COPPER

1. Introduction

Copper [7440-50-8], was one of the first metals to be used by early humans because, like gold and silver, it occurs in nature in the metallic state. The Chalcolythic Age marked the transition from man's use of stone implements to those made from copper. Humans first used copper for utilitarian objects. The “Ice Man” recently found in the Italian Alps carried a copper axe, an example of the copper tools believed to be prevalent during this time. The earliest recorded use of copper occurred in northern Iraq about 8500 B.C. Copper appeared elsewhere in Asia Minor and in Egypt around 7000 B.C. The oldest known copper smelting, dating to 3600 B.C., was conducted near the Timna mine in Elot, Israel, a site believed to be that of King Solomon's Mine (1). Indeed, copper is referenced several times in the Old Testament. Deposits on Cyprus were known as early as 3000 B.C. These mines became prized possessions of the empires that followed the Egyptians and became the chief source of copper for the Roman Empire. The metal was named *aes syprium* and subsequently *cuprum*, from which derives the English name, *copper*, and the symbol, *Cu*.

Copper is a soft metal, and although it was easy to work, it was not ideal for knives, axes, and other weapons. Thus, when humans learned how to alloy copper with tin to form bronze, about 3500 B.C., the harder and tougher alloy replaced copper in many of its uses. Because of its gold color, bronze quickly became a metal for decorative as well as utilitarian objects, giving rise to the Bronze Age. In time, humans learned how to smelt iron and to form steel, and since steel could cut through bronze, it largely replaced bronze in applications other than decorative items. Copper then fell into disuse until the advent of electricity in the late 1800s. Around 1850, with the invention of the dynamo, the electric motor and later, the telephone, copper became the preferred metal for electrical wire and other conductros. With electrification, copper rapidly came into its own, and its use has grown every year since. Maximum growth in the rate of production, about 6% per year, occurred during the period between the two world wars. Figure 1 tracks the production of copper in the Western world during the period 1810–1998 (2,3).

Agricola described the antecedents of today's copper smelting processes in *De Re Metallica*, published in 1556 (4). At that time, smelting was conducted at Mansfeld, Germany and Swansea, in Wales. Early copper production utilized so-called direct-smelting ores: ores with a grade in excess of 7% copper that could be smelted without first having to be concentrated. These ores were found in veins between rock masses, and early copper mines were therefore entirely located underground. Large-scale mining of low grade ores began early in the twentieth century, when Daniel Jackling developed the open-pit mining method at the Bingham Canyon Mine, located near Salt Lake City, Utah. Jackling's breakthrough, combined with development of the froth flotation process for concentrating low grade ores (by the Minerals Separation Company of London), made possible the exploitation of the massive porphyry copper ore bodies mined today in Arizona, New Mexico, Utah, and elsewhere (see section on occurrence).

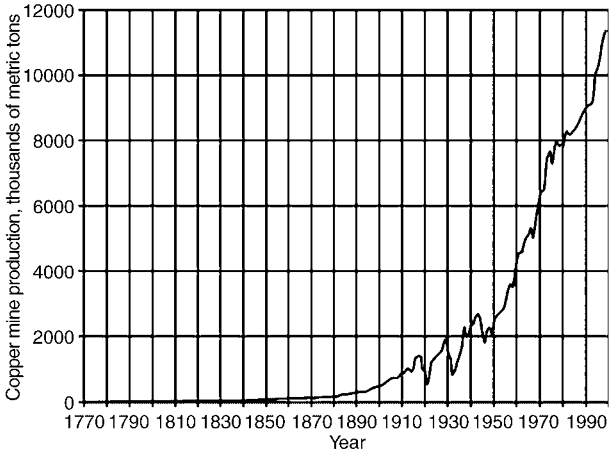

Fig. 1. Historical world copper production, 1770–1998 (2,3).

Today, the large porphyry copper ore bodies in Chile and Peru have made South America the world's leading copper-producing region. The United States ranks second, and it comprises the only region in which production and consumption are in balance. Central Africa, the Congo and Zambia, and the CIS follow the United States in production. Other important deposits are found in southern Oceania (Papua New Guniea, the Philippines, and Indonesia), Canada, Mexico and Poland. Since the United States is essentially self-sufficient in copper, copper-producing regions outside the United States supply Asia and Europe.

The copper industry is composed of *producers* and *fabricators*. Producers mine, smelt, and refine copper for sale in the form of cathodes or ingots, output that is collectively referred to as *refined copper*. Some producers also manufacture *wire rod*, selling it as a *refinery product*. Producers may additionally recover molybdenum disulfide, various precious metals, selenium, tellurium, copper sulfate, nickel sulfate, and sulfuric acid as byproducts. Fabricators manufacture useful shapes using combinations of refined copper, copper scrap, and alloying ingredients, as appropriate. The shapes include wire, rod and bar, tube, sheet, strip, plate, and foil and are known as *semifabricates*, or more commonly, *semis*. Fabricators known as *wire mills* manufacture electrical and mechanical wire. The broad term, *brass mills*, refers to fabricators that make tube and pipe, rod, and flat-rolled items, whether or not those products are made from brass. Other fabricators produce powered metal and speciality chemicals. Fabricators' products (semis) may be sold directly to manufacturers for the production of finished goods such as electrical and electronic equipment and automotive heat exchangers. Fabricators may also sell directly to end users in building construction and other industries. Smaller quantities of copper semis are sold to distributors.

2. Occurrence

Copper is one of the most abundant of the metallic elements in the earth's crust. Its average estimated concentration is 55 mg/kg (5), placing it below chromium

(200 mg/kg) and zinc (132 mg/kg) but above tin (40 mg/kg) and lead (24 mg/kg). It is estimated that there are 3×10^{18} tonnes of copper diffusely distributed in uppermost mile (1.6 km) of the continental crust (6). Only a small fraction of this copper is relatively concentrated, comprising an estimated 10^{10} tonnes concentrated in deposits with a grade of $\geq$0.25% Cu (2). At the current global mine production rate, approximately 110 million tonnes per year, this fraction represents a million years' supply of copper theoretically available in the mineable portion of the earth's crust. There are also appreciable quantities of copper in deep-sea clays, in ocean manganese-based nodules scattered on the ocean floor, and in effluents from undersea fumaroles. None of these undersea sources have been economically exploited (see OCEAN RAW MATERIALS).

2.1. Minerals and Ores. Almost all crustal copper is contained within igneous rock. Copper's strong chemical affinity for sulfur chiefly determines its manner of occurrence. Copper–iron sulfides have relatively low melting points and therefore crystallized last, between the other minerals that make up igneous rocks. Other sulfides were transported and deposited by hydrothermal processes, and are found in cracks and fissures. Copper ore minerals are classified as *primary, secondary, oxidized*, and *native* copper. Primary minerals were concentrated in ore bodies by secondary enrichment as a result of hydrothermal processes.

Secondary minerals formed when copper sulfides exposed at the surface became weathered, leached (dissolved) by groundwater, and precipitated near the water table (see METALLURGY, EXTRACTIVE). Copper, like gold and silver, can also occur as a primary mineral, in its metallic (native) form. A good example of the latter minerals are the lava-associated deposits of the Keweenaw Peninsula in Upper Michigan, which formed a significant portion of global copper production in the nineteenth century.

The five classifications of economically viable copper ore include porphyry deposits and vein replacement deposits; strata-bound deposits in sedimentary rocks; massive sulfide deposits in volcanic rocks; magmatic segregates associated with nickel in mafic intrusives, and native copper. A sixth type of deposit, one consisting of oxide minerals, is now recognized as a result of the development of leaching and solution purification technologies (see section on SXEW process).

Almost two-thirds of the world's copper resources are porphyry deposits. (The term *porphyry* is generally applied to a copper deposit that is hydrothermal in origin, and in which a large portion of the copper minerals is uniformly distributed as small particles in fractures and small veins.) Porphyry deposits usually contain $\leq$1% copper. The most extensive of these deposits are located in western Canada, southwestern United States, Mexico, and the Andes Mountains of western South America. In addition to the porphyries, there are large bedded copper deposits in Germany, Poland, the CIS, Australia and central Africa. Most near-surface copper sulfide deposits have an oxidized cap of secondary mineralization. Since these oxide minerals are not treatable in a smelter, such deposits were previously not regarded as ores. Modern leaching technology now makes their recovery possible, and these minerals, together with oxidized portions of previously mined material, currently account for about 15–20% of primary-copper production.

3. Properties

Copper, with symbol Cu and atomic number 29, is one of the "noble" metals, and like gold and silver, it is a member of subgroup IB in the periodic chart of the elements. Its atomic electronic structure is described by the notation $1s^22s^22p^63s^23p^63d^{10}4s^1$, which depicts an argon core plus a filled 3*d* orbital and a single 4*s* electron. Copper owes its unique properties to this structure. For example, the filled 3*d* states limit compressibility and, consequently, scattering of conductance electrons due to thermal lattice vibrations. Lattice incompressibility and the loosely bound 4*s* and 3*d* electrons give the copper its high electrical and thermal conductivity (7). Copper's distinctive red color arises from absorption due to optical transitions between filled 3*d* states and empty conduction-band 4*s* states. Alloying alters this structure; additions of zinc, for example, produce progressively lighter golden yellows, while nickel additions yield pink to silver-white hues. (The cladding on U.S. coins other than the dollar contains 75% copper, 25% nickel.) The low ionization potential of the 4*s* electron, 7.724 eV, is responsible for the relative ease with which copper forms the Cu^+ ion, which is important to both industrial copper chemistry and the behavior of copper in the environment. The electron given up to form the Cu(II) state arises from the 3*d* orbital, whose ionization potential is only $\sim$2 eV higher than that of the 4*s*.

Copper has a face-centered cubic (fcc) crystal structure (space group: *A1*, *Fm3m*; *cF4*) at all temperatures below its melting point, 1358.03 K (1084.88°C). The lattice parameter at 298 K (25°C) is 0.361509 ± 0.000004 nm, the distance of closest approach (Burgers vector) is 0.255625 nm and the Goldschmidt atomic radius for 12-fold coordination is 0.1276 nm (8, 9). Copper's high ductility, an important commercial attribute is in large part due to the 12 (111)[110] slip systems in the fcc crystal structure. To a lesser extent, copper also deforms by twinning across {111} planes in the [112] direction.

Copper's atomic weight is 63.546; its nucleus contains 29 protons and 34–36 neutrons. There are two stable isotopes, ^{63}Cu (occurrence 69.09%) and ^{65}Cu (30.91%). Unstable isotopes range from ^{58}Cu to ^{68}Cu (9–11). All unstable isotopes are β emitters; however naturally occurring copper is not radioactive.

3.1. Physical Properties.

The density of pure, single-crystal copper at 278 K (20°C) is 8.95285 g/cm^3. As with all metals, density depends significantly on thermomechanical treatment, and densitities of 8.90526 g/cm^3 and lower have been reported for severely cold-drawn copper wire (12). The value 8.94 g/cm^3 at 298 K (25°C) is generally accepted in practice. A compilation of copper's physical properties can be found in Table 1.

From both technical and commercial standpoints, copper's most important physical property is its high electrical conductivity, highest among "engineering" metals and second only to silver. Copper's electrical properties are described by the International Annealed Copper Standard (IACS), which is defined as the volume conductivity of an annealed pure copper wire, one meter long, weighting one gram, having a density of 8.89 g/cm^3 at 298 K (25°C) and a resistance of exactly 0.15328 Ω. Designated "100% IACS" and corresponding to a volume resistivity of 16.70 $\Omega \cdot m$, this value is the standard against which all electrical copper products (wire, connector alloys, etc) are compared (13). Volume conductivity as high as 103.6% IACS has been reported for high purity copper (14), whereas

Table 1. **Physical Properties of Pure Copper**

Property	Value
atomic weight	63.546
atomic volume, cm^3/mol	7.11
mass numbers, stable isotopes	63 (69.1%), 65 (30.9%)
oxidation states	1, 2, 3
standard electrode potential, V	$Cu/Cu^+ = 0.520$ $Cu^+/Cu^{2+} = 0.337$
electrochemical equivalent, mg/C[a]	0.3294 for Cu^{2+} 0.6588 for Cu^+
electrolytic solution potential, V(SCE)[a]	0.158 ($Cu^{2+} + e^- = Cu^+$) 0.3402 ($Cu^{2+} + 2e^- = Cu$) 0.522 ($Cu^+ e^- = Cu$)
density, g/m^3	8.95285 (pure, single crystal) 8.94 (nominal)
metallic (Goldschmidt) radius, nm	0.1276 (12-fold coordination)
ionic radius, M^+, nm[b]	0.096
covalent radius, nm[b]	0.138
crystal structure	fcc, *A1*, *Fm3m: cF4*
lattice parameter	0.0361509 ± 0.000004 nm (25°C)
electronegativity[b]	2.43
ionization energy, kJ/mol[b]	
first	745
second	1950
ionization potential, eV[a]	7.724 Cu(I) 20.29 Cu(II) 36.83 Cu(III)
Hall effect[a]	
Hall voltage, V at 0.30–0.8116 T	-5.24×10^{-4}
Hall coefficient, mV/(mA)(T)	−5.5
heat of atomization, kJ/mol[b]	339
thermal conductivity, W/(m)(K)	394[b], 398[a]
electrical resistivity at 20°C, nΩ · m	16.70
temperature coefficient of electrical resistivitiy, 0–100°C[a]	0.0068
melting point	1358.03 K (1084.88°C)[a] 1356 K (1083°C)[b]
heat of fusion, kJ/kg	205, 204.9, 206.8[a] 212[b]
boiling point	2868 K (2,595°C), 2,840 (2,567°C)[a] 2595 K (2,868°C)[a]
heat of vaporization, kJ/kg	7369[b] 4729, 4726, 4793[a]
specific heat, kJ/(kg)(K)	0.255 (100 K)[a] 0.384 (293 K)[b] 0.386 (293 K)[a] 0.494 (2000 K)[a]
coefficient of expansion, linear, μm/m	16.5
coefficient of expansion, volumetric, $10^{-6}\ K^{-1}$	49.5
tensile strength, MPa	230 (annealed)[b] 209 (annealed)[a] 344 (cold drawn)[a]
elastic modulus, GPA	125 (tension, annealed)[a] 102–120 (tension, hard-drawn)[b] 128 (tension, cold drawn)[a] 46.4 (shear, annealed)[a] 140 (bulk)[a]

Table 1 (*Continued*)

Property	Value
magnetic susceptibility, 291 K, mks	-0.086×10^{-6}[b]
	-1.08×10^{-6}[a]
emissivity	0.03 (unoxidized metal, 100°C)[b]
	0.8 (heavily oxidized surface)[a]
spectral reflection coefficient, incandescent light	0.63[a]
nominal spectral emittance, $\lambda = 655$ nm, 800°C	0.15[a]
absorptivity, solar radiation	0.25[a]
viscosity, mPa · s (cP)	3.36 (1085°C)[a]
	3.33 (1100°C)[a]
	3.41 (1145°C)[b]
	3.22 (1150°C)[a]
	3.12 (1200°C)[a]
surface tension, mN/m (dyn/cm)	1300 (99.99999% Cu, 1084°C, vacuum)[a]
	1341 (99.999% Cu, N_2, 1150°C)[a]
	1104 (1145°C)[b]
	(see Ref. 15 for additional data)
coefficient of friction	4.0 (Cu on Cu) in H_2 or N_2[a]
	1.6 (Cu on Cu) in air or O_2[a]
	1.4 (clean)[a]
	0.8 (in paraffin oil)[a]
velocity of sound, m/s	4759 (longitudinal bulk waves)[a]
	3813 (irrotational rod waves)[a]
	2325 (shear waves)[a]
	2171 (Rayleigh waves)[a]

[a] Data from Ref. 12.

[b] Data from Ref. 3.

commercial oxygen-free electronic copper [Unified Numbering System (UNS) alloy C10100], oxygen-free copper (UNS C10200), and electrolytic tough pitch copper (UNS C11000) exhibit conductivities of at least 101% IACS. Alloying, even with minute additions of other metals, increases resistivity (decreases conductivity), as shown in Table 2 (9).

Copper's high thermal conductivity, 398 W(m) · (K) at 298 K (25°C), is exploited in applications ranging from ordinary heat exchangers to superconducting cables used in magnetic resonance imaging (MRI) equipment (although copper itself is not a superconductor). Maximum thermal conductivity, 19,600 W/(m) · (K), occurs near 10 K (−263°C). Conductivity decreases by only ~7% between room temperature and the melting point, an important consideration in the design of heat exchagners. Alloying reduces thermal conductivity, but from an engineering standpoint higher strength and/or better corrosion resistance normally compensates for this loss. Copper's relatively high coefficient of thermal expansion, 16.7 m/(m) · (K) at 298 K, is one reason why bonds between copper and silicon semiconductor chips always include an transitional layer, usually of a metal, usually nickel, which has an intermediate expansion coefficient.

Copper is diamagnetic, although a number of ferromagnetic copper alloys are known. Ferromagnetism in such alloys arises not from copper itself but from the alloys' crystal structure or from precipitated ferromagnetic phases.

Table 2. **Increase in Resistivity of Copper Due to Small Solute Additions**

Solute	Room-temperature solubility, wt%	Copper, at%/cm	Observed range of copper, at%/cm
Ag	0.1	0.6	0.1–0.6
Al	9.4	0.95	0.8–1.1
As	6.5	6.7	6.6–6.8
Au	100.0	0.55	0.5–0.6
B	0.06	1.4	1.4–2.0
Be	0.2	0.65	0.6–0.7
Ca	<0.01	(0.3)[a]	
Cd	<0.05	0.3	0.21–3.4
Co	0.2	6.9	6.7–7.0
Dr	<0.03	4.0	3.8–4.2
Fe	0.1	8.5	805–8.6
Ga	20.0	1.4	1.3–1.5
Ge	11.0	3.7	3.6–3.75
Hg		(1.0)[a]	
In	3.0	1.1	1.0–1.2
Ir	1.5	(6.1)[a]	
Li	<0.01	(0.7)[a]	
Mg	1.0	(0.8)[a]	
Mn	24.0	2.9	2.8–3.0
Ni	100.0	1.1	1.1–1.15
O	~0.0002	5.3	4.8–5.8
P	0.5	6.7	6.7–6.8
Pb	0.02	3.3	3.0–4.0
Pd	40.0	0.95	0.9–1.0
Ot	100.0	2.0	1.9–2.1
Rh	20.0	(4.4)[a]	
S	~0.0003	9.2	8.7–9.7
Sb	2.0	5.5	5.4–5.6
Se	~0.0004	10.5	0.2–10.8
Sn	1.2	3.1	3.0–3.2
Te	~0.0005	8.4	2.8–3.5
Ti	0.4	(16.0)[a]	
U	~0.1	(10.0)[a]	
W		3.8	0.3
Zn	30.0	1.3	

[a] Ref. 9.

Copper's low magnetic permeability avoids energy losses in electromagnetic devices such as motors and generators. Special heat treatments are employed to avoid traces of ferromagnetism in copper alloys in critical applications such as minesweepers.

Since pure copper does not undergo allotropic transformations, its mechanical properties depend entirely on grain size and on thermomechanical history, specifically, the degree of hot and cold working and/or annealing imparted during manufacture. Yield and tensile strengths (in MPa), respectively, of annealed oxygen-free (OF) copper between 4 K (−269°C) and 300 K (27°C) are described by the expressions (9)

$$\sigma_y = -8.60 - 0.0329\,T + 292\,d^{1/2} + 150\,I(SD = 9\,MPa)$$

$$\sigma_u = 419 - 1.19\,T + 0.00144\,T^2 \;+\; 156^{1/2}\,I\;(SD = 18MPa)$$

and for cold-worked OF copper by

$$\sigma_y = 124 - 0.241\ T + 14.1(CW) - 0.166(CW)^2(SD = 32\ MPa)$$

$$\sigma_u = 412 - 0.664\ T + 2.73(CW) - 0.00695(CW)^2\ (SD = 32\ MPa)$$

where T is temperature in degrees K, d is grain size in μm, I is the impurity content in wt.%, CW is the degree of cold work expressed by the percent reduction in thickness and S.D. is the standard deviation. Uses of pure copper based on mechanical properties alone are quite limited, and most applications in which high strength, ductility or other such properties are required—usually often in combination with other attributes—are served by copper alloys, of which several hundred are now produced worldwide. Mechanical properties of representative wrought Nort American copper alloys are listed in Table 3 (15).

Alloying improves mechanical properties through solid-solution strengthening (α brasses, tin bronzes), precipitation hardening (beryllium coppers, chromium copper, zirconium copper), spinodal decomposition (copper–nickel–tin alloys), order–disorder transformations (β-brasses), diffusionless transformations (aluminum bronzes, aluminum brasses, nickel–aluminum bronzes), or combinations thereof. Alloys such as beryllium coppers and aluminum and manganese bronzes can attain strengths comparable with those of quenched and tempered steels. High strength, combined with the alloys' high corrosion resistance, enables copper-base alloys to compete against stainless steels and other advanced alloys for a large variety of industrial applications such as pump and valve components.

Many alloys are devised primarily to facilitate manufacturing processes. It can be argued that cast implements created in the Bronze Age exemplify this process. In the late twentieth century, copper alloy development centered on improvements in machining characteristics (lead-free brasses), corrosion resistance (marine and plumbing alloys), elevated-temperature resistance (electrical connector- and leadframe alloys), and, as in ancient times, castability.

3.2. Chemical Properties. Compared with alkali metals, copper's higher ionization energy and smaller ionic radius contribute to its forming oxides that are much less polar, less stable, and less basic than those of the alkali metals (16). The relative instability of copper's oxides is responsible for the occurrence of native, that is metallic, copper in nature (17). Cu(I) forms compounds with the anions of both strong and weak acids. Many of these compounds are stable and insoluble in water. Compounds and complexes of Cu(I) are almost colorless because the 3d orbital of the copper is completely filled. There is, however, a very strong tendency for Cu(I) to disproportionate in aqueous solutions into (Cu(II) and metallic copper.

$$2\ Cu^+ \rightarrow Cu^0 + Cu^{2+}$$

Whereas the cuprous (I) state is generally unstable in aqueous solutions, the cupric (II) state is quite stable. Ligands that form strong coordinate bonds bind Cu(II) readily to form complexes in which the copper has coordination numbers of 4 or 6. Formation of Cu(II) complexes in aqueous solution depends on the

Table 3. **Mechanical Properties of Selected Wrought Copper Alloys**[a]

Alloy [Unified Numbering System (UNS)]	Description of previous name	Form of specimen	Tensile strength, MPa	Yield strength, 0.5% extension (0.2% extension), MPa	Elongation in 50 mm, %	Shear strength, MPa	Fatigue strength, 10^6 cycles, MPa	Hardness, Rockwell B/F
C10200	oxygen-free	Rod	221–375	69–345	10–55	152–186	117	47–60/40/94
C11000	electrolytic tough pitch	Rod	221–379	39–345	16–55	152–200	177	45–60/40–87
C12200	phosphorus deoxidized	Tube	221–379	69–76	8–45	152–200	76–131	35–60/40–95
C14500	tellurium-bearing	Rod	221–296	76–338	10–50	152–200	NA	36–64/40–43
C15720		Rod	441–552	400–531	16–25	NA	NA	66–74/NA
C17200	beryllium copper	Rod	469–1379	(172–1227)	3–48	NA	NA	3–95/NA
C18200	chromium copper	Rod	310–593	97–531	5–40	NA	NA	65–83/NA
C19500		Plate	552–669	(448–655)	2–15	NA	179–200	NA
C26000	cartridge brass, 70%	Rod	331–483	110–359	30–65	234–290	NA	60–80/65
C28000	muntz metal, 60%	Rod	359–496	138–345	25–52	269–310	NA	78/78–80
C36000	free-cutting brass	Rod	338–400	124–359	25–53	207–262	138	75–80/68
C37700	forging brass	Rod	359	138	45	NA	NA	NA/78
C50500	phosphor bronze 1.25% E	Plate	276–517	97–345	4–48	NA	221	64–79/68
C51000	phosphor bronze, 5% A	Rod	483–517	400–448	25	NA	NA	78/NA
C54400	phosphor bronze, B2	Rod	469–517	393–434	15–20	NA	NA	80–83/NA
C61300	aluminum bronze	Rod	552–586	331–400	35–40	276–331	NA	88–91/NA
C61800	aluminum bronze	Rod	552–586	269–293	23–28	296–324	179–193	88–89/NA
C63000	nickel–aluminum bronze	Rod	689–814	414–517	15–20	427–483	248–262	96–98/NA
C65500	high-silicon bronze A	Rod	400–745	152–414	13–60	296–427	NA	60–95/NA
C70600	copper–nickel, 10%	Tube	303–414	110–393	10–42	NA	NA	15–72/65–100
C71500	copper–nickel, 30%	Tube	372–414	172	45	NA	NA	35–45/77–80

[a] *Source*: Ref. 9.

ability of the ligands to compete with water for coordination sites. The stability and ease of formation of Cu(II) complexes are important factors influencing the bioavailability of copper in aqueous and marine environments. Until the late 1990s, copper's ecologic toxicity was grossly overestimated because of an inadequate awareness of the implication of this phenomenon, namely, that the bioavailability (and associated toxicity) of copper in aqueous environments can be several orders of magnitude lower than its concentration due to complexation with other ions.

3.3. Corrosion Resistance.

Copper's third most important property is the collection of attributes generally termed its intrinsically high corrosion resistance. To a degree, copper exhibits the thermodynamic stability of silver and gold. Native copper nuggets found in Michigan, for example, are estimated to have remained stable in subterranean brines for as long as 10^9 years. Numerous copper and bronze archaeologic artifacts, some of them retrieved from the sea, have survivied for centuries. Although copper is thermodynamically stable in a few environments, its corrosion resistance is more often based on kinetics, that is the low rates of speed at which corrosion reactions proceed. Thus, in many potentially corrosive media (including, importantly, air, steam, and potable and marine waters) the metal tends to form adherent and protective surface films that, once established, effectively inhibit further attack unless the films are damaged or altered by changes in the environment (18). Copper's long and successful history of use for plumbing tube rests on this phenomenon, as does the formation of protective—and attractive—patina on copper roofs and bronze statuary. Copper roofing in certain rural atmospheres corrodes less than 0.4 mm in 200 years, whereas the copper skin of the Statue of Liberty has lost only 0.1 mm to corrosion in 100 years despite exposure to a marine/industrial atmosphere. Pure copper resists aerated alkaline solutions except in the presence of ammonia. Copper does not displace hydrogen from acid but dissolves readily in oxidizing acids such as nitric acid or sulfuric acid solutions containing an oxidizer such as ferric sulfate. Copper is also attacked by soft, low pH waters, ammonia solutions, amines, cyanide solutions, nitrates and nitrites, oxidizing heavy-metal salts, and certain sulfides. Aqueous solutions containing ammonia, amines, cyanide, nitrates, and nitrites attack copper and can, under certain conditions, generate stress corrosion cracking. Although copper is biostatic, the metal can exhibit microbially induced corrosion (MIC) (19–22). Chlorides, including seawater, do not seriously attack copper and its alloys, and this has led to many applications for which, for example, stainless steels are less well suited. On the other hand, titanium alloys have begun to replace copper alloys in naval and seawater-cooled power plant condensers. Despite the metal's known biostatic properties, it can exhibit microbially induced corrosion (MIC) (20,21).

4. Sources and Supplies

Copper enters into trade primarily in the form of concentrates, blister, anodes, refined copper ingots and cathodes, and copper semis. The former are provided by copper producers (miners, smelters, and refiners) the latter by fabricators, respectively.

4.1. Concentrates and Blister. Concentrates, the product of mines and associated *concentrators*, contain 27–35% copper in the form of sulfide minerals. Most trade in concentrates is carried out by mines that do not have an associated smelter, or mines that produce more than their smelters can accommodate, in which case the surplus is sold. Some mines produce concentrates strictly for sale on world markets or for processing in foreign smelters. Concentrates also become available from time to time when the smelters that treat them are closed down for one reason or another. Blister copper is the first product from a smelter. It contains about 98% copper, some oxygen and iron, plus the noble metals and other impurities carried over from the ore. Blister copper may enter international trade when there is insufficient refinery capacity in the country in which it is produced, or as the result of contractual arrangements for the shipment of blister from the smelter for refining elsewhere. The price of concentrates and blister are negotiated on the basis of their copper content and the current price of copper on one of the commodity exchanges (see section on economic on aspects).

4.2. Refined Copper. The term *refined copper* refers to metal with a copper content of $\geq$99.99%, although some special grades are as pure as 99.9999%. Refined copper is the product of either electrolytic refining of anode copper or electrowinning from hydrometallurgic or leach solutions. Commercial *refinery shapes* include electrorefined or electrowon copper cathodes and several types of continuously cast wire rod. Cathode and wire rod are now by far the most important forms of copper in international trade. There is a substantial international trade in refined copper since fabricators of copper and copper alloy semis often obtain their supplies from refineries in other countries.

4.3. Semis. Semis (semifabricates) are fabricated product forms, such as rod, wire, sheet, plate, and tube. They are the products of wire mills, brass mills (which include rod mills and, tube mills and sheet and strip manufacturers), ingotmakers, and powdermakers. The price of semis is based on the commodity exchange price of copper; however, because their cost also includes alloying materials, energy, and labor input, the market price of semis is somewhat buffered and does not fluctuate to the extent that the price of refined copper does. End users often purchase semis directly from the fabricator when large quantities are involved; small quantities are purchased from distributors or supply houses.

4.4. Stockpiles. The London Metal Exchange (LME) and the Commodity Exchange of New York (COMEX) (see Economic Aspects) maintain warehouses of stocked with refined copper. These warehouses are located at strategic locations close to major consuming centers of the world.

5. Recovery and Processing

Most copper is produced using a combination of mining, concentrating, smelting, and refining. About 15% of refined copper is produced through the leaching of mine and concentrator wastes, depleted tailings, and oxide ores with sulfuric acid derived from the smelting process's off-gases. The copper-containing leach solutions are purified and concentrated by *solvent extraction* (SX), and copper is recovered by *electrowinning* (EW). Whether from the traditional or SXEW paths, the final product is a high purity copper cathode.

5.1. Mining. Copper ore is obtained from either open-pit or underground mines; the open-pit source is predominant today. The choice of mining method is a function of the ore grade, including its geologic setting (depth, shape, and amount of overburden) and economic considerations. Underground mining is generally more expensive and requires a higher ore grade (nominally $>2\%$ Cu) than does open-pit mining. In some instances a combination of open-pit and underground mining is used once a depth is reached in which open-pit mining is uneconomical. Conversely (e.g, San Manuel, Ariz.) open-pit mining has been used over areas that had previously been excavated underground. Open-pit mining can economically accommodate ore containing $\leq 1\%$ copper and as lean as 0.2% copper where byproducts such as molybdenum and precious metals are present in sufficient concentration. Run-of-mine U.S. porphyry ores currently contain about 0.6% copper.

In underground mining, the ore body is accessed via tunnels or shafts and ore is excavated using *room and pillar* or *block caving* mining methods. Following excavation, the ore may be broken up in an underground crusher or hauled directly to the surface using hoists or specialized trucks. Underground copper mines dominated the U.S. industry in the nineteenth century but are now rare due to the widespread exploitation of low grade porphyry deposits. The world's largest underground copper, *El Teniente*, is located in Chile. In 1998, it produced more than 35 million metric tons of ore with an average grade of 1.16% Cu ($>$400,000 tons of copper contained).

In open-pit mining, nonmineralized overburden is first stripped away to reveal the orebody, which is then drilled, blasted, and excavated. Because the surface area of an open-pit mine continually increases with pit depth in order to maintain a safe pit wall angle, the overburden:ore *stripping ratio* is an important factor in a mine's economics. Most breaking of rock takes place during blasting, but in some cases primary crushers are located in the pit. Crushed ore is transported to the mill for concentration using trucks or conveyors, while overburden is hauled to waste dumps surrounding the mine.

Open-pit mining has become a highly efficient mining method, due to technological innovations in explosives, shovels, haulage trucks, computer modeling of the ore body for mine planning, and computerized control of the equipment. Electric shovels with a bucket capacity of 15–25 m^3 (500–900 ft^3)—sufficient to hold an average pickup truck comfortably—and haul trucks capable of hauling 100–350 short tons of ore per load are now common. Geosatellite positioning systems (GPSs) are used to control the position and dispatch of shovels and trucks. This system is so precise that one company has a completely robotic haul truck under test. Most of the open-pit mines in the southwestern United States move 30,000–250,000 tons of ore plus overburden per day. The world's largest copper mine is the *Escondida* open pit, located in Chile. Its sulfide and oxide operations currently produce more than 800,000 tons of copper contained per year.

5.2. Concentration. *Concentrating* consists of crushing and grinding to liberate the copper mineralization from the host rock, followed by *flotation*, in which copper mineralization and waste materials, or *gangue* are separated. *Milling* refers to the crushing and grinding steps; however, the term *mill* is used interchangeably with the term *concentrator* to describe the facility in which the process takes place. Copper concentrators serving U.S. copper mines individually process 30,000–160,000 tonnes of low–grade ore per day.

Two or three stages of cone crushers are normally used for the first stage of size reduction. These crushers contain an eccentrically driven grinding cone that rotates in a fixed conical bowl, creating a moving wedge-shaped space. Ore is pinched and crushed as it drops into this space. Typical product sizes for three crushing stages in series are <20, <3, and <1 cm, respectively. Further size reduction is achieved by several stages of grinding in water to produce an ore slurry. In one process, grinding is conducted in large cylindrical vessels called *mills* into which ore, water, and steel rods or balls, called *grinding media*, are charged. These reduce the ore's particle size to <3 mm. Today, dry crushing, screening, and rodmilling is increasingly being replaced by semiautogenous (SAG) milling, in which large blocks of ore and hardened grinding balls are tumbled in very large mills. Impact of the ore against itself and the steel balls reduces the ore to the desired particle size. Effluent from the first stage of milling is passed to ball mills where the ore is further ground such that 75% of it is <0.25 mm in size. Wet cyclones classifiers recycle oversized ore particles between grinding stages.

Crushing and grinding are followed by *froth flotation* (see FLOTATION) where copper minerals are separated from the gangue and recovered. Copper concentrates commonly contain 25–35% copper; the upper limit is determined by the copper content of the mineral in question. Figure 2 shows a simplified flowchart for a typical copper concentrator. Flotation is conducted in large tanks, or *cells* into which air is injected or drawn, creating bubbles. Chemicals known as *collectors* are added to the cell, where they selectively coat and create a water-repelling film on exposed surfaces of sulfide minerals, causing the sulfides to cling to the rising bubbles. Other chemicals adjust pH, stabilize the froth, and depress unwanted minerals. The bubbles and their copper–mineral freight are skimmed from the surface froth. Gangue minerals, which are not attracted to the air bubbles, fall to the bottom of the cell, where they are removed. Common collectors include xanthates, dithiophosphates, or xanthate derivatives. Calcium or sodium cyanide and lime are used as depressants. Pine oil or long-chain alcohols are used as frothers. The pH is adjusted with lime, which optimizes the action of all of the reagents and depresses pyrite. Most copper flotation plants operate *rougher cells*, *cleaner cells*, and *scavenger cells* in series. Flow between these cells is illustrated in Figure 2. The froth from scavenger cells may be removed and reground in a special ball mill, from which it is reintroduced into rougher cells to further separate copper minerals from the gangue minerals.

The product, or *concentrate*, produced by the mill contains between 25 and 35% copper, depending on the copper content of the mineral(s) involved. The concentrate is dried by filtration and shipped to the smelter. Waste products, called *tailings*, are pumped to large *tailing ponds* where the water is decanted off and returned to the mill.

Molybdenite, MoS_2, occurs in many prophyry copper ore bodies. If the grade is sufficient, it can be recovered in the cocentrator as a byproduct of the copper mineral recovery. Molybdenite normally floats with the copper sulfides (see MOLYBDENUM AND MOLYBDENUM ALLOYS). Therefore, as shown in Figure 2, the copper

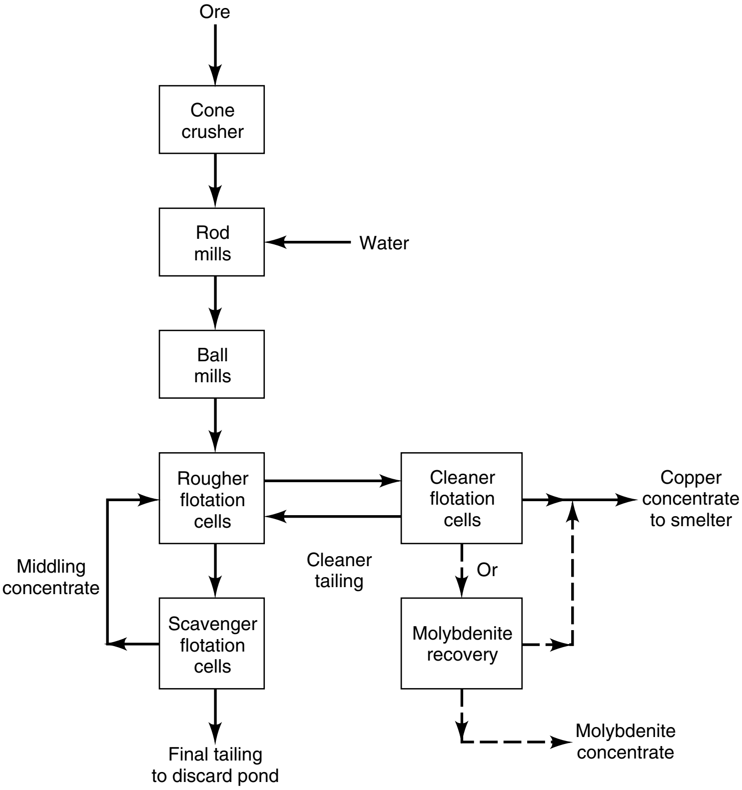

Fig. 2. Simplified flow diagram of a copper concentrator.

concentrate from the cleaner cells has to be separated from molybdenite in a separate flotation circuit.

5.3. Smelting. Copper concentrate usually (but not always) contains a mixture of copper and iron sulfides together with small amounts of gangue minerals. *Smelting* comprises the two operations needed to extract copper from concentrate using heat, flux, and oxidation. The first step, also called *smelting*, separates copper from the sulfur and iron and the gangue. In this step, much of the iron and a portion of the sulfur in the concentrate are oxidized, producing a mixture of molten copper and iron sulfides (known as *matte*), iron oxide (which is removed in the form of an iron silicon oxide slag and either discarded or processed further to remove additional copper), and sulfur dioxide gas.

Sulfur dioxide gas is recovered from the smelter and converted into sulfuric acid or other products. In a few installations, the gas is captured by lime and made into gypsum (crystallized calcium sulfate) for use in building materials. Sulfuric acid is normally sold, but in some cases it is used at the mine to leach copper oxide minerals in ores, waste dumps, and tailings. In 1998, sulfuric acid from copper (and other metal) smelting amounted to 4 million tonnes, or nearly 10% of U.S. production (23).

Figure 3 is a simplified flowchart for the smelting process. Material flows are given in metric tons per day. There are at least a dozen different versions

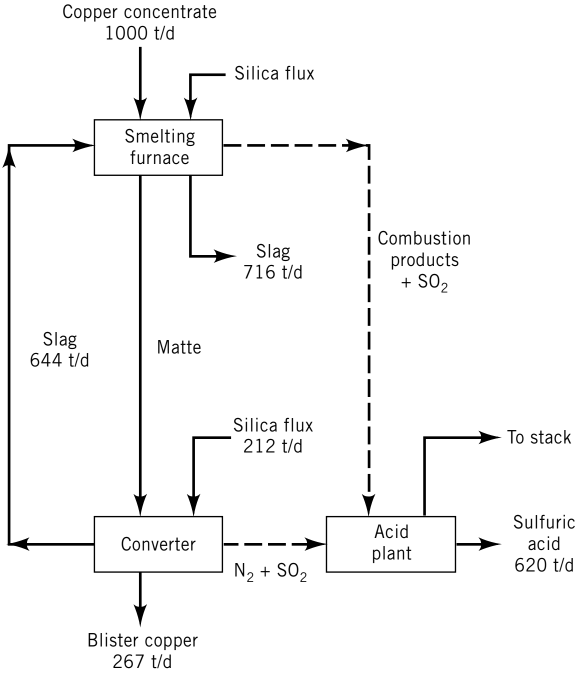

Fig. 3. Flow diagram for smelting and converting.

of smelting furnaces; the most prevalent, in order of current tonnage processed worldwide, are Outokumpu (50%), reverberatory (25%), blast furnace (7%), El Teniente (7%), and Inco (5%). These furnaces differ mainly in the manner in which oxygen (in the form of air, oxygen-enriched air, or oxygen) is introduced into the reaction. The Outokumpu and Inco units are known as *flash furnaces* in that concentrates are blown into the furnace with oxygen or oxygen air.

Once in the furnace, the concentrates burn, or "flash." The oxidation reaction is *autogenous*, supplying nearly all the heat to sustain the furnace, operation; however, some natural gas is added to maintain proper heat balance. In the *reverberatory furnace*, copper concentrates and silica flux are introduced into a fuel-fired bed-shaped furnace hearth, where they are melted to form a low copper matte and slag. Fuel oil or natural gas provides the necessary energy and only a negligible amount of the heat value of the concentrate is utilized. Reverberatory and blast furnaces are being phased out because they are inefficient and the low sulfur dioxide concentration in their offgas renders the production of sulfuric acid difficult and costly.

5.4. Converting. In a *converter* or *converting furnace*, matte from the smelting furnace is further oxidized to form copper and slag. The most common type of furnace, the Pierce–Smith converter—developed in the United States in 1906 and changed little since—consists of a simple cylindrical vessel with a large opening along one side and equipped to rotate about its longitudinal axis. In conventional converting, matte is charged into the furnace from open ladles, silica is added to flux iron in the matte, and air is blown into the charge through injectors, called *tuyeres*, located on the side of the converter. The sulfides are oxidized to sulfur dioxide, which is collected and sent to the sulfuric acid plant. Iron sulfide in the matte is oxidized by injecting air in a *slag blow*. The resulting iron oxide combines with silica to form an iron silica slag, which floats to the top of the melt and is poured off into ladles for either further processing or disposal. Following pouring, the now iron-free copper sulfide is oxidized by continued air injection in the *finish blow*. The product is *blister copper* (or simply *blister*) containing $>98\%$ Cu plus some sulfur, oxygen, and other impurities. This blister is then tapped into ladles for transport to the fire refining and anode casting operations.

Several continous (i.e., combined smelting–converting) technologies were introduced in the late 1990s. In the *Mitsubishi process*, oxygen or oxygen-enriched air is injected using lances, and process streams move continuously from one step to the next (24,25). In the *Kennecott–Outokumpu process* in which a flash furnace is used to smelt concentrates, matte is solidified, pulverized, and fed to a flash converter (26). Both processees avoid many of the air-quality problems associated with conventional smelting and converting operations. Most importantly, they avoid transfer of molten matte in large ladles, a procedure that generates ambient emissions of sulfur dioxide. The Mitsubishi and Kennecott–Outokumpu processes also produce concentrated sulfur dioxide gas, which is well suited for use in sulfuric acid plants.

5.5. Sulfur Recovery from Smelter Gases. The environmentally driven need to convert smelter gases to acid has been the most importent force driving the development of new smelting technologies. Until the mid–Twentieth Century, sulfur dioxide gas was simply vented to the atmosphere via tall stacks. Today, it is normally captured and sent to a sulfuric acid plant, where it is catalytically converted to sulfur trioxide, then contacted with water to form sulfuric acid (see SULFURIC ACID AND SULFUR TRIOXIDE). The key to the operation is obtaining the sulfur dioxide in sufficient concentration (minimum $\sim 5\%$) to make acid efficiently. Today, the most modern smelters produce gases containing $\geq 35\%$ sulfur dioxide. Since the maximum sulfur dioxide concentration that can be treated by most acid plants is $\sim 14\%$, the rich offgas from the smelter is mixed with weaker gas steams from the converters and from fugitive sources to prepare the gas feed to the acid plant.

Simple scrubbers, the devices first used to remove sulfur dioxide from offgases, are now employed primarily to treat gases with very low sulfur dioxide concentrations, such as those from dryers, anode furnaces, and building ventilation. Lime is the most commonly used absorbent; the resulting product is calcium sulfate. Scrubbers are used mainly in Japan, where the process has been taken one step further to the manufacture of *gypsum*, a crystallized form of calcium sulfate used in the manufacture of wallboard (see CALCIUM COMPOUNDS, CALCIUM SULFATE; SULFUR REMOVAL AND RECOVERY). Today, about 26% of the world's smelters are ranked "high capture" with regard to sulfur dioxide. The most efficient smelters exceed 99.5% SO_2 recovery.

5.6. Fire Refining. Fire refining adjusts the sulfur and oxygen levels in blister copper, removing impurities as slag or volatile products. The process is needed because excessive sulfur and oxygen levels result in excessive gas evolution during anode casting (the next step in the production of cathode), producing unacceptably rough anode surfaces, which, in turn, lead to low current efficiences in the refining cell, uneven cathode deposits and excessive impurities. Fire-refined copper also is also marketed directly for fabrication into copper products.

Fire refining takes place in a reverberatory furnce or a rotary furnace that resembles a converter. Both types have capacities of 100–800 short tons (90–720 t). Most plants fire-refine and cast anodes within the smelter building to facilitate the supply of blister copper to the fire-refining furnace. Once charged, air is blown into the molten copper through tuyeres to complete the oxidation of some of the impurities and remove volatile impurities. Sodium carbonate flux may be added to remove arsenic and antimony. Blowing the blister copper raises the oxygen content to 0.6–1.0%, which is too high for casting. This oxygen content is reduced by a process known as *poling*, after the outdated method of feeding green tree trunks into the furnace as a reducing medium. Today, the oxygen content is reduced by feeding a reducing gas such as ammonia, re-formed gas, or a mix of natural gas and steam into the copper. The end product is cast directly into anodes for electrolytic refining or, rarely, into ingots for sale as fire-refined copper. Anode casting requires an oxygen content of 0.05–0.2% whereas copper to be used directly for fabrication into such things as bar stock, water tubing, or ingots for alloying (known as *tough pitch* copper) requires an oxygen content between 0.03 and 0.05%.

5.7. Electrorefining. Copper intended for electrical uses requires further refining by electrolysis in order to raise its purity and electrical conductivity to the degree needed for electrical products. Total impurity content in the highest-grade copper is restricted to fewer than a few parts per million.

In electrofining, anodes produced from fire refined copper are dissolved electrolytically in acidic copper sulfate solutions and the copper concurrently electrodeposited (electroplated) onto copper *starting shets* to produce *cathodes*. Starting sheets are made beforehand on insoluble stainless steel or titanium cathodes called *mother blanks*. In some modern refineries, cathode copper is plated entirely onto stainless-steel blanks. Electrorefining is conducted in large tanks, and refineries are known as *tank houses*. A refinery having an annual production of 175,000 short tons might have as many as 1250 cells in the tank house, which may encompass several hectares. The volume of electrolyte in a modern tank house is typically 6000 m^3 for a copper production level of 500 short tons per day. Copper circulating in the electrolyte comprises approximately 10% of the refinery's annual production. Copper in the undissolved anodes represents an additional inventory. Cathodes are sold directly or are melted and cast into wire rod, ingots, and other forms. Some producers cast wire rod in their own refineries; others sell cathode to fabricators, where they are remelted and cast to rod or other intermediate products.

The basic process for electrorefining was developed around 1900. It remains essentially the same today, although several engineering improvements have been introduced. Periodic current reversal (PCR), for example, has enabled an increase in current density from the normal maximum of 240 A/m^3 to 300–350 A/m^3. Automation has led to significant cost savings. Figure 4 shows a simplified flowchart of a modern electrolytic refinery. There are four basic operations:

1. Anodes are dissolved and copper redeposited on starter sheets to form cathodes.

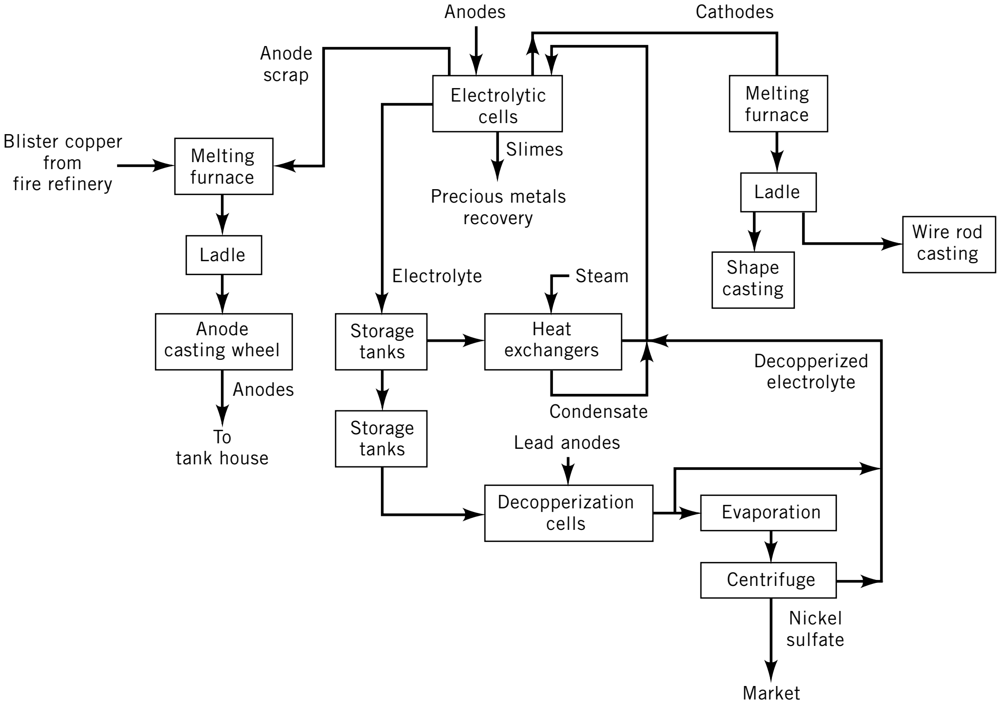

Fig. 4. Flow diagram for an electrorefinery.

2. Impurities (with the exception of silver) from the anode fall to the bottom of the cell and are collected as a sludge known as *anode slime*.
3. Electrolyte is treated to control the concentrations of copper and impurities circulating in it.
4. The refined copper cathodes are melted and cast into commercial shapes.

Anode slimes are shipped to a precious-metal refinery, where gold, silver, platinum, selenium, and tellurium are recovered. Sulfur, selenium, and tellurium in the slimes are combined with copper. The slimes may also contain lead and tin in the form of lead sulfate and tin sulfate.

Electrodeposition is the most important of the unit processes in electrolytic refining. It is performed in lead- or plastic-lined concrete cells, or more recently, in polymer–concrete cells. Composition, temperature, and flow rate of the electrolyte are of great importence to the quality of the cathode deposit. Changes in any one of these parameters can have a serious effect. Current density and voltage are two additional important variables. The trend is toward increased current density and cell voltage in order to change the ratio of copper produced to copper circulating in the electrolyte. In addition, some refineries have changed from the traditional 25–30-day anode cycle to a 9–14-day cycle using smaller anodes to reduce the copper inventory (27). This has reduced the amount of copper in inventory by ~60% (28). The majority of refineries operate at 175–240 A/m^3, copper concentrations of 30–50 gm/L, electrolyte temperatures of 55–65°C, and a circulation rate of 10–20 L/min.

The quality of the cathode deposit is extremely importent since off-grade cathode cannot command established prices on metal exchanges. Dendrites, for example, can occlude electrolyte and insoluble particulate matter, thereby reducing quality. Surface quality is controlled by the addition of organic chemicals that influence nucleation through surface adsorption or complexation. The intent is to produce a cathode product that (*1*) is free from deep striations or fissures that would entrap electrolyte impurities, (*2*) does not develop nodular growths that might cause short circuits as well as entrap electrolyte impurities, and (*3*) is not so hard as to preclude straightening bent sheets.

Common additives include animal glue modified with lignin derivatives such as Orzan or Goulac, sulfonated oils (Avitrone), casein, and thiourea, as well as other proprietary reagents.

5.8. Hydrometallurigic Processes. Hydrometallurgical processes for copper can be categorized as:

1. Acid extraction of copper from oxide ore
2. Oxidation and solution of sulfides in waste rock from the mine, concentrator tailings (*dump leaching*), or slag piles
3. Dissolution of copper in concentrates to avoid conventional smelting
4. *In situ* leaching, otherwise known as *solution mining*

Copper ores have been leached in the United States since the 1920s, but hydrometallurgical processing did not become a major part of the copper industry until the availability of large amounts of sulfuric acid from the smelters. Hydrometallurgy was further enhanced by adoption of a solvent extraction and solution purification process developed in 1957 by General Mills (29). Combination of the solvent extraction process with electrowinning led to the development of the (*solvent extraction/electrowinning* (SXEW)) process. Previous leaching processes used *cementation*, the replacement of copper in solution for iron by contacting acidic copper-rich solutions with scrap iron. The product, known as *cement copper*, was fed to the smelter. The SXEW process enables the direct recovery of high purity copper, in cathode form.

An increasing portion of U.S. copper production is being obtained by the leaching of waste rock and tailings. There are currently over 30 installations of this type in the country; their production capacity is now about 850,000 tonnes of copper (30). Hydrometallurgy is also gaining importance in other parts of the world, and it has been predicted that by 2005, leaching and SXEW will account for 20% of the newly mined copper in the world (31).

Leaching of oxide ores is also becoming common; however, this practice is contrained by the availability of oxide mineralization at the mine site. Extraction of copper from oxide ore is accomplished by contacting the ore in a heap or pile, which is underlain by a plastic membrane. The ore is fragmented by blasting and is deposited in the pile in a manner so as to preserve porosity. Acid is dispersed over the top of the pile through a system of plastic garden sprinklers and allowed to percolate through the pile to be collected at the bottom as pregnant liquor. This liquor is piped to the solvent extraction copper recovery system, and spent acid is piped back to the pile for reuse. The acid is ultimately consumed by the limestone in the ore to form calcium sulfate—a very insolouble mineral—and by hydrated ferric sulfate. In fact, the amenability of an oxide ore for acid leaching is determined by the amount of limestone in the ore. Too much limestone consumes too much acid making the process uneconomical for that particular ore.

Copper sulfide minerals per se, cannot be leached by acid unless they are first oxidized. In practice oxidation is accomplished by long-term exposure to the atmosphere and by contact with naturally occuring *Thiobacillus thiooxidans and Thiobacillus ferroxidans* bacteria. Under the right conditions of moisture, temperature, and air, these bacteria have the ability to oxidize sulfide minerals to oxides and elemental sulfur. For example, in an environment maintained at a pH 1.5–4.0, *T. ferrooxidans*, combined with *T. thiooxidans* readily oxidizes the ferrous iron in solution to ferric iron. The ferric iron, in turn, has the capability of oxidizing cuprous sulfide to cupric oxide that is then leached by the addition of acid (32).

Heap leaching of waste rock and mill tailings is conducted in the same manner as leaching oxide ore. The exception is that attention must be paid to maintaining conditions in the heap that are conducive to bacterially induced oxidation and to the prevention or delay in the precipitation of hydrated ferric sulfate, which can lower the percolation rate of the heap.

Leaching of *copper concentrates* is not currently practiced except in a few special cases due to the lack of an efficient and cost-effective process to oxidize the copper minerals. A number of processes were developed for this purpose during the 1960s and 1970s, several using ferric chloride or sulfate as the oxidative agent; however, with the increased cost of energy beginning in 1974, all of these processes were passed over for commercial application. Work has been conducted using elevated pressure leaching following processes developed in the 1950s for the commercial leaching of nickel and cobalt sulfide ores (33,34). None of these processes have been reduced to commercial practice in view of the high cost of pressure leaching relative to the low value of copper.

In-situ leaching is defined as the in-place extraction of metals from ores in a mine or in dumps, heaps, slag piles or tailing piles. Unfortunately, many statistical compilations refer to copper recovered in this manner as *in-situ mining*. In fact, the term rightfully refers to *solution mining*, which involves the pumping of a leach solution underground where it contacts the ore body directly. Boreholes drilled into the ore body provide sites for injection and return of the leach solution. The orebody may be fractured *in situ* using explosives or hydro-fracture techniques developed by the petroleum industry (35).

Leach solutions are characteristically too dilute to be sent directly to an electrowinning cell. The solutions are therefore first concentrated by a process called solvent extraction. A flow sheet of the entire SXEW process is shown in Figure 5 (36). The process is conduced in three stages, each of which has two substages; mixing and settling. The equipment used is therefore called a *mixer*/settler. In the first stage, copper is extracted from the pregnant leach solution by contacting it with chemicals called *extractants*, which are based on a family or organic chemicals known as *oximes*. Early extractants were members of this family called ketoximes. A variety of extractants based on aldoximes are now available that show performance superior to that of the ketoximes (37). The

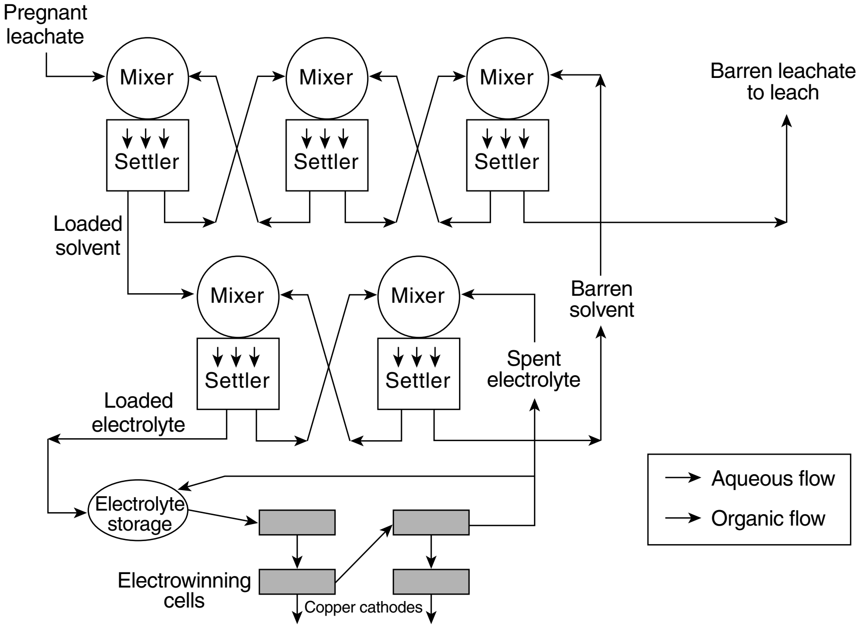

Fig. 5. Flow diagram for the SXEW process (36).

extractants are dissolved in a kerosene-like diluent, forming what is called the *organic phase*. The extractants selectively remove copper from the weakly acidic leach solution and, in turn, increase its acidity. In the second stage, a process called *extraction*, the organic phase is separated from the depleted aqueous phase by settling. The copper is next recovered from the organic phase by contacting it with a strongly acidic aqueous solution. This operation is called *stripping*. Finally, the resulting copper-rich acidic aqueous solution is fed to an electrowinning cell, where copper is deposited onto cathodes much as in conventional electroplating. The stripped organic phase is returned to the loading stage, while the barren but now strongly acidified leach liquor is returned to the leaching operation.

Electrowinning is highly energy intensive in that only about 0.3 kg of copper per kilowatt–hour is deposited. This contrasts with about 3 kg of copper per kilowatt–hour deposited in electrorefining. Electrowinning cells must also operate above is a minimum potential of about 1.67 V, below which there is no deposition.

6. Fabrication

Copper and copper alloy shapes, known in the trade as *semifabricates*, or more commonly, *semis*, are made from refined copper, and/or copper and copper alloy scrap, with or without the addition of alloying ingredients. Fabricator's facilities are classified as *wire mills, brass mills, foundries*, and *powder plants*. Wire mills and foundries produce wire products and castings, respectively. The general term, *brass mills*, encompasses a variety of plants that produce, respectively, extruded rods and shapes, tube and fittings, and sheet and strip. Only some of these products are made from brass.

6.1. Wire. In order to make wire, refined copper cathodes are melted and cast into *wire rod*, an intermediate product for wire drawing. Wire rod production may take place in the refinery or at the wire mill. Common copper rod diameters and coil sizes are

- 8.0-mm (0.315-in.) or 11.7-mm (0.46-in.)-diameter rod in 113-kg (250-lb) coils
- 8.0-mm (0.315-in.)-diameter rod in 272 (600-lb) or 2268–2722-kg (5000–7000-lb) coil sizes
- Melting is generally conducted in an Asarco shaft furnace. Rod is continuously cast by one of four major processes: the Southwire process; the Properzi process; the Hazelett process, and the Hazelett–Contirod process. The General Electric dip-forming process and the Outokumpu upcast process are also used, but less frequently (38).

Wire rod is fed from coils into a drawing machine, or *drawbench*, which reduces the size of the wire by drawing it through a series of successively smaller-diameter dies. Dies used for drawing copper are made from diamond or tungsten carbide. Natural-diamond dies are used to draw wire diameters ranging from 0.01 to 4.06 mm (0.0004 to 0.16 in.). Tungsten carbide dies are used for sizes AWG (American Wire Gauge) 16 (1.291 mm, 0.05 in.) and larger. The dies are lubricated and cooled by water containing soaps and high fat emulsions. Wire from the drawing machine is taken up and packaged by one of four types of machines known as *spoolers, dead-block coilers, line-block coilers*, or a combination of spooler and line-block coiler known as a *Bundpacker* (39).

Most wire is insulated, standed, jacketed, and bundled into cable. Stranded copper wire and cable are made on machines known as *bunchers* or *stranders*. Various synthetic polymers are used for insulation depending on the service requirement. The most commonly used polymers are poly(vinyl chloride) (PVC), polyethylene, ethylenepropylene rubber (EPR), silicone rubber, polytetrafluoroethylene (PTFE), and fluorinated ethylene propylene (FEP). These insulation materials are formed on the wire by a coextrusion process. Fine magnet wire (otherwise known as *winding wire*, the type used in electric motors, transformers, and similar devices) is coated with a thin, flexible, heat-resisting enamel film. Enamels used include polyvinyl acetals, polyesters, and epoxy resins. Enameling is accomplished by multiple dipping or wiping with curing between stages, or by powder coating. The latter process requires no solvents and therefore simplifies environmental control measures. Oil-impregnated cellulose paper is used to insulate high voltage cable of the sort used in underground transmission lines. The paper is applied by winding tape around the individual conductors in a tight helix, with successive layers wrapped in alternating directions. The entire bundle is then pressure-impregnated with oil, assembled and encased in a sheath, which may be polymeric, metallic, or a combination of materials (40).

Stranded cable is made by paying individual filaments of wire off reels located alongside the stranding equipment. The wires are then fed over flyer arms that rotate about the takeup reel, giving the wires their twist. The bundles of twisted wires can themselves be twisted, bundled, and insulated using the same sort of stranding equipment (39).

High purity copper wire for electrical uses is by far the principal product manufactured by wire mills. Some mills do, however, also manufacture pure and alloyed copper wires for nonelectrical applications such as fasteners, springs, and cold-headed products (this is known as *mechanical wire*) and welding and brazing rods.

6.2. Alloying.

The principal products of brass mills are not limited to brass alone but include copper itself and many alloys. Alloys are prepared by the brass mills or by scrap recyclers and secondary refiners known in the trade as *ingotmakers*. Raw materials include refined copper cathodes, copper ingots, high quality copper or alloy scrap, and the various alloying ingredients required for each product. Alloying elements are usually added in the form of refined metal, although some clean scrap of known composition is also used. Melting and alloying take place in an electric melting furnace where some fire refining may also be performed in order to control oxygen content and other impurities. Once melted, the alloy is cast into a *billet* or *slab* for processing into the required shape.

6.3. Continuous Casting.

In the past, billets with large cross sections were cast statically: those for round products in the form of cylinders (or *logs*) of various dimensions, and those for flat products as thick rectangular slabs called *cakes*. Most mills now use continuous casting machines to produce these intermediate products. In the *vertical* continuous casting process (which is actually semicontinuous), molten metal is poured into the top of an open-ended mold cavity having water-cooled sides and a movable bottom. Hot metal is poured into the mold, where it freezes from the walls inward, forming a solid slug. As the metal solidifies, the bottom of the mold cavity is slowly withdrawn downward while more metal is poured into the top. The result is a continuous shape, up to about 7.6 m (25 ft) long and having the external geometry of the mold cavity. The cavity may be round, square, or rectangular. It may also be profiled for such things as gear blanks, or hollow, for sleeve-bearing blanks. The *horizontal* continuous casting process is similar, except that the mold's axis is oriented horizontally and molten metal is fed from one side. The opposite or exit side of the mold is initially plugged by a starter bar of the same diameter or cross-sectional shape as the finished casting. Grips or a set of pinch rolls slowly withdraw the starter bar followed by the billet that has solidified against it. Horizontal continuous casters generally produce solid rods, billets or flat slabs. Unlike vertical units, which are limited by the depth of the casting pit beneath the mold, horizontal casters can produce large cross-section products in any length. Cast rods used for wire drawing are normally <25 mm (<1 in.) in diameter. Billets for subsequent extrusion range up to about 305 mm (12 in.) in diameter, while cast slabs are normally between 9.5 and 16 mm (3/8 and 5/8 in.) thick. In either case, the casting is sawed into appropriate lengths for further processing in rolling mills, drawbenches, or extrusion presses, depending on the product from desired.

6.4. Rod, Bar, Shapes, Plate, Sheet, Strip, and Foil. In the terminology of copper products, *rod* designates round, hexagonal, or octagonal products supplied in straight lengths, that is, not coiled. *Bar* products are square or rectangular in cross section when sold in straight lengths. *Shapes* can have oval, half-round, geometric, or custom-ordered cross sections and are also sold in straight lengths. *Wire* can have any cross section; the term simply means that the product is sold in coils, reels, or spools. The remaining product designations are straightforward: *plate* is a thick, wide, flat product; *sheet* is a thin, wide, flat product; *strip* is a thin, narrow, flat product usually slit from coils of sheet; while *foil* is very thin sheet.

Rod, bar, and other shapes are normally made by extrusion, a process frequently likened to squeezing toothpaste from a tube. The billet is heated to temperatures approaching 815°C (1500°F) and placed in the extrusion press's cylindrical chamber. A hydraulically driven ram forces the softened metal through a steel die, which may be located at either end of the extrusion chamber. The die opening determines the profile of the finished extrusion. With *direct extrusion*, the extruded metal exits from the end opposite to the ram and in the same direction as the ram travels; with *indirect extrusion*, the die is contained in the face of a hollow ram and metal exits in a direction opposite to the ram's travel. Indirect extrusion produces products with better internal cleanliness. Some rod, bar and profiled wire products are also made by hot and/or cold rolling. Cold rolling hardens the metal, raising its *temper*.

Plate, sheet, strip, and foil are made by rolling continuously cast slabs of copper or copper alloys. For alloys that can be hot worked without cracking, the reduction process begins by heating the slabs, then hot-rolling them on very sturdy two-high roll stands. The rolling process is efficient since the hot metal is quite compliant. The rolls are reversible to permit rolling in forward and reverse directions, and several passes may be used to reduce the thickness to that required for the next stage of rolling. Horizontally oriented rolls reduce the strip's thickness while a pair of vertical edging rolls located in the same roll stand maintains the proper width. Progressively smaller working rolls are required as the strip gets thinner. Small-diameter rolls are normally supported by larger-diameter backup rolls in order to increase the stiffness across the width of the mill. Very thin gauges (such as foil) are rolled on Sendzimir, or "Z" mills, in which a cluster of rolls provides the necessary stiffness. The strip may be annealed between rolling passes; however, final dimensional tolerance is achieved by cold rolling. Cold rolling also imparts the temper required for the intended application. The rolling process must be carefully controlled since different alloys require different rolling conditions, and errors in hot-rolling or annealing temperatures or improper degrees of reduction can result in the production of expensive scrap.

6.5. Tube. Plumbing tube and commercial tube are made from refined (cathode) copper and/or high-grade copper scrap that has been fire-refined and deoxidized with phosphorous. Mills that operate reverberatory or induction (electric) furnaces can utilize scrap, which is usually cheaper than cathode, as delivered, since the furnaces can be used to fire refine the melt to the required purity. Such mills will only use cathode if scrap is in short supply or more costly because of high freight charges. Mills that operate simple shaft furnaces must use cathode as their raw material since no refining takes place in this type of furnace. On average, the North American copper tube industry uses about 65% scrap in its manufacturing process. Whether from cathode or scrap, the resulting metal must, when used for water tube, meet the composition requirements of UNS C12200 [deoxidized high residual phosphorus (DHP)] copper. This grade is quite pure (minimum 99.90% Cu); only phosphorus is added to remove oxygen, which makes the tube more formable and brazeable. Alloy tube or pipe may be brass or any other copper-based alloy.

Tubular products are produced by extrusion and drawing, by seam welding sheet that has been roll-formed into a tube, by continuous casting a shell and rolling the shell into a tube, and by the centrifugal casting process. For extrusion, a tube shell is first produced by continuous casting if a vertical casting machine is available. The tube shell is heated, placed in the extrusion press and extruded over a mandrel that extends through the shell and the die opening. If a horizontal casting machine is used, solid billets are pierced and extruded over a mandrel in a single operation. Extrusion produces a somewhat oversized, thick-walled tube, which is cold-drawn to final size. Drawing also reduces the tube's wall thickness. Copper or copper alloy tube is then drawn in multiple passes on draw blocks (*bull blocks*) or draw benches until it attains its finished size. Tube sold in coils is softened by annealing after drawing. Tube sold in straight lengths is straightened, cut to the appropriate length and shipped in the *hard-drawn* temper.

Plumbing tube has smooth surfaces inside and out. *Commercial tube* requires a more precisely controlled diameter but is otherwise quite similar. Some commercial tube is ridged or grooved inside and/or outside to improve heat conductivity. External grooving is accomplished using a roll-forming process; internal grooving is accomplished using an internal die. To produce inside-and-outside grooved tube a suitably formed die is rocked back and forth along the tube while a grooved and tapered mandrel controls the tube's internal diameter (41).

Extrusion and drawing lubricants used with annealed tube should not leave a carbonaceous film on the interior surface of the tube, since any remaining lubricant will be cracked to carbon during the annealing process. In some cases, the presence of carbon films on the interior surface of water tube may lead to pitting corrosion of the underlying copper (42). In North America, this problem is avoided by using a noncarbonizing lubricant. In Europe, special precautions are taken to either oxidize the carbonaceous material during annealing or to remove the internal residual film by a form of abrasive blasting (43).

Welded tube is made by drawing copper strips through a conical die such that the strip assumes a tubular shape. The mating edges of the strip are joined by induction or resistance seam welding as they exit the die. Excess metal (flashing) inside the tube is cleaned off by passing a broaching die through the tube. Large-diameter tube can be formed directly by this process; small-diameter tube is formed by drawing the as-welded tube to progressively smaller sizes. The welded tube process lends itself well to small-to-medium scale production (40).

The relatively new *cast and roll process* developed by Outokumpu OY is also suitable for modest production volumes, although the developer claims that it can compete with large-scale extrusion processes, as well. A tube shell is first continuously cast to yield a hollow cylinder with an external diameter of 87 mm (3.4 in.), a wall thickness between 18 and 20 mm (0.79 to 1.2 in.) and a length of 12.5 m (41 ft.). This shell is then reduced in size up to 95% by working it over an internal mandrel using planetary rollers. The size of the rolled tube can be reduced further by cold drawing (44).

Centrifugal and, occasionally, continuous casting processes are used to produce thick-walled pipe. For centrifugal casting, molten metal is poured into, and solidifies against, the walls of a spinning, hollow cylindrical steel or cast iron mold, forming a shell. As the metal solidifies, dross and impurities, which are lighter than the molten metal, segregate to the shell's inside diameter, where they are later removed by machining. The centrifugal casting process results in an exceptionally clean product with a fine, dense microstructure. Centrifugally cast copper alloy products can be used in such demanding applications as high pressure hydraulic cylinders.

6.6. Forging. Many copper and copper alloy products can be produced by forging (or *hot stamping*, as the process is called in the United Kingdom). Thick disks, called *slugs*, are sawed from continuous-cast and extruded billets and used as starting materials. Size and weight of the slugs are chosen such that the forged metal fills the die completely, producing some excess flashing—later trimmed off—at the die's mating surfaces. The cumulative deformation of extrusion and forging yields an extremely dense and fine-grained structure that makes forgings suitable for products such as high pressure valve and pump components. High metallurgical quality and the capability to produce near-net shapes enable the forging process to compete with permanent mold casting, investment casting, and machining processes, some of which are less costly. Copper and many copper alloys can be forged, but the overwhelming majority of copper-based forgings are made from *forging brass*, UNS C37700.

6.7. Cold Forming. Copper itself is quite ductile as a result its face-centered cubic (FCC) crystal structure (see section on properties). Many copper alloys, particularly those that share copper's crystal structure are also ductile and easy to form into useful products. Aside from pure copper for roofing products, most copper alloys produced in the form of sheet, plate, or strip are cold-formed in some manner. The large number of different sheet alloys derives in part from the need to optimize several properties (formability, electrical conductivity, corrosion resistance, color, etc) concurrently for various and diverse products. A detailed description of the many forming processes applied to copper alloys is beyond the scope of this article, but excellent literature on the subject is available (18).

Formability is influenced by alloy composition, temper (hardness or strength, often a function of grain size), thickness, and surface condition. From a commercial standpoint, the most important cold-forming alloys are brasses, the large variety of which range in zinc content from 5% to ~40%. As zinc content increases over this range, both strength and elongation increase, and formability increases accordingly. *Cartridge Brass*, UNS C26000 (70% Cu, 30% Zn), is among the most formable of all metals. Copper–tin alloys (known as *phosphor bronzes* for the deoxidizing phosphorus they contain) are also readily formable. *Nickel silvers*, which are brasses containing some nickel (and no silver), form well, although they tend to work-harden faster than do ordinary brasses and consequently require more frequent annealing. Lead, added to many brasses and other alloys to improve machinability impairs formability, but small amounts can be tolerated, a valuable feature in products that must be both drawn and machined (picture a threaded garden hose fitting). Grain size is controlled by a combination of deformation and annealing. Optimum formability for drawing and stretching operations is frequently that which provides maximum elongation. The situation is complex, however, and such factors as the influence on grain size of intermediate annealing operations must be taken into consideration. Grain sizes that are too coarse impair surface finish, a condition aptly called *orange peeling*. Grain orientation (actually crystal orientation, a phenomenon known as *texture*) must also be considered, since the drawing and bending properties of rolled sheet vary with respect to rolling direction, specifically, parallel or perpendicular to the length of the sheet.

6.8. Casting. Copper alloys are known for their excellent castability and, indeed, early cast artifacts were some of the first applications of copper. Statues, bells, and works or art are still cast in bronze, although such products now comprise a small fraction of the copper alloy casting market.

Casting is performed using any of the conventional methods: *sand, permanent mold, die, investment, continuous*, and *centrifugal*. Some alloys are better suited to one or more of these processes than are others, which is one of many factors that dictates process selection. In all cases, the melt is prepared in a furnace using scrap, prealloyed ingot, alloying elements, or combinations thereof. Refined cathode copper is rarely used in the foundry industry. Intermediate frequency induction furnaces are preferred for their fast melting rate and versatility. Low frequency induction furnaces, which must be kept energized and partially filled with molten metal, are used in foundries that primarily cast only one alloy.

The *sand casting process* continues to account for about 75% of copper-base castings in North America, largely because of its versatility in terms of casting size, weight, complexity, and number, and its relatively low capital requirements. It can be used with most copper alloys. Sand casting is less popular in Europe, where various permanent mold processes predominate. The North American situation is slowly changing, however, as environmental regulations, particularly those involving metal-containing offgases and the disposal of spent, lead-contaminated foundry sand have forced many sand foundries to choose between bearing the cost of pollution abatement and converting to a more environmentaly favorable process.

Large copper-base castings such as nickel-aluminum bronze marine propellers and bronze church bells are cast in molds made from sand bonded with resin or Portland cement and supported by a steel shell. Small castings are also made in resin-bonded sand, a process known as *shell molding*. The shell mold is formed by pressing resin-containing sand against a heated steel pattern. The resin sets under heat, forming a thin but strong crust. The shell molding process is capable of producing castings with fine surface detail and good dimensional fidelity.

Use of the *permanent mold casting process* (known as *gravity die casting* in the United Kingdom) for copper alloys is very popular in many parts of the world and is gradually gaining acceptance in North America. Plumbing hardware items, especially faucets, are now commonly produced by this casting method.

Here, split metallic molds, usually made from beryllium copper, beryllium nickel, die steel, or cast iron, are not truly "permanent" but are durable enough to last for tens of thousands of castings. Resin-bonded sand cores are inserted in the die cavity when the finished casting contains internal contours (as in a faucet). An automated version of the permanent mold casting method known as *low pressure die casting* utilizes a few inches of metallostatic head to force metal into the mold. In another version of the process, vacuum draws metal in the mold cavity.

The pore-free surface attainable with permanent mold casting is important to the plumbing fixture industry. Fine grain size, a result of rapid solidification, inputs strength, and an permanent-mold cast alloy cast will be significantly stronger than when cast in sand. This is advantageous in copper alloys applications competing against materials such as stainless steels. The casting process is best suited to castings weighing from one to several kilograms, although castings as heavy as 25 kg (55 lb) have been produced. Alloys such as yellow brass that narrow freezing ranges are best suited to the process. Aluminum bronzes, high-strength manganese bronzes and even pure copper are routinely cast in permanent molds.

Copper and its alloys can also be *die-cast* (*pressure die-cast* in the United Kingdom), although use of this process for copper alloys is uncommon in North America. Here, molten metal is forced into a water-cooled, split metallic mold under very high pressure. The process is fast, mechanized and labor-saving. Copper itself can be die-cast, but doing so requires special mold alloys that can resist thermal cycling to copper's high melting temperature. A large multiple-sponsor research project to enable the die-casting of electric induction motor rotors (almost all of which are currently made from aluminum) was launched in the late 1990s. If the project is successful and if die-cast copper motor rotors become widely accepted, they could increase worldwide demand by up to 400,000 tonnes of copper annually.

The *investment casting* or *lost wax process* dates to at least ancient Egypt. Here, wax patterns are dipped into a slurry of plaster or other refractory until a sufficient thickness is built up to form a mold. The wax is subsequently burned out of the mold. Numerous copper-based products are manufactured using investment casting, among them jewelry items (nickel silver), dental crowns (aluminum bronze), and mechanical components (yellow brass).

Copper alloys are routinely centrifugally cast to produce a large variety of industrial and military products. In addition to the hydraulic cylinders mentioned earlier, products include controllable-pitch marine propeller hubs, fittings, flanges, and a large variety of pump and valve housings. One relatively recent development is the ability to introduce two different alloys into the spinning mold sequentially, forming a composite structure. The alloys bond metallurgically, producing a casting with different properties on its inner and outer surfaces (45).

6.9. Machining. Machined products constitute an important copper market. Understandably, a large number of copper alloys are made in such a way as to provide optimum machining characteristics. The most popular machining alloy is *free-cutting brass*, UNS C36000, which contains nominally 60–63% copper, 2.5–3.7% lead, balance zinc. (Versions of the alloy can be found in all international specification systems.) Approximately 500,000 tonnes of free-cutting brass is consumed annually in the United States alone, all of it made entirely from scrap, about half of which is in the form of turnings recycled to the brass mills from machine shops. Free-cutting brass is widely accepted as having the best machining characteristics of all engineering metals. It is theoretically capable of attaining cutting rates nearly 5 times higher than those used with leaded free-machining steel, the alloy's major competition in the screw-machined products market.

High machinability in free-cutting brass and most other alloys derives from the addition of a few percent of lead. The lead breaks up machining chips (turnings), making the turnings easy to remove from the cutting zone. It also provides a measure of internal lubrication as it smears across the face of the cutting tool, enabling higher machining speeds. Leaded versions of numerous wrought copper alloys are commercially available. Many cast copper alloys contain lead to improve castability; enhanced machinability is a supplemental benefit. Leaded plumbing alloys, including free-cutting brass, have come under scrutiny by health authorities because of the possibility that small amounts of lead may leach into certain aggressive drinking waters. The U.S. Environmental Protection Agency's "Lead and Copper Rule" limits the level of such releases. All plumbing goods sold in the United States are now certified to meet these limitations. Plumbing product's whose shape or internal volume makes excessive leaching unavoidable can be cast in brasses containing bismuth and selenium (designated by the industry as *EnviroBrass*) in place of lead (45).

6.10. Powder Metallurgy (PM) and Composites. Products made from pressed and sintered metal powders constitute a small (1% of total consumption) but interesting market for copper. Copper and copper alloy powders used in such products are produced by gas or water atomization of molten metal, by electrolysis, and by solid-state reduction. Most copper-base powders are made from scrap. It is possible to achieve 100% of theoretical density in PM products, but items such as "oil-less" bearings—a high volume product—are intentionally left porous to retain lubricants. PM makes possible the creation of composite materials, which may or may not be entirely metallic and whose properties cannot be obtained by other means. Copper–graphite brushes for electric motors and copper-containing brake pads are examples of mixed structures. Modern examples of metal-matrix composites are the copper/refractory metal materials from which liquid-fueled rocket engine nozzles are made. Copper provides high thermal conductivity for efficient heat transfer, while the refractory metal (tungsten, molybdenum or niobium plus chromium) provides strength at elevated temperatures (46).

7. Economic Aspects

Copper is a world-traded commodity. Base prices of the several accepted grades of refined copper are established by buying and selling on the London Metal Exchange (LME), the Commodity Exchange of New York (COMEX), and the Chicago-based Mid-America Commodity Exchange (MACE). The main function of these commodity exchanges is to separate the manufacturing and speculating activities of the participants in the marketplace. The exchanges also provide the means by which natural market fluctuations can be mitigated to the benefit of both producers and consumers. While most refined copper is sold directly to customers, the prices that are negotiated between the buyer and seller are based generally on one of the major exchange prices at the time of delivery. The prices of the various grades of scrap are also generally derived as some fraction of the current LME or COMEX copper price.

Because copper is produced in many different parts of the world, there has never been a successful effort to control prices centrally such as in the case of as occurred with the Organization of Petroleum Exporting Countries (OPEC) vis-à-vis petroleum production. About 40% of global copper production was briefly controlled under a French organization, called Conseil Intergouvernemental des Pays Exportateurs de Cuivre (CIPEC), which represented eight producing countries, largely in Africa and Latin America. However, the cartel never successfully controlled prices, and it disbanded in 1992. The International Copper Study Group (ICSG) was formed in 1994 as an intergovernmental assemblage of copper producing and copper consuming countries in an attempt to stabilize prices by making the market more transparent. The United States and Canada are members of the ICSG.

The basis for copper pricing is simply the state of the world economy, which establishes the level of demand, counterbalanced against the installed capacity to produce and the unit costs of production, which establish the level of supply. Copper is an energy-intensive material; hence, the cost of energy-producing commodities, coal, oil and natural gas, have a direct effect on copper supply. Figure 6 (for which data were compiled from Metallgesellschaft, the American Bureau of Metal Statistics, and various industrial sources) shows a plot of the historic price of copper in both actual and constant 1994 dollars. It should be noted that ever since the 1974 "energy crisis," the constant dollar price of copper has trended downward. This occurred despite the fact that the average ore grade has also trended downward.

Measures taken by copper mining companies to reduce drastically both energy and labor costs enabled companies to absorb the lower prices for their

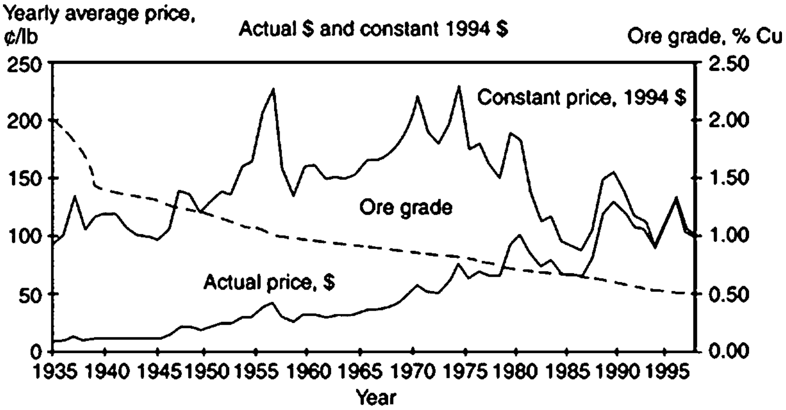

Fig. 6. Copper price versus ore grade. (*Data*: Metallgesellschaft, the American Bureau of Metal Statistics and various industrial sources.)

products. As indicated in Figure 6, which has been smoothed by using annual averages, the price of copper fluctuates. The reason for this is that copper world mining companies compete on the basis of lowest cost production. Thus, in times of surplus, the global copper price tends to follow production costs downward. As high cost producers temporarily close their mines and thus reduce production, or if copper consumption increases as a result of normal business cycle fluctuations, a copper shortage is created and the price of copper increases above the lowest cost producers' marginal price. Unfortunately, the inertia of the system caused by time delays in shutdown and start-up of production facilities causes a ratcheting of world copper prices.

8. Specifications, Standards, and Quality Control

Numerous national and international organizations specify standards for copper and copper alloy products, including the International Organization for Standardization (ISO), the British Standards Institution (BSI), the Deutsches Institut fur Normung (DIN), the Japanese Industrial Standards Committee (JISC), and the American Society for Testing and Materials (ASTM).

8.1. Refinery Products. ASTM B224 defines the standard classifications of copper according to the method of refining and characteristics determined by the method of casting or processing (47). The accepted basic standard for cathodes is given in ASTM B115 (48). ASTM B5 gives specifications for electrolytic tough pitch (ETP) copper in cakes, slabs, billets, ingots, ingot bars, and other refinery shapes. Electrolytic copper is one of the purest of all materials of commerce, and commercial ETP copper usually far surpasses the specifications of ASTM B5. In fact, ETP copper ranges from 99.94 to 99.96% Cu; even the highest level of impurities other than oxygen occur at concentrations of only 0.0015–0.003% (15–30 ppm). Oxygen, present as copper(I) oxide, is present up to 0.05% (500 ppm). In those coppers exceeding the specifications of ASTM B5, it is not uncommon to find conductivities of IACS of $\geq$101%. Oxygen–free (OF) copper is copper that has been specially processed to reduce the oxygen content in order to raise electrical conductivity and improve weldability. Oxygen-free copper C10200, for example, contains a maximum of 0.001% (10 ppm) oxygen. Oxygen-free electronic copper C10100, for electronic use, contains $\leq$0.005% (5 ppm) oxygen and $<$0.01% (100 ppm) total impurities.

8.2. Mill Products. Published specifications for copper semis deal with specific applications, such as building construction, and with certain copper alloys. ASTM B248M specifies the general requirements for wrought copper and copper alloy plate, sheet, strip, and rolled bar (metric); ASTM B249M contains requirements for wrought copper and copper alloy rod, bar, and other shapes (metric); ASTM B1 and B2 govern hard- and soft-drawn copper wire; ASTM B42 gives specifications for seamless copper pipe, while ASTM B68, B75, and B88 contain specifications for bright annealed copper tube, seamless copper tube, and copper water tube, respectively. In addition, ASTM B280 provides specifications for seamless copper tube used in air conditioning and refrigeration field service and ASTM B819, for seamless copper tube for medical gas systems.

8.3. Influence of Impurities. All *dissolved* impurities reduce the conductivity of copper (49) however, those impurities that form insoluble phases have little or no effect. For example, phosphorus, which is often used as a deoxidizer, sharply reduces electrical conductivity in OF copper, but it has little effect if the copper contains excess oxygen because insoluble phosphorus oxide then forms. Impurities also affect mechanical behavior; however, impurities in electrolytic copper are present at such low levels that they have little effect on the hot- or cold-working operations, including wire drawing and sheet rolling. The effect of impurities on annealing behavior is important in magnet wire. Enamels used to insulate the wire cure at a relatively low (baking) temperature. It is important that the copper also anneals at this temperature, so that the finished wire retains a minimum amount of spring-back after winding (50–52). Impurities such as antimony, sulfur, tellurium, and selenium raise the softening temperature of copper and thus raise its springback. Impurities such as bismuth, selenium, and sulfur have a strong effect in increasing springiness (53). Other impurities, such as silver, iron, nickel, cobalt and oxygen have no effect (54).

Impurities can affect the influence of thermal history on the mechanical properties of rolled copper products. For example, many impurities in commercial copper are present in metastable concentrations (above their solid solubility limits) at low (eg., 300°C) temperatures, but they can precipitate at somewhat elevated temperatures, thereby changing the metal's mechanical properties. Other impurities can revert from solution as oxides (in oxygen-bearing copper) as temperature is raised. In both cases, changes in temperature change the state of the impurities, and thereby the metal's hot-deformation characteristics. Since uniform deformation characteristics are obviously advantageous, efforts are normally made to ensure that most impurities are taken out of solid solution before deformation is attempted.

8.4. Quality Control.

The spectrometer is the most suitable analytic instrument for quantifying the presence of most low–level residual impurities in copper. ASTM E414 specifies the standard method for the measurement of impurities in copper by the briquette dc arc technique (55).

Conductivity is measured using a 0.48-cm (12-gauge) wire, which is annealed at 500°C for 20 min, given a sulfuric acid pickle, quenched, and dried. The resistance of the prepared specimen is then compared with that of a standard wire of the same dimensions and structure.

Annealability, or the ease and rapidity with which copper softens on heating after cold working, is important in the drawing of wire products. Annealability is most often described by the half-hardness temperature, defined as the temperature at which annealing for one hour returns the metal's tensile or yield strength to the midpoint between that for the fully worked metal and that the fully annealed state. High purity copper, after cold working, reaches the half-hard stage when annealed for one hour at 140°C. Other tests for annealability include residual hardness after cold working and annealing and by spring elongation after work hardening and annealing.

9. Analytical Methods

The previous section described the analytic methods used in the quality control of refined copper. For general copper analyses, techniques such as atomic absorption analysis and X-ray fluorescence are used for control of operations and environmental measurements. Microquantities of copper are readily detected and identified by the formation of either the deep blue cupramine complex ion $[Cu(NH_3)_4]^{2+}$, a red-brown precipitate in the presence of potassium ferrocyanide, or a green precipitate with α-benzoin oxime. When substances containing copper are moistened with hydrochloric acid and heated on a platinum wire, a blue-green tinge to the flame results. Numerous other reagents, chiefly organic compounds applied in spot tests, have been employed for the detection of microquantities of copper.

10. Environmental Concerns

Copper production, and to some extent copper use and disposal practices, are regulated in the United States and elsewhere in the world by both state and federal regulations related to air and water quality and to waste disposal. The concerns regarding copper and the byproducts of its production in the natural environment can be divided into four categories:

- Natural flux to the atmosphere and the oceans
- Effluents from production
- Effluents from uses
- Lifecycle environmental impact

10.1. Natural Flux to Atmosphere and Oceans. As noted earlier, copper is relatively abundant in the earth's crust. It can enter the natural environment in various forms and by a variety of mechanisms 56–59:

- In mists dispersed into the atmosphere from the sea where salt spray is generated in breaking waves
- As wind-blown powder and dust of geologic origin—mainly from deserts and other arid regions
- As wind-blown biogenic particles from agricultural areas, forests, and other vegetated areas
- As volcanic dust, ashes, and the like dispersed into the upper atmosphere
- As the result of volcanic and hydrologic activities at midocean ridges
- As biogenic refuse from aquatic flora and fauna
- By erosion of the seabed
- By erosion of riverbeds

It is estimated that as much copper is dispersed into the natural environment by natural forces as is by anthropogenic point sources—specifically, a total of ~20,000–51,000 tonnes/year (59).

10.2. Effluents from Production. Most copper minerals are sulfides. Since many of these minerals are copper/iron sulfides, more sulfur is liberated from the ore by the smelting process than copper. During the smelting processes, these sulfides are oxidized to form gaseous sulfur dioxide. In the United States, under the Clean Air Act of 1970, stringent limitations are placed on the emission of sulfur dioxide from copper smelters. Similar regulations exist elsewhere in the world. As a result, measures have been taken by most smelters to restrict sulfur dioxide emissions to some extent. Today, two-thirds of the world's major smelters recover 95–99.5% of the sulfur in the ore. The majority of the remaining smelters recover at least 85% of the sulfur dioxide they generate. Sulfur dioxide is most often recovered in the form of sulfuric acid but also as elemental sulfur and calcium sulfate, an extremely insoluble and inert material that is similar in composition to the naturally occurring mineral, gypsum. Acid is either sold into the acid market or used to leach oxidized copper ores (see section on recovery and processing).

Copper mining operations have always been faced with a large solid-waste disposal problem. Waste consists of overburden (unmineralized rock and soil), tailings (copper mineral-depleted waste material from the mill), and slag (largely iron oxide, calcium oxide, and silica with low concentrations of other metals fused into a lavalike mass in the smelter) and depleted leach residues. All this material must be stored onsite. The wastes are regulated in the United States under the Solid Waste Disposal Act as amended in 1976 by the Resources Conservation and Recovery Act (RCRA). In addition, under the Emergency Planning Management and Community Right to Know Act of 1986 (EPCRA), otherwise known as the *Toxic Release Inventory* (TRI), the amount of any substance in the wastes that is listed among the 644 substances considered to be toxic under this act must be measured and reported to the USEPA annually. No risk to the public is implied, yet an operation as simple as moving unprocessed broken rock from one part of a mine to another must be reported as a "release to the land." Wastes naturally contain small concentrations of copper but may also contain other substances such as lead, manganese, and zinc, all of which are considered toxic under the Act.

Water effluents include process water and wastewater related to specific mining, milling, and smelter operations, plus storm water runoff that may come in contact with a facility's operations. Such effluents are monitored and regulated under the Clean Water Act of 1977. In general, in a copper mining/milling operation, most of the water used in the milling process is recycled back to the mill. In the U.S. Southwest as in other arid areas, the major water loss from a mining/milling site occurs by evaporation.

10.3. Effluents from Uses. A large portion of all of the copper in use is ultimately recycled for other uses (see section on recycling and disposal), although there is a finite amount of attrition into the environment. Copper contamination in the soil is not a major issue, since surface soils in the United States naturally contain, on the average, 18.2 ppm copper (range: 6.4–63.4 ppm) (60). In certain agricultural soils, where there is a copper deficiency, copper must be added as a mineral supplement to fertilizer. Surplus copper is remineralized into the soil.

The major concern over contamination due to copper uses is introduction of the metal to bodies of freshwater and saltwater where aquatic life may be adversely affected. (Because copper is an essential element, adverse effects only appear at copper intake levels higher than those required for metabolism.

Toxicity levels vary widely among species.) Most of copper's uses in aquatic applications utilize the metal's algicidal and fungicidal properties. In the United States, under the Clean Water Act of 1977, copper is regulated in freshwater at levels on the order of 6.5-34 ppb (61) and in saltwater at levels on the order of 2.9 ppb (data also from Ref. 63, but based on 1-h average concentration not to exceed once every 3 years). In both cases, the actual number is calculated under the law as a function of a number of variables, including water composition and pH. It should be noted that the restrictions on copper in wastewater discharge are significantly lower (measured in parts per billion) than the restrictions of copper in drinking water (in 1.0–1.3 ppm maximum; — see section on health and safety factors).

Copper enters bodies of water in rainwater runoff, through the use of copper algaecides in lakes and ponds, through the breakdown of copper-based antifouling paints, or in sewage effluent. Copper enters rainwater runoff from several sources: road traffic, through wear of brake linings and pads, tires, roadway surfaces; spillage of fuels, oils and antifreeze; chemicals, wood preservatives, antifouling paints, algicides; buildings, as corrosion products from copper roofs and facades and from plumbing systems; agriculture, by leaching of soils; and landfills, as seepage.

Road traffic–based sources are reportedly the main contributors of copper to the environment at large and are major contributors to aquatic systems, as well. Copper-based chemicals used as antifoulants, algicides, and similar products are the principal contributors to the aquatic environment and a major contributor to the total environment. These are followed in magnitude by landfills and agricultural sources. Plumbing systems, roofing and facades contribute only minor amounts of copper to the environment (62).

10.4. Lifecycle Assessment (LCA). There is growing interest in quantifying the environmental impact of materials by performing "cradle to grave" analyses of the energy consumed in the materials' production and use, and by the materials' impact on the environment at each stage of their lifecycle. One objective of this LCA exercise is to compare the results obtained for various materials when making materials selection decisions for items ranging from consumer goods to sports arenas. LCA analysis potentially poses a threat to certain metals, especially ones whose production is particularly energy intensive. LCA is still in its infancy, and quantitative data are scarce for any material, however, copper should fare well in any LCA by virtue of the large amount of copper scrap that is recycled. Since scrap represents energy that has already been expended, its use in products significantly lowers the products' net energy content. For example, it is estimated that the mining, smelting, and refining of primary copper by traditional means requires about 62 MJ/kg. However, refined copper is now derived from smelting, leaching (SXEW) and scrap recycling. When the latter two energy-efficient sources are factored in, it is estimated that the resulting refined copper requires (in the United States) an average of only about 36 MJ/kg (63).

LCA-type comparisons can, for example, be applied to copper plumbing tube and chlorinated poly (vinyl chloride) (CPVC) pipe—products that compete in several global markets. Using the energy intensity for copper in the United States and recognizing that 65% of U.S. copper plumbing tube is currently manufactured from recycled scrap, it is estimated that 27 MJ/kg of energy are required to manufacture copper tube (64). It can further be shown that the energy required to manufacture the tube, transport it to an average-sized home in California, install it and to ultimately recycle it back to the manufacturer is 2118 MJ. The comparable amount of energy required for CPVC pipe is 2335 MJ. However, the estimated energy requirements for copper plumbing tube range from 760 MJ (if 100% scrap copper were used to make the tube) to 3900 MJ (100% primary copper). The corresponding range for CPVC is 1500 MJ to 3300 MJ, based on manufacturing data from a European Plastics manufacturers' association (65). From an environmental-impact viewpoint, it is significant to note that whereas copper is recycled for further use at the end of its useful life, CPVC must be disposed of in a landfill.

11. Recycling and Waste Disposal

Because of its high value, copper is among the most throughly recycled metals. A large and sophisticated industry gathers, grades, remelts, and returns copper-base metals to fabricators for reuse in commercial products. Recycled copper is known as *secondary copper* or simply *scrap*, of which there are three categories:

- *Prompt, home*, or *direct scrap*, which originates in smelting and/or fabrication operations. This scrap is recycled within the plant
- *New scrap*, which is metal returned to the fabricator by manufacturers as leftover material. Machine shop turnings (chips) are one example
- *Old scrap*, which includes all worn out, discarded, or salvaged products, such as telephone cable and plumbing tube from demolished buildings.

In North America, copper scrap is graded, according to standard definitions established by the Institute of Scrap Recycling Industries (ISRI). Definitions are based on form and the presence of contaminants (66):

No. 1 Scrap. Scrap that is of cathode quality and that requires only melting and casting. Examples include waste copper rod and bare wire.

No. 2 Scrap. Unalloyed copper scrap that is contaminated with other metals (such as might have been introduced by electroplating or soldering). It may be recycled to a primary smelter, where it is re-refined, reentering the market in the form of high grade cathode.

No. 3 Scrap. Low grade scrap of variable composition (10–88% copper) is processed in smelting furnaces, where it may be fire-refined to high purity. It may additionally be electrorefined to high grade cathode. Refining is performed by *primary* or *secondary smelters*. The latter specialize in scrap recover.

No. 4 Scrap. Alloyed scrap, consisting mainly of brasses, bronzes, and copper–nickels, is recycled to ingot makers or brass mills for the production of new alloys. The scrap is carefully sorted according to composition. The scrap is then melted and compositional adjustments made using air oxidation to

Table 4. **Average Lifetime of Recyclable Copper in Various Applications**[a]

Application	Estimated life in service, years
automobiles	8–15
small electric motors	10–12
electric cable	30–40
brass and other alloy parts	50–60
copper plumbing systems	60–80
roofing and facade sheet	>100

[a] Refs. 67–69.

remove aluminum, chromium, silicon, iron, and sometimes tin in the form of slag. Care is taken to avoid the loss of valuable metals such as zinc in brasses and tin in bronzes. High lead-content scrap (soldered copper–brass automobile radiators are a good example) is used to manufacture leaded brasses and lead-bearing casting alloys, providing a safe repository for lead that might otherwise enter the environment.

Scrap prices are established by the market and are posted daily in the trade press. Published prices generally fluctuate with the market price of refined copper, although supply–demand factors and supplier–client agreements often set the final prices.

Much like steel, copper is an industrial commodity that exists *within* the infrastructure—as electric motor windings, telecommunications cable, and components, where it may remain in service for 50, 80, or even 100 years before entering the scrap cycle. Table 4 lists estimated lifetimes for recyclable copper in various applications (67–69). As a result, the availability of old scrap for recycling is a function of the amount of copper that was used in the past. This situation differs from that for aluminum, whose main uses are short-term and for which metal returns to the scrap cycle within a matter of weeks or months. It has been estimated that the global copper reservoir in installed uses was about 33 million tonnes in 1940 and had grown to 190 million tonnes in 1991 (70). The latter figure corresponds to some 70–80% of all copper mined since 1900. The average growth rate of the installed copper reservoir was about 3 million tons/year over the 50-year period. In the United States, the growth rate of the installed copper reservoir was about 1.2 million tonnes/year during the period 1983–1991.

Because of the delay in the reappearance of scrap copper and the complex nature of scrap flow through the economy, statistical records of copper recycling are difficult to establish and it is impossible to determine precisely how much copper is actually recycled in any given year. The flow of scrap through the copper industry is shown in Figure 7, data for which were taken from, among others, the International Copper Study Group (71). Prompt scrap, which is internally recycled, does not appear in scrap recycling statistics. Available statistical data, however, do allow several important observations to be made:

1. In the United States, between 1978 and 1998, the fraction of the total consumption of copper derived from scrap varied between 35.5% (1998) and

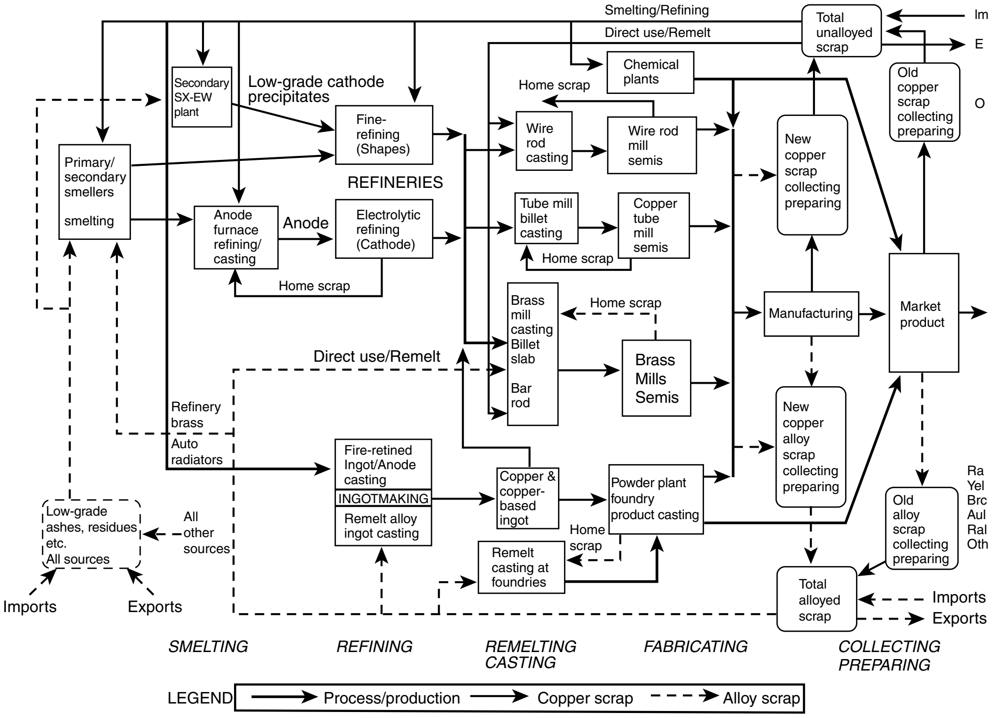

Fig. 7. Copper and copper alloy flowchart. [Data from ICSG (71)].

49.3% (1982). The average for the 21-year period was 43.3% (72). Of this, 68% was new scrap and 32%, old scrap.

2. Approximately 67% of all recovered copper scrap in Western countries does not undergo refining; specifically, it is melted and used directly by brass mills and other fabricators in the fabrication of alloy products. This is equivalent to 35% of all the copper used in the these countries (73). In the United States, where there is a domestic supply of refined copper, between 1978 and 1998 an average of 29% of all copper consumed was consumed directly by fabricators, mainly by brass mills (7). Of this scrap consumed, 52% was alloyed and the remainder unalloyed.
3. The functional distribution of copper uses suggests that approximately 92% of all copper consumed is recyclable. That is, the metal is used in forms and products that are not dissipative (74). Copper chemicals and powders, for example, are dissipative in their use, whereas, solid shapes, such as wire, plate, sheet, and bar, are not. Thus, very few copper or copper alloy products ever reach a landfill for final disposal. Only an estimated 0.5% of copper is lost from nondissipative forms, such as electronic circuitry (70). This factor is discussed in the section on environmental concerns.
4. Figure 8 shows that the amount of scrap used in any given year is a direct function of the price of refined copper (75). The higher the copper price, the greater the amount of scrap that is available for use. Copper scrap is itself a

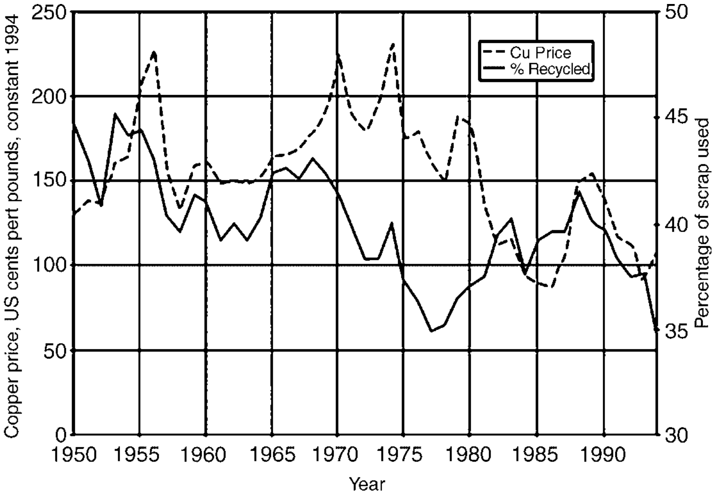

Fig. 8. World percentage of scrap used in refined copper versus copper price (61).

commodity, and scrap dealers tend to speculate by warehousing copper scrap when its price is depressed and offering it for sale when the price rises. As discussed in the environmental concerns section, the production of refined copper from scrap is significantly cheaper than that from ores and concentrates largely because of the reduced amount of energy required.

12. Health and Safety Factors

12.1. Human Metabolism. Copper is an essential trace element required for human metabolism. The total amount of copper in humans, based on individual tissue analyses, is estimated at 50–120 mg for adults and 14 mg for a full-term newborn infant. The concentration of copper in adults and infants is 0.7–1.71 milligrams per kilograms (mg/kg) of body weight and 4 mg/kg of body weight, respectively. The higher concentration of copper in newborn infants compensates for the lack of copper in mothers' milk. This additional copper is imparted to the fetus by the mother in the third trimester of pregnancy. The liver, brain, and heart have the largest concentrations of copper of all the organs in the body. The liver and the brain contain together one-third of the total copper content of the body. The liver plays a central role in copper metabolism and takes part in the storage, distribution, and disposal of copper from the body. All body tissues require copper in their metabolism, but some have greater metabolic needs than others. Copper is normally obtained from food and to a lesser extent, water intake; however, it is also provided in some vitamin and mineral supplements and it is added to baby formulae. According to the safe and adequate intake values established by the U.S. National Academy of Sciences, daily intake of copper should be 1.5–3 mg for adults and 0.7–2 mg for children (76).

Copper is a cofactor for many enzymes that act as catalysts for body functions. It plays a role in erythrocyte formation and development of bone, central nervous system (CNS), and connective tissue. It is necessary for the release of tissue iron and its movement to plasma. Copper is an antioxidant essential for cardiovascular health (77). It is also essential for the production of collagen, the fibrous component that binds heart muscles together, and elastin, a protein substance that makes heart and artery walls elastic. In addition to its metabolic role in the human body, copper acts as an antiinflammatory agent in rheumatoid arthritis and other diseases involving damaged tissue (78).

Copper deficiency is rare in Western countries since diets provide the necessary amount. However, the World Health Organization has expressed its opinion that copper deficiency is more of a potential problem than copper toxicity in humans (79). Children afflicted with chronic diarrhea or fed cow's milk exclusively are prone to copper deficiency (80). A deficiency of copper restricts the pickup of iron and thus inhibits the synthesis of hemoglobin leading to anemia. It can also lead to neutropenia, osteoporosis, arterial disease, and, in the case of severe deficiency, brain damage (81). The effects of copper deficiency are best observed in patients suffering from Menkes disease, a genetic disorder associated with a defect of copper transport and absorption in the body (82). The disease is characterized by rapidly progressive cerebral degeneration, bone lesions resembling those seen in scurvy, and elongation and tortuosity of the cerebral arteries. Death caused by severe, progressive neurodegeneration almost invariably occurs by the age of 3 years. There is no pharmacologic treatment available for Menke's disease.

12.2. Toxicity. Acute environmentally related copper toxicosis is not a major problem in humans as ingestion of excessive quantities of copper salts (25–50 mg of Cu) usually induces immediate expulsion by vomiting (83). In fact, 300 mg of copper sulfate in an 8-oz (0.24-l) glass of water was at one time prescribed extensively by the medical profession as an emetic (84). Death from the intake of huge excesses of copper sulfate has been reported in India, where it has been used as a vehicle for committing suicide (85). However, in at least one instance a patient survived the ingestion of 250 g of copper sulfate (86). Present regulations for the copper content of drinking water are based on the minimum level at which copper can be tasted in the water, about 2.6 mg/l, (87) and the level at which a nauseous feeling is felt by individuals exhibiting a sensitivity to the metal, 3-5 mg/l, (88). However, it has been observed in some communities with a copper content in drinking water of $\leq$8–10 mg/l that people become accustomed to the taste and do not exhibit nausea. In the United States, the regulatory level has been established at 1.0 mg/l and the action level, at 1.3 mg/l. The World Health Organization recommends a level of 2 mg/l based on acute effects (89). The WHO established no limits based on chronic effects.

Since copper is an essential nutrient, humans and other forms of life requiring copper in their metabolism have a variety of mechanisms that function to prevent overdose. Tolerance mechanisms (e.g., homeostasis) make copper generally innocuous (90). However, in the case of direct introduction of copper into the bloodstream, as has occurred in several cases of improperly constructed blood dialysis machines, death can result for copper overdose (88). A small proportion of the population, approximately 1 individual in 30,000, suffers from a genetic deficiency whereby copper is not efficiently removed from the system by the liver. This is known as *Wilson'*s disease (91). If not treated, patients can suffer severe neurologic and psychiatric disturbances and ultimately die of cirrhosis of the liver. The disease, however, can be very effectively treated pharmaceutically. Liver transplantation is the only permanent cure for the disease as it corrects the metabolic defect. In addition, it has been discovered that a very small population of infants suffer from what has been termed an *ecogenetic* disorder whereby affected infants, if exposed to excessive amounts of copper in their diets, succumb within the first year of life of cirrhosis of the liver (92). It appears that this disease is the same as what was previously called *Indian childhood cirrhosis*—a disease endemic to India where it has been customary to prepare infant food by boiling milk and cereal in copper or brass pots (93).

12.3. Medicinal and Antibacterial Qualities. Copper has been used in medicine for thousands of years. The first written record of its use is in the Smith *Papyrus*, an ancient medical record written between 2600 and 2200 B.C. (94). The *Papyrus* records the use of copper (probably in the form of the mineral malachite) to treat chest wounds and to sterilize drinking water. The ancient Egyptians used copper vessels for cooking and serving their food and bronze cups for drinking water (95). Modern research has shown certain copper compounds to be valuable in the treatment of inflammatory diseases, in some forms of cancer, and as an anticonvulsant agent (96). Likewise, copper plumbing tube has been found to be effective in restricting the growth of bacteria, including *Legionella pneumophila*, the cause of Legionnaires' disease (97). Copper–silver ionizers have been found to be effective in controlling *L. pneumophila* in hospital drinking water (98). Such systems have been widely used in the disinfecting of swimming pools (99). Further, research strongly suggests that the pathogen *Escherichia coli* O157 is killed within several hours' exposure to copper surfaces; *E. coli* O157 has caused countless outbreaks of foodborne and waterborne disease around the world and has caused tens of thousands of cases of bacterial gastroenteritis and numerous deaths among the very young and the elderly (100). The bacteriostatic properties of copper-bearing surfaces such as ordinary brass doorknobs and pushplates have also been credited for reducing infection in hospitals and other public buildings (101).

12.4. Worker Health and Safety. With the exception of vineyard sprayer's disease, no significant chronic effects of copper have been reported as a result of occupational exposure. In the case of vineyard sprayer's disease, 5 out of 15 patients who had used Bordeaux mixture, a mixture of copper sulfate and lime long used as a fungicide in agriculture, exhibited lung condensations varying from diffuse reticulonodular shadows to tumorlike opacities (102). A study of copper miners who had spent at least 20 years in copper mines showed no adverse effects (103). Metal fume fever, a 24–48-h illness characterized by dryness in the mouth and throat and headache has been reported in factory workers exposed to copper dust or fumes (104).

Copper mining activities fall under the aegis of the Federal Mine and Safety Act of 1977. The Act sets mandatory standards and requires training for new employees plus annual refresher training for all mine workers. It is administered by the Mine Safety and Health Administration (MSHA). The Occupational Safety and Health Act, which covers mills, smelters, refineries, and fabricators, is similar except that it is administered by the Occupational Safety and Health Administration (OSHA). Both MSHA and OSHA are part of the U.S. Department of Labor.

13. Uses

Figure 1 indicates that the demand for copper has increased continually since the first use of electrical power. Between 1994 and 1997, for example, the rate of growth in copper consumption was approximately 4.5% worldwide, one of the fastest-growth periods in history. Table 5 shows the consumption of copper in the western World from 1992 to 2000 (105).

Copper's useful properties and intrinsic attributes are exploited in the many commercial products in which the metal is used. In the United States, copper and copper alloy consumption, based on the metal's five most important attributes, is as follows (106):

> Electrical conductivity 62%; corrosion resistance 20%; heat transfer 11%; structural 5%; aesthetic 2%.

Electrical and communications wire and cable together with plumbing products account for 85% of refined copper consumption and 63% of total consumption, including scrap. Electrical products are primarily manufactured from refined copper, whose degree of purity ensures high electrical conductivity. About 65% of the copper in plumbing products is derived from copper scrap. Most other applications, including most copper alloys, except those used in coinage, are also based mainly on scrap as a raw material.

Electrical uses constitute the largest single market for refined copper. In the United States, for example, wire and cable accounted for 67% of all refined copper consumed in 1998 (2). In rapidly emerging economies where power and communications infrastructures are being installed, the fraction of refined copper consumed as wire and cable can be as high as 80%. Likewise, in the United States, copper uses are found the markets described in the following subsections.

13.1. Building Construction.

Copper's use in homes and in commercial and industrial buildings is by far the metal's largest market, amounting to approximately 41% of total consumption. Electrical products, plumbing goods, and roofing sheet, respectively, make up the bulk of copper's building-construction applications. An average modern U.S. home, for example, contains approximately 439 lb (200 kg) of copper (see also BUILDING MATERIALS, SURVEY).

Electrical conductors in homes and commercial–industrial buildings are classified as *building wire and cable*. House wiring is almost exclusively copper; the main exception is service entrance cable (from the street to the primary electrical panel), which is often aluminum (see ELECTRICAL CONNECTORS). Penetration by aluminum of the interior house-wiring market, a factor in the 1960s, ebbed quickly after numerous fires were attributed to aluminum wire connections. Today little aluminum is used as interior house wire in the United States, and nearly none is used in Canada. Aluminum house wiring is not, however, uncommon in some developing countries.

Table 5. **Western World Consumption of Refined Copper ('000 Metric Tons)**

Region	1992	1993	1994	1995	1996	1997	1998	1999	2000 e
Western Europe[a]	3,268	3,097	3,341	3,388	3,345	3,534	3,728	3,763	3.920
United States	2,176	2,359	2,560	2,534	2,621	2,790	2,883	2.988	3,005
Japan	1,411	1,384	1,375	1,415	1,480	1,441	1,255	1,294	1,325
Other Asia	1,416	1,620	1,833	1,955	2,128	2,240	2,132	2,527	2,700
Latin America	450	469	503	511	619	714	874	894	984
Canada	156	186	199	190	218	225	246	267	280
Oceania	126	150	148	174	170	166	166	171	175
Africa	104	109	123	117	115	118	110	111	115
Total	*9,107*	*9,374*	*10,082*	*10,283*	*10,694*	*11,228*	*11,394*	*12,015*	*12,504*
Annual growth, (%)	*2*	*3*	*8*	*2*	*4*	*5*	*1*	*5*	*4*

Sources: World Bureau of Metal Statistics, International Copper Study Group and Codelco, Chile, e = estimated.

[a] Includes former German.

Plumbing tube, faucets, valves, and fittings for both potable water and heating use constitute copper's second largest use, accounting for approximately 14% of all copper consumed. Copper plumbing tube is overwhelmingly preferred in the U.S., Canadian, and British markets, and it is widely used in many other industrialized countries. Copper's reliability, based on its corrosion resistance in all but highly aggressive (acidic or exceedingly soft) waters, is the principal reason for the metal's continuing popularity. Ease of installation and ready availability are also important factors, as is, increasingly, appreciation of copper's ability to immobilize certain waterborne pathogens (see section on health and safety factors), thereby ensuring high water quality. Plastic plumbing products for potable water use made from poly (vinyl chloride) (PVC), chlorinated poly (vinyl chloride) (CPVC), crosslinked polyethylene (PEX), and at one time, poly-(butene-1) have encroached on copper tube markets in the United States. In Europe, plastics are challenging copper in the transition from galvanized steel pipe to alternative tubular products. In less developed countries, the plastic products' initial low cost and local availability has gained them market dominance. For energy efficiency reasons, copper tube has become the material of choice for most residential and commercial air-conditioning–refrigeration (ACR) systems. ACR applications represent about 9% of the market for copper and copper alloys in the United States. The desire for increased energy efficiency is driving a trend toward the increased use of thinner tubes, longer lengths, and enhanced-surface tubes.

Roofing sheet and related products such as gutters and downspouts are important (and highly visible) uses for copper. Much of the copper used in such applications is refined from scrap. In the past, copper roofing was relegated mainly to public buildings. This trend continues, although the 1990s saw significant growth of copper for architectural purposes in private homes, as well. In addition to roofing products, copper, brasses, and bronzes are used as wall and column sheathing, fascia, banisters and railings, architectural hardware, and decorative trim. Copper competes with many other building products in these applications, but the metal's wide spectrum of pleasing colors and textures and "natural" origin are seen by architects as unique advantages.

Copper, in the form of brass and bronze alloys, is widely used in builders' hardware, such as lock sets, doorknobs, hinges, and push- and kickplates. Coatings developed in the 1990s have ensured lifetime tarnish-resistant service in such products.

13.2. Electrical and Electronic Products. Copper's use in electrical and electronic products constitutes about 26% of the total market for copper in the United States (see also ELECTRONIC MATERIALS). Power utilities contribute to about 9% of total consumption. Included here are both electric-utility applications and equipment that connects to utility lines, such as switchgear and load centers. Copper cable competes well with aluminum in industrial applications, its position strengthened by the metal's higher electrical conductivity, which reduces the amount of energy otherwise lost as heat. Copper is not widely used for overhead transmission or distribution cables (except in parts of Japan and Africa) since its high density, compared with aluminum, requires more closely spaced towers. Many underground transmission and distribution cables are copper, however. Copper is preferred for ultra-high-voltage lines, 345 kV, because the metal's high electrical conductivity per unit volume and high thermal conductivity enable it to conduct large currents in narrow conduits. Copper's corrosion resistance is also advantageous here. There has been a trend, seen mainly in Europe, toward conversion of low to medium voltage (1–60-kV) overhead lines to underground cables.This shift has opened a new market for copper. Market drivers include underground cables' favorable lifecycle economics, increased safety and security, and aesthetics.

Copper magnet wire—that used in electric motors, transformers, and similar devices—continues to be an important copper product. About 60% of all electricity is used to drive electric motors, and a global need for better energy conservation has consequently led to a growing adoption of so-called high efficiency or premium-efficiency motors. For example, a standard 100-hp 74,57-kW AC motor, type D, having 73.5 lb (27.43 kg) of copper in its windings, exhibits an energy efficiency of 93.0%. A premium-efficiency motor of the same horsepower will have 125 lb (46.65 kg) of copper in its windings and will operate at 95.4% efficiency. Besides energy savings, there is a cost savings since the payback time for the premium motor is normally 2 years or less, depending on power cost, motor size, and duty cycle.Telecommunications represents about 9% of the market for copper in the United States. Copper ("twisted pair") communications cable, once seen as obsolescent, is actually an *increasing* market for copper. Fiber optic cable and to a lesser extent coaxial cable and microwave transmission have replaced copper in long lines. However, copper still dominates the subscriber loop (that part of the system located between the telephone central office and the customer), primarily in that portion of the loop between the digital loop carrier and the customer, where most of the copper used in telecommunications can be found. Market factors favorable to copper include its low cost relative to fiber, rapid growth in data communications, growth in Internet usage, recyclability, introduction of high-bandwidth products such as enhanced Category 5 cable and growing availability of digital subscriber line (DSL) telephone service. It is now possible, for example, for twisted-pair copper cables to accommodate data transfer at a rate greater than one gigabyte per second.

Approximately 4.5% of copper and copper alloy products are used in the electronics industry in the United States. Electrical contacts, connectors, and switch components are important outlets for copper and copper alloy strip. Pure copper foil, produced either by rolling, or more often by electrodeposition, is used in many printed circuits. Copper interconnects for integrated circuits, announced in the late 1990s, promise to increase processing speed several-fold over traditional circuitry, which rely on aluminum. While this application will account for only a few thousand pounds of copper annually, it clearly grants the metal standing as a "high technology" material.

Other important copper electrical products include busbar (which is made from plate or heavy tube), superconducting cable (in which copper acts as a thermal buffer), plus a countless variety of switch and contact components, connectors, leadframes, pole-line hardware, and high voltage switchgear products. Many of these products are made from brass, phosphor copper, and copper alloys that were specifically developed for their respective service conditions. Copper has no serious competitors here.

13.3. Transportation Equipment. Transportation uses (automobiles, trucks, buses, ships, aircraft, and aerospace) constitute about 12% of the market for copper and copper alloys in the United States. Automobile wiring harnesses represent the largest portion, about 8%, of this copper. The proliferation of electronic and electrical features in modern automobiles has increased the use of copper in wiring harnesses, motors, contacts, switches, and power supplies to the extent that these devices constitute most of the 25 kg (50 lb) of copper used in a modern American automobile. The remainder can be found in the cooling and brake systems and as an alloying ingredient in various aluminum alloy castings. The change from 12/14- to 36/42-V electrical systems will permit the use of thinner wires. However, the continuing proliferation of electrical and electronic devices will require larger number of wires, and the total amount of copper in wiring harness is therefore expected to remain about the same, if not increase.

Thin-gauge copper and brass strip for automotive radiators, once an important market, declined steadily after the introduction of aluminum radiators in the 1970s. However, radiators for trucks as well as those for the automobile after market continue to consume approximately 200,000 tonnes of copper annually, worldwide. Copper–brass radiators for new cars are also preferred in tropical countries where use of corrosion-inhibiting antifreeze compounds (necessary with aluminum but not copper) is uncommon. Many technical deficiencies in traditional copper–brass radiators were associated with the units' soldered assembly. An improved lightweight *brazed* copper–brass radiator developed by the International Copper Research Association and the International Copper Association, introduced in 1998, may regain some of copper's former original-equipment market share.

Copper alloys are widely used in marine applications ranging from propellers to seawater piping, pumps, heat exchangers, condensers, and other equipment. Alloys most commonly used include copper–nickels (condenser tubes), leaded brasses (tubesheets), aluminum bronzes (pipe, pump, and valve components), nickel–aluminum bronzes (propellers), aluminum brasses (tube), manganese bronzes (pump and valve components), and silicon bronzes (pump and valve components). Copper's traditionally large market share in these applications is being challenged by stainless steels and titanium, which offer properties comparable to copper alloys except for biofouling resistance. Copper–nickel sheathing applied to the legs of offshore platforms prevents buildup of algae, thereby increasing safety and reducing costs. Although technically viable, this market has been slow to develop. Ship hull sheathing, historically an important use for copper, has in modern times been limited to small craft. Copper, in the form of cuprous oxide and other specialty compounds is widely used in antifouling hull paints. Copper hull paints are environmentally superior to organotin coatings, which once threatened copper in this market but are now widely banned.

13.4. Industrial Machinery and Equipment. This market sector, which includes in-plant equipment, nonelectrical instruments, and off-highway vehicles, is the fourth largest for copper in the United States, representing approximately 11% of total consumption. A wide variety of copper alloys are used in industrial valves and fittings, sintered and cast bronze bearings, and heat exchanger (see also HEAT EXCHANGE TECHNOLOGY, HEAT PIPES) and condenser pipe and tube for both fresh water and seawater cooling.

13.5. Consumer and General Products. Approximately 9% of the total copper and copper alloys used in the United States are found in consumer and general products. Copper used in home appliances constitutes about 3% of this volume. Other uses are spread over an enormous variety, including consumer electronics, appliance cords, coinage, agricultural fungicides, wood preservatives, food additives, military and commercial ordnance, fasteners and closures, and utensils and cutlery.

Also included in this category are copper chemicals that, as a product form, represent about 1% of the copper market. Copper's unique chemical, toxicologic and nutritional properties enable it to serve a number of niche markets in both the agricultural and industrial sectors. Agriculturally, copper compounds are used as fungicides (55% of consumption) (see Fungicides, agricultural) livestock feeds (8%), crop nutrients (6%), and other uses. Among industrial uses, wood preservative (12%), antifouling paints (7%), mining and metallurgy (4%) chemicals and petroleum processing (4%), and textile and leather treatment (2%) are major uses (107). Copper sulfate, copper oxides and oxychlorides, and copper hydroxide are the dominant chemical product forms.

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K. J. A. KUNDIG
Metallurgical Consultant
W. H. DRESHER
WHD Consulting