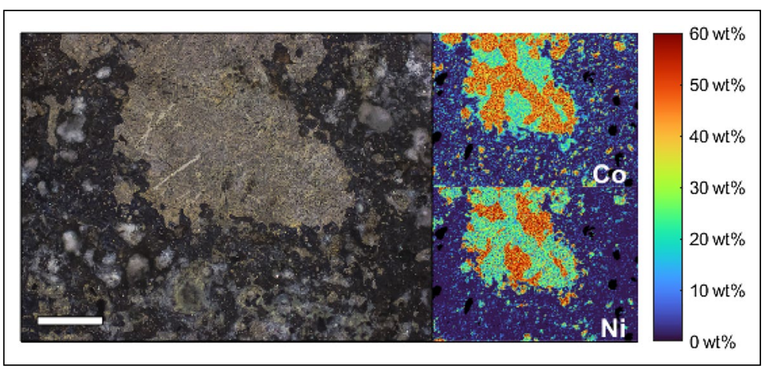
Metal extraction by selective sulfidation of compounds is beneficial for recycling

Environmental protection and sustainability are generally considered incompatible with the expanding industrialization of electronics. This is because metals like copper, manganese, and cobalt are crucial to electronics-related technologies, such that demand has risen by 40% since 2010. Antoine Allanore, a professor at the Massachusetts Institute of Technology (MIT), has explored new methods to answer this question: "Can we mitigate the extraction of metals in electronics technology?" In their study published in *Nature* (https://doi.org/10.1038/s41586-021-04321-5), Allanore and co-author Caspar Stinn of MIT found that sulfidation rather than oxidation is a more environmentally friendly and selective method of extracting metals, especially *d*-block and *f*-block metals, from compounds. An anion exchange reaction has been referred to as the selective pathway of sulfidation to physically isolate metals. Their research showed that high purity metal extraction through sulfidation is possible using physical separation techniques (rather than chemical separation) with just a few reaction steps.

An anion exchange reaction selectively reacts a metal (M) from a compound mixture containing M–X to target the formation of a new compound M–Y. The researchers reported that the novel chemical, M–Y, in which Y is sulfur (S) and X is oxygen, is formed when sulfur combines with metal (M) from the compound mixture—sulfidation is thermodynamically selective because of the relative stabilities of oxides and sulfides. The compound M–Y is targeted to enable subsequent physical separation. Due to their high reactivity, low selectivity, and tendency to produce several side products, gases like H_2S, C_2S, and SO_2 were traditionally considered less desirable. The sulfide product also forms in a solid matrix that is very simple to physically separate without using any energy to extract the liquid–liquid layer.



Optical image (left) and scanning electron microscope energy-dispersive x-ray spectroscopy element maps (right) show the product of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111 or NMC333) processed using selective sulfidation for lithium-ion battery cathode recycling. Cobalt and nickel are observed to partition into sulfide phases that are amenable to physical separation. Manganese and lithium are found to form separate oxysulfide and sulfate phases, respectively. Scale bar corresponds to 200 μm. Credit: Caspar Stinn and Antoine Allanore.

The researchers are developing efficient protocols to find solutions for supply diversification and lower gas emissions due to the acute shortage of cobalt and nickel. They have also shown that carbon-free sulfidation of nickel-manganese-cobalt oxide (NMC) cathode material, a crucial component in lithium-ion battery recycling, is possible. Their research showed that using a single pyrometallurgical sulfidation phase can improve physical separation methods for metal extractions while also providing effective selectivity and reduced gas emission.

A case study of rare earth metal (Ln) extraction and separation from (Nd, Pr, Dy)-Fe-B magnets was chosen to demonstrate this process in the recycling of rare earth magnets. Sulfidation was shown to be very selective because of the difference in thermal activation energy of sulfidation reaction between Fe and Ln oxides. This method therefore offers a means of solving the unbalanced supply and demand of different rare earth metals.

The method developed at MIT is not only technically feasible but was also shown to be cost-effective. This study is expected to be beneficial for various recycling industries including lithium-ion battery recycling, rare earth magnet recycling, and rare earth mineral processing.

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