Tapping into a new lithium source

Deep geothermal drilling is one of the brightest rays of hope for the transition to green heating. It also comes with the positive side effect that it can not only be used to generate eco-friendly electricity and heat, but also to extract lithium for battery manufacturing.

By Dr. Janine van Ackeren

Geothermal systems carry heat from far below the Earth's surface — and soon, they may also be bringing the chemical element lithium (Li³) with them, thanks to Fraunhofer technology.

1 mbry

D

eep geothermal systems seem like something of a magical panacea for our climate-conscious age. Their most attractive feature is their potential for generating green

electricity and heat, even to the point of serving as an alternative to heat pumps. The systems bore down to depths of thousands of meters to tap into saline aquifers with a temperature of around 80 degrees; this hot groundwater is then transported to the surface, where it powers electricity generation turbines and supplies many households with heating via district heating networks. But the benefits of geothermal systems don't stop there: The boreholes also represent a new avenue for extracting lithium resources — in Germany, without harming the environment and with very little extra effort. Researchers at the Fraunhofer Institute for Physical Measurement Techniques IPM in Freiburg and the Karlsruhe Institute of Technology (KIT) have teamed up to prove that this goal is technically feasible. "The salty water that gets

pumped to the Earth's surface through geothermal boreholes contains around 200 milligrams of lithium per liter," explains Dr. Carl Basler, a project manager at Fraunhofer IPM. "In other words, one borehole should be able to deliver enough lithium for around 20,000 car batteries every year — and that more or less as a side product. In the Upper Rhine Valley alone, it would be possible to set up ten of these facilities."

Lithium-ion batteries are used on a mass scale in many modern products, ranging from electric cars to smartphones and tablets. These batteries could also play an important role when it comes to electrifying applications

during the heating transition — i.e., heat pumps — by serving as storage for the electricity produced by photovoltaic systems. However, as lithium has yet to be mined in Germany, the country is entirely dependent on imports, leaving it vulnerable to all the pitfalls associated with such international relationships. A domestic source of lithium could significantly reduce the pressure in this area.

Researchers at KIT are working to develop the technology required to extract lithium from the water that is pumped to the surface. To do this, they feed the groundwater through a sorbent, i.e., a material that specifically

"One borehole should be able to deliver enough lithium for around 20,000 car batteries every year — and that more or less as a side product."

Dr. Carl Basler, Fraunhofer IPM

binds the lithium salt, while allowing all the other salts that are dissolved in the water to flow on through unimpeded. If all the binding sites in the sorbent material are occupied, then the sorbent is saturated with lithium, and the team can disconnect it from the borehole water supply and send a desorption solution through instead. This redissolves the bound lithium, which can then be precipitated out of the solution by means of standard processes. The KIT researchers are currently focusing their energies on developing the optimal sorbent material.

Analysis process supports lithium extraction

One important question that crops up in the course of this mode of lithium extraction is: when does the sorbent material reach saturation? After all, the lithium content in the groundwater varies from borehole to borehole, and once the sorbent is saturated, the water will flow on through, taking its dissolved lithium with it. Until

> now, it has only been possible to answer this question by means of lab-based analysis processes that take around half a day to complete. This is obviously far too long for adaptive control, but fortunately, Fraunhofer IPM has the necessary expertise to speed things up. "We are developing a process that can be used to measure the water's lithium concentration at the outlet from the sorbent in real-time - which allows for extremely rapid feedback cycles. If the concentration increases, then the sorbent material's saturation levels are rising, meaning it needs to be cleaned out," explains Dr. Basler.

For this process, the researchers use laser-induced breakdown

spectroscopy, which involves focusing short laser pulses (lasting around 10 nanoseconds each) on the water's surface through a lens. This applies so much energy to the water that some of it forms a plasma — i.e., a gas that no longer consists of atoms or molecules like a normal gas, but rather of ions and electrons — because the laser's high energy ejects the electrons out of the atoms. If the ions capture the electrons again, they emit a characteristic radiation in the process, which allows scientists to extrapolate the type of the atom in question. The researchers can then analyze the spectrum to identify and quantify the elements dissolved in the water. "Based on the ▶

spectrum, we can see how much lithium is in the water, which also tells us whether the sorbent is saturated and requires cleaning," says Dr. Basler.

The laser-induced breakdown spectroscopy process has been around for quite some time and is used in industry settings to identify aluminum alloys, for example. However, the materials that the process has been used to investigate thus far are all solids. In the case of liquids, things become more tricky — and the hunt for commercial solutions has been unsuccessful. "With solids, the majority of the laser energy is absorbed by the medium, which makes it easy to apply enough energy to the material to ignite a plasma. However, with liquids, the energy

is carried much further into the material," explains Dr. Basler. This means that in most cases, the energy is not enough for plasma ignition in liquids. However, by following a sort of "the more, the merrier" logic, the researchers managed it eventually. They created a setup in which a gas layer lies on top of the liquid, so that they could apply so much energy to the liquid via the laser that the plasma is ignited right at the liquid's surface; the plasma then expands through the gas rather than the liquid.

However, that is not quite as easy as it sounds here. The water is subjected to a pressure of 20 bars, that is, 20 times the atmospheric

pressure, and the gas must be adapted to these conditions but this high pressure also influences the generation and expansion of the plasma. Which gases are most suitable? What effect does the pressure have on plasma expansion? The temperature also has an impact on plasma ignition after all, the groundwater does not run through the system at room temperature, but rather at around 80 degrees Celsius. What's more, if a certain proportion of iron is dissolved in the water, the lines in the analytic spectrum can shift due to what are known as matrix effects. "We will study the matrix effects caused by all elements found in the water and calibrate the system as needed to account for them," says Dr. Basler.

But there are still other challenges to tackle: Plasma expansion often sprays the water beneath away, which results in the spatter hitting the viewing glass that the laser shines through to reach the pressure chamber. The next laser pulse will then be absorbed and deflected, meaning that proper plasma ignition can no longer take place. Consequently, the researchers are working on a setup that will block this spatter effect. They are hoping to overcome all these challenges by the end of 2024, so they can take the next step: testing out the system at an existing geothermal facility alongside the KIT technology that will be used to extract the lithium from the water.

Recycling lithium from used batteries

In

2022

lithium prices

surged by

a factor of

Given the imminent electrification of mobility and heat generation, lithium demand could soon rise to such heights that even this technology will not be enough to cover it all. This is why the research team is also working

> on methods of recycling lithium from used batteries as well as extracting it from geothermal water. The German federal government is also driving progress in this area.

> Various processes are already being applied in the industry sector in order to recover the materials that batteries contain, such as nickel, manganese, cobalt and aluminum and copper foils. "Unfortunately, lithium is still too cheap to make the recovery process pay off," explains Dr. Basler. However, based on the price trends for lithium over the last year alone, it is safe to assume that this state of affairs will not last for long. In 2022, lithium prices surged by a

affairs will not last for long. In 2022, lithium prices surged by a factor of ten. "The question of recovering lithium from used batteries could become really pressing within a period of around ten years. However, we need to develop the necessary technologies now, so they work when that time comes," affirms Dr. Basler.

The sorbent from KIT has been specially developed for binding lithium — so it should also be suitable for battery recycling. In this process, the battery slurry (a mixture of cobalt, manganese, nickel, lithium, graphite and binding agents) is dissolved in an aqueous solution and passed through the sorbent. It should also be possible to transfer the technology developed by Fraunhofer IPM to this application — and to other approaches, such as processes where the lithium is spun out of an aqueous solution by means of a centrifuge. In short, the process can be used in any situation that involves measuring lithium concentrations in a liquid media — and as such, it has a valuable role to play in driving lithium production in Germany and Europe.