Recovery of Radiogenic Osmium-187 from Sulfide Copper Ores in Kazakhstan

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There are 41 osmium isotopes with mass numbers from 162 to 196 and the majority are unstable. Only seven stable osmium isotopes occur naturally; these are the ones with mass numbers 184, 186, 187, 188, 189, 190 and 192. Their abundance varies and they differ in some of their nuclear characteristics (1, 2). Osmium isotopes were naturally formed as a result of two different processes. Isotopes 184, 186, 188, 189, 190, 192 and a portion of 187 originated during the initial nucleosynthesis of elements. Another portion of isotope ^{187}Os originated as a result of β disintegration of one of the rhenium isotopes:

$$^{187}_{75}\mathrm{Re} \rightarrow {}^{187}_{76}\mathrm{Os} + \beta^- + \bar{\nu}$$

where β^- is a β-particle, $\bar{\nu}$ is a β-disintegration antineutrino, see Figure 1. This process is continuous and has resulted in the gradual accumulation of the radiogenic osmium isotope 187, especially in natural materials having a high rhenium content. As a consequence, the proportions between ^{187}Os and the other osmium isotopes varies over a wide range (2–5).

Researchers S. K. Kalinin and E. E. Fain from Kazakhstan have developed a set of analytical techniques, including the direct quantitative determination of osmium in ores and process products, a highly sensitive spectrochemical analysis of source materials and an isotopic analysis of osmium in concentrated samples (2, 6–10). The techniques make use of high-resolution spectroscopic equipment, as well as an appropriate consideration of physical and chemical properties of osmium and its spectral features. The limits of detection are within 10^{-4} to 10^{-7} per cent. The methods developed are believed to be highly reliable and capable of determining osmium with minimal error in samples of various compositions and with a wide range of concentrations.

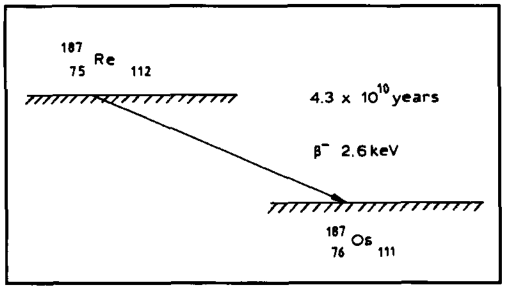

Fig. 1 Scheme of the disintegration of rhenium-187 to osmium-187

Types of Osmium Deposits

The techniques developed (2, 6–10) have assisted the authors in studying ores and minerals that occur in various deposits in the territory of the former Soviet Union, and in distinguishing the following major types of deposits where osmium isotopes are concentrated:

[i] Platinum ore and osmiridium deposits. The proportion of ^{187}Os relative to the total amount of osmium ranges from 1.4 to 1.7 per cent. The major isotope present is ^{192}Os. Isotopes ^{190}Os, ^{189}Os and ^{188}Os are also present.

[ii] Sulfide deposits of copper-nickel and other ores enriched in platinum elements where the isotope ^{187}Os is found in concentrations of 2 to 3 per cent and higher.

[iii] Copper-molybdenum deposits in secondary quartz rocks with rhenium content in molybdenites of 300 to 3000 g t^{-1}. Usually these ores contain only insignificant concentrations of non-radiogenic osmium isotopes. However, they do contain practically pure ^{187}Os isotope, in the range 99.0 to 99.9 per cent of the total osmium content.

[iv] Some rhenium-containing copper deposits, such as copper-bearing sandstones and shale, where the content of radiogenic osmium-187 (in

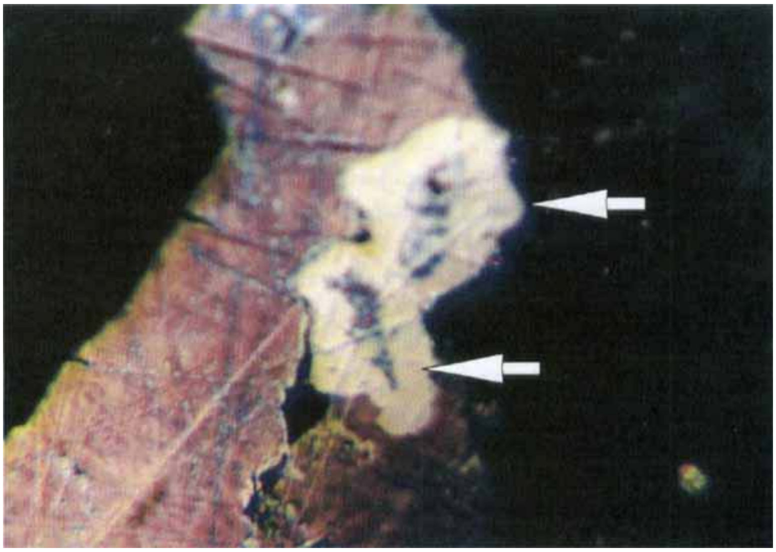

Fig. 2 A sample of bornite ore from the Zhezkazgan deposit in Kazakhstan, containing the mineral zhezkazganite $CuReS_4$. The arrows indicate:
pale area – zhezkazganite
pink area – bornite
black area – quartz
This mineral is very rare; similar samples are mined for copper, rhenium and radiogenic osmium-187

The photo was made in the reflective light immersion field.
Magnification × 1500

the osmium identified) is higher than 99.4 per cent.

The fourth type of deposit includes the Zhezkazgan sulfide copper ore deposit in Kazakhstan, see Figure 2, where the authors have discovered radiogenic osmium and have thoroughly studied its isotopic composition (2, 11). The research has shown that Kazakhstan has stable raw materials for the production of osmium-187 isotope. In this connection the possibility that radiogenic osmium production might be a byproduct of the comprehensive processing of sulfide copper ores has been addressed.

Distribution of Osmium in the Products from Sulfide Processing

Copper concentrates are processed via smelting operations, resulting in the production of cathode copper, sulfuric acid and ammonium perrhenate. However, because the initial osmium-187 content in concentrates is less than 0.000005 wt.% (0.05 g t^{-1}) the recovery of osmium from concentrates is not possible.

Therefore, in order to identify products with the highest osmium concentration, for the first time during processing of copper raw materials we studied the distribution of osmium giving the content in the gaseous phase of products generated in metallurgical, sulfuric acid and rare metal production (12). The results obtained demonstrated that during electric smelting of the charge, there is almost no sublimation of osmium. The major quantity of osmium (91 per cent of its content in the charge) remains in the matte (which has a high collecting capacity) and more than 6 per cent passes into the slag. In the conversion of matte, 56.8 per cent of the osmium passes into converter gases, 8.5 per cent into ventilation gases, and 26.5 per cent into various dusts in the gas purification systems (12).

During scrubbing the gases, before their use in the sulfuric acid production process, 40.2 per cent of the osmium passes into wash solution (wash sulfuric acid) and 17 per cent passes into slime. The osmium content of the slime is increased 400 times compared to its initial concentration.

The major source of rhenium production is the wash sulfuric acid which contains 100 to 400 mg l^{-1} rhenium and 0.3 to 0.5 mg l^{-1} osmium. Rhenium is recovered from wash sulfuric acid by liquid-liquid extraction, using trialkylamine in kerosene. Rhenium is recovered from impregnated organic matter in the form of solid ammonium perrhenate salt by treatment with ammonia solution. In the liquid-liquid extraction of the wash sulfuric acid, about 15 per cent of the osmium passes into the organic phase, while 25 per cent remains in the spent sulfuric acid – raffinate.

In the subsequent rhenium stripping, 9 per cent of the osmium is concentrated in the mother liquor generated from the solid-phase stripping. The osmium concentration in the mother liquor is 80 to 100 times higher than in the wash sulfuric acid. (The stripping, carried out by the ammonia solution, results in the formation of three phases: organic, mother liquor and salt. Over 20 years of practice at the plant have shown that there are no essential problems in separating these phases.)

Hence, it has been determined that the major osmium concentrators are wash sulfuric acid processing products – mother liquor generated from the solid-phase stripping of rhenium and lead slimes containing 15 to 40 mg l^{-1} and 15 to 50 g t^{-1} osmium, respectively. (Although more than 26 per cent of the osmium passes into various dusts, osmium concentration in dusts is not higher than 1 g t^{-1}, which does not make the dusts osmium concentrators (12).)

Recovery of Osmium

To develop effective processes for recovering osmium from solutions it is necessary to know the chemical forms in which osmium occurs. Therefore, the behaviour and chemical reactions of osmium compounds most probably formed during gas purification (in the system used for copper production: OsO_4 - H_2SO_4 - SO_2 - H_2O) have been studied (13).

A number of osmium(VI) sulfite complexes $[OsO_2(SO_3)_2(H_2O)_2]^{2-}$, $[OsO_2(SO_3)_{4-x}(H_2O)_x]^{-6+2x}$, and $[OsO_2(HSO_3)_x(SO_3)_{4-x}]_n^{-6+x}$ ($x = 0$ to 1, $n = 1$ to 4) were shown to form in solution, depending upon concentration, ratio of the constituents, the temperature, and time of interaction (ageing). The complex $[OsO_2(SO_3)_2(H_2O)_2]^{2-}$ is the most readily extracted into trialkylamine and during the extraction of rhenium from the wash sulfuric acid this complex is extracted with trialkylamine. (The other two complexes tend to aggregate and polymerise. This has been confirmed by comparative extraction of the complexes.)

The osmium extraction mechanism has been identified as outer-sphere substitution (13). During stripping with ammonia solution, the rhenium precipitates as a solid salt, but the osmium complex passes into the aqueous phase – the mother liquor generated from the solid-phase stripping of rhenium. This is a multicomponent ammonium sulfate system. To develop the process for recovering osmium from the mother liquor, the effect of varying physical and chemical factors which affect osmium(VI) conversions (concentration of constituents, temperature and solution ageing) have been investigated, during formation and storage of the mother liquor, in the following system: $[OsO_2(SO_3)_2(H_2O)_2]^{2-}$ - NH_4OH - $(NH_4)_2SO_4$ - H_2O (14).

The results of the investigations suggest possible chemical processes which may be occurring during osmium stripping (14). Decreases in ammonia concentration and increases in the ammonium sulfate content and temperature during stripping result in the formation of the insoluble ammonium form $(NH_4)_2[OsO_2(SO_3)_2(H_2O)_2]$ and its water-soluble N-coordinated ammine derivative, the anion part of which can be represented as $[OsO_2(SO_3)_2(NH_3)_2]^{2-}$. With increasing mother liquor storage time, the portion of soluble complex is increased. We have determined that water-soluble ammine derivatives of osmium are converted into the insoluble form $(NH_4)_2[OsO_2(SO_4)_2(NH_3)_2]$ in sulfuric acid solution (14).

The method for recovering osmium from the process mother liquor is based on the formation of the insoluble form. To produce concentrate suitable for refining, recovered osmium-containing residue was roasted under reducing conditions. Metallic radiogenic osmium was produced from concentrate using well-known methods of distillation, precipitation and high-temperature hydrogen reduction (15).

The implementation of this technology of processing mother liquor derived from solid-phase stripping of rhenium results in an average recovery from these solutions of 80 per cent of the osmium metal. (80 per cent is direct recovery of osmium from the mother liquor, the other 20 per cent in solid and liquid byproducts is recycled.) Analysis carried out by various methods (6–9) has shown that the chemical purity is 99.95 per cent and the isotopic purity is 99.4 ± 0.2 per cent of osmium-187.

Lastly, it should be noted that another source of radiogenic osmium production is sulfuric acid slimes resulting from copper production. The basis of the slime is lead sulfate. For effective osmium recovery at the refining stage, a preliminary enrichment of the slime by removal of lead compounds is beneficial. In this connection studies have been undertaken to develop a process for the production of osmium concentrate and tribasic lead sulfate (TBLS).

The process includes pre-carbonisation of slimes with sodium carbonate solution followed by leaching of the carbonate cake with nitric acid, precipitation of lead sulfate from the nitrate solutions, and production of TBLS from it (16). Osmium is concentrated in the resulting insoluble residue. Osmium in the concentrate is 25 times higher than in the initial slime. It is suitable for the separation and production procedures described above.

Conclusions

The technical feasibility of producing natural stable radiogenic osmium-187 isotope from rhenium-containing raw materials available in Kazakhstan has been demonstrated. The research performed suggests that osmium-187 could be produced in larger quantities and with higher purity than physical methods of separation allow. Further ways of utilising the ^{187}Os isotope would be a powerful incentive to commercialise production and could also contribute to the development of work on other naturally-occurring stable isotopes.

References

1 A. O. Nier, 'The isotopic constitution of osmium', *Phys. Rev.*, 1937, 52, (8), 885

2 S. K. Kalinin, E. E. Fain and K. E. Egizbaeva, "Stable Isotope Osmium-187", Publishing House 'Nauka', Alma-Ata, 1975 (in Russian)

3 S. N. Naldrett and W. F. Libby, 'Natural radioactivity of rhenium', *Phys. Rev.*, 1948, 73, (5), 47

4 H. Hintereberger, W. Herr and H. Voshage, 'Radiogenic osmium from rhenium-containing molybdenite', *Phys. Rev.*, 1954, 95, (6), 1690

5 W. Herr and E. Merz, 'Zur Bestimmung der Halwertszeit des 187 Re. Weitete Datierunden nach der Re/Os – Methode', *Z. Naturforsch.*, 1958, 13a, (3), 231

6 S. K. Kalinin and E. E. Fain, "Emissive Spectral Analysis of Mineral Raw Materials", Publishing House 'Nedra', Moscow, 1969 (in Russian)

7 K. E. Egizbaeva, S. K. Kalinin and E. E. Fain, 'Spectrographic determination of radiogenic osmium', *Zh. Priklad. Spektr.*, 1967, 7, (6), 924 (in Russian)

8 E. E. Fain, 'Spectrographic determination of rhenium and osmium', *Vestn. AN KazSSR*, 1963, (2), 53–59 (in Russian)

9 K. E. Egizbaeva and E. E. Fain, 'Spectrographic determination of osmium in ores and process products', in "Improvement of Methods for Spectral Analysis of Noble Metals", Publishing House 'Nedra', Moscow, 1967, 46–52 (in Russian)

10 S. K. Kalinin and E. E. Fain, 'Rhenium and radiogenic osmium in natural objects', *Izv. AN KazSSR, Ser. Geol.*, 1977, (6), 1–7 (in Russian)

11 T. A. Satpaeva, S. K. Kalinin and E. E. Fain, 'About contents of osmium in Zhezkazgan ore deposit', *Vestn. AN KazSSR*, 1960, (8), 29–31 (in Russian)

12 A. N. Zagorodnyaya, Z. S. Abisheva and T. N. Bukurov, 'Rhenium and osmium distribution with respect to products resulting from the processing sulfide copper raw materials', *Tsvetn. Met.*, 1997, (9), 47–50 (in Russian)

13 Z. S. Abisheva, N. M. Bodnar and T. N. Bukurov, 'Osmium behavior during extraction of rhenium from sulfuric acid solutions', *Tsvetn. Met.*, 1994, (9), 33–35 (in Russian)

14 Z. S. Abisheva, I. N. Parshina, E. G. Bochevskaya and V. Zh. Ushanov, 'Chemical conversions of osmium(VI) sulfite complexes in ammonia-sulfate solutions', *Hydrometallurgy*, 1998, 50, 271–280

15 A. Illis, B. I. Brandt and A. Manson, 'The recovery of osmium from nickel refinery anode slimes', *Metall. Trans.*, 1970, 1, (2), 431–434

16 Z. S. Abisheva, A. N. Zagorodnyaya, B. B. Beisembaev and M. C. Abaidildinov, 'Complex treatment of lead slimes of copper production', Proc. 7th Int. Symp. Mineral Processing, Istanbul, Turkey, 15th–17th Sept., 1998, A. A. Balkema, Rotterdam, 1998, p. 451

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