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Sent:	Thursday, April 27, 2017 4:32 PM
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Subject:	Stabilization of mercury waste
Attachments:	ENV__126.pdf; ENV__125.pdf

Under RCRA, waste that is hazardous for mercury must contain <260 ppm total mercury in order to be stabilized and landfilled. If it contains >260 ppm, it must go to mercury recovery. Wastes that are hazardous for mercury are not common. The stabilization recipe for treating mercury includes the addition of a sulfide reagent; we use polysulfide. This is based on the fact that mercury sulfide is a very insoluble salt (see Table 4-12) of Jesse Connor's book on Chemical Fixation. The polysulfide is added first, then the CKD binder. The second attachment is from an EPA paper titled Volatility of Mercury from Soils Amended with Various Mercury Compounds. The conclusion is that the less water-soluble a mercury salt is, the less volatile it is. As mercury sulfide is very insoluble, the study found that only 0.2 to 0.3% evolved from sand, soil and clay. As we convert the mercury to a sulfide upon placement in the tank, before completing the treatment, this seemed like a reasonable factor to use for the release during stabilization.

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VOLATILITY OF MERCURY FROM SOILS AMENDED WITH VARIOUS MERCURY COMPOUNDS

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INTRODUCTION

Studies involving the transformation and fate of mercury (Hg) in the environment have been intensely pursued in recent years. Investigations have been conducted involving both aquatic and terrestrial environments in which mercuric ion (Hg^{++}) is added to the environment of interest and its transformation with time is determined. One transformation which is often overlooked is that Hg^{++} can rapidly be reduced and lost from the study system as elemental Hg.

Some work on the volatilization of reduced Hg^{++} from aquatic systems has been conducted (Avotins and Jenne, 1975), and it has also been noted that Hg applied to soil can be volatilized as elemental Hg (Alberts et al., 1974; Kimura and Miller, 1964; Hitchcock and Zimmerman, 1957). However, since large losses of Hg have not been suspected, no effort has generally been made to monitor the amount of Hg liberated from either deliberately or accidentally contaminated soils. In addition, work is necessary to determine the actual loss rate of Hg from several soil types as a function of various inorganic mercuric sources.

Because of the need for more information, a study was conducted to determine the effect of inorganic mercuric sources on Hg volatilization from soil. Since the possibility exists that soil type could influence Hg loss, because of chemical and/or physical properties, three different soil types were amended with solutions of a variety of inorganic mercury compounds.

CONCLUSIONS

The following conclusions can be drawn from the study:

1. Considerable amounts of Hg can be volatilized from soil but the loss depends on the soil type and the inorganic form of Hg used. These data indicate that mercury can be volatilized from soil amended with any of the water-soluble Hg compounds used.

2. The maximum loss of Hg occurred within the first week after amendment of the soil with such Hg compounds.

or was the result of the Hg becoming more bound with time could not be determined with this experiment.

The type of soil had a distinct effect on the amount of mercury volatilized. In all cases except sand and loam soils amended with $Hg(C_2H_3O_2)_2$ and the HgS amended soils, the loss rates were sand>loam>clay (Table 2).

TABLE 2. PERCENT OF APPLIED Hg EVOLVED FROM SOILS WITHIN 144 HOURS

Hg Compound	Sand	Soil Loam	Clay
		% evolved	
$HgCl_2$	38.3	32.9	14.2
$Hg(NO_3)_2$	36.5	24.1	13.4
$Hg(C_2H_3O_2)_2$	26.4	30.5	12.1
HgO	19.6	15.0	6.4
HgS	0.2	0.3	0.2

These soils decreased in clay and organic matter in the same order. Since Hg is bound to both clay and organic matter this could explain the decreased volatility.

With both the loam and clay soil, maximum volatilization of Hg followed immediately after amendment. However, with the sand soil there was a 22 to 29-hour lag before a maximum volatility rate was obtained. The cause of this phenomenon was not ascertained.

This study amply shows that substantial quantities of Hg can be lost due to volatilization from soils amended with a variety of inorganic Hg compounds. The species of Hg being lost from the soil was not determined. However, work with these soils (Rogers 1977, 1976) has shown that the rate of Hg being transformed into a volatile organic compound (methylmercury) is not sufficient to account for the amounts of Hg lost. Other investigators have shown that elemental Hg is the species being volatilized from treated soils (Alberts et al., 1974; Kimura and Miller, 1964; Hitchcock and Zimmerman, 1957). Whether the reason for this loss was the result of chemical or biochemical reduction of Hg was not determined. However, the percent clay and/or organic matter in the soil does mediate the loss rate.

The data presented here clearly show that there can be large, unsuspected losses of Hg from amended soils. In addition, this loss of Hg is not related to nor would it be detected in experiments designed to detect the transformation of Hg compounds into organic species. These data also indicate

CHEMICAL FIXATION AND SOLIDIFICATION OF HAZARDOUS WASTES

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TABLE 4-12 Solubilities of Metal Sulfides

Species	Solubility (mol/l)	K_{sp}
Cadmium sulfide	6.0×10^{-15}	3.6×10^{-29}
Copper sulfide	9.2×10^{-23}	8.5×10^{-45}
Iron sulfide	6.1×10^{-10}	3.7×10^{-19}
Lead sulfide	1.8×10^{-14}	3.4×10^{-28}
Mercuric sulfide	4.5×10^{-25}	2.0×10^{-49}
Nickel sulfide	1.2×10^{-12}	1.4×10^{-24}
Zinc sulfide	3.5×10^{-12}	1.2×10^{-23}

Source: Adapted from K. F. Cherry, *Plating Waste Treatment*, Ann Arbor Science Publishers, Ann Arbor, MI, 1982.

the reaction must be carried out in an alkaline environment in any case and H_2S is very dangerous to handle in CFS treatment scenarios. The soluble sulfide is usually added as a solution. The stoichiometry is difficult to calculate in CFS systems because the total contents and proportions of sulfide reactive metals are seldom known with any degree of accuracy. Therefore, the addition of sulfide is determined empirically by making up a number of mixtures and determining the minimum addition level that achieves the target leaching goal. The sulfide is added *before* any of the solidification reagents, since the latter contain calcium, magnesium, iron, and other metals that will compete for the soluble sulfide. However, calcium sulfide, which has limited solubility, may act as a sulfide buffer to maintain a small excess available sulfide level in the system, similar to the action of the alkalies in hydroxide precipitation. In fact, one commercial process has been described using CaS for treatment of copper-bearing waste water.

"Insoluble" inorganic sulfides. One answer to the problems encountered with the use of soluble sulfides is the use of very low-solubility species such as FeS or elemental sulfur. In the case of FeS, its solubility is about 0.0001 mg/l in water. The former technology has been commercialized as the Sulfex process by the Permutit Company [24, 30, 31]. The advantage of this approach is that very little excess sulfide is present in the system at any time, so the problem of H_2S odor and toxicity is eliminated.

However, since the solubility of FeS is considerably higher than that of the RCRA toxic metals, the latter will precipitate the available S^{-2} ion, causing more FeS to dissolve. This process continues until all of the metals have been precipitated, or until all of the FeS has been used up. It would also tend to respeciate the hydroxides as sulfides, given sufficient time.

Table 4-13 compares the solubilities of hydroxides and sulfides of a number of metals of interest. The advantage of sulfide precipitation, and the driving force for respeciation, are evident from these data. Cadmium, lead, nickel, and mercury hydroxides all have water solubilities above the recent landban levels (see Chapter 1 and the individual metals later in this chapter), and the leaching levels in tests such as the TCLP are even higher.

The data given in the table apply to an environment in the alkaline pH range. Under acid conditions and/or oxidizing

TABLE 4-13 Comparison of Hydroxide and Sulfide Solubilities

	Approximate Solubility (mg/l)		
Metal	Hydroxide	Sulfide	Difference Factor
Iron	5×10^{1}	1×10^{-4}	5×10^{3}
Cadmium	3×10^{0}	1×10^{-8}	3×10^{8}
Chromium	1×10^{-3}	None	None
Copper	2×10^{-2}	2×10^{-13}	1×10^{11}
Lead	2×10	6×10^{-9}	3×10^{8}
Mercury	6×10^{-4}	1×10^{-21}	6×10^{17}
Nickel	7×10^{-1}	6×10^{-8}	1×10^{7}
Silver	2×10	4×10^{-12}	5×10^{12}
Zinc	3×10^{2}	1×10^{-6}	3×10^{8}

$$\text{Difference factor} = \frac{\text{hydroxide solubility}}{\text{sulfide solubility}}$$

Source: Adapted from Permutit Company, *Sulfex™ Heavy Metals Waste Treatment Process*, Tech. Bull. XIII, No. 6, Paramus, NJ.

by far the largest category, and disposal under controlled landfill conditions, the likelihood of resolubilization is minimal.

One interesting exception in sulfide precipitation is that of chromium, which does not precipitate as the sulfide, but as the hydroxide. Therefore, chromium leaching will be controlled by hydroxide precipitation, and hence by pH, at least in theory. As we shall see later in this chapter, chromium's expected solubility at higher pH takes place only at very high pH levels, and is generally not a problem at the present regulatory levels. It is also claimed by Permutit [32] that FeS has the ability to reduce Cr^{+6} to the trivalent state by the reaction:

$$CrO_4^{-2} + FeS + 4H_2O \longrightarrow Fe(OH)_3 + Cr(OH)_3 + S^0 + 2OH^- \qquad (4\text{-}3)$$

It is also claimed that the Sulfex process is effective with complexed metals, a claim also made for soluble sulfides. Feigenbaum [31] has given the test results shown in Table 4-14. Obviously, FeS is more effective on some species than on others. This is not too surprising, given the considerable differences in the complexes.

TABLE 4-14 Sulfex Treatment of Complexed Metals[a]

		Complex		
Metal	Precipitant	Rochelle Salt	Na EDTA	Rochelle Salt/EDTA
Cadmium	Hydroxide	0.67	4.8	4.4
	Sulfide	<0.005	2.9	2.9
Chromium	Hydroxide	0.20	0.05	0.47
	Sulfide	0.20	0.05	0.40
Copper	Hydroxide	0.18	1.8	1.2
	Sulfide	0.01	0.01	0.01
Nickel	Hydroxide	1.2	1.3	1.8
	Sulfide	0.18	1.4	0.88
Zinc	Hydroxide	0.02	2.2	1.5

leaching test scenario with neutral water as the leachant, lead leaching is very low. Cote *et al.* [106] found only 0.177 percent of the lead to be leached from a cement/flyash waste form after an 11-month test duration in such a system. In this case, lead leaching was somewhat higher than that of chromium or cadmium, but much lower than that of arsenic. Other CFS systems—lime/flyash, bentonite/cement, and cement/soluble silicate—leached lead at somewhat higher rates than cement/flyash, but still below 1 percent. It is obvious that the leaching scenario used is critical when evaluating lead leachability from the products of any CFS process, with pH, and perhaps redox potential, being factors of prime importance. Meaningful estimation of leaching potential must include tests using the actual environmental conditions expected at the disposal site, especially the groundwater composition. Testing with actual or simulated groundwater should include control of redox potential as well as the compositional parameters.

MERCURY

Mercury and its prime ore, cinnabar or vermillion (HgS), have been known since antiquity. They were used for cosmetic and medical preparations and as a pigment. Mercury is estimated to occur in natural rocks at the level of 10 to 1000 ppb, and in petroleum in the range of 2000 to 20,000 ppb. Today, mercury is used in the chemical industries, in the manufacture of paints and paper, in pesticides, and in the electrical industries. The metal is produced by retorting the sulfide ores to liberate the metal as a vapor, then condensing it to the liquid metal. Other methods include the leaching of ores and concentrates with sodium sulfide and sodium hydroxide, or with sodium hypochlorite, but these techniques are not used now [8]. World production of mercury in 1978 was about 6000 metric tons. The standard unit of trade is the "flask," which weighs 76 pounds.

Mercury salts exist in two valence states, +1 and +2. The mercurous compounds often exist as double salts, for example, Hg_2Cl_2. Many mercury compounds are volatile; they are also labile and easily decomposed by light, heat, and reducing agents, even weak reducing agents such as amines, aldehydes, and ketones. Because of their covalent nature and ability to form a variety of organic complexes, mercury compounds have unusually wide solubility. Small amounts of amines, ammonia, and so forth, can exercise a large solubilizing effect [8].

Although the toxic nature of mercury and its compounds was known for centuries, the relatively small scale of use and its familiarity prevented recognition of the environmental hazards. The metal, its vapors, and most of its compounds are protoplasmic poisons that can be fatal to all forms of life, including man. Poisoning may occur through oral, dermal, and inhalation routes. The most toxic forms of mercury are the alkyl organic compounds. In 1960, it was reported that more than 100 people had died or suffered severe neurological damage from eating fish and shell fish contaminated with methyl mercury and mercuric chloride from plastics manufacturing near Minamata, Japan [87]. Later, it was demonstrated that inor-

Commercial Uses

Consumption of mercury in the United States by use is given in Table 4-29. Ottinge *et al.* [87] divide mercury's uses into recyclable and dissipative. Recyclable uses in clude its important use as a cathode in caustic-chlorine production by electrolysis and in various electrical and electronic applications, the two largest consumers o mercury in the United States. The others are basically dissipative uses.

Caustic-Chlorine Production. Even though it is classified as a recyclable use, ther is a large loss of mercury from this process into the environment, and it has bee by far the largest single source of mercury pollution. This waste is classified by th EPA as:

K071— Brine purification muds from mercury cell process in chlorine production, where separately prepurified brine is not used.

K106—Wastewater treatment sludge from the mercury cell process in chlorine production.

Both of these listed wastes are in the first-third landban, but K106 final BDAT stan dards were not set by the EPA and have been deferred until later. K071 BDAT stan dards require solubilizing of the mercury in the waste so that it can subsequently b respeciated as the very low-solubility sulfide. This is the only case to date whe such respeciation has been formally required prior to fixation, and may constitut

TABLE 4-29 Uses of Mercury in the United States (Metric Tons)

Use	1959	1968	1978
Agriculture	110	118	21[a]
Amalgamation	9	9	<0.5[a]
Catalysts	33	66	29[a]
Dental preparations	95	106	18
Electrical applications	426	677	619
Caustic-chlorine	201	602	385
General laboratory	38	69	14
Industrial and control	351	275	120
Paint			
Antifouling	34	14	
Mildew proofing	87	351	309
Paper and pulp	150	14	
Pharmaceuticals	59	15	15[a]
Other	298	285	216
Totals	1892	2600	1681

[a] 1975 figures.

Source: Adapted from Kirk-Othmer, *Encyclopedia of Chemical Technology,* 3d ed., Wiley, New York, 1979.

a precedent. In all other cases, CFS or fixation techniques have been left to the treater, with only the performance level being a requirement.

The brine sludge contains small amounts of mercury as well as mercuric ions, mostly in the form of the tetrachloro complex, $HgCl_2^{-2}$. This waste is being reduced by the use of other chlorine production methods that do not require mercury. Nevertheless, there is still a significant amount of brine sludge being generated, and probably a large number of lagoons and other areas contaminated by mercury from this source. These will require cleanup in the future, probably using CFS technology. Waste from caustic-chlorine production is definitely the most important of all sources to CFS technology.

Agriculture. As is obvious from Table 4-29, this use has declined drastically, due to the 1972 banning of all mercury compounds in agriculture in the United States. At present, only mercuric and mercurous chloride are permitted for use on turf as fungicides [8]. However, in view of the past consumption, it is likely that significant amounts of mercury may be encountered in the cleanup of old pits, ponds and lagoons, contaminated soils, and underwater sediments under CERCLA and in private remediation work.

Electrical Applications. Mercury and its compounds may be found in wastes from certain manufacturing operations, for example, battery manufacture, but these are not important impacts on CFS technology.

Catalysts. Mercury is used as a catalyst for the production of vinyl chloride monomers and urethane foams. Discharges from these plants are sources of mercury-containing wastes, and may require CFS treatment to clean up old disposal areas.

Industrial and Control. Most of these uses involve elemental mercury, and the environmental effects are primarily of an occupational health nature, or result from the disposal of the products (thermometers, batteries, etc.) into landfills. There is little impact from these sources on CFS technology.

Paint. This use of mercury and its compounds has decreased drastically in recent years.

Paper and Pulp. The use of mercury compounds as slimicides in the pulp and paper industry has also decreased greatly since 1970.

Other. Mercury from mine tailings may be an important issue to CFS work in the future, but such wastes are exempted from the RCRA at this time.

Major Compounds

Mercuric Chloride. This salt is very soluble in water and in polar organic solvents. It is used as a catalyst and an intermediate in organic synthesis. $HgCl_2$ is also a component of fungicides and antiseptics, and is used in photography and in hat

Mercuric Oxide. Mercuric oxide exists in both red and yellow forr is more dense, and is used in the Ruben-Mallory dry cell, where graphite and serves as a depolarizer.

Mercuric Nitrate. This compound is used as the starting material inorganic mercury salts, and is also used in organic synthesis.

Mercuric Sulfate. Mercuric sulfate is used as a catalyst.

Mercuric Sulfide. The red hexagonal form of mercuric sulfide is as cinnabar, while the black sulfide is a tetrahedral form. Both are due to color and insolubility.

Organomercury Compounds. Alkyl compounds of the general fo no longer manufactured in most of the world because of extreme toxicity. They were previously used as seed disinfectants. Phenyln or PMA, finds its primary use in latex paint as a preservative an Other organomercury compounds are also used for this purpose.

CFS Treatment Processes

Nearly all of the literature references refer to the removal of mer water. Some exceptions are listed below, including mercury leachin processes.

Process	*Reference*
Portland cement	[115]
Cement/soluble silicate	[143]
Cement + thiourea	[140]
Cement + Fe^{+2} + thiourea	[141]
Cement + metal cyanides	[149]
Cement + vermiculite	[151]
Cement + coal	[150]
Coprecipitation with Fe^{+2}/Fe^{+3}	[156]
Fe/Cu salt + polydithiocarbamate	[142]
Calcium polysulfide	[153]
Inorganic sulfur compounds	[155]
Sulfides	
Thiosulfates	
Dithionates	
Hypophosphorous acid reduction	[144]
Formaldehyde reduction	[145]
Sodium borohydride reduction	[146]
Zinc or iron reduction	[48], [154]
Ion exchange	[48], [147]
Activated carbon	[48], [148]

Process	*Reference*
Sulfide	[8], [48], [98], [156]
Bacteria	[157]
Absorption	[87]

Table 4-30 summarizes fixation processes for mercury in both CFS systems and in waste water treatment. These data are presented because waste water fixation methods have been found to work, and be necessary, for fixation of mercury to sufficiently low levels in CFS systems. The requirement for mercury fixation under the RCRA, especially in the first-third BDAT standards, is lower than that for any other metal except arsenic (0.025 mg/l in K071). In the nonlisted waste categories, the mercury leaching standard is also the lowest of the metals (0.2 mg/l).

Precipitation with Sulfur Compounds. Most of the information in the preceding list comes from processes for treatment of brine, brine-sludge, or waste water from caustic-chlorine production. Mercury in wastes does not form low-solubility hydroxides that would allow pH control to be effective in its fixation, and the oxide solubility is too high. The most common way to remove mercury from waste water or fix it in CFS systems is by the use of various sulfur compounds, typically sodium or calcium sulfide. The solubility of the sulfide, HgS, at 18°C is 0.0107 mg/l. However, the use of excess sulfide increases the solubility of HgS, as shown in Table 4-31 [8]. In view of Table 4-31, it is advisable to use no more than a 20 percent excess of the alkali sulfide over the calculated requirement. In doing a treatability study, a range of alkali sulfide additions should be used, and the results graphed to obtain the minimum requirement. Also, HgS typically precipitates in a very fine particle size, making filtration of the leachate difficult and risking the carryover of solid HgS particles into the filtrate. Obviously, this has been a problem in waste water treatment, and has been resolved in many cases by using flocculating agents such as ferric chloride, ferric sulfate, or starch.

Other sulfur compounds that may be used are in the preceding list. Several patents describe the use of thiourea and cement, with or without other additives, to reduce mercury leaching to low levels—0.001 mg/l and below. Another uses polydithiocarbamates along with iron or copper salts. Unfortunately, all of these investigators used the Japanese leaching test, with water as the leachant, to assess the success of the process. Their results are not directly translatable for use in the United States. One study in the United States [143] achieved excellent TCLP leaching results (0.0006 mg/l) with hexadecyl mercaptan as an additive to a cement/soluble silicate process. The leaching of other metals was not affected by this additive; the sulfhydryl group apparently is highly specific to mercury, at least in this system.

Kaczur *et al.* describe a process [155] for insolubilizing mercury in situ, using inorganic sulfur compounds. The additives, in this case, were sprinkled on the surface of the waste and eluted into and through the waste by flushing with water. The additives dissolve in the eluting water and subsequently react with mercury in the waste or landfilled material, "insolubilizing" it. Typical results from this process showed soluble mercury in the effluent reduced by factors of 55 to 90 percent. Ottinger *et al.* [87] reference various processes for precipitating mercury from solutions by Na_2S and H_2S. Sittig [48] also references a number of reported

TABLE 4-30 Summary of Mercury Fixation Data

Reference^a	Waste Description	Waste Code	CFS System	Mix Ratio	Treatment Scale	Leaching Test	*Mercury Content (mg/kg or mg/l)* Total	Leachate
4:98	Metal/cyanide	F006-8	Lime	—	Commercial	EPT		
4:98	Metal finishing	F006-9, D002-3	Lime/sulfide	—	Commercial	EPT	<1	<0.002
4:98	Metal finishing	F006-9, D002-3	Lime/sulfide	—	Commercial	TCLP		<0.002
4:98	Metal finishing	F006-9, D002-3	Lime/sulfide	—	Commercial	EPT	<1	<0.002
4:98	Metal finishing	F006-9, D002-3	Lime/sulfide	—	Commercial	TCLP		<0.002
4:98	Oil waste		Flyash	1.20	Commercial	TCLP		<0.100
4:98	Paint sludge		Flyash	0.35	Commercial	EPT		<0.100
4:98	Paint sludge		Flyash	0.35	Commercial	TCLP		<0.100
4:98	Biological sludge		Flyash	1.10	Commercial	TCLP		<0.100
4:100	TSD incinerator ash	Various	Cement kiln dust	0.50	Lab	TCLP	<0.007	<0.001
4:100	TSD incinerator filter cake	Various	Cement kiln dust	0.50	Lab	TCLP	3	0.003
4:100	TSD landfill leachate	Various	Cement kiln dust	0.50	Lab	TCLP	<0.007	<0.001
4:100	TSD incinerator ash	Various	Cement kiln dust	0.50	Lab	TCLP	0.048	<0.001
4:104	Arc furnace dust	K061	Proprietary		Lab	EPT	<1	<0.002
4:105	Mixed wastes	Various	Proprietary		Commercial	EPT	<1	0.005
4:114	Electroplating sludge	F006	Lime, sulfide		Commercial	EPT	<1	<0.002
						TCLP		<0.001
4:119	Arc furnace dust	K061	Portland cement	0.05	Lab	TCLP	3.8	0.001
4:119	Arc furnace dust	K061	Kiln dust	0.05	Lab	TCLP	3.8	<0.001
4:119	Arc furnace dust	K061	Lime/flyash	0.10	Lab	TCLP	3.8	0.002
	Arc furnace dust	K061	Potassium silicate		Lab	EPT		<0.001

(continued)

TABLE 4-30 Summary of Mercury Fixation Data (*Continued*)

Reference[a]	Waste Description	Waste Code	CFS System	Mix Ratio	Treatment Scale	Leaching Test	*Mercury Content (mg/kg or mg/l)* Total	Leachate
4:140	Cl-caustic brine sludge	K071	Cement + thiourea	0.65	Lab	Water	15	<0.010
4:140	Cl-caustic brine sludge	K071	Cement + NaS	0.65	Lab	Water	15	0.017
4:141	Acetylene sludge		Cement + Fe^{+2}+ thiourea	2.5	Lab	Water	381	<0.001
4:142	Seabed sediment		Fe^{+2}/Cu^{+2} + polydithiocarbamate	0.01	Lab	Water	10	<0.001
4:143	Synthetic sludge		Raw waste			TCLP		2.070
4:143	Synthetic sludge		Cement/silicate + hexadecyl mercaptan	0.2	Lab	TCLP		<0.001
4:159	Mixed waste		Cement/flyash		Lab	EPT	0.377	0.003
4:159	Mixed waste		Cement/flyash		Lab	MEP[b]	0.377	0.027
4:160	Zinc phosphate waste		Cement/flyash		Lab	ELT,[c] 1 d	2.6	<0.002
4:160	Zinc phosphate waste		Cement/flyash		Lab	ELT,[c] 28 d	2.6	<0.002
4:160	Zinc phosphate waste		None		Lab	ASTM,[c] 2 d	2.6	<0.002
4:160	Zinc phosphate waste		None		Lab	ASTM,[c] 10	2.6	<0.002
4:160	Zinc phosphate waste		Cement/flyash		Lab	ASTM,[c] 2 d	2.6	0.003
4:160	Zinc phosphate waste		Cement/flyash		Lab	ASTM,[c] 10	2.6	0.002

[a] References are listed at the end of Chapter 4.

[b] Maximum concentration.

[c] Sequential batch test, CO_2-saturated water.

TABLE 4-31 Solubility of HgS in Excess Na_2S

Na_2S in g/100g of Solution	HgS in Solution (mg/l)
0.95	2100
1.50	5700
2.31	14500
3.58	29100
4.37	41200
6.07	72700
9.64	155900

Source: Adapted from Kirk-Othmer, *Encyclopedia of Chemical Technology*, 3d ed., Wiley, New York, 1979.

uses of sulfur-based "getter" systems, including elemental sulfur and thiourea-type organics [170].

Chemical Reduction. Reductants are used to reduce mercury to the elemental state in water, after which it can be removed and reclaimed. This technique probably has limited use in CFS processes, since the mercury would remain in the waste and could be leached out by acidic leachants under oxidizing conditions. Under reducing conditions, organomercury compounds may be formed. It is also claimed that bacteria [157] become resistant to mercuric salts by metabolizing the salts to elemental mercury, the end result of which is reduction. Processes [48] where the reduction is accompanied by amalgamation—for example, with zinc or iron—may produce a species more resistant to leaching, but no data are available on leachability of the amalgams in a CFS matrix.

Ion Exchange and Sorption. A number of references show the use of ion exchange for waste water treatment. In both ion exchange and absorption, the metal species remains in the matrix and the process is reversible, so these processes are probably less effective in CFS treatment than they are with waste water. Exceptions may be when the mercury is fixed with thiol-type [145] or other reactive resins. Also, Jones [150] reports the removal of mercury from water with powdered coal. Although described as an absorbent, the sulfur content of the coal may comprise the real fixing agent. Chen and Majewski [151] claim that vermiculite, usually considered an absorbent, mixed with cement is effective in fixing mercury.

Other Precipitants. A Japanese patent [149] claims the fixation of mercury with cement containing copper cyanide. According to the authors, both the mercury and the cyanide were "strongly fixed" in the solidified product. Nippon Electric developed a process for fixing mercury as magnetic ferrite by coprecipitation with Fe^{+2} ion. The reaction is described as shown in Eq. (4-7).

$$xM^{++} + Fe^{+2}_{(3-x)} + 6(OH)^- \longrightarrow M_xFe_{(3-x)}(OH)_6 \qquad (4\text{-}7)$$

Oxidation with air converts the product in Eq. (4-7) to a black ferrite, $M_xFe_{(3-x)}O_4$. This latter compound can be separated by magnetic means. Mercury in the effluent is claimed to be 0.005 mg/l, compared with 6.0 mg/l in the influent. Since the ferrite

Bhatty [115] found that while mercury in a dilute tricalcium silicate (the major component of cement) slurry was strongly fixed at short hydration times, it was released at longer times, suggesting that cement-based systems alone may not fix mercury in a stable form. Other metals (see prior sections in this chapter) did not display this effect. No explanation was given for possible mechanisms.

With the exception of a few very specific waste streams such as K061, it can probably be said that mercury leaching is not a major problem in the CFS field. Most wastes show leaching levels below routine detection limits. For K061 and other residuals where mercury leaching is a problem, sulfides or other sulfur compound additives provide the most fruitful approach in every case, although the best additive may vary from waste source to waste source. This is especially true now, in view of the allowable mercury leaching levels set in recent landbans and those likely to be set in the near future.

NICKEL

Nickel comprises about 3 percent of the earth's composition, but only about 0.009 percent of the earth's crust. Two types of ores are mined commercially: sulfide and laterite. The former is currently the most important, and the most common form is pendlandite, $(Ni,Fe)_9S_{16}$, which is found along with chalcopyrite, $CuFeS_2$, and pyrrhotite, Fe_7S_8. Lateric ores were formed as a result of weathering, and nickel silicate in solid solution in other minerals, or nickel in solid solution in hydrated iron oxides [8]. Nickel is produced from sulfide ores by pyrometallurgical processes, followed by electrolytic or carbonyl refining where pure nickel is required.

Nickel is a Group VIII transition element, along with iron and cobalt. It forms compounds in which the nickel atom has the oxidation states of -1, 0, $+1$, $+2$, $+3$, and $+4$. The Ni^{+2} valence state, however, represents the majority of all nickel compounds. The most common structural form for nickel is the octahedral configuration, in which nickel has the coordination number 6 and the compounds are the familiar green color. Less common forms exist where the coordination number is 4. Nickel is not amphoteric, but the ease with which it forms coordination complexes at high pH gives it the appearance of being so.

Nickel and its compounds are inhalation hazards, and some aqueous solutions of nickel compounds are skin irritants and may cause allergic dermatitis. Nickel and most of its salts are not considered to cause systemic poisoning. Some nickel compounds are carcinogenic via the inhalation route, and are regarded as carcinogenic via ingestion on an experimental basis [178].

Major Compounds

Nickel Oxide. Nickel oxide (NiO) has the characteristic "nickel green" color, but there is also a black crystalline form that is an incomplete calcination product with slightly more than the stoichiometric oxygen content. The oxides are used in alloying, in catalysts, ceramic frits, ferrites, and pigments, and in the manufacture of other nickel chemicals.

Nickel Sulfate. The common commercial form is the hexahydrate, $NiSO_4 \cdot 6H_2O$. Its principal use is in formulating the electrolyte in nickel electroplating; it is also used in electrorefining and electroless nickel plating. Other uses include catalyst intermediates and the manufacture of other nickel chemicals.

Nickel Nitrate. Also a hexahydrate, the nitrate decomposes on heating to form nickel oxide. It is used in the manufacture of nickel catalysts and in nickel–cadmium batteries.

Nickel Halides. The chloride hexahydrate is used with nickel sulfate in the conventional Watts electroplating bath. It is also used in catalysts, to absorb ammonia in gas masks, and as an intermediate in the formation of coordination compounds.

Nickel Carbonate. There are two carbonates, $NiCO_3$ and basic nickel carbonate, $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$. Carbonates are used in catalysts, in the manufacture of colored glass in pigments, and in electroplating solutions.

Nickel Hydroxide. Nickel hydroxide $[Ni(OH)_2]$ has low water solubility, which accounts for the adequate fixation of nickel in most wastes by simple pH control. It is used as a catalyst intermediate and in nickel–cadmium batteries.

Nickel Fluoroborate. Nickel fluoroborate $[Ni(BF_4)_2 \cdot 6H_2O]$ is used in specialty high-speed nickel plating.

Nickel Cyanide. The simple cyanide is used in organic chemical manufacture. The complex cyanides, formed when $Ni(CN)_2 \cdot 4H_2O$ is dissolved in bases, are water soluble and quite stable. $K_2[Ni(CN)_4]$ does not precipitate with H_2S from aqueous solution.

Nickel Sulfamate. Nickel sulfamate $[Ni(SO_3NH_2)_2 \cdot 4H_2O]$ is used as an electrolyte in electroforming of nickel.

Nickel Sulfide. Nickel sulfide (NiS) occurs naturally as the mineral millerite, and has low water solubility. It is found in nickel wastes from waste water treatment polishing operations.

Other Inorganic Nickel Compounds. A number of other nickel compounds are used in industry and may be present in waste streams. These include: nickel arsenate (hydrogenation catalysts), nickel phosphate (steel pretreatment before coating), a number of double salts with NH_4^+ (dye mordants and metal finishing), and nickel amine complexes.

Organonickel Compounds. Organic compounds of interest in CFS chemistry are primarily salts such as the acetate, formate, oxalate, stearate, and nickel chelates. Nickel acetate is found in metal finishing operations such as aluminum anodizing and electroplating. The fatty acid salts are used in the dying of synthetic fibers. Various soluble chelates are formed, and these are the source of most of the problems encountered with fixation of nickel. They are quite stable and very difficult to "break" so that the nickel can be precipitated as an insoluble species.