ARSENIC AND ARSENIC ALLOYS

1. Introduction

Arsenic [7440-38-2], although often referred to as a metal, is classified chemically as a nonmetal or metalloid and belongs to Group 15 (VA) of the Periodic Table (as does antimony). The principal valences of arsenic are +3, +5, and −3. Only one stable isotope of arsenic having mass 75 (100% natural abundance) has been observed.

Elemental arsenic normally exists in the α-crystalline metallic form which is steel-gray in appearance and brittle in nature, and in the β-form, a dark-gray amorphous solid. Other allotropic forms, ie, yellow, pale reddish-brown to dark brown, have been reported (1), but the evidence supporting some of these allotropes is meager. Metallic arsenic, heated under ordinary conditions, does not exhibit a discrete melting point but sublimes. Molten arsenic can be obtained by heating under pressure.

2. Occurrence

Arsenic is widely distributed about the earth and has a terrestrial abundance of ~5 g/t (2). Over 150 arsenic-bearing minerals are known (1). Table 1 lists the most common minerals. The most important commercial source of arsenic, however, is as a by-product from the treatment of copper, lead, cobalt, and gold ores. The quantity of arsenic usually associated with lead and copper ores may range from a trace to 2–3%, whereas the gold ores found in Sweden contain 7–11% arsenic. Small quantities of elemental arsenic have been found in a number of localities.

World resources of copper and lead contain ~11 million tons of arsenic. Substantial resources of arsenic occur in copper ores in northern Peru and the Philippines and in copper–gold ores in Chile. World gold resources, particularly in Canada, contain substantial resources of arsenic. World reserves and reserve base are thought to be ~20 and 30 times, respectively, annual world production (see Table 2). U.S. reserve base in estimated to be ~80,000 tons (3).

Table 1. **Naturally Occurring Arsenic-Bearing Minerals**

Name	CAS Registry Number	Formula	Name	CAS Registry Number	Formula
loellingite	[12255-65-1]	$FeAs_2$	sperrylite	[12255-87-7]	$PtAs_2$
safforlite	[12044-43-8]	$CoAs_2$	arsenopyrite (mispickel)	[1303-18-0]	FeAsS
niccolite	[1303-13-5]	NiAs	cobaltite	[1303-15-7]	CoAsS
rammelsbergite	[1303-22-6]	$NiAs_2$	enargite	[14933-50-7]	Cu_3AsS_4
realgar	[12044-30-3]	AsS	gersdorffite	[12255-11-7]	NiAsS
orpiment	[12255-89-9]	As_2S_3	glaucodot	[12198-14-0]	(Co,Fe)AsS

Table 2. **World Production, Reserves, and Reserve Base, 10^3 t**[a]

	Production[b]	
Country	2000	2001[c]
Belgium	1,500	1,500
Chile	8,200	8,000
China	16,000	16,000
France	1,000	1,000
Kazakhstan	1,500	2,000
Mexico	2,400	2,600
Russia	1,500	1,500
other countries	1,800	2,000
World total (may be rounded)	33,900	35,000

[a] Ref. 3.

[b] As arsenic trioxide.

[c] Estimated.

3. Properties

Physical properties of α-crystalline metallic arsenic are given in Table 3. The properties of β-arsenic are not completely defined. The density of β-arsenic is 4700 kg/m^3; it transforms from the amorphous to the crystalline form at 280°C; and the electrical resistivity is reported to be 107 Ω cm.

Metallic arsenic is stable in dry air, but when exposed to humid air the surface oxidizes, giving a superficial golden bronze tarnish that turns black upon further exposure. The amorphous form is more stable to atmospheric oxidation. Upon heating in air, both forms sublime and the vapor oxidizes to arsenic trioxide [1327-53-3], As_2O_3. Although As_4O_6 represents its crystalline makeup, the oxide is more commonly referred to as arsenic trioxide. A persistent garliclike odor is noted during oxidation.

Elemental arsenic combines with many metals to form arsenides. When heated in the presence of halogens it forms trihalides; however, pentahalides with the exception of AsF_5 (4) and the unstable $AsCl_5$ are not readily formed. It reacts with sulfur to form the compounds As_2S_3, AsS, As_2S_5, and complex mixtures in various proportions (see ARSENIC COMPOUNDS).

Arsenic vapor [12187-88-5], As_4, does not combine directly with hydrogen to form hydrides. However, arsine (arsenic hydride) [7784-42-1], AsH_3, a highly poisonous gas, forms if an intermetallic compound such as AlAs is hydrolyzed or treated with HCl. Arsine may also be formed when arsenic compounds are reduced using zinc in hydrochloric acid. Heating to 250°C decomposes arsine into its elements.

Metallic arsenic is not readily attacked by water, alkaline solutions, or nonoxidizing acids. It reacts with concentrated nitric acid to form orthoarsenic acid

Table 3. **Physical Properties of Arsenic**

Property	Value
atomic weight	74.9216
mp at 39.1 MPa[a], °C	816
bp, °C	615[b]
density at 26°C, kg/m^3	5,778
latent heat of fusion, J/(mol · K)[c]	27,740
latent heat of sublimation, J/(mol · K)[c]	31,974
specific heat at 25°C, J/(mol · K)[c]	24.6
linear coefficient of thermal expansion at 20°C, μm/(m·°C)	5.6
electrical resistivity at 0°C, μ Ω cm	26
magnetic susceptibility at 20°C	-5.5×10^{-6}[d]
nuclear absorption cross section[e]	4.3 ± 0.2
crystal system	hexagonal (rhombohedral)
lattice constants at 26°C, nm	$a = 0.376$, $c = 1.0548$
hardness, Mohs' scale	3.5

[a] To convert MPa to psi, multiply by 145.

[b] Sublimes.

[c] To convert to cal/(mol · K), divide by 4.184.

[d] From cgs system units.

[e] Thermal neutrons 2200 m/s of arsenic mass 75.

[7778-39-4], H_3AsO_4. Hydrochloric acid attacks arsenic only in the presence of an oxidant.

Arsenic may be detected qualitatively as a yellow sulfide, As_2S_3, by precipitation from a strongly acidic HCl solution. Other members of this group that are normally precipitated with hydrogen sulfide do not interfere if the solution contains 25% or more hydrochloric acid. Trace quantities of arsenic may be detected by first converting to arsine (5). The arsine is decomposed by heating the gas in a small tube and an arsenic mirror is formed (Marsh test). Alternatively, the arsine may be allowed to react with test paper impregnated with mercuric chloride (Gutzeit test).

4. Metallurgy

Metallic arsenic can be obtained by the direct smelting of the minerals arsenopyrite or loellingite. The arsenic vapor is sublimed when these minerals are heated to about 650–700°C in the absence of air. The metal can also be prepared commercially by the reduction of arsenic trioxide with charcoal. The oxide and charcoal are mixed and placed into a horizontal steel retort jacketed with firebrick that is then gas-fired. The reduced arsenic vapor is collected in a water-cooled condenser (6). In a process used by Boliden Aktiebolag (7), the steel retort, heated to 700–800°C in an electric furnace, is equipped with a demountable air-cooled condenser. The off-gases are cleaned in a scrubber system. The yield of metallic arsenic from the reduction of arsenic trioxide with carbon and carbon monoxide has been studied (8) and a process has been patented describing the gaseous reduction of arsenic trioxide to metal (9).

The demand for metallic arsenic is limited and thus arsenic is usually marketed in the form of the trioxide, referred to as white arsenic, arsenious oxide, arsenious acid anhydride, and also by the generally accepted misnomer arsenic.

Arsenic trioxide was recovered from smelting or roasting of nonferrous metal or as concentrates in at least 16 countries in 2000.

Arsenic trioxide is readily volatilized during the smelting of copper and lead concentrates, and is therefore concentrated with the flue dust. Crude flue dust may contain up to 30% arsenic trioxide, the balance being oxides of copper or lead, and perhaps of other metals such as antimony and zinc. This crude flue dust is further upgraded by mixing with a small amount of pyrite or galena concentrate and roasting (10). The pyrite or galena is added to prevent arsenites from forming during roasting and to obtain a clinkered residue which can be returned for additional processing. The gases and vapors are passed through a cooling flue which consists of a series of brick chambers or rooms called kitchens. The temperature of the gas and vapor is controlled so that they enter the first kitchen at 220°C and by the time the gas and vapor reach the last kitchen they are cooled to 100°C or less. The arsenic trioxide vapor that condenses in these chambers is of varying purity analyzing from 90–95%. A higher purity product is obtained by resubliming the crude trioxide, an operation normally carried out in a reverberatory furnace. The vapors pass first through a settling chamber and then through ~39 kitchens that cover a length of ~68.6 m. The temperature of the settling chamber is kept at ~295°C, which is above the condensation temperature of the trioxide. A black, amorphous mass containing about 95% As_2O_3 condenses in the kitchens nearest the furnace and is reprocessed. The bulk of the trioxide is condensed in the kitchens having temperature ranges of 180–120°C giving a product of 99–99.9% purity. The dust which exits from the kitchens at a temperature of 90–100°C is caught in the baghouse. It assays ~90% As_2O_3 and may be sold as a crude grade or reprocessed. (A typical flow sheet for the production of arsenic trioxide at a copper smelter is depicted in Fig. 1.)

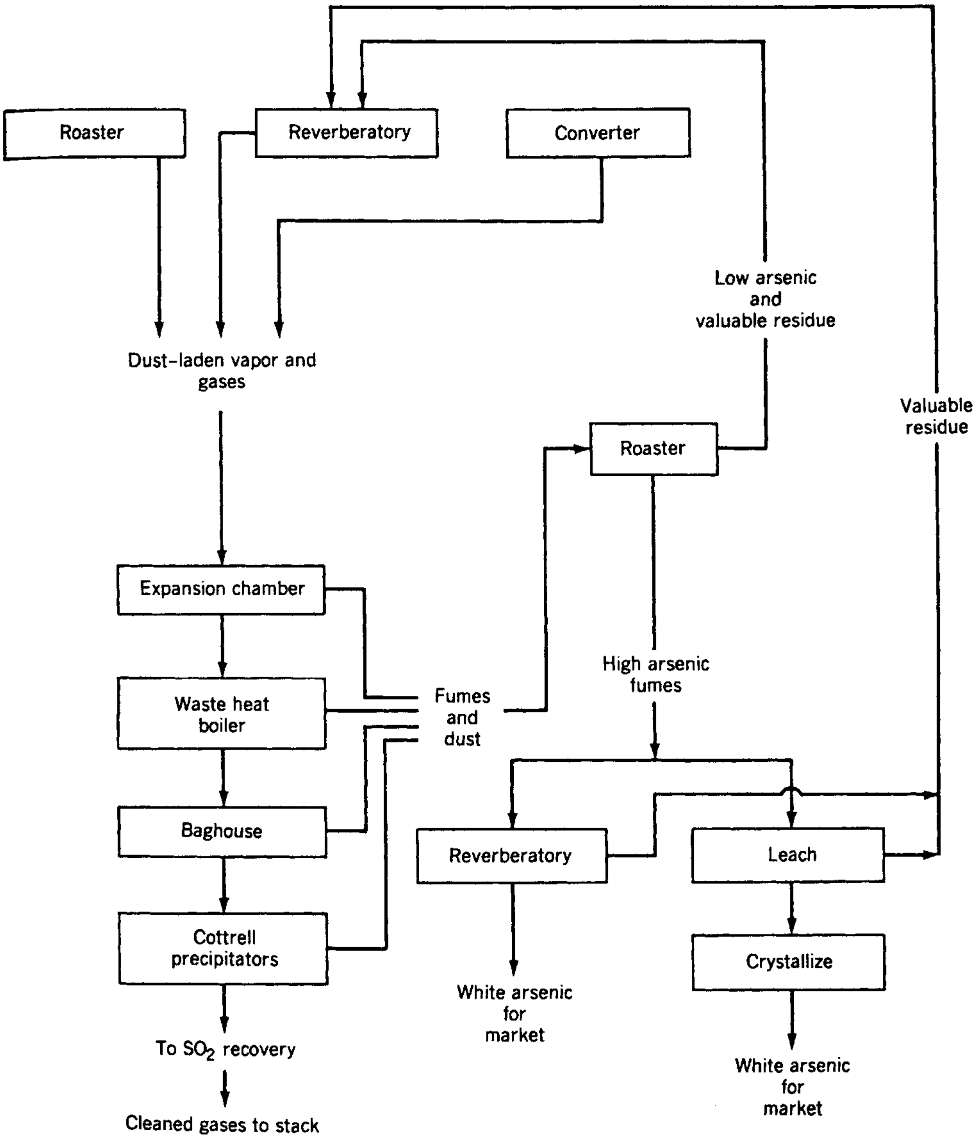

Fig. 1. Arsenic trioxide copper smelter-flow sheet.

In addition to pyro-refining, crude oxide analyzing 80–95% can be refined by a wet process (7). In this process, advantage is taken of the fact that the solubility of arsenic trioxide in water increases with temperature as follows:

Temperature, °C	Solubility, g/L
0	12.1
20	18.1
98.5	81.8

Most of the common impurities present in crude arsenic have a low solubility.

The crude oxide is pressure-leached in a steam-heated autoclave using water or circulating mother liquor. The arsenic trioxide dissolves, leaving behind a residue containing a high concentration of heavy metal impurities and silica. The solution is vacuum-cooled and the crystallization is controlled so that a coarse oxide is obtained that is removed by centrifuging. The mother liquor is recycled. The oxide (at least 99% purity) is dried and packaged in a closed system.

The refined arsenic trioxide is analyzed for purity and also tested for solubility, a term referring to its rate of reactivity with nitric acid; this test is important if the arsenic is used in the manufacture of insecticides and herbicides. The product is graded for marketing as white soluble having 99% min As_2O_3, white insoluble, or crude having 95% min As_2O_3.

Minor quantities of arsenic trioxide have been obtained from the roasting of arsenopyrite, but the presence of copious amounts of SO_2 in the gas and vapor stream requires the use of lead-lined kitchens (10).

5. Economic Aspects

The United States had no domestic production of arsenic in 2000 and needed to rely on imports for its needs. The United States did import some arsenic metal, but most of its imports were in the form of arsenic trioxide. China remains the principal supplier to the United States. See Table 4 for U.S. import data (11).

The estimated value of arsenic consumed by the United States during 2001 was ~$20 million (3).

Economic statistics for the United States are given in Table 5.

5.1. Prices. During the 1970s demand for arsenic was growing. During the late 1970s, regulations related to exposure and emissions were adopted. Arsenic prices peaked in 1980 at $6612/t ($3.00/lb). In 2001, it was $110.2/t ($0.50/lb) (3,12).

Table 4. **U.S. Imports for Consumption of Arsenicals**[a,b]

	1999		2000	
Class and country	Quantity metric tons	Value $\times 10^3$ \$	Quantity metric tons	Value $\times 10^3$ \$
arsenic trioxide				
Belgium	724	429	576	356
Bolivia	280	159	212	118
Canada			1	2
Chile	8,870	3,340	9,110	3,620
China	15,500	8,380	15,400	7,800
France	1,410	862	1,340	871
Germany	3	34	4	15
Hong Kong	70	42	406	232
Mexico	1,680	1,090	1,900	1,330
Morocco	148	90	2,180	1,150
Spain				
Switzerland				
Vietnam	437	251		
Total	*29,100*	*14,700*	*31,100*	*15,500*
arsenic acid	4	24		
arsenic acid, arsenic metal				
France				
China	1,240	1,600	612	694
Germany	16	3,210	21	3,410
Hong Kong			41	36
Japan	45	3,580	157	5,660
Taiwan				
United Kingdom	[c]	7	[c]	2
Total	*1,300*	*8,390*	*830*	*9,800*

[a,b] Ref. 11. Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Less than 1/2 unit.

Table 5. **United States Economic Statistics for Arsenic**[a]

	t^b		Year		
Statistic	1993	1998	1999	2000	2001[b]
production					
imports for consumption:					
metal, t	909	997	1,300	830	1,200
compounds, t	22,800	29,300	22,100	23,600	24,000
exports, metal, t	61	177	1,350	41	60
estimated consumption, t^b	23,700	30,100	22,000	24,000	25,000
value, cents per pound, average[c]					
metal (China)	32	57	59	51	50
trioxide (Mexico)	31	32	29	32	31
net import reliance[d] as a percentage of apparent consumption	100	100	100	100	100

[a] Ref. 3.

[b] Estimated to be the same as net imports.

[c] From U.S. Census Bureau import data. To convert to \$/t, multiply by 2.204.62.

[d] Defined as imports—exports + adjustments for government and industry stock changes.

6. Recycling

Arsenic was not recovered from consumer end-product scrap. However, process water and contaminated runoff collected at wood treatment plants were reused in pressure treatment, and gallium arsenide scrap from the manufacture of semiconductor devices was reprocessed for gallium and arsenic recovery. In the United States, no arsenic was recovered from arsenical residues and dusts at nonferrous smelters, although some of these materials are processed for recovery of other metals (3).

7. Health and Safety Factors

The toxicity of arsenic ranges from very low to extremely high depending on the chemical state. Metallic arsenic and arsenious sulfide [1303-33-9], As_2S_3, have low toxicity. Arsine is extremely toxic. The toxicity of other organic and inorganic arsenic compounds varies (13).

Arsenic is classified as a carcinogen by the International Agency for Research on Cancer (IARC) (14). An association between high and lengthy exposures to inorganic arsenic compounds and cancer has been reported (15), but evidence supporting this relationship is equivocal (16). Ulceration and perforation of the nasal septum is caused by airborne As_2O_3 if proper precautions are not observed. However, these injuries have not been associated with malignancy (17).

The handling of arsenic in the workplace should be in compliance with the Occupational Safety and Health Administration (OSHA) regulations: the maximum permissible exposure limit for arsenic in the workplace is 10 $\mu g/m^3$ of air as determined as an average over an 8-h period (18).

The National Institute for Occupational Safety and Health (NIOSH) has established an exposure level of 0.002 mg/m^3 as a recommended ceiling (15 min) for inorganic arsenic; no level for organic arsenic and an REL of 0.002 mg/m^3 as a 15-min celling concentration (19).

The American Conference of Governmental Industrial Hygienists (ACGIH) has established air TLV for arsenic, elemental and inorganic compounds (except arsine), at 0.01 mg/m^3).

Precaution should be taken to avoid accidental generation of arsine gas; the maximum permitted exposure is 0.05 ppm in air per 8-h period five days per week (20). Disposal of arsenical products should be in compliance with federal and local government environmental regulations.

8. Environmental Concerns

The location and extent of arsenic in ground water was the subject of a U.S. Geological Survey study in 2000 (21). The presence of arsenic in ground water is due largely to minerals dissolving. Data on 19,000 samples of potable water showed that the arsenic concentration was lower that the 50 μ/L, which was the EPA standard at that time. Ten percent of the samples exceeded to 10 μ/L, which is the World Health Organization standard.

The United States EPA has adopted a new standard for drinking water of 10 μ/L based on a study by the National Academy of Sciences (http://www.epa.gov/safewater/arsenic/html).

For a detailed discussion of this topic see ARSENIC, ENVIRONMENTAL IMPACT, HEALTH EFFECTS, AND TREATMENT METHODS.

9. Uses

Table 6 gives the United States demand patterns for specific end uses.

The use of many arsenical chemicals are subject to registration and must comply with federal and local government environmental regulations.

9.1. Wood Preservative. The largest use for arsenic (as arsenic trioxide) is in the production of wood preservatives. The demand will probably continue to correlate closely with housing construction, renovations, and replacements of existing structures using pressure-treated lumber (3,22,23). In 2000, the three principal U.S. producers of arsenical wood preservatives wer Hudson Corp. (Smyrna, Ga.), Chemical Specialties, Inc. (Harrisburg, NC) Osmose Wood Preserving, Inc. (Buffalo, N.Y.) (11).

9.2. Semiconductor Applications. A limited but important demand for metallic arsenic of 99.99% and greater (exceeding 99.999 + %) purities exists in semiconductor applications (see SEMICONDUCTORS). In 2001, are estimated 30 t/process used in the United States. This high purity arsenic may be prepared by the reduction of a highly purified arsenic compound using a high purity gaseous or solid reductant.

High purity (HP) arsenic, when alloyed with aluminum, gallium, and indium, form the III–V semiconductor compounds, aluminum arsenide [22831-42-1], AlAs, gallium arsenide [1303-00-0], GaAs, and indium arsenide [1303-11-3], InAs, respectively. These compounds or variations such as GaAlAs, GaAsP, and InGaAs, are used in device manufacture. Gallium aluminum arsenide, GaAlAs, is used in the manufacture of solar cells having efficiencies exceeding 20% (see SOLAR ENERGY). $GaAs_xP_y$ is used in the manufacture of light emitting diodes (LEDs) of red light; yellow LEDs are produced by increasing the phosphorus content (see LIGHT GENERATION, LIGHT EMITTING DIODES). GaAs infrared (ir) emitters and ir detectors have use in fiber optic applications (see FIBER

Table 6. **U.S. Arsenic Demand Pattern, metric tons, arsenic content**[a,b]

Use	1996	1997	1998	1999	2000
agricultural chemicals	950	1,400	1,500	1,100	1,000
glass	700	700	700	700	700
wood preservatives	19,200	20,000	27,000	19,000	21,000
nonferrous alloys and electronics	250	900	1,000	1,300	800
other	300	300	300	300	300
total	*21,400*	*23,700*	*30,100*	*22,000*	*24,000*

[a,b] Ref. 11. Data are rounded to no more than three significant digits; may not add to totals shown.

optics). GaAs is also used in the manufacture of microwave devices (see Microwave technology), integrated circuits (qv), lasers (qv), laser windows, and optoelectronic devices. Indium arsenide has been used to produce Hall effect and infrared devices (see Infrared and Raman spectroscopy; Magnetohydrodynamics). InGaAs is used as lasers and photodetectors (qv). GaAs is also used in the manufacture of microwave devices (see Microwave technology), integrated circuits (qv), lasers (qv), laser windows, and optoelectronic devices. Indium arsenide has been used to produce Hall effect and infrared devices (see Infrared and Raman spectroscopy; Magnetohydrodynamics). InGaAs is used as lasers and photodetectors (qv).

HP arsenic is used in the manufacture of photoreceptor arsenic-selenium alloys for xerographic plain paper copiers (see Electrophotography). The level of arsenic may be 0.5, 5.0, or 35% present as arsenic triselenide [1303-36-2], As_2Se_3.

Arsenic from the decomposition of high purity arsine gas may be used to produce epitaxial layers of III–V compounds, such as InAs, GaAs, AlAs, etc, and as an *n*-type dopant in the production of germanium and silicon semiconductor devices. A group of low melting glasses based on the use of high purity arsenic (27–30) were developed for semiconductor and ir applications.

9.3. Other. Other uses for arsenic metal are as an additive to improve corrosion resistance and tensile strength in copper alloys and as a minor additive (0.01–0.5% 0 to increase strength of posts and grids in lead storage batteries (11). Arsenic acid is used by the glass industry as a fining agent to disperse air bubbles (11,24,25). Arsenic is also used in some herbicides (11,26).

10. Alloys

Arsenic metal is used primarily in alloys in combination with lead and, to a lesser extent, copper.

Trace quantities of arsenic are added to lead-antimony grid alloys used in lead–acid batteries (31) (see Batteries, lead acid). The addition of arsenic permits the use of a lower antimony content, thus minimizing the self-discharging characteristics of the batteries that result from higher antimony concentrations.

No significant loss in hardness and casting characteristics of the grid alloy is observed (32,33).

Arsenic added in amounts of 0.1–3% improves the properties of lead-base babbitt alloys used for bearings (see Bearing materials). Arsenic (up to 0.75%), has been added to type metal to increase hardness and castability (34). Addition of arsenic (0.1%) produces a desirable fine-grain effect in electrotype metal without appreciably affecting the hardness or ductility. Arsenic (0.5–2%) improves the sphericity of lead ammunition. Automotive body solder of the composition 92% Pb, 5.0% Sb, and 2.5% Sn, contains 0.50% arsenic (see Solders and brazing alloys).

Minor additions of arsenic (0.02–0.5%) to copper (qv) and copper alloys (qv) raise the recrystallization temperature and improve corrosion resistance. In some brass alloys, small amounts of arsenic inhibit dezincification (35), and minimize season cracking.

Table 7. **Arsenical Copper Alloys**

Alloy number	Composition, wt %						
	Cu	As	Pb	Fe	Sn	P	Al
142	99.4	0.015–0.50				0.015–0.040	
366[a]	58–61	0.02–0.10	0.40–0.9	0.15	0.25		
443[a]	70–73	0.02–0.10	0.07	0.06	0.9–1.2		
465[a]	59–62	0.02–0.10	0.20	0.10	0.5–1.0		
687[a]	76–79	0.02–0.10	0.07	0.06			1.8–2.5

[a] Zinc constitutes the remainder of composition.

Phosphorized deoxidized arsenical copper (alloy 142 (36)) is used for heat exchangers and condenser tubes. Copper-arsenical leaded Muntz metal (alloy 366), Admiralty brass (alloy 443), naval brass (alloy 465), and aluminum brass (alloy 687), all find use in condensers, evaporators, ferrules, and heat exchanger and distillation tubes. The composition of these alloys is listed in Table 7.

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