

Electronic Supplementary Information

Synthesis of dense porous layered double hydroxides from struvite

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Table of Contents

S1. General instrument details	S2
S2. Experimental details	S4

S.1 General instrument details

The specific surface area of the samples was determined by the Brunauer-Emmett-Teller (BET) method using the N₂ adsorption and desorption isotherms collected at 77 K on a Micromeritics TriStar II 3030 instrument. Struvite samples were degassed at 30 °C overnight before analysis. LDH samples were degassed at 110 °C overnight before analysis.

Fourier transform infra-red (FTIR) spectra were collected on a Bruker VERTEX 80 spectrometer fitted with a DuraSamplIR II diamond ATR (attenuated total reflection) accessory. The instrument was set to record 50 scans between 4000–500 cm⁻¹ at 4 cm⁻¹ resolution. The diamond gave rise to absorption bands between 2300–1800 cm⁻¹. These did not interfere with the analysis.

Elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS) was performed by Dr Alaa Abdul-Sada (University of Sussex). Analyses were conducted on 20–30 mg samples digested in concentrated nitric acid (c. HNO₃) and diluted. Each solution was analysed three times.

Powder X-ray diffraction (XRD) spectra were collected on a PANAnalytical X'Pert Pro Diffractometer in scanning mode using Cu K α radiation ($\alpha_1 = 1.540598 \text{ \AA}$, $\alpha_2 = 1.54426 \text{ \AA}$, weighted average = 1.541847 \AA). Scans were recorded between $2\theta = 5.0100\text{--}72.9760^\circ$, with step size 0.0170° and scan step time 55.8800 s. The samples were mounted on stainless steel holders that gave rise to peaks at 43.36, 44.29, and 50.51°. These did not interfere with the analysis.

Scanning electron microscopy (SEM) images were collected at the David Cockayne Centre for Electron Microscopy (Department of Materials, University of Oxford) on a Zeiss EVO MA10 microscope with an acceleration voltage of 3 kV. Samples were mounted onto 12 mm pin stubs using silver dag at least 24 hours prior to imaging to allow the dag to dry and out gas.

High resolution scanning electron microscopy (HR-SEM) with energy-dispersive X-ray spectroscopy (EDX) was performed at the David Cockayne Centre for Electron Microscopy (Department of Materials, University of Oxford) on a Zeiss Merlin-EBSD microscope with an operating voltage of 5 kV. Samples were mounted onto 12 mm pin stubs using silver dag at least 24 hours prior to imaging to allow the dag to dry and out gas.

Transmission electron microscopy (TEM) images were taken at the David Cockayne Centre for Electron Microscopy (Department of Materials, University of Oxford) on a JEOL JEM-2100 microscope with an accelerating voltage of 200 kV. Samples were prepared by dispersion in ethanol using sonication and cast onto copper grids coated with carbon mesh.

Tap density was calculated by a standard testing method (ASTM D7481-09). The powder was filled into a volumetric cylinder and a precise weight of sample (m) was measured. The volume was measured before (V_0) and after 1000 taps (V_t), with the volume recorded after every 100 taps. The loose bulk and tap densities are defined as:

$$\text{Loose bulk density} = m/V_0$$

$$\text{Tap density} = m/V_t$$

Thermogravimetric analysis (TGA) was carried out on a Mettler Toledo TGA/DSC 1 instrument. Samples (~10 mg) were heated in an alumina crucible from 25 to 800 °C at a rate of 5 °C min⁻¹ under N₂ (~100 cm³ min⁻¹).

S.2 Experimental details

Materials

Synthetic struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) was purchased from Alfa Aesar and used without further purification. Hydrochloric acid (HCl, 37%), nitric acid (HNO_3 , 70%), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were purchased from Sigma Aldrich and used without further purification.

Two Waste Water Treatment Plant (WWTP) struvites were also obtained and used for comparison (named WWTP A and WWTP B).

Mg₃Al-CO₃-SLDH

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (37.5 mmol) was dispersed in 33 cm³ 1 M NaOH in a three-neck round bottom flask. The mixture was stirred (1000 rpm) at 85 °C for 1 hour under a flow of N₂. The ammonia off-gases were collected via a trap containing 1 M HCl. Na_2CO_3 (50.0 mmol) was added to the mixture and stirred for a further 5 minutes. A solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (12.5 mmol) in 33 cm³ D.I. water was added to the basic struvite mixture dropwise (2 cm³ min⁻¹), keeping the temperature at 85 °C and maintaining pH 11.5 by addition of 1 M NaOH. Once the addition was complete, the mixture was stirred at 65 °C for 2 hours. After the ageing period, the slurry was filtered and washed with D.I. water until the supernatant was pH 7. The solid was then dried in a vacuum oven at 30 °C overnight.

Decomposition of struvite in alkali

$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (37.5 mmol) was dispersed in 33 cm³ 1 M NaOH in a three-neck round bottom flask. The mixture was stirred (1000 rpm) at 85 °C for 1 hour under a flow of N₂. The ammonia off-gases were collected via a trap containing 1 M HCl. After the ageing period, the flask was cooled rapidly, and the slurry was filtered and washed with D.I. water until the supernatant was pH 7. The solid was dried in a vacuum oven at 30 °C overnight.

CO₂ adsorption studies

CO₂ adsorption was carried out using a Micromeritics 3Flex instrument fitted with a chemisorption attachment. The LDHs were first calcined *ex situ*. Typically, 100 mg of the sample was calcined at 400 °C at a ramp of 100 °C min⁻¹ for 2 hours. The sample was cooled to 40 °C using a ramp of 30 °C min⁻¹ and left to evacuate under vacuum at 40 °C for 3 hours. The CO₂ measurements were then carried out twice at 40 °C. The first value provides the total

adsorption value (chemisorption and physisorption), while the second measurement provides physisorption value. The difference between the two values provides the chemisorption value.

Table S1 Summary of ICP-MS elemental analyses of struvite and Mg_3Al-CO_3 SLDH

	Mg/wt%	Al/wt%	P/wt%	Mg/Al	Mg/P
Struvite	10.35	0.03	13.26	0.0026	1
Mg_3Al-CO_3 SLDH	21.77	8.19	1.4	2.99	20

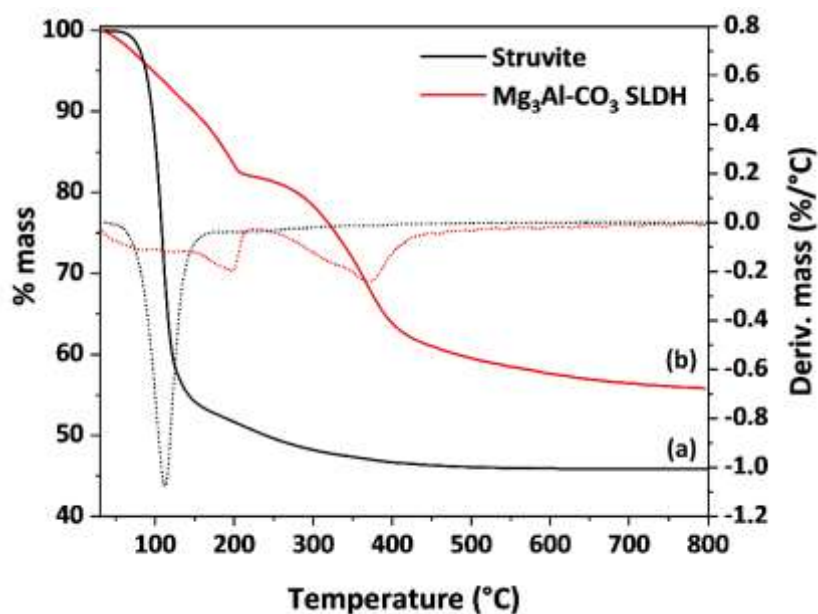


Fig. S1. TGA and dTGA profiles of (a) struvite and (b) Mg_3Al-CO_3 SLDH.

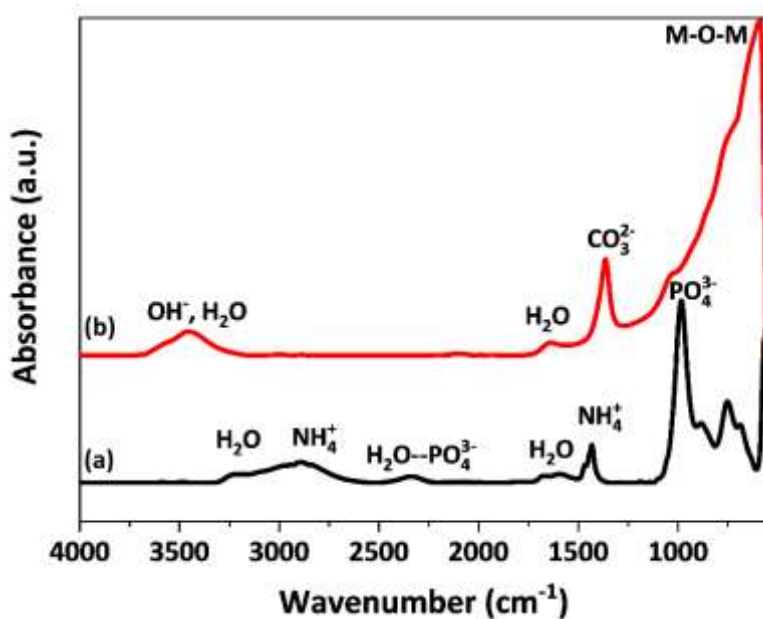


Fig. S2. FTIR spectra of (a) struvite and (b) Mg_3Al-CO_3 SLDH.

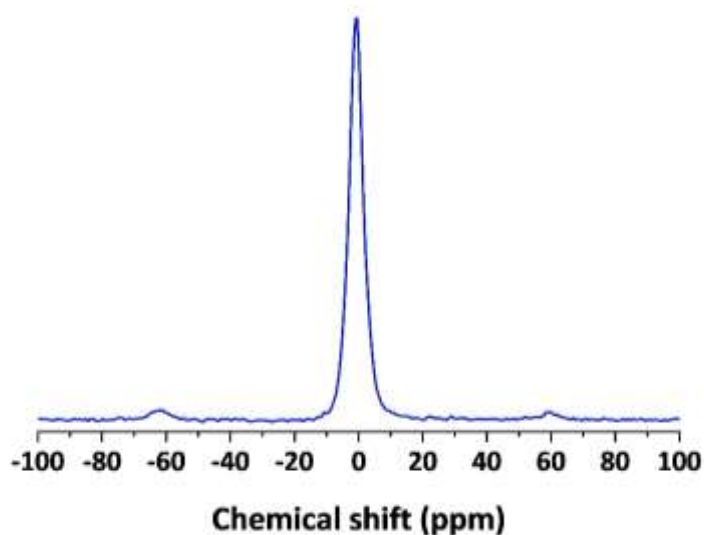


Fig. S3. Solid state ^{31}P NMR spectra of $\text{Mg}_3\text{Al-CO}_3$ SLDH.

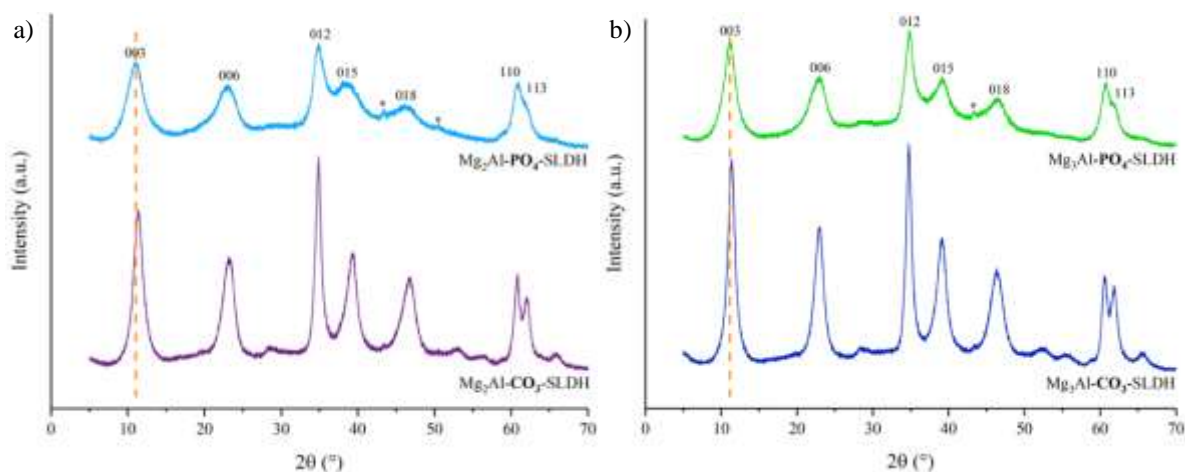


Fig. S4. Powder XRD diffractograms of carbonate and phosphate SLDHs for 2 different Mg/Al ratios. a) Mg/Al = 2 and b) Mg/Al = 3. *Reflections due to the sample holder.

Table S2. d -spacing of SLDHs calculated from powder XRD diffractograms.

Mg/Al ratio ^a	Interlayer species	003 ^b (°)	d_{003} (Å)	FWHM (°)
2	CO_3^{2-}	11.36864	7.78	1.743
2	PO_4^{3-}	11.05112	8.00	2.294
3	CO_3^{2-}	11.35719	7.78	1.094
3	PO_4^{3-}	11.15139	7.93	1.822

^aRatio of metals used in the synthesis

^bPosition of 003 Bragg reflection (2θ)

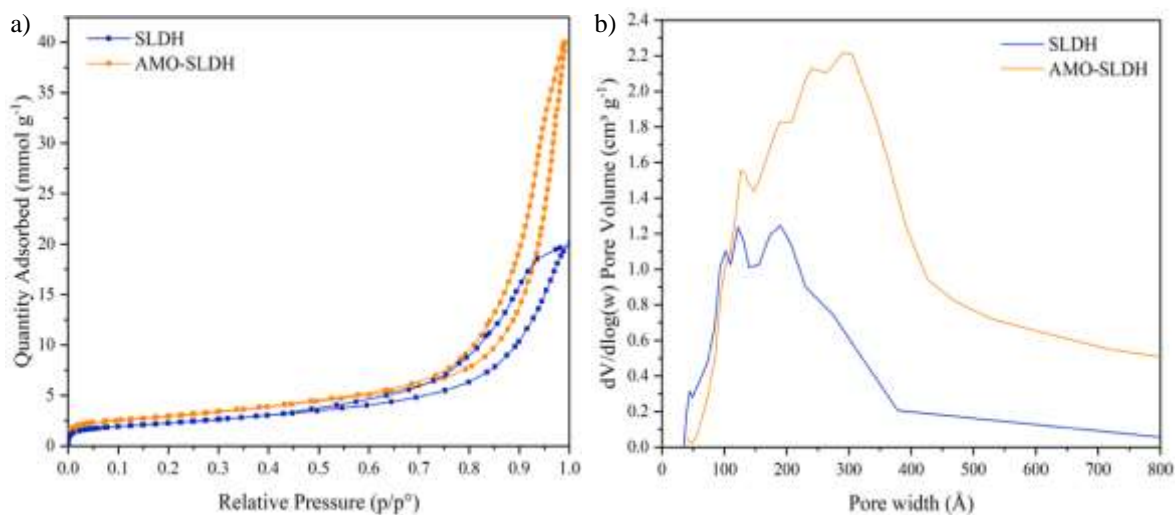


Fig. S5. a) N_2 adsorption and desorption isotherms and b) BJH pore size distributions of SLDHs with and without AMOST. Mg/Al = 3. AMO solvent = EtOH.

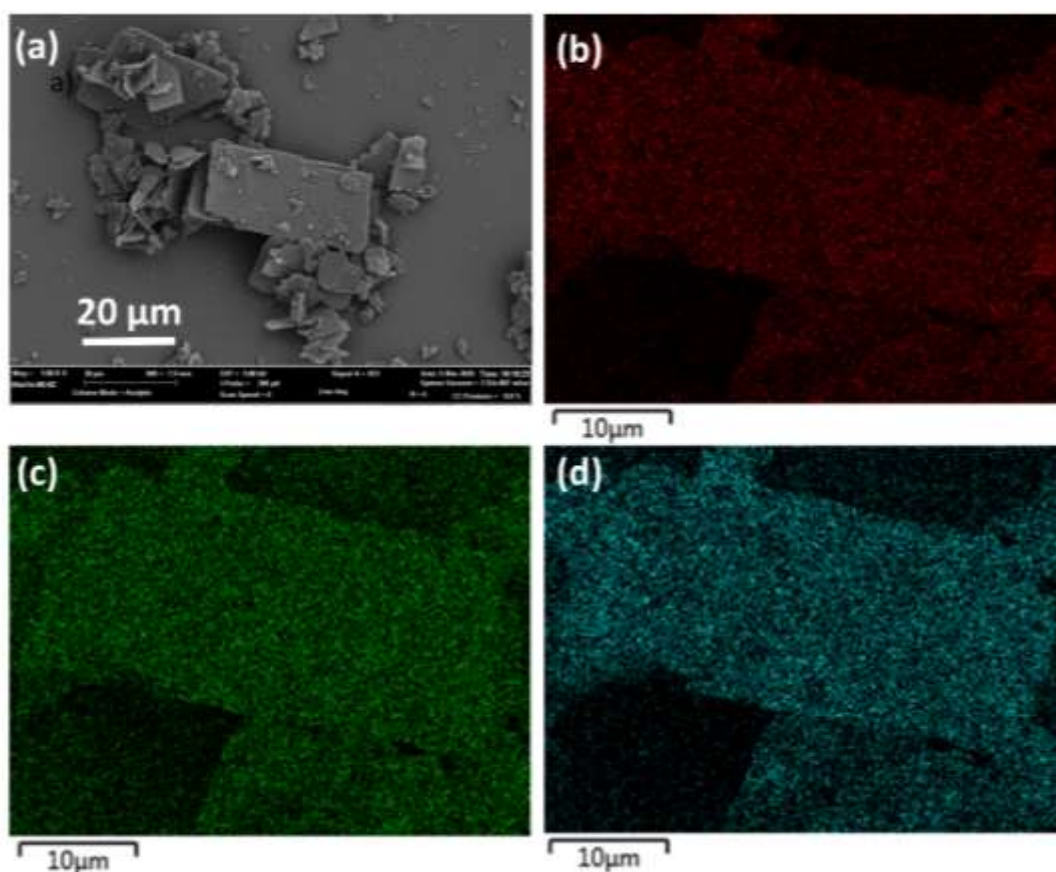


Fig. S6. (a) HR-SEM image of struvite decomposed in NaOH aqueous solution at 85 °C for 1 hour and HR-SEM EDX mapping images of (b) Mg, (c) P and (d) Na.

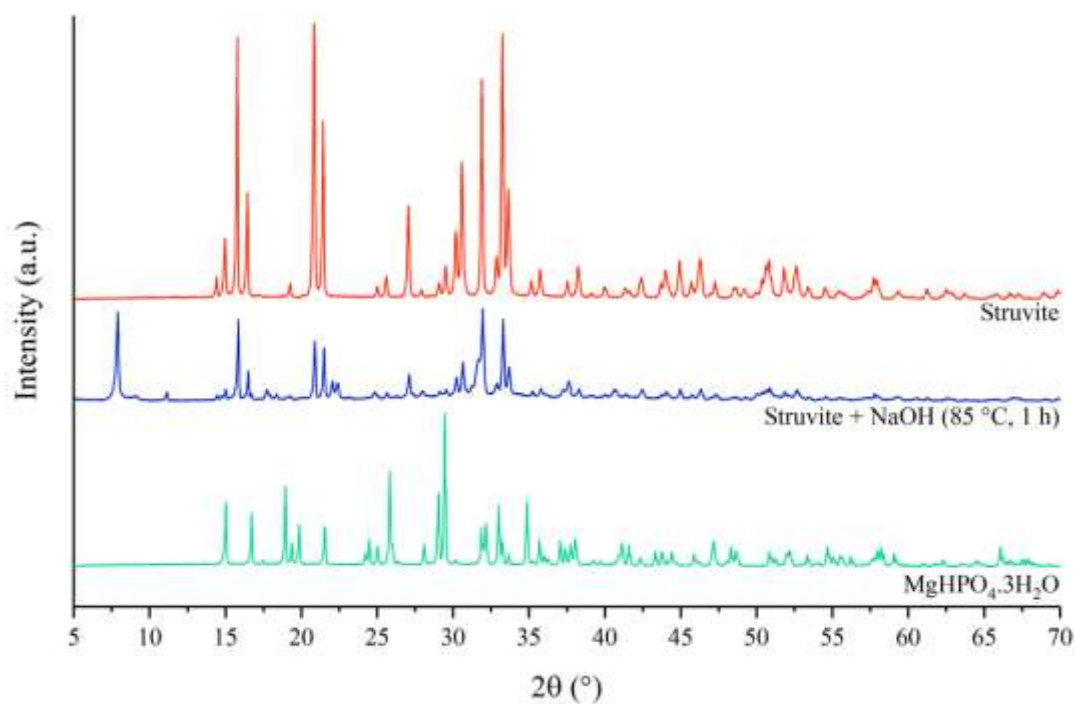


Fig. S7. Powder XRD diffractograms of struvite, struvite decomposed in NaOH (85 °C, 1 h) and magnesium hydrogen phosphate, MgHPO₄·3H₂O. XRD patterns were recorded for different Mg, Na, PO₄ compounds for comparison to the spectrum of the decomposition product.

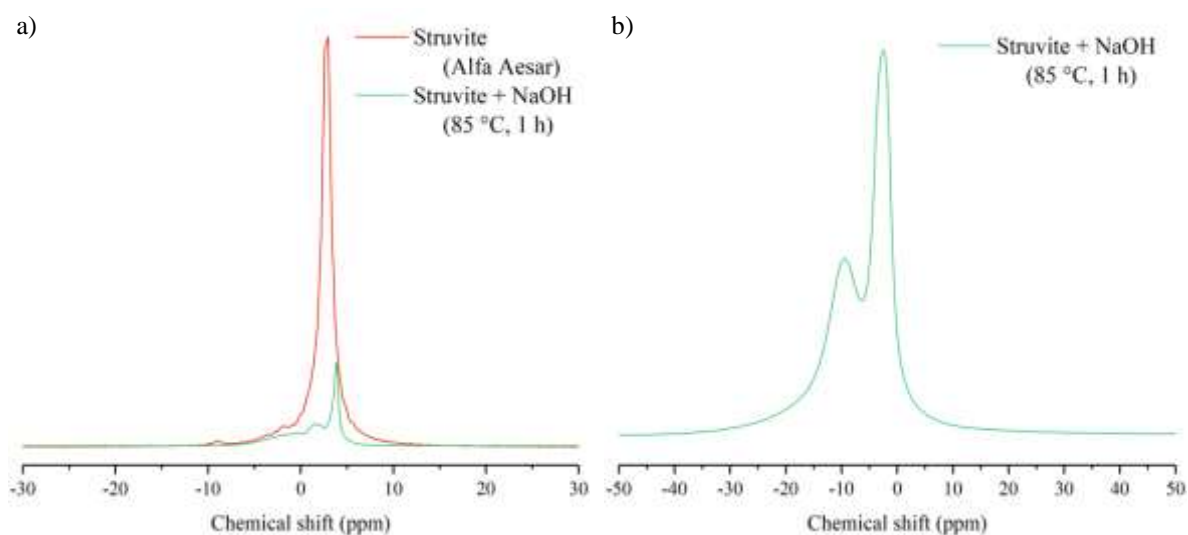


Fig. S8. a) ³¹P DPMAS ssNMR of struvite and struvite decomposed in NaOH (85 °C, 1 h) and b) ²³Na DPMAS ssNMR of struvite decomposed in NaOH (85 °C, 1 h).

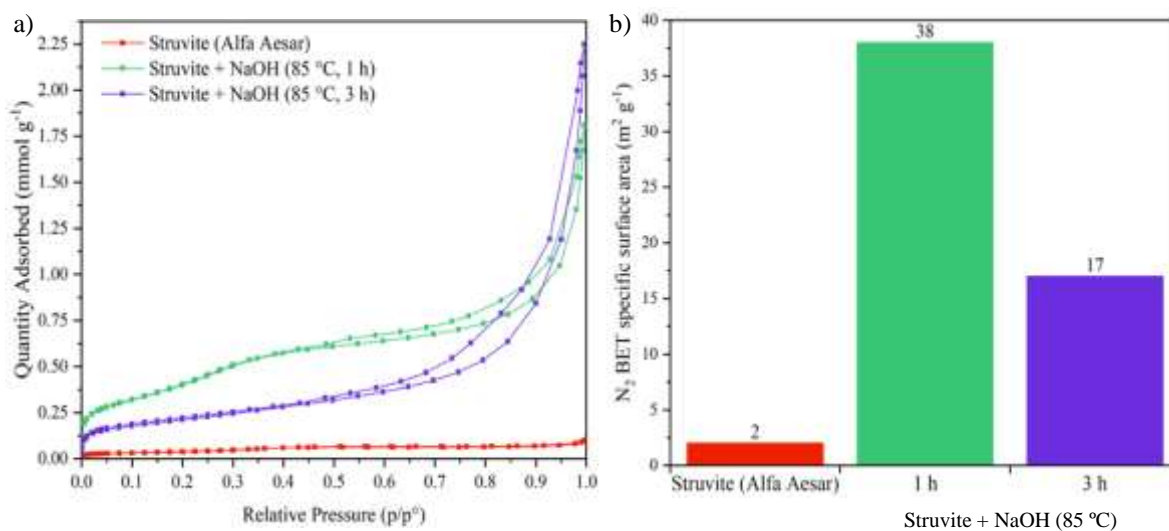


Fig. S9. a) N_2 adsorption and desorption isotherms and b) N_2 BET specific surface areas of struvite and struvite decomposed in NaOH (85 °C, 1 and 3 h).

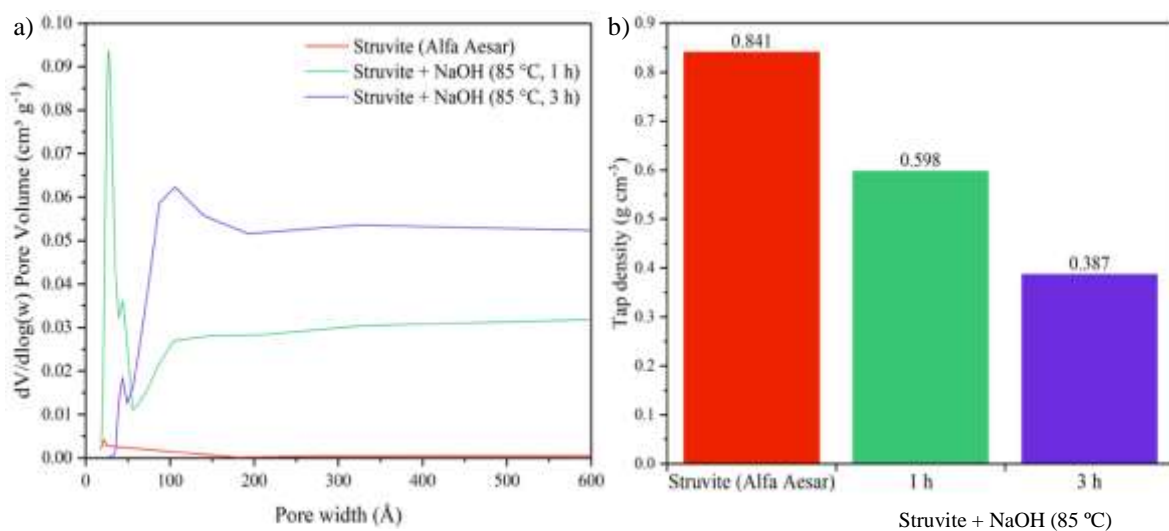


Fig. S10. a) BJH pore size distributions and b) tap densities of struvite and struvite decomposed in NaOH (85 °C, 1 and 3 h).

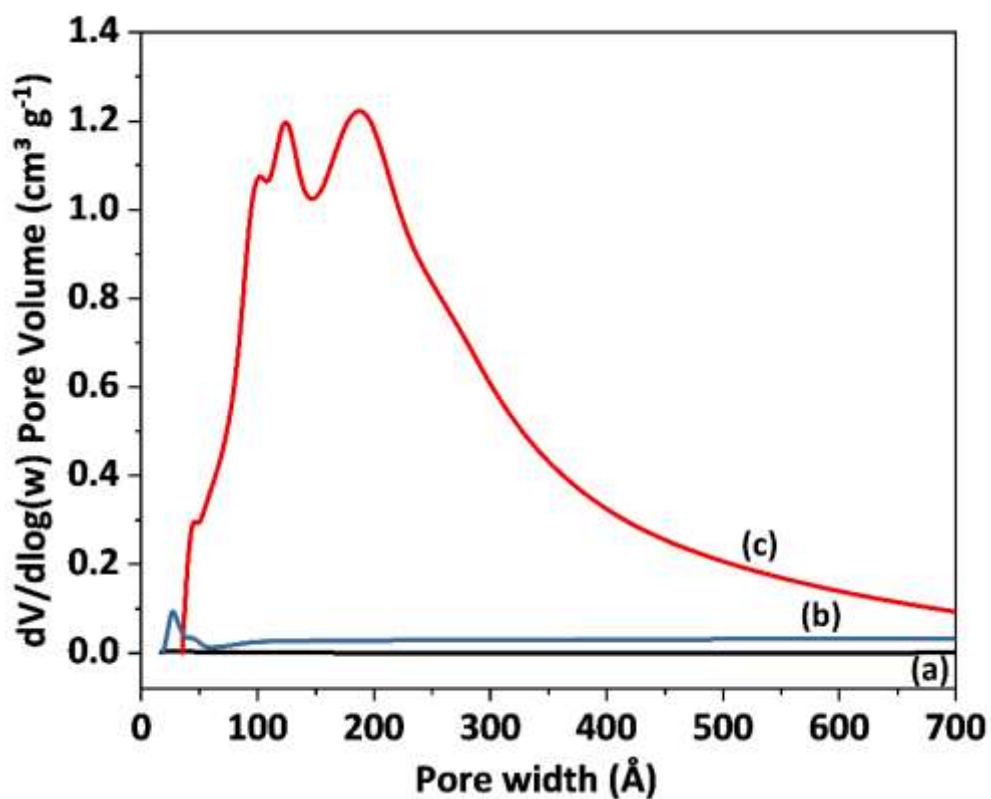


Fig. S11. BJH desorption pore size distributions of (a) struvite, (b) struvite decomposed in NaOH at 85 °C for 1 hour, and (c) Mg₃Al-CO₃ SLDH.

Table S3. Summary of the ICP-MS elemental analyses of struvite decomposed in NaOH at 85 °C.

Av. wt.%	MgNH ₄ PO ₄ ·6H ₂ O + NaOH (85 °C)	
	1 h	3 h
Na	3.46	7.33
Mg	12.81	15.95
P	13.36	16.30

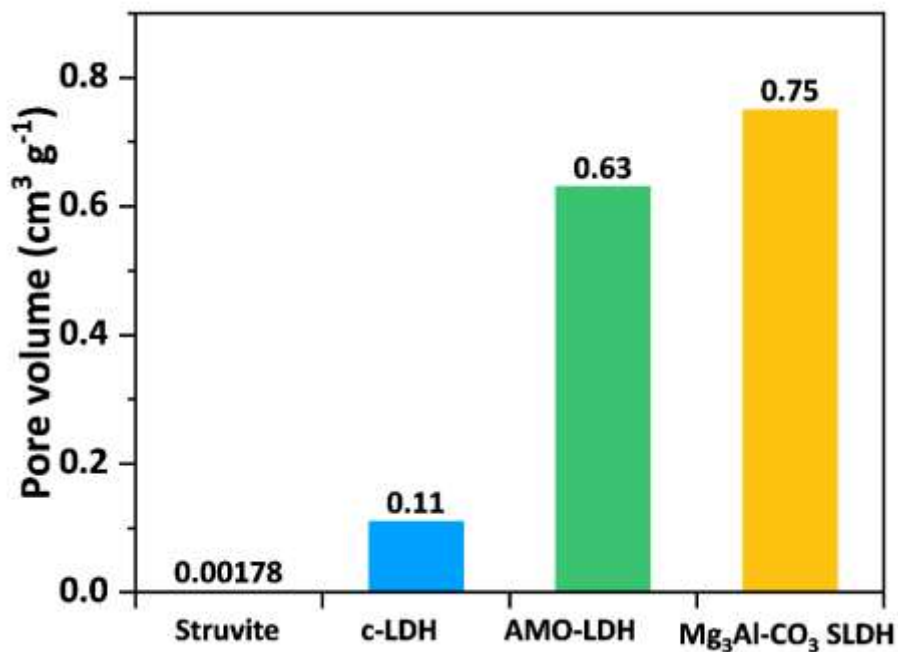


Fig. S12. Pore volumes of struvite, c-LDH, AMO-LDH, and Mg₃Al-CO₃ SLDH (c-LDH is a conventional water-washed Mg₃Al-CO₃ LDH, AMO-LDH is acetone-dispersed Mg₃Al-CO₃ AMO LDH).

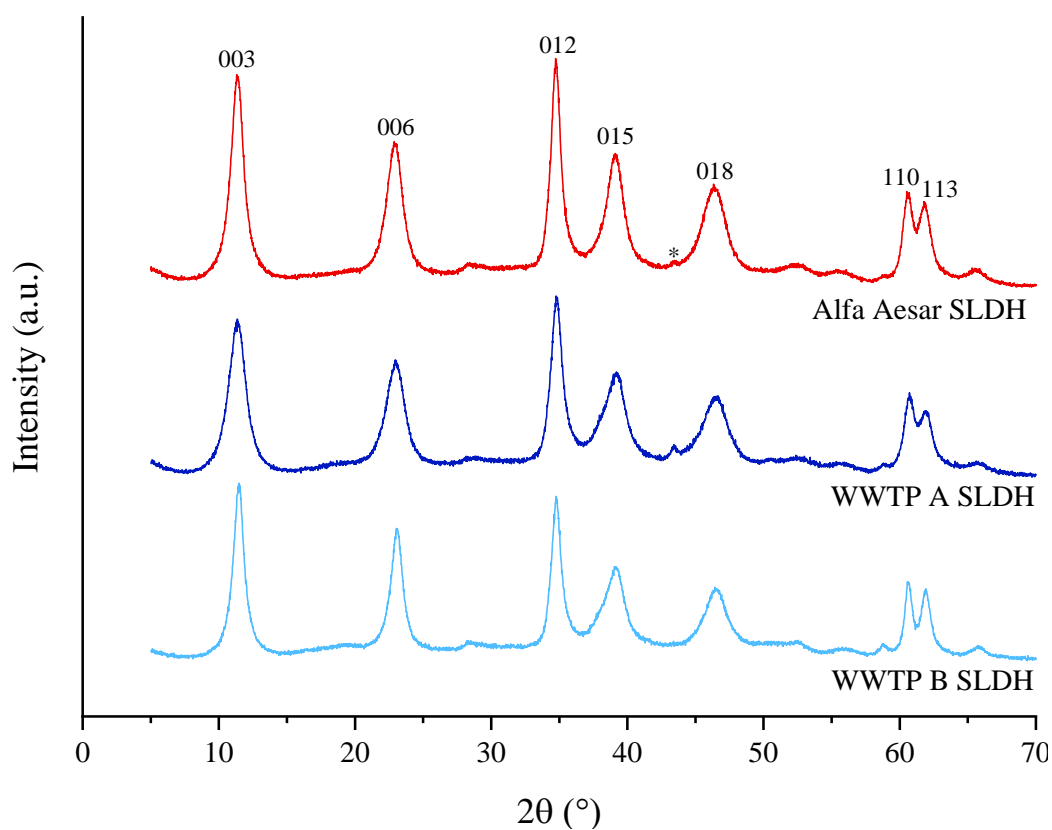


Fig. S13. Powder XRD diffractograms of SLDHs prepared from Alfa Aesar, WWTP A and WWTP B struvites. Mg/Al = 3. *Reflection due to the sample holder.

Table S4. Lattice parameters and mean CDLs of SLDHs. Mg/Al = 3.

SLDH Commercial Struvite source	<i>d</i> -spacing (Å)		Lattice parameter (Å)		CDL (Å)	
	<i>d</i> ₀₀₃	<i>d</i> ₁₁₀	<i>c</i> [†]	<i>a</i> [‡]	<i>c</i> -axis	<i>ab</i> -plane
Alfa Aesar	7.78	1.53	23.37	3.06	77.9	203.3
WWTP A	7.77	1.52	23.31	3.04	54.9	197.5
WWTP B	7.72	1.53	23.16	3.06	88.8	260.6

[†]Lattice parameter $c = 3d_{003}$

[‡]Lattice parameter $a = 2d_{110}$

CDL = $0.89\lambda/\beta\cos\theta$

$\lambda = 1.541847$ Å, β = FWHM in radians

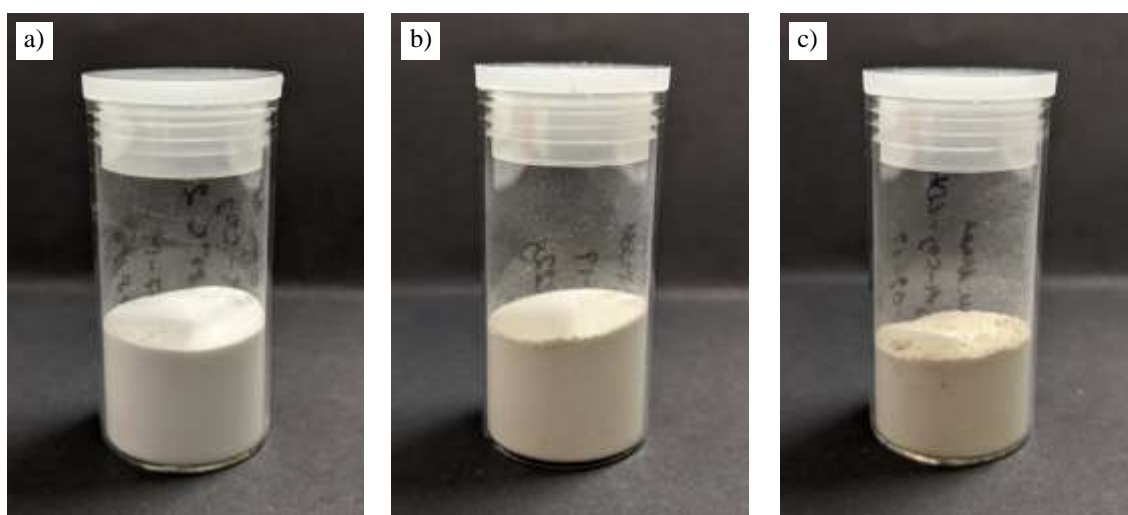


Fig. S14. Photos of SLDHs (Mg/Al = 3) using three different commercial struvite sources. a) Alfa Aesar, b) WWTP A and c) WWTP B.

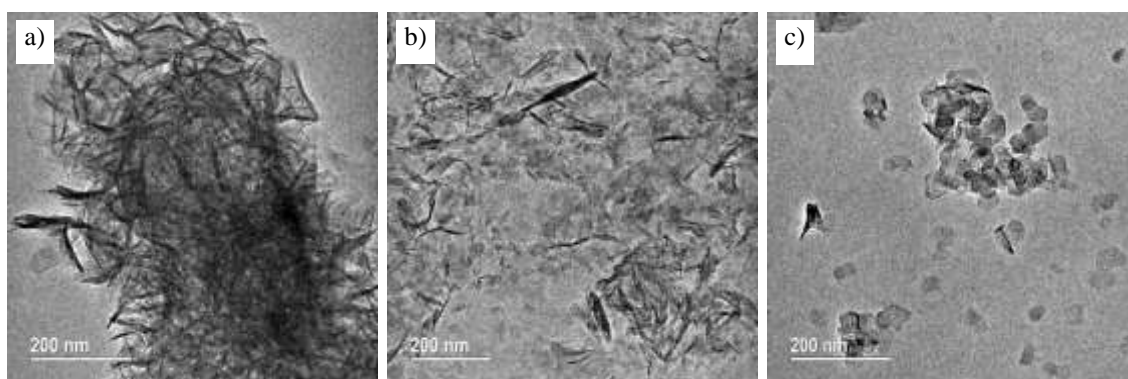


Fig. S15. TEM images of SLDHs (Mg/Al = 3) using three different commercial struvite sources a) Alfa Aesar, b) WWTP A and c) WWTP B.

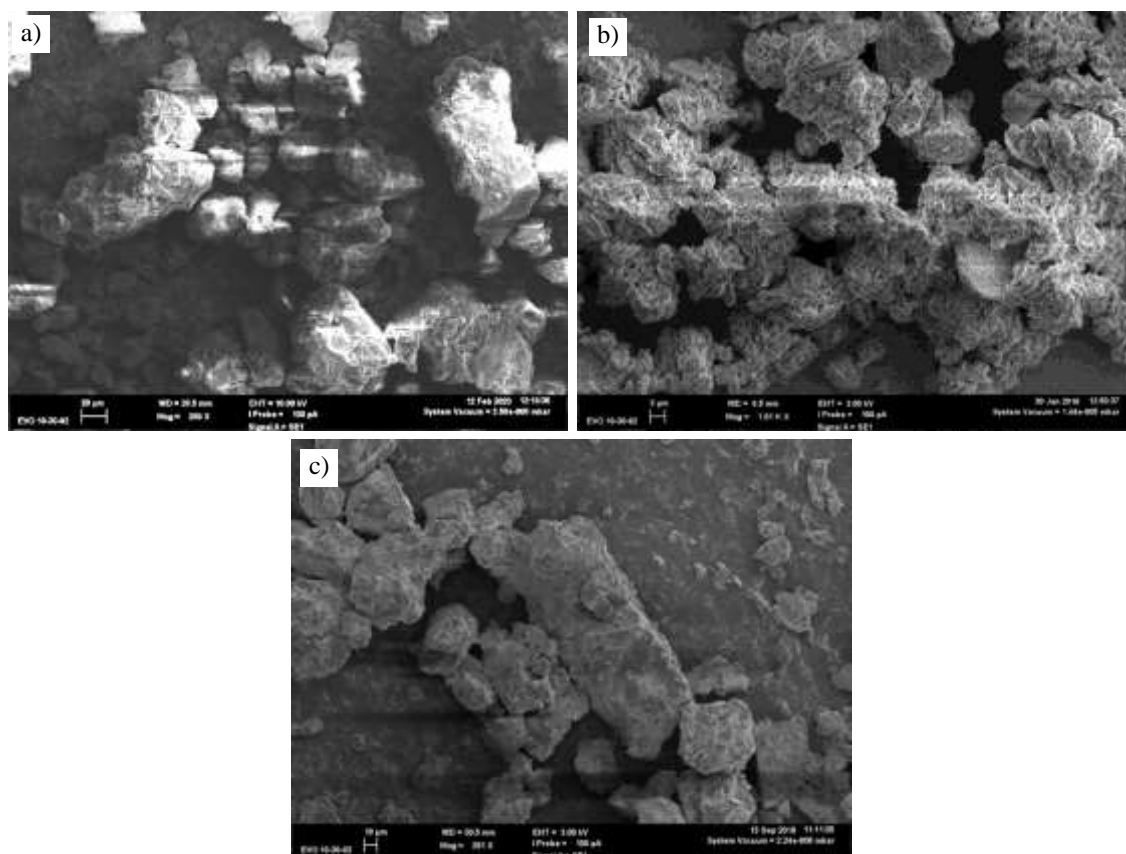


Fig. S16. SEM images of SLDHs Mg/Al = 3 from commercial struvite sources a) Alfa Aesar, b) WWTP A and c) WWTP B.

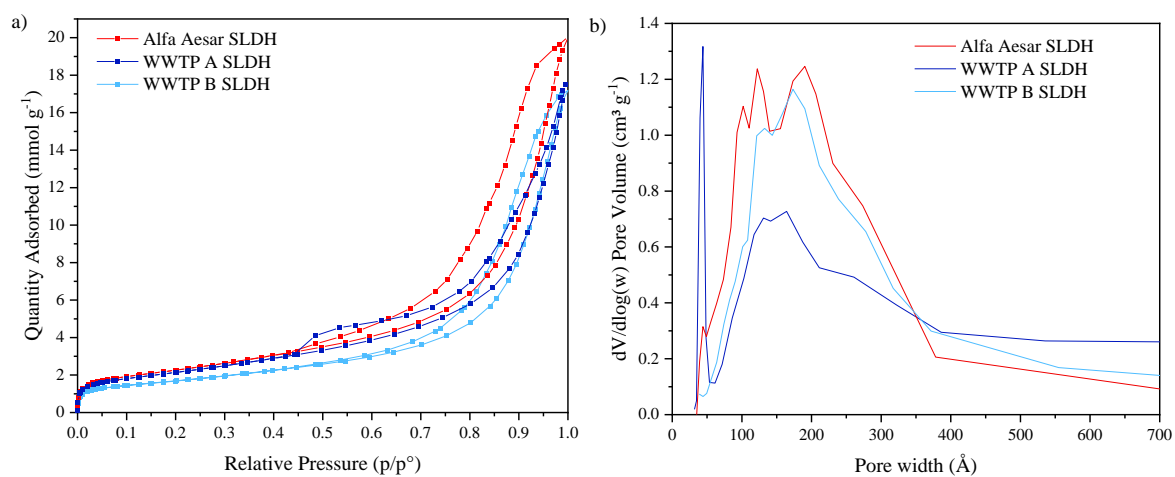


Fig. S17. a) N_2 adsorption and desorption isotherms and b) BJH pore size distributions of SLDHs. Mg/Al = 3 using three commercial struvite sources.

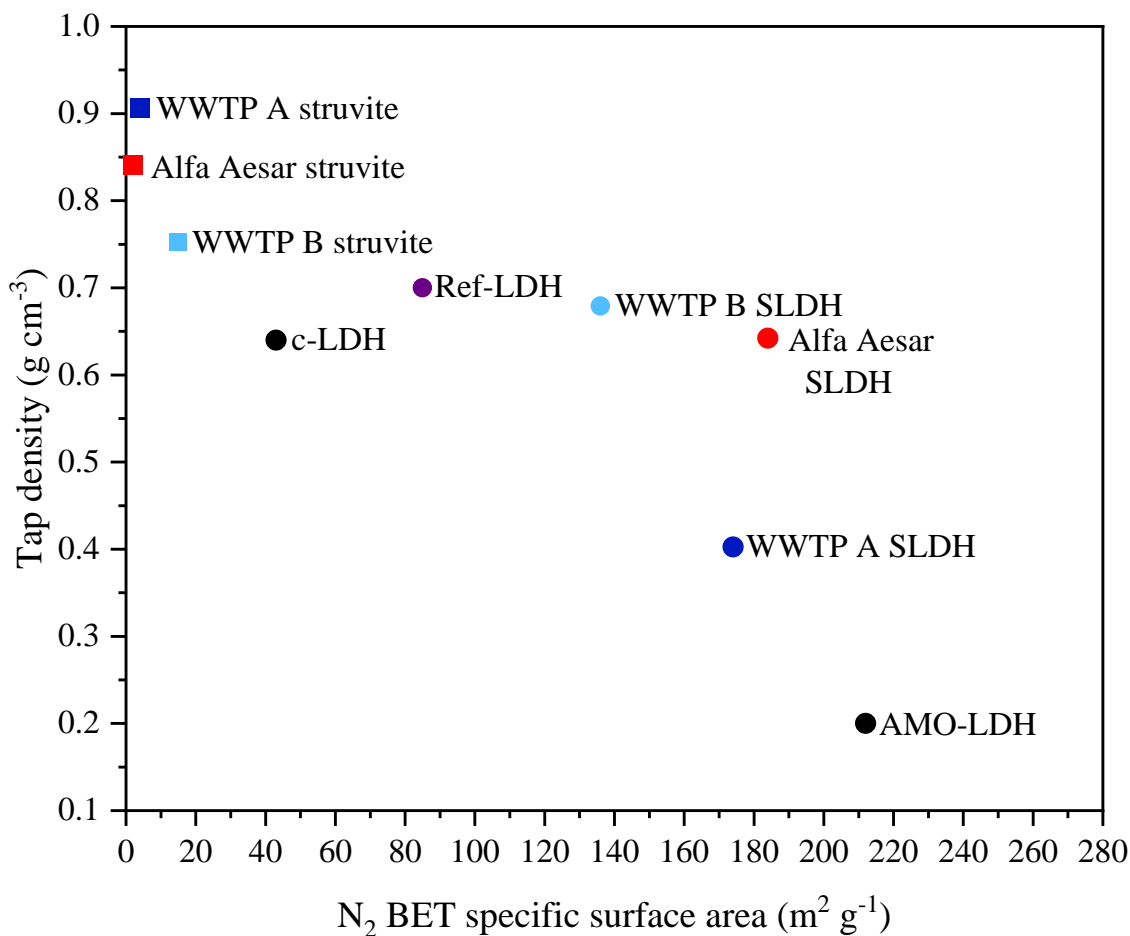


Fig. S18. Tap density plotted as a function of BET area for struvite, SLDHs and reference LDHs.

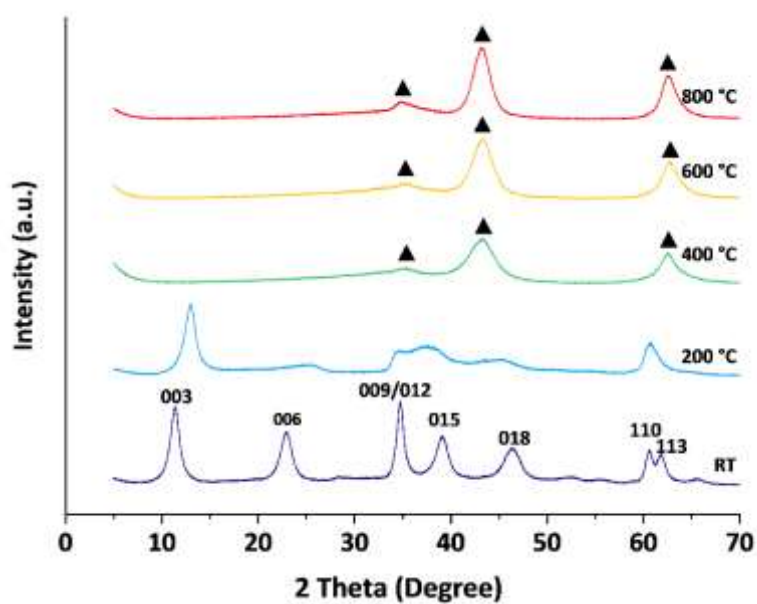


Fig. S19. Powder XRD diffractograms of Mg₃Al-CO₃ SLDH and SLDOs calcined at different temperatures. ▲ MgO

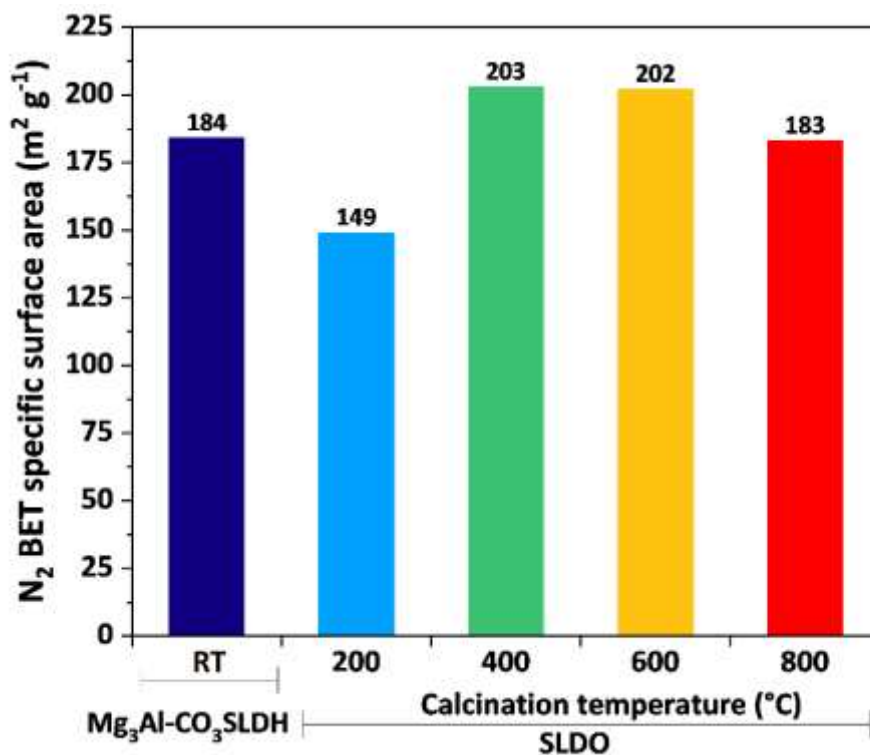


Fig. S20. N₂ BET specific surface areas of Mg₃Al-CO₃ SLDH and SLDOs calcined at different temperatures.

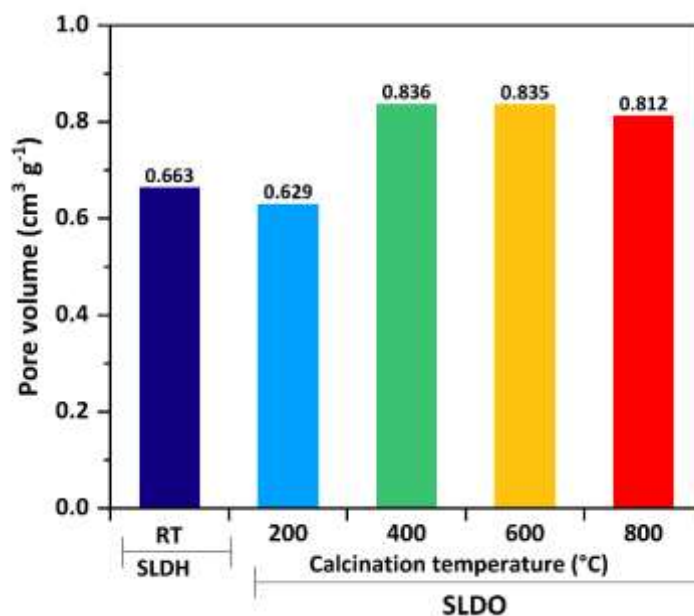


Fig. S21. Pore volumes of Mg₃Al-CO₃ SLDH and SLDOs calcined at different temperatures.