

## Capturing Carbon Dioxide with Wastewater

*The O'Hare group has developed a novel method of synthesising carbon-capture compounds from wastewater by-products. By Victoria A M Atkinson*

Struvite ( $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ) is a naturally occurring mineral which, since its discovery, has been causing problems wherever it has been found. In mammals, struvite is one of the major components of kidney stones, hard crystalline deposits which form in the kidneys and which are incredibly difficult to remove owing to their complete insolubility in water. In the presence of high concentrations of ammonium ( $\text{NH}_4^+$ ), magnesium ( $\text{Mg}^{2+}$ ) or phosphate ( $\text{PO}_4^{3-}$ ) ions any trace of dissolved struvite immediately precipitates out to form insoluble off-white crystals (**Figure 1**).



**Figure 1:** Struvite crystals. ©pinfa

In the 1930s, this was identified as a particular problem for wastewater treatment plants. The treatment process resulted in changes to concentrations of ions present in the water and consequently uncontrolled precipitation of struvite in water pipes began to occur, causing serious blockages (**Figure 2**).

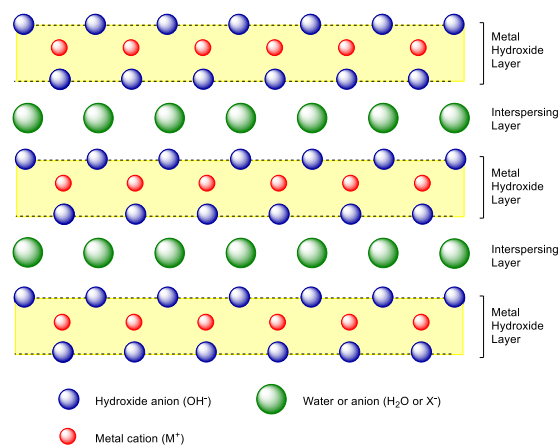


**Figure 2:** Serious pipe blockages caused by struvite deposits. ©apexengineering

Modern water treatment now incorporates a chemical sedimentation step to

remove the struvite at an early stage in the process. The wastewater is held in a sedimentation tank and treated with specific quantities of ammonium, magnesium, and phosphate ions, forcing the struvite to precipitate out of solution to be collected as a solid sediment.

The addition of this chemical sedimentation step has drastically increased the efficiency of wastewater treatment plants but has unfortunately also resulted in the production of large amounts of waste struvite for which there is currently no commercial use. However, an important application of this waste compound has recently been developed by the O'Hare group at the University of Oxford, focused on layered double hydroxides (LDHs).



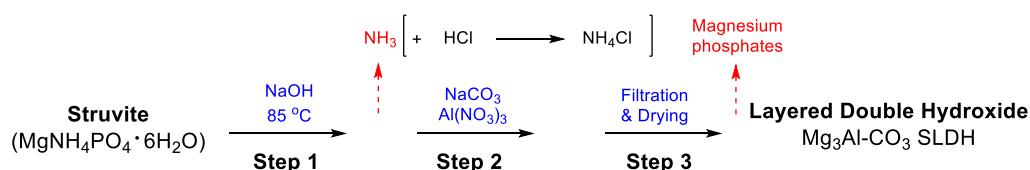
**Figure 3:** Representation of a layered double hydroxide (LDH). Sheets of metal hydroxides (yellow) are interspersed by a layer of weakly-bound water or anion particles (green).

LDHs (**Figure 3**) are a class of ionic solid comprising sheets of metal hydroxides (indicated in yellow), interspersed with a layer of either water molecules or anions (represented by the green particles).

Importantly, the interspersing anion layer is weakly bound to the hydroxide sheets, meaning these ions are easily exchangeable. As a result of this unique structure, LDHs have many useful and tuneable properties making them highly suitable for applications in fields as diverse as medicine, energy and the environment.

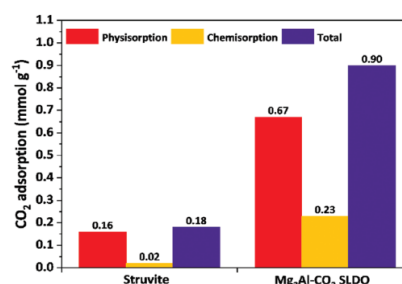
Usually LDHs are prepared industrially, using a variety of expensive (and often toxic) metal salts. However, the O'Hare group in Oxford have developed an alternative method, using the waste struvite from water treatment plants to prepare LDHs directly (**Figure 4**). The struvite is first suspended in a solution of sodium hydroxide (NaOH) at 85 °C, causing the ammonium ions in the struvite to be released as ammonia gas (NH<sub>3</sub>). This gas is passed through a hydrochloric acid (HCl) gas trap and collected as ammonium chloride (NH<sub>4</sub>Cl), itself a useful product. In the second step, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and aluminium nitrate (Al(NO<sub>3</sub>)<sub>3</sub>) are added to the solution to introduce both carbonate (CO<sub>3</sub><sup>2-</sup>) and aluminium (Al<sup>3+</sup>) ions into the product. Finally, filtration of the reaction mixture removes the waste magnesium phosphates, and the resultant solid is dried to give the product Mg<sub>3</sub>Al-CO<sub>3</sub> SLDH (struvite layered double hydroxide).

Carefully considered adjustments to both the ratios of reagents and the reaction conditions enable different double-layered structures with modified properties to also be prepared using this method. One such example of this is calcination, the prolonged heating of the solid product in the absence of oxygen, and when applied to Mg<sub>3</sub>Al-CO<sub>3</sub> SLDH, the resultant product is actually the mixed metal



**Figure 4:** Synthesis of layered double hydroxides (LDHs) from struvite. Blue indicates treatments on the struvite. Red indicates side products removed during synthesis.

oxide Mg<sub>3</sub>Al-CO<sub>3</sub> SLDO (struvite layered double oxide). This compound is of particular interest because of its ability to adsorb carbon dioxide and hence act as a carbon-capture material. The Mg<sub>3</sub>Al-CO<sub>3</sub> SLDO product has a larger surface area and larger pore volumes than both struvite and the parent SLDH, making it particularly effective as a physical adsorber of carbon dioxide. In addition to this, the greater acid/base reactivity of the SLDO product compared with struvite also enables it to act as a chemical adsorber by forming new chemical bonds with the carbon dioxide. In fact, preliminary studies have already demonstrated that Mg<sub>3</sub>Al-CO<sub>3</sub> SLDO is over four times more effective as a carbon capture material (**Figure 5**).



**Figure 5:** Comparison of carbon dioxide adsorption of struvite and Mg<sub>3</sub>Al-CO<sub>3</sub> SLDO. Physorption refers to physical adsorption processes. Chemisorption refers to chemical adsorption processes.

Such research clearly demonstrates the value of repurposing waste products of human activities. The full potential of struvite layered double hydroxides is still under investigation, but if the journey from wastewater to carbon capture is anything to go by, they could prove to be a revolutionary development in the fight against climate change!