

Neglected neptunium

Jim Ibers talks about neptunium, an element that has remained largely unnoticed despite the flurry of activity devoted to its neighbours in the periodic table, uranium and plutonium.

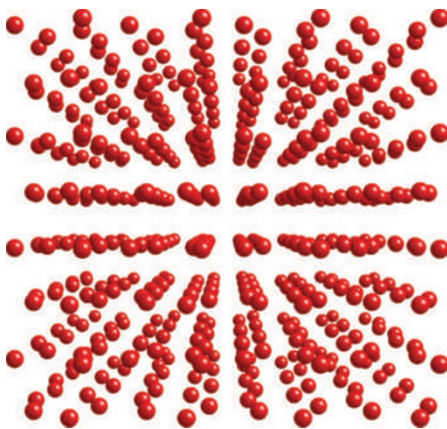
The actinides, the radioactive chemical elements beginning with element 89 (actinium) and extending to element 103 (lawrencium), are a neglected part of chemical pedagogy, at least in the USA. As a result, some chemists may not know the names of most of these elements, or where they lie in the periodic table, but most would guess correctly from knowledge of the Solar System that somewhere in the periodic table uranium, neptunium and plutonium would be found in that order. Some might even guess correctly that this order reflects their year of discovery.

However, it does not reflect the relative attention these elements have received. Although neptunium is barely talked about, uranium and plutonium are famous — some would say infamous — because in the early 1940s isotopes of uranium and plutonium were found to be fissile, meaning they can sustain a nuclear chain reaction, and hence had weapons applications. Neptunium was also known to be fissile, but the quantity needed made it unattractive for such applications.

Yet neptunium ought to be famous because it was the first actinide element to be synthesized. In a classic study in 1940, McMillan and Abelson bombarded a thin layer of UO_3 with neutrons from a cyclotron¹. Investigation of the chemistry of the product that possessed a 2.3-day half-life led them to conclude that it was element 93 with a mass of 239, now written as $^{239}_{93}\text{Np}$. They also speculated on the nature of the daughter product obtained from the radioactive decay of their new element, soon characterized² by Seaborg and co-workers as an isotope of element 94 (plutonium). Much of this work was classified for the next five years.

Now, about 22 isotopes of neptunium have been characterized. Of these, ^{237}Np is the most stable, with a half-life of 2.14×10^6 years — too short for any significant

quantity of primordial ^{237}Np to remain today, 4.5×10^9 years after the Earth's formation. The mass of ^{237}Np being formed from various nuclear-decay processes in the Earth's crust is estimated to be only about 10^{-12} times that of uranium-containing minerals. Thus, neptunium could not be 'discovered'; it had to be synthesized. Today, the production of plutonium in nuclear reactors is the main source of neptunium.



Extended view of the crystal structure of neptunium.

The need to characterize new actinide elements, and to separate their compounds from each other and those of the lanthanides, has led to extensive knowledge of actinide solution chemistry. Here, oxidation states are critical: these dictate acid–base properties, coordination chemistry and solubilities in aqueous and non-aqueous solvents. In solution the elements americium to lawrencium closely resemble one another and often exhibit oxidation states of +3, as do the lanthanides. In contrast, uranium has formal oxidation states of +3 to +6, and neptunium and plutonium have those oxidation states as well as +7.

These differences are the basis for sophisticated procedures, such as the PUREX (plutonium–uranium extraction) process for removing uranium and

plutonium from nuclear spent fuels, in which neptunium and small amounts of the heavier actinides are rejected into a high-level radioactive liquid waste. New advanced commercial processes are needed to remove ^{237}Np , which will otherwise become the main contributor to the total radiation from these wastes in about 10^4 years — a time being discussed at present for their containment.

As opposed to their solution chemistry, knowledge of the solid-state chemistry of the lighter actinides is far less extensive. Even here, neptunium is the 'stepchild'. Pure metals and compounds of uranium and plutonium have been produced in far greater quantities than those of neptunium. In the solid state one finds some surprising differences in structures and properties. For example, the crystal structure of neptunium under ambient conditions differs from those of uranium and plutonium, although the structural complexity of plutonium metal is another subject altogether. The intermetallic compounds UCoGa_5 and NpCoGa_5 do not superconduct, whereas PuCoGa_5 is a non-conventional high-temperature superconductor. Unlike isotopes of uranium or plutonium, ^{237}Np is one of the best Mössbauer nuclei in the periodic table — Mössbauer spectroscopy is a valuable tool for probing valence electrons, and hence oxidation states and chemical bonding.

Many surprises await the development of more extensive knowledge of the chemistry of neptunium compounds, particularly the solid-state chemistry. The renaissance of nuclear energy may well accelerate this development. □

JIM IBERS is in the Department of Chemistry at Northwestern University, USA.
e-mail: ibers@chem.northwestern.edu

References

1. McMillan, E. & Abelson, P. H. *Phys. Rev.* **57**, 1185–1186 (1940).
2. Seaborg, G. T., McMillan, E. M., Kennedy, J. W. & Wahl, A. C. *Phys. Rev.* **69**, 366–367 (1946).

