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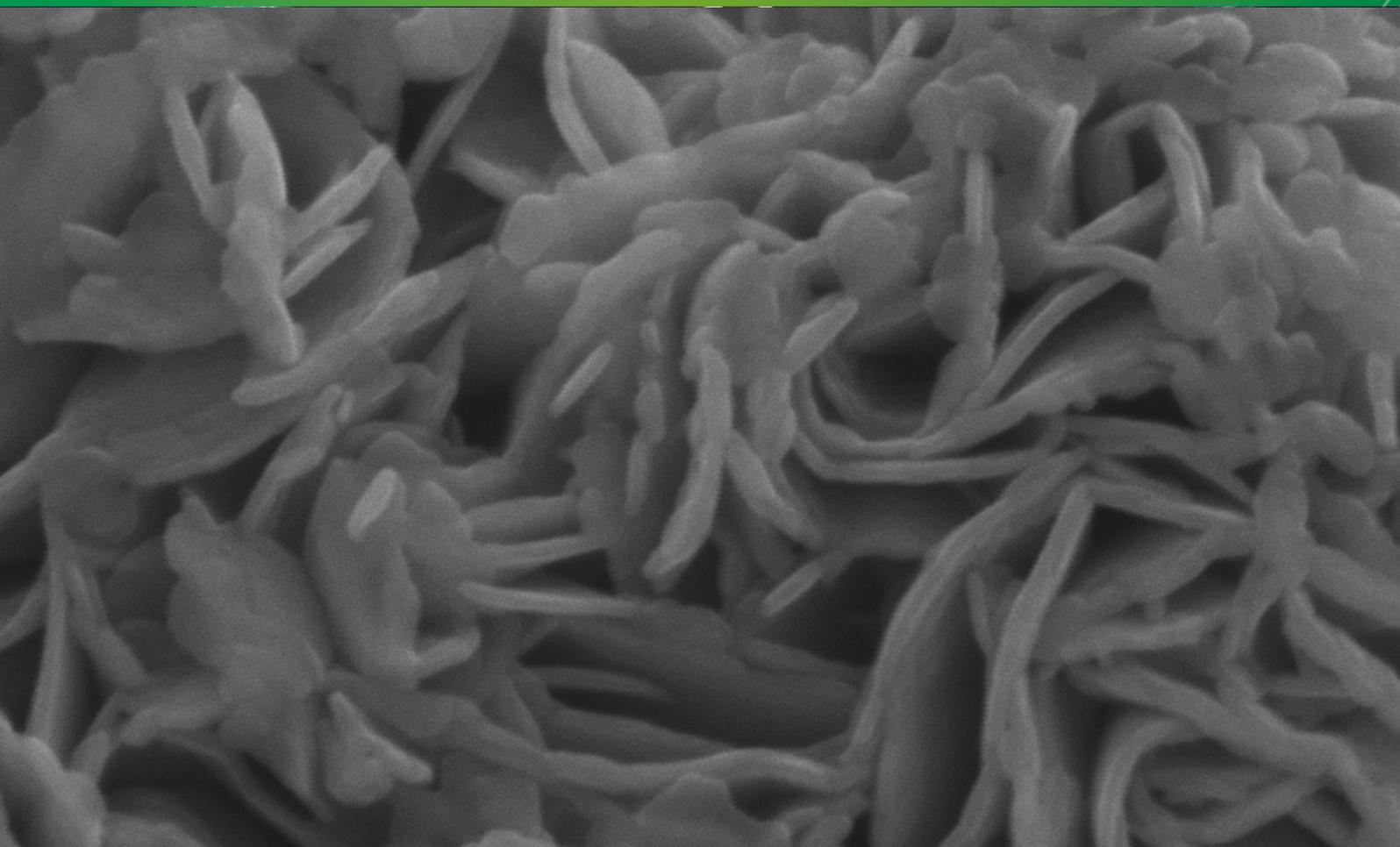


## Project Report

# Nanotechnology for phosphorus recovery from effluent

A report of a study funded by the  
Australian Water Recycling Centre of Excellence

TH Muster, GB Douglas, TG Harvey, SG Hardin, April 2015



# Nanotechnology for phosphorus recovery from effluent

## Project Leader

Dr Tim H. Muster  
CSIRO  
Waite Road  
Urrbrae SA 5064 Australia  
Telephone: +61 8 8273 8133

Contact: [tim.muster@csiro.au](mailto:tim.muster@csiro.au)

## Contributing Partners

Incitec Pivot, ACTEW, Melbourne Water, SA Water, Unity Water, Water Corporation, Queensland Urban Utilities.

## About the Australian Water Recycling Centre of Excellence

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### Cover image:

Mg-Al hydrotalcite produced in this study by induced hydrolysis. Image width is ca. 3 microns.

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## Executive summary

The AWRCE Nanotechnology for Phosphorus recovery from effluent project has sought to deliver P-absorbent materials that are easily separable from water, possess direct agronomic value, and are economically viable. This would achieve the combined goals of improving water recycling and enabling nutrient recovery from wastewater. The project thus attempted to meet the current P recovery challenge by shifting P removal towards a routine recovery and reuse opportunity yielding a P-rich solid, along with treated, recyclable water. The fiscal and agronomic/environmental benefit is the production of a new, sustainable agricultural P source partially addressing on a regional basis, the risk of limitation on global P supply.

From the outset of the project, industry partners advised on: (i) the sourcing of appropriate low-cost starting materials to be used as absorbent media, and (ii) on appropriate methodologies for the introduction of absorbent media into wastewater treatment processes. In addition, prior CSIRO research on the synthesis and characterisation of P-absorbent materials was also utilised.

Initially, a series of selected industrial materials including steelmaking by-product, calcined magnesia, and Neutralised Unused Acid (NUA) from heavy mineral processing were characterised for their P-uptake performance and ability to make P available upon application in agricultural systems. Secondly, a range of hydrotalcite materials prepared in-house by CSIRO, including clay-hydrotalcite hybrids, were developed and their P-uptake characteristics assessed. Results showed that when presented in an appropriate form, up to 35 g P/kg of solid could be incorporated into these absorbents. Furthermore, the P-absorbents were demonstrated to be effective in both synthetic and actual wastewaters. The extent of uptake is thought to have industrial relevance to augment existing fertilizer materials such as superphosphate, which typically contain 80-90 g P/kg. In addition to demonstrating effective P-uptake, P availability testing showed that the nutrients contained within the P-absorbents were effectively 100% available when exposed to citrate extraction solutions, commonly used as an indicative measure of soil availability, thus giving them a competitive edge over existing precipitation/coagulation methods such as alum or ferric dosing for the removal of P from wastewaters.

Engagement with wastewater experts from SA Water, Unity Water and Queensland Urban Utilities provided technical and practical guidance on tailoring developments in absorbent performance and morphology to meet widespread industry challenges. With their assistance, the most likely deployment of the technology was established as being the introduction into waste streams via rapid mixing, followed by a coagulation-like retention time prior to disk/cloth filtration.

Given the above operational constraints, three aspects of development were focussed upon; P-absorbent optimisation, P-absorbent application and recovery, and an operational cost-benefit analysis. The goals and outcomes of the developmental program are summarised below:

**P-absorbent optimisation:** Initial P-absorbent material development and screening identified the most promising materials as: (i) calcined magnesia, (ii) hybrid nanoclays and (iii) hydrotalcite formed at < 60°C (to minimize production costs).

The performance of absorbent materials was made by assessing the total P removal and uptake capacity of the absorbents. A range of wastewaters was sourced from processing facilities throughout Australia, several of which had specific concerns with P concentrations. The utilisation of absorbents was targeted towards lowering P concentrations in anaerobic digester centrate and secondary treated effluent. Those wastewaters tested included:

- secondary treated effluent from two large activated sludge plants;
- anaerobic digester centrate from dairy processing facility; and
- anaerobic digester (with enhanced pre-treatment) centrate from municipal treatment plant.

The P-uptake experiments were based on industry recommendations that the most feasible use of absorbents would involve dosing the solid into a well-mixed solute stream and removing the solid using existing recovery facilities. It was estimated that the residence time in such a stream would be no longer than 15-20 minutes, so rapid P-uptake times were critical.

Experimental results revealed that absorption capacities were extended beyond original results (i.e. 35 g P/kg) and exceeded 100 g P/kg for freshly calcined MgO, and 57 g P/kg for a series of hydrotalcite materials.

Nanoclay hybrid materials were demonstrated to absorb up to 18 g P/kg. Furthermore, the inherent advantages and disadvantages of each absorbent were detailed through careful examination of performance data. It follows that the most effective means of removing P from water was via addition of MgO. For example, MgO can comfortably reduce the P concentration of an anaerobic digester effluent from 64 mg/L to less than 10 mg/L in five minutes and to around 2 mg/L in 20 minutes at a loading of 1 kg MgO per kL of wastewater. However, MgO did not generally remove P to concentrations below 2 mg/L. In secondary treated effluent containing 6 mg/L P, the same loading of MgO could only reduce the P to a concentration of 2-3 mg/L. This limit was also confirmed with a synthetic 2.6 mg/L P solution, where MgO (used at 1 kg/kL) does not remove P below approximately 2 mg/L. Thus, the utility of MgO is primarily as a gross P-absorbent to remove the majority of P from high strength streams.

Hydrotalcites could be considered complementary to MgO in that, while lacking the ability to remove large amounts of P from solution (e.g. from digester effluent) as efficiently as MgO, they offer the potential to scrub remaining P to very low concentrations. For instance, with a synthetic 2.6 mg/L P solution, all synthetic hydrotalcites could remove P to lower concentrations than MgO, leaving < 1 mg/L P after five minutes. Indeed some hydrotalcites proved to be capable of leaving no detectable P in solution (< 0.1 mg/L) after 10-20 minutes. This performance, however, was not matched with actual effluent, but even with secondary effluent containing 6.2 mg/L P, certain hydrotalcites were capable of reducing P concentrations down to 1 – 1.5 mg/L ( $\frac{1}{2}$  to  $\frac{1}{3}$  of that of MgO within the same period, 10-20 minutes). Thus, hydrotalcites seem to be ideally suited as a supplementary treatment step to scrub remaining P from solution where the majority of the P has already been removed by MgO. In situations where the P concentrations are already low and much lower final concentrations are required (e.g. < 0.5 mg/L), hydrotalcites would appear to be suitable for use alone. A number of hydrotalcites were synthesized and while some were extremely effective, it is considered that the most effective material was a commercial product purchased from Aldrich. One critical proviso is, however, it was found that the material must be heat-treated prior to use as, in its as-received form, it is extremely hydrophobic and is essentially unusable.

Nanoclay hybrid materials were found to have rapid P uptake kinetics, due to the accessibility of the hydrotalcite coating on clay particles. However, they are limited in their overall capacity due to dilution by the inactive clay substrate. In low strength P wastewaters (0.87 mg/L and 0.38 mg/L) nanoclay hybrids removed approximately 56% of the P after only 5 minutes and 70% after 30 minutes (leaving 0.26 mg/L P). In addition to rapid uptake kinetics, an advantage of the nanoclay hybrid is the clay component itself which may constitute a useful addition to sandy soils with poor nutrient retention if the adsorbent is reused as a soil conditioner.

***P-absorbent application and recovery:*** A series of trials were undertaken to evaluate P-absorbent materials in the context of potential methods of P absorbent introduction and enhancing separability for efficient recovery. The potential 'competitive edge' of absorbent technologies developed in this study are their ability to be directly substituted to replace coagulants, and enable productive use of P incorporated into a solid form. The preferred application relies upon a rapid settling and/or filtration of the P-loaded absorbent in wastewater. Particle separation characteristics were explored through a variety of approaches:

- the use of unmodified dead-burned magnesia (DBM-S);
- through the binding of primary particles using acidified aluminosilicate binders; and
- utilising the distinct density contrast and "handleability" of hybrid nanoclays.

Whilst it was shown that particles with enhanced separability could be formed, production methods that lead directly to larger primary particles would be important in lowering manufacturing costs. Importantly, MgO is produced from the calcination of naturally occurring magnesite ( $\text{MgCO}_3$ ) that would require minimal treatment as it possesses a natural sheet-like atomic lattice structure. It can be directly sourced in various size fractions which directly influence its ability to be separated from wastewater. Exploration of the influence of particle size on efficacy showed the MgO particle sizes up to 10 mm diameter were still effective at lowering soluble P concentrations. Further improvements in separability may be achieved by sourcing larger size fractions of vermiculite as substrates/carriers for the hybrid nanoclays. The hydrotalcites utilised in this work exhibited small particle sizes and proved more difficult to settle.

This study also highlighted that careful preparation and adequate storage conditions are required for absorbents. For instance, magnesia should be calcined prior to utilisation and particle sizes should be selected to ensure a balance between separability and maximisation of uptake kinetics.

***Operational risk and cost-benefit analysis:*** The absorbent technologies developed were evaluated against coagulation methodologies for the polishing of secondary treated effluent, and the crystallisation of struvite from anaerobic digestion centrate. The table below presents a summary of the scientific, operational

and commercial benefits and risks of MgO, nanoclay hybrid and hydrotalcite absorbents in the context of their performance, utilisation and comparison against existing wastewater treatment technologies.

	Scientific		Operational		Commercial	
	Benefits	Risks	Benefits	Risks	Benefits	Risks
<b>MgO absorbent</b>	Minor advances in know-how can be made.	High levels of Mg in product may not be desirable for widespread utilisation as soil conditioner.	Can treat water containing >5 mg/L. No significant infrastructure needed.	Chemical storage, handling, dewatering costs may be high. May not find market for recovered absorbent. May only find application to treat shocks in water quality (i.e. not implemented in regular wastewater treatment process).	Materials available in Australia and would require limited pre-treatment.	Direct competition against coagulant technologies may not offer a competitive edge if recovered absorbent cannot demonstrate benefits as a soil conditioner. Not competitive financially against other recovery processes (i.e. struvite crystallisation).
<b>Nanoclay hybrid</b>	Novel products and processes can be developed.	Existing patents in the manufacturing processes.	Can be deployed as an on-demand treatment for shocks in water quality. No significant infrastructure needed. Reduces P < 1 mg/L.	Chemical storage, handling, dewatering costs may be high. May not find widespread market for recovered absorbent.	Novel technology that may find diverse application in wastewater treatment and environmental remediation.	Recovered absorbent may not find local application is clay fraction is not valued in soil conditioning.
<b>Hydrotalcite</b>	Novel products and processes can be developed.	Existing patents in the manufacturing processes.	Reduces P to lower levels than other absorbents (i.e. < 1 mg/L).	Specialised manufacture needed to bring costs down. Would likely result in limited suppliers. High dewatering costs. May not find widespread market for recovered absorbent.	Exceptional performance in being able to lower P concentration when compared to other absorbents.	High cost would restrict to niche application.

The costs for the implementation of MgO to remove and recover P from more concentrated wastewater were evaluated against existing struvite crystallisation from digester centrate. The latter technology has been implemented in the global wastewater industry according to two approaches: (i) direct manufacture of a high grade fertilizer prill (akin to a fertilizer granule); and (ii) rapid precipitation of fine struvite particles yielding a product resembling a fine powder upon drying. The costings for MgO absorbents showed comparatively higher chemical costs, and whilst capital costs may be substantially lower than for struvite crystallisation processes, MgO absorbent deployment for widespread application does not appear economically attractive. The high cost is primarily associated with the high loading of MgO (10:1) required to remove an equivalent proportion of P, whereas soluble Mg sources remove P at a ratio of 1:1 in struvite precipitation. The use of MgO adsorbents also contains significantly higher material handling costs. The low retrofitting costs of absorbent technologies does however offer an option for one-off or occasional treatments should shocks in P concentration arise. However, the cost effectiveness of using absorbent MgO in place of a soluble Mg source would need to be demonstrated.

For wastewaters containing P concentrations in the range of approximately 1-5 mg/L (i.e. secondary treated effluent), nanoclay hybrid absorbents offer an alternative to the use of traditional coagulants. The competitive edge for the nanoclay material is their potential ability to reduce sludge handling costs and the improved potential for recovery as a saleable soil conditioner (though both of these suggested advantages require confirmation). Best estimates suggest that the cost of supply of nanoclay hybrid absorbents, whilst possibly being up to two times more expensive than coagulants, is similar to the increased sludge management costs that would arise due to the use of coagulant technologies. Where biosolids handling costs are not an imposition for a wastewater facility, it would appear that traditional coagulants would still be more cost-effective. However, nanoclay materials may also offer productivity benefits for agriculture in rural areas, particularly in regions with sandy soils, whereby the combined benefits of clay and P additions to soil could be realized. Demonstration of the agronomic value of the P-enriched absorbents will therefore be an important part in subsequent development of absorbent materials.

Recommendations for future work are to:

- explore the cost effectiveness of using coarse MgO as a means to manage one-off or occasional treatments of high P concentration waters;
- further develop nanoclay hybrid materials as a soil remediation tool and for the treatment of wastewaters and environmental waters containing low P concentration (1-5 mg/L);
- ensure that the exceptional performance of hydrotalcite materials in lowering P concentration to less than 1 mg/L is communicated in scientific literature, with the hope that decreased manufacture costs may lead to future technology deployment;
- continue to develop scientific understanding where possible of the effects of water quality (i.e. pH, ionic strength, competitive species) on performance would also assist improved absorbent development.

# Introduction

Approximately 2000 GL of municipal wastewater is produced in Australia p.a. with only 15% being effectively recycled due to barriers such as treatment efficiency, environmental management, social acceptance and licence-to-operate [1]. Australia's wastewater industry has been progressing towards energy-efficiency goals, however, environmental sustainability is placing increased emphasis on effective nutrient recovery [2]. Discharge limits for phosphorus (P) in treated wastewater are becoming increasingly stringent, and new technologies are required to address these evolving criteria [2]. This is particularly crucial to the urban water environment in Australian cities and also internationally, where high population density gives rise to potentially valuable P-enriched waste streams. These streams are contained within extensive capture and delivery infrastructure, but are presently being poorly exploited for P recovery.

Global and Australian government policy agendas are becoming increasingly aware of food security issues and the pending complications of the declining availability of P fertilizers.[3-6] Australia is known to have P-deficient soils and limited ongoing resources of phosphate. The price of phosphate rock has risen by an average of 25% each year for the past eight years (2006-14), yet changed by less than 10% in total during the previous 25 years [7]. Long-term P prices are predicted to continue to increase, and thus advances in P recovery and productive reuse are of interest to agri-businesses. The purity of P fertilizers has also been of concern in some parts of Australia. For instance, the Victorian Dept. Primary Industrials found that during a 2008-09 study, 15 out of 18 P fertilizers contained cadmium concentrations exceeding industry guidelines [8]. The development and implementation of large-scale recyclability of P from effluent aims to partially address impending limitations to global P supply that may arise in the future.

Internationally, current P recovery technologies from wastewater generally involve the precipitation of P-containing struvite and hydroxyapatite [9] and recover less than 30% total P. Given this marginal P recovery, an opportunity exists to develop and implement novel technology-based P removal techniques of potential lower cost, and with increased efficiency. Asahi Kasei Chemical Corporation (Japan) has developed absorbent materials for P removal, demonstrating high selectivity and P removal efficiencies approaching 99%.[10] In this case P is recovered using chemical treatment to precipitate calcium phosphate. Such techniques, however, may be inherently expensive, not only in absorbent synthesis and lifespan, but also due to the use of chemical precipitation and associated recovery infrastructure. During the lifetime of the project, work has been published on a novel dispersed magnesium oxide (brucite) nanoflake-modified diatomite adsorbent (MOD) developed for the removal of excess phosphate from lakes [11].

High-surface area materials have been widely demonstrated to have exceptional P adsorption at low concentration, thus being able to treat water to meet defined P discharge limits. P-uptake by high surface area materials is generally achieved at a higher efficiency and increased rate relative to biological-based phosphate treatment [12]. Numerous P-absorbent materials have been assessed internationally and over the past four years, in our laboratories [13-14] and in large-scale field trials (e.g. [15-16]).

As large quantities of low-cost raw materials are required, the by-products from energy and mining industries have been a dominant source of P-based absorbents. Absorbent materials most suitable for environmental remediation purposes in Australia have already been identified as partly summarised by CSIRO in earlier work (Table 1). More detailed information on the identification and characterisation of P-absorbents already conducted by CSIRO can be obtained in references [17-19] and electronically at: (<http://www.water.wa.gov.au/PublicationStore/first/97296.pdf>). Despite many potential candidates being available for P-adsorption (Table 1), a number of factors inhibit their wide-scale application, including raw material or synthesis cost, availability or inadequate P-uptake capacity or kinetics. This is particularly the case in P recovery from wastewaters (Figure 1).

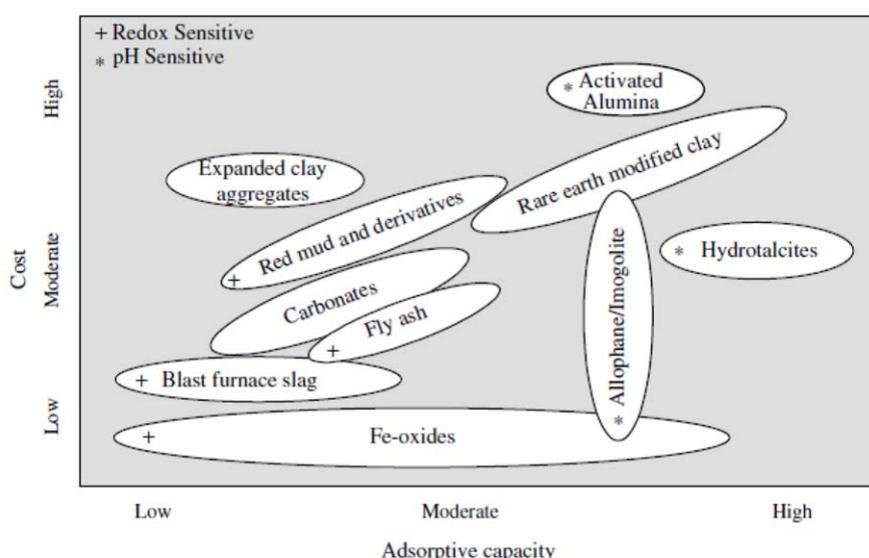


Figure 1. Cost vs Adsorptive capacity of various materials.

Source [18].

Table 1. Summary of nutrient and DOC addition or removal by low-cost mineral-based by-products or mixtures of by-products in laboratory trials after 60 days of column operation<sup>†</sup>. Mineral-based by-products are ranked in order of increasing DOC removal.

Experimental column contents	Cumulative analyte added or removed (mg/kg material)						
	NO <sub>x</sub> -N	NH <sub>3</sub> -N	DON	TN	PO <sub>4</sub> -P	TP	DOC
Inlet water (mg/L)	0.4	0.4	1.4	2.2	0.6	0.8	58
Bassendean Sand	+13.0 <sup>‡</sup>	+14.5	+0.4	+27.8	+7.8	+10.7	+50
GWTP <sup>#</sup> Fe/CaCO <sub>3</sub> residue	<b>-135.8<sup>§</sup></b>	<b>-92.6</b>	+85.7	-142.7	-2.6	-0.8	+4,732
Red mud (RM)	<b>-112.4</b>	-28.8	-5.6	-146.8	<b>-71.0</b>	<b>-75.8</b>	+197
Fly ash	<b>-120.5</b>	<b>-106.9</b>	-3.1	<b>-230.4</b>	-21.8	-31.5	-170
Laterite	-53.2	-22.6	-78.5	-47.9	<b>-76.5</b>	<b>-91.5</b>	-372
Vermiculite	<b>-126.5</b>	-27.1	<b>-101.6</b>	<b>-255.1</b>	<b>-47.1</b>	<b>-69.2</b>	-721
GWTP lime residue (GWTPL)	<b>-130.1</b>	<b>-95.2</b>	+64.0	-161.2	<b>-81.5</b>	<b>-105.9</b>	-794
NUA <sup>@</sup> /steel by-product	-71.6	-49.5	<b>-122.1</b>	<b>-243.2</b>	<b>-75.1</b>	<b>-95.7</b>	-1,626
Limestone	<b>-80.0</b>	<b>-71.1</b>	<b>-103.0</b>	<b>-254.0</b>	<b>-52.3</b>	<b>-77.4</b>	-2,030
Steel by-product (SS)	<b>-110.8</b>	-27.4	<b>-92.6</b>	<b>-230.8</b>	<b>-44.4</b>	<b>-70.0</b>	-2,283
Red sand (RS)	<b>-132.1</b>	-29.2	+10.7	-150.6	<b>-74.1</b>	<b>-77.7</b>	-2,738
NUA/GWTP lime residue	<b>-81.9</b>	-39.4	+57.5	-63.8	<b>-86.6</b>	<b>-109.3</b>	-3,033
NUA/carbonated red mud (CRM)	<b>-144.4</b>	<b>-117.7</b>	-84.4	<b>-346.5</b>	<b>-83.4</b>	<b>-109.9</b>	-3,664
Steel by-product/activated carbon	<b>-182.9</b>	<b>-112.9</b>	<b>-213.9</b>	<b>-509.8</b>	<b>-87.0</b>	<b>-128.5</b>	-4,167
NUA/red sand	<b>-125.2</b>	<b>-95.9</b>	-71.3	<b>-292.4</b>	<b>-89.2</b>	<b>-117.6</b>	-4,408
Calcined magnesia (CM)	<b>-102.4</b>	<b>-76.2</b>	-34.6	-213.2	<b>-82.9</b>	<b>-106.8</b>	-4,452
NUA	<b>-121.1</b>	<b>-104.6</b>	-61.1	<b>-286.8</b>	<b>-87.2</b>	<b>-109.9</b>	-4,561
NUA/calcined magnesia	<b>-89.6</b>	<b>-80.6</b>	<b>-137.9</b>	<b>-308.1</b>	<b>-88.8</b>	<b>-117.2</b>	-6,309
NUA/activated carbon	-56.2	<b>-144.6</b>	<b>-194.8</b>	<b>-395.6</b>	<b>-135.6</b>	<b>-173.6</b>	-7,638
Granular activated carbon (GAC)	+22.0	<b>-456.9</b>	<b>-564.5</b>	<b>-1,000.6</b>	+47.7	+1.5	-21,165

<sup>#</sup> Groundwater Treatment Product

<sup>†</sup> Columns that failed or were terminated due to poor performance prior to 60 days operation not included in summary.

<sup>‡</sup> +xx=net increase as compared to inlet water.

<sup>§</sup> Cumulative reductions of >50% as compared to inlet water in **bold**.

<sup>@</sup> NUA – Neutralised Used Acid – a combination of Fe-oxide and gypsum produced from heavy mineral processing.

Source [16].

Two examples of P absorbent materials below highlight some of the challenges in developing a suitably low-cost, high-capacity P-absorbent suitable for P removal from wastewaters:

- Phoslock™, developed by CSIRO is a commercially-available P-absorbent but is not well suited to P-removal from wastewater due to its substantial cost and the (intentional) difficulty in recovering absorbed P [20]. Thus, its application is best suited to high value environmental applications such as in lakes or rivers where a permanent sink for P is required.
- Calcium silicate hydrate (CSH) as a by-product produced from blast furnaces in steel product has undergone extensive trials in treating wastewater. It has been suggested that it acts as a seed crystal [21] and as a filter of nutrients [22]. Most recently CSH has been introduced to operational wastewater treatment plants in Darmstadt, Germany, where calcium phosphate crystallisation is induced on the surface of CSH during secondary treatment of the wastewater [23]. A potential drawback, however, may be the presence of potentially leachable contaminants that are often present in blast furnace by-products [24].

Many of the properties required to address broader environmental remediation goals such as soil amendments overlap with those required for a P-absorbent in wastewater treatment. This project, however, seeks to develop a novel, low-cost P-absorbent that is able to release P for reuse applications such as in soil amendments or for P-recovery for fertiliser manufacture, with the adjunct goal of a separate economic return to offset wastewater treatment costs.

Herein, the aims for this *Nanotechnology for Phosphorus Recovery from Effluent* project were:

- Development of innovative microbead nanotechnology to enable a larger fraction of P contained in wastewater to be effectively captured and recycled.
- Technology transfer to wastewater treatment utilities, government departments and agricultural bodies enabling ongoing technological development for wastewater recycling.
- Further development of key capability within Australia in the modification of high-surface area absorbents, and in solid-liquid separation media, particularly in wastewaters.

Initial testing within the project explored the performance of a series of selected materials for their ability to absorb soluble phosphate. Appendix I contains information on the materials, sourcing and performance. The most promising materials for further development were identified as: (i) calcined magnesia, (ii) hybrid nanoclays, and (iii) hydrotalcite formed at < 60°C. Kinetic tests demonstrated that P adsorption was characterised by a rapid initial adsorption where typically 60-80% of total adsorption occurred in 2-5 hours followed by a slower uptake, over 30-40 hours. All absorbents demonstrating good P-uptake from synthetic wastewater solutions showed comparable performance in real wastewater (secondary treated effluent and anaerobic digester centrate), with the exception of NUA, which showed a lower uptake capacity.

Appendix II provides data on the potential for recycling or reuse of absorbed P. A neutral pH ammonium citrate test widely used in industry as a proxy for P bioavailability in soil, demonstrated that all of the absorbed P is labile from the absorbents tested. On this basis, a potential exists for the further concentration of absorbed P, direct incorporation as an alternative P source in commercial fertiliser manufacture, and/or for use of spent P absorbents as a direct soil amendment.

# Industry Guidance

The development of novel P-absorbent technologies has been guided through interaction with contacts from both the wastewater treatment and fertilizer industries. Formal discussions/meetings were undertaken with Incitec Pivot and ACTEW, as well as informal conversations with Melbourne Water and Water Corporation. Most recently the project team has sought guidance from wastewater industry experts to ensure that developments in P-absorbent technologies are able to meet common industry challenges, amongst the most important being P-uptake capacity, hydraulic retention time, and spent absorbent recovery.

The key points from all discussions are summarized below. Interaction of project members in an aligned project, "*Identifying and enabling the capture of recycled water opportunities in sustainable food production and manufacture*", has gained insights into the needs of City West Water and Southern Rural Water. Southern Rural Water indicated that they would also be interested in trialling P-absorbent technologies, however, restructures within the company inhibited further discussions and trials from taking place. The absorbent materials have been trialled on anaerobic digester centrate from the dairy processing industry where significant amounts of P are found in waste streams.

## The fertilizer perspective

Nationally, Incitec Pivot Limited (IPL) [25] produce  $10^6$  tonnes/yr MAP/DAP (mono-ammonium and di-ammonium phosphates), some of which is exported. It has a range of P-containing products, including liquid fertilizers, ammonium/Ca phosphates (no Mg products however) and rock phosphate. For pastures, superphosphate is preferred and it is produced at Geelong and Portland. IPL has found that the  $\text{CaSO}_4$  in superphosphate is valued by farmers, despite the fact that it is lower in P (~9%) compared to DAP/MAP (20-22%). In some areas, for instance sandy soils in Western Australia, superphosphate can be lost too quickly but this can be overcome by applying less material but more frequently (twice yearly) or through the use of lower solubility products. The rapid release of P is valued in some cases as it may be distributed throughout the soil more efficiently to encourage vigorous crop growth to compete with weeds. The consumption of MAP/DAP in Australia is around 1.3 mt p.a. and can vary considerably. In Australia, the cost of MAP and DAP varied between \$300 and \$2000 per tonne over the period of 2008 to 2012. Total Australian consumption of P was ~500k tonnes at the turn of the 21<sup>st</sup> century, but has subsequently decreased, and Australia exports fertiliser in the quiet (local) season but imports in the high season. There is a peak in use in autumn and a smaller peak in spring emphasising the fundamental seasonality of fertiliser use in Australia. Large reserves of phosphate cannot be maintained as the storage capacity does not exist and the fertiliser granules tend to decompose over time.

A growth area for the fertilizer industry is in efficiently controlled release of P. In general, P-containing materials must not possess Al or Fe as it will tie up the P too effectively (due to poor solubility). Consideration must also be given to Ca:Mg ratios in soils, and IPL generally support the view that a Ca:Mg ratio of between 3:1 to 5:1 is ideal, although this depends on the soil type and it is more important to ensure there is enough Ca and Mg in the soil. There are, for instance, calcareous soils in South Australia (particularly around the Eyre Peninsula for example) that would be as high as 20:1 and yet still grow excellent crops. The main issue is often one of soil structure and friability rather than nutrient concentration, although if there is too much Mg in the soils they often seal and become water repellent. The most productive soils are neutral and slightly alkaline vertosols (e.g. Liverpool Plains, Darling Downs, Wimmera) and therefore slightly acidic forms would be preferred for any soil additive to enable P utilisation.

Organic P is already available in the form of biosolids, but is only ever applied on a local basis as a soil amendment from municipal recycling of sewage. Most manure is now sold either directly or indirectly (i.e. via blending), rather than disposed of as a waste. For these reasons, in addition to the generally low nutrient content, manure is usually used within 20-50 km of where it is generated. IPL do not operate in this business area at all, chiefly due to low nutrient concentrations and difficulty in logistics, storage and volatility.

There are around twenty elements commonly found in wastewater, most of which are required by crops, but not all of the time. For example, Zn is often needed in alkaline soils, but not in acid soils. Selenium (Se) deficiency is widespread in pastoral situations (causing white muscle disease in lambs). To provide these minor constituents, it is normal to use combinations of fertilisers. The development of fertilizers with blends of major and minor nutrients are generally done on a regional basis, but not finer than that, as logistics/supply issues for individual farms become too complex. However, a significant portion (up to 15%) of IPL's business is custom blends which are formulated to specific paddock needs.

Materials that are undesirable in any soil include heavy metals (e.g. Cd, Hg, Pb) and F, although certain others (e.g. hormones, endocrine disruptors) could also be problematic. Addition of Na to soil should also be avoided. The ability of recovered products to be stored and transported is also critical. Similarly, quality control should be tightened wherever possible. IPL suggested that using C-based absorbents may not be the best option as previous research undertaken on the addition of carbon to soils indicates that whilst it can improve some soils, there are issues in keeping carbon in the soil and preventing run down, particularly in the light of existing farming practices.

Any new product should not affect the logistics of fertiliser delivery (e.g. the number of trucks needed) or application (how a product is applied). The cost of superphosphate is sufficiently low on a cost per mass of P basis that it is unlikely that a recycled P form will be able to compete against superphosphate in the present market although IPL would consider the addition of a low-P filler to enable traditional products (i.e. MAP/DAP) to meet concentration specifications [25].

## The water treatment perspective

In Australia and globally, wastewater treatment facilities are tasked to ensure the socially acceptable and legislative requirements for the management of water, odours, contaminants and pathogenic and disease carrying organisms. The need for removal of nutrients from treated water has arisen from their tendency to promote eutrophication, where the most detrimental occurrences are associated with increased phosphorus in freshwater. As a result, project stakeholders, ACTEW and Melbourne Water represent the diversity of discharge requirements based on their geographic location, both in terms of in-land and ocean discharge.

ACTEW [26] cleans treated wastewater to tertiary quality with the philosophy that “water should be of improved quality than it was before use”. Present limits for treated wastewater effluent are 0.4 mg/L total P and this cannot be achieved by means of biological treatment alone. Therefore, ferric chloride is currently dosed upon primary (settling) treatment and again after secondary treatment. In most cases the effluent quality of 0.15 mg/L total P is achieved and DOC typically < 10 mg/L. ACTEW are also regulated on N:P ratio as decreasing P further can affect N-fixing bacteria as well. At 0.15 mg/L the P concentration is still sufficient in some cases to cause environmental concern, particularly as they release into the upper Murrumbidgee system. The addition of Fe can lead to discolouration, which is also of some concern to ACTEW. The introduction of an absorbent into the current treatment process used by ACTEW at the Lower Molonglo plant would either be during Primary treatment but most likely in line with final polishing of tertiary treated water. In the latter case the absorbent would need to treat a high volume, low P stream.

Melbourne Water [27] operates two major wastewater treatment plants, the Western Treatment Plant (WTP) at Werribee and the Eastern Treatment Plant (ETP) in Bangholme. The latter was chosen as having appropriate wastewater streams to assess the capability of absorbent materials. The ETP treats approximately 40% of Melbourne’s sewage, which amounted to over 425 megalitres per day on average in 2012 [26]. The NH<sub>3</sub>-N concentration limit imposed on the ETP for release of treated water is 5 mg/L, with typical annual average released of < 3 mg/L achieved. There is, however, no current concentration limit for P. Samples from two ETP streams were sourced; secondary treated effluent and dewatering centrate from the anaerobic digester. Soluble P concentrations entering ETP are typically 12 mg/L.

From wider consultation with the industry (with SA Water, Unity Water, Queensland Urban Utilities) there is clear evidence of a growing need for technologies to assist in the cost-effective compliance to P discharge concentration limits, as well as the ability to recover P such that it can be beneficially used to decrease dependence on new P resources. Two general areas are considered for the implementation of the P-absorbent nanomaterials:

*A concentrated stream:* This would best suit the centrate from a dewatering facility (anaerobic centrate, WAS centrate or centrifuge or belt filter press). The concentrated ‘waste’ stream of the dewatering process will contain high P concentrations. The most likely applications would be in:

- Dewatered liquor from waste activated sludge (WAS) may benefit from lowering P concentrations where the liquor is returned to the plant. Best practice suggests it would be optimal to combine it with the anaerobic centrate where possible.
- Anaerobic digester centrate, where it could be possible to compete against struvite crystallisation if a low-cost process could be implemented).

*A dilute stream:* This would likely be the effluent stream from a typical sewage treatment facility. All of or a portion of the stream could be treated as follows; cleaning treated water (effluent) after the biological process. This would typically contain 5-6 mg P/L, or where Biological-P removal is unable to achieve low P concentrations (i.e. to sub mg/L) in which case it would be competing against the use of alum/ ferric addition. Industry advice has been that the use of alum or ferric dosing is not seen as sustainable. P-adsorbents, on the other hand, would be very suitable for potential future plant designs similar to the two stage A-B process [28-29] if they were to be adopted within Australia.

There is a demand for recycled water both with and without nutrients. The use of adsorbents at the input or output of storage lagoons would enable nutrients to be removed on demand. This gives the option to sell water and P separately to farmers, while many industrial customers would not want any P in water (e.g. to prevent scale build-up in boilers).

The recovered adsorbents may or may not be incorporated into sludge. This would depend on the particular capability of the plant concerned and the cost to recover the adsorbents as a “non-biological” stream that could be transported off-site for application independent of biosolids. Alternatively, if it added value to the biosolids, or was more cost-effective, it may be incorporated to improve value (such as in the lime-amended biosolids developed by Water Corporation).

The technology could be implemented for wastewater treatment in several ways:

- Packed column
- Sand filter
- Rapid mixing followed by settling/filtration or removal via the normal wasting process of biomass to control the sludge age of an STP.

Industry advisors considered that the P-adsorbent technology would most likely be retrofitted to existing treatment facilities. This would provide the benefit of being able to respond to any regulatory demands for increases in treatment capacity at low cost and with relatively few changes to plant. A number of alternative existing technologies could also be modified to effectively utilise the P-adsorbents.

*Sand filters:* The hydraulic retention time (HRT) for a sand filter is in the order of 15-20 minutes and is somewhat dependent upon the rate of dewatering. Existing technologies for precipitating P using ferric/alum coagulants have a HRT of up to approximately 1 hr depending on the dose location. In instances where a sand bed is used to remove particles to meet recycled water quality (or as an oxidation reactor to remove manganese-based colour concerns), the sand filter may offer an additional removal of P (i.e. classic coagulant, mix then settle and filter through a sand filter). It was suggested that the industry is moving away from sand filters as there is a high capital cost for the concrete tanks. Therefore, a disk filter or a cloth filter may be preferable. Cloth/disk filters are generally smaller with the entire package having a lower capital cost.

*Cloth/disk filters:* To incorporate the P-adsorbent nanomaterials, a flash mixer could be used, along the lines of those used to mix coagulants. Sufficient reaction time would need to provide adequate time for P capture. This would likely also require an extra balance tank. Alternatively, the transit time in the distribution pipeline could be built in to match reaction time needs, which would allow sufficient reaction time followed by a cloth filter. This would take a few minutes to treat the same flow at a lower capital cost. Bench-scale testing used in an earlier phase of this work was similar to the mixing regime that would be encountered in an industrial setting if this approach was used.

*Key experimental challenges:* Experimental focus should centre on measuring uptakes after 5/10/15 minutes. Rapid adsorption rates would lead to more rapid treatment throughput and smaller infrastructure. This would also provide a comparison with existing coagulant performance. The development of reliability in performance is also required (e.g. HRT for 90% P removal). Should pilot trials be undertaken, they should provide the following operational details: reaction times, chemical cost, capital cost (i.e. comparison of tank volumes, HRT), net change in sludge volume, how much water is retained (i.e. to avoid haulage of contained water), and any other potential additional benefits that might be factored in. This data will assist to understand what scale of plant would be suited to the P-adsorbent technology.

# Materials and Methods

Three absorbent substrates were selected for optimisation of P uptake capacity and reaction kinetics (to reduce the hydraulic retention time), these being: (i) calcined magnesia, (ii) hybrid nanoclays, (iii) hydrotalcite formed at < 60°C.

## Magnesia

Four magnesia products were used in the present work, each of which was sourced from Sibelco, Qld magnesia.

MgO: is a purified fine calcined magnesium oxide. Received as a 4:6 mixture of periclase and brucite. Thermal Gravimetric Analysis (TGA) in earlier work showed transition to 100% periclase at 400°C [30] - 95% passes 45 µm. The specific surface area is estimated to be 35 m<sup>2</sup>/g. In this work, MgO was used either as received, or heated to 700°C for 20 hours prior to use.

EMAG1000: is calcined natural magnesium oxide with chemical analysis: MgO 94%, SiO<sub>2</sub> 2.4%, CaO 3.0%, Al<sub>2</sub>O<sub>3</sub> 0.2%, Fe<sub>2</sub>O<sub>3</sub> 0.26%, Mn<sub>3</sub>O<sub>4</sub> 0.14%. 100% is less than 1mm in size and 70% smaller than 500 µm.

EMAG2100: is calcined natural magnesium oxide with chemical analysis: MgO 94%, SiO<sub>2</sub> 1.7%, CaO 4.0%, Al<sub>2</sub>O<sub>3</sub> 0.1%, Fe<sub>2</sub>O<sub>3</sub> 0.1%, Mn<sub>3</sub>O<sub>4</sub> 0.1%. 10% is less than 2 mm in size and 2% greater than 10 mm.

QMAG DBM-S: is a high purity deadburned natural magnesia with typical chemical analysis: MgO 96%, SiO<sub>2</sub> 0.8%, CaO 2.2%, Cr<sub>2</sub>O<sub>3</sub> 0.13%, Al<sub>2</sub>O<sub>3</sub> 0.26%, Fe<sub>2</sub>O<sub>3</sub> 0.27%, Mn<sub>3</sub>O<sub>4</sub> 0.12%. 85% of the sample is less than 250 µm in diameter.

## Hybrid nanoclay

Clay-hydrotalcite nanohybrids were synthesised using partial acid digestions of clays to liberate Mg and some Al. Further Al was added to achieve an appropriate Mg:Al stoichiometry for the formation of hydrotalcite. Hybrid nanoclays were synthesised in the laboratory in kilogram quantities. This key intermediate step in the upscaling process has facilitated a better understanding of possible problems when manufacturing tonne quantities for pilot-scale trials. An external contractor was engaged to realise production of tonne quantities of hybrid nanoclay.

## Hydrotalcite preparation

Hydrotalcites are a class of naturally occurring anion exchange materials based on the platelike mineral Brucite, Mg(OH)<sub>2</sub>. Partial substitution of a trivalent cation of comparable ionic radius and octahedral stereochemistry for Mg yields a structure with a similar structure but net positive charge. Such positively charged platelets alternating with exchangeable anions form the hydrotalcite structure.

A number of divalent cations, such as Mn, Fe, Co, Ni and Zn, and trivalent cations, including Cr and Fe, may form this structure. However, the Mg/Al system is the most stable and best understood in the series.

The general formula of the Mg/Al system may be written: [Mg<sub>(1-x)</sub>Al<sub>x</sub>(OH)<sub>2</sub>]<sub>A<sub>x</sub></sub>·yH<sub>2</sub>O, where A is a monovalent anion or the charge equivalent of a multivalent species. The composition range, i.e. degree of substitution of Al for Mg ranges approximately from x=0.2 to x=0.33 i.e. Mg:Al 4:1 to 2:1. The anion exchange capacity increases linearly with x. The degree of tenacity of the anions in the structure increases with charge and decreases with size: ClO<sub>4</sub><sup>-</sup><NO<sub>3</sub><sup>-</sup><CH<sub>3</sub>CO<sub>2</sub><sup>-</sup><Cl<sup>-</sup><OH<sup>-</sup><SO<sub>4</sub><sup>2-</sup><CO<sub>3</sub><sup>2-</sup><PO<sub>4</sub><sup>3-</sup>.

Hydrotalcites are thus well-suited to sequestration of phosphate by ion exchange. Although normally synthesised in the carbonate form, other forms can be synthesised.

In the current work, Mg/Al hydrotalcites with a Mg:Al ratio of 2:1 are preferred, due to higher ion exchange capacity. However, a commercial 3:1 hydrotalcite in the carbonate form was used in some experiments (Aldrich). As far as possible, the presence of carbonate in the final product was minimised, as previous work show that the commercial carbonate form exchanged poorly with phosphate. The chloride form is preferred

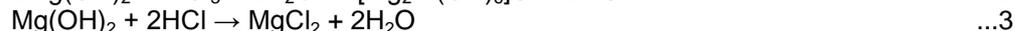
from the standpoint of cost, low environmental impact and rapid reactivity. The optimum theoretical material could be written as:  $[\text{Mg}_2\text{Al}(\text{OH})_6]\text{Cl}\cdot y\text{H}_2\text{O}$ . As an alternative, an acetate form was also explored. For an anhydrous  $\text{Mg}_2\text{Al}$  product ( $y=0$ ) fully exchanged with phosphate, the formula could be written as:  $[\text{Mg}_2\text{Al}(\text{OH})_6](\text{PO}_4)_{0.33}$ . This represents a product with a theoretical maximum P content of 4.93% w/w or 49.3 gP/kg.

Synthetic methods for the production of hydrotalcites have been comprehensively reviewed by Reichle [31]. In the current work, three methods have been explored:

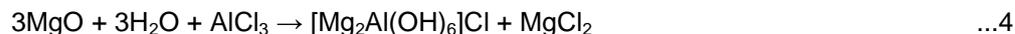
1) *Direct co-precipitation*:  $\text{MgCl}_2$  and  $\text{AlCl}_3$  in a 2:1 ratio are precipitated with  $\text{NaOH}$  just sufficient to cover the Mg and Al, in the presence of a large excess of  $\text{NaCl}$  to favour the chloride form. The reaction may be carried out at ambient temperature, or at  $60^\circ\text{C}$  to enhance crystallisation. Care is taken to exclude atmospheric  $\text{CO}_2$ . It is hoped that the mixtures will produce mainly the chloride form, possibly with some hydroxide present.

2) *Induced hydrolysis*: Previous work studied the reaction of calcined  $\text{MgO}$  with an excess of aqueous  $\text{AlCl}_3$  with exclusion of  $\text{CO}_2$  at ambient temperature. Under these conditions, the  $\text{MgO}$  is largely hydrated to  $\text{Mg}(\text{OH})_2$ , followed by partial substitution of Al in the structure. Although the reaction was incomplete, with other phases being present, the mixture was highly active for the absorption of phosphate. A second series of materials were prepared where the reaction was performed with enough  $\text{AlCl}_3$  only to give a 2:1 product. This approach sought to minimise the formation of amorphous Al hydrated oxide by-products. Excess  $\text{NaCl}$  was added in some cases to increase the proportion of the chloride form. The reaction was carried out at ambient temperature and  $60^\circ\text{C}$ .

Theoretical reactions are written as:



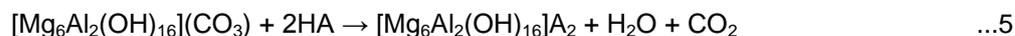
With a net reaction of:



Note that one equivalent of  $\text{MgO}$  is required to absorb the by-product of  $\text{HCl}$  formed (equation 3).

3) *Acid conversion*: Reaction of the carbonate form of a hydrotalcite with dilute  $\text{HCl}$  (0.01M) results in expulsion of  $\text{CO}_2$  and conversion into the chloride form. This reaction proceeds smoothly at ambient temperature, provided that a good dispersion of the hydrotalcite in water can be achieved. A 3:1 carbonate hydrotalcite obtained from Aldrich appears to be hydrophobic and may need pre-treatment with an organic solvent or dispersion with a surfactant prior to exchange. A successful demonstration of this method would demonstrate that a large-scale conversion of commercial 2:1 Mg/Al hydrotalcite in the carbonate form to the chloride form is feasible. In addition, reaction of the 3:1 carbonate with acetic acid may yield the acetate form. Due to the weak acidity of acetic acid, a higher concentration of acid may be feasible to speed the conversion, without dissolution of the hydrotalcite structure.

A theoretical reaction with the monobasic acid HA is:



The synthesised hydrotalcite materials are detailed in Table 2. All products were characterised by XRD, SEM and ICP.

**Table 2. Experimental matrix for hydrotalcite syntheses.**

Method (Sample No.)	Desired Product (form)	Reactants (ratio)	Temperature/Time	Expected Morphology
Co-precipitation (S-1608)	Mg <sub>2</sub> Al (Cl <sup>-</sup> )	MgCl <sub>2</sub> :AlCl <sub>3</sub> :NaOH:NaCl (2:1:7:10)	Ambient/7 days	Plates < 0.1 μm
Co-precipitation (S-1622)	Mg <sub>2</sub> Al (Cl <sup>-</sup> )	MgCl <sub>2</sub> :AlCl <sub>3</sub> :NaOH:NaCl (2:1:7:10)	60 <sup>o</sup> C/3 days	Plates 0.1-0.5 μm
Induced Hydrolysis (S-1620)	Mg <sub>2</sub> Al (Cl <sup>-</sup> )	MgO (calcined 700 <sup>o</sup> C):AlCl <sub>3</sub> :NaCl (3:1:10)	Ambient/14 days	Plates < 0.1 μm
Induced Hydrolysis (S-1621)	Mg <sub>2</sub> Al (Cl <sup>-</sup> )	MgO (calcined at 700 <sup>o</sup> C):AlCl <sub>3</sub> :NaCl (3:1:10)	60 <sup>o</sup> C/3 days	Plates 0.1-0.5 μm
Acid conversion (S-1606)	Mg <sub>2</sub> Al (Cl <sup>-</sup> )	Mg <sub>3</sub> Al (Aldrich):0.01M HCl 1:2	Ambient/14 days	Plates 0.1-0.5 μm
Acid conversion (S-1607)	Mg <sub>3</sub> Al (Cl <sup>-</sup> )	Mg <sub>3</sub> Al (Aldrich): 0.01M HCl (1:2) Base: H <sub>2</sub> O/C <sub>2</sub> H <sub>5</sub> OH/CH <sub>3</sub> OH 3:2:2 (vol)	Ambient/7 days	Plates 0.1-0.5 μm
Acid conversion (S-1616)	Mg <sub>3</sub> Al (acetate)	Mg <sub>3</sub> Al (Aldrich):0.1M CH <sub>3</sub> COOH (1:10) Base: C <sub>2</sub> H <sub>5</sub> OH	Ambient/14 days	Plates 0.1-0.5 μm
Thermal Activation (S-1626)	Mg <sub>3</sub> Al (OH <sup>-</sup> )	Mg <sub>3</sub> Al (Aldrich)	500 <sup>o</sup> C/20hrs	Plates 0.1-0.5 μm

## Phosphorus uptake experiments

### MODEL SOLUTIONS

Model solutions containing 30 mg/L P (a P concentration commensurate with many effluents) and 2.6 mg/L P (representative of a dilute secondary treated effluent) were prepared through the combination of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>.

The dilute solution achieved a final pH of 7.0 ± 0.2. The more concentrated solution was made up of NaH<sub>2</sub>PO<sub>4</sub> (50 mM) and Na<sub>2</sub>HPO<sub>4</sub> (50 mM) corrected to pH 7.2 ± 0.2. The total phosphorus concentration was 100 mM (approximately 30 mg/L). The latter solutions were utilised for the initial performance screening of a wide number of absorbents. P uptake experiments involved adding a sample of 250 mg of (dried) powder to a magnetically stirred 250 g of the P-containing solution (ie. a mass ratio of 1:1000). Samples (10 mL) were collected at intervals for up to 48 hrs, filtered and analysed by ICP-OES to give P-uptake data. Where treated effluent was being tested, a range of other elements were also analysed by ICP-OES.

Uptake studies using the dilute solution were carried out as follows. A stock solution of 1mM of each of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> was made up and volumes were withdrawn (10.41 g) and diluted to 250 g. This made up standard solutions of approximately 2.5 mg/L P at pH 7.0. Uptake experiments were carried out in rapidly stirred solutions for 5, 10, 15, 20, 30 and 40 minutes. Samples (250 mg) of the absorbent were added to the stirred solution. Thirty seconds before the completion of the test, stirring was halted and the suspension allowed to settle for 30 seconds before filtering under pressure through a 0.22 μm syringe filter. The solutions were then capped for ICP and pH analysis. The basis of the above test was developed in discussion with wastewater treatment engineers, who indicated that the preferred method of implementation of P-absorbents would be via rapid mixing into the waste stream for a period not exceeding 15-20 minutes followed by removal using existing solid recovery processes. This meant that rapid P-removal was the priority rather than extraction until the solid was exhausted. In the light of this information, experiments were set up to model short periods in a turbulent stream.

## ISOTHERM (HIGH-P UPTAKE) EXPERIMENTS

Isotherm absorbance experiments were carried out to test standard absorbents (MgO and nanoclay hybrid) at various higher P concentrations. The uptake solutions were made up using equi-molar amounts of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  in the range 15 - 120 mg/L. The percentage P reductions were then calculated from the lowering of soluble P concentrations, as measured after 96 hrs equilibrium. The ratio of sample to solution was 250 mg : 250 mL (1:1000). After 96 hrs, samples were passed through a 0.22  $\mu\text{m}$  syringe filter prior to P analysis. Mg/Si were also analysed to see how much (if any) of the absorbent dissolved as well. Phosphorus-uptake experiments were run in duplicate and the results averaged.

## P-UPTAKE CAPACITY ASSESSMENT

Long terms saturation uptake capacity of P by the hydrotalcite and magnesia samples was carried out using a solution of equimolar  $\text{NaH}_2\text{PO}_4$  +  $\text{Na}_2\text{HPO}_4$  at pH ~ 7.50. The total nominal P concentration was 5 mM or 155 mg/L. The actual P measured was 145 mg/L.

The solid adsorbent (250 mg) under test was placed in 250  $\text{cm}^3$  of the P solution. The mixture was stirred vigorously for 5 days at ambient temperature in a sealed flask. At the conclusion of the exchange period, the suspension was passed through a 0.22  $\mu\text{m}$  syringe filter to give a transparent water-white solution which were analysed by ICP for Mg, Al and P. The P differential (in ppm)  $P_0 - P_{obs}$  for each sample scaled directly to the P uptake in g/kg solid.

## EFFLUENT

Effluent was received from various sources:

- Melbourne Water Eastern Treatment Plant (ETP) secondary treated effluent and anaerobic digester centrate;
- Anaerobic digester centrate from a large dairy manufacturer;
- SA Water Bolivar secondary treated effluent;
- Water Corporation Western Australia Woodman Point anaerobic digester centrate;
- Unity Water Burpengary raw wastewater; and
- Queensland Urban Utilities Oxley Cambi pre-treated anaerobic digester centrate.

Each of the effluent samples was stored at 4°C and thermally (steam) sterilised using an autoclave prior to use.

Due to a minimal amount of some of the hydrotalcite samples, the experiments were reduced to 125 mg of absorbent to 125 g of effluent. These were tested for 5 - 20 minutes, with the longer periods (30/40 min) removed due to the small amounts of the hydrotalcites that were available. The samples were, again, tested for uptake with vigorous stirring and then filtered using a syringe filter prior to storage for analysis.

## Granulation studies

Where the preparation of absorbent materials leads to the generation of primary particle sizes not amenable for implementation into the wastewater process, there is a need to upsize primary particles into larger particles/granules.

A series of approaches to granulate powders was explored in the present work, with the pre-request that the process should not significantly reduce anion adsorption sites, it should be carried out using granulation (as opposed to more energy intensive processes such as spray drying / extrusion / pelletisation) and at low temperature. The following variations were explored:

1. Lignite
2. Aluminosilicate colloids
3. Metakaolin
4. Ca addition
5. Combinations of the above.

## LIGNITE

Products based upon the granulation of lignite already exist on the fertilizer market. It is claimed that lignite increases cation exchange capacity (CEC) and supports microbial activity (<http://www.aitkens.co.uk/>) [32]. Studies into lignite granulation have also been performed on the basis of dust suppression methods for the handling of brown coal [33].

Samples of Lignite were sourced from Loy Yang, Victoria. The organic component of Victorian brown coals have been characterised as comprising 25% oxygen, where about half is this is accounted for in acidic functional groups (phenolic hydroxyl, free carboxylic acid, carboxylate) and the other half in ether linkages/heterocyclic ring structures. The moisture holding capacity of Loy Yang coal is approximately 42%. The total inorganic component is approximately 1-2 wt% (measured as ash), where the inorganic components on a wt% basis decrease in the order of:  $\text{CaO} > \text{Fe}_2\text{O}_3 > \text{MgO} > \text{SiO}_2 > \text{Na}_2\text{O} > \text{Al}_2\text{O}_3$  (Perry et al., 1984) [34].

## ALUMINOSILICATE COLLOIDS

The presence of free silicate during binding will likely be detrimental as adsorption of silicate will decrease the number of P-adsorption sites. For this reason, acidified silicate gels were explored as a means to provide rigidity to aggregated primary absorbent powders.

Metal salt sols consist of dense particles and not of loose networks (i.e. polymeric clusters). For silica particles formed from silicic acid, the particles initially formed are very small (i.e.  $< 5$  nm), after which they go through Oswald ripening where the particle sizes increase with time (Brinker and Scherer (1989) [35]. Typically gelation occurs over time and is dependent upon pH, temperature and concentration. The presence of a small amount of aluminium enables the silicate solutions to be prepared at slightly higher pH.

Aluminosilicate gels were prepared using sodium metasilicate (Grade N, PQ Australia), aluminium chloride (Aldrich) and hydrochloric acid. Starting solutions were prepared with 1, 2, 5 and 10 wt% silicate and were adjusted to pH 2.8 and allowed to stand for one week prior to use. Dynamic light scattering (Brookhaven, Zetaplus90) confirmed the size of individual particles in the 1wt% solution to be in the range of 400-500 nm.

## METAKAOLIN

A semi-dehydroxylated form of kaolin, metakaolin is typically supplied as a finely divided powder with a size range of 100 nm – 2.5  $\mu\text{m}$ . Typically, metakaolin has a 1:1  $\text{Al}_2\text{O}_3:\text{SiO}_2$  ratio and is heavily utilised to make porcelain materials. Whilst being amorphous structure due to it being a dehydroxylated form, it maintains its long-range sheet structure. Metakaolin is known to readily participate in pozzolanic reactions (i.e. silicate/aluminate binding at high pH).

## GRANULATION AND CHARACTERISATION

Granulation was carried out by mixing a quantity of the absorbent with a binding solution and/or, additional binders. Granulation was carried out at 30 rpm, typically for a period of one hour. Following granulation, the samples were dried at either 80°C or 400°C.

The integrity of granules was explored using a water stability test. The Water Stability test was carried out by placing a representative granule within a vial containing 5 mL of deionised water. The sample was then mixed on a sample rotator at 20 rpm.

## Analytical and Characterisation Methods

### SEM-EDS PRECIPITATE ANALYSIS

For SEM analyses, powdered samples were mounted on standard 10 mm SEM pin stubs using double-sided conducting adhesive tape and dusted with a jet of dry nitrogen. The samples were then coated with a conductive carbon film approximately 15 nm in thickness using an Edwards Auto 306 carbon arc evaporative

coater. A planetary rotating stage was used to ensure an even coating thickness and full coverage of the individual particulates from the samples.

After coating, the samples were mounted in a suitable SEM specimen holder designed to accommodate standard 10 mm mounts. SEM imaging was conducted under high vacuum conditions in a FEI, Quanta 400 F, field emission, environmental scanning electron microscope (ESEM). Secondary and backscattered electron images were taken using a beam energy of 15 kV and a probe current of approximately 150 pA. Energy Dispersive Spectrometry (EDS) was carried out using a probe current of approximately 1 nA and a beam energy of 15kV. Spectra collection times were 30 seconds (spectrometer live time). The backscattered electron image provides information on the average atomic number of each phase in the sample. Phases with a high average atomic number produce a higher backscattered yield and so result in a whiter pixel at that point in the image. Phases with a lower average atomic number produce a lower yield and so result in a darker image pixel.

## **ICP-OES CHEMICAL ANALYSIS**

ICP-OES analyses for various metallic elements (including common impurities), silicon, phosphorus, sulphur and chloride (where applicable) were carried out for a number of the samples.

Solid samples were digested in duplicate with 1:1 Nitric acid/Milli-Q (High purity) water, and the resultant solution analysed by ICP-OES. Certified multi-element solutions were also used to check the accuracy of the calibration and the method. For samples containing chloride, chloride analysis was performed after digestion in 1:1 Nitric acid/Milli-Q (High purity) water, and analysed by Potentiometric titration using a Metrohn 785 DMP Titrino Auto-titrator.

## **XRD MINERALOGICAL ANALYSIS**

For powder XRD characterisation, a Bruker D8 Diffractometer using CuK $\alpha$  radiation operating at 40 kV and 40 mA was employed to determine the X-ray diffraction (XRD) patterns. Each sample was scanned over the 2-theta range 5° to 85° with a step size of 0.02° and a count time of 0.4 seconds per step. XRD data was captured using a LynxEye silicon strip detector.

Analyses were performed on the collected XRD data for each sample using the Bruker XRD search match program EVA™. Crystalline phases were identified using the ICDD-PDF+4 2011 Powder diffraction database. Phase assignment was further qualified by knowledge of the reaction mixture composition (e.g. when the database assigned a Zn-hydrotalcite phase, it was re-assigned as Mg). Relative amounts of phases in the hydrotalcite reaction mixtures were estimated from peak heights.

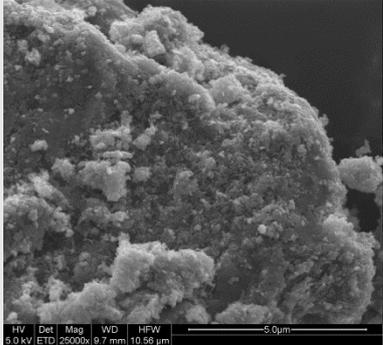
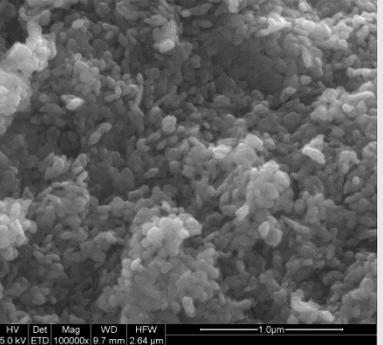
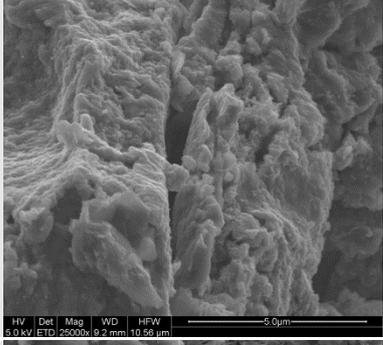
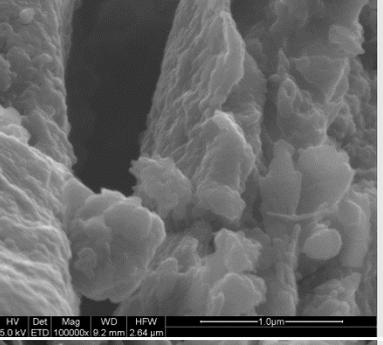
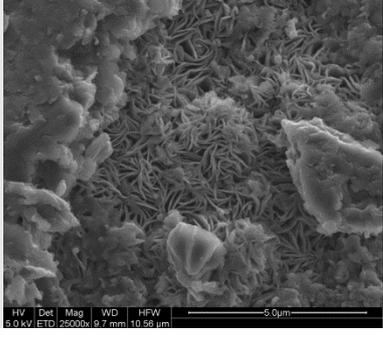
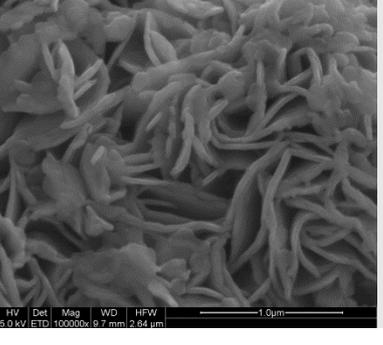
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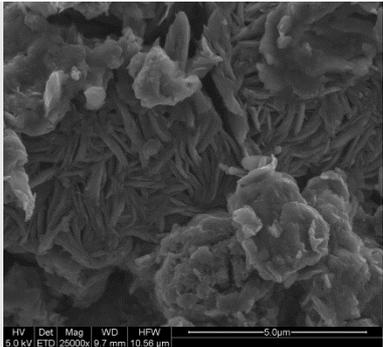
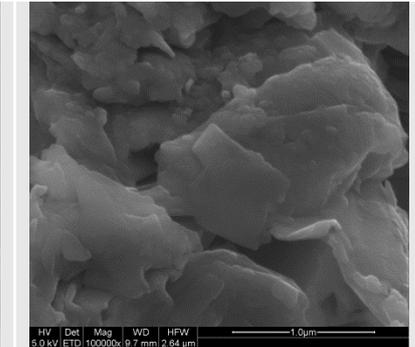
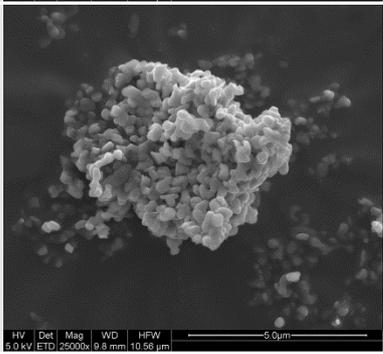
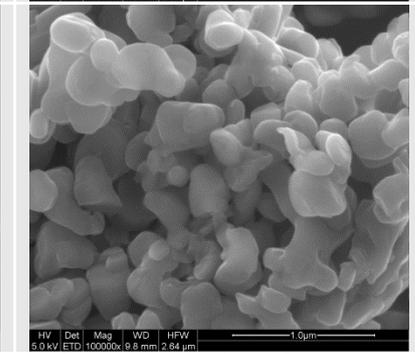
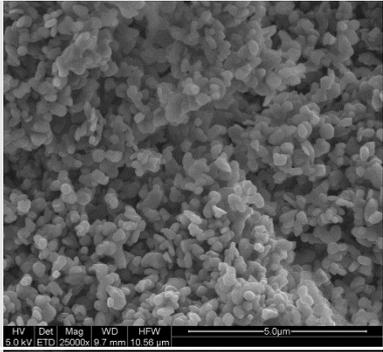
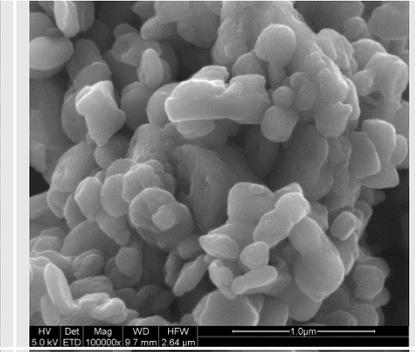
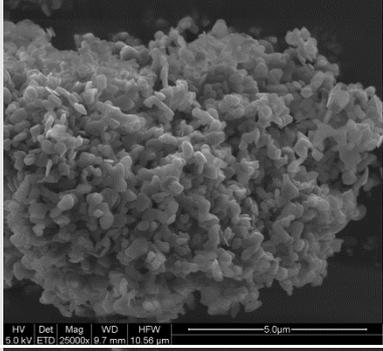
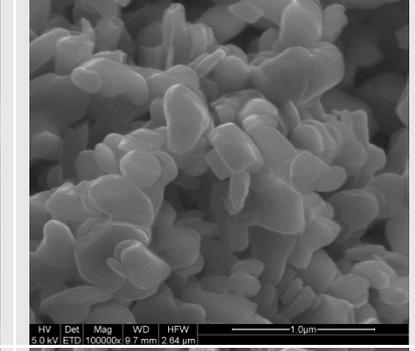
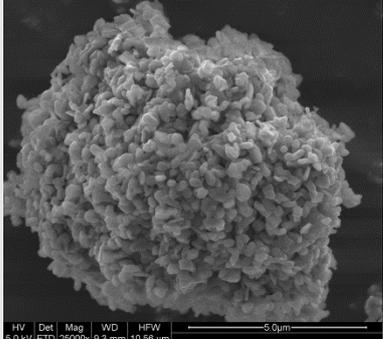
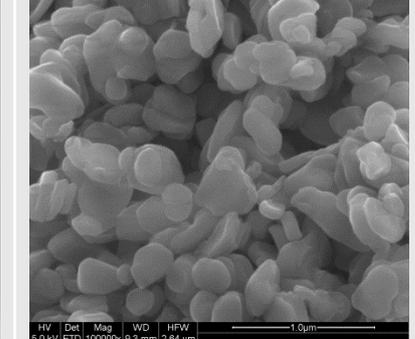
## Materials development

### HYDROTALCITE

A number of hydrotalcites were manufactured, with preparations done at both room temperature and 60°C. Both high and low magnification morphologies of the products are shown in Table 3. Generally, a mixture of amorphous materials and either twisted sheets or small tablets was produced. EDS was semi-quantitative only, but indicated that differing Mg:Al ratios in some phases, as well Cl enrichment in some phases of the Cl<sup>-</sup> exchanged mixtures. X-ray diffraction (XRD) spectra for each of the hydrotalcites can be found in Appendix III.

**Table 3. Hydrotalcite absorbent materials.**

Method	Desired Product	SEM X25k Magnification	SEM X100k Magnification	EDS Results
Co-precipitation S-1608 CSIRO-developed	Mg <sub>2</sub> Al, Cl <sup>-</sup> form			Good Cl concentrations seen across most regions; Mg:Al ~2:1
Co-precipitation S-1622 CSIRO-developed	Mg <sub>2</sub> Al, Cl <sup>-</sup> form			Al:Cl ~1, showing good Cl <sup>-</sup> exchange, Mg:Al ~2.5, Al lower than in S-1608
Induced hydrolysis S-1620 CSIRO-developed	Mg <sub>2</sub> Al, Cl <sup>-</sup> form			Mg:Al ~2:1, Al:Cl ~1 in most regions – very good Cl <sup>-</sup> exchange.

<p>Induced hydrolysis S-1621 CSIRO-developed</p>	<p>Mg<sub>2</sub>Al, Cl<sup>-</sup> form</p>			<p>As for S-1620</p>
<p>Acid conversion S-1606 Modified Aldrich</p>	<p>Mg<sub>3</sub>Al, Cl<sup>-</sup> form</p>			<p>Relatively poor degree of Cl<sup>-</sup> exchange but some particles showed enhanced Cl<sup>-</sup> concentrations. Mg:Al as expected.</p>
<p>Acid conversion S-1607 Modified Aldrich</p>	<p>Mg<sub>3</sub>Al, Cl<sup>-</sup> form</p>			<p>As for S-1606, but improved Cl<sup>-</sup> concentrations seen in most regions.</p>
<p>Acid conversion S-1616 Modified Aldrich</p>	<p>Mg<sub>3</sub>Al, acetate form</p>			<p>Mg:Al ~3:1, Cl<sup>-</sup></p>
<p>Thermal Activation S-1626 Modified Aldrich</p>	<p>Mg<sub>3</sub>Al, dehydrated layer, interlayer OH<sup>-</sup></p>			<p>Cl<sup>-</sup> N/A, Mg:Al ~3</p>

**Table 4. Hydrotalcite absorbent materials, phase assignment.**

Sample Ref.	Approximate % crystalline phases
S-1606	100% hydrotalcites
S-1607	100% hydrotalcites
S-1608	100% hydrotalcites
S-1616	95% hydrotalcites, 5% orthorhombic AlO(OH)
S-1620	90% hydrotalcites, 10% MgAl <sub>2</sub> (OH) <sub>8</sub>
S-1621	90% hydrotalcites, 10% MgAl <sub>2</sub> (OH) <sub>8</sub>
S-1622	80% hydrotalcites, 20% Mg(OH) <sub>2</sub>
S-1626	90% hydrotalcite, 10% hydrotalcite

**Table 5. Hydrotalcite absorbent materials, ICP.**

Sample Ref.	Mg wt%	Mg rel. mol	Al wt%	Al rel. mol	Mg/Al molar ratio
S-1606	37.33	1.536	17.86	0.662	2.32
S-1607	36.4	1.498	17.59	0.652	2.30
S-1608	22.63	0.931	10.64	0.394	2.36
S-1616	36.59	1.505	16.74	0.620	2.43
S-1620	22.23	0.915	10.90	0.404	2.26
S-1621	20.34	0.837	10.68	0.396	2.11
S-1622	25.11	1.033	8.60	0.319	3.24
S-1626	40.22	1.655	17.75	0.658	2.52

The Aldrich material, with a nominal Mg:Al ratio of 3.0, displayed an actual ratio near 2.5, as shown in S-1626, which had no treatment other than calcination. Samples S-1606, 1607 and 1616, derived from the Aldrich material by treatment with dilute acid, showed slightly lowered Mg:Al ratios compared to S-1626, suggesting that some leaching of Mg from the sample had occurred. As expected, this was slightly more pronounced for the samples treated with HCl rather than acetic acid.

The samples produced by direct co-precipitation, S-1608 and 1622, showed Mg:Al ratios considerably higher than the nominal 2:1. This was especially pronounced for the sample produced at 60°C. This may be due to loss of some of the Al as laminate in the filtrate.

The induced hydrolysis samples, S-1620 and 1621, showed Mg:Al ratios much closer to the desired value of 2:1. Unlike the co-precipitation samples, these are formed in an acidic environment, so that loss of Al as aluminate is unlikely.

Phase assignments are qualitative only, by visual comparison of peak heights. In general, the products were composed predominately of hydrotalcite phases, with lesser amounts of Al or Mg/Al hydroxides. The degree of Cl-substitution (where applicable) was difficult to ascertain, as ICP methods caused loss of Cl and EDS was qualitative only.

Looking at the ICP/XRD/SEM/EDS results overall, it would appear that induced hydrolysis methods produce materials which are predominately hydrotalcites, with higher Al and Cl content than obtained by other methods. Simple calcinations of a commercial material, however, has the advantage of producing an active material without the need for labour-intensive wet chemistry or workup.

## NANOCLAY

In May 2014, a trial to scale up the manufacture of the nanoclay hybrid (bentonite-hydrotalcite co-precipitate) was undertaken at a commercial metallurgical laboratory in Welshpool, Western Australia under the supervision of CSIRO and the Western Australian Department of Water (Figure 2). The latter organisation funded the manufacture of the hybrid nanoclay for use in field trials.

In a 13 m<sup>3</sup> mixing tank fitted with an overhead impellor, 750 kg of dry Na-bentonite was dispersed into 7000 L of Perth domestic tap water. This suspension was sparged with industrial grade N<sub>2</sub> via a submerged

manifold with a positive pressure  $N_2$  blanket maintained in the tank headspace throughout the nanoclay hybrid manufacture.

To initiate formation of the hydrotalcite, 750 kg of commercial grade  $MgCl_2 \cdot 6H_2O$  was added. Upon dissolution of the  $MgCl_2 \cdot 6H_2O$ , 356 kg of commercial grade  $AlCl_3 \cdot 6H_2O$  was then added until dissolved to give a Mg:Al; molar ratio of 2.5 consistent with hydrotalcite stoichiometry. A stream of 20% w/w commercial grade NaOH was then added with constant stirring until the suspension in the tank attained a pH of 10. Constant agitation and pH of the suspension was maintained for 24 hours to ensure complete formation of the hydrotalcite precipitate. Thereafter, the pH was reduced to approximately 9 via the addition of dilute HCl. The nanoclay hybrid was then allowed to settle with approximately 1000 L of the NaCl-bearing supernatant discarded. The remaining nanoclay hybrid suspension estimated to be a total of 1160 kg in 6000 L of water was then resuspended and transferred to six 1000 L Intermediate Bulk Containers (IBC's) for storage.



**Figure 2. (a) Addition of bentonite clay to mixing tank prior to dispersion in water using an overhead impellor; (b) Stacked IBC's ( $1\text{ m}^3$  capacity) filled with nanoclay hybrid suspension.**

## P-uptake from synthetic solutions

### P ADSORPTION ISOTHERMS

Isotherm experiments are carried out in order to measure the capacity for adsorption as a function of adsorbate concentration. As demonstrated in Figure 3 and Figure 4, MgO was shown to have good adsorption properties irrespective of the P concentration, particularly in the range of 60-120 mg/L. However, MgO did show signs of tapering off in terms of percentage P removal in lower P concentration solutions. In contrast, nanoclay hybrid demonstrated improved P removal behaviour (albeit with poorer overall performance) at lower P concentration.

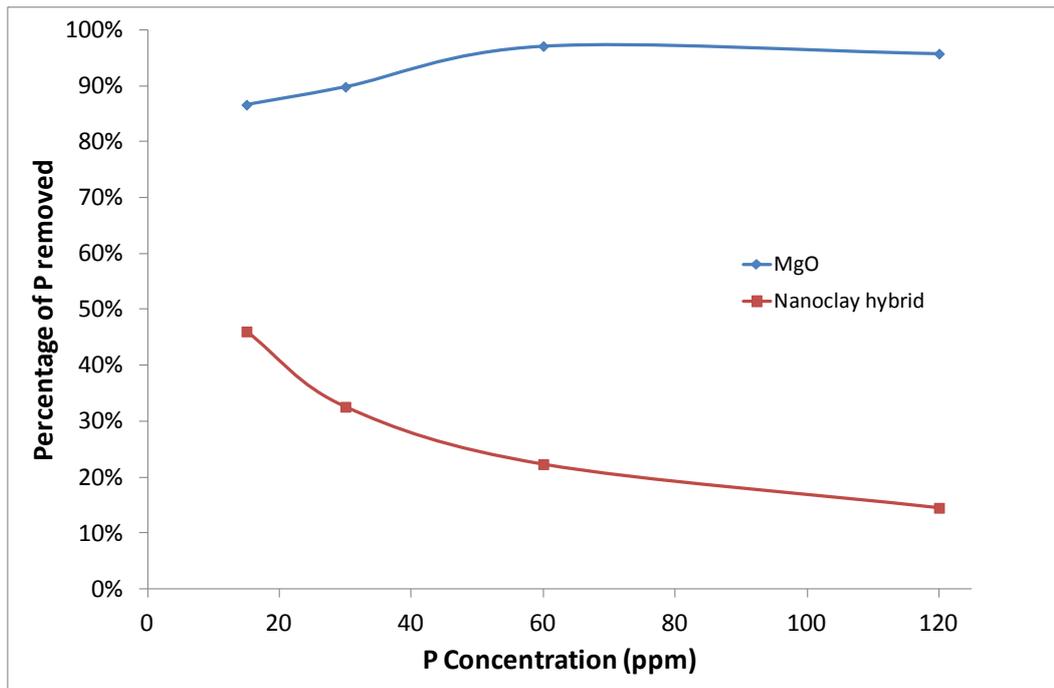


Figure 3. Percentage of P removed from solution after 96 hrs equilibrium as a function of P concentration.

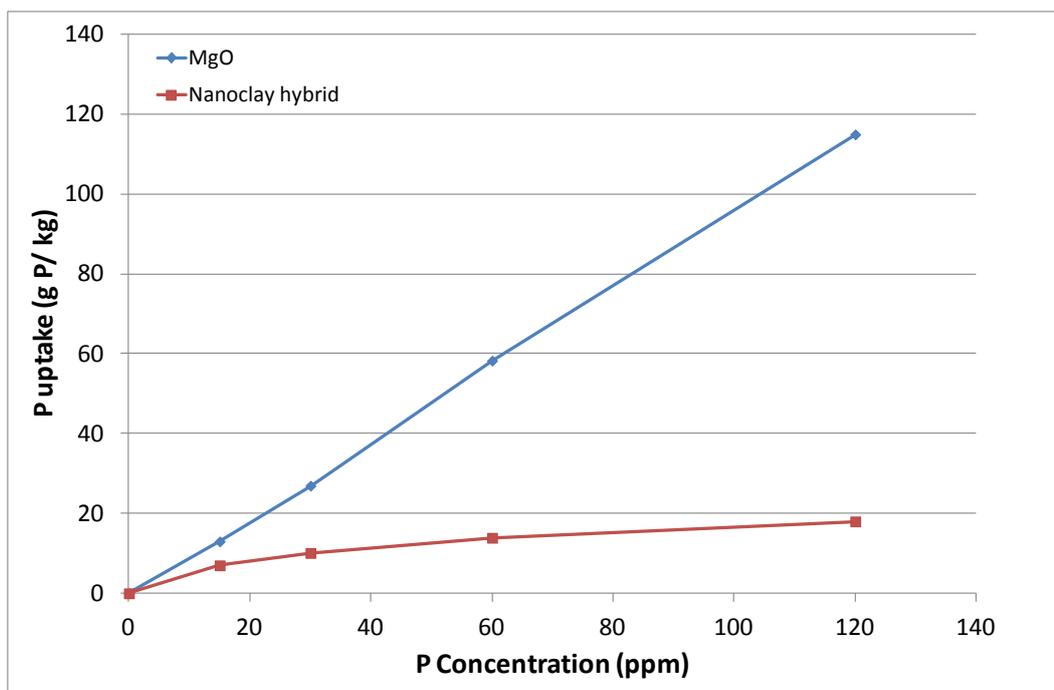


Figure 4. P uptake per unit of solid after 96 hrs equilibrium as a function of starting P concentration.

## P CAPACITY DETERMINATIONS

Table 6 details the total capacity of various P-absorbent materials was assessed via the addition of 250 mg of solid material into 250 mL of 5 mM P solution comprised of equimolar concentrations of  $\text{Na}_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  (Table 1). Previous hydrotalcite, MgO and nanoclay hybrid absorbents were tested for their uptake capacity, showing that the best materials could achieve 35 g P/kg [30]. In Table 6, it can be seen that many of the synthesized hydrotalcite materials demonstrated increased P capacities; reaching up to 57 g P/kg. Interestingly, freshly calcined MgO showed an ability to take up 101 g P/kg, which exceeds the phosphorus contents of some commercial fertilizers. As has been discussed in earlier work [30], the form of MgO (i.e. brucite vs. Periclase) and history has been demonstrated to be important in determining P-uptake efficiency.

Table 6. Maximum capacity of P measured in 5 mM phosphate synthetic solution.

Original Sample No. and Description	g P/kg
Reference Solution	0
S-1606: Mg3Al Aldrich H/T exchanged with 0.01M HCl/ambient/14d	17
S-1607: Mg3Al Aldrich H/T exchanged with 0.01M HCl/H2O/MeOH/EtOH/ambient/14d	25
S-1608: Mg2Al H/T Cl- form; direct precipitation/ambient/7d	44
S-1616: Mg3Al Aldrich H/T exchanged with 0.1M HOAc/EtOH/ambient/14d	10
S-1620: Mg2Al H/T Cl- form; induced hydrolysis from MgO/ $\text{AlCl}_3$ /ambient/14d	57
S-1621: Mg2Al H/T Cl- form; induced hydrolysis from MgO/ $\text{AlCl}_3$ /60C/3d	52
S-1622: Mg2Al H/T Cl- form; direct precipitation/60C/3d	35
S-1626: Mg3Al Aldrich H/T calc 500C/20h	50
Nanoclay-hybrid	18
Calcined MgO aged in air	69
Calcined MgO freshly re-calc 700C/20h	101

## RAPID UPTAKE FROM SYNTHETIC SOLUTIONS

The uptake results for several adsorbents from a low-P synthetic solution are shown in Figure 5. The adsorbents include MgO, HTClay and a range of hydrotalcite preparations. S-1608 and S-1622 are co-precipitated materials developed by CSIRO. S-1620 and S-1621 are CSIRO formulations based upon induced hydrolysis. S-1606, S-1607 and S-1616 are acid conversions of a commercially available hydrotalcite (Aldrich) and S-1626 is a thermally activated sample of the same Aldrich hydrotalcite. (Further information on these hydrotalcites is provided in Table 3, Table 4 and Table 5).

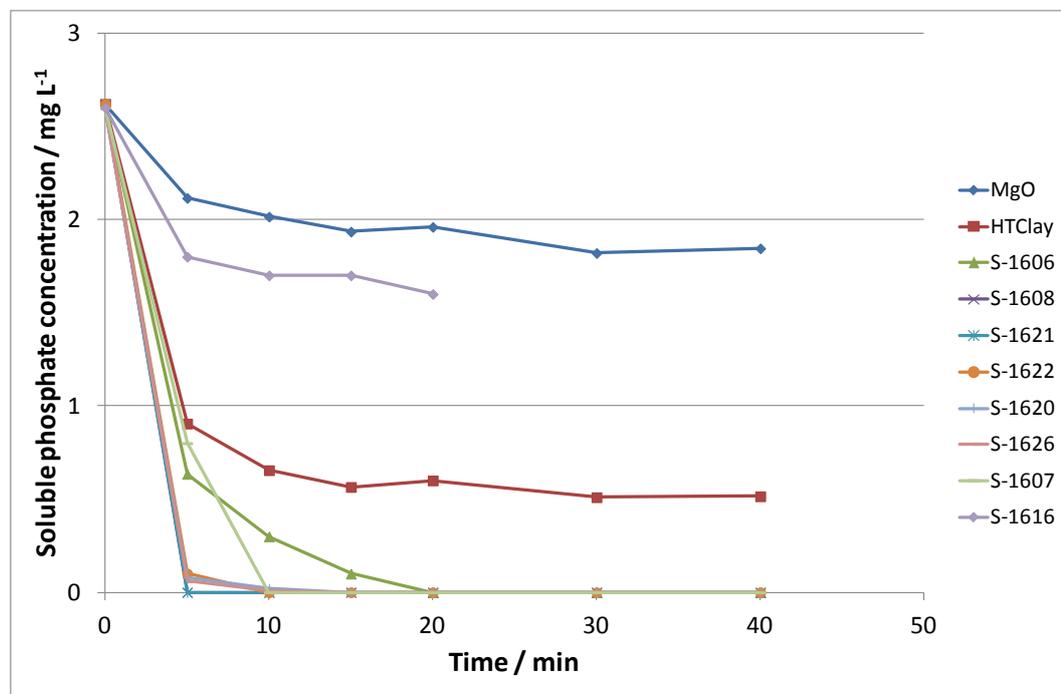


Figure 5. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of adsorbent in 250 mL of synthetic solution.

In these tests, MgO appeared to act slowly and appears to have difficulty in reducing the P level to much below 2 mg/L. The nanoclay hybrid (HTClay) showed good performance, scrubbing much faster than MgO and levelling out at 0.5 mg/L after 15 minutes.

Each of the CSIRO-produced hydrotalcites via co-precipitation and induced hydrolysis, and the thermally-treated Aldrich hydrotalcites, scrubbed P at even faster rates than HTClay and result in < 0.1 mg/L soluble P within five minutes.

To better understand the importance of particle size of MgO adsorbents, three variations of particle size were explored; MgO used in previous experiments was compared with two calcined natural magnesia products supplied by QMAG (EMAG®1000 and EMAG®2210). The EMAG®1000 had improved performance compared to the finer MgO material and the much coarser EMAG®2100 (Figure 6). It was noted that in two cases, the coarser EMAG products fragmented or disintegrated in solution, but overall, this wasn't a uniform behaviour as coarser particles tended to retain their structure during testing. Given that the particle size of MgO did not significantly affect the P-uptake performance, there would appear to be added benefit in utilising larger particle sizes for wastewater treatment, where coarser particles could be separated easily through sedimentation or even filtration processes.

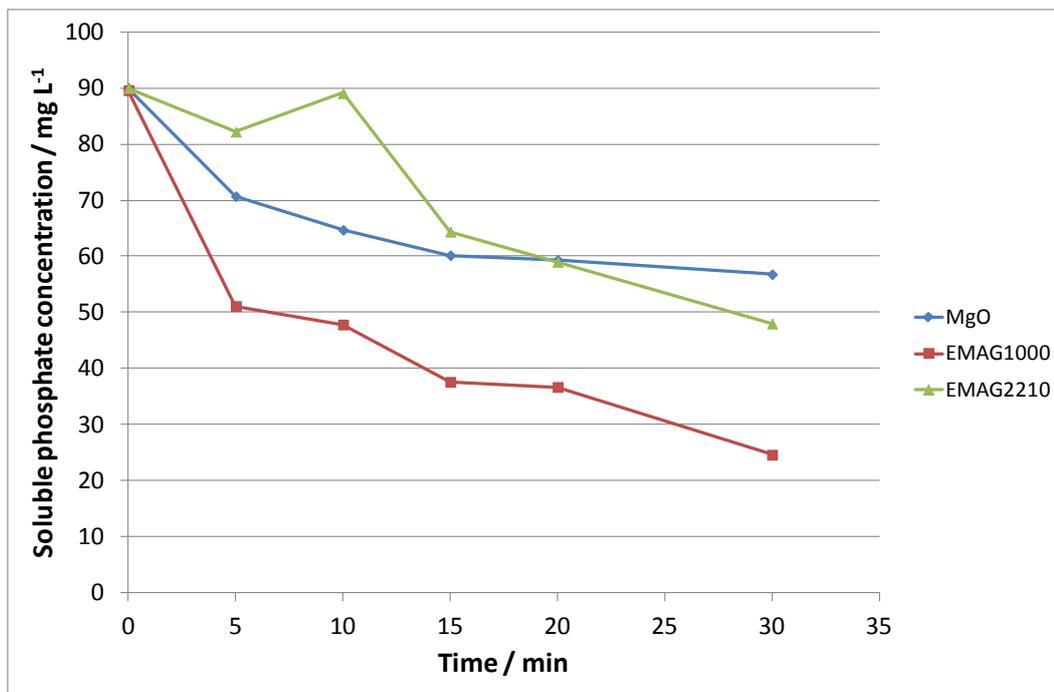


Figure 6. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of absorbent in 250 mL of a synthetic  $\text{NaH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$  solution made to 90 mg/L P and pH 7.0.

## P-uptake from effluent solutions

### LOW STRENGTH (SECONDARY TREATED EFFLUENT)

The most promising absorbents for removing P were tested in secondary treated effluent and the data is presented in Figure 7 and Figure 8. These experiments were conducted with the view that the absorbent materials should act quickly to lower P concentrations, such that they could be implemented into a treatment system with a retention time of less than 30 minutes. Previous studies reported on absorbance performance in secondary treated effluent from Melbourne Water ETP [31]. The characteristics of SA Water Bolivar secondary treated effluent are provided in Table 7.

From trials with model solutions the best appear to be: S-1620, S-1621, S-1622, S-1626, S-1607 and S-1608, while the secondary effluent trials indicate that the best are: S-1620, S-1621, S-1622, S-1626, with the nanoclay hybrid and MgO doing well also. Although MgO lowered the P concentration from 6.15 mg/L to 2.7 mg/L (Figure 6) and 0.86 mg/L to 0.36 mg/L (Figure 7) for ETP and Bolivar, respectively, its superior performance demonstrated in earlier work was not replicated.

The acid-modified form of the Aldrich product (S-1616 and S-1606) showed no affinity for P-uptake in the secondary treated effluent and in fact, appeared to increase P concentration, which could potentially occur if the material already contained P or if the product facilitated hydrolysis of organic P into organic forms. In contrast, S-1606 showed good performance in synthetic solutions, which suggests that other constituents in the effluent such as organic matter may inhibit P-uptake. The heat treated hydrotalcite from Aldrich (S-1626) showed good performance in ETP secondary treated effluent, reducing P from 6.15 mg/L to 1.25 mg/L, and being a commercially available product, was further trialled in Bolivar effluent (Figure 8). In this case it was able to remove P to lower levels than MgO and nanoclay hybrid, achieving a final P concentration of 0.05 mg/L.

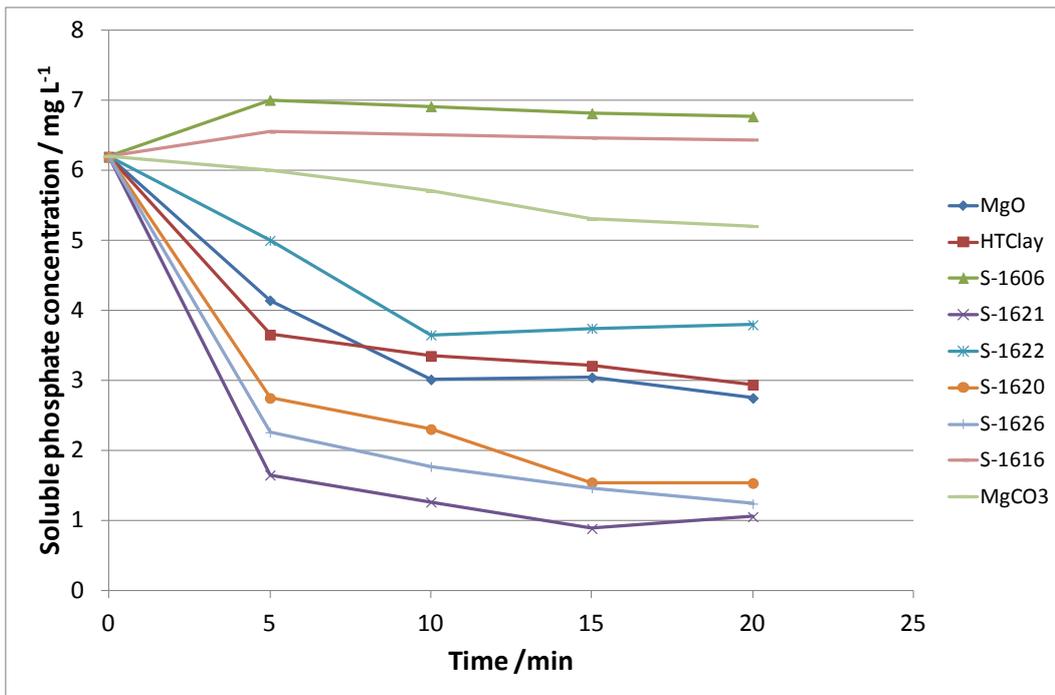


Figure 7. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of absorbent in 250 mL of secondary treated effluent (Melbourne ETP).

Table 7. Typical data from SA Water on quality of secondary treated effluent quality in storage lagoon (2011-12). Flow through the plant is approximately 165 ML/day. This equates to 561 kg P per day [36].

	BOD	Suspended Solids	COD	pH	NH <sub>3</sub> -N	NO <sub>3</sub> -N	TKN	N-Total	P-Total
	mg/L	mg/L	mg/L	pH units	mg/L	mg/L	mg/L	mg/L	mg/L
Maximum	23	90	209	7.6	10	32	16	36	16
Minimum	2	4	51	6.9	0	5	2	9	1
Median	7	14	97	7.3	0	18	4	23	3
Average	8	17	102	7.3	0	18	5	23	4

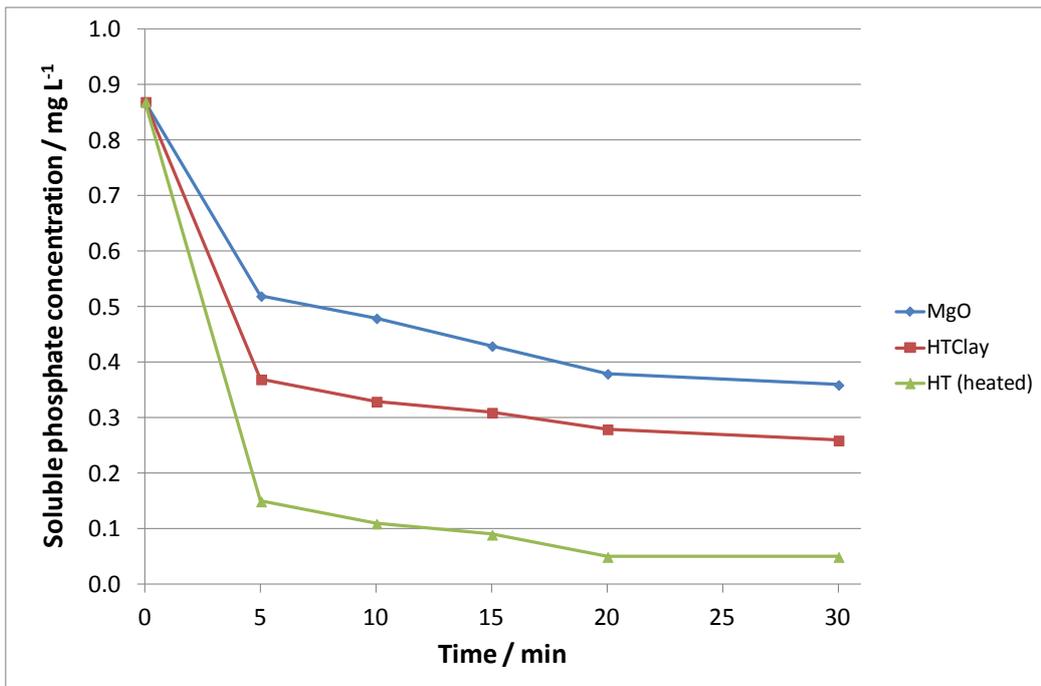


Figure 8. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of absorbent in 250 mL of secondary treated effluent (SA Water, Bolivar).

### LOW STRENGTH (RAW EFFLUENT)

The ability of MgO, Nanoclay hybrid and HT to remove P from the raw wastewater feed to the Burpengary East treatment facility was tested and the results are presented in Figure 9. This facility has a noxious industries estate in its catchment and there is always a baseline level of biological inhibition at the plant. There was also a period in recent times in which the plant was “turned upside down” due to this trade waste.

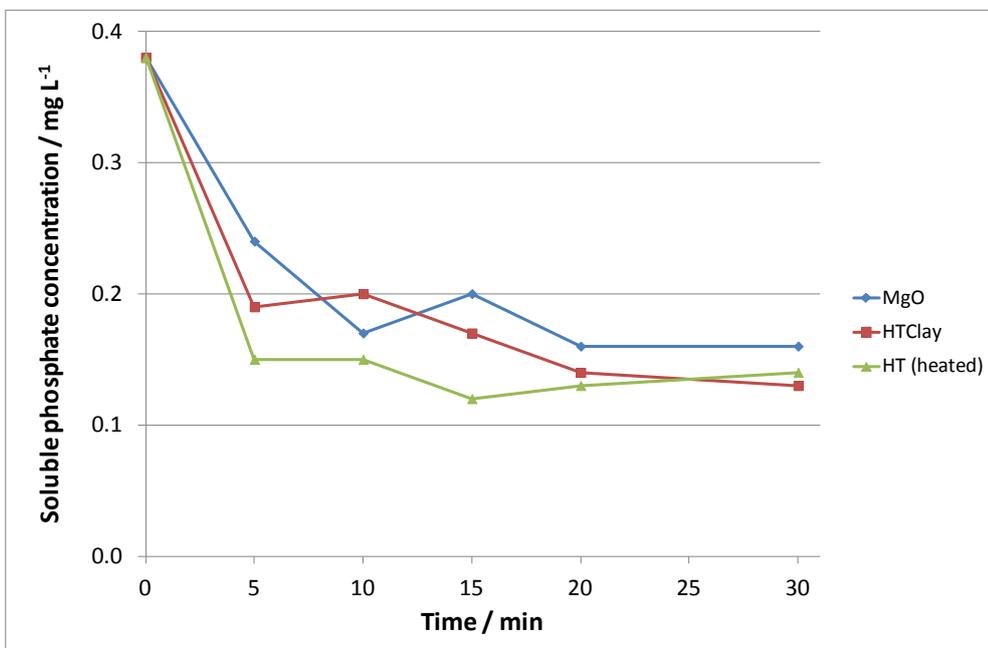


Figure 9. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of absorbent in 250 mL of raw wastewater (Unity Water, Burpengary East).

In this case, all the adsorbents tested demonstrated a similar ability to lower P concentration, each decreasing from 0.38 mg/L to  $0.14 \pm 0.02$  mg/L.

One curious aspect of the Burpengary and Bolivar data is that the final P levels are significantly lower than could be achieved in either ETP or synthetic solutions. This suggests that there are different water chemistries or variations of P compounds, which are affected differently by the adsorbent materials. This suggests that the adsorbents used may have to be selected specifically for the particular application.

## ANAEROBIC CENTRATE

The ability of adsorbents to uptake soluble phosphate from concentrated centrate solutions was briefly explored in phase 1 of the project [30]. The aim of this earlier work was to explore the interaction of nanoclay materials and individual salts of magnesium and aluminium, with anaerobic centrate sourced from Water Corporation of Western Australia, Woodman Point site. Testing of the Woodman Point anaerobic effluent indicated a dissolved P concentration of approximately 270 mg/L, and salts were added in stoichiometries of 1:1 and 4:1 (i.e. Al:P) at unadjusted pH and at a consistent pH of 8. Table 8 provides a summary of results from the testing, which showed that magnesium salts had equivalent effectiveness in removing phosphate from solution as commonly used aluminium-based coagulants, and secondly, that nanoclay materials were offered similar efficacy to individual salt additions.

**Table 8. Percentage P-uptake (in order of increasing uptake, mean  $\pm$  1 standard deviation) for Woodman Point anaerobic effluent samples after addition of Al and/or Mg salts, P-adsorbent materials, after mixing for two hours, after re-adjustment to  $\text{pH } 8.0 \pm 0.1$  and after further mixing for two hours.**

Material added	Alum 4:1	$\text{AlCl}_3 + \text{MgCl}_2$	Solid HT	$\text{MgCl}_2$ only	Vermic +Al+Mg	$\text{AlCl}_3$	Alum 1:1
<b>Unadjusted pH</b>	$71.8 \pm 0.1$	$83.6 \pm 4.8$	$88.5 \pm 0.4$	$97.5 \pm 0.0$	$98.1 \pm 0.2$	$98.7 \pm 0.1$	$98.7 \pm 0.1$
<b>pH 8</b>	$100 \pm 0.0$	$99.9 \pm 0.4$	$96.8 \pm 0.2$	$98.7 \pm 0.1$	$98.5 \pm 0.0$	$97.2 \pm 0.1$	$97.5 \pm 0.3$

Further studies were carried out using MgO, nanoclay and hydrotalcite materials, exploring their interaction with concentrated centrates when mixed for shorter periods of time. The results of these are provided in Figure 10 and Figure 11, when the materials were contacted with an anaerobic centrate from a dairy processing site, and anaerobic centrate from a municipal wastewater treatment facility using Cambi thermal hydrolysis to pre-treat the anaerobic digester feed.

MgO was very effective at lowering soluble phosphate in solution, decreasing P from 63 mg/L down to 1.8 mg/L within a 30-minute period (Figure 10). The MgO was also more effective at lowering P concentration than hydrotalcite materials, however in the case of Figure 11, it appeared that the 1 g/L loading of MgO was only sufficient to lowering P from around 591 mg/L down to 398 mg/L within 30 minutes. This surprisingly equates to a significant P uptake of 193 gP/kg of added MgO.

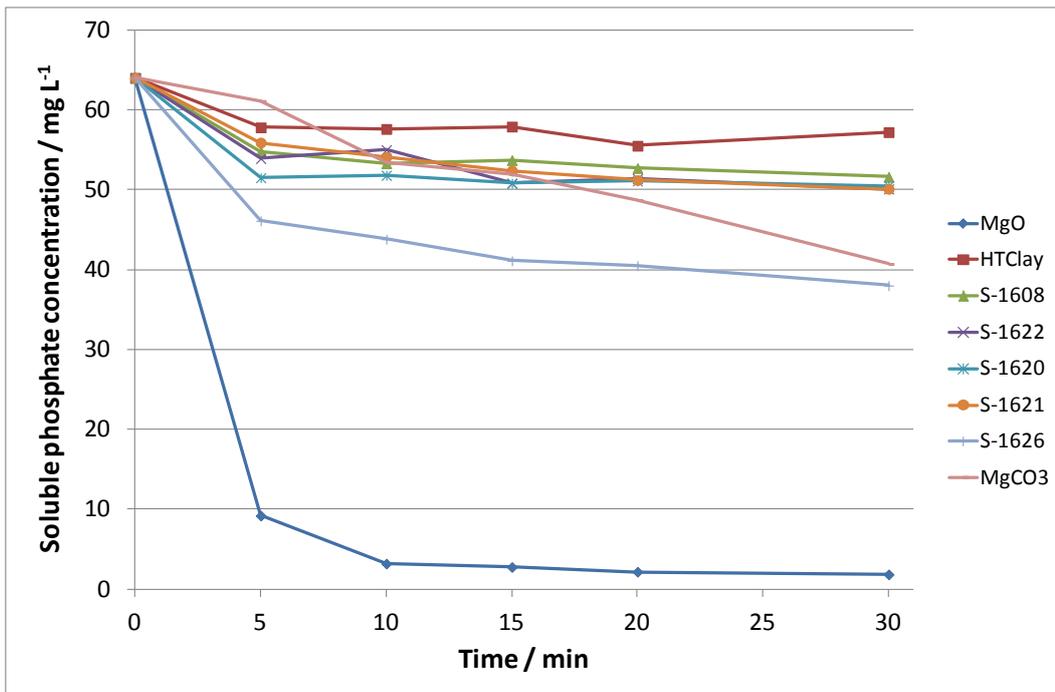


Figure 10. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of adsorbent in 250 mL of anaerobic digester effluent from a Dairy Processing site.

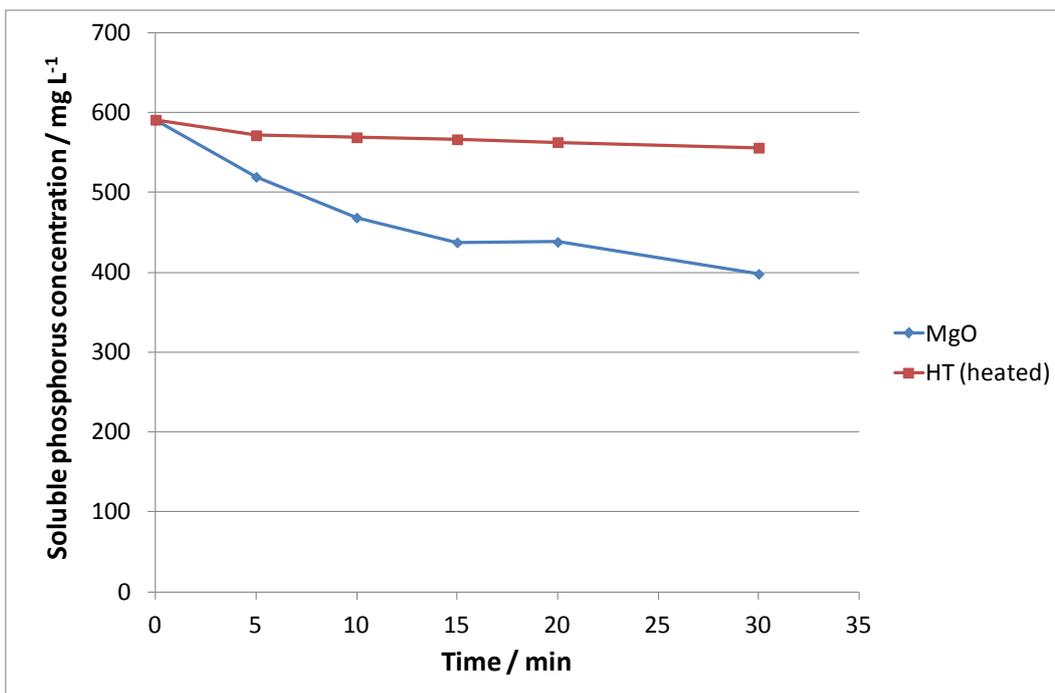


Figure 11. Soluble phosphate concentration measured as a function of time in rapidly stirred solutions containing 250 mg of adsorbent in 250 mL of anaerobic digester effluent pre-treated with thermal hydrolysis.

# Discussion

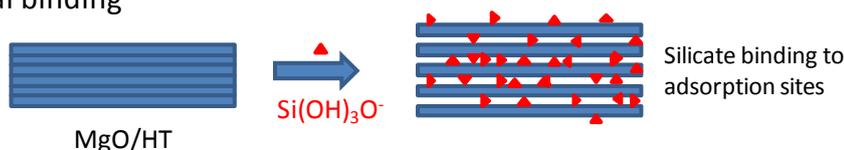
## Separability from wastewater

The separability of particulate matter from wastewater is important to enable the effective physical removal of gross solids, coagulated material (including BOD, metal oxides and phosphates). In introducing an absorbent material where there is a desire to recover it for beneficial use, it is imperative that it has superior separability from the wastewater.

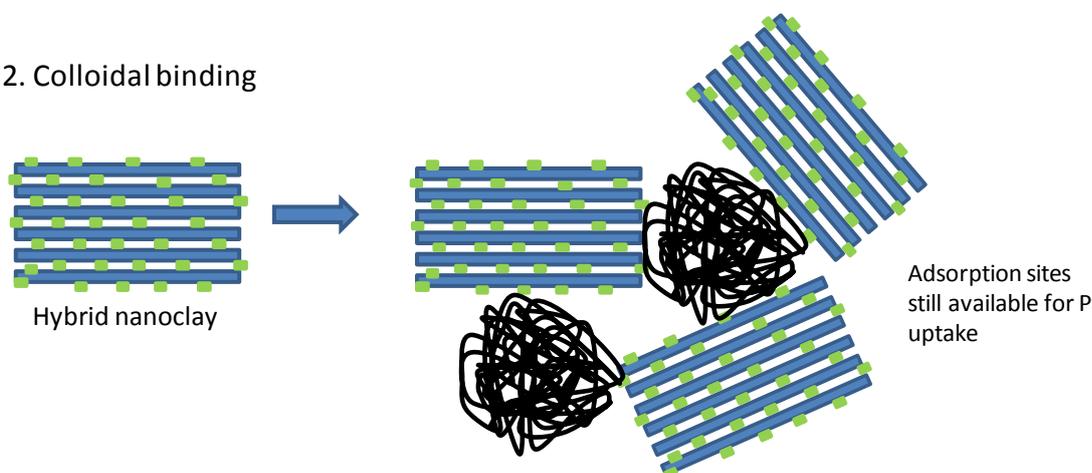
Earlier reports of the project [37] reported on the ability of binders and additives to enable the upsizing of primary powder particles into larger granules. Advances in binding capability would ultimately enable fine powders to be delivered to wastewater, maintaining their high surface area and structural integrity. The binding mechanisms explored were largely based on aluminosilicate chemistry and included the use of sodium silicate, metakaolin, and acidified aluminosilicates. The product formed by mixing equal proportions of 10 wt% acidified aluminosilicate and metakaolin showed potential promise as a binding material, forming inorganic bonds at low temperature (80°C). However, the robustness of bonds was not as strong as when using sodium metasilicate in its alkaline form.

Figure 12 shows a schematic which assists in understanding the difference between molecular binding such as occurs with sodium metasilicate, versus colloidal binding mechanism. In the latter case, the colloidal sized entities are too large to enter between the platelets of the bound material.

### 1. Molecular binding



### 2. Colloidal binding



**Figure 12. Schematic showing the difference between using a molecular binder (i.e. sodium metasilicate) and a colloidal binder (i.e. acidified aluminosilicate). The choice of MgO, HT or Hybrid Nanoclay is arbitrary.**

The ability to granulate magnesia powders to bind primary particles was explored using a series of different binding compositions, primarily based upon aluminosilicate chemistry. The addition of acidified aluminosilicate colloidal gels, metakaolin and calcium ions led to the improved properties of calcined magnesia to be separated from water. However, the formation of large granules with stability in water was not achievable using colloidal binding mechanisms. The use of sodium metasilicate demonstrated that robust granules could be formed, however, further testing beyond the scope of this project, is required in order to investigate the extent of anionic binding sites that are occupied by the silicates.

The ability of cloth filters to remove particulates has been documented previously. Furuya et al. found that removal rates for particles increased significantly where the size increased above 15  $\mu\text{m}$  [38]. Market products such as OptiFiber® PES are suggested to have a 5-10  $\mu\text{m}$  pore size [39]. The estimated settling rates from the present study suggest that the adsorbent powders have sufficient size to be removed using disk/cloth filters, however, a particle size of approximately 100  $\mu\text{m}$  diameter would be advantageous to ensure that clogging of the filters does not occur. Alternatively, for use in sand filter arrangements the adsorbents should have a particle size between 600  $\mu\text{m}$  and 1200  $\mu\text{m}$ .

The fine MgO used for the majority of the project was a relatively soft material in its hydrated (or semi-hydrated) form and was demonstrated to be problematic in its separation from water. Both coarser size fractions and “dead-burned” magnesia were explored further to assess their ability to uptake P and to improve settling performance. Dead-burned magnesia showed that it could be easily separated from water based upon its size and density distinction, however, it showed no affinity for P uptake. The data in Figure 6 demonstrated that coarser MgO particles in the range of 500  $\mu\text{m}$  diameter, or even in the range of 2-10 mm diameter could be potentially useful for P removal/recovery in wastewater treatment. Practically, to avoid disintegration of MgO (as was observed on occasions for EMAG products) quality control measures may need to be established to demonstrate reliability.

Hybrid nanoclays show promise in that they have a good density contrast with water and settle to form a solid with good handling characteristics. Despite these properties, the formation of robust granules based on hybrid nanoclays did not seem feasible using aluminosilicate binding (i.e. nanoclay granules showed less integrity than calcined MgO). The good inherent properties of the primary particles of hybrid nanoclays may be built upon by using coarser starting materials, such as vermiculites sourced from Mud Tank Australia [40]. The following products were suggested to be available from MudTank Mine, Australia, however samples of these materials were not obtained within the project.

**Table 9. Vermiculite clay grades offered by MudTank Mine [40].**

Size	Grade	Minimum size (mm)	Maximum size (mm)
Medium	G3	-4.75	1.70
Fine	G2	-2.20	0.90
Superfine	G1	-1.20	0.50

The likelihood of synthetic hydrotalcites to be used in wastewater treatment will be dependent on the ability to synthesize primary particles with a large particle diameter. The ability to up-size particles is not out of the question for future work, however, it would seem that the production of hybrid nanoclays and/or magnesia with larger particle sizes are more likely to succeed in the short-term. Should the hydrotalcite preparations in the current work not be suitable for disk/cloth filtration, the precipitation of primary hydrotalcite particles will likely hinder their practicability.

## Upscaling of hybrid nanoclay production

A cornerstone of the continuing assessment of P adsorptive nanomaterials will be the ability to upscale manufacture to quantities sufficient to meet pilot- or full-scale trials with industry partners. In the specific context of the hybrid nanoclay, a major milestone was achieved in the laboratory where small kilogram quantities of this material were manufactured. This manufacturing process within 20 L plastic containers went on to allow further upscaling to produce significant quantities in the order of 1 tonne per batch. A key factor that preserves the P uptake capacity of the hybrid nanoclay (ca. 3% P w/w) is the pre-acidification of the solution after the addition of Na-clay (as residual  $\text{Na}_2\text{CO}_3$  used in the Na-substitution may remain) and the maintenance of an  $\text{N}_2$  atmosphere to displace any remaining dissolved  $\text{CO}_2$  from the reaction vessel. While solid-solution ratios and mixing times have yet to be optimised, this optimisation process can occur as successive batches of the hybrid nanoclay are manufactured.

In order to expedite the manufacture of sufficient quantities of the hybrid nanoclay for manufacture, the CSIRO is partnering with the Western Australian Department of Water who require large batches of similar material to undertake environmental remediation field trials in collaboration with CSIRO. This supplementary use of the hybrid nanoclay is viewed as an enhancement to the present project as it allows for a more rapid upscaling of manufacture, true costing of manufacture, in addition to further performance validation in aquatic systems, albeit with substantially lower dissolved P concentrations. To this end, the Western Australian Department of Water in collaboration with CSIRO secured the services of a manufacturing

company to procure raw materials and devise (with CSIRO oversight) the most technically and cost-efficient method of clay manufacture. Indeed, this information provides invaluable cost-benefit analysis of any hybrid nanoclay adoption.

Commercial IBC containers will be used to transport high solid content slurries to trial locations around Australia. In the medium-term, once the hybrid nanoclay manufacture is optimised, and given its relative simplicity as a “one-pot” synthesis it is envisaged that this material could be made at any number of locations within Australia as required. Further to the above, research continues to investigate the most appropriate methods to produce a dry hybrid nanoclay product which may include one or both of centrifugation followed by paste extrusion or spray drying. An option also exists, where/as required, to integrate research findings of the incorporation of binding materials to enhance bead or pellet integrity and in turn recoverability.

A further option to enhance separability and recovery of spent hybrid nanoclay currently being investigated is to use larger grain size clays such as vermiculite as the substrate for hybrid nanoclay synthesis. In particular, expanded vermiculite may offer the option of semi-concealed clay surfaces in between the expanded sheets for hydrotalcite precipitation, and thus, also for an effective barrier against abrasive loss during hybrid nanoclay deployment and recovery. In addition, during synthesis of the hybrid nanoclay, Mg contained within the vermiculite may be partially leached under low pH conditions and hence offer a latent source of “free” Mg to be utilised in the hydrotalcite precipitation reaction.

## Absorbent Performance and Cost-Benefit Analysis

The benefits and risks of the absorbent materials have been explored in a scientific, operational and commercial framework. The range of current technologies that are utilised to lower phosphorus loads in wastewater provides some commentary on the benefits of each in terms of meeting environmental compliance. These, along with some notes on fertilizer profitability and the complexities of solids handling are summarised in Table 10. The absorbent materials developed within this work lend themselves to two implementations within wastewater treatment: MgO absorbent for the treatment of anaerobic digester centrate; and nanoclay materials for the polishing of secondary treated effluent to low P concentrations.

**Table 10. Technology vs benefits evaluation.**

Technology / Benefit	Comparative Capital Cost	Comparative Operational Costs	Environmental Compliance	Fertilizer profitability	Solids handling complexity
Absorbent additive for Digester centrate treatment	Low-Moderate	High	Moderate usefulness	40% of P recovered as a filler for fertilizer production	Moderate
Struvite Crystallisation	High	Low-Moderate	Moderate usefulness	40% of P recovered and can directly produce a niche product with high purity	Low
Absorbent for sand filtration	Moderate	Moderate-High	Very helpful in meeting discharge targets	Low	High
Absorbent for polishing secondary treated effluent	Moderate	Moderate-High	Very helpful in meeting discharge targets	10% of P recovered	Moderate
FeCl <sub>3</sub> /Alum	Low	Moderate	Very helpful in meeting discharge targets	Low	Moderate
Biological removal of P into sludge	Moderate - high	Low-Moderate	Very helpful in meeting discharge targets	Moderate	Moderate

A range of MgO absorbent materials of different particle size and purity may be used to remove P from anaerobic digester centrate. This will compete directly with magnesium additions used in the production of struvite (magnesium ammonium phosphate). Commercial processes based on struvite manufacture currently utilise two variations of magnesium addition: (i) magnesium chloride and sodium/potassium hydroxide (i.e. Ostara process) [41]; or (ii) through the addition of a magnesium hydroxide slurry, such as that used in existing facilities (Oxley, Qld) and pilot trials coordinated through the Australian Meat Processors Corporation (AMPC) in Australia [42]. Each of these struvite products may be managed in different ways within the Australian market. The competitive edge for the absorbent materials in this instance is the potentially lower capital investment required in order to produce a recovered P product, and the avoidance of high sludge handling costs associated with the use of traditional coagulants such as ferric and alum.

The use of nanoclay absorbents to polish P concentrations down to < 1 mg/L provides a means to compete against traditional coagulation, thus providing an opportunity to produce a P-rich soil amendment and again, avoid sludge handling costs associated with traditional coagulants. Whilst the hydrotalcites examined within the project are extremely effective in their ability to lower P concentrations, their high cost (in comparison to nanoclay materials) would limit their industrial application at this point in time.

Estimated costs for struvite precipitation facilities have been detailed for both Australian and International facilities. Internationally, a recent review by Latimer [43] has been conducted within the Water Environment Research Foundation (WERF) NTRY1R12 [43] project to look at the business cases for the installation of struvite recovery facilities. For several facilities, struvite crystallisation was found to be more cost-effective than ferric chloride addition in the management of P concentrations.

### ***Struvite Crystallisation Example 1 [43]:***

The following annual savings were noted for an Ostara process treating a sidestream flow of 0.379 ML/day with 351 mg/L P, which through the implementation of P removal would lower P concentrations to 54 mg/L. The capital cost would be approximately US\$4.1m and annual operating inputs of:

Ferric chloride costs = US\$290,000, Cost of caustic = US\$25,000

Sludge savings = US\$155,000 (sludge disposal US\$40/wet ton)

Revenue from struvite production = US\$135,850 (incorporates the value of magnesium chloride).

From the above, the business case for investment is shared between lowering the costs for chemicals (in comparison to ferric chloride), the revenue from struvite sales and savings on the amount of sludge that needs to be managed.

### ***Struvite Crystallisation Example 2 [43]:***

A second example of struvite manufacture is provided below for a Multifarm Harvest facility managing 0.265 ML/day sidestream and decreasing P from 200 mg/L P to 20 mg/L P (i.e. 80-90% of soluble P).

Total cost for full scale plant was US\$735,000, with design an additional US\$150,000. Annual costs were:

Power US\$12,000, Chemicals (magnesium and caustic) = US\$25,000, Cleaning chemicals = US\$1,500, Miscellaneous = US\$600.

Based on the above calculations, the facility would be uneconomical based upon the revenue of struvite alone, however, if sludge savings were assumed to be similar to the example above, payback would be in around 12 years at 5% interest rate.

### ***Struvite Crystallisation Example 3 [42]:***

Recent pilot trials carried out by Jensen [42] suggest that P removal and recovery via struvite crystallisation through magnesium hydroxide liquid dosing can remove phosphorus at a net cost of AU\$1/kg P, compared to approximately AU\$11/kg P for iron or alum dosing. Assuming a fertiliser value of phosphorus at AU\$3.5/kg P, it was suggested that investment in struvite crystallisation for the treatment of P-rich streams from meat processing could payback within 8 years and even sooner if avoidance of trade waste fees was relevant to the case.

#### Struvite Crystallisation Example 4:

Batstone et al. [44] investigated the feasibility for the treatment of poultry manure in Australia using a combined energy (Upflow Anaerobic Sludge Blanket) and nutrient facility where struvite was recovered through the addition of MgO. MgO was valued at AU\$800/tonne and the recovered struvite/MgO product was valued at AU\$560/tonne.

Capital costing for the complete treatment system was estimated to scale from AU\$130,000 for a 20,000 bird farm, to AU\$800,000 for a 200,000 bird farm, to AU\$3.5 million for a 1 million bird farm (assuming degradability of 50% of organics). Taking the 200,000 bird farm as a base case, capital costs were distributed approximately 60% in vessels and civil construction, and 40% in mechanicals (mainly the cogeneration engine), fixed piping and wiring, and engineering. A summary of estimated operating costs is presented in Table 11 which demonstrates the value of recovered electricity and nutrients exceeds input costs and operational expenses. Payback for this scheme was estimated as being 11 years.

**Table 11: Annual operating costs for a 200,000 bird anaerobic digestion facility with different litter degradability. Negative values represent income [44].**

Cost (AU\$)	50%
Operator salaries	\$14,332
Vessel and piping maintenance	\$10,723
Costs (maintenance)	\$5,650
Pump and mixing energy	\$3,772
Chemical MgO	\$11,915
Cogeneration electricity	-\$99,042
Nitrogen in $MgNH_4PO_4$	-\$7,611
Phosphorous in $MgNH_4PO_4$	-\$44,940
Nitrogen in stripped $NH_3$ <sup>1</sup>	-\$20,127
Input cost of litter	\$19,337
Value of digested litter	\$0
Cost of wastewater treatment	\$5,304
Total yearly cost	-\$100,686

#### MgO absorption Example 1:

Using the same operational parameters presented in the Struvite Crystallisation Example 1, an estimated cost for MgO absorbants to decrease P concentrations from 351 mg/L P to 54 mg/L P was assessed. This study has shown that MgO can remove P with an uptake of 69 g P/kg and this can be achieved within short time frames, as evidenced by high P removals from anaerobic digester centrate from a dairy manufacturing facility. At these rates, the following annual operational figures can be calculated:

Total amount of MgO = 595 t (annual cost presented in Table 12).

**Table 12. Indicative costs for the supply of bulk MgO to two locations in Australia [45].**

MgO product	Location	Indicative cost (AU\$/t)	Cost MgO (AU\$/yr)
Calcined MgO	Brisbane	680	-404,600
EMAG1000	Brisbane	520	-309,400
EMAG2210	Brisbane	480	-285,600
Calcined MgO	Adelaide	780	-464,100
EMAG1000	Adelaide	620	-368,900
EMAG2210	Adelaide	580	-345,100

Total cost of sludge management if incorporated into biosolids = AU\$137,770

Revenue of sales based on P value of AU\$3/kg = AU\$123,165.

The implementation of MgO absorbent technology can be compared to that of struvite precipitation. Capital expenditure for ½ hr retention basin (30 m<sup>3</sup>), rapid mixing, sludge extraction and drying is estimated to be in the order of AU\$0.7m. If recovered MgO is incorporated into biosolids, the capital would be substantially reduced, estimated to be approximately AU\$0.5m, as detailed below:

Estimated capital items (AU\$):

Storage area (shed)	\$50,000
30m <sup>3</sup> tank	\$150,000
Transfer hopper and rapid mixing	\$150,000
MgO extraction/handling	\$150,000
Drying	\$200,000

Table 13 provides a summary of estimated costs for MgO absorbents, compared to the costs reported by Latimer [43]. From this comparison, the ability of MgO absorbents to compete against struvite precipitation technology for treating anaerobic digester centrate is shown to be highly dependent upon the ability to create a market for the recovered product such that it is not incorporated into biosolids and therefore incur sludge management costs. Where MgO absorbents can be recovered, the technology appears to offer financial and environmental benefits when compared to ferric chloride dosing, however, should MgO be incorporated into biosolids, the cost of implementation would become very similar to the case for ferric chloride and would offer marginal benefit.

**Table 13. Comparison of estimated costs for the implementation of struvite recovery, MgO absorbents and ferric chloride dosing for the removal of P from anaerobic digester centrate.**

AU\$	Struvite	MgO/P product (with sales)	MgO/P (incorporated in biosolids)	Ferric chloride (incorporated in biosolids)
Capital	-\$5.1m	-\$0.7m	-\$0.5m	-\$0.5m
Chemical cost	-\$31,250	-\$285,000 to - \$464,000	-\$285,000 to - \$464,000	-\$362,500
Revenue	\$169,810 (adjusted for MgCl <sub>2</sub> cost/value)	\$123,165	0	0
Sludge management	0	0	-\$137,770	-\$193,750

Whilst it is true that additional drivers may influence a business-case decision (i.e. decrease in maintenance, or ability to achieve P environmental limits), a direct comparison with struvite precipitation does not make MgO absorbents look attractive, as put simply, the cost to supply MgO absorbents is likely to be greater than the achievable revenue for the product. Using a payback period calculation with a 5% discount rate, the revenue from the sale of the product would need to be a factor of three higher in order to achieve a return on investment within a 20-year timeframe. In comparison to Struvite Crystallisation Example 4, it follows that the amount of MgO required for effective absorption of P is approximately 10 times the amount of soluble Mg hydroxide required to induce struvite crystallisation. Operationally, this also corresponds to the handling of greater volumes of recovered product and potentially increases the risk of high material management costs (i.e. dewatering, stockpiling, transport).

### **Polishing of secondary treated effluent Example 1:**

Inland treatment facilities usually have the tightest phosphorus limits in order to avoid eutrophication issues. Here, we look at the theoretical cost scenario of implementing the use of nanoclay materials for the polishing of secondary treated effluent at the Lower Molonglo facility in the Australian Capital Territory, which handles approximately 90 ML/day of municipal wastewater. Historically, this facility used around 15 mg/L of ferric chloride and high lime dosing to lower P concentrations to < 0.4 mg/L during primary treatment (at pH 11.2) [46]. Subsequent advances have led to the facility carrying out a dual removal of phosphorus, both in the primary treatment and at the end of secondary treatment. The phosphate concentrations after secondary treatment are in the range of 0.42 mg/L (on average) and ideally, P concentrations need to be further decreased to <0.15 mg/L for environmental release. Typically, a Al:P ratio of 5:1 to 7:1 is required to achieve P < 0.1 mg/L [47]. For the Lower Molonglo scenario, Fe:P ratios of 4:1 are sufficient, consuming 5.5 mg/L for secondary polishing. The cost of ferric chloride is estimated to be \$300/t; suggesting annual chemical costs of \$52,800 for secondary polishing.

The difference in solids production due to the use of coagulants was estimated in the following manner: Biosolids production in Australia is typically about 0.25 t (dry solids) per megalitre of treated effluent, which, without the addition of ferric chloride, would equate to approximately 8000 t/year and with coagulants would increase solids by 10-25%. Assuming 10% for calculations, and that biosolids handling costs are \$300/dry tonne (value from AWA average reported costs for biosolids management in Australia), the additional sludge management costs for using coagulants are estimated as \$240,000.

Indicative costs for the same treatment performed by nanoclay absorbents may be calculated based upon a 1.8% P uptake, where absorbent cost is approximately \$500/t assuming economies of scale. On this basis, the annual requirement for absorbent material would be 480 t at an estimated cost of \$240,000. Revenue from the sale of nanoclay materials as a soil conditioner is uncertain at this point in time. The closest estimate of what may be achievable is the lime-amended bioclay produced by Water Corporation WA, which has estimated value in the range of \$40 /t [48]. This revenue would equate to \$19,200 per annum.

Based on the above scenario for the required polishing of secondary treated effluent, the economics of using nanoclay appear to be comparable to removing P with alum and ferric chloride. The competitive edge for the nanoclay material is the ability to reduce sludge handling costs, and the potential recovery of a saleable soil conditioner. Where biosolids handling costs are not an imposition for a wastewater facility, it would appear that traditional coagulants would still be more cost-effective. However, nanoclay materials may also offer productivity benefits for agriculture in rural areas, particularly in regions with sandy soils, whereby the combined benefits of clay and P additions to soil could be realized.

## Future work

Based on the outcomes of the project, the following recommendations are made for future work:

- The ability of large MgO particles to remove significant P loads from a range of wastewaters has general application. The deployment of such a technology would enable an on-demand or one-off means to reduce P and could be subsequently used as a local soil conditioner. The technology may be developed for rapid response, and may compete or complement Phoslock or similar products.
- Nanoclay hybrids should be further developed as both an environmental remediation tool and a secondary effluent polishing option. Where possible, large-scale manufacture and pilot trials should be undertaken to improve the understanding of reactions times, chemical cost, capital cost, changes in sludge volume and solids water retention.
- The ability of hydrotalcites to decrease P to low concentrations should be published in scientific literature, with the intention that their cost of production can be reduced over time.
- Results have indicated that, depending on water characteristics, some feeds are easier to scrub than others. This indicates that factors such as pH, EC, alkalinity have a strong effect on how well a particular adsorbent performs its task. Further knowledge on the competition for phosphorus adsorption sites is required where possible.

# Conclusions

This report has focussed on the evaluation of P-absorbent materials in the context of potential methods of P absorbent introduction and enhancing separability for efficient recovery.

With assistance from wastewater engineers, the most suitable introduction methods for the absorbents have been identified as being the introduction via rapid mixing, followed by a coagulation-like retention time prior to disk/cloth filtration.

Sourcing of absorbent materials with suitable settling/separation characteristics has been demonstrated via (i) the use of particles with large primary particle sizes (i.e.  $> 100 \mu\text{m}$ ), (ii) through the binding of primary particles using acidified aluminosilicate binders, and (iii) the good density contrast and “handleability” of hybrid nanoclays. Future work aims to bypass the need for the binding of primary particles, and therefore improvements in separation beyond those observed in the present study will not be built upon in the foreseeable future.

Testing of the uptake kinetics demonstrated variations in P absorption and identified more specific uses for MgO, nanoclay hybrids and hydrotalcites:

- MgO was the most effective means of removing large quantities of P from water, taking up to 101 g P/kg of absorbent. This amount of phosphorus exceeds levels found in single superphosphate fertilizer. However, MgO did not generally remove P to concentrations below 2 mg/L. Thus, the utility of MgO is primarily as a gross P-absorbent to remove the majority of P from high strength streams. That said, MgO absorbents do not appear to be cost-competitive with existing technologies, particularly when matched against struvite crystallisation which uses approximately one tenth of the Mg in comparison. P absorbents are therefore not likely to find widespread application but may be used in one-off and emergency situations where P concentrations in water need to be reduced. However, the cost-effectiveness of using absorbents in the place of ferric or alum dosing would need to be further explored.
- Hydrotalcites could be considered complementary to MgO in that, while lacking the ability to remove large amounts of P from solution, they offer the potential to scrub remaining P to very low concentrations. For instance, with a synthetic 2.6 mg/L P solution, some hydrotalcites proved to be capable of leaving no detectable P in solution ( $< 0.1 \text{ mg/L}$ ) after 10-20 minutes. To achieve such a P removal hydrotalcite would need to be dosed at approximately 44 kg/ML. A number of hydrotalcites were synthesized and while some were extremely effective, it is considered that the most effective material was a commercial product purchased from Aldrich. One critical proviso is, however, it was found that the material must be heat-treated prior to use as, in its as-received form, it is extremely hydrophobic and is essentially unusable. Practical application is thought to be limited at present due to the high cost of hydrotalcite materials.
- Nanoclay hybrid materials were found to have rapid P uptake kinetics, due to the accessibility of the hydrotalcite coating on clay particles. However, they are limited in their overall capacity due to dilution by the inactive clay substrate which accounts for approximately 70% of the total mass. In low strength P wastewaters (0.87 mg/L and 0.38 mg/L), nanoclay hybrids removed approximately 56% of the P after only 5 minutes and 70% after 30 minutes (leaving 0.26 mg/L P). For this removal to occur nanoclay hybrid materials would need to be dosed at approximately 34 kg/ML, assuming an uptake of 18 gP/kg of absorbent. In addition to rapid uptake kinetics, an advantage of the nanoclay hybrid is the clay component itself which may constitute a useful addition to sandy soils with poor nutrient retention if the adsorbent is reused as a soil conditioner.

A range of recommendations have been made to allow future research on phosphorus absorbent technologies to be undertaken in a more focused manner.

# Appendix I: Materials sourced for initial characterisation

Table 14. Materials sourced for initial characterisation, and as starting materials to possibly develop into high-surface area absorbents.

By-product	Source	Sourcing	Modification	P uptake (g P/kg)
Serpentines (Mg,Fe) <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Lizardite (Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> ) from Mineral Resources Tasmania.	Yes	Cheap feedstock for HT formation. Grind, acid leach out Mg/Al (Fe) adjust stoichiometry for HT and neutralise to induce HT precipitation, with added Al if necessary. Alkali Cracking?	<1
NUA	TiWest, Iluka (Capel, WA, Jacinth Ambrosia, SA).	Yes	Blend with other materials to optimise nutrient removal.	< 20 dependence on solid:solution and time
Calcined magnesia (MgO)	Queensland Magnesia. Received as 4:6 mixture of periclase and brucite. TGA showed transistion to 100% periclase at 400°C.	Yes	Mg and alkalinity source for hydrotalcite synthesis by induced hydrolysis with Al. Sodium aluminate and AlCl <sub>3</sub> .	< 35
Magnesite (MgCO <sub>3</sub> )	Magnesite for HT manufacture use analytical reagent.	Yes	Test reaction as above with Al compounds.	<1
Nano clays	Exfoliation of clays by acid digestion of clays, addition of complexing agents and ratio correction. Precipitation of HT onto clay backbone.	Produced at CSIRO	Mg-rich clays as precursors (Vermiculite, Smectitie etc.). Vermiculite+HT batch tests 60% of expectations. Work to isolate Si during prep to increase P-uptake.	2-9
Limestone (CaCO <sub>3</sub> )	Local garden suppliers. Beams Bros. Smithton (NW Tasmania) can supply calcite "fines".	†		
Cement Kiln Dust (CaCO <sub>3</sub> /CaO)	Initially utilize ordinary Portland cement if required and optimize with Dust?	†		<2
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	Local garden suppliers identified. Also Beams Bros., Smithton (NW Tas).	†	Feedstock for hydrotalcite synthesis but not ideal.	<1
Ca slurry from acetylene production		†		
Hydrotalcite	Mg <sub>6</sub> Al <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>16</sub> ·4H <sub>2</sub> O. Layered double hydroxides. (1) co-precipitation of di-(Mg) and tri-valent (Al/Fe) cations at high pH or (2) induced hydrolysis of Al salt with Mg(OH) <sub>2</sub>	Produced at CSIRO	Vary anion, Al source and Mg:Al ratio to optimize P-uptake. Blend with other materials as required. Mg/Fe system could be absorbed if necessary.	< 25
CaSO <sub>3</sub>	From SO <sub>2</sub> scrubbing.	†		
Synergistic combinations			Synergies by combining by-products, i.e. to remove DOC, N and P.	

† Materials high in Ca and containing limited Mg are less desired for hydrotalcite formation. These materials, whilst being potentially useful were not envisaged to provide additional benefit.

Note: HiSmelt was previously shown to offer some potential as an absorbent for nutrients. This material will no longer be available due to Rio Tinto decommissioning the plant. Two carbonaceous-based materials were also explored; Iluka Carbon and Brown Coal from Loy Yang, La Trobe Valley Victoria.

## Appendix II: Phosphorus release summary

The internationally recognised neutral ammonium citrate (NAC) test was suggested by Incitec Pivot as being an appropriate first pass to evaluate the agronomic properties of the P-adsorbent materials. The test was conducted according to EN15957:2011 and specifies a method for the extraction of phosphorus soluble in neutral ammonium citrate [49].

### NEUTRAL AMMONIUM CITRATE SOLUTION

370 g of citric acid was dissolved in 1.5L of deionised water and 28% ammonium hydroxide was added to adjust the pH to 7. The solution was made up to 2L in a volumetric flask at 20°C and the pH checked again. A small amount of neutral ammonium citrate (NAC) solution was heated to 65°C just prior to use.

### SAMPLE PREPARATION

Solids remaining from P-uptake experiments from model solutions were separated using a 0.2 µm Millipore filter, rinsing twice with a small quantity of deionised water. The solids were dried overnight in an oven at 60°C. After cooling, an amount of solids was weighed out into an Erlenmeyer flask (200 ml) and preheated NAC solution added using a pipette in a ratio of 1 g : 100 mL citrate solution. All materials examined were conducted in replicate. For comparison, both aluminium phosphate ( $\text{AlPO}_4$ ) and iron phosphate ( $\text{FePO}_4$ ) compounds synthesised in our laboratory were also tested.

### EXTRACTION

The stoppered Erlenmeyer flasks were shaken to disperse any obvious lumps and placed into water bath stirrer preheated to 65°C. After exactly one hour the flasks were removed from the water bath and cooled to ambient temperature. The contents of the flasks were transferred to 200 mL volumetric flasks and made to volume using deionised water. A small volume was extracted through a 0.2 µm syringe filter and P concentration analysed using ICP-OES.

### RESULTS

Table 15 provides a summary of P release tests using NAC. All hydrotalcites and nanoclay hybrids displayed 100% extraction of P, suggesting that these materials have good promise as agronomic fertilizer supplements. In comparison, both  $\text{AlPO}_4$  and  $\text{FePO}_4$  demonstrated decreased concentrations of extractable P, in the range of 70%. Interestingly, MgO, which was the best performer during P-uptake tests, exhibited decreased concentrations of P in the NAC test. The estimated total P in the starting material is decreased in the case of MgO as result of water rinsing during preparation of the material.

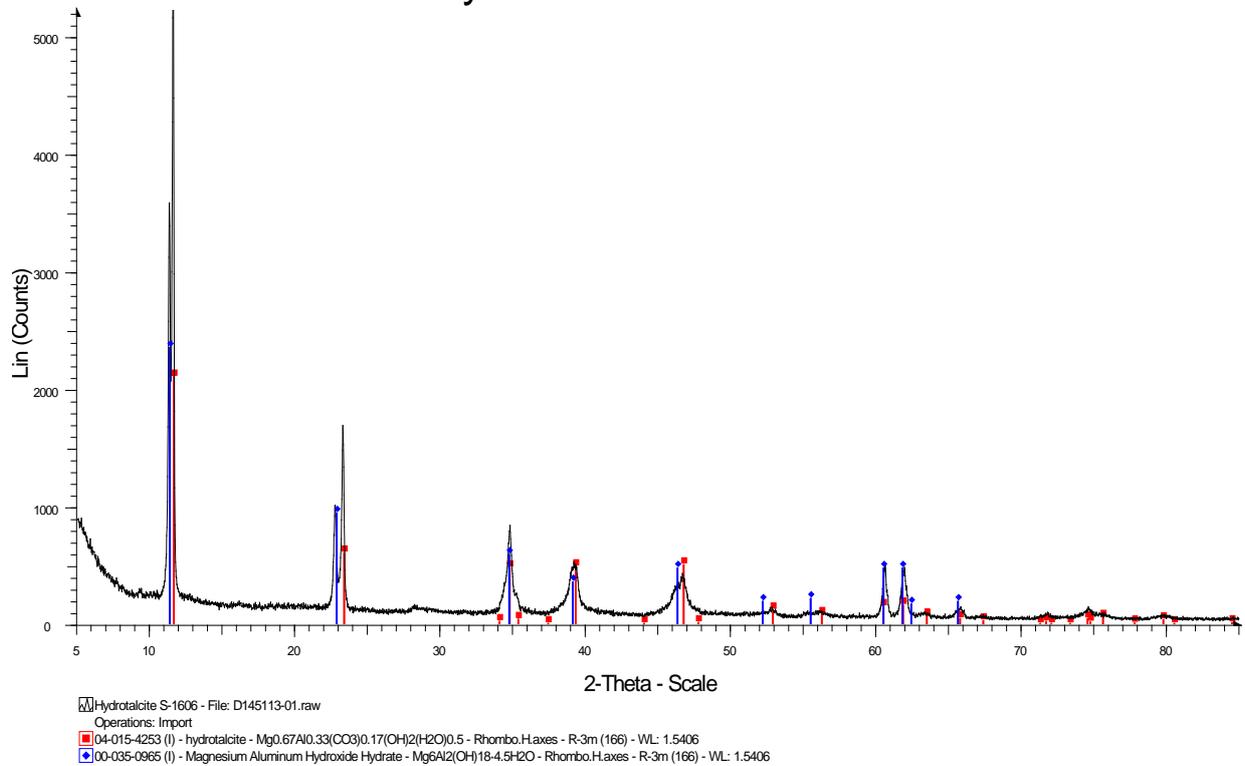
**Table 15. Estimated phosphorus concentrations in starting solids and extractable phosphorus from neutral ammonium citrate test (mean  $\pm$  total error).**

Sample	P from uptake experiment (gP/kg)	Estimate total P (mg/l)	Measured total P (mg/l)	Final Concentration (mg/l)	P release (%)
S1590-A	24.8	12.4 $\pm$ 0.3		15.3 $\pm$ 0.2	100
S1590-B	18.0	9.0 $\pm$ 0.6		11.6 $\pm$ 0.0	100
S1590-C	14.3	7.2 $\pm$ 1.1		9.2 $\pm$ 0.3	100
S1590-D	19.5	9.8 $\pm$ 0.4		12.1 $\pm$ 0.1	100
S1590-E	22.2	11.1 $\pm$ 0.4		17.8 $\pm$ 0.6	100
Nanoclay hybrid	9.1	4.6 $\pm$ 0.0		1.2 $\pm$ 0.1	100
NUA	22.9	11.5		21.2 $\pm$ 0.3	100
MgO	37.4	18.7	12.9 †	12.8 $\pm$ 0.4	99
FePO <sub>4</sub>		205.3		147 $\pm$ 17	71
AlPO <sub>4</sub>		254.0		182.8 $\pm$ 0.9	72

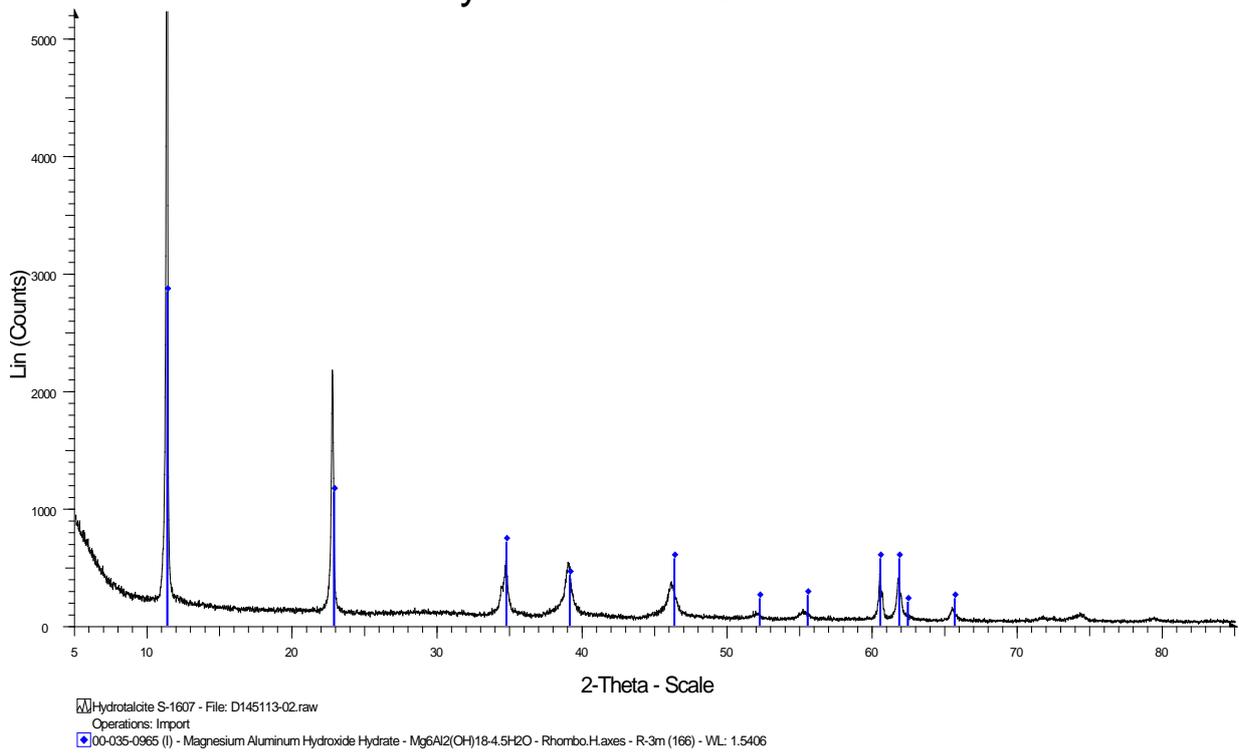
† Measured total concentration achieved by digestion of 0.1 mg MgO into HCl solution adjusted to pH 4.5. Concentration determined using phospho-molybdate method [9].

# Appendix III: Materials characterisation supporting information – X-ray diffraction

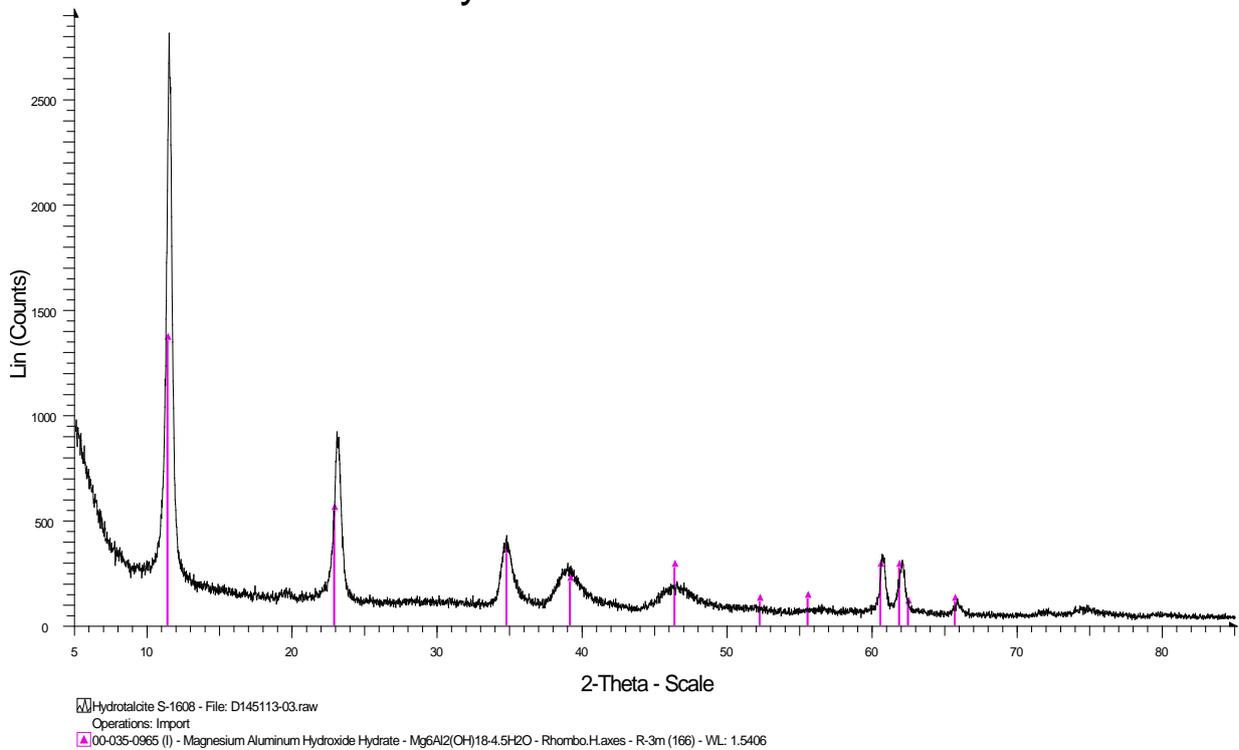
## Hydrotalcite S-1606



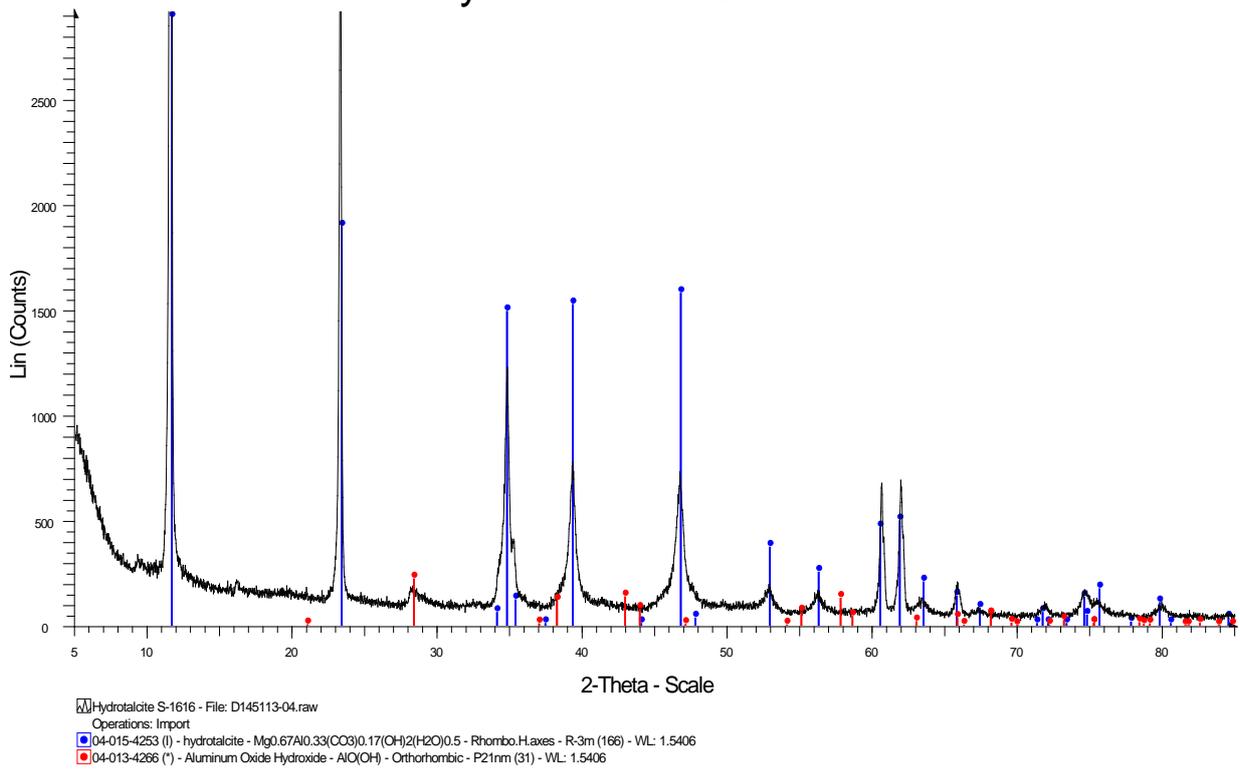
## Hydrotalcite S-1607



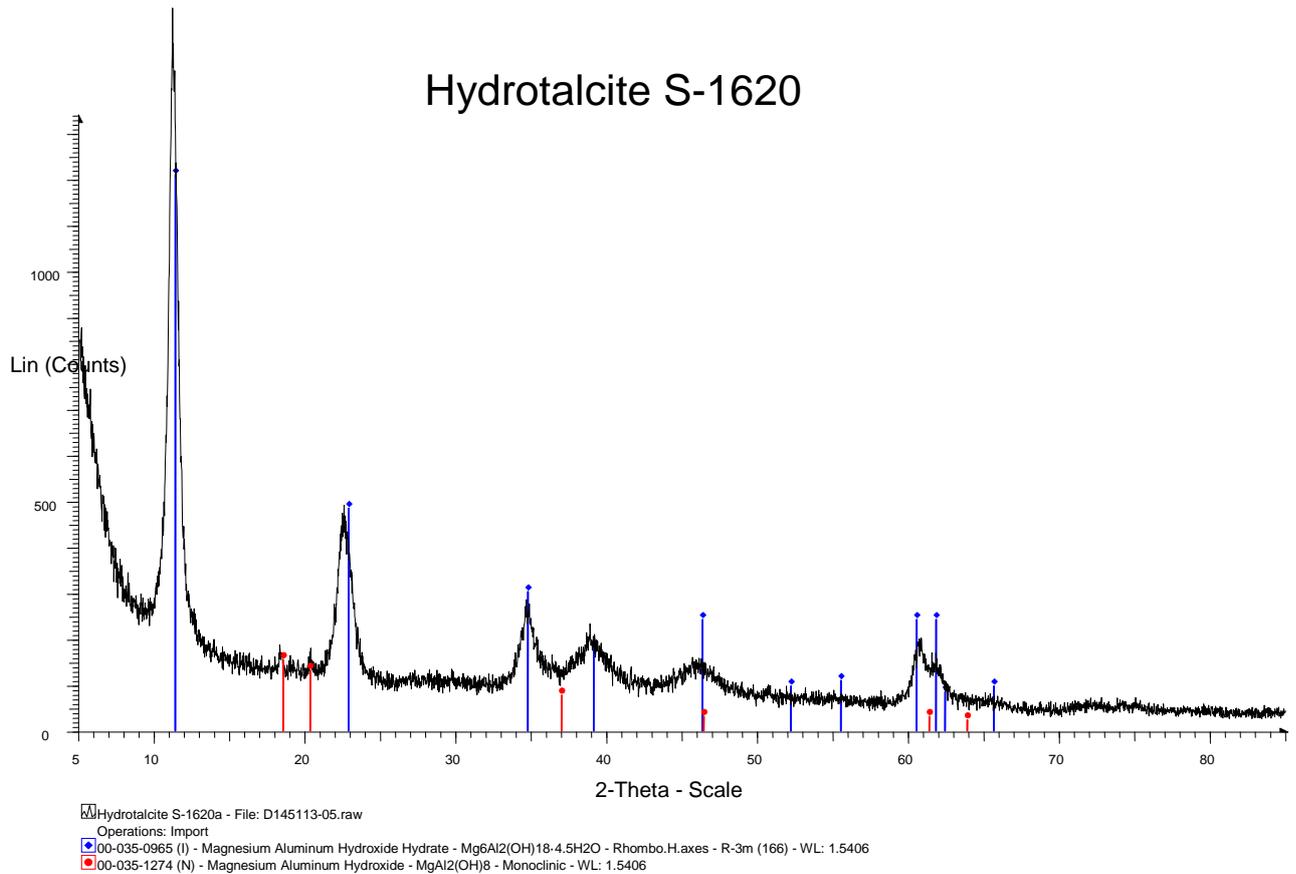
## Hydrotalcite S-1608



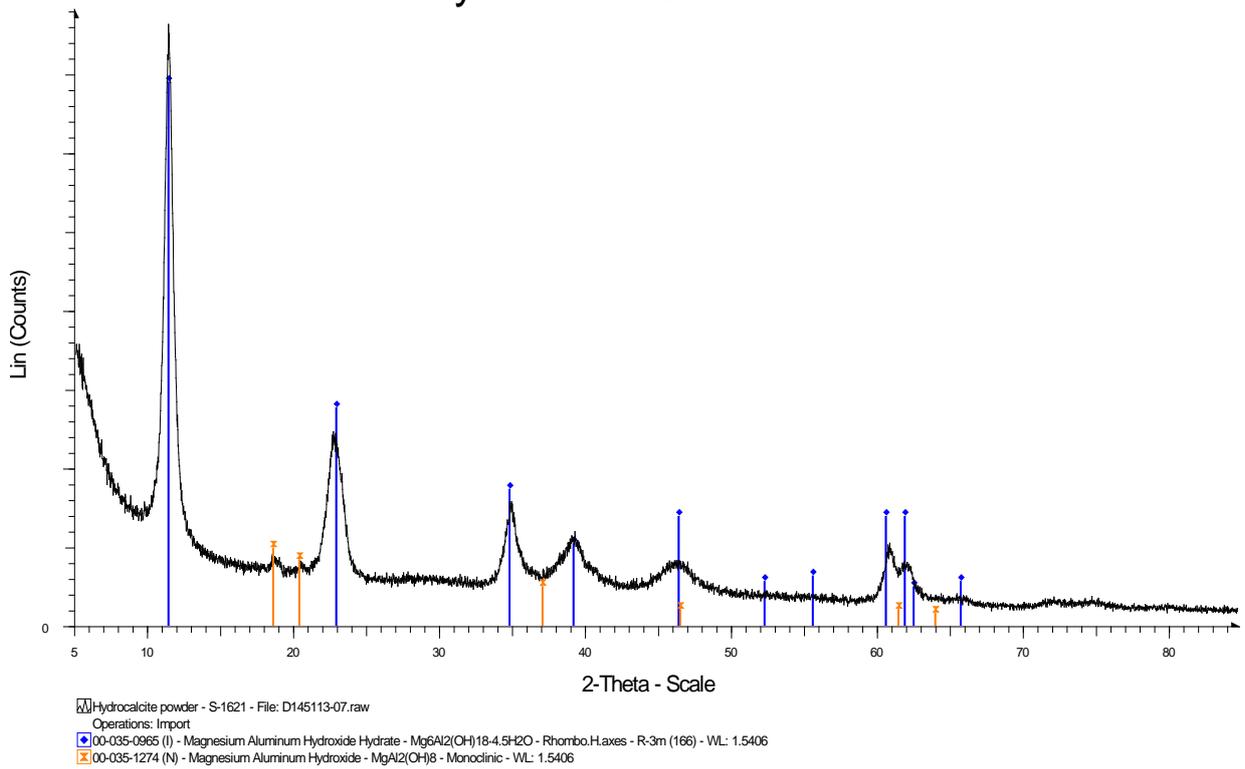
## Hydrotalcite S-1616



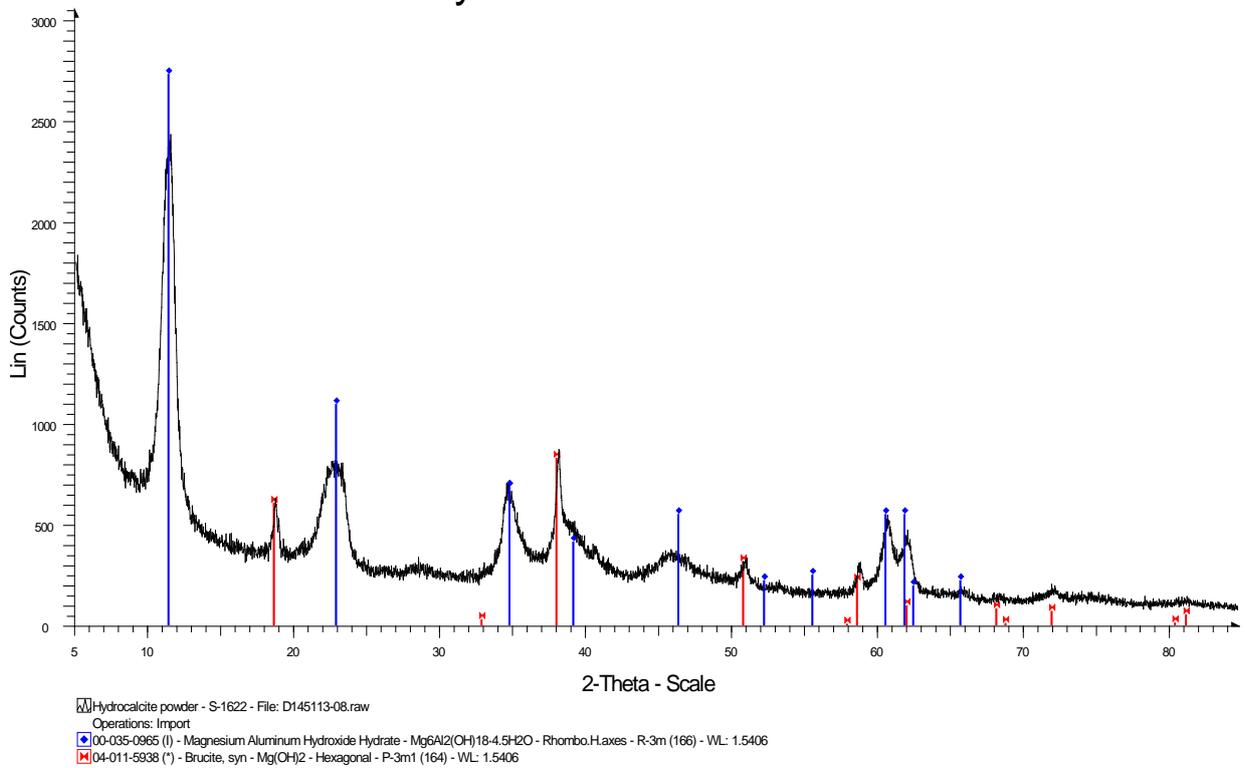
## Hydrotalcite S-1620



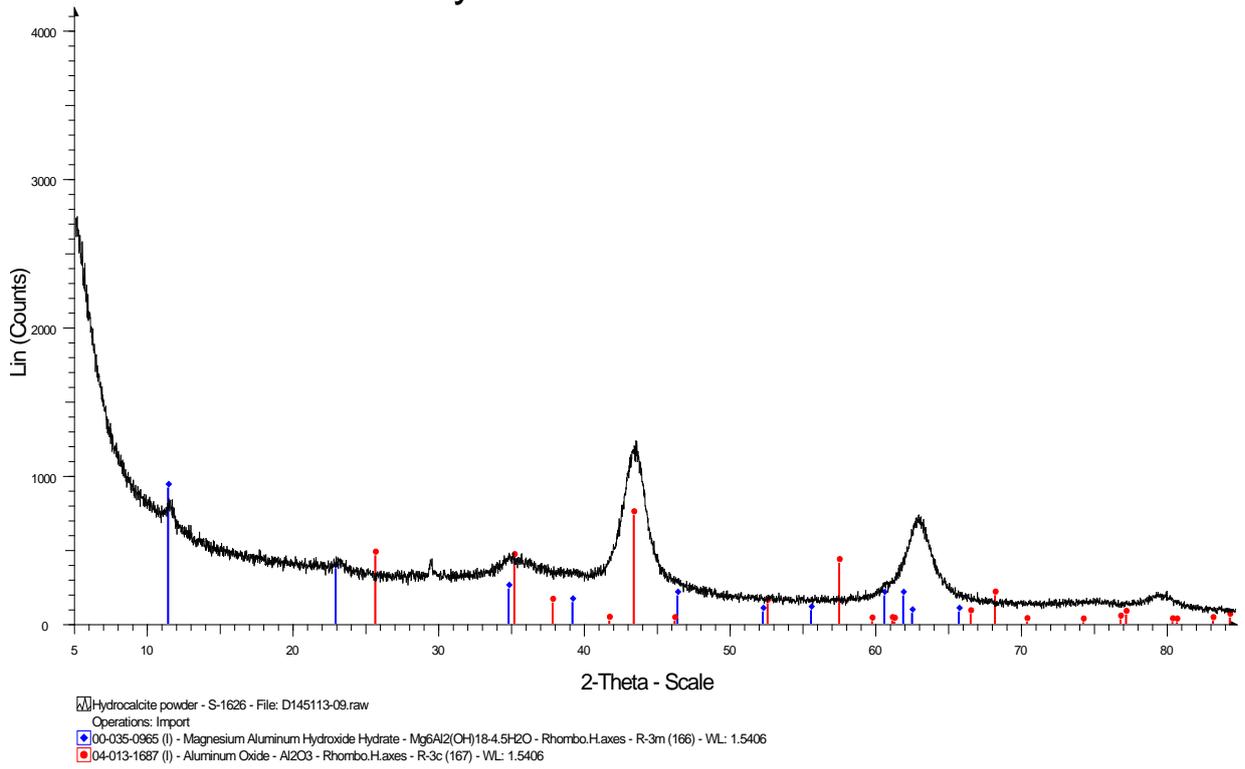
## Hydrotalcite S-1621



## Hydrotalcite S-1622



# Hydrotalcite S-1626



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