

22

Metals I: Metallurgy



OUTLINE

Metals

22-1 Occurrence of the Metals

Metallurgy

22-2 Pretreatment of Ores

22-3 Reduction to the Free Metals

22-4 Refining of Metals

Metallurgies of Specific Metals

22-5 Magnesium

22-6 Aluminum

22-7 Iron

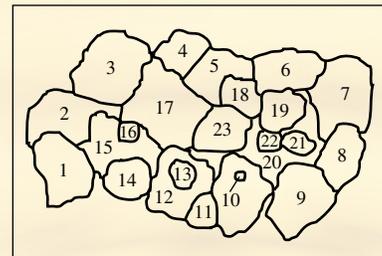
22-8 Copper

22-9 Gold

OBJECTIVES

After you have studied this chapter, you should be able to

- Describe major sources of metals
- Describe some pretreatment techniques for ores
- Describe some reduction processes that produce free metals
- Describe some techniques for refining (purifying) metals
- Describe the specific metallurgies of five metals: magnesium, aluminum, iron, copper, and gold



A cluster of 21 minerals that are present in ores, plus two samples of native ores (free metals, Ag and Bi). These are identified in the following list.

1. Bornite (iridescent)—COPPER
2. Dolomite (pink)—MAGNESIUM
3. Molybdenite (gray)—MOLYBDENUM
4. Skutterudite (gray)—COBALT, NICKEL
5. Zincite (mottled red)—ZINC
6. Chromite (gray)—CHROMIUM
7. Stibnite (*top right*, gray)—ANTIMONY
8. Gummite (yellow)—URANIUM
9. Cassiterite (rust, *bottom right*)—TIN
10. Vanadinite crystal on Goethite (red crystal)—VANADIUM
11. Cinnabar (red)—MERCURY
12. Galena (gray)—LEAD
13. Monazite (white)—RARE EARTHS: cerium, lanthanum, neodymium, thorium
14. Bauxite (gold)—ALUMINUM
15. Strontianite (white, spiny)—STRONTIUM
16. Cobaltite (gray cube)—COBALT
17. Pyrite (gold)—IRON
18. Columbinite (tan, gray stripe)—NIOBIUM, TANTALUM
19. Native BISMUTH (shiny)
20. Rhodochrosite (pink)—MANGANESE
21. Rutile (shiny twin crystal)—TITANIUM
22. Native SILVER (filigree on quartz)
23. Pyrolusite (black, powdery)—MANGANESE

METALS

Metals are widely used for structural purposes in buildings, cars, railroads, ships, and aircraft. They also serve as conductors of heat and electricity. Medical and nutritional research during recent decades has provided much insight into important biological functions of metals. The metals Na, K, Ca, and Mg, as well as some nonmetals (C, H, O, N, P, and S), are present in the human body in substantial quantities. Many other metals are present in lesser quantities in the human body, but they are essential to our well-being (see essay “Trace Elements and Life” in Chapter 23). In this chapter, we shall study the occurrence of metals and examine processes for obtaining metals from their ores.

22-1 OCCURRENCE OF THE METALS

In our study of periodicity we learned that metallic character increases toward the left and toward the bottom of the periodic table (Section 4-1) and that oxides of most metals are basic (Section 6-8, part 2). The oxides of some metals (and metalloids) are amphoteric (Section 10-6). In Section 13-17 we described metallic bonding and related the effectiveness of metallic bonding to the characteristic properties of metals.

The properties of metals influence the kinds of ores in which they are found, and the metallurgical processes used to extract them from their ores. Metals with negative standard reduction potentials (active metals) are found in nature in the combined state. Those with positive reduction potentials, the less active metals, may occur in the uncombined free state as **native ores**. Examples of native ores are Cu, Ag, Au, and the less abundant Pt, Os, Ir, Ru, Rh, and Pd. Cu, Ag, and Au are also found in the combined state.

Many “insoluble” compounds of the metals are found in the earth’s crust. Solids that contain these compounds are the **ores** from which metals are extracted. Ores contain **minerals**, comparatively pure compounds of the metals of interest, mixed with relatively large amounts of **gangue**—sand, soil, clay, rock, and other material. Soluble compounds are found dissolved in the sea or in salt beds in areas where large bodies of water have evaporated. Metal ores can be classified by the anions with which the metal ions are combined (Table 22-1 and Figure 22-1).

Pronounce “gangue” as one syllable with a soft final g.

METALLURGY

Metallurgy is the commercial extraction of metals from their ores and the preparation of metals for use. It usually includes several steps: (1) mining the ore, (2) pretreatment of the ore, (3) reduction of the ore to the free metal, (4) refining or purifying the metal, and (5) alloying, if necessary.

TABLE 22-1 *Common Classes of Ores*

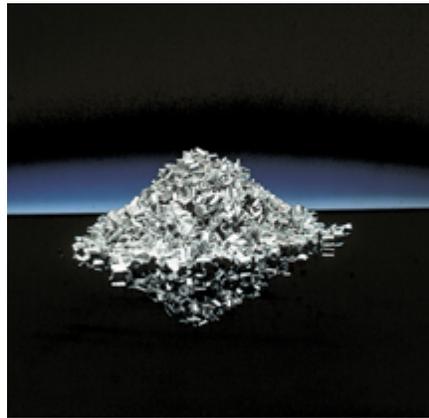
Anion	Examples and Names of Minerals
none (native ores)	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd, As, Sb, Bi, Cu
oxide	hematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; bauxite, Al_2O_3 ; cassiterite, SnO_2 ; periclase, MgO ; silica, SiO_2
sulfide	chalcopyrite, CuFeS_2 ; chalcocite, Cu_2S ; sphalerite, ZnS ; galena, PbS ; iron pyrites, FeS_2 ; cinnabar, HgS
chloride	rock salt, NaCl ; sylvite, KCl ; carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
carbonate	limestone, CaCO_3 ; magnesite, MgCO_3 ; dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$; rhodochrosite, MnCO_3
sulfate	gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; barite, BaSO_4
silicate	beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; kaolinite, $\text{Al}_2(\text{Si}_2\text{O}_8)(\text{OH})_4$; spodumene, $\text{LiAl}(\text{SiO}_3)_2$

The most widespread minerals are silicates. But extraction of metals from silicates is very difficult. Metals are obtained from silicate minerals only when there is no other more economical alternative.

Key																			
 Sulfides	 Phosphates																		
 Oxides	 Silicates																		
 Occur uncombined	 C from coal, B from borax																		
 Halide salts	 Carbonates																		

H																						H	He
Li	Be													B	C	N	O				F	Ne	
Na	Mg													Al	Si	P	S				Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo		Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi								Rn	
Lanthanides																							
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								

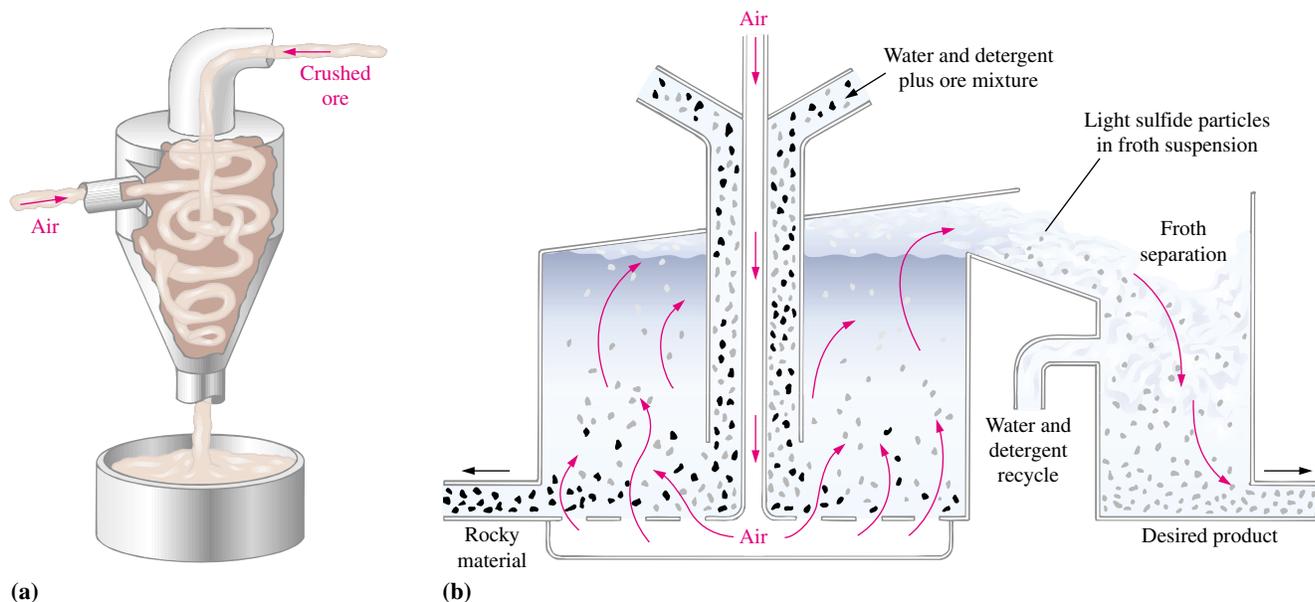
Figure 22-1 Major natural sources of the elements. The soluble halide salts are found in oceans, salt lakes, brine wells, and solid deposits. Most helium is obtained from wells in the United States and Russia. Most of the other noble gases are obtained from air.



(Left) The pink mineral rhodochrosite is manganese carbonate, MnCO_3 . (Right) A pile of manganese metal. Manganese is an important element in steels that must withstand great shock, such as those used to construct rock crushers.

22-2 PRETREATMENT OF ORES

After being mined, many ores must be concentrated by removal of most of the gangue. Most sulfides have relatively high densities and are denser than gangue. After pulverization, the lighter gangue particles are removed by a variety of methods. One involves



Some sulfide minerals: iron pyrite (fool's gold), FeS_2 ; black galena, PbS ; yellow orpiment, As_2S_3 .



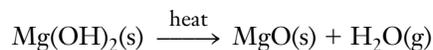
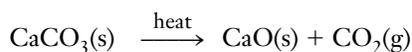
Panning for gold is possible because of the high density of the native metal.

Figure 22-2 (a) The cyclone separator enriches metal ores. Crushed ore is blown in at high velocity. Centrifugal force takes the heavier particles, with higher percentages of metal, to the wall of the separator. These particles spiral down to the collection bin at the bottom. Lighter particles, not as rich in the metal, move into the center. They are carried out the top in the air stream. (b) A representation of the flotation process for enrichment of copper sulfide ore. The relatively light sulfide particles are suspended in the water–oil–detergent mixture and collected as a froth. The denser material sinks to the bottom of the container.

blowing the lighter particles away via a cyclone separator (Figure 22-2a). These particles can be sifted out through layers of vibrating wire mesh or on inclined vibration tables.

Hydrophilic (“water-loving”) particles are made wet by water; hydrophobic (“water-hating”) particles are not made wet by water. These two kinds of particles are separated in the **flotation process**. This method is particularly applicable to sulfides, carbonates, and silicates, which are not “wetted” by water or else can be made water-repellent by treatment. Their surfaces are easily covered by layers of oil or other flotation agents. A stream of air is blown through a swirled suspension of such an ore in water and oil (or other agent). Bubbles form in the oil on the mineral particles and cause them to rise to the surface. The bubbles are prevented from breaking and escaping by a layer of oil and emulsifying agent. A frothy ore concentrate forms at the surface. By varying the relative amounts of oil and water, the types of oil additive, the air pressure, and so on, it is even possible to separate one metal sulfide, carbonate, or silicate from another (Figure 22-2b).

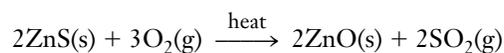
Another pretreatment process involves chemical modification. This converts metal compounds to more easily reduced forms. Carbonates and hydroxides may be heated to drive off CO_2 and H_2O , respectively.



Some sulfides are converted to oxides by **roasting**, that is, heating below their melting points in the presence of oxygen from air. For example,



Figure 22-3 Trees damaged by acid rain and air pollution in the southwestern United States.



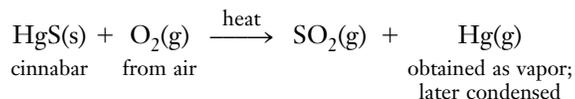
Roasting sulfide ores causes air pollution. Enormous quantities of SO_2 escape into the atmosphere (Section 6-8, part 4), where it causes great environmental damage (Figure 22-3). Federal regulations now require limitation of the amount of SO_2 that escapes with stack gases and fuel gases. Now most of the SO_2 is trapped and used in the manufacture of sulfuric acid (Section 24-12).

Some of these environmental problems are discussed in the Chemistry in Use essay “Acid Rain.”

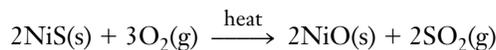
22-3 REDUCTION TO THE FREE METALS

The method used for reduction, or smelting, of metal ores to the free metals depends on how strongly the metal ions are bonded to anions. When the bonding is strong, more energy is required to reduce the metals. This makes reduction more expensive. The most active metals usually have the strongest bonding.

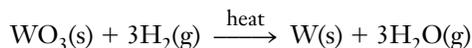
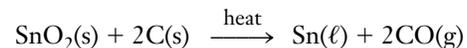
The least reactive metals occur in the free state and thus require no reduction. Examples include Au, Ag, and Pt. This is why gold and silver have been used as free metals since prehistoric times. Some less active metals, such as Hg, can be obtained directly from their sulfide ores by roasting. This reduces metal ions to the free metals by oxidation of the sulfide ions.



Roasting sulfides of the more active metals produces metal oxides, but no free metals.



The resulting metal oxides are then reduced to free metals with coke or CO. If C must be avoided, another reducing agent, such as H_2 , Fe, or Al, is used.

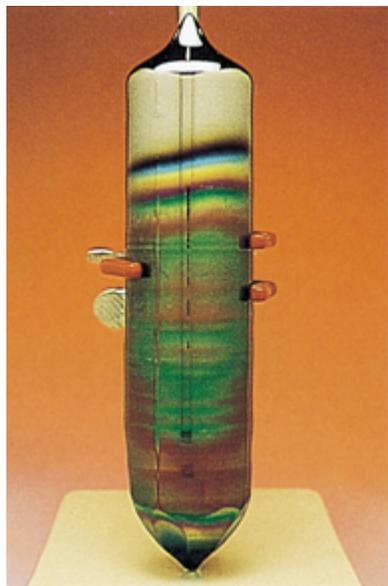


Rutile contains TiO_2 .

Coke is impure carbon.

TABLE 22-2 Reduction Processes for Some Metals

	Metal Ion	Typical Reduction Process
 Increasing activity of metals	lithium, Li^+ potassium, K^+ calcium, Ca^{2+} sodium, Na^+ magnesium, Mg^{2+} aluminum, Al^{3+}	Electrolysis of molten salt
	manganese, Mn^{2+} zinc, Zn^{2+} chromium, Cr^{2+} , Cr^{3+} iron, Fe^{2+} , Fe^{3+}	Reaction of oxide with coke (carbon) or carbon monoxide (CO)
	lead, Pb^{2+} copper, Cu^{2+} silver, Ag^+ mercury, Hg^{2+} platinum, Pt^{2+} gold, Au^+	Element occurring free, or easily obtained by roasting the sulfide or oxide ore



Ultrapure silicon is produced by zone refining.

The end containing the impurities can be sliced off and recycled.

The very active metals, such as Al and Na, are reduced electrochemically, usually from their anhydrous molten salts. If H_2O is present, it is reduced instead of the more active metals. Tables 22-2 and 22-3 summarize reduction processes for some metal ions.

22-4 REFINING OF METALS

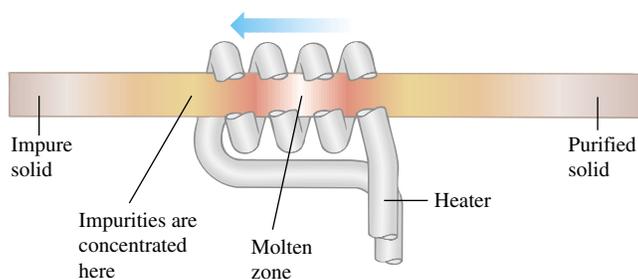
Metals obtained from reduction processes are almost always impure. Further refining (purification) is usually required. This can be accomplished by distillation if the metal is more volatile than its impurities, as in the case of mercury. Among the metals purified by electrolysis (Sections 21-3 to 21-7) are Al (Section 22-6), Cu (Section 22-8), Ag, and Au (Section 22-9).

Zone refining is often used when extremely pure metals are desired for such applications as solar cells and semiconductors (Section 13-17). An induction heater surrounds a bar of the impure solid and passes slowly from one end to the other (Figure 22-4). As it passes, it melts portions of the bar, which slowly recrystallize as the heating element moves away. The impurity does not fit into the crystal as easily as the element of interest, so most of it is carried along in the molten portion until it reaches the end. Repeated passes of the heating element produce a bar of high purity.

After refining, many metals are alloyed, or mixed with other elements, to change their physical and chemical characteristics. In some cases, certain impurities are allowed to remain during refining because their presence improves the properties of the metal. For example, a small amount of carbon in iron greatly enhances its hardness. Examples of alloys include brass (Cu and Zn), bronze (Cu and Sn), duralumin (Al, Cu, Mg, and Mn), and stainless steel (Fe, Cu, Mn, plus others).

TABLE 22-3 *Some Specific Reduction Processes*

Metal	Compound (ore)	Reduction Process	Comments
mercury	HgS (cinnabar)	Roast reduction; heating of ore in air $\text{HgS} + \text{O}_2 \xrightarrow{\text{heat}} \text{Hg} + \text{SO}_2$	
copper	sulfides such as Cu ₂ S (chalcocite)	Blowing of oxygen through purified molten Cu ₂ S $\text{Cu}_2\text{S} + \text{O}_2 \xrightarrow{\text{heat}} 2\text{Cu} + \text{SO}_2$	Preliminary ore concentration and purification steps required to remove FeS impurities
zinc	ZnS (sphalerite)	Conversion to oxide and reduction with carbon $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\text{heat}} 2\text{ZnO} + 2\text{SO}_2$ $\text{ZnO} + \text{C} \xrightarrow{\text{heat}} \text{Zn} + \text{CO}$	Process also used for the production of lead from galena, PbS
iron	Fe ₂ O ₃ (hematite)	Reduction with carbon monoxide produced from coke $2\text{C} (\text{coke}) + \text{O}_2 \xrightarrow{\text{heat}} 2\text{CO}$ $\text{Fe}_2\text{O}_3 + 3\text{CO} \xrightarrow{\text{heat}} 2\text{Fe} + 3\text{CO}_2$	
titanium	TiO ₂ (rutile)	Conversion of oxide to halide salt and reduction with an active metal $\text{TiO}_2 + 2\text{Cl}_2 + 2\text{C} \xrightarrow{\text{heat}} \text{TiCl}_4 + 2\text{CO}$ $\text{TiCl}_4 + 2\text{Mg} \xrightarrow{\text{heat}} \text{Ti} + 2\text{MgCl}_2$	Also used for the reduction of UF ₄ obtained from UO ₂ , pitchblende
tungsten	FeWO ₄ (wolframite)	Reduction with hydrogen $\text{WO}_3 + 3\text{H}_2 \xrightarrow{\text{heat}} \text{W} + 3\text{H}_2\text{O}$	Used also for molybdenum
aluminum	Al ₂ O ₃ · xH ₂ O (bauxite)	Electrolytic reduction (electrolysis) in molten cryolite, Na ₃ [AlF ₆], at 1000°C $2\text{Al}_2\text{O}_3 \xrightarrow{\text{heat}} 4\text{Al} + 3\text{O}_2$	
sodium	NaCl (sea water)	Electrolysis of molten chlorides $2\text{NaCl} \xrightarrow{\text{heat}} 2\text{Na} + \text{Cl}_2$	Also for calcium, magnesium, and other active metals in Groups IA and IIA

**Figure 22-4** A representation of a zone refining apparatus.

METALLURGIES OF SPECIFIC METALS

Mg and Al are active metals, Fe and Cu are moderately active, and Au is relatively inactive.

The metallurgies of Mg, Al, Fe, Cu, and Au will be discussed as specific examples. The order of increasing standard reduction potentials of these metals indicates the order of increasing ease of reduction to the free metals.

Reduction Half-Reaction	Standard Reduction Potential E^0 , Volts
$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337
$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.50

22-5 MAGNESIUM

Magnesium occurs widely in carbonate ores, but most Mg comes from salt brines and from the sea (Figure 22-5). Sea water is 0.13% Mg by mass. Because of its low density (1.74 g/cm^3), Mg is used in lightweight structural alloys for such items as automobile and aircraft parts.

Magnesium ions are precipitated as $\text{Mg}(\text{OH})_2$ by addition of $\text{Ca}(\text{OH})_2$ (slaked lime) to sea water. The slaked lime is obtained by crushing oyster shells (CaCO_3), heating them to produce lime (CaO), and then adding a limited amount of water (slaking).

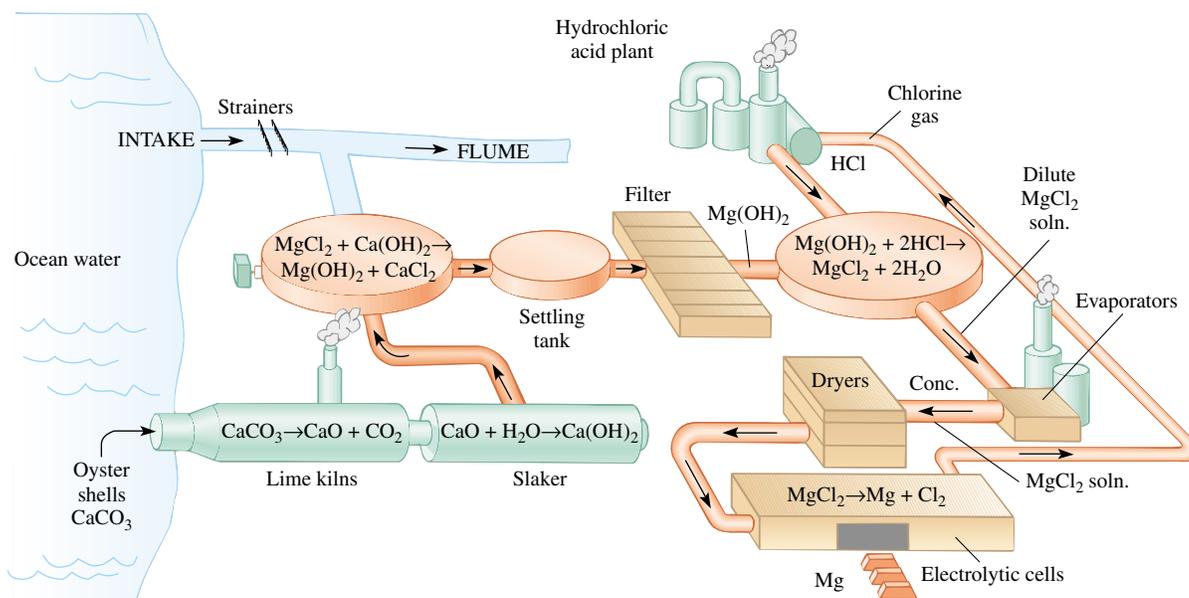


Figure 22-5 Schematic diagram of an industrial plant for the production of magnesium from the Mg^{2+} ions in sea water.

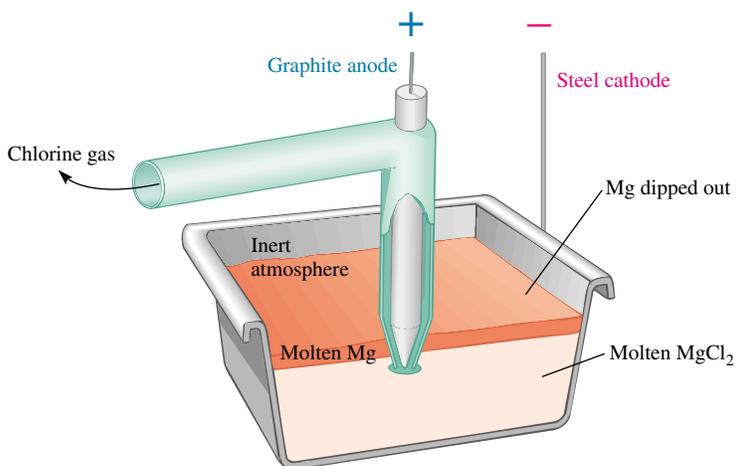
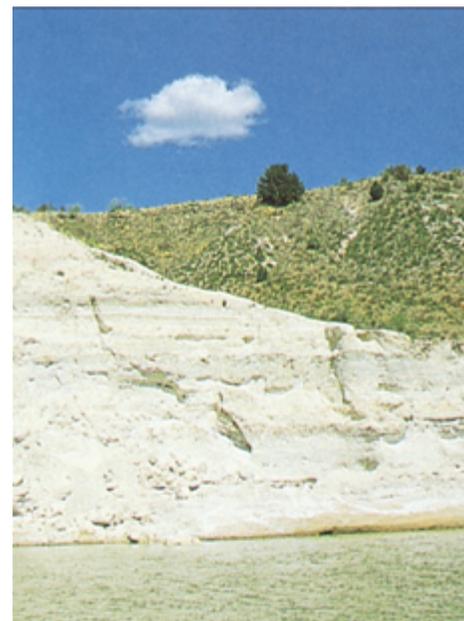
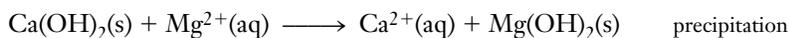


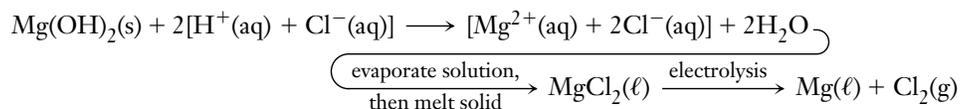
Figure 22-6 A cell for electrolyzing molten MgCl_2 . The magnesium metal is formed on the steel cathode and rises to the top, where it is dipped off periodically. Chlorine gas is formed around the graphite anode and is piped off.



A bed of limestone, CaCO_3 , along the Verde River, Arizona.



The last reaction occurs because K_{sp} for $\text{Mg}(\text{OH})_2$, 1.5×10^{-11} , is much smaller than that for $\text{Ca}(\text{OH})_2$, 7.9×10^{-6} . The milky white suspension of $\text{Mg}(\text{OH})_2$ is filtered, and the solid $\text{Mg}(\text{OH})_2$ is then neutralized with HCl to produce a MgCl_2 solution. Evaporation of the H_2O leaves solid MgCl_2 , which is then melted and electrolyzed (Figure 22-6) under an inert atmosphere to produce molten Mg and gaseous Cl_2 . The products are separated as they are formed, to prevent recombination.

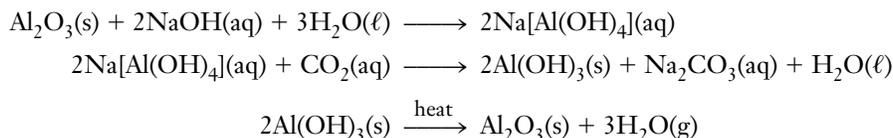


Magnesium is cast into ingots or alloyed with other light metals. The Cl_2 by-product is used to produce more HCl for neutralization of $\text{Mg}(\text{OH})_2$.

22-6 ALUMINUM

Aluminum is the most commercially important nonferrous metal. Its chemistry and uses will be discussed in Section 23-7. Aluminum is obtained from bauxite, or hydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Aluminum ions can be reduced to Al by electrolysis only in the absence of H_2O . First the crushed bauxite is purified by dissolving it in a concentrated solution of NaOH to form soluble $\text{Na}[\text{Al}(\text{OH})_4]$. Then $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ is precipitated from the filtered solution by blowing in carbon dioxide to neutralize the unreacted NaOH and one OH^- ion per formula unit of $\text{Na}[\text{Al}(\text{OH})_4]$. Heating the hydrated product dehydrates it to Al_2O_3 .

Recall that Al_2O_3 is amphoteric. Impurities such as oxides of iron, which are not amphoteric, are left behind in the crude ore.

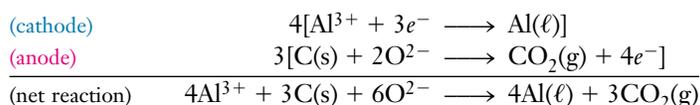


For clarity, we have not shown waters of hydration.

A mixture of compounds typically has a lower melting point than any of the pure compounds (Chapter 14).

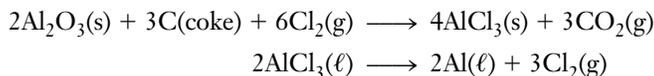
The melting point of Al_2O_3 is 2045°C ; electrolysis of pure molten Al_2O_3 would have to be carried out at or above this temperature, with great expense. It can be done, however, at a much lower temperature when Al_2O_3 is mixed with much lower-melting cryolite, a mixture of NaF and AlF_3 often represented as $\text{Na}_3[\text{AlF}_6]$. The molten mixture can be electrolyzed at 1000°C with carbon electrodes. The cell used industrially for this process, called the **Hall–Héroult process**, is shown in Figure 22-7.

The inner surface of the cell is coated with carbon or carbonized iron, which functions as the cathode at which aluminum ions are reduced to the free metal. The graphite anode is oxidized to CO_2 gas and must be replaced frequently. This is one of the chief costs of aluminum production.



Molten aluminum is denser than molten cryolite, so it collects in the bottom of the cell and is drawn off and cooled to a solid.

A more economical approach, the Alcoa chlorine process, has now been developed on a commercial scale. The anhydrous bauxite is first converted to AlCl_3 by reaction with Cl_2 in the presence of carbon. The AlCl_3 is then melted and electrolyzed to give aluminum, and the recovered chlorine is reused in the first step.



This process uses only about 30% as much electrical energy as the Hall–Héroult process.

The use of large amounts of electrical energy in electrolysis makes production of aluminum from ores an expensive metallurgy. Methods for recycling used Al use less than 10% of the energy required to make new metal from bauxite by the Hall–Héroult process.



Many consumer items are made of aluminum.

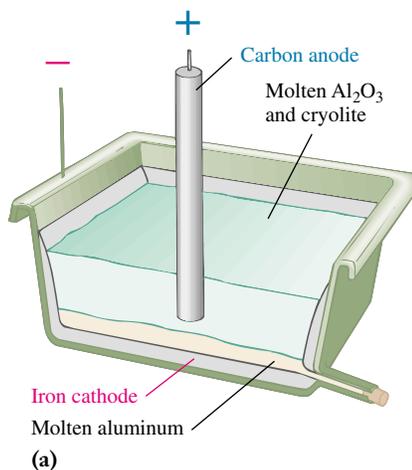


Figure 22-7 (a) Schematic drawing of a cell for producing aluminum by electrolysis of a melt of Al_2O_3 in $\text{Na}_3[\text{AlF}_6]$. The molten aluminum collects in the container, which acts as the cathode. (b) Casting molten aluminum. Electrolytic cells used in the Hall–Héroult process appear in the background.



(b)

Processing of recycled Al now accounts for more than half of the production of this metal. Recycling of aluminum drink cans is now so successful that more than two thirds of this aluminum is used to produce new cans. The typical time elapsed from collection of cans until new ones made from the same aluminum appear on supermarket shelves is only a few weeks.

22-7 IRON

The most desirable iron ores contain hematite, Fe_2O_3 , or magnetite, Fe_3O_4 . As the available supplies of these high-grade ores have dwindled, taconite, which is magnetite in very hard silica rock, has become an important source of iron. The oxide is reduced in blast furnaces (Figure 22-8) by carbon monoxide. Coke mixed with limestone (CaCO_3) and crushed ore is admitted at the top of the furnace as the “charge.” A blast of hot air from the bottom burns the coke to carbon monoxide with the evolution of more heat.

In Fe_3O_4 , the formal oxidation state of iron is $+\frac{8}{3}$. Two thirds of the Fe atoms are in the +3 state and the other one third are in the +2 state. The formula is sometimes written as $\text{Fe}_2\text{O}_3 \cdot \text{FeO}$.

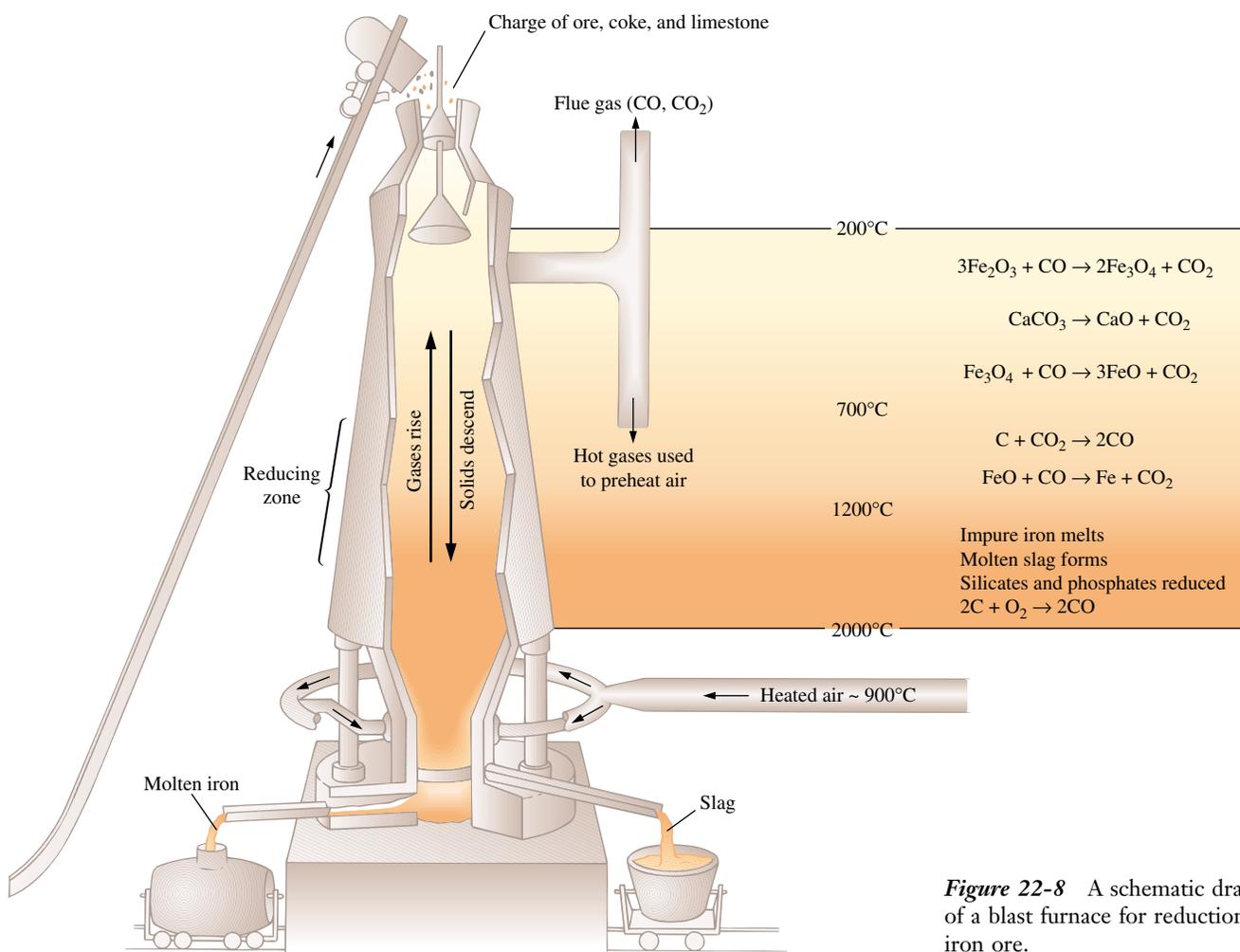


Figure 22-8 A schematic drawing of a blast furnace for reduction of iron ore.



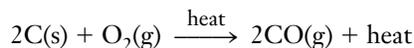
Iron ore is scooped in an open-pit mine.

Reaction of a metal oxide (basic) with a nonmetal oxide (acidic) forms a salt.

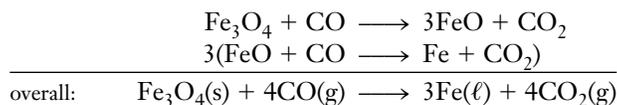
Considerable amounts of slag are also used to neutralize acidic soil. If there were no use for the slag, its disposal would be a serious economical and environmental problem.



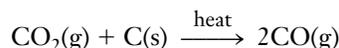
Molten steel is poured from a basic oxygen furnace.



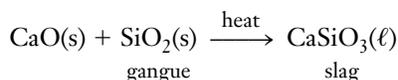
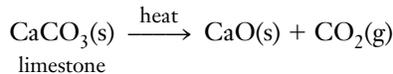
Most of the oxide is reduced to molten iron by carbon monoxide, although some is reduced directly by coke. Several stepwise reductions occur (see Figure 22-8), but the main reactions for Fe_3O_4 can be summarized as follows:



Much of the CO_2 reacts with excess coke to produce more CO to reduce the next incoming charge.



The limestone, called a **flux**, reacts with the silica gangue in the ore to form a molten **slag** of calcium silicate.



The slag is less dense than molten iron; it floats on the surface of the iron and protects it from atmospheric oxidation. Both are drawn off periodically. Some of the slag is subsequently used in the manufacture of cement.

The iron obtained from the blast furnace contains carbon, among other things. It is called **pig iron**. If it is remelted, run into molds, and cooled, it becomes **cast iron**. This is brittle because it contains much iron carbide, Fe_3C . If all the carbon is removed, nearly pure iron can be produced. It is silvery in appearance, quite soft, and of little use. If *some* of the carbon is removed and other metals such as Mn, Cr, Ni, W, Mo, and V are added, the mixture becomes stronger and is known as **steel**. There are many types of steel, containing alloyed metals and other elements in various controlled proportions. Stainless steels show high tensile strength and excellent resistance to corrosion. The most common kind contains 14–18% chromium and 7–9% nickel.

Pig iron can also be converted to steel by burning out most of the carbon with O_2 in a basic oxygen furnace (Figure 22-9). Oxygen is blown through a heat-resistant tube inserted below the surface of the *molten* iron. Carbon burns to CO, which subsequently escapes and burns to CO_2 .

22-8 COPPER

Copper is so widely used, especially in its alloys such as bronze (Cu and Sn) and brass (Cu and Zn), that it is becoming very scarce. The U.S. Bureau of Mines estimates that the known worldwide reserves of copper ore will be exhausted during the first half of the twenty-first century (Figure 22-10). It is now profitable to mine ores containing as little as 0.25% copper. The increased use of fiber optics in place of copper in communications cables may help to lessen the demand for this metal. The use of superconducting materials in electricity transmission lines could eventually provide enormous savings.

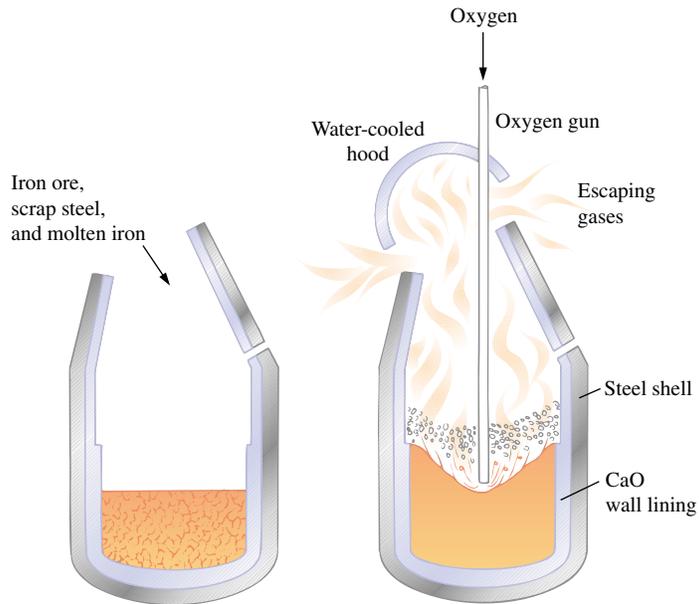


Figure 22-9 A representation of the basic oxygen process furnace. Much of the steel manufactured today is refined by blowing oxygen through a furnace that is charged with scrap and molten iron from a blast furnace. After the refined iron is withdrawn into a ladle, alloying elements are added to produce the desired steel. The steel industry is one of the nation's largest consumers of oxygen.



Figure 22-10 An open-pit copper mine near Bagdad, Arizona.



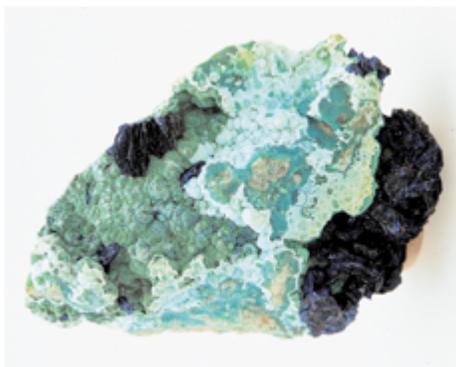
Figure 22-11 A copper ore being enriched by flotation.



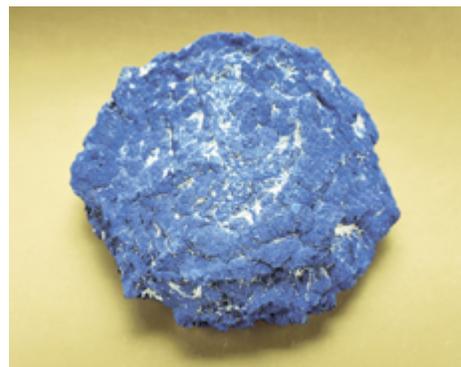
Mining low-gold ore in an open-pit mine.

The steps of this process are described in Exercise 36 at the end of the chapter.

A sludge called anode mud collects under the anodes. It contains such valuable and difficult-to-oxidize elements as Au, Pt, Ag, Se, and Te. The separation, purification, and sale of these elements reduce the cost of refined copper.



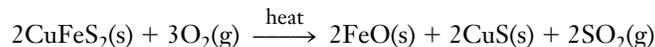
(a)



(b)

Two copper-containing minerals. (a) Malachite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ or $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, is green. (b) azurite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$ or $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, is blue.

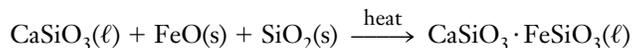
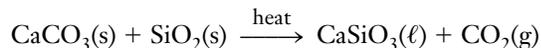
The two main classes of copper ores are the mixed sulfides of copper and iron—such as chalcopyrite, CuFeS_2 —and the basic carbonates, such as azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, and malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$. Let's consider CuFeS_2 (or $\text{CuS} \cdot \text{FeS}$). The copper compound is separated from gangue by flotation (Figures 22-2b and 22-11) and then roasted to remove volatile impurities. Enough air is used to convert iron(II) sulfide, but not copper(II) sulfide, to the oxide.



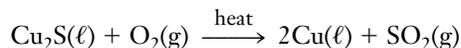
The roasted ore is then mixed with sand (SiO_2), crushed limestone (CaCO_3), and some unroasted ore that contains copper(II) sulfide in a reverberatory furnace at 1100°C . CuS is reduced to Cu_2S , which melts.



The limestone and silica form a molten calcium silicate glass. This dissolves iron(II) oxide to form a slag less dense than the molten copper(I) sulfide, on which it floats.



The slag is periodically drained off. The molten copper(I) sulfide is drawn off into a Bessemer converter, where it is again heated and treated with air. This oxidizes sulfide ions to SO_2 and reduces copper(I) ions to metallic copper. The overall process is



The impure copper is refined using an electrolytic cell like the one shown in Figure 22-12. Thin sheets of very pure copper are made to act as cathodes by connecting them to the negative terminal of a dc generator. Chunks of impure copper connected to the positive terminal function as anodes. The electrodes are immersed in a solution of copper(II) sulfate and sulfuric acid. When the cell operates, Cu from the impure anodes is oxidized and goes into solution as Cu^{2+} ions; Cu^{2+} ions from the solution are reduced and plate out as metallic Cu on the pure Cu cathodes. Other active metals from the impure

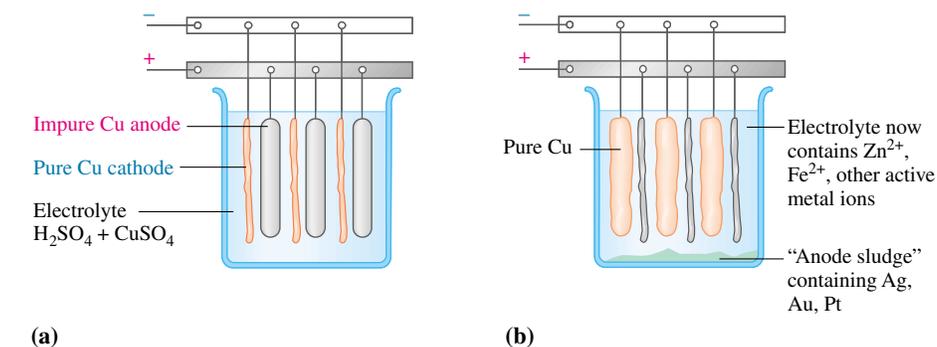
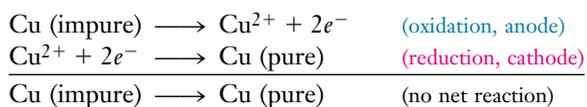


Figure 22-12 A schematic diagram of the electrolytic cell used for refining copper (a) before electrolysis and (b) after electrolysis. (c) Commercial electrolysis cells for refining copper.

(c)

bars also go into solution after oxidation. They do not plate out onto the cathode bars of pure Cu because of the far greater concentration of the more easily reduced Cu^{2+} ions that are already in solution. Overall, there is no net reaction, merely a simultaneous transfer of Cu from anode to solution and from solution to cathode.



Nevertheless, the net effect is that small bars of very pure Cu and large bars of impure Cu are converted into large bars of very pure Cu and small bars of impure Cu.

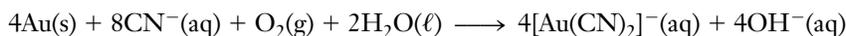
The energy provided by the electric generator forces a decrease in the entropy of the system by separating the Cu from its impurities in the impure bars.

22-9 GOLD

Gold is an inactive metal (sometimes called a noble metal), so it occurs mostly in the native uncombined state. It is sometimes found as gold telluride. Because of its high density, metallic gold can be concentrated by panning. In this operation, gold-bearing sand and gravel are gently swirled with water in a pan. The lighter particles spill over the edge, and the denser nuggets of gold remain. Gold is concentrated by sifting crushed gravel in a stream of water on a slightly inclined shaking table that contains several low barriers. These impede the descent of the heavier gold particles but allow the lighter particles to pass over. In a modern extension to this centuries-old process, the gold is then alloyed with mercury and removed. The mercury is distilled away, leaving behind the pure gold.

Because of environmental concerns about mercury toxicity, the cyanide process is increasingly preferred. This is not to suggest that mercury is more toxic than cyanide. The problems due to mercury are greater in that it persists in the environment for a long time, and mercury poisoning is cumulative.

Gold is also recovered from the anode sludge from electrolytic purification of copper Section 21-7. Gold is so rare that it is also obtained from very low-grade ores by the cyanide process. Air is bubbled through an agitated slurry of the ore mixed with a solution of NaCN. This causes slow oxidation of the metal and the formation of a soluble complex compound.



After filtration, free gold can then be regenerated by electrolytic reduction or by reduction of $[\text{Au}(\text{CN})_2]^{-}$ with zinc.



Key Terms

Alloying Mixing of a metal with other substances (usually other metals) to modify its properties.

Cast iron The brittle iron obtained when the pig iron from the blast furnace is remelted, run into molds, and cooled; contains much iron carbide, Fe_3C .

Charge A sample of crushed ore as it is admitted to a furnace for smelting.

Flotation A method by which hydrophobic (water-repelling) particles of an ore are separated from hydrophilic (water-attracting) particles in a metallurgical pretreatment process.

Flux A substance added to react with the charge, or a product of its reduction, in metallurgy; usually added to lower a melting point.

Gangue Sand, rock, and other impurities surrounding the mineral of interest in an ore.

Hall-Héroult process A process in which a molten mixture of Al_2O_3 , NaF, and AlF_3 is electrolyzed to obtain pure aluminum.

Metallurgy The overall processes by which metals are extracted from ores.

Mineral A naturally occurring inorganic solid substance having a definite chemical composition and characteristic crystalline structure, color, and hardness; contains a metal that can be extracted in a metallurgical process.

Native ore A metal that occurs in an uncombined or free state in nature.

Ore A natural deposit containing a mineral of an element to be extracted.

Pig iron The iron obtained from the blast furnace.

Refining Purifying of a substance.

Roasting Heating a compound below its melting point in the presence of air.

Slag Unwanted material produced during smelting.

Smelting Chemical reduction of a substance at high temperature in metallurgy.

Steel Iron alloyed with other metals, such as Mn, Cr, Ni, W, Mo, and V, and sometimes with C and Si.

Zone refining A method of purifying a bar of metal by passing it through an induction heater; this causes impurities to move along in the melted portion.

Exercises

General Concepts

- List the chemical and physical properties that we usually associate with metals.
- Define the term “metallurgy.” What does the study of metallurgy include?
- What kinds of metals are most apt to occur in the uncombined (native) state in nature?
- List the six anions (and their formulas) that are most often combined with metals in ores. Give at least one example of an ore of each kind. What anion is the most commonly encountered?
- How does an ore differ from a mineral? Name the three general categories of procedures needed to produce pure metals from ores. Describe the purpose of each.
- Briefly describe one method by which gangue can be separated from the desired mineral during the concentration of an ore.
- Give the five general steps involved in extracting a metal from its ore and converting the metal to a useful form. Briefly describe the importance of each.
- Describe the flotation method of ore pretreatment. Are any chemical changes involved?
- Smelting is the process by which a metal ore is reduced. In this context, what does the term “reduced” mean?
- Which metals are likely to be found in the free state in nature? Why are these metals in the free state in nature? Describe the location of these elements on the periodic table. Is there a pattern?

11. What kinds of ores are roasted? What kinds of compounds are converted to oxides by roasting? What kinds are converted directly to the free metals?
12. Of the following compounds, which would you expect to require electrolysis to obtain the free metals: KCl; $\text{Cr}_2(\text{SO}_4)_3$; Fe_2O_3 ; Al_2O_3 ; Ag_2S ; MgSO_4 ? Why?
13. At which electrode is the free metal produced in the electrolysis of a metal compound? Why?
- *14. Write the equation that describes the electrolysis of a brine solution to form NaOH, Cl_2 , and H_2 . What mass of each substance will be produced in an electrolysis cell for each mole of electrons passed through the cell? Assume 100% efficiency.
15. The following equations represent reactions used in some important metallurgical processes.
- (a) $\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}(\text{g}) \longrightarrow \text{Fe}(\ell) + \text{CO}_2(\text{g})$
 (b) $\text{MgCO}_3(\text{s}) + \text{SiO}_2(\text{s}) \longrightarrow \text{MgSiO}_3(\ell) + \text{CO}_2(\text{g})$
 (c) $\text{Au}(\text{s}) + \text{CN}^- + \text{H}_2\text{O}(\ell) + \text{O}_2(\text{g}) \longrightarrow [\text{Au}(\text{CN})_2]^- + \text{OH}^-$
- Balance the equations. Which one(s) represent reduction to a free metal?
16. Repeat Exercise 15 for
- (a) Al_2O_3 (cryolite solution) $\xrightarrow{\text{electrolysis}}$ $\text{Al}(\ell) + \text{O}_2(\text{g})$
 (b) $\text{PbSO}_4(\text{s}) + \text{PbS}(\text{s}) \longrightarrow \text{Pb}(\ell) + \text{SO}_2(\text{g})$
 (c) $\text{TaCl}_5(\text{g}) + \text{Mg}(\ell) \longrightarrow \text{Ta}(\text{s}) + \text{MgCl}_2(\ell)$
17. Suggest a method of obtaining manganese from an ore containing manganese(III) oxide, Mn_2O_3 . On what basis do you make the suggestion?
18. What is the purpose of utilizing the basic oxygen furnace after the blast furnace in the production of iron?
19. A blast furnace utilizes or produces five species that include carbon. (a) List the five species that contain carbon. (b) Explain the function of each step in the chain of events from heating the ore to the production of steel.
20. Magnesium hydroxide can be precipitated from sea water by adding slaked lime, $\text{Ca}(\text{OH})_2$. (a) Why does this precipitation occur? (b) Could this process be used to remove sodium from sea water? Why?
21. Describe the metallurgy of (a) copper and (b) magnesium.
22. Describe the metallurgy of (a) iron and (b) gold.
23. Briefly describe the Hall–Héroult process for the commercial preparation of aluminum.
24. (a) Compare the refining of aluminum by the Hall–Héroult process and by the Alcoa chlorine process. (b) Which process is less expensive and why? (c) The Alcoa chlorine process is potentially more dangerous to the workers than is the Hall–Héroult process. Why?
25. A common iron ore is magnetite, Fe_3O_4 . In this formula for magnetite the oxidation number of iron is not an integer. Write the formula in a form that includes only integer oxidation numbers.
26. Name some common minerals that contain iron. Write the chemical formula for the iron compound in each. What is the oxidation number of iron in each substance?
27. What is steel? How does the hardness of iron compare with that of steel?
28. (a) What is the difference in composition between pure iron and steel? (b) What is the name of the process by which steel is produced?
29. (a) What is an alloy? (b) Why are alloys produced? (c) How are alloys produced?
30. Describe and illustrate the electrolytic refining of Cu.
31. Name the undesirable gaseous product formed during the roasting of copper and other sulfide ores. Why is it undesirable?

CONCEPTUAL EXERCISES

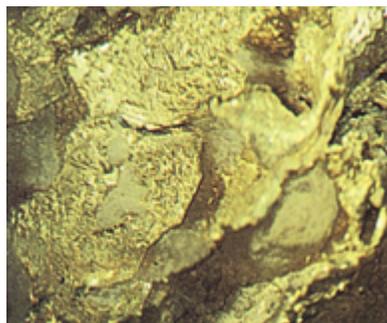
32. One of the problems with roasting sulfide ores is the air pollution caused by the gas that is produced. Describe some consequences of releasing this gas into the atmosphere.
33. Gold can be obtained by the separation of gold from the anode sludge of the electrolytic purification of copper. (a) Considering the nature of gold and copper, is this source of gold to be expected? Explain. (b) Would finding silver in the sludge also be expected? Explain.

BUILDING YOUR KNOWLEDGE

34. The reaction



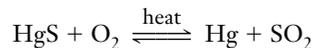
takes place in the blast furnace at a temperature of 800 K. (a) Calculate ΔH_{800}^0 for this reaction, using $\Delta H_{\text{f}, 800}^0 = -268$ kJ/mol for FeO, -111 kJ/mol for CO, and -394 kJ/mol for CO_2 . Is this a favorable enthalpy change? (b) Calculate ΔG_{800}^0 for this reaction, using $\Delta G_{\text{f}, 800}^0 = -219$ kJ/mol for FeO, -182 kJ/mol for CO, and -396 kJ/mol for CO_2 . Is this a favorable free energy change? (c) Using your values of ΔH_{800}^0 and ΔG_{800}^0 , calculate ΔS_{800}^0 .



Native gold.

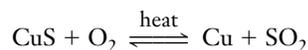
35. During the operation of a blast furnace, coke reacts with the oxygen in air to produce carbon monoxide, which, in turn, serves as the reducing agent for the iron ore. Assuming the formula of the iron ore to be Fe_2O_3 , calculate the mass of air needed for each ton of iron produced. Assume air to be 21% O_2 by mass, and assume that the process is 93% efficient.
36. The following reactions take place during the extraction of copper from copper ore.
- (a) $2\text{Cu}_2\text{S}(\ell) + 3\text{O}_2(\text{g}) \longrightarrow 2\text{Cu}_2\text{O}(\ell) + 2\text{SO}_2(\text{g})$
 (b) $2\text{Cu}_2\text{O}(\ell) + \text{Cu}_2\text{S}(\ell) \longrightarrow 6\text{Cu}(\ell) + \text{SO}_2(\text{g})$
 Identify the oxidizing and reducing agents. Show that each equation is correctly balanced by demonstrating that the increase and decrease in oxidation numbers are equal.
- *37. Assuming complete recovery of metal, which of the following ores would yield the greater quantity of copper on a mass basis? (a) an ore containing 3.60 mass % azurite, $\text{Cu}(\text{OH})_2 \cdot 2\text{CuCO}_3$, or (b) an ore containing 4.95 mass % chalcopyrite, CuFeS_2 .
- *38. What mass of copper could be electroplated from a solution of CuSO_4 , using an electric current of 2.50 A flowing for 5.00 h? (Assume 100% efficiency.)
- *39. (a) Calculate the weight, in pounds, of sulfur dioxide produced in the roasting of 1 ton of chalcocite ore containing 10.3% Cu_2S , 0.94% Ag_2S , and no other source of sulfur. (b) What weight of sulfuric acid can be prepared from the SO_2 generated, assuming 85% of it can be recovered from stack gases, and 88% of that recovered can be converted to sulfuric acid? (c) How many pounds of pure copper can be obtained, assuming 78% efficient extraction and purification? (d) How many pounds of silver can be produced, assuming 81% of it can be extracted and purified?
- *40. Forty-five pounds of Al_2O_3 , obtained from bauxite, is mixed with cryolite and electrolyzed. How long would a 0.900-A current have to be passed to convert all the Al^{3+} (from Al_2O_3) to aluminum metal? What volume of oxygen, collected at 775 torr and 125°C , would be produced in the same period of time?
- *41. Calculate the percentage of iron in hematite ore containing 61.5% Fe_2O_3 by mass. How many pounds of iron would be contained in 1 ton of the ore?

42. The roasting of cinnabar, HgS , is a process by which free mercury is obtained.



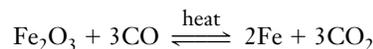
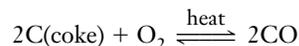
Assuming that the roasting process is 100% efficient, what mass, in tons, of SO_2 is released into the air by the roasting of 500. tons of cinnabar?

43. The roasting of covellite, CuS , is a process by which free copper is obtained.



Assuming that the roasting process is 91.5% efficient, what mass, in tons, of SO_2 is released into the air by the roasting of 500. tons of covellite?

44. Consider the separation of iron from hematite, Fe_2O_3 , in a blast furnace which has an overall efficiency of 98.0% in order to leave a specific amount of carbon in the final product.



Calculate the mass of coke, in tons, necessary for the ultimate reaction with 100. tons of hematite.

- *45. Using data from Appendix K, calculate ΔG_{298}^0 for the following reactions.
- (a) $\text{Al}_2\text{O}_3(\text{s}) \longrightarrow 2\text{Al}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$
 (b) $\text{Fe}_2\text{O}_3(\text{s}) \longrightarrow 2\text{Fe}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$
 (c) $\text{HgS}(\text{s}) \longrightarrow \text{Hg}(\ell) + \text{S}(\text{s})$
 Are any of the reactions spontaneous? Are the ΔG_{298}^0 values in line with what would be predicted based on the relative activities of the metal ions involved? Do increases in temperature favor these reactions?
- *46. Find the standard molar enthalpies of formation of Al_2O_3 , Fe_2O_3 , and HgS in Appendix K. Are the values in line with what might be predicted, in view of the methods by which the metal ions are reduced in extractive metallurgy?