Comparison of Struvite and Brushite Recovery: Model-based Technical and Economic Evaluation and Case Studies

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Stantec

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Outline

- Background
- Modeling and Cost Comparison
- CalPrex^{TM} Feasibility Studies
- Visual MINTEQ Modeling for P Recovery
- Summary

Background - P Recovery

- Phosphorus (P) Recovery can be implemented in different stages of treatment, from the liquid to the sludge phase, and also from sludge post-treatment.
- Close to 90% P removal from the sidestream P load is achievable

Brushite - Source: NRU

Struvite - Source: NuReSys

Background - P Recovery

- P recovery is achieved by precipitation/crystallization.
- The product is in the form of calcium phosphate or magnesium ammonium phosphate hexahydrate/MAP (struvite).
- Struvite crystallization is one of the current leading technologies for P recovery.
- Brushite recovery is a newer technology

Struvite: pK_{sp} (25°C): 13.26 — Taylor et al. (1963)

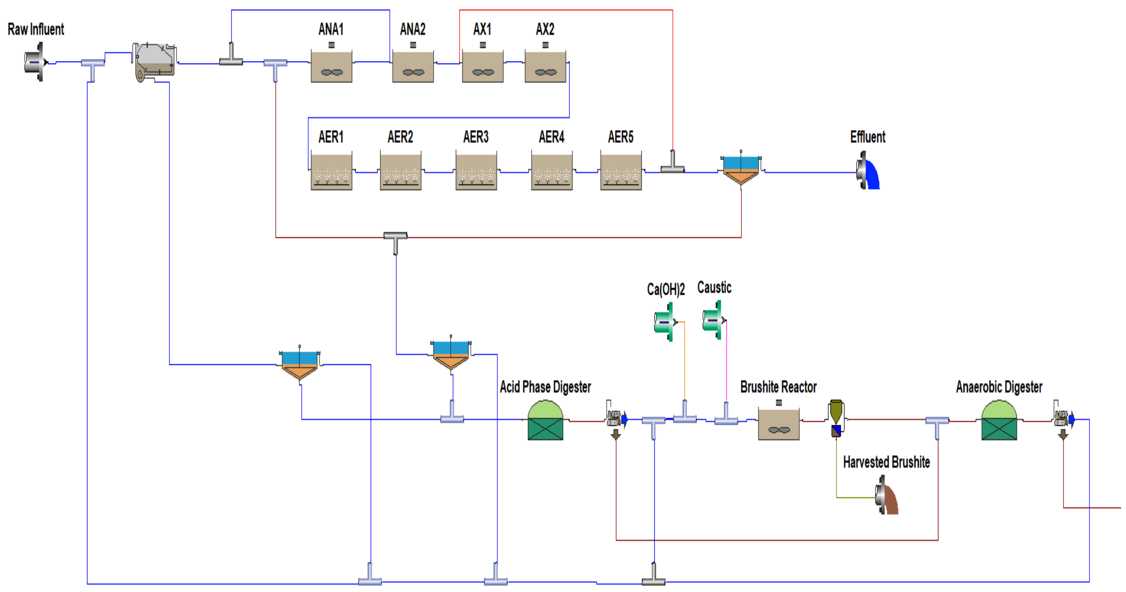
$Ksp = -\log([Mg^{+2}][NH_4^{+}][PO_4^{-3}])$

Brushite: pK_{sp} (25°C): 6.6 — Stumm and Morgan (1981)

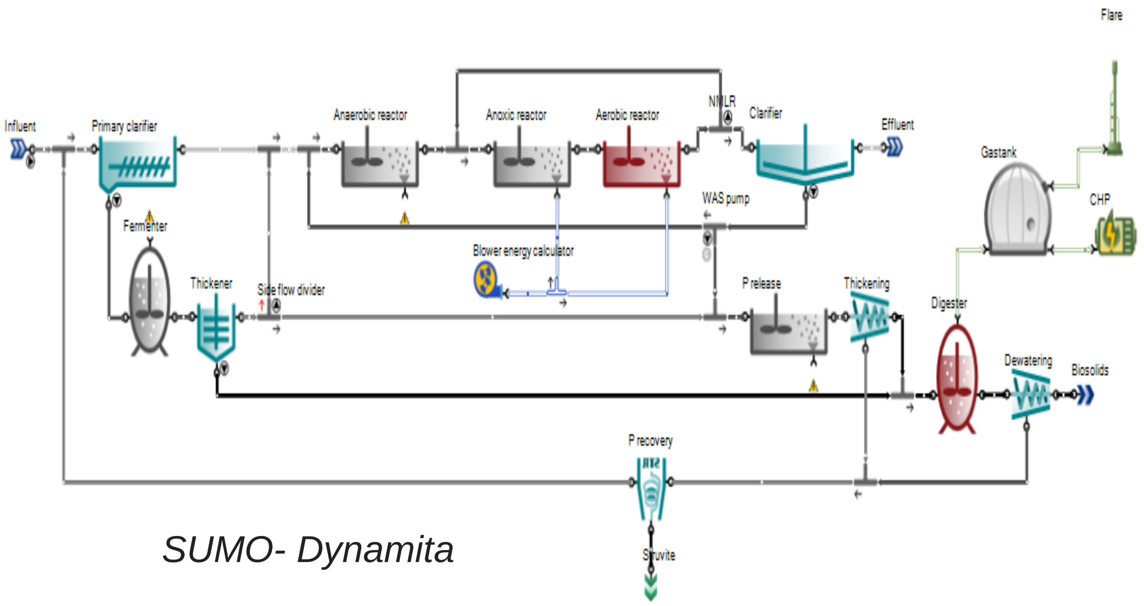
$K_{sp} = -\log([Ca^{+2}][HPO_4^{-2}])$

Modeling of P Recovery Processes

- In the past, predicting P recovery product yield relied on pilot testing and empirical analysis.
- Recent advances in simulators better account for biomass impacts on chemistry, kinetic limitations, and surface chemistry.
- Digester chemistry evaluations are improved and whole plant models more accurately predict P recovery
- Allows for investigation of a broader number of P-recovery scenarios, improved comparison of P-recovery alternatives, and optimization of P-recovery processes.



BioWin - EnviroSim



SUMO- Dynamita

Modeling-based Comparison for Brushite and Struvite Recovery

Modeling of P Recovery Processes

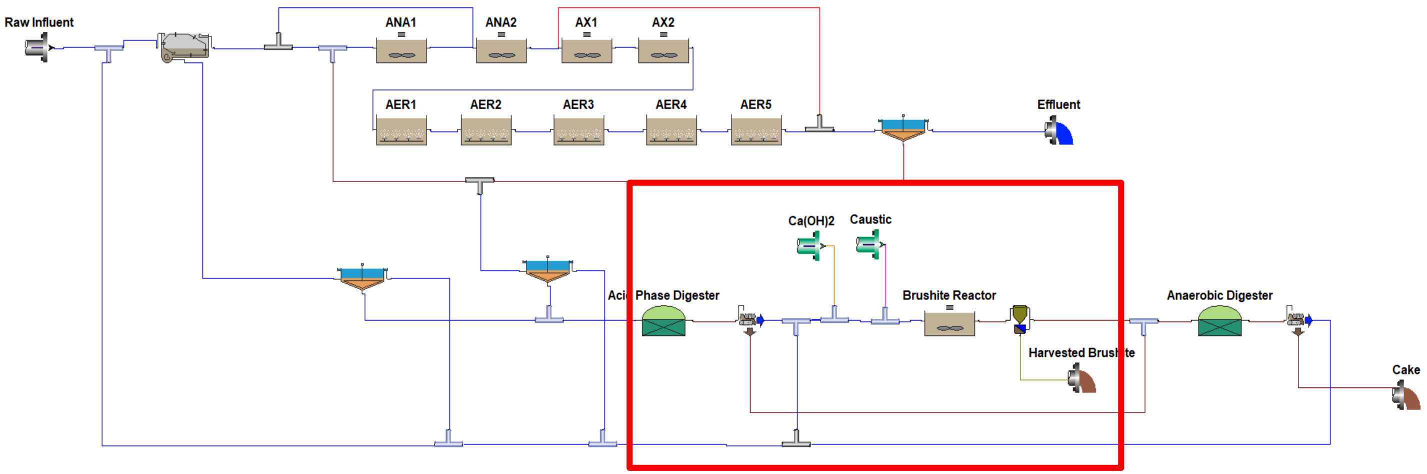
- Develop a comparative economic and technical assessment of the two most common P-recovery options of struvite and brushite.
- For a 20 MGD WRRF and typical medium strength influent wastewater
- Compared the model with full-scale data and technology providers' design basis.

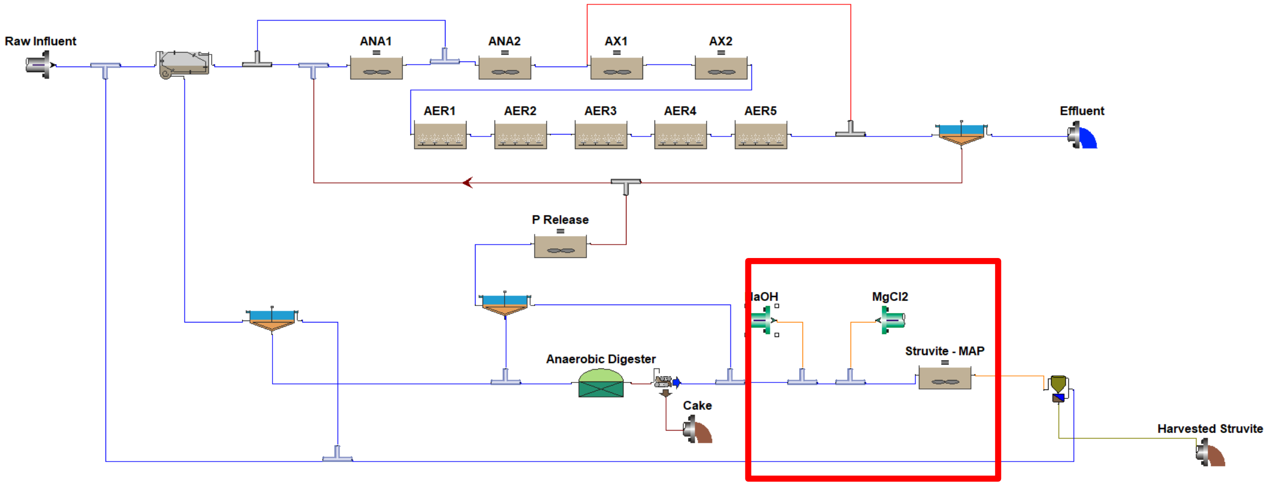
Modeling - Method

- Modeling evaluation was completed in two steps.
- Step 1: a plant model was setup to demonstrate that the model is able to predict P-recovery from an existing facility.
- Step 2: A “mock” plant model was setup to compare struvite and brushite recovery.
- Step 1- Confirmed that the model is capable of predicting P recovery reasonably well for struvite recovery
- For brushite recovery, comparison of the model output with the technology provider design basis was conducted.

Modeling

Parameter	Average Value
Flow (MGD)	20
COD (mg/L)	507
BOD_5 (mg/L)	240
pH	7.5
TKN (mg-N/L)	42.5
TP (mg-P/L)	5.7
TSS (mg/L)	230
Ca (mg/L)	87
Mg (mg/L)	46
Ammonia (mg-N/L)	27
Alkalinity (meq/L)	4.8





Comparison of Brushite and Struvite Recovery

Modeling

- Mg/P and Ca/P ratios for struvite and brushite recovery are similar to the values reported in the literature based on full-scale and pilot-plant studies

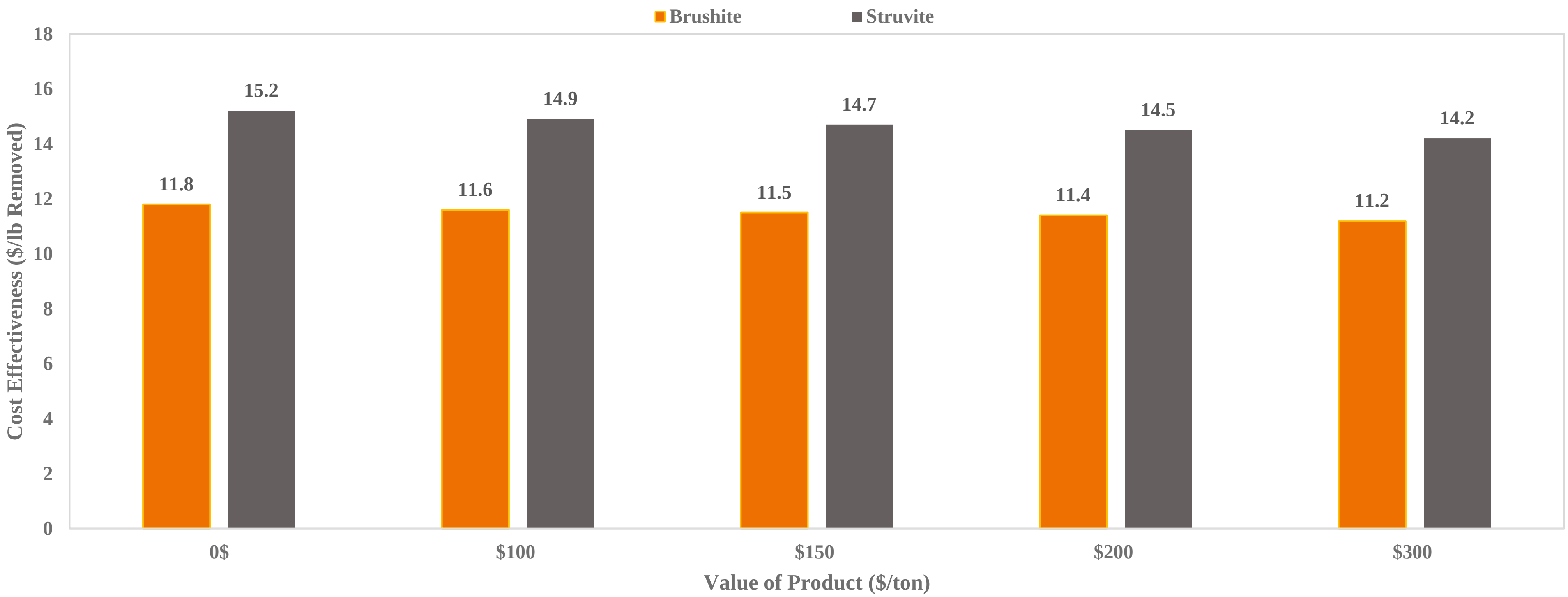
Parameter	Brushite Recovery	Struvite Recovery
Acid Phase Digester		
HRT	1.2 days	--
Operating temperature	20 ˚C	--
Soluble P	362 mg/L	--
pH	4.3	--
VSS Destruction	29%	--
TS	3.80%	--
P release	36%	--
P-Release Tank		
Soluble P	--	96 mg-P/L
Mg	--	92 mg/L
Ammonia	--	41 mg-N/L
Supernatant to P recovery		
Soluble P	363 mg/L	197 mg-P/L
pH	4.3	7
Mg	112 mg/L	11 mg/L
Ammonia	401 mg/L	980 mg-N/L
Ca	160 mg/L	15 mg/L
P Recovery Reactor		
pH	5.7	8.9
Ammonia	397 mg/L	394 mg/L
Effluent Soluble P	58 mg/L	31 mg/L
P Recovered	218 lb/d	256 lb/d
Chemical demand (Molar Ratio)	Ca:P = 1	Mg:P = 1

Results: Cost Comparison

Process	Struvite Recovery	Brushite Recovery
CAPEX	$12,161,000	$9,159,00
Annual OPEX	$757,000	$566,000
Annual Revenue	$35,000	$49,000
Annual mass of $P_{removed}$ (lb)	114,763	110,957
Annualized Cost without Product Revenue	$1,745,000	$1,313,000
Annualized Cost with Product Revenue	$1,709,000	$1,274,000
$/lb $P_{removed}$ without Product Revenue	$15.2	$11.8
$/lb $P_{removed}$ with Product Revenue	$14.9	$11.4

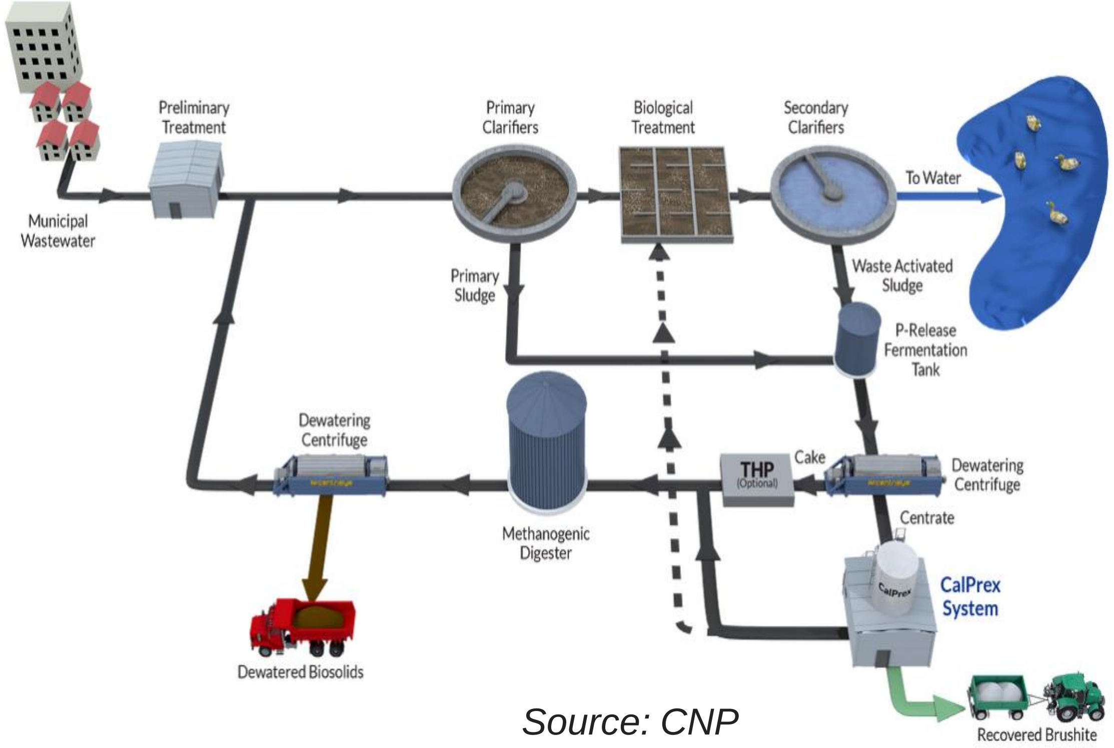
- Brushite recovery has a lower capital cost and is cheaper to operate (the cost of acid phase digester not included)
- Brushite recovery is slightly more cost effective, but this is sensitive to product or offtake value

Results: Sensitivity Analysis



Mode details : S. Arabi, E. Evans , M. Benisch, and C, Bye, Comparison of Struvite and Brushite Recovery: Model Based Technical and Economic Evaluation and Sensitivity Analysis, Proceedings of WEFTEC 2020.

Source: CNP



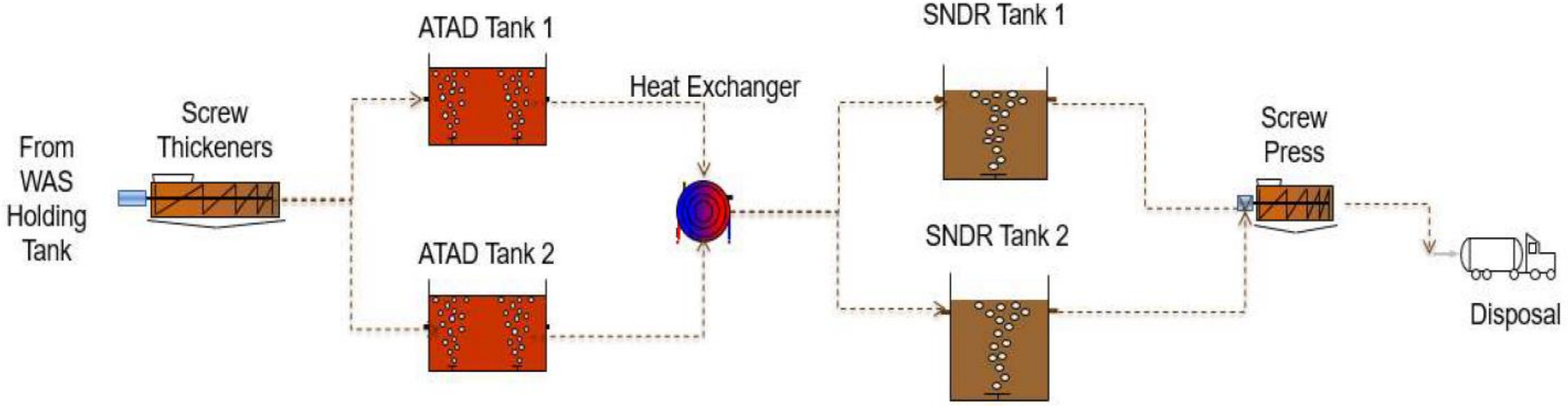
Source: CNP

Case Studies: Feasibility of Brushite Recovery/Sequestration

Case Study 1

Case Study 1 – Facility Background

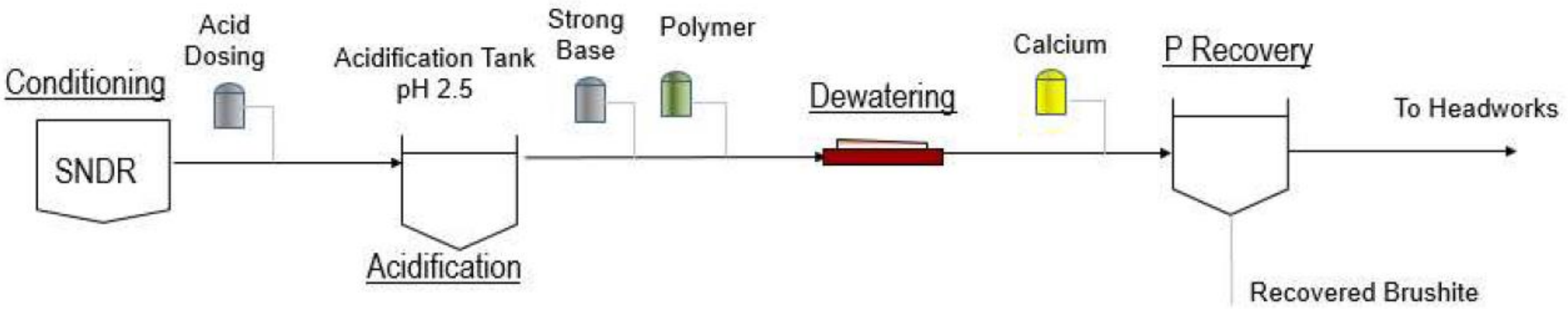
- Facility in central Colorado and is currently under design for expansion to 6 MGD.
- The average influent TP concentration is 7.9 mg/L
- Existing liquid treatment processes is based on an oxidation-ditch system.
- Historically used ferric sulfide for improvement of dewatering



ATAD: Autothermal thermophilic Aerobic Digestion

Case study 1 – Proposed Improvements

- Brushite recovery is proposed instead of struvite recovery given the low pH of the ATAD sludge.
- Modified CalPrex™ system is proposed



Case study 1 – Testing

- ATAD/SNDR samples were taken and tested in the lab by Thermal Process System
- Tested for the proposed solution (acidification, phosphorus release, dewatering and phosphorus capture with brushite crystallization)
- Compared with ferric sulfide and polymer addition.
- Lab testing indicates over 90% soluble P removal using the proposed solution.

Case Study 1- Testing

Parameter	Proposed Solution Value	Current Practice
SNDR Sludge		
Total Solids (%)	2.7	
pH	7.3	
TP (mg/L)	3,554	
SP (mg/L)	1,757	
Acidification		
H_2SO_4 (50%)	0.6 ml/100 ml	--
	265 lb/dry ton	--
Ferric Sulfate Addition		
Ferric sulfate (42%)	--	0.7/100 ml
	--	769 lb/dry ton
Polymer Addition		
EM640LOB Polymer (0.5%)	11 ml/100 ml	29 /100 ml
	53.4 lb/dry ton	141 lb/dry ton
Gravity Dewatering		
Filtrate Ortho-P	2,203	153
Brushite Formation		
Calcium Hydroxide	0.334 g	--
	249 lb/dry ton	--
Filtrate Ortho-P	50 mg/L	--
Ca:P Ratio	1.35	--

Case Study 1

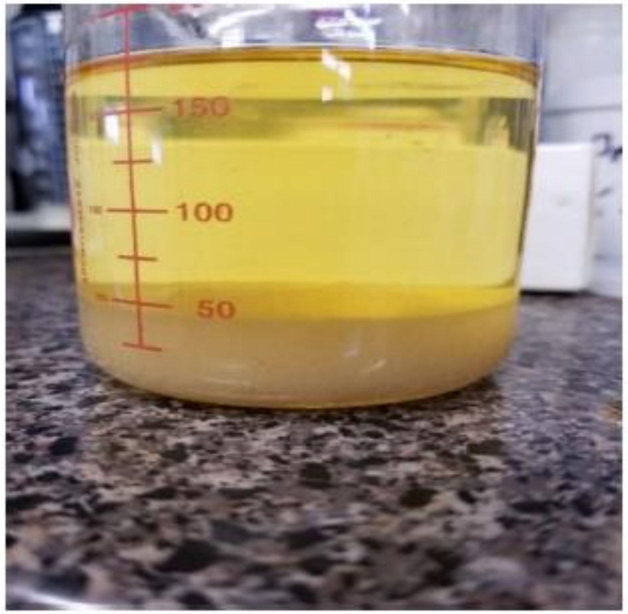
Case Study 1- Testing

Gravity Filtered Cake (Ferric Sulfate and Polymer

Sulfuric Acid and Polymer

P Rich Filtrate

Settled Brushite



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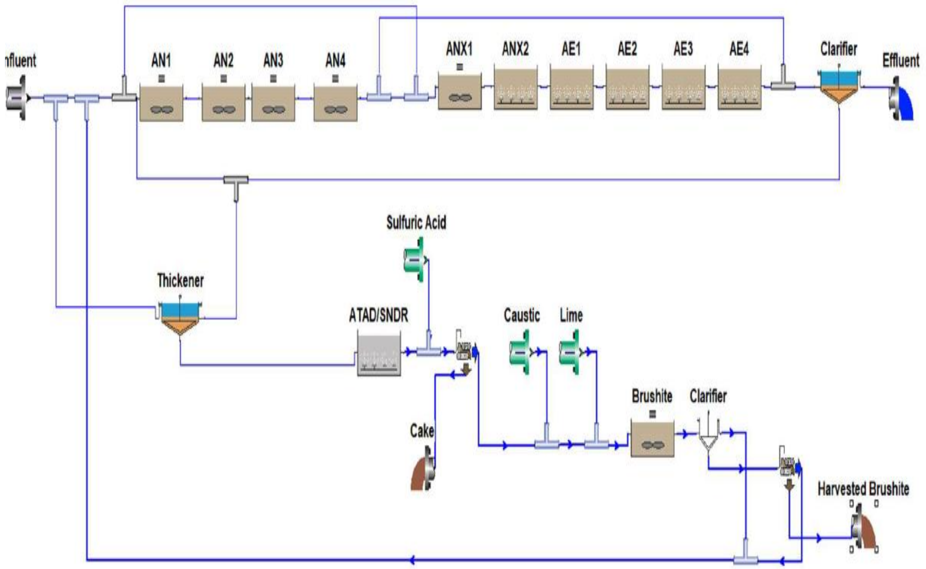
Photos provided by Thermal Process Systems

Case Study 1 - Process Modeling

Parameter	Model Predicted Value	Modified CalPrex™
ATAD/SNDR effluent		
Flow (MGD)	0.02	
Ammonia (mg/L)	263	
TP (mg/L)	800 (144 lbs/day)	
SP (mg/L)	600 (101 lbs/day)	
Sulfuric Acid addition (gpd)	55	30
Caustic addition (gpd) (50%)	0	0
Brushite Reactor		
Effluent SP (mg/L)	53	50
Ca:P Ratio (Lime addition)	1.4	1.4
pH	6.4	
Recovered P (lb/d)	71	82
P Capture %	87%	90%
Brushite Production (lb/d)	406	475



Case Study 1

Case Study 1 – Cost Estimate

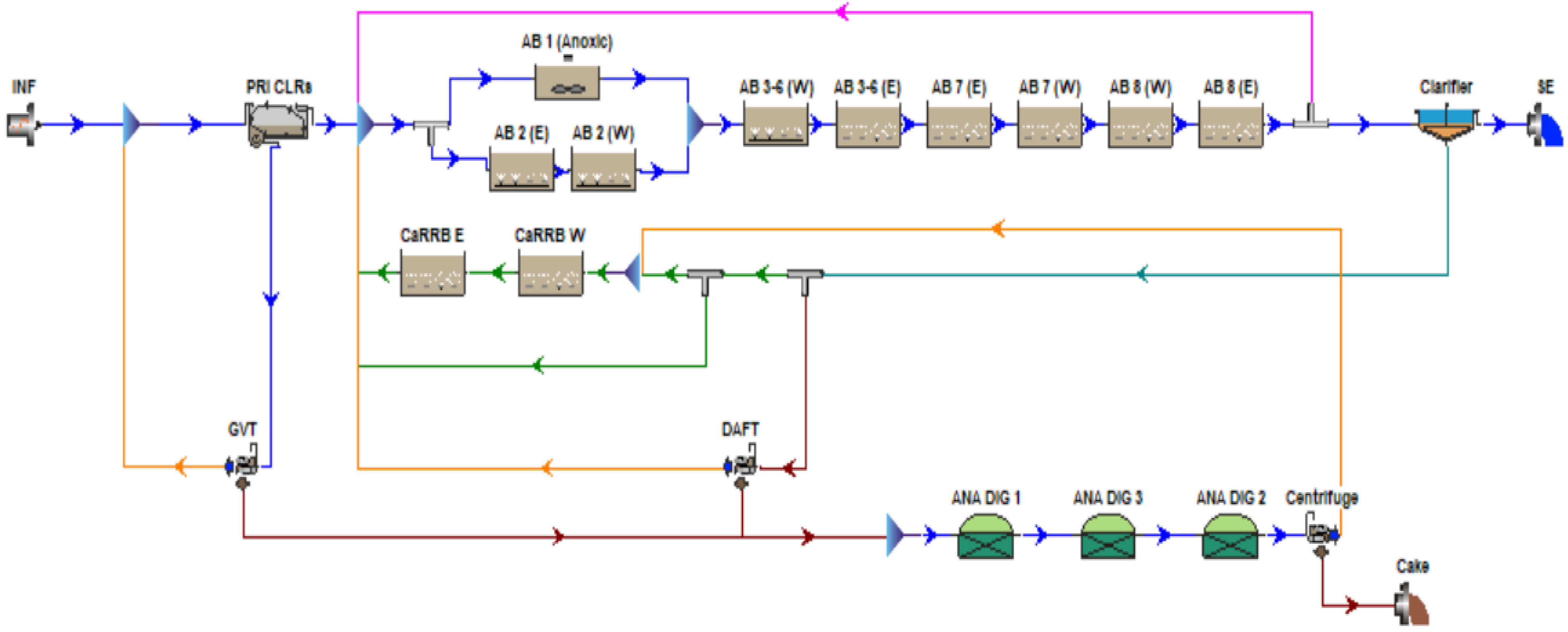
Item	Existing Practice	P Recovery with brushite
CAPEX*	$0	$2,091,700
OPEX **	$587,500	$213,800
NPW	$14,468,00	$7,357,700
Dewatering Chemical Cost		
H_2SO_4 (50%)	---	$44/dry ton
Polymer	$167/dry ton	$64/dry ton
Ferric sulfate	$188/dry ton	---
Calcium hydroxide ***	---	$25/dry ton
Total Chemical Cost	$350/dry ton	$133/dry ton

** includes brushite drying; ** OPEX includes chemical cost, polymer cost, and sludge hauling cost; *** based on 249 Ib/dry ton*

Mode details : S. Arabi, T. Gulliver, C. Bye, M. Tabanpour, and J. Wippo, Brushite Recovery from Autothermal Thermophilic Aerobic Digestion (ATAD) Sludge to Improve Dewatering Characteristics, Proceedings of WEFTEC 2021.

Case Study 2

- Facility in central Colorado with rated capacity of 13 MGD

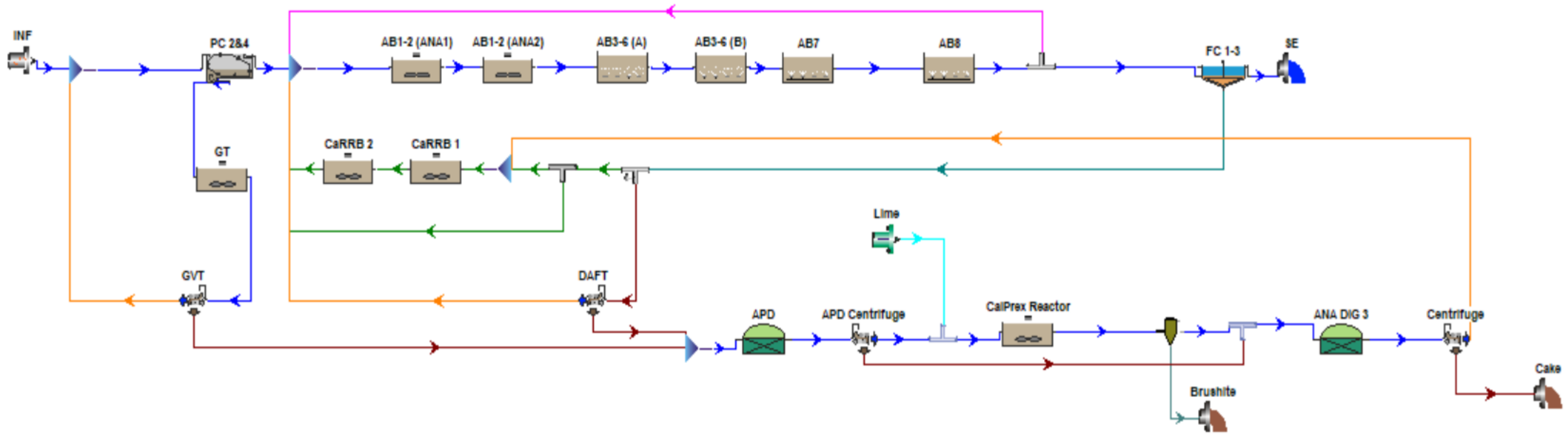


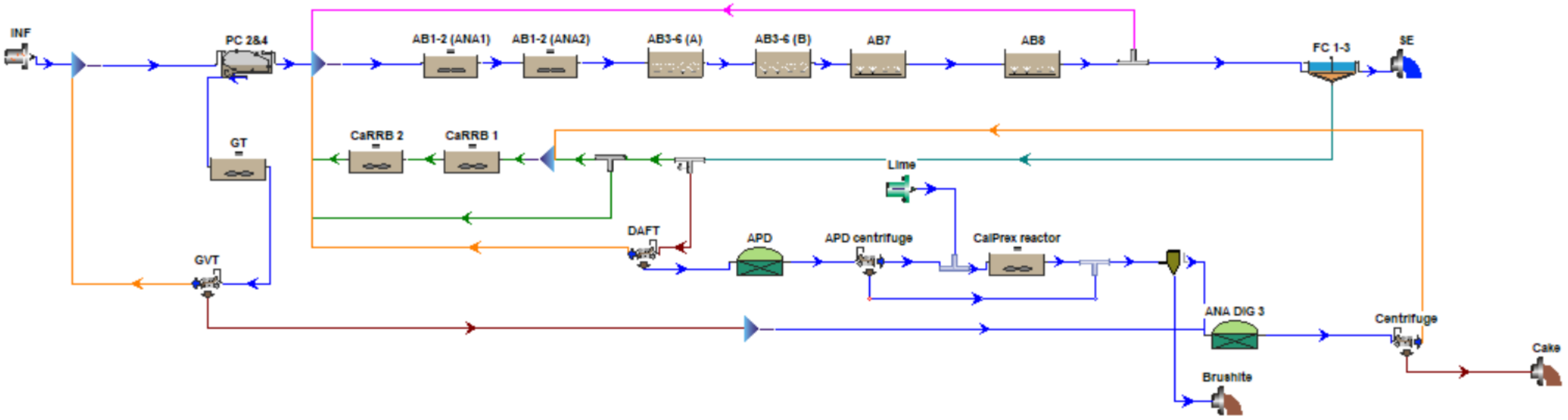
Case Study 2 – Proposed Improvements

- Conversion of sideatream tanks to anaerobic tanks (A2O process)
- Using existing infrastructure for P recovery
- One of the two existing small digesters to be used as acid phase digester
- Existing lime silo
- Existing gravity thickener
- Process modeling for brushite recovery for WAS only and combined sludge

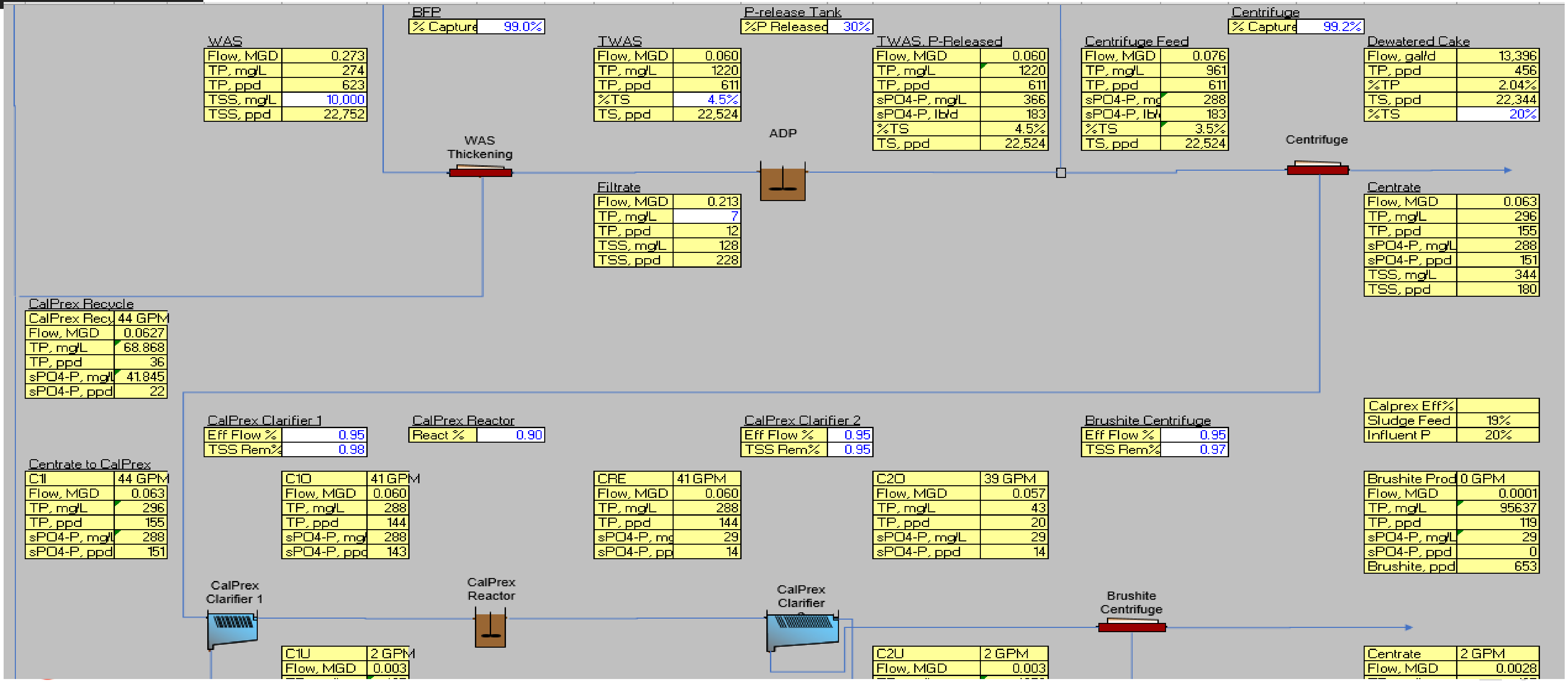
Case Study 2

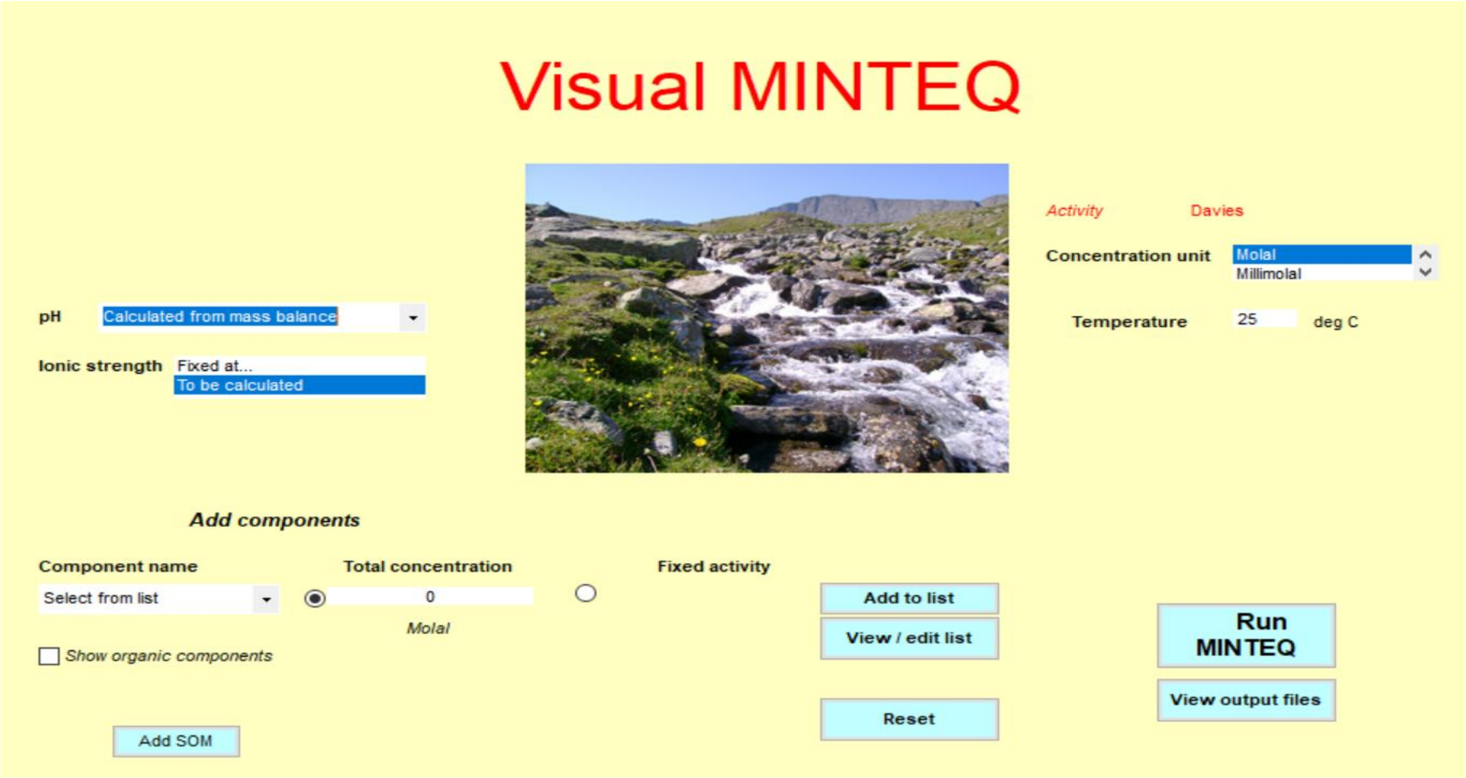
Case Study 2 – Process Modeling





Case Study 2- Mass Balance





Visual MINTEQ Modeling

VISUAL MINTEQ Modeling

- Chemical equilibrium model for calculation of metal speciation, solubility equilibria, equilibrium of solved and dissolved chemicals in aqueous system (Gustafsson, 2008).
- Visual MINTEQ has been used for struvite recovery studies (bench scale testing and/or synthetic wastewater)
- Visual MINTEQ used for brushite precipitation in anaerobic digester effluent and compares the results with BioWin and XRD analysis.

Visual MINTEQ

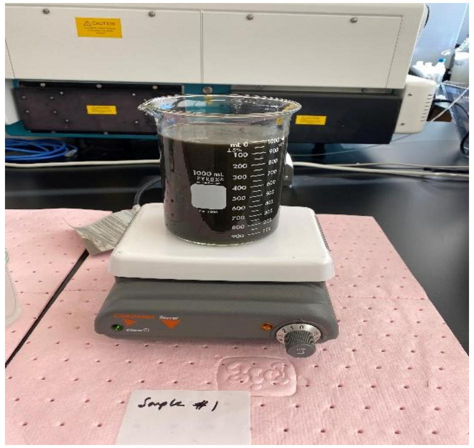
Bench scale Testing and VISUAL MINTEQ Modeling

- Debye–Huckel method for activity correction

- Precipitates employed in the model include struvite, bobierrite, newberyite, monetite, brushite, monetite (DCP), $MgCO_3$, calcite, vivianite, strengite, and ferrous sulfide.

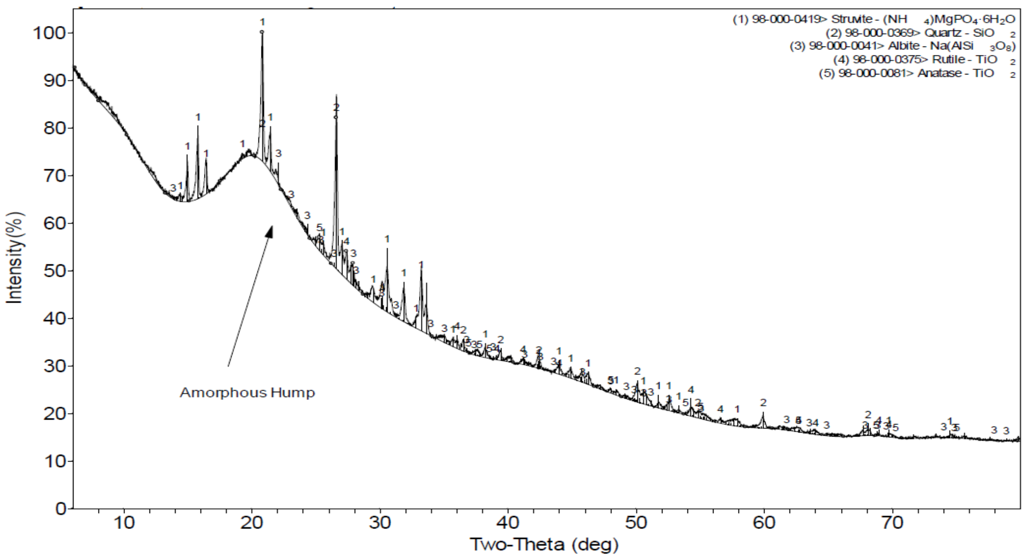
- Sample 2: Ca/P : 1.5
- Sample 3: Ca/P : 2.5
- Sample 4: Ca/P : 3.5

Parameter	Unit	Sample 1
Ammonia	mg/L	1,346
Orthophosphate	mg/L	230
Total Mg	mg/L	97
Total Ca	mg/L	326
Total Fe	mg/L	95
Alkalinity	mg/L as $CaCO_3$	3,300
pH		7.27
Mg/Ca, calculated	mole/mole	0.6



Visual MINTEQ

XRD Analysis



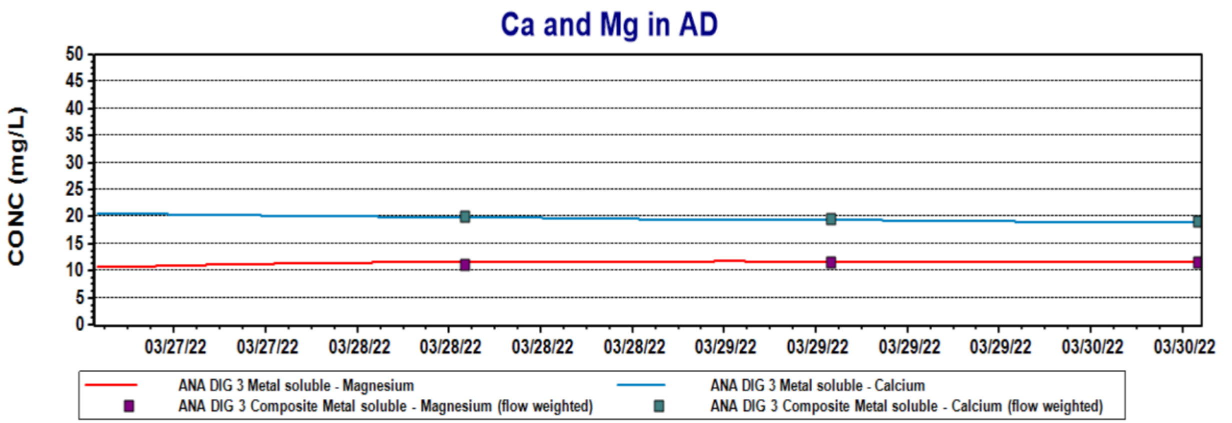
Parameter	Quantitative Crystalline Phase Analysis (wt%)
Sample 1	Quartz (SiO_2): 6.7% Struvite ($NH_4MgPO_4.6H_2O$): 21.2% Albite ($NaAlSi_3O_8$): 3.5% Rutile (TiO_2): 1.2% Anatase: 0.4% Amorphous content: 33%
Sample 2	Quartz (SiO_2): 14.8% Albite ($NaAlSi_3O_8$): 9.9% Rutile (TiO_2): 1.7% Anatase: 0.6% Amorphous content: 27%
Sample 3	Quartz (SiO_2): 17.3% Albite ($NaAlSi_3O_8$): 8% Rutile (TiO_2): 2.0% Anatase: 1.3% Iron (Fe): 6.4% Amorphous content: 35%
Sample 4	Quartz (SiO_2): 12% Albite ($NaAlSi_3O_8$): 5% Rutile (TiO_2): 2.4% Anatase: 0.6% Amorphous content: 20%

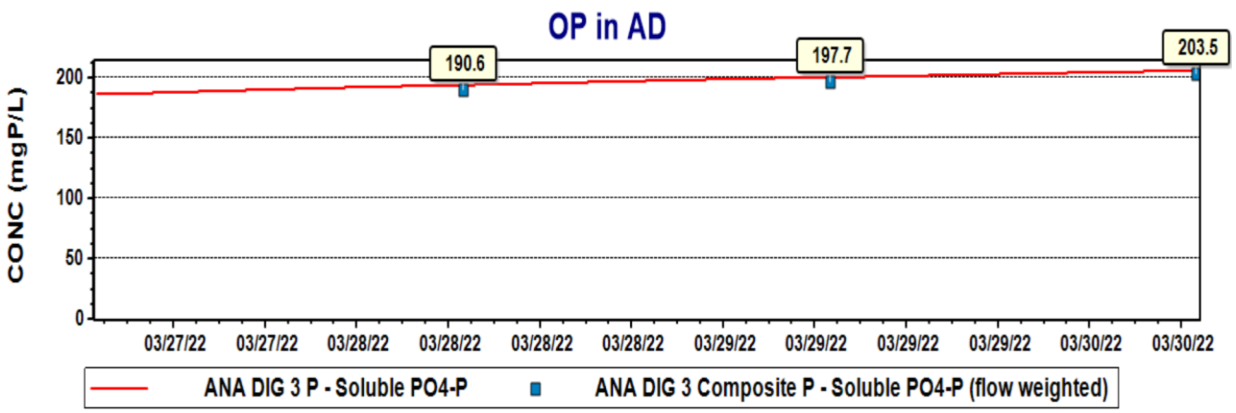
Visual MINTEQ

- For Samples 1-4, Visual MINTEQ predicts calcite being in equilibrium with $CaHPO_4$ (DCP), and vivianite. Struvite present for Sample 1.
- Visual MINTEQ confirmed that the calcium phosphate mass increased with additional of Ca.
- Results of Visual MINTEQ was consistent with XRD analysis indicating that Struvite was predicted in Sample 1 but not in Sample 2-4.

Comparison with BioWin

Visual MINTEQ



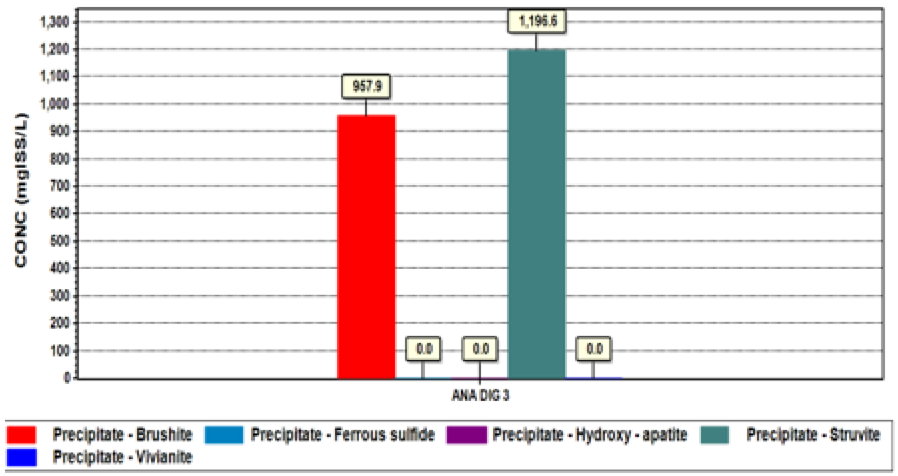


Parameter	BioWin Model Output	Actual Data
Sample 1		
Orthophosphate (mg/L)	206	230
Ammonia (mg/L)	1,100	1,346
pH	7.07	7.2
Alkalinity (mg/L $CaCO_3$)	3,900	3,300
Total Ca (mg/L)	298	326
Total Magnesium	109	97
Total Iron (mg/L)	0	95
Sample 2 – Ca/P: 1.5		
Orthophosphate (mg/L)	57	78
Ortho-P Removal Efficiency %	72%	66%
Sample 3 – Ca/P: 2.5		
Orthophosphate (mg/L)	16	62
Ortho-P Removal Efficiency %	92%	73%
Sample 4- Ca/P: 3.5		
Orthophosphate (mg/L)	9	48
Ortho-P Removal Efficiency %	96%	79%

Visual MINTEQ

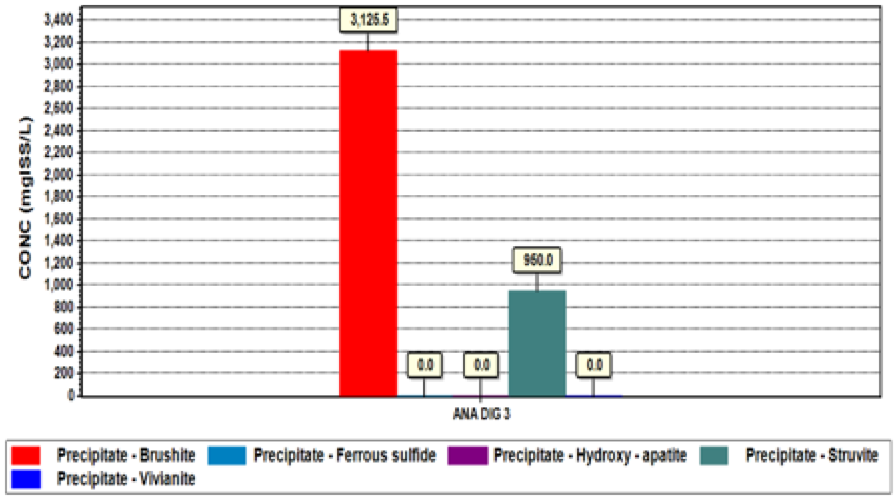
BioWin Modeling

Sample 1



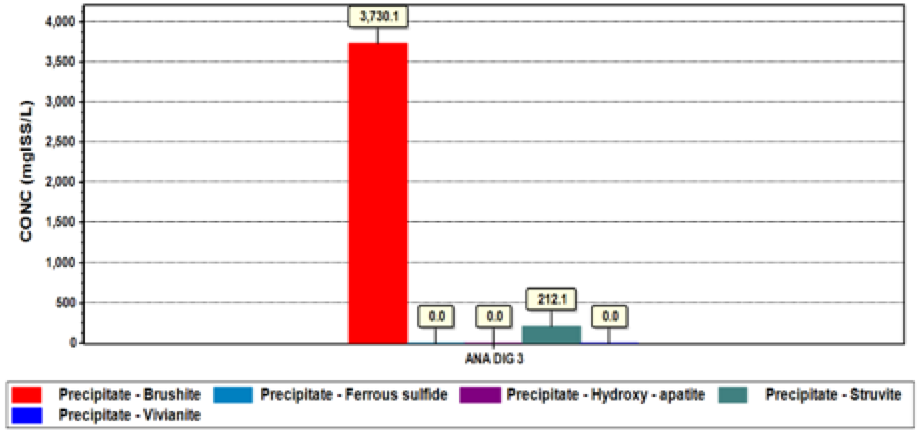
(a)

Sample 2

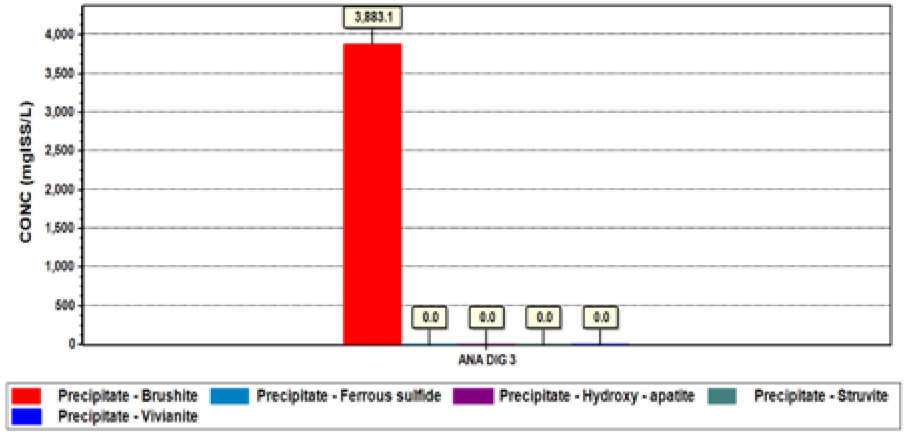


(b)

Sample 3



Sample 4



Visual MINTEQ

Modeling Comparison

Parameter	Visual MINTEQ Predicted OP Reduction %	BioWin Predicted OP Reduction %	Actual OP Reduction %
Sample 2	49%	72%	66%
Sample 3	56%	92%	73%
Sample 4	63%	96%	79%

Parameter	Major Solids Species - XRD	Major Solids Species - BioWin	Major Solids Species – Visual MINTEQ
Sample 1	Calcite, struvite, amorphous content, Albite, Rutile, Anatase, amorphous content (amorphous calcium phosphate)	Brushite Struvite	Stregnite, $CaHPO_4$ (DCP), Calcite, magnetite, struvite, $Ca_3(PO_4)_2$ (beta)
Sample 2	Calcite, amorphous content, Albite, Rutile, Anatase, amorphous content (amorphous calcium phosphate)	Brushite Struvite	Stregnite, $CaHPO_4$ (DCP), Calcite, magnetite, $Ca_3(PO_4)_2$ (am2), $Ca_3(PO_4)_2$ (beta)
Sample 3	Calcite, amorphous content, Albite, Rutile, Anatase, amorphous content (amorphous calcium phosphate))	Brushite Struvite	Stregnite, $CaHPO_4$ (DCP), Calcite, magnetite, $Ca_3(PO_4)_2$ (am2), $Ca_3(PO_4)_2$ (beta)
Sample 4	Calcite, amorphous content, Albite, Rutile, Anatase, amorphous content (amorphous calcium phosphate)	Brushite	Stregnite, $CaHPO_4$ (DCP), Calcite, magnetite, $Ca_3(PO_4)_2$ (am2), $Ca_3(PO_4)_2$ (beta)

Summary

- Modeling tools compared reasonably well with the actual data and technology provider design basis.
- While both brushite and struvite recovery are viable P-recovery options, for the testing conditions modeled in this paper, brushite recovery appears to be more cost effective ($/lb $P_{removed}$).
- Final choice between these two products mainly depends on process requirements and final application of the recovered product.
- Visual MINTEQ can be helpful in predicting the precipitation of brushite and other phosphate-bearing minerals (not a kinetic model)
- Default parameters available in BioWin provide a reasonable prediction of phosphorus removal performance for process engineering purposes for brushite recovery/sequestration

Questions

Thank you

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