

Phosphorus Removal from Wastewater and Manure Through Hydroxylapatite Formation

An Annotated Bibliography

Hydroxylapatite – $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ – is the main mineral in bones, giving them their compressive strength, and, as found in nature, is often called phosphate rock. Phosphate rock is commercial mined for its phosphorus, for use in fertilizers and other purposes. Its formation is sometimes used to remove phosphorus from wastewaters, including manures. It is often also known as hydroxyapatite (that is, without the "l"), as HAP, and as calcium apatite.

This annotated bibliography – while not exhaustive – summarizes some of the research to provide a possible foundation for knowledge and an evaluation of this technique for the removal of phosphorus from livestock manure.

1. "Phosphate removal & recovery from wastewaters", *Phosphorus & Potassium*, Issue 213, January-February, 1998, 12 pages

This article reviews the state-of-the-art of phosphate removal & recovery from wastewaters. One such process is the Crystalactor system, which was developed by the Dutch consulting engineers DHV in the late 1970s. It has been used commercially in water softening and other water purification applications for some years. For phosphate removal, the process aims to produce calcium phosphate (hydroxylapatite) in a granular form using a fluidized-bed reactor/crystallizer. The phosphate crystallizes on seed grains, usually sand.

The process involves preliminary degasification (carbon dioxide removal) of the phosphate-laden wastewaters with 96% H_2SO_4 sulfuric acid and then crystallization of calcium phosphate by the controlled addition of lime or caustic soda. It has been found that dosing with caustic soda (OH ions) is often more effective than dosing with lime (Ca ions), since it increases the driving force for the conversion of the phosphate to tricalcium phosphate. In practice, dosing with lime is only necessary in "soft" wastewaters.

A demonstration plant was built at Westerbork, The Netherlands in 1988, where the phosphorus loading (including organic phosphorus) in raw sewage of 16 mgP/liter is first reduced by conventional sewage treatment to 9 mgP/liter. Here, the Crystalactor process reduced the phosphorus loading in the final effluent to less than 0.5 mgP/liter while producing up to 40 tonnes of 2 mm diameter calcium phosphate pellets per year. These typically consist of 40-50% calcium phosphate, 30-40% sand, and up to 10% calcium carbonate. Employing ground pellets as seed materials reduces the sand content, so that a product with higher calcium phosphate content is obtained.

Another technique is the CSIR process, which was developed in South Africa. It is a fluidized bed crystallization column at a laboratory scale for removal of phosphate from a variety of influent streams. Phosphate can be removed either as hydroxylapatite or struvite, according to the make-up of the feed stream, and retention times in the range of 3-10 minutes result in over 90% P removal with the pH controlled between 8.0 and 9.5. The process claims to be capable of reducing phosphate loadings to less than 0.1 mgP/liter from raw sewage intake containing 30-80 mgP/liter. Conditions for struvite precipitation are optimum at pH above 8.0, while those for hydroxylapatite are best at pH above 9.5.

Using similar chemistry to that in the DHV and CSIR processes described above, Kurita Water Industries, Japan, has developed a process based around a fixed bed crystallization column. The Kurita process is designed to remove phosphate from the secondary effluent of sewage treatment works using phosphate rock as seed material.

The fixed bed column reactor is packed with 0.5-1.0 mm phosphate rock particles. The secondary effluent passes upward through the column, having been conditioned with the addition of calcium chloride and caustic soda. Hydroxyapatite is precipitated. It is claimed that the residual phosphorus content of the effluent lies below 1.0 mgP/liter. However, it is not clear how the crystals are removed from the reactor.

2. Valsami-Jones, E., "Calcium phosphate precipitation", *SCOPE Newsletter*, No. 41, pages 8-15, January 2001

Although there has been considerable work on phosphorus recovery from wastewaters, there is still limited recovery due to a number of scientific and technical problems that need to be resolved, including:

- the role of interfering ions, such as carbonates and organic ligands
- the role of pH

- interference from fines
- the quality and use of the recovered material
- improved reactor design
- optimum positioning of the reactor within the wastewater flow
- how phosphorus recovery fits into normal wastewater treatment

This article reviews the chemical principles of calcium phosphate precipitation, reviews recent work on the scientific and technical developments and considers the remaining challenges. A table shows six forms of calcium phosphates, their molar ratios and solubilities and the text notes that the precipitated phase will most likely eventually transform in the thermodynamically more stable hydroxylapatite (HAP), and it is for this reason that the majority of published experimental solubility studies focus on HAP.

Compound	Formula	Molar ratios	Solubility
Brushite or dicalcium phosphate dihydrate (DCPD)	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	1	$\text{SP} = 2.49 \times 10^{-7}$
Monetite (DCPA)	CaHPO_4 (Anhydrous DCPD)	1	$\text{SP} = 1.26 \times 10^{-7}$
Octacalcium phosphate (OCP)	$\text{Ca}_8\text{H}(\text{PO}_4)_3 \cdot 2.5\text{H}_2\text{O}$	1.33	$\text{SP} = 1.25 \times 10^{-47}$
Amorphous calcium phosphate (ACP)	$\text{Ca}_3(\text{PO}_4)_2$	1.5	$\text{SP} = 1.20 \times 10^{-29}$
Hydroxylapatite (HAP)	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	1.67	$\text{SP} = 4.7 \times 10^{-59}$
Tricalcium Phosphate (TCP)	$\text{Ca}_3(\text{PO}_4)_2$	undefined	SP = variable, more soluble than crystalline phosphates

The formation of precipitates from solution are controlled by the two steps of nucleation and growth. For nucleation, aggregation of crystallites on existing materials (for example, seed crystals) is less energetically demanding than the spontaneous growth of crystals. Growth takes place in a number of steps and may first be in a precursor stage, although the precipitate will eventually recrystallise to form HAP. The type of precursor will be influenced by pH, ion inhibition, the impact of organic ligands, seed materials and other factors.

While the design of reactors for removal of phosphorus from water and wastewater has been of interest for over 30 years, the design of reactors to foster the recovery of the phosphorus has been much less studied, although does include research done in Australia, Germany, Holland, Italy, Japan, Korea, South Africa, and Turkey. However, in most cases, this work has focused on struvite formation.

Most working reactors are variations of a fluidized bed principle and use seeding material, most often sand. A high state of supersaturation is necessary, which is achieved by an extreme increase in pH and the addition of other ions, such as calcium or magnesium.

Research in Germany has tested seeds of sand, apatite and calcite. It was found that the surface area of the seed is important, versus the composition of the seed.

The article summarizes both scientific research in Germany, Greece and the UK, along with technical developments in Australia, Germany, Holland, and Japan. In Holland, the firm DHV developed the Crystalactor® technology, which was installed at several locations in The Netherlands and in the UK. However, this technology is no longer economic in Holland and is only in operation at one location there; at the Geestmerambacht sewage works. A challenge with this technology is the need for carbon dioxide stripping and high pH.

In order to move this process along, additional research is needed on the factors listed at the beginning of the article, and described in more detail at the end of the article.

3. Regy, Sylvia, et. al., "Phosphate Recovery by Struvite Precipitation in a Stirred Reactor", June 2002, 66 pages. Found at http://www.nhm.ac.uk/research-curation/projects/phosphate-recovery/LagepReport.PDF?bcsi_scan_991819FA721D10BC=0&bcsi_scan_filename=LagepReport.PDF on August 15, 2007

This work focuses on phosphate removal by precipitation, testing existing systems and developing a new approach. Numerous studies have been reported in literature on this subject. The reactors tested are mainly fluidised bed reactors (FBR) and the phosphate is mainly recovered as calcium phosphate or struvite (MAP, Magnesium Ammonium Phosphate, principally). Owing to the need of having a simple and flexible technology, a new reactor was designed, based on struvite precipitation.

After a description of the theory on crystallization and precipitation, a brief description of the calcium phosphate and struvite chemistry is presented. Then, we will describe the different processes developed in literature for P-recovery are described.

In the section on the theory of crystallisation and precipitation, information is provided in seven sections:

1. Generality
2. Solubility
3. Supersaturation
4. Nucleation
5. Induction time
6. Growth
7. Agglomeration

The report next looks specifically at calcium phosphate formation, and focuses on four areas:

1. Solubility
2. The thermodynamics “drive force”
3. Precursor phases
4. Inhibitors

The different forms of calcium phosphate are reported in the following table:

Compounds	Formula	Molar ratios	pK*	pK à 20°C
DCPD (dicalcium phosphate dihydrate)	CaHPO ₄ *2H ₂ O	1	pKDCPD=3649.6/T-18.181+0.04203T	6.59
DCPA (monetite)	CaHPO ₄ (Anhydrous DCPD)	1		
OCP (octacalcium phosphate)	Ca ₄ H(PO ₄) ₃ *2.5H ₂ O	1.33	pKOCP=50.606 à 20°C	
ACP (amorphous calcium phosphate)	Ca ₃ (PO ₄) ₂	1.5	No solubility product for an amorphous	
HAP (hydroxylapatite)	Ca ₅ (PO ₄) ₃ OH	1.67	pKHAP=8219.41/T+1.6657 + 0.098215T	58.5
TCP (tricalcium phosphate)	Ca ₃ (PO ₄) ₂	undefined	pKTCP=45723.26/T-287.4536+0.546763T	28.8

* reference is Y. Song, H.H. Hahn, and E. Hoffmann, “The effects of pH and Ca/P ratio on the precipitation of calcium phosphate”, *Second international conference on Recovery of Phosphate from sewage and animal wastes, Holland, 12th and 13th March 2001.*

The most important factors are the temperature of the reaction, the chemical speciation of the solution and the solubility product of the mineral. The solubility of calcite decreases with increasing temperature whereas the solubilities of calcium phosphate minerals increase with the temperature. However, for both HAP and OCP, the solubility trends reverse at higher temperatures in the region of 15-20°C .

Two HAP systems were evaluated – a system by Battistoni and the Crystalactor®.

For the system by Battistoni, the precipitation of phosphates in these tests was very low whereas the crystallization varied from 59 to 88%. Efficiency is strongly related to the operating pH, the lowest result being 58.2% at pH 7.94, but even in this case no significant increase of precipitated fines is observed. The different molar ratios exercise a strong control on HAP or MAP formation:

- If the ratio Ca/Mg increases, the HAP formation increases and MAP formation decreases.
- For a ratio Ca/Mg equal to 3.1, the HAP/MAP formation is 50-50.
- A ratio Ca/Mg equal to 1.8 gives a MAP formation ranging from 80 to 100%.
- If the ratio Ca/Mg is equal to 3.6, the MAP/HAP formation is 35/65.
- If Mg is superior at 53 mg/L, only MAP precipitates, the magnesium ions exert a strong inhibitory effect on HAP formation and the ratio Mg/PO₄ increases.

The low operating pH induced by the air stripping limits the loss of fines. The contact time and the pH are the main operating parameters to define the process efficiency.

For the Crystalactor, the report says:

DHV, a multi-national group of consulting engineers and general contractors with headquarters in the Netherlands, has developed and patented a fluid-bed type of crystallizer in which phosphate is removed and recovered from the wastewater while phosphate pellets with a typical diameter of 1 mm are produced. The major advantage of the crystallization technology, the so-called Crystalactor®, is that in the compact high purity phosphate pellets are produced which have proven to be reusable. Phosphate has been successfully recovered in the form of calcium phosphate, magnesium phosphate and magnesium ammonium phosphate.

The pellet reactor is partially filled with a suitable seed material like sand or minerals. The wastewater is pumped in an upward direction maintaining the pellet bed in a fluidized state. In order to crystallize the target component on the pellet bed, a driving force is created by a reagent dosage and pH-adjustment. By selecting the appropriate process conditions, co-crystallization of impurities is minimized and high-purity crystals are obtained. The pellets grow and move towards the reactor bottom. At regular intervals, a quantity of the largest fluidized pellets is discharged from the reactor and fresh seed material is added. After atmospheric drying, readily handled and virtually water-free pellets are obtained.

4. Giesen, Andreas, "Crystallization Process Enables Environmental Friendly Phosphate Removal at Low Costs", no date, 9 pages. Accessed at <http://www.nhm.ac.uk/research-curation/projects/phosphate-recovery/crystalct.htm> on August 16, 2007

The author is with DHV Water BV, and the article describes the Crystalactor technology and several of its current applications – including the municipal wastewater treatment plant Geestmerambacht.

In the technology section, it says that the Crystalactor enables phosphate removal and recovery by means of several process routes. The most important routes are:

- crystallisation as calcium phosphate (CP)
- crystallisation as magnesium phosphate (MP)
- crystallisation as magnesium ammonium phosphate (MAP)
- crystallisation as potassium magnesium phosphate (KMP)

5. The Crystalactor®, <http://www.procorpinc.com/The%20Crystalactor.htm>, <http://www.crystalactorusa.com/>, <http://www.crystalactorusa.com/resources/Alto%20-%20Crystalactor.pdf>, accessed August 16, 2007

Procorp, located in Wauwatosa, Wisconsin, is the sole US licensee of the Crystalactor technology. It has installed a Crystalactor system at the Alto Dairy Cooperative cheese plant in Wisconsin. The Crystalactor technology is said to be installed at over 50 locations worldwide.

The description of the technology on the web is as follows:

The Crystalactor® utilizes a fluidized-bed crystallizer for water softening, phosphorus removal and the recovery of other inorganic compounds found in process water. The heart of the treatment process is a "pellet reactor", partially filled with a suitable seed material such as sand. The wastewater is pumped in an upward direction maintaining the pellet bed in a fluidized state. In order to crystallize the target component on the pellet bed, a driving force is created by a pH-adjustment and the addition of a reagent such as soda ash, lime or caustic soda. By selecting the appropriate process conditions, co-crystallization

of impurities is minimized and high-purity crystals are obtained. The pellets grow and move towards the reactor bottom where they are discharged from the reactor and fresh seed is added with no disruption to the cycle. After atmospheric drying, readily handled pellets are obtained.

The following is from the description of the installation at the Alto Dairy Cooperative, as found on the Internet:

During production of dairy and cheese products, water containing organic and phosphorus compounds is produced and must be treated. Alto has long engaged in safe environmental practices including production and reuse of energy from their on-site anaerobic digester. Using a biological activated sludge (AS) system, the organics in the Alto wastewater are removed, leaving phosphorus that must be treated prior to groundwater discharge.

Located after the AS treatment system, the Alto Crystalactor handles about 125 m³/h of wastewater with a maximum phosphorus concentration of 25 mg/L. The heart of the Crystalactor is the "pellet" reactor, 10 feet in diameter, which is partially filled with a seed material such as sand or minerals. Wastewater is pumped to maintain the pellet bed in a fluidized condition. In order to crystallize the target component on the pellet bed, a driving force is created by a reagent dosage and pH adjustment. By selecting the appropriate conditions, co-crystallization of impurities is minimized and high-purity crystals are obtained.

At Alto, quartz sand was used in the pellet reactor with lime as the reagent. This combination allowed calcium phosphate to crystallize on the sand particles forming "pellets", which eventually sink to the reactor bottom and are easily discharged and replaced with fresh seed with no disruption to the process. After atmospheric drying, readily handled pellets are obtained and the need for sludge dewatering or hauling of sludge is eliminated. Due to their excellent composition, the pellets can often be recycled or reused. In the event that the pellets must be hauled off-site, the resultant solid equates to approximately 1 ft³ per 100,000 gallons of wastewater treated.

6. Szögi, A.A., et. al., "Innovative Technology for Recycling Manure Phosphorus with Rapid Amorphous Phosphate Precipitation", September 12, 2006 12th RAMIRAN International Conference, USDA-ARS Coastal Plains Research Center Florence, 24 slides

A three stage process has been developed by the USDA ARS to remove phosphorus from manure, consisting of (1) solids removal, (2) biological N removal and (3) phosphorus precipitation. The phosphorus removal process produces calcium phosphate and a patent has been applied for. The presentation describes the system as used for a swine production facility.

The solids separation system appears to be a stationary wedgewire separator, while the nitrogen system is a biological nitrification-denitrification system. The phosphorus removal system is an ARS invention that adds lime or calcium or magnesium hydroxide to produce an adjustment of the pH to 10.5, followed by the settlement of phosphate sludge. A 94% removal rate for phosphorus was achieved. The calcium phosphate was dried and then bagged for recovery. The composition of the recovered material averaged 24.4% P₂O₅, 27.3% calcium, 0.9% potassium and 1.8% magnesium.

The study concluded:

- The technology presented was developed to solve problems of excess nutrient land application due to confined animal production by removing P from animal wastewater.
- Phosphorus is selectively precipitated using an alkaline earth metal after carbon and ammonia buffers are reduced with a nitrification pretreatment.
- The final product is amorphous calcium phosphate that can be reused as a slow release P fertilizer.

7. Vanotti, Matias, et. al., "Solids Separation, Nitrification-Denitrification, Soluble Phosphorus Removal, Solids Processing System", North Carolina Animal Waste Management Workshop, no date (2003 or later), 6 pages

The opening paragraph of this paper reads in part:

Systems of treatment technologies are needed that capture nutrients, reduce emissions of ammonia and nuisance odors, and kill harmful pathogens. A system of swine wastewater treatment technologies was developed to accomplish many of the tasks listed above. The system greatly increases the efficiency of

liquid/solid separation by injection of polymer to increase solids flocculation. Nitrogen management to reduce ammonia emissions is accomplished by passing the liquid through a module where immobilized bacteria transform nitrogen. Subsequent alkaline treatment of the wastewater in a phosphorus module precipitates calcium phosphate and kills pathogens. Treated wastewater is recycled to clean hog houses and for crop irrigation. The system has been pilot tested and is going through full-scale demonstration and verification as part of the Smithfield Foods|Premium Standard Farms|Frontline Farmers Agreement with the North Carolina Attorney General to identify technologies that can replace current lagoons with Environmentally Superior Technology

Turning to the section on phosphorus removal, it says, in part:

After biological N treatment, the liquid flows by gravity to the phosphorus separation module developed by USDAARS, where P is recovered as calcium phosphate and pathogens are destroyed by alkaline pH. Liquid from which ammonia nitrogen and carbonate buffers have already been removed is mixed with hydrated lime in a reaction chamber. A pH controller is linked to the lime injector and keeps the process pH at 10.5-11.0. The liquid and precipitate are separated in a settling tank. The precipitated calcium phosphate sludge is further dewatered in filter bags with a capacity of about 50 lb each. Polymer is added to the precipitate to enhance P separation. Automation to the system is provided by sensors integrated to a programmable logic controller (PLC) for 24 hr/day operation; treatment parameters such as process pH are set by the operator using another tactile screen in the plant control panel. Removal efficiencies of the soluble phosphate averaged 91% for wastewater containing 90 to 185 ppm PO₄-P.

Note: Other presentations on this project are:

Szögi, A.A., Vanotti, M.B. 2005. "Removal of phosphorus from animal manures. Experiences of the USDA - Agricultural Research Service", In: *Proceedings of the Workshop on Technologies to Remove Nutrients from Animal Waste, August 25, 2005, Florianopolis - Santa Catarina, Brazil*. p. 26-33.

and

Szögi, A.A., Vanotti, M.B., Bauer, P.J., Scheckel, K.G., Hudnall, W.H. 2006. "Innovative technology for recycling of manure phosphorus with rapid amorphous phosphate precipitation", In: Petersen, S.O., editor. *Proceedings of 12th Recycling of Agricultural Municipal and Industrial Residues (RAMIRAN), September 9-12, 2006, Aarhus, Denmark*. p. 103-105.

8. Wastewater treatment system, United States Patent 6,893,567, <http://www.uspto.gov/patft/index.html>, accessed August 16, 2007

This patent was granted in 2005 and the abstract reads:

Wastewater treatment systems and processes for: removal of solids, pathogens, nitrogen, and phosphorus from municipal and agricultural wastewater include nitrification of wastewater and increasing the pH of the nitrified wastewater by adding a metallic-containing salt and hydroxide to precipitate phosphorus to form a useable effluent having a specified nitrogen:phosphorus ratio that is useful as a fertilizer or spray for remediation of contaminated soils. The presence of infectious microorganism such as enteropathogenic bacteria and picornaviruses will be reduced in the useable effluent. The precipitated phosphorus is recovered and used to form useable phosphorus products.

9. Vanotti, M.B. , et. al., "Blue Lagoons on Pig Farms? A new waste-handling system can make it a reality", *Agricultural Research*, USDA ARS, March 2005, 2 pages

A year-long evaluation was conducted of a swine manure process system built at the Goshen Ridge Farm, a 4,360-head swine-finishing facility in Mount Olive, North Carolina. Excerpts from the article point out:

The system performs three critical processes in animal-waste management: It separates solids and liquids from swine wastewater while recovering organic matter; it removes ammonia from wastewater, using acclimated nitrifying bacteria; and it transforms phosphorus removed from wastewater into a solid, marketable fertilizer while converting leftover effluent into an environmentally friendly liquid crop fertilizer.

"Results showed that this system can have a great impact in animal-waste treatment," says Szogi.

It removed more than 97 percent of total suspended solids from wastewater during the tests. It stripped the water of 95 percent of its total phosphorus, 99 percent of its ammonia, 98 percent of its copper, 99 percent of its zinc, more than 99 percent of its biochemical oxygen demand, and more than 97 percent of its odor-causing components.

The reduction in fecal microorganisms achieved in this system resulted in disinfected effluent. Says microbiologist Patricia Millner, a project cooperater from ARS's Environmental Microbial Safety Laboratory in Beltsville, Maryland, "This prevents dispersion of pathogens into soil, water, or air when the treated effluent is sprayed onto fields or recycled into storage ponds."

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August 16, 2007