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Technology Offer

Exploitation of mineral cesium from mineral sources

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Prof. Klaus-Richard Pörschke and co-workers at the MPI for Coal Research developed a novel cyclic process for the quantitative extraction of cesium with 100% selectivity from any given aqueous or acidic solution, irrespective of the other components.

Background

Natural cesium is used in small quantities in a variety of contexts, especially with experimental or developmental purposes.

Natural cesium finds applications in the chemical process industry, primarily as an ingredient of metal-ion catalysts and in the petroleum refining industry for the removal of sulfur from crude oil. It is used as an ingredient in specialty glasses for fiber optics and night-vision devices. Thanks to a wide-spectrum of photo-emissive properties cesium is used in television image devices, solar photovoltaic cells, and other types of photoelectric cells. Perhaps one of its best known applications is the use in the super-accurate atomic cesium clock for the world's timekeeping systems standard. The application that requires the most cesium is probably as a specialty high-density component in drilling mud used for petroleum exploration. The main source of cesium that is economically viable is pollucite [$\text{Cs}_2\text{Al}_2\text{Si}_4\text{O}_{12}$], with the largest deposit being in located at Bernic Lake, Canada.

Cesium is extracted from pollucite mainly by acid digestion using hydrobromic, hydrochloric, hydrofluoric, or sulfuric acids. Digestion of pollucite in hydrochloric acid at elevated temperature yields an impure CsCl solution that is converted to double chloride salts, such as cesium antimony chloride [$4\text{CsCl}:\text{SbCl}_3$], cesium iodine chloride [Cs_2ICl], or cesium hexachloroacetate [$\text{Cs}_2(\text{CeCl}_6)$], which are purified and then decomposed by hydrolysis to yield purified CsCl.

Pollucite may also be digested in hot 35 to 45 percent sulfuric acid to yield a solution from which cesium alum is precipitated. The alum is roasted with 4 percent carbon and then leached to yield a Cs_2SO_4 solution; the sulfate may then be converted to CsCl.

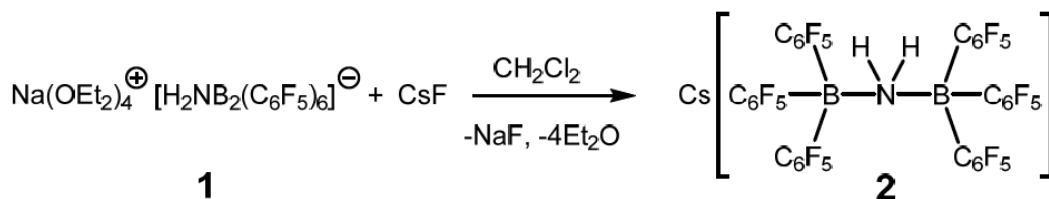
Cesium chloride obtained by the methods described above can be reduced at 700 to 800 °C with calcium or barium and the cesium metal is distilled and collected.

Technology

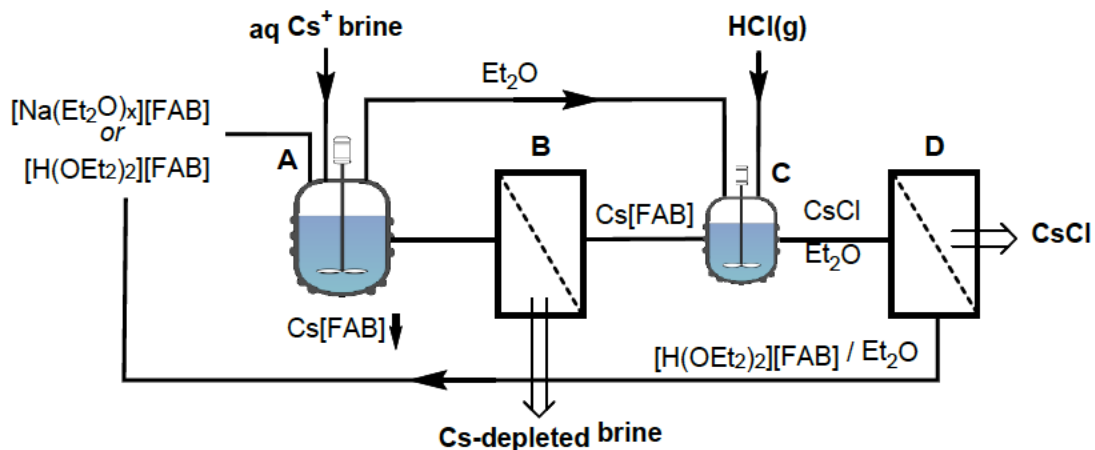
The technology described herein allows a cyclic process for the quantitative extraction of cesium with 100% selectivity from any given aqueous or acidic solution, irrespective of the other components.



After grinding and acidic digestion of the mineral, the acidic aqueous cesium ion containing brine may be treated with the highly hydrophobic perfluoroaryl borate (FAB) ligand of (1).



The complex $\text{Cs}[\text{H}_2\text{NB}_2(\text{C}_6\text{F}_5)_6]$ (**2**) precipitates or can be extracted quantitatively from water (dielectric constant 78.4) or acidic solutions containing the cesium ions in concentration as low as a few ppm. Once (**2**) is isolated from water, it can be cleaved, e.g. by HCl gas in diethyl ether to quantitatively precipitate pure CsCl, with recovery of the perfluoroaryl borate weakly coordinating anion (**1**) in the form of $[\text{H}(\text{OEt}_2)_2]^+[\text{H}_2\text{NB}_2(\text{C}_6\text{F}_5)_6]^-$. Feeding the latter compound back to an aqueous cesium brine and evaporating the organic solvent allows for a cyclic process in which the cesium ion is 100% selectively and quantitatively extracted from any aqueous or acidic cesium ion solution and converted into, e.g., pure CsCl without formation of byproducts. This cyclic process has the potential to substitute the multistep recrystallization processes currently used, which are responsible for the high price of cesium compounds.



FAB process for the exploitation of cesium-containing mineral brines

Compound (**1**) can be synthesized by reacting 2 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ in a suspension of sodium amide in diethyl ether to obtain a colorless crystal in high yield.

Patent Information

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EP2017710178, AP/P2018010989, AU2017230853, CA3015721, EA201892546,
IN201817033737, US16/083043 currently under examination.

Literature

David Pollak, Richard Goddard, Klaus-Richard Pörschke: "Cs $[\text{H}_2\text{NB}_2(\text{C}_6\text{F}_5)_6]$ Featuring an Unequivocal 16-Coordinate Cation", *J. Am. Chem. Soc.* 2016, **138**, 9444–9451

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