

# Copper Compounds

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## 1. Introduction

The importance of copper and its alloys to today's society is well documented in the articles on → Copper and on → Copper Alloys. Copper compounds, although they represent a small fraction of total copper production, play an important and varied role in industry and agriculture. One of the oldest known fungicides was copper-based and was used extensively in the early part of the century. The last 20 years have brought about a resurgence in the use of copper-based fungicides partly because of a lack of tolerance by fungi to copper and also because of its relatively low toxicity to higher plants and animals (see, however, Chaps. 7 and 9). Although copper is an essential trace element for higher plants and animals, it is acutely toxic in higher doses. Copper compounds are used as nutritional additives in animal feeds and fertilizers, and are found in a variety of dietary supplements. Copper salts are used in the control of algae in lakes and ponds, and the oxides are used in antifouling paints and coatings. Copper acetarsenite, Paris green, is used as an insecticide,

and copper chromium arsenate is an effective alternative to creosote for the preservation of wood.

Copper and its compounds are used catalytically in numerous organic reactions, e.g., polymerization, isomerization, and cracking reactions. They are used in the textile and dye industries in the preparation of rayon and acrylonitrile, as mordants and oxidants in textile dyeing and printing, and in the preparation of azo dyes. Copper compounds are used as pigments in glass, ceramics, porcelains, varnishes, and artificial gems, and in the manufacture of the copper phthalocyanine pigments. Copper salt solutions are used for electroplating, in brazing and burnishing preparations, and as brighteners for aluminum. Solutions of copper(I) complexes are used to selectively absorb carbon monoxide, butadiene, and alkenes from gas streams. In the petroleum industry, copper compounds are used as deodorizing (desulfurization) and purifying agents. Copper(II) carbonate is used in drilling muds to protect against release of poisonous hydrogen sulfide gas, and copper(I) iodide is used in acid muds to bind corrosion inhibitors

to the iron drills. More recent applications of copper compounds are in pollution control and solar technology.

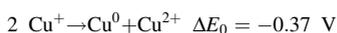
The multitude of applications of copper compounds in the biosphere is largely responsible for the extent of academic interest in them. Also, the facile reduction – oxidation of the copper(I) – copper(II) couple, the ease of theoretical treatment of the  $d^9$  copper(II) system, and the varied stereochemistries and magnetic behaviors associated with copper ions enhance their theoretical appeal. Since this treatment of copper compounds is primarily from an industrial perspective, the reader whose interest is academic is referred to the classic references [1–4] as well as to more recent materials [5–11] that are attune to the subtle chemistries of copper and its compounds. Compounds of primary industrial importance (Chaps. 3 and 4) are distinguished from compounds of minor importance (Chap. 5) in this article.

## 2. The Copper Ions

Copper, Cu [7440-50-8],  $M_r$  63.546,  $[\text{Ar}]3d^{10}4s^1$ , is a member of the first transition series. It is classified as a transition element in the broader definition because the copper(II) valence state,  $[\text{Ar}]3d^9$ , comprises such a large proportion of the defined chemistry of copper. Copper in its compounds exists primarily in two oxidation states, + 1 and + 2. Although copper(0) and copper(III) compounds have been identified, they are not presently of commercial importance. The stabilities of the various valence states of copper are illustrated by the following standard reduction potentials:

			$E_0$
$\text{Cu}^+ + e$	$\rightarrow$	$\text{Cu}^0$	+ 0.52 V
$\text{Cu}^{2+} + 2 e$	$\rightarrow$	$\text{Cu}^0$	+ 0.34 V
$\text{Cu}^{2+} + e$	$\rightarrow$	$\text{Cu}^+$	+ 0.15 V
$\text{Cu}^{3+} + e$	$\rightarrow$	$\text{Cu}^{2+}$	+ 1.80 V

From the above, it is seen that



with  $pK = -5.95$

In other words, the free copper(I) ion does not exist to any appreciable extent in aqueous solu-

tion. In the presence of ligands such as ammonia, chloride, or cyanide, solutions of copper(I) can be prepared that are stable with respect to disproportionation. For example, the colorless solution of tetraamminedicopper(I) sulfate is prepared readily by contact of blue tetraamminecopper(II) sulfate with metallic copper in the absence of air. Upon acidification with sulfuric acid, copper powder and a copper(II) ammonium sulfate solution are produced. The insoluble copper(I) chloride can be produced by sulfuric acid acidification of a copper(I) ammine chloride solution. If the solution is acidified with hydrochloric acid, a solution of  $[\text{CuCl}_2]^-$ ,  $[\text{CuCl}_3]^{2-}$ , or  $[\text{CuCl}_4]^{3-}$  species is produced, depending on chloride concentration. Copper(I) chloride is stable to water because of its insolubility, which is a result of the polymeric structure that arises from the chloride's ability to bridge copper. This contrasts with the sulfate's inability to coordinate or bridge strongly. Consequently, copper(I) sulfate can be produced only in nonaqueous media.

The electronic structure of the copper(I) ion is  $[\text{Ar}]3d^{10}$ . The compounds are diamagnetic and colorless except where charge-transfer bands arise. Copper(I) is isoelectronic with zinc(II) and the preferred stereochemistries are similar. As a result of the filled  $3d$  level, no ligand field stabilization occurs and electronic distortions are minimized. The stereochemistry around the copper(I) ion is determined mainly by the size of the anions, as well as by the electrostatic and covalent bonding forces. The preferred stereochemistry is tetrahedral, with linear and trigonal planar compounds also being common.

The majority of copper(II) compounds exhibit square planar or distorted octahedral configurations about the copper ion. The  $3d^9$  electronic structure gives rise to the classic example of Jahn – Teller distortion in which the four planar metal – ligand distances are smaller than the two axial distances. Copper(II) ions are also found in distorted tetrahedral and various five-coordinate environments.

The copper(II) ion,  $[\text{Ar}]3d^9$ , is predominantly blue or green, and the unpaired  $3d$  electron results in magnetic phenomena. In most copper compounds, the unpaired electrons of the copper ions are sufficiently isolated from each other so that the compounds exhibit paramagnetic behavior. However, there are many polynuclear copper compounds in which the spins are coupled, which

lowers the magnetic moment. The coupling may be so weak that it must be observed near the absolute zero of temperature, or it may be strong enough to render the compound diamagnetic at room temperature or above.

### 3. Basic Copper Compounds

#### 3.1. Copper(I) Oxide

$\text{Cu}_2\text{O}$  [1317-39-1],  $M_r$  143.09,  $mp$  1235 °C,  $d_4^{25}$  5.8 – 6.2, decomposes above 1800 °C. It occurs in nature as the red or reddish brown mineral cuprite with a cubic or octahedral crystal morphology. Depending on the method of preparation and particle size, the synthetic material is yellow, orange, red, or purple. The yellow material has erroneously been referred to as copper(I) hydroxide, but X-ray diffraction patterns indicate that there are no differences in the crystal structures of the colored forms. Their thermodynamic data are as follows:  $c_p$  (298 K) 429.8 J kg<sup>-1</sup> K<sup>-1</sup>,  $c_p$  (290 – 814 K) 519.2 J kg<sup>-1</sup> · K<sup>-1</sup>,  $c_p$  (290 – 1223 K) 565.2 J kg<sup>-1</sup> K<sup>-1</sup>,  $\Delta H^\circ$  (25 °C) – 166.6 kJ/mol. Copper(I) oxide is stable in dry air but slowly oxidizes to copper(II) oxide [1317-38-0] in moist air. It is practically insoluble in water but dissolves in aqueous ammonia. In excess hydrochloric acid, soluble copper(I) chloride complexes are formed; however, in dilute sulfuric or nitric acids, disproportionation to the soluble copper(II) salts and copper powder results.

**Production.** Copper(I) oxide is produced easily by a variety of methods; its instability with respect to oxidation requires careful consideration. Copper(I) oxide produced pyrometallurgically is usually coated with isophthalic acid or pine oil to preserve its integrity [12]. Hydrometallurgically produced material can be stabilized by mixing the particle slurry with glue, gelatin, casein, or dextrin before drying [13–16].

*Pyrometallurgical Processes.* Copper(I) oxide is formed when copper powder is heated above 1030 °C in air; to prevent further oxidation, it must be cooled quickly in an inert atmosphere. To allow for lower temperature production of copper(I) oxide, carbon can be blended with copper(II) oxide and heated to 750 °C in an inert atmosphere. The material must be stabilized

by coating the formed particles with isophthalic acid or pine oil [12]. A more stable copper(I) oxide results when stoichiometric amounts of copper powder and copper(II) oxide are blended, heated to 800 – 900 °C in an inert atmosphere, and allowed to cool. The production can be effected at lower temperature if ammonia or certain ammonium salts are added to the blend [17–19]. The autoclave oxidation of copper metal at 120 °C and about 0.6 MPa gauge pressure with air in the presence of water and small amounts of sulfuric and hydrochloric acids produces a red, pigment-grade product [20]. By varying the pressure and temperature, considerable differences in particle size, coloring, apparent bulk density, and buoyancy have been found.

*Hydrometallurgical Processes.* Tetraamminedicopper(I) sulfate,  $\text{Cu}_2(\text{NH}_3)_4\text{SO}_4$ , prepared by leaching an excess of copper with a solution of ammonia and ammonium sulfate, with air as the oxidant, yields a red copper(I) oxide upon acidification to pH 3 – 5 [21]. The less corrosive ammonium carbonate leach system in which  $\text{Cu}_2(\text{NH}_3)_4\text{CO}_3$  is produced is more common (see Section Production). Upon vacuum distillation, a very stable red  $\text{Cu}_2\text{O}$  product remains [21]. If sodium hydroxide is added to the leach liquor, a yellow microcrystalline powder is precipitated [22]. When the yellow  $\text{Cu}_2\text{O}$  is heated in an excess of sodium hydroxide, it is converted to an orange material of somewhat larger particle size.

Steam stripping of the copper(I) ammine carbonate solution yields a brown, impure product [23] which can be converted to a red material by washing it in an organic acid, e.g., formic or acetic acid [24]. An impure, brown product can also be converted to a red material by boiling it in 20 % sodium hydroxide solution [25].

If a saturated solution of copper(I) ammine carbonate is agitated over copper metal, a layer of red copper(I) oxide is continuously produced which can be broken loose and recovered [26]. When copper salts are leached with chelating agents such as ethylenediaminetetraacetic acid [27] or ammonia [28] under pressure of carbon monoxide or hydrogen, and sodium hydroxide is subsequently added, a relatively stable, yellow copper(I) oxide is obtained; the reaction is catalyzed by an alkali metal iodide [29].

The reduction of a boiling slurry of basic copper(II) sulfate with sulfur dioxide at a pH of

about 3 produces a reddish product [30]. Red copper(I) oxide has also been prepared by mixing a slurry of basic copper(II) sulfate with neutral copper(II) sulfate and adding sodium sulfite to a pH of 5.2. The mixture is then acidified to pH 3.5 – 5 and heated to boiling. The intermediate copper(I) sulfite slurry is decomposed to copper (I) oxide and sulfurous acid. Alkali is subsequently added to maintain a pH of 2.6 – 2.8 [31].

When a solution of copper(I) chloride and sodium chloride is neutralized with sodium hydroxide and then heated to 138 °C under pressure, a red copper(I) oxide is obtained which has an average particle diameter of about 2.5 μm [32]; an orange product (about 1-μm particles) is prepared by neutralizing the solution to pH 8.5 at 60 °C [33]. Simultaneous mixing of copper(I) chloride solutions with sodium chloride and sodium hydroxide solution in the presence of copper(I) oxide seed crystals at a controlled pH of 10.0, 55 °C, and under nitrogen, gives a reddish purple material (average diameter 48 μm). At pH 7.0, a yellow material is obtained with an average particle size of 0.4 μm [34].

The *electrolytic production* of copper(I) oxide between copper electrodes in brine yields a yellow product at room temperature. At higher temperature, an orange or red material is produced.

**Uses.** The largest commercial use of copper (I) oxide is in antifouling paints for boat and ship bottoms; it is an effective control for barnacles and algae. The yellow or orange copper(I) oxide is used as a seed and crop fungicide, and the red material is used as a pigment in ceramic glazes and glass. Copper(I) oxide is also used in rectifiers and in brazing. Numerous organic reactions are catalyzed by copper(I) oxide, and it is an effective absorbent for carbon monoxide.

**Analysis and Specifications.** The ASTM approved analysis and specification for pigment-grade copper(I) oxide [35] and the military specification for the pigment grade [36] are listed in Table 1.

### 3.2. Copper(II) Oxide

CuO [1317-38-0],  $M_r$  79.54,  $mp$  1330 °C,  $d_4^{25}$  6.48, occurs in nature as the black minerals tenorite (triclinic crystals) and paramelaconite

**Table 1.** Specifications for pigment-grade copper(I) oxide

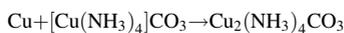
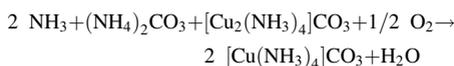
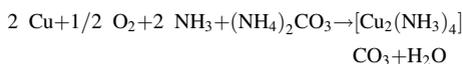
Assay	Mass fraction, %	
	Navy I [36], [37]	Navy II [36]
Copper(I) oxide	97.0	90.0
Total copper (min.)	86.0	80.0
Reducing power (min.)	97.0	90.0
Nitric acid-insolubles (max.)	0.3	0.3
Chloride (max.)	0.4	0.4
Sulfate (max.)	0.1	0.1
Zinc oxide (max.)	–	10.0
Other metals (max.)	0.5	0.5
Acetone-soluble material (max.)	0.5	0.5

(tetrahedral, cubic crystals). Commercially produced copper(II) oxide is usually black, although a brown product (particle size  $< 10^{-6}$  m) can also be produced. Thermodynamic data:  $c_p$  (298 K) 531.1 J kg<sup>-1</sup> K<sup>-1</sup>,  $c_p$  (290 – 1253 K) 682.4 J kg<sup>-1</sup> · K<sup>-1</sup>,  $\Delta H^\circ$  (25 °C) –155.3 kJ/mol. Copper(II) oxide is stable to air and moisture at room temperature. It is virtually insoluble in water or alcohols. Copper(II) oxide dissolves slowly in ammonia solution but quickly in ammonium carbonate solution; it is dissolved by alkali metal cyanides and by strong acid solutions. Hot formic acid and boiling acetic acid solutions readily dissolve the oxide. Copper(II) oxide is decomposed to copper(I) oxide and oxygen at 1030 °C and atmospheric pressure; the reduction can proceed at lower temperature in a vacuum. Hydrogen and carbon monoxide reduce copper(II) oxide to the metal at 250 °C and to copper(I) oxide at about 150 °C. Ammonia gas reduces copper(II) oxide to copper metal and copper(I) oxide at 425 – 700 °C [17].

**Production.** Copper(II) oxide can be prepared *pyrometallurgically* by heating copper metal above 300 °C in air; preferably, 800 °C is employed. Molten copper is oxidized to copper (II) oxide when sprayed into an oxygen-containing gas [37]. Ignition of copper(II) nitrate trihydrate [10031-43-3] at about 100 – 200 °C produces a black oxide. Basic copper(II) carbonate [12069-69-1], when heated above 250 °C, produces a black oxide if a dense carbonate is employed; a brown material is produced when the light and fluffy carbonate is used. An alkali-free oxide can be prepared by ignition of copper (II) carbonate produced from ammonium carbon-

ate and a copper(II) salt solution. Copper(II) hydroxide [20427-59-2], when heated above 100 °C, is converted to the oxide.

*Hydrometallurgy* is the most common method for the production of copper(II) oxide. A solution of ammonia and ammonium carbonate in the presence of air effectively leaches metallic copper; the process is represented by the following reactions:

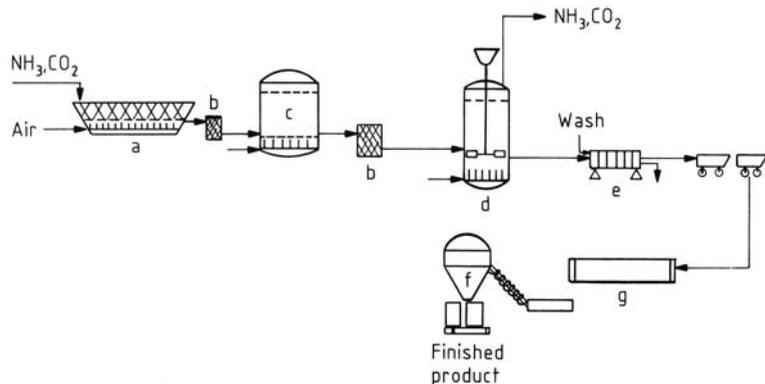


The second and third reactions proceed readily; the first is slow. Consequently, in batch operations the leach is usually begun with a small charge of the copper solution, but continuous operations offer significantly improved rates. The leach liquor is then filtered to remove iron impurities and metallic copper, and is subsequently oxidized by air sparging. If necessary, lead and tin are removed by treatment with strontium, barium, or calcium salts [38–41]. The solution is filtered again and stripped of ammonia and carbon dioxide by steam injection or pressurized boiling to produce a black copper(II) oxide [38]. The ammonia and carbon dioxide are recycled for further use. The process is illustrated in Figure 1. Alternatively, the leach liquor

can be treated with strong alkali to precipitate the intermediate copper(II) hydroxide, and then boiled to remove ammonia, with subsequent decomposition of the hydroxide to the black oxide.

The copper(II) ammine sulfate and chloride systems are treated similarly although they are utilized much less frequently because of their highly corrosive nature. However, the copper ammine chloride system, a byproduct of circuit board etching, is recycled out of economic and environmental necessity to copper(II) oxide [42] (see Chap. 6).

**Uses.** Copper(II) oxide is used as a precursor to a number of copper(II) salts. One of the largest commercial applications is in the production of compounds for wood preservation. Copper(II) oxide is also used extensively as a feed additive and as a pigment in glass, ceramic, and porcelain enamels [43]. In combination with manganese dioxide, it is used as an oxidative catalyst for exhaust gas [44], in the removal of  $\text{NO}_x$ , CO, and  $\text{O}_3$  [45], [46], and in the purification of formaldehyde-containing waste gas [47]. Supported on aluminum phosphate, copper(II) oxide is active in reducing tar and polycyclic hydrocarbons in smoke by absorption and catalytic conversion [48]. Copper(II) oxide is used as a catalyst in the preparation of acrylates [49] and in the production of magnetic storage devices [50]. It has limited application in the petroleum industry as a gas sweetener and is used in welding fluxes for bronze.



**Figure 1.** Process flow diagram for production of copper(II) oxide from ammonia – ammonium carbonate leach a) Leach vat; b) Filter; c) Treatment tank; d) Strip tank; e) Press; f) Bag house; g) Drying kiln

**Table 2.** Typical analysis of commercial copper(II) oxide

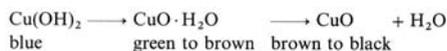
Assay	Mass fraction, %
Copper	78.5
Iron	0.09
Lead	0.08
Water	0.10
Nitric acid-insolubles	0.10
Zinc	0.05
Surface area, m <sup>2</sup> /g	10.0

**Analysis and Specifications.** Electrolytic deposition from a solution or iodometric analysis with sodium thiosulfate is standard for copper determination [51]. The technical specification is shown in Table 2.

### 3.3. Copper(II) Hydroxide

Cu(OH)<sub>2</sub> [20427-59-2], *M*<sub>r</sub>97.54, *d*<sub>4</sub><sup>25</sup>3.37, Δ*H*<sup>o</sup> (25 °C) 446.7 kJ/mol, decomposes over 100 °C or over 50 °C in the presence of an excess of alkali.

Copper(II) hydroxide is virtually insoluble in water (0.003 mg/L), and decomposes in hot water to the more stable copper(II) oxide and water:



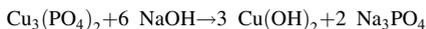
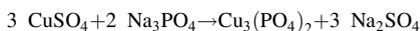
Copper(II) hydroxide is readily soluble in mineral acids and ammonia solution. When freshly precipitated, it is soluble in concentrated alkali, with the formation of [Cu(OH)<sub>3</sub>]<sup>−</sup> or [Cu(OH)<sub>4</sub>]<sup>2−</sup>. Copper(II) hydroxide is inherently unstable but can be kinetically stabilized by a suitable production method.

**Production.** There are two classes of copper(II) hydroxide. The first is stoichiometrically rather precise, with a copper content as high as 64 %; the theoretical copper content of Cu(OH)<sub>2</sub> is 65.14 %. This class is produced by the ammonia process [52–55], which yields a pure product of relatively good stability and large particle size. The best product results from the addition of strong alkali to the soluble copper(II) ammine complex [52], [55]. A relatively large particle-size product, deep blue in color and high in copper content, is precipitated below 35 °C. The resulting mate-

rial is fairly stable or can be coated with gelatin to enhance its stability [56].

In the copper(II) hydroxide made by the ammonia process, the solubility of the copper(II) ammine complexes provides for crystallite growth. This affords a large particle size, a limited surface area (point of dehydration), and hence a relatively stable product, in contrast with the unstable product (variable assay) that results from the addition of hydroxide solutions to copper(II) salt solutions at 20 °C or above. The reaction with hydroxide is diffusion-controlled, allowing essentially no time for crystallite growth. The product is obtained as a gelatinous, voluminous precipitate with a large surface area, which is quite unstable and difficult to wash free of impurities. If the same reaction, with the same order of addition, is allowed to occur at 0 – 10 °C, a product of defined particle size and measurable surface area results, with greater stability but low assay.

The second class of copper(II) hydroxide, which represents a “stable” product but has lower assay and greater impurity, is produced from an insoluble precursor such as basic copper(II) carbonate or copper(II) phosphate. The first stable copper(II) hydroxide of this kind was made from copper(II) phosphate with alternate additions of copper(II) sulfate and sodium hydroxide solutions [57]. The process is illustrated by the following series of reactions:



The alternate copper(II) sulfate – sodium hydroxide addition is continued through 15 or 20 cycles and yields a stable product with 58 – 59 % copper and 3 – 5 % phosphate. The product has a small particle size and a high surface area, and is used as an agricultural fungicide.

Other stable copper(II) hydroxides of high surface area and fine particle size have been produced more recently [58–60]; the processes include the use of a copper(II) oxychloride precursor in the presence of an anionic surfactant [59] or a magnesium sulfate-precipitated precursor [58]. An electrolytically produced material has also been made by using trisodium phosphate as the electrolyte [61].

The classic Bordeaux slurry of copper(II) sulfate and lime in water has been replaced by a powdered stabilized product. This is obtained by mixing copper(II) nitrate solution and lime, adding cellulose pitch liquor (a waste product of the paper industry), and drying to yield a powder which is effective as a fungicide [62]. Sodium carbonate can be used as the precipitating agent instead of lime [63].

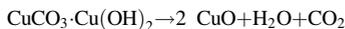
**Uses.** Copper(II) hydroxide is used as an active precursor in the production of copper(II) compounds. Ammonia-processed copper(II) hydroxide is used in the production of copper(II) naphthenate, copper(II) 2-ethylhexanoate, and copper soaps. Ammonia-processed copper(II) hydroxide is also used in the production of rayon (Schweitzer's reagent) and in the stabilization of nylon. Copper(II) hydroxides of the second class are often used as fungicides because of their small particle size. Copper(II) hydroxide is also used as a feed additive, a catalyst in the vulcanization of polysulfide rubber, and an antifouling pigment.

**Analysis and Specifications.** Copper is determined iodometrically with sodium thiosulfate [51]. The analysis of typical ammonia-processed copper(II) hydroxide (mass fractions in %) is copper 63.0, iron 0.05, zinc 0.05, lead 0.05, naphthenic acid-insoluble material 2.0, sulfate 0.3.

### 3.4. Copper(II) Carbonate Hydroxide

Copper(II) carbonate hydroxide, also called basic copper(II) carbonate, occurs in nature as the metastable mineral *azurite* [12070-39-2], also called chessylite, a blue, monoclinic crystalline or amorphous powder with a formula approximating  $2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ,  $M_r$  344.67,  $d_4^{24}$  3.8,  $\Delta H^\circ$  (20 °C)  $-87.4$  kJ/mol, and *malachite* [12069-69-1], green, monoclinic crystals with a formula approximating  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ,  $M_r$  221.12,  $d_4^{25}$  3.9–4.0,  $\Delta H^\circ$  (20 °C)  $-57.7$  kJ/mol. The copper(II) carbonate of commerce, malachite, is also known as Bremen green. Pure copper(II) carbonate,  $\text{CuCO}_3$ , has not been isolated. Copper(II) carbonate is virtually insoluble in water but dissolves readily in aqueous ammonia and alkali metal cyanide solutions. Copper(II) carbonate dis-

solves quickly in mineral acid solutions and warm acetic acid solution, with the formation of the corresponding copper(II) salt. Malachite is much more stable than copper(II) hydroxide but slowly decomposes to the oxide according to the following reaction:



Malachite is rapidly decomposed to the oxide above 200 °C.

**Production.** Two grades of copper(II) carbonate are available commercially, the light and the dense. The light grade is a fluffy product of high surface area. It is precipitated by adding a copper(II) salt solution, usually copper(II) sulfate solution, to a concentrated solution of sodium carbonate at 45–65 °C. Azurite is formed initially, and complete conversion to malachite usually occurs within two hours. The conversion is accelerated by the addition of malachite nuclei to the reactor.

A dark green, dense product results when a copper(II) salt solution is added to a solution of sodium hydrogen carbonate at 45–65 °C; conversion to malachite requires about one hour in this case. The density is maximized if the reactor is washed with acid prior to the precipitation to prevent premature nucleation on malachite nuclei. (A less dense product would be produced if malachite nuclei are added to the slurry of azurite.) Solutions of copper(II) salt and sodium carbonate can also be added simultaneously at a pH of 6.5–7.0 and a temperature between 45 and 65 °C; conversion to malachite is usually complete within one hour.

When a solution of copper(II) ammonium carbonate is boiled, ammonia and carbon dioxide are expelled from the solution, and a deep green, dense copper(II) carbonate precipitates [38].

**Uses.** Copper(II) carbonate is used as a precursor in the production of copper salts and soaps. It is used in animal feeds as a source of copper, in the sweetening of petroleum, and in electroplating for the control of pH. Copper(II) carbonate is used as a hydrogenation catalyst and as an accelerator in polymerization reactions. The light grade is somewhat effective as a fungicide and is used as a seed protectant.

**Table 3.** Typical analysis of commercially available copper(II) carbonate hydroxides

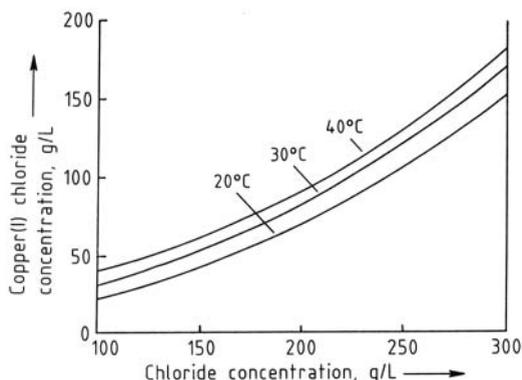
Assay	Mass fraction, %	
	Light	Dense
Copper	55.5	55.0
Sulfate	0.6	0.6
Iron	0.1	0.1
Zinc	0.01	0.02
Lead	0.003	0.005
Hydrochloric acid-insoluble material	0.05	0.05
Water	1.0	2.0

**Analysis and Specifications.** Copper is analyzed by iodometric titration with sodium thio-sulfate solution [51]. Table 3 gives typical analyses of light and dense technical-grade copper (II) carbonates.

## 4. Salts and Basic Salts

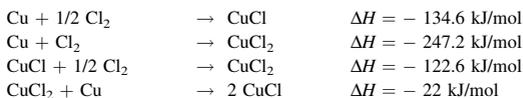
### 4.1. Copper(I) Chloride

Copper(I) chloride [7758-89-6],  $\text{CuCl}$ ,  $M_r$  99.00,  $mp$  422 °C,  $bp$  1367 °C,  $d_4^{25}$  4.14,  $\Delta H^\circ$  (25 °C) – 134.6 kJ/mol, occurs in nature as the colorless or gray cubic-crystal nantokite. The commercially available product is white to gray to green and of variable purity. Copper(I) chloride is fairly stable in air or light if the relative humidity is less than about 50 %. In the presence of moisture and air, the product is oxidized and hydrolyzed to a green product that approaches copper(II) oxychloride,  $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$  [12356-86-4]. In the presence of light and moisture, a brown or blue product is obtained. Copper(I) chloride is slightly soluble to insoluble in water, with values from 0.001 to 0.1 g/L being reported. It is readily hydrolyzed to copper(I) oxide by hot water. Copper(I) chloride is insoluble in dilute sulfuric and nitric acids, ketones, alcohols, and ethers, but it quickly dissolves in hydrochloric acid, alkali halide, or ammonia solutions with the formation of complex compounds that are readily oxidized by air. Copper(I) chloride is soluble in solutions of alkali metal cyanides or thiosulfates and of coordinating amines, pyridines, and nitriles, notably, acetonitrile [64]. The increase in solubility of copper(I) chloride with chloride ion concentration illustrated in Figure 2 [65]. When the

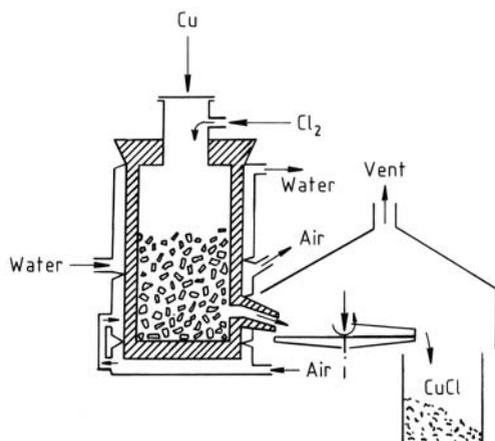
**Figure 2.** Solubility of copper(I) chloride in excess chloride ion solution at different temperatures

chloride concentration is decreased by dilution with water, the pure white copper(I) chloride precipitates.

**Production.** The direct combination of the elements is the most common method of production. The reaction of copper metal and chlorine is not spontaneous at ambient temperature. Once the metal is heated to red heat in the presence of chlorine, the reaction is self-sustaining and requires external cooling to prevent the metal from melting. A number of similar patents exist [66–69] in which copper metal is reacted with chlorine gas to produce a molten copper(I) chloride that is cast and pulverized. The primary difference in conditions is the use of a shaft furnace [66] as opposed to the use of crucibles. The recommended process temperature varies from 450 to 800 °C [66], [67] or 500 to 700 °C [68], [69]. The conditions required for the high-temperature production of a pure copper(I) chloride can be illustrated by the following:

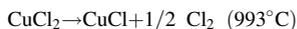


Higher temperature and excessive contact with copper metal favor the production of a very pure copper(I) chloride. The lowest possible temperature is obviously 422 °C, the melting point of copper(I) chloride. As the temperature approaches the decomposition temperature for



**Figure 3.** Crucible used in the production of copper(I) chloride

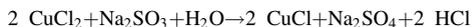
the reaction



a product of higher purity is obtained. Operationally, a temperature between 750 and 900 °C is ideal, and results in a product of > 98 % purity. The process of Degussa [67] illustrates a commonly used commercial process for the high-temperature production of copper(I) chloride; Figure 3 shows a suitable crucible for the production of technical-grade copper(I) chloride. Once the reaction is initiated, chlorine and copper metal (shot, chopped wire, or briquettes) are added continuously. As the molten product is formed on the surface of the upper metal layer, it flows by gravity down through the porous copper bed to effect further reduction of any copper(II) chloride, and out the exit port onto a rotating table where the product is allowed to cool and solidify. The flakes that form are packaged as is or ground to a powder and packaged. Because of the high temperature during the reaction and the volatility of copper(I) chloride, the exit port must be vented to a caustic scrubber. When the molten product is allowed to fall onto a high-speed, horizontally rotating disk constructed of quartz, graphite, or porcelain, small prills of uniform size are produced [70]. The product is spun out onto a water cooled diaphragm and collected. If the copper is contaminated with oxides, hydrogen chloride gas should be added to the chlorine gas stream to prevent the production of basic copper(II) chlorides that would contaminate the product [66].

If the product is packaged quickly and sealed properly, no extreme precautions are required. Otherwise, the product must be stored under nitrogen to preserve its integrity or coated with mineral oil as a barrier to moisture.

Copper(I) chloride is also produced hydro-metallurgically by the reduction of copper(II) in the presence of chloride ions [71]:



Other reducing agents can be used, such as metallic copper, sulfurous acid, hydroxylamine, hydrazine, or phosphorous acid. The copper(I) chloride solution is produced, for example, by mixing a copper(II) chloride solution with metallic copper in the presence of hydrochloric acid or sodium chloride. The colorless to brown solution is stable only in the absence of air. Continuous preparations of copper(I) chloride solutions have been developed [72], [73]. When they are diluted with water, a white crystalline material precipitates which can be vacuum dried or washed with sulfurous acid, then with alcohol and ether, and carefully dried. Zinc has also been used as a reducing agent in a more recent process [74].

Production of copper(I) chloride by treatment of ores with iron(III) chloride solutions [75], [76] and recovery of the product through chlorination in pit furnaces above 800 °C [77] have also been attempted.

**Uses.** Copper(I) chloride is used as a precursor in the production of copper(II) oxychloride and copper(I) oxide, as well as fine copper powder [78]. The production of silicone polymers, the vulcanization of ethylene – propene rubbers (EPDM) [79], and acrylonitrile production are other applications. Copper(I) chloride is also used in the purification of carbon monoxide gas [80–83] and the production of phthalocyanine pigments [84], [85]. More recently, copper(I) chloride has been found to be an effective catalyst in the production of dialkyl carbonates [86–88].

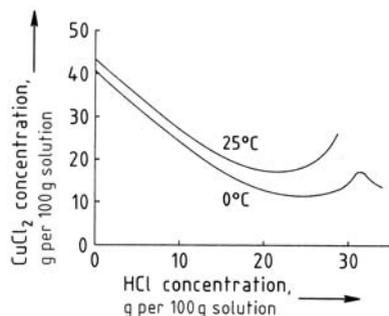
**Analysis and Specifications.** Copper(I) chloride is analyzed according to [51]. Table 4 lists specifications for technical- and reagent-grade material.

**Table 4.** Specifications for copper(I) chloride

Assay	Mass fraction, %	
	Technical-grade	Reagent-grade
Copper (min.)	97.0	90.0
Acid-insolubles (max.)	0.1	0.02
Iron (max.)	0.01	0.005
Sulfate (max.)	0.3	0.10
Arsenic (max.)	–	0.001
Not precipitated by H <sub>2</sub> S as sulfate (max.)	–	0.2

## 4.2. Copper(II) Chloride

Copper(II) chloride [7447-39-4], CuCl<sub>2</sub>, *M<sub>r</sub>* 134.45, *mp* (extrapolated) 630 °C, *d*<sub>4</sub><sup>25</sup> 3.39, begins to decompose to copper(I) chloride and chlorine at about 300 °C. The often reported melting point of 498 °C is actually a melt of a mixture of copper(I) chloride and copper(II) chloride. Decomposition to copper(I) chloride and chlorine is complete at 993 °C. The deliquescent monoclinic crystals are yellow to brown when pure; their thermodynamic data are as follows: *c<sub>p</sub>* (298 K) – 579.2 J kg<sup>-1</sup> K<sup>-1</sup>, *c<sub>p</sub>* (288–473 K) – 621.7 J kg<sup>-1</sup> K<sup>-1</sup>, *c<sub>p</sub>* (288–773 K) – 661.9 J kg<sup>-1</sup> K<sup>-1</sup>, Δ*H*<sup>o</sup> (25 °C) – 247.2 kJ/mol. In moist air, the dihydrate is formed. Figure 4 shows the solubility of copper(II) chloride in water and hydrochloric acid at two temperatures [89]. At higher concentrations of hydrogen chloride, [CuCl<sub>3</sub>]<sup>-</sup> and [CuCl<sub>4</sub>]<sup>2-</sup> complexes are formed. Copper(II) chloride is easily soluble in methanol and ethanol and moderately soluble in acetone.

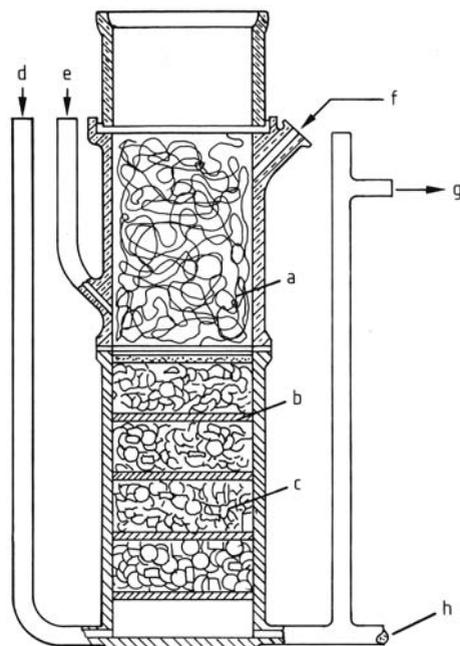
**Figure 4.** Solubility of copper(II) chloride in hydrochloric acid solutions at different temperatures

The more common commercial form of copper(II) chloride is the dihydrate [10125-13-0], CuCl<sub>2</sub> · 2 H<sub>2</sub>O, *M<sub>r</sub>* 170.45, *mp* around 100 °C (with decomposition to the anhydrous form). This occurs in nature as blue-green orthorhombic, bipyramidal crystals of eriochalcite, *d*<sub>4</sub><sup>25</sup> 2.51. Its solubility characteristics are proportionally similar to those of the anhydrous form. In moist air the dihydrate deliquesces, and in dry air it effloresces.

**Production.** Because of the relative stabilities of copper(I) chloride and copper(II) chloride at high temperature, it is improbable that a pure anhydrous copper(II) chloride can be prepared by excessive chlorination of copper in a melt, even though such methods have been reported. The most common method for the production of anhydrous copper(II) chloride is by dehydration of the dihydrate at 120 °C. The product must be packaged in air-tight or desiccated containers.

The dihydrate can be prepared by the reaction of copper(II) oxide, copper(II) carbonate, or copper(II) hydroxide with hydrochloric acid and subsequent crystallization. Commercial production of copper(II) chloride dihydrate uses a tower packed with copper. An aqueous solution is circulated through the tower. Sufficient chlorine is passed into the bottom of the tower to oxidize the copper completely [72], [73]; to prevent hydrolysis [precipitation of copper(II) oxychloride] of concentrated copper(II) chloride solutions, they are kept acidic with hydrochloric acid. The tower can be operated batchwise or continuously; Figure 5 shows the continuous operation. A hot, concentrated liquor is circulated continuously through the tower, and the overflow from the tower is passed through a crystallizer where the liquor is cooled; the product is then centrifuged, dried, and packaged. The addition of hydrogen chloride is pH controlled; the addition of water is controlled by specific gravity. Copper is added daily or twice daily, as needed.

**Uses.** Copper(II) chloride dihydrate is used in the preparation of copper(II) oxychloride [90], [91]. It serves as a catalyst in numerous organic chlorination reactions such as the production of vinyl chloride [92] or 1,2-dichloroethane [93]. Copper(II) chloride dihydrate is used in the textile industry as a mordant and in the petroleum industry to sweeten sulfidic crude oil. Copper(II)



**Figure 5.** Reactor for the production of copper(II) chloride solutions a) Copper metal; b) Porous plates; c) Raschig rings; d) Chlorine inlet; e) Steam inlet; f) Solution recycle; g) Solution to crystallizer; h) Drain

chloride solutions are used for plating copper on aluminum, and in tinting baths for tin and germanium. Copper(II) chloride dihydrate is used as a pigment in glass and ceramics, as a wood preservative, and in water treatment.

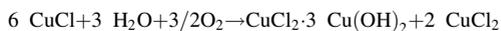
**Analysis and Specifications.** Copper is analyzed iodometrically with sodium thiosulfate [51]. A typical analysis of technical-grade copper(II) chloride dihydrate (mass fractions in %) is as follows: copper(II) chloride dihydrate 99.0 (min.), iron 0.02, zinc 0.05, sulfate 0.05, water-insoluble material 0.01, material not precipitated by hydrogen sulfide as sulfate 0.15.

### 4.3. Copper(II) Oxychloride

Copper(II) oxychloride,  $\text{Cu}_2\text{Cl}(\text{OH})_3$  [1332-65-6],  $M_r$  213.56, is usually written as  $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$ . The trade name is copper oxychloride or basic copper chloride; the internationally accepted name (IUPAC) is dicopper chloride trihydroxide. Copper oxychloride is found in

nature as the minerals paratacamite, green hexagonal crystals, and atacamite, green rhombic crystals,  $d_4^{25} 3.72 - 3.76$  [94]. It is virtually insoluble in water, dissolves readily in mineral acids or warm acetic acid, and is soluble in ammonia and alkali-metal cyanide solutions. The green oxychloride is converted into blue copper(II) hydroxide in cold sodium hydroxide solution [59] and into the oxide in hot sodium hydroxide solution. With a lime suspension, copper oxychloride is converted into the blue calcium tetracuproxochloride, calcium tetracopper(II) chloride tetrahydroxide,  $\text{CaCl}_2 \cdot 4 \text{Cu}(\text{OH})_2$  [95]. It is decomposed to the oxide at 200 °C.

**Production.** Copper(II) oxychloride is most often prepared commercially by air oxidation of copper(I) chloride solutions [90], [91], [96], [97]. For this purpose, a concentrated sodium chloride solution containing about 50 g/L copper(II) is contacted with copper metal to produce a solution containing about 100 g/L copper(I). The copper(I) chloride – sodium copper(I) chloride solution, with or without the copper metal, is then heated to 60 – 90 °C and aerated to effect oxidation:

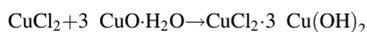


The mother liquor is separated from the precipitate and recycled into the process. The particles that are obtained by the above process are generally less than 4  $\mu\text{m}$  in diameter and are suitable as crop fungicides. The particle size can be reduced further by increasing the agitation during oxidation and by utilizing a lower temperature [96]. Also, spray-drying of the product slurry gives a micronized product [98] as a result of deagglomeration of the material.

Copper(II) oxychloride can also be prepared by reaction of a copper(II) chloride solution with sodium hydroxide [94]:



or by reaction of a copper(II) chloride solution with freshly precipitated, hydrated copper(II) oxide [99]:



Copper oxychloride has also been produced as a byproduct in the electrolytic production of copper(I) chloride [100].

**Uses.** Copper oxychloride is used primarily as a foliar fungicide [90], [101–105]; it is also used as a pigment.

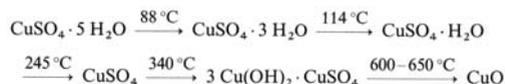
**Analysis and Specifications.** A typical analysis of technical-grade copper(II) oxychloride (mass fractions in %) is as follows: copper 56.0, chloride 14.0 – 15.0, sulfate 2.0 – 2.5, hydroxide 22.5 – 23.5, water 3.0 – 6.0. Copper is analyzed by iodometric titration with sodium thiosulfate [51].

## 4.4. Copper(II) Sulfates

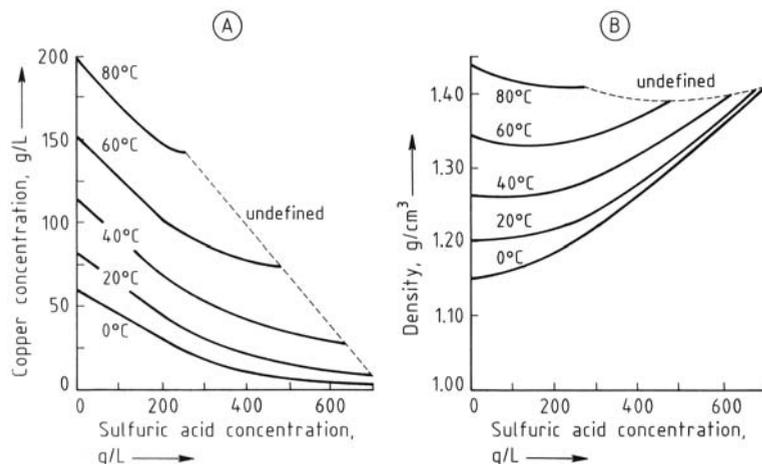
### 4.4.1. Copper(II) Sulfate Pentahydrate

$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  [7758-99-8],  $M_r$  249.61,  $d_4^{25}$  2.285,  $c_p$  (273 – 291 K)  $1126 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $\Delta H^\circ$  (25 °C) – 850.8 kJ/mol, bluestone, blue vitriol, is found in nature as the mineral chalcantite, blue trichlinic crystals that can be ground to a light blue powder. Copper(II) sulfate pentahydrate slowly effloresces in dry air or above 30.6 °C with the formation of the trihydrate,  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ . At 88 – 100 °C the trihydrate is produced more quickly. Thermal anal-

ysis of the pentahydrate gives the following:



Above about 114 °C, the monohydrate is formed, and between about 245 and 340 °C, the anhydrous product  $\text{CuSO}_4$ , results. Figures 6 A and 6 B show solubility of  $\text{CuSO}_4$  in water and density of the solution as a function of temperature and sulfuric acid concentration [106], [107]. The pentahydrate can be crystallized from the solution either by addition of sulfuric acid or by evaporation. Although the addition of sulfuric acid appears to be more economical, the concentration of the solution by evaporation is preferred because the crystals obtained from a “neutral” (pH 3.5 – 4.0) medium are less prone to hard cake formation than the acid crystals. As the particle size of the pentahydrate decreases, the tendency toward hard cake formation increases, and the necessity to increase the pH during crystallization is enforced. When a free-flowing, commercial product of fine particle size is required, such alkaline additives as calcium oxide or calcium stearate must be incorporated into the final product to assure flowability. The incorporation of excess acid into the product accelerates the in situ dehydration of the pentahydrate and promotes



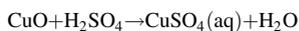
**Figure 6.** Saturated solutions of copper(II) sulfate A. Solubility of copper(II) sulfate (as copper) as a function of sulfuric acid concentration and temperature; B. Density of copper(II) sulfate solutions as a function of sulfuric acid concentration and temperature Reprinted with permission [107]

hard cake formation. Lower temperature and lower humidity slow the caking process.

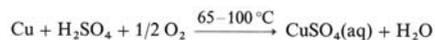
Copper(II) sulfate pentahydrate is soluble in methanol (15.6 g/100 mL solution) but insoluble in ethanol. It readily forms soluble alkaline complexes at sufficiently high concentrations of amines or alkali cyanides (see Chap. 5), but basic sulfates are precipitated from solution by ammonia at an intermediate pH (about 4.2 – 6.8).

Copper(II) sulfate pentahydrate is the most commonly used copper compound because of the economics and the availability of starting materials, the ease of production, and the extent of byproduct utilization (primarily copper electro-winning liquors).

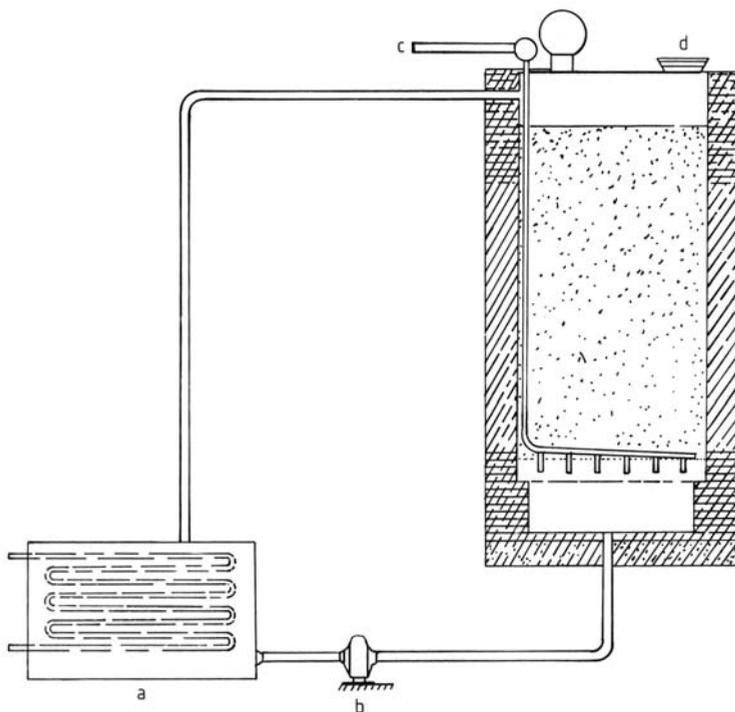
**Production.** Copper(II) sulfate pentahydrate is prepared most easily by the reaction of a basic copper(II) compound with a sulfuric acid solution (100 – 200 g/L  $\text{H}_2\text{SO}_4$ ), e.g.:



Copper metal, sulfuric acid, and air are the most common starting materials for the production of copper sulfate pentahydrate:



*Harike Process.* The Harike process [108] is the best commercial example of the preceding reaction (Fig. 7). Blister shot copper up to 25 mm in diameter is added to the reaction tower (2.9 m<sup>2</sup> cross – sectional area) to give a bed of copper metal 2.74-m high. Two different reaction conditions are given in Table 5. Condition A allows for the production of concentrated copper (II) sulfate solutions and subsequent crystallization from acid media. Condition B gives a concentrated neutral solution of copper(II) sulfate that can be crystallized or diluted with water and used for direct production of other copper products. The rate of oxygen consumption by the



**Figure 7.** Harike tower process for production of copper(II) sulfate solutions a) Heat exchanger; b) Circulation pump; c) Air inlet; d) Copper input

**Table 5.** Production of copper(II) sulfate by the Harike method

	A*	B*
Initial concentration, Cu (g/L)	100	100
H <sub>2</sub> SO <sub>4</sub> (g/L)	160	80
Final concentration, Cu (g/L)	160	160
H <sub>2</sub> SO <sub>4</sub> (g/L)	80	0
Temperature, °C	85	85
Circulation rate, m <sup>3</sup> /h	34 – 45	34 – 45
Air to tower, m <sup>3</sup> h <sup>-1</sup> m <sup>-2</sup>	46	46
Entering oxygen, vol %	20.9	20.9
Exiting oxygen, vol %	2.6	7.3
Oxygen consumed, vol %	90	70
Production rate (CuSO <sub>4</sub> · 5 H <sub>2</sub> O)		
t/m <sup>2</sup> of tower cross section	4.65	3.6
t/tower	13.2	10.3

\* For processes A and B, see text.

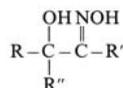
system is directly proportional to the mass of copper metal dissolved. Air flows of 46 m<sup>3</sup> h<sup>-1</sup> m<sup>-2</sup> are used in order to fill with air the voids that are created by the packing of the copper shot. The solution is circulated cocurrently with the air flow to wet the particles continuously and enhance mixing of the solution with the copper metal. If the air flow is decreased and the voids in the copper metal bed are not filled sufficiently, the hot acid solution oxidizes the copper metal in the absence of air with the formation of a copper sulfide film. This film renders the copper metal inert to further oxidation and would lower the efficiency of the tower. On the other hand, an increase in air flow above 46 m<sup>3</sup> h<sup>-1</sup> m<sup>-2</sup> decreases the fraction of oxygen consumed and would also result in a lowered efficiency of the tower. If an increased production (greater oxygen consumption) with good tower efficiencies is required, the height of the tower must be increased. This would also be necessary if a copper metal of lower surface area was used such as scrap copper instead of the blister shot copper. The use of cement copper and fine chopped wire creates insufficient voids for adequate air passage; such fine copper must be leached in agitated vessels.

*Two-Tower Process.* Another commercial method for the preparation of copper(II) sulfate pentahydrate utilizes two towers filled with copper shot. One of the towers is filled with a sulfuric acid solution, whereas the other is sparged with air and steam to oxidize the surface of the copper metal and form a layer of copper(II) oxide. The solution is pumped alternately to the other tower

to dissolve the layer of oxide while the now drained tower is sparged with air and steam. This process is continued until the desired copper(II) sulfate concentration is reached.

*The Trickle Method* is also used commercially: a copper-filled tower is continuously sprayed from the top with leach liquor from an adjacent reservoir. The liquor drains through the tower and is pumped back to the reservoir. Steam and air are sparged continuously into the tower from the bottom. The process is continued until the copper sulfate solution has the desired concentration.

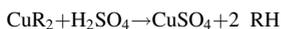
*Solvent Extraction.* Copper(II) sulfate pentahydrate is produced from alkaline ammoniacal copper(II) solutions by solvent extraction [107], [109]. The alkaline copper(II) solution is first contacted with an organic extractant that is selective to copper. One of the most common extractants can be represented by the following general formula:



where R and R' are preferably unsaturated alkyl groups and R'' is preferably hydrogen [110].



The now copper-barren aqueous layer is continuously separated from the copper-containing organic layer which is subsequently contacted with a sulfuric acid solution:



The saturated copper(II) sulfate liquor produced is cooled or concentrated by evaporation to crystallize the pentahydrate. The copper-barren ammonia – ammonium salt solution is continuously returned to the copper leach tank. Figure 8 shows a flow diagram for a typical solvent extraction ammonia leach circuit utilizing mixer – settlers. With the exception of small quantities of wash water and loss of ammonia, the plant produces no effluent. Also, this process allows for lower overall energy input than acid dissolution, primarily as a result of the more facile oxidation



**Table 6.** Typical analysis of copper(II) sulfate pentahydrate

Assay	Mass fraction, %			
	Industrial, granular	Large, medium	Snow, superfine	Powdered
Copper	25.2	25.2	25.2	25.2
Iron	0.008	0.007	0.008	0.17
Silicon dioxide	0.006	—	0.42	—
Water-insolubles	0.008	0.06	0.11	0.11
Calcium oxide	—	—	0.001	0.15
Large crystals:	on 9.5 mm×19.0 mm through 28.6 mm screen;			
Medium crystals:	on 3.2 mm×12.7 mm through 19.0 mm screen;			
Granular crystals	on U.S. 20 mesh through U.S. 6 mesh;			
Industrial crystals:	on U.S. 14 mesh;			
Snow crystals:	through U.S. 18 mesh;			
Superfine crystals:	through U.S. 25 mesh;			
Powdered:	85 % through U.S. 100 mesh			

#### 4.4.2. Anhydrous Copper Sulfate

$\text{CuSO}_4$  [7758-98-7],  $M_r$  159.61, occurs in nature as the mineral hydrocyanite [14567-54-5]. It is gray to white and has a rhombic crystal morphology. It decomposes to the green basic copper(II) sulfate at 340 °C, and at 600 – 650 °C it decomposes to copper(II) oxide. Some of the properties of the anhydrous salt are as follows:  $d_4^{25}$  3.6,  $c_p$  (273 – 291 K) 631.8 J kg<sup>-1</sup> K<sup>-1</sup>,  $c_p$  (273 – 373 K) 657.3 J kg<sup>-1</sup> K<sup>-1</sup>,  $\Delta H^\circ$  (25 °C) – 771.6 kJ/mol. The compound is soluble in water (Section 4.4.1), somewhat soluble in methanol (1.1 g/100 mL), but insoluble in ethanol. It readily dissolves in aqueous ammonia and excess alkali metal cyanides, with the formation of complexes. The material is hygroscopic, with conversion to the pentahydrate in moist air below 30 °C.

The anhydrous salt is prepared by careful heating of the pentahydrate salt to 250 °C. It can also be prepared by the reaction of hot concentrated sulfuric acid with copper metal, but purification is rather difficult.

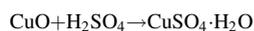
**Table 7.** Specifications of electroless-grade copper(II) sulfate pentahydrate

Assay	Mass fraction, %
Copper	25.1
Iron	<0.0015
Lead	<0.003
Nickel	<0.001
Manganese	<0.0005
Chromium	<0.0005
Chlorine	nil
Water-insolubles	0.01

The compound has limited commercial use, but it can be used as a desiccant for removing water from organic solvents and is a sensitive indicator of the presence of moisture in such solvents.

#### 4.4.3. Copper(II) Sulfate Monohydrate

$\text{CuSO}_4 \cdot \text{H}_2\text{O}$  [10257-54-2],  $M_r$  175.63,  $d_4^{20}$  3.25, is a whitish powder. The solubility of the monohydrate in water is identical to the pentahydrate on a copper basis. The product is hygroscopic and must be packaged in containers with moisture barriers. It is commercially produced by dehydration of the pentahydrate at 120 – 150 °C. A novel preparation is to triturate stoichiometric ratios of copper(II) oxide and sulfuric acid:



The uses of the monohydrate are analogous to those of the pentahydrate. Although there can be slight economic advantages (primarily freight costs) in using the monohydrate, market acceptance has not been great. Presently, less than 5 % (copper basis) of copper(II) sulfate is marketed in the monohydrate form.

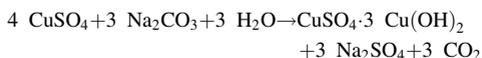
#### 4.4.4. Basic Copper(II) Sulfates

Four distinct basic copper(II) sulfates can be identified by potentiometric titration of a copper(II) sulfate solution with sodium carbonate or

sodium hydroxide solution [115], [116]:  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  (langite),  $\text{CuSO}_4 \cdot 2 \text{Cu}(\text{OH})_2$  (antlerite),  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$  (brochantite), and  $\text{CuSO}_4 \cdot \text{CuO} \cdot 2 \text{Cu}(\text{OH})_2 \cdot x \text{H}_2\text{O}$ . Their unique crystal morphologies are confirmed by X-ray diffraction.

The most important commercial basic copper (II) sulfate, commonly referred to as *tribasic copper sulfate* [12068-81-4], is  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$ ,  $M_r$  452.27,  $mp$  ca. 380 °C (decomp.),  $d_4^{25}$  3.78, occurs in nature as the green monoclinic mineral brochantite. It is readily soluble in mineral acids, acetic acid solution, and ammonia solution; it is insoluble in water. Above 650 °C it decomposes to copper(II) oxide. If anhydrous copper(II) sulfate is heated cautiously to 650 °C, another naturally occurring mineral is obtained, dolerophane,  $\text{CuSO}_4 \cdot \text{CuO}$ , which reacts readily with water at 20 °C to form  $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$  or at 100 °C to form  $\text{CuSO}_4 \cdot 2 \text{Cu}(\text{OH})_2$  [117].

**Production.** Tribasic copper(II) sulfate, the commercially available basic copper(II) sulfate, is most often prepared by the addition of sodium carbonate solution to hot solutions of copper(II) sulfate:

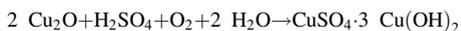


Great variation of particle size can be achieved by control of the precipitation temperature. As the temperature is increased, larger particles with greater bulk density are formed. If a small particle size is desired, lower precipitation temperature should be used. However, as the precipitation temperature is lowered, multiple hydrates and larger amounts of sulfate are incorporated into the product; e.g., around 50 °C, the dried product contains only about 50 % copper. A precipitation temperature around 90 °C is required to make a pure tribasic copper(II) sulfate.

The single largest use of the compound is as a crop fungicide, and small particles are preferred because they give a greater degree of coverage. These small particles can be obtained by high-energy attrition of the product or by carefully controlled precipitation conditions.

Another method of making tribasic copper(II) sulfate is the aeration of a suspension of copper(I)

oxide in the presence of stoichiometric quantities of sulfuric acid or copper(II) sulfate [118]:



A purified, concentrated solution of copper(II) sulfate containing ammonium sulfate can be neutralized to pH 6.0 – 6.5 with ammonia to give a blue precipitate of approximate stoichiometry  $4 \text{CuSO}_4 \cdot 12 \text{Cu}(\text{OH})_2 \cdot 5 \text{H}_2\text{O}$ . When this is dried, a green tribasic copper(II) sulfate is formed with up to 1 mol of hydration water per mole of tribasic salt [119]; the water content depends on the drying temperature.

A continuous process has been developed in which copper(II) sulfate solutions are neutralized to pH 5.9 at 30 °C by addition of gaseous ammonia to an agitated vessel [120]. A unique, germicidally active, basic copper(II) sulfate whose X-ray diffraction pattern differs from langite and brochantite has been prepared in this way [121].

Reaction of copper(II) sulfate with  $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$  and sodium hydroxide in aqueous solution gives a fine, blue, basic copper(II) sulfate powder (16 %  $\text{SO}_4$ , 2.6 %  $\text{PO}_4$ , and 54.9 % Cu) that is formulated into a germicidal powder.

Tribasic copper(II) sulfate can also be prepared by cautiously heating copper(II) sulfate to 340 °C or by the aeration of a hot copper(II) sulfate solution in contact with copper metal.

Other basic copper(II) sulfates of commercial interest are the classic fungicidal mixtures, Bordeaux and Burgundy slurries, in which copper(II) sulfate solution is mixed with lime and soda ash, respectively. They are of variable stoichiometry. More recently, the aqueous Bordeaux suspension has been dried to yield a stable basic copper(II) sulfate powder of variable composition [122].

**Uses.** As stated earlier, basic copper(II) sulfate is primarily used as a crop fungicide [123], [124]. It has also been utilized as a precursor in the separation of copper from metallic impurities [125].

**Analysis and Specifications.** The analysis of a typical technical-grade tribasic copper(II) sulfate is (mass fractions in %) as follows: copper

53.5, iron 0.08, sulfate 19.0, carbonate 2.0, water 2.0 – 5.0. This is analyzed according to [51].

## 5. Compounds and Complexes of Minor Importance

### 5.1. Copper Compounds

**Copper(I) Acetate** [598-54-9],  $\text{CuCH}_3\text{COO}$ ,  $M_r$  122.6, is obtained as white crystals which are stable when dry but decompose on exposure to water. The product is obtained by reducing an ammoniacal solution of copper(II) acetate; on acidification with acetic acid, the crystals precipitate. Ammoniacal solutions of copper(I) acetate are used commercially to absorb olefins.

**Copper(II) Acetate Monohydrate** [6046-93-1], neutral verdigris,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ ,  $M_r$  199.65,  $mp$  115 °C,  $d_4^{25}$  1.88, decomposes at 240 °C; it forms dark green, monoclinic crystals; its solubility in water at 25 °C is 6.8 g/100 g solution; the compound is slightly soluble in methanol, diethyl ether, and acetone.

Copper(II) acetate monohydrate is produced by the reaction of copper(II) carbonate or copper(II) hydroxide with a solution of acetic acid or by the reaction of copper(II) oxide with hot dilute acetic acid. Alternatively, the material can be made by refluxing aqueous acetic acid in the presence of copper metal and air. The technical product is generally 99% pure.

Copper(II) acetate monohydrate is used in textile dyeing and as a ceramic pigment. It is used as a fungicide, as a precursor in the production of Paris green [copper(II) acetoarsenite], and as a polymerization catalyst in organic reactions.

**Copper(II) Acetate, Basic** [52503-63-6],  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{CuO} \cdot 6 \text{H}_2\text{O}$  (variable),  $M_r$  369.26, exists as blue to green salts, depending on the amount of water of hydration. Blue verdigris has the above formula, while green verdigris has fewer molecules of water of hydration. The salts are slightly soluble in water or ethanol, and soluble in dilute mineral acid or aqueous ammonia.

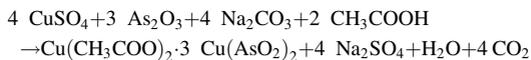
The basic salts are produced by neutralizing copper(II) acetate solutions. They can also be

prepared by refluxing acetic acid over copper in the presence of air until the basic salt precipitates.

The basic copper(II) acetates are used as precursors in the manufacture of Paris green [copper(II) acetoarsenite] and as fungicides. They are used as pigments in oil- and water-based paints and in textile dyeing.

**Copper(II) Acetoarsenite** [12002-03-8], (acetato)trimetaarsenitodicopper(II),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3 \text{Cu}(\text{AsO}_2)_2$  (variable),  $M_r$  1013.77, also known as Paris green, is an emerald green, poisonous powder. It is virtually insoluble in water and ethanol but dissolves in dilute mineral acids and aqueous ammonia.

Copper(II) acetoarsenite is primarily made by the reaction of a solution of copper(II) sulfate with arsenic(III) oxide, sodium carbonate, and acetic acid



or by the reaction of copper(II) oxide with a hot solution of acetic acid and arsenic(III) oxide. A solution of copper(II) acetate or a suspension of basic copper(II) acetate can also react with arsenic(III) oxide. The product is used as an insecticide, in the preservation of wood, and as an antifouling pigment.

**Copper(II) Arsenate** [7778-41-8],  $\text{Cu}_3(\text{AsO}_4)_2 \cdot 4 \text{H}_2\text{O}$  (variable),  $M_r$  540.52, is a blue-green to blue insoluble powder. It is most often prepared by reaction of copper(II) sulfate solutions with arsenic(V) oxide and sodium hydroxide. Copper(II) arsenate is used as an insecticide, fungicide, rodenticide, wood preservative, and antifouling pigment.

**Copper(II) Arsenite**,  $\text{CuHAsO}_3$  (variable),  $M_r$  187.47, Scheele's green, an insoluble green powder, is prepared by the reaction of a copper(II) sulfate solution with arsenic(III) oxide and sodium hydroxide and is used as pigment and insecticide.

**Copper(I) Bromide** [7787-70-4],  $\text{CuBr}$ ,  $M_r$  143.45,  $mp$  504 °C,  $bp$  1345 °C,  $d_4^{25}$  4.72, forms white cubic crystals that slowly decompose on exposure to light or to moist air; it is soluble in hydrochloric and hydrobromic acids and in

aqueous ammonia, but very slightly soluble in water. This compound is prepared pyrometallurgically [see copper(I) chloride, Section 4.1] or by reducing a copper(II) sulfate solution in the presence of sodium bromide, usually with sulfur dioxide or metallic copper. Copper(I) bromide is used as a polymerization catalyst for organic reactions.

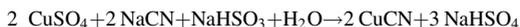
**Copper(II) Bromide** [7789-45-9],  $\text{CuBr}_2$ ,  $M_r$  223.36,  $mp$  498 °C,  $d_4^{25}$  4.77, crystallizes from warm solution as black, deliquescent, monoclinic crystals. Below 29 °C, the green tetrahydrate,  $\text{CuBr}_2 \cdot 4 \text{H}_2\text{O}$ , results. The anhydrous product is very soluble in water (55.7 g/100 g solution) and soluble in ethanol and acetone. It is insoluble in diethyl ether, benzene, or concentrated sulfuric acid. Copper(II) bromide is most conveniently prepared by dissolving copper(II) oxide in hydrobromic acid; it can also be prepared by the direct action of bromine water on metallic copper. Copper(II) bromide is used as a brominating reagent and catalyst in organic synthesis and as an intensifier in photography.

**Copper(II) Chromate(VI)** [13548-42-0],  $\text{CuCrO}_4$ ,  $M_r$  179.55, is obtained as reddish brown crystals. Numerous insoluble basic salts can be formed from solutions. Neutral copper(II) chromate is prepared by direct heating of a mixture of copper(II) oxide and chromium(VI) oxide. It decomposes around 400 °C, with the formation of copper(II) chromate(III). Copper(II) chromate (VI) is used in wood preservation and in the weatherproofing of textiles.

**Copper(II) Chromate(III)** [12018-10-9],  $\text{CuCr}_2\text{O}_4$ ,  $M_r$  231.56, forms black, tetragonal crystals which are insoluble in water. It is prepared by heating neutral copper(II) chromate(VI) to 400 °C. Copper(II) chromate(III) is used as a hydrogenation catalyst.

**Copper(I) Cyanide** [544-92-3],  $\text{CuCN}$ ,  $M_r$  89.56,  $mp$  474 °C (in nitrogen),  $d_4^{25}$  2.92, is usually a white to cream-colored powder, which is practically insoluble in water, cold dilute acids, and ethanol, but dissolves in ammonia and alkali cyanide solutions with the formation of complexes. Copper(I) cyanide is produced by the addition of an alkali cyanide and sodium hydro-

gensulfite to a solution of copper(II) sulfate:



Copper(I) cyanide is very poisonous and must be handled cautiously. It is used in electroplating and in organic reactions as a polymerization catalyst or as a means of introducing the cyanide moiety. Copper(I) cyanide has also been used as an antifouling pigment for marine paints and is an active fungicide and insecticide.

**Copper(II) Formate** [544-19-4],  $\text{Cu}(\text{HCOO})_2$ ,  $M_r$  153.58,  $mp$  ca. 200 °C (decomp.),  $d_4^{25}$  1.831, is soluble in water and slightly soluble in ethanol. The reaction of copper(II) oxide, carbonate, or hydroxide with formic acid is used to prepare the product. The most common commercial form, a royal blue material, is prepared by crystallization from water at 75 – 85 °C. A metastable dihydrate is produced by crystallization at 50 – 60 °C. Copper(II) formate tetrahydrate is prepared by crystallization from cool solutions. Copper(II) formate is used to prevent bacterial and mildew growth in cellulosic materials.

**Copper(II) Gluconate** [527-09-3],  $\text{Cu}(\text{C}_6\text{H}_{11}\text{O}_7)_2$ ,  $M_r$  453.85, forms light blue to blue-green crystals from water; it is soluble in water and slightly soluble in ethanol. Copper(II) gluconate is prepared by the reaction of gluconic acid solutions with basic copper(II) carbonates or copper(II) hydroxide. It is used as a dietary supplement for copper deficiency and in mouth deodorants or breath fresheners.

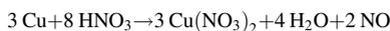
**Copper(I) Iodide** [7681-65-4],  $\text{CuI}$ ,  $M_r$  190.49,  $mp$  605 °C,  $bp$  1290 °C,  $d_4^{25}$  5.62, occurs in nature as the mineral marshite, white to reddish brown cubic crystals. It is virtually insoluble in water but dissolves in ammonia solution, alkali iodide and cyanide solutions, and dilute hydrochloric acid. Copper(I) iodide is manufactured pyrometallurgically by the reaction of hot copper with iodine vapor. Alternatively, copper(II) salt solutions are reacted with alkali iodides to precipitate copper(I) iodide.

Copper(I) iodide is used as a heat and light stabilizer in polymers, photographic emulsions, and light-sensitive papers, and in oil drilling to

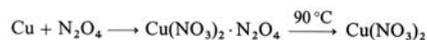
aid in corrosion inhibition in highly acid environments. It is also used as a feed additive, in cloud seeding, and as a double salt with mercury (II) iodide as a temperature indicator.

**Copper(II) Nitrate Trihydrate** [10031-43-3],  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ ,  $M_r$  241.59,  $mp$  114.5 °C,  $d_4^{25}$  2.32, is a blue, deliquescent salt that crystallizes as rhombic plates. It is very soluble in water (77.4 g/100 g solution) and ethanol. When crystallized from solution below the transition point (26.4 °C), the hexahydrate is produced,  $\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  [13478-38-1],  $M_r$  295.64,  $mp$  26.4 °C (with loss of 3 mol of water of hydration),  $d_4^{25}$  2.07, blue, deliquescent, prismatic crystals. The anhydrous nitrate is not produced by heating the hydrates; instead, decomposition to the basic copper(II) nitrate [12158-75-7],  $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$ , begins around 80 °C. Conversion to copper(II) oxide is complete at 180 °C.

Copper(II) nitrates are obtained by dissolving copper(II) oxide, basic copper(II) carbonate, or copper(II) hydroxide in nitric acid solution. The various hydrate crystals obtained depend on the conditions of crystallization. Basic copper(II) nitrate can be precipitated directly from solution by neutralization. Copper(II) nitrate salts are often produced by dissolving copper metal in nitric acid solution. The reaction is vigorous, and oxides of nitrogen are evolved:



The second reaction is favored by a lower temperature and dilute acid. Anhydrous copper (II) nitrate [3251-23-8] can be produced in ethyl acetate:



It is not available commercially.

The hydrates of copper(II) nitrate are used in the textile industry as oxidants and mordants in dyeing. They are used to prepare a copper(II) oxide of high surface area, which is useful as a catalyst in numerous organic reactions. The nitrate salts are used as colorants in ceramics, in the preparation of light-sensitive papers, and in the

burnishing of iron, as well as the browning of zinc and brightening of aluminum. They are also used in pyrotechnics and as an oxidative component in solid rocket fuels.

**Copper(II) Oxalate** [814-91-5],  $\text{CuC}_2\text{O}_4$ ,  $M_r$  151.56, is a blue-white powder, which is very slightly soluble in water. Copper(II) oxalate is prepared by precipitation from a mixture of a copper(II) salt and sodium oxalate solution. The product is used as a stabilizer for acetylated polyformaldehyde and as a catalyst in organic reactions.

**Copper(II) Phosphate Trihydrate** [7798-23-4],  $\text{Cu}_3(\text{PO}_4)_2 \cdot 3 \text{H}_2\text{O}$ ,  $M_r$  434.61, is a light blue powder which is insoluble in cold water, slightly soluble in hot water, and soluble in ammonia solution and mineral acids. This compound is prepared by reaction of copper(II) sulfate solution with soluble alkali phosphates; it precipitates as a voluminous, almost gelatinous, product. Copper(II) phosphate trihydrate is used as a fungicide and corrosion inhibitor.

**Copper(II) Diphosphate Hydrate** [10102-90-6],  $\text{Cu}_2\text{P}_2\text{O}_7 \cdot x \text{H}_2\text{O}$  (variable), has the following typical analysis: Cu 33 – 36 %,  $\text{P}_2\text{O}_7$  45 – 49 %. Copper(II) pyrophosphate is a light blue powder which is insoluble in water, but soluble in solutions containing an excess of diphosphate. It is prepared by the precipitation reaction of solutions of copper(II) sulfate and alkali diphosphate. Solutions are used for plating copper on plastics, aluminum, and zinc.

**Copper(II) Selenide** [1317-41-5],  $\text{CuSe}$ ,  $M_r$  142.5,  $mp$  not defined,  $d_4^{25}$  6.0, decomposes at dull red heat; it is insoluble in water but dissolves in hydrochloric acid with evolution of  $\text{H}_2\text{Se}$ . Copper(II) selenide is prepared by reducing copper (II) selenite with hydrazine. It is used as a catalyst in the digestion of organic chemicals by the Kjeldahl method.

**Copper(II) Soaps** are water-insoluble copper salts of long-chain fatty acids. They are usually sold as 6 – 10 % copper solutions in a kerosene diluent. The copper(II) soaps are commonly prepared by direct reaction of the fatty acid with copper(II) hydroxide or basic copper(II) carbonate in an organic diluent, or by precipitation from

aqueous media when copper(II) sulfate solution is mixed with the sodium salt of the respective fatty acid. The common commercially available soaps, concentrations, and uses follow.

*Copper (II) naphthenate* [1338-02-9] contains 8 % copper and is used as a mildewcide in textiles, woods, and paints, and to prevent barnacle growth on ship bottoms.

*Copper (II) oleate* (9-octadecenoate) [1120-44-1],  $M_r$  626.43, contains between 6 and 9 % copper, and is used as a combustion improver in fuel oils, as an emulsifier and dispersant, and as an antifouling coating for fish nets and lines.

*Copper (II) stearate* (octadecanoate) [660-60-6],  $M_r$  630.46, contains 10 % copper, and is used in antifouling paints and in the preservation of wood and textiles.

**Copper(I) Sulfide** [22205-45-4],  $\text{Cu}_2\text{S}$ ,  $M_r$  159.15,  $mp$  1100 °C,  $d_4^{25}$  5.6, occurs in nature as the mineral chalcocite [21112-20-9], blue to gray rhombic crystals, also known as copper glance. It has a lustrous metallic look. Copper(I) sulfide is virtually insoluble in water, but is soluble with decomposition in nitric acid and concentrated sulfuric acid, and soluble in alkali cyanide solution through complex formation. It is decomposed to copper(II) oxide, copper(II) sulfate, and sulfur dioxide by heating in air, and to copper(II) sulfide and copper by heating in the absence of air. Copper(I) sulfide is prepared by heating copper and sulfur in a hydrogen atmosphere or by precipitation with hydrogen sulfide from an ammoniacal copper(II) salt solution. It is used in luminous paints, lubricants, solar cells, thermoelements, and semiconductors.

**Copper(II) Sulfide** [1317-40-4],  $\text{CuS}$ ,  $M_r$  95.60,  $d_4^{25}$  4.6, decomposes at 220 °C and occurs in nature as the mineral covellite [19138-68-2], as blue-black hexagonal or monoclinic crystals. It is virtually insoluble in water, but soluble in alkali cyanides and in ammonia solution with complex ion formation. This compound is decomposed by hot nitric acid. It is stable in dry air, but is slowly oxidized to copper(II) sulfate in moist air. Copper(II) sulfide can be prepared by melting an excess of sulfur with copper(I) sulfide or by precipitation with hydrogen sulfide from a

solution of anhydrous copper(II) chloride in anhydrous ethanol. It is used in the dye industry for the preparation of aniline black dyes and as an antifouling pigment.

**Copper(II) Tetrafluoroborate** [38465-60-0],  $\text{Cu}(\text{BF}_4)_2$ ,  $M_r$  237.15, is prepared commercially by the neutralization of tetrafluoroboric acid with copper(II) hydroxide or basic copper(II) carbonate. It is generally produced as a concentrated solution and is used in the production of printed circuits and in copper plating.

**Copper(I) Thiocyanate** [1111-67-7],  $\text{CuSCN}$ ,  $M_r$  121.62,  $mp$  1084 °C (under nitrogen),  $d_4^{25}$  2.84, is a white to yellow amorphous powder, which is very slightly soluble in water and dilute mineral acids, and soluble in ammonia solution, alkali thiocyanate solutions, and diethyl ether. It is stable to dry air but slowly decomposes in moist air. The material is prepared by reacting a copper(I) chloride solution with an alkali metal thiocyanate at 80 – 90 °C. The recovered product is dried under nitrogen. Copper(I) thiocyanate is used as an antifouling pigment.

## 5.2. Copper Complexes

Copper(I) and copper(II) ions form many stable complexes with halides, amines, azo compounds, cyanides, and other complexing media. This, in part, accounts for the fact that more X-ray crystal structures have been determined for copper complexes than for any other first-row transition metal ion. Many of these complexes are of great commercial significance. The dissociation constants for a number of copper complexes are given in Table 8.

**Copper Ammine Complexes.** Copper(II) salts form complexes of the type  $[\text{Cu}(\text{NH}_3)_n]^{2+}$  where  $n = 1 - 5$ . The pentaammine complex is favored only in concentrated ammonia solution (Table 8). The hexaammine complex is formed only in anhydrous ammonia. The tetraammine complex of copper(II) is favored at low ammonia concentrations. For the copper(I) complexes of ammonia, the diammine complex is favored. Tetraammine copper(II) hydroxide,  $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ , Schweizer's reagent, is used in the dissolution of cellulose and in the production

**Table 8.** Dissociation constants of copper(I) and copper(II) complexes ( $pK = -\log K$ )

Complex ion	Dissociation products	$pK$
$[\text{CuCl}_3]^-$	$\text{CuCl} + 2 \text{Cl}^-$	-2.0
$[\text{CuCl}_2]^-$	$\text{Cu}^+ + 2 \text{Cl}^-$	4.7
$[\text{CuBr}_2]^-$	$\text{CuBr} + \text{Br}^-$	-3.3 to -2.3
$[\text{CuBr}_2]^-$	$\text{Cu}^+ + 2 \text{Br}^-$	5 to 6
$[\text{Cu}(\text{CN})_3]^{2-}$	$[\text{Cu}(\text{CN})_2]^- + \text{CN}^-$	11.3
$[\text{Cu}(\text{CN})_2]^-$	$\text{Cu}^+ + 2 \text{CN}^-$	16
$[\text{Cu}(\text{NH}_3)_2]^+$	$\text{Cu}^+ + 2 \text{NH}_3$	10.8
$[\text{Cu}(\text{NH}_3)]^{2+}$	$\text{Cu}^{2+} + \text{NH}_3$	4.1
$[\text{Cu}(\text{NH}_3)_2]^{2+}$	$\text{Cu}^{2+} + 2 \text{NH}_3$	3.5
$[\text{Cu}(\text{NH}_3)_3]^{2+}$	$\text{Cu}^{2+} + 3 \text{NH}_3$	2.9
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\text{Cu}^{2+} + 4 \text{NH}_3$	2.1
$[\text{Cu}(\text{NH}_3)_5]^{2+}$	$\text{Cu}^{2+} + 5 \text{NH}_3$	-0.5
$[\text{CuCl}_4]^{2-}$	$[\text{CuCl}_3]^- + \text{Cl}^-$	0.01
$[\text{CuCl}_3]^-$	$\text{CuCl}_2 + \text{Cl}^-$	0.06
$\text{CuCl}_2$	$\text{CuCl}^+ + \text{Cl}^-$	0.4
$\text{CuCl}^+$	$\text{Cu}^{2+} + \text{Cl}^-$	1
$[\text{Cu}(\text{OH})_4]^{2-}$	$[\text{Cu}(\text{OH})_3]^- + \text{OH}^-$	0.9
$[\text{Cu}(\text{OH})_3]^-$	$\text{Cu}(\text{OH})_2 + \text{OH}^-$	-5

of rayon ( $\rightarrow$  Cellulose). Copper(I) diammine salt solutions are used in the absorption of olefins and carbon monoxide. Many copper circuit boards are etched with ammoniacal ammonium salt solutions; copper ammine solutions, which can be used in the production of copper compounds, are byproducts of this process.

**Copper Chloride Complexes.** Copper(I) and copper(II) ions form complexes with hydrochloric acid or soluble metal chlorides. Dilute solutions of copper(II) chloride are blue. As the chloride concentration increases, the color of the solution shifts toward green, intensifying as the concentration of the distorted tetrahedral  $[\text{CuCl}_4]^{2-}$  ion increases. Copper(II) compounds have been isolated that contain either the  $[\text{CuCl}_4]^{2-}$  anion or the  $[\text{CuCl}_3]^-$  anion, e.g.,  $\text{CsCuCl}_4$  and  $\text{KCuCl}_3$ , respectively.

The insoluble copper(I) chloride can be solubilized by chloride-containing solutions, with the formation of the  $[\text{CuCl}_2]^-$  ion. The benzene-insoluble copper(I) chloride dissolves readily in the presence of anhydrous aluminum chloride, with formation of the  $\text{Al}[\text{CuCl}_4]$  complex. In acetonitrile, copper(I) chloride is solubilized with the formation of the isolable  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{Cl}$  complex.

**Copper(I) Cyanide Complexes.** Alkali cyanides readily dissolve copper(I) cyanide, with

the formation of  $[\text{Cu}(\text{CN})_2]^-$  and  $[\text{Cu}(\text{CN})_3]^{2-}$  complexes. Solutions of the complexes are of great importance in the electroplating industry because of their versatility. From saturated copper and sodium cyanide baths, crystals of the double salt  $\text{Na}_2\text{Cu}(\text{CN})_3 \cdot 2 \text{H}_2\text{O}$  can be obtained readily.

**Other Copper Complexes of Industrial Significance.** Solvent extraction of copper(II) ions relies on the ability of copper to form complexes and to break those complexes as a function of pH [110], [126], [127]. The most common reagents used commercially are substituted salicylaldehydes, 1,8-hydroxyquinolines, and  $\alpha$ -hydroxyoximes.

Copper(II) is solubilized in alkaline media by complex formation with tartrates for use as Fehling's solution, which is utilized in the analysis of reducing sugars. Copper(II) bis(1,8-dihydroxyquinoline) is used as a textile fungicide and as a pigment. Copper phthalocyanines [128], [129] are exceptionally stable blue and green pigments, as are the azo dye complexes of copper ( $\rightarrow$  Azo Dyes, 3. Direct (Substantive) Dyes;  $\rightarrow$  Phthalocyanines).

## 6. Copper Reclamation

The reclamation or recycling of copper wastes and byproducts is environmentally imperative and, in many cases, economically sound. Better technologies have been developed to produce useful materials from wastes and byproducts, many of which are now considered hazardous wastes. The establishment of the Resource Conservation and Recovery Act (RCRA) by the EPA defined procedures to assure proper disposal or reclamation of hazardous wastes [130]. However, no distinction is made between waste buried in an approved landfill and waste recovered as useful products. Unfortunately, in many cases this encourages the burial of recyclable waste materials.

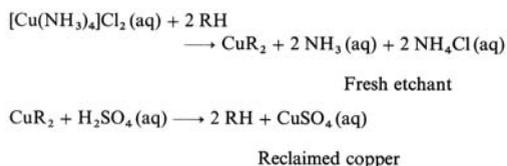
The largest sources of reclaimable byproduct copper are the electronics and plating industries, as well as spent electrowinning baths [113]. Electrowinning baths are most often crystallized (Section 4.4.1) or precipitated as tribasic copper (II) sulfate for use in agriculture.

In the manufacture of circuit boards, a copper laminate is selectively dissolved (etched). This

dissolution process yields the desired circuit board and a byproduct copper solution, the spent etchant. The earliest etching solutions used iron (III) chloride – hydrogen chloride or chromium trioxide – sulfuric acid solutions which were difficult to recycle. Later, the sulfuric acid etchants that used hydrogen peroxide [131], [132] or persulfate [133–135] as oxidants were developed. Recycling of the copper is achieved through crystallization, precipitation [135], ion exchange [136], or cementation [137], [138]. Alkaline etchants utilized a mixture of ammonia and ammonium sulfate with persulfate as the oxidant [139] or a mixture of ammonia and ammonium chloride with chlorite as the oxidant [140]. The primary etchants used today are the ammonia – ammonium chloride system with air as the oxidant and the hydrochloric acid system with stabilized hydrogen peroxide as the oxidant [141].

Copper is recovered from the acid chloride etchants (1) by neutralization and precipitation of copper(II) oxochloride or copper(II) oxide [42]; (2) by reduction with sodium hydrogen-sulfite, for example, to precipitate copper(I) chloride which can then be converted to copper(I) oxide by sodium hydroxide treatment [142]; or (3) by cementation with scrap iron [143]. From the alkaline etchants, copper is recovered (1) by distillation to strip ammonia and precipitate copper(II) oxide [144]; (2) by addition of base to precipitate copper(II) hydroxide, followed by steam stripping of the ammonia [145]; (3) by reduction to copper with formaldehyde [146] or  $\text{Na}_2\text{S}_2\text{O}_4$  [147]; or (4) by electrolysis [148].

One of the more elegant methods for the recovery of copper from ammonia – ammonium chloride etchants utilizes solvent extraction [149] (Fig. 8). Not only is the copper recovered, but the etchant is simultaneously regenerated:



where R is an  $\alpha$ -hydroxyoxime as shown in.

The copper can be further reclaimed by crystallization or electrowinning.

## 7. Copper and the Environment

The reclamation of copper byproducts and wastes and the regulation of plant effluents and sanitary waters have resulted in lower indiscriminate release of copper into natural waters [150]. Where large quantities of copper in high concentration exist (see Chap. 6), recovery of the copper can, in many cases, be economical. Regulations have been established to control or limit altogether the introduction of copper into waters [151–155]. The Federal Water Pollution Control Act Amendments of 1972 set up a comprehensive program to “restore and maintain the chemical, physical, and biological integrity of the nation’s waters” [151].

Limitations of copper in drinking water have also been established: the World Health Organization recommends 0.05 – 1.5 mg/L [156]. No specific drinking water standards for copper have been established by the Environmental Protection Agency [157].

A variety of technologies presently exist for the removal of copper from wastewaters and drinking water [158], [159]. The most common treatment methods include direct precipitation [151–153], [160–163] or electrolysis [164], [165].

Although copper is toxic in exceedingly low concentrations to certain lower life forms, notably fungi and algae, it is a necessary constituent of higher plants and animals (see, however, Chap. 9). Copper plays a necessary role as an oxidation catalyst and oxygen carrier, probably second only to iron in importance [166]. Copper aids plants in photosynthesis and other oxidative processes. In higher animals, it is responsible for oxidative processes and is present in many proteins such as phenolase, hemocyanin, galactose oxidase, superoxide dismutase, ceruloplasmin, tyrosinase, monoamine oxidase, and dopamine  $\beta$ -hydroxylase [167], [168].

Copper compounds are regularly applied for their nutrient value to agricultural crops in European countries [169–171]. In the United States, more emphasis is now being placed on the value of copper as a nutritional feed additive [169], [172], [173]: it increases the rate of gain and feed efficiencies of the animals. The increased use of copper as a feed additive has caused concern about the environmental impact of high levels of copper in manure [174], [175]. The approved

**Table 9.** Maximum copper levels in Western European animal feeds

Use	Total copper, mg/kg
Fattening pigs, up to 16 weeks	175
Fattening pigs, 17th week to 6th months	100
Fattening pigs, over 6 months	50
Breeding pigs	50
Calves, fed milk-based products	30
Calves, other feeds	50
Sheep	20
Other animals	50

maximum total copper content in animal feeds for Western European countries is shown in Table 9 [169].

The largest single application of copper compounds is as an agricultural fungicide (see Chap. 8). Although copper is a necessary constituent of higher plants and animals, it is highly toxic to certain fungi. In human medicine, the importance of copper as a nutrient in proper development and growth is receiving increased study [167], [176]. Also, copper is being used in the production of new copper antibiotics and copper anti-inflammatory drugs [176]. The recommended daily requirement of copper is as follows [176]:

Humans	2.5 – 5.0 mg
Cattle	50 – 70 mg
Horses	50 – 60 mg
Sheep	10 – 15 mg
Swine	10 – 20 mg

## 8. Economic Aspects

The world's production of copper compounds represents less than 2 % of the total production of primary metal [65]. In 1974,  $7.65 \times 10^6$  t of primary copper was produced, with 1.3 %

**Table 10.** Production and valuation of copper(II) sulfate pentahydrate in the United States

Year	Production		Price of copper(II) sulfate penta-hydrate, U.S. \$/kg
	Quantity, t	Copper content, t	
1978	31 880	8551	1.04
1979	35 005	9286	1.18
1980	31.010	8445	1.23
1981	35 640	9413	1.14
1982	32 230	8385	1.08

**Figure 9.** Production of copper(II) sulfate pentahydrate in Italy and the United States (1950 – 1976)

(100 000 t) used in the production of copper compounds. Of these 100 000 t, 80 % is used to prepare copper(II) sulfate pentahydrate.

Historically, the United States and Italy have led the world in producing copper sulfate pentahydrate (Fig. 9) [65]. The U.S. production and valuation of copper sulfate pentahydrate are given in Table 10 [177].

According to estimates about 70 % (70 000 t) of the total world's production of copper compounds is used in agriculture [169]. Table 11 gives a breakdown by region, country, and use. Copper sulfate pentahydrate can be blended directly with feed or fertilizers for animal feeds or crop nutrients, respectively. For application as a foliar fungicide, it must be rendered insoluble to prevent it from being easily washed off the leaf. The first copper fungicide on the market was Bordeaux mixture (1882), a combination of lime and copper sulfate [178]. The inherent phytotoxicity of Bordeaux mixture led to the development of the "fixed coppers" in the 1920s and 1930s. The fixed coppers are grouped into four categories: (1) basic sulfates, (2) basic chlorides, (3) oxides, and (4) miscellaneous – silicates, phosphates, etc. [179], [180]. To enhance their performance, the fixed coppers are usually blended with wetting agents, dispersants, sticking agents, and diluents. Since better coverage and enhanced efficacy are obtained with smaller particles, the basic coppers are usually ground before packaging [181]. Table 12 gives a partial list of available fixed copper fungicides.

## 9. Toxicology and Occupational Health

Copper is an essential trace element in humans. In larger quantities it can be lethal. The salts are usually considered to be more toxic than the

**Table 11.** Annual use of copper in agriculture [169]

Country	Total, t	Fungi- cide, %	Animal feed, %	Crop nutrient, %
<i>Europe</i>				
France	5 380	83.6	14.9	0.9
Federal Republic of Germany	2 800	35.7	28.6	35.7
Greece	1 410	97.9	1.4	0.7
Italy	6 220	96.5	3.2	0.3
Portugal	1 120	89.3	8.9	1.8
Spain	2 800	89.3	10.7	0.0
Others	15 563	49.8	34.5	15.8
<i>Asia and Australia</i>				
Australia	1 556	19.3	6.4	74.3
India	3 500	0.0	0.0	100.0
Japan	2 040	98.0	1.2	0.7
Others	1 811	78.7	0.6	20.3
<i>Africa</i>				
Algeria	1 750	100.0	0.0	0.0
Kenya	1 000	100.0	0.0	0.0
Tanzania	2 000	100.0	0.0	0.0
Others	2 635	96.4	0.6	3.0
<i>America</i>				
Brazil	7 160	97.8	1.4	0.8
Mexico	1 650	100.0	0.0	0.0
United States	6 400	46.9	9.4	43.8
Others	3 540	40.7	2.8	56.6
Total	70 305	76.4	12.1	11.4

metal. The acute oral toxicity in humans, LD<sub>Lo</sub>, is about 100 mg/kg; however, recovery has occurred after ingestion of up to 600 mg/kg. The symptoms of copper poisoning include nausea,

vomiting, gastric disturbances, apathy, anemia, cramps, convulsions, coma, and death.

Many reported cases of illness were once attributed to chronic copper poisoning, but they are now thought to be caused by impurities in the refining of copper, e.g., lead, arsenic, and selenium [182], [183]. The question of chronic poisoning is still open to debate. Prolonged exposure to copper dust can cause skin irritation and discoloration of skin and hair. Whether pathological changes occur is uncertain, although there is evidence of accumulation of copper in the liver. Attempts to induce chronic copper poisoning in animals have been unsuccessful.

The inhalation of dusts of copper compounds irritates the upper respiratory tract [184], [185]. Ulceration and perforation of the nasal septum have occurred. Workers exposed to dusts of copper salts complained of metallic tastes and irritation of the oral and nasal mucosa. Smokers complained of an intense sweet taste during inhalation of the smoke. Long-term exposure to copper-containing dust has resulted in atrophic changes in the mucous membranes. Mild nasal discomfort was noted in workplace concentrations as low as 0.08 mg/m<sup>3</sup>. A very small fraction of the workers exhibited allergic skin reactions from exposure to copper-containing dust [186], [187].

Copper compounds embedded in the eye produce a pronounced foreign body reaction with discoloration of the ocular tissue. Conjunctivitis, ulceration, and turbidity have been reported [188], [189].

**Table 12.** Commercially available fixed coppers

Manufacturer/representative	Trade name	Active ingredient	Cu content, %
BASF	BASF-Grünkupfer	copper oxychloride	45
	Kauritil	copper oxychloride	47
Bayer	Cupravit-Spezial	copper oxychloride	45
	Cupravit-Forte	copper oxychloride	50
CP Chemicals	Basic Copper Sulfate	tribasic copper sulfate	53
	Champion WP	copper hydroxide	50
Cuproquim	Hydrox	copper hydroxide	50
Hoechst	Vitigran, Conc.	copper oxychloride	45
Kocide/Griffin	Kocide 101	copper hydroxide	50
Merck	Perenox	copper(I) oxide	50
Norddeutsche-Aff.	Cobre Nordox	copper(I) oxide	50
Phelps-Dodge	Tribasic Copper Sulfate	tribasic copper sulfate	53
Sandoz	Cobre Sandoz	copper(I) oxide	50
Simplot	Blue Shield	copper hydroxide	50
Spiess Urania	Funguran	copper oxychloride	45
	Cuprasol	copper oxychloride	50
Tennessee Copper	Tribasic Copper Sulfate	tribasic copper sulfate	53
Wacker	Wacker-Kupferkalk	copper oxychloride	15 – 18

The workplace standard for copper dust concentration in air, MAK and TLV, is 1 mg/m<sup>3</sup> [190–192]. Copper fume standards are 0.2 mg/m<sup>3</sup> [190] and 0.1 mg/m<sup>3</sup> [191], [192]. A number of reviews and books of a more specific nature report detailed animal and workplace studies [193–197].

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