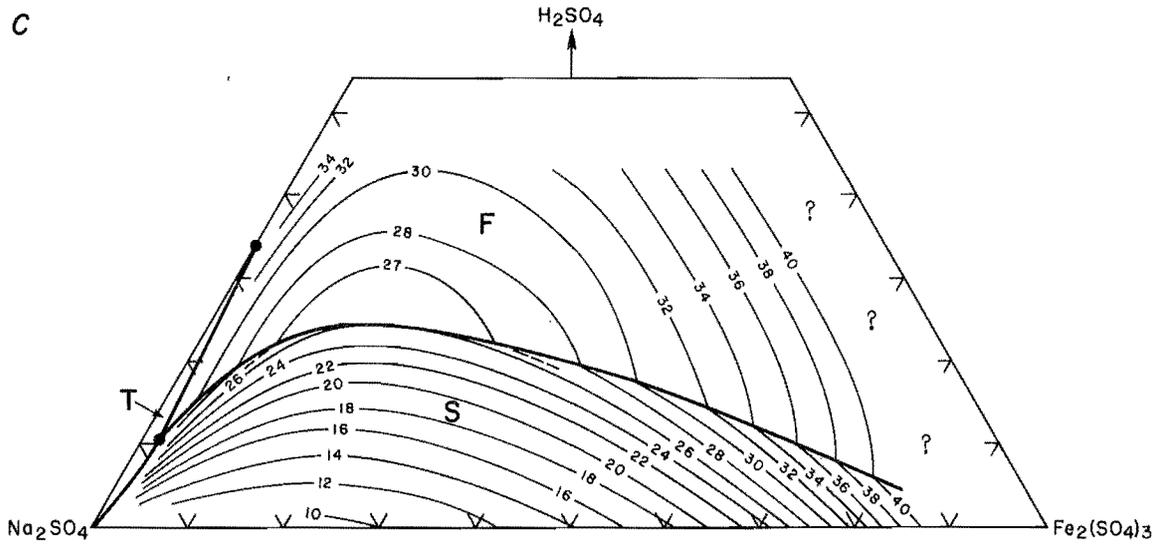
FIGURE 1.—Continued.

the triangle, the proportions of solutes Na_2SO_4, $Fe_2(SO_4)_3$, and H_2SO_4 are 60, 30, and 10 pct (dry basis), respectively. The composition of the solution is, in percent, 10.08 Na_2SO_4, 5.04 $Fe_2(SO_4)_3$, 1.68 H_2SO_4, and 83.2 H_2O (solution basis). The solid phase at point * is sideronatrite (S).

Solution stoichiometry is also specified in terms of Na^+-Fe^{3+} and $H^+-SO_4^{2-}$ mol ratios. The mol ratio $H^+-SO_4^{2-}$ was adopted as a measure of acidity because the acidity is controlled primarily by the dissociation of HSO_4^-. The data in figure 1 resulted from systematic determinations at the following solution mol ratios: Na^+-Fe^{3+} = 0.50 to $\geq$100 (Na_2SO_4 saturation) and $H^+-SO_4^{2-}$ = 0 to 1.00.

Experimental limitations prevented determinations at certain solution stoichiometries. Solubilities were not systematically determined at Na^+-Fe^{3+} mol ratios below 0.50 because equilibrium was difficult to establish; this region is noted by question marks in figure 1. Factors contributing to this difficulty were high solubilities, high solution viscosities, and inability to crystallize hydrates of $Fe_2(SO_4)_3$. Sideronatrite is metastable with respect to sodium jarosite except at high acidity and low temperature. It can easily be obtained throughout the range of compositions for which its solubility data are reported, without interference from sodium jarosite formation, because the rate of formation of sodium jarosite is very low. Data on the solubility and formation kinetics of sodium jarosite will be published in subsequent papers. The sideronatrite and ferrinatrite solubility determinations required 4 to 20 days at 25° C. The time required decreased with increasing temperature and was 6 to 10 h at 90° C. Only at low acidity and high solution Na^+-Fe^{3+} mol ratios at 60° and 90° C did formation of sodium jarosite or other hydrolysis products prevent determination of sideronatrite solubilities, as shown in figures 1C and 1D.

Because the solubility contours in the Na_2SO_4-rich region are congested in figure 1, this region is shown in greater detail in figure 2. The angle at the Na_2SO_4 corner is 90° in figure 2 versus 60° in figure 1 because the limited composition range included in figure 2 is amenable to presentation on orthogonal coordinates. For example, in figure 2A, at the point of intersection of the mirabilite, sideronatrite, and ferrinatrite fields, the proportions of solutes $Fe_2(SO_4)_3$, H_2SO_4, and Na_2SO_4 are (dry basis) 5.0, 13.2, and 81.8 pct, respectively.

EFFECT OF ACIDITY

Figures 1 and 2 show that sideronatrite is the stable phase at low acidity and ferrinatrite is the stable phase at high acidity. The greatest acidity at which sideronatrite is stable, equivalent to the lowest acidity at which ferrinatrite is stable, depends on the solution Na^+-Fe^{3+} mol ratio, and is given by the sideronatrite-ferrinatrite boundary shown in figures 1 and 2. At solution Na^+-Fe^{3+} mol ratios of 3 to 20, the sideronatrite field extends to a maximum acidity, $H^+-SO_4^{2-}$ = 0.56 to 0.62. At lower and higher solution Na^+-Fe^{3+} mol ratios, ferrinatrite becomes the stable phase at relatively lower acidity. The sideronatrite-ferrinatrite boundary extends to solution $H^+-SO_4^{2-}$ mol ratio ~0.3 at Na_2SO_4 saturation and $\leq$0.2 at solution Na^+-Fe^{3+} mol ratio = 0.5.

TEMPERATURE DEPENDENCE

The variation of the solubilities of sideronatrite and ferrinatrite with temperature is modest over most of the composition range, so figures 1A, 1B, 1C, and 1D are similar. One major difference pertains to the sideronatrite-ferrinatrite phase boundary, represented by the solid curve dividing the sideronatrite and ferrinatrite fields in figure 1. At 25°, 40°, and 60° C, the sideronatrite-ferrinatrite boundary extends to a point on the edge of the triangle very close to the $Fe_2(SO_4)_3$ corner. At these temperatures, ferrinatrite is not stable in solutions that do not contain H_2SO_4. At 90° C, this boundary terminates on the $Na_2SO_4-Fe_2(SO_4)_3$ side of the

triangle at 79 pct $Fe_2(SO_4)_3$ (dry basis). In this composition region, above 60° C, the solubility of sideronatrite increases with temperature faster than the solubility of ferrinatrite, so that the lower solubility of ferrinatrite at 90° C results in its phase field extending to solution compositions containing no H_2SO_4, represented by the Na_2SO_4-$Fe_2(SO_4)_3$ edge of the triangle. The other major difference pertains to Na_2SO_4-rich solutions, in which $Na_2SO_4 \cdot 10H_2O$ is present at 25° C but not at the higher temperatures, as seen by comparing the A diagrams in figures 1 and 2 with diagrams B, C, and D in those figures. The solubility of $Na_2SO_4 \cdot 10H_2O$ at 25° C is significantly lower than the solubility of Na_2SO_4 at the higher temperatures and results in a larger field for $Na_2SO_4 \cdot 10H_2O$ at 25° C relative to Na_2SO_4 at the higher temperatures.

The temperature dependence of solubility varies in a complex way with solution stoichiometry. Additional data were obtained at selected solution stoichiometries to more precisely characterize the temperature dependence of the solubility equilibria (fig. 3). The ordinate in figure 3 is total percent solutes, $Fe_2(SO_4)_3$ + Na_2SO_4 + H_2SO_4, which is the same as the quantity contoured in figures 1 and 2. For any of the curves in figure 3, solution stoichiometry (Na^+-Fe^{3+} and H^+-SO_4^{2-} mol ratios) is constant, so $Fe_2(SO_4)_3$ solubility in percent is proportional to total percent solutes and is obtained via the equations in the previous "Calculations" section. Approximate generalizations may be stated. Solubility increases monotonically with temperature at low Na^+-Fe^{3+} mol ratios, e.g., Na^+-Fe^{3+} = 1. At Na^+-Fe^{3+} mol ratios >3, solubilities decrease to a shallow minimum, then increase as temperature increases. With increasing Na^+-Fe^{3+} mol ratio, the temperature dependence becomes less pronounced.

As shown in figure 1, the maximum acidity at which sideronatrite is stable is almost constant versus temperature, namely, 23, 24, 25, and 24 pct H_2SO_4 (dry basis) at 25°, 40°, 60°, and 90° C, respectively. The Na_2SO_4 content at that

maximum acidity increases with temperature; the respective values are 48, 53, 59, and 62 pct (dry basis). Corresponding respective values of H^+-SO_4^{2-} mol ratio are 0.57, 0.60, 0.62, and 0.61 and of Na^+-Fe^{3+} mol ratio are ~4, ~6, ~10, and ~13.

SOLUBILITY OF SIDERONATRITE IN BASE-TREATED SOLUTIONS

Concentrated solutions of $Fe_2(SO_4)_3$ containing Na_2SO_4 can be treated with up to 0.5 equivalent of base per mol iron(III) without precipitating amorphous hydrous oxides or basic sulfates. Such solutions are part of the Na_2SO_4-Fe_2O_3-$Fe_2(SO_4)_3$-H_2O system. Solubility data for sideronatrite at 25° and 40° C in base-treated Na_2SO_4-$Fe_2(SO_4)_3$ are shown below the Na_2SO_4-$Fe_2(SO_4)_3$ side of the triangle in figures 1A and 1B. Determinations are less extensive at 40° C than at 25° C because of interference by sodium jarosite formation. At constant Na^+-Fe^{3+} mol ratio, the solubility of sideronatrite decreases almost linearly with decreasing H^+-Fe^{3+} mol ratio or increasing OH^--Fe^{3+} mol ratio. The maximum OH^--Fe^{3+} mol ratio attainable without precipitation of amorphous hydrous oxides or basic sulfates decreases with increasing Na^+-Fe^{3+} mol ratio. The amorphous phase that precipitates at OH^--Fe^{3+} ratios just above the maximum is rust-orange amorphous basic iron(III) sulfate [$Fe_4(OH)_{10}(SO_4) \cdot {\sim}2H_2O$]. The sideronatrite-$Fe_4(OH)_{10}(SO_4) \cdot {\sim}2H_2O$ boundary was determined by plotting the solubility data for $Fe_4(OH)_{10}(SO_4) \cdot {\sim}2H_2O$ (to be published in a subsequent paper) with the data for sideronatrite. This boundary is shown in figures 1A, 1B, 2A, and 2B.

SIMULTANEOUS SATURATION WITH IRON COMPOUND AND Na_2SO_4

Figures 1 and 2 show the phase boundaries sideronatrite-Na_2SO_4 and ferrinatrite-Na_2SO_4. At 25° C and the lower acidities, in figure 2A, the boundaries are sideronatrite-$Na_2SO_4 \cdot 10H_2O$ and ferrinatrite-$Na_2SO_4 \cdot 10H_2O$, and they intersect the sideronatrite-ferrinatrite boundary
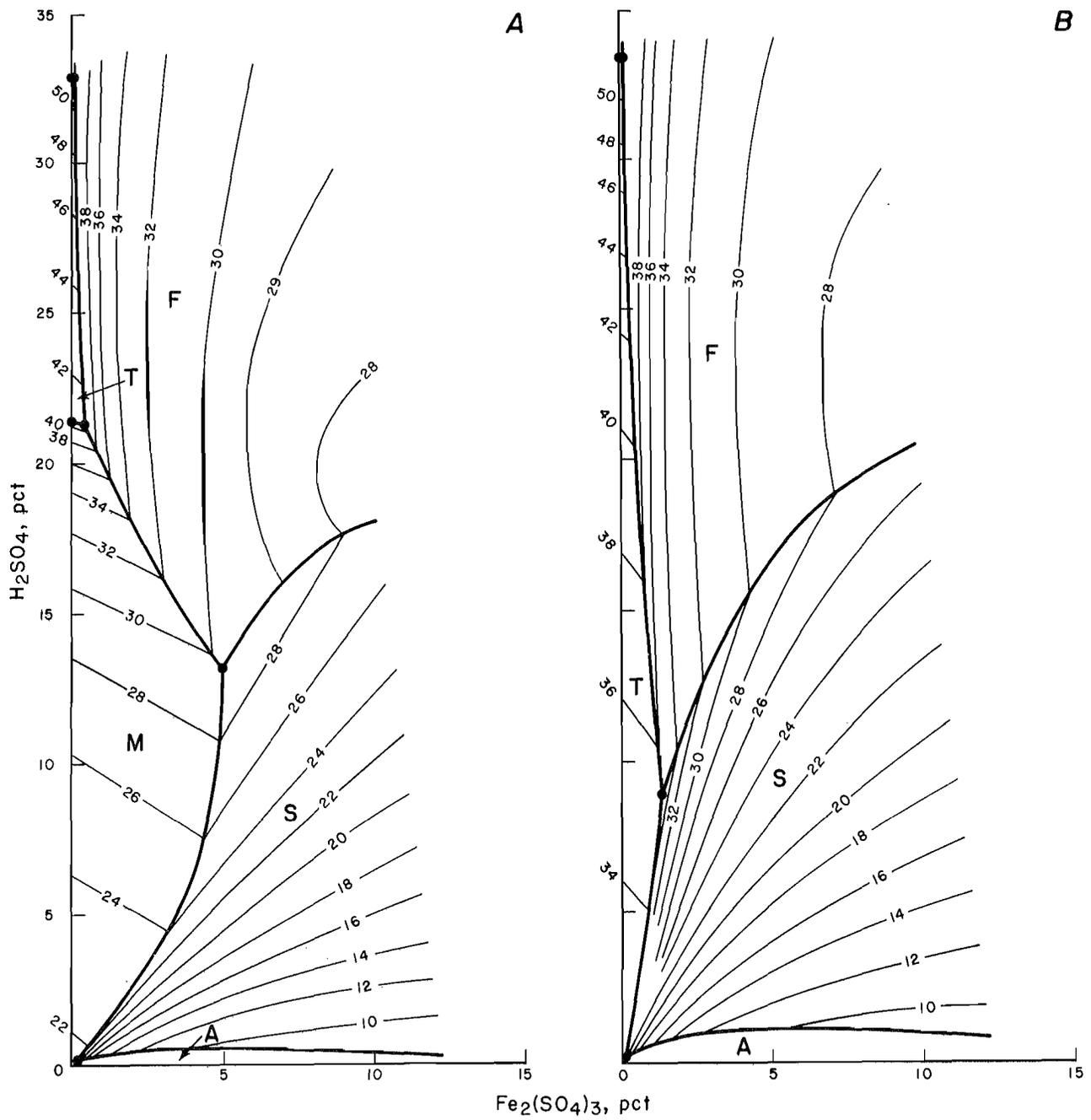
FIGURE 2.—Na₂SO₄-rich portion of Na₂SO₄·Fe₂(SO₄)₃·H₂SO₄·H₂O system. *A*, 25° C; *B*, 40° C; *C*, 60° C; *D*, 90° C. These are magnifications of the Na₂SO₄-rich sides of the diagrams in figure 1; see figure 1 caption for explanation.
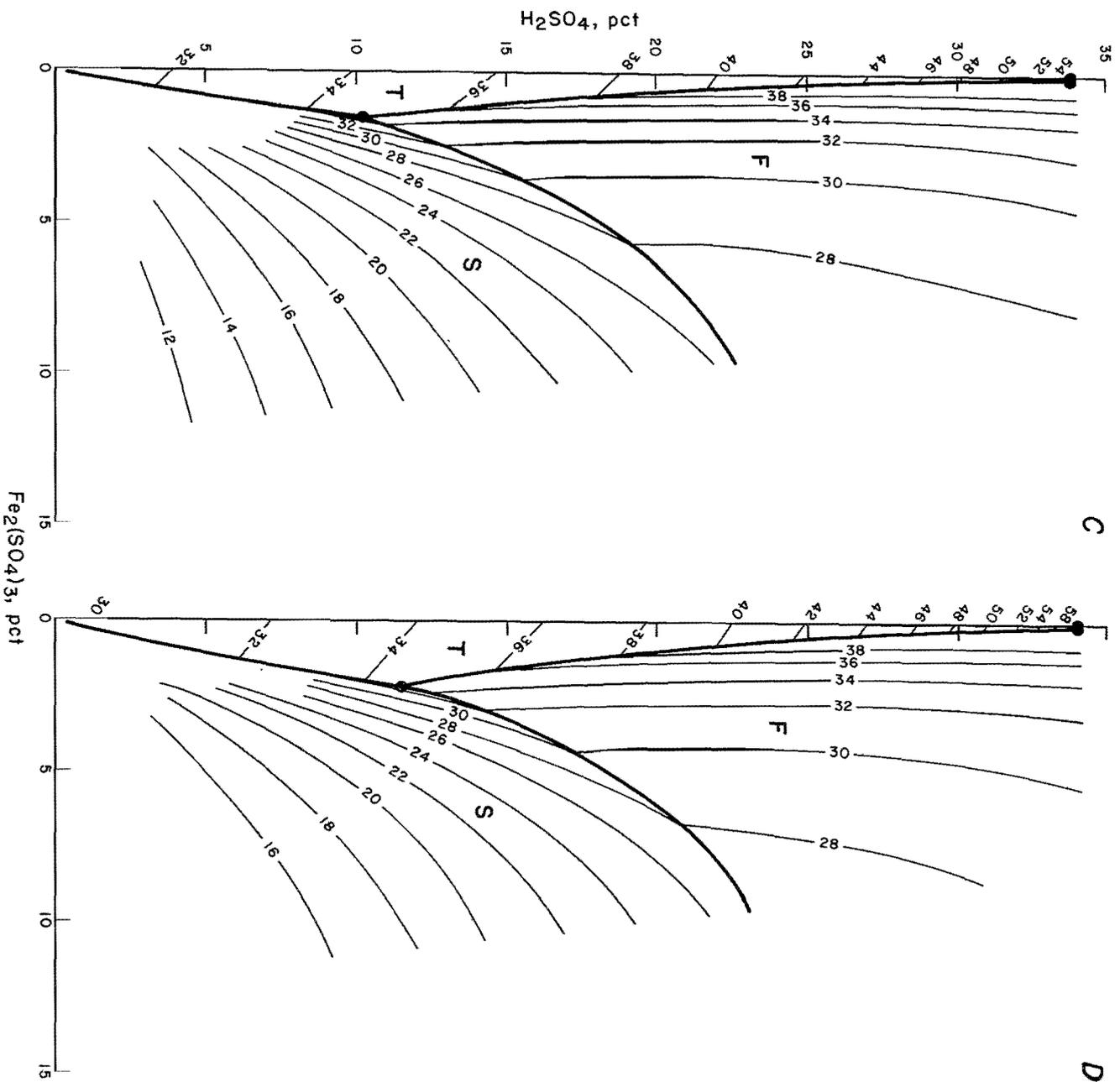
FIGURE 2.—Continued.

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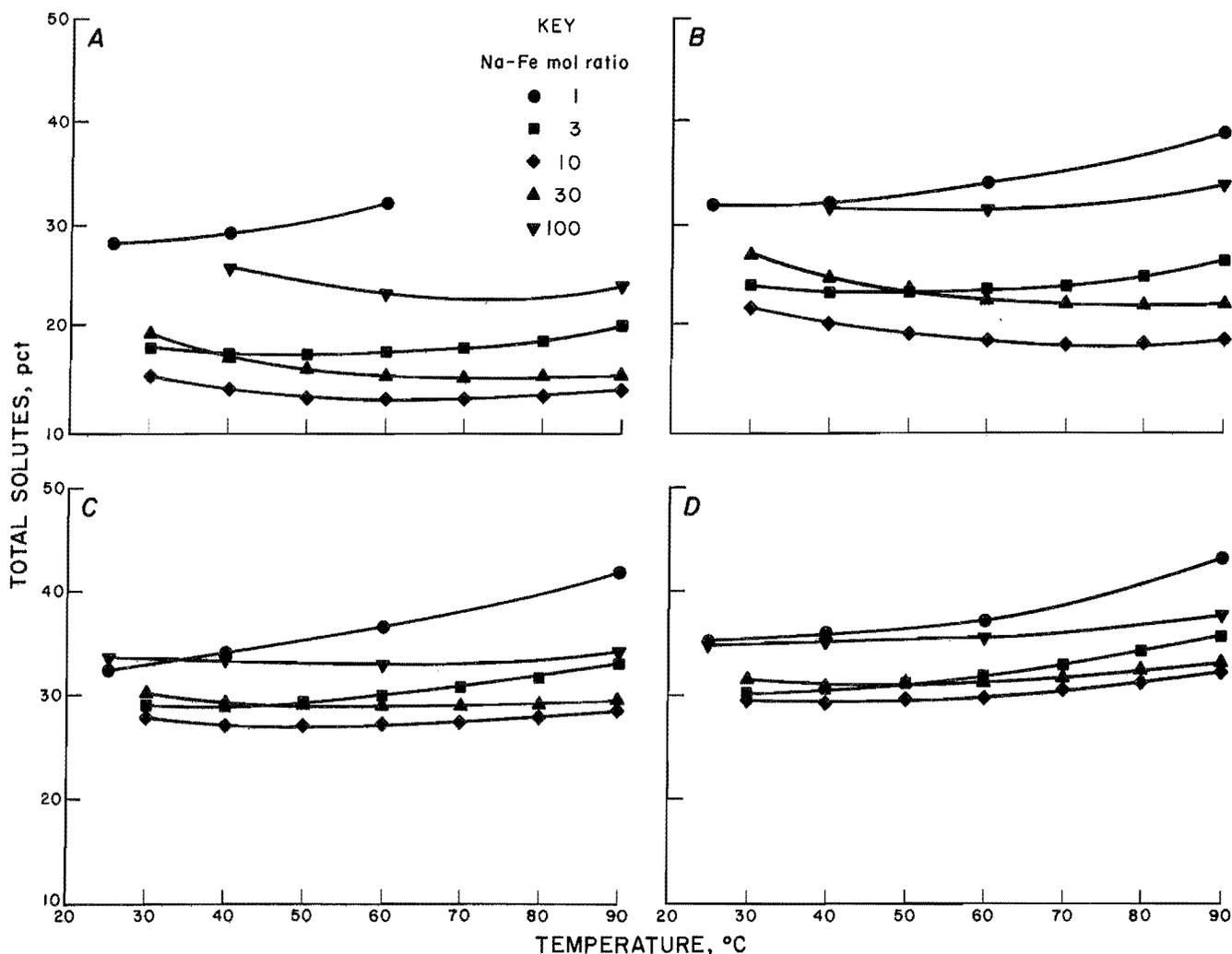
FIGURE 3.—Temperature dependence of solubilities at selected solution H^+-SO_4^{2-} mol ratios. A, 0.20; B; 0.40; C, 0.80; D, 1.00.

at the sideronatrite-ferrinatrite-Na_2SO_4 ·$10H_2O$-solution quadruple point. At higher acidities the ferrinatrite-Na_2SO_4 ·$10H_2O$ and ferrinatrite-Na_2SO_4 boundaries intersect the Na_2SO_4·$10H_2O$-Na_2SO_4 boundary at the ferrinatrite-Na_2SO_4·$10H_2O$-Na_2SO_4-solution quadruple point. At 40°, 60°, and 90° C, in figures 2B, 2C, and 2D, the boundaries sideronatrite-Na_2SO_4 and ferrinatrite-Na_2SO_4 intersect the sideronatrite-ferrinatrite boundary at the sideronatrite-ferrinatrite-Na_2SO_4-solution quadruple point. At all temperatures and the higher acidities, the ferrinatrite-Na_2SO_4 boundary and the ferrinatrite-$Na_3H(SO_4)_2$ boundary intersect the Na_2SO_4-$Na_3H(SO_4)_2$ boundary at the ferrinatrite-Na_2SO_4-$Na_3H(SO_4)_2$-solution

quadruple point (left side of the diagrams in figures 1 and 2, near 35 pct H_2SO_4 (dry basis)).

Plots of the phase boundaries involving Na_2SO_4 saturation are shown in figure 4, which emphasizes the correlation with the Na_2SO_4-H_2SO_4-H_2O system. Linke's compilation (9) contains data for the Na_2SO_4-H_2SO_4-H_2O system at different temperatures, but none for 40° and 90° C. The triple points in the Na_2SO_4-H_2SO_4-H_2O system at 25° C given by Linke are in fair agreement with the data reported here, as indicated in figure 4A. Linke's 60° C data, shown in figure 4C, are ~3 pct higher than the present results. The triple points in the Na_2SO_4-H_2SO_4-H_2O system correspond to quadruple points
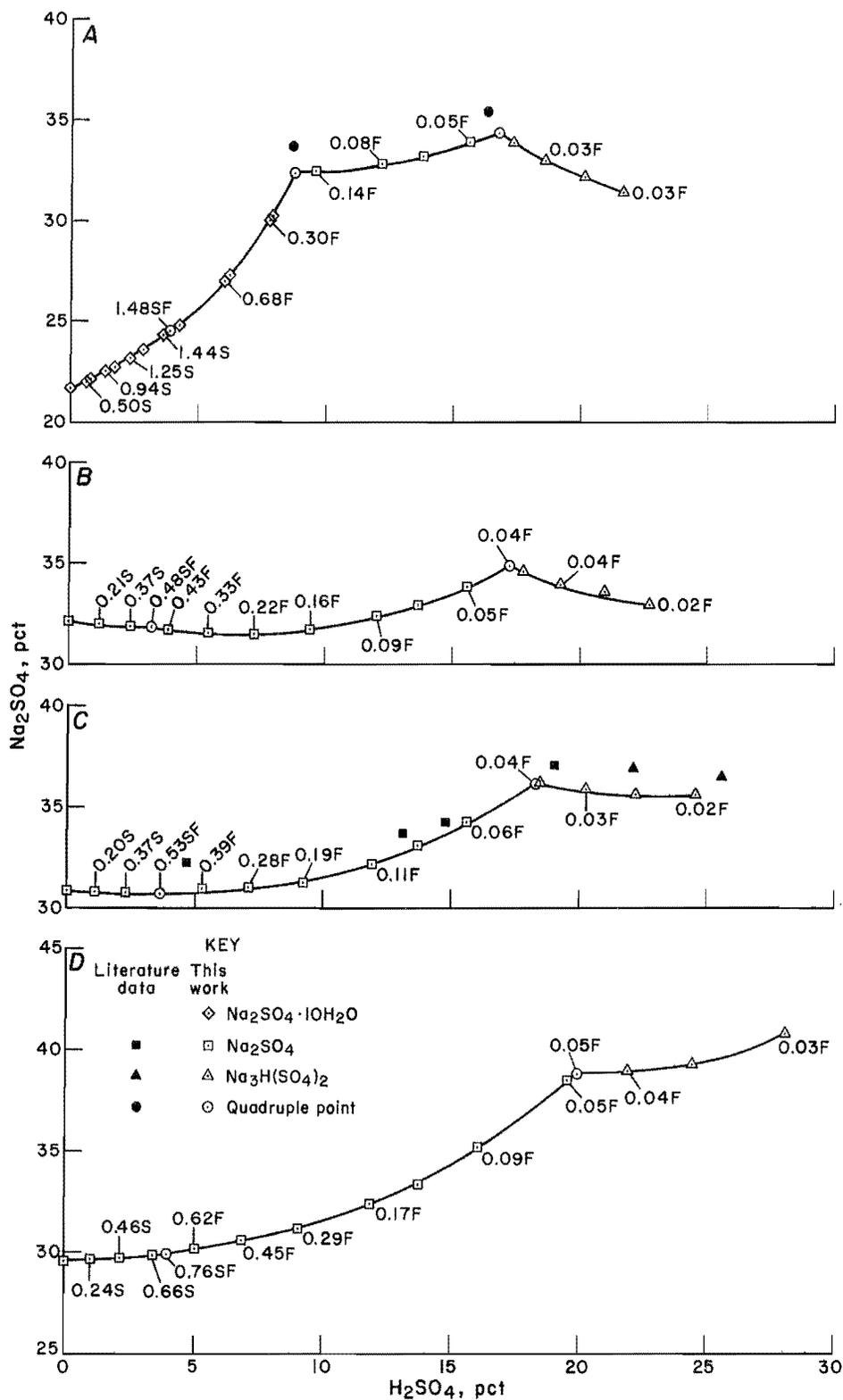
FIGURE 4.—System $Na_2SO_4-H_2SO_4-H_2O$ and $Fe_2(SO_4)_3$ solubility. A, 25° C, B, 40° C; C, 60° C; D, 90° C. Compositions are given on solution basis. Numbers adjacent to data points indicate weight percent $Fe_2(SO_4)_3$; the saturating iron-containing phase is sideronatrite (S) or ferrinatrite (F).

in the presence of $Fe_2(SO_4)_3$, as indicated in figure 4. Because of the low $Fe_2(SO_4)_3$ concentration, the Na_2SO_4 and H_2SO_4 concentrations at these quadruple points differ insignificantly from the values at the corresponding triple points in the $Na_2SO_4-H_2SO_4-H_2O$ system.

The iron solubilities on the Na_2SO_4-sideronatrite and Na_2SO_4-ferrinatrite boundaries are shown more clearly in figure 5. The iron solubilities on these boundaries are at a minimum relative to iron solubilities in solutions unsaturated with Na_2SO_4. Along the Na_2SO_4-sideronatrite boundary, the iron (sideronatrite) solubility increases with increasing acidity from a minimum of <0.05 pct $Fe_2(SO_4)_3$ at <0.2 pct H_2SO_4. At 25° and 40° C, the sideronatrite-Na_2SO_4 boundary at its low-acid end intersects the sideronatrite-$Fe_4(OH)_{10}(SO_4)$ $\cdot\sim2H_2O$ boundary at the sideronatrite-$Fe_4(OH)_{10}(SO_4)\cdot\sim2H_2O-Na_2SO_4$-solution quadruple point, as shown in figures 2A and 2B. At that point, the iron solubility is at a minimum, 0.03 pct $Fe_2(SO_4)_3$ at 25° C and 0.012 pct at 40° C. Along the Na_2SO_4-ferrinatrite boundary, the iron

(ferrinatrite) solubility decreases with increasing acidity to ≤0.05 pct $Fe_2(SO_4)_3$ at the ferrinatrite-$Na_2SO_4-Na_3H(SO_4)_2$-solution quadruple point, as shown in figure 2. At the sideronatrite-ferrinatrite-Na_2SO_4-solution quadruple point, the iron solubility is at a maximum relative to the iron solubilities in Na_2SO_4-saturated solutions at lower or higher acidities. These maximum iron solubilities are 1.48, 0.48, 0.53, and 0.76 pct $Fe_2(SO_4)_3$ at 25°, 40°, 60°, and 90° C, respectively. Complete data for all of the quadruple points are given in table 1.

EFFECTIVENESS OF IRON REMOVAL FROM SOLUTIONS

The solubilities of sideronatrite and ferrinatrite are lowest in solutions saturated with Na_2SO_4. Figure 5 and table 1 show that the $Fe_2(SO_4)_3$ solubility at Na_2SO_4 saturation is <0.8 pct, or <2.2 g Fe/kg solution, at all acidities at 40° to 90° C. At 25° C, acidity must be <1.2 pct or >5.8 pct H_2SO_4 to attain $Fe_2(SO_4)_3$ solubility of <0.8 pct. To attain a

TABLE 1. - Quadruple points in the $Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O$ system

Temp, °C	Solid phases	Composition, pct (solution basis)		
		$Fe_2(SO_4)_3$	Na_2SO_4	H_2SO_4
25...	Sideronatrite, ferrinatrite, $Na_2SO_4\cdot10H_2O$..	1.48	24.4	3.9
	Ferrinatrite, $Na_2SO_4\cdot10H_2O$, Na_2SO_4.........	.15	[1]32.4	[1]8.8
	Ferrinatrite, Na_2SO_4, $Na_3H(SO_4)_2$...........	.03	[2]34.3	[2]16.8
	Sideronatrite, $Fe_4(OH)_{10}SO_4\cdot\sim2H_2O$, $Na_2SO_4\cdot10H_2O$.	.03	21.7	.03
40...	Sideronatrite, ferrinatrite, Na_2SO_4........	.48	31.9	3.2
	Ferrinatrite, Na_2SO_4, $Na_3H(SO_4)_2$............	.04	34.7	17.4
	Sideronatrite, $Fe_4(OH)_{10}SO_4\cdot\sim2H_2O$, Na_2SO_4..	.012	32.2	.06
60...	Sideronatrite, ferrinatrite, Na_2SO_4........	.53	30.7	3.6
	Ferrinatrite, Na_2SO_4, $Na_3H(SO_4)_2$...........	.04	36.1	18.4
90...	Sideronatrite, ferrinatrite, Na_2SO_4........	.76	29.9	4.0
	Ferrinatrite, Na_2SO_4, $Na_3H(SO_4)_2$...........	.05	38.7	19.8

[1]Linke (9) gives 33.6 pct Na_2SO_4 and 8.7 pct H_2SO_4 in the ternary (iron-free) system.

[2]Linke (9) gives 35.3 pct Na_2SO_4 and 16.3 pct H_2SO_4 in the ternary (iron-free) system.
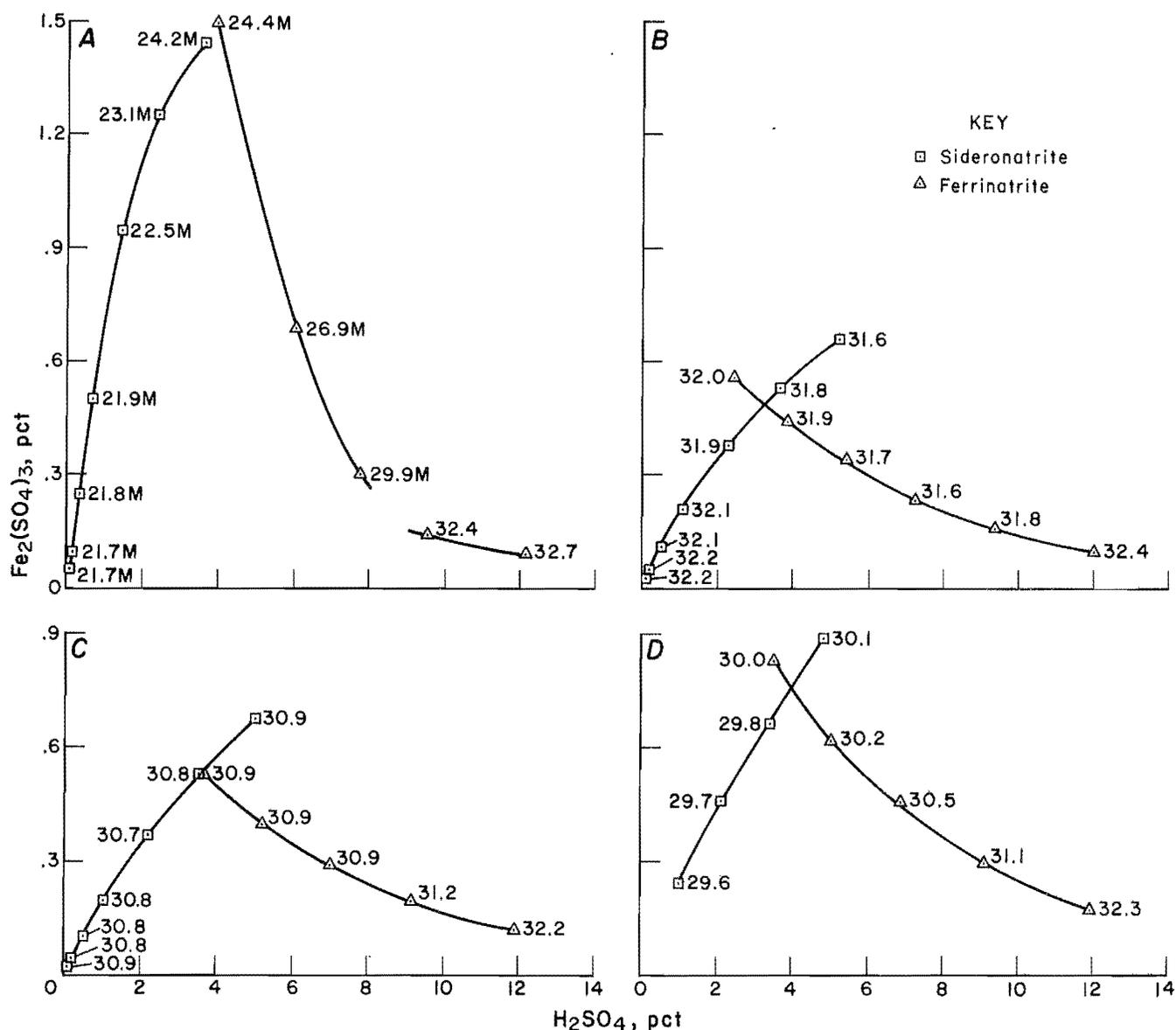
FIGURE 5.—$Fe_2(SO_4)_3$ solubility versus H_2SO_4 concentration at Na_2SO_4 saturation. A, 25° C; B, 40° C; C, 60° C; D, 90° C. Compositions are given on solution basis. Numbers adjacent to data points indicate weight percent Na_2SO_4. The sodium sulfate phase is Na_2SO_4 except for the data points marked M (mirabilite) in graph A.

$Fe_2(SO_4)_3$ solubility of <0.36 pct, or <1 g Fe/kg solution, acidity must be <2 pct H_2SO_4 at 40° to 90° C, <0.5 pct H_2SO_4 at 25° C, or >6 to 8 pct H_2SO_4 at all temperatures.

In solutions undersaturated with Na_2SO_4 and containing no H_2SO_4, the Na_2SO_4 concentration required for a $Fe_2(SO_4)_3$ solubility of 1 g Fe/kg solution increases from ~8 to ~15 pct Na_2SO_4 as temperature

increases from 25° to 90° C, by estimation from figure 2. Likewise, to obtain the same iron solubility at high acidity requires 36 to 38 pct total Na_2SO_4 + H_2SO_4, ≥20 pct of which is H_2SO_4, at all temperatures. To summarize, iron removal as sideronatrite or ferrinatrite is effective for solutions with high Na_2SO_4 concentrations, preferably at temperatures 40° to 60° C. (Much of the Na_2SO_4

TABLE 2. - Densities of iron compounds

Compound	Source	Size,[1] μm	Bulk density of powder,[2] g/cm^3	Crystal density[3]	
				Calculated	Observed
Sideronatrite....	Preparation.......	ND	0.2-1.1	2.28	2.15-2.35
Ferrinatrite.....	Preparation.......	ND	≥.5	2.55	2.55-2.61
Sodium jarosite..	Preparation[4]......	1- 3	.8	3.26	3.18
Do.............	...do.............	10-20	1.6		
Hematite.........	Commercial reagent	≤1	1.0	5.26	5.26

ND Not determined.
[1]Range (diameter) of ≥80 pct of material, by SEM.
[2]Determined by measuring weight and volume of tamped powder samples.
[3]From references 3-4.
[4]$0.10M$ Na_2SO_4-$0.05M$ $Fe_2(SO_4)_3$, 60° C.

can be crystallized as $Na_2SO_4 \cdot 10H_2O$ by cooling the solutions if they contain little or no H_2SO_4; its solubility in water decreases to 8 pct at 10° C and 4 pct at 0° C (9).

The precipitation rates of sideronatrite and ferrinatrite are slow at 25° C; up to 2 days are required, depending on seed dosage. At 40° and 60° C, rates are much faster. The rates are much faster than for sodium jarosite precipitation. Quantitative kinetic studies were not conducted. The slow rates are attributed to the polymeric nature of the crystal structures of the two compounds (6-8).

Ferrinatrite precipitates as a dense granular solid which filters rapidly, comparable to jarosites. Sideronatrite precipitates as a fine-grained solid. If precipitated slowly, it filters fairly rapidly, though more slowly than ferrinatrite. If sideronatrite is precipitated rapidly, filtration is slower, but still much faster than gelatinous iron(III) hydrous oxide filtration. Concentrated sideronatrite slurries are viscous and possibly thixotropic. The bulk densities of the isolated, dried substances vary greatly, as shown in table 2, which also lists data for some other iron compounds for comparison.

SUMMARY

The solubilities of sideronatrite [$Na_2Fe(OH)(SO_4)_2 \cdot 3H_2O$] and ferrinatrite [$Na_3Fe(SO_4)_3 \cdot 3H_2O$] have been determined in the system Na_2SO_4-Fe_2O_3-H_2SO_4-H_2O at 25°, 40°, 60°, and 90° C. The solubilities were determined by seeding supersaturated solutions of known composition to precipitate the solid phase, followed by incremental addition of water during agitation at controlled temperature until the last remaining solid dissolved. The estimated accuracy of the data is 1 to 2 pct. The data show that the solid phase is sideronatrite at low acidity and ferrinatrite at high acidity. The relative change in solubilities with temperature over the 25° to 90° C range of the data is variable, ranging from ~3 to ~70 pct, and depends on solution Na^+-Fe^{3+} and H^+-SO_4^{2-} mol ratios.

Minimum iron solubilities occur in solutions saturated with Na_2SO_4. The maximum $Fe_2(SO_4)_3$ solubility in Na_2SO_4-saturated solutions is 1.48, 0.48, 0.53, and 0.76 pct at 25°, 40°, 60°, and 90° C, respectively, at corresponding H_2SO_4 concentrations of 3.9, 3.2, 3.6, and 4.0 pct. At all temperatures, the $Fe_2(SO_4)_3$ solubility decreases to <0.3 pct at lower and higher acidities.

The solubilities of sideronatrite and ferrinatrite are <0.36 pct $Fe_2(SO_4)_3$, or <1 g Fe/kg solution, at high Na_2SO_4 concentrations; therefore, industrial application for iron removal is limited to Na_2SO_4-rich solutions. In solutions containing no H_2SO_4, the minimum required Na_2SO_4 concentration is ~8 pct. In very acidic solutions, the total required Na_2SO_4 + H_2SO_4 is at least 36 to 38 pct, of which at least 20 pct is H_2SO_4. Sideronatrite or ferrinatrite can form from evaporating Na_2SO_4-containing acidic sulfate waste solutions or acid mine drainage.

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