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Thorium dioxide pellets could be the nuclear fuel of the future if proliferation concerns can be addressed.

## Thorium fuel has risks

Simple chemical pathways open up proliferation possibilities for the proposed nuclear ‘wonder fuel’, warn **Stephen F. Ashley** and colleagues.

**T**horium is being touted as a potential wonder fuel. Proponents believe that this element could be used in a new generation of nuclear-power plants to produce relatively safe, low-carbon energy with more resistance against potential nuclear-weapons proliferation than uranium. Although thorium offers some benefits, we contend that the public debate is too one-sided: small-scale chemical reprocessing of irradiated thorium can create an isotope of uranium that could be used in nuclear weapons, raising proliferation concerns.

Global stocks of thorium are uncertain, but the element is thought to be three to four times more naturally abundant than uranium

(see ‘World thorium deposits’). The silver-white metal is often encountered as oxide waste from the mining of rare-earth elements, and substantial thorium deposits are found in Australia, Brazil, Turkey, Norway, China, India and the United States. The last three of these, together with the United Kingdom, are exploring the potential use of thorium in civil nuclear-energy programmes.

One of many voices proposing the deployment of new thorium-based molten salt reactors (see page 26) is the Weinberg Foundation, a non-profit organization based in London that promotes thorium-fuelled technologies to combat climate change. Molten salt reactors were developed in the 1960s and

use liquid nuclear fuels, that can incorporate thorium, rather than solid fuel rods. They are claimed to be more efficient and less susceptible to meltdown-related accidents than existing technologies. Small modular reactors, such as high-temperature gas-cooled reactors that use solid thorium-based fuels, are also being pursued, most notably by China.

Naturally-occurring thorium is made up almost entirely of thorium-232, an isotope that is unable to sustain nuclear fission. When bombarded with neutrons, thorium is converted through a series of decays into uranium-233, which is fissile and long-lived — its half-life is 160,000 years. A side product is uranium-232, which decays into other ▶

► isotopes that give off intense  $\gamma$ -radiation that is difficult to shield against. Spent thorium fuel is typically difficult to handle and thus resistant to proliferation.

We are concerned, however, that other processes, which might be conducted in smaller facilities, could be used to convert  $^{232}\text{Th}$  into  $^{233}\text{U}$  while minimizing contamination by  $^{232}\text{U}$ , thus posing a proliferation threat. Notably, the chemical separation of an intermediate isotope — protactinium-233 — that decays into  $^{233}\text{U}$  is a cause for concern.

Thorium is not a route to a nuclear future that is free from proliferation risks. Policies should be strengthened around thorium's use in declared nuclear activities, and greater vigilance is needed to protect against surreptitious activities involving this element.

### PROTACTINIUM PATHWAY

The decay path of thorium is well understood. If bombarded with neutrons, isotopically pure  $^{232}\text{Th}$  forms  $^{233}\text{Th}$ , which has a half-life of 22 minutes and  $\beta$ -decays to  $^{233}\text{Pa}$ . That isotope has a half-life of 27 days and  $\beta$ -decays to  $^{233}\text{U}$ , which can undergo fission. The International Atomic Energy Agency (IAEA) considers 8 kilograms of  $^{233}\text{U}$  to be enough to construct a nuclear weapon<sup>1</sup>. Thus,  $^{233}\text{U}$  poses proliferation risks.

Although  $^{233}\text{U}$  is not used today in commercial reactors, the United States accumulated two tonnes of it during the cold war. Plans to dispose of much of it by burial are controversial and pose security and safety risks, according to a 2012 report<sup>2</sup>.

The chemical reprocessing needed to separate  $^{233}\text{U}$  from spent nuclear fuel requires major infrastructure, such as large

reprocessing plants, which are difficult to hide. With thorium fuel, the presence of highly radiotoxic  $^{232}\text{U}$  means that the spent fuel must be handled using remote techniques in heavily-shielded containment chambers.

After irradiating thorium with neutrons for around one month, chemical separation of  $^{233}\text{Pa}$  could yield minimal  $^{232}\text{U}$  contamination, making the  $^{233}\text{U}$ -rich product easier to handle. If pure  $^{233}\text{Pa}$  can be extracted, then it merely needs to be left to decay to produce pure  $^{233}\text{U}$ . The problem is that neutron irradiation of  $^{232}\text{Th}$  could take place in a small facility, such as a research reactor, of which around 500 exist worldwide. The  $^{232}\text{Th}$  need not be part of a nuclear-fuel assembly nor be involved in energy generation.

It has been demonstrated that around 200 g of thorium metal could produce 1 g of  $^{233}\text{Pa}$  — and hence 1 g of  $^{233}\text{U}$  — if exposed to neutrons at levels typically found in power reactors and some research reactors for a month, followed by protactinium separation<sup>3</sup>. Thus, only 1.6 tonnes of thorium metal would be required to produce the 8 kg of  $^{233}\text{U}$  required for a weapon. This amount of  $^{233}\text{U}$  could feasibly be obtained by this process in less than a year.

The separation of protactinium from thorium is not new. We highlight two well-known chemical processes — acid-media techniques<sup>3,4</sup> and liquid bismuth reductive extraction<sup>5-7</sup> (see 'Ways to obtain pure protactinium') — that are causes for concern, although there may be others. Both methods use standard nuclear-lab equipment and hot cells — containment chambers in which highly radioactive materials can be manipulated safely. Such apparatus is not

necessarily subject to IAEA safeguards.

The most common acid-media technique uses manganese dioxide to precipitate the protactinium as protactinium oxide<sup>4</sup>. Any radiotoxic uranium by-products are dissolved in acid and removed during the precipitation. This method was used in the 1960s by researchers at Oak Ridge National Laboratory in Tennessee to extract 1 g of  $^{233}\text{Pa}$  from 200 g of an irradiated thorium compound<sup>3</sup>.

The main difficulty is that  $\beta$ -decay from each gram of  $^{233}\text{Pa}$  produces 50 watts of heat<sup>3</sup>, which complicates the handling. Scaling up the production of  $^{233}\text{Pa}$  would not be easy, but given the possibility of parallel processing of small quantities, our concerns over this technique remain.

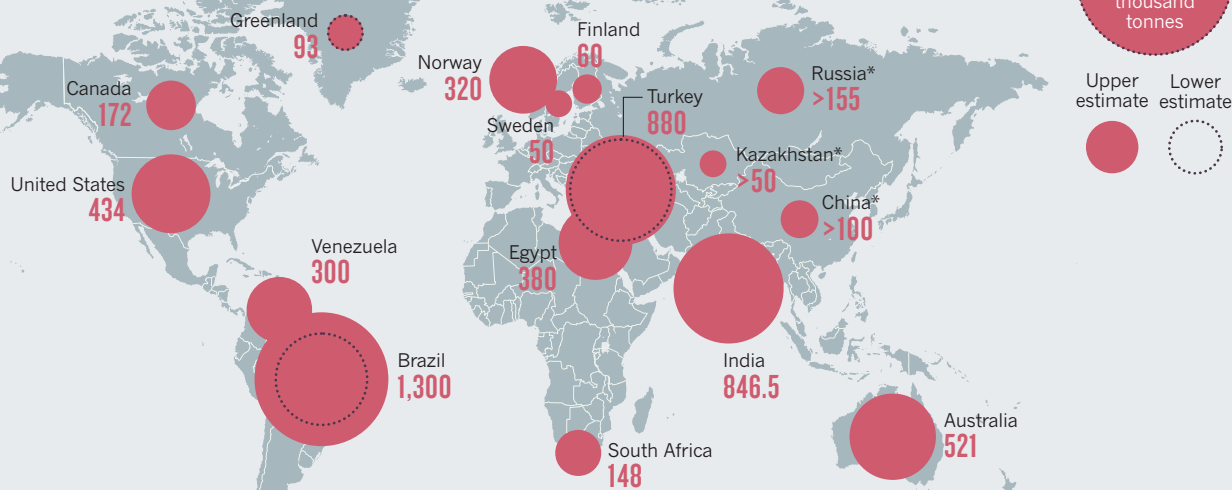
A second chemical method, suggested in the 1970s (refs 5,7), is being revisited for next-generation molten salt reactors (see, for example, ref. 8). These use thorium-based liquid fuels containing a fluoride-based salt with the typical composition  $^7\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ . The process is pyrochemically based, using high temperature oxidation-reduction reactions. It involves first fluorination and then extraction using molten bismuth to obtain protactinium.

The infrastructure for pyrochemistry is more complex than for acid-media techniques, and scaling it up is even more challenging. Pyrochemical reprocessing technologies are in their infancy. But we are concerned that such a technique could be used in small batches<sup>9</sup> to slowly accumulate protactinium.

Given the need for access to a research or power reactor to irradiate thorium, the most likely security threat stems not from terrorist

## WORLD THORIUM DEPOSITS

Thorium oxides, silicates and phosphates are found worldwide, often alongside rare-earth elements. Thorium is not yet mined commercially, and abundances are only approximately known in most countries. Numbers show upper estimates of identified thorium reserves (in thousand tonnes).



\*Upper estimate not known.

## THORIUM CHEMISTRY

## Ways to obtain pure protactinium

**Acid-media techniques**

After irradiating thorium-based materials for one month, the canisters are removed and dissolved in nitric acid<sup>3,4</sup>. The resultant sludge goes through three stages of filtration. Protactinium is separated during the second stage, by co-precipitation with MnO<sub>2</sub> (ref. 3). It is separated further in the third stage using iodic acid and combustion to form protactinium oxide, containing only <sup>233</sup>Pa. Any traces of <sup>232</sup>Pa (half-life of 1.3 days) and <sup>234</sup>Pa (half-life of 6.7 hours), formed by competing reactions, decay to <sup>232</sup>U and <sup>234</sup>U during the dissolution stage, in which they are removed. Left to decay, <sup>233</sup>Pa becomes ultra-pure (>99%) <sup>233</sup>U.

**Liquid bismuth reductive extraction**

Fluorine is passed over the irradiated molten-salt fuel<sup>6</sup> to convert approximately 99% of the uranium to UF<sub>6</sub>, which can then be removed<sup>5-7</sup>. The remaining protactinium, fission products and unreacted uranium are fed into a column containing liquid bismuth, lithium and thorium. The fission products are retained in the salt, and the protactinium and uranium are extracted in the liquid bismuth. Further fluorination of the bismuth removes the remaining uranium, including <sup>232</sup>U, <sup>234</sup>U and other isotopes. The <sup>233</sup>Pa left behind is highly pure and decays into <sup>233</sup>U.

organizations but from wilful proliferating nation states. We have three main concerns:

First, nuclear-energy technologies that involve irradiation of thorium fuels for short periods could be used covertly to accumulate quantities of <sup>233</sup>U by parallel or batch means, perhaps without raising IAEA proliferation flags.

Second, the infrastructure required to undertake the chemical partitioning of protactinium could be acquired and established surreptitiously in a small laboratory.

Third, state proliferators could seek to use thorium to acquire <sup>233</sup>U for weapons production. These three points should be included in debates on the proliferation attributes of thorium.

**MONITORING THORIUM**

The emergence of thorium technologies will bring problems as well as benefits. There is a need for appropriate monitoring of thorium-related nuclear technologies within declared and undeclared facilities. The IAEA and the Nuclear Suppliers Group, the group of countries that controls nuclear exports, have a role to play in observing such developments.

Steps are needed to control the short-term irradiation of thorium-based materials with neutrons. Similarly, civil nuclear-fuel cycles involving in-plant reprocessing of thorium-based fuels should be avoided.

Hot cells are a key technology in protactinium separation. The Additional Protocol of the Nuclear Non-Proliferation Treaty<sup>10</sup> requires disclosure of large hot-cell facilities. The associated size cut-off is potentially important with protactinium pathways in mind. We are comforted that large hot-cell facilities are treated by the IAEA as nuclear technologies that can be 'dual use' for military or peaceful purposes, but concerns will always remain about hidden undeclared facilities.

Thorium is not as benign as has been suggested and we call for greater debate on its associated risks. In this way, a safer nuclear future can be assured. ■

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