Mystical Material Might Help Solve Global Energy Problems

Daniel T. Sun and Wendy L. Queen

Laboratory for Functional Inorganic Materials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL-Valais), CH-1051 Sion, Switzerland

A team led by Guangshan Zhu of Northeast Normal University in China has cleverly developed a porous material that can extract uranyl species from the sea. This type of work is becoming exceedingly important as there is an overwhelming amount of data that make the existence of climate change undeniable. For instance, since 1998, we have experienced 10 of the hottest years on record. In addition to heat-waves, Arctic glaciers are melting and oceans are rising, and we are experiencing extreme weather patterns globally. The potentially dire consequences that currently face humanity necessitate our conversion from fossil fuels toward sustainable, cleaner energy sources. Although science aims to develop a diverse portfolio of prospective energy sources, nuclear power is an important avenue to explore; however, for nuclear energy production to become feasible long-term and on larger scales, a sustainable supply of uranium is essential.

Uranium-235 is a naturally occurring fissile isotope that is used in nuclear power production. Unfortunately, current uranium reserves on land, estimated to be ~4.85 million tons, will likely be exhausted in the coming decades. This limited, diminishing supply is driving efforts to develop new technologies able to harvest uranyl species (UO$_2^{2+}$) directly from the sea. While it is estimated that the sea contains approximately 4.5 billion tons of this commodity, an amount able to help supply the world with energy, uranyl extraction is extremely challenging. This difficulty stems from low concentrations that are less than 3 μg per liter. To put this in perspective, over 300,000 L of seawater would need to be filtered to extract a single gram of uranyl.

While it is estimated that the sea contains approximately 4.5 billion tons of this commodity, an amount able to help supply the world with energy, uranyl extraction is extremely challenging. This difficulty stems from low concentrations that are less than 3 μg per liter. To put this in perspective, over 300,000 L of seawater would need to be filtered to extract a single gram of uranyl.
To mitigate the selectivity issue, Zhu et al. have designed a porous aromatic framework referred to as MISS-PAF-1, which is constructed from predefined organic building units. Such porous organic and hybrid frameworks are an emergent topic in separation science that is popularized due to the easy chemical modification of the organic struts. Using simple synthetic techniques, various chemical functionality can be readily appended to the internal pore surface that is tailored for a specific use. This designability, in combination with high internal surface areas, promotes a wide range of applications such as gas and liquid separations, small-molecule storage, and catalysis.

The unique aspect of the work published in this issue of *ACS Central Science* is how the authors engineer selective moieties onto the internal pore surface of PAF-1.

This work illustrates a novel methodology to endow materials with selectivity for a separation that is deemed highly difficult. Not only were the authors able to engineer specific functional groups into the framework, but they also encode specific coordination environments, which lends to an impressive performance that clearly surpasses state of the art materials.

The resulting material, MISS-PAF-1, has a BET surface area of 412 m²/g and offers unprecedented selectivity for uranyl over the aforementioned common inorganic interferents. The selectivity factors, which are greater than 100, are far superior to materials prepared using the traditional approach. In fact, MISS-PAF-1 can extract 99.97% of uranyl from a 5 ppm solution, reducing concentrations below 1.6 ppb in less than 120 min. It should be noted that 1.6 ppb is below the aforementioned concentration of uranyl in seawater, which provoked the authors to think about extraction directly from the sea. The material also exhibits a maximum adsorption capacity of 253 mg of uranyl per gram of adsorbent, and the calculated distribution coefficient is $1.4 \times 10^3$ mL/g, also illustrating an extremely high affinity toward the targeted species. In addition to these already strong points, MISS-PAF-1 has been regenerated 10 times with minimal to no loss in extraction capacity. Last and most impressively, the authors soaked the material in the sea for 56 days. Afterward, it was found to contain 5.79 mg of uranyl per gram of adsorbent. This value is already 4 times higher than other reported materials tested under similar conditions.

Uranyl is indeed found in one of the world’s most complex matrices, the sea. As such, this work illustrates a novel methodology to endow materials with selectivity for a separation that is deemed highly difficult. Not only were the authors able to engineer specific functional groups into the framework, but they also encode specific coordination environments, which lends to an impressive performance that clearly surpasses state of the art materials. While the material’s extraction capacity from the sea is still quite low, the tunability of this class of frameworks provides much hope for future optimization. It is envisioned that these synthetic methods could certainly be employed in a number of different types of porous organic and hybrid frameworks that have varying pore shapes, sizes, and volumes, allowing one to significantly enhance capacities and potentially also extraction rates.
The scientific advancement made by Zhu et al. is related to the precision with which the authors are able to design a material for a targeted species. As such, this work provokes the question: what will futuristic mining activities look like? One can think of many other high-value commodities that are likewise found in inconceivable places like the sewage or the sea. Should capacities and extraction rates be boosted, work of this kind could aid in the development of a number of new, energetically efficient, and environmentally mindful extraction processes.

Author Information
E-mail: wendy.queen@epfl.ch.

ORCID
Wendy L. Queen: 0000-0002-8375-2341

REFERENCES
(1) Yuan, Y.; Meng, Q.; Faheem, M.; Yang, Y.; Li, Z.; Wang, Z.; Deng, D.; Sun, F.; He, H.; Huang, Y.; Sha, H.; Zhu, G. A Molecular Coordination Template Strategy for Designing Selective Porous Aromatic Framework Materials for Uranyl Capture. ACS Cent. Sci. 2019, in press. DOI: 10.1021/acscentsci.9b00494
(2) The Intergovernmental Panel on Climate Change: Global Warming of 1.5 °C. https://www.ipcc.ch/sr15/.
(3) Kottasova, I. France endures its hottest day ever as Europe swelters in heat wave. https://edition.cnn.com/2019/06/28/europe/france-record-temperature-heatwave-intl/index.html.
(4) Winski, D.; Osterberg, E.; Kreutz, K.; Wake, C.; Ferris, D.; Campbell, S.; Baum, M.; Bailey, A.; Birkel, S.; Introne, D.; Handley, M. A. 400-Year Ice Core Melt Layer Record of Summertime Warming in the Alaska Range. Journal of Geophysical Research: Atmospheres 2018, 123, 3594–3611.
(5) Melet, A.; Meyssignac, B.; Almar, R.; Cozannet, D. L. Underestimated wave contribution to coastal sea-level rise. Nat. Clim. Change 2018, 8, 234–239.
(6) Sholl, D. S.; Lively, R. P. Seven chemical separations: to change the world: purifying mixtures without using heat would lower global energy use, emissions and pollution– and open up new routes to resources. Nature 2016, 532, 435.
(7) Abney, C. W.; Mayes, R. T.; Saito, T.; Dai, S. Materials for the Recovery of Uranium for Seawater. Chem. Rev. 2017, 117 (23), 13935–14013.
(8) Das, S.; Heasman, P.; Ben, T.; Qiu, S. Porous Organic Materials: Strategic Design and Structure-Function Correlation. Chem. Rev. 2017, 117 (3), 1515–1563.
(9) Singh, D. K.; Mishra, S. Synthesis and characterization of UO₂²⁺-ion imprinted polymer for selective extraction of UO₂²+. Anal. Chim. Acta 2009, 644, 42.