Kirk-Othmer Encyclopedia of Chemical Technology.

SELENIUM AND SELENIUM COMPOUNDS

1. Selenium

Selenium [7782-49-2], Se, atomic no. 34, atomic wt 78.96, lies between sulfur and tellurium in Group 16 (VIA) and between arsenic and bromine in Period 4 of the Periodic Table (1–4). Its outer electronic configuration is $3d^{10}$ $4s^2$ $4p^4$, ie, the three inner electron shells of selenium are completely filled. Strikingly similar to sulfur in most of its chemistry, important selenium oxidation states are -2, 0, $+2$, $+4$, and $+6$. The $+2$ state is not known to occur in nature. Selenium exists in various allotropic modifications and forms many inorganic and organic compounds, often analogous and isomorphous with their sulfur equivalents. Selenium was discovered in 1817 and its name derived from *selene*, the Greek goddess of the moon.

1.1. Physical Properties

The six stable isotopes of selenium are ^{74}Se [13981-33-4], ^{76}Se [13981-32-3], ^{77}Se [14681-72-2], ^{78}Se [14833-16-0], ^{80}Se [14681-54-0], and ^{82}Se [14687-58-2]. These occur naturally in the approximate abundances of 0.87, 9.02, 7.58, 23.52, 49.82, and 9.19%, respectively. A number of artificial radioactive isotopes have been prepared by neutron activation. One of these, the γ-emitting ^{75}Se [14265-71-5], which has a half-life of 120.4 d, is a diagnostic tool in medicine (see Medical imaging technology; Radioactive tracers).

Solid selenium has several allotropic forms, including an amorphous one resembling plastic sulfur. The stable form at ordinary temperatures, ie, the gray or hexagonal selenium, is the most dense and is semimetallic in appearance. Selenium crystallizes in a hexagonal lattice with $a = 0.4366$ nm and $c = 0.4954$ nm. The electrical conductivity, which makes gray selenium useful in photoelectrical and photochemical applications, is low in the dark but increases several hundredfold on exposure to light. Crystalline red selenium exists in two monoclinic forms obtained by evaporation of carbon disulfide extracts of amorphous red selenium. The α-monoclinic form, where $a = 0.9054$ nm, $b = 0.9083$ nm, $c = 1.1060$ nm, and $\beta = 90.81^\circ$, has a unit cell formed of four puckered Se_8 ring molecules. The β-monoclinic form, where $a = 1.285$ nm, $b = 0.807$ nm, $c = 0.931$ nm, and $\beta = 93.13^\circ$, is also made up of puckered Se_8 [13494-81-0] rings. Amorphous selenium exists in black and red forms. Black amorphous selenium is vitreous and is formed by rapid cooling of liquid selenium; red amorphous selenium is colloidal and is formed in reduction reactions. Heating and/or catalysts transform all the amorphous forms and both monoclinic crystalline forms to gray selenium. Liquid selenium is black in the bulk and brownish red in thin films. The liquid probably contains chains and rings of variable numbers of atoms. Selenium vapor is also complex in nature. The most abundant species are Se_2 [12185-17-0], Se_5 [12597-28-3], Se_6 [12597-30-7, 20721-13-5], Se_7 [12597-32-9], and Se_8. Se_2 is an important species at 900°C, whereas at 2000°C the vapor is mainly monatomic. The saturated vapor pressure is given (5), when T is in K, by the following:

$$\log P_{\text{kPa}} = 7.2355 - 5010.7/T$$

Table 1. Physical Constants of Selenium[a]

Property	Value
melting point, °C	217
boiling point, °C	ca 685
heat of fusion, trigonal liquid, kJ/mol[b]	5.2–5.4
heat of vaporization, kJ/mol[b]	59.7
heat of combustion, at 298 K, kJ/mol[b]	−225.1
heat capacity, J/(gK)[b]	
trigonal	24.52
vitreous	25.627
liquid	29.288
thermal conductivity, W/(m·K)	248.1
thermal expansion coefficient[c], °C^{-1}	$3.24 \times 10^{-5} - 7.5 \times 10^{-5}$
viscosity, mPa·s(= cP)	
at 220°C	221
360°C	70
density, g/cm^3	
trigonal at 298 K	4.819
monoclinic	4.4
liquid at 490 K	4.05
vitreous	4.285
standard reduction potential, V	
$Se + 2\,e^- \longrightarrow Se^{2-}$	−0.78
$Se + 2\,H^+ + 2\,e \longrightarrow H_2Se$ (aq)	−0.36
surface tension, liquid, mN/m(=dyn/cm)	
at 220°C	105.5
310°C	95.2
electronegativity, Pauling scale	2.4

[a] Refs. 2 and 4.
[b] To convert J to cal, divide by 4.184.
[c] Value depends on form.

To convert P_{kPa} to log P_{mmHg}, subtract 0.8751 from the constant. The saturated vapor pressure increases from 133 Pa (1 mm Hg) at 343.7°C to 101.3 kPa (760 mm) at 685.4°C, the boiling point of selenium.

Some physical constants for selenium are given in Table 1. More extensive data and many sources are available (1–5). For a selenium atom, the covalent radius is ca 0.115 nm, the electron affinity for two electrons is ca −2.33 eV, ie, energy absorbed, and the first ionization potential is 9.75 eV.

1.2. Chemical Properties

The chemical properties of selenium are intermediate between those of sulfur and tellurium. Whereas selenium reacts with active metals and gains electrons to form ionic compounds containing the selenide ion, Se^{2-}, selenium forms covalent compounds with most other substances. The oxidation states in elemental and combined forms are as follows (5): −2 in disodium selenide [1313-85-5], Na_2Se; −1 in disodium diselenide [39775-49-0], Na_2Se_2; 0 in Se_8; +1 in diselenium dichloride [10025-68-0, 21317-32-8], Se_2Cl_2; +2 in selenium dichloride [14457-70-6], $SeCl_2$; +4 in sodium selenite [10102-18-8], Na_2SeO_3; and +6 in sodium selenate [13410-01-0], Na_2SeO_4.

Selenium combines with metals and many nonmetals directly or in aqueous solution. The selenides resemble sulfides in appearance, composition, and properties. Selenium forms halides by reacting vigorously with fluorine and chlorine, and less so with halogen compounds bromine and iodine. It does not react with pure hydrogen fluoride or hydrogen chloride but decomposes hydrogen iodide to liberate iodine and form hydrogen selenide [7783-07-5], H_2Se. Selenium combines with oxygen yielding a number of oxides, the most stable being selenium dioxide [7446-08-4], SeO_2. Under proper conditions, selenium forms selenides with hydrogen, carbon, nitrogen, phosphorus, and sulfur. Crystalline selenium does not react with water, even at 150°C.

Selenium remains unaffected by dilute sulfuric acid or hydrochloric acid, but dissolves in a nitric–hydrochloric acid mixture, concentrated nitric acid (qv), and concentrated sulfuric acid. It is oxidized by ozone and solutions of alkali metal dichromates, permanganates, and chlorates and calcium hypochlorite. Selenium dissolves in strong alkaline solutions yielding selenides and selenites. It forms selenocyanates, MSeCN, with alkali metal cyanides, MCN, as well as many inorganic and organic derivatives of the corresponding acid, HSeCN [13103-11-2]. Selenium also dissolves in alkali metal sulfites, M_2SO_3, forming selenosulfates, M_2SeSO_3 and, because tellurium does not undergo this reaction, this method can be used to separate the two elements. Selenium mixes in all proportions with sulfur and tellurium forming a continuous series of solid solutions and alloys.

In many reactions, selenium is an oxidant as well as a reductant. Strong oxidants convert selenium dioxide and its derivatives to the hexavalent state. Although hexavalent selenium compounds are oxidants, these are less active and difficult to reduce. Selenium salts resemble the corresponding sulfur and tellurium salts in behavior.

Selenium also forms a large number of organic compounds. Of special interest are the oxidizing and reducing actions of selenium and its compounds. Chemical reactions are described in detail elsewhere (1–9). Organic reactions are reviewed in References 10 and 11. The organic chemistry and biochemistry of selenium is also available (12–16).

1.3. Occurrence

The occurrence of selenium is discussed in References 17–19. At 0.68 atom per 10,000 atoms Si, selenium is the 30th most abundant element. Selenium is widely dispersed in igneous rocks probably as selenide minerals; in volcanic deposits where it substitutes for some of the sulfur; in hydrothermal deposits, where it is associated isothermally with silver, gold, antimony, and mercury; and in massive sulfide and porphyry copper deposits, where it appears in large quantities but only in small concentrations. In sedimentary rocks such as sandstones, carbonaceous siltstones, phosphorite rocks, and limestones, selenium is syngenetic, ie, it was introduced during deposition, probably by adsorption on precipitated ferric hydroxide. Like vanadium, phosphorus, arsenic, and antimony, selenium has been reported in sedimentary iron ores in amounts larger than its average abundance in the crust.

The estimated selenium content of the oceans is only ca 0.5 ppb, and only a small fraction of the selenium is transported into the sea by weathering and erosion (20). The principal species in the seas is $SeO^{2-}{}_4$. Adsorption by some marine organisms contributes to the removal of selenium from seawater. Thus selenium often, though not always, occurs in the pyrite and marcasite of sedimentary formations as well as in soils derived from them. Selenium is particularly concentrated in soils of the drier regions, eg, the North American great plains from Mexico to the prairie provinces of Canada and westward to the Pacific Ocean at California, but especially in Wyoming and South Dakota, and in localities in Colombia, Ireland, Israel, and the People's Republic of China. It is also found in much smaller quantities in Argentina, Venezuela, Bulgaria, Algeria, Morocco, Australia, and some regions of the former USSR, as shown by analyses of locally grown crops. Selenium occurs in coals in 0.5–12 ppm concentrations, probably associated with pyrite and marcasite (21). Crude oil from different locations contains variable amounts of selenium, usually less than 0.5 ppm.

There are areas (22) where selenium levels in the soil are very low; these include regions of volcanic activity like that adjacent to the Cascade mountains in the Pacific Northwest states of the United States and the central north island of New Zealand. There, because the heat of eruption volatilized the selenium, the residual soil parent material is virtually devoid of selenium. Other areas of low soil-selenium reflect leaching of selenium out of the top soil, as in the Canterbury plain on New Zealand's south island. Areas of selenium deficiency have negative implications for animal and human health.

1.3.1. Biosphere

Selenium occurs in alkaline soils chiefly as selenates which, when water soluble, are readily available to plants. In acid soils, selenides and to some degree elemental selenium are prevalent but little is available to plants. The concentration of selenium in most soils is between 0.01 and 2.0 mg/kg. However, levels as high as 1200 mg/kg have been reported in seleniferous areas. High selenium soils have developed from Cretaceous shales such as those found in the Dakotas and Wyoming in the United States, whereas low selenium soils include those derived from sedimentary rocks (northeastern U.S.) and volcanic ash (Pacific Northwest U.S.). The topsoils can be enriched by certain native plants that accumulate high selenium concentrations from the seleniferous soils and earth formations. These plants, which require selenium for their growth, include about 24 species and varieties of *Astragalus* (milk vetch), *Machaeranthera* (woody aster), *Haplopappus* (goldenweed), and *Stanlea* (Princes' plume). Other species, eg, *Atriplex* (salt bush) and *Grindelia* (gumweed), absorb moderately large quantities when growing in soils with high available selenium concentrations. These so-called secondary selenium absorbers and the primary selenium indicators aid in locating seleniferous regions. Some selenium-tolerant plants may contain up to 1.5 wt % selenium.

Indicator plants generally have an offensive odor, which varies with the selenium concentration. Other vegetable matter grown on seleniferous soils may have a sufficiently high selenium content to be toxic when ingested by animals or humans. Apart from appearance in these seleniferous plants, selenium has been considered as a variable contaminant. Selenium is a necessary micronutrient in living organisms, needed by humans as well as animals (see Mineral nutrients).

Data on selenium in water are limited. The drinking water content is usually less than 1 μg/L, and seldom exceeds the 50 μg/L upper limit established in 1993 by the U.S. EPA (23). It may be higher in wells in seleniferous areas, and markedly higher in some river waters where irrigation drainage from seleniferous soil contains up to 2680 μg/L.

1.3.2. Deposits

Selenium forms natural compounds with 16 other elements. It is a main constituent of 39 mineral species and a minor component of 37 others, chiefly sulfides. The minerals are finely disseminated and do not form a selenium ore. Because there are no deposits that can be worked for selenium recovery alone, there are no mine reserves. Nevertheless, the 1998 world reserves, chiefly in nonferrous metals sulfide deposits, are ca 70,000 metric tons and total resources are ca 130,000 t (24). The principal resources of the world are in the base metal sulfide deposits that are mined primarily for copper, zinc, nickel, and silver, and to a lesser extent, lead and mercury, where selenium recovery is secondary.

1.4. Manufacture and Recovery

Electrolytic copper refinery slimes are the principal source of selenium and its sister element, tellurium, atomic numbers 34 and 52, respectively. Electrolytic copper refinery slimes are those constituents in the copper anode which are not solubilized during the refining process and ultimately accumulate in the bottom of the electrorefining tank. These slimes are periodically recovered and processed for their metal values. Slimes generated by the refining of primary copper, copper produced from ores and concentrates, generally contain from 5–25% selenium and 2–10% tellurium.

Selenium occurs in the slimes as intermetallic compounds such as copper silver selenide [12040-91-4], CuAgSe; disilver selenide [1302-09-6], Ag_2Se; and $Cu_{2-x}Se_x$ [20405-64-5], where $x < 1$. The primary purpose of slimes treatment is the recovery of the precious metals gold, silver, platinum, palladium, and rhodium. The recovery of selenium is a secondary concern. Because of the complexity and variability of slimes composition throughout the world, a number of processes have been developed to recover both the precious metals and selenium. More recently, the emphasis has switched to the development of processes which result in early recovery of the higher value precious metals. Selenium and tellurium are released in the later stages. Processes in use at the primary copper refineries are described in detail elsewhere (25–44).

1.4.1. Soda Ash Roasting

Some of the first processes to recover selenium on a commercial basis were based on roasting of copper slimes with soda ash to convert both selenium and tellurium to the +6 oxidation state. Figure 1 shows flow sheets for two such processes. Slimes are intensively mixed with sodium carbonate, a binder such as bentonite, and water to form a stiff paste. The paste is extruded or pelletized and allowed to dry. Care in the preparation of the extrudates or pellets is required to ensure that they have sufficient porosity to allow adequate access to the air required for oxidation.

Roasting occurs between temperatures of 530–650°C. Virtually no volatilization of selenium or tellurium takes place during roasting. Conversion of both elements to the hexavalent form is complete.

The roasted pellets or extrudes are ground and leached in water. The hexavalent selenium dissolves as sodium selenate [13410-01-0], Na_2SeO_4. Sodium tellurate, being highly insoluble in the now very strongly alkaline solution, remains in the residue. The separation between selenium and tellurium is readily achieved, provided all tellurium is oxidized to the hexavalent state.

1.4.1.1. Selenium Recovery. There are two processes commonly employed for reducing selenium from solution. There are many variations on these processes. In the first process, employed commercially for many years, selenium is leached from the slimes in the form of the hexavalent sodium selenate. It is recovered from solution by crystallization (qv) and the crystalline sodium selenate is mixed with charcoal. Under controlled conditions of heating, the Na_2SeO_4 is reduced to sodium selenide. The sodium selenide cake is leached with water to form a typically liver-red solution of sodium selenide which is readily oxidized to the elemental form by blowing air through the solution. This precipitation technique allows the recycling of much of the solution, a significant advantage considering the particularly severe restrictions placed on the discharge of selenium-bearing solutions.

In the second process, reduction of the hexavalent selenium is accomplished using concentrated hydrochloric acid or ferrous iron salts catalyzed by chloride ions as the reductant. This process was developed during the 1940s in Germany and is still apparently employed at a variety of refineries for dealing with hexavalent selenium. It generates a large effluent stream of iron chlorides containing small quantities of selenium which can be burdensome to discharge or control. Additionally, the solution is extremely corrosive and considerable care must go into the selection of process equipment to avoid severe corrosion problems.

1.4.2. Alkaline Autoclaving

A variety of research experiments have been performed on the oxidation of slimes under pressure in an alkaline solution (32, 35, 40). Although many different process conditions are stipulated, a temperature of approximately 200°C is generally preferred when using sodium hydroxide concentrations on the order of 100–500 g/L, depending on the concentration of selenium in the slimes and solids of the slimes slurry employed. Oxygen partial pressures vary from 172–1720 kPa (25–250 psig). Reaction time is generally greater than four hours, and can be as much as 12 hours to achieve acceptable selenium extraction. The reactions for selenium and tellurium are shown in the following equations.

$$Se + 1.5\ O_2 + 2\ NaOH \longrightarrow Na_2SeO_4 + H_2O$$

$$Te + 1.5\ O_2 + 2\ NaOH \longrightarrow Na_2TeO_4 + H_2O$$

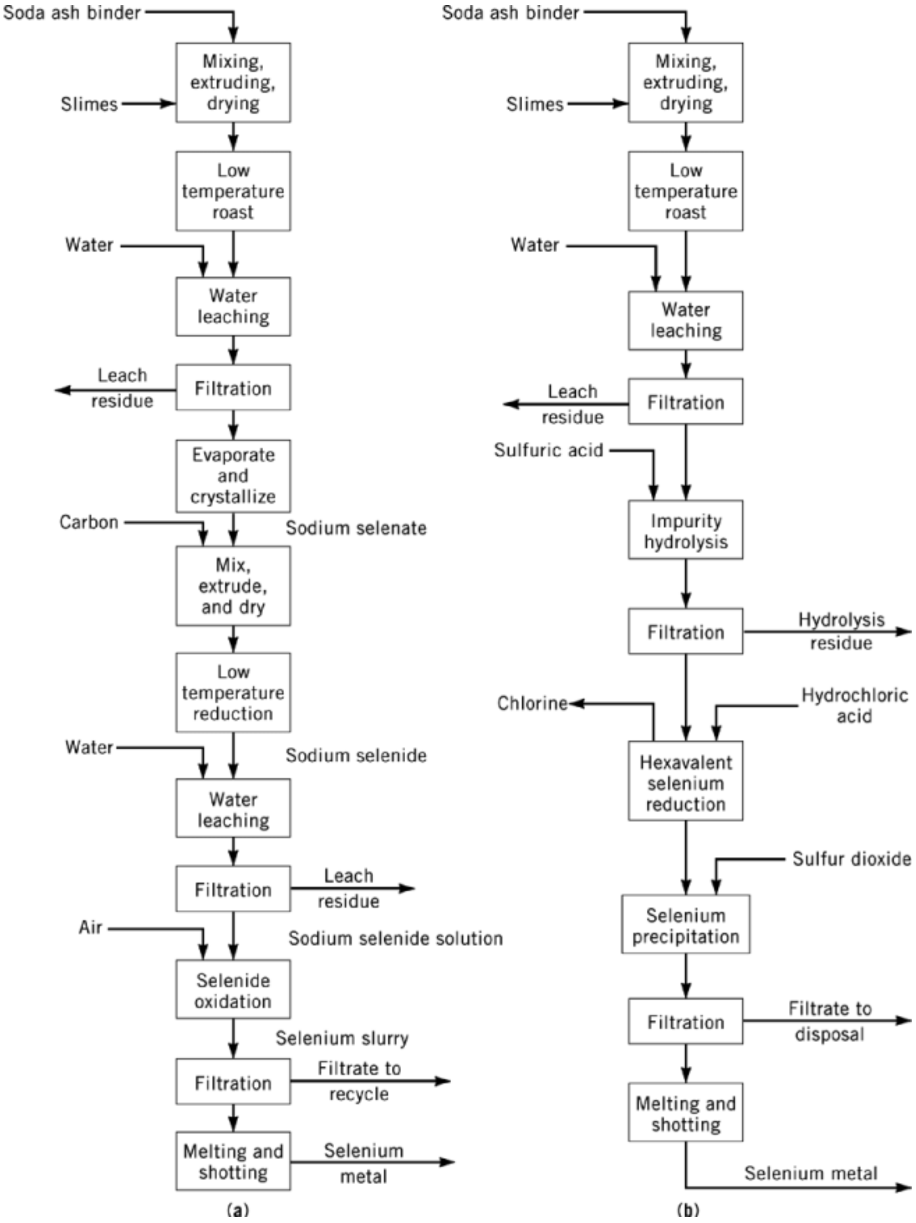

Fig. 1. Recovery of selenium by soda ash roasting of slimes: (**a**) process 1 and (**b**) process 2.

Conversion of tellurium to the hexavalent form is complete. The extent of selenium oxidation to the hexavalent form is a function of temperature, alkalinity, and oxygen pressure. Total conversion of tellurium to the hexavalent form ensures its virtually complete insolubility in the alkaline leach liquor, thereby allowing an essentially quantitative separation from the soluble selenium compounds. The advantages of the alkaline pressure leach process include its comparatively low corrosivity, no volatile selenium loss, no scrubbing or gas cleaning circuit, and a substantially quantitative separation of tellurium and selenium.

The process is not without its disadvantages. The drawbacks include high oxygen consumption, because oxygen is used not only for the oxidation of the selenium and tellurium but for a variety of other constituents in slimes, including organic constituents introduced through the additives employed as growth modifiers in the copper refinery. Sodium hydroxide consumption may also be high, because lead sulfate in the slimes is converted to lead plumbate and silica present in the slimes from mold washes is converted to sodium silicate. In fact, substantially all metal sulfates present in the slimes are converted to sodium sulfate and their respective metal oxide, hydroxide, or sodium salts. In addition, alkaline autoclaving has the same drawbacks as soda ash roasting with regard to reduction of hexavalent selenium and tellurium compounds.

1.4.3. Sulfation Roasting

Acid roasting technology (Fig. 2) relies on differences in the volatility of the tetravalent oxides of selenium and tellurium at roasting temperatures of 500–600°C to selectively volatilize selenium from slimes. Acid roasting uses sulfuric acid as the oxidant for the conversion of selenium/selenides and tellurium/tellurides to their respective tetravalent oxides. Typical oxidation reactions are as follow:

$$\mathrm{Se^0\ (s) + 2\ H_2SO_4\ (l) \longrightarrow SeO_2\ (g) + 2\ H_2O\ (g) + 2\ SO_2\ (g)}$$

$$\mathrm{Ag_2Se\ (s) + 4\ H_2SO_4\ (l) \longrightarrow Ag_2SO_4\ (s) + SeO_2\ (g) + 4\ H_2O\ (g) + 3\ SO_2\ (g)}$$

$$\mathrm{Cu_2Te\ (s) + 6\ H_2SO_4\ (l) \longrightarrow 2\ CuSO_4\ (s) + TeO_2\ (s) + 4\ SO_2\ (g) + 6\ H_2O\ (g)}$$

It is apparent from these equations that significant quantities of sulfur dioxide are generated. For selenium, the reaction shown for oxidation of elemental selenium reverses itself at the lower temperatures employed for water scrubbing, thus regenerating sulfuric acid. The tellurium dioxide remains in the sulfated slimes.

$$\mathrm{SeO_2\ (g) + 2\ SO_2\ (g) + 2\ H_2O\ (l) \longrightarrow Se^0\ (s) + 2\ H_2SO_4\ (l)}$$

1.4.3.1. Selenium Recovery. Because the oxidation reactions take place well below the temperature at which significant volatilization of elemental selenium occurs, only the readily scrubbable selenium dioxide is present in the vapor phase. Thus, the scrubbing of the off-gases is highly efficient, resulting in virtually complete recovery of the selenium from the gas stream. Although some sulfuric acid is recovered in dilute form during the scrubbing, this process consumes more sulfuric acid than is recovered, because only sulfur dioxide associated with the oxidation of selenium from the elemental state to the tetravalent state is reoxidized to sulfuric acid. All sulfuric acid associated with the oxidation of tellurium, copper, and silver is irretrievably lost as sulfur dioxide.

It is generally unacceptable to emit sulfur dioxide, thus the scrubber effluent must be treated for sulfur dioxide removal. If the plant already possesses facilities for the production of sulfuric acid, this rather concentrated sulfur dioxide stream can be easily fed into the wet gas cleaning circuit and disposed of in the sulfuric acid plant. The quantity is so small that it does not put any additional burden on the sulfuric acid plant. Because no tellurium is carried over with the selenium dioxide during roasting, it is possible to produce a selenium product which can be purified to commercial grade (99.5–99.7%).

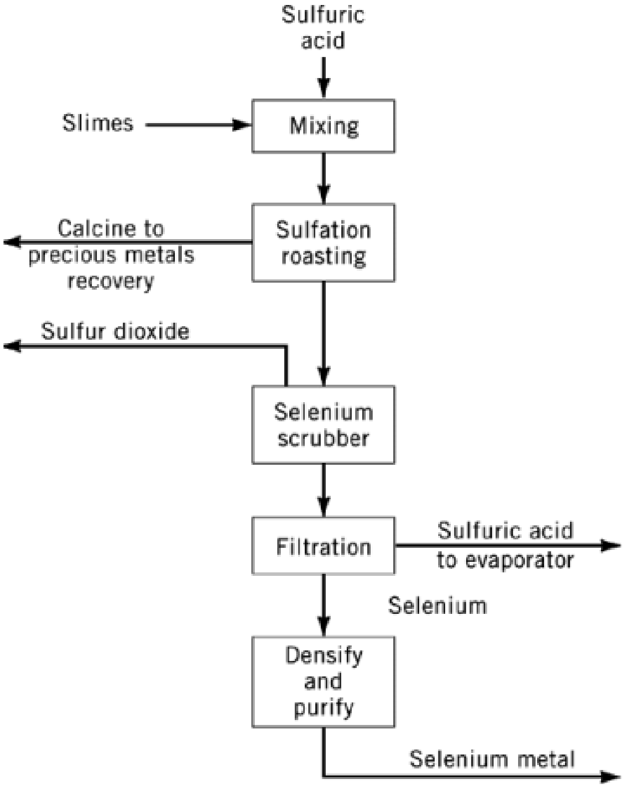

Fig. 2. Recovery of selenium by sulfation roasting.

The process is not without its difficulties. These include the rather long reaction times required for the oxidation of the selenium/selenides and extensive foaming owing to sulfur dioxide liberation during the reaction. This mandates large allowances for freeboard, making the equipment large and cumbersome. Also, the equipment must be designed so that selenium formed in the scrubber does not plug scrubber nozzles or pipelines (qv) during its phase transformation from monoclinic to hexagonal crystal structure, which ordinarily occurs at about 60°C. This problem is sometimes dealt with by the introduction of lignone or similar compounds into the scrubber solution. These interdict the phase transformation but may cause serious problems downstream in producing a selenium of saleable density and purity.

Several refineries use this process which was invented by Outokumpu Oy (Finland) in the 1970s. The original batch process hearth roasted a slurry of decopperized slimes and concentrated sulfuric acid. The off-gases, containing selenium dioxide and sulfur dioxide, were scrubbed using water and a venturi jet ejecter. Phelps Dodge Refining Corporation (El Paso, Texas) has converted this to a continuous process. Outokumpu has modified their process so that trays of dry decopperized slimes are contacted with a gaseous mixture of sulfur dioxide and water in an oven. Sulfur trioxide is generated *in situ* and converts the selenium to selenium dioxide which is volatilized from the trays into the overall gas stream. The gases pass through a venturi scrubber and selenium is precipitated as before.

Another variation is practiced by CCR Division of Noranda (Canada) (37) in which the selenium is vaporized from the sulfated decopperized slimes in a top-blown rotary converter (TBRC). The advantage of using a TBRC is that further refining can be carried out in the furnace to directly produce a doré bullion containing the precious metals. In the Outokumpu process the deselenized slimes must be transferred from the trays to a separate refining furnace if bullion is to be produced.

1.4.4. Chlorination Processes

Both aqueous (wet) and high temperature (dry) chlorination processes have been developed for processing decopperized and detellurized slimes (29, 30). Dry chlorination processes have not achieved the acceptance of wet processes because of problems in controlling temperature during fixed-bed chlorination, difficulty in separating the volatile chlorides of selenium and tellurium from those of gold and platinum metals, and loss of bed porosity owing to fusion of silver chloride. In particular, problems associated with heat transfer to avoid bed fusion, owing to the low melting point of silver chloride, are a principal barrier to the commercialization of this process.

On the other hand, wet chlorination of refinery slimes has proven to be a rapid and simple method of obtaining high extractions of selenium from slimes. A simple wet chlorination flow sheet is shown in Figure 3. Slimes chlorination *per se* is not a simple deselenization operation, but rather a process wherein virtually all the constituents of slimes which form soluble chlorides report as a complex solution of mixed chlorides. Thus the use of wet chlorination requires a complete change in the process to recover the metal values in slimes. The first plant to use wet chlorination of slimes was started by Kennecott (Salt Lake City, Utah) in 1995.

Wet chlorination is performed by sparging slimes slurried either in water or hydrochloric acid using chlorine gas, or other oxidants such as sodium chlorate or hydrogen peroxide which liberate chlorine from hydrochloric acid, at about 100°C. Under these conditions, selenium and selenides rapidly oxidize and dissolve.

$$\mathrm{Se^0 + 2\ Cl_2 \longrightarrow SeCl_4}$$

$$\mathrm{Ag_2Se + 3\ Cl_2 \longrightarrow 2\ AgCl + SeCl_4}$$

Selenium tetrachloride hydrolyzes to form hydrochloric acid, the degree of hydrolysis depending on the acidity of the solution.

$$\mathrm{SeCl_4 + 3\ H_2O \longrightarrow H_2SeO_3 + 4\ HCl}$$

Chlorine may initially convert the selenium in solution to the hexavalent state, but as the hydrochloric acidity increases, reduction to the tetravalent state occurs spontaneously.

Losses of selenium and tellurium from the solution are negligible, provided the reactor is equipped with a reflux condenser. The wet chlorination is easily controlled. The reaction is rapid, allowing fast turnover of the precious metals in the slimes and yielding all the selenium and tellurium in soluble form.

Selenium and precious metals can be removed selectively from the chlorination liquor by reduction with sulfur dioxide. However, conditions of acidity, temperature, and a rate of reduction must be carefully controlled to avoid the formation of selenium monochloride, which reacts with elemental selenium already generated to form a tar-like substance. This tar gradually hardens to form an intractable mass which must be chipped from the reactor. Under proper conditions of precipitation, a selenium/precious metals product substantially free of other impurities can be obtained. Selenium can be recovered in a pure state by vacuum distillation, leaving behind a precious metals residue.

1.4.5. Miscellaneous

Where a copper refinery is adjacent to a lead (qv) plant it is feasible to recover the selenium in slimes by smelting them in conjunction with lead-bearing materials. Utilizing the lower temperatures needed to melt

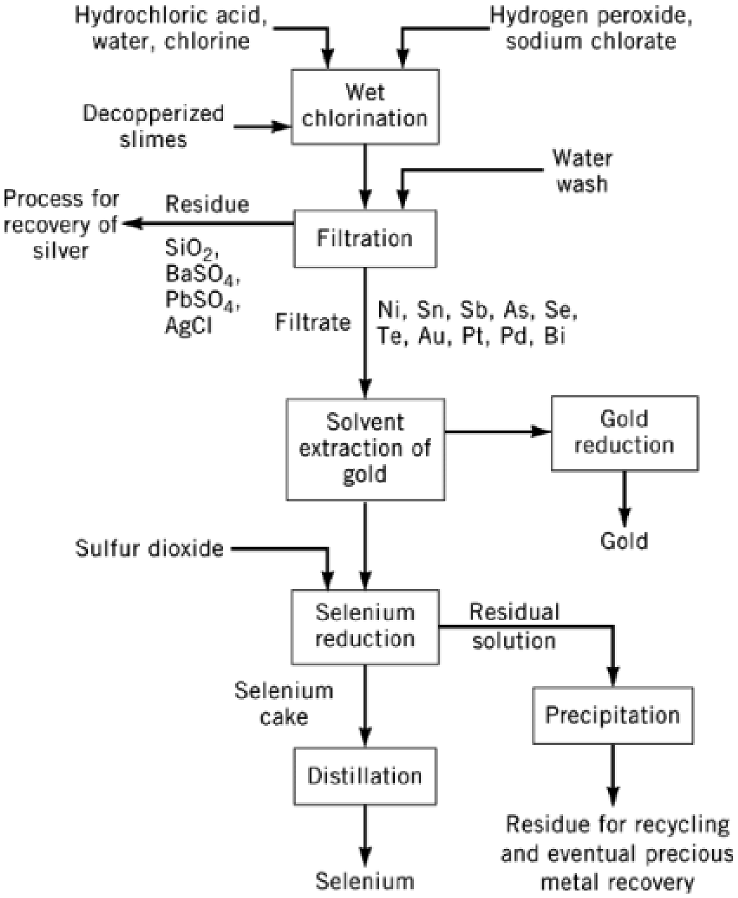

Fig. 3. Recovery of selenium by wet chlorination.

lead, the selenium is volatilized from a lead bath or cupel blown with air. The selenium is recovered from flue dust and fume by scrubbing. This is the process used by Union Miniere at its Hoboken plant in Belgium.

1.5. Purifying Selenium and Tellurium

Selenium recovery processes generally yield a metal product which contains some tellurium, and, correspondingly, recovered tellurium generally contains some small amount of selenium (37, 41).

Classically, the purification of elemental selenium from tellurium is achieved by distillation because of the much greater volatility of selenium compared to tellurium. The advantages of distillation, typically at 1.0–0.255 kPa (0.015–0.037 psi) and 300–400°C, are its simplicity and the absence of emission problems, if performed under vacuum on properly dried, acid-free material. Single-stage distillation can also be carried out at atmospheric pressure at 680°C from cast-iron or iron alloy retorts. In this manner most of the occluded impurities such as sulfur dioxide, water, organic matter, halogens, sulfuric acid, and mercury are expelled to a scrubber, leaving the bulk of the nonvolatile impurities such as tellurium and other metals in the residue. Distillation from a quartz retort upgrades the quality of the selenium.

Complete separation of selenium from tellurium cannot be achieved owing to classical Raoult's law considerations and what appears to be the formation of a Se–Te azeotrope at about 1–2 mol % selenium. A simpler and highly effective purification can be achieved by fluxing molten selenium at about 300°C in the presence of a eutectic mixture of potassium and sodium nitrates (40). At 300°C, selenium does not react significantly with the eutectic nitrate mixture; however, tellurium is oxidized, as are many other impurity metals, and passes into the molten flux layer.

This process can be readily substituted for distillation and proves equal and in some cases superior to distillation. It does not, however, remove precious metals and requires the disposal of the spent sodium/potassium nitrate slag as well as the need to treat any NO_x emissions.

In a cyclic method selenium is dissolved in hot sodium sulfite solution to form sodium selenosulfate [25468-09-1].

$$Se^0 + Na_2SO_3 \longrightarrow Na_2SeSO_3$$

Tellurium and many other impurities remain undissolved. The solution is filtered and cooled to reverse the reaction and to deposit solid selenium. Deselenized liquor is recycled to the dissolution step.

Selenium purification by zone refining is not feasible. At practical zone-refining speeds, crystallization does not occur and impurities do not segregate. However, a controlled differential thermal treatment of selenium in a long vertical glass tube has been described (45). The treatment time is several weeks to several months.

2. Selenium Compounds

Selenium is incorporated into a large variety of commercially used compounds. The most common are listed in Table 2.

Also reported as commercial products are selenium amino acid chelate, selenium ascorbate, selenium aspartate, and selenium citrate triturations, as well as selenium dibromide, selenium dichloride, selenium lysinate, and selenium sulfide bentonite.

2.1. Inorganic Compounds

Inorganic selenium compounds are similar to those of sulfur and tellurium. The most important inorganic compounds are the selenides, halides, oxides, and oxyacids. Selenium oxidation states are -2, 0, $+1$, $+2$, $+4$, and $+6$. Detailed descriptions of the compounds, techniques, and methods of preparation, and references to original work are available (1–3, 5–10, 51–54). Some important physical properties of inorganic selenium compounds are listed in Table 3.

2.1.1. Selenides

Selenium forms compounds with most elements. Binary compounds of selenium with 58 metals and 8 nonmetals, and alloys with three other elements have been described (55). Most of the selenides can be prepared by a direct reaction. This reaction varies from very vigorous with alkali metals to sluggish and requiring high temperature with hydrogen.

2.1.1.1. Hydrogen Selenide. The only important hydride of selenium is hydrogen selenide, H_2Se, although there is some evidence for H_2Se_2. Deuterium selenide [13536-95-3], D_2Se, has been prepared and its properties studied. Hydrogen selenide may be prepared by the action of acids or water on some metal selenides, usually aluminum selenide or iron selenide, or by passing hydrogen and selenium vapor over pumice at 177°C resulting in a ca 58% yield. Thermodynamically, hydrogen selenide is unstable at room temperature, but the rate of decomposition is very slow. The gas is colorless, flammable, highly toxic, and has an offensive odor.

Table 2. Commercial Selenium Products

Product	CAS Registry Number	Formula	Synthetic method	Se content,[a] %	Refs.[b]
barium selenite	[13718-59-7]	$BaSeO_3$		29.9	
barium selenate	[7787-41-9]	$BaSeO_4$		28.2	
cadmium sulfoselenide	[11112-63-3]	CdSSe		35.3	46
calcium selenite	[13780-18-2]	$CaSeO_3$		47.3	
ferroselenium[c] (iron–selenium)	[1310-32-3]	FeSe	melting a mixture of powdered iron and selenium	58.6	
nickel–selenium[c]	[1314-05-2]	NiSe	melting a mixture of powdered nickel and selenium	57.2	
potassium selenocyanate	[3425-46-5]	K(SeCN)		54.9	
selenic acid	[7783-08-6]	H_2SeO_4	oxidizing selenous acid with hydrogen peroxide; electrolyzing selenous acid[d]	54.5	47
selenous acid	[7783-00-8]	H_2SeO_3		61.2	
selenium diethyldithiocarbamate (Selenac) 0.0pt1,120.0pt	[5456-28-7]	 $[(C_2H_5)_2N\overset{S}{\overset{\|}{C}}S]_4Se$	reaction of diethylamine, carbon disulfide, and selenium dioxide in alcoholic solution		48
selenium dioxide[e]	[7446-08-4]	SeO_2	oxidizing selenium with nitric acid and evapo-rating; oxidizing selenium with air or oxygen	71.1	
selenium disulfide	[7488-56-4]	SeS_2		55.2	
selenium oxychloride	[7791-23-3]	$SeOCl_2$	chlorinating mixture of selenium and selenium dioxide dry or suspended in CCl_4	47.6	49
selenium tetrachloride	[10026-03-6]	$SeCl_4$		35.7	
selenourea	[630-10-4]	$(NH_2)_2CSe$		64.2	
sodium selenate	[13410-01-0]	Na_2SeO_4	neutralizing selenic acid with soda ash; electrolyzing sodium selenite solution[f]	41.8	50
sodium selenide	[1313-85-5]	Na_2Se		63.2	
sodium selenite	[10102-18-8]	Na_2SeO_3	neutralizing selenous acid with soda ash	45.7	

[a] Theoretical value.

[b] The patents cited are basic; improvements have been made, but little has been published.

[c] Grade is crushed lump.

[d] The electrolyzed product contains no selenous acid.

[e] Grade is commercial and high purity.

[f] The electrolyzed product contains no selenite.

It irritates the mucous membranes, nose, throat, and eyes. Dry oxygen has no effect on hydrogen selenide. Moist air decomposes it, liberating elemental selenium. It burns in air with excess oxygen to SeO_2 and with insufficient oxygen, to Se. Hydrogen selenide is a strong reductant. The aqueous solution is weakly acidic, although it is stronger than aqueous acetic acid.

2.1.1.2. Binary Selenides. Most binary selenides are formed by heating selenium in the presence of the element, reduction of selenites or selenates with carbon or hydrogen, and double decomposition of heavy-metal salts in aqueous solution or suspension with a soluble selenide salt, eg, Na_2Se or $(NH_4)_2Se$ [66455-76-3]. Atmospheric oxygen oxidizes the selenides more rapidly than the corresponding sulfides and more slowly than the tellurides. Selenides of the alkali, alkaline-earth metals, and lanthanum elements are water soluble and readily hydrolyzed. Heavy-metal selenides are insoluble in water. Polyselenides form when selenium reacts

Table 3. Physical Properties of Inorganic Selenium Compounds[a]

Compound	CAS Registry Number	Formula	Mp, °C	Bp, °C	ΔH_f, 25°C, kJ/mol[b]
hydrogen selenide	[7783-07-5]	H_2Se	−65.7	−41.3	85.7
carbon diselenide	[506-80-9]	CSe_2	−40 – 45	125	155.2
selenium monochloride	[10025-68-0]	Se_2Cl_2	−85	127 dec	−43.7
selenium monobromide	[7789-52-8]	Se_2Br_2		227 dec	
selenium dichloride	[14457-70-6]	$SeCl_2$			
selenium tetrafluoride	[13465-66-2]	SeF_4	−13.2	101	
selenium tetrachloride	[10026-03-6]	$SeCl_4$	305	196 sub	−188.3
selenium tetrabromide	[7789-65-3]	$SeBr_4$	75 dec		
selenium hexafluoride	[7783-79-1]	SeF_6	−34.6	−46.6 sub	−1029.3
selenium dioxide	[7446-08-4]	SeO_2	340	315 sub	−238.5
selenium trioxide	[13768-86-0]	SeO_3	118	180 dec	−184
selenous acid	[7783-00-8]	H_2SeO_3			−531.3
selenic acid	[7783-08-6]	H_2SeO_4	60		−538.0
selenium oxyfluorides	[7783-43-9]	$SeOF_2$	15	125–126	
	[14984-81-7]	SeO_2F_2	−99.5	−8.4	
selenium hypofluorite	[27218-12-8]	$SeOF_6$	−54	−29	
selenium oxychloride	[7791-23-3]	$SeOCl_2$	10.8	177.6	
selenium oxybromide	[7789-51-7]	$SeOBr_2$	41.7	217	

[a] Refs. 1, 2, and 4.

[b] To convert J to cal, divide by 4.184.

with alkali metals dissolved in liquid ammonia. Metal (M) hydrogen selenides of the M HSe type are known. Some heavy-metal selenides show important and useful electric, photoelectric, photo-optical, and semiconductor properties. Ferroselenium and nickel selenide are made by sintering a mixture of selenium and metal powder.

The carbon selenides CSe_2 [506-80-9], COSe [1603-84-5], and CSSe [5941-19-9] are not very stable, especially when exposed to light. Nitrogen selenide [12033-88-4], Se_4N_4, is an orange-red amorphous powder and is unstable. It detonates easily when scratched or when heated to 200°C. The phosphorous selenides, P_4Se_3 [1314-86-9] and the readily flammable P_2Se [12137-67-6], are known. Sulfur and selenium form homogeneous solutions in the liquid state, and these form a series of solid solutions on crystallization. Orange SeS [7446-34-6] has been prepared by precipitation. Selenium and tellurium form a continuous series of solid solutions or alloys, which probably contain different simple and mixed chains of various lengths.

2.1.2. Halides and Oxyhalides

2.1.2.1. Halides. Selenium combines directly with fluorine, chlorine, bromine, and iodine, and forms the monohalides, Se_2X_2; the dihalides, SeX_2; the tetrahalides, SeX_4; and the hexafluoride, SeF_6 [7783-79-1]. The compounds are covalent and volatile. The stability decreases from the fluorides to the iodides. Although SeF_6 is stable on an electric-arc discharge, SeI_2 [81256-76-0] and SeI_4 [13465-68-4] exist in solution only. Selenium halides and sulfur halides have similar properties. The tetrahalides are more stable than the dihalides. When heated, the dihalides decompose into selenium and a tetrahalide. The chlorides and bromides are easily hydrolyzed and the hexafluoride hydrolyzes very slowly. The hydrolysis products are selenous or selenic acids and halogen acid.

Selenium tetrafluoride, SeF_4, is a colorless liquid which fumes in air. It is a powerful oxidant. It attacks silicon, phosphorus, arsenic, antimony, and bismuth; dissolves sulfur, selenium, bromine, and iodine; reacts violently with water; and attacks glass if wet. Selenium tetrachloride, $SeCl_4$, is a white or pale yellow crystalline substance. It forms addition compounds with metal and nonmetal chlorides, ammonia, thiourea, and amines. It is a strong chlorinating substance; it is readily hydrolyzed to selenous acid and is reduced to the monochloride and lower chlorides by sulfur and selenium. Selenium monochloride, Se_2Cl_2, is a brownish red oily liquid. It is decomposed by a number of substances and reacts with many metals and nonmetals. Selenium tetrabromide, $SeBr_4$, is orange-red, crystalline, hygroscopic, and readily hydrolyzed. In carbon disulfide solution and with ammonia, it forms the highly explosive Se_4N_4. Selenium monobromide is a dark red (almost black), pungent smelling, oily liquid. It is hygroscopic and is readily hydrolyzed by water and alkalies and forms addition compounds with amines and heterocyclic bases.

2.1.2.2. Oxyhalides. Selenium oxyhalides, $SeOX_2$, are prepared by the addition of a halogen to a dry mixture or a carbon tetrachloride suspension of selenium and selenium dioxide. Selenium oxyfluoride is conveniently prepared by treating selenium oxychloride with silver fluoride. The product is a colorless liquid with a pungent odor. It reacts with water, silica, silicon, and very violently with red phosphorus, and it forms addition compounds with hydrofluoric acid. Selenium oxychloride is also a colorless liquid with a pungent odor, is readily hydrolyzed, and fumes in moist air. It is a strong chlorinating agent and oxidant; it reacts with many metals, nonmetals, and organic substances. It dissolves many metal chlorides and chalcogenides, and it forms solvates and addition compounds. When mixed with sulfur trioxide, it dissolves alumina, chromic oxide, and rare metal oxides. Selenium oxychloride has been called the universal solvent. It has a high dielectric constant and has been used extensively as an ionizing solvent. Selenium oxybromide is an orange solid and is very easily hydrolyzed, decomposing in moist air at 50°C. It is a brominating agent with solvent properties similar to those of the oxychloride.

2.1.3. Oxides, Acids, and Salts

2.1.3.1. Oxides. Selenium monoxide [12640-89-0] has only been detected spectroscopically as the gas. Selenium dioxide, SeO_2, is prepared by burning selenium in a current of air or oxygen and, optionally, by passing it over a catalyst or by oxidation with nitric acid to selenous acid followed by evaporation to dryness by heating. The compound is white and crystalline with a tetragonal structure and is yellowish green as the vapor. It dissolves easily in water forming selenous acid and less readily in acetone, alcohols, glacial acetic acid, and dioxane. Selenium dioxide is less stable than sulfur dioxide or tellurium dioxide. Like sulfur dioxide it is an acid anhydride, but unlike SO_2 it is a strong oxidant and is reduced to elemental selenium by sulfur dioxide, hydrogen, hydrogen sulfide, ammonia, phosphorus, carbon, and even organic dust particles in moist air. The reaction with sulfur dioxide does not occur without the presence of water vapor. Selenium dioxide strongly catalyzes the oxidation of nitrogen compounds in Kjeldahl digestion. The use of selenium dioxide as an oxidant in organic chemistry has been reviewed (56). In the gaseous state it is reduced by ammonia and hydrocarbons with emission of light. This gaseous reaction with ammonia was used at one time and in the production of high purity selenium. Selenium dioxide is oxidized by fluorine to SeO_2F_2 and by hydrogen peroxide and potassium permanganate to form selenates.

Selenium trioxide, SeO_3, is white, crystalline, and hygroscopic. It can be prepared by the action of sulfur trioxide on potassium selenate or of phosphorous pentoxide on selenic acid. It forms selenic acid when dissolved in water. The pure trioxide is soluble in a number of organic solvents. A solution in liquid sulfur dioxide is a selenonating agent. It is stable in very dry atmospheres at room temperature and on heating it decomposes first to selenium pentoxide [12293-89-9] and then to selenium dioxide.

2.1.3.2. Acids and Salts. The important oxyacids are selenous acid, H_2SeO_3, and selenic acid, H_2SeO_4. Selenous acid is formed by wet oxidation of the element or by dissolving selenium dioxide in water. It is colorless, crystalline, and highly soluble in water, forming a weakly acidic solution and two series of salts: selenites and hydrogen selenites. Selenous acid is an oxidant. It is easily reduced by nascent hydrogen, hydrogen sulfide, and sulfur dioxide. It is also readily oxidized to selenic acid by fluorine, bromine, chlorine, chloric acid, ozone, hydrogen peroxide, or permanganate; the oxidation by chlorine or bromine is reversible. Electrolysis of selenous acid yields selenic acid free of selenous acid. The selenate and hydrogen selenate salts are similar in their

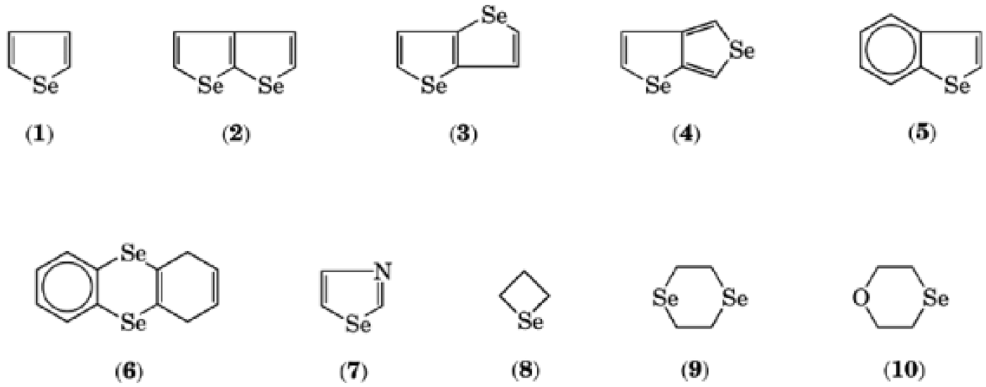

Fig. 4. Simple organic ring compounds containing selenium: selenophene [288-05-1] (**1**), selenolo[2,3-*b*]selenophene [250-85-1] (**2**), seleno[3,2-*b*]selenophene [251-49-0] (**3**), seleno[3,4-*b*]selenophene [250-71-5] (**4**), benzo[*b*]selenophene [272-30-0] (**5**), selenanthrene [262-30-6] (**6**), selenazole [288-52-8] (**7**), selenetane [287-28-5] (**8**), and cyclic ethers 1,4-diselenane [1538-41-6] (**9**) and 1,4-selenoxane [5368-46-7] (**10**).

properties to the sulfates and hydrogen sulfates. Selenic acid and selenates are stronger oxidants than sulfuric acid or sulfates.

Some of the other selenium oxyacids are permonoselenic acid [81256-77-1], H_2SeO_5; perdiselenic acid [81256-78-2], $H_2Se_2O_8$; and pyroselenic acid [14998-61-9], $H_2Se_2O_7$. Selenosulfuric acid, H_2SeSO_3, is not known but its alkali metal salts have been prepared.

Other inorganic selenium compounds include sodium selenocyanate [4768-87-0], NaSeCN, which is prepared by melting together selenium and sodium cyanide; selenocyanogen [27151-67-3] $(SeCN)_2$; sodium selenosulfate [25468-09-1], Na_2SeSO_3, which is prepared by dissolving selenium in aqueous sodium sulfite (acidification decomposes this compound); and selenate alums, eg, $Al_2(SeO_4)_3 \cdot K_2SeO_4$ [13530-59-1].

2.2. Organic Compounds

The chemical properties of organosulfur, organoselenium, and organotellurium compounds are markedly similar. Because bond stability decreases with increasing atomic number of the element, thermal stability and stability on exposure to light of all wavelengths decrease and oxidation susceptibility increases. Thus, selenium compounds often turn red when exposed to light or air. These factors as well as the unpleasant odor of many compounds and difficulties in analytical determination in the early 1900s hindered the development of organoselenium chemistry. Since the 1960s interest has grown appreciably. A large and steadily increasing number of selenium analogues of organosulfur compounds have been prepared and their properties and possible uses have been studied. They range from the simple COSe, CSSe, and CSe_2 to complex heterocyclic compounds, selenium-containing coordination compounds, and selenium-containing polymers.

Selenocysteine was identified in 1976 (57) in a protein produced by *Clostridium stricklandii*, and it is thought to be the form in which selenium is incorporated, stoichiometrically, into proteins. Studies with rats show that over 80% of the dietary selenium given them is incorporated into proteins, thus selenocysteine takes on metabolic importance. Selenoproteins having known enzymatic activities contain selenocysteine at the active sites. Two other forms of metabolic selenium are recognized: methylated selenium compounds are synthesized for excretion, and selenium is incorporated into some transfer ribonucleic acids (tRNAs) in cultured cells (58). Some of the more important seleno-compounds are listed in Table 4. Examples of simple ring compounds are shown in Figure 4.

Table 4. Types of Organoselenium Compounds

Type	Formula[a]
selenols (selenomercaptans)	RSeH
selenides	RSeR
diselenides	RSeSeR
triselenides	RSeSeSeR
selenenic acids	RSeOH
selenamides	$RC(Se)NH_2$
selenocyanates	RSeCN
seleninic acids	RSeO(OH)
selenonic acids	$RSeO_2(OH)$
halides	R_3SeX
dihalides	R_2SeX_2
trihalides	$RSeX_3$
selenoxides	R_2SeO
selenones	R_2SeO_2
selenonium compounds	$R_3Se^+X^-$
selenoaldehydes	RCHSe
selenoketones, cyclic selenoketones	RC(Se)R
sulfenoselenides	RSSeR
selenourea [630-10-4]	$(NH_2)_2CSe$
selenocarboxylic acids, esters, and *N*-derivatives of selenourea	$(RNH)_2CSe$
selenocycloalkanes	$CH_2(CH_2)_xSe$
selenophenols	C_6H_5SeH
selenosemicarbazides	$H_2NC(Se)NHNHR$
selenium-containing *N*-heterocycles	
selenium-containing carbohydrates (selenogluconides, selenosugars)	
selenium-containing dyes (cyanine and noncyanine)	

[a] R = organic aliphatic or aromatic group.

The organoselenium compounds, their chemistry, and methods of preparation are discussed in the literature (3, 4, 7, 11, 12, 14, 59). Selenium-containing polymers are of interest because of their semiconducting and plastic properties. The biologically important compounds include selenoaminocarboxylic acids and derivatives, selenium-containing peptides, and selenium derivatives of pyrimidines, purines, cholines, steroids, coenzyme A, and other compounds (4, 14). The biochemical and medical aspects and uses of organoselenium compounds have also been discussed (13, 14, 60–62).

Organoselenium compounds, such as phosphine selenides, are being evaluated in solvent extraction systems for silver and gold (63). Also, potential pharmaceuticals containing selenium have been prepared (64).

3. Economic Aspects

Commercial production of selenium started in the United States in 1910 when ca 4500 kg was produced. Prior to that selenium was imported from Germany. Demand remained small for several decades, but in the 1940s selenium use in electronics began to increase and selenium became, in many cases, an essential industrial material. All primary selenium producers are electrolytic copper refiners. Leading world producers of selenium are Japan, Canada, Belgium, and Germany. Table 5 lists world production for the years 1994–1998. U.S. data for 1997–1998 are considered proprietary. U.S. production in 1996 was 379 metric tons. Worldwide about 250 metric tons of secondary selenium was produced (65).

Table 5. Selenium: World Refinery Production, by Country, kg, contained selenium[a, b, c]

Country[d]	1994	1995	1996	1997	1998[e]
Belgium[e]	250,000	250,000	250,000	250,000	200,000
Canada[f]	566,000	553,000	694,000	592,000[g]	384,000
Chile[e]	43,000[h]	51,000	50,000	49,500[g]	49,000
Finland[e]	29,690[h]	29,000	28,000	28,000	26,000
Germany[e]	120,000	115,000	115,000	115,000	100,000
India[i]	11,582	11,449	11,500[e]	11,500[e]	11,500
Japan	614,134	547,731	588,186	546,372[g]	551,000[h]
Peru[e]	21,000[h]	21,000	21,000	21,000	21,000
Philippines[e]	40,000	40,000	40,000	40,000	40,000
Serbia and Montenegro[e]	30,000	30,000	30,000	30,000	30,000
Sweden[e]	50,000	30,000	26,000	20,000	20,000
United States[j]	360,000	373,000	379,000	[g],[k]	[k]
Zambia[l]	21,290	18,550	15,161[g]	20,165[g]	15,000
Zimbabwe	2,009	2,000[e]	2,000[e]	[g]	
Total	*2,160,000*	*2,070,000*	*2,250,000*	*1,720,000*	*1,450,000*

[a] Ref. 65.

[b] World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.

[c] Insofar as possible, data relate to refinery output only; thus, countries that produced selenium contained in copper ores, copper concentrates, blister copper and/or refinery residues, but did not recover refined selenium from these materials indigenously were excluded to avoid double counting. Table includes data available through June 3, 1999.

[d] In addition to the countries listed, Australia produced refined selenium, but output is not reported; available information is inadequate for formulation of reliable estimates of output levels. Australia is known to produce selenium in intermediate metallurgical products and has facilities to produce elemental selenium. In addition to having facilities for processing imported anode slimes for the recovery of selenium and precious metals, the United Kingdom has facilities for processing selenium scrap.

[e] Estimated.

[f] Excludes selenium intermediates exported for refining.

[g] Revised.

[h] Reported figure

[i] Data are for Indian fiscal year beginning April 1 of year stated

[j] Includes production of semirefined selenium exported for further refining

[k] Withheld to avoid disclosing company proprietary data; not included in "Total."

[l] Data are for year beginning April 1 of year stated. Gross weight, purity unknown.

Three U.S. copper refiners (ASARCO Inc., Amarillo, Texas), Phelps Dodge Refining Corp. (El Paso., Texas), and Kennscott Copper Corp. (Salt Lake City, Utah) recover selenium from anode slimes generated in the electrolytic production of copper (65).

U.S. import information is given in Table 6.

Producer price in 1998 was $2.50/lb ($5.50/kg) (66). Since 1990, worldwide production has exceeded or matched demand. Fairly constant oversupply has kept prices low (67).

There is no U.S. government stockpile of selenium (24).

Table 6. U.S. Imports for Consumption of Selenium kg, contained selenium[a, b]

Class and country	1997 Quantity	1997 Value	1998 Quantity	1998 Value
Unwrought waste and scrap				
Australia	18,000	$86,200		
Belgium	46,500	1,710,000	43,300	$1,550,000
Canada	95,300	1,880,000	100,000	1,550,000
Finland	4,200	26,100	12,800	48,200
France	2,370	12,600	10,700	53,100
Germany	250	9,590	2,040	65,200
Japan	2,740	645,000	19,100	320,000
Korea, Republic of	3,590	133,000	1,000	3,530
Netherlands	500	15,000	999	4,410
Peru	14,000	97,600		
Philippines	100,000	478,000	116,000	597,000
Russia	1,590	7,010	2	2,740
United Kingdom	19,500	117,000	18,500	102,000
Total	*333,000*	*5,220,000*	*325,000*	*4,290,000*
Selenium dioxide[c]				
Belgium	1	6,620	1,410	79,100
China			1,350	76,600
Germany	10,900[d]	125,000[d]	9,350	103,000
Japan	1,870[d]	20,100[d]	2,160	23,900
Spain	160[d]	4,530[d]	178	2,870
United Kingdom	710[d]	13,400[d]		
Total	*13,700*[d]	*169,000*[d]	*14,400*	*285,000*
Grand total	*346,000*[d]	*5,390,000*[d]	*339,000*	*4,580,000*

[a] Bureau of the Census. Ref. 65

[b] Data are rounded to three significant digits; may not add to totals shown.

[c] Totals revised to 71% of original quantities and values.

[d] Revised.

World producers of selenium are listed in Table 7 (68).

Like all minor metals, the unique physical and chemical properties of selenium determine its technological uses. Consumption of selenium by industry in 1998 follows: 25%, glass, 22%, metallurgy, 19%; agricultural/biological; 14%, miscellaneous chemical and articles; 12%, photoreceptors; 8% pigments.

The use of organic photoreceptors has resulted in a decline of use of selenium in xerography. Use of selenium in cadmium sulfoselenide pigments is declining because of environmental regulations. Research has shown a positive correlation between selenium supplementation and cancer prevention in humans. However, the small doses required would not significantly add to demand (69). Declining markets have resulted in prices for commercial 99.7% grade to fall $4.89/lb ($8/kg) in 1995 to $2.50/lb ($5.50/kg) in 1998 (66).

Table 7. World Producers of Selenium[a]

Country	Company
Australia	Hydromet Operations Ltd., Marrickville
Belgium	UM Electro-Optic Materials, Hoboken
Canada	Inco Limited, Toronto
	Noranda Minerals Inc., CCR Did., Montreal East, Québec
Chile	Codelco Chile Chuquicamata
	Cormiquim SA Chile, Santiago, Maipu (Santiago)
	Enami–Empresa Nacional de Mineria, Santiago
China, P.R.[b]	Guangzhou Smelter, Guangzhou
	Guixi Smelter, Guixi
	Shanghai Smelter, Shanghai
	Shenyang Smelter, Shenyang
	Zhuzhou Smelter, Zhuzhou
CIS[b]	Amalysky Metallurgical Plant, Tashkent Region, Almalyk, Uzbekistan
	Balashmed Plant, Dzheskazgen Region, Russia
	Copper Refinery Uralelektromed, Yekaterinburg, Russia
	Krasny Chimik, St Petersburg Russia
	Krastsvetmet (Krasnoyarsky Plant of Nonferrous Metals), Krasnoyarsk, Russia
	Kyshtym Copper Electrolytical Plant, Chelyabinsk Region, Russia
	Norilsk Nickel Plant, Krasnoyarsk Region, Russia
	Shelkovskoje Plant Agrochim, Shelkovo, Moscow Region, Russia
	Ust-Kamenogorsky Lead-Zinc Plant, East Kazakhstan, Russia
Finland	Outokumpu Harjavalta Metals Oy, Pori
Germany	Norddeutsche Affinerie AG, Hamburg
Japan	Japan Energy Corp., Tokyo
	Mitsubishi Materials Corp., Tokyo
	Mitsui Mining & Smelting Co., Ltd., Tokyo
	Nippon Rare Metal, Inc.; Yokohama
	Shinko Chemical Co., Ltd., Hyogo
	Sumitomo Metal Mining Co., Ltd., Tokyo
Peru	Doe Run-Peru, La Oroya
Philippines	Pacific Rare Metal Industries Inc., Quezon City, (Manila)
Spain	Atlantic Copper SA, Madrid
Sweden	Boliden Ore & Metals AB, Stockholm
United Kingdom	Mining & Chemical Products Ltd., Alperton, London
United States	Asarco Inc., New York
	Kennecott Corp., Salt Lake City, UT
	Phelps Dodge Refining Corp., El Paso, Tex.
Zambia	Zambia Consolidated Copper Mines Ltd., Kalulushi

[a] Ref. 68

[b] May not be exact.

4. Specifications and Standards

There are no official specifications for selenium, apart from those of the U.S. Government for purchases under the national stockpile plan (at present there is no U.S. stockpile (24)). Some producers publish standards, and some users specify a screen analysis and maximum content of certain impurities. Four grades of selenium are available. There is the commercial or refined grade, which contains >99.5 wt% selenium and various impurities, usually <0.2 wt% tellurium, <0.1 wt% iron, <0.005 wt% lead, and <0.005 wt% copper. This grade is sold mainly as 75-μm (200-mesh) powder as well as in smaller quantities of coarser size and as lump. A second, more select pigment grade has a purity of 99.7%. The third grade, high purity selenium, contains 99.999 wt % selenium, although this figure of purity is obtained by difference and not by a direct determination. This grade is sold usually in shotted form but also in small amounts as a powder. Some users have their own specifications which reflect a particular application of selenium. Impurities, eg, mercury, tellurium, iron, arsenic, and nonferrous metals that are harmful in electronic and electrostatic uses must be $<1-2$ ppm each. A somewhat higher concentration of inert contaminants, eg, sodium, magnesium, calcium, aluminum, and silicon, can be tolerated. The concentration of halogens, sulfur, and oxygen must be low, depending on the use. The fourth grade, called ultrahigh purity selenium, is claimed to contain 99.999–99.9999 wt % selenium.

5. Analytical Methods

Comprehensive accounts of the various gravimetric, polarographic, spectrophotometric, and neutron activation analytical methods have been published (1, 2, 5, 17, 19, 70–72). Sampling and analysis of biological materials and organic compounds is treated in References 60 and 73. Many analytical methods depend on the conversion of selenium in the sample to selenous acid, H_2SeO_3, and reduction to elemental selenium when a gravimetric determination is desired.

Several common acid treatments for sample decomposition include the use of concentrated nitric acid, aqua regia, nitric–sulfuric acids, and nitric–perchloric acids. Addition of potassium chlorate to nitric acid assists in dissolving any carbonaceous matter. Perchloric acid is an effective oxidant, but its use is hazardous and requires great care. Loss of selenium may occur on preparing the sample or during determination. For example, the practice of dissolving a sample of some metals in a nonoxidizing acid could lead to some loss of selenium as the volatile hydrogen selenide.

Organic selenium compounds and siliceous materials (rock, ore, concentrates) are fused with mixtures of sodium carbonate and various oxidants, eg, sodium peroxide, potassium nitrate, or potassium persulfate. For volatile compounds, this fusion is performed in a bomb or a closed system microwave digestion vessel. An oxidizing fusion usually converts selenium into Se(VI) rather than Se(IV).

When the sample contains $<0.1\%$ selenium or if interfering substances are present, selenium may be preconcentrated by distillation from a bromine–hydrobromic acid mixture:

$$H_2SeO_3 + 4\ HBr \longrightarrow SeBr_4 + 3\ H_2O$$

The $SeBr_4$ which forms is distilled from the solution leaving the interfering elements behind. The only other metallic elements that can also distill over by this procedure are arsenic, antimony, tellurium (partly), and germanium.

A number of substances, such as the most commonly used sulfur dioxide, can reduce selenous acid solution to an elemental selenium precipitate. This precipitation separates the selenium from most elements and serves as a basis for gravimetry. In a solution containing both selenous and tellurous acids, the selenium may be quantitatively separated from the latter by performing the reduction in a solution which is 8 to 9.5 *N* with respect to hydrochloric acid. When selenic acid may also be present, the addition of hydroxylamine hydrochloride is recommended along with the sulfur dioxide. A simple method for the separation and determination of selenium(IV) and molybdenum(VI) in mixtures, based on selective precipitation with potassium thiocarbonate, has been developed (74).

There are also numerous titrimetric methods for determining macro amounts of selenium including the iodometric, thiosulfate, and permanganate methods. In one of the several iodometric methods, the dissolved selenium is reduced from Se(IV), if an excess of potassium iodide is added:

$$H_2SeO_3 + 4\ HCl + 4\ KI \longrightarrow Se^0 + 2\ I_2 + 4\ KCl + 3\ H_2O$$

The liberated iodine is titrated with standard sodium thiosulfate solution. In the thiosulfate method, selenous acid is treated with an excess of standard sodium thiosulfate solution:

$$H_2SeO_3 + 4\ Na_2S_2O_3 + 4\ HCl \longrightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 4\ NaCl + 3\ H_2O$$

The excess $Na_2S_2O_3$ is back-titrated with standard iodine solution. The permanganate method is based on the oxidation of Se(IV) to Se(VI).

From a toxicological and physiological point of view, the determination of micro amounts of selenium is becoming increasingly important. Interest in environmental and human health has promoted development of analytical techniques and methods at the trace and ultratrace levels (see Trace and residue analysis). The classical, highly selective and sensitive 3,3′-diaminobenzidine method is used widely in the spectrophotometric determination of low levels of selenium. Some instrumental analysis methods used to determine trace amounts of selenium include flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, hydride generation atomic absorption spectrometry, inductively coupled argon plasma optical emission spectrometry, inductively coupled plasma mass spectrometry, and neutron activation analysis.

Other methods of instrumental analysis include polarography, potentiometry, emission spectroscopy, x-ray diffraction, and x-ray fluorescence.

A widely used procedure for determining trace amounts of selenium involves separating selenium from solution by reduction to elemental selenium using tellurium (as a carrier) and hypophosphorous acid as reductant. The precipitated selenium, together with the carrier, are collected by filtration and the filtered solids examined directly in the wavelength-dispersive x-ray fluorescence spectrometer (75). Numerous spectrophotometric and other methods have been published for the determination of trace amounts of selenium (76–93).

6. Health and Safety Factors

Commercial elemental selenium along with the stable metallic selenides are considered relatively nontoxic. However, other selenium compounds which include the reactive selenides; the gaseous, volatile, and soluble compounds; and particularly hydrogen selenide, the halides, oxides, and the organics are highly toxic and must be handled with care (94). Selenium can enter the body through inhalation, ingestion, or absorption through the skin where it accumulates primarily in the liver and kidney. Symptoms of selenium poisoning include bronchial irritation, gastrointestinal distress, nasopharyngeal irritation, and garlic odor on the breath (95).

Selenium plays a dual role in a living organism, depending on the compound and the amount adsorbed. Controlled small doses of some compounds are used in medicine and as diet supplements, for example, ca 0.1 ppm of diet dry matter for livestock (see Feed additives; Mineral nutrients). Larger amounts can be toxic.

Contact with elemental selenium does not injure the skin. Selenium dioxide, however, upon contact with water, sweat, or tears, forms selenous acid, a severe skin irritant. Selenium oxyhalides are extremely vesicant and cause burns when in contact with human skin (96, 97). Hydrogen selenide affects the mucous membranes of the upper respiratory tract and the eyes (98).

Industrial precautions include the common-sense measures of good housekeeping, proper ventilation, personal cleanliness, frequent changes of clothing, and provision of respirators (where needed), gloves, and either safety glasses or chemical goggles. Food should be consumed in a clean room separate from the handling area and after washing hands and face. Workers should change out of their work clothes and shower at the end of the working day. Selenium and its commercial products are not a fire hazard. The toxicity of seleniferous plants ingested by domestic animals and instances of poisoning among humans consuming the products of these animals and food (cereal grains) grown on highly seleniferous soils have been reported (19). Measures have been taken to cease grazing and cultivation on such soils. The aspects of selenium in human and animal biology and in medicine have been treated (14, 73, 94–101). Toxicity is discussed in References 103–108.

The ACGIH TWA-TLV is 0.05 ppm measured as selenium. This is equivalent to the OSHA limit for selenium hexafluoride. The National Institute for Occupational Safety and Health (NIOSH) indicated that 2 ppm is immediately dangerous to life or health (IDLH) (95).

6.1. Environmental Concerns and Recycling

Selenium scrap was banned from shipment from Europe to Africa, Pacific and Carbbean nations (APC countries) per the Basel Convention (1997). This directive was an attempt to prevent dumping of toxic materials in those countries. However, some of these countries were already importing scrap for processing (102).

There is no U.S. secondary production of selenium. An estimated 45 t of selenium metal recovered from scrap was imported in 1998 (24).

6.2. Glass and Ceramics

Selenium is used to decolorize the greenish tinge in glass caused by the presence of iron as an impurity. This application was introduced into the United States in 1915 (4). Until that time manganese dioxide imported from Russia was used in conjunction with arsenic trioxide. Selenium is usually used in the elemental form although other forms such as selenites of sodium, barium, or zinc and frits containing selenium may be used. The quantity required for a glass batch depends on the iron content of the sand used, preferably 0.02–0.05 wt % Fe_2O_3, and the selenium is added typically at a level of 10–30 g/t of glass. Selenium retention efficiencies are generally around 20%. Utilization is being addressed by improving the form of the additive, modifying the furnace design, and improving the off-gas cleaning system (109).

Significant amounts of selenium are used to decolorize glass for container applications and to a lesser extent for table, lighting, and industrial glass applications. The flat plate glass industry uses selenium to produce gray to nearly black and bronze tinted heat-absorbing glasses for architectural and automotive applications. These glasses contain selenium in the range of 0.1–0.5 g/kg in addition to measured amounts of cobalt and iron.

Selenium is combined with cadmium sulfide in various ratios to produce glasses colored in the range of orange to ruby red for the art and novelty glass industry. To produce the desired color, a glass batch containing the appropriate ratio of selenium and cadmium sulfide is melted under reducing conditions and rapidly cooled. The rapid cooling retains the color particles in solution and the glass takes on a faint yellow color. It is then subjected to a heat treatment called striking to develop the desired color. To produce a ruby red glass, which is influenced by melting conditions, Se, on the order of 0.5–1.0 kg, and CdS, 1.5–2.0 kg, are added to a 100-kg batch of sand. Selenium ruby glass exhibits very good transmission in the red part of the spectrum with a sharp cut-off of other colors and for this reason has found application in the United States since 1895 for signal light lenses, in addition to religious articles, vases, dinnerware, etc.

Selenium pink or rosaline glasses are obtained with the addition of 0.05–1.0% Se under oxidizing melting conditions. Selenium also imparts a yellow color to glass when oxides of antimony, arsenic, and bismuth are added. Addition of neodynium oxide and selenium produces purple glass and additions of cobalt or iron oxide with selenium yield black glasses. Selenium and silicon are used together to color glasses in conjunction with a third additive, eg, ferrous oxalate, to produce amber, bismuth oxide to produce topaz, and chromium oxide to produce emerald glass.

Selenium pigments are used in ceramic applications. These pigments may be encapsulated in zirconium silicate (110) which combines the brilliance of the pigments with high temperature and corrosion resistance under conditions of firing. Colored glazes of selenium are used in the ceramic industry for chinaware, porcelain and pottery, sanitary ware, and in printing inks for glass and other containers (see Colorants for ceramics).

Selenium chalcogenide glasses exhibit good infrared transmission properties. These are used as lenses (ZnSe, CdSe) in laser applications and have potential applications in fiber optics (qv) and in data storage and retrieval.

6.3. Metallurgical

The metallurgical applications of selenium normally involve its use as a minor alloying additive to enhance the properties of both ferrous and nonferrous metals and alloys (see Iron; Steel).

6.3.1. Ferrous Metals

In small concentrations, selenium decreases the surface tension of molten steel more than S, N, O, P, and C, but probably less than Te. In cast iron of low (0.02%) Mn content, selenium, in the presence of hydrogen, suppresses graphite nucleation and promotes carbide formation. However, at higher Mn levels graphite nucleation is favored. In steels, small amounts of Se act as a mild deoxidizer and selenium promotes fine-grained equiaxial crystals which minimize differences in directional properties, reduces hardenability, and is less sensitive to overheating and quench cracking. These properties result in improved steels for carburizing and hot-rolled applications. Selenium is also added to steel to counteract, on hot rolling, the elongation of globular MnS inclusions frequently encountered which lead to directional properties. It dissolves in the MnS, hardening the inclusion so that it will remain more oval during rolling. As little as 0.2% Se added to stainless steel casting alloys prevents the pinhole porosity ascribed to hydrogen.

The principal use of selenium in ferrous alloys is to improve machinability, ie, production rate and surface finish. Based on a machinability rating of 100 for AISI1112 steel, the machinability of low carbon steel 12L14, with the addition of 0.04–0.08% Se and 0.15–0.35% Pb, is increased 2.5 times. Similarly, the addition of a minimum of 0.15% Se to 302 and 430 stainless steels improves the machinability by 25 and 50%, respectively. The influence of selenium on improving the machinability of higher carbon grades of stainless steels is less pronounced. Even though sulfur also imparts free machining properties, selenium on a weight basis is preferred for better machinability and surface finish because selenium has a less deleterious effect on corrosion resistance, hot shortness, cold working, and strength properties of the finished product.

Selenium is added up to 0.1% to silicon steels (2–4% Si) used in transformer cores to enhance the development of the secondary recrystallization texture which, in turn, improves the magnetic characteristics. Selenium alloying additions to the melt may be made as elemental Se, nickel–selenium, or ferroselenium. The recovery depends on the melting practice and method of addition. Normally, it is in the range of 66%, but may be as high as 90%.

6.3.2. Copper and Copper Alloys

In liquid copper, selenium, owing to its surface activity, forms a monomolecular surface layer. The addition of selenium in the amount of 0.025–1% improves the machinability of copper. The microstructure of the alloy consists of primarily copper and a eutectic of copper plus cuprous selenide. The presence of the cuprous selenide phase acts as a chip breaker. Selenized copper has favorable brazing and soldering characteristics, although its weldability is degraded (see Solders and brazing filler metals; Welding).

Selenium has also been shown to act synergistically with bismuth to improve the machinability of brasses (111). The machining properties are similar to those of the leaded brasses used in plumbing applications. Environmental concerns arising from the leaching of lead brasses necessitates a replacement of the lead. The use of selenium as an additive to no-lead free-machining brasses for plumbing applications continues to increase as more stringent regulations on lead in drinking water increase (24).

6.3.3. Lead and Lead Alloys

Selenium is reported to lower the surface tension of lead. The addition of 0.1% selenium and tellurium to solder improves its fluidity.

Selenium acts as a grain refiner in lead antimony alloys (112, 113). The addition of 0.02% Se to a 2.5% antimonial lead alloy yields a sound casting having a fine-grain structure. Battery grids produced from this alloy permit the manufacture of low maintenance and maintenance-free lead–acid batteries with an insignificant loss of electrolyte and good performance stability.

6.3.4. Nickel–Iron and Cobalt–Iron Alloys

Selenium improves the machinability of Ni–Fe and Co–Fe alloys which are used for electrical applications. Neither sulfur nor tellurium are useful additives because these elements cause hot brittleness. The addition of 0.4–0.5% selenium promotes a columnar crystal structure on solidification, doubling the coercive force of cobalt–iron–titanium alloy permanent magnets produced with an equiaxial grain structure.

6.3.5. Chromium Plating

Sodium selenate or selenic acid are added to chromium-plating baths to improve corrosion protection from pitting, blistering, and rusting, especially of plated automobile articles exposed to salt in the North American snow belt. Such chromium plate has a dull luster with a decreased glare. A similar microporous, decorative, corrosion-protective plate has been developed (114) (see Electroplating).

6.3.6. Miscellaneous

Addition of selenium to magnesium and magnesium alloys is claimed to improve corrosion resistance by seawater. However, the technique of making this addition requires great care. Selenium dioxide has been added to baths used in etching, formation of decorative colors on galvanized iron and nonferrous metals and alloys, and corrosion-protective coatings in magnesium alloys. Inorganic and organic selenium compounds are brighteners in electroplating. Selenous acid improves the current efficiency in electrowinning of manganese. Diffusion coating of ferrous metals with selenium in a molten salt bath improves resistance to wear and to seizure of contact surfaces. In the manufacture of friction brake facings by powder metallurgy, the addition of selenium to copper oxide followed by reduction, mixing with nonmetallic particles, pressing, and sintering improves the adhesion of the metallic to the nonmetallic particles and increases the pressed green strength by 30%.

6.4. Agriculture

In 1956 selenium was identified (115) as an essential micronutrient in nutrition. In conjunction with vitamin E, selenium is effective in the prevention of muscular dystrophy in animals. Sodium selenite is administered to prevent exudative diathesis in chicks, a condition in which fluid leaks out of the tissues; white muscle disease in sheep; and infertility in ewes (see Feed additives). Selenium lessens the incidence of pneumonia in lambs and of premature, weak, and stillborn calves; controls *hepatosis dietetica* in pigs; and decreases muscular inflammation in horses. White muscle disease, widespread in sheep and cattle of the selenium-deficient areas of New Zealand and the United States, is insignificant in high selenium soil areas. The supplementation of animal feeds with selenium was approved by the U.S. FDA in 1974 (see Feed additives). Much of selenium's metabolic activity results from its involvement in the selenoprotein enzyme, glutathione peroxidase.

6.5. Electrical and Optical

The electrical and optical uses are based on the semiconducting and photoresponsive properties of selenium in its amorphous and crystalline trigonal forms. In the metastable amorphous form, the electrical conductivity is very low, making selenium almost an insulator, but when exposed to light the conductivity is greatly increased. This effect is exploited in xerography and in vidicons. The crystalline trigonal form has a higher electrical conductivity, which also increases under illumination. This conductivity increase, or photoconductivity, has its principal maximum at a wavelength of about 700 nm. The photoconductive effect in selenium was discovered by Smith in 1873 (116).

Trigonal selenium is a *p*-type semiconductor with an energy gap of 1.85 eV (117) and a work function of about 6 eV (118), which is the largest value reported for all the elements. Accordingly, a Schottky barrier should be created at the contact of selenium with any metal. This is consistent with the observed nonsymmetric current–voltage characteristics for metal–Se contacts, particularly where the metal has a low work function. This property is used in rectifiers.

The photovoltaic effect, where an internal elecromotive force is created, was discovered by Becquerel (119) in 1839 in an electrolyte with selenium but the effect in a metal–Se contact was first reported by Adams and Day (120) in 1876. The first practical photovoltaic cell was constructed by Uljanin (121) in 1888.

6.5.1. Rectifier

The selenium rectifier typically has the form Al–Ni–Se–CdBi as a layer structure. A base plate of steel or aluminum, sandblasted or etched, is plated with a film, about 1 μm thick, of bismuth or nickel to form a low resistance back contact. Next, a layer 50–60 μm thick of selenium doped with a halogen, is evaporated on the Ni- or Bi-covered heated plate. During or after this, the selenium is converted completely into the trigonal polycrystalline form by annealing at a temperature below the melting point of selenium (217°C). Then the selenium is coated with a counterelectrode of cadmium alloy, usually by spraying. Following this, the rectifier must be electrically formed, which is done by applying a reverse voltage continuously to the device for a period of hours or days. This process causes the reverse breakdown voltage to increase, without excessively increasing the forward resistance, thus improving the rectification ratio. The action has been ascribed to the formation of CdSe at the interface between the selenium and the counterelectrode. However, more recent work (122) indicates that the forming is more likely to be a partial sweep-out of acceptors in the selenium near the contact by ionic field drift.

Selenium rectifiers were extensively used in electrical power equipment from the 1940s to the 1960s. In this period, there were many variations in the processes used by the rectifier manufacturers. For example, it was found that the electrical characteristics were improved by the addition of some thallium to the selenium or the counterelectrode. Subsequent work showed that a counterelectrode of thallium alone gave even better rectification but the device suffered from rapid degradation owing to the chemical reactivity of thallium with the selenium. As of 1998, selenium rectifiers have been almost completely displaced by silicon diodes, which have a larger reverse breakdown voltage, smaller reverse leakage current, operate up to a higher temperature, and have more precise and controlled characteristics. Nevertheless, the selenium rectifier in single-plate form has a self-healing property not possessed by the silicon device. This property is demonstrated when breakdown by thermal runaway occurs at a hot-spot and localized melting takes place, producing a small crater with a wall of high resistance amorphous selenium, which avoids a short circuit. When silicon melts, it becomes metallic and the short circuit destroys the rectifier.

6.5.2. Photovoltaic Cell

The selenium photovoltaic cell is similar in basic structure to the rectifier, but instead of the opaque cadmium alloy, this cell has a transparent counterelectrode, usually of cadmium oxide deposited by reactive sputtering, on which an annular metal ring is deposited as the top contact the device has been replaced to a large extent in this application by the CdS photoconductive cell. Under standard sunlight (AM1.5), the commercial selenium photovoltaic photometric cell yields an open-circuit voltage of 0.6 volt, a short-circuit current density of about 2 mA/cm^2, and a solar energy conversion efficiency below 1%. However, somewhat higher performance has been obtained in laboratory cells.

6.5.3. Xerography

Photocopiers and laser printers, using the xerographic principle of operation are an application for selenium and selenium-based alloys. A large number of such machines use selenium in the drum or belt photoconductor, which is the critical component for both the image generation and image development functions. The selenium is typically deposited on the metal belt or aluminum drum used in these machines, as a 50-μm vitreous layer, using a process which involves the thermal evaporation of high purity grades of selenium under vacuum. Early copiers used pure selenium coatings, but these have been almost totally replaced by alloys using additions of arsenic, chlorine, and tellurium in order to improve the lifetime of the drums, to modify their photoconductive or spectral response, and to improve their resistance to abrasion. As a result of these changes, some types of selenium-based photocopiers and printers can operate at very fast speeds and deliver hundreds of thousands of pages of output before the drum or belt needs to be replaced. Used selenium drums or belts are returned to the supplier for recycling. In the lower speed, lower cost, desktop digital copier, selenium has been largely replaced by organic-based photoconductors, which offer better performance and are free of environmental concerns(65).

Selenium has also been used for xeroradiography. In this case the photoconductor is typically in the form of a flat plate and the image is formed by x-rays rather than by light. The original units of this type produced an x-ray image on paper, but these machines, which were primarily used in mammography, are nearly obsolete. Newer techniques for electronically developing the latent image formed on the reusable, selenium plate have been proposed (123, 124). These could be the base for a new generation of digital radiographic systems, which would not require the use of traditional x-ray films.

6.6. Organic Chemistry and Pharmaceuticals

Selenium dioxide is an important oxidizing agent and catalyst in the synthesis of organic chemical and drug products (125) (see Hormones; Vitamins). It has been used in the manufacture of cortisone and nicotinic acid (niacin). Selenium and its compounds are useful in a wide variety of organic reactions, eg, oxidation, ammoxidation, reduction, hydrogenation, dehydrogenation, and polymer treatment. Dehydrogenation of hydroaromatic compounds $\geq 250^\circ\mathrm{C}$ with the evolution of hydrogen selenide has been valuable in elucidating the structure of some natural products. Selenium is often used as a catalyst in Kjeldahl determinations to hasten the digestion of nitrogenous materials. Some organoselenium compounds act as miticides. Others have neuroleptic and antidepressant properties. An antibiotic selenomycin is known. An orgonselenium compound is claimed to possess psychotropic activity (126) (see Psychopharmacological agents).

One area of research is the replacement of sulfur with selenium to enhance the potency of organic compounds in pharmaceutical applications. This has seldom been successful and often the toxicity is increased. There are some exceptions, eg, selenazofurin, phenylaminoethyl selenide, ebselen, and selenotifen (64). Selenazofurin is a cytotoxic compound having antitumor properties, phenylaminoethyl selenide is used to reduce hypertension, ebselen inhibits a variety of inflammatory and tissue damaging reactions, and selenotifen is an antiallergic agent.

6.7. Medicine and Nutrition

A stabilized buffered suspension of selenium sulfide has been marketed for many years as Selsun Blue (Abbott Laboratories) for control of seborrheic dermatitis of the scalp. A similar sulfur or selenium sulfide shampoo containing a metallic cation complex has been prepared (127). Topical application of selenium sulfide controls dermatitis, pruritis, and mange in dogs.

Selenium deficiency has been identified in humans in a broad area of China, stretching from the northeast to the southwest. Two syndromes are evident: Keshan disease, an endemic cardiomyopathy which affects children, and Kashin-Beck disease, an edemic osteoarthropathy (big-joint), also mainly involving children, which occurs in eastern Siberia and parts of China. As a result of these observations, a protective effect for selenium has been proposed, and various selenium-containing preparations have been applied to preserve animal and human health.

Sufficient empirical data have been assembled to justify a broad research program enquiring into the protective effects of selenium against certain types of cancer, including colorectal and breast cancers (128). A massive field experiment was conducted in China in 1992 which showed that a treatment including selenium and some other antioxidants gave significant protection in an area of known high cancer incidence (129). Research continues on selenium supplementation and human cancer prevention(130).

Inorganic and organic selenium compounds, including selenoproteins, have been used to treat selenium deficiency in humans and warm-blooded animals, control stress and high blood pressure in poultry and animals, combat aging, and improve the healing of surgically incised, lacerated, and burned tissue (see Antiaging agents; Memory-enhancing drugs). Some organoselenium compounds are useful in immunoassays (qv). Tablets containing several micrograms of selenium as sodium selenite or as selenized yeast are sold over-the-counter in the United States and Europe.

6.8. Pigments

Selenium combines with cadmium sulfide to produce cadmium sulfoselenide pigments with colors in the range of orange to maroon depending on the Cd–S–Se ratio. These are characterized by high temperature stability, brilliance of color, high chemical and light resistance, high opacity, and good dispersion in plastics and paints which are critical properties for use in ceramic, plastic, and glass applications. The olive-drab zinc–chromium–selenate pigments have corrosion-resistant properties (see Corrosion and corrosion control). A zinc sulfide-based pigment containing copper–indium–selenide sulfide exhibits an intensely golden yellow color (131) (see Pigments, inorganic).

6.9. Rubber

The rubber industry consumes finely ground metallic selenium and Selenac (selenium diethyl dithiocarbamate, R. T. Vanderbilt). Both are used with natural rubber and styrene–butadiene rubber (SBR) to increase the rate of vulcanization and improve the aging and mechanical properties of sulfurless and low sulfur stocks. Selenac is also used as an accelerator in butyl rubber and as an activator for other types of accelerators, eg, thiazoles (see Rubber chemicals). Selenium compounds are useful as antioxidants, uv stabilizers, bonding agents, carbon black activators, and polymerization additives. Selenac improves the adhesion of polyester fibers to rubber.

6.10. Lubricants

Selenium and its compounds are added to lubricating oils and greases for normal and extreme pressure service (see Lubrication and lubricants). Dialkylselenides are oxidation inhibitors in lubricants. Barium, calcium, and zinc salts of selenic acids, RSe(O)OH, where R is an alkaryl radical with 10–40 carbon atoms, improve the detergent properties of lubricating oils. Dry, powdered lubricants containing diselenides of tungsten, niobium, tantalum, and molybdenum are manufactured for use at elevated temperatures in an ultrahigh vacuum. Under such conditions, they possess lower outgassing properties, lower coefficients of friction, and higher stability than graphite and the corresponding metal sulfides. Some self-lubricating iron alloys contain selenium.

6.11. Miscellaneous

Sodium selenite is used in photography to produce prints with warm brown tones; sodium selenosulfate gives similar results. Derivatives of selenazole, benzoselenazole [273-91-6], and naphthoselenazole and selenium-containing dyes are used in supersensitive photographic emulsions. Selenocarbazides are used in photographic bleach fixing baths. Some photographic antifogging agents contain selenium.

Sodium selenate has been used on a small scale in commercial greenhouses, primarily for growing carnations and chrysanthemums. It is transformed by the plants into volatile selenides, which repel red spiders, mites, thrips, and aphids. Sodium selenite is not intended for crops which could ultimately be used as food for humans or domestic animals.

Sodium selenite has also been incorporated into styrene–butadiene rubber and used in a pellet form which results in the slow release of selenium into water. These pellets have been placed in lakes in Sweden which have fish contaminated with mercury owing to high levels of that element in the water. The selenium released by the pellets reacts with mercury to form insoluble, heavy mercury selenide which settles to the lake bottom and removes mercury from the ecosystem (132).

Selenium and selenium compounds are also used in electroless nickel-plating baths, delayed-action blasting caps, lithium batteries, xeroradiography, cyanine- and noncyanine-type dyes, thin-film field effect transistors (FET), thin-film lasers, and fire-resistant functional fluids in aeronautics.

The Selenium-Tellurium Development Association (STDA), located in Grimbergen, Belgium, and supported by the principal selenium producers, sponsors activities promoting the use of selenium, the development of new markets, and provides information in all areas where selenium is used. A newsletter is published semiannually. STDA technical efforts as of 1996 were being focused on the use of selenium as an additive to free machining plumbing brasses owing to the phase-out of leaded alloys in this application. When selenium is used in conjunction with bismuth, the elements act synergistically such that alloys with only 1–2% selenium and bismuth have close to the same machining properties as alloys containing the traditional 7% lead.

The use of high purity selenium in digital imaging is considered a potential market. Selenium-based plates can be used to replace conventional silver-based x-ray film, and in 1994 the Xerox Corporation introduced a selenium-based product, Verdefilm, for use in graphic arts applications.

Selenium is also used in thin-film photovoltaic cells which contain copper indium diselenide [12018-95-0],. Use is quite small as of 1998.

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J. E. HOFFMANN
Jan Reimers and Associates USA Inc.
M. G. KING
Selenium–Tellurium Development Association