Kirk-Othmer Encyclopedia of Chemical Technology.

TELLURIUM AND TELLURIUM COMPOUNDS

Tellurium [13494-80-9], Te, at no. 52, at wt 127.61, is a member of the sixth main group, Group 16 (VIA) of the Periodic Table, located between selenium and polonium. Tellurium is in the fifth row of the Table, between antimony and iodine, and has an outer electron configuration of $5s^25p^4$. The four inner principal shells are completely filled. Tellurium is more metallic than oxygen, sulfur, and selenium, yet it resembles them closely in most of its chemical properties. Whereas oxygen and sulfur are nonmetals and electrical insulators, selenium and tellurium are semiconductors, and polonium is a metal. Tellurium forms inorganic and organic compounds superficially similar to the corresponding sulfur and selenium compounds, yet dissimilar in properties and behavior. The valence states assigned to the central atom in tellurium compounds are -2, 0, +2, $+4$, $+6$.

Tellurium was discovered in 1782 in Transylvanian gold ore. Its name is derived from the Latin *tellus,* meaning earth (1). At 0.047 atoms per 10,000 atoms Si, tellurium is about the fortieth element in the order of cosmic abundance. Along with platinum, palladium, and ruthenium, it ranks about seventy-first in the order of crustal abundance. The average amount in crustal rocks is 0.01 ppm. The chalcogens, sulfur, selenium, and tellurium, are primarily components of intrusive and extrusive magmas and volcanic gases, and hence of volcanic sulfur deposits. Nevertheless, selenium and tellurium are not essential components of the common igneous rock-forming minerals. Tellurium is widely distributed in the earth's crust in deposits of many different types, from magmatic and pegmatitic to hydrothermal, especially where these deposits are associated with epithermal gold and silver deposits (2–4).

Small concentrations but large quantities of tellurium are present in copper porphyries, massive pyritic copper sulfide and nickel sulfide deposits, and frequently in lead sulfide deposits. In pyritic deposits, tellurium is concentrated chiefly in pentlandite [53809-86-2], $(FeNi)_9S_8$; chalcopyrite [1308-56-1], $CuFeS_2$; and pyrite [1309-36-0], FeS_2 in decreasing order; and least in sphalerite [12169-28-7], ZnS, and pyrrhotite [12063-67-1], FeS. Other tellurium-bearing deposits are copper–molybdenum, lead–zinc, gold, tungsten–bismuth, uranium, and mercury–antimony. The S:Se:Te ratio varies widely among the deposits and within the same deposit. At times, tellurium concentration exceeds that of selenium, and often it increases with depth. Little is known about tellurium in sedimentary rocks, though some shales contain 0.1–2 ppm; manganese nodules from the Pacific and Indian Ocean floors contain 0.5–125 ppm (see Ocean raw materials).

Like selenium, tellurium usually forms binary minerals; but whereas selenium isomorphously replaces a part of the sulfur in sulfides, tellurium occurs only as discrete tellurium minerals of microscopic size. Tellurium is a main component of ca 40 mineral species, including 24 tellurides, two tellurates, native tellurium, and a selenium–tellurium alloy. It is a minor constituent of an undetermined number of minerals. It occurs in combination with oxygen, sulfur, and 10 other elements with high atomic numbers. At least ten tellurium minerals occur with gold and silver, ten with bismuth, and six with iron. Some of the better known minerals are hessite [12002-98-1], Ag_2Te; petzite [1317-73-3], Ag_3AuTe_2; calaverite [37043-71-3], $AuTe_2$; sylvanite [1301-81-1], $AuAgTe_4$; altaite [12037-86-4], PbTe; tetradymite [1304-78-5], Bi_2Te_2S; rickardite [12134-39-31], Cu_4Te_3; nagyagite [12174-01-5], $Au(Pb,Sb,Fe)_8(Te,S)_{11}$; and tellurite [14832-87-2], TeO_2.

Like selenium, tellurium minerals, although widely disseminated, do not form ore bodies. Hence, there are no deposits that can be mined for tellurium alone, and there are no formally stated reserves. Large resources however, are present in the base-metal sulfide deposits mined for copper, nickel, gold, silver, and lead, where the recovery of tellurium, like that of selenium, is incidental.

1. Physical Properties

At least 21 tellurium isotopes are known, with mass numbers from 114 to 134. Of these, eight are stable, ie, 120, 122–126, 128, 130. The others are radioactive and have lifetimes from 2 min to 154 d; the heaviest six, 131m, 131, 132, 133m, 133, and 134, are fission products (see Radioisotopes). Tellurium illustrates the rule that elements having even atomic numbers have more isotopes than elements having odd atomic numbers.

The physical properties of tellurium are given in Table 1. The vapor pressure between 511 and 835°C is given by the equation shown where temperature, T, is in K (5): Pressures in kPa may be converted to mm Hg by multiplying by 7.5.

$$\log p_{\mathrm{kPa}} = 6.7249 - (5960.2/T)$$

At ordinary temperature and pressure, solid tellurium, unlike sulfur and selenium, has only one structural form. Tellurium crystallizes in a trigonal lattice with a space group $P3_121$ (or $P3_221$). Lattice parameters are $a = 44.6$ pm, $c = 593$ pm, and a bond angle of 103.2°. The crystal structure may be considered as a set of helical chains parallel to the c-axis, held together by relatively weak atomic forces. The helical screw directions can be either right-handed or left-handed, and a plane-polarized electromagnetic wave travelling along the c-axis can be rotated in a clockwise or anticlockwise direction. Light is strongly absorbed by tellurium for wavelengths, λ, smaller than about 3.5 micrometers, corresponding to the energy gap of this semiconductor. Above this absorption edge wavelength, the element is essentially transparent, having weak absorption owing to free carriers, characterized by the absorption coefficient α increasing as a function of λ^2. For plane-polarized infrared light where the electric vector E is parallel to the c-axis, there is a pronounced absorption peak at $\lambda = 11\ \mu$m. This is absent for E perpendicular to c. Below room temperature, tellurium shows photoconductivity for wavelengths smaller than about 4 μm and has been considered as a cooled infrared detector for this wavelength range.

Single crystals of tellurium can readily be grown from the melt by the Czochrlaski method. Where the seed is parallel to the c-axis, the resulting crystal ingot is usually six-sided, with (1010) planes, reflecting the three-fold symmetry of the material. Crystals can also be grown perpendicular to the c-axis. The prismatic (1010) planes can be etched to reveal characteristic four-sided etch pits; six-sided etch pits having a 3-fold symmetry can be obtained on the (0001) basal plane. Thermal etch pits of these symmetries can also be revealed by heating tellurium crystals under reduced pressure.

The physical properties of tellurium are generally anistropic. This is so for compressibility, thermal expansion, reflectivity, infrared absorption, and electronic transport. Owing to its weak lateral atomic bonds, crystal imperfections readily occur in single crystals as dislocations and point defects. Tellurium is diamagnetic below its melting point. Its intrinsic electrical resistivity at room temperature is about $0.25\ \mathrm{ohm{\cdot}cm}$, when the current is parallel to the c-axis, and decreases with increasing temperature and pressure. The element forms a continuous range of isomorphous solutions with selenium, consisting, in the solid state, of chains of randomly alternating Se and Te atoms.

Tellurium has a semiconducting thermal energy gap of 0.33 eV and, if sufficiently purified by zone refining in hydrogen, is intrinsic at room temperature with a carrier concentration of about $4 \times 10^{15}\ \mathrm{cm^{-3}}$. At liquid nitrogen temperature (77 K), tellurium has always shown p-type extrinsic behavior; n-type extrinsic conduction has never been observed. Thus, whereas no donors have been found, the Group 15 (V) elements Bi, Sb, As, and P act as acceptors and can increase the extrinsic hole concentration. As the temperature of sufficiently

Table 1. Physical Properties of Tellurium

Property	Value
specific gravity[a] at 18°C	
crystalline	6.24
amorphous	6.0–6.2
hardness, Mohs[b]	2.0–2.5
modulus of elasticity, MPa[c]	4140
Poisson ratio at 30°C	0.33
heat capacity at 25°C, kJ/mol[d]	25.70
entropy at 25°C, J/(K·mol)[d]	49.70
heat of fusion, kJ/mol[d]	17.87
mp, °C	450
viscosity at mp, mPa·s(=cP)	1.8–1.95
bp, °C[e]	990
heat of formation[f], kJ/mol[d]	171.5
heat of vaporization, kJ/g[d]	46.0
thermal conductivity at 20°C[g], W/(m·K)	0.060
Te–Te bond energy, kJ/mol[d]	138
covalent radius, pm	137
electronegativity[h]	ca 2.1
first ionization potential, eV	9.01
electron affinity, eV	
first	2.3
second	ca 3.0
volume shrinkage on solidification, %	5–7

[a] Increases under pressure.
[b] Anisotropic.
[c] To convert MPa to psi, multiply by 145.
[d] To convert J to cal, divide by 4.184.
[e] Extrapolated.
[f] Te (g) atom to Te_2 (g) molecule.
[g] Polycrystalline material; in single crystals, it is anisotropic and affected by impurities and lattice imperfections.
[h] Pauling scale.

pure tellurium is raised from 77 K, the Hall coefficient changes sign from positive to negative at an inversion temperature which increases with the extrinsic hole concentration. However, another sign reversal of the Hall coefficient takes place at 514 K from negative back to positive again. This time the reversal temperature is fixed and does not vary with the extrinsic hole concentration. The first sign reversal results from the larger mobility of the electrons compared to that of holes; the second reversal has been attributed to the existence of higher conduction band having a very low mobility.

An excellent review of the semiconducting properties of tellurium is available (6).

2. Chemical Properties

Although tellurium resembles sulfur and selenium chemically, it is more basic, more metallic, and more strongly amphoteric. Its behavior as an anion or a cation depends on the medium, eg:

$$TeO_2 + 2\ KOH \longrightarrow K_2TeO_3 + H_2O$$

$$TeO_2 + 4\ HCl \rightleftarrows TeCl_4 + 2\ H_2O$$

In an acid medium, the following reactions take place:

$$Te^0 - 4e^- \longrightarrow Te^{4+} \qquad Te^{4+} + 4e^- \longrightarrow Te^0 \qquad Te^{4+} - 2e^- \longrightarrow Te^{6+}$$

In an alkaline medium:

$$Te^0 - 4e + 3\ H_2O \longrightarrow TeO_3^{2-} + 6\ H^+$$

$$TeO_3^2 + 4e^- + 6\ H^+ \longrightarrow Te^0 + 3\ H_2O$$

$$TeO_3^2 - 2e^- + H_2O \longrightarrow TeO_4^{2-} + 2\ H^+$$

Tellurium forms ionic tellurides with active metals, and covalent compounds with other elements. The valence states are -2, $+4$, and $+6$. Solid crystalline tellurium tarnishes slightly in the air, and more rapidly and to a greater degree in the powdered state. Moist, precipitated tellurium oxidizes on drying, especially above 100°C. Molten tellurium is readily oxidized to tellurium dioxide, which can be volatilized by blowing air through the melt. Tellurium reacts with halogens and halogenating agents, and mixes in all proportions with sulfur and selenium. Oxidation with nitric acid, and ignition of the resulting 2 $TeO_2 \cdot HNO_3$ [23624-18-2] yields very pure TeO_2. Tellurium dioxide can be used as an oxidant for acetoxymethylation reactions (7):

$$ArH \xrightarrow[\text{LiBr, 120 or 160°C}]{TeO_2,\ CH_2COOH} ArCH_2O\overset{\overset{O}{\|}}{C}CH_3$$

where Ar = aryl. Tellurium reacts with concentrated, but not with dilute, sulfuric acid to form tellurium sulfite [84074-47-5]:

$$Te^0 + H_2SO_4 \rightleftarrows TeSO_3 + H_2O$$

Dilution with water reverses the reaction, and heating the solution liberates sulfur dioxide. Upon being added to a solution of tellurides, tellurium forms colored polytellurides. Unlike selenium, tellurium is not soluble in aqueous sodium sulfite. This difference offers a method of separating the two elements. Like selenium, tellurium is soluble in hot alkaline solutions except for ammonium hydroxide solutions. Cooling reverses the reaction. Because tellurium forms solutions of anions, Te^{2-}, and cations, Te^{4+}, tellurium films can be deposited on inert electrodes of either sign.

Elemental tellurium liberates chlorine from compounds such as $AsCl_3$ and $AuCl_3$; it reduces $FeCl_3$ partially to $FeCl_2$, and SO_2Cl_2 to SO_2 and Cl_2 gases. Oxidation of metals by tellurium gives metallic tellurides. Tellurium itself is oxidized by strong reagents such as $Na_2Cr_2O_7$, $KMnO_4$, $Ca(OCl_2)_2$, H_2O_2, and $HClO_3$. Tellurium dioxide and tellurous acid and its salts are readily reduced to the element, Te^0 with $SnCl_2$, H_2S, and $Na_2S_2O_4$. These compounds are oxidized to the Te(VI) state with PbO_2, and $KMnO_4$. Selenium, H_2S, and HCl reduce $TeO_4{}^{2-}$ ions to TeO^{2-}. Solid tellurium oxides can be reduced by heating with hydrogen, carbon, and carbon monoxide.

The stability of organic chalcogen compounds decreases mostly in the order $\text{sulfur} > \text{selenium} > \text{tellurium} \cdot$

3. Manufacture

3.1. Recovery

No attention is paid to the recovery of tellurium in the mining, flotation and concentration of copper ores. In the further process steps of roasting, smelting, and refining, tellurium is found in detectable quantities but only on rare occasions are operations altered to enhance recovery or deliberately redistribute tellurium. Pyrometallurgical lead refineries do, however, actively monitor tellurium and recover tellurium-bearing intermediates when concentrations are high enough ($>0.025\%$).

Most commercial tellurium is recovered from electrolytic copper refinery slimes (8–16). The tellurium content of slimes can range from a trace up to 10% (see Selenium and selenium compounds). Most of the original processes developed for the recovery of metals of value from slimes resulted in tellurium being the last and least important metal produced. In recent years, many refineries have changed their slimes treatment processes for faster recovery of precious metals (17, 18). The new processes have in common the need to remove the copper in slimes by autoclave leaching to low levels ($<1\%$). In addition, this autoclave pretreatment dissolves a large amount of the tellurium, and the separation of the tellurium and copper from the solution which then follows places tellurium recovery at the beginning of the slimes treatment process.

Typically, the removal of copper in slimes is accomplished by the autoclaving of slimes at elevated temperature with sulfuric acid and oxygen. Use of temperatures of 120°C and oxygen pressures of 345 kPa (50 psig) allows almost complete copper extraction and tellurium extractions ranging from 50 to 80%. The range of tellurium extraction is wide because the mode of occurrence in slimes varies significantly (19). Selenium and intermetallic selenides are more resistant to oxidation and these remain essentially unchanged in the residue. The tellurium solubilized by autoclaving may be present in both the tetravalent and hexavalent forms, the proportion of hexavalent rising with increasing oxygen pressure, acidity, and temperature. The overall reactions are:

$$Cu_2Te + 2\ O_2 + 2\ H_2SO_4 \longrightarrow 2\ CuSO_4 + H_2TeO_3 + H_2O$$

$$H_2TeO_3 + 1/2\ O_2 \longrightarrow H_2TeO_4$$

Tellurium is recovered from solution by cementation with copper at elevated ($>90^\circ C$) temperature.

$$H_2TeO_3 + 4\ Cu^0 + 2\ H_2SO_4 \longrightarrow Cu_2Te + 2\ CuSO_4 + 3\ H_2O$$

Table 2. Electrolysis Conditions for Tellurium Recovery[a]

Parameter	CCR Refinery	PRM Refinery
Te, g/L		
in fresh electrolyte	150–200	250
in spent electrolyte	90–140	80
NaOH, g/L		
in fresh electrolyte	40	85
in spent electrolyte	80	200
electrolyte temperature, °C	40–45	45
flow rate, L/min	60	40
number of anodes	15	9
number of cathodes	14	8
cathodic current density, A/m^2	160	160
cell voltage, V	2.0–2.5	2.5
deposition time, days	3	8
current efficiency, %	ca 90	90

[a] Ref. 20.

$$H_2TeO_4 + 5\ Cu^0 + 3\ H_2SO_4 \longrightarrow Cu_2Te + 3\ CuSO_4 + 4\ H_2O$$

Although this procedure yields tellurium as the same compound found in the original feedstock, the copper telluride is recovered in a comparatively pure state which is readily amenable to processing to commercial elemental tellurium or tellurium dioxide. The upgraded copper telluride is leached with caustic soda and air to produce a sodium tellurite solution. The sodium tellurite solution can be used as the feed for the production of commercial grade tellurium metal or tellurium dioxide.

If the final product desired is tellurium metal, excess free caustic soda is required in the sodium tellurite solution. The solution is electrolyzed in a cell using stainless steel anodes to produce tellurium metal (20). This technology is used at the CCR Division of Noranda Metallurgy Inc., Canada, and at Pacific Rare Metals Industries Inc., the Philippines. Typical electrolysis conditions are given in Table 2.

Alternatively, if tellurium dioxide is the product desired, the sodium tellurite solution can be neutralized in a controlled fashion with sulfuric acid. As the pH is lowered, precipitates containing impurities such as lead and silica that form are filtered off. At pH 5.6 the solubility of tellurous acid reaches a minimum and essentially all of the tellurium precipitates ($>98\%$). After filtration and drying, commercial tellurium dioxide is obtained. A diagram for the process of detellurizing of slimes and recovering tellurium products is shown in Figure 1.

Tellurium is still recovered in some copper refineries by the smelting of slimes and the subsequent leaching of soda slags which contain both selenium and tellurium. The caustic slags are leached in water and, using the controlled neutralization process, tellurium is recovered as tellurium dioxide.

To produce commercial (99.5%) tellurium, tellurium dioxide is dissolved in hydrochloric acid. The tellurium solution is saturated with sulfur dioxide gas to yield commercial tellurium powder, which is washed, dried, and melted.

$$H_2TeO_3 + H_2O + 2\ SO_2 \longrightarrow Te^0 + 2\ H_2SO_4$$

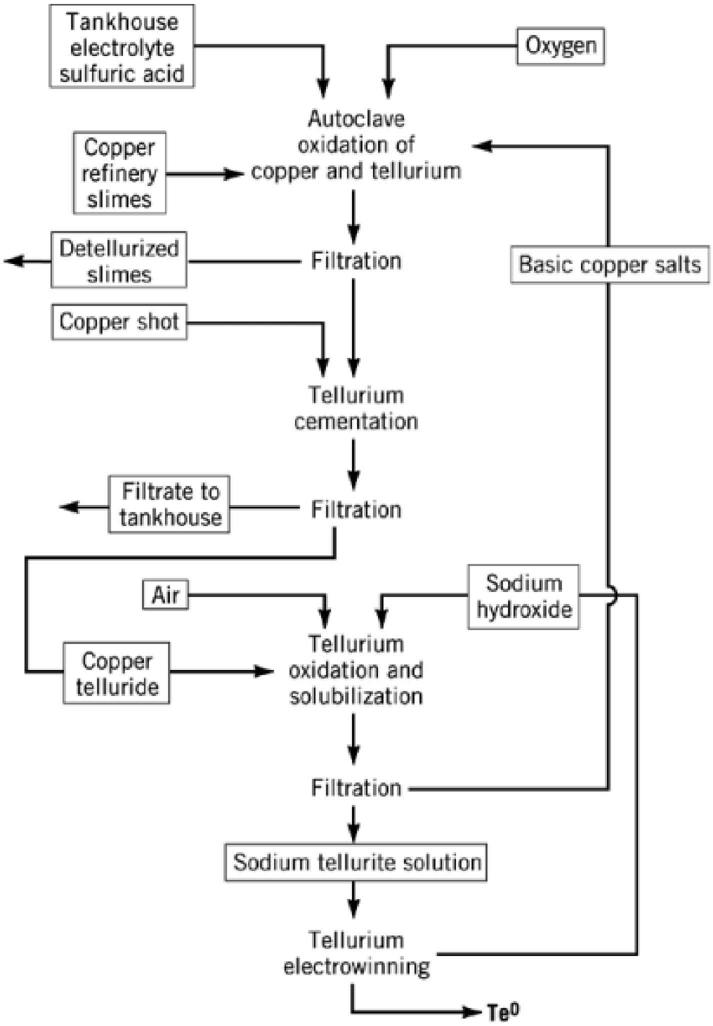

Fig. 1. Flow sheet for recovery of tellurium from copper slimes.

3.2. Purification

Tellurium can be purified by distillation at ambient pressure in a hydrogen atmosphere. However, because of its high boiling point, tellurium is also distilled at low pressures. Heavy metal (iron, tin, lead, antimony, and bismuth) impurities remain in the still residue, although selenium is effectively removed if hydrogen distillation is used (21).

Ultrahigh ($99.999+\%$) purity tellurium is prepared by zone refining in a hydrogen or inert-gas atmosphere. Single crystals of tellurium, tellurium alloys, and metal tellurides are grown by the Bridgman and Czochralski methods (see Semiconductors).

3.3. Commercial Products

Tellurium dioxide [7446-07-3], TeO_2 (79.9% Te theoretically), is made by heating an aqueous suspension of tellurous acid. The acid is purified, if necessary, by redissolving in caustic soda solution and neutralizing with sulfuric acid.

Sodium tellurate [10101-25-8], Na_2TeO_4, (53.7% Te theoretically), is made by oxidizing sodium tellurite solution with hydrogen peroxide. The reaction is exothermic.

Ferrotellurium or iron telluride [12125-63-2], FeTe, which usually has a Te content near the theoretical 69.5%, is made by the exothermic melting iron and tellurium powders in stoichiometric proportions.

Tellurium diethyldithiocarbamate [20941-65-5], $[(C_2H_5)_2NC(S)S]_4Te$, is made by the reaction of diethylamine, carbon disulfide, and tellurium dioxide in an alcoholic solution.

Metal tellurides for semiconductors are made by direct melting, melting with excess tellurium and volatilizing the excess under reduced pressure, passing tellurium vapor in an inert gas carrier over a heated metal, and high temperature reduction of oxy compounds with hydrogen or ammonia.

4. Economic Aspects

Tellurium has been produced commercially in the United States since 1918 and in Canada since 1934 (10). The principal world recoverers and producers are given in Table 3 (22).

Production and trade figures are published by the U.S. Geological Survey (23), the American Bureau of Metal Statistics (24), the Canadian Department of Energy, Mines, and Resources (25), and the World Bureau of Metal Statistics (26). Production figures are often incomplete because of the need to avoid disclosure of proprietary data. Hence, marketing data is often estimated.

The world's largest producers of tellurium are Canada, Japan, Peru, and the United States. ASARCO in Amarillo, Texas, produces commercial grade tellurium and tellurium dioxide from copper anode slimes and lead refinery skimmings. ASARCO produces high purity tellurium in its plant in Denver, Colorado

World production of tellurium in 1998 is shown in Table 4 (27). U.S. production for the years listed is proprietary.

U.S. consumption increased in 1998. Imports decreased from 27,400 kg of contained metal in 1994 to 73,700 kg in 1996 down to 63,900 in 1997 and back up to 88,900 in 1998 (27). Producer price decreased from \$26/lb (\$57/kg) in 1994 to \$18/lb (\$39/kg) in 1998 due to an oversupply situation (28). Production decreased, but demand decreased more (29). U.S. imports for consumption of tellurium for 1997 and 1998 are listed in Table 5 (27).

There is no United States government stockpile of tellurium (23). The world producers of tellurium are listed in Table 4 (8).

The main uses for tellurium are as a free-machining addititive in ferrous metallurgy (50%), as a free-machining additive in nonferrous metallurgy (10%), in chemicals (25%), in electrical applications such as solar cells and thermoelectrics (8%), and miscellaneous (7%) (23).

Technical efforts to develop new applications have been concentrated in the area of electronics. Steady improvements in performance for cadmium telluride [1306-25-8], CdTe, based solar cells have been noted and similarly for bismuth telluride [1304-82-1], Bi_2Te_3, thermoelectrics. Neither application has yet become a principal market for tellurium and, consequently, the price of tellurium has been related to variations in output from producers rather than to market demand.

However, demand for high-purity tellurium for solar cells could increase. the most promising use would be in remote power supplies in developing countries, Cadmium telluride is one of the most promising thin-film photovoltaic module compounds (27).

Table 3. World Producers of Tellurium in 2000[a]

Belgium	UM Electro-Optic Materials, Hoboken
Canada	Inco Limited, Toronto
	Noranda Minerals Inc., CCR Div., Montreal East, Québec
China, P.R.	Guangzhou Smelter, Guangzhou
	Guixi Smelter, Guixi
	Shenyang Smelter, Shenyang
	Zhuzhou Smelter, Zhuzhou
C.I.S.	Almalysky 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
Germany	Norddeutsche Affinerie A.G., Hamburg
Japan	Japan Energy Corp., Tokyo
	Mitsubishi Materials Corp., Tokyo
	Mitsui Mining & Smelting Co., Ltd., Tokyo
	Sumitomo Metal Mining Co., Ltd., Tokyo
Peru	Centromin-Peru, La Oroya
Philippines	Pacific Rare Metal Industries Inc., Quezon City (Manila)
Spain	Atlantic Copper SA, Madrid
United Kingdom	Mining & Chemical Products Ltd., Alperton (London)
U.S.A.	Asarco Inc., New York, NY
	Phelps Dodge Refining Corp., El Paso, TX

[a] Ref. 22

Table 4. Tellurium: World Refinery Production, by Country, kg, contained tellurium[a, b, c]

	Year				
Country[d]	1994	1995	1996	1997	1998[e]
Canada[f]	42,000	102,000	59,000	59,000[g]	57,000
Japan	47,256	43,129	37,945	25,260[g]	33,000
Peru	28,000	30,087	25,102	25,100[e]	25,100
United States	W[h]	W[h]	W[h]	W[h]	W[h]

[a] Ref. 27.

[b] Estimated data are rounded to three significant digits.

[c] Insofar as possible, data relate to refinery output only; thus, countries that produced tellurium contained in copper ores, copper concentrates, blister copper and/or refinery residues, but did not recover refined tellurium are excluded to avoid double counting. Table is not totaled because of exclusion of data from major world producers, notably the former USSR and the United States. Table includes data available through June 3, 1999.

[d] In addition to the countries listed, Australia, Belgium, Chile, Germany, Philippines, and the former USSR are known to produce refined tellurium, but output is not reported; available information is inadequate for formulation of reliable estimates of output levels.

[e] Estimated.

[f] Excludes selenium intermediates exported for refining.

[g] Revised.

[h] Withheld to avoid disclosing company proprietary data.

Table 5. U.S. Imports for Consumption of Tellurium, kg, gross weight[a, b]

	1997		1998	
Class and country	Quantity	Value	Quantity	Value
Unwrought and waste and scrap:				
Australia	1,200	$43,000	6,800	$183,000
Belgium	10,200	271,000	21,900	385,000
Canada	6,410	503,000	7,810	645,000
China	21	5,460	24	17,000
France	1,060	19,800		
Japan	2,330	245,000	13,200	540,000
Mexico	154	2,110	173	2,370
Philippines	19,600	635,000	17,800	325,000
Russia			4	13,400
United Kingdom	22,900	383,000	21,200	317,000
Total	63,900	2,110,000	88,900	2,430,000

[a] Bureau of the Census, Ref. 27.
[b] Data are rounded to three significant digits; may not add to totals shown.

Table 6. Tellurium Grades

Element, wt %	Commercial	High purity
tellurium	99.7	99.999
copper	0.01	
lead	0.003	
selenium	0.01	
silica	0.04	
iron	0.01	
other impurities		10[a]

[a] Value is maximum in units of ppm.

5. Specifications and Grades

There are no official U.S. specifications for tellurium and producers publish their own standards. Typically the producer specifies the weight and shape of the pieces, a screen analysis of powders, and a maximum content of certain impurities.

The common grades marketed in the U.S. and Canada are given in Table 6. Commercial-grade tellurium is available in tablets (1 and 3 g), slabs (2.27 kg (5 lbs)), sticks (0.454 and 0.908 kg (1 and 2 lbs)) and powder (-100 and -200 mesh (<149 and <74 μm)). High purity tellurium is sold as cast cakes or chunks.

6. Analytical Methods

Comprehensive accounts of the analytical chemistry of tellurium have been published (5, 30–34). The analytical methods for the determination of tellurium are to a considerable extent influenced by the element's resemblance, in many of its properties and in its limited terrestrial abundance, to selenium.

A solution of tetravalent or hexavalent tellurium is commonly detected by precipitation as the black elemental tellurium, Te^0, when sulfur dioxide is bubbled through dilute hydrochloric acid solutions. Tellurium(IV) or tellurium(VI) are also detected as elemental tellurium when treated with reducing agents such as tin(II) chloride, hypophosphorous acid, hydrazine hydrochloride, aluminum amalgam, zinc, or magnesium. A solution of tellurium(IV) reacts with hydrogen sulfide to form the reddish-brown tellurium sulfide [16608-21-2], TeS. Elemental tellurium and tellurides, TeO^{2-}, but not the oxidized tellurium compounds such as tellurites, $TeO^{2-}{}_3$, or tellurates, $TeO^{2-}{}_3$, give a purplish-red color when warmed in concentrated sulfuric acid solutions.

Several common acid treatments for sample decomposition include the use of concentrated nitric acid, aqua regia, nitric–sulfuric acids, and nitric perchloric acids. Perchloric acid is an effective oxidant, but its use is hazardous and requires great care. Addition of potassium chlorate with nitric acid also assists in dissolving any carbonaceous matter.

Organic tellurium compounds and siliceous materials, ie, rock, ore, or concentrates, are fused with mixtures of sodium carbonate and alkaline oxidants, ie, 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 tellurium into Te(VI) rather than Te(IV).

Many analytical methods depend on the conversion of the tellurium in the sample to tellurous acid, H_2TeO_3. Should tellurous acid precipitate on dilution, it can be redissolved with hydrochloric acid. Although tellurium is not as readily volatile as selenium, precautions should be taken to prevent the volatilization of tellurium when halogen or hydrohalide media are used during sample decomposition.

Depending on the tellurium content and the nature of the material being analyzed, tellurium can be determined by a number of gravimetric methods, notably precipitation as the element using either sulfur dioxide or hydrazine hydrochloride as reductants. This method suffers from coprecipitation of other elements and oxidation of the precipitate on drying. Alternatively, tellurium can be precipitated from Te(IV) solutions using ammonia, pyridine, and hexamethylenetetramine, but heavy metals and other elements are coprecipitated, unless complexed with ethylenediaminetetraacetic acid (EDTA) (35), citric acid, or tartaric acid. Not all of the many ions that can precipitate at the recommended pH can be complexed effectively, and the possibility of interferences must be carefully considered in each case when applying a gravimetric method.

Although gravimetric methods have been used traditionally for the determination of large amounts of tellurium, more accurate and convenient volumetric methods are favored. The oxidation of tellurium(IV) by ceric sulfate in hot sulfuric acid solution in the presence of chromic ion as catalyst affords a convenient volumetric method for the determination of tellurium (36). Selenium(IV) does not interfere if the sulfuric acid is less than 2 N in concentration. Excess ceric sulfate is added, the excess being titrated with ferrous ammonium sulfate using *o*-phenanthroline ferrous–sulfate as indicator. The ceric sulfate method is best applied in tellurium-rich materials such as refined tellurium or tellurium compounds.

The oxidation of tellurium(IV) by permanganate as an analytical method has been studied in some detail (30). The sample is dissolved in 1:1 nitric– sulfuric acid mixture; addition of potassium bisulfate and repeated fuming with sulfuric acid volatilizes the selenium. The tellurite is dissolved in 10 vol % sulfuric acid, followed by threefold dilution with water and titration with potassium permanganate:

$$4\ H_2TeO_3 + 2\ KMnO_4 + 5\ H_2SO_4 + 4\ H_2O \longrightarrow 4\ Te\,(OH)_6 + 2\ KHSO_4 + Mn_2\,(SO_4)_3$$

Any manganese(IV) which is produced can be sequestered by the addition of fluoride. Satisfactory results can be obtained by titration of a solution containing approximately 3 vol % H_2SO_4 and 1 % NaF and not more than 0.10 g of tellurium per 300 mL. The potassium permanganate solution containing 3.485 g/L of $KMnO_4$ (Te equivalence approximately 0.005 g/mL Te) is standardized against pure tellurium or telluric acid. Dissolution of the sample and its preparation for titration must be carried out so that tellurium is maintained in the tetravalent state while other elements are fully oxidized. There is a tendency for this method to give slightly high results.

From a toxicological and physiological point of view, the determination of very small amounts of tellurium is becoming increasingly important. Interest is environmental and human health has promoted development in analytical techniques and methods for the trace and ultra trace levels (see Trace and residue analysis).

Numerous methods have been published for the determination of trace amounts of tellurium (37–46). Instrumental analytical methods (qv) used to determine trace amounts of tellurium include: atomic absorption spectrometry, flame, graphite furnace, and hydride generation; inductively coupled argon plasma optical emission spectrometry; inductively coupled plasma mass spectrometry; neutron activation analysis; and spectrophotometry (see Mass spectrometry; Spectroscopy, optical). Other instrumental methods include: polarography, potentiometry, emission spectroscopy, x-ray diffraction, and x-ray fluorescence.

A widely used procedure for determining trace amounts of tellurium involves separating tellurium in (1:1) hydrochloric acid solution by reduction to elemental tellurium using arsenic as a carrier and hypophosphorous acid as reductant. The arsenic, reduced from an addition of arsenite to the solution, acts as a carrier for the tellurium. The precipitated tellurium, together with the carrier, is collected by filtration and the filter examined directly in the wavelength-dispersive x-ray fluorescence spectrometer.

7. Health and Safety Factors

Elemental tellurium and the stable tellurides of heavy nonferrous metals are relatively inert and do not represent a significant health hazard (47–51). Other, more reactive tellurides, including soluble and volatile tellurium compounds such as hydrogen telluride [7783-09-7], tellurium hexafluoride [7783-80-4], and alkyl tellurides, should be handled with caution. Some of these materials can enter the body by absorption through the skin or by inhalation and ingestion of dust or fumes. No serious consequences or deaths have been reported in workers exposed to tellurium and its compounds in industry (52).

The soluble tellurites are more toxic than the selenites and arsenites. Hydrogen telluride, formed by the action of water on aluminum telluride [12043-29-7], Al_2Te_3, is a toxic gas (47).

The unusual physical complaints and findings in workers overexposed to tellurium include somnolence, anorexia, nausea, perspiration, a metallic taste in the mouth and garliclike odor on the breath (52). The unpleasant odor, attributed to the formation of dimethyltelluride, has not been associated with any adverse health symptoms. Tellurium compounds and metabolic products have been identified in exhaled breath, sweat, urine, and feces. Elimination is relatively slow and continuous exposure may result in some accumulation. No definite pathological effects have been observed beyond the physical complaints outlined. Unlike selenium, tellurium has not been proved to be an essential biological trace element.

Industrial precautions for handling tellurium include the common-sense measures of good housekeeping, adequate ventilation, personal cleanliness, and frequent changes of clothing. Gloves and safety glasses should be worn at all times, and dust masks and chemical goggles should be used where needed. Oral administration of ascorbic acid (or chlorophyll) was recommended at one time to alleviate unpleasant breath, but such treatment may enhance toxic effects by reducing the tellurium compounds to more toxic constituents, and could also serve to give workers a false sense of security (53).

The threshold limit value (TLV) set by the American Conference of Industrial Hygienists (ACGIH) for tellurium and its compounds is 0.1 mg/m^3 which is about ten times the amount which has been known to produce the adverse garlic odor (49, 54). The ACGIH TLV for tellurium hexafluoride is 0.2 mg/m^3 or 0.02 ppm of air (47). Likewise, the U.S. Occupational Safety and Health Administration (OSHA) has established its permissible exposure limit (PEL) for tellurium and its compounds at 0.1 mg/m^3; the PEL for tellurium hexafluoride is 0.2 mg/m^3 or 0.02 ppm of air (54).

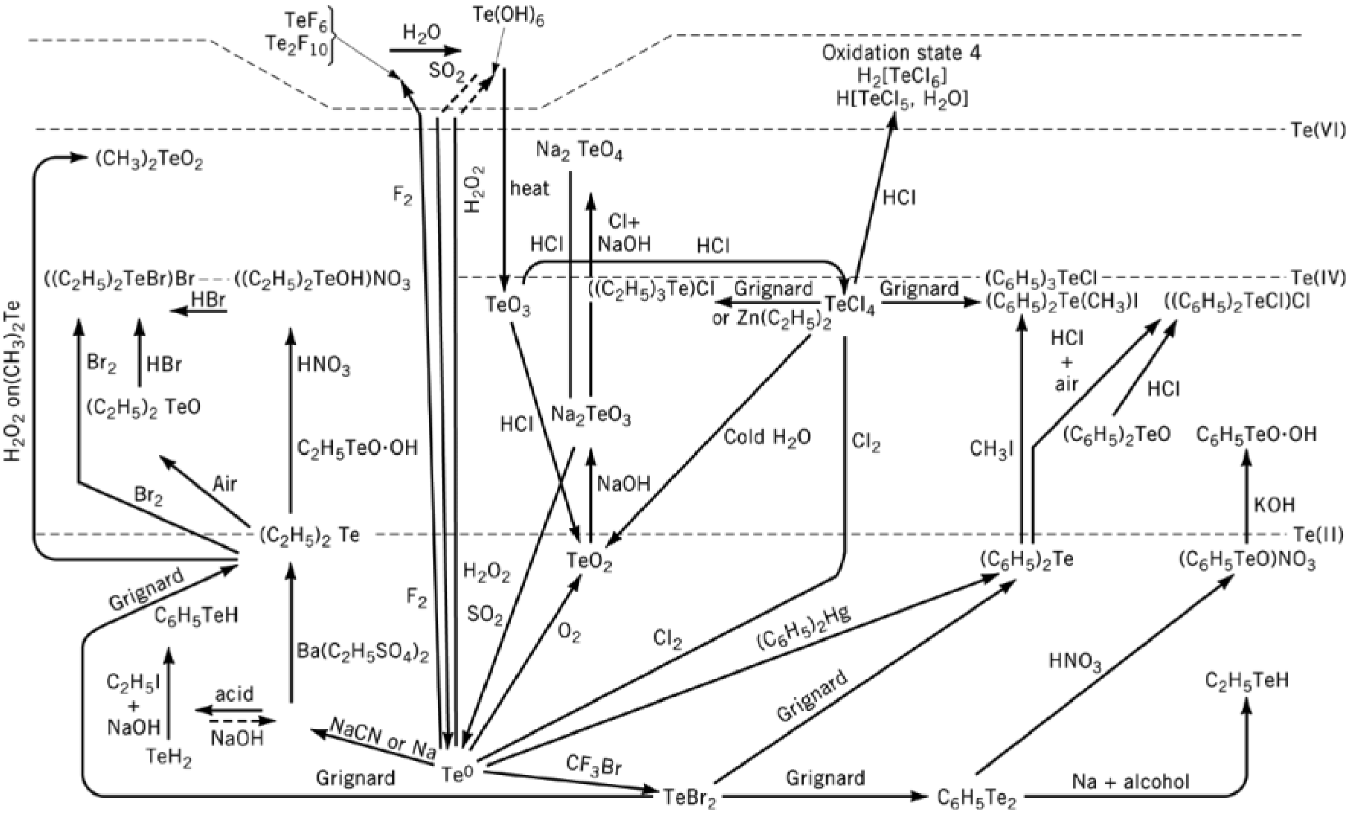

Fig. 2. Chemical relations of the compounds of tellurium (59).

8. Environmental Concerns and Recycling

Tellurium scrap was banned from shipment from Europe to Africa, Pacific and Caribbean 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 (55).

There is no U.S. secondary production of tellurium (23).

Tellurium is not toxic and was removed from the EPA most hazardous list because of its insolubility (56).

9. Inorganic Compounds

Tellurium forms inorganic compounds very similar to those of sulfur and selenium. The most important tellurium compounds are the tellurides, halides, oxides, and oxyacids (5). Techniques and methods of preparation are given in the literature (57, 58). The chemical relations of tellurium compounds are illustrated in Figure 2 (53).

9.1. Tellurides

Most elements form compounds with tellurium. Binary compounds of tellurium with 69 elements and alloys of two others have been described (5, 60); 58 are metals, 3 are metalloids, and 10 are nonmetals. Most tellurides are prepared by direct reaction, varying from very vigorous with alkali and some alkaline-earth (Fig. 2) metals to sluggish and requiring a high temperature with hydrogen. The alkali and alkaline-earth tellurides are colorless ionic solids rapidly decomposed by air, especially in the presence of atmospheric moisture. In aqueous solutions, these hydrolyze less than sulfides and selenides but are very easily oxidized. The solutions dissolve excess tellurium, forming dark red tellurides. The alkali metal tellurides are strong reductants. Hydrotellurides, such as sodium hydrotelluride [23624-18-2], NaHTe, are also known. Some metals form more than one telluride, and some metal tellurides show nonstoichiometry; many of them exhibit semiconductor properties.

9.1.1. Hydrogen Telluride

Hydrogen telluride, H_2Te, is a colorless, toxic gas having an odor resembling that of arsine. It is also colorless in the liquid and solid states. Hydrogen telluride is prepared by the action of water on aluminum telluride in the absence of air, or by electrolysis of cold 15–20% sulfuric acid at a tellurium cathode. Hydrogen telluride and its aqueous solution decompose slowly in air. Unless perfectly dry, the compound also decomposes when exposed to light. Hydrogen telluride is a strong reductant and is rapidly oxidized. It reacts with alkalies and the solutions of many metal salts to form the corresponding tellurides. Hydrogen telluride solutions are weakly acidic and ionize to HTe^- and Te^{2-}.

9.1.2. Tellurium Sulfide

In the liquid state, tellurium is completely miscible with sulfur. The Te–S phase diagram shows a eutectic at 105–110°C when the sulfur content is 98–99 atom % (94–98 wt %). Tellurium–sulfur alloys have semiconductor properties (see Semiconductors). Bands attributed to tellurium sulfide [16608-21-2], TeS, molecules have been observed.

9.1.3. Tellurium Selenides

Tellurium selenides or selenium tellurides are unknown. The molten elements are miscible in all proportions. The mixtures are not simple solid solutions but have a complex structure. Like the sulfides, the selenides exhibit semiconductor properties.

9.1.4. Carbon Sulfotelluride

Carbon sulfotelluride [10340-06-4], CSTe, exists as a yellow-red liquid having a garliclike odor. It is decomposed by light, even at $-50^\circ C$, to carbon disulfide, carbon, and tellurium.

9.1.5. Carbonyl Telluride

Little is known about carbonyl telluride [65312-92-7], COTe. It is formed in poor yield by passing carbon monoxide over tellurium at a high temperature. It is less stable than the selenide.

9.1.6. Tellurium Nitride

Tellurium nitride [12164-01-0], Te_3N_4, is an unstable, citron-yellow solid that detonates easily when heated or struck, but it can be kept under dry chloroform. It is said to explode on contact with water, possibly because of the heat of wetting.

9.2. Tellurium Halides

Tellurium forms the dihalides $TeCl_2$ and $TeBr_2$, but not TeI_2. However, it forms tetrahalides with all four halogens. Tellurium decafluoride [53214-07-6] and hexafluoride can also be prepared. No monohalide, Te_2X_2, is believed to exist. Tellurium does not form well-defined oxyhalides as do sulfur and selenium. The tellurium halides show varying tendencies to form complexes and addition compounds with nitrogen compounds such as ammonia, pyridine, simple and substituted thioureas and anilines, and ethylenediamine, as well as sulfur trioxide and the chlorides of other elements.

9.2.1. Tellurium Tetrafluoride

Tellurium tetrafluoride [15192-26-4], TeF_4, forms white, hygroscopic needles melting at 129.6°C. It decomposes at 194°C to TeF_6 and is readily hydrolyzed. Tellurium tetrafluoride attacks glass, silica, and copper at 200°C, but it does not attack platinum below 300°C.

9.2.2. Tellurium Decafluoride

Tellurium decafluoride [53214-07-6], Te_2F_{10}, is a stable, volatile, colorless liquid, melting at $-33.7°C$ and boiling at 59°C.

9.2.3. Tellurium Hexafluoride

Tellurium hexafluoride, TeF_6 melts at $-38°C$ and sublimes at $-39°C$, forming a colorless gas. It hydrolyzes slowly to orthotelluric acid and is reduced by tellurium to TeF_4.

9.2.4. Tellurium Dichloride

Tellurium dichloride [10025-71-5], $TeCl_2$, is a black hygroscopic solid, melting at 208°C to a black liquid; it boils at 328°C to a bright red vapor. The solid is stable when pure. It disproportionates in organic solvents and is decomposed by acids and alkalies. It is hydrolyzed to H_2TeO_3, Te, and HCl, and decomposed by HCl to Te and H_2TeCl_6 [17112-43-5]. Air oxidizes tellurium dichloride to TeO_2 and HCl.

9.2.5. Tellurium Tetrachloride

Tellurium tetrachloride [10026-07-0], $TeCl_4$, forms white, hygroscopic crystals which melt at 225°C to a dark red liquid. The vapor (bp ca 390°C) is also red. It is prepared by the action of chlorine on tellurium, or of SCl_2, CCl_4, or $AsCl_3$ on tellurium or TeO_2. The crystals are soluble in benzene, toluene, and ethyl alcohol, but not in ethyl ether. It hydrolyzes in cold water to TeO_2, and in hot water gives a clear solution. With dilute HCl, it yields H_2TeO_6 [56367-33-0], TeO_2, $HTeCl_5$ [22742-12-7], and H_2TeCl_6, and with concentrated HCl, $TeCl^{2-}{}_3$. On evaporation of the acid solution to dryness, $TeCl_4$ forms $H_2TeCl_62{\cdot}H_2O$ [12192-31-3], which decomposes at 350°C to TeO_2. With phenylmagnesium chloride, it yields $Te(C_6H_5)_3Cl$ [1224-13-1]. Tellurium tetrachloride forms addition compounds with various ligands.

9.2.6. Tellurium Dibromide

Tellurium dibromide [7789-54-0], $TeBr_2$, must be prepared very carefully, because it is unstable and has a strong tendency to disproportionate to $TeBr_4$ and Te.

9.2.7. Tellurium Tetrabromide

Tellurium tetrabromide [10031-27-3], $TeBr_4$, forms yellow hygroscopic crystals which decompose above 280°C and melt at 363°C under bromine vapor. It boils at 414–427°C, dissociating into $TeBr_2$ and bromine. It is soluble in ether and chloroform but not in CCl_4, and is readily hydrolyzed in water.

9.2.8. Tellurium Tetraiodide

Tellurium tertaiodide [7790-48-9], TeI_4, forms gray-black volatile crystals which above 100°C decompose into the elements. They melt at 280°C in a sealed tube.

9.2.9. Tellurium Oxychlorides

Tellurium oxychlorides, $Te_6O_{11}Cl_2$ [12015-54-2], and $TeOCl_2$ [16981-34-2], have been reported.

9.2.10. Tellurium Oxydibromide

Tellurium oxydibromide [66461-30-1], $TeOBr_2$, has been prepared.

9.3. Tellurium Oxides, Oxyacids, and Salts

The white crystals of tellurium dioxide [7446-07-3], TeO_2, melt at 733°C to a clear, dark red liquid which vaporizes at 790–940°C. Tellurium dioxide is made by dissolving tellurium in strong HNO_3 solution and decomposing the resultant 2 $TeO_2{\cdot}HNO_3$ at 400–430°C; by heating Te in air or oxygen; or by thermal dehydration of H_6TeO_6. It is slightly soluble in water with the formation of H_2TeO_3, and readily soluble in halogen acids, forming complex anions such as $TeCl_3^{2-}$. It dissolves in solutions of alkali–metal carbonates only on boiling. The standard redox potential is between those of SO_2 and SeO_2. In solution, TeO_2 is a weaker oxidant for SO_2 than SeO_2. Tellurium dioxide is amphoteric, having minimum solubility at pH 3.8–4.2, its isoelectric point. It forms tellurites, $MTeO_3$, with alkali metals, but not with NH_3. With some acids it forms basic salts such as $TeO_2{\cdot}2\ HCl$ [83543-00-4], $TeO_2{\cdot}3\ HCl$, $TeO_2{\cdot}2\ HBr$ [83543-02-6], 2 $TeO_2{\cdot}HNO_3$, 2 $TeO_2{\cdot}SO_3$ [1206584-8], and 2 $TeO_2{\cdot}HClO_4$. Heating with metal oxides yields tellurites, but with higher oxides, such as PbO_2, or with oxidants such as KNO_3 or $KClO_3$, tellurates are formed. Heating with metals such as Al, Cs, and Zn, with C (at red heat), or with S, ZnS, HgS, or PbS, reduces TeO_2 to Te. Hydrogen does not reduce it completely even at high temperatures, and H_2O_2 oxidizes aqueous TeO_2 suspension to H_4TeO_6 [41673-77-2].

9.3.1. Tellurium Trioxide

Tellurium trioxide [13451-18-8], TeO_3, exists in two modifications, the yellow-orange α-form and the grayish β-form. The α-form, sp gr 5.07, decomposes above 360°C to TeO_2. It is prepared by dehydrating H_6TeO_6 at 300–360°C, α-Tellurium trioxide is a strong oxidant, it reacts violently with metals such as Al or Sn, and with nonmetals such as C, P, and S. Although insoluble in water, dilute mineral acids, and dilute alkalies, it dissolves in hot concentrated alkalies with the formation of tellurates. α-Tellurium trioxide is reduced to TeO_2 and $TeCl_4$ by boiling with concentrated HCl (with the liberation of Cl_2). The β-form, a grayish solid, sp gr 6.21, is obtained by heating orthotelluric acid or α-TeO_3, alone or with H_2SO_4, for 10–12 h at 300–350°C. It is soluble in concentrated Na_2S solution. Less reactive than the α-form, it is reduced by hydrogen at 400°C. The β-form does not react with water at 150°C in the presence of acid or alkali. Most likely it is a polymer, but there are no structural data for either modification.

9.3.2. Tellurous Acid

Tellurous acid [10049-23-7], H_2TeO_3 is an unstable white solid that dehydrates readily to TeO_2. It is prepared by the acidification of a tellurite solution with HNO_3 or by cold hydrolysis of a tetrahalide. Tellurous acid is a much weaker acid than H_2SeO_3. Both normal and acid tellurites are known. Alkali–metal tellurites are obtained from alkali hydroxides and TeO_2; other tellurites are prepared by double decomposition with metal tellurites, or by fusing TeO_2 with metal oxides or carbonates. The alkali metal tellurites are water soluble, the alkaline-earth tellurites are less so. Other tellurites are insoluble. Tellurites are oxidized to tellurates by heating in air or by treating a solution with H_2O_2 and other oxidants. In acid solution, the salts are reduced to Te by SO_2, Sn, Zn, Cu, and some organic compounds.

9.3.3. Orthotelluric Acid

The white crystals of orthotelluric acid [7803-68-1], H_6TeO_6, are sparingly soluble in cold water and easily soluble in hot water and mineral acids, with the exception of HNO_3. It is made by oxidizing Te or TeO_2, for example by refluxing with H_2O_2 in concentrated H_2SO_4. It exists in a cubic form and a monoclinic β-form, which is stable at room temperature. The β-form is obtained from the α-form by heating. Orthotelluric acid tends to polymerize. It is weakly dibasic, forming salts such as KH_5TeO_6 [15855-68-2], $Li_2H_4TeO_6$ [20730-51-2], and $Na_2H_4TeO_6$ [20730-46-5]. An exception is Ag_6TeO_6. Heating dehydrates H_6TeO_6 to TeO_3, further heating gives TeO_2 and oxygen. The acid is fairly strong oxidant; it liberates iodine from KI and oxidizes HCl and HBr. It is reduced by H_2S, SO_2, Zn, Fe^{2+} and hydrazine. It forms complex acids and salts with other elements.

9.3.4. Polymetatelluric Acid

Polymetatelluric acid, H_2TeO_{4n} (where $n \simeq 10$), is a white, amorphous, hygroscopic solid obtained by partial dehydration of orthotelluric acid at 100–200°C in air. Polymetatelluric acid always contains some of the ortho acid and reverts to it in solution. It forms esters and salts. Orthotelluric and polymetatelluric acids are the only two telluric acids known. The so-called allotelluric acid [13520-55-3], a colorless syrup, is a mixture of orthotelluric and polymetatelluric acids. It is prepared by heating the ortho acid in a sealed tube at 305°C.

9.3.5. Tellurates

The water-soluble alkali metal and alkaline-earth tellurates are prepared by chlorinating alkaline solutions of the tellurites or by heating solid tellurites with KNO_3, $KClO_3$, or PbO_2 to form, for example, potassium tellurate [7790-58-1], K_2TeO_3. The insoluble tellurates are made by double decomposition of alkali–metal salt solutions.

9.4. Other Inorganic Compounds

Alkali–metal and ammonium telluropentathionates $(Te(S_2O_3)_2)^{2-}$, have been prepared. The S_2O_3 group can be replaced by ethyl xanthate or diethyl dithiocyanate.

Tellurium pseudohalides, such as the dicyanide [14453-24-8] $Te(CN)_2$, the dithiocyanate [83543-04-8] $Te(SCN)_2$, and thiourea complexes with $Te(SCN)_2$, have been prepared. These are similar to the halides in properties.

Basic tellurium nitrate, TeO_2, is made by dissolving Te in HNO_3. Thermal decomposition begins at 190°C and is complete at 300°C.

Basic tellurium sulfate $2\ TeO_2{\cdot}SO_3$ [12068-84-8]; $2\ TeO_2{\cdot}SeO_3$ selenate; and tellurate, $2\ TeO_2{\cdot}TeO_3$, are known. The sulfate is made by the slow evaporation of a TeO_2 solution in H_2SO_4. It is stable up to 440–500°C and is hydrolyzed slowly by cold, and rapidly by hot water.

Tellurium perchlorate, iodate, and methylthiosulfate, as well as Te(IV) salts of aliphatic and aromatic acids, have been prepared.

10. Organic Compounds

The chemical properties of organosulfur, organoselenium, and organotellurium compounds are markedly similar. Because bond stability with carbon decreases with the increasing atomic number of the element, thermal stability decreases, whereas oxidation susceptibility increases to such an extent that alkyl tellurides are oxidized rapidly by air at room temperature. As a result, less has been written concerning the chemistry of organotellurium than organoselenium compounds. Nevertheless, a sizable literature exists (33, 61–65).

Organotellurium compounds range from the simple carbon sulfotelluride to complex heterocyclic compounds and organotellurium ligands (66). Tellurium analogues of alcohols and mercaptans are prepared by

Table 7. Isolated Organic Tellurium Compounds[a]

Compounds	CAS Registry Number	Formula	Mp, °C	Bp, °C
tellurols or tallanes		RTeH		>90
ethanetellurol	[83270-38-6]	C_2H_5TeH		
benzenetellurol	[69577-06-6]	C_6H_5TeH		
alkyl, aryl, and cyclic tellurides				
dimethyltelluride (methyl telluride)	[593-80-6]	$(CH_3)_2Te$		82
diphenyl telluride	[1202-36-4]	$(C_6H_5)_2Te$	53.4	182
tetraphenyl telluride	[64109-07-5]	$(C_6H_5)_4Te$	104–106	
tetrahydrotellurophene	[3465-99-4]	$\underline{TeCH_2(CH_2)_2CH_2}$		
ditellurides		R_2Te		
diphenyl ditelluride	[32294-60-3]	$C_6H_5Te–TeC_6H_5$	53–54	
alkyltellurium dihalides		$RTeX_3$		
methyltellurium tribromide	[20350-53-2]	CH_3TeBr_3	dec 140 C	
dialkyltellurium dihalides		R_2TeX_3		
dimethyltellurium dichloride	[24383-90-3]	$(CH_3)_2TeCl_2$	92(α), 134(β)	
tellurium salts		R_3TeX		
trimethyltellurium iodide	[18987-26-3]	$(CH_3)_3TeI$		
telluroxides		RTeO		
diphenyl telluroxide	[51786-98-2]	$(C_6H_5)_2TeO$	185	
tellurones		R_2TeO_2		
dimethyl tellurone	[83270-39-7]	$(CH_3)_2TeO_2$		
telluroketones		R_2CTe		
dimethyl telluroketone	[83270-40-0]	CH_3CTeCH_3	63–66	
tellurinic acid		RTeO·OH		
phenyltellurinic acid	[83270-41-1]	$C_6H_5Te·OH$	211	
heterocyclic compounds				
1,4-oxatellurane	[5974-87-8]	$\overline{OCH_2CH_2TeCH_2CH_2}$		
3,5-telluranedione	[24572-07-4]	$\underline{CH_2COCH_2TeCH_2CO}$		

[a] Ref. 43.

reacting their vapors with aluminum telluride and protecting the products in an atmosphere of hydrogen. Ditellurides, R–Te–Te–R, are also sensitive to atmospheric oxygen. Dimethyltellurium dihalides, R_2TeX_2, have been prepared as *cis-trans* isomers (67), and organometallic compounds including both Group III and Group IV elements, involve a metal–tellurium bond. Various types of tellurium compounds and specific examples are listed in Table 7. Not included are the many organic complexes of inorganic tellurium compounds and their ions. For detailed descriptions of the laboratory preparation of organotellurium compounds, see References 62 and (68–70).

11. Uses

11.1. Free-Machining Steels

Tellurium has been shown to be the best additive for improving machinability in several types of ferritic steel (71–73). Its effectiveness in this area represents over 50% of tellurium consumption. The Inland Steel Company (East Chicago, Indiana) developed the largest single outlet for tellurium as an additive to plain-carbon, leaded, and leaded resulfurized steels (74). The presence of 0.023–0.057% tellurium in cold drawn steels, containing 0.06–0.09% carbon, 0.28–0.37% sulfur, and 0.15–0.22% lead, increases their machinability by 30–50% and increases the feed rates. The machined surface finish is superior, the life of the cutting tool is extended, the metal chips are more uniform, and there is less buildup on the tool edges. Tellurium addition affects the mechanical properties very little, raises the recrystallization temperature only slightly without affecting the heat-treating properties, and has a minor effect on grain refining. In addition, it is less detrimental than sulfur in lowering the corrosion resistance. The addition of Te and Ca has been found to enhance the machining performance of a number of steels by controlling the morphology of sulfide and oxide inclusions. In the case of silicon-killed free-machining steels, the addition of Ca forms the plastic-type silicate inclusion $(Ca,Mn)O–Al_2O_3–2\,SiO_2$, which acts as an internal lubricant while the addition of Te promotes the globularization of MnS inclusions and increases their rigidity, preventing them from elongating in hot-rolled products which cause directional properties. The presence of well-distributed globular inclusions of MnS significantly improves the machinability of steel (75). Tellurium can also be added to low and high alloy steels that are normally difficult to machine (76) and tellurium improves the machinability of powder-metallurgy steels (77).

11.2. Chilled Castings

Since about 1940, tellurium has been used to control the chill depth of iron castings (see Iron). Hard, wear-resistant, chilled surfaces were originally produced on gray iron castings by pouring molten iron over a metal surface. A thin layer of white iron formed on rapid cooling. By the addition of less than 0.1% Te to the melt, chilled surfaces could be obtained, with higher yields and extended mold life.

Tellurium is 100–150 times as effective as chromium in producing a given depth of chill. It is a powerful carbide stabilizer and minute quantities convert gray iron to white. Because tellurium is highly volatile, it is added to the ladle just before pouring. It may be added as pellets, tablets, powder (in aluminum or copper containers), ferrotellurium or copper telluride [12181-15-6], Cu_2Te, granules, or any other convenient form. Alternatively, the mold is treated by coating the desired areas of the mold surface with a tellurium-bearing wash, surfacing the sand mold with a layer of tellurium-rich sand, or using tellurium-containing tape (78).

The result is a hard, abrasion-resistant surface, important in many applications of cast iron. The depth of the chill may be controlled by regulating the amount of tellurium added. The casting shows a sharp demarcation line between the chilled and unchilled regions; there is no intermediate or mottled zone. Yet, the chilled portion shows excellent resistance to spalling from thermal or mechanical shock. Tellurium-treated iron is more resistant to sulfuric and hydrochloric acids than is untreated, unchilled gray iron. The amount added ranges from 0.005 to 0.1%; ca 60% is lost by volatilization. Excessive addition causes porosity in the castings.

Tellurium-chilled iron has been used in mining, automotive, railroad, and other equipment. Tellurium used as a coating for molds and cores, so-called corewashes, eliminates troublesome localized shrinkage in castings. These corewashes may contain ca 25% tellurium; the remainder consists mainly of silica and some bentonite.

11.3. Other Ferrous Metal Uses

Tellurium shows an extremely high surface activity in liquid metals (72, 79–81). As a result, addition of tellurium sharply decreases the rate of nitrogen absorption in liquid iron and steel (80). This allows the use of cheaper, lower purity oxygen in pneumatic or basic oxygen steelmaking, and decreases the nitrogen pickup during supplementary scrap melting.

In 0.1% and smaller additions, tellurium acts as a mild deoxidizer of liquid steel, improves the soundness of castings, refines the grain size, and counteracts the detrimental effect of sulfur on the ductility (81). The addition of 0.002–0.009% Te reduces impact and ductility anisotropy in plain carbon steels by controlling the Te addition so as not to exceed its solubility limit in the MnS inclusions and form tellurides. The globular shape of MnS inclusions is optimized with the presence of about 2% Te in solid solution, resulting in the enhancement of both the transverse and through thickness properties. In highly deoxidized steels, Te is also reported to improve the inclusion distribution and eliminates sulfide clustering at the grain boundaries (82).

The low temperature impact strength of structural steels was found to be significantly improved with the additions of 0.022–0.008% Te. The low ($-40^{\circ}\mathrm{C}$) temperature impact strength of a steel annealed at blue brittle temperature of 350°C did not show any embrittlement effect with the addition of .002% Te (76).

The presence of 0.004–0.0062% Te in a welding rod or wire produces a positive surface tension coefficient which enhances the heat transfer to the weld root, producing a weld pool fluid flow that results in solidified weld beads with high depth to width ratios. This characteristic is particularly desirable for stainless steel weldments (82).

The addition of 0.002–0.02% Te to a bearing steel is reported to improve the fatigue strength and antifriction characteristics by promoting the spheroidicity of the sulfide inclusions. It is specified that the ratio of Te to S be 0.1:1.0 (82).

Tellurium also improves the properties of electrical steels by aiding in the magnetic anisotropy, malleable cast iron (83), and spheroidal (graphitic) cast irons (see also Metal surface treatments).

11.4. Copper Alloys

Tellurium is alloyed with copper for various purposes. Frequently the tellurium is added to molten copper as a copper telluride (46.3% Te) master alloy, taking advantage of the peritectic melting point of 1051°C.

A 99.5% Cu–0.5% Te alloy has been on the market for many years (84). The most widely used is alloy No. CA145 (number given by Copper Development Association, New York), nominally containing 0.5% tellurium and 0.008% phosphorous. The electrical conductivity of this alloy, in the annealed state, is 90–98%, and the thermal conductivity 91.5–94.5% that of the tough-pitch grade of copper. The machinability rating, 80–90, compares with 100 for free-cutting brass and 20 for pure copper.

Unlike lead and other additives, tellurium has no adverse effect on the hotworking properties of copper, and does not cause segregation and firecracking. Although the alloy is somewhat less ductile at room temperature than pure copper, it may be extensively hot- and cold-worked, and intermediate annealing is required when the cross section reduction is $>40\%$. Machining methods are the same as for free-cutting brass. Because the copper telluride particles are harder than the lead particles in free-machining brass, carbide-tipped cutting tools are recommended.

A copper alloy, containing 0.02–0.04% tellurium, 0.002–0.015% phosphorous, and 0.002–0.05% oxygen is recommended for use in automobile radiators (85). A continuously cast Amtel copper alloy, containing 0.4–0.6% tellurium, 0.007–0.012% phosphorous, 0.02% sulfur max, and a copper– silver–tellurium–phosphorous alloy (99.90% max) was developed by AMAX Base Metals R&D, Inc. (86).

Tellurium–copper alloys are recommended for situations demanding a high production rate with no significant sacrifice in conductivity. These alloys can be soldered, brazed, or welded without incurring embrittlement. They are used in vacuum applications, forgings, screw-machine parts, welding-torch tips, transistor bases, semiconductor heat sinks, electrical connectors (qv), motor and switch parts, and nuts, bolts, and studs. Addition of tellurium significantly improves the surface of machined parts.

Copper–lead–tellurium alloys have high wear resistance in sliding contacts. In copper–zinc alloys, the benefits of tellurium decrease with increasing zinc content and almost disappear when the zinc content exceeds 35%.

Telnic bronze, Copper Development Association (CDA) No. 191, an alloy that hardens with age, contains 98.3% Cu, 1.1% Ni, 0.5% Te, and 0.2% P. It was developed by Chase Division, Kennecott Copper Corp., in 1950. The machinability rating is 80. The hot-working properties are comparable to those of a high copper commercial bronze and are superior to lead-containing free-machining copper alloys. The tensile strength is high, and the electrical and thermal conductivities are similar to those of nickel bronze CDA No. 191, and about one half those of copper (see Copper alloys).

11.5. Lead Alloys

A tellurium–lead alloy containing 0.02–0.1% tellurium, with or without antimony, was introduced in 1934 (87) as tellurium lead or Teledium. This alloy has higher recrystallization temperatures and corrosion resistance and takes a significantly longer time to soften at 25°C after cold work.

The addition of tellurium has a deoxidizing action and confers on lead useful work and precipitation-hardening properties. It also improves resistance to wear, vibration, and mechanical breakdown. These properties, along with improved corrosion resistance, are utilized in the sheathing of power communication and marine cables, in chemical equipment (especially those exposed to sulfuric acid), or where resistance to fatigue is important. Tellurium has successfully replaced tin (1–3% Sn) in the sheathing. Thinner sheaths can be extruded, and the extrusion pressure for 0.05% Te-bearing lead is about the same as for a 3% Sn alloy.

Adding tellurium to lead and to lead alloyed with silver and arsenic improves the creep strength and the charging capacity of storage battery electrodes (see Batteries). These alloys have also been suggested for use as insoluble anodes in electrowinning.

11.6. Other Metals

Tellurium has been added to copper-base, lead-base, and tin-base bearing alloys. In babbit-type alloys, tellurium controls the structure and improves uniformity and fatigue resistance by restraining the tendency to segregation (see Bearing materials).

Adding 0.05–1% tellurium to tin and tin-base bearing alloys improves the workhardening properties, tensile strength, and creep resistance.

Tellurium has been recommended as an additive to magnesium to increase corrosion resistance (see Corrosion and corrosion control). The addition is highly exothermic but can be controlled by adding one tellurium tablet at a time to a sufficiently large bath of liquid magnesium. The addition to tellurium and chromium improves the stress-corrosion resistance of aluminum–magnesium alloys.

In permanent-magnet alloys of high cobalt–titanium type, tellurium significantly increases the coercive force. Tellurium alloyed with gold produces a yellowish-green color useful for ornamental applications. A gold alloy with 43% Te, centrifically cast, appears light yellowish-green after polishing.

11.7. Metal Coatings

Tellurium chlorides, as well as tellurium dioxide in hydrochloric acid solution, impart permanent and attractive black antique finish to silverware, aluminum, and brass. Anodized aluminum is colored dark gold by tellurium electrodeposition. A solution containing sodium tellurate and copper ions forms a black or blue-black coating on ferrous and nonferrous metals and alloys. Addition of sodium tellurite improves the corrosion resistance of electroplated nickel. Tellurium diethyldithiocarbamate is an additive in bright copper electroplating (see Electroplating).

11.8. Pigments and Glass

Tellurium has served as base for ultramarine-type cadmium sulfotelluride (88) and cadmium telluride pigments (89) (see Pigments, inorganic). In addition, small amounts of tellurium have been used in glass and ceramics to produce blue to brown colors (see Colorants for ceramics).

11.9. Catalysts

In industrial practice the composition of catalysts are usually very complex. Tellurium is used in catalysts as a promoter or structural component (90). The catalysts are used to promote such diverse reactions as oxidation, ammoxidation, hydrogenation, dehydrogenation, halogenation, dehalogenation, and phenol condensation (91–93). Tellurium is added as a passivation promoter to nickel, iron, and vanadium catalysts. A cerium tellurium molybdate catalyst has successfully been used in a commercial operation for the ammoxidation of propylene to acrylonitrile (94).

11.10. Lubricants

Tellurides of titanium, zirconium, molybdenum, tungsten, and other refractory metals are heat- and vacuum-stable. This property makes them useful in solid self-lubricating composites in the electronics, instrumentation, and aerospace fields (see Lubrication and lubricants). Organic tellurides are antioxidants in lubricating oils and greases.

11.11. Rubber

At one time the largest single market for tellurium was the rubber industry. This has been replaced by the steel industry. Suspected health hazards of tellurium compounds used in rubber have hampered its applications (95). Traditionally, small additions of powdered tellurium have been used in the rubber industry as a secondary vulcanizing agent in hard natural rubber compositions to reduce curing time and increase flexibility and abrasion resistance. It is also used in the production of soft natural rubber and styrene–butadiene rubber vulcanizates of enhanced toughness and heat resistance. In many cases an addition of 0.5% Te increases the rate of vulcanization and improves the aging and mechanical properties of sulfurless and low sulfur stocks. Tellurium is particularly effective when used with tetramethylthiuram disulfide, 2(bis(dimethylthiocarbamoyl)disulfide) and with selenium diethyldithiocarbamate in sulfurless cures. It is frequently used to eliminate porosity in thick-molded sections. Tetrakis (dimethylthiocarbamato) tellurium(IV), when added to natural rubber, was found to offer an advantage over elemental tellurium in prevulcanizates because it reacts fast at low temperatures normally employed in natural rubber latex technology and, along with certain organic activators, results in a rubber with vastly enhanced high temperature and oxidation resistance and superior processing qualities in extrusion and calendering applications (96). Tellurium dioxide improves the heat stability and aromatic fuel resistance in cured polysulfide elastomers, such as Thiokol. Tellurium rubber is extremely resistant to heat and abrasion. It is used in all-rubber-jacketed portable cables in mining, dredging, welding, etc and conveyor belts for special applications (see Rubber chemicals).

Tellurium dimethylthiocarbamate in combination with mercaptobenzothiazole, with or without tetramethylthiuram disulfide, is the fastest known accelerator for butyl rubber. It is used extensively in butyl tubes for buses and similar vehicles and in other butyl applications (see Elastomers, synthetic; Rubber, natural).

Tellurium is also useful in the coupling of rubber to metals.

11.12. Explosives

Sodium tellurite is used as a jelling promoter in explosive compositions that can be readily poured or pumped into drillholes (97) (see Explosives and propellants, explosives).

11.13. Medical and Biological

A very small, yet very important application of tellurium is in organic derivatives and radioactive isotopes for use as biological tracers, x-ray-contrast agents, and diagnostic aids, and for the treatment of thyroid diseases (see Medical imaging technology; Radioactive elements). Binary tellurides involving antimony, bismuth, cadmium, cobalt, or copper have found uses as fungicides (98). Some organic tellurobromides show strong bacterial activity (99). Terpene ether tellurocyanates are effective parasiticides, used either alone or with carriers (100).

11.14. Electronic and Optoelectronic Applications of Tellurides

Most metal tellurides are semiconductors with a large range of energy gaps and can be used in a variety of electrical and optoelectronic devices. Alloys of the form HgCdTe and PbSnTe have been used as infrared detectors and CdTe has been employed as a gamma ray detector and is also a promising candidate material for a thin-film solar cell.

A slow but growing area of use has been for thermoelectric applications. Here, cooling by the Peltier effect has been used to make refrigerators of relatively low efficiency for special purposes. Such devices, which have no moving parts (except for a fan), employ modules containing a Bi_2Te_3–Sb_2Te_3 alloy for the *p*-type region of each junction and a Bi_2Te_3–Sb_2Se_3 alloy for the *n*-region. From the inverse thermoelectric phenomenon of the Seebeck effect, heat can be used to generate electrical power if one junction is heated and the other is kept at a lower temperature. For such power conversion, the modules employed have been based on PbTe [1314-91-6], SnTe [12040-02-7], and MnTe [12032-88-1] as well as bismuth telluride alloys (101).

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