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SELENIUM

By

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Introduction

Selenium is one of the paradoxical elements in nature that can be both useful and harmful. The element was discovered in 1817 by Berzelius, a Swedish chemist, who found it in the flue dust of the sulfuric acid works at Grupsholm, Sweden. For many years selenium was an obnoxious by-product of copper refineries and was discarded. After World War I, commercial uses for selenium began to develop, particularly in glass factories, but it wasn't until after World War II that the element came into its own through the great demand for selenium rectifiers in the electrical industry. Today selenium is considered to be one of the most critical metals for industry and the national stockpile.

In spite of selenium's important contributions to industry, its detrimental qualities cannot be overlooked. The highly toxic and corrosive effects of certain selenium compounds are well-known industrial hazards. Poisoning of livestock by selenium-absorbing plants growing on seleniferous soils has long been a problem in certain range lands of western United States. Recent studies by public health agencies of population groups have shown that daily ingestion of small amounts of selenium may render teeth more susceptible to decay.

Properties of Selenium

Selenium is a grayish solid occurring usually in needlelike crystals and sometimes in glassy droplets (Palache and others, 1944). It has a metallic luster, red streak, and a specific gravity of 4.47. One of the most remarkable properties of this element is the difference shown in its ability to conduct electricity in darkness and in light. When illumination is increased its conductivity is increased.

Selenium is closely related to sulfur and tellurium with which it is commonly associated in nature. It occurs in native form, like sulfur, and also in selenides of copper, silver, lead, mercury, bismuth, and thallium. About twenty-five minerals contain selenium in varying amounts, but none of these is considered a commercial source at the present time.

Economic Importance of Selenium

Uses

The principal consumer of selenium is the electrical industry which makes extensive use of selenium rectifiers, particularly the minature type suitable for radio and television sets. Military uses of the selenium rectifier are numerous and include aircraft controls, guided missiles, radar equipment, and others.

Selenium has been employed in the glass industry for many years. It alters the normal greenish tinge to a neutral gray, and when added in relatively large quantities it produces ruby-red glass which has a wide variety of uses from tableware to tail lights.

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Selenium improves the quality of rubber and increases the machinability of stainless steel and the tensile strength of copper alloy. It is used extensively as a pigment to produce various shades of red in paint, paper, printing inks, dyes, and many other products. It is widely employed in industrial chemistry in the manufacture of products such as soaps, waxes, plastics, pharmaceuticals, and insecticides. Selenium is the catalyst in the synthesis of cortisone, used to treat arthritis, and isonicotinic acid, used to treat tuberculosis.

Statistics show (Sargent 1954) that the electrical and the chemical industries each consume about 40 percent of the nation's production of selenium. The glass industry uses about 13 percent, and the steel industry consumes most of the remainder.

Production of selenium

According to the U.S. Bureau of Mines (Sargent, 1954), the only commercial source at present is the anode mud or slime produced in the electrolytic refining of blister copper. The slimes generally contain from 4 to 25 percent selenium.

Production of primary selenium in the United States was 687,384 pounds in 1952 and 923,887 pounds in 1953. Demand exists at the present time for larger quantities of selenium than are available. The American Mining Congress Bulletin Service for September 1954 reports that negotiations are underway by General Services Administration for the purchase of 40,000 pounds of commercial selenium produced from accumulations of flue dust at lead smelters.

Selenium as a Hazard to Man and Animals

Selenium and most of its compounds are very toxic and certain compounds, particularly selenium oxychloride, are exceedingly corrosive. Considerable experimental data are available on selenium poisoning in animals, but the physiological effects of the element and its compounds on human beings are not entirely understood.

Industrial hazards

Poisoning by selenium is an industrial hazard but adequate safeguards to prevent exposure minimize the dangers. Exposures to selenium may result during smelting and refining of sulfide ores containing selenium and from the use of selenium compounds in the manufacturing of the numerous items mentioned above. Selenium poisoning may result from the inhalation of dust and volatile compounds, by ingestion, and to some extent by absorption through the skin (Patty, 1949).

Standards for maximum allowable concentrations of selenium have been established as 0.1 ppm* selenium in air, 4 ppm in foodstuffs, and .05 ppm in drinking water.

Toxic vegetation

Naturally occurring selenium compounds in soils of semiarid lands of western United States are capable of producing toxic vegetation.

Two types of livestock poisoning are caused by the seleniferous vegetation (Williams and others, 1941). One type is chronic and results from daily ingestion of small amounts of selenium which may be present in cereals, grasses, and other forage plants. It manifests itself in horses and cattle by deformity of hoofs, loss of hair, and emaciation. In severe cases, the animal either is permanently impaired or dies. In poultry, eggs either do not hatch or weak chicks result. The other type of poisoning is acute and results from the ingestion of larger amounts of selenium which are present in the indigenous range plants particularly certain species of Astragalus. These plants sometimes accumulate as much as 10,000 ppm of selenium. Only 10 ounces of green Astragalus bisulcatus rich in selenium will cause death of sheep in 30 minutes (Trelease, 1942).

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*Ppm: parts per million.

Publications concerning health hazards caused by seleniferous foodstuffs coming into markets outside seleniferous areas prompted a comprehensive survey of grain from widely different sources by the U.S. Department of Agriculture (Williams and others, 1941). Nearly 1,000 samples of wheat and wheat products were examined. Results showed that 75 to 80 percent contained 1 ppm or less of selenium while 90 percent contained less than 4 ppm and thus the great majority could not be considered toxic.

Public-health surveys have been made to determine the effects of selenium on persons living in known seleniferous areas. These investigations revealed that a great majority of the urine specimens of these people contained selenium in various amounts, indicating absorption of selenium. The results did not evidence any definite symptoms of selenium poisoning according to Patty (1949). However, it was observed that among families examined there existed a prevalence of bad teeth, varying from marked discoloration through all stages of decay.

A recent study (Hadjimarkos and others, 1952) of Oregon school children showed that there may be a relationship between dental caries and presence of selenium in the body. A group of high school children born and reared in Clatsop County where the rate of dental caries is said to be the highest in the State, was compared to a group of high school children from Klamath County where the caries rate is the lowest. It was found that a direct relationship was indicated between the prevalence of dental caries and urinary selenium concentrations of the subjects.

Investigations of Seleniferous Soils

History

Poisoning of livestock in the semiarid range lands of western United States was for many years unexplained. At first the disease was attributed to alkali waters and was known as alkali disease. Losses were great. For example, a herder in Huerfano County, Colorado, drove 200 sheep into a gulch in the evening and in the morning 197 sheep were dead (Beath and others, 1946). The origin of the disease remained a mystery until 1933 when O. A. Beath and associates at the University of Wyoming discovered that certain wild plants growing on some of the range soils were able to absorb and accumulate sufficient quantities of selenium to be highly toxic to animals.

As a result of these findings, a Presidential order on September 5, 1933, authorized the Secretary of Agriculture to set aside a sum of money for conducting surveys and other investigations in an effort to "definitely determine the areas injuriously affected by the presence of selenium in soils" (Byers 1935). Out of this survey came a series of seven reports published between 1935 and 1948 under the title "Selenium occurrence in certain soils in the United States with a discussion of related topics."

Distribution of seleniferous soils

It was early recognized that concentration of selenium in soils was directly related to certain geologic formations which served as the parent material from which the soil was derived. At first, selenium soils were thought to be limited to marine shales of Cretaceous age, but with broadening of field studies, it was found that seleniferous soils were derived from a variety of formations ranging in age from Late Paleozoic to Recent. Highly seleniferous soils were found in Eocene tuffs in Wyoming (Beath and others, 1946). They were found in glacial, lacustrine (lake bed), and recent alluvial materials which had been transported from seleniferous regions and deposited in marginal basins. Up to the present time, seleniferous soils capable of producing toxic vegetation have been found in the semiarid portions of the fifteen states which make up the Great Plains and Rocky Mountain region, and in Canada.

Indicator plants

One of the valuable aids in locating seleniferous soils is the presence of certain native plants which seem to require selenium for normal growth. These include 28 species of <u>Astragalus</u> (legumes with pealike flowers, such as vetches), and probably all species of

Xylorrhiza (woody aster), Oonopsis (a composite related to goldenrod) and Stanleya (prince's plume) (Trelease 1942). All of these are handsome and conspicuous western wild flowers. They not only absorb selenium but concentrate it in large amounts. They give off volatile selenium compounds and hence have a very offensive garlicky odor.

A number of domestic plants such as wheat, barley, corn, oats, and rye although capable of absorbing large quantities of selenium are not restricted to seleniferous soils and are therefore not selenium indicators.

Properties of seleniferous soils

Irrigation of seleniferous soils in semiarid regions has resulted in a very marked decrease of selenium in plants (Byers and others, 1938). The soluble compounds formerly available to the plants were removed and the residual selenium was essentially unavailable as plant food. Selenium, Byers explains, may be present in soils in three forms which become available to plants only by slow processes of hydrolytic action. These forms are free selenium, pyritic selenium, and basic ferric selenites, the last being the most common, particularly in soils containing iron oxide. Selenium may also be present in forms immediately available to plants as selenates and as more or less evanescent organic compounds resulting from decay of seleniferous plants. These two soluble forms are subject to eluviation and removal by percolating water, which accounts for the low content of selenium in plants grown on irrigated and humid soils even when selenium is fairly abundant in the soils.

Thus it is that soils which produce toxic vegetation are limited to arid or semiarid regions where rainfall is too low for percolating waters to carry away the soluble selenium compounds. In humid regions, on the other hand, soluble selenium compounds are removed by leaching and probably also by erosion.

Geology of Selenium

The reason for the variable concentrations of selenium in the rocks of the earth's crust is not fully understood. It is known that selenium accompanies sulfur both in the sulfides that separate from magma and in emanations from volcanoes. Igneous rocks contain about 0.09 ppm selenium, while certain volcanic tuffs have been shown to contain as much as 187 ppm.

Selenium brought into solution through weathering is carried to the sea, but little of it remains in the sea water. Part is removed during the precipitation of hydroxides of iron and manganese which are able to adsorb selenium nearly quantitatively, and part during the precipitation of carbonate sediments (Rankama and Sahama, 1949). Selenium in sea water averages only 0.004 ppm, while that contained in sea-bottom sediments averages 1 to 2 ppm.

Byers and others (1938) propose that formations which are notably seleniferous were deposited contemporaneously with periods of great volcanic activity and that selenium came wholly from volcanic dust and gases. Trelease and Beath (1949) suggest that, although some of the selenium may have been thus contributed, most of it was a primary constituent of magmas and molten materials intruded into or poured out upon the land mass from which the seleniferous sediments were derived.

Selenium is associated with uranium and vanadium in carbonaceous deposits of the Jurassic Morrison formation in New Mexico (Cannon, 1953). A selenium area known as the Poison Basin in Wyoming coincides with the outcrop of the uranium-bearing sandstone of the Miocene Browns Park formation in Wyoming (Vine and Prichard, 1954). Soils formed on the outcrops of both formations support selenium indicator plants, and hence these plants can be useful guides to uranium prospecting.

Selenium in Oregon

The first indication that there were seleniferous soils in Oregon came in 1940 when the U.S. Department of Agriculture made a reconnaissance investigation of lacustrine and alluvial materials along the Snake River basin (Lakin and Byers, 1948). Because seleniferous soils had

(Continued on page 68.)

Selenium Content of Soils, Minerals, and Vegetation From Malheur County, Oregon*

Sample No.	Place of collection	Material	Selenium in -	
			Soil or mineral P.p.m.	Vege-tation P.p.m.
1.	Oregon State Exper. Sta. at Vale.	Grayish-brown silt loam, 0-8 in.	0.1	---
2.	1 mi. E of Vale, on Oreg. 28.	Light-brown silt loam, 0-10 in.	0.1	---
3.	same	*A. nudisiliquus*	---	0.5
4.	22 mi. S of Ontario, on Oreg. 201.	Rotten ferruginous sandstone	0.8	---
5.	same	*A. nudisiliquus*	---	1
6.	In Sucker Creek Canyon, approaching Rockville.	*Astragalus* sp.	---	1
7.	1½ mi. SE of Jordan Valley.	*Astragalus* sp.	---	0.5
8.	30 mi. W of Jordan Valley	Light-brown loam, 0-10 in.	0.2	---
9.	same	*Astragalus* sp.	---	0.5
10.	In cut along Owyhee River at Rome.	Yellowish-brown silt loam	0.2	---
11.	4 mi. W of Rome.	Light-gray silt loam, in creek cut	2.0	---
12.	same	*Stanleya* sp.	---	360
13.	6 mi. W of Rome.	Yellowish-brown calcareous gravelly loam, 0-10 inches	0.8	---
14.	same	*Stanleya* sp.	---	220
15.	½ mi. N of No. 13.	Gravelly grayish-brown loam, 0-10 in.	2.0	---
16.	same	*Stanleya* sp.	---	60
17.	6½ mi. W of Rome.	Gray sandy loam, 0-10 in.	0.8	---
18.	same	Sandstone	0.05	---
19.	same	*Stanleya* sp.	---	650
20.	4 mi. N. of Rome, on road to Follyfarm	Yellowish-brown sandy loam, 0-10 in.	0.8	---
21.	same	*Stanleya* sp.	---	180
22.	6 mi. NW of Rome, on road to Follyfarm	Light gravelly sandy loam, 0-10 in.	0.8	---
23.	same	*Stanleya* sp.	---	10
24.	same	*A. beckwithii*	---	1
25.	8 mi. NW of Rome, on road to Follyfarm	Light-gray sandy loam, 0-10 in.	0.2	---
26.	same	*Stanleya* sp.	---	7
27.	same	Indian paintbrush	---	4
28.	5 mi. S of U.S. 20, on road to Riverside	Light-brown silt loam, 0-10 in.	0.2	---
29.	same	*Astragalus* sp.	---	1
30.	5 mi. E. of crossroad to Riverside, on U.S. 20	Diatomaceous earth	0.1	---
31.	5 mi. E of Juntura, on U.S. 20	Gray sandy loam	0.05	---
32.	same	*A. stenophyllus*	---	2
33.	7 mi. E of Juntura, on U.S. 20	Gravelly gray silt loam, 0-10 in.	0.05	---
34.	same	*A. stenophyllus*	---	1
35.	20 mi. W of Vale, on U.S. 20	Diatomaceous earth	0.2	---
36.	10 mi. W of Vale, on U.S. 20	Brown silt loam, 0-10 in.	0.1	---
37.	same	Alfalfa	---	1

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*Adapted from Lakin and Byers, 1941.

been found on the Payette formation in Idaho, a search was made for selenium in similar deposits in Malheur County in eastern Oregon. A total of 37 samples of soil, rock, and vegetation was collected in Malheur County in a circuit from Vale to Jordan Valley, to Rome, to Riverside, and back to Vale. As a result, a seleniferous area was located in the vicinity of Rome, about 60 miles west of Jordan Valley. Eighteen samples were collected at eight localities in this area (Nos. 10 to 27 in table on p. 67). The eight soil samples ranged in selenium content from 0.2 ppm to 2.0 ppm. Samples of an indicator plant Stanleya growing on this soil ranged from 7 ppm to 650 ppm. The sediments in the vicinity of Rome are believed to be in the Idaho formation of Pliocene age.* This is the only known study of selenium in Oregon soils.

The Quality of Water Branch of the U.S. Geological Survey reports that there are no analyses for selenium in the ground and surface waters of Oregon.

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HORSE HEAVEN WILL PRODUCE AGAIN

It is reported that Cordero Mining Company will install a small furnace at the Horse Heaven mine in Jefferson County, Oregon, to treat ore already broken in the mine left when the property shut down in December 1944. At that time a fire burned the furnace plant and caused closure of the property.

The Horse Heaven was one of the best known quicksilver producers before and during World War II. Cinnabar, the ore of quicksilver, was discovered in the area by A.J.Champion in 1933. Claims covering the property were acquired by Ray Whiting and cinnabar was discovered in place at the base of Horse Heaven Mountain by Ray Whiting, Jr., and Harry Hoy. The mine began production in 1934. Horse Heaven Mines, Inc., acquired the property in 1936 and produced continuously until the fire in 1944.

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DEPARTMENT DIRECTOR RETIRES

The Governing Board of the State Department of Geology and Mineral Industries has announced that F. W. Libbey, Director of the Department, will retire on November 1 under the State Retirement Act. At the same time the Board announced that Hollis M. Dole, Department geologist, has been appointed to succeed Mr. Libbey as Acting Director.

Mr. Dole is a graduate of Oregon State College and did graduate work in geology at U.C.L.A. and the University of Utah. During World War II he served in the Navy for three years and after the war was employed by the U.S. Geological Survey Ground-Water Division in Arizona. He joined the Department as geologist in charge of the Grants Pass office in 1946 and in 1947 was transferred to the head office. Mr. Dole was appointed Assistant to the Director in September 1954.

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CONVERTING SALT WATER TO FRESH WATER

According to Reclamation News published by the National Reclamation Association, Washington, D.C., the U.S. Department of the Interior will start field tests next spring on converting saline to fresh water at Miller, South Dakota. A contract on this research program has been let to Ionics, Inc., Cambridge, Massachusetts, to develop and operate field equipment. It is stated that the Ionics equipment makes use of plastic membranes and electric current to remove salt from salt water. It is stated that the equipment will be tested on irrigation water in Arizona this winter.

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OREGON STATE PROFESSORS TO GO TO THAILAND

Oregon State College has entered into a 2½-year contract with Kasetsart University, Bangkhen, Bangkok, Thailand, to supply technical assistance for the purpose of strengthening the educational and research programs of the University. The program is financed by the Thai government.

Oregon State College has agreed to send to Thailand as soon as practicable an initial group of six staff members to assist the University in improving teaching methods and curricula, research projects and methods, laboratory and classroom facilities, libraries, etc., and in advising the University on the selection and use of the necessary books, equipment, apparatus, supplies, and teaching aids.

Dr. Ira S. Allison, Head of the Department of Geology at Oregon State College has been appointed Chief Advisor of the group of visiting professors. Other fields to be represented include agricultural engineering, chemistry, physics, agricultural economics, plant pathology, and entomology.

Kasetsart University was founded in 1943 and is growing rapidly in enrollment and facilities. It includes colleges of agriculture, forestry, cooperative science, irrigation, and fisheries. In its expansion program several new buildings have been erected and others are contemplated.

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NEW OIL PERMITS

Recent permits to drill new oil tests have been secured by the following groups:

(1) Oil Developers, Inc., Roseburg, Oregon.

Scott No. 1 located in SW¼ of SW¼ of sec. 5, T. 27 S., R. 6 W., Douglas County. Elevation of the ground is 482 feet. Permit approved October 4, 1954.

(2) H. K. Riddle, Moore Hotel Building, Ontario, Oregon.

Kiesel Estate No. 1, located in SW¼ of sec. 8, T. 19 S., R. 47 E., Malheur County. Elevation of the ground is 2176 feet. Permit approved September 2, 1954.

Earlier permits were issued to Roderick Stamey, Ontario, Oregon, on March 26, 1954, to drill at a location in sec. 14, T. 19 S., R. 44 E., Malheur County, and to Walter Kernin, Roseburg, Oregon, on March 22, 1954, to drill in the NE¼ SE¼ sec. 30, T. 28 S., R. 6 E., Douglas County.

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QUICKSILVER

The price of quicksilver continues to soar because, according to E&MJ Metal and Mineral Markets, the supply situation is very tight. The quotation reported in the October 14 issue is $325 to $330 per flask for spot metal. Interest in re-opening old quicksilver mines has been stepped up both in California and Oregon since potential producers feel that the government's new program, under which a ceiling of $225 per flask is guaranteed over a 3-year period, will be some assurance that a new operation could pay off before the bottom drops out of the market.

The General Services Administration has issued a statement that the government has not contracted with foreign producers to deliver quicksilver to the account of the United States Government and that present and future procurement efforts of GSA are being directed toward obtaining the metal in this hemisphere.

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GEOLOGIC MAP OF CORVALLIS, OREGON, AREA

A new geologic map of a section of western Oregon near Corvallis prepared by the U.S. Geological Survey with the cooperation of the Oregon State Department of Geology and Mineral Industries has just been issued. It is designated OM-150 of the Oil and Gas Investigations series. Authors are H. E. Vokes, D. A. Myers, and Linn Hoover. Price of the map is 50 cents and it may be procured from the Distribution Section, U.S. Geological Survey, Denver, Colorado, or from the Chief of Distribution, U.S. Geological Survey, Washington, D.C.

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