

Mining gold with moly

Modern electronic gadgets contain dozens of metals crammed into the smallest possible space. The construction is such that they are nearly impossible to disassemble for recycling. Highly reactive supercritical water can facilitate “mining” of precious-metals from this electronic waste. Because of the corrosive process environment, molybdenum containing nickel alloys are needed for the vats.

It is estimated that there were approximately 7.3 billion mobile device subscriptions active globally as of November 2016, about 3.3 billion of which were for smartphones. These numbers are expected to grow to 8.9 billion and 6.8 billion, respectively, by 2022. Moreover, these estimates do not include unused and unconnected phones that lie around gathering dust. This mountain of electronic waste, or e-waste, contains tiny nuggets of valuable metals that are part of a giant “ore deposit” distributed around the world. Gold, palladium, silver, and copper can all be “mined” by recycling this never-ending stream of e-waste discarded in the quest for ever more efficient and entertaining devices. The recovery of precious and specialty metals contained in electronic equipment has even been given a name – “urban mining.” Instead of being deposited in rocks, the metals of interest are contained in the intricate circuitry of silicon devices and are firmly secured to polymer substrates, so extracting them presents a new set of problems.

Current recycling processes

Recyclers now use pyrometallurgy, hydrometallurgy, and electrolytic processes to extract metals from e-waste. Pyrometallurgy, which involves heating, is the most common approach because it is relatively energy efficient compared to other current alternatives. This is because the combustible portion of the scrap stream, such as plastics, is a supplemental source of “free” process energy. The modern plants found in Japan, Europe and North America are relatively

inexpensive and environmentally efficient compared to competitive processes. Pyrometallurgical processing usually extracts precious metals and elements such as nickel into a metallic copper phase, which is electrorefined to extract copper and separate the remainder for subsequent production of pure gold, silver and other precious metals. Copper electrorefining is highly efficient, requiring only the electric energy of 0.35 kWh per kilogram of copper extracted. Conventional hydrometallurgical techniques (chemical extraction using aqueous acid solutions) are also used to recover precious metals from e-scrap.

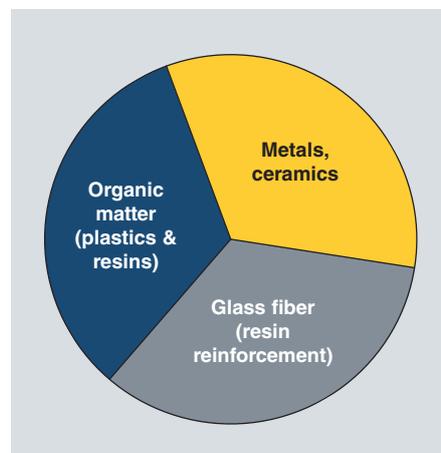
Conventional technologies such as those noted above are efficient, have low to moderate energy requirements, and possess good environmental records; but there can always be a better approach around the corner. Any process that

lowers cost and reduces environmental risks will generate considerable interest. However, new technologies always require lengthy steps of small-scale laboratory experimentation and larger-scale piloting before they can eventually move to full-scale commercial operation.

One new innovative process that generates high hopes for more efficient and environmentally friendly technology is well along this arduous development path. It uses a common and seemingly unlikely candidate – water – as a tool to lay bare the treasures of mobile devices and other electronic components.

An abundant and powerful resource, and a new idea

The water used in the process is not water as normally seen in rivers, lakes, and drinking-water systems; it is *supercritical water*. When heated above 374°C under pressures above 221 bars (22.1 GPa, or about 221 times atmospheric pressure), water is in a *supercritical state*. Under these conditions water’s gaseous and liquid states cannot be distinguished from one another, and the phase present is an ever-boiling cauldron of many different pieces of the lowly water molecule, H₂O. Supercritical water is a strong oxidizer and a highly-corrosive reactant. It turns carbon-containing matter into gas and dissolves other substances that are insoluble in plain water. Because it reacts with materials that require the use of hazardous chemicals for processing, supercritical water is currently used for the processing of toxic waste such as biomass and chemical weapons stocks. ➤



Electronic circuit boards: three main types of materials



The electronic devices of today are the “urban mines” of tomorrow. © iStockphoto/xuanhuongho

A French research team working on the Remotox project deserves credit for the idea to change the focus of supercritical water processing from toxic waste to e-waste. The project’s approach is to destroy the polymeric materials of e-waste using supercritical water, without deteriorating or melting the metal components. The team members hail from the French Geological Survey (BRGM), Orléans University, and France’s National Center for Scientific Research (CNRS), in association with Terra Nova Development (a company specializing in electronic-waste management). Drawing from knowledge of organic waste treatment processes like gasification and hydrothermal oxidation, the team envisioned plunging electronic circuit boards into supercritical

water to extract the contained metals. They designed a laboratory-scale supercritical-water reactor that could operate at 500°C and 250 bars pressure. Their next problem was to choose the best material of construction for their equipment, one that would withstand the aggressive supercritical-water environment.

A superalloy derived from nuclear technologies

Experience acquired in supercritical-water reactors for biomass processing, toxic waste treatment, and nuclear power generation guided the material choices for the vat, valves and metallic seals. These crucial components must resist stress-corrosion cracking and retain their strength at high temperatures. The team chose the nickel-base superalloy Inconel® Alloy 718 containing 3 percent molybdenum to meet these requirements. The alloy possesses excellent strength, toughness, and stress-corrosion-cracking resistance, and has a decades-long history of reliable performance in safety-critical nuclear-reactor components like fuel-assembly support grids.

The Remotox team’s laboratory-scale results have been impressive. When electronic circuit boards are immersed >

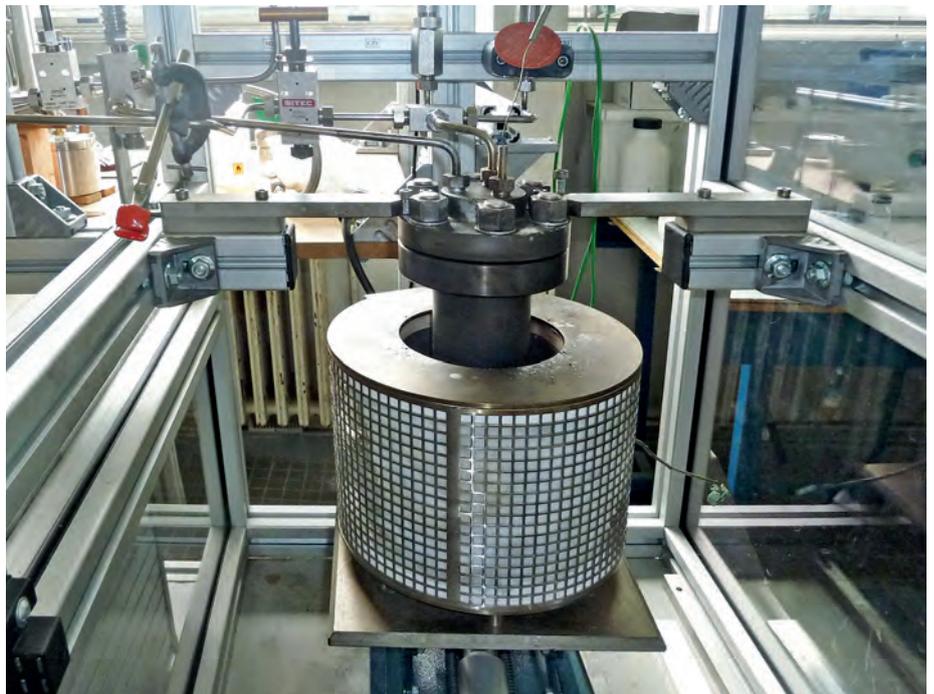
An ore deposit of continental proportions, by the number

It is difficult to know accurately how much e-waste is produced globally. The EU reports that about 1.1 million tonnes were collected in 2014 from information-technology, telecommunications, and consumer equipment. This number is probably lower than the amount of e-waste actually generated. The reported weight incorporates all parts of the various components in these categories, including the circuit boards and electronic devices that contain valuable metal resources. Using the iPhone as a reference, the BBC estimated in 2016 that one million such smartphones alone would yield 15 tonnes of copper, 340 kg of silver, 34 kg of gold, and 15 kg of palladium. On a weight basis, circuit boards in electronic devices contain 300 times more gold than a typical gold ore and 6–7 times more silver than typical silver ore. These numbers do not include other elements present in iPhones and other electronic equipment, such as nickel, tin, cobalt and tantalum. The figures highlight the potential of “urban mining” to maintain an economical supply of precious and specialty metals.

in supercritical water for a few hours the water decomposes their polymer resins, leaving behind a crumbly residue. On the other hand, the circuit boards' metal components and glass fiber reinforcement remain intact. These various materials can then be separated by a sorting step and directed to appropriate recycling processes.

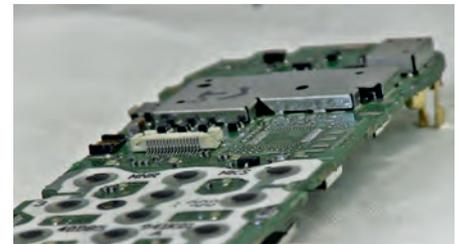
A modest but highly promising industrial goal

The project now operates experimental vats with capacities of 0.3 and 2 liters. A 10-liter vat designed to handle relatively small quantities of electronic scrap is scheduled to begin operating in 2020. This next development phase will employ a semi-continuous closed cycle that feeds batches of circuit boards to the reactor while maintaining supercritical conditions. Treatment times will range from 30 minutes to a few hours, depending upon the quantity of material contained in the batch. The gases produced by the reaction – mostly methane – will be recovered and fed back into the loop to reduce energy consumption and process cost. The commercial process envisioned by the team aims to handle the components of about 1 million phones annually.



Prototype reactor for environmentally friendly electronic-waste treatment. © CNRS

One million phones seems like a large number, but it is actually quite modest considering that global smartphone sales for 2016 alone are estimated to be nearly 1.5 billion. Even so, Orléans University's moly-containing vats may be a first step towards a new technology to treat electronic waste. (Thierry Pierard)



Electronic circuit board before treatment. © CNRS



The recipe: plunge the board into supercritical water and cook it for about 30 minutes. © CNRS



Resin and fiberglass crumble and turn into ashes while precious metal components remain intact and can be sorted. © CNRS