Curious curium

From secretive beginnings to serving in missions on Mars, **Rebecca J. Abergel** and **Eric Ansoborlo** take a look at the glowing mark curium has left on contemporary science and technology.

Ithough perhaps not as renowned as its actinide siblings plutonium and uranium, the fourth transuranic element — named in honour of Pierre and Marie Curie — has a story that is intertwined with that of the twentieth century.

The first isotope of element 96, ²⁴²Cm, was prepared in 1944 by Seaborg, James, and Ghiorso through bombardment of ²³⁹Pu with helium nuclei. This finding was quickly followed by that of element 95 (americium) but the news of both discoveries were kept under wraps during the war and only announced by Seaborg himself on 11 November 1945, Armistice Day, in a somewhat impromptu manner on the 'Quiz Kids' American radio program.

Today curium is mostly produced by irradiation of uranium and/or plutonium oxides with neutrons in nuclear reactors: about 20 g of curium can be produced from 1 ton of spent nuclear fuel. We now know over twenty isotopes of curium with mass numbers ranging from 232 to 252, all of which are radioactive and primarily α -particle emitters, with ²⁴²Cm and ²⁴⁴Cm (respective half-lives of 163 days and 18.1 years) accounting for 90% of those produced in the nuclear fuel cycle.

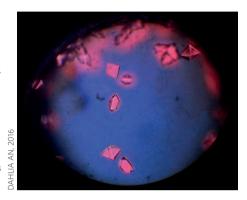
Because of their high specific activities $(10^{12} \text{ to } 10^{15} \text{ Bq g}^{-1})$, ²⁴²Cm and ²⁴⁴Cm were investigated as heat sources for power generation in spacecraft programmes, but abandoned as costs and shielding requirements proved prohibitive. ²⁴⁴Cm still went on to be sent to space, as a source of a-particles in alpha particle X-ray spectrometers for analysis of rocks and soil on Mars. ²⁴²Cm served to produce the more stable ²³⁸Pu for thermoelectric generation in devices including cardiac pacemakers. Although less common, isotopes ²⁴⁵Cm and ²⁴⁸Cm recently made headlines as targets in the synthesis of one of the newest elements of the periodic table, livermorium.

Despite these uses, the high activity of curium isotopes has mainly been considered

Cf

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Es



an issue because it significantly contributes to the radiotoxicity of nuclear waste. Most curium research has therefore focused on characterizing its physico-chemical properties in the quest for actinide separation, recovery, and recycling processes.

In most compounds and solutions curium is present in the trivalent oxidation state +3, the stability of which is attributed to the half-filled $5f^7$ electron shell configuration although a few +4 and +6 compounds are also known, such as CmO₂ and CmO₃. The similarities between curium and the other lanthanides, which stem from the predominance of this +3 state, make their separation a challenging task. In fact, elements 95 and 96 were so difficult to separate from each other, and from the rare-earth metals, that the Seaborg group nicknamed them 'pandemonium' (demons or hell in Greek) and 'delirium' (madness in Latin).

Setting curium aside from other actinides is its inherent strong fluorescence (attributed to relaxation through f-f electronic transitions), which gives rise to bright orange luminescence¹. Because the energy and intensity of curium emission depend on the coordination of the metal ion, time-resolved laser-induced spectroscopy has been used extensively to characterize curium compounds. The high sensitivity of this technique is important for the detection and analysis of different species of curium in environmental and biological media², especially relevant to current issues involving waste storage, remediation and potential transport in terrestrial and freshwater ecosystems. As hard Lewis acids, curium ions form strong hydrolysis complexes in neutral to basic solutions and very stable compounds with hard bases such as oxygen or fluoride donors. Sorption studies of $\rm Cm^{3+}$ at the hydrated $\rm Al_2O_3$ surface using an $\rm Al_{31}O_{60}H_{21}$ model cluster have evidenced bonding with both ionic and covalent character³.

Even on a small scale, accidental release of curium into the environment would be disastrous because it is extremely hazardous to humans, and is in particular strongly retained by the liver and skeleton. The high radioactivity of its isotopes would result predominantly in radiation-induced injury rather than chemical toxicity: the lethal ²⁴⁴Cm dose for a 70 kg human is only ~250 MBq, or ~80 μ g. Fear of such an event has sparked the use and development of hard oxygen-donor, high-affinity ligands that may serve as sequestering agents⁴.

Its radioactive properties and its ability to form fluorescent complexes have inspired much curiosity about curium, and will no doubt continue to do so, perhaps in particular towards curium remediation and decontamination strategies.

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Mt

Rg

Cn

113

Ds

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Hs

Lr

Rf

Db

Sg

Bh

Fm Md No

516

An

Pu