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# SOLID AND AQUEOUS SPECIES OF SIGNIFICANCE FOR THE SITING OF A HIGH-LEVEL NUCLEAR WASTE REPOSITORY IN ROCK SALT: AN EVALUATION OF DATA NEEDS FOR LEAD, TIN, STRONTIUM, AND SELENIUM

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by

Kenneth L. Brubaker

Energy and Environmental Systems Division
Engineering Geosciences Group

June 1987

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## CONTENTS


ABSTRACT ..... 1

1 INTRODUCTION ..... 1

2 METHODOLOGY ..... 3

2.1 General Description ..... 3
2.2 Specific Procedures ..... 4

3 LEAD RESULTS ..... 8

3.1 Background ..... 8
3.2 Solid Species ..... 8
3.2.1 Data Errors ..... 8
3.2.2 Calculations ..... 17
3.2.3 Galena ..... 18
3.2.4 Phosphate Minerals ..... 22
3.2.5 Cumengeite ..... 25
3.2.6 Hydrocerrusite ..... 25
3.2.7 $(KPbCl_3)_3 \cdot H_2O$ and $KCl \cdot (PbCl_2)_2$ ..... 26
3.2.8 Recommendations for Further Study ..... 26
3.3 Aqueous Species ..... 32
3.3.1 Pb-Cl Complexes ..... 32
3.3.2 Pb-$CO_3$ Complexes ..... 43

4 TIN RESULTS ..... 48

4.1 Background ..... 48
4.2 Solid Species ..... 48
4.2.1 Cassiterite ..... 48
4.2.2 $SnSO_4$ ..... 55
4.2.3 Recommendations for Further Study ..... 55
4.3 Aqueous Species ..... 56

5 STRONTIUM RESULTS ..... 64

5.1 Background ..... 64
5.2 Solid Species ..... 64
5.2.1 Celestite ..... 64
5.2.2 Strontianite ..... 64
5.2.3 $Sr_3(PO_4)_2$ ..... 70
5.2.4 $Sr_2SiO_4$ ..... 70
5.2.5 Recommendations for Further Study ..... 70
5.3 Aqueous Species ..... 70

6 SELENIUM RESULTS ..... 76

6.1 Background ..... 76
6.2 Solid Species ..... 76
6.2.1 $MgSeO_3$ ..... 76
6.2.2 $CaSeO_3$ ..... 76

## CONTENTS (Cont'd)

6.2.3 $Fe_2(SeO_3)_3$ ..... 81
6.2.4 Recommendations for Further Study ..... 82
6.3 Aqueous Species ..... 82

REFERENCES ..... 87

## FIGURES

1 Methodology for Identification of Significant Solid and Aqueous Species ..... 4

2 Oxidation Potential-pH Diagram for Lead ..... 17

3 Calculated Solubilities of Selected Lead Compounds ..... 18

4 Comparison of Predicted and Observed Solubility for Galena in 3 m NaCl ..... 45

5 Oxidation Potential-pH Diagram for Tin ..... 55

6 Oxidation Potential-pH Diagram for Selenium ..... 81

## TABLES

1 Species Assumed to Be Present in Brine in Significant Amounts ..... 5

2 Assumptions Concerning the Composition of Standard Brine and the Thermodynamic Activities of Its Components ..... 6

3 Solid Species Containing Lead ..... 9

4 Aqueous Species Containing Lead ..... 15

5 Solids Containing Lead for Which Data Are Available ..... 19

6 Solubility of Galena at 25-30°C ..... 20

7 Solubility of Galena at Temperatures up to 100°C ..... 23

8 Solid Species Containing Lead for Which Data Are Not Available ..... 27

9 Aqueous Species Containing Lead for Which Data Are Available ..... 33

10 Aqueous Species Containing Lead for Which Data Are Not Available ..... 35

11 Computed Aqueous Speciation in Alkaline Solution ..... 36

## TABLES (Cont'd)


12 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 0.0 ..... 37

13 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 1.0 ..... 40

14 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 3.0 ..... 42

15 Reported Values of Lead-Chloride Stability Constants at Elevated Temperatures ..... 44

16 Reported Values of Lead-Carbonate Complex Stability Constants ..... 46

17 Solid Species Containing Tin ..... 49

18 Aqueous Species Containing Tin ..... 54

19 Solid Species Containing Tin for Which Data Are Available ..... 56

20 Solid Species Containing Tin for Which Data Are Not Available ..... 57

21 Aqueous Species Containing Tin for Which Data Are Available ..... 62

22 Aqueous Species Containing Tin for Which Data Are Not Available ..... 63

23 Solid Species Containing Strontium ..... 65

24 Aqueous Species Containing Strontium ..... 68

25 Solid Species Containing Strontium for Which Data Are Available ..... 69

26 Solid Species Containing Strontium for Which Data Are Not Available ..... 71

27 Aqueous Species Containing Strontium for Which Data Are Available ..... 73

28 Aqueous Species Containing Strontium for Which Data Are Not Available ..... 74

29 Solid Species Containing Selenium ..... 77

30 Aqueous Species Containing Selenium ..... 80

31 Solid Species Containing Selenium for Which Data Are Available ..... 82

32 Solid Species Containing Selenium for Which Data Are Not Available ..... 83

33 Aqueous Species Containing Selenium for Which Data Are Available ..... 85

34 Aqueous Species Containing Selenium for Which Data Are Not Available ..... 86

# SOLID AND AQUEOUS SPECIES OF SIGNIFICANCE FOR THE SITING OF A HIGH-LEVEL NUCLEAR WASTE REPOSITORY IN ROCK SALT: AN EVALUATION OF DATA NEEDS FOR LEAD, TIN, STRONTIUM, AND SELENIUM

by

Kenneth L. Brubaker

## ABSTRACT

The literature on the solubility of solids and the formation of aqueous complexes containing lead, tin, strontium, and selenium was surveyed for the purpose of identifying substances that are likely to limit the concentrations of these elements in brines associated with rock salt deposits. Initial lists of candidate solids were developed from the Nuclear Energy Agency and EQ3/6 thermodynamic data bases; *Chemical Abstracts* and a comprehensive list of known minerals were also used. The initial lists were then screened using solubility computations for those substances for which thermodynamic data were available. Qualitative criteria were used for those for which data were lacking. The potentially most limiting substances found were galena (PbS) and pyromorphite ($Pb_5(PO_4)_3Cl$) for lead, cassiterite ($SnO_2$) for tin, celestite ($SrSO_4$) for strontium, and the calcium and magnesium selenites ($CaSeO_3$ and $MgSeO_3$) for selenium. The well-known chloride complexes are the dominant aqueous species expected for lead in brines. Insufficient experimental data exist for the other three elements to assess with any confidence their likely speciation in brines, although chloride complexes would probably be important for tin and strontium.

## 1 INTRODUCTION

This report describes the methodology and presents the results of a survey of the literature concerning the solubility of solid substances containing lead, tin, strontium, and selenium, and the formation of aqueous complexes containing those elements. Radionuclides of these four elements are among those whose release from a repository for high-level nuclear waste may be of environmental concern. This literature survey was undertaken to identify relevant existing data and areas that require experimental investigation. Scientists at other research facilities are surveying the literature concerning other elements of concern.

The U.S. Department of Energy (DOE) is considering three candidate sites for a repository. The site in Deaf Smith County, Texas, consists of a thick deposit of bedded

salt. If the emplaced waste containers were to degrade and leak after a period of time, radionuclides might be transported away from the repository. Fluid inclusions or freely flowing brine might be the transport medium.

To evaluate such potentialities, information is required on the solubility of radionuclides of interest in brine. Thermodynamic data on solid substances containing certain elements and on aqueous species containing those elements are also required for computing the theoretical total concentration of each element in the fluid phase. The results of such computations could be used in arguments presented by DOE to the U.S. Nuclear Regulatory Commission as part of an application for a license to construct a repository. This report covers such thermodynamic data to a limited extent.

All projects related to the Deaf Smith County site are being managed for DOE's Salt Repository Project Office by the Office of Nuclear Waste Isolation, which is part of the Project Management Division of Battelle Memorial Institute in Columbus, Ohio.

# 2 METHODOLOGY

## 2.1 GENERAL DESCRIPTION

The original goal of the overall effort was to identify all solid substances containing elements of interest that might be sufficiently insoluble so that they would limit the extent to which an element would be present in brines near the Deaf Smith County candidate site. However, the technical literature concerning individual elements was so voluminous that a comprehensive search would have been too time consuming and expensive. After the work was underway, the decision was made to review only for substances in the Nuclear Energy Agency (NEA) and the EQ3/6 thermodynamic data bases.* These data bases were provided by Lawrence Berkeley National Laboratory and Lawrence Livermore National Laboratory.

Once lists of solid and aqueous species potentially important for repository siting had been produced, it was decided that all researchers involved in generating the final body of information would follow a reasonably uniform procedure (see Fig. 1). The two paths shown correspond to species for which solubility data or thermodynamic data from which solubilities could be estimated are or are not available. If such data were available, some type of objective and quantitative evaluation as to the importance of the given solid or aqueous species was made. The specific details of the evaluation in each case were left to the individual investigators. If data were not available, the solid substance was to be examined in light of the following five considerations and eliminated from further consideration if it met any one of them:

I Conditions for the stability of the mineral do not correspond to anticipated repository conditions.

II Solid species is highly soluble in brines.

III One compound is picked as being representative of a class of chemical compounds.

IV At least one constituent required for the formation of the solid or aqueous species is present at too low a concentration.

V Compounds containing two radionuclides contain at least two elements present at too low a concentration.

Slightly different criteria were used to cull the aqueous species.

---

*The EQ3/6 data base comprises computer codes developed at Lawrence Livermore National Laboratory to perform thermodynamic calculations for systems of geochemical interest.

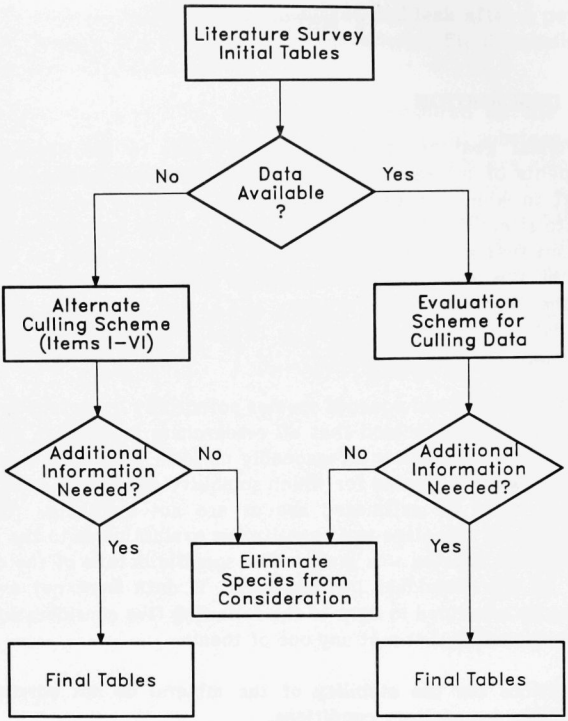


**FIGURE 1 Methodology for Identification of Significant Solid and Aqueous Species**

Two lists of potentially significant substances were produced in this way, one of solid species and one of aqueous species, for each branch of the flowchart. The literature was then surveyed in detail for each substance, and the need for additional experimental measurements was evaluated.

## 2.2 SPECIFIC PROCEDURES

Initial efforts were directed toward compiling comprehensive lists of solid and aqueous species and the associated *Chemical Abstracts* registry numbers. The sources used for preparing these lists were *Chemical Abstracts*, the NEA and EQ3/6 thermodynamic data bases, and a comprehensive list of minerals provided by the Office of Nuclear Waste Isolation. In preparing the initial lists, many substances were omitted. Some of these involved an oxidation state of the element of interest that is not expected to be present in aqueous solution under anticipated repository conditions (criterion I). Others contained an element or species not expected to be present in

repository brines in significant amounts (criterion IV). Indeed, many minerals were initially eliminated by this last consideration, but the example concerning cumengeite (Sec. 3.1) indicates that many of these may merit further investigation. The species assumed to be present in the brine in significant amounts are given in Table 1.

**TABLE 1 Species Assumed to Be Present in Brine in Significant Amounts**

| Major Anions | Major Cations |
|---|---|
| $Cl^{-1}$ | $Na^{+1}$ |
| $Br^{-1}$ | $K^{+1}$ |
| $OH^{-1}$ | $Ca^{+2}$ |
| $HCO_3^{-1}$, $CO_3^{-2}$ | $Mg^{+2}$ |
| $SO_4^{-2}$, $HSO_4^{-1}$ | |
| **Minor Anions** | **Minor Cations** |
| $F^{-1}$ | $Fe^{+2}$ |
| Silicate | $Fe^{+3}$ |
| $PO_4^{-3}$, etc. | $Al^{+3}$ |
| $HS^{-1}$, $S^{-2}$ | |
| Acetate | |
| Propionate | |
| n-Butyrate | |
| Isobutyrate | |
| n-Valerate | |

Source: Material handed out by the Office of Nuclear Waste Isolation at a meeting in October 1986.

For the purpose of quantitative evaluation, some specific assumptions were made about brine composition. Table 2 presents the assumed thermodynamic activities of major and minor standard brine species that were used to compute the solubility of various solid species in brine. Because no ionic strength effects were included in the computations, no effort was made to ensure charge neutrality in the assumed brine. In addition, the combined effects of pH and Eh could not be thoroughly investigated in a consistent way for each solid because of time and budget restrictions. The brine composition given in Table 2 is not intended to be consistent with any particular value for Eh; however, it does indicate the activities that were assumed in screening candidate solid substances. For example, the ratio of total sulfate to total sulfide is $1.75 \times 10^6$, which corresponds to an Eh value of approximately -0.26 V at a neutral pH. This value happens to correspond to a relatively reducing environment. In many calculations, however, a much more oxidizing environment was assumed, either explicitly or implicitly, and the presence of sulfide ion was essentially ignored.

The values in Table 2 are intended to represent nothing more than typical values. The silicate, phosphate, aluminum, copper, and iron activities represent extrapolations from the seawater values given in Horne (1969) and Stumm and Morgan (1981). The sulfide activity is representative of the amount of sulfide that would be in equilibrium with a gas-phase partial pressure of $1 \times 10^{-7}$ atm, an amount that would be noticeable to the human nose, but not toxic. The other values are representative of a brine intermediate in composition between a fluid inclusion brine and a dissolution brine.

**TABLE 2 Assumptions Concerning the Composition of Standard Brine and the Thermodynamic Activities of Its Components**

| Species | Activity × $10^3$ | p[activity] = $-\log_{10}$[activity] |
|---|---|---|
| Anions | | |
| $Cl^{-1}$ | 5660.0 | -0.753 |
| $Br^{-1}$ | 15.2 | 1.818 |
| Total carbonate | 0.250 | 3.602 |
| Total sulfate | 17.5 | 1.757 |
| $F^{-1}$ | 0.030 | 4.523 |
| Total silicate | 0.52 | 3.28 |
| Total phosphate | 0.013 | 4.89 |
| Total sulfide | 0.00001 | 8.00 |
| Cations | | |
| $Na^{+1}$ | 3180.0 | -0.502 |
| $K^{+1}$ | 135.0 | 0.870 |
| $Ca^{+2}$ | 203.0 | 0.693 |
| $Mg^{+2}$ | 1100.0 | -0.040 |
| $Al^{+3}$ | 0.015 | 4.82 |
| $Cu^{+2}$ | 0.0019 | 5.73 |
| Total iron | 0.0072 | 5.14 |

The solubilities were computed for all solid substances for which standard free energies of formation ($\Delta G_f^o$) were available and that contained only one radionuclide of interest plus assumed brine species. For this purpose, no distinction was made between the activity, molality, or molarity of a species in solution; all activity coefficients were implicitly equal to unity. Examination of the NEA data base in particular, but also of the set of volumes entitled *Critical Stability Constants* (Smith and Martell, 1976; Martell and Smith, 1977, 1982) showed that many aqueous complexes of lead, tin, and strontium are expected to be present and that complexes involving chloride ion might be of particular significance.

A computer program was written to compute aqueous equilibrium speciation and other relevant quantities (e.g., total dissolved lead) for the assumed brine. The required $\Delta G_f^o$ values were taken from the NEA and EQ3/6 data bases, as well as from other sources as needed. From the results of these computations, a list of "critical" substances was prepared, these substances being those that were found to be the most insoluble within the pH range of interest $3 \leq pH \leq 10$. The literature was then reviewed to determine the extent and quality of any existing solubility measurements for these substances. A

*Chemical Abstracts* computer search covering 1967 to the present was conducted for most of the critical substances; exceptions are noted in the discussion below. Solubility measurements were sought that covered part or all of the following experimental conditions:

1. $3 \leq pH \leq 10$.

2. Both oxidizing and reducing Eh, if relevant.

3. $25°C \leq$ temperature $\leq 100°C$.

4. $0 \leq$ ionic strength $\leq$ as high as possible.

The list of substances for which no data were available was examined with the five criteria given earlier in mind; substances meeting even one of these criteria were eliminated. Generally speaking, substances for which no thermodynamic data were available were also substances for which no solubility data were available. Solubility measurements represent one type of experiment from which thermodynamic data can be obtained. The substances for which no data were available, but which could not reasonably be eliminated, were not subjected to an intensive literature survey because of funding and time constraints.

A list of critical aqueous species was also prepared, simply by identifying those species expected from the computations to be present in the largest amounts under saturation conditions for the various critical solids. This list identifies those species that require the most accurate treatment in any theoretical solution model.

# 3 LEAD RESULTS

## 3.1 BACKGROUND

Tables 3 and 4 present the initial lists of solid and aqueous species containing lead and indicate if $\Delta G_f^o$ values are available or not. A total of 236 solid and 87 aqueous species are included.

Figure 2 is a simplified Eh-pH diagram for lead, showing only the dominant aqueous species in the absence of any additional ligands. For Eh values near the upper $H_2O$ stability limit, particularly in basic solution, Pb(IV) becomes thermodynamically stable, with the dominant species being $Pb(OH)_4^o$, based on the limited treatment of Baes and Mesmer (1976). Studies at Pacific Northwest Laboratory indicate that Eh values can substantially exceed the upper $H_2O$ stability limit in brines in contact with spent nuclear fuel (Pederson et al., 1985). The implication is that Pb(IV) solid and aqueous species may be important in a repository environment.

## 3.2 SOLID SPECIES

### 3.2.1 Data Errors

The primary source of the free energy data used in the solubility calculations was the NEA thermodynamic data base. In the NEA data base for lead, the following three solids are listed with their standard Gibbs free energies of formation: $Pb_2Cl(OH)_3$ (-1056.7 kJ/mol), PbClOH (laurionite, -480.3 kJ/mol), and PbClOH (paralaurionite, -391.2 kJ/mol). Calculations based on these values indicate that both $Pb_2Cl(OH)_3$ and laurionite are many orders of magnitude less soluble than galena (PbS), a mineral known for its extreme insolubility. However, paralaurionite is predicted to be rather soluble in the assumed brine. On general chemical grounds, all three substances would be expected to be rather soluble. Upon consulting the reference given in the NEA data base for $Pb_2Cl(OH)_3$, the value actually cited was -840.7 kJ/mol, a difference of 216 kJ/mol! When the correct value was used, $Pb_2Cl(OH)_3$ turned out to be as soluble as expected.

The case of laurionite is less straightforward. The reference given in the NEA data base (Naumov et al., 1974) gives the quoted value of -480.3 kJ/mol. Further investigation turned up a paper by Humphreys et al. (1980) in which a value cited in the 1968 National Bureau of Standards compilation of -408.3 kJ/mol is mentioned, with a remark that even this value is clearly too high. The authors state that any difference in $\Delta G_f^o$ between laurionite and paralaurionite would be so small as to make no apparent difference and that paralaurionite is appreciably soluble in aqueous solution. It seems likely that two digits were transposed in preparing Naumov et al. (1974), resulting in a value that is far too large. In the final computations, no distinction was made between laurionite (actually $PbCl_2 \cdot Pb(OH)_2$) and paralaurionite ($PbCl_2 \cdot PbO \cdot H_2O$), and both are soluble in the assumed brine.

**TABLE 3 Solid Species Containing Lead**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Pb | Yes (1) | |
| PbO | Yes (1) | Litharge |
| PbO | Yes (1) | Massicot |
| PbO | No | Hokutolite |
| PbO | Yes (1) | Crystalline |
| PbO·3H2O | No | |
| PbO2 | Yes (1) | Plattnerite |
| Pb2O3 | Yes (4) | |
| Pb3O4 | Yes (1) | Minium |
| Pb(OH)2 | Yes (1) | |
| PbO·Pb(OH)2 | Yes (4) | |
| Pb(OH)4 | No | |
| (PbO)3·H2O | Yes (1) | |
| Pb2O | No | |
| [PbO]4·[Pb(OH)2]2 | No | |
| [PbO]8·[Pb(OH)2]5·H2O | No | |
| PbFe4O7 | No | Plumboferrite |
| K2PbO3 | No | |
| Na2PbO3 | No | |
| Na2PbO2 | No | |
| K2PbO4 | No | |
| K2Pb3O7 | No | |
| K4PbO4 | No | |
| PbF | No | |
| PbF2 | Yes (1) | |
| PbF3 | No | |
| PbF4 | Yes (1) | |
| Pb3F8 | No | |
| KPbF3 | No | |
| NaPbF3 | No | |
| K2PbF6 | No | |
| PbCl | No | |
| PbCl2 | Yes (1) | Cotunnite |
| PbCl4 | No | |
| (KPbCl3)3·H2O | Yes (1) | |
| K2PbCl4 | No | |
| Na3PbCl5 | No | |
| CaPbCl6 | No | |
| K2PbCl6 | No | |
| Na2PbCl6 | No | |
| K4PbCl6 | No | |
| KPbCl3 | No | |
| NaPbCl3 | No | |
| KCl(PbCl2)2 | Yes (1) | |
| PbBr | No | |

**TABLE 3 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| PbBr2 | Yes (1) | |
| PbBr2·H2O | No | |
| PbBr4 | No | |
| KPbBr3 | No | |
| NaPbBr3 | No | |
| K2PbBr4 | No | |
| PbO·PbCl2 | No | |
| (PbO)2PbCl2 | Yes (4) | Mendipite |
| (PbO)3PbCl2 | No | |
| (PbO)6PbCl2 | No | |
| PbClOH [ PbCl2·Pb(OH)2 ] | Yes (1) | Laurionite |
| PbClOH [ PbCl2·PbO·H2O ] | Yes (1) | Paralaurionite |
| Pb2(OH)3Cl | Yes (1,4) | |
| [Pb(OH)2]3PbCl2 | No | |
| (PbO)7PbCL2 | No | Cassel yellow |
| PbO·PbBr2 | No | |
| (PbO)2PbBr2 | No | |
| (PbO)3PbBr2 | No | |
| PbFCl | Yes (1) | Matlockite |
| PbFBr | Yes (1) | |
| PbS | Yes (1) | Galena |
| PbS2 | No | |
| (PbS)3PbCl2 | No | |
| (PbO)3(PbS)3(PbCl2)2 | No | |
| PbS·Pb(OH)2 | No | |
| (PbS)2·(PbBr2)5 | No | |
| Pb(HS)2 | No | |
| PbSO4 | Yes (1) | Anglesite |
| Pb(SO4)2 | No | |
| (K,Na)Pb(SO4)2 | No | Palmierite |
| K2Pb(SO4)2 | Yes (1) | |
| K2Pb(SO4)3 | No | |
| Pb2(SO4)3 | No | |
| Pb(HSO4)2 | No | |
| PbO·PbSO4 | Yes (1) | Lanarkite |
| (PbO)2PbSO4 | Yes (1) | |
| (PbO)3PbSO4 | Yes (1) | |
| (PbO)3PbSO4·H2O | No | |
| (PbO)4PbSO4 | No | |
| Pb4SO4(OH)6 | Yes (4) | |
| Pb10SO4Cl2O8 | No | Sundiusite |
| Pb4SO4(OH)2O2 | No | |
| PbFe6(SO4)4(OH)12 | No | Plumbojarosite |
| Na3Pb2(SO4)3Cl | No | |
| PbCO3 | Yes (1) | Cerrusite |

**TABLE 3 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Pb3(CO3)2(OH)2 | Yes (1) | Hydrocerrusite |
| Pb10(CO3)6(OH)6O | Yes (1) | Plumbonacrite |
| PbCO3·PbCl2 | Yes (1) | Phosgeneite |
| PbO·PbCO3 | Yes (1) | |
| (PbO)2PbCO3 | Yes (1) | |
| PbO(PbCO3)2 | No | |
| Pb4SO4(CO3)2(OH)2 | Yes (4) | Leadhillite |
| NaPb2(CO3)2OH | Yes (4) | |
| Na2Pb3(CO3)3(OH)2 | No | |
| PbAl2(CO3)2(OH)4·H2O | Yes (1) | Dundasite |
| Pb(CO3)2 | No | |
| Pb-H3PO4 salts | | |
| (+2)(1:1) [ PbHPO4 ] | Yes (1) | |
| (+2)(2:1) [ Pb(H2PO4)2 ] | Yes (1) | |
| (+2)(2:3) [ Pb3(PO4)2 ] | Yes (1) | |
| (+4)(4:1) | No | |
| (+4)(6:1) | No | |
| (+4)(2:1)·H2O | No | |
| (+4)(2:1)·2H2O | No | |
| (+2)(+4) | No | |
| (+2)K(3:4:1) | No | |
| (+2)K(3:4:1)·4H2O | No | |
| (+2)Na(3:4:1) | No | |
| (+2)Na(3:4:1)·5H2O | No | |
| Pb10(PO4)6(OH)2 | Yes (4) | |
| Pb,K apatite | No | |
| Pb,Na apatite | No | |
| KPb3PO4(SO4)2 | No | |
| PbAl3(PO4)2(OH)5·H2O | Yes (4) | Plumbogummite |
| PbAl3PO4SO4(OH)6 | No | |
| PbFe3PO4SO4(OH)6 | Yes (4) | Corkite |
| Pb2ClPO4 | No | |
| Pb5Cl(PO4)3 | Yes (1) | Pyromorphite |
| Pb5F(PO4)3 | Yes (1) | |
| Pb5Br(PO4)3 | Yes (1) | |
| Pb5(OH)(PO4)3 | Yes (1) | Hydoxypyromorphite |
| PbO·Pb3(PO4)2 | Yes (1) | |
| (PbO)5Pb3(PO4)2 | No | |
| PbO·[Pb3(PO4)2]3 | No | |
| Pb(H2PO4)2SO4 | No | |
| PbSiO3 | Yes (1) | Alamosite |
| Pb-H2SiO4 salts | | |
| (+2)(1:1) | No | |
| (+2)K(1:1:2) | No | |
| Pb(+2)-H6SiO5 salt | No | |

**TABLE 3 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Pb4OSiO4SO4 | No | |
| Pb6O(SiO4)2SO4 | No | |
| Na3Pb(AlSiO4)3SO4 | No | |
| Pb4SiO6 | No | |
| (PbO)2SiO2 | Yes (1) | |
| Pb2SiO4 | Yes (1) | |
| Pb2Si2O7 | No | |
| (PbO)4SiO4 | No | |
| Pb5Si4O8(OH)10 | No | Plumbotsumite |
| Pb2Fe2O(SiO4)2 | No | Melanotekite |
| Pb(Ac)2 | No | |
| Pb(Ac)2·3H2O | No | |
| Pb(Ac)2·10H2O | No | |
| PbAc4 | No | |
| Pb(Pr)2 | No | |
| Pb(Pr)4 | No | |
| Pb(n-Bu)2 | No | |
| Pb(n-Bu)4 | No | |
| PbSnO3 | No | |
| Pb2SnO3 | No | |
| Pb3SnO4 | No | |
| Pb6SnO7 | No | |
| PbSnS2 | No | Teallite |
| PbSnS3 | No | |
| PbSnF4 | No | |
| Pb-H2SeO3 salts | | |
| (+2)(1:1) | No | |
| (+4)(2:1) | No | |
| (+4)K(3:1:2) | No | |
| PbSeO3 | No | Molybdomenite |
| PbSeO4 | No | Kerstenite |
| PbSe | No | Clausthalite |
| Pb2Se2 | No | |
| PbSrO3 | No | |
| PbSr2O4 | No | |
| Pb2SrO5 | No | |
| Pb(Cu,Fe,Al)3(SO4)2(OH)6 | No | Beaverite |
| Cu10(Fe,Pb)S6 | No | Betekhtinite |
| Pb2Cl(O,OH)2 | No | Blixite |
| Pb5Cu2CO3(SO4)3(OH)6 | Yes (4) | Caledonite |
| Pb3CuCl(OH)2O2 | Yes (4) | Chloroxiphite |
| Pb2Cu2Fe2Si5O17·6H2O | No | Creaseyite |
| PbCuCl2(OH)2 | No | Cumengeite |
| Pb19Cu24Cl42(OH)44 | Yes (4) | Also cumengeite |
| Pb2U5O17·4H2O | No | Curite |

**TABLE 3 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| $Pb(UO_2)_2(PO_4)_2 \cdot 3H_2O$ | No | |
| $Pb_2CuCl_2(OH)_4$ | Yes (4) | Diaboleite |
| $Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot H_2O$ | Yes (4) | Dewindtite |
| $Pb_2(Fe,Al)(PO_4)_2OH \cdot H_2O$ | No | Drugmanite |
| $Pb_2(UO_2)_3(PO_4)_2(OH)_4 \cdot 3H_2O$ | Yes (4) | Dumontite |
| $(Th,U)(Ca,Fe,Pb)_2Si_8O_{20}$ | No | Ekanite |
| $PbU_4O_{13} \cdot 4H_2O$ | No | Fourmarierite |
| $Pb_6Ca_4Si_6O_{21}(OH)_2$ | No | Ganomalite |
| $Pb_4Fe_3O_8(OH,Cl)$ | No | Hematophanite |
| $PbAl_3PO_4SO_4(OH)_6$ | Yes (4) | Hinsdalite |
| $Pb_3F_3Si_3O_{10}(OH,Cl)$ | No | Jagoite |
| $PbUO_2SiO_4 \cdot H_2O$ | No | Kasolite |
| $PbCuSO_4(OH)_2$ | Yes (4) | Linarite |
| $PbCuAl_2(SO_4)_2(OH)_6$ | No | Osarizamaite |
| $Pb_2UO_2(PO_4)_2 \cdot 2H_2O$ | Yes (4) | Parsonsite |
| $Pb_2UO_2(PO_4)_2$ | No | Anhydrous parsonsite |
| $Pb(UO_2)_2(PO_4)_2 \cdot 4H_2O$ | Yes (4) | Przhevalskite |
| $Pb(UO_2)_2(PO_4)_2$ | No | Anhydrous przhevalskite |
| $Pb_5Cu_4Cl_{10}(OH)_8 \cdot 2H_2O$ | No | Pseudoboleite |
| $Pb(UO_2)_4(PO_4)_2OH \cdot 7H_2O$ | Yes (4) | Renardite |
| $(Pb,Cu)_2SeO_4(OH)_2$ | No | Schmeiderite |
| $Pb_6(IO_3)_2Cl_4O_2(OH)_2$ | No | Schwartzembergite |
| $Pb(Pb,Ca)(Al,Fe,Mg)_2 - (Si,Al)_4O_{10}(OH)_2(CO_3)_2$ | No | Surite |
| $Pb_2CuPO_4SO_4OH$ | Yes (4) | Tsumebite |
| $PbU_7O_{22} \cdot 12H_2O$ | No | Vandendriesscheite |
| $Pb_3CaAl_2Si_{10}O_{24}(OH)_6$ | No | Wickenburgite |
| $Pb_2UO_2(CO_3)_3$ | No | Widenmannite |
| $(Pb,Ca)U_2O_7 \cdot 2H_2O$ | No | Woelsendorfite |
| $Cu_4Pb_2SO_4Cl_6(OH)_4 \cdot 2H_2O$ | No | Arzrunite |
| $Na_3Pb_2(SO_4)_3Cl$ | No | Caracolite |
| $(Na,Ca,Pb)_2U_2(O,OH)_7$ | No | Clarkeite |
| $Pb_2Cu_5(UO_2)_2(SeO_3)_6(OH)_6 \cdot 2H_2O$ | No | Demesmaekerite |
| $Pb_4CuSO_4(OH)_8$ | No | Elyite |
| $(Th,Pb)_{(1-x)}Al_3(PO_4,SiO_4)_2(OH)_6$ | No | Eylettersite |
| $Pb_3Cl_4(OH)_2$ | No | Fiedlerite |
| $(Th,Pb,Ca)PO_4 \cdot H_2O$ | No | Grayite |
| $(Pb,Ca,Sr)_2(Al,Fe)_3(SiO_4)_3OH$ | No | Hancockite |
| $(Th,Ca,Pb)H_2(UO_2)_4(PO_4)_2(OH)_8 \cdot 7H_2O$ | No | Kivuite |
| $Pb_7O_6Cl_2$ | No | Lorettoite |
| $(Sr,Pb)Fe_3(PO_4)_2(OH)_5 \cdot H_2O$ | No | Lusungite |
| $PbU_7O_{22} \cdot nH_2O$ ($n<12$) | No | Metavandendriesscheite |
| $Pb_2Mg_2Si_2O_7(OH)_2$ | No | Molybdophyllite |
| $PbSn_4S_5$ | No | Montesite |

**TABLE 3 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| PbCu6(O,Cl,Br)8 | No | Murdochite |
| Pb6ca4Si6O21Cl2 | No | Nasonite |
| Pb2(SeO4)SO4 | No | Olsacherite |
| Pb3(UO2)3(Si2O7)2·6H2O | No | Orlite |
| H6Pb10Al2O(PO4)12(SO4)5(OH)40·11H2O | No | Orpheite |
| Pb2Cl3OH | No | Penfieldite |
| PbCuCl2(OH)2 | No | Percylite |
| Pb4Al2(SiO2)7 | No | Plumalsite |
| (U and Pb) oxide | No | Richetite |
| Pb2Ca7Si6O14(OH)10(SO4)2 | No | Roeblingite |
| hydrous (Pb,Cu,Al) | No | Rosieresite |
| Pb3Ca6Cu2(CO3)8(OH)6·6H2O | No | Schuilingite |
| Pb2SO4(CO3)2(OH)2 | No | Susannite |
| (Ca,Pb)CO3 | No | Tarnowitzite |
| Pb4CuCO3(SO4)2(Cl,OH)2O | Yes (4) | Wherryite |

[a]1 = NEA data base and 4 = other sources.

**TABLE 4 Aqueous Species Containing Lead**

| Aqueous Species | Data Available[a] | Comment |
|---|---|---|
| Pb(+2) | Yes (1) | |
| Pb(+4) | Yes (4) | |
| PbO2(-2) | No | |
| PbO3(-2) | No | |
| PbOH(+1) | Yes (1,4) | |
| Pb(OH)2 | Yes (1,4) | |
| Pb(OH)3(-1) | Yes (1,4) | |
| Pb(OH)4(-2) | Yes (1) | No reference[b] |
| Pb2OH(+3) | Yes (1,4) | |
| Pb2(OH)3(+1) | No | |
| Pb3(OH)4(+2) | Yes (1,4) | |
| Pb3(OH)5(+1) | Yes (1) | No reference |
| Pb4(OH)4(+4) | Yes (1,4) | |
| Pb6(OH)8(+4) | Yes (1,4) | |
| Pb(OH)4 | Yes (4) | |
| Pb(OH)3(+1) | Yes (4) | |
| Pb(OH)6(-2) | Yes (4) | |
| PbF(+1) | Yes (1) | |
| PbF2 | Yes (1) | |
| PbF3(-1) | Yes (1) | No reference |
| PbF4(-2) | Yes (1) | No reference |
| PbF6(-6) | No | |
| PbF6(-2) | No | |
| Pb3F7(-1) | No | |
| PbCl(+1) | Yes (1) | |
| PbCl2 | Yes (1) | |
| PbCl3(-1) | Yes (1) | |
| PbCl4(-2) | Yes (1) | |
| PbCl5(-3) | No | |
| PbCl6(-4) | Yes (4) | |
| PbCl6(-2) | No | |
| PbBr(+1) | Yes (1) | |
| PbBr2 | Yes (1) | |
| PbBr3(-1) | Yes (1) | |
| PbBr4(-2) | Yes (1) | |
| PbBr5(-3) | Yes (4) | |
| PbBr6(-4) | No | |
| PbBrCl | Yes (1) | |
| PbBr6(-2) | No | |
| Pb2Br(+3) | Yes (1) | |
| PbBr2Cl(-1) | Yes (1) | |
| PbBr3Cl(-2) | Yes (1) | |
| PbBr4Cl(-3) | Yes (1) | |
| PbBrCl2(-1) | Yes (1) | |
| PbBr2Cl2(-2) | Yes (1) | |

**TABLE 4 (Cont'd)**

| Aqueous Species | Data Available[a] | Comment |
|---|---|---|
| PbBr3Cl2(-3) | Yes (1) | |
| PbBrCl3(-2) | Yes (1) | |
| PbSO4 | Yes (4) | |
| Pb(SO4)2(-2) | Yes (4) | |
| Pb(SO4)3(-4) | Yes (1) | No reference |
| Pb(SO4)4(-6) | Yes (1) | No reference |
| PbHS3(-1) | No | |
| Pb(HS)2 | Yes (4) | |
| Pb(HS)3(-1) | Yes (1) | |
| PbPO4(-1) | Yes (1) | No reference |
| Pb(PO4)2(-4) | Yes (1) | No reference |
| Pb(PO4)3(-7) | Yes (1) | No reference |
| Pb(PO4)4(-10) | Yes (1) | No reference |
| PbHPO4 | Yes (1) | |
| Pb(HPO4)2(-2) | Yes (1) | No reference |
| Pb(HPO4)3(-4) | Yes (1) | No reference |
| Pb(HPO4)4(-6) | Yes (1) | No reference |
| PbH2PO4(+1) | Yes (1) | |
| Pb(H2PO4)2 | Yes (1) | No reference |
| Pb(H2PO4)3(-1) | Yes (1) | No reference |
| Pb(H2PO4)4(-2) | Yes (1) | No reference |
| PbP2O7(-2) | Yes (1) | |
| Pb(P2O7)2(-6) | Yes (1) | |
| PbCO3 | Yes (1) | No reference |
| Pb(CO3)2(-2) | Yes (4) | |
| Pb(CO3)3(-4) | Yes (1) | No reference |
| Pb(CO3)4(-6) | Yes (1) | No reference |
| PbHCO3(+1) | Yes (1) | No reference |
| Pb(HCO3)2 | Yes (1) | No reference |
| Pb(HCO3)3(-1) | Yes (1) | No reference |
| Pb(HCO3)4(-2) | Yes (1) | No reference |
| Pb(acetate)(+1) | Yes (1) | |
| Pb(acetate)2 | Yes (1) | |
| [Sn(x)Pb(9-x)](-4) | No | x = 1 to 8 |
| Pb-H2SeO3 complex | No | |

[a]1 = NEA data base and 4 = other sources.

[b]Indicates that the data cannot be traced back to the original source.

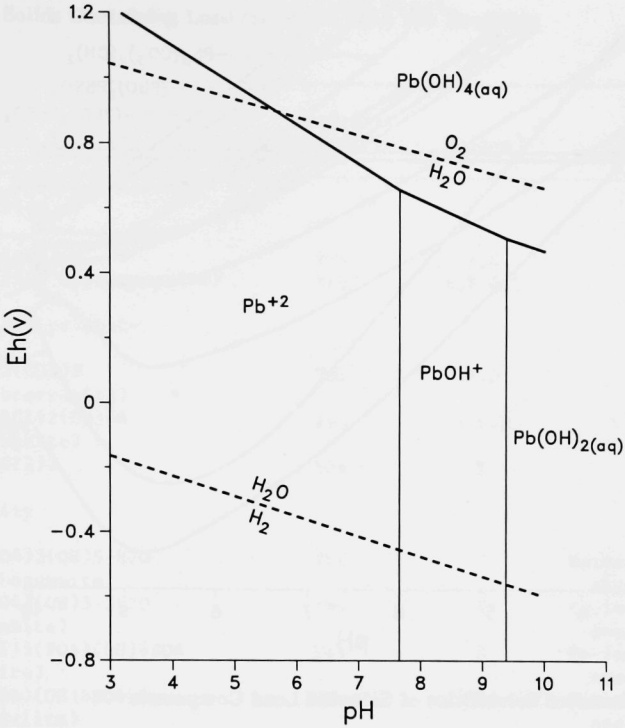


**FIGURE 2 Oxidation Potential-pH Diagram for Lead**

### 3.2.2 Calculations

Figure 3 shows the results of the solubility calculations for several Pb(II) solids. Galena and several phosphate minerals are predicted to be potentially limiting substances for lead. In addition, the mineral cumengeite, $Pb_{19}Cu_{24}Cl_{42}(OH)_{44}$, appears to be nearly as insoluble as galena under repository conditions. (The total Cu[II] concentration was assumed to be $1.9 \times 10^{-6}$ M, based on a rough extrapolation from seawater.) Other minerals of this type may also be potentially important. Because trace metals like copper are not expected to be present in the brine in large amounts, minerals like cumengeite that require such a trace metal for their formation were screened out of the lists of candidate solids before the computations were made. This step is in accordance with the agreed-upon procedure. It is entirely fortuitous that a calculation was made for cumengeite at all. The conclusion is that minerals may well exist that would limit the solubility of lead (and tin, strontium, and selenium) in brine to a greater extent than do those substances that have been identified. In most cases, only estimated free energies of formation exist, and actual solubility data are rare. Table 5 presents a list of critical solids for lead, based on these calculations.

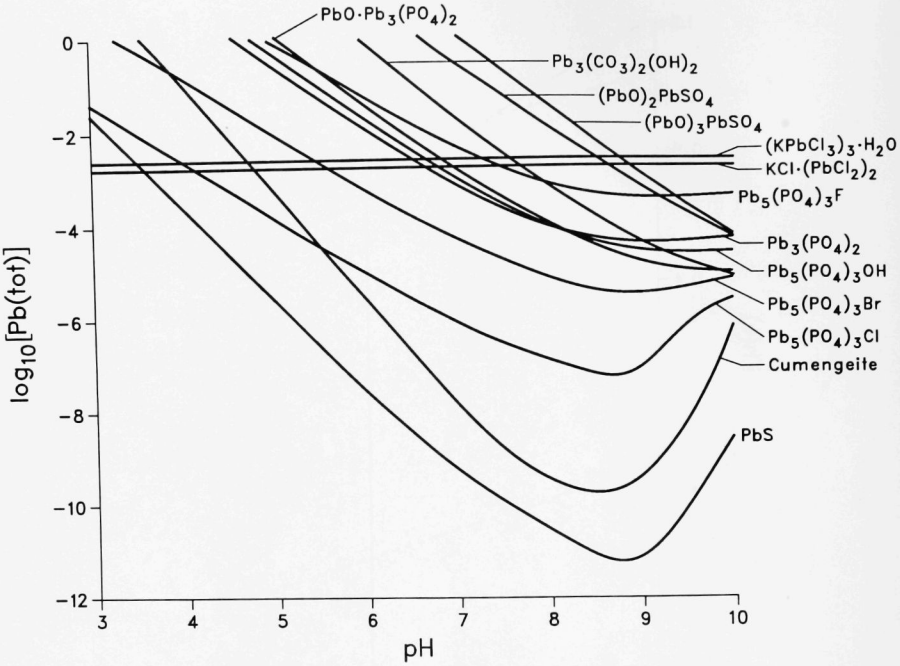


**FIGURE 3 Calculated Solubilities of Selected Lead Compounds**

### 3.2.3 Galena (PbS)

Even though several studies have been published on the solubility of galena under various conditions, the range of experimental conditions does not cover the desired ranges of ionic strength, temperature, and pH. In particular, even though data exist for concentrations as high as 3 M NaCl at temperatures up to and exceeding 100°C, no solubility data exist for highly concentrated brines like inclusion brines. In acidic brines, the data are reasonably consistent; however, at near-neutral to basic pH, the available data are somewhat contradictory. New measurements are needed.

The recent measurements at 25-30°C are summarized in Table 6. Hemley (1953) and Anderson (1962) reference earlier work that is not discussed here. Most experiments involved high sulfide concentrations, which were achieved either by adding significant amounts of NaHS solution or by using $H_2S$ gas. The PbS was precipitated from a solution of either $PbCl_2$ or $Pb(NO_3)_2$. In several cases, the authors report approaching equilibrium from below, using natural or synthetic galena, with results that were equivalent to those obtained from precipitated samples. The only study reported in Table 6 that did not involve adding sulfide in excess of the amounts arising from the dissolution

**TABLE 5 Solids Containing Lead for Which Data Are Available**

| Solid Species | Need for Further Study | Reason[a] | Comment |
|---|---|---|---|
| High priority | | | |
| PbS (galena) | Yes | A,C | |
| Pb5(PO4)3Cl (pyromorphite) | Yes | A,B,C,D | |
| Intermediate priority | | | |
| Pb3(OH)2(CO3)2 (hydrocerrusite) | Yes | A,D | |
| Pb19Cu24Cl42(OH)44 (cumengeite) | Yes | A,B,D | |
| NaCl(PbCl2)2 | Yes | E | |
| Low priority | | | |
| PbAl3(PO4)2(OH)5·H2O (plumbogummite) | Yes | E | Estimated free energy |
| Pb2Cu(PO4)(OH)3·3H2O (tsumebite) | Yes | E | Estimated free energy |
| PbFe(III)3(PO4)(OH)6SO4 (corkite) | Yes | E | Estimated free energy |
| PbAl3(PO4)(OH)6SO4 (hinsdalite) | Yes | E | Estimated free energy |

[a]A = available solubility data do not cover the necessary range of experimental conditions; B = experimental procedures are deficient in some respect (e.g., equilibrium from both undersaturation and oversaturation is not demonstrated); C = available solubility data are anomalous or contradictory; D = only one solubility study exists (no independent confirmation available); and E = no solubility data are known to exist.

**TABLE 6 Solubility of Galena (PbS) at 25-30°C**

| Reference | pH | $I^a$ (Medium) | Solubility | Comment |
|---|---|---|---|---|
| Hemley (1953) | 1-6 | 0.1 (NaCl) | $(1.5 \pm 0.5) \times 10^{-8}$ M | 25°C; saturated $H_2S$ solution; value read from figure |
| | 7 | ~0.1 ($Na^+$, $HS^-$) | $(3.8 \pm 0.7) \times 10^{-8}$ M | 25°C; saturated $H_2S$ solution; value read from figure |
| | 8 | ~1 ($Na^+$, $HS^-$) | $(5.0 \pm 0.4) \times 10^{-8}$ M | 25°C; saturated $H_2S$ solution; value read from figure |
| Anderson (1962) | 2.6-2.9 | (no NaCl) | $(6.3$ to $16) \times 10^{-9}$ M | 30°C; saturated $H_2S$; value read from figure |
| | 4.6 | (0.11 M NaCl) | $1.6 \times 10^{-8}$ M | 30°C; saturated $H_2S$; value read from figure |
| | 7.9 | (0.20 M NaCl) | $8 \times 10^{-8}$ M | 30°C; saturated $H_2S$; value read from figure |
| Nriagu (1971a) | 1.8 | 3.0 (HCl, NaCl) | $3.5 \times 10^{-4}$ m | 28°C; values taken from author's Fig. 1; more values are reported than are shown here; no excess sulfide added; sulfide not measured |
| | 2.6 | 3.0 (HCl, NaCl) | $7.1 \times 10^{-5}$ m | |
| | 4.1 | 3.0 (HCl, NaCl) | $2.0 \times 10^{-6}$ m | |
| Hamann and Anderson (1978) | 6.5 | 3.1 (3.0 m NaCl) | 23 ± 7 ppb | 25°C; $1.2 \times 10^{-7}$ M; saturated $H_2S$ solutions |
| | 7.0 | 3.0 (2.7 m NaCl) | <100 ppb | $<5.4 \times 10^{-7}$ M; saturated $H_2S$ solutions |
| | 9.7 | 3.0 (3.0 m NaCl) | 9 ± 2 ppb | $5 \times 10^{-8}$ M; saturated $H_2S$ solutions |

**TABLE 6 (Cont'd)**

| Reference | pH | I[a] (Medium) | Solubility | Comment |
|---|---|---|---|---|
| Giordano and Barnes (1979) | ~7 | >1 (NaHS) | 250 ppb ±180 ppb | 27-33°C; 250 ppb = $1.4 \times 10^{-6}$ [NaHS] = 1.0 m; varying $P(H_2S)$; no NaCl |
| Barrett and Anderson (1982) | ~1 | 3 m NaCl | $\sim 8 \times 10^{-6}$ m | 27°C; saturated $H_2S$ solutions; mean value of log (Pb) = -5.10 ± 0.30 (five values) |

[a]Ionic strength.

of solid PbS is that of Nriagu (1971a). His results are of limited usefulness because the dissolved sulfide in the solutions was not measured.

The results of Hemley (1953) and Anderson (1962) are in good agreement. Both authors show that, in saturated $H_2S$ solution, the solubility curve of PbS is flat up to pH values near neutral, with a slight increase in solubility in slightly alkaline solutions. They attribute this behavior to formation of lead-hydrosulfide complexes, although the exact nature of those complexes remained a matter for debate. Hemley added 0.1 M chloride to his experimental solutions and allowed for formation of $PbCl^+$ by using the stability constant value of Garrels and Gucker (1949). Anderson added up to 0.2 M NaCl to his runs at pH 4.6 and 7.9 in order to flocculate the PbS precipitate, but made no allowance for $PbCl^+$.

Nriagu (1971a) studied the solubility of galena in 3 m NaCl at several temperatures. In all cases, a linear dependence of log[Pb] on pH was found, with slopes near the expected value of -1.0. Nriagu's values at 28°C are considerably higher than those of Hemley and Anderson, presumably because of the formation of lead-chloride complexes. Because Nriagu did not measure or otherwise determine the sulfide content of his solutions, his data are of limited usefulness.

The other studies shown in Table 6 were undertaken primarily to examine the solubility of galena at elevated temperatures, and the values shown represent the few measurements taken at lower temperatures. These values should not be compared, either with each other or with the others shown, because the experimental conditions were not comparable.

The available data at temperatures up to 100°C are summarized in Table 7. The studies of Nriagu (1971a) and Giordano and Barnes (1979) also involved temperatures in excess of those shown in Table 6. Some of the data seem consistent. The data of Nriagu (1971b) at 90°C and 3 m NaCl are consistent with those of Barrett and Anderson (1982) at 95°C. However, the measurement of Hamann and Anderson (1978) at 90°C in 3 m NaCl at pH = 3.7-4.7 is about an order of magnitude lower than that of Nriagu (1971b) under the same conditions, although the sulfide content was different. Also, Barrett and Anderson (1982) found a much larger increase in solubility in going from 1 m NaCl to 3 m NaCl at 80°C than does Nriagu (1971b) at 90°C. Other comparisons are less direct, basically because of differences in experimental conditions. Systematic study is clearly needed.

### 3.2.4 Phosphate Minerals

Five lead-phosphate minerals have been identified as potentially limiting substances. One of them, $Pb_5(PO_4)_3Cl$ (pyromorphite), appears in Fig. 3. In addition, four other minerals have been identified based on limited calculations using $\Delta G_f^o$ values estimated by Nriagu (1984): plumbogummite, tsumebite, corkite, and hinsdalite. The four additional lead-phosphate solids shown in Fig. 3, $Pb_5(PO_4)_3F$, $Pb_5(PO_4)_3Br$, $Pb_3(PO_4)_2$, and $PbO \cdot Pb_3(PO_4)_2$, are not considered further because, in the presence of concentrated NaCl brine, all are expected to be converted to pyromorphite. The

**TABLE 7 Solubility of Galena (PbS) at Temperatures up to 100°C**

| Reference | Temp. (°C) | Solubility | Comment |
|---|---|---|---|
| Anderson (1962) | 50 | 3.7 ± 0.2 ppb | $1.8 \times 10^{-8}$ M; saturated $H_2S$ solution; pH - 2.8; 1 atmosphere |
| | 70 | 4.6 ± 0.7 ppb | $2.2 \times 10^{-8}$ M; saturated $H_2S$ solution; pH - 2.8; 1 atmosphere |
| | 90 | 1.7 ± 0.3 ppb | $8.2 \times 10^{-9}$ M; saturated $H_2S$ solution; pH - 2.8; 1 atmosphere |
| Nriagu (1971a) | 60 | $1.6 \times 10^{-3}$ m | pH = 2 (values read from author's Fig. 1; values shown |
| | | $1.8 \times 10^{-4}$ m | pH = 3 correspond to 3.0 m NaCl solutions to which no |
| | | $1.6 \times 10^{-5}$ m | pH = 4 excess sulfide was added) |
| | 90 | $5.0 \times 10^{-4}$ m | pH = 3 |
| | | $5.6 \times 10^{-5}$ m | pH = 4 |
| | 120 | $1.0 \times 10^{-2}$ m | pH = 2 |
| | | $1.3 \times 10^{-3}$ m | pH = 3 |
| | | $1.6 \times 10^{-4}$ m | pH = 4 |
| Nriagu (1971b) | 90 | 30.9 ppm | $1.5 \times 10^{-4}$ M; 1.0 m NaCl; pH = 2.0 (values in satu- |
| | | 0.25 ppm | $1.3 \times 10^{-6}$ M; 1.0 m NaCl; pH = 3.1 rated $H_2S$ solu- |
| | | 0.17 ppm | $8.5 \times 10^{-7}$ M; 1.0 m NaCl; $3.75 \leq pH \leq 5.9$ tion at 1 atmo- |
| | | 0.31 ppm | $1.6 \times 10^{-6}$ M; 1.0 m NaCl; pH = 6.5 sphere; data |
| | | 62.0 ppm | $3.3 \times 10^{-4}$ M; 3.0 m NaCl; pH = 2.0 selected from a |
| | | 0.25 ppm | $1.3 \times 10^{-6}$ M; 3.0 m NaCl; pH = 3.2 more extensive |
| | | 0.11 ppm | $5.9 \times 10^{-7}$ M; 3.0 m NaCl; $3.5 \leq pH \leq 6.25$ list) |
| | | 0.29 ppm | $1.6 \times 10^{-6}$ M; 3.0 m NaCl; pH = 6.7 |
| Hamann and Anderson (1978) | 90 | 14 ± 10 ppb | $7.5 \times 10^{-8}$ M; 3.0 m NaCl; pH = 3.7-4.7; 0.008 m sulfide |
| | | a | a 3.0 m NaCl; pH = 6.1-6.7; 0.008 m sulfide |
| | | 4 ± 3 ppb | $2.0 \times 10^{-8}$ M; 1.0 m NaCl; pH = 3.4; 0.01 m sulfide |
| | | 27 ± 19 ppb | $1.4 \times 10^{-7}$ M; 1.0 m NaCl; pH = 4.8; 0.01 m sulfide |
| | | a | a 1.0 m NaCl; pH = 5.4; 0.01 m sulfide |
| | | a | a 0.7 m NaCl; pH = 7.7; I = 1.0 |

**TABLE 7 (Cont'd)**

| Reference | Temp. (°C) | Solubility | Comment |
|---|---|---|---|
| Giordano and Barnes (1979) | 50 | 0.06-2.43 ppm | [NaHS] = 0 to 2.85 m; $P(H_2S)$ = 0.6-30.2 atm; no pH measurements reported; no NaCl added |
| | 100 | 0.13-6.80 ppm | [NaHS] = 0 to 2.85 m; $P(H_2S)$ = 1.5-63.9 atm. No pH measurements reported; no NaCl added |
| Barrett and Anderson (1982) | 60 | $2.5 \times 10^{-5}$ m | pH = 1.0; 3 m NaCl (measurements in saturated $H_2S$ solution at 1 atmosphere; authors report log (solubility), with an estimated error of ± 0.2 log units) |
| | 80 | $1.5 \times 10^{-4}$ m | pH = 0.8; 1 m NaCl |
| | | $5.0 \times 10^{-5}$ m | pH = 1.1; 1 m NaCl |
| | | $1.1 \times 10^{-5}$ m | pH = 1.3; 1 m NaCl |
| | | $4.8 \times 10^{-6}$ m | pH = 1.6; 1 m NaCl |
| | | $3.4 \times 10^{-4}$ m | pH = 1.0; 2 m NaCl |
| | | $4.2 \times 10^{-4}$ m | pH = 1.4; 2 m NaCl |
| | | $9.1 \times 10^{-4}$ m | pH = 1.0; 3 m NaCl |
| | | $3.8 \times 10^{-4}$ m | pH = 1.2; 3 m NaCl |
| | | $1.4 \times 10^{-4}$ m | pH = 1.4; 3 m NaCl |
| | | $7.3 \times 10^{-5}$ m | pH = 1.6; 3 m NaCl |
| | | $1.9 \times 10^{-5}$ m | pH = 2.0; 3 m NaCl |
| | 95 | $1.2 \times 10^{-3}$ m | pH = 1.6; 3 m NaCl |
| | | $3.7 \times 10^{-4}$ m | pH = 1.7; 3 m NaCl |
| | | $2.3 \times 10^{-4}$ m | pH = 2.0; 3 m NaCl |
| | | $1.0 \times 10^{-4}$ m | pH = 2.2; 3 m NaCl |
| | | $3.0 \times 10^{-5}$ m | pH = 2.5; 3 m NaCl |

[a]Below detection limit.

possibility of formation of solid solutions involving fluoro-, bromo-, and chloropyromorphite, as well as possibly the calcium analogs, is not considered further.

Most of the experimental work on these substances was done by Nriagu (1972, 1973a,b, 1974); otherwise, the literature is very sparse. In most instances, Nriagu made no direct solubility measurements, but rather determined $\Delta G_f^o$ from equilibration or interconversion experiments. For example, he showed that in NaCl brine (0.1 M), $PbHPO_4$ is converted to pyromorphite, stating that $Pb_3(PO_4)_2$ is also unstable with respect to pyromorphite under these conditions. This statement is in agreement with Jowett and Price (1932). Given Nriagu's estimate for $\Delta G_f^o$ of $PbO \cdot Pb_3(PO_4)_2$, this substance would also be unstable. Unfortunately, Nriagu's results often disagree with those of other workers. For example, he reports $pK_{sp}$ (pyromorphite) as 84.4 (Nriagu, 1973a), whereas Jowett and Price (1932) report it as 79.1, and reports $\Delta G_f^o$ (pyromorphite) as -3792 kJ/mol, whereas Baker (1964) reports it as -3526 kJ/mol. Because pyromorphite is predicted to be the dominant lead-phosphate mineral, it certainly merits further investigation. No direct solubility measurements are available.

Nriagu often estimates $\Delta G_f^o$ of substances that he has not studied experimentally, but his estimation procedures in several cases appear questionable. The uncertainty involved in Nriagu's estimates of $\Delta G_f^o$ can be illustrated by the case of hinsdalite. Baker's (1964) experimental value of -4673 kJ/mol can be compared with Nriagu's estimated value of -5724 kJ/mol. A recalculation from Baker's analytical data yielded values of $pK_{sp}$ and $\Delta G_f^o$ close to those reported by him. Nriagu (1984) provides no details on his estimation method, and the references cited provide insufficient details to check his calculations. Baker's value was discovered as this report was being written, and no solubility calculations have been made using it. If this discrepancy is not simply a typographical error, the huge difference in the two $\Delta G_f^o$ values would have a very large effect on the potential of hinsdalite to limit lead concentrations in brines.

### 3.2.5 Cumengeite

The only data available are the solubility measurements of Humphreys et al. (1980), which were taken at 25°C. Very few experimental details are given in support of the reported free energy ($\Delta G_f^o$ = -15,163 ∓ 20 kJ/mol). Neither the final pH nor the chloride ion concentration is reported. This free energy of formation indicates that cumengeite may be a definite limiting substance, even with $Cu^{+2}$ levels as low as $2 \times 10^{-6}$ M. This last value is approximate and is based on an extrapolation to the brine from seawater. For this $Cu^{+2}$ concentration, the computed solubility of cumengeite is only one to two orders of magnitude greater than that of galena (Fig. 3). From its formula, cumengeite appears to be a mixture of Pb(II) and Cu(II) chlorides and hydroxides. The very low solubility implied by the free energy value above seems rather anomalous and requires verification.

### 3.2.6 Hydrocerrusite ($Pb_3(OH)_2(CO_3)_2$)

The only available data on hydrocerrusite, with the single exception of a $K_{sp}$ value dating from 1913, seem to be those of Taylor and Lopata (1984), who evaluated

$\Delta G_f^o$ from equilibration experiments and made no direct solubility measurements, and the solubility data of Bilinski and Schindler (1982). Bilinski and Schindler's data were taken at 25°C, I = 0.3 ($NaClO_4$), and at various partial pressures of $CO_2$. They concluded that hydrocerrusite would be the thermodynamically stable phase in the presence of the normal atmospheric $CO_2$ level and for pH values in the range seen in natural waters. They demonstrated by x-ray diffraction that hydrocerrusite is converted to cerrusite ($PbCO_3$) at low pH and high $pCO_2$ values, but that hydrocerrusite is not converted at $pCO_2$ less than 0.005 and acid concentrations less than 0.02 M. They did not investigate other temperatures or ionic strengths, nor did they carry out any experiments in brines.

### 3.2.7 $(KPbCl_3)_3 \cdot H_2O$ and $KCl \cdot (PbCl_2)_2$

These substances or those like them may be the limiting substances in highly acidic (pH < 4) brines (Fig. 3). The $\Delta G_f^o$ values used were those of Wagman et al. (1982); no primary sources were cited. Because of time and budget constraints, the literature was not searched further for these substances. The corresponding sodium salts would presumably be even more limiting with respect to solubility in NaCl brines because of a larger common ion effect.

### 3.2.8 Recommendations for Further Study

Data on Pb(IV) compounds and aqueous complexes are absent. Free energy values are available for $PbO_2$, $Pb_2O_3$, and $Pb_3O_4$; all three are computed to be quite soluble in the assumed brine. No data exist for Pb(IV) sulfides, phosphates, or carbonates, for example, nor for aqueous complexes with chloride ion or for any other ligand except $OH^-$. According to Baes and Mesmer (1976), Pb(IV) hydrolyzes extensively, but the hydrolysis products are not well known. The situation does not seem to have changed since then.

In preparing Table 8 on solid species containing lead for which data are not available, the following considerations were taken into account when recommending further study:

- Need to study Pb(IV) compounds.
- Need for more data on Na-Pb-Cl compounds.
- Lack of data for different types of substances such as chloro-sulfides, oxy-sulfides, or hydroxy-sulfides.
- Belief that if a substance is a known mineral, then preliminary data should be acquired, if only to eliminate it from more extensive studies.

With respect to the last point, the cumengeite example discussed above seems to suggest that minerals excluded because their formation requires a constituent expected to be present only in minute quantities should perhaps be reexamined.

**TABLE 8 Solid Species Containing Lead for Which Data Are Not Available**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| PbO | No | III | Hokutolite |
| PbO·3H2O | No | II,III | |
| Pb(OH)4 | Yes | | |
| Pb2O | No | I | |
| [PbO]4·[Pb(OH)2]2 | No | III | |
| [PbO]8·[Pb(OH)2]5·H2O | No | III | |
| PbFe4O7 | Yes | | Plumboferrite |
| K2PbO3 | No | II | |
| Na2PbO3 | No | II | |
| Na2PbO2 | No | II | |
| K2PbO4 | No | II | |
| K2Pb3O7 | No | II | |
| K4PbO4 | No | II | |
| PbF | No | I | |
| PbF3 | No | I | |
| Pb3F8 | No | II | |
| KPbF3 | No | II | |
| NaPbF3 | No | II | |
| K2PbF6 | No | II | |
| PbCl | No | I | |
| PbCl4 | Yes | | |
| K2PbCl4 | No | II,III | |
| Na3PbCl5 | Yes | | |
| CaPbCl6 | No | II | |
| K2PbCl6 | No | II,III | |
| Na2PbCl6 | Yes | | |
| K4PbCl6 | No | II,III | |
| KPbCl3 | No | II,III | |
| NaPbCl3 | Yes | | |
| PbBr | No | I | |
| PbBr2·H2O | No | III | |
| PbBr4 | Yes | | |
| KPbBr3 | No | II,III | |
| NaPbBr3 | Yes | | |
| K2PbBr4 | No | II,III | |
| PbO·PbCl2 | No | III | |
| (PbO)3PbCl2 | No | III | |
| (PbO)6PbCl2 | No | III | |
| [Pb(OH)2]3PbCl2 | No | III | |
| (PbO)7PbCL2 | No | III | Cassel yellow |
| PbO·PbBr2 | No | III | |
| (PbO)2PbBr2 | No | III | |
| (PbO)3PbBr2 | No | III | |
| PbS2 | Yes | | |
| (PbS)3PbCl2 | Yes | | |

**TABLE 8 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| (PbO)3(PbS)3(PbCl2)2 | No | III | |
| PbS·Pb(OH)2 | Yes | | |
| (PbS)2·(PbBr2)5 | No | III | |
| Pb(HS)2 | No | II | |
| Pb(SO4)2 | Yes | | |
| (K,Na)Pb(SO4)2 | Yes | | Palmierite |
| K2Pb(SO4)3 | No | II | |
| Pb2(SO4)3 | No | II | |
| Pb(HSO4)2 | No | II | |
| (PbO)3PbSO4·H2O | No | III | |
| (PbO)4PbSO4 | No | III | |
| Pb10SO4Cl2O8 | Yes | | Sundiusite |
| Pb4SO4(OH)2O2 | No | III | |
| PbFe6(SO4)4(OH)12 | Yes | | Plumbojarosite |
| Na3Pb2(SO4)3Cl | No | III | |
| PbO(PbCO3)2 | No | III | |
| Na2Pb3(CO3)3(OH)2 | No | III | |
| Pb(CO3)2 | Yes | | |
| Pb-H3PO4 salts | | | |
| (+4)(4:1) | Yes | | |
| (+4)(6:1) | Yes | | |
| (+4)(2:1)·H2O | Yes | | |
| (+4)(2:1)·2H2O | No | III | |
| (+2)(+4) | Yes | | |
| (+2)K(3:4:1) | No | III | |
| (+2)K(3:4:1)·4H2O | No | III | |
| (+2)Na(3:4:1) | No | III | |
| (+2)Na(3:4:1)·5H2O | No | III | |
| Pb,K apatite | No | III | |
| Pb,Na apatite | Yes | | |
| KPb3PO4(SO4)2 | No | III | |
| Pb2ClPO4 | Yes | | |
| (PbO)5Pb3(PO4)2 | No | III | |
| PbO·[Pb3(PO4)2]3 | No | III | |
| Pb(H2PO4)2SO4 | No | II | |
| Pb-H2SiO4 salts | | | |
| (+2)(1:1) | Yes | | |
| (+2)K(1:1:2) | No | III | |
| Pb(+2)-H6SiO5 salt | No | III | |
| Pb4OSiO4SO4 | Yes | | |
| Pb6O(SiO4)2SO4 | No | III | |
| Na3Pb(AlSiO4)3SO4 | No | III | |
| Pb4SiO6 | No | III | |
| Pb2Si2O7 | No | III | |
| (PbO)4SiO4 | No | III | |

**TABLE 8 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| Pb5Si4O8(OH)10 | Yes | | Plumbotsumite |
| Pb2Fe2O(SiO4)2 | Yes | | Melanotekite |
| Pb(Ac)2 | No | II | |
| Pb(Ac)2·3H2O | No | II | |
| Pb(Ac)2·10H2O | No | II | |
| PbAc4 | No | II | |
| Pb(Pr)2 | No | II | |
| Pb(Pr)4 | No | II | |
| Pb(n-Bu)2 | No | II | |
| Pb(n-Bu)4 | No | II | |
| PbSnO3 | No | V | |
| Pb2SnO3 | No | V | |
| Pb3SnO4 | No | V | |
| Pb6SnO7 | No | V | |
| PbSnS2 | No | V | Teallite |
| PbSnS3 | No | V | |
| PbSnF4 | No | V | |
| Pb-H2SeO3 salts | | | |
| (+2)(1:1) | No | V | |
| (+4)(2:1) | No | V | |
| (+4)K(3:1:2) | No | V | |
| PbSeO3 | No | V | Molybdomenite |
| PbSeO4 | No | V | Kerstenite |
| PbSe | No | V | Clausthalite |
| Pb2Se2 | No | V | |
| PbSrO3 | No | V | |
| PbSr2O4 | No | V | |
| Pb2SrO5 | No | V | |
| Pb(Cu,Fe,Al)3(SO4)2(OH)6 | Yes | | Beaverite |
| Cu10(Fe,Pb)S6 | Yes | | Betekhtinite |
| Pb2Cl(O,OH)2 | No | III | Blixite |
| Pb2Cu2Fe2Si5O17·6H2O | Yes | | Creaseyite |
| Pb2U5O17·4H2O | No | V | Curite |
| Pb(UO2)2(PO4)2·3H2O | No | V | |
| Pb2(Fe,Al)(PO4)2OH·H2O | Yes | | Drugmanite |
| (Th,U)(Ca,Fe,Pb)2Si8O20 | No | V | Ekanite |
| PbU4O13·4H2O | No | V | Fourmarierite |
| Pb6Ca4Si6O21(OH)2 | Yes | | Ganomalite |
| Pb4Fe3O8(OH,Cl) | Yes | | Hematophanite |
| Pb3F3Si3O10(OH,Cl) | Yes | | Jagoite |
| PbUO2SiO4·H2O | No | V | Kasolite |
| PbCuAl2(SO4)2(OH)6 | Yes | | Osarizamaite |
| Pb2UO2(PO4)2 | No | V | Anhydrous Parsonsite |

**TABLE 8 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| $Pb(UO_2)_2(PO_4)_2$ | No | V | Anhydrous Przhevalskite |
| $Pb_5Cu_4Cl_{10}(OH)_8 \cdot 2H_2O$ | Yes | | Pseudoboleite |
| $(Pb,Cu)_2SeO_4(OH)_2$ | No | V | Schmeiderite |
| $Pb_6(IO_3)_2Cl_4O_2(OH)_2$ | No | IV | Schwartzemberg |
| $Pb(Pb,Ca)(Al,Fe,Mg)_2$ - $(Si,Al)_4O_{10}(OH)_2(CO_3)_2$ | Yes | | Surite |
| $PbU_7O_{22} \cdot 12H_2O$ | No | V | Vandendriessche |
| $Pb_3CaAl_2Si_{10}O_{24}(OH)_6$ | Yes | | Wickenburgite |
| $Pb_2UO_2(CO_3)_3$ | No | V | Widenmannite |
| $(Pb,Ca)U_2O_7 \cdot 2H_2O$ | No | V | Woelsendorfite |
| $Cu_4Pb_2SO_4Cl_6(OH)_4 \cdot 2H_2O$ | Yes | | Arzrunite |
| $Na_3Pb_2(SO_4)_3Cl$ | Yes | | Caracolite |
| $(Na,Ca,Pb)_2U_2(O,OH)_7$ | No | V | Clarkeite |
| $Pb_2Cu_5(UO_2)_2(SeO_3)_6(OH)_6 \cdot 2H_2O$ | No | V | Demesmaekerite |
| $Pb_4CuSO_4(OH)_8$ | Yes | | Elyite |
| $(Th,Pb)_{(1-x)}Al_3(PO_4,SiO_4)_2(OH)_6$ | No | V | Eylettersite |
| $Pb_3Cl_4(OH)_2$ | Yes | | Fiedlerite |
| $(Th,Pb,Ca)PO_4 \cdot H_2O$ | No | V | Grayite |
| $(Pb,Ca,Sr)_2(Al,Fe)_3(SiO_4)_3OH$ | No | V | Hancockite |
| $(Th,Ca,Pb)H_2(UO_2)_4(PO_4)_2(OH)_8 \cdot 7H_2O$ | No | V | Kivuite |
| $Pb_7O_6Cl_2$ | Yes | | Lorettoite |
| $(Sr,Pb)Fe_3(PO_4)_2(OH)_5 \cdot H_2O$ | No | V | Lusungite |
| $PbU_7O_{22} \cdot nH_2O$ ($n<12$) | No | V | Metavandendries |
| $Pb_2Mg_2Si_2O_7(OH)_2$ | Yes | | Molybdophyllite |
| $PbSn_4S_5$ | No | V | Montesite |
| $PbCu_6(O,Cl,Br)_8$ | Yes | | Murdochite |
| $Pb_6Ca_4Si_6O_{21}Cl_2$ | Yes | | Nasonite |
| $Pb_2(SeO_4)SO_4$ | No | V | Olsacherite |
| $Pb_3(UO_2)_3(Si_2O_7)_2 \cdot 6H_2O$ | No | V | Orlite |
| $H_6Pb_{10}Al_2O(PO_4)_{12}(SO_4)_5(OH)_{40} \cdot 11H_2O$ | Yes | | Orpheite |
| $Pb_2Cl_3OH$ | Yes | | Penfieldite |
| $PbCuCl_2(OH)_2$ | Yes | | Percylite |
| $Pb_4Al_2(SiO_2)_7$ | Yes | | Plumalsite |
| (U and Pb) oxide | No | V | Richetite |
| $Pb_2Ca_7Si_6O_{14}(OH)_{10}(SO_4)_2$ | Yes | | Roeblingite |
| hydrous (Pb,Cu,Al) | Yes | | Rosieresite |
| $Pb_3Ca_6Cu_2(CO_3)_8(OH)_6 \cdot 6H_2O$ | Yes | | Schuilingite |

**TABLE 8 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| $Pb_2SO_4(CO_3)_2(OH)_2$ | Yes | | Susannite |
| $(Ca,Pb)CO_3$ | Yes | | Tarnowitzite |

[a]I = conditions for the stability of the mineral do not correspond to anticipated repository conditions; II = solid species is highly soluble in brines; III = one compound is picked as being representative of a class of chemical compounds; IV = at least one constituent required for the formation of the solid or aqueous species is present at too low a concentration; and V = compounds containing two radionuclides contain at least two elements present at too low a concentration.

## 3.3 AQUEOUS SPECIES

Tables 9 and 10 present the results for aqueous species that contain lead. An examination of the aqueous speciation for solutions saturated with respect to the substances in Table 5 shows that chloride-Pb(II) complexes are dominant over most of the pH range of interest, with phosphate complexes and possibly carbonate complexes being important at high pH values. Table 11 shows by way of example the major species for the galena and pyromorphite solubility calculations.

### 3.3.1 Pb-Cl Complexes

The existing literature on $Pb^{+2}$-$Cl^{-}$ complexes is extensive. Comparison of results reported by different workers is complicated by the effect of ionic strength and by the fact that experimentally determined values of the stability constants depend not only on ionic strength but also on the cationic composition of the medium (Millero and Byrne, 1984; Byrne and Miller, 1984; Byrne et al., 1981; Mironov, 1961). Table 12 gives the reported literature values of the thermodynamic cumulative formation constants for the first four chloride complexes of Pb(II). The formation constant for even the first complex in the table is not as well established as might be expected, especially given the amount of work done over the past 50 years. In addition, the three most recent determinations (Lozar et al., 1984; Millero and Byrne, 1984; Seward, 1984) do not agree with each other within the reported uncertainties. Thus, one cannot even claim that opinion on the matter is converging. As Table 12 shows, the situation is still worse for the higher complexes. The summary statistics given in Table 12 are defined as follows: the weighting factor $f_i$ for the i-th value of a given stability constant $\beta_n$ was taken to be inversely proportional to the quoted uncertainty $\sigma_i$ of the i-th value, and the weight factors were then normalized to unity. The quantities reported at the bottom of the table are defined by:

$$\langle\beta_n\rangle = \sum_{i=1}^{N} f_i \beta_{ni}$$

$$s_n^2 = \sum_{i=1}^{N} f_i (\beta_{ni} - \langle\beta_n\rangle)^2$$

$$\langle\sigma_n^2\rangle = \sum_{i=1}^{N} f_i \sigma_{ni}^2$$

$$\text{s.e.m.} = [(s_n^2 + \langle\sigma_n^2\rangle)/(N - 1)]^{1/2}$$

where $\beta_{ni}$ denotes the i-th reported value of $\beta_n$, the cumulative stability constant for $PbCl_n^{2-n}$. Twice the standard error of the mean (s.e.m.) gives an approximate 95% confidence limit.

**TABLE 9 Aqueous Species Containing Lead for Which Data Are Available**

| Aqueous Species | Low I[a] | | Intermediate I[b] | | High I[c] | |
|---|---|---|---|---|---|---|
| | Low T | High T | Low T | High T | Low T | High T |
| Pb(+2) | D[d] | | | | | |
| Pb(+4) | D | | | | | |
| PbOH(+1) | D | | | | | |
| Pb(OH)2 | D | | | | | |
| Pb(OH)3(-1) | D | | | | | |
| Pb2OH(+3) | D | | | | | |
| Pb3(OH)4(+2) | D | | | | | |
| Pb4(OH)4(+4) | D | | | | | |
| Pb6(OH)8(+4) | D | | | | | |
| Pb(OH)4 | A | - | - | - | - | - |
| Pb(OH)3(+1) | A | - | - | - | - | - |
| Pb(OH)6(-2) | B | - | - | - | - | - |
| PbF(+1) | D | | | | | |
| PbF2 D | | | | | | |
| PbCl(+1) | B | B | B | B | - | - |
| PbCl2 B | B | B | B | - | - | |
| PbCl3(-1) | B | B | B | B | - | - |
| PbCl4(-2) | B | B | B | B | - | - |
| PbCl6(-4) | A | - | - | - | - | - |
| PbBr(+1) | D | | | | | |
| PbBr2 D | | | | | | |
| PbBr3(-1) | D | | | | | |
| PbBr4(-2) | D | | | | | |
| PbBr5(-3) | D | | | | | |
| PbBrCl | A | - | - | - | - | - |
| Pb2Br(+3) | D | | | | | |
| PbBr2Cl(-1) | A | - | - | - | - | - |
| PbBr3Cl(-2) | A | - | - | - | - | - |
| PbBr4Cl(-3) | A | - | - | - | - | - |
| PbBrCl2(-1) | A | - | - | - | - | - |
| PbBr2Cl2(-2) | A | - | - | - | - | - |
| PbBr3Cl2(-3) | A | - | - | - | - | - |
| PbBrCl3(-2) | A | - | - | - | - | - |
| PbSO4 D | | | | | | |
| Pb(SO4)2(-2) | D | | | | | |
| Pb(HS)2 | D | | | | | |
| Pb(HS)3(-1) | D | | | | | |
| PbHPO4 | A | - | - | - | - | - |
| PbH2PO4(+1) | D | | | | | |
| PbP2O7(-2) | D | | | | | |
| Pb(P2O7)2(-6) | D | | | | | |
| PbCO3 C | - | - | - | - | - | |
| Pb(CO3)2(-2) | C | - | - | - | - | - |

**TABLE 9 (Cont'd)**

| Aqueous Species | Low I[a] | | Intermediate I[b] | | High I[c] | |
|---|---|---|---|---|---|---|
| | Low T | High T | Low T | High T | Low T | High T |
| Pb(acetate)(+1) | D | | | | | |
| Pb(acetate)2 | D | | | | | |

[a]Low I = low ionic strength (I < 0.1).

[b]Intermediate I = intermediate ionic strength (0.1 < I < 3).

[c]High I = high ionic strength (3 < I).

[d]A = a single stability constant value or free energy of formation value exists, B = several mutually inconsistent values exist, C = satisfactory data apparently exist, and D = data are not required.

**TABLE 10 Aqueous Species Containing Lead for Which Data Are Not Available**

| Aqueous Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| PbO2(-2) | No | V | Equivalent to Pb(OH)4(-2) |
| PbO3(-2) | Yes | | |
| Pb(OH)4(-2) | No | I | |
| Pb2(OH)3(+1) | No | V | No evidence for existence |
| Pb3(OH)5(+1) | No | I | |
| PbF3(-1) | No | I | |
| PbF4(-2) | No | I | |
| PbF6(-6) | No | I | |
| PbF6(-2) | Yes | | |
| Pb3F7(-1) | No | V | Lead level too low |
| PbCl5(-3) | Yes | | |
| PbCl6(-2) | Yes | | |
| PbBr6(-4) | No | I | |
| PbBr6(-2) | Yes | | |
| Pb(SO4)3(-4) | No | I | |
| Pb(SO4)4(-6) | No | I | |
| PbHS3(-1) | No | II | |
| PbPO4(-1) | Yes | | |
| Pb(PO4)2(-4) | Yes | | |
| Pb(PO4)3(-7) | Yes | | |
| Pb(PO4)4(-10) | Yes | | |
| Pb(HPO4)2(-2) | Yes | | |
| Pb(HPO4)3(-4) | Yes | | |
| Pb(HPO4)4(-6) | Yes | | |
| Pb(H2PO4)2 | No | I | |
| Pb(H2PO4)3(-1) | No | I | |
| Pb(H2PO4)4(-2) | No | I | |
| Pb(CO3)3(-4) | No | V | No evidence for existence |
| Pb(CO3)4(-6) | No | V | No evidence for existence |
| PbHCO3(+1) | No | I | |
| Pb(HCO3)2 | No | I | |
| Pb(HCO3)3(-1) | No | I | |
| Pb(HCO3)4(-2) | No | I | |
| [Sn(x)Pb(9-x)](-4) | No | III | |
| Pb-H2SeO3 complex | No | III | |

[a]I = computations using estimated free energies imply negligible contribution to the total dissolved radionuclide concentration, II = one constituent is present at too low a concentration, III = two or more radionuclides are needed, and V = other (see comment and/or text).

**TABLE 11 Computed Aqueous Speciation in Alkaline Solution[a]**

| | Galena (with $PbCl_6^{-4}$)[b] | | | Pyromorphite (without $PbCl_6^{-5}$) | | |
|---|---|---|---|---|---|---|
| Species | pH = 10 | 9 | 8 | pH = 10 | 9 | 8 |
| $Cl^-$ | 0.2 | 74.7 | 99.4 | 0.6 | 45.8 | 97.6 |
| $Cl^-$-$Br^-$ | 0.0 | 0.5 | 0.6 | 0.0 | 0.9 | 2.2 |
| $PO_4^{-3}$ | 99.4 | 24.7 | 0.0 | 98.5 | 52.3 | 0.0 |
| $CO_3^{-2}$ | 0.1 | 0.2 | 0.0 | 0.8 | 0.4 | 0.0 |

[a]Values given are percentages of total dissolved Pb(II) that are present as complexes with the indicated ligand.

[b]The complex $PbCl_6^{-4}$ was included in the computations for galena, but not for pyromorphite.

**TABLE 12 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 0[a]**

| Reference | PbCl(+1) | PbCl2 | PbCl3(-1) | PbCl4(-2) | Method[b] | Notes |
|---|---|---|---|---|---|---|
| Seward (1984) | 25.7 (3.1) | 93.3 (9.0) | 45.7 (9.3) | 28.8 (3.6) | S | c |
| Millero and Byrne (1984) | 30.0 (0.6) | 106.7 (2.2) | 73.0 (1.5) | - | S | d,e |
| Lozar et al. (1984) | 40.3 (1.0) | 47.2 (3.0) | 420.0 (10) | - | Sol | f |
| Bendiab et al. (1982) | 7.8 (1.1) | 20.8 (3.2) | 6.8 (1.8) | - | S,P | g |
| Prasad and Prasad (1980) | 38.9 (4.8) | - | - | - | P | h,i |
| Yurchenko et al. (1976) | 22.9 (5.5) | - | - | - | S | |
| Smith and Martell (1976) | 38.9 (1.5) | 63 | 50 | 25 | - | g |
| Fedorov et al. (1972a) | 30.2 (3.6) | 120 (15) | 64.6 (7.8) | 7.1 (3.1) | P | c |
| Nancollas (1955) | 39.4 (1.5) | - | - | - | C | c,h |
| Biggs et al. (1955a) | 36.6 (2.6) | - | - | - | S | h,i |
| Biggs et al. (1955b) | 38.9 (2.8) | - | - | - | S | h,i |
| Papoff et al. (1955) | 12.6 (2.8) | 180 (40) | 72.7 (22) | 65 (50) | Pol | g |
| James (1949) | 43.2 (4.0) | - | - | - | P | h,i,j |
| James (1949) | 37.8 2.0) | - | - | - | C | h,i,k |
| Garrels and Gucker (1949) | 34.1 (1.6) | - | - | - | P | h,i,j |
| Garrels and Gucker (1949) | 34.6 (2.0) | - | - | - | P | h,i,l |
| Guntelberg (1938) | 26.3 (1.2) | - | - | - | P | m |

**TABLE 12 (Cont'd)**

| Reference | PbCl(+1) | PbCl2 | PbCl3(-1) | PbCl4(-2) | Method[b] | Notes |
|---|---|---|---|---|---|---|
| Number | 15 | 4 | 3 | n | | |
| Mean value ($<\beta_n>$) | 33.76 | 85.54 | 68.55 | - | | |
| SQRT ($s_n^2$) | 5.00 | 28.41 | 8.89 | - | | |
| SQRT ($<\sigma_n^2>$) | 2.01 | 30.24 | 4.54 | - | | |
| 2*(s.e.m.) | 2.88 | 33.41 | 14.12 | - | | |

[a]Cumulative stability constants; numbers in parentheses are estimated uncertainties.

[b]S = spectrophotometry, Sol = solubility, P = potentiometry, C = conductivity, Pol = polarography.

[c]Value reported by authors is log(stability constant).

[d]Value reported by authors is ln(stability constant).

[e]Data of Byrne and Miller (1984).

[f]For PbCl(+1), the uncertainty is my estimate; the authors' estimate was 0.2.

[g]Values are not included in the statistical summary.

[h]Authors do not provide uncertainties; quoted values are my estimates.

[i]Value reported by authors is 1/(stability constant).

[j]Data of Carmody (1929).

[k]Data of Norman and Garrett (1947).

[l]Data of Hannan (1936).

[m]Cited in Tobias (1958).

[n]Insufficient data are available for a meaningful statistical summary.

The values cited by Papoff et al. (1955), Smith and Martell (1976), and Bendiab et al. (1982) are excluded from the computation of the summary statistics. Bendiab et al. made measurements at only five ionic strengths (I = 0.5, 1, 2, 3, and 4 M) and fitted their log $\beta_n$ values with a second-degree polynomial in I in order to make an extrapolation to the I = 0 limit. That this procedure is inadequate can be seen from the results of Millero and Byrne (1984), for example, who show that $\beta_n$ is a sensitive function of ionic strength at low ionic strength, but not at the values used by Bendiab et al. Their empirical curve fails to show the true behavior of $\beta_n$ at low ionic strength, and their quoted values at I = 0 are clearly erroneous. The results of Papoff et al. (1955) are also suspect simply from a comparison with the results of other workers. The article of Papoff et al. is written in Italian, and their work has not been critically evaluated. However, Kivalo (1956) points out that the method used by Papoff et al. is capable of yielding only approximate results. Accordingly, their values are not included in the statistical computations. The values given by Smith and Martell (1976) are the results of their own critical review and therefore are not independent experimental values.

Tables 13 and 14 show values from the literature for the apparent cumulative formation constants for the first few complexes at ionic strengths of 1.0 and 3.0, respectively. These values represent the appropriate combinations of experimentally measured concentrations and involve no assumptions regarding activity coefficients or limiting behavior. The results are reasonably consistent over a wide range of experimental methods, with the values for I = 1.0 of Papoff et al. (1955) being obvious exceptions.

The cationic medium effect can be seen in the results of Byrne and Miller (1984) for I = 1.0. It seems to become more pronounced in going from $PbCl^+$ to $PbCl_3^-$. Differences between media in which the dominant cation is $H^+$, $Na^+$, or an alkaline earth ion such as $Ca^{+2}$ or $Mg^{+2}$ can be seen, especially for $PbCl_3^-$. Millero and Byrne (1984) analyzed the data of Byrne and Miller in terms of the Pitzer (1973) formulation of individual ion activity coefficients, with excellent results at ionic strengths up to 1.0, the limit of Byrne and Miller's data. Pitzer parameters for the interaction of the first three Pb-Cl complexes with the other major aqueous species were determined.

The statistical summaries presented in Tables 13 and 14 are based on the same expressions for $\langle\beta_n\rangle$, $s_n^2$, and $\langle\sigma_n^2\rangle$ used earlier, except that equal weights are assumed: $f_i = 1/N$, independent of i. Media effects, including those discussed by Millero and Byrne (1984), are ignored in the statistical calculations.

As the chloride activity is increased, higher Pb-Cl complexes become important. Several studies (Mironov et al., 1965; Vierling, 1973; Bendiab et al., 1982; Seward, 1984) show that in NaCl solutions up to 3.0 m, spectrophotometric and potentiometric data can be explained by assuming that only the first four complexes are present in significant amounts. Papoff et al. (1955) report values for the stability constant of $PbCl_6^{-4}$, but, as indicated above, this work is somewhat suspect. At present, no reliable information exists on the importance of lead-chloride complexes $PbCl_n^{2-n}$ higher than n = 4 in brines with chloride concentrations up to 6 m.

The effect of temperature on the formation constants of the Pb-Cl complexes has been studied by several authors; reported values up to a temperature of 100°C are

**TABLE 13 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 1.0[a]**

| Reference | $PbCl^+$ | $PbCl_2$ | $PbCl_3^-$ | Medium | Notes[b] |
|---|---|---|---|---|---|
| Byrne and Miller (1984) | 8.14 (0.13) | 16.4 (0.3) | 14.6 (0.5) | 0.7 $HClO_4$/0.3 HCl | S |
| | 7.66 (1.9) | 15.0 (3.5) | 13.8 (3.7) | 1.0 HCl | S |
| | 7.79 (0.05) | 15.4 (0.13) | 12.7 (0.15) | 0.7 $NaClO_4$/0.3 NaCl | c,S |
| | 7.49 (2.0) | 14.2 (0.7) | 12.4 (3.2) | 1.0 NaCl | c,S |
| | 7.38 (0.3) | 12.7 (0.5) | 9.85 (0.4) | 0.33 $CaCl_2$ | c,S |
| | 7.30 (0.2) | 12.7 (0.4) | 9.48 (0.3) | 0.33 $MgCl_2$ | c,S |
| Byrne et al. (1981) | 8.05 (0.22) | 16.4 (0.8) | 14.6 (1.6) | HCl + $HClO_4$ | S |
| Lozar et al. (1984) | 13.7 (2.7) | 10.2 (2.0) | 32.9 (6.6) | HCl + $HClO_4$ | d,Sol |
| Bendiab et al. (1982) | 7.1 (0.4) | 17.4 (1.0) | 12.4 (1.0) | NaCl + $NaClO_4$ | P |
| | 9.5 (1.4) | 19.9 (3.8) | 14.7 (6.1) | NaCl + $NaClO_4$ | S |
| Smith and Martell (1976) | 7.9 (1.2) | 20.0 (5.1) | 25.1 (15) | - | e |
| Hutchinson and Higginson (1973) | 12.0 (1.5) | - | - | $NaClO_4$ | f,Kin |
| Bond and Hefter (1973) | 8.7 (0.5) | 12 (1.0) | 53 (8.0) | $NaClO_4$ | g,Pol |
| Fedorov et al. (1972a,b) | 7.1 (1.2) | 18.2 (1.3) | 15.8 (2.0) | $LiClO_4$ | P |
| Papoff et al. (1955) | 17.0 (-) | 200 (-) | 125 (-) | $KClO_4$, $NaClO_4$ | e,Pol |
| Kivalo (1955) | 9.1 (0.9) | 7.4 (0.7) | 23.4 (2.3) | unknown, pH = 5-6 | Pol |

**TABLE 13 (Cont'd)**

| Reference | $PbCl^+$ | $PbCl_2$ | $PbCl_3^-$ | Medium | Notes[b] |
|---|---|---|---|---|---|
| Number | 14 | 13 | 12 | | |
| Mean value ($<\beta_n>$) | 8.64 | 14.45 | 15.55 | | |
| SQRT ($s_n^2$) | 1.88 | 3.30 | 6.23 | | |
| SQRT ($<\sigma_n^2>$) | 1.25 | 1.96 | 3.14 | | |
| 2*(s.e.m.) | 1.25 | 2.21 | 4.21 | | |

[a]Apparent cumulative stability constants.

[b]S = spectrophotometry, Sol = solubility, P = potentiometry, Pol = polarography, and Kin = kinetic method.

[c]pH adjusted to 2.0 with HCl.

[d]Authors did not estimate uncertainties; quoted values are my estimates.

[e]Values are excluded from statistical summary.

[f]Authors report log(stability constant) value.

[g]Value for PbCl3(-1) is not included in statistical summary.

**TABLE 14 Reported Values of Lead-Chloride Stability Constants at 25°C, I = 3.0[a]**

| Reference | $PbCl^+$ | $PbCl_2^\circ$ | $PbCl_3^-$ | $PbCl_4^{-2}$ | Medium | Notes[b] |
|---|---|---|---|---|---|---|
| Bendiab et al. (1982) | 11.3 ± 2.2 | 33.6 ± 8.2 | 67.9 ± 4.6 | - | $Na(Cl,ClO_4)$ | Pot |
| Smith and Martell (1976) | 14.8 ± 1.0 | 50.1 ± 13 | 79.4 ± 20 | 15.8 ± 10 | - | c |
| Fedorov et al. (1972a) | 14.1 ± 1.2 | 50.1 ± 3.3 | 89.1 ± 4.0 | 24 ± 14 | $LiClO_4$ | Pot |
| Nriagu and Anderson (1971) | 15.7 ± 2.9 | 130 ± 38 | 300 ± 114 | - | $Na(Cl,ClO_4)$ | d,Sol |
| Mironov et al. (1965) | 15 ± 2 | 52 ± 5 | 100 ± 10 | 11 ± 2 | $Li(Cl,ClO_4)$ | Pot |
| Mironov et al. (1964a) | 16.0 ± 3 | 50.6 ± 5 | 97.6 ± 10 | - | $LiClO_4$ | e,Sol |
| Mironov et al. (1964b) | 17 ± 2 | 74 ± 10 | 95 ± 5 | - | $LiClO_4$ | Pot |
| Number | 6 | 5 | 5 | 2 | | |
| Mean value ($<\beta_n>$) | 14.9 | 52.1 | 89.9 | 17.5 | | |
| SQRT ($3_n^2$) | 1.66 | 11.5 | 10.4 | 6.50 | | |
| SQRT ($<\sigma_n^2>$) | 2.30 | 6.75 | 7.24 | 10.0 | | |
| 2*(s.e.m.) | 2.54 | 13.3 | 12.7 | - | | |

[a]Apparent cumulative stability constants.

[b]Pot = potentiometry and Sol = solubility.

[c]Values are omitted from the calculation of the summary statistics.

[d]28°C, near neutral pH; $PbCl_2$ and $PbCl_3^-$ values are omitted from summary statistics.

[e]Authors provide no error estimates; quoted values are my estimates.

given in Table 15. The estimated values of Helgeson (1969) are also presented. Except for the value of Prasad and Prasad (1980), the values of $\beta_1$ do not seem too discordant, although not enough data are available at different ionic strengths. The situation is much worse for the higher complexes, and the exact order of magnitudes of their formation constants are unknown in some cases.

The recommendations in Tables 9 and 10 concerning aqueous lead species reflect the need for better understanding of the Pb-Cl complexes. In particular, data are needed on the higher complexes that may be important in brines and on the temperature dependence of the formation constants for all the complexes. Finally, Tsai and Cooney (1976a,b) present evidence for the existence of polynuclear Pb(II)-hydroxo-chloride complexes in Red Sea brines at 56°C. Nothing is known about the stability of these complexes or if they are important with respect to the type of brine of interest here.

Accurate prediction of the solubility of a particular lead-containing solid in brine requires knowing the lead-chloride stability constants and the free energy of formation of the solid (or, equivalently, its solubility product constant). In the case of galena, recent measurements by Uhler and Helz (1984) imply a much higher solubility than do the $\Delta G_f^o$ values in the compilations of Robie et al. (1978) or Wagman et al. (1982). During the course of this survey, I realized that the values of the lead-chloride stability constants in Table 14 can be used in combination with the PbS solubility data of Barrett and Anderson (1982) in 3 M NaCl at 27°C to effectively rule out Uhler and Helz's value.

Considering the solubility of PbS in 3 M NaCl saturated with $H_2S$ leads to the following equation, which is valid for acidic solutions:

$$[Pb(tot)] = \alpha[H^+]^2$$

where $\alpha$ is a particular combination of equilibrium constants for PbS solubility, $H_2S$ dissociation in aqueous solution, $H_2S_{(gas)} = H_2S_{(aq)}$ equilibrium, Pb-Cl complex formation, and activity coefficients. The quantity $\alpha$ can be computed using Barrett and Anderson's (1982) experimental data, tabulated thermodynamic data, and the stability constants at an ionic strength of 3.0 (Table 14), together with $\Delta H_f^o$ data to correct the predictions to 27°C and Millero and Byrne's (1984) Pitzer parameter values to compute activity coefficients. Figure 4 compares Barrett and Anderson's (1982) solubility data with predictions based on the free energies of formation tabulated by Robie et al. (1978) and Wagman et al. (1982), as well as the results of Uhler and Helz (1984). The predictions based on Robie et al. (1978) are in excellent agreement with observations, but those based on the results of Uhler and Helz (1984) are too high by two and one-half orders of magnitude. It seems inescapable that Uhler and Helz's results are erroneous, and it appears that complexation at 25°C in 3 M NaCl is understood well enough to accurately predict the solubility of galena under these conditions.

### 3.3.2 Pb-$CO_3$ Complexes

Carbonate ($CO_3^{-2}$) complexes may also be significant at high pH. Several studies found stability constants for $PbCO_3^o$ and $Pb(CO_3)_2^{-2}$ (Table 16). As the table shows, the reported stability constants for $PbCO_3^o$ and $Pb(CO_3)_2^{-2}$ are reasonably consistent at 25°C

**TABLE 15 Reported Values of Lead-Chloride Stability Constants at Elevated Temperatures**

| Reference | Temp. (°C) | $PbCl^+$ | $PbCl_2^\circ$ | $PbCl_3^-$ | $PbCl_4^{-2}$ | Notes |
|---|---|---|---|---|---|---|
| Seward (1984) | 50 | 29.4 | 148 | 50.1 | 36.3 | a |
| | 100 | 46.8 | 417 | 162 | 85.1 | |
| Rafalsky and Masalovich (1981) | b | | | | | |
| Prasad and Prasad (1980) | 40 | 84.7 | - | - | - | c |
| Yurchenko et al. (1976) | 100 | 69.5 | 7.5 | - | - | d |
| Nriagu and Anderson (1971) | 40 | 19.7 | 205 | 330 | 310 | e |
| | 60 | 25.5 | 354 | 430 | 640 | |
| | 90 | 40.0 | 708 | 420 | 140 | |
| Mironov et al. (1964a) | 45 | 16.0 | 70 | 120 | 17 | f |
| | 55 | 16.8 | 73 | 155 | 15 | |
| Helgeson (1969) | 50 | 42.7 | 70.8 | 64.6 | 38.9 | g |
| | 100 | 53.7 | 110 | 135 | 112 | |

[a] $I = 0$; $\beta_1 - \beta_3$ at 25,50(50)300°C; $\beta_4$ at 25,50(50)150°C; spectrophotometry.

[b] $\beta_1 - \beta_3$; 190-240°C; solubility of PbS in HCl.

[c] $I = 0$; $\beta_1$ at 5(5)40°C.

[d] $I = 0.1$; $\beta_1$ and $\beta_2$ at 21, 100, 150, and 200°C; data of Aksenova and Kolonin (1975).

[e] Stepwise constants for n = 1-4 at 28, 40, 60, and 90°C; pH ≈ 7; $PbCl_2$ solubility in 3 m $Na(Cl,ClO_4)$.

[f] 3 m $Li(Cl,ClO_4)$; $\beta_1 - \beta_4$ at 5(10)55°C; highly uncertain.

[g] Estimates based on $\beta_1 = 39.8$, $\beta_2 = 60.3$, $\beta_3 = 47.9$, and $\beta_4 = 24.0$ at 25°C.

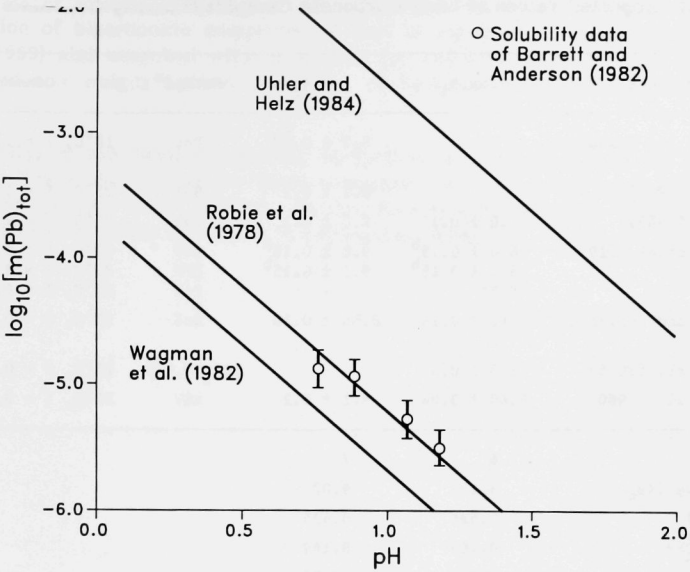


**FIGURE 4 Comparison of Predicted and Observed Solubility for Galena in 3 m NaCl**

and at ionic strengths up to 1.0, although no extensive study exists of the effect of ionic strength similar to that of Byrne and Miller (1984) for the Pb-Cl complexes. The two constants are known to within factors of approximately 3.0 under these conditions. There are no data available on the stability constants at higher ionic strengths.

The effect of an increase in temperature has been studied by Baranova and coworkers (Baranova and Barsukov, 1965; Baranova, 1968, 1969). Baranova (1968) reports $\beta_1 = 7.7 \times 10^{11}$ and $1.6 \times 10^{12}$ at 250°C and 300°C, respectively, and notes that no evidence was found for the species $Pb(CO_3)_2^{-2}$. When combined with her value for 25°C, reported in the same paper, a reasonably straight Arrhenius plot can be drawn, from which a value $\beta_1 = 2.5 \times 10^{10}$ at 100°C is obtained. This result would seem to indicate that the relative importance of carbonate complexes may increase with temperature, although the temperature dependence of the chloride complexes is very poorly known. Baranova (1969) reports an additional value of $\beta_1$ at 200°C, in addition to $\beta_1$ and $\beta_2$ at 25°C, but this new point is inconsistent with the Arrhenius plot from her 1968 results. No other information on the temperature dependence of carbonate complexes of Pb(II) is available.

Baranova and Barsukov (1965) and Baranova (1968, 1969) interpret their results at 25°C in terms of bicarbonate rather than carbonate complexes. Bilinski et al. (1976) point out that the data could be interpreted equally well in terms of the formation of

**TABLE 16 Reported Values of Lead-Carbonate Complex Stability Constants**

| Reference | log $\beta_1$ | log $\beta_2$ | Method[a] | Comments |
|---|---|---|---|---|
| Faucherre and Bonnaire (1959) | - | 8.2 ± 0.2[b] | Pot | 18°C, I = 1.7 M ($KNO_3$) |
| Baranova (1968) | - | 9.1 ± 0.1 | Sol | 25°C, I = 1.0 m ($NaClO_4$) |
| Baranova (1969) | 7.0 ± 0.1 | 9.0 ± 0.1 | Sol | 25°C, I = 1.0 m ($NaClO_4$) |
| Bilinski et al. (1976) | 6.4 ± 0.15[b] | 9.8 ± 0.15[b] | ASV | 25°C, I = 0.1 M ($KNO_3$) |
| | 6.1 ± 0.15[b] | 9.1 ± 0.15[b] | DPP | 25°C, I = 0.1 M ($KNO_3$) |
| | 8.2[c] | - | Pol | 25°C, I < 0.76 M |
| Bilinski and Schindler (1982) | 5.40 ± 0.10 | 8.86 ± 0.10 | Sol | 25°C, I = 0.3 m ($NaClO_4$) |
| Ernst et al. (1975) | 6.3 ± 0.3 | - | DPASV,DPP | 25°C, I = 0.1 M ($KNO_3$) |
| Sipos et al. (1980) | 5.60 ± 0.06 | 9.1 ± 0.2 | ASV | 25°C, I = 0.7 M ($NaClO_4$) |
| Number | 6 | 7 | | |
| Mean value ($<\beta_n>$) | 6.13 | 9.02 | | |
| SQRT ($S_n^2$) | 0.528 | 0.435 | | |
| SQRT ($<\sigma_n^2>$) | 0.163 | 0.149 | | |
| 2*(s.e.m.) | 0.494 | 0.375 | | |

[a]Pot = potentiometry, Sol = solubility, ASV = anodic stripping voltammetry, DPP = differential pulse polarography, and DPASV = differential pulse anodic stripping voltammetry.

[b]My estimate of error.

[c]Value is excluded from computation of summary statistics. Recalculated from data of Baranova and Barsukov (1965).

$Pb(CO_3)_2^{-2}$; more recently, Sipos et al. (1980) and Byrne (1981) report evidence against the formation of bicarbonate complexes of lead at significant levels. Faucherre and Bonnaire (1959) also searched without success for evidence of bicarbonate complexes. Current evidence weighs against formation of bicarbonate complexes in significant amounts.

Finally, mixed bromide-chloride complexes are calculated to be marginally significant. The available data for these complexes come from two papers (Fridman et al. (1960) and Fedorov et al. (1972b). Further investigation would be required if these complexes needed accurate treatment in a speciation model.

# 4 TIN RESULTS

## 4.1 BACKGROUND

Tables 17 and 18 present the initial lists of solid and aqueous species containing tin and indicate if $\Delta G_f^o$ values are available. The number beside each "Yes" has the same significance as for lead. A total of 196 solid and 47 aqueous species were considered. Figure 5, a simplified Eh-pH diagram for tin, shows only the dominant aqueous species in the absence of any additional ligands. Sn(IV) dominates in the region of interest.

Standard free energies of formation are available for a much smaller number of solid tin compounds than was the case for lead. The results of computations indicate that cassiterite ($SnO_2$) is definitely the most insoluble of them. However, the $\Delta G_f^o$ value for $SnSO_4$ given in the NEA data base implies that, for Eh values near the lower $H_2O$ stability line, $SnSO_4$ might also be a limiting substance. Accordingly, both are given in the list of critical solids for tin (Table 19). All other solids for which computations were made, including those in Table 17 with available $\Delta G_f^o$ values, are expected to be rather soluble in the assumed brine and are of no further interest.

## 4.2 SOLID SPECIES

### 4.2.1 Cassiterite ($SnO_2$)

Barsukov and coworkers (Barsukov and Klintsova, 1970; Klintsova and Barsukov, 1973; Kurilchikova and Barsukov, 1970) measured the solubility of $SnO_2$ at 25°C, 100°C, and higher temperatures for several pH values ranging from 2 to 14. Dadze et al. (1981) measured the solubility of $SnO_2$ in acid solution at high temperatures and pressures. In addition, Kurilchikova and Barsukov (1970) found from x-ray diffraction measurements that the solid phase at equilibrium varied from cassiterite ($SnO_2$ at 300°C to varlamoffite ($SnO_2 \cdot xH_2O$) at or below 100°C. Their starting material was freshly precipitated and washed "$Sn(OH)_4$," and equilibrium was attained in only 24 hours at temperatures above 100°C. Barsukov and Klintsova (1970), on the other hand, report that, starting with purified synthetic $SnO_2$, equilibrium was attained in a month at 25°C. The $SnO_2$ system is clearly characterized in practice by varying water content, depending on experimental conditions. Feitknecht and Schindler (1963) report results consistent with those of Barsukov and coworkers.

Additional measurements at room temperatures were carried out in the 1920s by Gruner and Lin (1926) and Boydell (1928); both papers are cited in Jackson and Helgeson (1985). Jackson and Helgeson (1985) reviewed and summarized the scanty available information on the solubility of cassiterite and on the aqueous complexes of Sn(II) and Sn(IV). No data exist on $SnO_2$ solubility in chloride solutions at any pH between 25°C and 100°C. Extensive studies will be required.

**TABLE 17 Solid Species Containing Tin**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Sn | Yes (1) | |
| SnO | Yes (1) | Romarchite |
| $SnO_2$ | Yes (1) | Cassiterite |
| $SnO_2 \cdot H_2O$ | No | |
| $SnO_2 \cdot 2H_2O$ | No | |
| $SnO_2 \cdot 4H_2O$ | No | |
| $Sn_2O_2$ | No | |
| $Sn_2O_3$ | No | |
| $Sn_3O_3$ | No | |
| $Sn_3O_4$ | No | |
| $Sn_3O_6$ | No | |
| $Sn_4O_4$ | No | |
| $Sn_5O_9$ | No | |
| $Sn(OH)_2$ | Yes (1) | |
| $Sn(OH)_4$ | Yes (1) | |
| $SnO(OH)_2$ | No | |
| $Sn_3O_2(OH)_2$ | No | |
| $Na_2SnO_2$ | No | |
| $PbSnO_2$ | No | |
| $K_2SnO_3$ | No | |
| $Na_2SnO_3$ | No | |
| $SrSnO_3$ | No | |
| $MgSnO_3$ | No | |
| $CaSnO_3$ | Yes (1) | |
| $CaSnO_3 \cdot 3H_2O$ | No | |
| $FeSnO_3$ | No | |
| $K_4SnO_4$ | No | |
| $Na_4SnO_4$ | No | |
| $Ca_2SnO_4$ | No | |
| $Mg_2SnO_4$ | No | |
| $Sr_2SnO_4$ | No | |
| $K_2Sn_2O_3$ | No | |
| $K_2Sn_3O_7$ | No | |
| $Sr_3Sn_2O_7$ | No | |
| $K_2Sn(OH)_6$ | No | |
| $Na_2Sn(OH)_6$ | No | |
| $CaSn(OH)_6$ | No | |
| $MgSn(OH)_6$ | No | |
| $SrSn(OH)_6$ | No | |
| SnS | Yes (1) | Herzenbergite |
| $SnS_2$ | Yes (1) | Berndtite |
| $SnS_4$ | No | |
| $Sn_2S_3$ | Yes (1) | Ottemannite |
| $Sn_3S_4$ | Yes (1) | |
| $CaSnS_3$ | No | |

**TABLE 17 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| SrSnS3 | No | |
| Na4SnS4 | No | |
| Mg2SnS4 | No | |
| Ca2SnS4 | No | |
| SnF | No | |
| SnF2 | No | |
| SnF4 | No | |
| Sn2F4 | No | |
| Sn3F6 | No | |
| Sn3F8 | No | |
| Sn4F8 | No | |
| Sn7F16 | No | |
| Sn10F34 | No | |
| KSnF3 | No | |
| KSnF3·0.5H2O | No | |
| NaSnF3 | No | |
| Sr(SnF3)2 | No | |
| H2SnF4 | No | |
| Na2SnF4 | No | |
| SrSnF4 | No | |
| KSnF5 | No | |
| NaSnF5 | No | |
| K2SnF6 | No | |
| K2SnF6·H2O | No | |
| Na2SnF6 | No | |
| CaSnF6 | No | |
| CaSnF6·2H2O | No | |
| MgSnF6 | No | |
| MgSnF6·6H2O | No | |
| SrSnF6 | No | |
| SrSnF6·2H2O | No | |
| KSn2F5 | No | |
| NaSn2F5 | No | |
| SrSn2F5 | No | |
| SnF(OH)3 | No | |
| Sn4F4O2 | No | |
| SnCl | No | |
| SnCl2 | Yes (1) | |
| SnCl2·H2O | No | |
| SnCl2·2H2O | No | |
| SnCl2·1.5H2O | No | |
| SnCl3 | No | |
| SnCl3·5H2O | No | |
| SnCl4 | No | |
| SnCl4·H2O | No | |

**TABLE 17 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| $SnCl_4 \cdot 3H_2O$ | No | |
| $SnCl_4 \cdot 4H_2O$ | No | |
| $SnCl_4 \cdot 5H_2O$ | No | |
| $Sn_2Cl_4$ | No | |
| $Sn_2Cl_6$ | No | |
| $H_2SnCl_4$ | No | |
| $H_2SnCl_6$ | No | |
| $KSnCl_3$ | No | |
| $KSnCl_3 \cdot H_2O$ | No | |
| $NaSnCl_3$ | No | |
| $K_2SnCl_4 \cdot H_2O$ | No | |
| $K_2SnCl_6$ | Yes (1) | |
| $Na_2SnCl_6$ | No | |
| $CaSnCl_6 \cdot 6H_2O$ | No | |
| $SnCl(OH)_3$ | No | |
| $SnClOH \cdot H_2O$ | Yes (1) | |
| $Sn_2Cl_2O$ | No | |
| $Sn_2Cl(OH)_3$ | No | |
| $Sn_3Cl_2F_4$ | No | |
| SnFCl | No | |
| $Sn_2F_3Cl$ | No | |
| SnBr | No | |
| $SnBr_2$ | Yes (1) | |
| $SnBr_3$ | No | |
| $SnBr_4$ | Yes (1) | |
| $SnBr_2Cl_2$ | No | |
| $KSnBr_3$ | No | |
| $NaSnBr_3$ | No | |
| $K_2SnBr_6$ | Yes (1) | |
| SnBrF | No | |
| $Sn_3BrF_5$ | No | |
| $Sn_5Br_4F_6$ | No | |
| SnBrCl | No | |
| $SnBrCl_3$ | No | |
| $KSnBr_2Cl$ | No | |
| $NaSnBr_2Cl$ | No | |
| SnBrO | No | |
| $Sn_2Br_2O$ | No | |
| $Sn_3Br_4O$ | No | |
| $Sn_4Br_2O_3$ | No | |
| $Sn_2Cl_2S$ | No | |
| $Sn_4Cl_6S$ | No | |
| $Sn_5Cl_6S_2$ | No | |
| $Sn_7Br_{10}S_2$ | No | |
| $SnCO_3$ | No | |

**TABLE 17 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Sn-H2SO4 salts | | |
| (+2) [ SnSO4 ] | Yes (1) | |
| (+4) | No | |
| (+4)(2:1) [ Sn(SO4)2 ] | Yes (1) | |
| (+4)(2:1)·2H2O | No | |
| Sn2O3SO4 | No | |
| Sn4O3SO4 | No | |
| Sn-H3PO4 salts | | |
| (+2) | No | |
| (+2)(1:1) | No | |
| (+2)(2:1) | No | |
| (+2)(2:1)·H2O | No | |
| (+2)(2:1)·0.5H2O | No | |
| (+2)(2:3) | No | |
| (+4) | No | |
| (+4)(2:1) | No | |
| (+4)(2:1)·H2O | No | |
| (+4)(4:3) | No | |
| K(2:2:1) | No | |
| K(2:2:1)·2H2O | No | |
| K(3:1:2) | No | |
| Na(2:2:1) | No | |
| Na(2:2:1)·2H2O | No | |
| Na(3:1:2) | No | |
| Sr(6:7:1) | No | |
| SnF3PO4 | No | |
| Sn3O(OH)PO4 | No | |
| Sn2OHPO4 | No | |
| Sn2O(PO4)2 | No | |
| SnO(H2PO4)2 | No | |
| Sn(+4)-H2SiO3 salt | No | |
| Sn-acetic acid salts | | |
| (+2) | No | |
| (+4) | No | |
| Sr(+2) | No | |
| Sn-propionic acid salts | | |
| (+2) | No | |
| (+4) | No | |
| Sn-n-butyric acid salts | | |
| (+2) | No | |
| (+4) | No | |
| Sn(+4)-H2SeO3 salts | | |
| (2:1) | No | |
| Sn4Br6Se | No | |
| Sn5O6Se4 | No | |

**TABLE 17 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| SnSe | No | |
| SnSe2 | No | |
| Sn2Se2 | No | |
| Sn2Se3 | No | |
| SnSeS | No | |
| CaSnSiO5 | No | Malayaite |
| MgSn(OH)6 | No | Schoenfliesite |
| Cu2FeSnS4 | No | Stannite |
| CaSnSi3O9·2H2O | No | Stokesite |
| SnO(OH)F | No | |
| SnOHCl | No | |
| SnOHBr | No | |
| SnBr4·8H2O | No | |
| Sn(HS)2 | No | |
| Sn(HSO4)2 | No | |
| Sn(HCO3)2 | No | |
| SnSiO3 | No | |
| CaSnO4 | No | |
| K2SnOCl4 | No | |
| K2SnCl6·H2O | No | |
| Sn3O2(OH)2 | No | Hydromarchite |
| (Sn,Fe)(O,OH)2 | No | Varlamoffite |

[a]1 = NEA data base.

**TABLE 18 Aqueous Species Containing Tin**

| Aqueous Species | Data Available[a] |
|---|---|
| Sn(+2) | Yes (1) |
| Sn(+4) | Yes (2) |
| SnOH(+1) | Yes (1) |
| Sn(OH)2 | Yes (2) |
| Sn(OH)3(-1) | Yes (2) |
| Sn2(OH)2(+2) | Yes (4) |
| Sn3(OH)4(+2) | Yes (4) |
| SnOH(+3) | Yes (2) |
| Sn(OH)2(+2) | Yes (2) |
| Sn(OH)3(+1) | Yes (2) |
| Sn(OH)4 | Yes (2) |
| Sn(OH)6(-2) | Yes (4) |
| SnO2(-1) | No |
| SnO2(-2) | No |
| SnO4(-4) | No |
| SnCl(+1) | Yes (1) |
| SnCl2 | Yes (1) |
| SnCl3(-1) | Yes (1) |
| SnCl4(-2) | Yes (1) |
| SnCl4 | Yes (4) |
| SnCl5(-1) | No |
| SnCl6(-2) | Yes (4) |
| SnOHCl | Yes (1) |
| SnBrCl2(-1) | No |
| SnBrCl3(-2) | No |
| SnBr(+1) | Yes (1) |
| SnBr2 | Yes (1) |
| SnBr3(-1) | Yes (1) |
| SnBr4(-2) | Yes (4) |
| SnBr6(-2) | No |
| SnOHBr | Yes (1) |
| SnF(+1) | Yes (1) |
| SnF2 | Yes (2) |
| SnF3(-1) | Yes (2) |
| SnF4(-2) | No |
| SnF(+3) | Yes (2) |
| SnF2(+2) | Yes (2) |
| SnF3(+1) | Yes (2) |
| SnF4 | Yes (2) |
| SnF6(-2) | No |
| SnF(OH)3 | Yes (1) |
| SnF(OH)4(-1) | No |
| SnF(OH)5(-2) | No |
| SnSO4(+2) | No |

**TABLE 18 (Cont'd)**

| Aqueous Species | Data Available[a] |
|---|---|
| Sn(SO4)2 | Yes (1) |
| SnS4(-4) | No |
| Sn-Se(-2) complex | No |

[a]1 = NEA data base, 2 = EQ3/6 data base, and 4 = other sources.

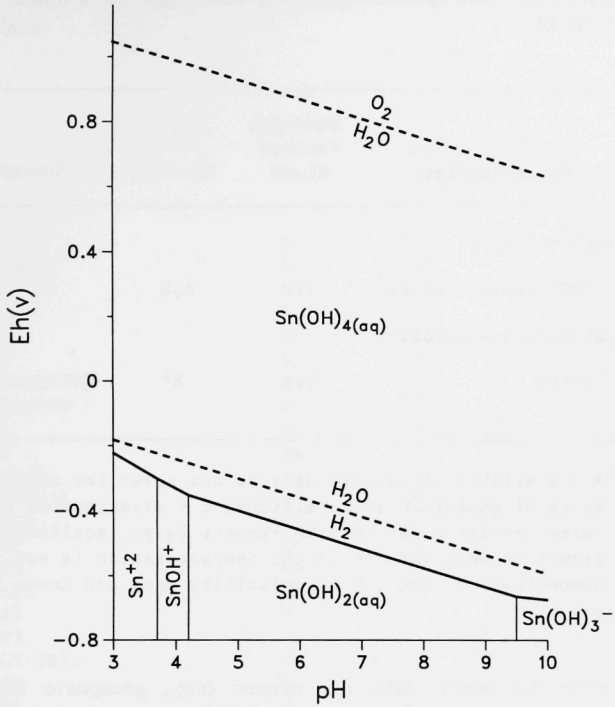


**FIGURE 5 Oxidation Potential-pH Diagram for Tin**

### 4.2.2 $SnSO_4$

On general chemical grounds, $SnSO_4$ might be expected to be moderately soluble; therefore, the value of its free energy of formation given in the NEA data base is suspect. The source of the information is Kubaschewski and Alcock (1979), but these authors give no primary source for the standard heat of formation that was used in calculating their reported $\Delta G_f^o$ value. The computer search in *Chemical Abstracts* did not turn up any useful information. Additional literature review is desirable, but I believe that the extensive solubility data required will not be found in the available literature.

### 4.2.3 Recommendations for Further Study

Table 20 presents the final recommendations for solid species containing tin for which data are not available. Essentially the same considerations were taken into account here as for lead. In the case of tin, a large number of general classes of

**TABLE 19 Solid Species Containing Tin for Which Data Are Available**

| Solid Species | Need for Further Study | Reason[a] | Comment |
|---|---|---|---|
| High priority | | | |
| SnO2 (cassiterite) | Yes | A,B | |
| Intermediate priority | | | |
| SnSO4 | Yes | E | Estimated free energy |

[a]A = available solubility data do not cover the necessary range of experimental conditions, B = experimental procedures are deficient in some respect (e.g., equilibrium from both undersaturation and oversaturation is not demonstrated), and E = no solubility data are known to exist.

compound exist for which data are needed (e.g., phosphate salts). The main requirements, however, are for data on Sn(IV) compounds because Sn(IV) is the thermodynamically stable form under the conditions of interest. Data are also needed for some classes of Sn(II) compounds that are potentially insoluble (e.g., phosphates).

## 4.3 AQUEOUS SPECIES

Tables 21 and 22 present the status concerning aqueous species containing tin, along with recommendations for further study. In the case of $SnO_2$, the dominant aqueous species by far is $Sn(OH)_4^o$. As was the case for lead, the hydrolysis of Sn(IV) has not been adequately studied. The primary references are Klintsova and Barsukov (1973 and references therein) and Nazarenko et al. (1971). No data exist for aqueous Sn(IV) complexes involving chloride phosphate and carbonate ions (Jackson and Helgeson, 1985). The computations for $SnSO_4$ indicate that only hydrolysis products and chloride complexes are likely to be important for Sn(II). The hydrolysis of Sn(II) has been studied more extensively (Baes and Mesmer, 1976, and references therein), but not over the entire range of temperatures and ionic strengths required. These considerations are reflected in Tables 21 and 22.

**TABLE 20 Solid Species Containing Tin for Which Data Are Not Available**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| $SnO_2 \cdot H_2O$ | No | III | |
| $SnO_2 \cdot 2H_2O$ | No | III | |
| $SnO_2 \cdot 4H_2O$ | No | III | |
| $Sn_2O_2$ | No | III | |
| $Sn_2O_3$ | No | III | |
| $Sn_3O_3$ | No | III | |
| $Sn_3O_4$ | No | III | |
| $Sn_3O_6$ | No | III | |
| $Sn_4O_4$ | No | III | |
| $Sn_5O_9$ | No | III | |
| $SnO(OH)_2$ | No | III | |
| $Sn_3O_2(OH)_2$ | No | III | |
| $Na_2SnO_2$ | No | I | |
| $PbSnO_2$ | No | V | |
| $K_2SnO_3$ | No | III | |
| $Na_2SnO_3$ | Yes | | |
| $SrSnO_3$ | No | V | |
| $MgSnO_3$ | No | III | |
| $CaSnO_3 \cdot 3H_2O$ | No | III | |
| $FeSnO_3$ | No | III | |
| $K_4SnO_4$ | No | III | |
| $Na_4SnO_4$ | Yes | | |
| $Ca_2SnO_4$ | Yes | | |
| $Mg_2SnO_4$ | No | III | |
| $Sr_2SnO_4$ | No | V | |
| $K_2Sn_2O_3$ | No | III | |
| $K_2Sn_3O_7$ | No | III | |
| $Sr_3Sn_2O_7$ | No | V | |
| $K_2Sn(OH)_6$ | No | III | |
| $Na_2Sn(OH)_6$ | Yes | | |
| $CaSn(OH)_6$ | Yes | | |
| $MgSn(OH)_6$ | No | III | |
| $SrSn(OH)_6$ | No | V | |
| $SnS_4$ | Yes | | |
| $CaSnS_3$ | Yes | | |
| $SrSnS_3$ | No | V | |
| $Na_4SnS_4$ | Yes | | |
| $Mg_2SnS_4$ | No | III | |
| $Ca_2SnS_4$ | Yes | | |
| SnF | No | I | |
| $SnF_2$ | No | II | |
| $SnF_4$ | Yes | | |
| $Sn_2F_4$ | No | III | |

**TABLE 20 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| Sn3F6 | No | III | |
| Sn3F8 | No | III | |
| Sn4F8 | No | III | |
| Sn7F16 | No | III | |
| Sn10F34 | No | III | |
| KSnF3 | No | II | |
| KSnF3·0.5H2O | No | II | |
| NaSnF3 | No | II | |
| Sr(SnF3)2 | No | V | |
| H2SnF4 | No | II | |
| Na2SnF4 | No | II | |
| SrSnF4 | No | V | |
| KSnF5 | No | II | |
| NaSnF5 | No | II | |
| K2SnF6 | No | II | |
| K2SnF6·H2O | No | II | |
| Na2SnF6 | No | II | |
| CaSnF6 | No | II | |
| CaSnF6·2H2O | No | II | |
| MgSnF6 | No | II | |
| MgSnF6·6H2O | No | II | |
| SrSnF6 | No | V | |
| SrSnF6·2H2O | No | V | |
| KSn2F5 | No | II | |
| NaSn2F5 | No | II | |
| SrSn2F5 | No | V | |
| SnF(OH)3 | Yes | | |
| Sn4F4O2 | Yes | | |
| SnCl | No | I | |
| SnCl2·H2O | No | III | |
| SnCl2·2H2O | No | III | |
| SnCl2·1.5H2O | No | III | |
| SnCl3 | No | I | |
| SnCl3·5H2O | No | I | |
| SnCl4 | Yes | | |
| SnCl4·H2O | No | III | |
| SnCl4·3H2O | No | III | |
| SnCl4·4H2O | No | III | |
| SnCl4·5H2O | No | III | |
| Sn2Cl4 | No | III | |
| Sn2Cl6 | No | III | |
| H2SnCl4 | No | II | |
| H2SnCl6 | No | II | |
| KSnCl3 | No | II | |

**TABLE 20 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| KSnCl3·H2O | No | II | |
| NaSnCl3 | No | II | |
| K2SnCl4·H2O | No | II | |
| Na2SnCl6 | No | II | |
| CaSnCl6·6H2O | No | II | |
| SnCl(OH)3 | Yes | | |
| Sn2Cl2O | Yes | | |
| Sn2Cl(OH)3 | No | III | |
| Sn3Cl2F4 | No | III | |
| SnFCl | Yes | | |
| Sn2F3Cl | No | III | |
| SnBr | No | I | |
| SnBr3 | No | I | |
| SnBr2Cl2 | No | III | |
| KSnBr3 | No | II | |
| NaSnBr3 | No | II | |
| SnBrF | Yes | | |
| Sn3BrF5 | No | III | |
| Sn5Br4F6 | No | III | |
| SnBrCl | Yes | | |
| SnBrCl3 | Yes | | |
| KSnBr2Cl | No | III | |
| NaSnBr2Cl | No | III | |
| SnBrO | No | I | |
| Sn2Br2O | Yes | | |
| Sn3Br4O | No | III | |
| Sn4Br2O3 | No | III | |
| Sn2Cl2S | Yes | | |
| Sn4Cl6S | No | II | |
| Sn5Cl6S2 | No | II | |
| Sn7Br10S2 | No | II | |
| SnCO3 | Yes | | |
| Sn-H2SO4 salts | | | |
| (+4)(2:1)·2H2O | No | II | |
| Sn2O3SO4 | Yes | | |
| Sn4O3SO4 | Yes | | |
| Sn-H3PO4 salts | | | |
| (+2)(1:1) | Yes | | |
| (+2)(2:1) | Yes | | |
| (+2)(2:1)·H2O | No | III | |
| (+2)(2:1)·0.5H2O | No | III | |
| (+2)(2:3) | Yes | | |
| (+4)(2:1) | Yes | | |
| (+4)(2:1)·H2O | No | III | |

**TABLE 20 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| (+4)(4:3) | Yes | | |
| K(2:2:1) | No | III | |
| K(2:2:1)·2H2O | No | III | |
| K(3:1:2) | No | III | |
| Na(2:2:1) | No | III | |
| Na(2:2:1)·2H2O | No | III | |
| Na(3:1:2) | No | III | |
| Sr(6:7:1) | No | V | |
| SnF3PO4 | Yes | | |
| Sn3O(OH)PO4 | Yes | | |
| Sn2OHPO4 | Yes | | |
| Sn2O(PO4)2 | Yes | | |
| SnO(H2PO4)2 | Yes | | |
| Sn(+4)-H2SiO3 salt | Yes | | |
| Sn-acetic acid salts | | | |
| (+2) | No | II | |
| (+4) | No | II | |
| Sr(+2) | No | V | |
| Sn-propionic acid salts | | | |
| (+2) | No | II | |
| (+4) | No | II | |
| Sn-n-butyric acid salts | | | |
| (+2) | No | II | |
| (+4) | No | II | |
| Sn(+4)-H2SeO3 salts | | | |
| (2:1) | No | V | |
| Sn4Br6Se | No | V | |
| Sn5O6Se4 | No | V | |
| SnSe | No | V | |
| SnSe2 | No | V | |
| Sn2Se2 | No | V | |
| Sn2Se3 | No | V | |
| SnSeS | No | V | |
| CaSnSiO5 | Yes | | Malayaite |
| MgSn(OH)6 | Yes | | Schoenfliesite |
| Cu2FeSnS4 | Yes | | Stannite |
| CaSnSi3O9·2H2O | Yes | | Stokesite |
| SnO(OH)F | Yes | | |
| SnOHCl | Yes | | |
| SnOHBr | Yes | | |
| SnBr4·8H2O | No | II | |
| Sn(HS)2 | No | II | |
| Sn(HSO4)2 | No | II | |
| Sn(HCO3)2 | No | II | |

**TABLE 20 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| $SnSiO_3$ | Yes | | |
| $CaSnO_4$ | Yes | | |
| $K_2SnOCl_4$ | No | III | |
| $K_2SnCl_6 \cdot H_2O$ | No | III | |
| $Sn_3O_2(OH)_2$ | Yes | | Hydromarchite |
| $(Sn,Fe)(O,OH)_2$ | Yes | | Varlamoffite |

[a]I = conditions for the stability of the mineral do not correspond to anticipated repository conditions, II = solid species is highly soluble in brines, III = one compound is picked as being representative of a class of chemical compounds, and V = compounds containing two radionuclides contain at least two elements present at too low a concentration.

**TABLE 21 Aqueous Species Containing Tin for Which Data Are Available**

| Aqueous Species | Low I[a] | | Intermediate I[b] | | High I[c] | |
|---|---|---|---|---|---|---|
| | Low T | High T | Low T | High T | Low T | High T |
| Sn(+2) | D[d] | | | | | |
| Sn(+4) | D | | | | | |
| SnOH(+1) | B | - | B | - | - | - |
| Sn(OH)2 | B | - | B | - | - | - |
| Sn(OH)3(-1) | B | - | B | - | - | - |
| Sn2(OH)2(+2) | B | - | - | - | - | - |
| Sn3(OH)4(+2) | B | - | - | - | - | - |
| SnOH(+3) | A | - | - | - | - | - |
| Sn(OH)2(+2) | A | - | - | - | - | - |
| Sn(OH)3(+1) | A | - | - | - | - | - |
| Sn(OH)4 | A | - | - | - | - | - |
| Sn(OH)6(-2) | A | - | - | - | - | - |
| SnCl(+1) | B | - | B | - | - | - |
| SnCl2 | B | - | B | - | - | - |
| SnCl3(-1) | B | - | B | - | - | - |
| SnCl4(-2) | B | - | B | - | - | - |
| SnCl4 | A | - | - | - | - | - |
| SnCl6(-2) | A | - | - | - | - | - |
| SnOHCl | B | - | - | - | - | - |
| SnBr(+1) | D | | | | | |
| SnBr2 | D | | | | | |
| SnBr3(-1) | D | | | | | |
| SnBr4(-2) | D | | | | | |
| SnOHBr | D | | | | | |
| SnF(+1) | D | | | | | |
| SnF2 | D | | | | | |
| SnF3(-1) | D | | | | | |
| SnF(+3) | D | | | | | |
| SnF2(+2) | D | | | | | |
| SnF3(+1) | D | | | | | |
| SnF4 | D | | | | | |
| SnF(OH)3 | D | | | | | |
| Sn(SO4)2 | D | | | | | |

[a]Low I = low ionic strength (I < 0.1).

[b]Intermediate I = intermediate ionic strength (0.1 < I < 3).

[c]High I = high ionic strength (3 < I).

[d]A = a single stability constant value or free energy of formation value exists, B = several mutually inconsistent values exist, C = satisfactory data apparently exist, and D = data are not required.

**TABLE 22 Aqueous Species Containing Tin for Which Data Are Not Available**

| Aqueous Species | Need for Further Study | Reason Culled[a] |
|---|---|---|
| SnO2(-1) | No | IV |
| SnO2(-2) | No | IV |
| SnO4(-4) | No | IV |
| SnCl5(-1) | Yes | |
| SnBrCl2(-1) | Yes | |
| SnBrCl3(-2) | Yes | |
| SnBr6(-2) | Yes | |
| SnF4(-2) | No | II |
| SnF6(-2) | No | II |
| SnF(OH)4(-1) | No | II |
| SnF(OH)5(-2) | No | II |
| SnSO4(+2) | Yes | |
| SnS4(-4) | No | II |
| Sn-Se(-2) complex | No | III |

[a]II = one constituent is present at too low a concentration, III = two or more radionuclides are needed, and IV = conditions for stability do not correspond to repository conditions.

# 5 STRONTIUM RESULTS

## 5.1 BACKGROUND

Tables 23 and 24 give the initial lists of solid and aqueous species containing strontium and indicate if $\Delta G_f$ values are available. The number beside each "Yes" has the same significance as for lead. A total of 99 solids and 51 aqueous species were considered.

The results of solubility calculations indicate that of the solids for which $\Delta G_f^o$ values were available, the four that merit closer attention are $SrSO_4$ (celestite), $SrCO_3$ (strontianite), $Sr_3(PO_4)_2$, and $Sr_2SiO_4$ (Table 25). As was the case for tin and lead, data are not available for a number of minerals and for many solid compounds.

## 5.2 SOLID SPECIES

### 5.2.1 Celestite ($SrSO_4$)

An extensive set of measurements of the solubility of celestite in pure water from 10°C to 90°C and in up to 5 m NaCl solutions from 10°C to 40°C is reported in Reardon and Armstrong (1987). Historically, as discussed in this paper, substantial disagreement had existed concerning reported solubilities for this substance because of the stability of supersaturated solutions, the propensity for surface poisoning, and the effects of particle size. Reardon and Armstrong carefully addressed these issues, and their work provides a firm basis for the new measurements that are needed to extend the range of conditions to somewhat higher NaCl concentrations, actual brines, higher temperatures, and pH values on either side of neutral. Reardon and Armstrong (1987) provide a good review of earlier solubility studies, including those of Strübel (1966), which include higher temperatures and NaCl concentrations up to 2.3 m.

### 5.2.2 Strontianite ($SrCO_3$)

An extensive set of solubility measurements of strontianite in water at temperatures from 0°C to 90°C is reported in Busenberg et al. (1984). Their results apparently brought some order to what had been an unsatisfactory situation, but the range of experimental conditions did not include the entire ranges of pH and ionic strength of interest here. In the work of Busenberg et al., the pH was kept essentially constant (near 9.6), and the ionic strength was kept under 0.1. Earlier solubility studies are reviewed in Busenberg et al. (1984).

Millero et al. (1984) report solubility measurements for $SrCO_3$ in NaCl solutions from 0.1 m to 6 m at 25°C. Their value for $pK_{sp}$ at infinite dilution is 9.13, compared with the Busenberg et al. (1984) value of 9.27. Pitzer's formulation was used to extrapolate to zero ionic strength. The Millero et al. measurements did not extend to higher temperatures; therefore, further work is needed. In addition, Millero et al. did not

**TABLE 23 Solid Species Containing Strontium**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| SrO | Yes (1) | |
| SrO2 | Yes (1) | |
| SrO2·8H2O | No | |
| Sr2O2 | No | |
| Sr2O | No | |
| SrOH | No | |
| Sr(OH)2 | Yes (1) | |
| Sr(OH)2·H2O | No | |
| Sr(OH)2·8H2O | No | |
| FeSrO3 | No | |
| FeSrO2 | No | |
| Sr(FeO2)2 | No | |
| (SrO)Al2O3 | No | |
| (SrO)2Fe2O3 | No | |
| (SrO)3Al2O3 | No | |
| (SrO)3Fe2O3 | No | |
| (SrO)3FeO3 | No | |
| (SrO)4Al2O3 (alpha) | No | |
| (SrO)4Al2O3 (beta) | No | |
| (SrO)7(Fe2O3)5 | No | |
| SrF | No | |
| SrF2 | Yes (1) | |
| SrF(HF2) | No | |
| Sr2H5F9 | No | |
| SrCl | No | |
| SrCl2 | Yes (1) | |
| SrCl2·2H2O | Yes (1) | |
| SrCl2·6H2O | Yes (1) | |
| SrCl2·H2O | Yes (1) | |
| SrCl2·0.5H2O | No | |
| (SrO)SrCl2·9H2O | No | |
| (NaCl)2(SrCl2)2 | No | |
| (AlCl3)4(SrCl2)3 | No | |
| SrClOH | No | |
| SrClOH·4H2O | No | |
| SrClF | No | |
| Sr2Cl2F2 | No | |
| SrBr | No | |
| SrBr2 | Yes (1) | |
| SrBr2·6H2O | Yes (1) | |
| SrBr2·H2O | Yes (1) | |
| (SrO)SrBr2·3H2O | No | |
| (SrO)SrBr2·9H2O | No | |
| SrBrF | No | |
| SrS | Yes (1) | |
| SrS2 | No | |

**TABLE 23 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| SrS3 | No | |
| SrS4·6H2O | No | |
| Sr(HS)2 | No | |
| SrSO4 | Yes (1) | Celestite |
| SrSO4·2H2O | No | |
| Sr(HSO4)2 | No | |
| (SrO)3·SrSO4 | No | |
| Na2SO4·SrSO4 | No | |
| (Na2SO4)2SrSO4 | No | |
| SrCO3 | Yes (1) | Strontianite |
| Sr(HCO3)2 | No | |
| Sr-H3PO4 salts | | |
| (1:1) [ SrHPO4 ] | Yes (1) | |
| (1:1)·H2O | No | |
| (2:1) [ Sr(H2PO4)2 ] | No | |
| (2:1)·H2O | No | |
| (2:3) [ Sr3(PO4)2 ] | Yes (1) | |
| (2:3)·4H2O | No | |
| (5:6) | No | |
| KSr3(SO4)2PO4 | No | |
| SrO·3Sr3(PO4)2 | No | |
| Sr5OH(PO4)3 | No | |
| Sr5F(PO4)3 | No | |
| Sr5Cl(PO4)3 | No | |
| Sr5Br(PO4)3 | No | |
| Sr7F2(PO4)4 | No | |
| SrSiO3 | Yes (1) | |
| SrSiO3·H2O | No | |
| SrSiO3·4H2O | No | |
| SrSiO4 | Yes (1) | |
| Sr3OSiO4 | No | |
| Sr2SiO4 | No | |
| SrH2SiO4 | No | |
| (1:3)Sr-H6O5Si salt | No | |
| Sr5Cl6Si4O10 | No | |
| (SrO)2Al2O3SiO2 | No | |
| Sr2Al2SiO7 | No | |
| SrSeO3 | Yes (4) | |
| Sr(HSeO3)2 | No | |
| SrO·SrSeO3 | No | |
| SrSeO4 | No | |
| SrSe | No | |
| SrSe2 | No | |
| SrSe3 | No | |
| Sr2Se3 | No | |

**TABLE 23 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Sr(acetate)2 | No | |
| Sr(acetate)2·0.5H2O | No | |
| Sr(propionate)2 | No | |
| SrAl2Si2O8 | No | Strontium anorthite |
| Na(Ca,Sr)3Al3(F,OH)16 | No | Calcjarlite |
| SrAl3(PO4)2(OH)5·H2O | No | Goyazite |
| (Sr,Ca)Al2(CO3)2(OH)4·H2O | No | Strontiodresserite |
| SrAl3(OH)6PO4SO4 | No | Svanbergite |
| Na3Sr4ThH(SiO3)8 | No | Umbozerite |

[a]1 = NEA data base and 4 = other sources.

**TABLE 24 Aqueous Species Containing Strontium**

| Aqueous Species | Data Available[a] | Comment |
|---|---|---|
| Sr(+2) | Yes (1) | |
| SrOH(+1) | Yes (1) | |
| Sr(OH)2 | Yes (1) | No reference[b] |
| Sr(OH)3(-1) | Yes (1) | No reference |
| Sr(OH)4(-2) | Yes (1) | No reference |
| SrF(+1) | Yes (1) | |
| SrF2 | Yes (1) | |
| SrF3(-1) | Yes (1) | No reference |
| SrF4(-2) | Yes (1) | No reference |
| SrF5(-3) | Yes (1) | No reference |
| SrF6(-4) | Yes (1) | No reference |
| SrCl(+1) | Yes (4) | |
| SrCl2 | Yes (1) | |
| SrCl3(-1) | Yes (1) | No reference |
| SrCl4(-2) | Yes (1) | No reference |
| SrCl5(-3) | Yes (1) | No reference |
| SrCl6(-4) | Yes (1) | No reference |
| SrBr(+1) | Yes (1) | No reference |
| SrBr2 | Yes (1) | |
| SrBr3(-1) | Yes (1) | No reference |
| SrBr4(-2) | Yes (1) | No reference |
| SrBr5(-3) | Yes (1) | No reference |
| SrBr6(-4) | Yes (1) | No reference |
| SrCO3 | Yes (1) | |
| Sr(CO3)2(-2) | Yes (1) | No reference |
| Sr(CO3)3(-4) | Yes (1) | No reference |
| Sr(CO3)4(-6) | Yes (1) | No reference |
| Sr(CO3)5(-8) | Yes (1) | No reference |
| SrHCO3(+1) | Yes (1) | |
| Sr(HCO3)2 | Yes (1) | No reference |
| Sr(HCO3)3(-1) | Yes (1) | No reference |
| Sr(H2PO4)2 | Yes (1) | No reference |
| Sr(H2PO4)3(-1) | Yes (1) | No reference |
| Sr(H2PO4)4(-2) | Yes (1) | No reference |
| Sr(H2PO4)5(-3) | Yes (1) | No reference |
| SrHPO4 | Yes (1) | |
| Sr(HPO4)2(-2) | Yes (1) | No reference |
| Sr(HPO4)3(-4) | Yes (1) | No reference |
| Sr(HPO4)4(-6) | Yes (1) | No reference |
| Sr(HPO4)5(-8) | Yes (1) | No reference |
| Sr(HPO4)6(-10) | Yes (1) | No reference |
| SrPO4(-1) | Yes (1) | |
| Sr(PO4)2(-4) | Yes (1) | No reference |
| Sr(PO4)3(-7) | Yes (1) | No reference |

**TABLE 24 (Cont'd)**

| Aqueous Species | Data Available[a] | Comment |
|---|---|---|
| Sr(PO4)4(-10) | Yes (1) | No reference |
| Sr(PO4)5(-13) | Yes (1) | No reference |
| Sr(PO4)6(-16) | Yes (1) | No reference |
| SrSO4 | Yes (1) | |
| Sr(SO4)2(-2) | Yes (1) | No reference |
| Sr(SO4)3(-4) | Yes (1) | No reference |
| Sr(SO4)4(-6) | Yes (1) | No reference |

[a]1 = NEA data base and 4 = other sources.

[b]Indicates that the data cannot be traced back to the original source.

**TABLE 25 Solid Species Containing Strontium for Which Data Are Available**

| Solid Species | Need for Further Study | Reason[a] |
|---|---|---|
| High priority | | |
| SrSO4 (celestite) | Yes | A |
| Intermediate priority | | |
| SrCO3 (strontianite) | Yes | A |
| Sr3(PO4)2 | Yes | A |
| Low priority | | |
| Sr2SiO4 | Yes | A |

[a]A = available solubility data do not cover the necessary range of experimental conditions.

demonstrate that equilibrium is attained from either direction, although it seems likely that equilibrium was in fact attained.

### 5.2.3 $Sr_3(PO_4)_2$

The free energy of formation of this substance was taken from the NEA data base, but the information could not be followed back to the primary sources. The computer search in *Chemical Abstracts* turned up no useful information for this substance. Further literature review is needed, but it is highly unlikely that the required solubility data will be found.

### 5.2.4 $Sr_2SiO_4$

As in the previous subsection, $\Delta G_f^o$ was taken from the NEA data base, but the information could not be followed back to the primary sources. The only recent data uncovered by the computer search in *Chemical Abstracts* are high-temperature (1100-1300°C) potentiometric measurements of the free energy of formation of $Sr_2SiO_4$ (Rog et al., 1974). Further investigation is needed, but it is extremely unlikely that the required solubility data will be found.

### 5.2.5 Recommendations for Further Study

Table 26 summarizes the recommendations concerning solid species that contain strontium but for which data were not available. In preparing this table, the same considerations were applied as in the cases of lead and tin, except that strontium has only one oxidation state under the conditions of interest. Data are needed for several minerals that contain strontium. Also, a series of compounds exists that is analogous to the pyromorphite series for lead; these compounds should certainly be examined.

## 5.3 AQUEOUS SPECIES

On the basis of the calculations, chloride complexes of strontium are expected to be by far the most significant aqueous species in the assumed brine at most pH values in the range of interest, with phosphate complexes becoming significant contributors at pH values greater than 9. As indicated in Table 24, most of the available data cannot be traced back to original sources. The current status and recommendations concerning aqueous species are given in Tables 27 and 28. Further investigations can probably be limited to chloride and phosphate complexes of strontium. Because of time and budget constraints, an extensive literature search was not conducted for these complexes.

The entries in the NEA data base and the results of the literature search indicate that the literature concerning strontium complexes is not extensive, and it is highly unlikely that these complexes will have been studied in adequate detail. It is interesting to note that both Millero et al. (1984), in their study of the solubility of $SrCO_3$ in up to 6.0 m NaCl, and Reardon and Armstrong (1987), in their study of the solubility of $SrSO_4$

**TABLE 26 Solid Species Containing Strontium for Which Data Are Not Available**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| $SrO_2 \cdot 8H_2O$ | No | III | |
| $Sr_2O_2$ | No | III | |
| $Sr_2O$ | No | I | |
| SrOH | No | I | |
| $Sr(OH)_2 \cdot H_2O$ | No | III | |
| $Sr(OH)_2 \cdot 8H_2O$ | No | III | |
| $FeSrO_3$ | Yes | | |
| $FeSrO_2$ | Yes | | |
| $Sr(FeO_2)_2$ | No | III | |
| $(SrO)Al_2O_3$ | Yes | | |
| $(SrO)_2Fe_2O_3$ | Yes | | |
| $(SrO)_3Al_2O_3$ | No | III | |
| $(SrO)_3Fe_2O_3$ | No | III | |
| $(SrO)_3FeO_3$ | No | III | |
| $(SrO)_4Al_2O_3$ (alpha) | No | III | |
| $(SrO)_4Al_2O_3$ (beta) | No | III | |
| $(SrO)_7(Fe_2O_3)_5$ | No | III | |
| SrF | No | I | |
| $SrF(HF_2)$ | No | III | |
| $Sr_2H_5F_9$ | No | III | |
| SrCl | No | I | |
| $SrCl_2 \cdot 0.5H_2O$ | No | III | |
| $(SrO)SrCl_2 \cdot 9H_2O$ | Yes | | |
| $(NaCl)_2(SrCl_2)_2$ | No | III | |
| $(AlCl_3)_4(SrCl_2)_3$ | No | III | |
| SrClOH | Yes | | |
| $SrClOH \cdot 4H_2O$ | No | III | |
| SrClF | Yes | | |
| $Sr_2Cl_2F_2$ | No | III | |
| SrBr | No | I | |
| $(SrO)SrBr_2 \cdot 3H_2O$ | No | III | |
| $(SrO)SrBr_2 \cdot 9H_2O$ | Yes | | |
| SrBrF | Yes | | |
| $SrS_2$ | No | I | |
| $SrS_3$ | No | I | |
| $SrS_4 \cdot 6H_2O$ | No | I | |
| $Sr(HS)_2$ | No | II | |
| $SrSO_4 \cdot 2H_2O$ | No | III | |
| $Sr(HSO_4)_2$ | No | II | |
| $(SrO)_3 \cdot SrSO_4$ | Yes | | |
| $Na_2SO_4 \cdot SrSO_4$ | No | III | |
| $(Na_2SO_4)_2SrSO_4$ | No | III | |
| $Sr(HCO_3)_2$ | No | II | |
| Sr-$H_3PO_4$ salts (1:1)$\cdot H_2O$ | No | III | |

**TABLE 26 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| (2:1) [ $Sr(H_2PO_4)_2$ ] | Yes | | |
| (2:1)·$H_2O$ | No | III | |
| (2:3)·$4H_2O$ | No | III | |
| (5:6) | No | III | |
| $KSr_3(SO_4)_2PO_4$ | No | III | |
| $SrO \cdot 3Sr_3(PO_4)_2$ | Yes | | |
| $Sr_5OH(PO_4)_3$ | Yes | | |
| $Sr_5F(PO_4)_3$ | Yes | | |
| $Sr_5Cl(PO_4)_3$ | Yes | | |
| $Sr_5Br(PO_4)_3$ | Yes | | |
| $Sr_7F_2(PO_4)_4$ | No | III | |
| $SrSiO_3 \cdot H_2O$ | No | III | |
| $SrSiO_3 \cdot 4H_2O$ | No | III | |
| $Sr_3OSiO_4$ | No | III | |
| $Sr_2SiO_4$ | No | III | |
| $SrH_2SiO_4$ | No | III | |
| (1:3)Sr-$H_6O_5Si$ salt | No | III | |
| $Sr_5Cl_6Si_4O_{10}$ | Yes | | |
| $(SrO)_2Al_2O_3SiO_2$ | Yes | | |
| $Sr_2Al_2SiO_7$ | No | III | |
| $Sr(HSeO_3)_2$ | No | V | |
| $SrO \cdot SrSeO_3$ | No | V | |
| $SrSeO_4$ | No | V | |
| SrSe | No | V | |
| $SrSe_2$ | No | V | |
| $SrSe_3$ | No | V | |
| $Sr_2Se_3$ | No | V | |
| Sr(acetate)2 | No | II | |
| Sr(acetate)2·0.5$H_2O$ | No | II | |
| Sr(propionate)2 | No | II | |
| $SrAl_2Si_2O_8$ | Yes | | Strontium anorthite |
| $Na(Ca,Sr)_3Al_3(F,OH)_{16}$ | Yes | | Calcjarlite |
| $SrAl_3(PO_4)_2(OH)_5 \cdot H_2O$ | Yes | | Goyazite |
| $(Sr,Ca)Al_2(CO_3)_2(OH)_4 \cdot H_2O$ | Yes | | Strontiodresserite |
| $SrAl_3(OH)_6PO_4SO_4$ | Yes | | Svanbergite |
| $Na_3Sr_4ThH(SiO_3)_8$ | No | V | Umbozerite |

[a]I = conditions for the stability of the mineral do not correspond to anticipated repository conditions, II = solid species is highly soluble in brines, III = one compound is picked as being representative of a class of chemical compounds, and V = compounds containing two radionuclides contain at least two elements present at too low a concentration.

**TABLE 27 Aqueous Species Containing Strontium for Which Data Are Available**

| Aqueous Species | Low I[a] | | Intermediate I[b] | | High I[c] | |
|---|---|---|---|---|---|---|
| | Low T | High T | Low T | High T | Low T | High T |
| Sr(+2) | B[d] | - | B | - | - | - |
| SrOH(+1) | D | | | | | |
| SrF(+1) | D | | | | | |
| SrF2 | D | | | | | |
| SrCl(+1) | - | - | A | - | - | - |
| SrCl2 | B | - | - | - | - | - |
| SrBr2 | D | | | | | |
| SrCO3 | D | | | | | |
| SrHCO3(+1) | D | | | | | |
| SrHPO4 | D | | | | | |
| SrPO4(-1) | A | - | - | - | - | - |
| SrSO4 | B | - | - | - | - | - |

[a]Low I = low ionic strength (I < 0.1).

[b]Intermediate I = intermediate ionic strength (0.1 < I < 3).

[c]High I = high ionic strength (3 < I).

[d]A = a single stability constant value or free energy of formation value exists, B = several mutually inconsistent values exist, and D = data are not required.

**TABLE 28 Aqueous Species Containing Strongium for Which Data Are Not Available**

| Aqueous Species | Need for Further Study | Reason Culled[a] |
|---|---|---|
| Sr(OH)2 | No | I |
| Sr(OH)3(-1) | No | I |
| Sr(OH)4(-2) | No | I |
| SrF3(-1) | No | I |
| SrF4(-2) | No | I |
| SrF5(-3) | No | I |
| SrF6(-4) | No | I |
| SrCl3(-1) | Yes | |
| SrCl4(-2) | Yes | |
| SrCl5(-3) | Yes | |
| SrCl6(-4) | Yes | |
| SrBr(+1) | Yes | |
| SrBr3(-1) | No | I |
| SrBr4(-2) | No | I |
| SrBr5(-3) | No | I |
| SrBr6(-4) | No | I |
| Sr(CO3)2(-2) | No | I |
| Sr(CO3)3(-4) | No | I |
| Sr(CO3)4(-6) | No | I |
| Sr(CO3)5(-8) | No | I |
| Sr(HCO3)2 | No | I |
| Sr(HCO3)3(-1) | No | I |
| Sr(H2PO4)2 | No | I |
| Sr(H2PO4)3(-1) | No | I |
| Sr(H2PO4)4(-2) | No | I |
| Sr(H2PO4)5(-3) | No | I |
| Sr(HPO4)2(-2) | No | I |
| Sr(HPO4)3(-4) | No | I |
| Sr(HPO4)4(-6) | No | I |
| Sr(HPO4)5(-8) | No | I |
| Sr(HPO4)6(-10) | No | I |
| Sr(PO4)2(-4) | No | I |
| Sr(PO4)3(-7) | No | I |
| Sr(PO4)4(-10) | No | I |
| Sr(PO4)5(-13) | No | I |
| Sr(PO4)6(-16) | No | I |
| Sr(SO4)2(-2) | No | I |
| Sr(SO4)3(-4) | No | I |
| Sr(SO4)4(-6) | No | I |

[a]I = computations using estimated (or otherwise unattributable) free energy values imply negligible contribution to the total dissolved radionuclide concentration.

in brines, do not consider $Sr^{+2}$-$Cl^{-}$ complexes at all, but make use of Pitzer's formulation for activity coefficients involving specific ion interaction terms, with excellent results in both cases. It seems reasonable to conclude that information on Sr-Cl complexes per se may not be needed for accurate prediction of the solubility in brines of strontium-containing solids.

# 6 SELENIUM RESULTS

## 6.1 BACKGROUND

Tables 29 and 30 present the initial lists of solid and aqueous species containing selenium and indicate if $\Delta G_f^o$ values are available. The number beside each "Yes" has the usual significance. A total of 104 solid and 21 aqueous species were considered.

Figure 6, a simplified Eh-pH diagram for selenium, shows the dominant aqueous species over the pH range of interest. The diagram indicates that, depending on conditions, the dominant aqueous species may be a selenide, a selenite, or a selenate (i.e., selenium in the -2, +4, and +6 oxidation states, respectively).

## 6.2 SOLID SPECIES

The results of solubility calculations indicate that none of the selenides or selenates for which $\Delta G_f^o$ values are available are sufficiently insoluble in the assumed brine to be of interest. For example, for a total dissolved selenide content of 0.1 m, the logarithms of the activity products for sodium, potassium, calcium, magnesium, and silicon selenide were at least 13 log units from zero (value at saturation) over the range $3 \leq pH \leq 10$. The calculated solubility in the assumed brine of $CaSeO_4$, the most insoluble selenate for which calculations could be done, corresponds to a selenate concentration of approximately 1.0 m. Additional $\Delta G_f^o$ data may reveal substances involving minor or trace brine cations, particularly those of heavy metals, that would limit the selenide content more than the major brine cations do.

Several relatively insoluble selenites exist. Masson (1986) critically reviews the available data. The results of the calculations indicate the existence of at least three candidates for a limiting solid (Table 31).

### 6.2.1 $MgSeO_3$

Masson (1986) describes two studies reporting $K_{sp}$ values for $MgSeO_3$ (Ripan and Vericeanu, 1968; Chukhlantsev, 1956). In the former, a conductometric method was used, and no direct solubility measurements were made. According to Masson, the $K_{sp}$ value cannot be regarded as reliable because of errors in the data analysis. In the latter, the solubility of $MgSeO_3$ was measured directly at 20°C in an initially acidic (pH = 2; HCl or $HNO_3$) solution. The resulting $pK_{sp}$ value was 4.89. This study did not cover the required range of conditions with respect to pH, ionic strength, or temperature; further studies are needed.

### 6.2.2 $CaSeO_3$

The same two references are cited in Masson (1986) as in the case of $MgSeO_3$; only the second is of interest here. The same conditions were used; consequently, further

**TABLE 29 Solid Species Containing Selenium**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| Se | Yes (1) | |
| SeO | No | |
| SeO2 | Yes (1) | Downeyite |
| SeO3 | Yes (1) | |
| Se2O5 | Yes (1) | |
| Se(OH)2 | No | |
| SeF | No | |
| SeF2 | No | |
| SeF4 | No | |
| SeF6 | No | |
| SeF6·H2O | No | |
| Se2F2 | No | |
| Se2F8O2 | No | |
| Se2F10O | No | |
| (FSeO)2O | No | |
| F2SeO2 | No | |
| SeCl | No | |
| SeCl2 | No | |
| SeCl4 | Yes (1) | |
| Se2Cl2 | No | |
| SeClF3 | No | |
| SeBr4 | No | |
| Se2Br2 | No | |
| K2SeBr6 | No | |
| F2SeO | No | |
| Cl2SeO | No | |
| Cl2SeO·H2O | No | |
| Br2SeO | No | |
| SeS | No | |
| SeS2 | No | |
| SeS3 | No | |
| SeS4 | No | |
| Se3S | No | |
| SeS7 | No | |
| Se2S6 | No | |
| Se3S5 | No | |
| Se4S4 | No | |
| Se5S3 | No | |
| Se6S2 | No | |
| Se7S | No | |
| Se2OS | No | |
| Al2Se | No | |
| Al2Se3 | No | |
| CaSe | Yes (1) | |
| FeSe | No | Achavalite |

**TABLE 29 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| FeSe2 | No | Ferroselite |
| Fe3Se4 | No | |
| Fe7Se8 | No | |
| K2Se | Yes (1) | |
| MgSe | Yes (1) | |
| NaSe | No | |
| Na2Se | Yes (1) | |
| Na2Se4 | No | |
| Na2Se2 | Yes (1) | |
| SiSe2 | Yes (1) | |
| Se8(HSO4)2 | No | |
| Se2O4·H2SO4 | No | |
| Se2F10SO4 | No | |
| Al2(SeO3)3 | No | |
| Al2(SeO3)3·6H2O | No | |
| CaSeO3 | Yes (4) | |
| CaSeO3·2H2O | Yes (1) | |
| FeSeO3 | No | |
| Fe2(SeO3)3 | Yes (4) | |
| Fe2(SeO3)3·7H2O | No | |
| Fe2(SeO3)3·H2O | No | |
| Fe2(SeO3)3·3H2O | No | |
| Fe2(SeO3)3·5H2O | No | |
| Fe2(SeO3)3·4H2O | No | |
| K2SeO3 | Yes (1) | |
| K2SeO3·4H2O | No | |
| KHSeO3 | No | |
| MgSeO3 | Yes (1) | |
| MgSeO3·2H2O | No | |
| MgSeO3·6H2O | Yes (1) | |
| Mg(SeO3)2·4H2O | No | |
| Na2SeO3 | Yes (1) | |
| Na2SeO3·8H2O | No | |
| Na2SeO3·5H2O | No | |
| NaHSeO3 | No | |
| H2SeO4·H2O | No | |
| CaSeO4 | Yes (1) | |
| FeSeO4·H2O | No | |
| FeSeO4·5H2O | No | |
| K2SeO4 | Yes (1) | |
| KHSeO4 | No | |
| MgSeO4 | Yes (1) | |
| MgSeO4·H2O | No | |
| MgSeO4·4H2O | No | |
| MgSeO4·6H2O | No | |

**TABLE 29 (Cont'd)**

| Solid Species | Data Available[a] | Comment |
|---|---|---|
| $MgK_2(SeO_4)_2$ | No | |
| $MgK_2(SeO_4)_2 \cdot 2H_2O$ | No | |
| $MgK_2(SeO_4)_2 \cdot 6H_2O$ | No | |
| $MgNa_2(SeO_4)_2 \cdot 2H_2O$ | No | |
| $Na_2SeO_4$ | Yes (1) | |
| $Na_2SeO_4 \cdot 10H_2O$ | No | |
| $Na_2SeO_4 \cdot H_2O$ | No | |
| $NaHSeO_4$ | No | |
| $Na_4(SeO_4)_5$ | No | |
| $Na_6(SeO_4)_5 \cdot 4H_2O$ | No | |
| $Cu_5Se_4$ | No | Athabascaite |
| $Cu_3Se_2$ | No | Umangite |
| $CaSeO_4 \cdot 2H_2O$ | Yes (1) | |
| $K_2SeCl_6$ | No | |

[a]1 = NEA data base and 4 = other sources.

**TABLE 30 Aqueous Species Containing Selenium**

| Species | Data Available[a] | Comment |
|---|---|---|
| H2Se | Yes (1) | |
| HSe(-1) | Yes (1) | |
| Se(-2) | Yes (1) | |
| Se2(-2) | No | |
| Se8(-2) | No | |
| Sex(-2) | No | Other polyselenides |
| H2SeO3 | Yes (1) | |
| HSeO3(-1) | Yes (1) | |
| SeO3(-2) | Yes (1) | |
| HSeO4(-1) | Yes (1) | |
| SeO4(-2) | Yes (1) | |
| Al-H2SeO4 complex | No | |
| Fe-H2SeO4 complexes | No | |
| Mg-H2SeO4 complexes | No | |
| SeCl3(+1) | No | |
| SeBr3(+1) | No | |
| SeBr6(-2) | No | |
| Metal-selenide complexes | | |
| Al | No | |
| Cu | No | |
| Fe | No | |
| Mg | No | |

[a]1 = NEA data base.

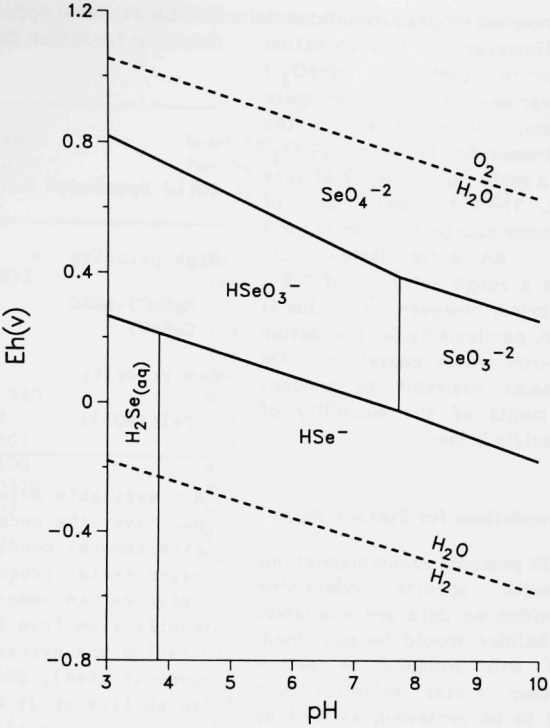


**FIGURE 6 Oxidation Potential-pH Diagram for Selenium**

studies are needed to cover the desired range of conditions. The reported value of $pK_{sp}$ for $CaSeO_3$ is 5.53.

### 6.2.3 $Fe_2(SeO_3)_3$

Masson (1986) cites Chukhlantsev and Tomashevsky (1957) and Pinaev and Volkova (1970). Both papers report the results of direct solubility measurements at low temperatures (20°C and "room temperature," respectively). The ionic strength in the first study was less than 0.1; in the second, it was fixed at 3.0. The pH in both studies was quite low -- less than 3 in the first and 1.4 in the second. The reported values for $pK_{sp}$ were 30.7 in the first and 35.43 in the second.

In spite of the small $K_{sp}$ value, the importance of $Fe_2(SeO_3)_3$ as a solid limiting the selenium level in an assumed brine is uncertain. The Eh value must be larger than

+0.771 V for ferric ion to predominate over ferrous ion. However, at this oxidation potential, selenite (actually, $HSeO_3^-$) predominates over selenate only under quite acidic conditions. In other words, the regions of dominance for $Fe^{+3}$ and $HSeO_3^-$ overlap only in a rather small region at very low pH (Fig. 6). The actual significance of $Fe_2(SeO_3)_3$ depends also on the iron content of the brine. An extrapolation from seawater yields a rough estimate of $7.2 \times 10^{-6}$ M in the brine; however, this value is highly uncertain, particularly for a situation involving cast-iron waste containers. On balance, it seems desirable to conduct further experiments of the solubility of $Fe_2(SeO_3)_3$ in acidic brines.

**TABLE 31 Solid Species Containing Selenium for Which Data Are Available**

| Solid Species | Need for Further Study | Reasons[a] |
|---|---|---|
| High priority | | |
| $MgSeO_3 \cdot 6H_2O$ | Yes | A,B,D |
| $CaSeO_3$ | Yes | A,B,D |
| Low priority | | |
| $Fe_2(SeO_3)_3$ | Yes | A,B,D |

[a]A = available solubility data do not cover the necessary range of experimental conditions, B = experimental procedures are deficient in some respect (e.g., equilibrium from both undersaturation and oversaturation is not demonstrated), and D = only one solubility study exists (no independent confirmation is available).

### 6.2.4 Recommendations for Further Study

Table 32 presents recommendations concerning solid species containing selenium for which no data are available. The selenium halides should be examined, although they will probably be rather soluble. Other metal selenites and selenates need to be reviewed, as well as the trace metal selenides that make up the four known minerals listed. Other selenium-containing solids were eliminated before the initial lists were compiled. A number of known minerals were eliminated because they required the presence of some trace constituents. These solids should be reexamined.

## 6.3 AQUEOUS SPECIES

Very few aqueous species containing selenium, other than the three acids and their ions, were identified. Because of time and budget constraints, the literature on the acids ($H_2Se$, $H_2SeO_3$, and $H_2SeO_4$), as well as their dissociation constants, was not reviewed extensively. Table 33 conveys the extent to which data on these species are available, as reported in Smith and Martell (1976) and Martell and Smith (1982). Additional information is given in Baes and Mesmer (1976) and in the NEA data base. Data are clearly needed at higher temperatures and ionic strengths; additional measurements at low temperatures and/or ionic strengths are almost certainly needed.

**TABLE 32 Solid Species Containing Selenium for Which Data Are Not Available**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| SeO | No | III | |
| Se(OH)2 | Yes | | |
| SeF | No | I | |
| SeF2 | Yes | | |
| SeF4 | Yes | | |
| SeF6 | Yes | | |
| SeF6·H2O | No | III | |
| Se2F2 | Yes | | |
| Se2F8O2 | Yes | | |
| Se2F10O | No | III | |
| (FSeO)2O | Yes | | |
| F2SeO2 | Yes | | |
| SeCl | No | I | |
| SeCl2 | Yes | | |
| Se2Cl2 | No | I | |
| SeClF3 | Yes | | |
| SeBr4 | Yes | | |
| Se2Br2 | No | I | |
| K2SeBr6 | Yes | | |
| F2SeO | Yes | | |
| Cl2SeO | Yes | | |
| Cl2SeO·H2O | No | | |
| Br2SeO | Yes | | |
| SeS | Yes | | |
| SeS2 | No | IV | |
| SeS3 | No | IV | |
| SeS4 | No | IV | |
| Se3S | No | IV | |
| SeS7 | No | IV | |
| Se2S6 | No | IV | |
| Se3S5 | No | IV | |
| Se4S4 | No | IV | |
| Se5S3 | No | IV | |
| Se6S2 | No | IV | |
| Se7S | No | IV | |
| Se2OS | No | IV | |
| Al2Se | Yes | | |
| Al2Se3 | No | III | |
| FeSe | Yes | | Achavalite |
| FeSe2 | Yes | | Ferroselite |
| Fe3Se4 | No | III | |
| Fe7Se8 | No | III | |
| NaSe | No | I | |
| Na2Se4 | No | III | |
| Se8(HSO4)2 | No | IV | |
| Se2O4·H2SO4 | No | II | |

**TABLE 32 (Cont'd)**

| Solid Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| Se2F10SO4 | No | III | |
| Al2(SeO3)3 | Yes | | |
| Al2(SeO3)3·6H2O | No | III | |
| FeSeO3 | Yes | | |
| Fe2(SeO3)3·7H2O | No | III | |
| Fe2(SeO3)3·H2O | No | III | |
| Fe2(SeO3)3·3H2O | No | III | |
| Fe2(SeO3)3·5H2O | No | III | |
| Fe2(SeO3)3·4H2O | No | III | |
| K2SeO3·4H2O | No | III | |
| KHSeO3 | No | II | |
| MgSeO3·2H2O | No | III | |
| Mg(SeO3)2·4H2O | No | I | |
| Na2SeO3·8H2O | No | III | |
| Na2SeO3·5H2O | No | III | |
| NaHSeO3 | No | II | |
| H2SeO4·H2O | No | II | |
| FeSeO4·H2O | Yes | | |
| FeSeO4·5H2O | No | III | |
| KHSeO4 | No | II | |
| MgSeO4·H2O | No | III | |
| MgSeO4·4H2O | No | III | |
| MgSeO4·6H2O | No | III | |
| MgK2(SeO4)2 | No | III | |
| MgK2(SeO4)2·2H2O | No | III | |
| MgK2(SeO4)2·6H2O | No | III | |
| MgNa2(SeO4)2·2H2O | No | III | |
| Na2SeO4·10H2O | No | III | |
| Na2SeO4·H2O | No | III | |
| NaHSeO4 | No | II | |
| Na4(SeO4)5 | No | III | |
| Na6(SeO4)5·4H2O | No | III | |
| Cu5Se4 | Yes | | Athabascaite |
| Cu3Se2 | Yes | | Umangite |
| K2SeCl6 | Yes | | |

[a]I = conditions for the stability of the mineral do not correspond to anticipated repository conditions, II = solid species is highly soluble in brines, III = one compound is picked as being representative of a class of chemical compounds, and IV = at least one constituent required for the formation of the solid or aqueous species is present at too low a concentration.

**TABLE 33 Aqueous Species Containing Selenium for Which Data Are Available**

| Aqueous Species | Low I[a] | | Intermediate I[b] | | High I[c] | |
|---|---|---|---|---|---|---|
| | Low T | High T | Low T | High T | Low T | High T |
| H2Se | X[d] | - | X | - | - | - |
| HSe(-1) | X | - | X | - | - | - |
| Se(-2) | X | - | X | - | - | - |
| H2SeO3 | X | - | X | - | - | - |
| HSeO3(-1) | X | - | X | - | - | - |
| SeO3(-2) | X | - | X | - | - | - |
| HSeO4(-1) | X | - | X | - | - | - |
| SeO4(-2) | X | - | X | - | - | - |

[a]Low I = low ionic strength (I < 0.1).

[b]Intermediate I = intermediate ionic strength (0.1 < I < 3).

[c]High I = high ionic strength (3 < I).

[d]X = data of unknown quality exist (table entries are based entirely on the compilations of Smith and Martell, 1976, and Martell and Smith, 1982).

Recommendations regarding aqueous species for which data are not available are given in Table 34. Essentially, the importance of complexes between any of the acids or ions and the significant metal ions present in the brine needs to be evaluated. In addition, if selenium can form complexes with chloride ion to any significant degree, this ability would affect the solubility of selenium compounds in brines in an important way. The importance of such complexes needs to be evaluated, although Smith and Martell (1976) do not consider such species.

**TABLE 34 Aqueous Species Containing Selenium for Which Data Are Not Available**

| Aqueous Species | Need for Further Study | Reason Culled[a] | Comment |
|---|---|---|---|
| Se2(-2) | No | II | |
| Se8(-2) | No | II | |
| Sex(-2) | No | II | Other polyselenides |
| Al-H2SeO4 complex | No | II | |
| Fe-H2SeO4 complexes | No | II | |
| Mg-H2SeO4 complexes | Yes | | |
| SeCl3(+1) | Yes | | |
| SeBr3(+1) | Yes | | |
| SeBr6(-2) | Yes | | |
| Metal-selenide complexes | | | |
| Al | No | II | |
| Cu | No | II | |
| Fe | No | II | |
| Mg | Yes | | |

[a]II = one constituent is present at too low a concentration.

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