P-RECOVERY ON THE MOVE

Instead of removing phosphates from waste streams, technology is now emerging to recover this vital resource

Unlike fossil fuels or precious metals, phosphorus has no alternatives — we (and all other life forms on the planet) need phosphorus; it's in our DNA, our bones and our energy-producing chemicals (ATP). We get it from our food — meat, grains and vegetables — so it's not surprising that phosphorus is a key ingredient in fertilizer, as well as a component of sewage, manure and slaughterhouse waste (bone meal).

Sewage, for example, contains about 1–2% phosphorus. Although some of this phosphorus can be "recycled" by land application of sewage sludge on farmland, plant uptake is limited because the phosphorus is bound as compounds that can't be metabolized. As a result, the unused phosphates find their way into waterways (runoff), causing eutrophication of rivers and lakes.

In addition, the practice of spreading manure and sewage sludge is coming under scrutiny for health and safety reasons due to the presence of other pollutants, such as organic compounds and heavy metals. In Germany, for example, about half of the sewage sludge generated is still used for land application, but the practice is now forbidden in two states (Bavaria and Baden-Württemberg); and environmental legislation tends to be one directional — more stringent, never less.

More critical than environmental concerns, perhaps, is the realization that phosphorus supplies are not only limited (some experts predict "peak phosphorus" occurring in 2030, and a depletion of phosphorus-rock mines occurring in the next 50–100 years), but are also in the hands of a few. Phosphate rock reserves (as P_2O_5) are estimated to be 71 billion tons, with 70% coming from Morocco and the Western Sahara region, according to U.S. Geological Survey (USGS; Reston, Va.; www.usgs.gov). Global mining production in 2011 was 191 million tons, according to the USGS.

The E.U. is particularly hard pressed, with only one phosphate mine (in Finland). As a result, efforts have been underway in recent years to develop technologies to recycle phosphorus, especially from sewage and other waste streams. Last May, these efforts also received a political impetus when the European Parliament adopted "A Resource-efficient Europe," a resolution that includes, among other things, a call to the Commission and Member States for "achieving virtually 100% reuse [of phosphorus] by 2020, and optimizing [its] use and recycling." E.U. funding for research into pilot projects was also emphasized.

Industry leads

Meanwhile, companies in the chemical process industries (CPI) have already developed technologies for removing phosphates from wastewater, not only for environmental reasons, but also to prevent fouling during the operation of wastewater treatment plants (WWTPs). These technologies are now being adapted — and new technologies are emerging — to recover, rather than simply remove, the phosphates in a form that can make money, namely as fertilizers.

Royal HaskoningDHV

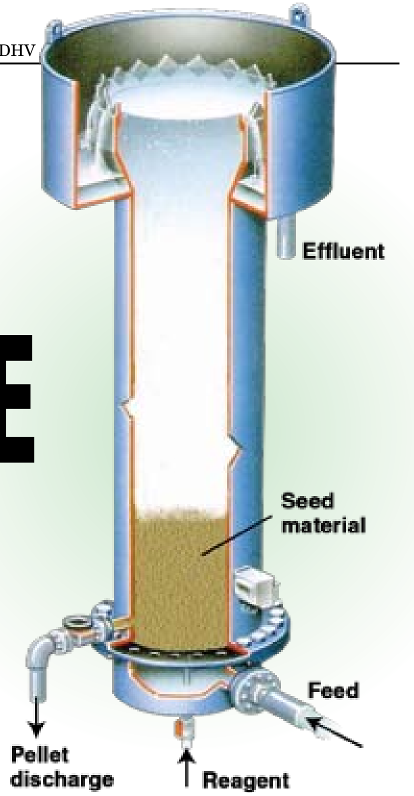

FIGURE 1. The Crystalactor technology recovers phosphorus as struvite crystals that form on seed particles

Already two years ago in a presentation at the International Conference on Nutrient Recovery and Management (Miami, Fla.; January 9–12, 2011), Christian Sartorious, project leader at the Fraunhofer Institute for Systems and Innovation Research (Karlsruhe, Germany; www.isi.fraunhofer.de) identified 22 phosphorus recovery (P-recovery) technologies at all stages of commercial development — from laboratory and pilot to full-scale implementation. These P-recovery methods can be broadly grouped into two categories: wet methods, in which the phosphorus is recovered at the WWTP; or thermo-chemical routes, which recover phosphorus from the ash left behind after sludge incineration. Some of these technologies are presented below.

Wet methods

Conventional phosphorus-treatment technology relies on chemicals (typically ferric chloride or alum) to convert dissolved phosphorus into an insoluble precipitate that can be settled and removed from the liquid stream as a sludge, explains Steve Wirtel, senior vice president for Nutrient Recovery at Ostara Nutrient Recovery Technologies Inc. (Ostara; Vancouver, B.C., Canada; www.ostara.com). Chemical addition is a simple process that requires minimal equipment, so it has a low capital cost. But, the process has a high operating cost because substantial amounts of chemicals are required. Chemical addition also falls short because the process binds the phosphorus into a chemical sludge where it cannot be recovered for its nutrient value as a fertilizer, says Wirtel. "And it is not environmentally friendly."

Instead of creating a chemical sludge, Ostara has developed its Pearl process, which converts dissolved phosphorus into pure (99.5%) struvite ($MgNH_4PO_4 \cdot 6H_2O$) crystals. "The process has virtually no carbon footprint and sustainably recovers a precious resource," says Wirtel. The struvite crystals are created and bagged onsite and marketed as a slow-release, enhanced-efficiency fertilizer to blenders that sell to nurseries, golf courses, and specialty agricultural growers under the brand name Crystal Green.

Ostara's proprietary Pearl process is based on the initiation and precise control of a chemical-precipitation reaction in a fluidized-bed reactor. The typical feedstreams in the process are sludge liquids produced at municipal WWTPs and "high strength" industrial used-water streams, says Wirtel. Pearl's chemical process removes phosphorus and other nutrients from the feedstreams, with phosphorus removal performance typically averaging approximately 90%, he says. The capital cost of a nutrient recovery system is recovered through the avoided cost of adding chemicals needed to precipitate phosphorus. The typical payback period range is 2–7 yr, says Wirtel.

The Pearl process was first scaled up in 2006, with the commissioning of a 500,000-L/d demonstration plant at the Edmonton Gold Bar sewage-treatment works (*CE*, November 2006, p. 13). The first commercial nutrient-recovery facility was launched with Clean Water Services (Hillsboro, Ore.) in 2009 at its Durham Advanced Wastewater Treatment Plant. Since then, Ostara has built facilities in Suffolk, Va.; York, Pa.; and a second facility with Clean Water Services at its Rock Creek Wastewater Treatment Facility in Hillsboro, Ore. In 2013, Ostara will launch three additional nutrient-recovery facilities: at Thames Water in the U.K., in Saskatoon — the first commercial facility in Canada — and in Madison, Wisc.

Another "wet" process for phosphorus recovery is the Crystalactor technology offered by Royal HaskoningDHV (Amersfoort, The Netherlands; www.royalhaskoningdhv.com). The process is based on the selective crystallization of targeted compounds, such calcium from water for water softening. Other pollutants can be crystallized as well, such as heavy metals or fluorides from the semiconductor industry or specific ions in the concentrate from desalination plants. The company has also adapted the Crystalactor technology for P-recovery from wastewater.

The heart of the patented Crystalactor process is a fluidized-bed pellet reactor (Figure 1). Wastewater is fed to the bottom of the reactor and flows upwards, fluidizing the bed of seed particles, such as sand or crushed and classified crystals. By adjusting the pH and dosing of reagents, phosphates from the waste stream crystallize as struvite or calcium phosphate onto the seed particles. As the pellets grow, they travel downwards to be discharged at the bottom of the reactor. The four steps commonly required in conventional phosphorus treatment processes — coagulation, flocculation, separation and dewatering — are combined in one by the Crystalactor, says the company.

One of the applications of the Crystalactor for P-removal is running at a dairy in Waupun, Wisc., where U.S.-licensee Procorp Enterprises (Milwaukee, Wisc.; www.procorp.com) installed a Crystalactor unit in 2005. The unit, with a 3-m dia. reactor, handles 125 m^3/h of wastewater with a phosphorus concentration of 25 mg/L, and uses quartz sand as seed. By adding lime, calcium phosphate is crystallized, and the pellets are dried for recycling.

Since the early 1990s, eight Crystalactor units have been built specifically for P-recovery, says the company.

Last August, pilot testing began on an electrochemical P-recovery process being developed at the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB; Stuttgart, Germany; www.igb.fraunhofer.de). Unlike conventional precipitation methods, which require the addition of magnesium salts (for struvite formation) along with NaOH for adjusting the pH, the patented process uses a sacrificial magnesium electrode that generates the required Mg^{+2} ions, as well as raises the pH to 9 by the water-splitting reaction that occurs at the other electrode ($2H_2O \rightarrow H_2 + 2OH^{-1}$). The Mg^{+2} ions react with phosphates in the wastewater and precipitate out of solution as struvite crystals that can be dried and used directly as fertilizer. Plant yield and plant nutrient-uptake with the struvite were found to be up to four-times higher than with commercially available mineral fertilizers, says IGB.

The 1-m^3 pilot plant is mobile, enabling tests to be performed at a variety of wastewater treatment plants. The first tests have commenced at an agricultural biogas plant that processes corn, manure and some waste from the food-processsing industry. IGB's commercial partners are Geltz Umwelt-Technologie GmbH (Niefern-Öschelbronn; www.geltz.de), E.R.S. GmbH & Co. KG (Osterburken; ers-gmbh.de) and Bamo IER (Mannhein; all Germany; www.bamo.de). All commercialization of the technology will be promoted within this consortium.

Meanwhile, an initiative to recover phosphorus from flyash was initiated in May 2011 between the phosphate-technology company, EcoPhos S.A. (Louvain-la-Neuve, Belgium; www.ecophos.com), the sludge-processing company Silbverwerking Noord-Brant N.V. (SNB; Moerdijk; www.snb.nl) and the utility company HVC (www.hvcgroep.nl). The two Dutch companies process more than half of the sewage sludge in The Netherlands at incineration plants in Dordrecht and Moerdijk, which generate flyash residue with a phosphorus content comparable to low-quality ore.

The companies have developed a hydrometallurgical method for recovering the phosphorus in the flyash, which is expected to yield up to 250 metric tons (m.t.) of phosphate from every 1,000 m.t. of flyash.

A commercial-scale plant is planned to go onstream in 2014, which will co-process phosphate rock supplemented with about 20% flyash. The product will then be used for the production of fertilizer. In the past, flyash has been used as filler in asphalt for roads and surfaces.

Thermo-chemical methods

Although wet P-recovery methods have the advantages of maturity (due to the need to remove phosphates to avoid scaling issues) and feasibility at the relatively small scales typical of municipal WWTPs, dairies and so on, they all have the disadvantage of recovering only the dissolved phosphates, says Ludwig Hermann, senior consultant, Energy at Outotec GmbH (Oberursel, Germany; www.outotec.com). Dissolved phosphorus is typically about 25% of the total phosphorus content in sewage, and sometimes much less, he says. The rest remains in the sludge, which must be treated by other methods. With the increasing use of sludge incineration, especially in Europe, the unrecovered phosphorus has typically found its final resting place in the discharged flyash, which ends up as supplements to road pavement and concrete. In developed countries, some few hundred incinerators are producing around 3 million m.t./yr of ash every year with phosphorus concentrations up to 25 wt.% (dry). Without treatment, such ash is unsuitable as fertilizer because of high heavy-metal content and limited plant availability, says Hermann. Now, methods to recover the phosphorus from the ash — so-called urban mining — are now slated for commercialization.

One such process is the Ash Dec technology, which Outotec acquired in 2011 from Ash Dec Umwelt AG (Vienna, Austria). The process recovers almost 100% of the phosphorus, as well as other metals present in the ash, while producing a marketable fertilizer.

Source: Outotec

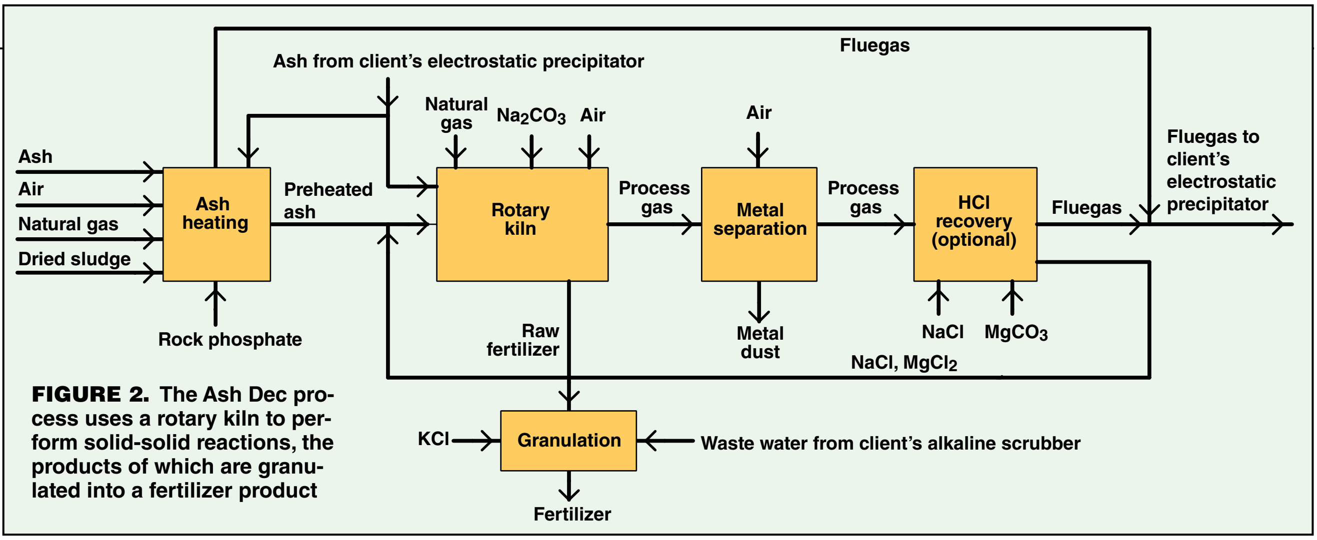

FIGURE 2. The Ash Dec process uses a rotary kiln to perform solid-solid reactions, the products of which are granulated into a fertilizer product

In Ash Dec (Figure 2), magnesium salts and ash are fed to a rotary kiln reactor operating at 1,000°C. Toxic metals are vaporized, and exit the kiln with the process gas to be captured as dust by the air-pollution control system. At the same time, the solid $MgCl_2$ reacts (residence time about 20 min) with the ash-borne phosphorus to produce calcined phosphate. This is then sent to a granulation unit, where it is combined with potassium salts to form granular fertilizer products. These fertilizers contain 99% less cadmium and 90% less uranium than most phosphate-rock-based fertilizers, and are equally effective in terms of crop uptake and yield, says Outotec.

The Ash Dec process has been demonstrated in a 7-m.t./d pilot unit operating between June 2008 and May 2010. The pilot plant, located in Leoben, Austria, treated the ash from Vienna and successfully produced nearly 1,000 tons of complex fertilizer. The process is commercially ready, says Hermann, and is economical for capacities of 30,000–32,000 m.t./yr, or smaller if integrated into a new sludge incineration facility.

Another thermal process is Mephrec (metallurgical phosphorus recycling), which is being developed by ingitec GmbH (Leipzig, Germany; www.ingitec.de). Mephrec takes place in an oxygen-blown, fixed-bed shaft ingitec

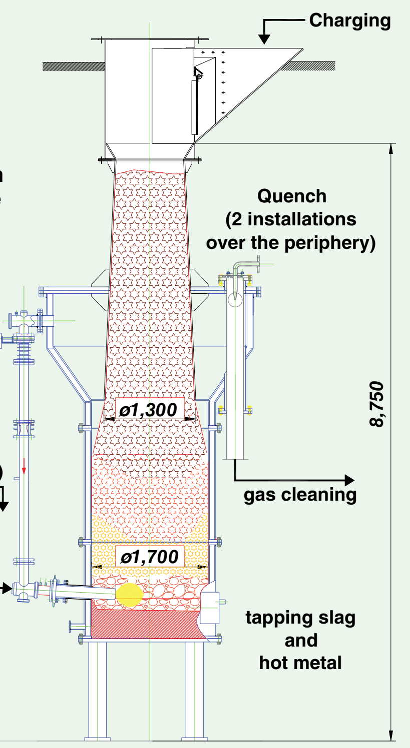

FIGURE 3. In the Mephrec process, phosphorus from ash reacts with coke in an O_2-blown furnace

furnace, with metallurgical coke used as the energy supply (Figure 3), explains consulting engineer Klaus Scheidig. Feed material is first agglomerated to ensure sufficient gas flow through the reactor. The briquettes are then fed at the top of the reactor and are heated as they pass down the reactor, countercurrent to the flow of hot gases. As they move downward, the briquettes are melted and gasified. Molten slag is tapped at the bottom at a temperature of about 1,450°C, then granulated with a water quench, resulting in a calcium-silico-phosphate with a high phosphorus-availability for plants.

Because Mephrec operates under reducing conditions, heavy-metal oxides are reduced to their metallic state, and either alloyed with the liquid-metal byproduct, or evaporated for subsequent recovery.

Another advantage of operating with O_2 is that the energy content of the sewage sludge is fully transferred to the offgas, and can be recovered for power generation. The accumulated revenues from power generation and the cost savings from sludge-disposal avoidance are sufficiently high to pay for the total recovery process, says Scheidig. As a result, the selling price of the product fertilizer is not a factor in the overall economic feasibility of the P-recovery process, he adds. A demonstration of the process is planned at a wastewater treatment facility in Nuremberg, Germany. The Mephrec plant will have a capacity of 12,000 m.t./yr when it starts up in 2013–2014. A future commercial unit will have a 70,000-m.t./yr capacity, says Scheidig.

Outotec and ingitec are also participants in the P-REX project, a three-year, €4.4-million research project under the European Commission's Seventh Framework Program (FP7). The project, which started in September 2012 and includes 15 partners from five countries, is said to be the first "holistic full-scale evaluation of the P-recovery techniques using municipal sludge or ashes in comparison with phosphorus recycling by land application of sewage sludge." It's looking at the complete life cycle, says Outotec's Hermann.

Another major E.U. project under the FP7 program is RecoPhos (www.recophos.org). Started in January 2012, the 36-month, €4.5-million project consists of a consortium of ten partners from six countries. The goal of the project is to develop a sustainable and highly efficient process to recover phosphorus from sewage-sludge ash.

RecoPhos is a thermo-chemical process involving the fractioned extraction of phosphorus and heavy metals. The chemical principle of the core reactor is the Wöhler process, whereby phosphates react with carbon and SiO_2 in a furnace, and is reduced to phosphorus. RecoPhos uses the InduCarb retort, where a coke bed is heated inductively, and the reduction of phosphates takes place in a thin melt film on the surface of the coke particles. The reduced phosphorus can be evaporated and recovered as either P_2O_5 or phosphoric acid.

The project aims to study the technology at the laboratory scale, along with modeling and simulation studies, which will provide the basis for the implementation of a fully operational bench-scale reactor and the design for a pilot-scale plant. ■

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