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Phosphorus Recovery from Animal Manures using Optimized Struvite Precipitation

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Current Incentives for Phosphorus Recovery

The over-application of phosphorus, as manure by animal feeding operations, is a threat to surface water quality. Concentration of animal feeding operations and over application of manures to cropland has lead to a build-up of phosphorus on many farms (Greaves et al., 1999). Relative to crop needs, manure slurries contain higher levels of phosphorus than nitrogen. When manure is applied to meet crop nitrogen needs, phosphorus is over applied. Recent laboratory studies show that phosphorus content in swine manure can be reduced by recovering a portion of the phosphorous as a crystalline precipitate containing struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4{\cdot}6H_2O$) (Beal et al., 1999; Burns et al., 2001; Kalyuzhnyi et al., 2001, Nelson et al., 2000; Wrigley et al., 1992). Precipitation of phosphorus prior to land application of manure offers the potential to recover excess phosphorus from manures and move it to cropping areas that require phosphorus fertilizer inputs. The cost effective relocation of excess phosphorus would allow existing animal feeding operations to successfully implement phosphorus-based nutrient management plans on their current land base. Proposed EPA regulations regarding concentrated animal feeding operations must be finalized by December 2002. These regulations will likely limit land application of manure to phosphorous-based rates. Comparisons of nitrogen and phosphorus-based nutrient management plans indicate that some poultry-broiler producers, swine producers, and diary producers may require as much as ten, eight, and four times more land, respectively, if required to shift to a phosphorus-based plan (Burns, et. al., 1998). Producers who do not have an adequate land base will be faced with transporting manure nutrients off-site. Recovery of phosphorus as precipitated struvite has the potential to substantially reduce transportation costs by isolating the excess phosphorous and converting it into a crystalline form for low-cost movement.

By amending manures with a magnesium source to precipitate phosphorus, manure could be applied at an application rate that met both nitrogen and phosphorous crop needs without the over application of phosphorus. This would reduce manure handling costs. While investigators have examined phosphorus precipitation in swine wastes on a laboratory scale, little work has been done to develop this process for field scale application (Nelson et al., 2000). Burns et al. (2001) has shown a 90% reduction in soluble phosphorus via struvite precipitation in a 140,000 L swine slurry holding pond under field conditions. The next step in the development of this technology is the farm-scale recovery of a phosphorus based precipitate for agronomic use and an economic assessment of the cost effectiveness of the method as a manure management option.

In Europe and Japan, large municipal sewage-handling facilities have already embraced phosphorus recovery technology (Batistoni et al., 2001; Gaterell et al., 2000; Liberti et al., 2001; Piekema and Giesen, 2001; Ueno and Fujii, 2001). Livestock producers have yet to benefit from these practices because farm-scale applications have not been developed.

Struvite Formation in Animal Waste Management Systems

Precipitation of struvite in waste streams is not a new idea. In as early as 1939, deposition of magnesium ammonium phosphate hexahydrate (struvite) inside pipes and pumps transporting wastes was recognized (Rawn et al., 1939). The precipitate forms a hard scale and was considered a nuisance due to the capacity reduction in the associated hydraulic network (Buchanan et al., 1994). Until management strategies were developed, the problem of struvite precipitation caused a serious setback to the recycle flush approach in confinement waste management (Safley et al., 1982). Therefore, a large portion of struvite research has been directed towards removal and prevention of struvite formation rather than towards its precipitation from solution for recovery and reuse.

Understanding struvite prevention and removal has lead to understanding its formation. Struvite formation is enhanced when the pH is between 7 and 11. In alkaline solutions, the solubility of struvite decreases, thus enhancing precipitation. To form struvite, magnesium, ammonium and phosphate must be available for reaction. Ammonium is not available when the solution pH exceeds 11. Magnesium is generally the limiting nutrient and must be supplemented for the solubility reaction (Buchanan et al., 1994; Westerman et al., 1985). Waste strength affects struvite solubility (Schulze-Rettmer, 1991). Specifically, struvite solubility is increased (and therefore less likely to form) in the presence of complexing agents, like organics, in wastewater. Schuiling and Andrade (1999) reported that total suspended solids interfere with the precipitation process at total suspended solids concentrations above 1000 mg L^{-1}. Animal waste slurries often contain high organic and total suspended solid concentrations.

Chemical Amendment for Struvite Precipitation

Because the limiting ion for struvite formation in animal manure slurries is usually magnesium, manure slurries are typically amended with magnesium to force the precipitation of struvite. Possible magnesium amendments include magnesium hydroxide, magnesium oxide, and magnesium chloride. Miles and Ellis (2001) initially used a 50% magnesium hydroxide slurry and phosphate fertilizer to reduce ammonia through struvite precipitation. However, they incurred insolubility problems with the magnesium hydroxide and changed to the use of magnesium oxide. Beal et al. (1999) used magnesium oxide (MgO) in bench scale reactions during initial struvite experiments. Phosphorus reductions of greater than 90% (1256 to 105 mg P L^{-1} and 1591 to 81 mg P L^{-1}) were achieved following the addition of MgO. Magnesium oxide had the additional benefit of increasing pH to aid the struvite reaction. However, because of the insolubility of the material, reaction time was long (20 min) and residual MgO existed after the reaction. Further bench scale experiments showed that magnesium chloride ($MgCl_2 \cdot 6H_2O$) is a good precipitant for struvite formation (Burns et al. 2001). Because of its solubility, magnesium chloride was easier to handle and it reduced the reaction time that was required to bring MgO into solution. However, because magnesium chloride is slightly acidic, it does not increase pH as MgO does. In laboratory experiments where magnesium chloride was added and the pH was not adjusted, there was a 76% reduction in soluble phosphorus (572 to 135 mg P L^{-1}) (Figure 1). When pH was adjusted, using sodium hydroxide, 91% of the soluble phosphorus was removed (572 to 50 mg P L^{-1}) (Figure 1). Magnesium chloride was added at a rate calculated to provide a 1.6:1 magnesium:total phosphorus molar ratio.

In a field experiment carried out in a swine manure holding pond (Figure 1) (Burns et al., 2001), a 90% (150 to 14.8 mg P L^{-1}) reduction in soluble phosphorus concentration was achieved in approximately 140,000 L of swine slurry treated before land application with 2000 L of magnesium chloride at ambient slurry temperatures ranging from 5 to 10ºC. In this experiment, pH was not adjusted by chemical amendment. It was adjusted using CO_2 stripping by mechanical stirring during agitation of the pond prior to land application. We found that agitation, as commonly practiced preceding land application of liquid manure, can effectively raise the pH in a swine manure holding pond by one pH point over a two hour agitation period (Burns, et al. 2001).

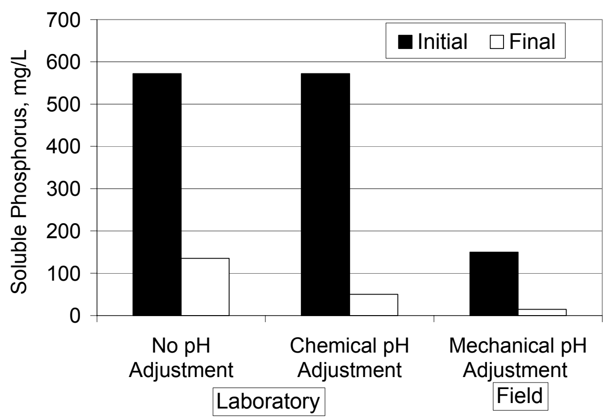

Figure 1. Soluble phosphorus reduction from swine manure slurry during laboratory and field tests.

Recovery Potential of Phosphorus as Struvite

Phosphorus precipitate recovered from swine manure (Figure 2) can be characterized by its physical and chemical properties. X-ray diffraction of the material can confirm the presence of struvite (magnesium ammonium phosphate hexahydrate). Chemical analysis of total nitrogen and total phosphorus can indicate the recovered materials value as a fertilizer. Figure 3 shows the results of an x-ray diffraction analysis performed on struvite recovered from swine manure. The presence of struvite is indicated by the location of the intensity peaks. Vertical lines on the graph represent where the struvite peaks should occur. Some of the more definite non-struvite peaks indicate presence of the mineral brushite ($CaPO_3(OH) \cdot 2H_2O$). This shows that phosphorus precipitates other than struvite are forming. The precipitate contained 34,250 mg kg^{-1} magnesium, 18,550 mg kg^{-1} of ammonia – nitrogen, 431,480 mg kg^{-1} of phosphate. The mass ratio of $Mg:NH_3:PO_4^{3-}$ of the precipitate was 1:0.54:12.6 and the molar ratio of the precipitate was 1:0.74:3.2. The phosphorus precipitate we have produced is not pure struvite, as the mass ratio of pure struvite is 1:0.74:3.9 and the molar ratio is 1:1:1, excluding the hexahydrate. The formed precipitate is enhanced with phosphorus from the formation of brushite and other phosphate containing compounds that may have been formed but not yet identified. Since our overall goal is to recover phosphorus, rather than produce pure struvite, this is a favorable result.

Figure 2. Precipitate recovered during lab tests.

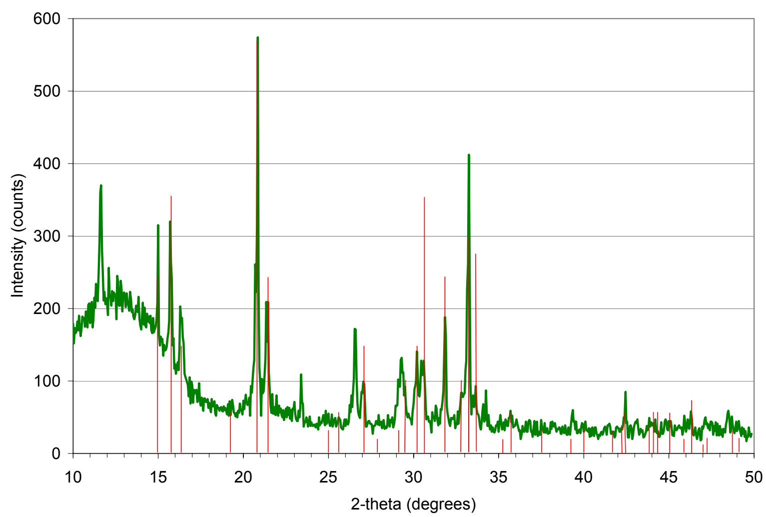

Figure 3. Results of x-ray diffraction analysis on struvite recovered from swine manure. Vertical lines indicate location of peaks identifying struvite.

In bench scale experiments, struvite is recovered by gravity settling, decanting, and washing the resulting sludge-like material. To obtain information about the potential to mechanically recover the struvite, a particle size distribution of the recovered precipitate using sieve analysis was performed (Figure 4). The particle size distribution of the material indicated that is was similar to course sand. As such we believe the potential for mechanical recovery of the precipitate is good.

To enhance recovery of the precipitated material, particle size can be increased. Particle formation is referred to as nucleation or induction. Homogenous nucleation occurs when the phosphorus precipitate is the nuclei. If other suitable nuclei are present, for example sand grains, the nucleation process is heterogeneous (Parsons, 2001). Amending the precipitation process with nuclei is referred to as seeding the reaction. While large municipal facilities in Europe and Japan are seeding to increase particle size and enhance recovery (Ueno and Fuji, 2001 and Battistoni et al., 2001), experiments to use this technology on animal manures have not yet been performed.

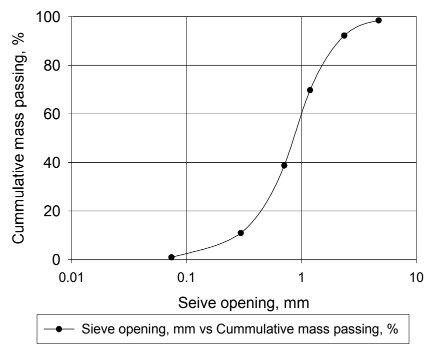

Figure 4. Sieve analysis of struvite recovered from swine manure slurry.

Conclusions

The recovery of phosphorus from animal waste as a struvite containing precipitate has been successfully demonstrated. The next step in the development of this technology is the development of a field-scale recovery unit at a commercial animal production unit. The operation of a field-scale recovery unit would supply the necessary data to complete a cost/benefit analysis to investigate the economics of the technology.

A cost-effective magnesium source and a fast, low-cost method of pH adjustment are needed to successfully implement this technology at the farm-scale. Drivers that could potentially provide positive economics for the recovery of phosphorus from animal waste in the United States include; 1) a dramatic increase in the cost of inorganic phosphorus, and 2) the implementation of enforceable regulations that require the land-application of animal manures on a phosphorus basis nationally.

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