Reprint from:

Handbook of Extractive Metallurgy

Edited by Fathi Habashi

ⓦ WILEY-VCH

17 Mercury

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17.1 Introduction

Mercury (also called quicksilver), symbol Hg from the Greek νδραρ = water and αργνρος = silver, was known as early as 1000 B.C. because of its liquid state at room temperature (*mp* -38.89 °C). The discovery in 1938 of 1 kg of the metal in 2500-year-old sand layers on the eastern coast of Greece indicates that mercury was used in the extraction of gold at an early date [1]. Mercury was mentioned about 200 B.C. in India as well as in China (Han dynasty).

As early as 1556, GEORGES BAUER, known as AGRICOLA, reported five different methods for extracting mercury from its ores [2]. He also realized that mercury vapors are heavier than air and that they could therefore conveniently be trapped in condensers beneath the reaction vessel.

Because of the considerable vapor pressure of mercury even at room temperature and the toxicity of its vapors, particularly safe and reliable methods must be used in the extraction of mercury to avoid releasing even the slightest trace of the metal into the environment. The problem of gas and water purification is therefore particularly important.

17.2 Properties

17.2.1 Physical Properties

Mercury is a silvery-white, shiny metal, which is liquid at room temperature. The most important physical properties are listed below:

Isotope masses (ordered according 202, 200, 199, 201
  to decreasing abundance) 198 204, 196
mp -38.89 °C
bp (101.3 kPa) 357.3 °C
Density (0 °C) 13.5956 g/cm^3
Specific heat capacity c_p (0 °C) 0.1397 J g^{-1} K^{-1}

Heat of fusion	11.807 J/g
Heat of evaporation (357.3 °C)	59.453 kJ/mol
Thermal conductivity (17 °C)	0.082 W cm^{-1}K^{-1}
Thermal expansion coefficient β (0-100 °C)	1.826 x 10^{-4} K^{-1}
Electrical conductivity (0 °C)	1.063 x 10^{-4} mΩ^{-1}mm^{-2}
Crystal structure	rhombohedral
Viscosity (0 °C)	1.685 mPa • S
Surface tension	480.3 x 10^{-5} N/cm
t_{critt}	1450 °C
p_{critt}	105.5 MPa
Critical density	5 g/cm^3
Evaporation number (25 °C)	0.085 mg K^{-1}cm^{-2}

Mercury has a relatively high vapor pressure, even at room temperature. Saturation vapor pressures at 0-100 °C are listed in Table 17.1 (corresponding to a specified mercury content in air). The temperature dependence of the density of mercury is given in Table 17.2.

Mercury vapor is excited to a state of luminescence by electrical discharge (mercury vapor lamps). Ultraviolet radiation is released primarily, it can be used to start and to promote chemical reactions.

Table 17.1: Saturation vapor pressure of mercury at different temperatures.

t, °C	p, Pa	Hg content in air, g/m^3
0	0.026	0.00238
10	0.070	0.00604
20	0.170	0.01406
30	0.390	0.03144
100	36.841	2.40400

Table 17.2: Density of mercury as a function of temperature.

t, °C	Density, g/cm^3	t, °C	Density, g/cm^3
-38.89	13.6902	200	13.1139
0	13.5956	250	12.9957
50	13.4733	300	12.8778
100	13.3524	350	12.7640
150	13.2327		

Table 17.3: Temperature dependence of the dynamic viscosity of mercury.

| t, °C	Density, g/cm^3	t, °C	Density, g/cm^3
-20	1.855	60	1.367
-10	1.764	80	1.298
0	1.685	100	1.240
10	1.615	200	1.052
20	1.554	300	0.950
30	1.499	340	0.921
40	1.450		

The surface tension of mercury is ca. six times greater than that of water, which is the reason for its poor wettability by water.

The dynamic viscosity η of mercury (Table 17.3) is of the same order of magnitude as that of water [3].

Some other metals, such as gold, silver, and zinc, dissolve readily in mercury to form amalgams. The solubility of mercury in water is strongly temperature dependent [4]. At room temperature, the solubility is ca. 60 µg/L; at 50 °C, ca. 250 µg/L; and at 90 °C, ca. 1100 µg/L. At low temperature, the addition of sodium chloride reduces the water solubility.

17.2.2 Chemical Properties

Mercury exists in the oxidation states 0, 1+, and 2+; monovalent mercury is found only in Hg-Hg bonds. The redox potentials E^0 at 298.15 K and 101.325 kPa relative to the standard hydrogen electrode are as follows [3]:

$$Hg^{2+} + 2e^- \rightleftharpoons Hg \qquad +0.851 \text{ V}$$

$$2Hg^{2+} + 2e^- \rightleftharpoons Hg_2^{2+} \qquad +0.920 \text{ V}$$

$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg \qquad +0.797 \text{ V}$$

$$Hg_2(CH_3COO)_2 + 2e^- \rightleftharpoons 2Hg + 2CH_3COO^- \qquad +0.511 \text{ V}$$
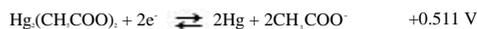
The standard potentials show that mercury is a relatively noble metal. Metallic mercury dissolves in nitric acid, aqua regia, warm concentrated hydrochloric acid and sulfuric acid. It is sparingly soluble in dilute HC1, HBr, and HI as well as in cold sulfuric acid. Most of its chemical compounds have densities of 5-9 g/cm^3. The oxide of mercury (HgO) decomposes at 400-500 °C. This effect is utilized in the extraction of mercury from oxidic sources. Mercury forms monovalent and divalent compounds with the halogens fluorine, chlorine, bromine, and iodine. It also forms monovalent and divalent compounds with sulfur.

17.3 Resources and Raw Materials

17.3.1 Deposits

All known mercury ores are relatively low-grade ores, the average mercury content being ca. 1 %. Because mercury ores lie close to the earth's surface, the mining depth is ca. 800 m at most. The overwhelming proportion of mercury has always been produced in Europe; some of the most important deposits are listed below. Over the last ten years, the former Soviet Union, Spain, China, Algeria, Turkey, and the United States have accounted for ca. 90 % of world mining production.

Spain. The deposits at Almadén have been mined for more than 2000 years. Almadén is situated in the southwest of the province of Ciudad Real in New Castile, about 200 km from Madrid, on the northern edge of the Sierra Morena. The ore-bearing deposits are porous sedimentary rocks (sandstone, bituminous shale, Silurian quartzite) that contain mercury sulfide (cinnabar). Needles of coarsely crystalline cinnabar as well as metallic mercury in lenticular ore-bearing bodies are also found over a roughly 20-km stretch in the valley of the Valdeazogues river. The ore is extracted in several mines (San Pedro y San Diego, San Francisco, San Nicolas). The richest strata contained 12-14% mercury at a depth of 170-200 m. Mining is carried out today at a depth of 500 m; 1 t of ore yields about one flask of mercury (= 34.473 kg of mercury, corresponding to a 3.5% mercury content in the ore).

This deposit was probably known to the Celts and Phoenicians, and was mined by the Romans from 150 B.C. These mines were subsequently worked by the Moors, then by the orders of knights, by the Spanish royal house, and from 1525-1645 by the Fuggers. Since then the mines have been under state management. From 1449 (when production records start) to the present, ca. 300 000 t of mercury has been mined.

In 1988 Almadén produced ca. 1380 t of mercury. The ore-bearing body has an average mercury content of 5%. Because of the low price of mercury the plant operates for only a few months of the year. The operating company, Minas de Almadén y Arrayanes SA, is state-owned [5,6].

Italy. A roughly 25-km-wide, 50-km-long belt running from Monte Amiata to the coast in southern Tuscany contains many closed mines as well as some that are still operating. Although these deposits had been mined by the Etruscans, they were not intensively worked by the Romans, to the benefit of the Spanish mines at Almadén. The Siele mine recommenced operation only in 1846, and the Abbadia San Salvatore mine, at present still the largest, in 1898.

Mercury occurs as cinnabar and metacinnabarite in pyrites, marcasite, antimonite, and realgar, mainly in Eocene sediments (shale, sandstone, marl, limestone) under a covering layer of trachyte. The gangue consists largely of clay or dolomite. The ores contain on average 0.2-0.8% mercury. Mercury extraction is organized by the Monte Amiata works, its latent production capacity being up to 2000 t/a. No mercury has been mined since 1983.

Former Yugoslavia. The third largest mercury deposits in Europe are situated in Idrija in Slovenia, about 40 km west of Ljubljana. These deposits have been worked since 1497. The mines were under Austrian ownership from 1580 to 1918, then under Italian ownership, and finally reverted to Yugoslavia after World War II.

The tectonics of this region are complicated. Shell marl and shale are impregnated with cinnabar and native mercury, and typically contain admixtures of pyrites, gypsum, and bitumen. The ore contains ca. 0.5% mercury. Idrija has a capacity of about 600 t/a. About 60 t mercury was mined in 1986. Additional deposits in Yugoslavia are located at Maškara in Croatia, Berg Avala to the south of Beograd in Serbia, Neumarkt in the Karavanken, and Montenegro.

Algeria. Algeria has become the second largest mercury producer in the western hemisphere after Spain, and in 1986 ca. 690 t of mercury was produced.

Germany. In 1936 a modern mercury works was built at Landsberg near Obermoschel in the northern Pfalz (Palatinate), which had to be closed in 1942 because working the very low-grade ore, containing only 0.1 % Hg, was uneconomical.

Austria. Fahl ore containing 1.8% mercury is mined in small amounts at Schwaz in the Tyrol. Other deposits at Dollach on the Drava are no longer mined.

Finland. Outokumpu obtains about 100 t of mercury per year from the processing of zinc concentrates.

Former Czechoslovakia. Three important deposits exist: at Kotrbachy, mercury is obtained as a by-product of a fahl ore. Cinnabar is found southwest of Gelnica in a workable ore containing 0.25% mercury. Finally, mercury has been obtained in the region between Mernik and Vranov since the end of the 17th century. This production ceased in 1937.

Romania. Romania has mercury ores at Zlatna and Baboja in Transylvania.

Turkey. In Turkey about 220 t of mercury is obtained annually from mining operations. At present, because of its low price, mercury is extracted from only two mines, which belong to the state-owned Etibank. The deposits are at Izmir-Odemis-Halikoy (1 X 10^6 t of ore containing 0.25% mercury), Konya-Ladik, and Konya-Sizma (1.15 x 10^6 t of ore containing 0.23% mercury). These deposits alone account for ca. 40% of the Turkish reserves of mercury [7].

Former Soviet Union. The most important deposits in the former Soviet Union are at Nikotovka in the Ukraine. Per year about 400 t of mercury is produced there from an antimonite ore containing 0.4% mercury. Cinnabar deposits have recently been discovered in the Crimea, although no further details are available. Additional ore deposits are mined in the

Northern Caucasus, Urals, Altai Mountains, and in Turkestan and Dagestan.

China. China has important deposits in the provinces of Yunnan, Hunan, and Kweitschan. The mines at Wanschantschang and Patschai are well known. Mined production was ca. 760 t of mercury in 1987.

Japan. In Japan, mercury is extracted on the island of Hokkaido.

Canada. Mercury ore deposits are situated in the west of Canada in British Columbia at Pinchi Lake and in the vicinity of Vancouver (Kamloops, Bridge River).

United States. The number of mines in the United States has decreased considerably in the last 20 years. Whereas 149 mines were operating in 1965, only 3 mines were still operating by 1981. The principal mining regions are California and Nevada. Placer, Inc., a subsidiary of the Canadian company Placer Development, accounts for ca. 99% of production. The average mercury content in the ore is 0.3—0.5%. Mining production in 1986 was ca. 400 t and falling.

Mexico. The 200 known mercury ore deposits are distributed over 20 states. The most important mines are in the provinces of Zacatecas, Guerero, Durango, Chihuahua, Guanajuato, San Luis Potosi Aguascalientes, and Queretaro; total mercury production is some 500 t/a.

South America. South America is of only minor importance as a mercury producer. Chile occupies first place among the mercury-producing countries. The Santa Barbara mine at Huancavelica in Peru is now exhausted, although it supplied substantial amounts of mercury in the 17th and 18th centuries: some 50 000 t was used for precious-metal extraction. Small amounts of mercury are mined in Venezuela and Bolivia.

A U.S. estimate made in 1983 gave the following amounts of mercury extracted by mining operations [8]:

Spain	50 000 t
China	17 200 t
Soviet Union	17 200 t
Yugoslavia	17 200 t

Italy	12	100 t
United States		12 100 t
Other countries		29 000 t
World total		154 800 t

Mining activities and exploitation of deposits are, as with most base metals, greatly dependent on current world market prices. Too low returns have led in recent years to a number of mines being closed, which has resulted in a concentration of plants (less plants with increased production).

17.3.2 Secondary Sources

Like primary ores, industrial waste containing mercury also contributes to its production. The majority of plants used in chlor-alkali electrolysis employ liquid mercury cathodes, resulting in residues containing 10% mercury or more. In addition to this major secondary source, mercury batteries, mercury fluorescent tubes, electrical switches, thermometer breakage, and obsolete rectifiers should be regarded as mercury sources.

Although the overall production of mercury has decreased over the last 20 years, sufficient potential uses and thus secondary sources remain for the foreseeable future, thanks to the unique properties of this metal.

17.4 Production

17.4.1 Extraction from Primary Sources

17.4.1.1 Beneficiation

Preliminary concentration is desirable, especially for working low-grade ores. This is often performed in the mine by classification. Because of the brittleness of cinnabar, pieces of ore break easily at the mercury sulfide veins. Crystalline mercury sulfide in brittle ore can be concentrated by using settling tables.

Another method of concentration is the use of a flotation stage to increase the mercury content. Separation of the antimony and arsenic fractions is particularly important, and the ores are comminuted to grain sizes of 0.075 mm (200 mesh) in the case of antimony and 0.5 mm (25 mesh) in the case of arsenic. After comminution, lead(II) nitrate $[Pb(NO_3)_2]$, butyl xanthate, and pine oil are added to the first flotation stage. Flotation is performed at pH 7.1. After purification, mercury is selectively floated, and a concentrate of ca. 50% antimony is obtained. Potassium dichromate $(K_2Cr_2O_7)$ is added as reactant. The end concentrate has a mercury content of ca. 70% [9]. Another way of concentrating mercury by flotation is to add potassium oleate as collector [10].

Only a coarse preliminary grinding to ca. 50-mm grain size is necessary for high-concentration mercury sulfide ores. During subsequent thermal treatment, the ore particles burst because of the high vapor pressure, resulting in further comminution.

17.4.1.2 Processing to Metallic Mercury [11,12]

The most important starting material for mercury extraction is mercury sulfide (cinnabar, cinnabarite); it is nonpoisonous and can be stored and transported without any problem.

The coarsely ground ore is processed in directly or indirecdy heated furnaces, retorts, or muffles. Reaction with oxygen begins at 300 °C, according to

$$HgS + O_2 \rightleftarrows SO_2 + Hg$$
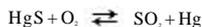
Quicklime can be added as flux to bind the sulfur in solid form. The overall reaction in the absence of oxygen is as follows:

$$4HgS + 4CaO \rightleftarrows 3CaS + CaSO_4 + 4Hg$$
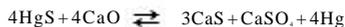
In the *presence of oxygen,* the reaction is

$$HgS + CaO + \frac{1}{2}O_2 \rightleftarrows Hg + CaSO_4$$
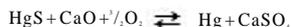
Addition of metallic iron in the form of iron filings enables the following reaction to occur:

$$HgS + Fe \rightleftarrows FeS + Hg$$
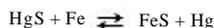
Instead of metallic iron, iron oxides can also be used:

$$7HgS + 2Fe_2O_3 \rightleftharpoons 4FeS + 3SO_2 + 7Hg$$
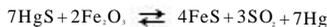
For this reason, sulfur-resistant steel should be used as construction material. Processing is normally performed with the addition of air, and the sulfur dioxide formed can be converted in a downstream wet scrubber.

17.4.1.3 Furnace Systems

Mercury sulfide-containing ores are processed pyrometallurgically. Distinction is made between *directly* and *indirectly* heated furnaces. This is important because the formation of *stupp* cannot be avoided in pyrometallurgical processing (the word stupp is an Austrian expression that simply means powder; in the case of mercury, a mercury-containing powder). The greater the formation of dust in the furnace, the greater is the occurrence of stupp. Because of the presence of combustion air in the furnace, directly heated furnaces generally create more dust than indirectly heated ones. Mercury in vapor form condenses to some extent on the small dust particles which act as condensation nuclei.

Another difference between directly and indirectly heated furnaces is that mercury vapor in indirectly heated systems is more highly concentrated because it is not diluted by combustion gases.

Directly Heated Furnaces. Cylindrical Bustamente furnaces, multiple-hearth furnaces, and rotary kilns are used.

The *Bustamente furnace* is still used in Spain (Almadén) [5]. The cylindrical vessel is heated outside the shaft, only the combustion gases come into contact with the ore. A historical feature is that mercury vapors are condensed in air-cooled terracotta pipes.

The *multiple-hearth furnace* is advantageous for working up rich concentrates, mercury waste of a similar type, or stupp. This kind of furnace has been used for many decades in various mercury mines in North America, and in Almadén most of the ore extracted since 1961 has been processed in multiple-hearth furnaces. The hearths and outer walls of the furnaces are built of shaped fire-clay bricks. The furnaces are lined with sheet steel. Cast steels with additions of titanium, chromium, and nickel have proved suitable for internal structural elements (stirrer shaft, raking arm). A modern furnace is up to 10 m high, has a diameter of ca. 5 m, and contains up to 16 hearths that are heated with wood, gas, or oil (mainly the upper and lower hearths). An attempt is made to keep the flow velocities for the reaction gas low (maximally 3 m/s) by skillful feeding of the material (if possible by special sliding surfaces at the throats in the case of small hearth interspacings) and by separately installed gas passageways. The amount of flue dust is thereby lowered (0.2-3% of the feedstock), and the formation of stupp is minimized. Addition of combustion air through the insulated hollow shaft and raking arm and, if necessary, preheating of the fuel oil both reduce fuel consumption. By accurate metering of the inlet air, a lower amount of gas can be passed through the furnace, and the capacity of the subsequent condensation unit can be reduced. Table 17.4 shows some operational examples of multiple-hearth furnaces.

With regard to environmental protection, multiple-hearth furnaces are relatively difficult to make gastight and, in some cases, have had to be shut down.

Rotary kilns have been used since 1913 to extract mercury. Rotary kilns and rotary drum furnaces provide a high mercury yield with a good throughput rate of the ore because the reaction temperature can be controlled accurately; the ore does not have to be specially preheated; and material throughput can be regulated.

Table 17.4: Operational data for multiple-hearth furnaces for mercury extraction.

	New Almadén	Pershing	Quicksilver Mines
Furnace diameter, m	4.9	4.9	5.5
Number of hearths	6	8	6
Worked material	ore	ore	ore
Throughput, t/d	38	77	50
Fuel consumption per tonne of material	47 L oil	21 L oil	0.15 m³ wood

The ore is ground to about 65-mm particle size before it is charged. Lime, charcoal, or low-temperature coke may be added as fluxes, and the furnaces are heated directly by oil or gas. The furnaces are operated at 320-400 °C at the charging head and 700-800 °C at the discharge end. For normal furnace sizes and ores, heat consumption is (1 to 1.25) x 10^6 kJ per tonne of throughput. Without the addition of coal as flux, this corresponds to up to 30 L of oil or 250 m^3 (STP) of fuel gas per tonne of ore throughput. A disadvantage of rotary kilns is the dust formed by the intense material movement, which leads to increased stupp formation in subsequent condensation and can cause stoppage in the waste-gas line. Flue dust amounting to 0.75-6% of the ore feedstock by weight is observed. In many cases, dust formation can be reduced by fluxes having a sintering effect. Some operating examples of older rotary kilns are listed in Table 17.5.

Indirectly Heated Furnaces. The basic advantage of indirect heating is the lower gas velocity in the reactor and the higher mercury concentration of the process gas. The furnaces are heated by gas, coal, or by electricity and consist in some cases of clay muffles, vessels lined with fireclay or ceramics, or iron vessels lined with silicon carbide.

F. Krupp-Grusonwerk AG has arranged several tubular individual muffles in a rotary kiln around a thermally insulated, centrally aligned shaft. A rotary kiln constructed from two concentric tubes was developed several years later. The ore passes continuously through the inner tube; the outer tube is heated. A highly thermally conducting, gastight silicon carbide is used as cladding. Several proposals for processing mercury-containing material in indirectly heated furnaces have been made, and patents have been issued [13-15].

The subsequent condensation of mercury from the furnace off-gas is treated later.

17.4.2 Extraction from Secondary Sources

Because of the relatively high toxicity of metallic mercury and some of its compounds, spent products must be reprocessed to a large extent. Storage of slurry-like residues is complicated and expensive, and is governed by the limited storage capacity of the closed mines. Active carbon slurries from the effluent concentration resulting from chlor-alkali electrolysis constitute the major proportion of mercury residues that must be reprocessed.

In addition to these residues, the processing of fluorescent bulbs, which contain about 15-50 mg of metallic mercury per lamp, is becoming increasingly important. Several plants dealing specifically with the disposal of these lamps already exist in Germany [16].

Table **17.5:** Operational data for rotary kilns for mercury extraction.

|	Gelnica	Abbadia San Salvatore	New Indria	Nevada, Quicksilver Mines	Pershing, Quicksilver Mines	Mercury Mining Company
Furnace length, m	14	16	17	12.2	18.3	21
Internal diameter, m	1.5	1.25	1.22	0.92	1.22	1.22
Thickness for lining, mm	250	200	150			
Gradient, %	4	5	4			
Time for one revolution, s	72		42	45	50	
Moisture content of ore, %	5-10					
Hg content of ore, %	0.2	0.6-0.8				
Grain size of ore, mm	50	5		64	40	50
Ore throughput, t/d	40	100	125	40	45	45
Fuel consumption per tonne of ore	100 m^3 (STP) gas + 0.3 m^3 wood	100 kg wood	19 L oil	26.5 L oil	30 L oil	29 L oil

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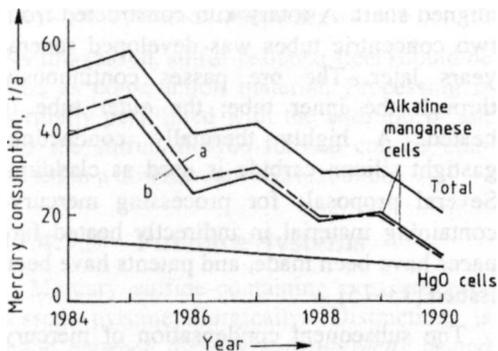
Figure 17.1: Reduction of mercury in primary batteries in Germany [17]: a) Mercury in sold primary batteries; b) Mercury in domestic refuse.

The mercury content of normal zinc-manganese dioxide batteries has been reduced considerably over the last few years (addition of mercury inhibits the formation of gas by zinc). In Germany, the mercury content of batteries will be reduced to 0.15% by 1990 (Figure 17.1), starting from a level of 1 % [17].

In addition to zinc-manganese dioxide batteries, zinc-mercury(II) oxide batteries are also widely used as round cells. These contain ca. 30 % mercury, which must be recovered. Mercury in concentrations of ca. 1% is also found in zinc-silver(II) oxide and zinc-oxygen batteries. A particular problem in reprocessing batteries is grading and sorting the various types, which are inadequately identified and, in some cases, have the same external dimensions for different electrochemical systems. Treatment processes have been developed in Japan [18], Germany [19, 20], and other countries [21], which can remove mercury by treatment in rotary kilns or in a distillation chamber. The individual types of batteries do not have to be sorted beforehand, and a mixture of batteries can be processed.

Because batteries also include a large number of plastics (e.g., as sealants), waste gases must be treated and burned if necessary.

Because a proportion of spent batteries end up in domestic refuse, high mercury concentrations can be found in waste gas from domestic refuse combustion. Mercury-containing older printing inks are another source. Because mercury can be precipitated

from waste gas most efficiently by adsorption on activated carbon or similar substances, mercury-containing charcoal from waste gas purification will also require reprocessing in the future.

The mercury-selenium residue formed in the primary smelting of mercury-containing sulfidic ores requires special reprocessing. This substance, which occurs as a slurry, has been reprocessed in a multiple-hearth furnace in which the mercury fraction is evaporated [22]. Another company converts the residue to metallic mercury in a rotary kiln by adding lime fluxes, with a relatively inert residue remaining behind [23]. A hydrometallurgical reprocessing treatment has been investigated on a pilot scale in a research project [24]. Mercury is extracted in the form of mercury(II) oxide and sulfide, and can be added to the conventional extraction processes. The method does not appear to be economically practical at present because of the relatively expensive reactants involved.

Additional secondary sources, such as thermometer breakage, electric switches, and amalgams, can generally be worked up by conventional distillation methods [25, 26]. A comprehensive monograph on the topic of evaporation and thermal dissociation of mercury sulfide is available [27]. Electrolysis has been proposed for the removal of mercury from gold-containing solutions: 90-95 % mercury and < 10 % gold are deposited at 1.0-1.5 V [28].

17.4.3 Condensation of Mercury from Furnace Off-Gas

The vapor pressure p (mbar of mercury) can be calculated according to a relationship given by BARIN and KNACKE [29]:

$$\log p = -\frac{3305}{T} - 0.795\log T + 10.47893$$

where T is measured in kelvin.

The degree of saturation s (kg of mercury per cubic meter) of the gas at t (°C) or T (K) and $p = 101.3$ kPa can be determined from the

pressure and density of mercury vapor (3.9091 kg/m³ at 357 °C) ($\alpha = 1/273$):

$$s = 3.9091 \frac{1 + 357\alpha}{1 + \alpha t} \frac{p}{101.3} = 3.9091 \frac{630}{T} \frac{p}{101.3}$$

The degree of saturation s of mercury vapor calculated according to this formula for different temperatures is summarized in Table 17.6. Figure 17.2 shows p and s plotted as a function of $1/T$ on a semilogarithmic scale.

Mercury losses during condensation can be calculated as follows: 1 m³ of saturated vapor at 140 °C (413 K) enters the condensation unit laden with 14.464 g of mercury. There it is cooled to 20 °C (293 K) ($s = 0.0141$ g/m³), and a volume contraction to $293/413 = 0.71$ m³ occurs. The saturated vapor leaving the unit therefore contains 0.71 x 0.0141 = 0.01 g of mercury. The loss of uncondensed mercury removed with the waste gas is thus 0.07% of the initial amount. With a condensation end temperature of 40 °C and otherwise identical conditions, the loss increases to 0.35 % Hg.

Table 17.6: Saturation content of mercury vapor at various temperatures.

p, kPa	T, K	Saturation content, s	
		g/m³	g/m³ (STP)
7.03 x 10⁻⁵	283	0.00604	0.00626
1.71 x 10⁻⁴	293	0.01406	0.01508
3.919 x 10⁻⁴	303	0.03144	0.03489
8.514 x 10⁻⁴	313	0.06612	0.07588
1.761 x 10⁻³	323	0.1325	0.1568
3.486 x 10⁻³	333	0.2545	0.3104
6.625 x 10⁻³	343	0.4695	0.5893
0.012138	353	0.8359	1.081
0.02150	363	1.440	1.915
0.03690	373	2.404	3.284
0.06154	383	3.906	5.478
0.100	393	6.187	8.906
0.1585	403	9.558	14.110
0.2457	413	14.464	21.385
0.3727	423	21.417	33.175
2.2894	473	117.65	203.65
3.8743	523	458.97	879.25
32.808	573	1391.5	2921.0
101.3	630	3909.1	9021.1

In practical operation the mercury content in the hot reaction waste gases is always far below the saturation limit because the theoretical vapor-liquid equilibrium is not reached. Directly heated mechanical roasting furnaces

require a heat input of ca. 1.2 x 10⁶ kJ per tonne of ore. The following amounts of waste gas [in m³ (STP)] are produced per 1000 kJ for the different fuels with 20% excess of air:

Wood	0.387
Generator gas	0.42
Oil	0.32

Per tonne of ore, this corresponds to about 470 m (STP) with wood or generator gas firing and 375 m³ (STP) with oil firing. With 5 % water content in the ore, 70 m³ (STP) of steam is produced in addition. If an ore containing 0.3% Hg is worked up, the mercury content with wood or gas firing is 5.56 g/m³ (STP), and with oil firing 6.75 g/m³ (STP), at 140 °C.

With a condensation end temperature of 20 °C at which the gas still contains 0.0141 g of mercury per cubic meter corresponding to the saturation limit a loss of 0.21-0.25% mercury occurs, and at a condensation end temperature of 40 °C, a loss of 1.1-1.3 % mercury from the waste gas occurs.

In general, the mercury residual content in waste gas, compared to the amount at 20 °C, increases with a temperature increase of

10 °C by a factor of 2.2
20 °C by a factor of 4.7
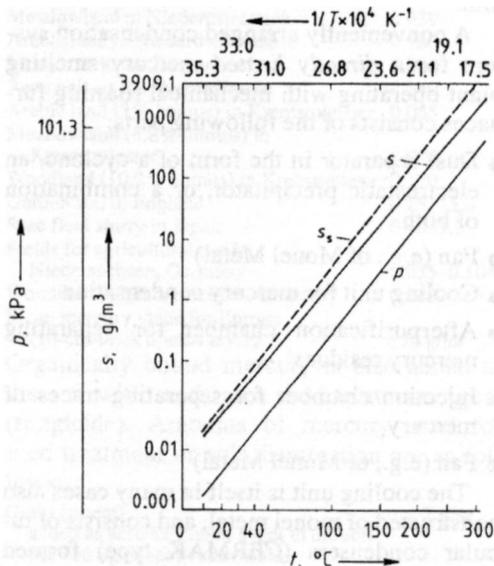
Figure 17.2: Vapor pressure p and saturation content s (g/m³) as a function of temperature; s_s saturation content under standard conditions [g/m³ (STP)].

30 °C by a factor of 9.4
40 °C by a factor of 18.1
50 °C by a factor of 33.4

Thus efficient cooling of the waste gas is necessary. In a plant that processes an ore with 5% moisture content, as much as 50% of the cooler capacity is used for condensation of evaporated moisture alone, without the steam originating from fuel combustion being taken into account.

Several practical requirements must be met for satisfactory operation: (1) The ore should be as dry as possible. (2) The amount of waste gas produced by the fuel should be low. (3) When the gas enters the condenser, its temperature should be only 10-20 °C above the mercury dew point. (4) The outlet temperature should be as low as possible. (5) Before entering the stack, the reaction gas should pass through an afterpurification section, if possible. Stupp formation can be kept low by (1) indirect heating, (2) separate processing of fine-grain classes of ore, (3) predrying of ore that is too wet, or (4) wetting of ore that is too dry. The flue dust should be separated as completely as possible from the still hot reaction gas before it enters the mercury condensation unit.

A conveniendy arranged condensation system for a *directly heated* mercury smelting plant operating with mechanical roasting furnaces consists of the following parts:

- Dust separator in the form of a cyclone, an electrostatic precipitator, or a combination of both
- Fan (e.g., of Monel Metal)
- Cooling unit for mercury condensation
- Afterpurification chamber for separating mercury residues
- Injection chamber for separating traces of mercury
- Fan (e.g., of Monel Metal)

The cooling unit is itself in many cases also constructed of monel metal, and consists of tubular condensers (CERMAK type) formed from six to ten trains arranged in parallel, each with eight inverted U-tubes of elliptical cross section whose arms terminate in acutely tapering, water-filled deflection boxes. The tubes are sprinkled with water. The mutually corresponding tubes of all the individual trains in each case end in a common box, and in this way the stupp can be classified. Gate valves in each train enable the draft to be regulated or even permit the train to be separately disengaged.

The ratio of tube cross section to fan output must be matched so that the gas flow velocity is maximally 0.75 m/s in narrow parts of the tubular condenser. The overall unit must be designed so that half of the tube trains can be decommissioned for cleaning and repair, whereas the remaining tube trains ensure satisfactory cooling of the reaction gas while maintaining draft conditions in the furnace.

Gases from *indirectly heated furnaces* that contain only a small amount of flue dust can be condensed by spraying water directly into the mercury-containing waste-gas stream. To ensure sufficient mercury condensation, the gas must pass through a succession of water curtains. Fewer parallel tubes of larger diameter are used in the cooling unit for directly heated furnaces. The last stage operates with fresh water; for the other cooling stages, water is circulated and recycled through suitably dimensioned settling tanks.

All setting tanks within the condensation unit have sloping floors and connecting pipes through which mercury metal flows to the lowest part of the system. The tanks stand on feet on a smooth cement floor, which slopes so that any leakage can be detected and escaping mercury collected. The material for these tanks is wood or cast iron; stupp-collecting tanks are also constructed of concrete. When the plant is operating continuously, all places prone to thick deposits must be mechanically cleaned once a week; the remaining areas can be cleaned at longer intervals.

17.4.4   Treatment of the Stupp

The amount of mercury contained in the stupp may represent a substantial proportion of production. In Idrija, when processing high-bituminous ore, for example, 78-91% of the

mercury is extracted from the stupp and only 9-22% is extracted directly. To extract mercury from the stupp, individual mercury droplets must be coagulated, which can generally be achieved by kneading and pressing the mass. Stirring the stupp with sievelike perforated rakes in iron vessels also gives good results. Addition of quicklime to the stupp neutralizes any acids contained in the condensate, saponifies any fats present, absorbs a large proportion of the water, and chemically reduces mercury sulfate.

Mercury and dust can also be mechanically separated by simple wash treatment with water. A tenfold mercury enrichment from the stupp by *flotation* was described in 1929 [30]. This very effective method of separating mercury enables the waste material to be dumped directly onto the waste tip in certain cases. Generally, however, extraction of mercury from the stupp is not so effective, with the result that the low-mercury fraction must be returned to the smelting process. For regularly occurring large amounts of stupp, a special furnace unit is worthwhile (retorts or multiple-hearth furnace).

17.5 Environmental Protection

17.5.1 Natural Distribution of Mercury

Because of its high vapor pressure, metallic mercury disperses relatively quickly into the atmosphere and, with suitable air movement, is taken up by plants and animals. The average concentration in the earth's crust is 0.08 ppm and in seawater 3×10^{-5} ppm. Mercury is thus one of earth's relatively rare elements. The natural mercury content of the atmosphere is 0.005-0.06 ng/m^3 [31]; in plants, 0.001-0.3 μg/g (generally < 0.01 μg/g); and in meat, 0.001-0.05 μg/g [32]. A comprehensive list of mercury in the environment appears in [33].

A quantitative summary of the occurrence, distribution, and utilization of mercury is given in the following material [34]:

Mercury content of the oceans	70 000 000 t
Mercury content of the earth's crust (1-m-thick layer)	100 000 000 t
Natural atmospheric mercury emission (volcanoes, wind erosion, degassing)	25-100 000 t/a
Natural mercury emission in water (weathering in rivers)	5000 t/a
Use of fossil fuels (minerals, deposits)	8-10 000 t/a
Use of mercury and its compounds	6000 t/a

Natural air emissions from mechanical activity, wind erosion, and degassing constitute the largest proportion of emitted mercury. By contrast, the utilization of mercury is relatively small, although this should not minimize or obscure the danger of mercury at high concentration.

17.5.1.1 Mercury in Soil, Plants, and Animals

Relatively large amounts of mercury are circulated due to the constant exchange of mercury among water, soil, and the atmosphere. Some of this migrating mercury is retained in the soil in the form of humus compounds and, in certain cases, is also concentrated [35]. The mercury content of various soils in Austria unless otherwise stated (mg per kilogram of soil) is as follows [36, 37]:

Meadowland in	Niederösterreich	0.039
Arable land in	Niederösterreich	0.180
Vineyards in the	Burgenland	0.080
Reed belt on the	Neusiedlersee	0.340
Arable land (3 % humus) in Kremsmünster		0.065
Meadowland (4.8% humus) in Kremsmünster		0.070
Woodland (10.2% humus) in Kremsmünster		0.170
Garden soil in England		0.25-15.0
Rice field slurry in Japan		0.40-1.8
Fields for agricultural use in Niedersachsen, Germany		0.055-0.104
Woodland in Niedersachsen, Germany		0.249-1.672
Mean mercury value for Europe (10-cm-thick humus layer)		120 g/ha

Organically bound mercury is also added to the soil with seeds as a seed treatment agent (fungicide). Amounts of mercury used for seed treatment or soil disinfection are as follows:

|	
Grain (wheat) added as seed treatment agent to the soil per 150 kg of seed material/ha	ca. 7 g/ha
Sugar beet (seed material in pill form) added as seed treatment agent to the soil per 200 000 pills/ha	ca. 1 g/ha
Cotton (seed treatment and disinfection)	ca. 20 g/ha
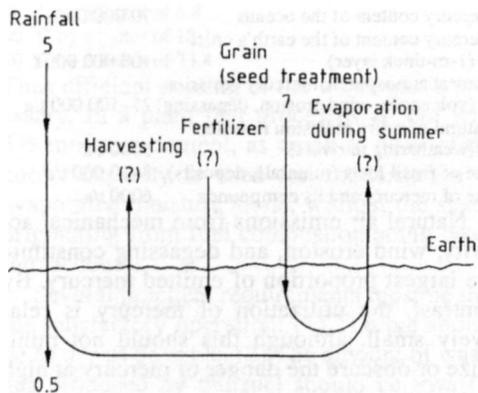
Figure 17.3: Microcirculation of mercury (in g h a - 1 a - l) in the soil [36].

Lawns (disinfection)　　　　　　ca.　　　　　　80 g/ha

However, neither soils that have received mercury-treated seeds for many years, nor plants grown on such soils, exhibit a high mercury content [35]. As pot tests have shown, the mercury is partly retained in the humus and partly evaporates from the soil [38, 39]. The amount of residue passing into groundwater is insignificant [40] (Figure 17.3).

According to investigations carried out in Norway, the mercury content of soil varies between 0.022 and 0.55 ppm (mean value 0.19), without any "recognizable" effect due to human activity [41]. The mercury content in soil is higher in geothermal or ore-containing regions and can be as high as several parts per million. Thus, mercury is often used as a tracer metal in geological exploration [42].

Mercury content has been investigated in soil and lichen in the mercury mining region around Monte Amiata (Italy). The mercury content in the soil and in the lichen decreases sharply with increasing distance from the mine. Mine waste gases and worked ore are the main sources of emission [43].

Mercury in Fungi and Mushrooms. The fleshy parts of fungi and mushrooms can contain unexpectedly high concentrations of mercury [44, 45]. Because of the affinity of mercury for the sulfur-containing constituents of fungi, the latter can absorb and concentrate mercury from the local soil. Mercury-rich fungi and mushrooms are found everywhere, regardless of whether the soil has been anthropogenically contaminated [46]. With more serious contamination, especially atmospheric, the mercury content of fungi and mushrooms increases considerably [47].

Mercury in Fish and Seals. The mercury content in *fish* varies depending on type and habitat [48]. The assumption that fish concentrate mercury to 2000 times its concentration in the ambient medium is neither valid nor statistically relevant and has no significance as a rule of thumb [48]. Mercury uptake in warm, tropical waters is higher than in cold northern waters [49]. Because of the concentration of mercury in sediment, dabbling fish, which collect their food from the bottom of the water, absorb more mercury than nondabbling fish. Predatory fish (e.g., pike) contain higher than normal levels of mercury only if they preferentially feed on dabbling fish.

The controversy surrounding canned tuna in the United States has revealed that tuna preparations in the Smithsonian Institute from ca. 1880 have the same mercury concentration as present-day fish. Under the assumption that the values found in museum preparations constitute a lower limit—some of the mercury might well have evaporated over the course of time—the fact that present-day values are the same as previous values means that no concentration has occurred.

Data from the Danube upstream of large cities and industrial regions, where trout have been found with a mercury content of > 1 mg of mercury per kilogram of fish, point to factors other than industrialization. The high mercury concentration in the liver of seals in the northern section of the east coast of North America (Labrador), where no large cities or industrial regions are to be found, is attributed to underwater volcanic emissions.

17.5.1.2　Mercury in Food

Many investigations were carried out on foods from the 1920s and 1930s onward [50]. In Germany, the Zentrale Erfassungs- und Bewertungsstelle für Umweltchemikalien (central office for collecting and evaluating data on

environmental chemicals; ZEBS) of the Federal Ministry of Health in Berlin in particular, has collected data from 1975, 1979, and 1982. According to these data, if average consumption patterns are assumed, mercury uptake in 1979 was about 0.052 mg per week for the "average" inhabitant of Germany (i.e., only about one-sixth of the upper limit recommended by WHO). The major proportion of mercury is absorbed from animal foods [51]. The legal limits are given in Table 17.7.

The most recent ZEBS investigations [52], covering 1978-1982, are presented in Tables 17.8 and 17.9. The 1982 values essentially confirm the analytical data of 1979. The values for milk, condensed milk, cheese, and eggs; veal, beef, pork, calves liver, calves kidneys, poultry, sausages, and meat products; vegetable oils and fats; rice, rye, and potatoes;

leafy, sprouting, fruit, or root vegetables and canned vegetables; pomaceous, stone, berry, citrus, shell, or canned fruit; fruit and vegetable juices; and beverages such as wine, beer, and chocolate are all < 0.020 mg of mercury per kilogram of fresh substance and, in most cases, < 0.010 mg/kg.

The average amounts of mercury actually absorbed per week are compared in Table 17.9 with the limiting values specified by WHO. Foods contain the major proportion as follows: drinking water (14.8%), wheat (12.9%), milk (10.2%), mineral water (8.1%), canned fish (8.0%), coffee (7.2%), potatoes (6.0%), and fish (5.6%). Another detailed investigation carried out by ZEBS is concerned with the mercury, magnesium, and zinc content of breast milk, blood serum, and the fatty tissue of nursing mothers [53].

Table 17.7: Legal limiting values for total uptake of mercury (1980).

	Fish, mg/kg	Total uptake, mg/week
Switzerland	0.5	
Japan	0.4 (Hg) 0.3 (Hg methyl)	0.17 mg of Hg per 50 kg of body weight
United States	1.0	0.005 mg/kg ofbody weight (Hg) 0.0033 mg/kg ofbody weight (Hg methyl)
Sweden	no limit (lakes that contain fish with more than 1 ppm Hg are placed on ablacklist); fish with a high Hg content may be legally rejected.	
Germany	1.0	
WHO recommendation		0.3 (max.)

Table 17.8: Mercury in food.

Food	Content, kg/kg of fresh substance	
	1982	1979
Cow's liver	0.021	0.015
Pig's liver	0.047	0.058
Cow's kidneys	0.077	0.066
Pig's kidneys	0.246	0.260
Freshwater fish	0.271	0.257
Saltwater fish, except Hg-susceptible fish	0.196	0.127
Hg-susceptible fish[*]	1.070	0.859
Fish products	0.208	
Canned fish	0.206	0.188
Wheat	0.026	0.003
Coffee	0.041	

[*] **Hg-susceptible fish include: mackerel shark, dogfish, blue ling, halibut, black halibut, turbot, and Greenland shark.**

Table 17.9: Uptake amounts of mercury in absolute figures and as a proportion of WHO values.

	Hg
WHO value mg/week (70 kg) mg/week (58 kg)	 0.35 (0.290)
Men (70kg) mg/week[*] Proportion ofWHO figure, %	 0.1229 35.11
Women (58 kg) mg/week[*] Proportion of WGO figure, %	 0.0933 32.17

[*] **The median values of toxic substance levels were taken into account.**

17.5.2 Mercury Emissions

17.5.2.1 Gas Purification

In a large number of combustion processes, mercury is transferred to the gaseous phase and must be removed again by subsequent treatment. The largest amounts of secondary mercury occur in the smelting of sulfidic ores. Mercury which is present as mercury sulfide is released during roasting. At present, two methods are primarily used for waste-gas purification.

In the first method, the gas is treated with sulfuric acid (90%) at 200 °C. The mercury(I) sulfate formed is deposited in wash towers. Fine purification is performed by afterpurification with sodium sulfide [54].

In the second method, the cooled and dusted roast gas is treated with a mercury(II) chloride solution, and mercury precipitates as mercury(I) chloride (Hg_2Cl_2). Mercury is removed from the wash liquid by treatment with sodium sulfide. Part of the mercury(I) chloride produced is oxidized to mercury(II) chloride with gaseous chlorine and returned to the process. The final level of mercury in the waste gas is 0.05-0.1 mg/m³ [55, 56].

In a third method, waste gas containing mercury and sulfur dioxide is treated with a wash solution containing Cu^{2+} and Hg^{2+} ions in addition to H_2SO_4 (200-300 g/L) and HCl (5 g/L). Mercury in the vapor is thereby oxidized to Hg^+, and the Hg^0 values of the waste gas are 0.02-0.05 mg/m³ [57].
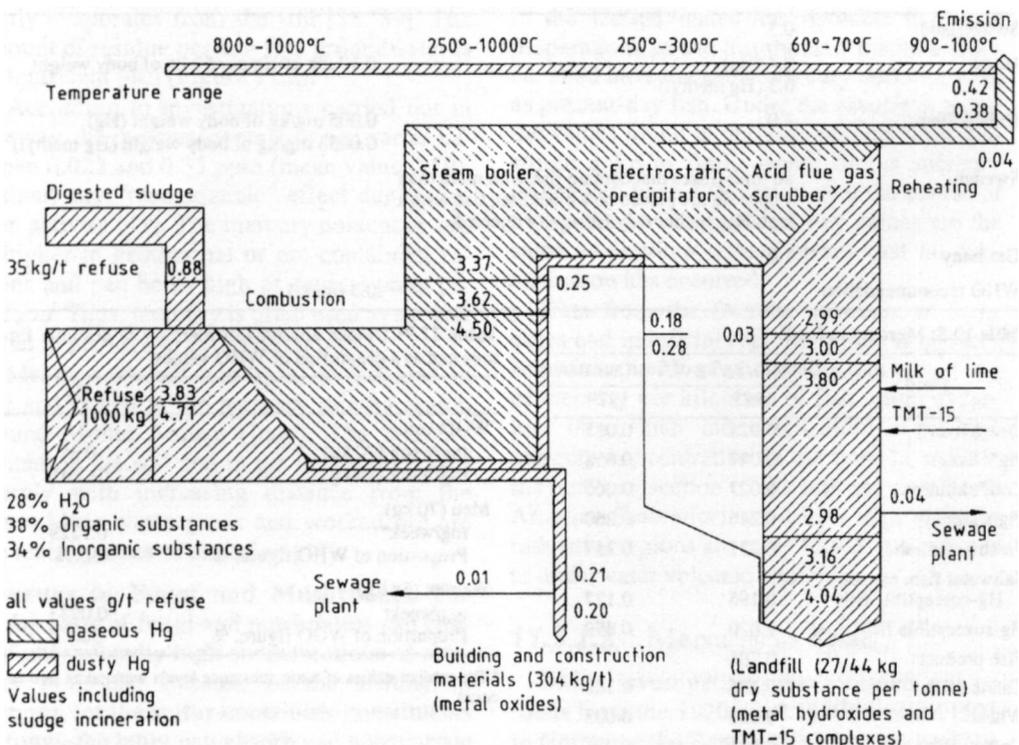

Figure 17.4: Specific mercury load distribution in the Bamberg refuse heating and power station with TMT-15 precipitation, with and without sludge combustion [63].

Another source of mercury emission is refuse combustion. Mercury occurs in the form of thermometer breakage, fluorescent tubes, switches, and batteries in domestic refuse. Investigations have shown that mercury in flue gases is present as mercury(II) chloride [58]. Below ca. 150 °C, the flue ash contained in flue gases adsorbs mercury(II) chloride and reduces it to mercury(I) chloride. Active carbon or active carbon impregnated with iodine compounds can also be used as a mercury adsorbent [59-62]. The mercury content of domestic refuse is 3-5 g/t [63]. The percentage distribution of mercury in a typical refuse combustion plant is shown schematically in Figure 17.4. Most of the mercury passes into the residue to be dumped.

17.5.2.2 Water Purification

The solubility of mercury in water depends strongly on the temperature. It decreases with decreasing temperature and can be reduced further by addition of salts (e.g., sodium chloride).

A whole range of equipment and devices can be used in purification methods to remove mercury from water. Examples are activated carbon filters, ion exchangers, and electrolysis systems. Mercury can also be removed from solution by addition of suitable reagents.

The level of 10-30 mg of mercury per liter in wastewater from chlor-alkali electrolysis can be reduced to 0.1 mg/L by using *activated carbon* and graphite powder. The carbon has a grain size of 5-100 μm [64, 65]. In principle, all types of activated carbon can be used for the fine purification of mercury-containing water. Carbon is dispersed in the water and then filtered.

For *ion exchangers,* a distinction can be made between reusable and disposable ones [65-67]. In some cases, sulfur-containing substances are used as active groups, which remove mercury from the solution in the form of a mercury sulfide compound.

Copper fluidized-bed electrolysis provides another method for mercury separation. The copper powder cathode is held in suspension by the flowing solution, and mercury is deposited as an amalgam. The copper amalgam is purified by distillation [68].

By adding *small amounts of oil* which are dispersed in the aqueous solution, mercury can be concentrated in the oil phase. The mercury content of the purified aqueous solution is in some cases < 10 μg/L. The oil is separated by centrifugation, and line purification is carried out by using a conventional oil-water emulsion splitting unit. The initial mercury concentration should be between 0.5 and 2.0 mg/L [4]. Tin(II) chloride dissolved in dilute hydrochloric acid has been proposed for treating mercury ion-containing wash water from combustion units. The reducing agent tin(II) chloride is added in above-stoichiometric quantities. Reduced mercury is added together with the wash water to an evaporation device and is expelled by passage of stripping gas at elevated temperature. Condensation is effected by cooling the gas stream. The mercury content is thus reduced from 5 mg/L to < 0.1 mg/L, depending on the concentration of tin(II) chloride [69].

To purify flue gas wash water from *refuse combined heating and power stations,* the additive TMT-15 developed by Degussa is used in some cases on an industrial scale (Figure 17.4). The active substance of the additive consists of trimercapto-*S*-triazine in the form of a sodium salt. Mercury is bound as $C_6N_6S_6Hg_3$, The compound is stable up to 210 °C and is only sparingly soluble in the elution test (a test to determine the soluble components of a solid material). The mercury content is reduced from ca. 4 mg/L to < 0.05 mg/L [70, 71]. The additional costs involved in TMT-15 precipitation amount to ca. 0.25 DM per tonne of refuse.

Mercury can be removed from *concentrated sodium hydroxide solution* by the use of ultrasound when the solution is filtered. The initial mercury content of ca. 20 mg/kg of aqueous sodium hydroxide is reduced to ca. 0.4 mg/kg after filtration [72].

The fine purification of crude phosphoric acid can be performed at pH 0.5-1.5 by using a diorganodithiophosphorus compound in

conjunction with activated carbon as adsorbent. The final mercury concentration is < 0.02 µg/g of solution [73]. Atpresent, no standard methods exist for removing mercury from sulfuric acid [74].

17.6   Quality Specifications

Fine Purification of Metallic Mercury [75]. Most of the mercury on the market is 4N material (99.99% mercury). Higher purity is seldom required. Impurities in the form of gold ppm) are manifested as dark particles after dissolution in nitric acid.Only a few purification methods exist.

- *Dry Oxidation*. In this method, readily oxidizable constituents such as magnesium, zinc, copper, aluminum, calcium, silicon, and sodium can be removed by passing air or oxygen through the liquid metal. The oxides formed have a lower density than mercury and float on its surface. They can be removed by filtration, scooping, or withdrawing the mercury through an opening in the bottom.

- *Wet Oxidation*. In an aqueous medium, mercury is dissolved by adding nitric, hydrochloric, or sulfuric acid with dichromate, permanganate, or peroxide, to oxidize impurities. Good dispersion of the mercury is extremely important in this method. The aqueous solution can be separated from the mercury by decanting, and traces of water can be removed with calcium oxide. A plant for the wet purification of mercury has been described [76].

- *Electrolytic Refining*. Perchloric acid containing mercury oxide serves as the electrolyte.

- *Distillation*. Mercury can be evaporated under atmospheric pressure or in vacuo. Distillation can be carried out in normal steel vessels or in a glass apparatus. Elements with a lower vapor pressure than mercury can be separated in this way. In many cases, mercury must be distilled repeatedly to achieve the desired purity, particularly if it is

to be used to produce cadmium-mercury telluride.

Additional methods, adapted to the relevant processes, are available for purifying and working up larger amounts of mercury [77, 78].

17.7   Chemical Analysis

The oldest and simplest method for determining mercury in minerals is described by ESCHKA; it involves a gravimetric method in which mercury is precipitated as an amalgam [79]. The ore sample is weighed in a porcelain crucible, intimately mixed with iron filings, and then covered with a layer of zinc oxide, magnesium oxide, or calcium oxide. The crucible is closed with a tightly fitting cover of gold foil having a cup-shaped depression in the middle, which is sprayed from above with cooling water. On careful heating of the sample, mercury is distilled and deposits on the underside of the cover. When a constant weight is reached at the gold foil, all the mercury has been collected. Measurements can be affected by cadmium and arsenic, which also condense on the gold foil. This method of mercury determination requires a high level of experimental skill and care on the part of the analyst, whose technique greatly affects the accuracy and reproducibility of the results. The reliably detectable minimum mercury content is between 10 and 50 ppm. Theoretically, the accuracy could be improved by increasing the amount of sample, although this would give rise to difficulties with regard to the apparatus.

A method for precipitating *monovalent* mercury as an iodate from a neutral or weakly acidic solution (nitric acid) is described in [80]. Mercury can be determined gravimetrically after the mercury(I) iodate precipitate is washed with ethanol and diethyl ether. Parallel gravimetric determination of the excess of potassium iodate precipitation agent is possible with thiosulfate after the mother liquor has been acidified with sulfuric acid and potas-

sium iodide has been added. Both methods give good results.

A quick method for determining mercury(II) is based on the fact that a complex is formed when an excess of potassium iodide is added to a neutral or weakly ammoniacal mercury solution. This complexes with copper diethylenediamine sulfate to form violet crystals of the complex double salt copper diethylenediamine mercury iodide, which is practically insoluble in ethyl alcohol or diethyl ether [81].

In a rapid classical qualitative method for detecting mercury, ca. 1 g of the substance to be tested is digested with acid; the resultant solution is oxidized with a drop of bromine (the solution must not turn yellow) and then boiled with a few milliliters of the reagent (10 g of KI and 100 g of NaOH in 100 mL of H_2O) and filtered. In the filtrate, mercury is determined by the black precipitate formed on dropwise addition of a Sn^{2+} solution [82].

Modern operational monitoring employs physical analytical methods and test tube methods suitable for quick detection. Both *X-ray fluorescence spectroscopy* and *atomic absorption spectroscopy* (AAS) have proved suitable for quantitative and qualitative mercury determination. The detection limit for these methods is so low that the maximum workplace concentration values can be monitored precisely [83].

Portable atomic absorption spectrometers, for example, are available, which indicate the atmospheric mercury concentration as an analog or digital display after a short warm-up time of the spectrometer. The result of the analysis is available immediately and simplifies the monitoring of a production plant. The measurement value can also be recorded continuously at stationary measurement sites with a recorder. The influence of interfering factors in AAS determination is discussed in [84].

Differential pulse anodic stripping voltammetry in conjunction with a gold electrode can be used to detect copper and mercury in natural water and wine [85, 86]. A mercury concentration of 0.02 µg/L can be measured.

Mercury in the air can be detected down to 0.1 ng/m³ with the *Coleman mercury analyzer* system (based on a very selective cold vapor atomic absorption), to an accuracy of 10%. One analysis takes about 3 min [83].

17.8 Storage and Transportation

A classification for the transportation of mercury, mercury oxide, mercury(I) chloride, and mercury(II) chloride is given in [87] (specification sheets 831, 863, 865, 868). DORIAS presents a detailed description of the properties, handling, storage, and transportation of dangerous substances [88], as well as a list of addresses of the relevant authorities (throughout Europe) for information purposes. The provisions differ from country to country and must be ascertained from the relevant authorities.

In general, containers of stainless steel, normal-quality steel, iron, glass, ceramics, and a range of plastics are suitable for storing mercury. When storing liquids that contain extremely low levels of mercury (µg/g–ng/g range) in plastic containers, mercury losses occur with a large number of plastics. When water containing 5 ng/g of mercury was stored in polyethylene bottles, only 5 % of the mercury was present after 21 d. Approximately 77 % of the mercury had been adsorbed on the side walls, and 18 % had evaporated. The Hg^{2+} ions are assumed to be reduced to Hg^+ ions, which in turn disproportionate to Hg^0 and Hg^{2+} [89]. Addition of Au^{3+} ions in trace amounts is sometimes recommended [90]. Further investigations on the storage of mercury in dilute solution are discussed in [91-95].

17.9 Uses

Because of its special properties, mercury has had a number of uses for a long time. The conventional application is the thermometer. Mercury is frequently used in pressure gauges and for thermal content measurements.

Table 17.10: Uses of mercury and its compounds [96].

Area of use	Form	Approximate amount, t/a	Emissions	Other sectors, waste elimination	Remarks
Chemicals, reagents	compound	40	laboratories		largely impossible to find suitable replacement; environmental damage can be reduced by other measures
Alkali-manganese batteries	chloride/metal	37		refuse combustion	reduced emission by separate collection possible
Mercury oxide batteries	oxide	20		refuse combustion	alternatives still too expensive; separate collection declining
Pesticides		27	distribution		now only for seed treatment; substitutes are available
Medicinal sector Dental amalgams Disinfection	metal compound	26		refuse combustion	separate collection possible
Fungicides for paints	compound	10	weathering	exploitation; removal of old paint coats	declining; in some cases restrictions on use
Catalysts	compound	8		chemical industry	declining
Thermometers, barometers, manometers	metal	8	instrument and apparatus breakage	refuse combustion	replacement by other methods and processes possible (e.g., electronics)
Electrical engineering components	metal	6		refuse combustion	declining; substitution possible largely through electronic components
interval switches				exploitation of scrap	
Fluorescent tubes	metal	3	lamp breakage	refuse combustion	demand for fluorescent tubes increasing, despite reduction in mercury use per tube; total use increasing
Pigments	sulfide	1		refuse combustion	declining

In mechanical engineering, mercury is used in mercury vapor diffusion pumps for producing a high vacuum.

One important area of use is the lighting industry, where mercury is added to various types of bulbs. Among electrical components, mercury switches, rectifiers, oscillators, and primary batteries can be mentioned, which contain up to 30% mercury.

Mercury is used as a liquid cathode in the production of chlorine and sodium hydroxide by chlor-alkali electrolysis. Because mercury forms alloys with a large number of metals, mercury alloys have a wide range of applications. Table 17.10 summarizes the areas of use of mercury and its compounds.

17.10   Mercury Alloys

The alloys of mercury (amalgams) occupy a special position among metal alloys because they can be solid, plastic, or liquid at room temperature.

Liquid amalgams are true solutions of the alloying elements in mercury, whereas plastic amalgams are suspensions of solid particles of the alloying partners in mercury or a saturated mercury solution. *Solid* amalgams are intermediary phases, often mixed with alloying partners or their primary mixed crystals. Solid amalgams may contain liquid-phase inclusions. An amalgam is sometimes difficult to identify experimentally. JANGG has suggested a suitable apparatus for synthesizing and analyzing amalgams [97].

The solubility of many metals in mercury depends strongly on temperature (Figure 17.5). The solubility of some metals in mercury at room temperature is given in Table 17.11. Amalgam formation may be exothermic (e.g., sodium) or endothermic (e.g., gold).
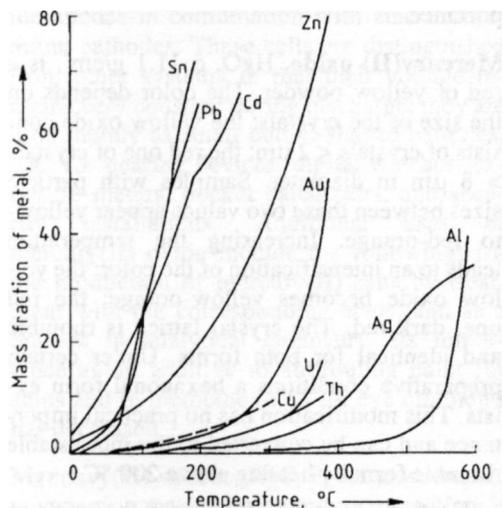

Figure 17.5: Solubility of some metals in mercury as a function of temperature [99].

Table 17.11: Solubility of some metals in mercury at 20 °C [97].

Metal	Solubility, %	Metal	Solubility, %
Tl	42.5	Mg	ca. 0.3
Cd	5.0	Au	0.131
Zn	1.99	Ag	0.035
Pb	147	Cu	ca. 0.002
Sn	ca. 0.9	Al	0.002
Na	0.62	Fe	ca. 10^5
K	ca. 0.4	Si	virtually insoluble

Ammonium amalgam, which has been known for a long time, is an interesting case of the NH_4 group acting as a metal-like alloying constituent. The synthesis of tetramethylammonium amalgam is described in [98].

Technically important amalgams are those of tin-copper precious metals used in conservative dental treatment.

Gold, silver, or tin amalgams are still used for much gold- and silver-plating work, as well as for production of certain types of mirrors. The measurement range of mercury thermometers can be extended to -58 °C by addition of thallium to mercury.

Alkali amalgam is an important intermediate in chlor alkali electrolysis by the amalgam method. Amalgams also play a role in the extraction of cadmium or aluminum [99].

A comprehensive list of thermodynamic data on amalgam formation has been collected by GUMINSKI [100]. After surveying the literature, he is of the opinion that liquid mercury greatly influences intermetallic compound formation. The reactions are comparable to the solid-state formation of ionic and nonionic substances in liquids.

Production of Amalgams. Three methods are used for the industrial production of amalgams:

- *Powder Metallurgy Method.* The powdered alloying components are mixed with mercury. The reaction rate of spontaneously occurring amalgam formation is determined by the degree of dispersion of the powder, the rate at which reactants diffuse into one another, and the wettability of the powder by liquid mercury. If other components besides mercury are added simultaneously, they are preferably pulverized as master alloy in the desired weight ratio. In many cases, the powder reacts with mercury more quickly in the presence of a salt of the element to be amalgamated.

- *Galvanic Method.* Many metals can be deposited from their aqueous solutions or from salt melts on mercury cathodes, with simultaneous formation of an amalgam. Because of the high overvoltage of hydrogen on mercury or amalgam cathodes, even nonprecious metals (Zn, Fe, Mn) can be deposited from acid solutions. Nonaqueous solutions may also be used (with Mg, Ti).

- *Reaction with Sodium Amalgam.* Metal exchange can occur in a fast and stoichiometric reaction through the phase boundary by reaction of sodium amalgam with the salt solution of a precious metal (or, generally, by reacting a nonprecious amalgam with a noble-metal salt solution).

17.11   Compounds

Mercury occupies a special position in group 12 of the periodic table. In contrast to the two other members of this group (zinc and cadmium), it forms compounds in two valence states.

Compounds of *monovalent* mercury contain ions in the unusual form Hg_2^{2+}. These compounds are not very stable and disproportionate easily to form elemental mercury and the corresponding divalent mercury derivative. Most of the monovalent compounds are sparingly soluble in water. The more soluble salts, e.g., the nitrate, are partially hydrolyzed in aqueous solution: after acidification of these solutions, the poorly soluble compounds can be obtained by precipitation. In addition, compounds of monovalent mercury can be prepared from those of the divalent element by reduction with metallic mercury.

The compounds of *divalent* mercury can be divided into those that are strongly dissociated and those that are weakly dissociated. The former, such as the sulfate and the nitrate, undergo considerable hydrolytic cleavage in water. The weakly dissociated compounds, e.g., the chloride and the cyanide, are less prone to hydrolysis by water. With excess anions they form complexes that are more soluble than the salts themselves.

The starting material for all of these compounds is elemental mercury: the metal is treated initially with a suitable oxidizing agent, e.g., chlorine or nitric acid. The other compounds are obtained from the resulting oxidation product by further reaction. Multistep processes are often necessary.

17.11.1   Mercury Chalconides

Chalconides of monovalent mercury are unknown: precipitation from a solution of mercury(I) nitrate with sodium hydroxide does not lead to the expected mercury(I) oxide, but rather to a mixture of finely divided elemental mercury and mercury(II) oxide. The chalconides of divalent mercury exist in nature as minerals: the oxide HgO as montroydite, the sulfide HgS as cinnabar and metacinnabar, the selenide HgSe as tiemannite, and the telluride HgTe as coloradoite. They can also be produced synthetically. Only the oxide and the sulfide are of practical importance.

Mercury(II) oxide, HgO, ρ 11.1 g/cm³, is a red or yellow powder. The color depends on the size of the crystals: the yellow oxide consists of crystals < 2 µm; the red one of crystals > 8 µm in diameter. Samples with particle sizes between these two values appear yellow- to red-orange. Increasing the temperature leads to an intensification of the color: the yellow oxide becomes yellow-orange; the red one, dark red. The crystal lattice is rhombic and identical for both forms. Under certain preparative conditions a hexagonal form exists. This modification has no practical importance and can be converted to the more stable rhombic form by heating above 200 °C.

Heating above 450 °C causes the oxide to decompose into elemental mercury and oxygen. Mercury(II) oxide is sparingly soluble in water and in ethanol. With dilute mineral acids, solutions of the corresponding salts are formed, a method that can be used to prepare these salts.

Production. Mercury(II) oxide can be prepared via the *anhydrous route* by reaction of the elements at 350-420 °C under oxygen pressure or by thermal decomposition of mercury nitrates at ca. 320 °C. Production via the *wet route* by precipitation is more important: the oxide is precipitated from solutions of mercury(II) salts by addition of caustic alkali [usually mercury(II) chloride solutions with sodium hydroxide]. Whether the yellow or the red form is obtained depends on reaction conditions: slow crystal growth during heating of mercury with oxygen or during thermal decomposition of mercury(I) nitrate leads to relatively large crystals (i.e., the red form). Rapid precipitation from solution gives finer particles (i.e., the yellow form). Nevertheless, depending on the conditions during precipitation such as stirring speed, pH, temperature, and

method of mixing the components, large crystals can be obtained by the wet route and, therefore, the red form is produced [101].

Uses. Red mercury(II) oxide in particular has become increasingly important for the production of galvanic cells with mercury oxide anodes in combination with zinc or cadmium cathodes. These cells are distinguished from other systems in that their voltage remains very constant during discharge; they are used mainly as small button-shaped batteries, e.g., for hearing devices, digital watches, exposure meters, pocket calculators, and security installations. Additional uses of mercury(II) oxide include the following: for the production of mercury(II) salts by treatment with the corresponding acids, and as a reagent in analytical chemistry. Its importance as an additive to antifouling paint for ships and in medicine (e.g., for eye ointment) has decreased.

Mercury(II) sulfide, HgS, is the most important starting material for mercury extraction; it can exist in two forms: α-HgS *(cinnabar,* cinnabarite) has a density of 8.1 g/cm^3, and (β-HgS (metacinnabar) has a density of 7.7 g/cm^3. The β-form slowly changes to α-HgS on heating. The latter sublimes at 583 °C. Of the two sulfide minerals, cinnabar is the most important ore for the production of mercury (see Section 17.4.1.2). When pure, the compound is bright red and forms hexagonal crystals. *Metacinnabar* is black and forms cubic crystals (zinc blende lattice). Both have extremely low water solubility; they are also insoluble in mineral acids and in caustic alkali. They dissolve only in aqua regia, to release sulfur, and in alkali sulfide solutions, to form thio complex-salt ions, such as $[HgS_2]^{2-}$.

Production by either the dry or the wet route is possible. In the former, a mixture of mercury and sulfur is heated. The elements react slowly together even on mixing. Production from aqueous solutions is more important. The sulfide is precipitated from solutions of mercury(II) salts by treatment with hydrogen sulfide, alkali, or ammonium sulfide solutions. Initially, the black sulfide is formed.

It can be converted to the more stable red form by heating in the presence of the mother liquor or with ammonium polysulfide solutions. The reaction of mercury and sulfur by heating with a solution of sodium polysulfide has been described [102].

17.11.2 Mercury Halides

Halides of both mono- and divalent mercury are known. Of these, only the fluorides are ionic compounds: they undergo hydrolysis with water; mercury(I) fluoride simultaneously undergoes disproportionation. The other halides either are already composed of molecules in the crystal lattice or form these by dissolution or evaporation. Accordingly, their melting and boiling points are low. The halides of monovalent mercury are sparingly soluble in water: the solubility of divalent mercury halides decreases with increasing molecular mass. Mercury halides form numerous basic compounds.

Mercury(II) fluoride, HgF$_2$, *mp* 645 °C, ρ 9.0 g/cm^3, forms colorless octahedral crystals with a cubic ionic lattice (fluorite type). It is unstable in humid air; hydrolysis yields a yellow color. Mercury(II) fluoride is insoluble in organic solvents.

The compound is *produced* from mercury and fluorine at elevated temperature or from mercury(II) oxide and hydrogen fluoride under oxygen pressure at 450 °C [103]. Synthesis from mercury(II) oxide and sulfur tetrafluoride has been suggested [104]. The compound is used in organic synthesis as a fluorinating agent.

Mercury(I) chloride, calomel, Hg$_2$Cl$_2$, ρ 7.15 g/cm^3, is rarely found as a mineral in nature. When pure, it exists as a heavy white powder or as colorless crystals with a silvery luster, having a tetragonal molecular lattice. It sublimes at 385 °C; above 400 °C the molecules decompose into a vapor composed of mercury and mercury(II) chloride. The substance is sparingly soluble in water, ethanol, diethyl ether, and acetone. A black color occurs in ammonia solution, whereby a mixture of

finely divided elemental mercury and mercury(II) ammonium chloride is formed by disproportionation—hence, the name *calomel,* from the Greek word meaning beautiful black.

Production. An intimate mixture of mercury and mercury(II) chloride is heated at 525 °C in closed iron or fused silica tubes, attached to cooled receivers in which calomel vapor condenses [105, 106]. Synthesis from the elements is also possible [101]. Very finely divided mercury(I) chloride can be obtained by precipitation from a dilute nitric acid solution of mercury(I) nitrate and sodium chloride [105].

Mercury(I) chloride finds *application* in calomel electrodes, which serve as standard electrodes for the measurement of electrochemical potential; it is also employed as a fungicide and insecticide in agriculture, and as a catalyst in organic synthesis. Mercury(I) chloride is mixed with gold for painting on porcelain.

Mercury(II) chloride, corrosive sublimate, $HgCl_2$, *mp* 280 °C, *bp* 303 °C, ρ 5.43 g/cm^3, is a white, heavy, crystalline powder with a rhombic crystal lattice. At the melting point the vapor pressure is 560 kPa; the substance can, therefore, sublime under reduced pressure. The sublimate is moderately soluble in cold water. Its solubility increases sharply with increasing temperature: the saturation limit is 6.2% at 20 °C and 36.0% at 100 °C; the compound may therefore be purified by recrystallization from water. The sublimate is readily soluble in organic solvents, in contrast to mercury(I) chloride, so that a clear solution, for example, in ether, is an indication of the absence of calomel. Molecules of mercury(II) chloride exist as such in all solvents; mixing Hg^{2+} ions with Cl^- in aqueous solution leads immediately to undissociated mercury(II) chloride molecules; this process is used analytically to bind chloride ions in determining the COD of effluents. Aqueous solutions of sublimate are weakly acidic, resulting from hydrolysis of a small amount of the chloride. The sublimate is much more soluble in alkali chloride solution than in pure water, because of the formation of chloro complex ions, e.g., $[HgCl_4]^{2-}$.

Production. For the formation of mercury(II) chloride from the elements, mercury is oxidized with chlorine in heated retorts; the reaction is carried out with the appearance of flame at > 300 °C. The escaping sublimate vapor is condensed in cooled receivers, where it settles as fine crystals. Formation of mercury(I) chloride is avoided by the use of excess chlorine [101]. Mercury and chlorine also react in the presence of water; in this case, intensive stirring is necessary. The chloride formed precipitates as crystals after the solubility limit has been exceeded. If an alkali chloride solution is used in place of water, solutions of chloro complex salts are formed, which are used mainly for the production of other compounds of divalent mercury [107].

Mercury(II) chloride can also be prepared from other mercury compounds. Mercury(II) sulfate, for example, is heated in the dry state with sodium chloride, and the evolving mercury(II) chloride vapor is condensed to a solid in receivers. A warm sublimate solution is obtained from the reaction of mercury(II) oxide and a stoichiometric amount of hydrochloric acid; the chloride separates as crystals on cooling.

Uses. Mercury(II) chloride is an important intermediate in the production of other mercury compounds, e.g., mercury (I) chloride, mercury(II) oxide, mercury(II) iodide, mercury(II) ammonium chloride, and organic mercury compounds. The compound is used as a catalyst in the synthesis of vinyl chloride, as a depolarizer in dry batteries, and as a reagent in analytical chemistry. It has minor importance as a wood preservative and retains some importance as a fungicide. Other uses (e.g., as a pesticide or in seed treatment) have declined considerably.

Mercury(II) bromide, $HgBr_2$, *mp* 236 °C, *bp* 320 °C, ρ 6.05 g/cm^3, forms colorless crystals with a rhombic layered lattice. Its water solubility is highly temperature dependent: the concentration limit is 0.6% at 25 °C and 18% at 100 °C. Mercury(II) bromide is readily sol-

uble in diethyl ether and ethanol. The compound is *produced* from mercury and bromine in the presence of water; by dissolution of mercury(II) oxide in hydrobromic acid; or by precipitation from a nitric acid solution of mercury(II) nitrate with addition of sodium bromide [108]. It is used as a reagent for arsenic and antimony, as an intermediate in the production of bromine-containing organomercury compounds (see Section 17.12), and as a catalyst in organic synthesis. The melt is used as a nonaqueous solvent.

Mercury(II) iodide, HgI_2, exists in a red and a yellow form. Red mercury(II) iodide is soluble in diethyl ether, chloroform, and methanol. The compound is produced by adding an aqueous solution of potassium iodide to an aqueous solution of mercury(II) chloride with stirring; the precipitate is then filtered off, washed, and dried at 70 °C. A yellow product is formed by sublimation; on cooling, it turns red.

Yellow mercury(II) iodide, *mp* 259 °C, *bp* 354 °C, is unstable at room temperature and is converted to the red form at the slightest touch or upon heating. The transition temperature is 127 °C. Yellow mercury(II) iodide is prepared by pouring an alcoholic solution of the red form into cold water, whereby a pale yellow emulsion is formed, from which the mercury(II) iodide crystallizes after a few hours.

Potassium mercury iodide, K_2HgI_4, readily soluble in water, is prepared by dissolving mercury(II) iodide in a concentrated potassium iodide solution.

17.11.3 Mercury Pseudohalides

The *cyanides* and *thiocyanates* of divalent mercury resemble the halides, in that they also exist in solution as undissociated molecules and form highly soluble complexes with an excess of the anion; moreover, numerous basic compounds are derived from them. Mercury(I) cyanide is unknown; the poorly soluble mercury(I) thiocyanate, which can be obtained by precipitation from mercury(I) nitrate solution, has no practical importance.

Mercury(II) thiocyanate, $Hg(SCN)_2$, ρ 3.71 g/cm³, is a white powder which is thermally unstable. Decomposition begins at 110 °C and becomes spontaneous at 165 °C, with the compound swelling to many times its normal volume. In air a blue flame appears, and a dark-colored, voluminous residue is left. The thiocyanate is sparingly soluble in cold water. It is produced by precipitation from mercury(II) nitrate solution with a stoichiometric amount of potassium thiocyanate solution and is used as an analytical reagent and as an intensifier in photography.

17.11.4 Acetates, Nitrates, Sulfates

The acetates, nitrates, and sulfates of mercury are composed of ions and undergo hydrolysis with water. The acetate and the sulfate of monovalent mercury are sparingly soluble and the nitrate is quite soluble in dilute acid. Compounds of divalent mercury are readily soluble in dilute acid.

Mercury(II) acetate, $(CH_3COO)_2Hg$, ρ 3.27 g/cm³, *mp* 178 °C, exists as a fine white powder or colorless shiny crystal flakes. It is soluble in diethyl ether and ethanol. It is produced by dissolution of mercury(II) oxide in dilute acetic acid and concentration of the resulting solution. Mercury(II) acetate is used for the synthesis of organomercury compounds, as a catalyst in organic polymerization reactions, and as a reagent in analytical chemistry.

Mercury(I) nitrate, $Hg_2(N0_3)_2 \cdot 2H_2O$, ρ 4.68 g/cm³, *mp* 70 °C, which forms colorless crystals (monoclinic ionic lattice), is produced by dissolving mercury in cold dilute nitric acid and crystallizing the compound from the resulting solution.

Uses. Mercury(I) nitrate is the most readily available soluble salt of monovalent mercury and is, therefore, an important intermediate for other mercury(I) derivatives; sparingly soluble compounds can easily be prepared from it by precipitation from aqueous solution. Thermal decomposition leads to red mercury(II) oxide. "Millons reagent", a solution of mercury nitrate and nitrous acid in dilute nitric

acid, is used as an analytical reagent for the indication of tyrosine-containing proteins.

Mercury(II)   nitrate, $Hg(NO_3)_2$ or $Hg(NO_3)_2 \cdot H_2O$,   forms colorless, hygroscopic crystals. Apart from the anhydrous salt and the monohydrate, several other hydrates and basic compounds are known. Mercury(II) nitrate is produced by dissolving mercury in hot concentrated nitric acid; the resulting solution is concentrated and the nitrate crystallized by cooling. Uses include the production of other divalent mercury derivatives, as a nitrating agent in organic synthesis, and as an analytical reagent.

Mercury(I) sulfate, Hg_2SO_4, ρ 7.56 g/cm^3, is a colorless microcrystalline powder (monoclinic crystal system) that is very sensitive to light. The compound is prepared by precipitation from a solution of mercury(I) nitrate with sulfuric acid or sodium sulfate solution, or by electrochemical oxidation of mercury in dilute sulfuric acid. It is used as a depolarizer in standard cells after Clark and Weston.

Mercury(II) sulfate. $HgSO_4$, ρ 6.49 g/cm^3, is a white powder (rhombic crystal type). It is prepared by fuming mercury with concentrated sulfuric acid or by dissolving mercury(II) oxide in dilute sulfuric acid and evaporating the resulting solution until the compound crystallizes. Mercury(II) sulfate is used in analytical chemistry to bind chloride ions in the determination of the COD of wastewater [109]; as a catalyst in the production of acetaldehyde from acetylene and of anthraquinonesulfonic acids; and as a depolarizer in galvanic elements.

17.11.5   Mercury-Nitrogen Compounds

Reaction of mercury(II) compounds with ammonia solution leads, depending on reaction conditions, to amine complexes or mercury(II) nitrogen compounds. Of the numerous compounds known, only mercury(II) amidochloride has any practical importance.

Mercury(II)   amidochloride, $HgNH_2Cl$, ρ 5.38 g/cm^3, is a fine, white crystalline powder with a rhombic crystal lattice. It is insoluble in water and in ethanol, and soluble in warm acid, ammonium carbonate solution, and sodium thiosulfate solution. On heating it decomposes without melting. The compound can be precipitated from mercury(II) chloride solution with an ammonia solution. Mercury(II) amidochloride is used in the treatment of severe skin disease, as an eye ointment, and as a veterinary preparation; its importance is declining because of the development of mercury-free products.

17.11.6   Analysis, Storage, and Transportation; Protective Measures

Analysis. Determination of the purity of mercury compounds, which consists of the determination of trace amounts of foreign cations and anions, involves specific reactions of these ions [110]. conventional methods for the trace analysis of cations have been supplemented or replaced by methods involving the simultaneous determination of several elements by means of plasma emission spectroscopy [111].

Storage and Transportation. Plastic-lined steel drums are normally employed for packing. Small amounts (e.g., for chemical laboratories) are usually placed in plastic or glass bottles. Many compounds are light-sensitive and must, therefore, be adequately protected from light sources. Proper consideration must be given to the chemical and toxic properties of mercury compounds and the necessary protective measures; this is particularly true in container labeling.

Protective Measures. Most mercury compounds, because of their toxicity, require the same protective measures during production and processing as metallic mercury. Furthermore, environmental protection necessitates appropriate precautions (see Section 17.5).

17.12 Selected Organic Compounds

Organic mercury derivatives [112, 113] are among the oldest known organometallic compounds. Organometallic compounds of *divalent mercury* are stable toward air, oxygen, and water. In contrast, organic derivatives of monovalent mercury are unstable and can be prepared only at low temperature. After 1990, use of organic mercury derivatives in Germany will be difficult because mercury will not be allowed in industrial effluent or wastewater.

Organomercury compounds can be divided into two major groups: compounds of the type $R^1\text{-Hg-}R^2$, where R^1 and R^2 are aliphatic or aromatic groups, and compounds of the type $R\text{-Hg-}X$, where R is aliphatic or aromatic and X is a halogen or an acid group.

Synthesis of organic mercury compounds can be carried out by reaction of Grignard reagents with mercury halides [114, 115]. To obtain pure products, the mercury salt and the Grignard reagent must contain the same anion

$$RMgX + HgX_2 \longrightarrow RHgX + MgX_2$$

Furthermore, organic mercury compounds can be produced by the reaction of sulfuric acids or their sodium salts with mercury(TI) halides [116]:

$$R\text{-}SO_2H + HgX_2 \longrightarrow R\text{-}HgX + SO_2 + HX$$

Hydroxy- or alkoxymercury derivatives can be obtained via the solvomercuration reaction (Hofmann-Sand reaction) by addition of mercury(II) compounds to alkenes in aqueous, alkaline, or alcoholic solutions [114, 117]:

$$R^1\text{-CH=CH-}R^2 + Hg(OAc)_2 + R^3OH \longrightarrow$$
$$(R^3O)CHR^1\text{-CHR}^2HgOAc + AcOH$$
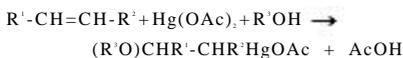
Organic mercury compounds can be converted to other organometallic derivatives by electrolysis or transmetallization [118].

Dialkyl- or Alkoxyalkylmercury Compounds. Dimethylmercury, $CH_3\text{-Hg-}CH_3$, a colorless, sweet-smelling liquid, is very toxic; it has a density of 3.069 g/cm³, *bp* 96 °C, and is soluble in ethanol and diethyl ether. In acidic aqueous solution, dialkylmercury compounds are hydrolyzed to monoalkylmercury derivatives. Dimethylmercury is formed in organisms by enzymatic methylation of elementary mercury or a mercury compound. In an organism it is easily converted to methylmercury $(CH_3\text{-Hg}^+)$ or methylmercury(II) chloride $(CH_3\text{-Hg-Cl})$. These species can react with free S-H groups of biologically important molecules, leading to the diseases that have been caused by mercury and its derivatives.

Mixed dialkylmercury compounds (e.g., methylpropylmercury compounds) are less volatile than symmetrical dialkylmercury compounds (e.g., diethylmercury). Dialkylmercury derivatives are generally very reactive and can also undergo transalkylation with simple alkyl halides (e.g., ethyl iodide).

Diarylmercury Derivatives. The best known diarylmercury derivative is diphenylmercury, $(C_6H_5)_2Hg$, which is produced by direct mercuration.

Analysis. Organic mercury compounds may be analyzed in the following ways: they can be determined *qualitatively* (1) by digestion with concentrated sulfuric acid and 30% hydrogen peroxide or (2) by digestion with 10% sulfuric acid and subsequent addition of dithizone (diphenylthiocarbazone) in carbon tetrachloride solution. In the presence of mercury the green solution turns orange. Organic mercury compounds can be determined *quantitatively* by atomic absorption spectroscopy.

17.13 Economic Aspects

A detailed description of the development of production is given in the metal statistics of Metallgesellschaft AG, Frankfurt [119] (Table 17.12). Over the last ten years, production figures have changed only slightly. According to U.S. estimates, current production is ca. 53% of the potential capacity. Because of reduced demand many mines and smelting plants are no longer operating or have greatly cut back production. Intervention by the former Soviet Union has seriously depressed the price of mercury to dumping price levels, although this has been resisted by Spain and Algeria. The change in the price of mercury

since 1979 is shown in Table 17.13 [119]. A survey of previous mercury prices is included in [120].

The main producers of mercury extracted by mining are as follows [121] (figures refer to flasks):

Algeria	23 000
China	20 000
Finland	2 300
Yugoslavia	2 000
Mexico	10 000
Spain	42 000
Former Czechoslovakia	4 400
Turkey	6 000
Former Soviet Union	66 000
United States	14 000[1]

The Algerian mercury producer, Entreprise nationale des non-ferreux et substances utiles (ENOF), quotes production prices of $300 per flask. Most of the Chinese production is exported to the United States. China claims to have the largest mercury resources in the world. Guizhou Province contains five mines, accounting for ca. 90% of Chinese production. Italy, once a large mercury producer, now imports mercury from Algeria, the Netherlands, and former Yugoslavia. In Mexico, ca.

[1] The sole producer in the United States discontinued mining operations from the middle of 1987 to February 1988. The production for 1988 is 14 000 flasks.

350 t of mercury (ca. 10 000 flasks) was extracted from mines in 1986, a large part of the production being exported to Brazil and Argentina. Spanish mercury production is ca. 40 000 fl. The main importers are the United States, Belgium, Luxemburg, and France. The former Soviet Union produces ca. 67 000 fl of mercury; in contrast to the high export level in 1986, almost the entire production is now reserved for domestic use. The capacity of production plants at the Anzob antimony mercury complex in Tajikistan has been doubled. The major proportion of former Yugoslav production of ca. 2000 fl of mercury is exported.

The development of prices and production figures will certainly be influenced substantially by acceptance of the metal mercury, and in large sectors no foreseeable substitute exists. The utilization of mercury in a highly industrialized country such as Germany is shown in Table 17.14 [122]. The purchase of mercury by individual sectors has decreased sharply since 1980. The main user of mercury is the electrical engineering industry, followed by the alkali chloride industry. The use of mercury in paints, pigments, and pesticides has fallen sharply.

Table 17.12: Production of mercury in tonnes [119].

	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994
Europe[a]	1672	1757	1693	1764	1704	1178	1140	135	128	734	475
Spain	1520	1539	1471	1553	1499	967	962	52	36	636	386
Finland	80	130	147	144	135	160	141	74	85	98	89
Yugoslavia	72	88	75	67	70	51	37	9[b]	7		
Asia[a] (Turkey)	182	226	262	211	97	202	60	25	5		
Africa (Algeria)	586	801	764	756	662	587	639	431	476	459	400
America	1043	965	695	264	724	1065	1195	398	85	82	80
Dominican Republic	2	1									
Mexico	384	394	185	124	345	651	735	340[b]	21[b]	12	10
United States	657	570	510[b]	140[b]	379[b]	414[b]	460[b]	58[b]	64[b]	70	70
Total Western countries	3483	3749	3414	2995	3187	3032	3034	989	694	1275	955
Czechoslovakia	152	158	168	164	168	131	126	75	60[b]	50	50
USSR[b]	1220	1200	1200	1200	1180	1180	2100	1900	1900	1700	1500
China[b]	800	800	850	900	900	1200	800	780	392	468	408
Total Eastern countries	2172	2158	2218	2264	2248	2511	3026	2755	2352	2218	1958
Total world	5655	5907	5632	5259	5435	5543	6060	3744	3046	3493	2913

[a] Excluding Eastern-Bloc countries.
[b] Estimates.

Table 17.13: Quoted prices for mercury in London and New York.

Year	European price £ per flask (34.473 kg)	£/kg	U.S. Price $ per flask (34.473 kg)	$/kg
1985	284.02-293.24	8.24-8.51	310.957	9.02
1986	187.49-200.36	5.44-5.81	232.785	6.75
1987	245.64-255.23	7.13-7.40	295.503	8.57
1988	297.17-310.49	8.62-9.01	335.517	9.73
1989	246.43-261.63	7.15-7.59	287.722	8.35
1990	200.91-218.79	5.83-7.22	249.218	7.23
1991	103.33-119.44	3.00-3.46	122.424	3.55
1992	126.85-173.35	3.68-5.03	201.390	5.84
1993	107.02-125.05	3.10-3.63	186.510	5.41
1994	103.23-119.32	2.99-3.46	194.453	5.64

17.14 Toxicology and Occupational Health [123]

Uptake, Mode of Action, Metabolism. The toxicity of mercury depends, among other things, on its state of aggregation and degree of dispersion. Both fine particulate dust containing mercury and mercury vapors are very toxic in comparison to the liquid metal. Various mercury compounds are very potent poisons. Compounds containing divalent mercury are generally more poisonous than monovalent ones. The toxicity of *inorganic* mercury compounds increases with increasing solubility. Still, in most cases, they are less toxic than *organic* mercury compounds.

The toxicity of mercury is based upon its action as a general cell and protoplasmic poison, i.e., bonding to the sulfhydryl groups of proteins; denaturing proteins; damaging membranes; and reducing the RNA content of cells. This leads to blocking of many enzyme systems. The kidneys and nervous system are especially vulnerable. In animal experiments, methyl mercury and mercury(II) chloride cause a dose-dependent suppression of spermatogenesis.

Acute poisoning occurs when mercury ion concentrations reach 0.2 mg per 100 mL of blood. Daily 5-h exposure to inhaled mercury vapor concentrations of 0.1 mg/m^3 leads to severe chronic mercury poisoning.

In foods, different mercury concentrations are tolerated: e.g., in the United States, 0.05 ppm; in Germany, 0.1 ppm. Environmental contamination with mercury leads to a critical concentration effect in animals that occupy higher positions in the food chain (large fish and fish-eating sea fowl). In certain fish, concentrations of 10 ppm of mercury and more have been found: fish and clams originating in Japan's Minamata Bay contained up to 9.6 mg of mercury per kilogram. Eggs of wild birds on the Finnish coast contained up to 3.5 mg of mercury per kilogram. Up to 270 mg of mercury per kilogram of organ tissue was found in dead seed-eating birds.

Table 17.14: Breakdown of mercury use (in tonnes) in former West Germany according to sector [122].

	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985
Alkali chloride industry (without changes in stock levels)	128.0	127.0	99.0	103.0	78.0	87.5	87.5	72.0	50.4	46.3	40.7	31.6	41.8
Catalysis	45.0	29.0	9.0	10.0	11.6	4.8	27.5	18.1	14.1	17.9	6.0	4.5	3.9
Paints, dyes	19.5	18.9	5.6	12.4	12.6	12.6	9.1	3.8	3.5	3.8	1.0	0.6	0.3
Pesticides	30.5	33.7	26.6	27.6	28.7	28.5	33.0	31.8	26.7	4.1	19.0	14.0	9.0
Electrical engineering	26.2	42.1	40.6	43.4	40.4	43.5	45.4	51.5	55.0	54.2	53.1	56.2	65.8
Control instruments and apparatus construction	14.8	17.3	8.7	10.3	14.6	13.4	13.3	16.5	15.7	17.1	7.0	6.1	7.2
Chemicals and reagents	25.3	7.0	33.1	45.8	22.0	31.4	43.2	35.5	27.1	53.9	36.2	24.7	
Medicine	24.2	25.2	25.0	26.0	23.9	24.3	24.2	24.2	22.9	23.6	23.5	24.3	24.1
Miscellaneous	32.8	31.1	44.2	46.7	30.0	30.0	30.0	42.1	32.5	35.7	30.1	30.2	30.2
Total	346.3	331.3	291.8	325.2	261.8	276.0	313.2	295.5	247.9	256.6	216.6	192.2	182.3
Total, % (1980= 100%)	117	112	99	110	89	94	106	100	84	86	73	65	62

Humans are estimated to consume 0.2 mg of mercury weekly in their diet. Mercury uptake with food leads to concentrations in the kidney of < 0.1-3 mg/kg; the corresponding concentrations with intoxication are 10-70 mg/kg.

Amalgam fillings are the most frequent cause of chronic mercury and tin intoxication. The metal is transformed to highly toxic organic compounds by oral microorganisms. During chewing (gum) up to 26 mg/L of mercury and 0.3 mg/L tin may be set free.

After 15 min, the mercury content of the respiratory air increased eightfold.

Toxicity of Metallic Mercury and Inorganic Mercury Compounds. The toxicity of mercury and its compounds depends predominantly on their solubility, which determines absorption and distribution in the organism. Thus metallic mercury and all mercury compounds are toxic, with the exception of red mercury sulfide, which is practically insoluble in the body. Mercury vapor causes acute damage to the lungs and chronic damage to the central nervous system. Mercury salts are caustic to the mucous membranes of the gastrointestinal tract and nephrotoxic when absorbed.

Metallic Mercury. Liquid mercury is not highly toxic; in earlier times, it was used as a treatment for ileus. Thermometers that break in the rectum lead to mercury intoxication only if a wound is created and mercury is pressed into the tissues from which it is slowly absorbed. Granulomas develop when mercury is injected into subcutaneous fat tissue; this can occur in suicide attempts or injuries to the hand caused by broken thermometers. Absorption occurs when the mercury depot is broken up into minuscule droplets, for example, after surgical excision. Occasionally liquid mercury has been injected intravenously, either suicidally [124, 125] or accidentally during intracardiac catheter studies when blood was drawn for blood gas analysis by using mercury-filled syringes. Mercury embolisms resulted, and some of the patients showed symptoms of intoxication. One of

nine patients died after five months as a result of the intoxication. Blindness as a result of occlusion of the central artery also occurred. Antisyphilitic treatment with gray mercury ointment caused numerous intoxications, with all grades of severity being encountered. They resulted from skin absorption and from inhalation of the mercury that vaporized on the skin.

Acute *inhalant poisoning* is very dangerous. In four cases, after several hour's exposure to mercury vapor concentrations of 1-3 mg/m^3, acute pneumonitis resulted. Chronic inhalant intoxication can be expected with mercury vapor concentrations of 0.1-1 mg/m^3. With < 0.1 mg of mercury per cubic meter, even mild intoxication is improbable. In sensitive persons, an increase in subjective signs (micromercurialism) has been observed at 0.02-0.1 mg/m^3 [125].

Mercury Salts. Salts of divalent mercury are more toxic than monovalent ones, regardless of the route of administration. In animal experiments the LD_{50} after parenteral injection for divalent salts is ca. 5 mg of mercury per kilogram. As a result of their poor absorption, they are much less toxic if administered orally, the LD_{50} in this case being of the order of 100 mg of mercury per kilogram [126]. Strongly dissociated salts are more caustic and generally more toxic than less dissociated ones. An exception to this is mercury oxycyanide [Hg(CN)$_2$HgO], which is highly poisonous even though it hardly dissociates. Cyanide ions may enhance the toxicity.

Acute Poisoning in Humans. Mercury(II) chloride (corrosive sublimate) is one of the strongest corrosive poisons; for adults, oral doses of 0.50-1.0 g (in several cases even 0.2 g) are fatal, even though people have survived after ingesting 5 g. A total of 0.2 g introduced into the vagina can be fatal. Administration of 1.5 g of *mercury oxycyanide* was lethal. The toxicity of *mercury(I) chloride* (calomel) depends on its retention time in the gastrointestinal tract. The lethal dosage for adults is generally 2-3 g; for children, 0.4 g [125]. However, in former times, therapeutically administered doses of 0.1 g of mercury(I) chloride have led to death, especially when the

laxative effect did not occur. Chronic intoxication with mercury salts is unusual; in industrial poisonings, exposition to mercury vapors generally exists concomitantly. Mercury salts act as direct skin irritants. Furthermore, they are sensitizing, especially mercury fulminate.

Toxicity of Organic Mercury Compounds. Most organic mercury compounds are lipid soluble. Some of them vaporize easily and thus also act in the gaseous phase. Organic mercury compounds can cause toxic dermatitis and, as a result of their lipid solubility, can severely damage the central nervous system. Hypersensitivity reactions, as well as kidney damage, also occur.

In the organism, *phenylmercury* and *alkoxyalkylmercury* compounds are metabolized to inorganic mercury compounds and act like mercury salts. The stable alkylmercury compounds are neurotoxic and embryotoxic.

Alkylmercury Compounds. Numerous toxicity studies on animals have been reported. The LD_{50} in rats and mice of most methyl- and ethylmercury compounds is 10-30 mg of mercury per kilogram. This holds true for parenteral and oral administration [126]. In humans, almost all alkylmercury poisoning has been caused by contaminated food, almost all involved chronic poisoning, the dose ingested is unknown, and estimated values are questionable. Mass poisoning in Iraq was caused by pita bread baked with flour made from seed grain; the grain contained ca. 15 mg of mercury per kilogram of alkylmercury (mainly methylmercury) salt.

The bread weighed 220 g and had a water content of 31 %. Affected adults are estimated to have eaten six to eight loaves per day; the first fatalities occurred six to eight weeks after distribution of the seed grain [126, 127].

Minamata disease developed in fishermen and their family members who ate fish daily or at least several times a week, consuming 250-500 g of fish with each meal. The average methylmercury concentration of the fish eaten is not known (estimates: 5-20 mg of mercury per kilogram of fish). Thus, a daily uptake of 1.5-4 mg of mercury would have resulted, respectively [4]. Affected patients had mercury concentrations of 200-2000 µg/L in their blood and 50-500 mg/kg in their hair [128]; the brain of patients who died contained > 5 mg of mercury per kilogram [126]. Mild symptoms are assumed to occur with concentrations of 100 µg of mercury per liter of blood and 30 mg of mercury per kilogram of hair. Daily ingestion of 5 µg of mercury per kilogram of body weight in the form of methylmercury compounds is considered the minimal toxic dose [128].

Mercury is *mutagenic, teratogenic,* and *embryotoxic,* especially in the form of alkylmercury compounds [129, 130]. The fetus is three to four times more sensitive to methylmercury than the pregnant woman [128]. Congenital brain damage occurred in 5-6% of the children from Minamata Bay, where the rate expected was 0.1-0.6%. The mothers belonged to the group of people heavily exposed to methylmercury but did not show any clear symptoms of intoxication [126].

Arylmercury Compounds. In animal experiments, arylmercury compounds are as toxic as alkylmercury compounds when administered parenterally; administered orally, however, they are less toxic. As a result of their instability they act like a combination of organically bound mercury and mercury vapor. In adults, ingestion of 100 mg of mercury in the form of phenylmercury nitrate led to abdominal pain and mild diarrhea; however, 120 mg was also tolerated without symptoms. Even after ingestion of 1.25 g of mercury, clinical chemistry values and kidney biopsy results were normal. Concentrations > 0.6 g/L are locally caustic [126].

Antagonism. Mercury and selenium are antagonists; within certain limits, selenium can reduce the toxicity of inorganic and methylmercury. In animal experiments, selenium predominantly delays the appearance of intoxication symptoms but reduces the lethality only slightly. Whether a high dietary selenium content can protect against methylmercury poisoning is still open to question: the fish that caused Minamata disease

contained, in addition to large amounts of mercury, a high proportion of selenium [128, 131].

Occupational Health. The MAK value for metallic mercury in Germany is presently 0.1 mg/m³ (0.01 ppm); for mercury vapor the MAK value is 0.05 mg/m³ [123]. The TWA of mercury is 0.05 mg/m³. The theoretically possible vapor pressure concentration can, however, far exceed this value. The odor threshold for mercury is 13 mg/m³.

The legal requirements covering industrial safety and hygiene when working with mercury and its compounds depend on the laws of individual countries. The measures adopted by a highly industrialized country such as Germany are described below.

The special safety measures for handling and working with mercury-containing materials are given in the TRgA (Technische Regeln für gefährliche Arbeitsstoffe; technical regulations for dangerous substances). They do not cover mercury(II) sulfide, inorganic compounds containing < 0.1 % mercury, or organic compounds containing < 0.05 % mercury. The working methods and procedures must basically be designed so that employees are not exposed to mercury vapor, mist, or dust. Further details are given in [132].

A series of specification sheets for handling mercury has been published, which describes the technical and personal safety measures to be adopted [133]. Explanatory information and instructions for work and health safety are summarized in a comprehensive poisons list [134].

Persons working with mercury should be monitored regularly. With metallic mercury, inorganic mercury compounds, and organic nonalkyl mercury compounds, mercury values in urine should not exceed 150 µg/L. The blood levels should be < 35 µg/L. With organic alkylmercury compounds, the limiting blood level is 75 µg/L.

17.15   References

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