

Chemical P removal – from lab tests through model understanding to full-scale demonstration

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Abstract

Chemical P removal with metal (Fe, Al) salts is widely used in practice to achieve low levels of effluent P in order to protect sensitive receiving water bodies. Based on laboratory experiments showing fast and slow reaction mechanisms, a new equilibrium and kinetic based model was formulated. The concept of slow kinetic sorption and surface aging was applied at the West Camden Sewage Treatment Plant, Australia. The system as designed uses a combination of biological phosphorus removal with *multipoint* chemical addition and *metal salt recycle* to achieve low effluent P at the lowest feasible chemical dosage. The metal salt usage is approximately half of what would normally be expected for these effluent goals. A key innovation in this design was the recycle of tertiary chemical sludge to the head of the plant to promote further sorption of phosphorus by the tertiary sludge in the secondary system in combination with the high shear alum addition dose.

Keywords

Chemical phosphorus removal, kinetic, equilibrium model, full-plant validation

INTRODUCTION

In spite of its wide use and relative straightforward design, the complex mechanism of P binding to metal complexes is not fully understood. This results in less than optimal designs (e.g. single-point dosage, low mixing, and inefficient flocculation) as well as costly operation (unnecessary overdose, excess sludge production, uncertainty of existing P removal capacity before a shock load event, suboptimal dosing strategy). Based on a detailed literature survey and a large range of laboratory experiments, a conceptual, engineering model was formulated with the objective of describing the complex processes occurring during metal salt addition in wastewater. The model is a combination of equilibrium precipitation and co-precipitation, as well as kinetic sorption and aging (surface consolidation) processes. This paper contains the description of the conceptual model and experimental evidence for the processes included. Model validation is the subject of a follow-up paper. The concept was applied at a full-scale plant to investigate its validity. The West Camden Sewage Treatment Plant, located in New South Wales, Australia, required upgrading for both increased capacity and to achieve new stricter nitrogen and phosphorus limits. The plant capacity was increased from 10000 m³/d to

23000 m³/d on an average day basis. Additionally, full nutrient removal was implemented with a target effluent TN value of 7.5 mg/L (median) and a target effluent total phosphorus of 0.04 mg/L (median). The West Camden STP was commissioned and placed into service in October 2009 using multi-point chemical dosage and recycled chemical sludge to promote further sorption of phosphorus on the metal hydroxides.

MATERIALS AND METHODS

An extensive review and summary of experiments performed to understand the various mechanisms involved in chemical P removal can be found in Szabó et al. (2008) and Smith et al., (2008). According to testing protocols described in the papers, it was demonstrated that fast P removal (termed co-precipitation) and slow sorption both play a significant role in binding phosphorus to the hydrous ferric or alum oxides (collectively termed hydrous metal oxides, HMO) that forms after metal salt addition (Figure 1).

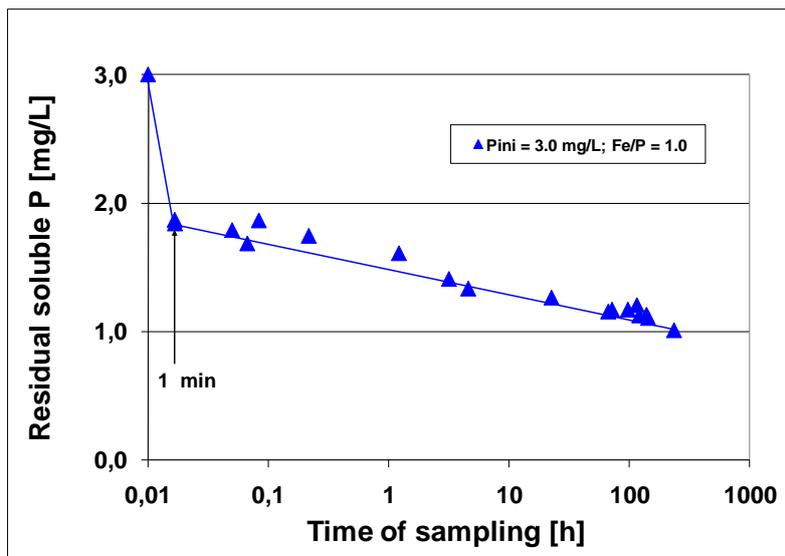


Figure 1. Fast co-precipitation and slow sorption

The freshly formed flocs quickly start losing their sorptive capacity, by rapid surface consolidation processes. This is demonstrated in Figure 2, after addition of one minute old

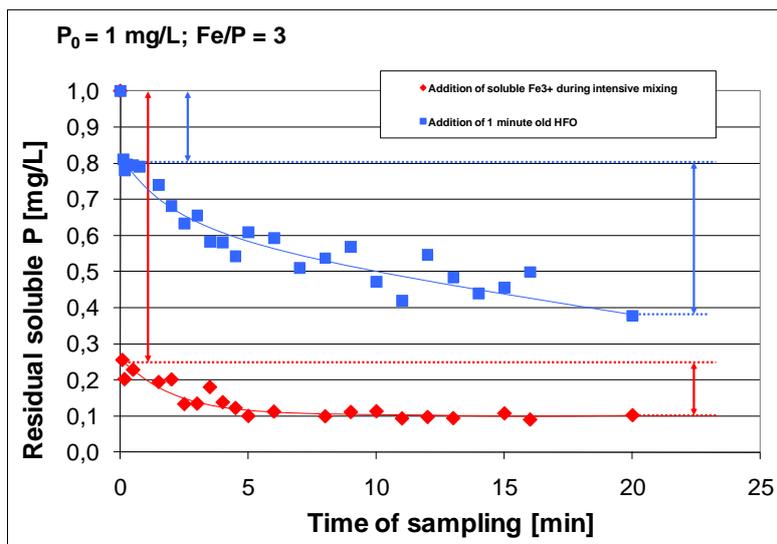


Figure 2. Older flocs have significantly lower capacity and slower P removal kinetics

preformed flocs, compared to metal salt addition.

The surface area and available sorptive capacity of the HMO particles depends to a large degree on the local mixing intensity, expressed as the mean velocity gradient (G, s^{-1}), as shown in Figure 3.

CONCEPTUAL MODEL DESCRIPTION

The equilibrium surface complexation model (SCM) for hydrous metal oxide (HMO) mediated removal of phosphate has been described for ferric (Smith et al., 2008a, Smith et al. 2008b) and for aluminum (Smith et al., 2010). Overall the model involves surface complexation reactions that are based on known

metal oxide surface reactions defined in the literature. The stoichiometry of these reactions and the nature of the surface sites are defined by crystallography and surface spectroscopy (i.e., infrared). The SCM for chemical P removal takes these literature defined surface reactions as the starting point. The equilibrium constants for the surface complexation

were calibrated (fit) to measured phosphorus removal in batch tests at variable pH and dose.

Finally an adjustable parameter was introduced, the Active Site Factor (ASF). This factor is the link to the kinetic part of the model, and relates the concentration of the surface sites to the amount of precipitated HMO. The surface binding constants are measured by jar tests that take into account dose and pH, and to fit data of variable kinetic conditions (reaction time, mixing, age) the ASF is the only required adjustable parameter. The model concept as defined below takes the ideas generated from HMO batch tests and extends them with the kinetic processes that affect the ASF.

Conceptually ASF is thought to represent all the sites available during rapid co-precipitation. In experiments where removal via HFO is monitored versus time (Szabó et al. 2008, Gilmore

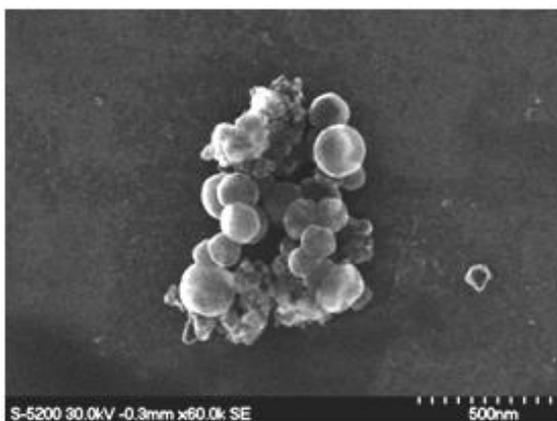


Figure 4. SEM image of one minute old ferric hydroxide floc. Image courtesy of Dr. Vladimir Kitaev (Wilfrid Laurier University).

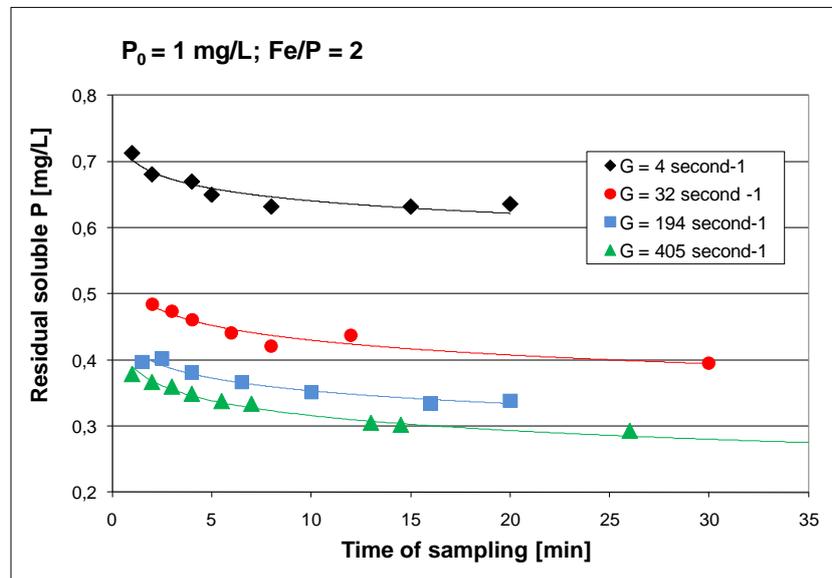


Figure 3. Mixing intensity (G) has a large effect on P removal efficiency

et al. 2010) an initial rapid removal step is seen (co-precipitation) followed by a slower removal step (surface sorption). For HAO this rapid removal is even faster (Smith et al. 2010). During this rapid co-precipitation initially HMO colloids will form. These colloids can associate via SCM mechanisms with phosphate. As the colloids grow and aggregate the phosphate is trapped or occluded within the growing particle. Thus, more rapid mixing can lead to more efficient removal as these nano-sized particles are exposed more to phosphate during their growth phase. After the initial precipitation of HMO and simultaneous removal of phosphorus

the particle surface can continue sorptive reactions as the particle ages. An SEM image of a minute old HFO particle is shown in Figure 4. The image clearly shows that the filterable sized floc is made up of many smaller aggregated particles.

It can be seen that this particle would be solid-liquid separable (size greater than 0.45 μm). Thus, P on the surface could be removed from the system. In addition, the particle is seen to be an aggregation of smaller particles which as they formed would accumulate phosphorus and trap that phosphorus as part of the larger aggregate particle.

MIXED EQUILIBRIUM-KINETIC MODEL CONCEPT FOR P PRECIPITATION

The following mechanism which can be directly transcribed into a mathematical model is proposed for chemical P removal.

1. Soluble metal (Fe^{3+} or Al^{3+}) salt is dosed into wastewater treatment plant. Mixing at point of dosage should be vigorous, but in practice it is frequently low energy.
2. Hydrous metal oxide (HMO) forms in very short timeframe (seconds). For engineering purposes this reaction can be approximated as an equilibrium precipitation process, slightly pH dependent. At very low pH values (dose dependent, $\text{pH} < 4-5$) the amount of HMO formed is reduced due to other soluble metal hydroxide and metal phosphate complexes forming. At high pH values ($\text{pH} > 10$) $\text{Me}(\text{OH})_4^-$ soluble species binds up the metal ions. In typical operating pH ranges the amount formed is stable, but pH affects surface charges of the HMO. The HMO formed has a variable surface available for P sorption:
 - a. High intensity mixing (high G values) will result in HMO with large specific surface area. In the model for ferric this HFO (termed High-HFO) has an active site factor of 1.2 molP/molFe.
 - b. Low intensity mixing (low G values) will result in HMO with low specific surface area. In the model this HFO (termed Low-HFO) has an active site factor of 0.2 molP/molFe.

The variable P/Metal ratio observed in practice is simulated in the model using the proper mixture of the two extreme HMO forms. The ratio of High-HMO to Low-HMO depends on mixing energy (as represented by G) in the vicinity of the dosing point. More research is required to determine the conversion process of the High and Low HMO forms from soluble to solid state, passing through a colloidal phase. Colloidal HMO (and bound P) can escape the plant and can be measured as soluble metal and phosphorus.

3. High-HMO sorbs (occludes) P instantaneously during its formation and forms a complex termed High-HMO-P. This process can be considered an equilibrium co-precipitation process, occurring in seconds.
4. Low-HMO sorbs P slowly and forms Low-HFO-P. This process can be described with a kinetic adsorption model.
5. Simultaneously, surface consolidation (depending on pH, mixing and residence time) occurs. In the model this is termed "HMO Aging". Unbound pure High-HMO "ages" to Low-HMO, that is the active surface gets consolidated and reduced. Low-HMO further

consolidates, and forms a component called old-HMO, which is inactive (has zero active surface sites).

- This model does not consider the release of P in lack of experimental evidence, except for very low and very high pH conditions. Under these conditions equilibrium processes dissolve HMO and form the appropriate soluble Fe or Al species with release of P.

A schematic representation of the conceptual model is shown in Figure 5.

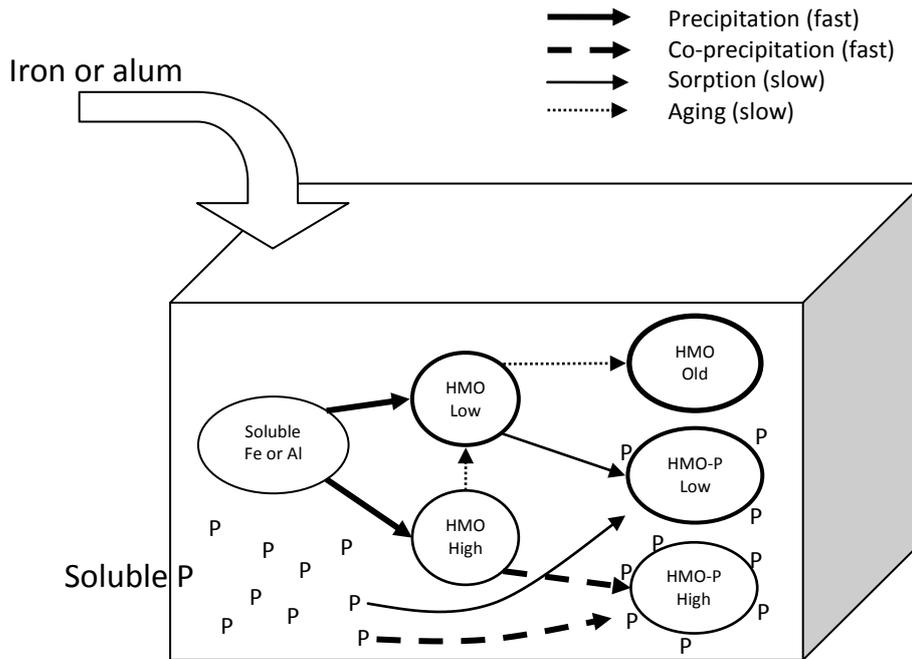


Figure 5. Schematic representation of equilibrium-kinetic chemical P model

FULL-SCALE CONCEPT VALIDATION

The West Camden Sewage Treatment Plant, located in New South Wales, Australia, required upgrading for both increased capacity and to achieve new stricter nitrogen and phosphorus limits. The project was awarded to the CHBM Water Joint Venture (a joint venture between CH2M HILL and Barclay Mowlem) late 2004 with the goal of increasing plant capacity from 10000 m³/d to 23000 m³/d on an average day basis. Additionally, full nutrient removal was implemented with a target effluent TN value of 7.5 mg/L (median) and a target effluent total phosphorus of 0.04 mgP/L (median).

The scope of the upgrade included modifying the existing aerobic activated sludge system to a MLE process with a capacity of 7000 m³/d, adding two new continuous feed sequencing batch reactors (IDALs) at 16000 m³/d with biological phosphorus removal capabilities, tertiary clarifiers for phosphorus removal with alum and polymer dosing, doubling the tertiary filter capacity, new chlorine contact tank with hypochlorite dosing, new centrifuge thickening and dewatering with associated centrate holding and balance tanks, anaerobic digestion, digested sludge holding tanks and dewatered cake loading facility. A process flow diagram of the facility is given in Figure 6.

The West Camden STP was commissioned and placed into service in October 2009. The upgrade has achieved its objectives of catering for future population growth in the wider

Camden area and is providing improved water quality in the Hawkesbury-Nepean River and is able to provide up to 5000 m³/d of high quality recycled water to the Elizabeth Macarthur Agricultural Institute.

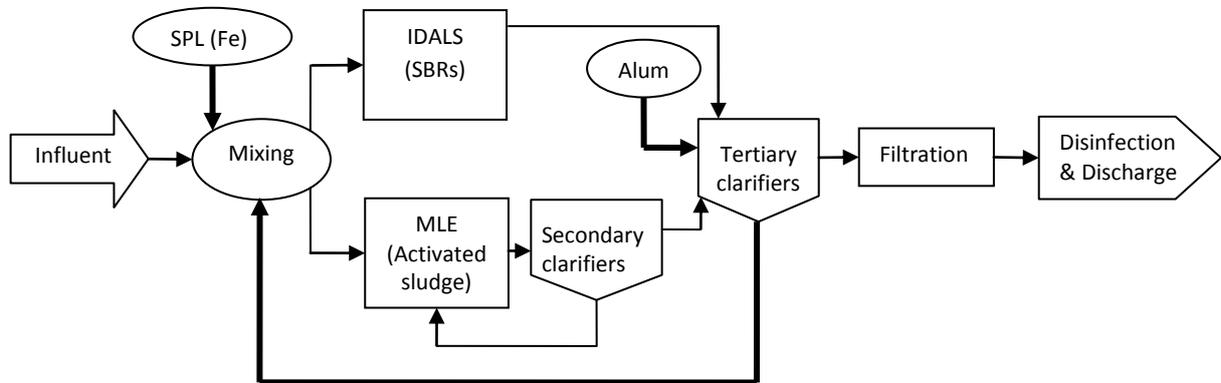


Figure 6: West Camden Liquid Process Flow Diagram

PHOSPHORUS REMOVAL DESIGN

The phosphorus removal system is staged to achieve the lowest feasible chemical usage. The IDALs are not specifically designed to accomplish biological phosphorus removal, but do show 2 mg/L of excess biological phosphorus removal attributable to the anaerobic conditions present during the decant step. The MLE system relies entirely upon chemicals for its phosphorus removal. During the period described in this paper, all the flow was directed to the IDAL's system. The first stage is therefore biological phosphorus removal, augmented with both Spent Pickle Liquor (SPL) addition and with the recycled alum sludge. After late August, the SPL dosage was 18 mg Fe/L and kept at that point for the remainder of the operating period.

One of the key features in this design is the recycle of tertiary sludge back to the head of the activated sludge basins. This allows reuse of the alum sludge to adsorb another fraction of the influent phosphorus, thus reducing overall chemical usage at the plant while still achieving the very low effluent TP limits required.

After secondary treatment the flow is directed to a solids contact tertiary clarifier system. The tertiary clarifiers used in the design have the solids contact center wells more commonly associated with water plant facilities. Alum is added (55 mg/L) in a high shear mixing box (30 to 60 seconds contact time) prior to splitting to the two clarifiers. This high shear mixing is a critical part of minimizing the amount of alum needed for phosphorus removal. After alum addition and flow splitting, flow goes to the clarifier flocculation wells where polymer (0.4 mg/L) is added to the tertiary clarifiers, and provides a high degree of contact between the alum solids and the secondary effluent, thus promoting phosphorus removal and the efficient use of alum. The clarifiers are 30.7 m in diameter to give a design overflow rate of 2 m/hr.

Finally, the plant effluent is filtered through a conventional granular media filter system prior to discharge from the facility.

Another interesting aspect of this design is the use of both spent pickle liquor (SPL) and alum for phosphorus precipitation. Alum is used only in the tertiary clarifier system while SPL is added, on an as needed basis, to the secondary influent (with the tertiary sludge alum solids). This was done because of the low cost of SPL in this region of Australia made it economic in the design. SPL was not used in the tertiary system because of concerns with its quality and

ability to adsorb P down to very low levels (given that it is mostly ferrous iron). It was also found that it was important to have some residual P in the secondary effluent to improve tertiary clarifier operation.

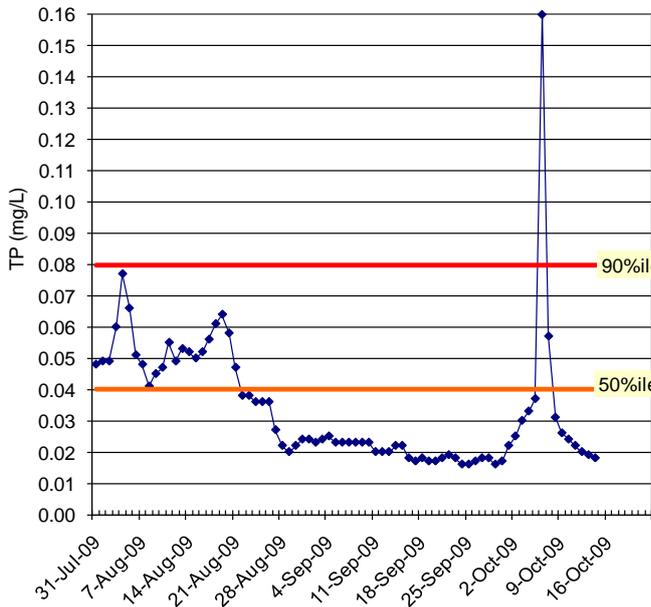


Figure 7: Effluent Total Phosphorus

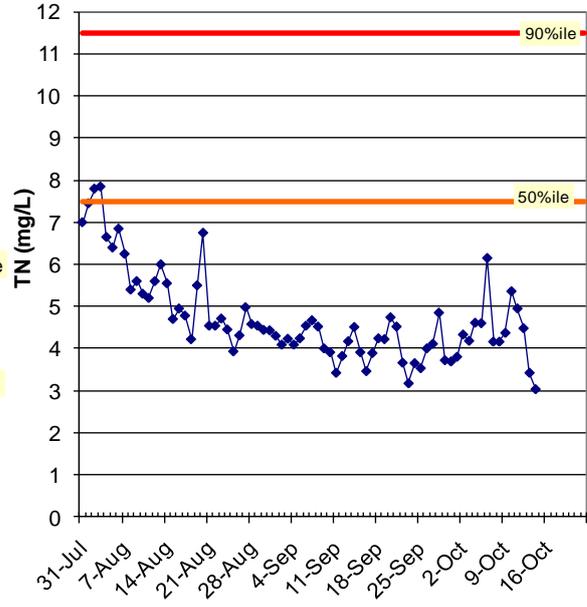


Figure 8: Effluent Total Nitrogen

Figure 7 shows a plot of the effluent total phosphorus for the plant during the startup and commissioning period. The two darker horizontal lines show the effluent limits at the facility. It can be seen that the effluent targets are easily achieved with this design, with an average

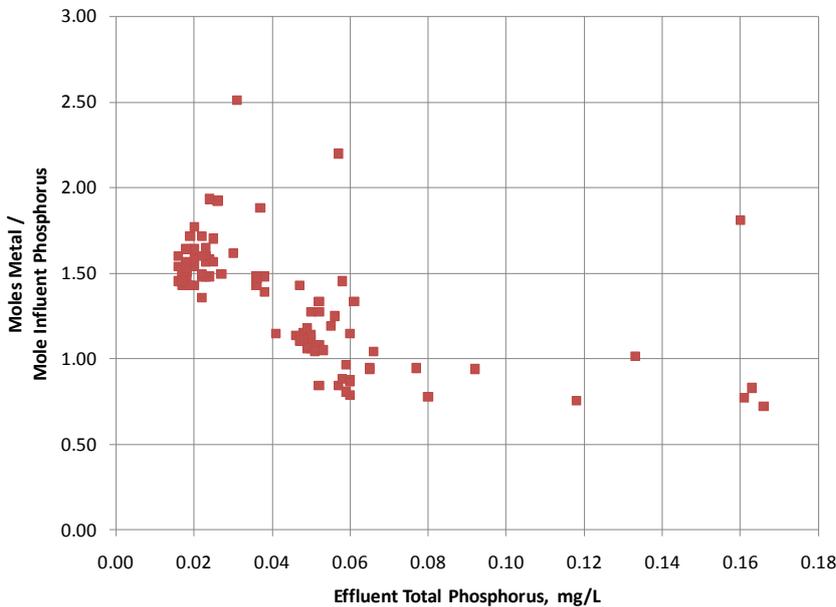


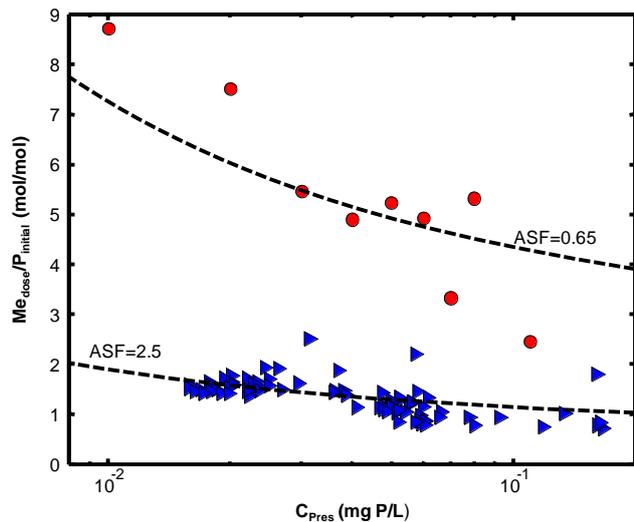
Figure 9. Metal Salt Usage Efficiency at West Camden

TP concentration, the molar ratio of metal dose to phosphorus was between 1 and 1.5. Normally this ratio would be expected to be in the 2 to 5 range for alum.

Two model runs were performed to compare the value of ASF of the West Camden plant with that of a traditional design. The results clearly show the advantage of intensive mixing and recycling of chemical sludge – the Me/P molar ratios are much lower, therefore the fitted ASF

effluent TP of 0.02 mg/L during the latter period. Figure 8 shows a plot of the effluent TN performance during the same period, averaging 4 mg/L after system stabilization.

The metal salt usage levels are much lower than industry standard in this system. This can be seen in the results shown in Figure 9. For example, at 0.05 mg/L



values are significantly higher for West Camden (ASF=2.5 vs. ASF=0.65 for the control plant (Figure 10).

Figure 10. Molar dose of aluminum versus measured residual phosphorus for West Camden Treatment Plant (blue ►) and for a plant utilizing tertiary phosphorus removal (red ●).

CONCLUSIONS

The underlying mechanisms of metal dosing for phosphorus removal are complex. The major mechanisms (hydrous metal oxide precipitation and co-precipitation, kinetic P sorption and surface consolidation or floc aging) were separated and demonstrated using extensive laboratory experiments. A conceptual model was constructed and is summarized in this paper. Model validation is the subject of a follow up paper. The concept was applied in a full-scale plant redesign. The ability of full scale wastewater treatment systems to reliably achieve very low phosphorus limits has been proven in the design and operation of the West Camden STP (Australia). The system uses a combination of biological phosphorus removal with multipoint chemical addition and metal salt recycle to achieve these goals at the lowest feasible chemical dosage. The metal salt usage is approximately half that would normally be expected for this quality of effluent. A key innovation in this design was the recycle of tertiary metal salts sludge to the head of the plant to promote further absorption of phosphorus by the tertiary sludge in the secondary system in combination with the high shear alum addition system.

Full scale operation of the West Camden STP has shown that design and operation of facilities to achieve very low phosphorus is feasible at low chemical usage rates.

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REFERENCES

- Gilmore, R.L., Murthy, S., Takács, I., Smith (2011). Application of a Factorial Design to Study Chemically Mediated Phosphorus Removal. Proceedings of the Nutrient Recovery and Management 2011 Conference, Miami, USA, January 9-12, 2011
- Smith, D. S., Takács, I., Murthy, S., Daigger, G., and Szabó, A. (2008). Phosphate complexation model and its implications for chemical phosphorus removal. *Water Environment Research* 80 (2008), 428-438
- Smith, D. S., Gilmore, R. L., Szabó, A., Takács, I., Murthy, S., and Daigger, G. (2008). Chemically mediated phosphorus removal to low levels: analysis and interpretation of data. In *WEFTEC Conference Proceedings* (2008), Water Environment Federation, pp. 3558-3574.
- Smith, D. S., Neethling, J. B. (2011). Surface Complexation Modeling and Aluminum Mediated Phosphorus Removal. Proceedings of the Nutrient Recovery and Management 2011 Conference, Miami USA January 9-12, 2011
- Szabó, A., Takács, I., Murthy, S., Daigger, G., Licskó, I., and Smith, D. S. (2008). The significance of design and operational variables in chemical phosphorus removal. *Water Environment Research* 80 (2008), 407-416.