Reinventing copper extraction with electricity

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Antoine Allanore, the Thomas B. King Assistant Professor of Metallurgy at MIT
Credit: Photo courtesy of Antoine Allanore

Copper is so valuable that its theft from worksites and power substations has become a national problem. Replacing the lost copper with new metal produced by the traditional method of cooking copper sulfide ores requires a multistep process to extract the copper and produces troublesome byproducts. Antoine Allanore, the Thomas B. King Assistant Professor of Metallurgy at MIT, wants to simplify copper extraction and eliminate noxious byproducts through electrolysis.

"If you look at the energy consumption of a copper smelter today, it's enormous," Allanore says. "They are dependent on electricity already to exist. My approach asks, why don't we try to do 100 percent electrical, starting from the concentrate and ending with the metal product, if I can use electricity to be more efficient as well as more environmentally friendly?"

In the traditional process, which still accounts for more than half of copper production, smelters roast a mixture of copper sulfide ore and oxygen. Besides copper, the process produces sulfur oxides, which are chemical precursors to acid rain. To prevent their release into the atmosphere, the sulfur oxides have to be trapped, filtered, and treated to make sulfuric acid, adding to capital costs. In contrast, the proposed electrochemical process of molten sulfides electrolysis melts the materials at high temperature (above 1,085 C or 1,985 F) and yields pure liquid copper and elemental sulfur gas.

The idea for direct sulfides electrolysis dates to as early as 1906. In a presentation for the Copper International Conference in Santiago, Chile, in December 2013, Allanore noted the proof of concept for producing copper and sulfur by electrodecomposition of copper sulfide, achieved by T.P. Hoar and R.G. Ward and published in the London-based Transactions of the Institute of Mining and Metallurgy in 1958.

In the electrolysis process, copper sulfide ore is added to a chemical stew called electrolyte, and the chemical transformation of the copper sulfide into its constituent parts takes place on two electrodes in the electrolyte—an anode and a cathode. The crucible, the vessel in which the process occurs, has to be nonreactive both to the electrolyte and to the copper sulfide.

Postdoc associate Sang-Kwon Lee is working on the electrolyte design. "The main strategy of our work is using the multicomponent molten sulfide in order to change the property of the supporting electrolyte and to reduce the melting temperature of the electrolyte," Lee says. See related article. The molten sulfides electrolysis research received funding from the Office of Naval Research and is continuing with support from an anonymous private investor. The research funds are managed through the Materials Processing Center.

The copper research builds on Allanore's previous work in the steel industry, where he developed new electrochemical processes to make iron without greenhouse gas emissions. One of those efforts, in collaboration with Donald R. Sadoway, John F. Elliott Professor of Materials Chemistry, focused on liquid iron production at 1,600 C, and resulted in a patent, a *Nature* paper, and a spinoff company, Boston Electrometallurgical Corp. (BEMC), in Woburn, Mass. BEMC is now scaling up the process to 1,000 times laboratory scale to demonstrate its commercial viability. Allanore addressed the fundamental scientific question of how to promote removal of oxygen from these systems in the paper "Electrochemical engineering of anodic oxygen evolution in molten oxides," published in November 2013 in Electrochimica Acta.

"The previous challenge was working with processing of an oxide system," Allanore says. "Here, the challenge is to work with a sulfide system, but in the molten state. We know surprisingly little about molten sulfides. We know their properties in the solid state, because they are used for thermoelectrics, magnetic material, and optical materials." Graduate student Cooper Rinzler, in Allanore's group, is studying the materials science that makes liquid sulfides different from their solid counterparts. "The challenge for us is really to predict the thermodynamic and physical properties of multicomponent sulfides, with the eventual objective of doing the electrolysis, which works very well if you don't have any electronic conductivity," Allanore says.

The fundamental electrolysis process is well understood—at one electrode, an electron reacts with an ionic compound in contact with the electrolyte to release the metal, and at the other electrode, a component in the electrolyte reacts to give back an electron. "In an ideal electrochemical process, you don't have electrons flowing in your electrolyte—they are stopped at the electrodes," Allanore says. "The problem in liquid sulfides is that some of them are allowed to go through." Allowing free electrons to pass through the solution without causing the desired chemical transformations on the electrodes allows their energy to be wasted as heat but doesn't contribute to metal separation. "The challenge right now is to probe how electrons are either flowing or not flowing in the system, so that we can design a system that works for metal extraction," Allanore says.

Allanore is optimistic, because his research documenting trends in metal refining reveals a historical trend of reduced overall energy consumption and higher electricity usage. "Interestingly, in the United States and some other countries, a significant reduction in energy consumption and CO_2 emissions for steelmaking occurred at the end of the 20th century, coinciding with a more intensive use of the electric arc furnace," Allanore wrote in the paper "Contribution of Electricity to Materials Processing: Historical and Current Perspectives," published in February 2013 in Journal of the Minerals, Metals & Materials Society. "This demonstrates that using electricity for steelmaking is a modern reality and actually provides benefits." Greater recycling of steel, which uses electric arc furnaces instead of coal-fired blast furnaces, has also fueled the improvements in energy consumption. "If you look carefully at the history of aluminum production, steel production, which are commodities where we speak about little numbers having a big impact, they show us the path," Allanore says. "They show us that we go for cheap electricity, and we go for more electricity as time goes by."

In traditional smelting processes for steel, for example, a plant has to put out four million tons a year and run for 20 to 30 years to be economical, requiring large consumers such as car makers to purchase its output. "Let's be honest," Allanore says. "If you don't pay for the environmental costs, and you have a steel plant that needs to be valuable for the next 30 years, there is no way you're going to change your technology. Now, there are always lags in metallurgical processing between when someone comes out with an idea, when it becomes ready for big-scale demonstration, and when the market is ready to buy it. One of the key factors is that this timing has to match the time when someone is willing to consider an investment. All of these things are dynamic, but the time constant is long." But the push for sustainability and environmental awareness are working in favor of the changes he advocates, Allanore argues.

Experience in the aluminum industry shows that it is actually fairly cheap to make the electrolysis device, Allanore says. "So if you can secure the supply of electrons, if you can make a device that is smaller or cheaper, now we are speaking about a different business scenario. We're not speaking about 20 or 30 years of investment at several billion [dollars]. It's something that you will pay once, hopefully, half the price, and therefore, the old business model changes completely. And I think that's the only way this innovative technology will be implemented, is if it is flexible enough to be integrated anywhere in the country and it has the ability to actually scale from lower capacity to extremely high capacity. And electricity allows that."

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