



# Selenium minerals and the recovery of selenium from copper refinery anode slimes

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## Synopsis

Since it was first identified in 1817, selenium has received considerable interest. Native selenium and a few selenium minerals were discovered several decades later. With the increasing number of selenium minerals, the occurrence of selenium minerals became the focus of much research. A great number of selenium deposits were reported all over the world, although few independent selenium deposits were discovered. Selenium is obtained mainly as a byproduct of other metals, and is produced primarily from the anode mud of copper refineries. This paper presents a comprehensive review of selenium minerals, as well as the treatment of copper refinery anode slimes for the recovery of selenium. Our focus is on the selenium minerals, including their discovery and occurrence, and the distribution of selenium resources. In addition, the main methods of recovering selenium from copper anode slimes are summarized.

## Keywords

selenium, selenium minerals, anode slimes.

## Introduction

Selenium (Se) was first observed in 1817 in a laboratory (Greenwood *et al.*, 1984). The discovery of selenium was made by the Swedish chemist J.J. Berzelius and J.G. Gahn, who isolated selenium from a red residue in sulphuric acid from pyrite mined at Fahlun, Sweden. Selenium was named from the Greek word selene (moon), since it resembled tellurium, which had been discovered a few years earlier and named from the Latin word *tellus* (Earth).

After the first observation of selenium in the laboratory, selenium received considerable interest. In 1954, E.P. Kaiser pointed out that Se is enriched in sulphide ores and often associated with Bi, Co, Sn *etc.* (Kaiser 1954). In 1959, Hawley and Nichol investigated selenium in Canadian sulphide minerals, and presented the content of selenium in sulphide from several deposits of different types. They also proposed that Se is enriched in low-temperature hydrothermal pyrite (Hawley and Nichol, 1959). The thermodynamic conditions for forming native selenium and selenium minerals in sedimentary rocks were discussed, as well as geochemical behaviour of selenium near the oxidation zones of sulphides in the 1970s (Howard III, 1977; Zhu *et al.*, 2003). Zhu *et al.* examined the morphology, features,

and genesis of native selenium from Yutangba, Enshi City, Hubei Province, China in 2004, and pointed out, from the different forms of native Se, that selenium can be activated, transformed, remobilized, and enriched at sites such as in the unsaturated subsurface zone or in the saturated zone (Zhu *et al.*, 2005). The transport and deposition of selenium in felsic volcanic-hosted massive sulphide deposits of the Yukon Territory, Canada was studied and reported by Layton-Matthews *et al.* (2005).

Selenium is a comparatively rare and greatly dispersed element. The average selenium content in the Earth's crust is considered to vary between 0.05 and 0.09  $\mu\text{g/g}$  (Lakin 1972; Greenwood *et al.*, 1984; Jiajun *et al.*, 1997). Elemental selenium is seldom found in nature; industrially, selenium is obtained as a by-product of mining other metals such as copper, iron, and lead (Fishbein 1983; Wen and Qiu 1999). It is produced primarily from the anode slimes of copper refineries (Butterman *et al.*, 2004). There are various reports in the literature on the treatment of copper anode slimes to recover selenium (Hoffmann 1989; Cooper 1990).

In this paper, we provide an overview of selenium minerals, as well as the recovery of selenium from copper refinery anode slimes. Our focus is on the occurrence of selenium minerals and selenium deposits. We also examined the research work reported in the literature on the treatment of copper refinery anode slimes for the recovery of selenium.

## Selenium minerals

In 1956, Thompson *et al.* discovered felty

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© The Southern African Institute of Mining and Metallurgy, 2016. ISSN 2225-6253. Paper received Dec. 2012; revised paper received Feb. 2016.



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native selenium, which is violet acicular crystal. Coleman and Delevaux (1957) investigated the occurrence of selenium in sulphide from sandstone-type uranium ores in the western USA, and discovered trigonal and monoclinic native selenium, as well as clausthalite and ferroselite (Thompson *et al.*, 1956; Coleman and Delevaux, 1957). The occurrence of large particle of native selenium up to 20–30 mm in length in coal seams was reported by Zhu *et al.* (2005). In 1990, spherical and tubular native selenium was discovered in a hydrothermal U-Se-Re polymetallic deposit (Zhu *et al.*, 2003).

The selenide deposits in the eastern Harz Mountains, Germany were intensively studied. The selenide-bearing deposits at Tilkerode, Lerbach, Clausthal, Zorge, St. Andreasberg, and Trogthall, are recognized as typical selenide vein deposits of telethermal origin (Simon *et al.*, 1997). The polymetallic selenide mineralization at Tilkerode, Zorge, Lerbach, and Trogthall occurs mainly as small deposits not associated with larger base-metal deposits, while the selenide minerals at Clausthal and St. Andreasberg are associated with larger deposits mined primarily for silver, lead, zinc, and copper. The series of selenides from Tilkerode was identified mainly by Tischendorf: clausthalite (PbSe), naumannite (Ag<sub>2</sub>Se), tiemannite (HgSe), eskebornite (CuFeSe<sub>2</sub>), trogtalite (CoSe<sub>2</sub>), hastite (CoSe<sub>2</sub>), freboldite (CoSe), bornhardtite (Co<sub>3</sub>Se<sub>4</sub>), berzelianite (Cu<sub>2</sub>Se), umangite (Cu<sub>3</sub>Se<sub>2</sub>), klockmannite (CuSe), and stibiopalladinite (Pd<sub>5</sub>Sb<sub>2</sub>) (Davis *et al.*, 1977; Stanley *et al.*, 2002). Two unidentified minerals, noted by Tischendorf in 1958, represented two new species: chrisstanleyite (Ag<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>) and tischendorfit (Pd<sub>8</sub>Hg<sub>3</sub>Se<sub>6</sub>) (Stanley *et al.*, 1990, 2002). Wallis described a number of additional mineral species in the Tilkerode selenide assemblage: krütait (CuSe<sub>2</sub>), athabascaite (Cu<sub>5</sub>Se<sub>4</sub>), temagamite (Pd<sub>3</sub>HgTe<sub>3</sub>), eucairite (CuAgSe), trüstedtite (Ni<sub>3</sub>Se<sub>4</sub>), penroseite ((Ni,Co,Cu)Se<sub>2</sub>), and geffroyite ((Ag,Cu,Fe)<sub>9</sub>(S,Se)<sub>8</sub>) (Stanley *et al.*, 2002).

Davis *et al.* (1977) reported a new selenide of palladium, palladseite (Pd<sub>17</sub>Se<sub>15</sub>), which occurs in the residual concentrates from gold washing at Itabira, Minas Gerais, Brazil and is associated with arsenopalladinite, isomertieite, and atheneite.

Selenian miargyrite (AgSb(Se<sub>0.6</sub>S<sub>1.4</sub>)<sub>2</sub>), a new variety of miargyrite, was found in gold-bearing quartz veins in middle-lower Silurian quartzite of the Ailaoshan metamorphic belt, Yunnan province, China. It is intimately associated with freibergite, stibnite, ullmannite, and native gold and occurs as grains from 0.1 to 0.02 mm in diameter (Yunfen *et al.*, 1990).

Stanley *et al.* (1990) examined the precious and base metal selenide mineralization at Hope's Nose, Torquay, Devon, England. The selenide assemblage consists of clausthalite (PbSe), tiemannite (HgSe), klockmannite (CuSe), umangite (Cu<sub>3</sub>Se<sub>2</sub>), tyrrellite ((Cu,Co,Ni)<sub>5</sub>Se<sub>4</sub>), trüstedtite (Ni<sub>3</sub>Se<sub>4</sub>), penroseite (NiSe<sub>2</sub>), naumannite (AgSe), eucairite (AgCuSe), and fischesserite (Ag<sub>3</sub>AuSe<sub>2</sub>). A new mineral, chrisstanleyite (Ag<sub>2</sub>Pd<sub>3</sub>Se<sub>4</sub>), was discovered in gold-bearing carbonate veins in Middle Devonian limestones at Hope's Nose. It is associated with palladian and argentic gold, fischesserite, clausthalite, eucairite, tiemannite, umangite, cerussite, calcite, and bromian chlorargyrite (Paar *et al.*, 1998).

Selenio-sulfantimonide was discovered in the Laerma gold-copper-uranium deposit in China in 1993. It is associated with native gold, tiemannite, clasthalite, lautite, aurostibite, gersdorffite, quartz, barite, *etc.* and occurs as fine grains, about 0.01–0.5 mm (Minghua *et al.*, 1993).

As many selenium minerals were identified and discovered, numerous investigators conducted investigations on selenium minerals. More than 90 selenium minerals had been identified by 1998. Wen and co-workers reviewed the selenium minerals and their occurrence (Huayun, 1998).

Recently, a new series of selenium minerals was discovered. Stanley *et al.* (2002) reported a new mineral species from the Eskaborner Stollen at Tilkerode, Harz Mountains, Germany. Tischendorfit occurs as aggregates in a carbonate matrix, together with the associated metallic minerals clausthalite, tiemannite, chrisstanleyite, stibiopalladinite, and gold.

Schlemaite, a new mineral species from the Niederschlema-Alberoda vein-type uranium deposit, was discovered at Hartenstein, Erzgebirge, Germany. It occurs in aggregates of up to several hundred micrometres across, with berzelianite, eucairite, and clausthalite in a dolomite-ankerite matrix. Of the three vein-type uranium deposits in the Schneeberg-Schlema-Alberoda ore district, Niederschlema-Alberoda is considered the major occurrence of selenides in the Erzgebirge of Germany. In addition, rare selenides of Cu, Bi, Hg, Ni, and other elements were reported (Förster *et al.*, 2003).

Jaguéite, the copper analogue of chrisstanleyite, was discovered in a telethermal selenide vein-type deposit at the El Chire prospect, Los Llantenes District of La Rioja Province, Argentina. The new species is generally associated with chrisstanleyite, particularly in intimate intergrowths, clausthalite, naumannite, tiemannite, klockmannite, berzelianite, umangite, and aguilarite. In addition, two unnamed compounds, chemically (Ag, Cu)<sub>6</sub>Hg<sub>2</sub>Pb<sub>2</sub>Se<sub>3</sub> and (Ag, Cu)<sub>8</sub>Hg<sub>3</sub>(S, Se)<sub>7</sub>, occur as rare constituents (Paar *et al.*, 2004).

Jolliffeite, previously known only from Lake Athabasca, Saskatchewan, Canada was reported from the Niederschlema-Alberoda uranium deposit in the Erzgebirge region of Germany. Jolliffeite, an exotic mineral, is associated with haematite, Ni-Co-Se-bearing löllingite, clausthalite, tiemannite, mercurian hakite-giraudite solid solutions, sulphurian berzelianite, sulphurian umangite, hessite, Ni-Co-As-bearing pyrite, and Se-rich chalcopyrite (Förster *et al.*, 2004).

Three occurrences of clausthalite were reported in Poland, in abandoned polymetallic deposits at Kowary and Kletno and the Fore-Sudetic copper deposits (Thompson *et al.*, 1956; Kucha, 1982). A new occurrence of clausthalite, together with uraninite, was reported in the Sudetes, southwest Poland. Clausthalite forms veinlets in a breccia comprising <50% calc-silicate rock fragments (Thompson *et al.*, 1956).

Plumboselite, a new selenite from the Tsumeb mine, Namibia, occurs as fibres on clausthalite and is associated with smithsonite, mimetite, and vaterite. It occurs in subparallel to divergent clusters of thin, flattened, colourless fibres up to 0.3 mm in length (Kampf *et al.*, 2011).

All the reported selenium minerals are shown in Tables I–III. The minerals are mainly selenides, selenium sulphides

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Table I

### Selenide minerals (Huayun, 1998; Zhu *et al.*, 2003)

Name	Chemical formula	Name	Chemical formula
Antimonselite	Sb <sub>2</sub> Se <sub>3</sub>	Athabascaite	Cu <sub>5</sub> Se <sub>4</sub>
Bambollaite	Cu(Se, Te) <sub>2</sub>	Bellidoite	Cu <sub>2</sub> Se
Berzelianite	Cu <sub>2</sub> Se	Bohdanowiczite	AgBiSe <sub>2</sub>
Bornhardtite	Co <sup>+2</sup> Co <sub>2</sub> <sup>+3</sup> Se <sub>4</sub>	Bukovite	Tl <sub>2</sub> Cu <sub>3</sub> FeSe <sub>4</sub>
Cadmoselite	CdSe	Clausthalite	PbSe
Crookesite	Cu <sub>7</sub> (Tl, Ag) Se <sub>4</sub>	Dzharkenite	FeSe <sub>2</sub>
Eskebornite	CuFeSe <sub>2</sub>	Eucairite	CuAgSe
Ferroselite	FeSe <sub>2</sub>	Fischesserite	Ag <sub>3</sub> AuSe <sub>2</sub>
Freboldite	CoSe	Guanajuatite	Bi <sub>2</sub> Se <sub>3</sub>
Hastite	CoSe <sub>2</sub>	Jolliffeite	(Ni, Co) AsSe
Kitkaite	NiTeSe	Klockmannite	CuSe
Kullerudite	NiSe <sub>2</sub>	Luberoite	Pt <sub>5</sub> Se <sub>4</sub>
Makinenite	γ-NiSe	Mgriite	Cu <sub>3</sub> AsSe <sub>3</sub>
Merenskyite	(Pd, Pt) (Te, Se, Bi) <sub>2</sub>	Naumannite	Ag <sub>2</sub> Se
Oosterboschite	(Pd, Cu) <sub>7</sub> Se <sub>3</sub>	Padmaite	PdBiSe
Palladseite	Pd <sub>17</sub> Se <sub>15</sub>	Penroseite	(Ni, Co, Cu) Se <sub>2</sub>
Permingeatite	Cu <sub>3</sub> SbSe <sub>4</sub>	Petrovicite	PbHgCu <sub>3</sub> BiSe <sub>5</sub>
Sabatierite	Cu <sub>4</sub> TiSe <sub>3</sub>	Sederholmite	β-NiSe
Selen-tellurium	(Se, Te)	Stilleite	ZnSe
Tiemannite	HgSe	Trogtalite	CoSe <sub>2</sub>
Trustedtite	Ni <sub>3</sub> Se <sub>4</sub>	Tyrrellite	(Cu, Co, Ni) <sub>3</sub> Se <sub>4</sub>
Umangite	Cu <sub>3</sub> Se <sub>2</sub>	Wilkmanite	Ni <sub>3</sub> Se <sub>4</sub>
Schlemaite	(Cu, ?) <sub>6</sub> (Pb, Bi)Se <sub>4</sub>	(IMA99. 023)	Cu <sub>2</sub> HgSe <sub>2</sub>
Krutaite	CuSe <sub>2</sub>	Achavalite	FeSe
Sudovikovite	PtSe <sub>2</sub>	Chrisstanleyite	Ag <sub>2</sub> Pd <sub>3</sub> Se <sub>4</sub>
Jaguéite	Cu <sub>2</sub> Pd <sub>3</sub> Se <sub>4</sub>	Tischendorfite	Pd <sub>8</sub> Hg <sub>3</sub> Se <sub>9</sub>
Plumboselite	Pb <sub>3</sub> O <sub>2</sub> (SeO <sub>3</sub> ) <sub>2</sub>		

Table II

### Selenium sulphides (Huayun, 1998; Zhu *et al.*, 2003)

Name	Chemical formula	Name	Chemical formula
Aguilarite	Ag <sub>4</sub> SeS	Chameanite	(Cu, Fe) <sub>4</sub> As(Se, S) <sub>4</sub>
Csiklovaite	Bi <sub>2</sub> Te(S, Se) <sub>2</sub>	Drysdallite	Mo(Se, S) <sub>2</sub>
Geffroyite	(Ag, Cu, Fe) <sub>9</sub> (Se, S) <sub>8</sub>	Giraudite	(Cu, Zn, Ag) <sub>12</sub> (As, Sb) <sub>4</sub> (Se, S) <sub>13</sub>
Hakite	(Cu, Hg) <sub>3</sub> (Sb, As) (Se, S) <sub>3</sub>	Ikunolite	Bi <sub>4</sub> (S, Se) <sub>3</sub>
Jeromite	As(S, Se) <sub>2</sub>	Junoite	Pb <sub>3</sub> Cu <sub>2</sub> Bi <sub>8</sub> (S, Se) <sub>16</sub>
Kawazulite	Bi <sub>2</sub> (Te, Se, S) <sub>3</sub>	Kurilite	(Au, Ag) <sub>2</sub> (Te, Se, S)
Laitakarite	Bi <sub>4</sub> (Se, S) <sub>3</sub>	Laphamite	As <sub>2</sub> (Se, S) <sub>3</sub>
Nevskite	Bi(Se, S)	Nordstromite	Pb <sub>3</sub> CuBi <sub>7</sub> S <sub>10</sub> Se <sub>4</sub>
Paraguanajuatite	Bi <sub>2</sub> (Se, S) <sub>3</sub>	Pekoite	PbCuBi <sub>11</sub> (S, Se) <sub>18</sub>
Penzhinite	(Ag, Cu) <sub>4</sub> Au(S, Se) <sub>4</sub>	Petrovskaitite	AuAg(S, Se)
Platynite	(Pb, Bi) <sub>3</sub> (Se, S) <sub>4</sub>	Poubaite	PbBi <sub>2</sub> Se <sub>2</sub> (Te, S) <sub>2</sub>
Proudite	Cu <sub>0-1</sub> Pb <sub>7.5</sub> Bi <sub>9.3-9.7</sub> (S, Se) <sub>22</sub>	Selenostephanite	Ag <sub>5</sub> Sb(Se, S) <sub>4</sub>
Skippenite	Bi <sub>2</sub> Se <sub>2</sub> (Te, S)	Soucekite	PbCuBi(S, Se) <sub>3</sub>
Tsnigriite	Ag <sub>9</sub> SbTe <sub>3</sub> (S, Se) <sub>3</sub>	Watkinsonite	PbCu <sub>2</sub> Bi <sub>4</sub> (Se, S, Te) <sub>8</sub>
Weibullite	Pb <sub>6</sub> Bi <sub>8</sub> (S, Se) <sub>18</sub>	Wittite	Pb <sub>3</sub> Bi <sub>4</sub> (S, Se) <sub>9</sub>
Crerarite	(Pt, Pb) Bi <sub>3</sub> (S, Se) <sub>4-x</sub> (x=0.7)	Vihorlatite	Bi <sub>8+x</sub> (Se, Te, S) <sub>11-x</sub>
Babkinite	Pb <sub>2</sub> Bi <sub>2</sub> (S, Se) <sub>3</sub>	Mozgovaite	PbBi <sub>4</sub> (S, Se) <sub>7</sub>

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Table III

### Oxygen-containing selenides (Huayun, 1998; Zhu *et al.*, 2003)

Name	Chemical formula	Name	Chemical formula
Ahlfeldite	(Ni,Co)SeO <sub>3</sub> ·2H <sub>2</sub> O	Carlosruizite	K <sub>6</sub> (Na, K) <sub>4</sub> Na <sub>6</sub> Mg <sub>10</sub> (Se <sub>6</sub> O <sub>4</sub> ) <sub>12</sub> (IO <sub>3</sub> ) <sub>12</sub> ·12H <sub>2</sub> O
Chalcomenite	CuSeO <sub>3</sub> ·2H <sub>2</sub> O	Chloromenite	Cu <sub>9</sub> O <sub>2</sub> (SeO <sub>3</sub> ) <sub>4</sub> Cl <sub>6</sub>
Clinochalcomenite	CuSeO <sub>3</sub> ·2H <sub>2</sub> O	Cobaltomenite	CoSeO <sub>3</sub> ·2H <sub>2</sub> O
Demesmaekerite	Pb <sub>2</sub> Cu <sub>5</sub> (UO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>6</sub> (OH) <sub>6</sub> ·2H <sub>2</sub> O	Derriksite	Cu <sub>4</sub> (UO <sub>2</sub> ) <sub>2</sub> (SeO <sub>3</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Downeyite	SeO <sub>2</sub>	Francisite	Cu <sub>3</sub> Bi (SeO <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> Cl
Georgbokiite	Cu <sub>5</sub> O <sub>2</sub> (SeO <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	Guilleminite	Ba(UO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> (OH) <sub>4</sub> ·3H <sub>2</sub> O
Haynesite	(UO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub> ·5H <sub>2</sub> O	Ilinskite	NaCu <sub>5</sub> O <sub>2</sub> (SeO <sub>3</sub> ) <sub>2</sub> Cl
Kerstenite	PbSeO <sub>4</sub> (?)	Mandarinoite	Fe <sub>2</sub> Se <sub>3</sub> O <sub>9</sub> ·6H <sub>2</sub> O
Marthozite	Cu(UO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub> ·7H <sub>2</sub> O	Molybdomenite	PbSeO <sub>3</sub>
Olsacherite	Pb <sub>2</sub> (SeO <sub>4</sub> )(SO <sub>4</sub> )	Orlandiite	Pb <sub>3</sub> (Cl, OH) <sub>4</sub> (SeO <sub>3</sub> )·H <sub>2</sub> O
Piretite	Ca(UO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> (OH) <sub>4</sub> ·4H <sub>2</sub> O	Schmiederite	Pb <sub>2</sub> Cu <sub>2</sub> (SeO <sub>3</sub> )(SeO <sub>4</sub> )(OH) <sub>4</sub>
Selenolite	SeO <sub>2</sub>	Sophiite	Zn <sub>2</sub> (SeO <sub>3</sub> )Cl <sub>2</sub>
(IMA2000-050)	KCdCu <sub>7</sub> O <sub>2</sub> (SeO <sub>3</sub> ) <sub>2</sub> Cl <sub>9</sub>	(IMA96.002)	Ca <sub>0.75</sub> (H <sub>3</sub> O) <sub>0.25</sub> (UO <sub>2</sub> ) <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> (OH) <sub>3.75</sub> ·2.5H <sub>2</sub> O

Table IV

### Mode of occurrence of some selenium minerals (Zuomin, 1997)

Modes of occurrence	Typical combination of selenium minerals
Placer deposits	Clausthalite, makineneite, ferroselite, cadmoselite, selenium
Tin deposits	Laitakarite, clausthalite, guanajuatite
Kustelite deposits	Fischesserite, naumannite, clausthalite, berzelianite, guanajuatite, paraganajuatite
Uranium deposits	Demesmaekerite, derriksite, guilleminite, haynesite, marthozite, antimonelite, umangite, dzharkenite, berzelianite
Contact metasomatic deposits	Clausthalite, guanajuatite, paraganajuatite
Oxidation zone of copper-cobalt sulphide deposits	Eucairite, trogtalite
Carbonate gangue	Calcite veins Dolomitic gangue Siderite veins
Quartz vein	Kawazulite, laitakarite
Carbonate –albite veins	Clausthalite, kitkaite, paraganajuatite, penroseite, Ni-selenide
Quartz-anthophyllite veins	Laitakarite

and oxygen-containing selenides (Huayun, 1998). There are a few native selenium minerals, selenium oxides, as well as intermetallic compounds between selenium and metals.

Selenium is chemically very similar to sulphur, and sulphur is the primary accompanying element in selenium minerals. Many of its compounds are analogues of sulphur compounds, and selenium substitutes for sulphur in minerals and other compounds.

Cu, Bi, Pb, Ag, and Te are the main element in selenium minerals, followed by Co, Ni, Fe, and Sb. Based on the content of selenium in sulphides, Yang (Huayun, 1998) described the affinity between Se and related elements, which can be divided into three categories (with decreasing affinity): (1) Pb, Ag, Bi, Hg, Cu; (2) Co, Ni; (3) Fe, Zn. Se forms a few minerals with precious metals, *e.g.* Au, Ag, Pt, Pb.

Mineralogical studies of numerous selenium minerals have not been fully conducted due to their restricted occurrence, small particle size, and experimental limitations. For instance, there are five selenides of nickel: kullerudite,

makineneite, sederholmite, trustedtite, and wilkmanite, but no information has been reported about reflectivity or color index (Huayun, 1998).

#### Occurrence of selenium minerals

Selenium minerals occur in various forms, which can be divided primarily into three categories: independent minerals; isomorphism; adsorbed on clay minerals. Although there are about 100 selenium minerals, the metal rarely occurs in commercial concentrations. Selenium occurs mainly in sulphides or sulphosalt minerals in the form of isomorphism; there are rare selenium deposits that are commercially viable (Brown Jr, 1998; Huayun, 1998).

Selenium deposits can be divided into independent deposits and accompanying deposits. The occurrence of some selenium minerals is shown in Table IV. As regards independent selenium deposits, hydrothermal deposits are dominating type, and the Pakarharkar deposit in Bolivia is typical, while the Yutangba Se deposit in China, a sedimentary deposit, is an exception.

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Selenium resources occur mainly in combined deposit, which can be divided into several industrial types, *i.e.* magmatic, porphyry, skarn, hydrothermal, volcanogenic-sedimentary, and sedimentary. Among these, magmatic, porphyry, hydrothermal, and sedimentary type deposits are dominant.

Selenium minerals are often closely associated with other minerals in very fine particles. For example, clausthalite occurs mainly as finer particles in the size range from 0.005 mm to 0.01 mm in the Wolverine deposit, Yukon Territory, Canada. It occurs with sulphides and is often associated with tetrahedrite or silver stibnic clausthalite in the same grain (Figure 1).

The mechanism of selenium mineral formation remains unclear. Selenium minerals are often associated with gold, but no selenium-gold minerals have been discovered. Furthermore, the relationship between selenium and sulphur in minerals is still indistinct, *e.g.* the replacement of selenium is ordered or disordered.

### Distribution of selenium resources

According to the US Bureau of Mines (USBM), the world's selenium reserve base is  $1.34 \times 10^5$  t, and the proved reserves amount to  $7.1 \times 10^4$  t (Brown Jr, 1998). The reserves are dominated by America with 52.7% of the total reserves; Asia, Africa, Europe, and Oceania account for 15.4%, 15.4%, 12.2%, and 4.4%, respectively (Feng and Jiajun, 2002). Chile, America, Canada, China, Zambia, Zaire, Peru, the Philippines, Australia, and Papua New Guinea account for about 76.9% of the proved reserves. There are about 40 countries that lack selenium resources.

Independent industrial deposits of selenium are rare. No independent selenium deposits were reported until the discovery of the Pakarharkar deposit in Bolivia in the 1980s. Since then, a series of associated deposits have been discovered in Canada, America, Chile, Zambia, Zaire, *etc.* (Daming, 1996). The main Se deposits of the world are shown in Table V.

Recently, selenium resources were reported at the Wolverine and KZK deposits in the Finlayson Lake District (FLD) of the Yukon, Canada. In the mid-1990s, three polymetallic volcanic-hosted massive sulphide deposits were discovered in the FLD with a combined resource of 21.5 Mt. Elevated selenium levels in the Wolverine and KZK massive

sulphide ores were recognized during metallurgical testing and in the pre-feasibility stages of exploration. Selenium concentrations up to 3420 g/t are reported, with a mean value of approximate 700 g/t (Layton-Matthews *et al.*, 2005). The selenium in the Wolverine deposit occurs mainly as fine particles of clausthalite and silver stibnic clausthalite between 0.005–0.05 mm in diameter.

China is one of the major countries that hold selenium resources, with the fourth-largest recoverable reserves after Canada, America, and Belgium (Brown Jr, 1998). There are 10 ascertained Se deposits, including Jinshan gold deposit,

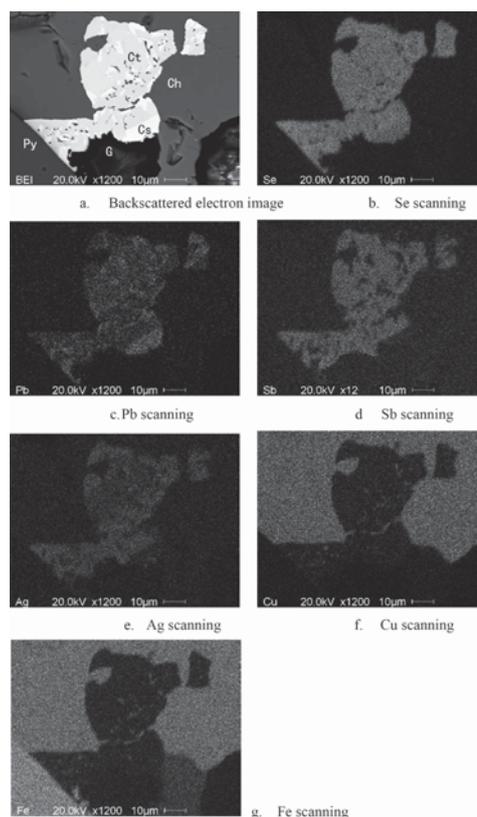


Figure 1—Scanning electron micrograph of clausthalite and silver stibnic clausthalite. Ct – silver stibnic clausthalite, contains Se, Ag, Sb, Pb; Cs – clausthalite, contains Se, Pb; Ch – chalcopyrite; Py – pyrite; G – gangue

Table V

### The main Se deposits of the world (Daming 1996)

Country	Name	Types	Mineral elements	Grade (10 <sup>-6</sup> )	Scale
America	Bingham	Magmatic	Se, Cu	21.5	Large
	Twin Buttes	Magmatic	Se, Cu	21.5	Large
Bolivia	Pakarharkar	Alteration	Se	>10	Small
Canada	Noranda	Volcanic hydrothermal	Se, Cu, Ni	64	Oversize
	Fiin Flon	Volcanic hydrothermal	Se, Cu, Ni	64	Oversize
Chile	Escondida	Magmatic	Se, Cu	>10	Large
	Chuquicamata	Magmatic	Se, Cu	>10	Large
The Philippines	Atlas	Magmatic	Se, Cu	>10	Large
Zaire	Kolwezi	Clastic sedimentary	Se	>10	Large
Zambia	Mufulira	Clastic sedimentary	Se	>10	Large
	Nchanga	Clastic sedimentary	Se	>10	Large

# Selenium minerals and the recovery of selenium from copper refinery anode slimes

Table VI

The main Se deposits of China (Daming 1996)

Province	Name	Types	Mineral elements	Grade (10-6)	Scale
An'hui	Tongguanshan		Se, Au, Cu		Large
Gansu	Baijiazuzi	Magmatic	Se, Au, Ni	>10	Over-size
Guangdong	Dabaoshan	Hydrothermal		>30	Large
Gansu	Laerma	Hydrothermal	U, Hg, Se, Au	29.4	Large
Hubei	Baiguoyuan		Ag, Se, V	67~79	Large
Hu'nan	Qibaoshan		Au, Ag, Se, S	>10	Large
Hubei	Shuanghe	Clastic sedimentary	Se	84.12	Medium
Hubei	Yutangba	Clastic sedimentary	Se	84.12	Medium
Jiangxi	Chengmenshan	Skarn	Polymetallic		Over-size
Jiangxi	Jinshan	Porphyry	Se, Cu, Au	15.4	Over-size
Qinghai	De'erni	Hydrothermal	Cu, Co, Au, Se, S		Large
Shanxi	Jinduicheng	Porphyry	Au, Se, Mo		Medium
Shanxi	Dashigou	Magmatic	Se, Mo	>10	Medium
Shanxi	Huayangchuan	Magmatic	Sr, Pb, Nb, Ag, Se, tobarthite	>10	Medium

Baijiazuzi Cu-Ni deposit, and Chengmenshan copper deposit (Zuomin, 1997). In addition, some independent selenium deposits have been discovered in China, *i.e.* the Yutangba Se deposit and Laerma Se-Au deposit (Wen and Qiu, 1999). Proven reserves of selenium occur mainly with copper and nickel ores, and are distributed in the northwest of China and the Lower Yangtze region. The main Se deposits of China are shown in Table VI.

### The recovery of selenium from copper anode slimes

The largest source of selenium is the anode slimes formed during the electrolytic refining of copper (Elkin and Margrave, 1982). Production usually begins by oxidation to produce selenium dioxide at an appropriate temperature. The selenium dioxide is then dissolved in water and the solution is acidified to form selenous acid (oxidation step). Selenous acid is sparged with sulphur dioxide (reduction step) to yield elemental selenium. In South Africa, Se is mostly removed to about 1 mg/L before the leach solution is sent to copper electrowinning. In South African refineries, Se is recovered mostly by precipitation using sulphurous acid. Different approaches to treating anode slimes are shown in Figure 2.

### Sulphatizing roast

In the sulphatizing roast, sulphuric acid is used as an oxidant in the presence of air for the conversion of selenium or selenides to their tetravalent oxides (Hoffmann *et al.*, 1976; Hoffmann, 1989). Selenium is volatilized as selenium dioxide and passes into the scrubbers. The scrubbing of the off-gases results in complete recovery of the selenium from the gas stream. The process is shown in Figure 3.

Although the process entails an advantage in that the sulphur dioxide produced in the roasting step reduces the selenous acid to elemental selenium and the sulphuric acid consumed in the roast is regenerated, this process is a net consumer of sulphuric acid. In addition, the rather long reaction times required for the oxidation of the selenium, extensive foaming due to sulphur dioxide liberation, as well as the cumbersome equipment due to large allowances for freeboard add difficulties to the process.

### Soda roast

Slimes are mixed with sodium carbonate, a binder clay, and water to form a stiff paste, and then pelletized, dried, and roasted at a low temperature (530–650°C) to convert all selenium and tellurium to the soluble hexavalent state. The roasted pellets are ground and leached in water. Selenium

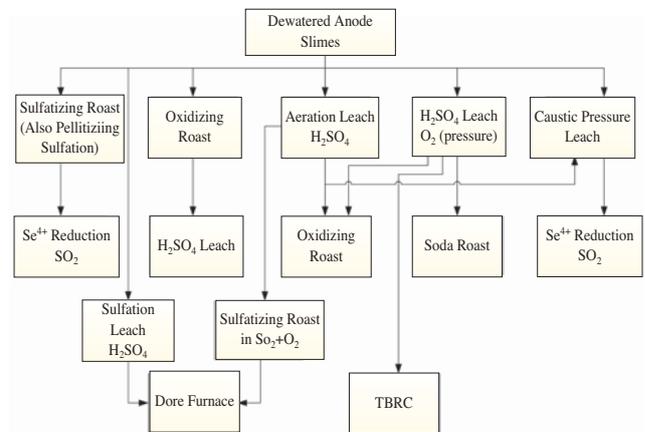


Figure 2—Flow sheet of different approaches to the treatment of copper anode slimes (Cooper, 1990)

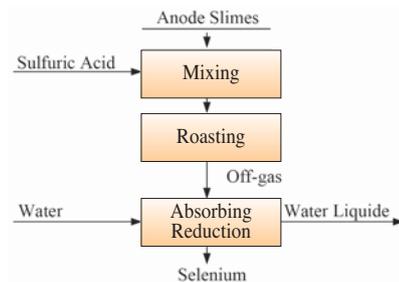


Figure 3—Flow sheet for anode slimes treatment with sulphation roasting (Yang *et al.*, 2005)

## Selenium minerals and the recovery of selenium from copper refinery anode slimes

goes into solution (as the selenate  $\text{Na}_2\text{SeO}_4$ ), while tellurium is insoluble in the alkaline solution; thus the two elements are separated in this stage (Figure 4).

Two processes are commonly employed for the reduction of hexavalent selenium from solution (Figure 5) (Hoffman 1997; Yang *et al.* 2005). In the first process, selenium is leached from the slimes and recovered from solution by crystallization. The crystalline sodium selenate is mixed with charcoal and reduced to sodium selenide under controlled conditions of heating. The sodium selenide cake is leached with water, and the dissolved sodium selenide is readily oxidized to the elemental form by blowing air through the solution. The recycling of much of the solution is a significant advantage considering the severe restrictions placed on the discharge of selenium-bearing solutions.

In the other process, the hexavalent selenium is reduced using concentrated hydrochloric acid or ferrous iron salts catalysed by chloride ions as the reductant. The process generates large volumes of ferric chloride effluent, which is extremely corrosive and problematic to discharge.

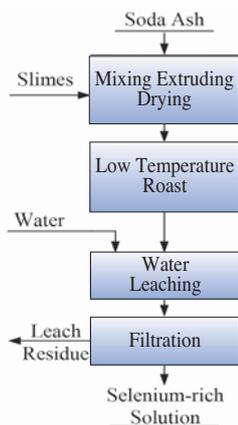


Figure 4—Flow sheet for anode slimes treatment with soda ash roasting (Hoffmann, 1989)

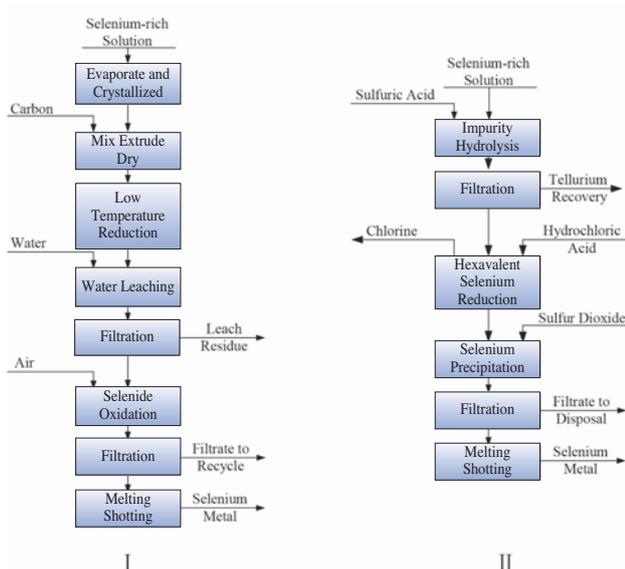


Figure 5—Flow sheet for selenium-rich solution treatment: (I) reduction by carbon; (II) reduction by ferrous ions (Hoffmann 1989)

### Oxidizing roast

Oxidation roasting of anode slimes can be employed to eliminate selenium following sulphuric acid leaching of the slimes (Morrison, 1977; Hyvarinen, *et al.*, 1984). Anode slimes are roasted to convert selenium to selenium dioxide, which reacts with water to form selenic acid in the dust collector. The selenic acid is reacted with copper powder, carbon (soot), and  $\text{SO}_2$  in the furnace gas, and it is reduced to selenium or insoluble selenide. The process is shown in Figure 6.

### Chlorination processes

The chlorination of anode slimes has been the focus of considerable research (Hyvarinen *et al.*, 1984). Both wet and dry chlorination processes have been developed. Dry chlorination processes have not proven to be industrially viable, while wet chlorination of refinery slimes is a rapid and simple method with high extraction of selenium from slimes. The wet chlorination process may involve changing all of the process chemistry, not just the removal of selenium (Hoffmann, 1989).

Wet chlorination of slimes involves sparging slimes slurried in water or hydrochloric acid with chlorine gas at about  $100^\circ\text{C}$  to oxidize and dissolve selenium and selenides. The selenium in solution may be converted initially to the hexavalent state by chlorine, and then reduced to the tetravalent state as the pH decreases. Selenium can be reduced selectively from the chlorination liquor by sulphur dioxide.

### Conclusion

Since the first observation of selenium in the laboratory, more than 100 selenium minerals have been discovered and reported. The minerals are mainly selenides, selenium sulphides, and oxygen-containing selenides. Sulphur is the primary element in selenium minerals as a consequence of its chemical similarity with selenium, while Cu, Bi, Pb, Ag, and Te are the other main elements, followed by Co, Ni, Fe, and Sb.

Selenium deposits can be divided into independent deposits and accompanying deposits. A few independent selenium deposits have been reported, such as the Pakarharkar deposit in Bolivia and Yutangba Se deposit in China. Se resources occur mainly in combined deposits.

Accompanying deposits can be divided into several genetic types, with magmatic, porphyry, hydrothermal, and sedimentary type deposits being dominant. Selenium

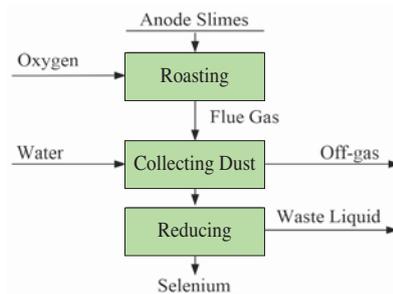


Figure 6—Flow sheet for anode slimes treatment with oxidizing roasting (Yang *et al.*, 2005)

# Selenium minerals and the recovery of selenium from copper refinery anode slimes

minerals are often closely associated with other minerals in very fine particles in combined deposits. Although numerous selenium deposits have been discovered all over the world, there are few deposits that are commercially viable. Industrial production of selenium is mainly as a by-product of other metals, such as copper, iron, and lead. Selenium is produced primarily from the anode mud of copper refineries, and this process has been investigated widely.

In investigations of the selenium minerals, comprehensive mineralogical studies of numerous minerals have not been conducted due to their restricted occurrence, small particle size, and experimental limitations. Furthermore, the mechanism of selenium mineral formation remains unclear. Selenium minerals are often associated with gold, although no independent minerals consisting of selenium and gold have been discovered. The relationship between selenium and sulphur in minerals is still unclear.

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