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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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S elenium 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 byproducts, 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 licensed capacity was 10,000 kg while annual installed produce selenium capacity to 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. As per the Annual Report 2022-23 of Hindalco Industries Ltd., in the electrolytic refining step in the copper manufacturing process, anode slime is generated as a by-product including tellurium, selenium. During the copper removal stage in slime leachate, about 50-60% of tellurium in anode slime gets co-dissolved. The remaining tellurium is present in a solid residue, resulting in the loss of this valuable element. At HIC Copper, Hindalco developed a process to recover this tellurium from slime leachate in the form of Copper Telluride (Cu,Te) powder at its Dahej Smelter in Gujarat.

USES

Selenium

Selenium is used as a decolourising agent in the Glass Industry. Selenium decolorises 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 sulphidebased 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) element lies on the borderland between metals and non-metals. It is added to nonferrous metals like aluminium, tin, copper and lead to modify certain physical properties, like ductility, hardness, mechinability, toughness, strength and resistance. Tellurium 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 cadmium-tellurium-based solar cells. In plain paper copiers and in thermoelectric and photoelectric devices, tellurium is used along with selenium. Mercury-cadmium 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 one substitute of selenium used as 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 81,000 tonnes or 0.08 million tonnes only cover the estimated selenium content of copper reserves, with the exception of China. Selenium was obtained as a byproduct with copper. Substantial resources also exist in association with other metals and in uneconomic copper deposits. Selenium reserves are mainly found in Russia (25%), Peru (16%), USA (12%), China (8%) and Canada (7%) (Table-1).

The world production of refined selenium is furnished in Table-2. The chief producers of selenium in the world in 2021 were China, Japan, Germany, Belgium and Russia. In addition to the countries listed, Australia, Iran, 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)	81000
Belgium	-
Canada	6000
China	6100
Finland	NA
Germany	-
Japan	-
Peru	13000
Poland	3000
Russia	20000
Sweden	500
Turkey	NA
United States	10000
Other countries	22500

Source: USGS, Mineral Commodity Summaries, 2023.

		(In tonne	
Country	2019	2020	2021
World total	3557	3543	3538
China	1358	1400	1400
Japan	740	740	750
Germany ^(a)	300	300	200
Belgium	200	200	200
Russia	184	190	194
Mexico	127	106	135
USA	144	66	112
Canada	57	102	100
Chile	90	100	100
Other countries	357	339	347

 Table – 2: World Production of Selenium, Refined

 (By Principal Countries)

Source: BGS, World Mineral Production, 2017-2021 (a): Includes selenium produced from imported material

Tellurium

The world reserves of tellurium were at 32,000 tonnes contained in copper resources. Tellurium reserves are mainly located in Russia (14%), USA (11%), China (9%), Canada & South Africa (3% each) and Sweden (2%). In addition to the countries listed, Australia, Belgium, Chile, Colombia, Germany, Kazakhstan, Mexico, Philippines and Poland may 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 quantity of tellurium in deposits of coal, copper and other metals that are of sub-economic 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-zinc ores. Other potential sources of tellurium include bismuth telluride and gold telluride ores. The chief producers of refined tellurium in the world in 2021 were China, Japan, Russia, Sweden, Canada and Bulgaria.These countries together contributed as an estimated 549 tonnes to the world production in 2021 as compared to 523 tonnes produced in 2020. 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 tonne	es of Tellurium content)
Country	Reserves
World: Total (rounded off)	32000
Bulgaria	NA
Canada	800
China	3000
Japan	-
Russia	4500
South Africa	800
Sweden	670
USA	3500
Other countries	19000

Source: USGS, Mineral Commodity Summaries, 2023.

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

			(In tonnes)
Country	2019	2020	2021
China	461	330	349
Japan	50	70	75
Russia	50	55	56
Sweden	41	42	41
Canada	15	23	25
Bulgaria	3	3	3

Source: BGS, World Mineral Production, 2017-2021.

To give a generalised view of the development in various countries, the counrywise description as sourced from latest available publication of Minerals Yearbook 'USGS' 2018 is furnished below.

China

China was the leading global producer of selenium and tellurium and accounted for 33% and 61% of world production, respectively. China produced an estimated 930 tonnes of selenium in 2018, unchanged from that in 2017. Estimated production of tellurium in China was 280 tonnes, a 3% decrease from 290 tonnes in 2017. In 2018, the Government of China's National Development and Reform Commission (NDRC) announced the installation of 30 GW of solar capacity, down from the 53 GW of solar capacity in 2017. The NDRC also announced a cut in the national subsidy for solar power generated, in order to reduce overcapacity of photovoltaic power stations. This shift in policy was to be kept in place until at least 2020

and new solar projects that required subsidies were unlikely to be approved.

According to the China Nonferrous Industry Association, the estimated selenium consumption in China decreased by 6% to 2,100 tonnes in 2018 from 2,240 tonnes in 2017. The electrolytic manganese industry remained the leading consumer of selenium in China, accounting for 46% of selenium consumption in 2018, followed by glass production, 19%; agriculture, 15%; electronics, 12%; and pigments, 8%. The selenium consumption was estimated to be less than the supply. Estimated tellurium consumption in China in 2018 increased to approximately 150 tonnes from 130 tonnes in 2017, and consumption was expected to be less than supply. Tellurium in China was consumed for various uses: thermal coolers (53%), metallurgy (27%), chemicals and photovoltaics (6% each), and other (8%).

Sweden

By product tellurium production at Boliden AB's Kankberg gold-tellurium mine increased by 28% in 2018 to 44,641 kg from 34,979 kg in 2017. Boliden reopened the Kankberg Mine in 2012, and the mine's life was expected to extend into 2020.

FOREIGN TRADE

Exports

Exports of selenium during 2021-22 decreased marginally by 2.5% to 39 tonnes from 40 tonnes in 2020-21. Exports were mainly to Philippines (31%), China (26%), Netherlands (13%), Ukraine (8%) and Canada & Indonesia (5% each). There were negligible amount of exports of selenium from Iran, UAE & USA (3% each) during 2021-22. Exports of tellurium were negligible during 2021-22 (Tables-5 & 6).

Imports

Imports of selenium during 2021-22 decreased substantially by 28% to 508 tonnes as compared to 701 tonnes in the preceding year. Imports were mainly from Japan (40%), Korea (23%), Belgium (16%), Germany (9%), Philippines Hong Kong & China (3% each), Netherlands (2%) and Italy (1%). Imports of tellurium increased substantially by 50% to 3 tonnes as compared to 2 tonnes in the preceding year. Imports were mainly from Belgium (67%) and China (33%). Negligible quantities were also imported from other countries (Tables-7 & 8).

Table – 5 : Exports of Selenium (By Countries)

Country	2020-21 (R)		2021-22 (P)	
	Qty (t)	Value (₹ '000)	Qty (t)	Value (₹'000)
All Countries	40	43423	39	81781
Philippines	1	555	12	16561
China	-	-	10	15139
Ukraine	3	13775	3	14741
Netherlands	5	4159	5	6965
Canada	4	12893	2	6089
Iran	1	5813	1	5999
USA	++	923	1	3538
Spain	-	-	++	2360
Indonesia	-	-	2	2277
UAE	1	1099	1	1895
Other Countries	25	4206	2	6217

Figures rounded off

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Table – 6 : Exports of Tellurium (By Countries)

Country	2020-21 (R)		2021-22 (P)	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹000)
All Countries	++	37	++	17
South Africa	-	-	++	6
Singapore	-	-	++	6
Azerbaijan	-	-	++	5
Belgium	++	37	-	-

Figures rounded off

Table – 7 : Imports of Selenium (By Countries)

Country	2020-21 (R)		202	21-22 (P)
	Qty (t)	Value (₹000)	Qty (t)	Value (₹000)
All Countries	701	681519	508	712159
Japan	186	187058	202	303678
Korea	142	128783	116	151179
Belgium	206	200846	83	96825
Germany	48	49138	48	70084
China	5	6959	14	35773
Philippines	47	42209	16	18344
Hong Kong	17	16582	15	18095
Netherlands	22	22370	10	10544
Italy	6	5551	4	3728
Canada	-	-	++	2738
Other countries	22	22023	++	1171

Figures rounded off

Table – 8 : Imports of Tellurium (By Countries)

Country	2020-21 (R)		2021-22 (P)	
	Qty (t)	Value (₹'000)	Qty (t)	Value (₹000)
All Countries	2	21250	3	18935
China	2	11901	1	5984
Canada	++	2633	++	5564
Belgium	++	8	2	3913
Germany	++	2494	++	1670
Japan	++	387	++	1037
Luxembourg	++	313	++	560
USA	++	295	++	207
Hong Kong	++	2948	-	-
Italy	++	271	-	-

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 copper and nickel.

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 in DVD's consumes only small amounts of tellurium and will, therefore, have minimal impact on tellurium demand.