Complexation and Solubility Reactions Controlling Cyanide Environmental Behavior

Literature Review and Speciation/Solubility Calculations

Technical Report

Complexation and Solubility Reactions Controlling Cyanide Environmental Behavior

Literature Review and Speciation/Solubility Calculations

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Cosponsor
Wisconsin Electric Power Company
333 W. Everett St.
Milwaukee, WI 53201

Principal Investigator
J. Lingle

EPRI Project Manager
A. J. Coleman

EPRI • 3412 Hillview Avenue, Palo Alto, California 94304 • PO Box 10412, Palo Alto, California 94303 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

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This report was prepared by

Battelle, Pacific Northwest Laboratories
Battelle Boulevard
Richland, WA 99352

Principal Investigators
K. M. Krupka
H. Bolton, Jr.

ISH Inc.
690 West Fremont Avenue
Sunnyvale, CA 94087

Principal Investigator
I. P. Murarka

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REPORT SUMMARY

This report presents information obtained from an extensive literature search on the geothermal behavior and thermodynamic properties of cyanide compounds. It also presents information on bioremediation technologies for degradation of cyanide. Available data on groundwater concentrations of cyanide compounds from several manufactured gas plant (MGP) sites indicate that free cyanide is a very minor fraction of the total dissolved cyanide complexes.

Background

Some former MGP sites may contain cyanide-contaminated soil and groundwater. This contamination is derived from the disposal of purifier box wastes containing iron-complexed cyanide solids, particularly Prussian Blue and Turnbull's Blue. The environmental risks associated with cyanide contamination are largely dependent on the presence of "free" cyanide species that are toxic. EPRI initiated this research project to compile thermodynamic data on cyanide compounds and species pertinent to defining aqueous forms and environmental fate of cyanide so that risks and remediation issues can be reliably addressed.

Objectives

To complete a literature review to identify aqueous species and solids that are potentially important to the release, transport, and fate of cyanide in soil/water systems; to summarize available information on bioremediation technologies for treatment of cyanide contaminated soil and water.

Approach

The project team searched computerized literature databases, the EPRI report database, and EPA Internet sites to identify published papers and reports that provided information on the geochemical and thermodynamic behavior of cyanide in soil/water systems. The team also conducted a computerized literature search to obtain information on bioremediation technologies for cyanide-contaminated soils and waters. These literature searches were limited to information published prior to 1998. In revising and finalizing this report, the team also utilized one EPRI report and two new papers on cyanide chemistry published in 1999. The team compiled equilibrium constants for cyano aqueous species and solids to identify those that may be important to the mobility and solubility limits of cyanide in soil/water environments. The researchers then completed a limited set of equilibrium thermodynamic calculations using the MINTEQA2 code to illustrate the possible importance of different cyanide aqueous species and solids in soil/water systems.

Results

The literature search resulted in the compilation of equilibrium constants for numerous cyanide aqueous species and solids. Available thermodynamic data indicate that cyanide anion readily forms metal complexes in aqueous phase as well as in solid phase. Therefore, a suite of easily dissociable, weak acid dissociable, and strong acid dissociable metal cyanide complexes may exist in groundwater. Thermodynamic calculations indicate that the speciation of dissolved cyanide complexes is a function of pH and pE (oxidation/reduction conditions). At pH values between 7 and 10, the iron-cyanide complexes are the dominant cyanide species both under oxidizing and moderately reducing conditions. Thermodynamic calculations further suggest that HCN^o (aq) is the dominant aqueous phase species in the acidic pH range. At pH values greater than 9 under oxidizing conditions and very low concentrations of dissolved cyanide, free CN^- may become dominant relative to the aqueous iron-cyanide complexes. However, field data on cyanide in groundwater at MGP sites show the preponderance of the iron-cyanide complexes at environmental pH values. This discrepancy is likely a result of slow kinetics for the decomposition of dissolved iron-cyanide complexes. Further research is needed to completely resolve this knowledge gap.

The available literature indicates that specific microorganisms can biodegrade cyanide when it is present as free cyanide and to a lesser extent when it occurs as metal cyanide complexes.

EPRI Perspective

This research project successfully identified and summarized available thermodynamic data on cyanide aqueous and solid species. This information is useful in evaluating leaching, transport, and fate of cyanide species in groundwater. Calculations using the available thermodynamic data over predict the presence of HCN^o (aq) and free CN^- species in the aqueous phase. This over prediction may be due to the occurrence of non-equilibrium reactions involving the kinetically controlled decomposition of dissolved iron-cyanide complexes. Further research is needed to clarify the importance of kinetics for the decomposition of dissolved iron-cyanide species. Development of water treatment technologies employing precipitation chemistry may provide cost effective methods to remediate groundwater contamination by cyanide species. Moreover, bioremediation technology demonstrations are warranted to determine the effectiveness and range of applications at MGP sites.

Keywords

MGP
Cyanide
Bioremediation
Geochemical modeling
Prussian Blue
Thermodynamics

ABSTRACT

A literature review was conducted to 1) identify cyanide aqueous species and solids (and their associated thermodynamic properties) that are potentially important to the geochemical behavior of cyanide in soil/water systems, and 2) summarize bioremediation technologies relevant to cyanide-contaminated water and soil. The review identified numerous references pertaining to the geochemical behavior and bioremediation technologies. However, the computerized literature search identified only one reference pertaining to the adsorption behavior of cyanide and metal-cyanide complexes on soil material. Metal-cyanide complexes are commonly present in anionic form, and therefore are not typically attenuated by adsorption processes in groundwater systems, especially at high pH values.

Equilibrium constants, log $K^\circ_{r,298}$, were compiled for numerous cyano aqueous species and solids using two internationally-recognized compilations of thermodynamic data. Solubility constants for Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ and Turnbull's Blue $\{Fe_3[Fe(CN)_6]_2\}$, which are dominant forms of cyanide in purifier box wastes at MGP sites, were obtained from the article by Ghosh et al. (1999). The thermodynamic calculations using the MINTEQA2 geochemical code indicate that the neutral species HCN° (aq) is the dominant aqueous cyanide complex at pH values typically less than 8 at these redox conditions and solution compositions. At pH values between 7 and 10, the iron-cyanide complexes $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are the dominant cyanide complexes under oxidizing and moderate-to-very reducing conditions, respectively. Increasing the concentration of total dissolved cyanide decreases the pH region where HCN° (aq) dominates to lower pH values, and increases the pH regions to lower pH values where iron-cyanide complexes dominate. The free cyanide species CN^- was present at less than 0.1 percent of the total mass of dissolved cyanide at pH values less than 7. The mass of aqueous CN^- increased with increasing pH and pE.

Speciation of dissolved cyanide predicted from equilibrium thermodynamic calculations do not accurately represent the cyanide speciation data observed in direct measurements of groundwater from MGP sites. Analytical measurements of groundwater samples from several MGP sites indicate that iron-cyanide complexes are dominant (about 99%) aqueous species of cyanide, and the concentrations of free cyanide [e.g., HCN° (aq) and CN^-] are a minor fraction (about 1%) of the total dissolved cyanide. The discrepancy between the analytically-determined versus equilibrium thermodynamically calculated speciation is attributed to the slow decomposition kinetics that have been observed for iron-cyanide complexes in the absence of sunlight.

There is increasing interest in bioremediation as a remediation strategy for treatment of toxic wastes such as cyanide-contaminated water and soil. The available literature indicates that specific microorganisms can biodegrade (transform) cyanide present as free cyanide or metal-cyanide complexes through various metabolic processes. However, there are fewer examples of the application of cyanide bioremediation in the field, although bioremediation in the field has been successful at select sites.

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INTRODUCTION AND BACKGROUND

1.1 Cyanide At Manufactured Gas Plants

Cyanide is used in several industrial processes because of its ability to form strong complexes with a range of metals. The cyanide products are predominantly used in steel, electroplating, mining, aluminum production, and chemical industries, and as an anti-caking agent in road salts. It was also produced in the purifier box wastes when sulfur in manufactured gas was removed by the scrubbing methods. The manufactured gas industry produced gas for lighting and heating, and produced feedstocks for the chemical industry from coal, coke, and oil in the United States from the mid-1800s to the 1950s. One manufacturing process used at manufactured gas plants (MGPs), coal carbonization, involved the heating of coal in a retort, the volatilization of hydrogen sulfide, and the generation of hydrogen cyanide. These gases were removed from the product gas stream through scrubbing with iron oxide particles. Some of the residuals of such processes were disposed of at landfills or on site. It was mainly disposed of in the form of cyanide compounds with iron, such as Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ (a common pigment) and Turnbull's Blue $\{Fe_3[Fe(CN)_6]_2\}$. See background discussions in EPRI (1999), Ghosh et al. (1999a, 1999b), Theis et al. (1994), and Meeussen et al. (1992a, 1992b, 1994).

Some of the MGP sites contain soils and groundwater contaminated with cyanide in appreciable concentrations, including the purifier box wastes characterized by the presence of Prussian Blue and Turnbull's Blue. Theis et al. (1994) reported that sulfur and iron are the major components of oxide box wastes, with significant quantities of cyanide, aluminum, titanium, and thiocyanate also present, based on the analysis of two purifier waste samples. Theis et al. (1994) further indicated that cyanide in these wastes exists entirely in complexed forms, with iron cyanide being the dominant solid phase, although small quantities of copper and nickel cyanide complexes were also found. Studies by Meeussen et al. (1992a, 1992b, 1994) and visual observations at former MGP sites (EPRI 1999) have established the presence of cyanide in a dark blue, iron complexed solid known as Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ or ferric ferrocyanide (FFC).

The solubility of Prussian Blue depends on pH and oxidation-reduction potential. Both Meeussen et al. (1992) and Theis et al (1994) reported that the solubility of Prussian Blue increases with increasing pH. More recently, Ghosh et al. (1999a) provided quantitative understanding of the aqueous stability and solubility of complex iron-cyanide compounds under equilibrium conditions. The authors investigated the stability of Prussian Blue, Turnbull's Blue $\{Fe_3[Fe(CN)_6]_2\}$, Prussian Brown $\{Fe[Fe(CN)_6]\}$, Berlin Green (composition not specified), and Berlin White (or Williamson's salt) $\{Fe_2[Fe(CN)_6]\}$, and found Prussian Blue and Turnbull's Blue to be the only two iron-cyanide solids stable under environmental aqueous conditions.

Ghosh et al. (1999a) report the importance of oxidation-reduction conditions to characteristics of Prussian Blue and Turnbull's Blue, and the stability of aqueous cyanide species. The authors report that total dissolved cyanide concentrations increase from oxic to anoxic conditions in the low pH region, but decrease at neutral to high pH regions. They also reconfirm that dissolution of complex iron-cyanide solids increases with increasing pH. Ghosh et al. (1999a) found that Prussian Blue and Turnbull's Blue were stable under higher and lower redox conditions, respectively

Studies indicate that complexed cyanide is the dominant cyanide species in soils because of its slow decomposition kinetics in the absence of sunlight. When exposed to sunlight, however, complexed cyanide rapidly decomposes to free cyanide (Meeussen et al. 1992a). The following two possible reactions are involved in the formation of dissolved cyanide species by the dissolution of Prussian Blue:

$$Fe_4[Fe(CN)_6]_3 \text{ (solid)} \rightarrow 4\ Fe^{3+} + 3\ Fe(CN)_6^{4-}$$

$$Fe_4[Fe(CN)_6]_3 \text{ (solid)} \rightarrow 3\ Fe^{2+} + Fe^{3+} + 3\ Fe(CN)_6^{4-}$$

Meeussen et al. (1994) provided the following overall dissolution reaction for Prussian Blue to yield solid $Fe(OH)_3$ and the ferricyanide species in the aqueous phases in mildly reducing to oxidizing soils (pH + pE ranging from 11 to 18):

$$Fe_4[Fe(CN)_6]_3 \text{ (solid)} + 12\ H_2O \rightarrow 4\ Fe(OH)_3 \text{ (solid)} + 3\ Fe(CN)_6^{4-} + 12\ H^+ + 2e^-$$

None of these studies indicate the formation of a significant mass of aqueous species HCN^o (aq) or CN^- when compared to aqueous complexed cyanide in these dissolution reactions.

Studies of MGP sites also indicate that cyanide release from oxide box wastes is primarily in the form of aqueous cyanide complexes and that these complexes are stable in groundwater systems [e.g., see Theis et al. (1999), Dzombak et al. (1999), Olsen et al. 1999)]. Murarka and Krupka (1999) summarize the observed maximum total cyanide concentrations in groundwater samples from four MGP sites, along with the range of analytically-determined concentrations of free cyanide species. The maximum measured concentrations of total cyanide at these sites ranged from 6.2 to 12.0 mg/L, compared to 0.001 to 0.020 mg/L for the range of free cyanide.

Theis et al. (1994) also reported very good confirming evidence of $Fe(CN)_6^{4-}$ in the leachates produced from two oxide box wastes. Based on their ion chromatography results, these authors however also noted a second peak containing an unknown iron-cyanide complex. Recent analyses of several groundwater samples from a number of MGP sites containing purifier box wastes have further confirmed the presence of this unknown iron-cyanide species as well as the occurrence of the $Fe(CN)_6^{4-}$ aqueous species (Theis et al. 1999). The unknown cyanide complex has a cyanide-to-iron molar ratio of between four and five, and may contain other ligands. Theis et al. (1999) suggest that the environmental significance of this unknown iron-cyanide complex may be intermediate between $Fe(CN)_6^{4-}$ and free cyanide.

The environmental risks associated with cyanide contaminated sites depend on the toxicity and geochemical behavior of cyanide. These two factors are related to the aqueous speciation of dissolved cyanide. Cyanide in its free aqueous form, $HCN°$ (aq) and CN^-, is highly toxic. The free form of cyanide is more toxic than its aqueous complexed species, such as metal-cyanide complexes like $Fe(CN)_6^{4-}$. Cyanide forms aqueous complexes with numerous metals (see examples in Table 1-1) which have a wide range of chemical and biological stabilities.

Table 1-1
Examples of Cyanide Aqueous Species and their Equilibrium Constants

[The sources of these equilibrium constants are discussed in Chapter 3 and Appendix A.]

Reaction	log $K°_{r,298}$	Reaction	log $K°_{r,298}$
$H^+ + CN^- = HCN°$ (aq)	+9.23	$Hg^{2+} + CN^- = HgCN^+$	+18.03
$Cd^{2+} + CN^- = CdCN^+$	+5.32	$Hg^{2+} + 2\ CN^- = Hg(CN)_2°$ (aq)	+34.51
$Cd^{2+} + 2\ CN^- = Cd(CN)_2°$ (aq)	+10.37	$Hg^{2+} + 3\ CN^- = Hg(CN)_3^-$	+38.26
$Cd^{2+} + 3\ CN^- = Cd(CN)_3^-$	+14.84	$Hg^{2+} + 4\ CN^- = Hg(CN)_4^{2-}$	+41.26
$Cd^{2+} + 4\ CN^- = Cd(CN)_4^{2-}$	+18.29	$Ni^{2+} + 2\ CN^- = Ni(CN)_2°$ (aq)	+14.59
$Co^{2+} + 3\ CN^- = Co(CN)_3^-$	+13.7	$Ni^{2+} + 3\ CN^- = Ni(CN)_3^-$	+22.63
$Co^{2+} + 5\ CN^- = Co(CN)_5^{3-}$	+23.0	$Ni^{2+} + 4\ CN^- = Ni(CN)_4^{2-}$	+30.12
$Cu^+ + 2\ CN^- = Cu(CN)_2^-$	+24.00	$Zn^{2+} + CN^- = ZnCN^+$	+4.98
$Cu^+ + 3\ CN^- = Cu(CN)_3^{2-}$	+28.62	$Zn^{2+} + 2\ CN^- = Zn(CN)_2°$ (aq)	+11.07
$Cu^+ + 4\ CN^- = Cu(CN)_4^{3-}$	+30.31	$Zn^{2+} + 3\ CN^- = Zn(CN)_3^-$	+16.05
$Fe^{2+} + 6\ CN^- = Fe(CN)_6^{4-}$	+45.63	$Zn^{2+} + 4\ CN^- = Zn(CN)_4^{2-}$	+16.76
$Fe^{3+} + 6\ CN^- = Fe(CN)_6^{3-}$	+52.61		

Some aqueous cyanide complexes (e.g., H^+, cadmium, and zinc) readily dissociate under neutral or mildly acidic conditions (“weak” acid dissociable), whereas other more stable cyanide complexes (e.g., iron) only dissociate rapidly under very low pH conditions (Theis et al. 1994). Complexed cyanide forms may interact more with the soil solid phase due to their ionic nature and solubility behavior. These processes in turn affect the migration rates of cyanide in soils. In the range of pH values and oxidation-reduction potentials of soil/water systems, the complex cyanide species may dissociate to more toxic free cyanide. The weaker cyanide complexes are considered more toxic than stronger complexes.

Several chemical methods (Aronstein et al. 1994 and others) have been proposed for the removal of cyanides from industrial solid waste and wastewaters, and for the remediation of cyanide-contaminated soils. Some of these methods include alkaline hydrolysis; anion exchange (e.g., clinoptilolite); bioremediation; circulating bed combustion; oxidation with chlorine and hypochlorite, UV/ozone, wet air, or hydrogen peroxide; photocatalytic oxidation; polymerization with formaldehyde; steam stripping; thermal desorption; and treatment with sulfur.

1.2 Objectives

The objectives of this effort were to conduct a literature review to 1) identify cyanide aqueous species and solids (and their associated thermodynamic properties) that are potentially important to the geochemical behavior of cyanide in soil/water systems, and 2) summarize bioremediation technologies relevant to cyanide-contaminated waters and soil materials. Based on the results of the literature review, speciation/solubility calculations were completed to demonstrate the relative importance of aqueous free cyanide species [HCN° (aq) and CN^-] and metal-cyanide complexes [e.g., $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $Ni(CN)_6^{4-}$], and to identify possible cyanide solubility controls that might affect the geochemistry of cyanide in contaminated soils and groundwaters.

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2
LITERATURE SEARCHES AND OTHER INFORMATION SOURCES

2.1 Introduction

Computerized literature and EPA Internet sites were searched and examined[1] to identify published information related to the geochemical and thermodynamic behavior of cyanide in soil/water systems and remediation technologies for cyanide-contaminated waters and soil materials. Results of these information searches were used to support all the objectives of this review.

2.2 Computerized Searches

The search criteria used to formulate the computerized literature searches are summarized below.[2]

- Purpose of search: Identify published sources describing thermodynamic data for cyanide-containing aqueous species and solids
  Search Criteria:
    - [cyanide or cyanate or thiocyanate or cyano]
      <u>and</u> [solid* <u>or</u> complex* <u>or</u> ligand*]
      <u>and</u> [thermodynamic <u>or</u> (equilibrium <u>or</u> stability <u>or</u> dissociation constant*) or solubility or Gibbs free energy]
      <u>and not</u> (gas*)
- Purpose of search: Identify published sources describing remediation technologies used for cyanide
  Search Criteria:
    - [cyanide <u>or</u> cyanate or thiocyanate <u>or</u> cyano]
      <u>and</u> [removal <u>or</u> remediation <u>or</u> destruction <u>or</u> treat* <u>or</u> restoration <u>or</u> in situ]

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[1] The literature searches were completed in late 1997 when this document was initially prepared for EPRI.

[2] The "*"character listed in above search strings refers to any additional characters. The search strings actually used by the library staff were refined from these summarized above.

- Purpose of search: Identify published sources describing environmental behavior of cyanide compounds
  Search Criteria:
  - [cyanide <u>or</u> cyanate <u>or</u> thiocyanate <u>or</u> cyano]
    <u>and</u> [Electric Power Research Institute <u>or</u> utility waste* <u>or</u> manufactured gas plants <u>or</u> groundwater <u>or</u> soil <u>or</u> environment*]
    <u>and</u> [solubility <u>or</u> adsorption <u>or</u> sorption <u>or</u> contam* <u>or</u> release <u>or</u> migration <u>or</u> groundwater transport]
    <u>and not</u> [air <u>or</u> atmospheric]

The computerized search was limited to documents published since 1975. Any relevant studies published prior to that time would likely be cited in the more recent publications.

The computerized literature searches also examined the Electric Power Research Institute (EPRI) computerized database. The EPRI database was searched for all reports and contracts pertaining to cyanide (or cyanate or thiocyanate or cyano) treatment and site contamination.

2.3 Other Information Sources

Additional information was identified from word searches of the electronic copies of several remediation-summary documents "downloaded" from EPA's Clean Up Information System (CLU-IN) site on the Internet. These sources included documents such as the report "*Remediation Technologies Screening Matrix and Reference Guide. Second Edition*" (EPA 1994).

2.4 Thermodynamic Properties and Adsorption Behavior of Cyanide Compounds

The literature searches identified numerous references to the geochemical behavior and remediation technologies for cyanide-contaminated waters and soil materials. However, except for the study by Meeussen et al. (1992) who reported an equilibrium constant for Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$, the literature searches did not identify any publications dealing specifically with thermodynamic data for cyano aqueous species or solids. Compilations of thermodynamic data by Smith and Martell (1997), Wagman et al. (1982), and Sehmel (1989) were known from prior experience and therefore were used as the sources of thermodynamic values for cyano aqueous species and solids.

As noted at the beginning of this chapter, the computerized literature searches were conducted in late 1997. Since that time, Ghosh et al. (1999) have reported the results of laboratory studies of the aqueous stabilities and solubilities of several iron-cyanide solids. Their experiments were conducted under a range of pH and oxidation-reduction conditions, and identified Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ and Turnbull's Blue $\{Fe_3[Fe(CN)_6]_2\}$ as being stable under environmental aqueous conditions. The equilibrium constants derived by Ghosh et al. (1999) are given in Chapter 3.

It should also be noted that only one relevant study was identified pertaining to the adsorption behavior of cyanide on soil materials. Theis et al. (1988) studied the adsorption rates of the ferricyanide ion [$Fe(CN)_6^{3-}$] and cadmium on goethite [α-FeO(OH)]. Their experiments, which were conducted at $5.1x10^{-6}$ M $Fe(CN)_6$, 0.6 g/L goethite, and I=0.01 M, indicated that the adsorption behavior observed for the ferricyanide ion was similar to that expected for an anion. At low pH values (less than pH 4.5), approximately 100% of the ferricyanide was removed by adsorption on goethite. The adsorption of ferricyanide then decreased at pH values between 5 to 9. At pH values greater than 9, essentially none of the dissolved ferricyanide was adsorbed by the goethite. Given the limited data available for the adsorption behavior of cyanide compounds on soil materials, this topic will not be discussed any further in this report.

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EQUILIBRIUM CONSTANTS FOR CYANO AQUEOUS SPECIES AND SOLIDS

3.1 Introduction

> Note that the term “cyano” will be used to collectively refer to all cyanide-related compounds, including cyanide (CN^-), thiocyanate (SCN^-), cyanate (OCN^-), etc. aqueous species and solids.

Equilibrium constants, log $K^\circ_{r,298}$, for cyano aqueous species and solids were compiled to identify aqueous species and solids that may be important to the mobility and solubility limits of cyanide in soil/water environments. Because cyanide (CN^-) is an anionic constituent, complexation reactions involving cyanide and environmentally important metals were also considered in our compilation and subsequent thermodynamic calculations.

3.2 Sources of Thermodynamic Values for Cyano Aqueous Species and Solids

Smith and Martell (1997), Beck (1987) Wagman et al. (1982), and Sehmel (1989) were used as the primary sources of thermodynamic values for cyano aqueous species and solids. Equilibrium constants, log $K^\circ_{r,298}$, for reactions involving cyano aqueous species and solids were compiled from the two internationally-recognized compilations of thermodynamic data (Smith and Martell 1997; Wagman et al. 1982), and from a published supplement to the thermodynamic database of the MINTEQ geochemical code (Sehmel 1989). Sehmel (1989) was considered a secondary source for data for cyano compounds possibly not listed or accepted in the other two references. Values were not compiled from the IUPAC (International Union of Pure and Applied Chemistry) sponsored critical review of cyano complexes by Beck (1987), because Smith and Martell (1997) included this source in their compilation.

Equilibrium constants for the solubilities of Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ and Turnbull’s Blue $\{Fe_3[Fe(CN)_6]_2\}$ were those derived by Ghosh et al. (1999) from precipitation and dissolution measurements.

3.3 Cyano Reactions and Equilibrium Constants

Our compilation of cyano reactions and associated log $K^\circ_{r,298}$ values is listed in Appendix A. Separate tables are included for reactions of aqueous species and solids containing cyanide

(CN^-), thiocyanate (SCN^-), cyanate (OCN^-), and cyano-metal compounds {e.g., hexacyanocobaltate ion [$Co(CN)_6^{3-}$], hexacyanoferrate(II), [$Fe(CN)_6^{4-}$], hexacyanoferrate(III) [$Fe(CN)_6^{3-}$], octacyanomolybdate(IV), [$Mo(CN)_8^{4-}$], selenocyanate ion ($NCSe^-$), and hexacyanotungstate(VI), [$W(CN)_8^{2-}$]}.

3.4Cyanide Aqueous Species

Based on the compiled thermodynamic data for cyano aqueous species (Appendix A), the cyanide aqueous species listed in Table 3-1 may be important to the mobility of cyanide in soil/water systems as well as to the complexation and thus mobility of environmentally important metals. Metals considered to be environmentally or geochemically important relative to the scope of this task include cadmium, cobalt, copper, iron, nickel, and zinc.

Table 3-1
Cyanide Aqueous Species Possibly Important to Mobility of Cyanide and Environmentally Important Metals in Soil/Water Systems.

[List of aqueous species based on availability of log $K°_{r,298}$ values.]

CN^-, $HCN°$ (aq)
$CdCN^+$, $Cd(CN)_2°$ (aq), $Cd(CN)_3$-, $Cd(CN)_4^{2-}$
$Co(CN)_3^-$, $Co(CN)_5^{3-}$
$Cu(I)CN_2^-$, $Cu(I)CN_3^{2-}$, $Cu(I)CN_4^{3-}$
$Fe(II)(CN)_6^{4-}$, $Fe(III)(CN)_6^{3-}$
$Ni(CN)_2°$ (aq), $Ni(CN)_3^-$, $Ni(CN)_4^{2-}NiH(CN)_4^-$, $NiH_2(CN)_4°$ (aq), $NiH_3(CN)_4^+$
$ZnCN^+$, $Zn(CN)_2°$ (aq), $Zn(CN)_3^-$, $Zn(CN)_4^{2-}$

3.5 Cyanide Solids

Based on the compiled thermodynamic data (Appendix A), the cyanide solids in Table 3-2 may be important to the solubility of cyanide in soil/water systems. In addition to the sources of thermodynamic data for cyano compounds listed above, Ghosh et al. (1999) recently studied the aqueous stabilities and solubilities of several iron-cyanide solids under a range of pH and oxidation-reduction conditions. They identified Prussian Blue {$Fe_4[Fe(CN)_6]_3$} and Turnbull's Blue {$Fe_3[Fe(CN)_6]_2$} as two iron-cyanide solids stable under environmental aqueous conditions. Based on their laboratory measurements, Ghosh et al. (1999) derived the following equilibrium constants for solubilities for these two solids:

$$Fe_4[Fe(CN)_6]_3 \text{ (Prussian Blue)} = 4\ Fe^{3+} + 3\ Fe^{2+} + 18\ CN^- \text{ , Log } K°_{r,298} = -257.45$$

$$Fe_3[Fe(CN)_6]_2 \text{ (Turnbull's Blue)} = 3\ Fe^{3+} + 2\ Fe^{2+} + 12\ CN^- \text{ , Log } K°_{r,298} = -173.44$$

The precipitation and dissolution of Prussian Blue has also been studied by Meeussen et al. (1992). They list a log $K°_{r,298}$ value of -84.5 for the reaction:

$$Fe_4(Fe(CN)_6)_3 \text{ (Prussian Blue)} = 4\ Fe^{3+} + 3\ Fe(CN)_6^{3-}\text{-} + 3\ e^- \text{ .}$$

For the sake of comparison to the solubility constant determined by Ghosh et al. (1999) for Prussian Blue, the log $K°_{r,298}$ in Meeussen et al. (1992) corresponds to a log $K°_{r,298}$ of -203.3 based on their reaction reformulated in terms of the species used by Ghosh et al. and ancillary thermodynamic data selected for our calculations. Ghosh et al. (1999) have criticized the accuracy of the solubility constant given by Meeussen et al. (1992) because the value was determined under non-equilibrium conditions and using superseded thermodynamic constants.

Table 3-2
Cyanide Solids Possibly Important to Solubility of Cyanide in Soil/Water Systems

[List of solids based on availability of log $K°_{r,298}$ and/or $\Delta G°_{f,298}$ values.]

$CrCN$, Cr_2CN, $CuCN$, $ZnCN_2$
$Cd_2Fe(CN)_6$, $Cd_2Fe(CN)_6{\cdot}7H_2O$, $K_2CdFe(CN)_6$, $K_{12}Cd_8[Fe(CN)_6]_7$,
$Cu_2Fe(CN)_6$, $K_2Cu(I)_2Fe(CN)_6$,
$K_4Fe(CN)_6$, $K_4Fe(CN)_6{\cdot}3H_2O$, $K_3Fe(CN)_6$,$Fe_4(Fe(CN)_6)_3$ (Prussian Blue), $\{Fe_3[Fe(CN)_6]_2\}$ (Turnbull's Blue)
$K_2Ni_3[Fe(CN)_6]_2$, $K_4Ni_4[Fe(CN)_6]_3$, $K_{12}Ni_8[Fe(CN)_6]_7$
$Pb_2Fe(CN)_6$, $Pb_2Fe(CN)_6{\cdot}3H_2O$
$Zn_2Fe(CN)_6$, $Zn_2Fe(CN)_6{\cdot}2H_2O$, $KZn_{1.5}Fe(CN)_6$

It should be noted from Table 3-2 that log $K°_{r,298}$ values (or $\Delta G°_{f,298}$ values) are available for a limited number of solids. Relative to cyano aqueous species, the thermodynamic data for cyano solids are relatively sparse. Wagman et al. (1982) lists several dozen additional solids which have only $S°_{298}$ or $\Delta H°_{f,298}$ values but no $\Delta G°_{f,298}$ values (see Table 3-3).

The solids listed in Tables 3-2 and 3-3 have relatively simple end-member compositions and may not represent the compositions of cyanide solids that might precipitate in soil/water systems. Rai et al. (1994) found that many hexacyanoferrate (or ferrocyanide) compounds exhibit a wide range of compositions due to solid solution and/or ion exchange factors. Many of these hexacyanoferrate (or ferrocyanide) compounds exhibit low solubilities.

Table 3-3
Cyanide Solids Listed in Wagman et al. (1982) Without $\Delta G^\circ_{f,298}$ Values

$Ba(CN)_2 \cdot 2H_2O$, $Ca(CN)_2$, $Ca_2Fe(CN)_6 \cdot 11H_2O$, $(CaO)_3 \cdot Ca(CN)_2 \cdot 15H_2O$

$Cd(CN)_2 \cdot CdO \cdot 5H_2O$, $CsCN$, $Fe_4(Fe(CN_6)_3$, $H_4Fe(CN)_6$

$Hg(CN)_2$, $(Hg(CN_2)_2) \cdot MgCl_2 \cdot 6H_2O$, $K_2Hg(CN)_4$, $K_3Co(CN)_6$, $Ni(CN)_2$

$Sr(CN)_2 \cdot 4H_2O$, $SrCl_2 \cdot 2Hg(CN)_2 \cdot 6H_2O$

$K_2Zn(CN)_4$, $Zn(CN)_2$, $(Zn(CN)_2)_3 \cdot ZnO$

3.6 References

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4

EQUILIBRIUM AQUEOUS SPECIATION AND SOLUBILITY CALCULATIONS

4.1 Introduction

A limited set of equilibrium thermodynamic calculations was completed to illustrate the possible importance of different cyanide aqueous species and solids (Tables 3-1 and 3-2) in soil/water systems. The calculations were limited to cyanide-containing soil/water systems and did not involve thiocyanate (SCN^-) reactions. The MINTEQA2 geochemical computer code was used to perform the calculations.

4.2 Calculation Method

The MINTEQA2 (Version 3.11) code and its predecessor versions are described by Allison et al. (1991, MINTEQA2), Brown and Allison (1987, MINTEQA1), Peterson et al. (1987a, MINTEQ), and Felmy et al. (1984, MINTEQ). The MINTEQ code was originally developed for EPA by combining the mathematical structure of the MINEQL code (Westall et al. 1976) with the thermodynamic database and geochemical attributes of the WATEQ3 code (Ball et al. 1981a). The MINTEQA2 code is used in conjunction with a thermodynamic database to calculate complex chemical equilibria among aqueous species, gases, and solids, and between dissolved and solid states. Version 3.11 of MINTEQA2 is the most current version of MINTEQ available from EPA. The code was obtained via the Internet from EPA's Center for Exposure Assessment Modeling (CEAM) in Athens, Georgia.

4.3 Geochemical Conditions

The geochemical conditions used for the thermodynamic calculations were arbitrarily selected for demonstration purposes only, but are based on general considerations of soil/water systems. Because pH and oxidation-reduction conditions are the most important parameters that affect aqueous speciation and solubility reactions, the thermodynamic calculations were completed over a range of pH and oxidation-reduction conditions that were thought to represent relevant soil conditions, as well as to demonstrate the relative importance of cyanide speciation.

4.3.1 pH Conditions

The cyanide speciation/solubility calculations were carried out at 0.5-pH unit increments between and including the pH values of 2 and 10. This range of pH values was selected for the cyanide calculations because it includes the pH values of most soil/water systems at the sites of interest.

4.3.2 Oxidation-Reduction Conditions

Three oxidation-reduction conditions were considered for the cyanide speciation/solubility calculations. Although oxidation-reduction conditions have no direct effect on the cyanide chemistry as considered in these calculations, they do affect the geochemical behavior of other constituents, such as iron which is ubiquitous in soil/water systems. Because Fe(II) and Fe(III) both form strong cyanide complexes [i.e., $Fe(II)(CN)_6^{4-}$ and $Fe(III)(CN)_6^{3-}$], the geochemical behavior of iron as affected by pH, oxidation-reduction conditions, and biological activity in turn affects and possibly enhances the mobility of cyanide in soils.

For the most oxidizing condition, pE[3] values were determined for each pH value from the equation

$$pE + pH = 18 ,$$

where Eh (mV) = 59.2 pE. This equation represents the most oxidizing conditions found in soil systems (Lindsay 1979), and is shown as the dotted line labeled A in Figure 4-1.

To represent an intermediate redox environment, it was assumed that the oxidation-reduction conditions were poised by the Fe(II)/Fe(III) redox couple (Lindsay 1979). The pH/pE boundary used for cyanide speciation/solubility calculations at these more reducing conditions was defined by the equilibrium between the dominant Fe(II) and Fe(III) aqueous species between pH values of 2 and 10. This boundary was determined from an Eh(or pE)-pH diagram [also known as Pourbaix diagram, see discussion in Nordstrom and Munoz (1985)] calculated with $\Delta G^\circ_{f,298}$ values for the Fe(II) and Fe(III) uncomplexed ions and hydrolytic species that are consistent with the log $K^\circ_{r,298}$ values for these same species in the MINTEQA2 database. This Fe(II)/Fe(III) oxidation-reduction boundary is shown as the dotted line labeled B in Figure 4-1.

For the most reducing condition, pE values were determined for each pH value from the equation

$$pE + pH = 2.6$$

This equation represents reducing conditions where dissolved sulfide and pyrite (FeS_2)[4] are stable in aqueous systems (see discussion of sulfide systems in Langmuir 1997), and is shown as the dotted line labeled C in Figure 4-1.

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[3] The reader is referred to Lindsay (1979) or Nordstrom and Munoz (1985) regarding the principles and equations governing the oxidation-reduction parameters pE and Eh.

[4] For a discussion of dissolved sulfide and pyrite (FeS_2) equilibria, see Langmuir (1997).

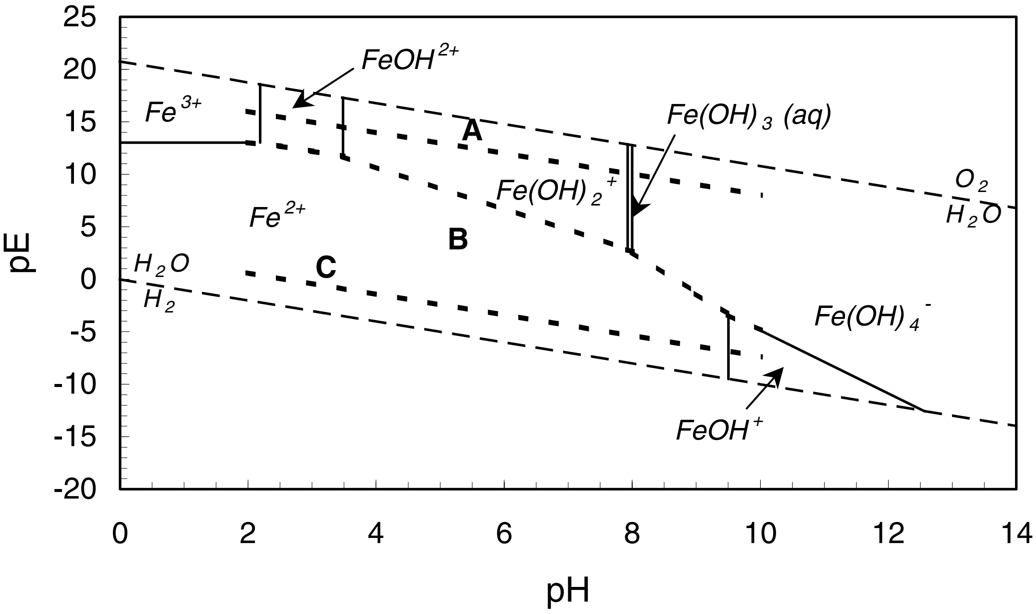

Figure 4-1
pE-pH (Pourbaix) Diagram Showing the Dominant Dissolved Fe(II) and Fe(III) Species Calculated for an Aqueous System Free of Dissolved Cyanide and Carbonate

[At these conditions, the pE-pH diagram is independent of the initial concentration of total dissolved iron. The dominant iron aqueous species are shown in italics within or near the Eh-pH region of dominance. The dotted line labeled A represents the most oxidizing conditions (pE + pH = 18) used for the cyanide speciation calculations. The dotted line labeled B represents the boundary between Fe(III) and Fe(II), and the intermediate redox conditions used for the speciation calculations. The dotted line labeled C represents the most reducing conditions (pE + pH = 2.6) used for the speciation calculations. The top and bottom dashed lines represent the boundaries for the 1-atm decomposition of water to O_2 and H_2, respectively.]

4.3.3 Cyanide and Other Ligand Concentrations

The cyanide speciation/solubility calculations were completed at the three redox conditions described above using a concentration of total dissolved cyanide (as CN) of 0.2 mg/L (7.70×10^{-6} mol/L). This concentration was selected because it corresponds to EPA's MCL (maximum contaminant level) for free cyanide. To demonstrate the effect of cyanide concentration on distribution of metal-cyanide complexes, cyanide speciation was also calculated at the most oxidizing condition using a concentration of total dissolved cyanide of 8.0 mg/L (3.07×10^{-4} mol/L), which is forty times greater than the MCL for free cyanide.

Other inorganic ligands (other than OH^-), such as carbonate and phosphate, that are naturally present in soil/water systems and potential complexants for dissolved metals were not included to simplify the speciation/solubility calculations. Although the review of thermodynamic data did not indicate any constants for reactions involving these ligands with cyanide, the formation of metal complexes with these ligands, especially carbonate at high pH values, could compete for the available dissolved metal concentrations and possibly reduce the calculated concentrations of metal-cyanide complexes. Given the magnitude of the equilibrium constants for the metal-cyanide complexes considered here, the impact on the speciation calculations from the omission of these ligands is expected to be minimal.

4.3.4 Iron and Other Metal Concentrations

As noted above, the geochemical behavior of iron affects the mobility of dissolved cyanide via the formation of strong Fe(II) and Fe(III) cyanide complexes. For this limited set of calculations, the concentrations of total dissolved iron at the two most oxidizing conditions and the most reducing conditions were assumed to be fixed by the equilibrium solubility of $Fe(OH)_3$ (soil) and pyrite (FeS_2), respectively. (Lindsay 1979).

To demonstrate the relative importance of the aqueous cyanide complexes listed in Table 3-1, dissolved cadmium, copper, iron, nickel, and zinc and their associated oxidation-reduction couples were also included in the speciation/solubility calculations. The concentrations of these trace metals are highly variable in soil/water systems, but are generally expected to be low. In reality, the concentrations of these metals will be controlled by solubility and/or sorption reactions in soil/water systems. At very reducing conditions, the solubilities of sulfide minerals may control the low concentrations of these dissolved metals. The initial total dissolved concentration of cadmium, copper, iron, nickel, and zinc was arbitrarily set at $1x10^{-6}$ mol/L.

4.4 Distribution of Cyanide Aqueous Species

4.4.1 Oxidizing Conditions

The calculated distribution of cyanide species for a total dissolved mass of cyanide (as CN) of 0.2 mg/L ($7.70x10^{-6}$ mol/L) is shown in Figure 4-2 as a function of pH at oxidizing conditions. At pH values less than 9, the speciation of dissolved cyanide is dominated by the presence of the neutral cyanide species HCN° (aq). The species HCN° (aq) comprises approximately 99% to 37% of the dissolved cyanide at pH values of 6.0 and 9.0, respectively, at the conditions assumed for these calculations. The anionic cyanide species CN^- dominates over the neutral species HCN° (aq) at pH values greater than 9.5 In a preliminary set of modeling calculations, the dominant cyanide complex was calculated to be $Ni(CN)_4^{2-}$ at pH values greater than 8. Because there is no evidence of nickel-cyanide complexes at MGP sites,[5] nickel was omitted from input data sets for all subsequent speciation calculations. Between pH values of 9.0 and 9.5, approximately 35% of the total mass of dissolved cyanide is present as $Fe(CN)_6^{3-}$. Based on thermodynamic constants used for these calculations, the speciation results indicate that cyanide complexation of cadmium and zinc would not be important over this pH range. At pH values greater than 8, less than a maximum of 6% of the total mass of dissolved cyanide would present as cadmium-cyanide complexes.

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[5] I. Murarka (Ish. Inc, Sunnyvale, California), personal communication.

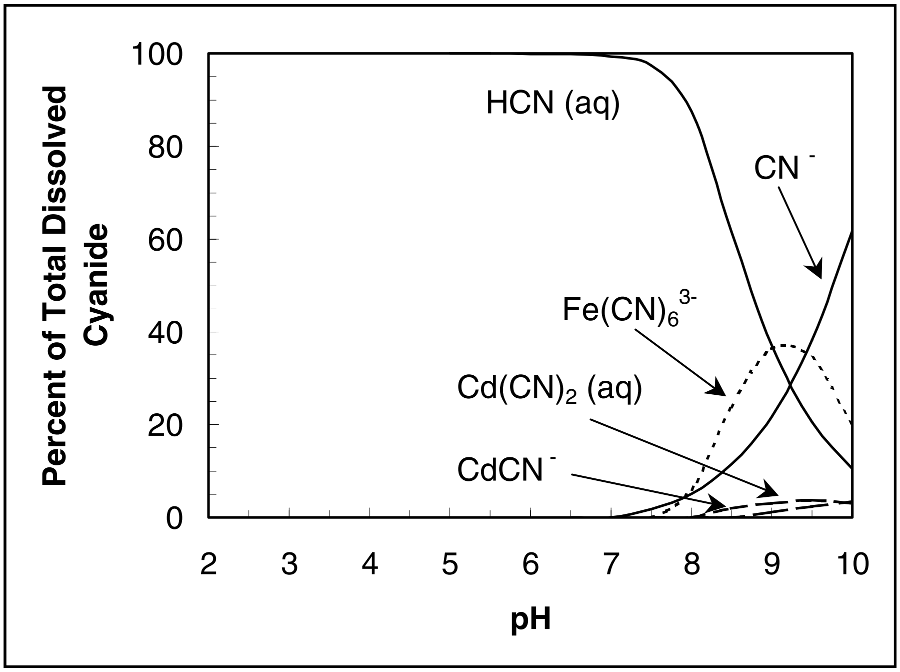

Figure 4-2
Distribution of Cyanide Aqueous Species as a Function of pH at the Most Oxidizing Conditions Considered in this Analysis and a Total Dissolved Mass of Cyanide (as CN) of 0.2 mg/L

Of the trace metals considered in this limited set of calculations at oxidizing conditions, cyanide complexation is most important to the geochemistry of dissolved Fe(III). At pH values greater than 7 and 0.2 mg/L total dissolved cyanide, the formation of $Fe(CN)_6^{3-}$ dominates the speciation of dissolved Fe(III). The importance of this Fe(III)-cyanide complex increases with increasing pH. At lower pH values, Fe(III) hydrolytic species [e.g., $FeOH^+$ and $Fe(OH)_2^+$] and uncomplexed Fe^{3+} will dominate the aqueous chemistry of iron at these conditions.

At these chemical conditions [i.e., oxidizing, equilibrium with respect to $Fe(OH)_3$(soil), and 0.2 mg/L total dissolved CN], the aqueous solutions calculate to be oversaturated with Prussian Blue $\{Fe_4[Fe(CN)_6]_3\}$ based on the equilibrium constant determined by Ghosh et al. (1999).

Increasing the total concentration of dissolved cyanide to 8.0 mg/L under these oxidizing conditions expands the pH region in which complex $Fe(CN)_6^{3-}$ is the dominant species (Figure 4-3). At this greater cyanide concentration, $Fe(CN)_6^{3-}$ is the dominant cyanide complex from pH 6.5 to 10, and uncomplexed CN^- constitutes less than 4% of the total dissolved cyanide at pH 10. At 8.0 mg/L total dissolved cyanide, the solution calculates to be oversaturated with respect Prussian Blue and Turnbull's Blue $\{Fe_3[Fe(CN)_6]_2\}$ at pH values less than 9 based on the equilibrium constants from Ghosh et al. (1999).

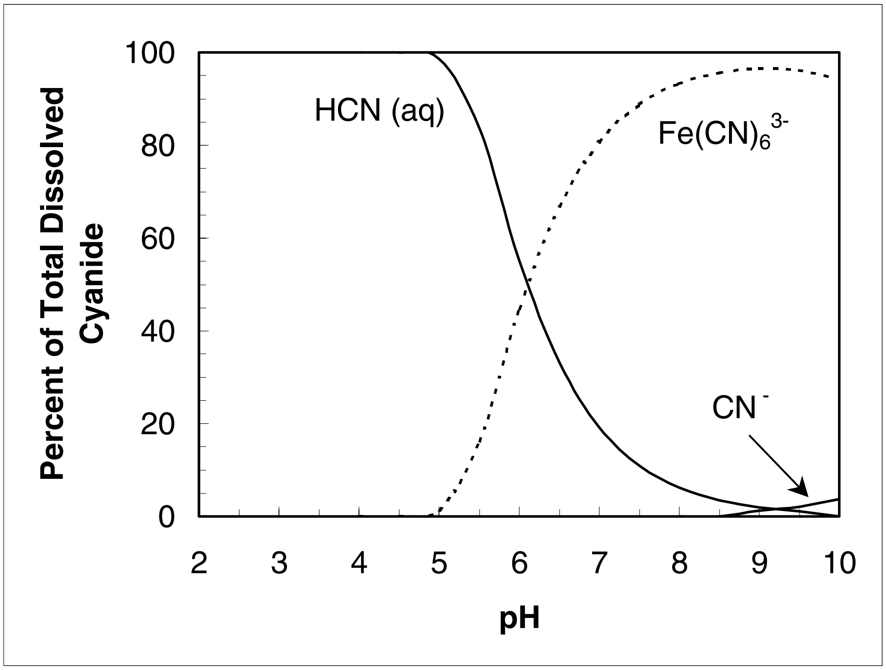

Figure 4-3
Distribution of Cyanide Aqueous Species as a Function of pH at the Most Oxidizing Conditions Considered in this Analysis and a Total Dissolved Mass of Cyanide (as CN) of 8.0 mg/L

4.4.2 Intermediate Oxidation-Reduction Conditions

The calculated distribution of cyanide species for a total dissolved mass of cyanide (as CN) of 0.2 mg/L is shown in Figure 4-4 as a function of pH at the intermediate redox conditions constrained by the Fe(II)/Fe(III) redox couple. Like the results based on oxidizing conditions, the speciation of dissolved cyanide at pH values less than 8 is dominated by the presence of the neutral cyanide species HCN° (aq). The species HCN° (aq) comprises approximately 95, 74, and 65% of the dissolved cyanide at pH values of 5.0, 6.0, and 7.5, respectively, at the conditions assumed for these calculations. At these more reducing conditions, there are greater concentrations of dissolved Cu(I) and Fe(II) present, especially at the higher pH values, which affect the speciation of dissolved cyanide. At pH values greater than 8, the iron-cyanide complex $Fe(CN)_6^{4-}$ is the dominant cyanide complex. This complex constitutes 72% of total dissolved cyanide at pH 10. At pH values from 5.5 to 10.0, the Cu(I) complex $Cu(CN)_2^-$ comprises approximately 25% of the total dissolved cyanide assumed for these calculations. At these intermediate redox conditions, the modeling calculations indicate that the uncomplexed species CN^- is never dominant, and constitutes a maximum of 2% of the total dissolved mass of cyanide at pH values between 7.5 and 10.0. Based on the solubility values determined by Ghosh et al. (1999), this solution is oversaturated with Prussian Blue at pH values less than 9.5 and with Turnbull's Blue over the entire pH range from 2 to 10.

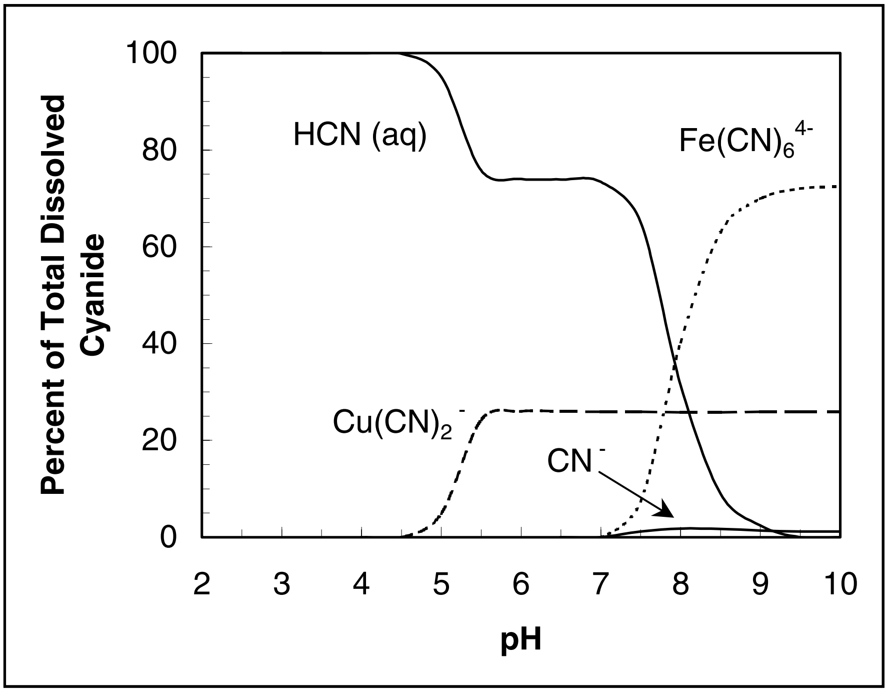

Figure 4-4
Distribution of Cyanide Aqueous Species as a Function of pH at Intermediate Redox Conditions Considered in this Analysis Based on the Fe(II)/Fe(III) Redox Couple and a Total Dissolved Mass of Cyanide (as CN) of 0.2 mg/L

Under these intermediate redox conditions, increasing the total concentration of dissolved cyanide to 8.0 mg/L extends the pH region in which complex $Fe(CN)_6^{4-}$ is dominant from pH 8 to 6.5 (Figure 4-5). At this greater cyanide concentration, $Cu(CN)_2^-$ is no longer an important cyanide complex. The calculations indicate that $Fe(CN)_6^{3-}$ is present at a significant mass over the pH range from 5 to 7. At pH 6.0, $Fe(CN)_6^{3-}$ constitutes a maximum 37% of the total dissolved mass of dissolved cyanide. At 8.0 mg/L total dissolved cyanide, the solution calculates to be oversaturated with respect to Prussian Blue and Turnbull’s Blue over the entire pH range from 2 to 10 based on the equilibrium constants from Ghosh et al. (1999).

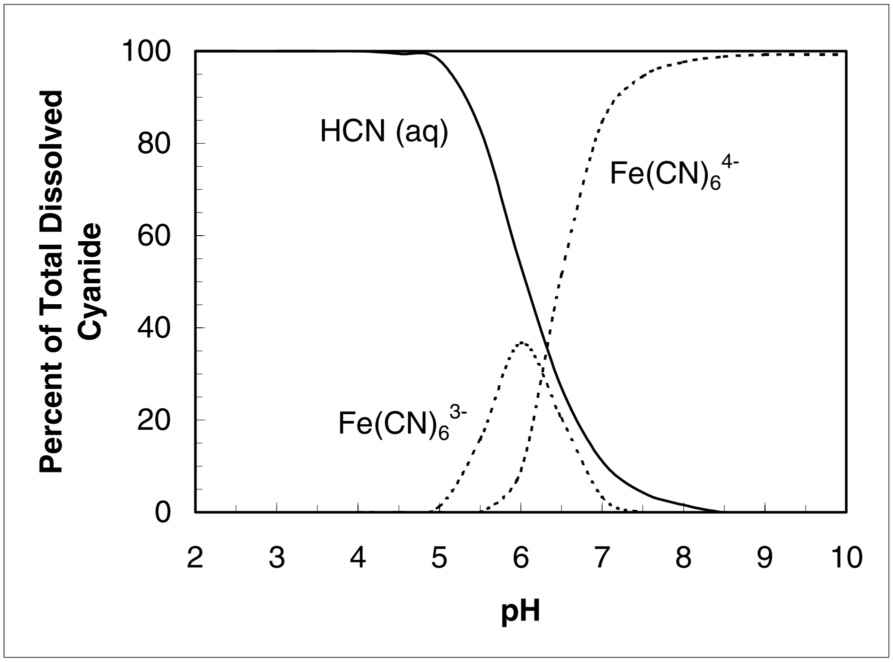

Figure 4-5
Distribution of Cyanide Aqueous Species as a Function of pH at Intermediate Redox Conditions Considered in this Analysis Based on the Fe(II)/Fe(III) Redox Couple and a Total Dissolved Mass of cyanide (as CN) of 8.0 mg/L

4.4.3 Reducing Conditions

The calculated distributions of cyanide species for a total dissolved mass of cyanide (as CN) of 0.2 and 8.0 mg/L are shown in Figures 4-6 and 4-7 as a function of pH at reducing conditions constrained by equilibrium with dissolved sulfide and pyrite. The results are similar to those obtained for the intermediate redox conditions. Like the results obtained for the two more oxidizing conditions, the speciation of dissolved cyanide at pH values less than 8 is dominated by the presence of the neutral cyanide species HCN° (aq). At basic pH values, the iron-cyanide complex $Fe(CN)_6^{4-}$ is the dominant cyanide complex. At 0.2 mg CN/L, the Cu(I) complex $Cu(CN)_2^-$ comprises approximately 26% of the total dissolved mass of cyanide in the pH range from 3 to 10. At these reducing conditions, the uncomplexed species CN^- is never dominant. At 0.2 mg CN/L, CN^- constitutes a maximum of 12% of the total dissolved mass of cyanide at pH values between 8.5 and 10.0. Both of these solutions calculate to be undersaturated with Prussian Blue and Turnbull’s Blue over the pH range from 2 to 10 based on the solubility constants from Ghosh et al. (1999).

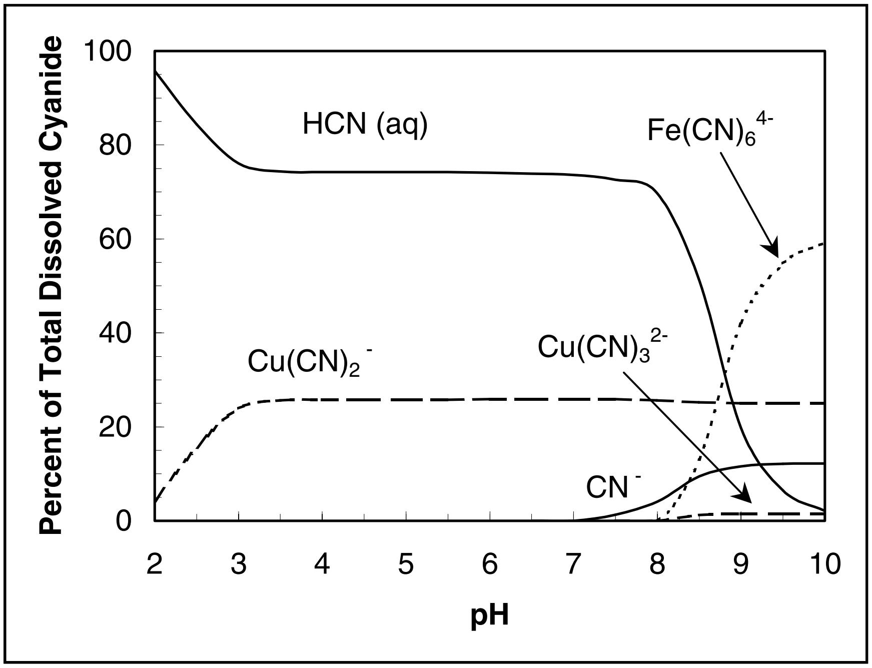

Figure 4-6
Distribution of Cyanide Aqueous Species as a Function of pH at the Most Reducing Conditions Considered in this Analysis and a Total Dissolved Mass of Cyanide (as CN) of 0.2 mg/L

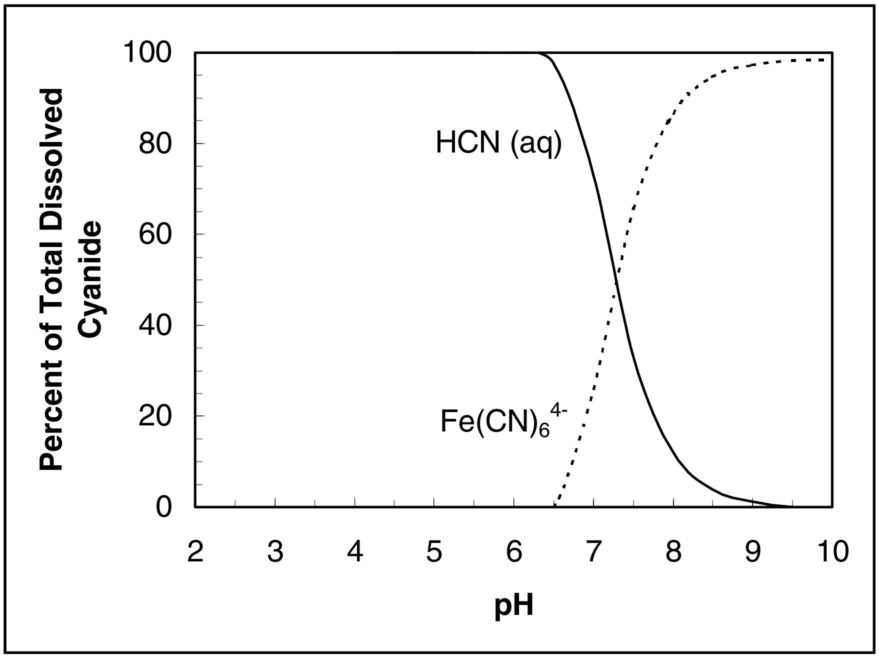

Figure 4-7
Distribution of Cyanide Aqueous Species as a Function of pH at the Most Reducing Conditions Considered in this Analysis and a Total Dissolved Mass of Cyanide (as CN) of 8.0 mg/L

4.5 Solubility of Cyanide Solid Phases

At MGP sites, the source of cyanide compounds is the purifier box wastes. These wastes have been characterized by the presence of Prussian Blue and Turnbull's Blue. Solubility constants reported by Ghosh et al. (1999) have been used to calculate the total concentrations of dissolved cyanide in equilibrium with the solubility of pure Prussian Blue (Figure 4-8) and Turnbull's Blue (Figure 4-9). The solubilities were calculated over the pH range from 2 to 10 and two pE values of 10 and 0. The solubilities plotted in Figures 4-8 and 4-9 indicate the range of solubility-limited concentrations of dissolved cyanide in soil porewater and groundwater that could be found near these source areas.

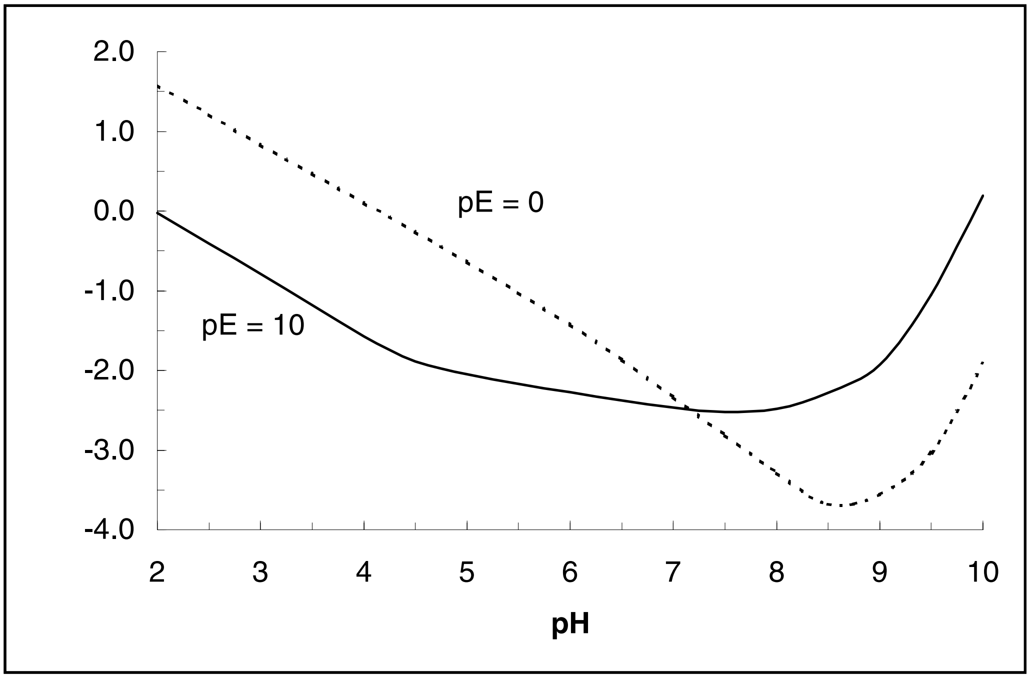

Figure 4-8
Concentration of Total Dissolved Cyanide as a Function of pH and pE Values of 10 and 0 Based on the Equilibrium Solubility of Prussian Blue from Ghosh et al. (1999)

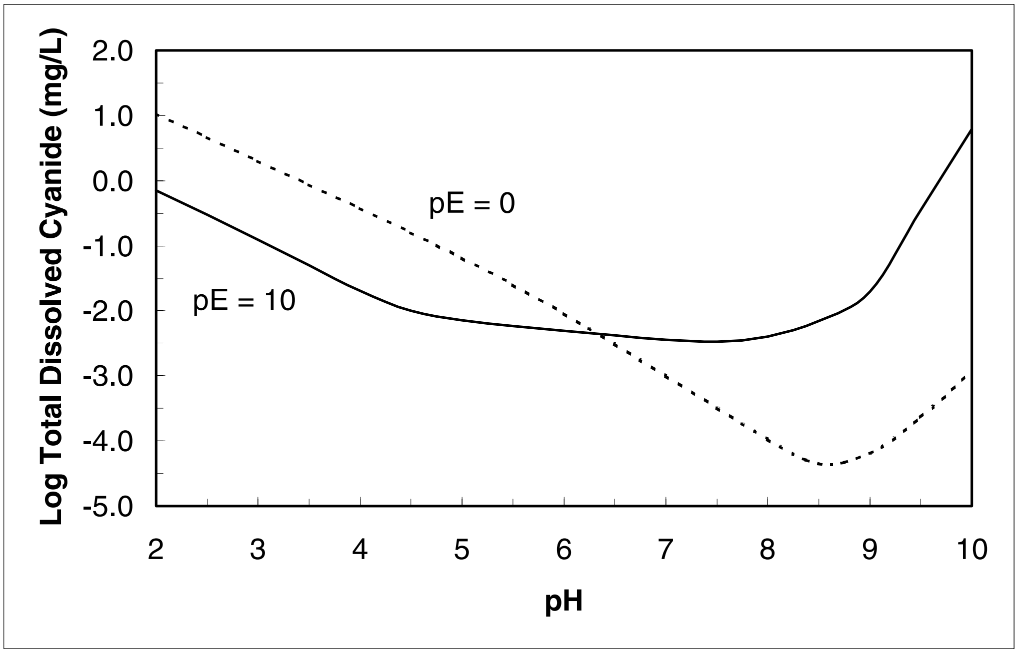

Figure 4-9
Concentration of Total Dissolved Cyanide as a Function of pH and pE Values of 10 and 0 Based on the Equilibrium Solubility of Turnbull's Blue from Ghosh et al. (1999)

4.6 Conclusions

The equilibrium speciation/solubility calculations demonstrate the importance of several metal-cyanide complexes. Based on the available thermodynamic data, a suite of easily dissociable, weak acid dissociable, and strong acid dissociable metal-cyanide complexes may exist in groundwater. Under the pH/pE and solution compositions used for these calculations, the neutral cyanide species HCN° (aq) is predicted to dominate the aqueous speciation of dissolved cyanide at pH values typically less than 8. Increasing the concentration of total dissolved cyanide decreases the pH region where HCN° (aq) dominates to lower pH values, and increases the pH regions where iron-cyanide complexes dominate.

However, cyanide speciation calculations based on equilibrium thermodynamics and the available equilibrium constants do not accurately represent the speciation of dissolved cyanide determined directly by chemical analyses of contaminated groundwaters. As noted by Murarka and Krupka (1999), the maximum measured concentrations of total cyanide in groundwater samples from four MGP sites ranged from 6.2 to 12.0 mg/L, whereas the concentrations of free cyanide in these same samples ranged from 0.001 to 0.020 mg/L. Theis et al. (1994) also reported very good confirming evidence of $Fe(CN)_6^{4-}$ in the leachates produced from two oxide box wastes. The discrepancy between the analytically-determined versus equilibrium thermodynamically calculated speciation of dissolved cyanide is attributed to the slow decomposition kinetics that have been observed for iron-cyanide complexes in the absence of sunlight (see Chapter 1).

Moreover, because cyanide solids, such as Prussian Blue {$Fe_4[Fe(CN)_6]_3$} and Turnbull's Blue {$Fe_3[Fe(CN)_6]_2$} are known to exist in purifier box wastes, cyanide will likely enter the soil porewater and groundwater systems as aqueous iron-cyanide complexes, as a result of the aqueous dissolution of these solids. In the near vicinity of such wastes, thermodynamic calculations indicate that the concentrations of total dissolved cyanide limited by the solubilities of these solids at circumneutral pH values should range from a few mg/L to several ppb. Because groundwater conditions (particularly pH and pE) typically do not change much within a few hundred feet on any specific MGP site, the dissociation of the iron-cyanide complexes is not expected to occur at a significant rate. Also, dissociation of the iron-cyanide complexes should precede the formation of other metal cyanide complexes, even when the other dissolved metals may be present in small concentrations in the groundwater.

4.7 References

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5
BIOREMEDIATION OF CYANIDE

5.1 Introduction

Bioremediation has gained increasing interest as a remediation strategy to treat wastes through the use of microorganisms (Bolton and Gorby 1995). Even a toxic waste such as cyanide may be treated using microorganisms. Specific microorganisms can transform cyanide to nontoxic forms through various metabolic processes. Although there have been numerous publications focused on cyanide biodegradation by microorganisms, there are fewer examples of applying cyanide bioremediation in the field. This short review will focus on factors influencing cyanide biodegradation by microorganisms and give examples of cyanide bioremediation in the field. Table 5-1 lists the key publications and environmental factors influencing cyanide biodegradation.

5.2 Toxicity to Microorganisms

Cyanide is toxic to most living organisms through its inhibition of cytochrome oxidase, a critical enzyme in the respiratory electron transport chain and to a lesser extent its binding to other metalloproteins (Solomonson 1981). Cyanide (i.e., CN^-) inhibits enzymatic activity by binding to the metallic co-factors in these enzymes (Fasset 1963). As an example, the CN^- binds to the Fe(III) in cytochrome oxidase and prevents the oxidation-reduction reactions necessary for the electron transport chain. Cyanide is toxic to a wide variety of microorganisms including fungi, bacteria, and algae (Dubey and Holmes 1995). For example, some bacterial *Pseudomonas* sp. are killed by only 1 mg/L cyanide (Dubey and Holmes 1995).

Although cyanide is toxic to most microorganisms, some microorganisms (e.g., bacteria, algae, and fungi) naturally produce cyanide in their environment (Dubey and Holmes 1995). This production of cyanide may offer a competitive advantage to these organisms if they are resistant to cyanide and can degrade it to nontoxic constituents. Also, some plant species naturally produce cyanide as evidenced by its concentration in the seeds of apples, apricots, cherries, peaches and plums (Wild et al. 1994). Because cyanide is produced naturally by select microorganisms and plants and anthropogenically released into the environment, microorganisms have adapted and developed methods to detoxify cyanide. As an example, microorganisms that produce cyanide can degrade cyanide intracellularly when its concentration reaches inhibitory levels using various pathways discussed below (Dubey and Holmes 1995).

Table 5-1
Key Publications and Environmental Factors Influencing Cyanide Biodegradation

Contaminated Material and/or Waste Type	Type of Study	Description	Reference(s)
Sediment from a Cyanide-Containing Storage Basin	Laboratory	—Investigated biodegradation of cyanide and various metal-cyanide complexes in batch, fed-batch, and continuous processes at pH~8.2 and total cyanides at 20-190 mg/L. Degradation occurred over days.	Boucabeille et al. (1994)
Waste Water from Gold Mining Operations	Field	—*Pseudomonas sp*. —Rotating biological contactors treat 4 million gallons/day (15 million L) at 4 mg cyanide/L and reduce the cyanide effluent concentration to 0.06 mg/L at pH 7-9.	Whitlock (1990)
Leachings From Gold Ore	Field	—*Pseudomonas pseudoalcaligenes* —Reduced cyanide from 20 mg/L to 8.5 mg/L after 15 weeks with flow rates starting at 50 gal/min for 2 weeks and increasing to 300 gal/min at pH 9.	Lien and Altringer (1993)
Bacterium	Laboratory	—*Pseudomonas fluorescens* —Biodegrade cyanide, $Ni(CN)_4^{2-}$ and $Cu(CN)_4^{2-}$ at pH 7, but not ferrocyanide [$Fe(CN)_6^{4-}$] or zinc cyanide [$Zn(CN)_4^{2-}$]. Metal toxicity was not a factor influencing the degradation of cyanide.	Rollinson et al. (1987)
Bacteria from Soil, Freshwater, and Sewage	Laboratory	—*Pseudomonas sp*., *Klebsiella sp*. —Biodegrade $Ni(CN)_4^{2-}$ with some $Ni(CN)_2$ formed at pH 7.	Silva-Avalos et al. (1990)
Bacterium from Gold Mining Effluent	Laboratory	—*Acinetobacter sp*. —Degraded (μg/ml): $Au(CN)_2^{2-}$ (0.25), $Ag(CN)_2^{2-}$ (1.0), $Cd(CN)_2^{2-}$ (5.0), $Zn(CN)_4^{2-}$ (5.0), $Cu(CN)_4^{3-}$ (5.0), $Fe(CN)_6^{4-}$ (80), $Fe(CN)_8^{3-}$ (100), $Co(CN)_4^{2-}$ (100), CN^- (100) at pH 6.5.	Finnegan et al. (1991)
Sewage Sludge	Laboratory	—Continuous stirred bench-scale bioreactor degraded cyanide and various metal-cyanide complexes at 20 mg/L.	Granato et al. (1996)
Contaminated Industrial Waste Waters	Laboratory	—Pseudomonas putide —Encapsulation in calcium alginate enhanced cyanide and metal-cyanide degradation	Babu et al. (1993), Babu et al. (1992), Chapatwala et al. (1993)
Sewage	Laboratory	—Anaerobic consortium —Degraded free cyanide at ~100 mg/L to 20 mg/L under methanogenesis conditions after 2 days, no metal-cyanide complexes degraded.	Fallon et al. (1991)
Sewage	Laboratory	—Anaerobic consortium —Degraded free cyanide at 50 mg/L (85%) and 250 mg/L (45%).	Nagle et al. (1995)

5.3 Biodegradation of Cyanide in Laboratory Studies

Cyanide is a simple compound (HCN). The form or speciation of cyanide (see Chapters 3 and 4) in the environment can vary and include HCN° (aq), CN^-, and various metal-cyanide complexes with ferri- and ferrocyanide complexes as stable forms in the environment. Understanding the form of cyanide or its speciation in the environment is critical to understanding the factors influencing the biodegradation of the C-N bond. Recent research on other metal complexing compounds, such as the synthetic chelating agents NTA and EDTA, indicate that the rate of biodegradation of these compounds was related to the complexed metal and the relative rate of dissociation of the metal-chelate complex (Bolton and Girvin 1996, Bolton et al. 1996, Bolton et al. 1996, Bolton and Gorby 1995, Bolton et al.[6]).

A similar hypothesis could be proposed for cyanide. The CN^- species is the toxic form of cyanide, because this is the species that binds to the Fe in metalloproteins. A hypothesis could be that the toxicity of various metal-cyanide complexes would depend upon the concentration and rate of formation of the free cyanide ion (CN^-) as determined by stability constants and the kinetics of dissociation of various metal-cyanide complexes. However, to our knowledge, research to investigate this hypothesis has not been conducted. Most of the research discussed below has either focused on the biodegradation of CN^- or metal-cyanide complexes (Boucabeille et al. 1994, Finnegan et al. 1991, Silva-Avalos et al. 1990) where it is unclear if the metal-cyanide complexes are being degraded or if the metal-cyanide complex is dissociating before degradation. Although the mechanism of cyanide biodegradation in the environment is currently unclear, the microorganisms may degrade the free cyanide in equilibrium with the various metal-cyanide complexes (Aronstein et al. 1995).

The iron-cyanide complexes $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are generally considered to be kinetically inert (Sharpe 1976) and do not rapidly dissociate. This was also shown when the thermodynamically predicted distribution of cyanide and iron-cyanide complexes should have had free cyanide, but field samples showed only the iron-cyanide complexes present (Meeussen et al. 1992). Aronstein et al. (1994) found that $Fe(CN)_6^{4-}$ was not degraded by either an aerobic mixed bacterial consortium of a methylotrophic culture, while free cyanide was readily degraded.

Earlier studies have demonstrated that microorganisms can utilize free cyanide (from dissociation of KCN or NaCN) for growth, mainly as a nitrogen source (Furuki et al. 1972, Harris and Knowles 1983, Ingvorsen et al. 1991, Meyers et al. 1991, Skowronski and Strobel 1969, Ware and Painter 1955, White et al. 1988). Relatively few studies have focused on the biodegradation of metal-cyanide complexes present in the environment. Early work by Rollinson et al. (1987) found *Pseudomonas fluorescens* could biodegrade cyanide when present as either CN^- or as various metal-cyanide complexes as a source of nitrogen. The fastest rate and most growth was with $Ni(CN)_4^{2-}$ followed by $Cu(CN)_4^{2-}$. There was little or no growth when ferrocyanide [$Fe(CN)_6^{4-}$] or zinc cyanide [$Zn(CN)_4^{2-}$] were present as sole nitrogen sources. The metal concentrations used in these growth studies (250 • M) were significantly lower than the

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[6] Bolton, H., Jr, L. Xun, A. E. Plymale, J. W. Payne, and D. C. Girvin. (In Preparation). "Biodegradation of Metal-Ethylenediaminetetraacetate Complexes - Implications for Radionuclide and Metal Mobility in the Environment." *Environmental Science and Technology*.

minimum inhibitory concentrations for nickel (800 • M), copper (950 • M), zinc (2000 • M), and iron (>5000 • M) indicating that metal toxicity was not a factor influencing the degradation of cyanide. Low concentrations of nickel were associated with the cell. It was not clear whether the $Ni(CN)_4^{2-}$ complex was transported into the cell or whether the complex must dissociate outside the cell and that CN^- is transported into the cell for degradation to occur.

Silva-Avalos et al. (1990) isolated bacteria from soil, freshwater, and sewage able to biodegrade cyanide as a sole source of nitrogen when present as $Ni(CN)_4^{2-}$, demonstrating that microorganisms able to biodegrade cyanide when present as metal-cyanide complexes can be widespread. The cyanide anion was biodegraded with some $Ni(CN)_2$ formed. The biodegradation of CN^- was much slower, because the CN^- was more toxic to the bacteria than $Ni(CN)_4^{2-}$. They did not identify whether the CN^- or $Ni(CN)_4^{2-}$ was transported into the cell. However, the formation of $Ni(CN)_2$ and the cells ability to utilize both $Ni(CN)_4^{2-}$ and KCN suggests that CN^- forms first before biodegradation can occur.

Finnegan et al. (1991) isolated an *Acinetobacter* sp. able to grow on cyanide when present as various metal-cyanide complexes. The various metal-cyanides were not identified or modeled in solution, but rather were dissolved in nutrient solution. Metal-cyanide complexes assayed included the following (and optimal growth concentration in mg/L): $Au(CN)_2^{2-}$ (0.25), $Ag(CN)_2^{2-}$ (1.0), $Cd(CN)_2^{2-}$ (5.0), $Zn(CN)_4^{2-}$ (5.0), $Cu(CN)_4^{3-}$ (5.0), $Fe(CN)_6^{4-}$ (80), $Fe(CN)_6^{3-}$ (100), $Co(CN)_4^{2-}$ (100), CN^- (100) at pH 6.5.

Boucabeille et al. (1994) isolated cyanide biodegrading microorganisms from cyanide contaminated sediments. They used batch, fed-batch, and continuous processes and found cyanide was degraded in wastewater from a mining storage basin. The composition of the solution was complex with cyanide, cuprocyanide, and ferrocyanide, although actual concentrations or speciation distributions were not provided.

Cyanide degrading bacteria (e.g., *Pseudomonas putida*, *P. fluorescens*) can also be encapsulated or immobilized in calcium alginate, zeolite, and other matrices and retain their ability to degrade cyanide and metal-cyanide complexes (Babu et al. 1992, Babu et al. 1993, Chapatwala et al. 1993, Suh et al. 1994). Encapsulation usually allows organisms to tolerate higher concentrations of cyanide and also permit higher cell densities in various bioreactor designs with varying flow rates (Babu et al. 1992).

Dubey and Holmes (1995) offer a table with various mechanisms for cyanide biodegradation by microorganisms. It is useful to look at this table because it offers insight into how microorganism can degrade cyanide compounds. Cyanide can be used by microorganisms as a nitrogen and/or carbon source through various pathways. The various enzymes involved include:

- Cyanide monooxygenase [*Pseudomonas* sp. (Dorr and Knowles 1989, Harris and Knowles 1983)]

$$HCN + O_2 + H + NADPH = HOCN + NADP^+ + H_2O$$

- Cyanide dioxygenase [*P. fluorescens*, *Bacillus pumillus, P. cereus* (Harris and Knowles 1983a)]

$$HCN + O_2 + 2\ H^+ + NADPH = CO_2 + NH_3 + NADP^+$$

- Cyanase [*Escherichia coli* (Dorr and Knowles 1989, Kunz and Nagappan 1989, Taussig 1960, Taussig 1965)]

$$HOCN + H_2O = CO_2 + NH_3$$

- Cyanide hydralase [fungi (Fry and Meyers 1981)]

$$HCN + H_2O = HCONH_2$$

- Cyanidase [*Alcaligenes xylosoxidans* (Ingvorsen et al. 1991)]

$$HCN + 2H_2O = HCOOH + NH_3$$

Dumestre et al. (1997) isolated a fungus, *Fusarium solani*, able to degrade cyanide under alkaline conditions (pH 9.2 - 10.7) via a two-step hydrolytic process with the conversion of cyanide to formamide and its subsequent conversion to formate, which is used for growth. This is the upper pH range found for cyanide biodegradation.

Granato et al. (1996) used a continuous stirred bench-scale bioreactor inoculated with sewage sludge to treat a synthetic gold milling effluent containing cyanide and various metal-cyanide complexes at 20 mg/L. Both free cyanide and thiocyanide were degraded in the bioreactor as compared to the uninoculated control. The bioreactors also removed zinc, copper, and to some extent iron, indicating that either free cyanide was being degraded and respeciating the metal-cyanide complexes resulting in precipitation of the metal, or that these metal-cyanide complexes were being degraded and the freed metal sorbed to biomass.

Most of the studies listed above are aerobic microbial processes requiring oxygen. Cyanide can also be biodegraded under anaerobic conditions. An anaerobic fixed-bed column degraded free cyanide at ≥100 mg/L to 20 mg/L under methanogenesis conditions after two days. Strongly complexed cyanides were resistant to degradation (Fallon et al. 1991). Nagle et al. (1995) found that an anaerobic consortium was able to degrade 85% of 50 mg cyanide/L and 45% of 250 mg cyanide/L. Only free cyanide was assayed. If anaerobic degradative systems are to be successfully deployed to treat cyanide containing waste streams, lower levels of effluent cyanide concentrations will have to be achieved as well as the ability to degrade not only free cyanide, but also the metal-cyanide complexes.

5.4 Field Studies of the Bioremediation of Cyanide

There has been a long-term commercial application of cyanide bioremediation at Homestake Mine near Lead, South Dakota (Whitlock 1990). This operation was started in August 1984. The advantage of this system, which is discussed in detail below, is that because it is a biological system it does not require significant electrical energy or chemical additions. This treatment has been scaled up to treat 4 million gallons (15 million L) of waste water per day from mining operations (Whitlock 1990). Rotating biological contactors containing *Pseudomonas* sp. are used to treat the wastewater containing 4.1 mg/L total cyanide, 2.3 mg/L weak acid dissociable cyanide, and 62.0 mg/L thiocyanate, and reduce the effluent concentrations to 0.06 mg/L total cyanide, <0.02 mg/L weak acid dissociable cyanide, and <0.5 mg/L thiocyanate. The *Pseudomonas* sp. was selectively enriched and may have adapted over time to the specific influent concentrations of various constituents. Although the microorganisms used at Homestake Mine may not be applicable to every cyanide containing waste stream, these results do suggest that this approach has merit and could be attempted for waste streams conducive to microbial growth. The selection of microorganisms for use in these processes should consider the waste stream composition, environmental conditions, and the source of the innoculum. The approach could include using known cyanide degrading microorganisms and/or adding sediment/soil samples with known cyanide degrading properties.

Dubey and Holmes (1995) discussed a second field site, the Green Bank Gas Works in Blackburn, England. Approximately 14,000 m^3 of sediment contaminated with cyanide and metal-cyanide complexes was encapsulated with clay and treated on-site. The cyanide was transformed to CO_2 and NH_3 through biodegradation. No mention is made of the field conditions used or time frame for the bioremediation. Lien and Altringer (1993) discussed bioremediation of the Green Springs gold heap leach operation near Ely, Nevada. Results include lab scale investigations of biodegradation of cyanide containing solution predominantly copper- and nickel-cyanide. *Pseudomonas pseudoalcaligenes*, which was previously isolated from the cyanide containing waste water at this site, degraded various cyanide compounds in laboratory studies. In 1992 they conducted studies of cyanide degradation in the field. Two sediment heaps (600,000 tons of ore) containing cyanides were leached, with the leachate entering a pond (capacity 1,000,000 gal), the solution was pumped from the pond into five carbon adsorption tanks inoculated with *P. pseudoalcaligenes*. The effluent from these tanks was then reintroduced to leach the sediment heaps to make a closed loop system. Cyanide was degraded from 20 mg/L to 8.5 mg/L after 15 weeks with flow rates starting at 50 gal/min for two weeks and increasing to 300 gal/min.

This short review shows that microorganisms can biodegrade cyanide when present as free cyanide and metal-cyanide complexes. The mechanism of degradation is still not yet clear; i.e., it is unknown what form of cyanide is biodegraded. There have been a few successful large scale applications at a selected number of sites of cyanide bioremediation in the field. These results suggest that cyanide bioremediation could be successful at other waste sites.

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A
COMPILATION OF EQUILIBRIUM CONSTANTS FOR CYANO AQUEOUS SPECIES AND SOLIDS

A.1 Sources of Cyano Thermodynamic Values

Equilibrium constants, log $K^\circ_{r,298}$, for reactions involving cyano aqueous species and solids were compiled from two internationally-recognized compilations of thermodynamic data (Smith and Martell 1997; Wagman et al. 1982), and from a published supplement to the thermodynamic database of the MINTEQ geochemical code (Sehmel 1989). Sehmel (1989) was considered a secondary source for data for cyano compounds possibly not listed or accepted in the other two references, because Sehmel also used Wagman et al. (1982) and Smith and Martell (1976) [a predecessor to the more recent compilation of Smith and Martell (1997)]. Values were not tabulated from the IUPAC (International Union of Pure and Applied Chemistry) sponsored critical review of cyano complexes by Beck (1987), because Smith and Martell (1997) used this source for their compilation.

Equilibrium constants for the solubilities of Prussian Blue {$Fe_4[Fe(CN)_6]_3$} and Turnbull's Blue {$Fe_3[Fe(CN)_6]_2$} were obtained from Ghosh et al. (1999).

Unlike Smith and Martell (1997), Wagman et al. (1982) list values of Gibbs free energy of formation ($\Delta G^\circ_{f,298}$) for each compound, and do not include equilibrium constant values. For data taken for cyano compounds from Wagman et al., equilibrium constants (log $K^\circ_{r,298}$) were calculated from Gibbs free energies of reaction ($\Delta G^\circ_{r,298}$) according to the equation:

$$\text{Log } K^\circ_{r,298} = \frac{-\Delta G^\circ_{r,298}}{2.303 \text{ x } R \text{ x } T} = \frac{-\Delta G^\circ_{r,298}}{2.303 \text{ x } 8.3143 \text{ x } 298}$$

where T is temperature in degrees Kelvin (298 K = 25°C), R is the gas constant (8.3143 J/mol·K = 1.9872 cal/mol·K), and $\Delta G^\circ_{r,298}$ is in units of J/mol. Values for $\Delta G^\circ_{r,298}$ were calculated from the Gibbs free energy of formation ($\Delta G^\circ_{f,298}$) taken from Wagman et al. (1982) for each product and reactant in the aqueous speciation or solubility reaction by the equation:

$$\Delta G^\circ_{r,298} = \sum \Delta G^\circ_{f,298} \text{ (products)} - \sum \Delta G^\circ_{f,298} \text{ (reactants)} \quad .$$

Values $\Delta G^\circ_{f,298}$ of the other non-cyano reactants and products (e.g., H_2O and Fe^{2+}) in a reaction were also taken from Wagman et al. (1982).

A.2 Cyano Reactions and Equilibrium Constants

The compilation based on the sources listed above includes log $K°_{r,298}$ values for reactions of aqueous species and solids containing cyanide (CN^-) (Table A-1), thiocyanate (SCN^-) (Table A-2),[7] cyanate (OCN^-) (Table A-3), and cyano-metal compounds (Table A-4). Within each table, the cyano aqueous species and associated log $K°_{r,298}$ values are listed first, followed by the reactions and log $K°_{r,298}$ values for the cyano solids. Table A-4 includes log $K°_{r,298}$ values for aqueous species and solids containing several different cyano-metal complex ions. In the order listed in Table A-4, these include the hexacyanocobaltate ion [$Co(CN)_6^{3-}$], hexacyanoferrate(II), [$Fe(CN)_6^{4-}$], hexacyanoferrate(III) [$Fe(CN)_6^{3-}$], octacyanomolybdate(IV), [$Mo(CN)_8^{4-}$], selenocyanate ion ($NCSe^-$), and hexacyanotungstate(VI), [$W(CN)_8^{2-}$]. Except for the reactions involving the Fe(II) and Fe(III) hexacyanoferrate ions, the other cyano-metal complex ion reactions are few in number.

Only a single log $K°_{r,298}$ value is listed for each cyano reaction in Tables A-1 through A-4. When log $K°_{r,298}$ values were available from both Wagman et al. (1982) and Smith and Martell (1997) for a certain cyano reaction, the value derived from $\Delta G°_{f,298}$ data from Wagman et al. (1982) was given preference over the log $K°_{r,298}$ listed in Smith and Martell (1997). Generally, there was less than a 1 log K unit difference between log $K°_{r,298}$ values for a cyano compound listed in both Wagman et al. (1982) and Smith and Martell (1997). Sehmel (1989) was listed as the source of a log $K°_{r,298}$ only when he listed a cyano compound that was not included in Wagman et al. (1982) or Smith and Martell (1997).

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[7] Wagman et al. (1982) list compounds that contain the ions SCN^- and CNS^-. From a cursory review of general chemical reference texts and discussions with other staff, it could not be determined if these formula represent equivalent or different ions. It was therefore assumed for the sake of completeness that these two formulations represent the same thiocyanate ion.

Table A-1
Reactions and Associated Log $K^\circ_{r,298}$ Values for Cyanide Aqueous Species and Solids.

[Unless otherwise noted, log $K^\circ_{r,298}$ values are for T = 25°C, I = 0.0.]

Cyanide—Aqueous Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$H^+ + CN^- = HCN^\circ$ (aq)	+9.23	Wagman et al. (1982)
$Ag^+ + 2\ CN^- = Ag(CN)_2^-$	+20.39	Wagman et al. (1982)
$Ag^+ + 3\ CN^- = Ag(CN)_3^{2-}$	+21.7	Smith and Martell (1997)
$Ag^+ + OH^- + CN^- = Ag(OH)CN^-$	+13.45	Wagman et al. (1982)
$Au(III)O_3^{3-} + 2\ CN^- + 6\ H^+ + 2\ e^- = Au(I)(CN)_2^- + 3\ H_2O$	+125.89	Wagman et al. (1982)
$Cd^{2+} + CN^- = CdCN^+$	+5.32	Wagman et al. (1982)
$Cd^{2+} + 2\ CN^- = Cd(CN)_2^\circ$ (aq)	+10.37	Wagman et al. (1982)
$Cd^{2+} + 3\ CN^- = Cd(CN)_3^-$	+14.84	Wagman et al. (1982)
$Cd^{2+} + 4\ CN^- = Cd(CN)_4^{2-}$	+18.29	Wagman et al. (1982)
$Co^{2+} + 3\ CN^- = Co(CN)_3^-$	+13.7	Smith and Martell (1997), I=1.0
$Co^{2+} + 5\ CN^- = Co(CN)_5^{3-}$	+23.0	Smith and Martell (1997), I=1.0
$Cu^+ + 2\ CN^- = Cu(CN)_2^-$	+24.00	Wagman et al. (1982)
$Cu^+ + 3\ CN^- = Cu(CN)_3^{2-}$	+28.62	Wagman et al. (1982)
$CuCN_2^- + CN^- = Cu(CN)_3^{2-}$	+5.30	Smith and Martell (1997)
$Cu^+ + 4\ CN^- = Cu(CN)_4^{3-}$	+30.31	Wagman et al. (1982)
$CuCN_3^{2-} + CN^- = Cu(CN)_4^{3-}$	+1.5	Smith and Martell (1997)
$Fe^{2+} + 6\ CN^- = Fe(CN)_6^{4-}$	+45.63	Wagman et al. (1982)
$Fe^{3+} + 6\ CN^- = Fe(CN)_6^{3-}$	+52.61	Wagman et al. (1982)
$Hg^{2+} + CN^- = HgCN^+$	+18.03	Wagman et al. (1982)
$Hg^{2+} + 2\ CN^- = Hg(CN)_2^\circ$ (aq)	+34.51	Wagman et al. (1982)
$Hg^{2+} + 3\ CN^- = Hg(CN)_3^-$	+38.26	Wagman et al. (1982)
$Hg^{2+} + 4\ CN^- = Hg(CN)_4^{2-}$	+41.26	Wagman et al. (1982)
$Hg^{2+} + OH^- + CN^- = Hg(OH)CN^\circ$ (aq)	+28.9	Smith and Martell (1997), 30°C, I=2.0
$Hg^{2+} + Cl^- + 2\ CN^- = Hg(Cl)_2Cl^-$	+34.25	Wagman et al. (1982)
$Hg^{2+} + Cl^- + 3\ CN^- = Hg(Cl)_3Cl^{2-}$	+37.73	Wagman et al. (1982)
$Mn^{2+} + CN^- = MnCN^+$	+1.9	Smith and Martell (1997), I=1.0
$Mn^{2+} + 2\ CN^- = Mn(CN)_2^\circ$ (aq)	+3.36	Smith and Martell (1997), I=1.0
$Ni^{2+} + 2\ CN^- = Ni(CN)_2^\circ$ (aq)	+14.59	Sehmel (1989)

Cyanide—Aqueous Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$Ni^{2+} + 3\ CN^- = Ni(CN)_3^-$	+22.63	Sehmel (1989)
$Ni^{2+} + 4\ CN^- = Ni(CN)_4^{2-}$	+30.12	Wagman et al. (1982)
$Ni(CN)_4^{2-} + H^+ = NiH(CN)_4^-$	+5.4	Smith and Martell (1997), I=0.1
$NiH(CN)_4^- + H^+ = NiH_2(CN)_4^\circ$ (aq)	+4.5	Smith and Martell (1997), I=0.1
$NiH_2(CN)_4^\circ$ (aq) $+ H^+ = NiH_3(CN)_4^+$	+2.6	Smith and Martell (1997), I=0.1
$Ni^{2+} + 4\ CN^- + 3\ H^+ = NiH_3(CN)_4^+$	+43.95	Sehmel (1989)
$Pd^{2+} + CN^- = PdCN^+$	+10.49	Wagman et al. (1982)
$Pd^{2+} + 4\ CN^- = Pd(CN)_4^{2-}$	+41.71	Wagman et al. (1982)
$Pd^{2+} + 5\ CN^- = Pd(CN)_5^{3-}$	(+45.3)	Smith and Martell (1997)
$Pt^{2+} + 4\ CN^- = Pt(CN)_4^{2-}$	+40.98	Wagman et al. (1982)
$Tl^{3+} + 4\ CN^- = Tl(CN)_4^-$	+35.25	Wagman et al. (1982)
$Zn^{2+} + CN^- = ZnCN^+$	+4.98	Smith and Martell (1997), I=3.0
$Zn^{2+} + 2\ CN^- = Zn(CN)_2^\circ$ (aq)	+11.07	Smith and Martell (1997)
$Zn^{2+} + 3\ CN^- = Zn(CN)_3^-$	+16.05	Smith and Martell (1997)
$Zn^{2+} + 4\ CN^- = Zn(CN)_4^{2-}$	+16.76	Wagman et al. (1982)
Cyanide—Solid Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$AgCN = Ag^+ + CN^-$	-16.22	Wagman et al. (1982)
$Ag_2(CN)_2 = 2\ Ag^+ + 2\ CN^-$	-10.9	Smith and Martell (1997), 20°C, I=0.1
$CrCN = Cr^{2+} + CN^- + e^-$	+23.89	Sehmel (1989)
$Cr_2CN = 2\ Cr^{2+} + CN^- + 3\ e^-$	+56.65	Sehmel (1989)
$CuCN = Cu^+ + CN^-$	-19.46	Wagman et al. (1982)
$Hg_2(CN)_2 = 2\ Hg^+ + 2\ CN^-$	-39.3	Smith and Martell (1997)
$KCN = K^+ + CN^-$	+1.58	Wagman et al. (1982)
$NaCN = NaK^+ + CN^-$	+2.29	Wagman et al. (1982)
$Zn(CN)_2 = Zn^{2+} + 2\ CN^-$	-15.5	Smith and Martell (1997), I=3.0

Table A-2
Reactions and Associated Log $K^\circ_{r,298}$ Values for Thiocyanate (SCN^-) Aqueous Species and Solids

[Unless otherwise noted, log $K^\circ_{r,298}$ values are for T = 25°C, I = 0.0.]

Thiocyanate—Aqueous Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$H^+ + SCN^- = HSCN^\circ$ (aq)	-0.85	Wagman et al. (1982)
$Ac^{3+} + SCN^- = AcSCN^{2+}$	+0.05	Smith and Martell (1997), I=1.0
$Ag^+ + SCN^- = AgSCN^\circ$ (aq)	+4.75	Wagman et al. (1982)
$Ag^+ + 2\ SCN^- = Ag(SCN)_2^-$	+8.31	Wagman et al. (1982)
$Ag^+ + 3\ SCN^- = Ag(SCN)_3^{2-}$	+9.52	Wagman et al. (1982)
$Ag^+ + 4\ SCN^- = Ag(SCN)_4^{3-}$	+9.77	Wagman et al. (1982)
$Al^{3+} + SCN^- = AlSCN^{2+}$	+0.42	Smith and Martell (1997) 22°C
$Au^+ + SCN^- = AuSCN^\circ$ (aq)	+15.27	Smith and Martell (1997), I=3.0
$Au^+ + 2\ SCN^- = Au(SCN)_2^-$	+16.98	Smith and Martell (1997), I=3.0
$AuO_3^{3-} + 2\ SCN^- + 6\ H^+ + 2\ e^- = Au(SCN)_2^- + 3\ H_2O$	+103.91	Wagman et al. (1982)
$AuO_3^{3-} + 4\ SCN^- + 6\ H^+ = Au(SCN)_4^- + 3\ H_2O$	+82.14	Wagman et al. (1982)
$AuO_3^{3-} + 5\ SCN^- + 6\ H^+ = Au(SCN)_5^{2-} + 3\ H_2O$	+82.10	Wagman et al. (1982)
$AuO_3^{3-} + 6\ SCN^- + 6\ H^+ = Au(SCN)_6^{3-} + 3\ H_2O$	+82.14	Wagman et al. (1982)
$Be^{2+} + SCN^- = BeSCN^+$	-0.16	Smith and Martell (1997), I=4.0
$Be^{2+} + 2\ SCN^- = Be(SCN)_2^\circ$ (aq)	-0.6	Smith and Martell (1997), I=4.0
$Bi^{3+} + SCN^- = BiSCN^{2+}$	+2.21	Smith and Martell (1997)
$Bi^{3+} + 2\ SCN^- = Bi(SCN)_2^+$	+2.7	Smith and Martell (1997)
$Bi^{3+} + 3\ SCN^- = Bi(SCN)_3^\circ$(aq)	+4.4	Smith and Martell (1997)
$Bi^{3+} + 4\ SCN^- = Bi(SCN)_4^-$	+5.2	Smith and Martell (1997)
$Bi^{3+} + 5\ SCN^- = Bi(SCN)_5^{2-}$	+5.8	Smith and Martell (1997)
$Bi^{3+} + 6\ SCN^- = Bi(SCN)_5^{3-}$	+5.4	Smith and Martell (1997)
$Cd^{2+} + SCN^- = CdSCN^+$	+1.33	Wagman et al. (1982)
$Cd^{2+} + 2\ SCN^- = Cd(SCN)_2^\circ$ (aq)	+1.88	Wagman et al. (1982)
$Cd^{2+} + 3\ SCN^- = Cd(SCN)_3^-$	+1.91	Wagman et al. (1982)
$Cd^{2+} + 4\ SCN^- = Cd(SCN)_4^{2-}$	+2.3	Smith and Martell (1997)
$Ce^{3+} + SCN^- = CeSCN^{2+}$	+0.59	Smith and Martell (1997), I=5.0
$Co^{2+} + SCN^- = CoSCN^+$	+1.58	Wagman et al. (1982)

Thiocyanate—Aqueous Species

Reaction	log $K^\circ_{r,298}$	Reference
$Co^{2+} + 2\ SCN^- = Co(SCN)_2^\circ$ (aq)	+2.02	Smith and Martell (1997), I=0.1
$Cr^{2+} + SCN^- = CrSCN^+$	+1.09	Smith and Martell (1997)
$Cr^{2+} + 2\ SCN^- = Cr(SCN)_2^\circ$ (aq)	+0.77	Smith and Martell (1997)
$Cr^{3+} + SCN^- = CrSCN^{2+}$	+3.08	Smith and Martell (1997)
$Cr^{3+} + 2\ SCN^- = Cr(SCN)_2^+$	(+2.98)	Smith and Martell (1997)
$Cu^+ + 3\ SCN^- = Cu(SCN)_3^{2-}$	+11.60	Smith and Martell (1997), I=5.0
$Cu^+ + 4\ SCN^- = Cu(SCN)_4^{3-}$	+9.94	Wagman et al. (1982)
$2\ Cu^+ + 6\ SCN^- = Cu_2(SCN)_6^{4-}$	+24.34	Smith and Martell (1997), I=5.0
$Cu^{2+} + SCN^- = CuSCN^+$	+2.33	Wagman et al. (1982)
$Cu^{2+} + 2\ SCN^- = Cu(SCN)_2^\circ$ (aq)	+3.68	Wagman et al. (1982)
$Dy^{3+} + SCN^- = DySCN^{2+}$	+0.12	Smith and Martell (1997), 20°C, I=0.5
$Er^{3+} + SCN^- = ErSCN^{2+}$	+0.16	Smith and Martell (1997), 20°C, I=0.5
$Eu^{3+} + SCN^- = EuSCN^{2+}$	+0.70	Wagman et al. (1982)
$Fe^{2+} + SCN^- = FeSCN^+$	(+1.31)	Smith and Martell (1997)
$Fe^{3+} + SCN^- = FeSCN^{2+}$	+2.96	Wagman et al. (1982)
$Fe^{3+} + 2\ SCN^- = Fe(SCN)_2^+$	+4.6	Smith and Martell (1997), 20°C
$Fe^{3+} + 3\ SCN^- = Fe(SCN)_3^\circ$ (aq)	+3.9	Smith and Martell (1997), I=1.0
$Fe^{3+} + 4\ SCN^- = Fe(SCN)_4^-$	+6.4	Smith and Martell (1997), I=3.0
$FeSCN^{2+} + OH^- = Fe(OH)SCN^+$	-0.6	Smith and Martell (1997)
$Ga^{3+} + SCN^- = GaSCN^{2+}$	+2.04	Smith and Martell (1997)
$Ga^{3+} + 2\ SCN^- = Ga(SCN)_2^+$	+2.72	Smith and Martell (1997), 10°C, I=6.0
$Gd^{3+} + SCN^- = GdSCN^{2+}$	+0.21	Smith and Martell (1997), 20°C, I=0.5
$Hg^{2+} + SCN^- = HgSCN^+$	+9.08	Smith and Martell (1997), I=1.0
$Hg^{2+} + 2\ SCN^- = Hg(SCN)_2^\circ$ (aq)	+17.23	Wagman et al. (1982)
$Hg^{2+} + 3\ SCN^- = Hg(SCN)_3^-$	+19.98	Wagman et al. (1982)
$Hg^{2+} + 4\ SCN^- = Hg(SCN)_4^{2-}$	+21.70	Wagman et al. (1982)
$Hg(OH)SCN^\circ$ (aq) $+ H^+ = HgSCN^+ + H_2O$	+3.4	Smith and Martell (1997), I=1.0
$Hg^{2+} + SCN^- + 3\ CN^- = Hg(CNS)(CN)_3^{2-}$	+38.74	Wagman et al. (1982)
$Hg^{2+} + SCN^- + Cl^- = Hg(CNS)Cl^\circ$ (aq)	+15.89	Wagman et al. (1982)
$In^{3+} + SCN^- = InSCN^{2+}$	-11.47	Wagman et al. (1982)
$In^{3+} + 2\ SCN^- = In(SCN)_2^+$	+3.51	Wagman et al. (1982)

Thiocyanate—Aqueous Species		
Reaction	**log $K°_{r,298}$**	**Reference**
$In^{3+} + 3\ SCN^- = In(SCN)_3°$ (aq)	+2.67	Wagman et al. (1982)
$La^{3+} + SCN^- = LaSCN^{2+}$	+0.12	Smith and Martell (1997), 30°C, I=1.0
$Lu^{3+} + SCN^- = LuSCN^{2+}$	+0.20	Smith and Martell (1997), 30°C, I=1.0
$Mg^{2+} + SCN^- = MgSCN^+$	-0.9	Smith and Martell (1997), I=3.0
$Mn^{2+} + SCN^- = MnSCN^+$	+1.05	Wagman et al. (1982)
$Mn^{2+} + 2\ SCN^- = Mn(SCN)_2°$ (aq)	+1.32	Wagman et al. (1982)
$Ni^{2+} + SCN^- = NiSCN^+$	+1.65	Wagman et al. (1982)
$Ni^{2+} + 2\ SCN^- = Ni(SCN)_2°$ (aq)	(+2.18)	Smith and Martell (1997), I=0.1
$Ni^{2+} + 3\ SCN^- = Ni(SCN)_3^-$	+1.5	Smith and Martell (1997), I=1.0
$Pb^{2+} + SCN^- = PbSCN^+$	+0.89	Wagman et al. (1982)
$Pb^{2+} + 2\ SCN^- = Pb(SCN)_2°$ (aq)	+1.15	Wagman et al. (1982)
$Pb^{2+} + 3\ SCN^- = Pb(SCN)_3^-$	+1.0	Smith and Martell (1997), I=3.0
$Pd^{2+} + 2\ SCN^- = Pd(SCN)_2°$ (aq)	+8.34	Wagman et al. (1982)
$Pd^{2+} + 4\ SCN^- = Pd(SCN)_4^{2-}$	+23.97	Wagman et al. (1982)
$Pt^{2+} + 4\ SCN^- = Pt(SCN)_4^{2-}$	+33.6	Smith and Martell (1997), I=0.5
$Sc^{3+} + SCN^- = ScSCN^{2+}$	+1.14	Wagman et al. (1982)
$Sm^{3+} + SCN^- = SmSCN^{2+}$	+0.09	Smith and Martell (1997), 20°C, I=0.5
$Sn^{2+} + SCN^- = SnSCN^+$	+0.83	Smith and Martell (1997), I=1.0
$Sn^{2+} + 2\ SCN^- = Sn(SCN)_2°$ (aq)	+1.1	Smith and Martell (1997), I=1.0
$Sn^{2+} + 3\ SCN^- = Sn(SCN)_3^-$	+1.5	Smith and Martell (1997), I=3.0
$Tb^{3+} + SCN^- = TbSCN^{2+}$	+0.23	Smith and Martell (1997), 30°C, I=1.0
$Th^{4+} + SCN^- = ThSCN^{3+}$	+1.65	Wagman et al. (1982)
$Th^{4+} + 2\ SCN^- = Th(SCN)_2^{2+}$	+3.14	Wagman et al. (1982)
$Th^{4+} + 3\ SCN^- = Th(SCN)_3^+$	+3.53	Wagman et al. (1982)
$Th^{4+} + 4\ SCN^- = Th(SCN)_4°$ (aq)	+4.55	Wagman et al. (1982)
$Tl^+ + SCN^- = TlSCN°$ (aq)	+0.80	Wagman et al. (1982)
$Tl^+ + 2\ SCN^- = Tl(SCN)_2^-$	0.00	Smith and Martell (1997), I=0.5
$Tl^+ + 3\ SCN^- = Tl(SCN)_3^{2-}$	-0.4	Smith and Martell (1997), I=1.0
$U^{4+} + SCN^- = USCN^{3+}$	+2.97	Smith and Martell (1997)
$U^{4+} + 2\ SCN^- = U(SCN)_2^{2+}$	+4.2	Smith and Martell (1997)
$U^{4+} + 3\ SCN^- = U(SCN)_3^+$	+2.2	Smith and Martell (1997), 20°C, I=1.0

Thiocyanate—Aqueous Species

Reaction	log $K^\circ_{r,298}$	Reference
$UO_2^{2+} + SCN^- = UO_2SCN^+$	+1.31	Smith and Martell (1997)
$UO_2^{2+} + 2\ SCN^- = UO_2(SCN)_2^\circ$ (aq)	+1.6	Smith and Martell (1997)
$UO_2^{2+} + 3\ SCN^- = UO_2(SCN)_3^-$	+1.4	Smith and Martell (1997)
$V^{2+} + SCN^- = VSCN^+$	+1.43	Smith and Martell (1997), I=1.0
$V^{3+} + SCN^- = VSCN^{2+}$	+2.20	Smith and Martell (1997), I=0.5
$VO^{2+} + SCN^- = VOSCN^+$	+1.11	Wagman et al. (1982)
$VO^{2+} + 2\ SCN^- = VO(SCN)_2^\circ$ (aq)	+3.68	Smith and Martell (1997)
$VO^{2+} + 3\ SCN^- = VO(SCN)_3^-$	+3.08	Smith and Martell (1997), 30°C, I=3.0
$Y^{3+} + SCN^- = YSCN^{2+}$	-0.07	Smith and Martell (1997), 20°C, I=0.5
$Zn^{2+} + SCN^- = ZnSCN^+$	+1.33	Smith and Martell (1997)
$Zn^{2+} + 2\ SCN^- = Zn(SCN)_2^\circ$ (aq)	+0.92	Wagman et al. (1982)
$Zn^{2+} + 3\ SCN^- = Zn(SCN)_3^-$	+2.0	Smith and Martell (1997)
$Zn^{2+} + 4\ SCN^- = Zn(SCN)_4^{2-}$	+1.29	Wagman et al. (1982)
$Y^{3+} + SCN^- = YCNS^{2+}$	+0.76	Wagman et al. (1982)

Thiocyanate—Solid Species

Reaction	log $K^\circ_{r,298}$	Reference
$AgSCN = Ag^+ + SCN^-$	-11.99	Wagman et al. (1982)
$CuSCN = Cu^+ + SCN^-$	-14.77	Smith and Martell (1997), I=5.0
$KCNS = K^+ + SCN^-$	+2.15	Wagman et al. (1982)
$Hg_2(SCN)_2 = 2\ Hg^+ + 2\ SCN^-$	-19.52	Smith and Martell (1997)
$Hg(SCN)_2 = Hg^{2+} + 2\ SCN^-$	-21.41	Wagman et al. (1982)
$Pb(SCN)_2 = Pb^{2+} + 2\ SCN^-$	-4.68	Wagman et al. (1982)
$Pd(SCN)_2 = Pd^{2+} + 2\ SCN^-$	-22.36	Wagman et al. (1982)
$TlSCN = Tl^+ + SCN^-$	-3.77	Smith and Martell (1997)

Table A-3
Reactions and Associated Log K°$_{r,298}$ Values for Cyanate (OCN^-) Aqueous Species and Solids

[Unless otherwise noted, log K°$_{r,298}$ values are for T = 25°C, I = 0.0.]

Cyanate—Aqueous Species

Reaction	log K°$_{r,298}$	Reference
$H^+ + OCN^- = HOCN^\circ$ (aq)	+3.45	Wagman et al. (1982)
$Ag^+ + 2\ OCN^- = Ag(OCN)_2^-$	+5.00	Smith and Martell (1997), 30°C
$Co^{2+} + 4\ OCN^- = Co(OCN)_4^{2+}$	+2.67	Smith and Martell (1997), 27°C, I=1.5

Cyanate—Solid Species

Reaction	log K°$_{r,298}$	Reference
$AgOCN = Ag^+ + OCN^-$	-6.62	Wagman et al. (1982)

Table A-4
Reactions and Associated Log K°$_{r,298}$ Values for Cyano-Metal Aqueous Species and Solids

[Unless otherwise noted, log K°$_{r,298}$ values are for T = 25°C, I = 0.0.]

Co (Hexacyanocobaltate Ion)Aqueous Species

Reaction	log K°$_{r,298}$	Reference
$Cd^{2+} + Co(CN)_6^{3-} = CdCo(CN)_6^-$	+4.17	Smith and Martell (1997)
$Fe^{3+} + Co(CN)_6^{3-} = FeCo(CN)_6^\circ$ (aq)	+1.81	Smith and Martell (1997), I=0.5
$K^+ + Co(CN)_6^{3-} = KCo(CN)_6^{2-}$	+1.22	Smith and Martell (1997)
$La^{3+} + Co(CN)_6^{3-} = LaCo(CN)_6^\circ$ (aq)	+3.71	Smith and Martell (1997)

Solid Species

Reaction	log K°$_{r,298}$	Reference
$Ag_3Co(CN)_6 = 3\ Ag^+ + Co(CN)_6^{3-}$	-25.41	Smith and Martell (1997)
$Hg_6[Co(CN)_6]_2 = 6\ Hg^+ + 2\ Co(CN)_6^{3-}$	-36.72	Smith and Martell (1997)

Fe(II) [Hexacyanoferrate(II) Ion]Aqueous Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$H^+ + Fe(CN)_6^{4-} = HFe(CN)_6^{3-}$	+4.17	Wagman et al. (1982)
$H^+ + Fe^{2+} + 6\ CN^- = HFe(CN)_6^{3-}$	+50.00	Sehmel (1989)
$2\ H^+ + Fe(CN)_6^{4-} = H_2Fe(CN)_6^{2-}$	+6.39	Wagman et al. (1982)
$2\ H^+ + Fe^{2+} + 6\ CN^- = H_2Fe(CN)_6^{2-}$	+52.45	Sehmel (1989)
$H^+ + HFe(CN)_6^{3-} = H_2Fe(CN)_6^{2-}$	+2.4	Smith and Martell (1997)
$Ba^{2+} + Fe(CN)_6^{4-} = BaFe(CN)_6^{2-}$	+3.79	Smith and Martell (1997)
$Ca^{2+} + Fe(CN)_6^{4-} = CaFe(CN)_6^{2-}$	+3.80	Wagman et al. (1982)
$2\ Ca^{2+} + Fe(CN)_6^{4-} = Ca_2Fe(CN)_6^\circ$ (aq)	+5.19	Wagman et al. (1982)
$Ca^{2+} + 6\ CN^- + Fe^{2+} + H^+ + e^- = CaHFe(CN)_6^-$	+52.71	Sehmel (1989)
$Cs^+ + Fe(CN)_6^{4-} = CsFe(CN)_6^{3-}$	+2.8	Smith and Martell (1997)
$K^+ + Fe(CN)_6^{4-} = KFe(CN)_6^{3-}$	+2.35	Smith and Martell (1997)
$K^+ + Fe^{2+} + 6\ CN^- + H^+ = KHFe(CN)_6^{2-}$	+51.47	Sehmel (1989)
$2\ K^+ + Fe^{2+} + 6\ CN^- + 2\ H^+ = K_2H_2Fe(CN)_6^\circ$ (aq)	+52.31	Sehmel (1989)
$2\ K^+ + Fe^{2+} + 6\ CN^- = K_2Fe(CN)_6^{2-}$	+48.98	Sehmel (1989)
$3\ K^+ + Fe^{2+} + 6\ CN^- + H^+ = K_3HFe(CN)_6^\circ$ (aq)	+50.22	Sehmel (1989)
$La^{3+} + Fe(CN)_6^{4-} = LaFe(CN)_6^-$	+5.06	Smith and Martell (1997)
$Li^+ + Fe(CN)_6^{4-} = LiFe(CN)_6^{3-}$	+1.75	Wagman et al. (1982)
$Li^+ + Fe^{2+} + 6\ CN^- + H^+ = LiHFe(CN)_6^{2-}$	+51.22	Sehmel (1989)
$2\ Li^+ + Fe^{2+} + 6\ CN^- = Li_2Fe(CN)_6^{2-}$	+48.53	Sehmel (1989)
$Mg^{2+} + Fe(CN)_6^{4-} = MgFe(CN)_6^{2-}$	+3.82	Wagman et al. (1982)
$NH_4^+ + Fe(CN)_6^{4-} = NH_4Fe(CN)_6^{3-}$	+2.3	Smith and Martell (1997)
$NH_4^+ + Fe^{2+} + 6\ CN^- + H^+ = NH_4HFe(CN)_6^{2-}$	+51.40	Sehmel (1989)
$2\ NH_4^+ + Fe^{2+} + 6\ CN^- = (NH_4)_2Fe(CN)_6^{2-}$	+48.87	Sehmel (1989)
$Na^+ + Fe(CN)_6^{4-} = NaFe(CN)_6^{3-}$	+2.2	Smith and Martell (1997)
$Na^+ + Fe^{2+} + 6\ CN^- + H^+ = NaHFe(CN)_6^{2-}$	+51.43	Sehmel (1989)
$2\ Na^+ + Fe^{2+} + 6\ CN^- = Na_2Fe(CN)_6^{2-}$	+48.74	Sehmel (1989)
$Rb^+ + Fe(CN)_6^{4-} = RbFe(CN)_6^{3-}$	+2.6	Smith and Martell (1997)
$Sr^{2+} + Fe(CN)_6^{4-} = SrFe(CN)_6^{2-}$	+3.66	Smith and Martell (1997)
$Tl^+ + Fe(CN)_6^{4-} = TlFe(CN)_6^{3-}$	+3.0	Smith and Martell (1997)

Solid Species		
Reaction	**log $K^\circ_{r,298}$**	**Reference**
$Ag_4Fe(CN)_6 = 4\ Ag^+ + Fe(CN)_6^{4-}$	-44.07	Smith and Martell (1997)
$Ag_4Fe(CN)_6AH_2O = 4\ Ag^+ + Fe^{2+} + 6\ CN^- + H_2O$	-89.69	Sehmel (1989)
$Cd_2Fe(CN)_6 = 2\ Cd^{2+} + Fe(CN)_6^{4-}$	-17.38	Smith and Martell (1997)
$Cd_2Fe(CN)_6A7H_2O = 2\ Cd^{2+} + Fe^{2+} + 6\ CN^- + 7\ H_2O$	-62.98	Sehmel (1989)
$Cu_2Fe(CN)_6 = 2\ Cu^{2+} + Fe^{2+} + 6\ CN^-$	-61.42	Sehmel (1989)
$Fe_4[Fe(CN)_6]_3$ (Prussian Blue) $= 4\ Fe^{3+} + 3\ Fe^{2+} + 18\ CN^-$	-257.45	Ghosh et al. (1999)
$Fe_3[Fe(CN)_6]_2$ (Turnbull's Blue) $= 3\ Fe^{3+} + 2\ Fe^{2+} + 12\ CN^-$	-173.44	Ghosh et al. (1999)
$K_4Fe(CN)_6 = 4\ K^+ + Fe(CN)_6^{4-}$	-2.63	Wagman et al. (1982)
$K_4Fe(CN)_6{\cdot}3H_2O = 4\ K^+ + Fe(CN)_6^{4-} + 3\ H_2O$	-3.40	Wagman et al. (1982)
$KZn_{1.5}Fe(CN)_6 = K^+ + 1.5\ Zn^{2+} + Fe(CN)_6^{4-}$	-21.10	Wagman et al. (1982)
$K_2CdFe(CN)_6 = 2\ K^+ + Cd^{2+} + Fe(CN)_6^{4-}$	-17.12	Wagman et al. (1982)
$K_{12}Cd_8[Fe(CN)_6]_7 = 12\ K^+ + 8\ Cd^{2+} +7\ Fe(CN)_6^{4-}$	-120.96	Wagman et al. (1982)
$K_2Co_3[Fe(CN)_6]_2 = 2\ K^+ + 3\ Co^{2+} +2\ Fe(CN)_6^{4-}$	-27.76	Wagman et al. (1982)
$K_4Co_4[Fe(CN)_6]_3 = 4\ K^+ + 4\ Co^{2+} +3\ Fe(CN)_6^{4-}$	-45.12	Wagman et al. (1982)
$K_2Cu(I)_2Fe(CN)_6 = 2\ K^+ + 2\ Cu^+ + Fe(CN)_6^{4-}$	-26.53	Wagman et al. (1982)
$K_2Mn_3[Fe(CN)_6]_2 = 2\ K^+ + 3\ Mn^{2+} + 2\ Fe^{2+} + 12\ CN^-$	-121.00	Sehmel (1989)
$K_8Mn_6[Fe(CN)_6]_5 = 8\ K^+ + 6\ Mn^{2+} + 5\ Fe^{2+} + 30\ CN^-$	-293.68	Sehmel (1989)
$K_2Ni_3[Fe(CN)_6]_2 = 2\ K^+ + 3\ Ni^{2+} + 2\ Fe(CN)_6^{4--}$	-31.68	Wagman et al. (1982)
$K_4Ni_4[Fe(CN)_6]_3 = 4\ K^+ + 4\ Ni^{2+} + 3\ Fe(CN)_6^{4-}$	-134.77	Wagman et al. (1982)
$K_{12}Ni_8[Fe(CN)_6]_7 = 12\ K^+ + 8\ Ni^{2+} + 7\ Fe(CN)_6^{4-}$	-110.11	Wagman et al. (1982)
$Mn_2Fe(CN)_6 = 2\ Mn^{2+} + Fe^{2+} + 6\ CN^-$	-59.03	Sehmel (1989)
$Pb_2Fe(CN)_6 = 2\ Pb^{2+} + Fe(CN)_6^{4-}$	-18.02	Smith and Martell (1997)
$Pb_2Fe(CN)_6{\cdot}3H_2O = 2\ Pb^{2+} + Fe^{2+} + 6\ CN^- + 3\ H_2O$	-63.60	Sehmel (1989)
$Tl_4Fe(CN)_6{\cdot}2H_2O = 4\ Tl^+ + Fe^{2+} + 6\ CN^- + 2\ H_2O$	-56.92	Sehmel (1989)
$Zn_2Fe(CN)_6 = 2\ Zn^{2+} + Fe(CN)_6^{4-}$	-15.68	Smith and Martell (1997)
$Zn_2Fe(CN)_6{\cdot}2H_2O = 2\ Zn^{2+} + Fe^{2+} + 6\ CN^- + 2\ H_2O$	-61.23	Sehmel (1989)

Fe(III) [Hexacyanoferrate(III) Ion]Aqueous Species

Reaction	$\log K^{\circ}_{r,298}$	Reference
$Ba^{2+} + Fe(CN)_6^{3-} = BaFe(CN)_6^{-}$	+2.88	Smith and Martell (1997)
$Ca^{2+} + Fe(CN)_6^{3-} = CaFe(CN)_6^{-}$	+2.86	Wagman et al. (1982)
$Cs^{+} + Fe(CN)_6^{3-} = CsFe(CN)_6^{2-}$	+0.52	Smith and Martell (1997), I=3.0
$Dy^{3+} + Fe(CN)_6^{3-} = DyFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Er^{3+} + Fe(CN)_6^{3-} = ErFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Eu^{3+} + Fe(CN)_6^{3-} = EuFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Fe^{3+} + Fe(CN)_6^{3-} = Fe[Fe(CN)_6]^{\circ}$ (aq)	+1.61	Smith and Martell (1997), I=0.5
$Gd^{3+} + Fe(CN)_6^{3-} = GdFe(CN)_6^{\circ}$ (aq)	+3.67	Smith and Martell (1997)
$Ho^{3+} + Fe(CN)_6^{3-} = HoFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$K^{+} + Fe(CN)_6^{3-} = KFe(CN)_6^{2-}$	+1.44	Smith and Martell (1997)
$La^{3+} + Fe(CN)_6^{3-} = LaFe(CN)_6^{\circ}$ (aq)	+3.75	Smith and Martell (1997)
$Lu^{3+} + Fe(CN)_6^{3-} = LuFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Mg^{2+} + Fe(CN)_6^{3-} = MgFe(CN)_6^{-}$	+2.79	Wagman et al. (1982)
$Na^{+} + Fe(CN)_6^{3-} = NaFe(CN)_6^{2-}$	-0.3	Smith and Martell (1997), I=3.0
$Nd^{3+} + Fe(CN)_6^{3-} = NdFe(CN)_6^{\circ}$ (aq)	+3.78	Smith and Martell (1997)
$Pr^{3+} + Fe(CN)_6^{3-} = PrFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Sm^{3+} + Fe(CN)_6^{3-} = SmFe(CN)_6^{\circ}$ (aq)	+3.76	Smith and Martell (1997)
$Sr^{2+} + Fe(CN)_6^{3-} = SrFe(CN)_6^{-}$	+2.84	Wagman et al. (1982)
$Tb^{3+} + Fe(CN)_6^{3-} = TbFe(CN)_6^{\circ}$ (aq)	+3.8	Smith and Martell (1997)
$Tm^{3+} + Fe(CN)_6^{3-} = TmFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)
$Yb^{3+} + Fe(CN)_6^{3-} = YbFe(CN)_6^{\circ}$ (aq)	+3.7	Smith and Martell (1997)

Solid Species

Reaction	$\log K^{\circ}_{r,298}$	Reference
$Ag_3Fe(CN)_6 = 3\ Ag^{+} + Fe(CN)_6^{3-}$	-27.9	Smith and Martell (1997), 20°C, I=0.1
$K_3Fe(CN)_6 = 3\ K^{+} + Fe(CN)_6^{3-}$	-1.16	Wagman et al. (1982)
$Mn_3[Fe(CN)_6]_2 = 3\ Mn^{2+} + 2\ Fe(CN)_6^{3-}$	-18.2	Smith and Martell (1997)

Mo [Octacyanomolybdate(IV) Ion]Aqueous Species

Reaction	log $K^\circ_{r,298}$	Reference
$Fe^{3+} + Mo(CN)_8^{4-} = FeMo(CN)_8^-$	+4.06	Smith and Martell (1997), I=0.3
$Fe^{3+} + Mo(CN)_8^{4-} = Fe_2Mo(CN)_8^{2+}$	+9.21	Smith and Martell (1997), I=0.3

Se (Selenocyanate Ion)Aqueous Species

Reaction	log $K^\circ_{r,298}$	Reference
$Ag^+ + NCSe^- = AgNCSe^\circ$ (aq)	+13.90	Smith and Martell (1997), I=0.5
$Cd^{2+} + NCSe^- = CdNCSe^+$	+1.98	Smith and Martell (1997)
$Cd^{2+} + 2\ NCSe^- = Cd(NCSe)_2^\circ$ (aq)	+2.30	Smith and Martell (1997), I=1.0
$Cd^{2+} + 3\ NCSe^- = Cd(NCSe)_3^-$	+2.8	Smith and Martell (1997), I=1.0
$Cd^{2+} + 4\ NCSe^- = Cd(NCSe)_4^{2-}$	+4.04	Smith and Martell (1997), I=1.0
$Co^{2+} + NCSe^- = CoNCSe^+$	+1.49	Smith and Martell (1997)
$Hg^{2+} + 3\ NCSE^- = Hg(NCSe)_3^-$	+26.4	Smith and Martell (1997), I=0.5
$Hg^{2+} + 4\ NCSE^- = Hg(NCSe)_4^{2-}$	+28.9	Smith and Martell (1997), I=0.5
$Ni^{2+} + NCSe^- = NiNCSe^+$	+1.66	Smith and Martell (1997)
$Ni^{2+} + 2\ NCSe^- = Ni(NCSe)_2^\circ$ (aq)	+1.26	Smith and Martell (1997), I=1.0
$Zn^{2+} + NCSe^- = ZnNCSe^+$	+0.44	Smith and Martell (1997), I=1.0
$Zn^{2+} + 2\ NCSe^- = Zn(NCSe)_2^\circ$ (aq)	+0.64	Smith and Martell (1997), I=1.0

Se (Selenocyanate Ion) Solid Species

Reaction	log $K^\circ_{r,298}$	Reference
$AgNCSe = Ag^+ + NCSe^-$	-15.40	Smith and Martell (1997), 20°C

W [Octacyanotungstate(VI) Ion] Aqueous Species

Reaction	log $K^\circ_{r,298}$	Reference
$Cs^+ + W(CN)_8^{2-} = CsW(CN)_8^-$	+1.71	Smith and Martell (1997), I=3.0
$K^+ + W(CN)_8^{2-} = KW(CN)_8^-$	+1.36	Smith and Martell (1997), I=3.0
$Na^+ + W(CN)_8^{2-} = NaW(CN)_8^-$	+1.08	Smith and Martell (1997), I=3.0
$Rb^+ + W(CN)_8^{2-} = RbW(CN)_8^-$	+1.57	Smith and Martell (1997), I=3.0

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