Harvesting metals from water

Gold is a noble metal, used not only in jewelry, but also in industrial applications such as electronics, where it is employed in electrical contacts because it is an excellent conductor and very resistant to corrosion. Commercial ores have gold concentrations around 5 to 30 parts per million (ppm) - that's 5 to 30 grams per ton. Electronic scrap can contain hundreds of gold grams per ton. Methods to recover gold from electronics have been developed. Aqueous solutions are prepared from the scrap using acids or other chemicals to leech the gold, which is then recovered from the solution by a number of different methods.

Seawater also has gold, but in much lower concentrations: about 10 parts per trillion (ppt) - that's 10 grams per trillion tons of water. That may not seem much, but it amounts to more than

Crystal structure of $LiMn_2O_4$ spinel.
Figure credit: Adapted from Wikipedia.

10 billion tons of gold in the Earth's oceans. With worldwide gold demand at just over 4 thousand tons per year (World Gold Council 2016), that would be enough supply for millions of years, if one could extract it from the sea, in an economically viable way.

The methods developed to recover gold from electronic scrap are not suited for natural waters. They require specific chemicals, and also high concentrations of gold in the solution. Dr. Kenta Ooi and co-workers from the National Institute of Advanced Industrial Science and Technology in Shikoku, Japan, discovered in 1986 that microporous hydrogen-containing Mn_2O_4 (manganese oxide) powders absorb lithium ions in seawater with high selectivity (Kenta Ooi et al., 1986).

Dr. Hideki Koyanaka from the Nippon Bunri University, Japan, and co-workers, later concluded that the selectivity for Li is due to an ion exchange reaction which occurs only between lithium and hydrogen ions, and that this depended on the hydrogen content of the Mn_2O_4 powder (H. Koyanaka et al., 2003). Their next step was to tailor a nanostructured Mn_2O_3 powder with selective gold-hydrogen ion exchange that could recover 95% of gold in seawater samples, in small scale laboratory conditions (H. Koyanaka et al., 2005). The Mn_2O_3 gold adsorbent was prepared by low-temperature synthesis, followed by protonation of the particle surfaces by acid treatments.

Gold recovery is made simply by dispersing the adsorbent nanostructured powder in the seawater. The protonated Mn_2O_3 nanoparticles become covered by a single atomic layer of gold. The polydisperse nanometer-size gold particles formed initially subsequently grow to submicron sizes. The adsorbent is then filtered out and washed with an acid, which recovers the gold and re-protonates the nanoparticles at the same time, which means they can be reused.

Manganese oxide-based nanostructured materials have also been proposed for recovery of tritium, which is a radioactive isotope of hydrogen (H. Koyanaka and H. Miyatake, 2015), and for use in hydrogen gas sensors (Y. Ueda et al., 2012).
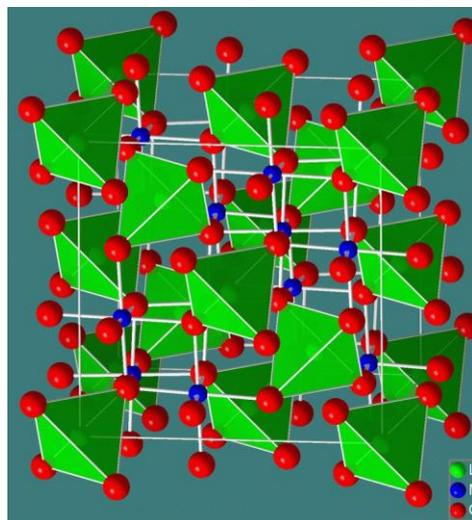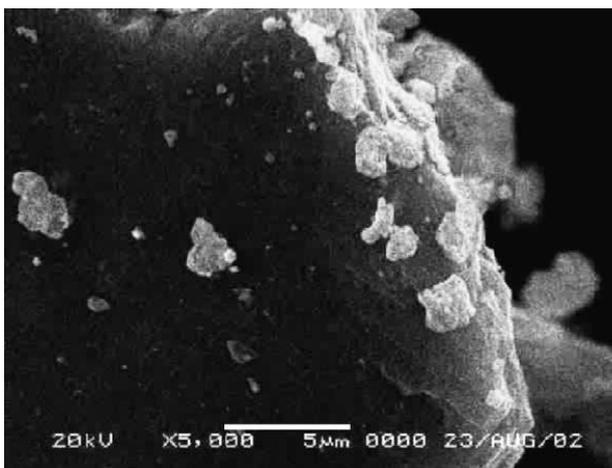
Scanning electron microscopy image showing gold particles (with lighter color) on the manganese oxide adsorbent.

Figure credit: (H. Koyanaka et al., 2005).

Neutron techniques played a crucial role in developing these systems. Inelastic neutron scattering was used, together with calculations, to understand the changes in the $LiMn_2O_4$ crystal structure when hydrogen is incorporated. The protons are associated to given oxygen atoms which induce displacements of the O from the ideal lattice positions. In addition, proton insertion is correlated to the quantity of defects due to Li deficiency (see P. Aitchison et al., 2000, C.-K. Loong et al., 2006). The Li-proton ion exchange depends strongly on these structural modifications.

The gold recovery mechanism in the protonated Mn_2O_3 nanoparticles could be elucidated with Small Angle Neutron Scattering (C.-K. Loong et al., 2006). Negatively charged gold chloride ($AuCl_2^-$) complexes are first deposited on the positively charged nanoparticles. There the protons are released and the gold chloride is decomposed into metallic gold that binds to the surface of the nanoparticles. Therefore, the larger the nanoparticle surface area, the more efficient is the harvesting reaction. Neutron scattering results also showed that the Mn_2O_3 nanoparticles have a fractal geometry, which leads to very high surface areas, and hence the high efficiency of the process.

What is Inelastic Neutron Scattering?

Inelastic neutron scattering is a technique used to obtain detailed information on atomic or molecular motions and electronic and magnetic excitations, individual or collective. In inelastic scattering processes there is energy and momentum exchange between the neutron and the scattering nucleus: an incident neutron interacts with a target nucleus forming a compound nucleus. This compound nucleus in unstable, and emits a neutron with energy different from the original neutron, leaving the nucleus in an excited state. Experimentally, one needs to measure not only the total number of neutrons scattered in a given direction, but also the number of neutrons scattered in a given direction *and* with a given energy. The method is experimentally challenging and also requires extensive calculations to interpret the data, but it can provide detailed information about both structure and dynamics of materials. That is, from the data one can determine both the positions and the motions of atomic nuclei.