

Sludge Reduction Benefits Observed When using Lanthanide Salt Technology in Wastewater Treatment

Introduction

In a wastewater treatment facility, the separation of solids from water is a very important task. Typically coagulants are added in an effort to aid the process. Recently, Lanthanide Salt (LS) technology has emerged as a new coagulant and has proven to be an effective alternative to traditional iron or aluminum based coagulants for phosphorus removal. Part of its effectiveness is the ability to remove phosphorus to extremely low levels. Although it was specifically designed for phosphorus removal in wastewater treatment facilities other benefits have been observed which include a reduction in sludge volume, improved settling, more efficient dewatering of solids, improved filter press performance and overall biosolids cost reduction. This paper is intended to explain the chemistry, application and toxicity of LE as it relates to solids in wastewater treatment.

Lanthanide Salt Chemistry and Solid Generation in Wastewater

The typical coagulants used in wastewater treatment are iron (Fe) and aluminum (Al) based. Fe based coagulants include ferric chloride, ferrous sulfate, and ferrous chloride among others. Al based coagulants include aluminum sulfate (alum), sodium aluminate, and polyaluminum chloride (PAC). LE technology is viable alternative to these coagulants but works differently. The principle difference between Fe, Al and LS based products is the mechanism by which they remove phosphate, as shown in Figure 1. There has been some debate about the mechanism of Fe and Al based products. Originally it was thought that Fe and Al formed FePO_4 or AlPO_4 , but recent studies have shown that the mechanism is more complicated. Smith has reported that the mechanism actually consists of a two-step process. A metal oxide such as Al_2O_3 or Fe_2O_3 initially forms which is followed by adsorption of phosphate onto the metal oxide surface.¹ This mechanism is consistent with the observed need for increasing amounts of Fe or Al at low phosphate concentrations, i.e. the adsorption process is less efficient when there is little phosphate present.



Figure 1. Depiction of phosphate removal reaction mechanism of RE vs. Fe

In contrast, the mechanism for lanthanide salt removal of phosphate is a straightforward metal phosphate precipitation resulting in the formation of the mineral rhabdophane, which is a stable form of LS found in nature. The precipitation reaction can be described by the equation



While RE can react in a similar mechanism to that of Fe and Al via the formation of a $\text{RE}(\text{OH})_3$ which can adsorb phosphate, the precipitation reaction with phosphate to form rhabdophane is greatly favored.

Another difference between Fe, Al, and LS based coagulants is the molar ratio of the coagulant metal to P that is needed to remove P to the desired level. The phosphate removal performance of various Fe, Al, and RE based coagulants vs the molar ratio of coagulant to P is shown in Figures 2 and 3. Regardless of starting P concentration, addition of the RE as CeCl_3 resulted in the lowest P concentration being achieved when the RE:P ratio was 1:1. By comparison, Fe and Al based coagulants need to be dosed at higher mole ratios (at least 2.5:1 (Fe or Al):P) in order to achieve similar P concentrations.

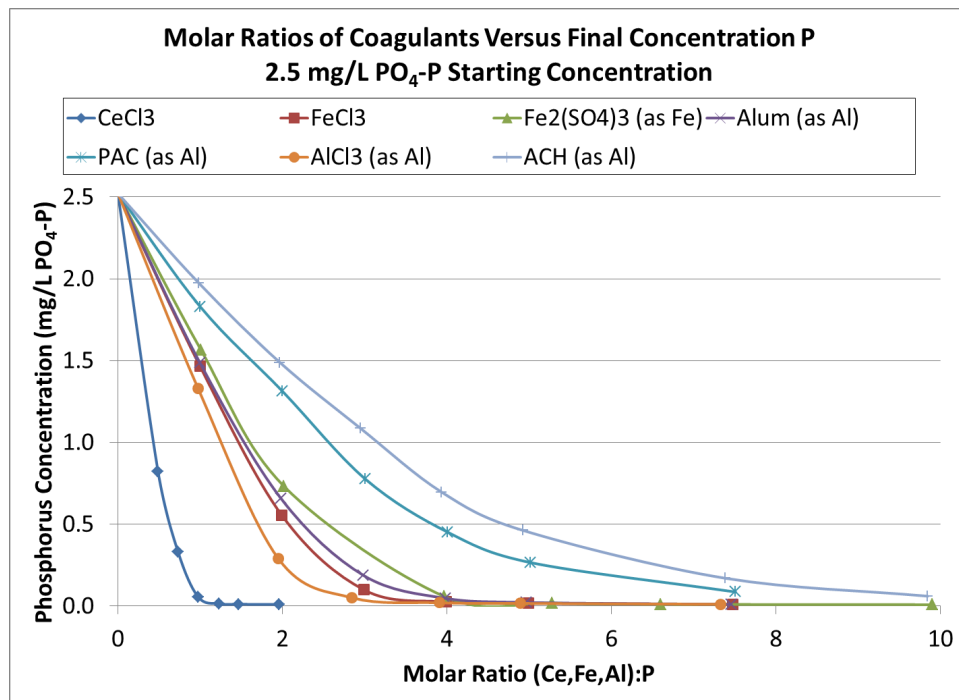


Figure 2. P removal vs. molar ratio for various coagulants. Beginning P concentration of 2.5 mg/L.

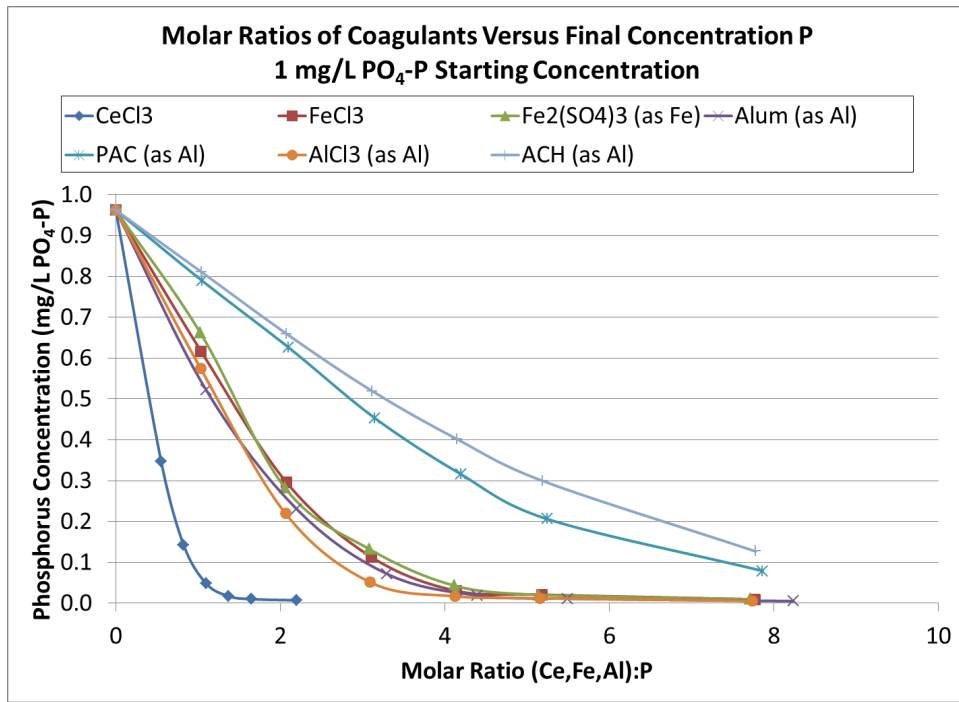


Figure 3. P removal vs. molar ratio for various coagulants. Beginning P concentration of 1.0 mg/L.

The LS to P reaction mechanism accounts for the near 1:1 RE:P molar ratio observed for P removal. In this way LS technology is unique among coagulants.

When comparing the amount of sludge generated from these coagulants it is clear that LS technology will produce less sludge. As an example if LS is compared with Fe and Al on an influent stream that has 0.8 mg/L P and a desired effluent P of 0.06 mg/L the data in Table I is generated.

Table I. Estimation of Sludge Generated From Coagulant Addition

	RE	Fe	Al
Influent P (mg/L)	0.8	0.8	0.8
Effluent P (mg/L)	0.06	0.06	0.06
M:P Molar Ratio	1	4	4
MW of M (g/mol)	140	56	27
MW of MPO ₄ (g/mol)	235	151	122
MW of M(OH) ₃ (g/mol)	191	107	78
M dosed (mg/L)	3.62	5.80	2.80
MPO ₄ sludge produced (mg/L)	5.63	3.61	2.92
M(OH) ₃ sludge produced (mg/L)	0.37	8.52	6.21
Total chemical sludge produced (mg/L)	6.00	12.13	9.13
Sludge produced per mg P removed (mg/L)	8.10	16.40	12.34
%Reduction using RE	-	51%	34%

In this example, the P concentration is reduced from 0.8 to 0.06 mg/L. The dose of coagulant is based on the molar ratio of the metal (M) to the influent P concentration. Fe and Al are multiplied by 4 due to the data in Figure 3 indicating a molar ratio of 4:1 is needed to achieve an effluent concentration of 0.06 mg/L P. The amount of MPO_4 produced is calculated based on a 1:1 M: PO_4 ratio. The excess M added is assumed to be converted to M(OH)_3 . Thus the total sludge produced is the sum of the MPO_4 and M(OH)_3 masses. In this example, the addition of LS will produce 6.00 mg of sludge per liter of solution. This is 51% less than the sludge produced by Fe and 34% less than the amount produced by Al addition. Dividing the amount of sludge produced by the amount of P removed yields a general estimate of the amount of sludge produced per mg/L of P removed. Based on this example, LS will produce 8.10 mg sludge/L of solution per mg/L of P removed.

LS technology will also enhance coagulation. This is accomplished by forming denser solids and removing the phosphates ability to disperse the solids. When comparing the solids formed in the precipitation of phosphate, the solids formed with iron or aluminum coagulants have a lower density than the solids formed with LS. See Table II below which lists the potential species formed, the molecular weights of the metal coagulants and the density of the precipitates.

Table II. Molecular Weights and Density of Solids Generated From Coagulant Addition

Precipitate formed	Molecular Weight of Metal (g/mol)	Density of Solids (g/ml)
Aluminum hydroxide Al(OH)_3	27	2.42
Aluminum phosphate AlPO_4	27	2.57
Iron phosphate dihydrate $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	55.85	2.87
Iron hydroxide oxide Fe(O)OH	55.85	3.4-3.9
Lanthanide Salt phosphate $\text{REPO}_4 \cdot \text{H}_2\text{O}$	138-175	4
Lanthanide Salt hydroxide RE(OH)_3	138-175	~4.3

The mechanism of precipitations described previously indicates that when Fe or Al salts are used a metal hydroxide is formed and phosphate binds to the surface. Phosphate is a known dispersion agent which means it will help keep particles suspended. Trisodium phosphate along with tetrasodium pyrophosphate have been shown to effectively suspend laterite type soils which contain high concentrations of iron and aluminum oxide.² Thus, when Fe or Al salts are added, iron or aluminum hydroxide forms, phosphate binds to the surface and as a result the particles are suspended. Thus coagulant added to remove phosphate ends up being a solid dispersed by phosphate. In contrast, the dominant mechanism for phosphate removal with LS is by formation of $\text{CePO}_4/\text{LaPO}_4 \cdot \text{H}_2\text{O}$ which effectively binds the phosphate rendering it incapable of suspending solids. This leads to the formation of a more compact solid which can be more easily dewatered.

Case Studies in Wastewater Treatment Plants

A 770,000 GPD plant that discharges to a stream leading to Lake Erie has been using LS technology since October 2014. Initially the use was to help meet the total aluminum (1.1 mg/L) and total phosphorus (1 mg/L) discharge limits. The use of LS technology quickly lowered the Eff TP and since Al based coagulants were no longer needed the Al limit was met as well.

The plant is set up to waste solids from the primary and secondary clarifier into an anaerobic digester. After the digester a gravity thickener is in place to thicken the solids prior to being separated by a belt filter press. The filtrate returns to the primary clarifier and the biosolids are hauled away in 20 yard dumpsters and disposed of in a landfill. Prior to the use of LS technology, the sludge had the appearance of dirty water and the belt filter press was run 8 hrs/day for 5 days/week. This is consistent with the Filter Press Cake Solids having a % Solids averaging around 15% (see Figure 4). After LS technology was adapted, the sludge increased in density, the % Solids of the Filter Press Cake Solids increased to an average of approximately 21%, and the gravity thickener prior to the belt filter press was no longer necessary. Furthermore the belt filter press run time was reduced to 8 hrs/day for 1 day/week. This translated into a reduction in power usage as the belt filter press is now run only 20% of the time (see Figure 5). However the clearest savings has been in the amount of 20 yard sludge containers hauled to the landfill. Prior to LS technology 75 containers were removed annually and after LS technology was implemented that number dropped and continued to drop with only 31 containers being hauled to the landfill in 2016. This represents a \$70,000 savings per year in sludge hauling alone. Thus the use of LS technology has reduced cost in electricity, man power, and sludge hauling.

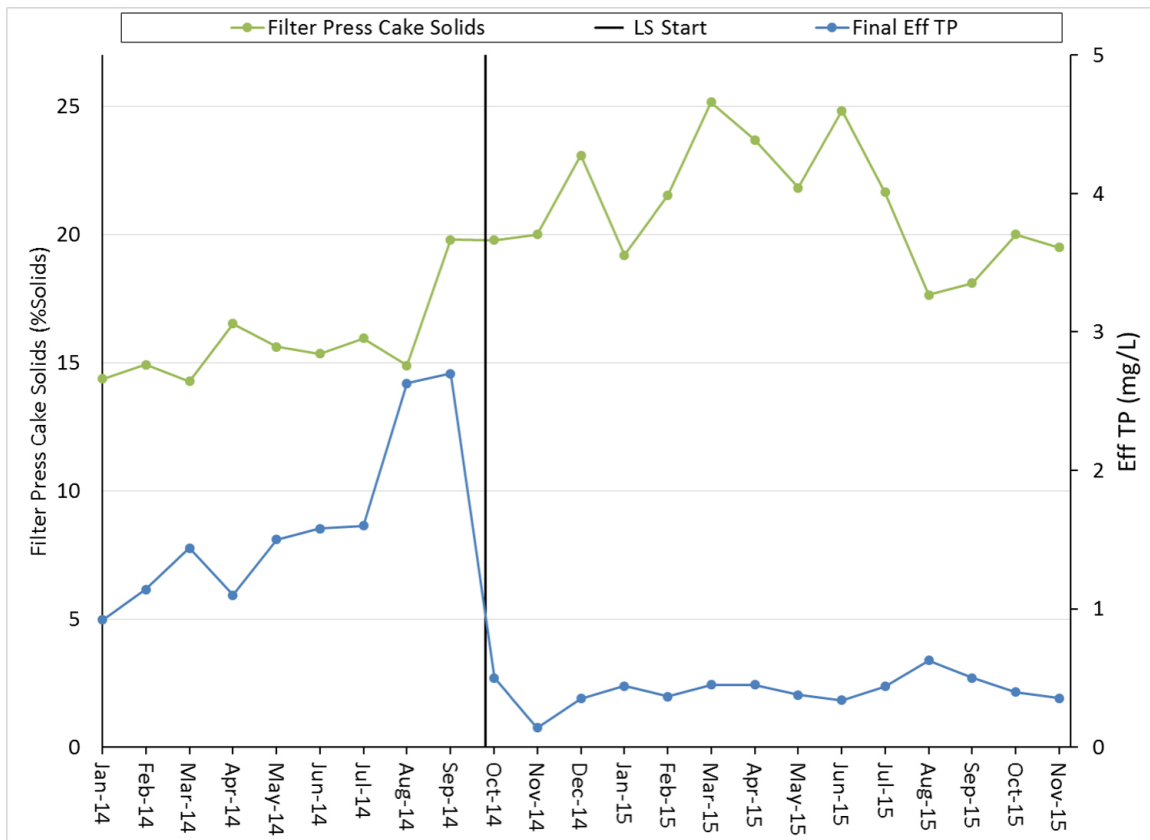


Figure 4. %Solids of Filter Press Cake Solids and Eff TP with and without LS

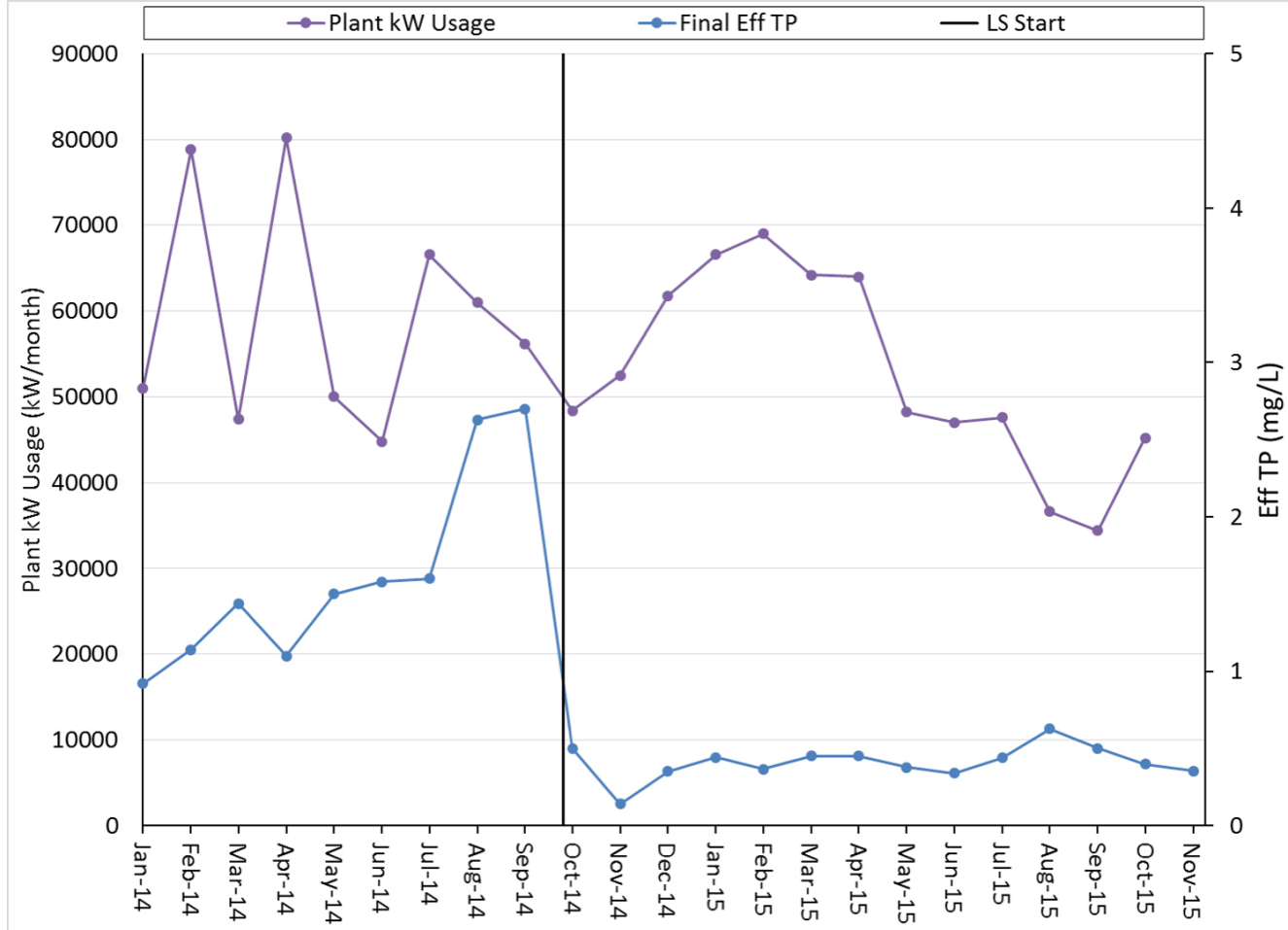


Figure 5. Plant kW Usage and Eff TP with and without LS

Table III. Sludge Hauling Pre and Post LS technology

Year	Containers of Sludge Hauled	Annual Hauling Costs	Cost Reduction
2013 (All Ferric)	75	\$103,000	-
2015 (All RE)	50	\$58,000	43.7%
2016 (All RE)	31	\$33,000	68.0%

Another plant using LS technology that is seeing beneficial sludge results is a 2 MGD plant discharging into a lake in Minnesota. This plant quantifies the sludge benefits by measuring the dewatering efficiency each month. What is measured is the total gallons of water separated from the solids, the average gallons per hour and the maximum gallons per hour. Below is the measured data for 5 month prior and 3 months after RE technology was implemented.

Table IV. Dewatering Efficiency per month Pre and Post LS technology

	Total Gallons	Avg GPH	Max GPH	Coagulant Used	Target P Limit (mg/L)
January	192400	9384.2	9931.0	Ferric Chloride	1
February	244000	7424.1	8312.5	Ferric Chloride	1
March	218300	7792.0	8173.1	Ferric Chloride	1
April	70600	3603.1	3898.6	Ferric Chloride	1
May	199500	7413.0	10500.0	Ferric Chloride	1
Avg	184960	7123.3	8163.0	Ferric Chloride	-
Avg w/o April	213550	8003.3	9229.2	Ferric Chloride	-
June	266600	8545.3	8712.1	RE Technology	0.075
July	225300	9001.1	10397.1	RE Technology	0.075
August	172100	9393.7	9824.6	RE Technology	0.075
Avg	221333	8980.0	9644.6	RE Technology	-

It is important to note that there is significant variability and many factors involved when assessing biosolids dewatering efficiency; however, based on this data (excluding April because the plant had some issues during April which skew the numbers lower) it appears that dewatering efficiency was improved by 977 more gallons removed per hour and 7,783 more gallons removed per month on average when RE technology is used. While this is a small increase in efficiency it is important to consider that the performance improvement occurred after only one month. Additional improvement may be evident over longer periods of time. LS technology was initially trialed to achieve P discharge limits of 0.075 mg/L. During the time period of the above data, not only did LS technology improve the biosolids dewatering efficiency, but it kept the P discharge below 0.07 mg/L. Thus at this facility two major benefits were observed 1) an increase in dewatering efficiency and 2) a low P discharge.

A plant in Wisconsin using LS technology has also observed a reduction in sludge. This plant doesn't do sludge digestion but stores the sludge in a 2 million gallon tank where farmers can pick up the sludge for land application. Although quantitative numbers are not currently available, they have seen a 50-70% reduction in sludge. This has been observed in the number of trucks hauling sludge and the level in the sludge tank. In years prior to LS usage, when ferric was used, the tank has reached capacity during winter. This has not been the case in years since LS has been implemented. In this case as well the P discharge achieved was 0.075 mg/L with LS and 1 mg/L with ferric. Thus a sludge reduction was observed even with the achievement of a significantly lower P discharge.

Toxicity of LS Technology Sludge

The sludge generated from rare earth addition to wastewater has been tested for toxicity. The typical concentration of RECl_3 in LS technology is 648 g/L, applied at a volumetric dosage rate of 1:53,000, yields approximately 12 mg $\text{CePO}_4/\text{LaPO}_4/\text{L}$. This value is lower than the conservatively calculated safe limit of 14 mg $\text{CePO}_4/\text{LaPO}_4/\text{L}$ for drinking water.³ The treated water is then further processed through a solids/liquid separation system such as a clarifier or filter. Any rare earth solids that precipitate would therefore be removed, with the actual rare earth phosphate concentration likely to

be much lower than 12 mg/L at the point of discharge.⁴ The primary potential for human exposure to RE technology treated water would be through consumption of treated water, whereas aquatic organisms could be exposed at any point after treatment of a water body with LS technology. Thus little to no harmful effects are expected from solids generated.

The toxicity of the sludge generated towards denitrification bacteria has also been studied in unpublished sludge respiration inhibition studies. The rare earth solids present in the sludge would be those discussed earlier such as $\text{CePO}_4/\text{LaPO}_4$, $\text{RE}_2(\text{CO}_3)_3$, and $\text{RE}(\text{OH})_3$. A study conducted by Intrinsic Technologies for Neo found no toxicity towards activated sludge microbes. As a comparison, for CeO_2 the EC50 for inhibition of respiration was greater than 1000 mg/L.⁵ Based on this the addition of RE to wastewater treatment should have no effect on the microbes.

Neo has also evaluated the effect of land applying the sludge generated in treatment plants using RE based coagulants. This study was performed by Richard Wolkowski, Ph.D. (Extension Soil Scientist at University of Wisconsin-Madison) at Alfisol Soil Management, LLC. In this study, P availability to corn from rare earth biosolids was investigated and compared to P availability from a commercial P fertilizer and ferric biosolids. Corn was chosen for the study as it is the most common crop treated with biosolids and is grown on four million acres in Wisconsin. Rare earth biosolids produced soil with P availability between P fertilizer and ferric biosolids as measured by the change in soil test P. The corn whole-plant dry matter yield either was unaffected by the rare earth biosolids. Thus, the application of rare earth biosolids is not expected to affect the growth and yield of corn when applied at normal rates that supply the corn N requirement.

Conclusion

The use of LS technology, a rare earth based coagulant, to remove P from water is quite effective. Due to the near 1 to 1 molar ratio of LS to P significantly less sludge will be produced as compared to Fe and Al based coagulants. Furthermore, LS will enhance the coagulation of the solids and produce a thicker sludge. All of this will improve the filtration process and help reduce the cost of dewatering the solids. Toxicity studies have also shown RE based coagulants and the precipitates formed when used in wastewater to be non-toxic to have low toxicity. Furthermore the presence of LS in the land applied sludge has no observed impact on the growth of corn plants.

Due to the chemistry of the lanthanide salt elements found in LS technology, highly insoluble solids are expected to form when LS is applied in wastewater treatment. These solids are dense and settle well. Lanthanide salts also enhance coagulation, which yields a thicker sludge and increases filterability. Lanthanide salts have been shown to have low toxicity and low environmental impact.

¹ Hanlon, C. Scott Smith: Understanding and Maximizing Phosphorus Removal *INFLUENTS*, Fall **2015**, p 8-9.

² Wintermyer, A. M.; Kinter, E. B. "Dispersing Agents of Particle-Size Analysis of Soils" Highway Research Board Bulletin, **95**, **1955**, p 1-14.

- ³ The oral reference dose for the similar compound Lanthanum Phosphate is 0.5 mg/kg-day (NSF International 2010 as cited by United States Environmental Protection Agency (USEPA). 2012. Rare earth elements: A review of production, processing, recycling, and associated environmental issues. EPA/600/R-12/5721. August.). Thus the safe daily exposure level of a rare earth phosphate is $0.5 \text{ mg/kg-day} \times 70 \text{ kg} = 35 \text{ mg/day}$ (assuming a 70 kg person). Using the 80% upper ceiling (United States Environmental Protection Agency (USEPA). 2000. Methodology for deriving ambient water quality criteria for the protection of human health. Office of Water, EPA-822-B-00-004. October. Available online: http://water.epa.gov/scitech/swguidance/standards/upload/2005_05_06_criteria_humanhealth_method_complete.pdf) contaminant exposure from water the safe concentration is $0.5 \text{ mg/kg-day} \times 70 \text{ kg} \times 0.8 / (2 \text{ L/day consumed}) = 14 \text{ mg/L}$.
- ⁴ $\text{CePO}_4/\text{LaPO}_4$ will be detected in a total phosphorus test. Assuming all 12 mg/L $\text{CePO}_4/\text{LaPO}_4$ was discharged, the TP measured would be 1.6 mg P/L, which is much higher than new discharge permits coming into effect (<1 or <0.1).
- ⁵ Toxicological Review of Nano Cerium Oxide. *Prospect* 2010