The Recovery of Osmium from Nickel Refinery Anode Slimes

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The commencement of pilot-scale production of high-purity osmium in 1965 increased to fifteen the number of elements recovered in marketable form from the Sudbury, Ontario, Ni-Cu ores. Detection of minute quantities of osmium in various plant intermediate products, development of a procedure for recovering and concentrating most of the osmium previously lost in processing, and the techniques for refining it into a metal powder of 99.98 pct purity, are described.

WITH the initial pilot-scale production of high-purity osmium in 1965, The International Nickel Co. of Canada, Ltd. has succeeded in increasing from fourteen to fifteen the number of elements recovered from its Sudbury district ores. These complex sulfide ore deposits have been worked by INCo and its predecessors since 1886, primarily for their nickel and copper content. The predominant source minerals for these two metals are pentlandite, (FeNi)_xS_y, and chalcopyrite, (CuFeS_2), which usually are accompanied by larger amounts of a nickel-bearing iron sulfide mineral, pyrrhotite (Fe_1-xS). In addition to the primary metals nickel, copper, and iron, the ores also contain smaller amounts of cobalt, selenium, and tellurium, and trace quantities of the precious metals, i.e., silver, gold, and members of the platinum group.

In early metallurgical practice, nickel was separated from copper and refined to nickel ingots by pyrometallurgical procedures which did not permit recovery of by-product metals. The blister copper, however, was treated at custom refineries by electrolysis, and some Au, Ag, Se, and Te were produced from the anode slimes. Somewhat later, nickel refining at Clydach, Wales, by the Mond carbonyl process permitted some precious metals recovery from the residues. When commercial electrolytic refining of nickel commenced at Port Colborne, Ontario, in 1926, the resulting anode slimes became INCo's major concentrate for shipment to INCo's refinery at Acton, England, where the individual precious metals were produced in marketable form.

More recently, the invention and adoption of the INCo matte separation process has substantially shortened the route to precious metals recovery by segregating the bulk of the platinum metals in a metallic phase which, being magnetic, is readily separated from the nonmagnetic sulfides of nickel and copper. Melting, casting into anodes, and electrolysis of the metallics results in a further concentration of the precious metals in the anode slimes, which are treated by chemical means for the recovery of Pt, Pd, Rh, Ir, and Ru.

INVESTIGATIONS INTO THE RECOVERY OF OSMIUM

The relationship of osmium to the other precious metals and base metals which are recovered from Sudbury district ores is illustrated below:

<table>
<thead>
<tr>
<th>Periodic Groups</th>
<th>VIII</th>
<th>IB</th>
<th>VIA</th>
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<tr>
<td></td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
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<td></td>
<td>Cu</td>
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<td>Pb</td>
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<td></td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
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<tr>
<td></td>
<td>Au</td>
<td>Se</td>
<td>Te</td>
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Osmium was first isolated and named in 1804 by Tennant. Its name is of Greek origin and means smell or odor which the discoverer probably associated with the chlorine-like odor of osmium tetroxide. The most outstanding chemical property of osmium is its reaction with oxygen to form the tetroxide which melts at 105°F and boils at 268°F. It is thus not surprising that this member of the group did not survive the severe pyrometallurgical operations long employed in the winning of nickel.

In spite of the fact that osmium was not reporting with the other platinum group metals in the final refining operations and that some opinions were expressed doubting its presence in the Sudbury ores, there was strong conviction by INCo Research personnel that osmium must be present. In 1952 analytical work utilizing neutron activation confirmed its presence, in minute concentrations, in the ores of the Sudbury district. In 1957, an analytical survey using a sensitive colorimetric method was made on selected samples from various locations in the metallurgical flowsheet. This survey showed the presence of osmium in smelter feed, traced its path through the various processing steps, and indicated the areas where osmium recovery might be favorable.

It was established that the metallic fraction from the matte separation process carried not only the five familiar platinum-group metals, but also a significant amount of osmium and that electrolysis of the metallics concentrated all of the platinum-group metals in the anode slimes. However, most of the osmium apparently was volatilized during the processes then employed for the production of a high-grade precious metals concentrate.

In the conventional treatment for base metals re-
moval, the slimes, analyzing about 50 pct Cu and 10 pct Ni, were digested with concentrated sulfuric acid to solubilize the base metals. During this sulfating operation the temperature often reached 600°F. The soluble salts were leached out with water, and the cycle was repeated until the residue contained less than 1 pct each of copper and nickel. The precious metals concentrate was then calcined in air at 1500°F to 1800°F to eliminate such impurities as S, Se, and As prior to its shipment for refining. Now we know that whatever amount of osmium survived the sulfating operation at 500°F to 600°F was probably lost in the subsequent calcining operation at 1500°F to 1800°F.

LABORATORY STUDIES

A laboratory duplication of this procedure showed that a careful control of the sulfating temperature is necessary to prevent a significant loss of osmium, see Fig. 1.

Scrubbing the off-gases from the sulfating operation was not attractive because of the large concentrations of associated acid fumes which would require neutralization.

When the sulfating temperature was maintained at about 400°F substantially all of the osmium was retained in the precious metals residue. It was now necessary to devise a means for its separation and recovery. Calcination of the platinum metals-containing residue was carried out in air at different temperatures and the results showed that gradual heating to about 1500°F to 1700°F gave satisfactory osmium elimination, see Fig. 2.

Scrubbing the off-gases from the calcination step appeared more attractive since alkali consuming constituents were now at a relatively low level. A scrubbing solution containing about 10 pct sodium hydroxide was adopted, to absorb not only osmium tetroxide but also the associated sulfur- and selenium dioxides. Due to the low concentration of osmium in the off-gases, we were not able to recover more than 85 pct of the osmium in the scrubbing solution. Typically, the osmium-containing scrubbing liquid analyzed in grams per liter: Os, 0.5; Se, 5.0; and S, 30.

Many different methods were tried for the recovery of osmium from the alkaline scrubbing solution. Among these were:

a) acidification and boiling under oxidizing conditions to volatilize osmium tetroxide with reabsorption in fresh sodium hydroxide solution to yield a more concentrated osmate solution,

b) partial reduction with alcohol and neutralization with acid to yield a precipitate of hydrated osmium dioxide,

c) pressure reduction of the alkaline solution with hydrogen at 200°F to 400°F to yield osmium sponge,

d) partial neutralization with sulfuric acid to pH 8 and gassing with sulfur dioxide to pH 6 to precipitate a complex Na-Os sulfite.

The precipitation with sulfur dioxide appeared the most attractive for ease of handling and economy. The precipitate was readily filterable to about 50 pct moisture, and usually analyzed 2 to 8 pct Os on a dry basis. Sulfur and selenium compounds were separated from the osmium by treating the crude precipitate first with sulfuric acid to evolve sulfur dioxide and then with an oxidizing agent which volatilized only osmium tetroxide and, if present, ruthenium tetroxide. The distillate vapors were absorbed in 20 pct sodium hydroxide yielding a solution containing about 60 g per liter Os. Methyl alcohol was then added to the osmium-rich solution to precipitate sodium ruthenate and to reduce the perosmate to the osmate state. Even at room temperature the rich perosmate solution showed a relatively high vapor pressure of osmium while in the osmate state the vapor pressure was negligible.

It was found possible to treat the filtered alkaline osmate solution in an autoclave with an over-pressure of hydrogen gas to precipitate osmium sponge, provided sufficient hydrochloric acid was added to give a final pH value between 3 and 8. This method was considered unsatisfactory as the hydrochloric acid additions were not always sufficiently accurate, and there was a tendency to volatilize osmium during the acid

![Fig. 1—Sulfation of nickel anode slimes: effect of temperature on osmium volatilization.](image1)

![Fig. 2—Calcination of precious metals concentrate: effect of temperature on osmium volatilization.](image2)