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(Part- II: Metals & Alloys)

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SELENIUM AND TELLURIUM

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GOVERNMENT OF INDIA MINISTRY OF MINES INDIAN BUREAU OF MINES

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14 Selenium and Tellurium

Selenium and tellurium are rare elements widely distributed within the Earth's crust. They do not occur in concentrations high enough to justify mining solely for their content. They are recovered as by-products, mostly from anode mud or slime obtained during electrolytic refining of copper. Tellurium is found mostly in tellurides associated with metals, such as, bismuth, lead, gold and silver. It is found with selenium in the anode slime from electrolytic copper refineries.

EXTRACTION

Selenium and tellurium metals were being recovered as allied products at Ghatsila Copper Smelter of HCL in Jharkhand, where the annual installed capacity to produce selenium was 14,600 kg. HCL has not reported production of selenium since 2006-07 and that of tellurium since 2004-05. HCL has developed its own Precious Metal Recovery Plant at ICC successfully. Presently, the plant is not operational. A tellurium recovery plant has also been developed by R & D Wing. Hindalco Industries Ltd reported 73,870 kg production of selenium from imported copper concentrates at its Dahej Smelter in Gujarat during 2010-11 and thereafter no production data is available.

USES

Selenium

Selenium is used as a decolourising agent in the Glass Industry. Selenium decolorizes the green tint caused by iron impurities in glass bottles. Approximately, 1 kg selenium is used for about 150 tonnes of glass production. It is also used in architectural plate glass to reduce solar heat transmission. High purity selenium compounds were used principally as photoreceptors on the drums of older plain paper copiers which are gradually being replaced by newer models that do not use selenium in the reproduction process. Dietary supplement for livestock is the largest agricultural usage of selenium. Also, selenium is known to be added to fertilizer to enrich selenium-poor soils.

Selenium is added to steel, copper and lead alloys to improve machinability which enables faster production with better surface finish and casting properties. Selenium is added to low antimony-lead alloys used in the support grids of lead acid storage batteries. The addition of 0.02% selenium by weight as a grain refiner improves the casting and mechanical properties of alloy. Metallurgical applications of selenium also include its use in the production of Electrolytic Manganese Metal (EMM) as a current efficiency enhancer wherein about 2 kg of SeO₂ is required per tonne of electrolytic manganese metal produced.

Selenium is proving to be a useful Solar PV material in increasing the efficiency of absorption of light.

Chemical uses of selenium are in industrial and pharmaceutical applications. The principal pharmaceutical use of selenium is in anti-dandruff hair shampoos. Selenium is also used as a human dietary supplement. Other industrial chemical uses are as lubricant, rubber compounding catalysts and as a promoter in the reformation of naptha.

In pigment applications, selenium is used to produce colour changes in cadmium sulphide-based pigments. Sulphoselenide pigments have good heat stability, resistant to light and chemical attack and hence are used in ceramics, plastics, paints, inks and enamels. Selenium is used in catalysts to enhance selective oxidation and in plating solutions to improve appearance and durability. It is also used in blasting caps and gun bluing.

The use of selenium in glass has increased due to higher colourless glass production. The use of selenium in fertilizer and supplements in the plantanimal human chain and as human vitamin supplements increased as its health benefits were documented. The use of selenium in copper-indiumgallium-diselenide (CIGD) solar cell has increased.

Selenium is recovered from used electronic and photocopier components and recycled. The estimated global use of selenium was in metallurgy (40%); glass (25%); agriculture/chemicals/pigments/electronic (10% each); and other industries (5%).

Tellurium

Tellurium (Te) demonstrates properties similar to those of elements known to be toxic to humans and has application in industrial processes, which is rapidly growing in importance and scale. Tellurium is used principally as an alloying element in the production of free-machining low carbon steel, where additions up to 0.1% tellurium greatly improves machinability. It is also used as a minor additive in copper alloys to improve machinability without reducing conductivity. Tellurium catalysts are used chiefly for the oxidation of organic compounds and also in hydrogenation and halogenation reactions. Tellurium chemicals are used as vulcanising and accelerating agents in processing of rubber compounds. It finds use as a component of catalysts for synthetic fibre production that is increasingly used in cadmiumtellurium-based solar cells. In plain paper copiers and in thermoelectric and photoelectric devices, tellurium is used along with selenium. Mercurycadmium telluride is used as a sensing material for thermal imaging devices. Tellurium is also used as an ingredient in blasting caps and as a pigment to produce colours in glass and ceramics. High purity tellurium is used in alloys for electronic applications.

SUBSTITUTES

The use of selenium as an alloy to substitute for lead in plumbing continued to increase in response to requirements of Public Law for safe drinking Water Act Amendment 1996. High-purity silicon has replaced selenium in high-voltage rectifiers and is the major substitute for selenium in low and medium voltage rectifiers and solar photovoltaic cells. Other inorganic semi-conductor materials, such as, silicon, cadmium, tellurium, gallium and arsenic as well as organic photoconductors are the substitutes for selenium in photoelectric applications. Cerium oxide is substitutes of selenium as either a colorant or decolorant in glass. Amorphous silicon and organic photoreceptors are substitutes of selenium in plain paper photocopiers. Sulphur dioxide can be used as a replacement for selenium dioxide in the production of electrolytic manganese metal.

Several materials can replace tellurium in most of its uses, but usually with loss in production efficiency or product characteristics. Bismuth, calcium, lead, phosphorus, selenium and sulphur can be used in place of tellurium in many free-machining steels. Several of the chemical process reactions catalysed by tellurium can be carried out with other catalysts or by means of non-catalytic processes. The chief substitutes for tellurium were selenium and sulphur in rubber compound applications and selenium, germanium and organic compounds in electronic applications.

WORLD REVIEW

Selenium

The world reserves of selenium at 99,000 tonnes only cover the estimated contents of economic copper deposits. Selenium was obtained as a by-product with copper. Substantial resources also exist in association with other metals and in uneconomic copper deposits. Selenium reserves are mainly found in China (26%), Russia (20%), Peru (13%), USA (10%) and Canada (6%) (Table-1).

The world production of refined selenium is furnished in Table-2. The chief producers of selenium in the world in 2018 were China, Germany, Japan & Belgium. In addition to the countries listed, Australia, Iran, the Republic of Korea and Zimbabwe are believed to produce refined selenium.

Global selenium and tellurium output cannot be determined easily because not all companies or countries report production and because trade in scrap and semi-refined products may be included with refined metal trade data.

Table – 1: World Reserves of Selenium (By Principal Countries)

(In tonnes of Selenium content)

| Country | Reserves |
|----------------------------|----------|
| World: Total (Rounded off) | 99000 |
| Canada | 6000 |
| China | 26000 |
| Peru | 13000 |
| Poland | 3000 |
| Russia | 20000 |
| USA | 10000 |
| Other countries | 21000 |

Source: USGS, Mineral Commodity Summaries, 2020

Table – 2: World Production of Selenium, Refined (By Principal Countries)

(In tonnes)

| Country | 2016 | 2017 | 2018 |
|---------------------------------|------------------|------------------|------------------|
| China | 750 | 930 | 1050 |
| Germany ^{(e)(a)} | 790 | 790 | 790 |
| Japan | 753 | 792 | 750 |
| Belgium(e) | 200 | 200 | 200 |
| Russia | 197 | 194 | 176 |
| USA ^(e) | 122 | 116 | 152 |
| Kazakhstan ^(e) | 130 | 130 | 130 |
| Finland | 104 | 100 | 109 |
| Mexico | 121 | 112 | 107 |
| Philippines(e) Other courtries | 70 431 | 70 294 | 70 298 |

Source: BGS, World Mineral Production, 2014-2018 (a): includes selenium produced from imported material.

Tellurium

The world reserves of tellurium were at 31,000 tonnes contained in copper resources. Tellurium reserves are mainly located in China (21%), USA (8%), Canada (3%) and Sweden (2%). In addition to the countries listed, Australia, Belgium, Chile, Colombia, Germany, Kazakhstan, Mexico, Philippines and Poland produce refined tellurium, but output was not reported and available information was inadequate to make reliable production and reserves estimates. Concentration of tellurium could also be found in lead and gold deposits. The quantities of tellurium in deposits of coal, copper and other metals that are of subeconomic grade are several times the amount of tellurium contained in identified economic copper deposits (Table-3).

More than 90% of tellurium is produced from anode slimes collected from electrolytic copper refining and the remainder is derived from skimmings at lead refineries and from flue dust and gases generated during the smelting of bismuth, copper and lead ores. The anode slimes of copper and lead refineries normally contain about 3% tellurium. The chief producers of refined tellurium in the world in 2018 were China, Japan, USA, Russia, Sweden, Canada and Bulgaria. These countries together contributed as an estimated 524 tonnes to the world production as compared to 476 tonnes produced in 2017. In addition to the countries listed Germany and Belgium are also believed to produce refined tellurium (Table-4).

Table – 3: World Reserves of Tellurium (By Principal Countries)

(In tonnes of Tellurium content)

| Country | Reserves |
|----------------------------|----------|
| World: Total (rounded off) | 31000 |
| Bulgaria | NA |
| Canada | 800 |
| China | 6600 |
| Japan | - |
| Russia | NA |
| South Africa | - |
| Sweden | 670 |
| USA | 3500 |
| Other countries | 19000 |

Source: USGS, Mineral Commodity Summaries, 2020

Table – 4: World Production of Tellurium, Refined (By Principal Countries)

| | | | (In tonnes) |
|----------|------|------|-----------------|
| Country | 2016 | 2017 | 2018 |
| China | 279 | 291 | 307 |
| Japan | 28 | 34 | 55 |
| USAe | 50 | 50 | 50 |
| Russia | 40 | 44 | 46 |
| Sweden | 39 | 35 | 45 |
| Canada | 18 | 17 | 17 ^e |
| Bulgaria | 4 | 5 | 4 |

Source: BGS, World Mineral Production, 2014-2018

To give a generalised view of the development in various countries, the counrywise description as sourced from latest available publication of Minerals Yearbook 'USGS' 2017 is furnished below.

China

China produced an estimated 930 tonnes of selenium in 2017, a slight increase from 2016. China's estimated production of tellurium in 2017 was 290 tonnes, a 4% increase from the year 2016.

In 2017, the Govt. of China's National Development and Reform commision announced the installation of 53 GW of solar capacity, to increase its PV capacity by 15 to 20 GW of annual solar power generation. These new solar plants could increase the consumption of minor metals, including cadmium, indium, gallium, selenium and tellurium.

According to China Nonferrous Industry Association, selenium consumption in China was expected to be more than production in 2017, with annual consumption of about 1,200 tones and production of 930 tonnes of selenium. The electrolytic manganese industry remained the leading consumer of selenium in China.

The tellurium market was expected to remain in surplus, owing to decrease consumption of tellurium because of increased efficiency in manufacturing thermoelectric devices. consumption of tellurium was around 210 tonnes from 2010 through 2012 but decreased in 2016 to 190 tonnes.

India

India planned to expand its solar capacity to 100 GW per year by 2022 from 5 GW per year in 2015 and announced a safeguard duty investigation in December 2017. This investigation was to determine if imports of cheap solar cells were a threat to the domestic industry. Indian Solar Manufacturing Association (ISMA), claimed that even though local demand increased, thier market share had not changed owing to cheap imports. According to CRISIL Ltd., imports from China and Malaysia accounted for around 80% of solar modules used in India.

Sweden

In Sweden, the production of by-product tellurium at Boliden AB's Kankberg gold-tellurium

mine decreased by 10% in 2017 to 34,979 kg from 38,680 kg in 2016. Boliden reopened the Kankberg mine in 2012 and the mine's life was expected to extend through 2020.

FOREIGN TRADE

Exports

Exports of selenium during 2018-19 decreased by 84% to 28 tonnes from 174 tonnes in 2017-18. Exports were mainly to China (39%), Hong Kong (32%), another hand Cananda, Iran, Netherlands, Egypt & Morocco (4% each), etc. There were negligible amount of exports of tellurium during 2018-19 as against no exports of tellurium reported in the previous year (Tables-5 & 6).

Imports

Imports of selenium during 2018-19 increased by 48% to 375 tonnes as compared to 254 tonnes in the preceding year. Imports were mainly from Japan (37%), Republic of Korea (22%), Netherlands (17%), Belgium (11%), Germany (4%) and China (3%). During 2018-19, imports of tellurium increased by 67% to 5 tonnes as compared to 3 tonnes in the preceding year. Imports were mainly from China (80%) & Hong Kong (20%). Negligible quantities was also contributed from other countries (Tables-7 & 8).

Table – 5: Exports of Selenium (By Countries)

| Country | 2017-18 (R) | | 2018-19 (P) | |
|-----------------|-------------|------------------|-------------|------------------|
| | Qty (t) | Value (`'000) | Qty (t) | Value (`'000) |
| All Countries | 174 | 374190 | 28 | 58603 |
| Hong Kong | 50 | 107425 | 9 | 28018 |
| China | 52 | 109235 | 11 | 15066 |
| Canada | 2 | 6226 | 1 | 4761 |
| Iran | ++ | 5 | 1 | 3690 |
| Egypt | ++ | 19 | 1 | 1810 |
| USA | ++ | 977 | ++ | 1739 |
| Netherlands | 10 | 21568 | 1 | 1367 |
| Uganda | ++ | 691 | ++ | 338 |
| Australia | ++ | 299 | ++ | 326 |
| Morocco | _ | _ | 1 | 302 |
| Other countries | 60 | 127743 | 3 | 1185 |

Figures rounded off.

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Table - 6: Exports of Tellurium (By Countries)

| Country | 2017-18 (R) | | 2018-19 (P) | |
|---------------|-------------|------------------|-------------|------------------|
| | Qty (t) | Value (`'000) | Qty (t) | Value (`'000) |
| All Countries | - | - | ++ | 419 |
| Sri Lanka | - | - | ++ | 419 |

Figures rounded off.

Table - 7: Imports of Selenium (By Countries)

| Country | 2017-18 (P) | | 2018-19 (P) | |
|-----------------|-------------|-------------------|-------------|------------------|
| | Qty (t) | Value (` '000) | Qty (t) | Value (`'000) |
| All Countries | 254 | 585920 | 375 | 936735 |
| Japan | 110 | 251824 | 138 | 332423 |
| Korea, Rep. of | 63 | 144927 | 81 | 196407 |
| Netherlands | 7 | 15294 | 64 | 163356 |
| Belgium | 43 | 100066 | 42 | 114028 |
| Germany | 16 | 37765 | 15 | 41810 |
| China | 7 | 17093 | 10 | 25405 |
| Italy | - | - | 7 | 16029 |
| USA | 2 | 6236 | 4 | 15899 |
| Hong Kong | - | - | 7 | 13058 |
| Brazil | - | - | 4 | 10712 |
| Other countries | 6 | 12715 | 3 | 7608 |

Figures rounded off.

Table - 8: Imports of Tellurium (By Countries)

| Country | 2017-18 (P) | | 2018-19 (P) | |
|---------------|-------------|------------------|-------------|------------------|
| | Qty (t) | Value (`'000) | Qty (t) | Value (`'000) |
| All Countries | 3 | 13734 | 5 | 31337 |
| China | 1 | 4890 | 4 | 21889 |
| Hong Kong | - | - | 1 | 5279 |
| Canada | ++ | 873 | ++ | 1329 |
| Belgium | 1 | 4086 | ++ | 1096 |
| UK | - | - | ++ | 809 |
| Netherlands | - | - | ++ | 705 |
| USA | ++ | 70 | ++ | 161 |
| Germany | ++ | 247 | ++ | 69 |
| Japan | 1 | 2991 | - | - |
| Philippines | ++ | 577 | - | - |

Figures rounded off.

FUTURE OUTLOOK

The supply of selenium is dependent on the supply of main product from which it is derived, copper and also to a lesser extent by the supply of nickel where the nickel production is from sulphide ore. The selenium prices are often inversely related to the supply of the major product from which it is derived—copper.

China has been purchasing large quantities of crude selenium. As this material becomes scarce, the prices for standard grade selenium may rise. The combination of these two factors, the decline of selenium containing concentrates from North America and the growth of Chinese demand, should firm up the prices for selenium in the short term.

Demand for selenium in photoreceptors is likely to see further decline as the cost of substituting organic compounds decreases. The Photoreceptor Industry which was once a major consumer of selenium and tellurium has reached the replacement stage. Selenium has been substituted by alternative material in newer models.

Further, use of selenium in cancer prevention and other health applications may eventually lead to increased consumption of the metal. Dosages taken directly for human consumption will not affect the demand for the metal because only minute quantities are necessary for effective therapy.

The demand and supply of tellurium has remained fairly balanced for a decade. In short term, significant increases are not anticipated in either consumption or production, although reduction in copper production may have a bearing on tellurium supply. An increase in demand for high purity tellurium for cadmium telluride solar cells might have a major impact on tellurium consumption. The use of tellurium alloys used in DVD's consumes only small amounts of tellurium and will, therefore, have minimal impact on tellurium demand.