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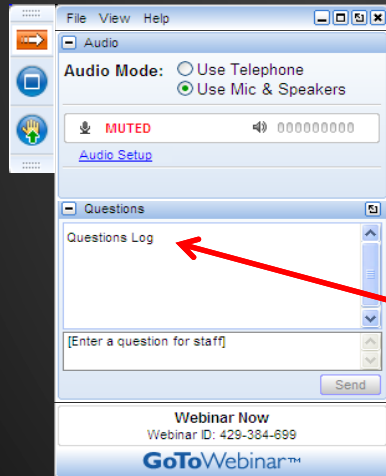
**Understanding And Modeling
Solids Stream Phosphorus
Release, Precipitation, And
Solids Handling**

Thursday, January 24, 2019
1:00 - 3:00 PM ET

The Water Environment Federation logo is located in the bottom right corner of the slide. It features the same stylized 'W' icon and text as seen in the first slide.

2

How to Participate Today



- **Audio Modes**
 - Listen using Mic & Speakers
 - Or, select "Use Telephone" and dial the conference (please remember long distance phone charges apply).
- Submit your questions using the Questions pane.
- A recording will be available for replay shortly after this webcast.



3

Today's Moderator

John B. Copp Ph.D.
Primodal Inc.
 Hamilton, Ontario



4

Solids Stream P – Jan. 24, 2019

An MRRDC Short Course
Solids Stream Phosphorus Modeling

• Topics:

- Basics of Phosphorus Removal
- Phosphorus Issues in the Solids Stream
- Digestion Phosphorus Chemistry
- Dewatering Impacts & Mitigation



5

Solids Stream P – Jan. 24, 2019

An MRRDC Short Course
Solids Stream Phosphorus Modeling

• Speakers:



**Patrick
Dunlap**
Black & Veatch



**Murthy
Kasi**
Smith & Loveless



**Hélène
Hauduc**
Dynamita



**Mario
Benisch**
HDR



6

Our Next Speaker



Patrick Dunlap, MS, PE
Process Engineer
Denver CO



7

Liquid Stream P Removal

Background to Impact on Residuals



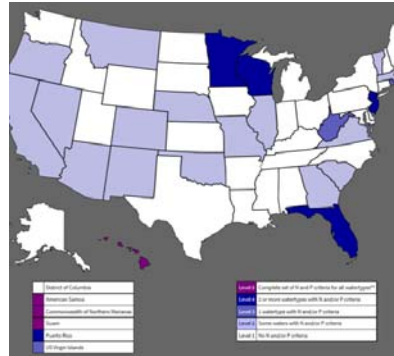
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Phosphorus Removal

Eutrophication



Phosphorus Limits



EPA, 2017

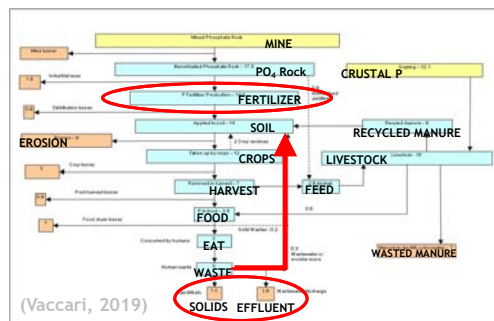


9

Phosphorus Scarcity

- Several hundred years of economically recoverable P reserved at current usage rates
- ... but the two largest P fertilizer producers (USA & China) will run out or recoverable reserves at current production rates within decades
- P Recovery potential at WWTPs is an important part of managing this challenge

USGS 2017 Report	2017 Prod (Mt/yr)	Prod % of global	Reserves (Mt)	Reserves % of global	Life (yrs)
Morocco_and_Western_Sahara	27	10%	50,000	71%	1,852
China	140	53%	3,300	5%	24
United_States	28	11%	1,000	1%	36
Rest of the World	68	26%	15,939	22%	234
World_total_(rounded)	263	100%	70,000	100%	266



(Vaccari, 2019)



10

Chemical vs Biological P Removal

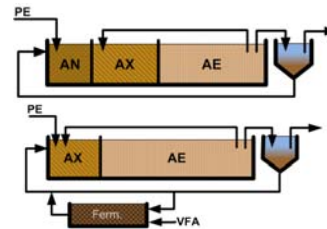
Chemical P Removal

- Consistent Performance
- Less disruptive/simpler operation
- Additional operational cost for chemical & residuals disposal
- Nuisance precipitates



Biological P Removal

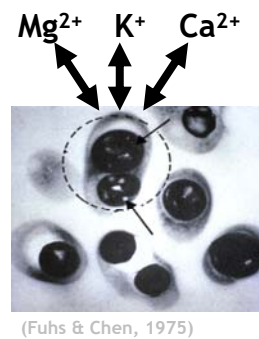
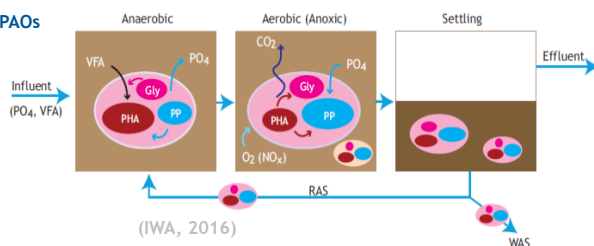
- Lower operational cost
- Creates opportunity for P Recovery
- Requires additional bioreactor vol.
- Dewatering Impacted
- Nuisance precipitates



11

Enhanced Biological Phosphorus Removal (EBPR)

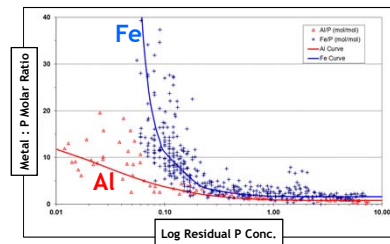
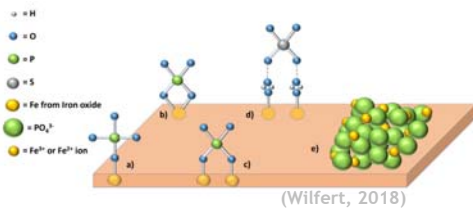
PAOs



12

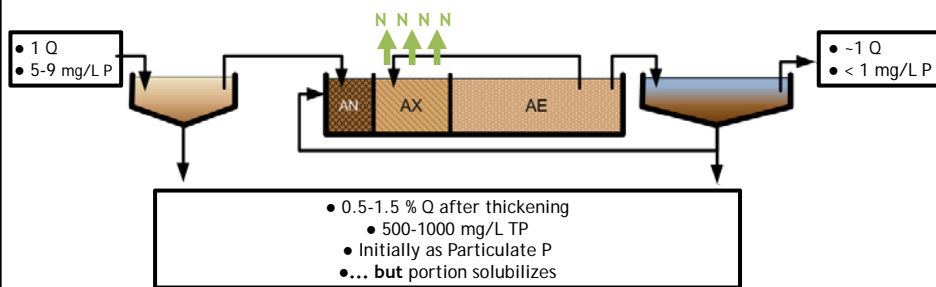
Chemical P Removal

- Phosphorus is removed by metal coagulants (Alum/Ferric) through co-precipitation and adsorption
- Metal:P molar ratio for additional removal increases lower PO_4 -P concentrations.



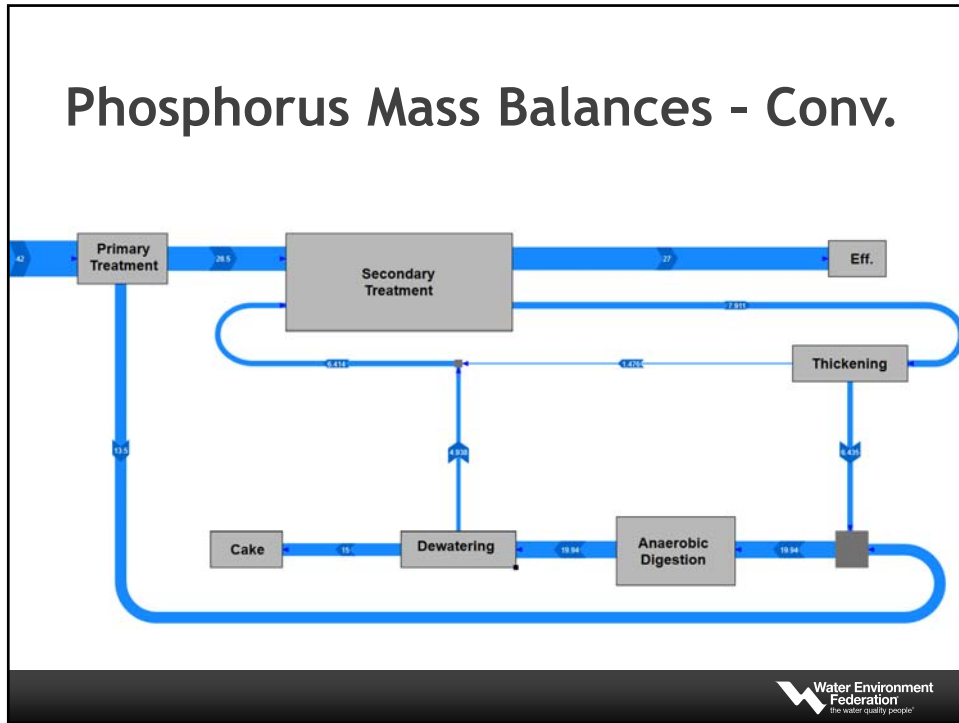
13

Nitrogen vs Phosphorus Removal



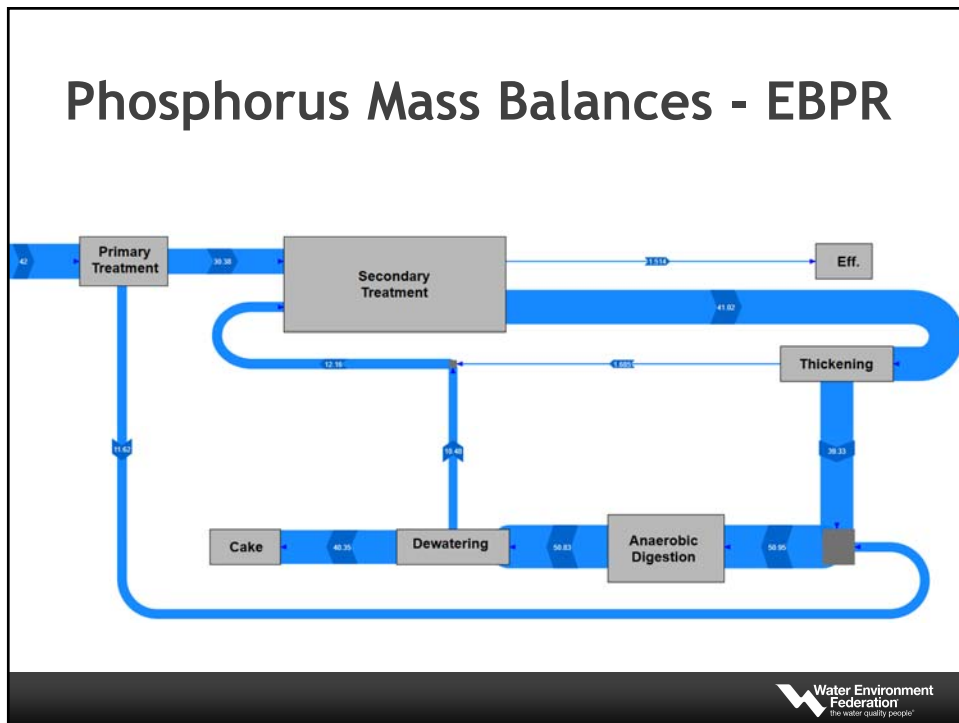
14

Phosphorus Mass Balances - Conv.

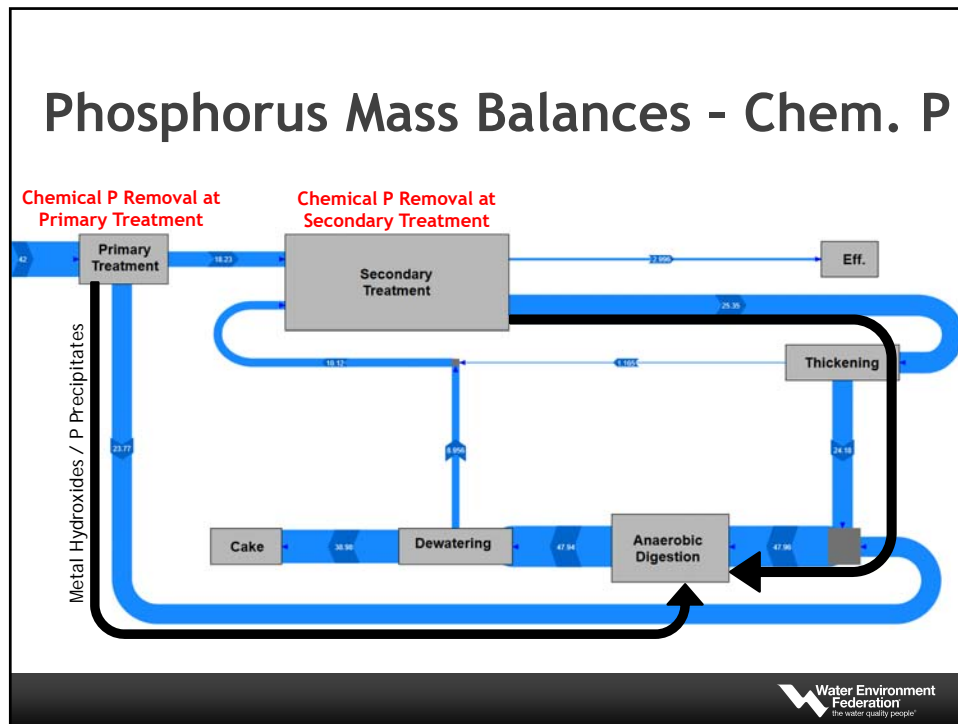


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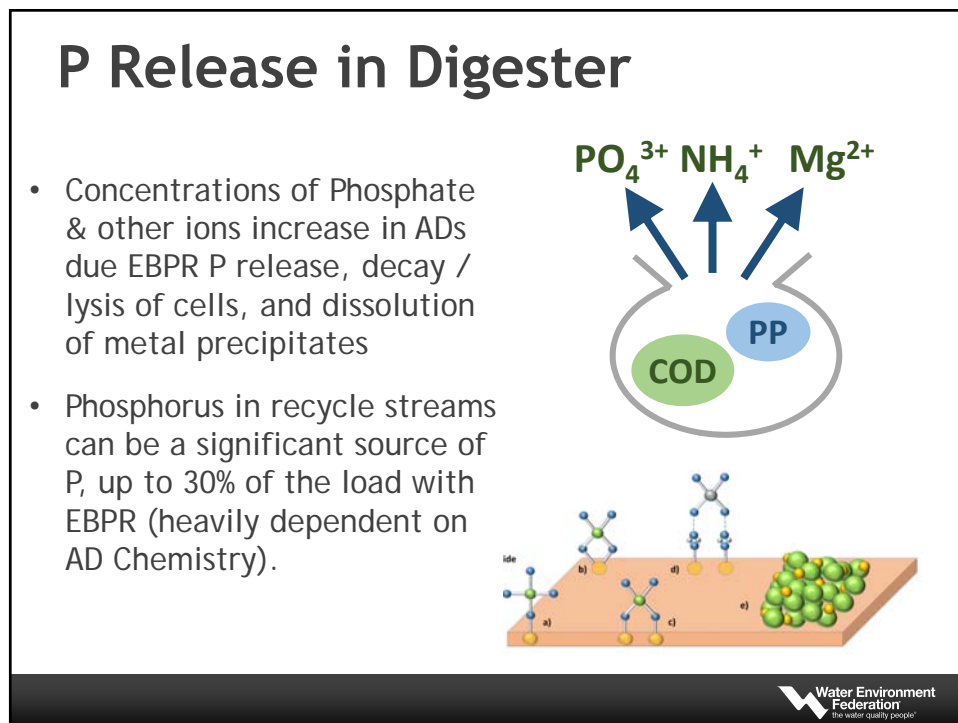
Phosphorus Mass Balances - EBPR



16

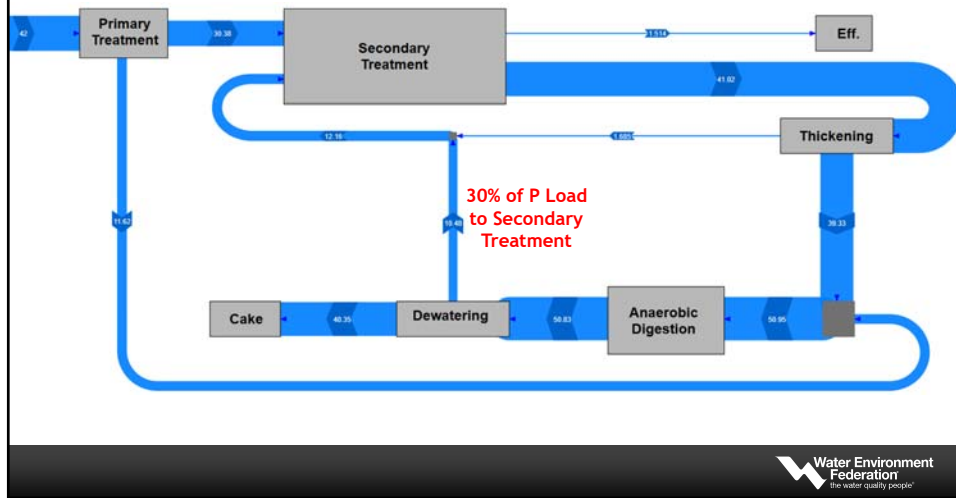


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18

Phosphorus Mass Balances - Recycles



19

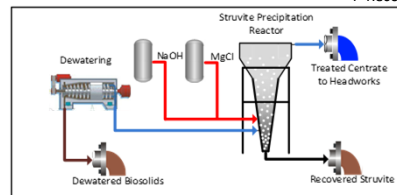
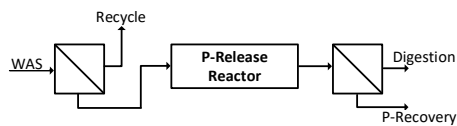
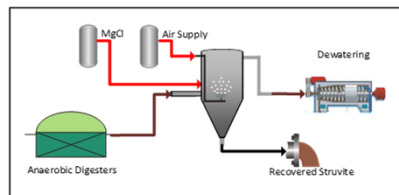
Recycle Phosphorus Management

Options for recycle stream P reduction

- Addition of coagulants to digesters
- Addition of coagulants to dewatering

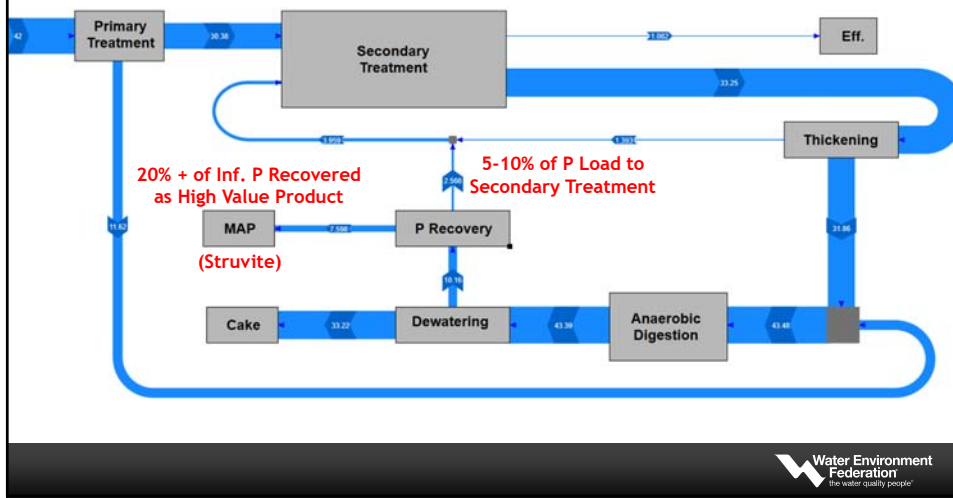
Options for recycle stream P reduction/recovery

- Phosphorus recovery (struvite/brushite precip.)
- Pre-digester P release w/ recovery



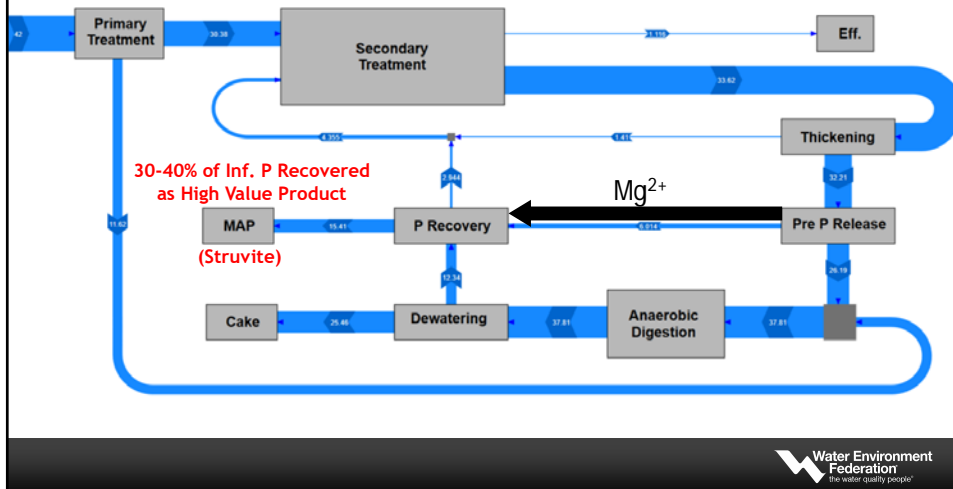
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Impact of P Recovery

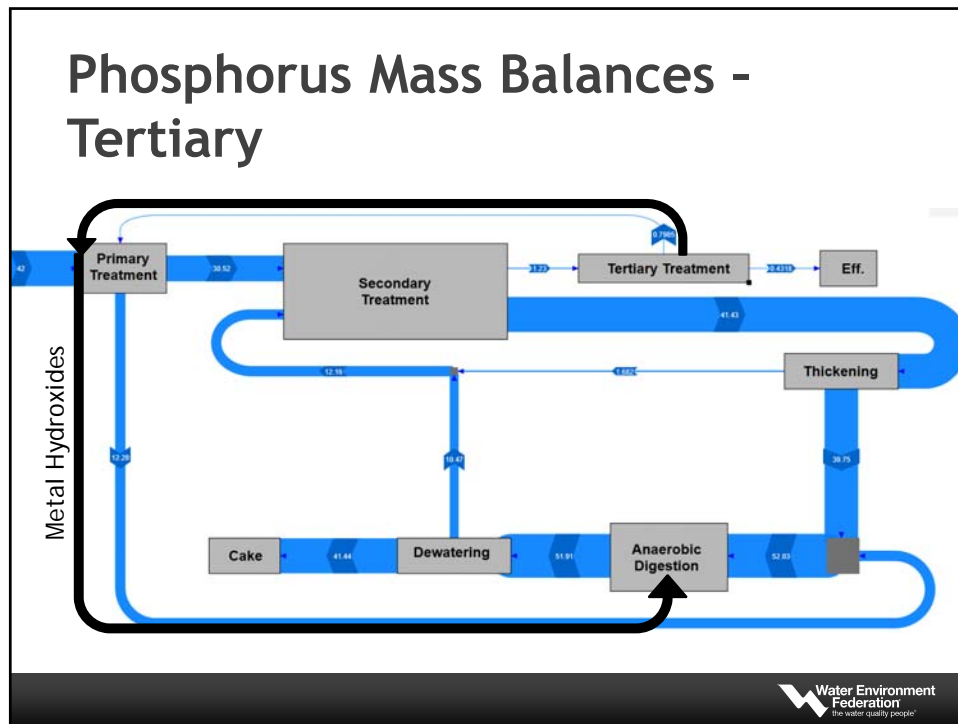


21

Impact of P Pre-Release / Recovery



22



23

Conclusions

- When P is removed from the mainstream it is sent to residuals in concentrated forms
- How P is removed in the mainstream will impact the form of P sent to residuals and other ions (Fe, Al, Mg, K Ca) which go along
- This can cause problems with nuisance precipitates and dewatering performance
- Heavily dependent on digester chemistry

24

Our Next Speaker



Murthy Kasi, PhD, PE
Process Engineering Manager
Lenexa, KS



Smith & Loveless Inc.



25

Phosphorus Precipitates: Nuisance and Mitigation



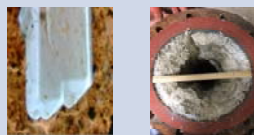


26

Outline

- Phosphorus Precipitates & Formation
- Operational Impacts
- Mitigation Strategies

27

Common Phosphorus Precipitates

Magnesium-based	Iron-based	Calcium-based
Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) <i>Magnesium Ammonium Phosphate</i>	Vivianite $(\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O})$ <i>Ferrous (Fe^{2+}) based</i>	Hydroxylapatite $\text{Ca}_5\text{H}(\text{PO}_4)_3\text{OH}$
		
	Strengite $(\text{FePO}_4 \cdot 2\text{H}_2\text{O})$ <i>Ferric (Fe^{3+}) based</i>	Octacalcium Phosphate $\text{Ca}_8\text{H}_2(\text{PO}_4)_6\text{OH}$
		Brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$

28

Where in Wastewater Treatment do these form?

Unintentional Precipitation is a **Nuisance**

Struvite is the most common nuisance

- Anaerobic digesters
- Digested sludge piping, valves, pumps, and mixers
- Dewatering equipment
- Filtrate and centrate piping, valves and pumps
- Rough surfaces preferred

29

What Promotes Phosphorus Precipitation?

- Concentrations of chemical species (e.g. Mg^{+2} , PO_4^{-3} , NH_4^+ , etc.)
- pH
- Temperature

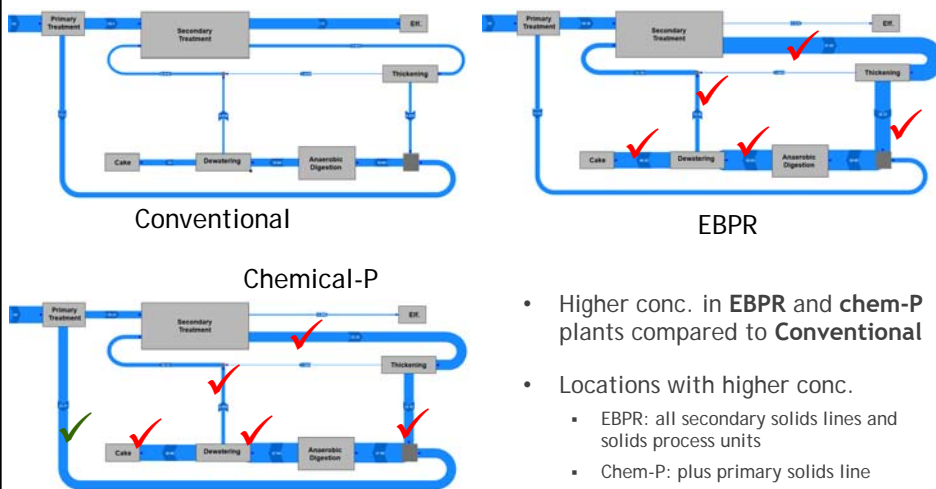
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Chemical Species for Phosphorus Precipitates

Struvite ($MgNH_4PO_4 \cdot 6H_2O$)	Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$)	Hydroxyapatite ($Ca_5H(PO_4)_3OH$)
	Strengite ($FePO_4 \cdot 2H_2O$)	Octacalcium Phosphate $Ca_8H_2(PO_4)_6$
		Brushite $CaHPO_4 \cdot 2H_2O$
Mg	Fe^{2+} or Fe^{3+}	Ca^{2+}
NH_4^+	PO_4^{-3}	PO_4^{-3} or HPO_4^{-2}
PO_4^{-3}		

31

Chemical Species Generation in Wastewater Treatment Processes



- Higher conc. in **EBPR** and **chem-P** plants compared to **Conventional**
- Locations with higher conc.
 - EBPR: all secondary solids lines and solids process units
 - Chem-P: plus primary solids line

32

Concentrations in Solids Streams

- Several factors impact concentrations of chemical species in solids streams
 - Efficiency Thickening prior to digestion % solids - 4, 5, 6, etc.
 - Thermal hydrolysis process included? increased digestion and higher orthophosphate
 - WASSTRIP Orthophosphate extracted from WAS before sent to digesters
 - Chemical type and addition points for phosphorus removal Iron, aluminum, cerium; Primary clarifier, aeration basins, secondary clarifiers



33

Concentrations in Anaerobic Digester

Concentrations for a specific scenario are presented here

Assumptions for the following Table:

- 4% Total Solids in Digester Feed for all 3 treatments
- No WASSTRIP
- Chemically Enhanced Primary Treatment with Fe-based salts

Treatment →	Conventional	EBPR	Chemical P (CEPT)*
Chemical Species ↓			
Mg ⁺² (mg/L)	40	→	140
Fe ⁺² or Fe ⁺³ (mg/L)	300		300
Ca ²⁺ (mg/L)	150	→	200
NH ₄ ⁺ (mg N/L)	1,100		1,100
PO ₄ ⁻³ (mg P/L)	300	→	750

*No Bio-P



34

pH & Temperature

Location in Wastewater Treatment Plant	pH	Temperature
Liquid Processes (raw influent, primary clarifiers, aeration basins, etc.)	6.7 to 8	10 to 25°C
Solids Processes (thickening, digestion, dewatering, phosphorus release, etc.)	6.5 to 7.5	35 to 55°C

35

Struvite Formation - Example Scenario

Consider the following concentrations in an anaerobic digester:



$Mg^{2+} = 40 \text{ mg/L}$
 $NH_4^+ = 1,100 \text{ mg/L}$
 $PO_4^{3-} = 300 \text{ mg/L}$

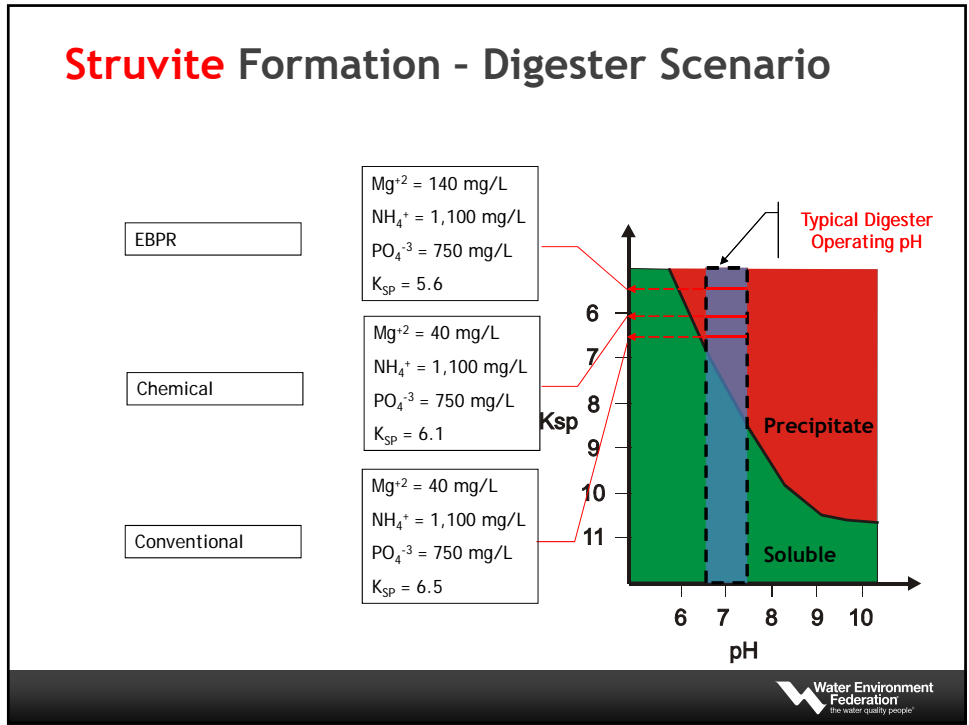
C in mol/L

$$K_{sp} = -\log\left([C_{Mg^{2+}}] \cdot [C_{NH_4^+}] \cdot [C_{PO_4^{3-}}]\right)$$

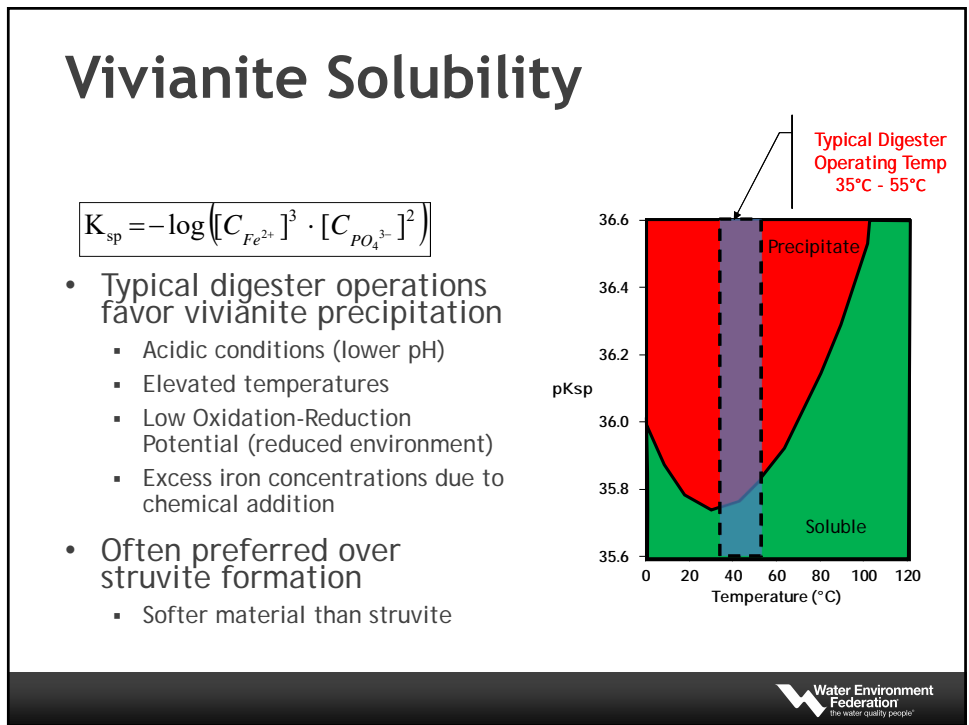
$$K_{sp} = -\log\left(\frac{40 \frac{\text{mg}}{\text{L}}}{24 \frac{\text{g}}{\text{mol}} \cdot 1000 \frac{\text{mg}}{\text{g}}} \cdot \frac{1100 \frac{\text{mg}}{\text{L}}}{18 \frac{\text{g}}{\text{mol}} \cdot 1000 \frac{\text{mg}}{\text{g}}} \cdot \frac{300 \frac{\text{mg}}{\text{L}}}{96 \frac{\text{g}}{\text{mol}} \cdot 1000 \frac{\text{mg}}{\text{g}}}\right)$$

$$K_{sp} = 6.5$$

36



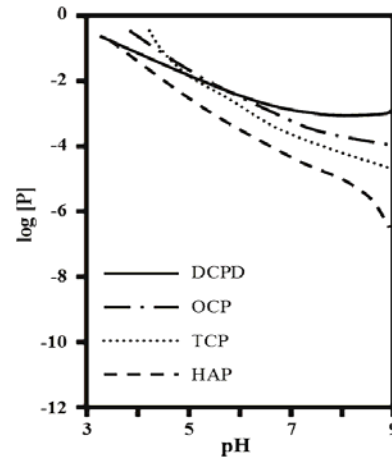
37



38

Calcium Phosphates Solubility

- Can be problematic in hard waters with high Ca^{+2} concentrations
- Struvite and vivianite have greater phosphorus precipitation potential than calcium phosphates, especially in low pH conditions



39

Nuisance or Resource??

Unintentional precipitation
can be a nuisance

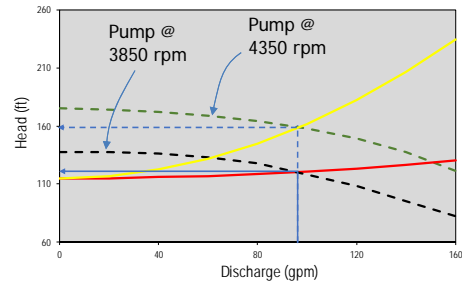
40

Impact on Plant Operation - Pipes & Pumps



Deposits in pipes

Meridian, ID
Wastewater Resource Recovery Facility



Reduction of pipe diameter changes system curve

- Higher energy cost
- Reduced equipment life
- Reduced capacity



41

Impact on Plant Operations - various processes/equipment

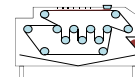
- **Digesters**

- Decrease of mixer speeds due to struvite deposits on blades and impellers
- Decrease in digester capacity and increased heating requirements



- **Dewatering**

- Decrease in filter press efficiency due to filter blinding; increased filter press operational time



42

Impact on Plant Operation



Deposits on digester wall



Deposits on mixer blade
in dewatering centrate
storage tanks



Deposits on belt
filter press rollers

43

Conditions Leading to Phosphorus Precipitation

Struvite

- Excess concentrations of Mg^{+2} , NH_4^+ , and PO_4^{-3}
- Increased pH of solution
- Turbulence
- Stripping of CO_2
- Rough surfaces

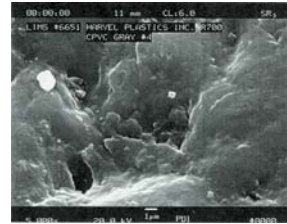
Fe-phosphates

- Excess iron and PO_4^{-3} concentrations
- Lower pH conditions
- Elevated temperatures

44

Struvite Control

- Minimize CO2 stripping
- Short straight pipes
- Cleaning loops
- Removable pipe lining
- Pinch valves
- Selecting right pipe material
- Magnesium dosing (1.3 Mg:1P)
- Iron salts addition (1.5 Fe:1P)
- pH adjustment (reduce pH to <7.5)



CPVC (5000 x)



Spears LXT (5000 x)

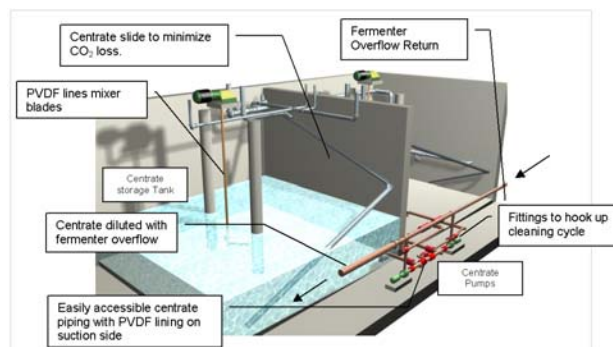
(C) Photos by SPEARS Inc



45

Facility Design Example

- Benefits:
 - Optimized Bio-P
 - Alum use was reduced from 150 to 20 ppm
 - FeCl3 costs reduced by \$15,000/yr



Centrate storage and conveyance system at Durham AWWTP and its struvite control features

Source: Baur, R., Benisch, M., Clark, D., Sprick, R.G., Struvite Control- Dealing With A Common and Nuisance, WEFTEC 2002



46

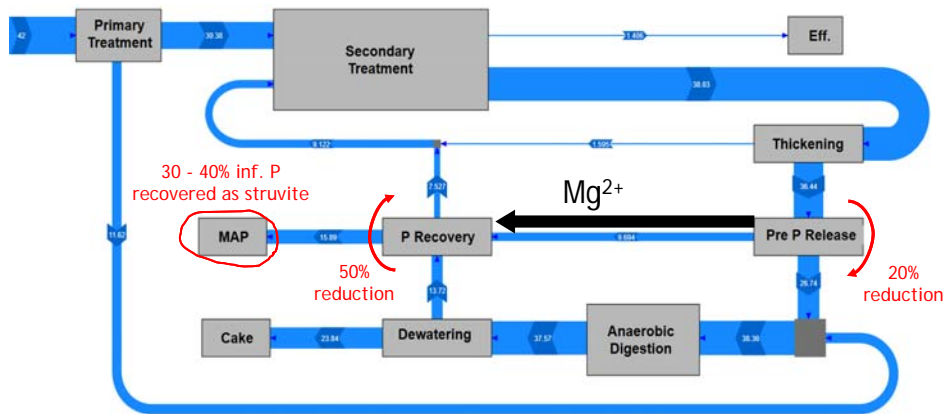
Other options?

Intentional Phosphorus Precipitation?

47

Phosphorus Recovery Benefits

- Reduces phosphorus concentrations in solids streams to anaerobic digester and dewatering processes
- Reduces the internal phosphorus recycle



48

Recovery Options

- Can be recovered in all three forms
 - Struvite (magnesium-based)
 - Brushite or hydroxyapatite (calcium-based)
 - Vivianite (iron-based)
- Recovery as struvite is the most common
 - Commercial recovery methods available for Ca-P
 - Recovery as Fe-P is still in research stage

P-recovery Methods

- | As struvite | As calcium phosphates | As sludge ashes |
|---|---|--|
| <ul style="list-style-type: none"> • Ostara® • Multiform harvest™ • Struvia™ • AirPrex™ • NuReSys™ • DHV Crystalactor | <ul style="list-style-type: none"> • P-Roc® • CalPrex™ • Quick Wash® • ExtraPhos® | <ul style="list-style-type: none"> • EcoPhos® <ul style="list-style-type: none"> ▪ Extracts as H₃PO₄ or Calcium phosphate • P-Bac (Incore)® <ul style="list-style-type: none"> ▪ Extracts as Struvite or Calcium phosphate |

For additional information:
 Law and Pagilla (2018) Phosphorus Recovery by Methods
 Beyond Struvite Precipitation, Water Environment Research, 2018, 90(9): 840-850

P-recovery Economics

	Struvite	Calcium phosphates
Recovery	80 to 90%	50 to 100%
Capital costs	\$28 to \$280 per ton per day	\$3.5 to \$4.5 per ton per day
Market value	\$50 to \$1,800 per ton	n/a

1 ton = 2,000 lb

Source: Vaneekhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P. A., Tack, F. M., & Meers, E. (2017). Nutrient recovery from digestate: systematic technology review and product classification. *Waste and Biomass Valorization*, 8(1), 21-40.



51

Conclusions

- EBPR or chemical-P removal:
 - Increase in concentrations of phosphorus precipitating species in solids streams
 - Struvite (magnesium-based phosphate) formation is the major nuisance
- Control options should be carefully evaluated before selection
 - Addition of iron salts - secondary nuisance due to vivianite formation; increased sludge production; high chemical costs; decreased P recovery
 - pH control by acid addition - agitation due to pumping and mixing still causes increase in pH
 - Proper pipe material - scratches/roughness over time favors struvite formation



52

Conclusions

- P-recovery can minimize impacts on downstream unit processes, e.g. digester, dewatering equipment
 - May still require chemical addition to control struvite in digesters
- Several commercial P-recovery options are available



53

Our Next Speaker



H el ene Hauduc, PhD

Senior Process Engineer

Toulouse, France



54

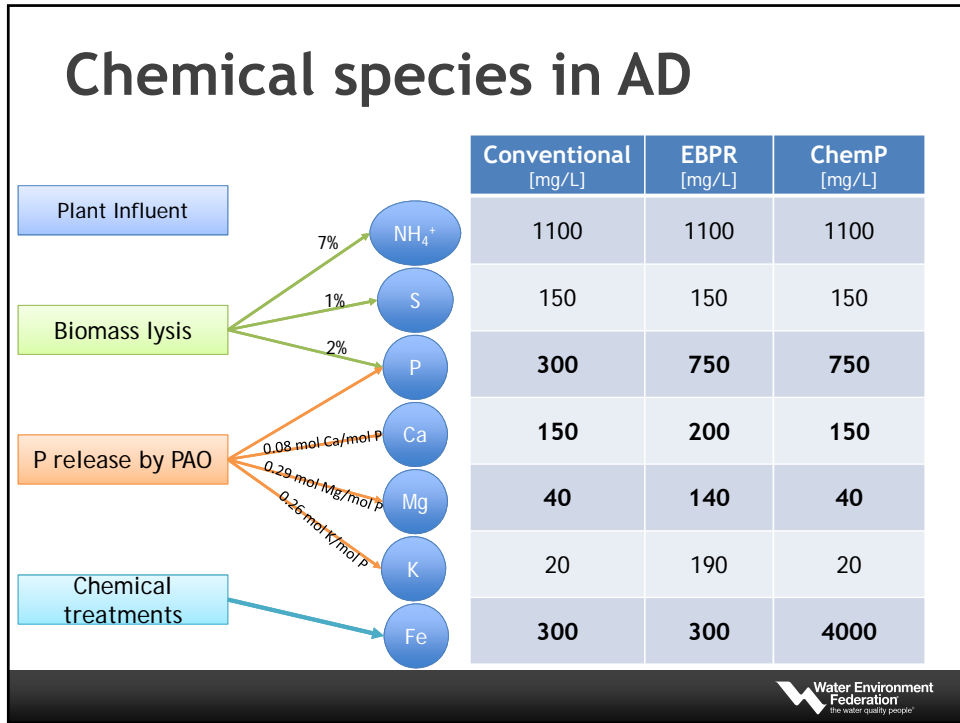
Chemical Processes in Anaerobic Digesters

55

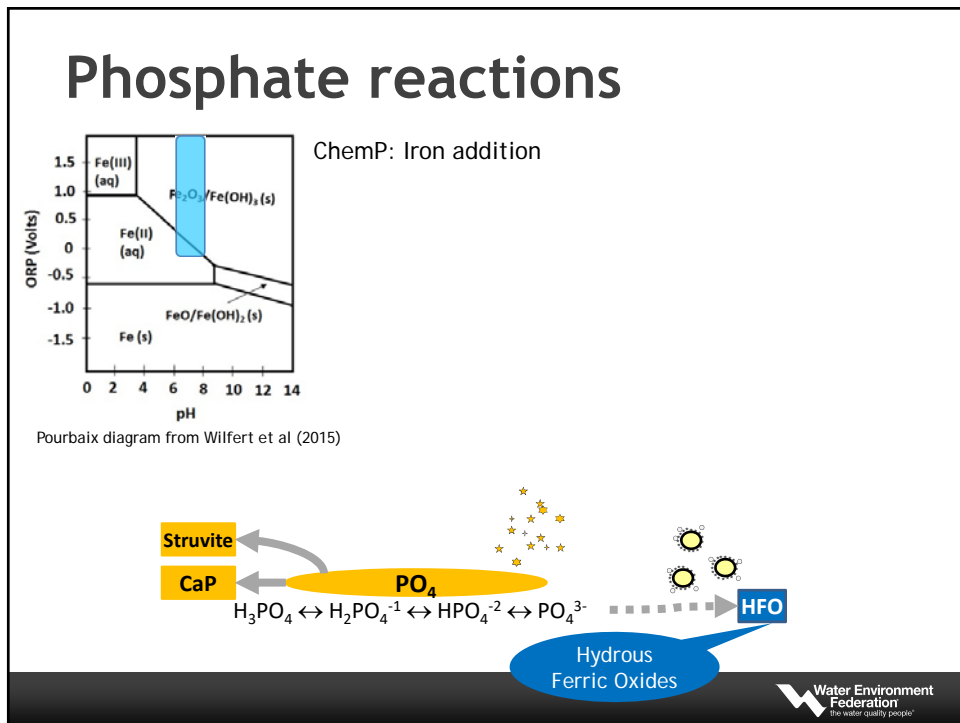
Outline

- P from EBPR and ChemP in AD
- Interactions between P, S and Fe cycles
- Mitigation Strategies
- Comprehensive model of relevant AD reactions

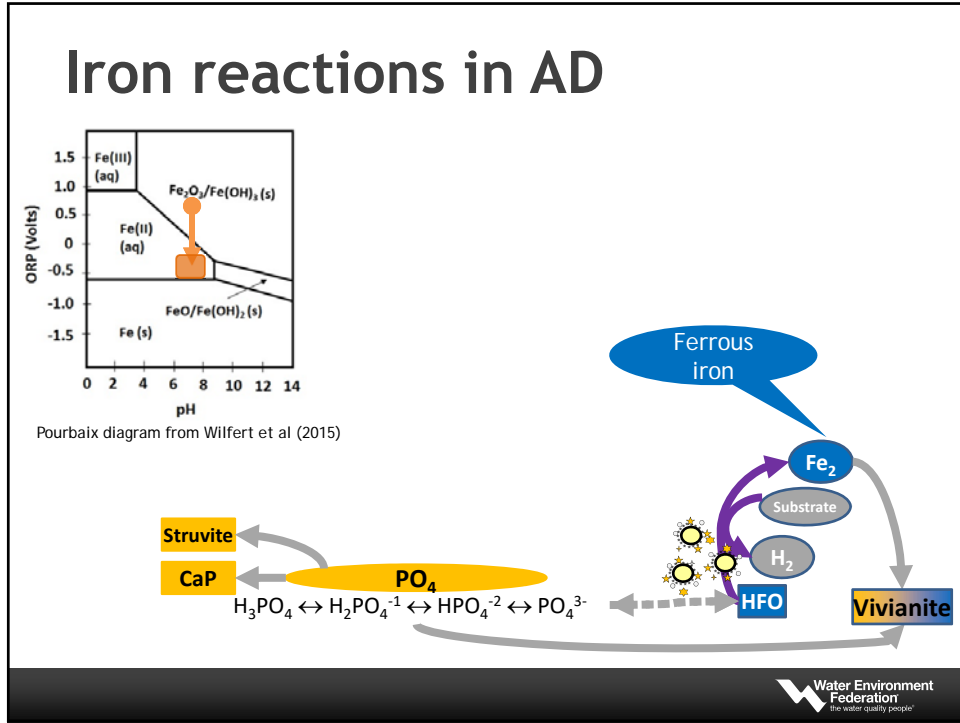
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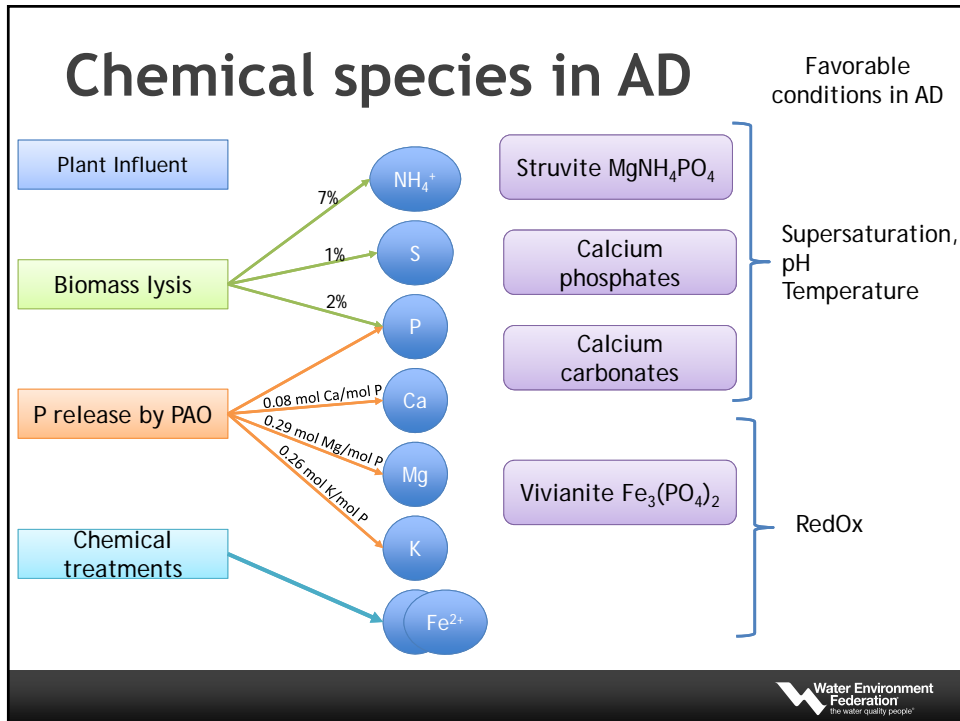
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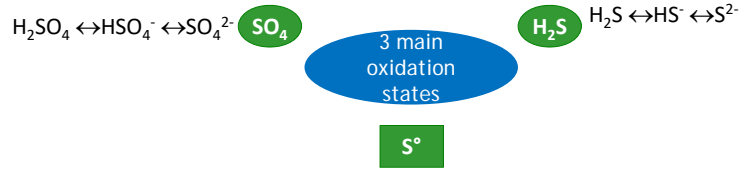


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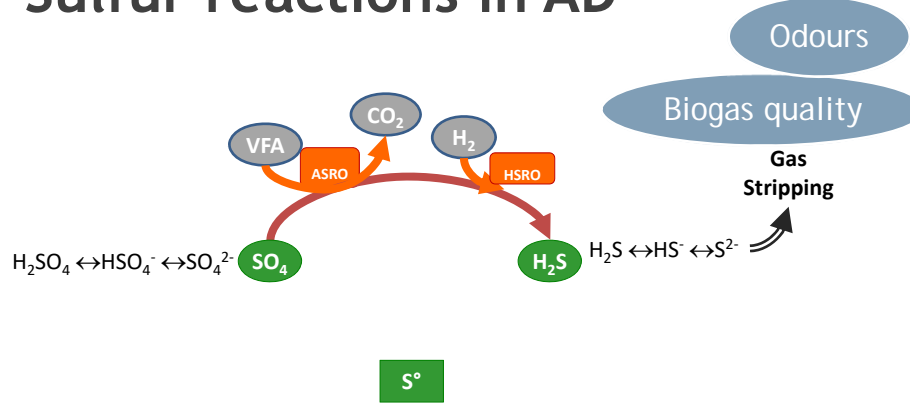
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Sulfur reactions in AD

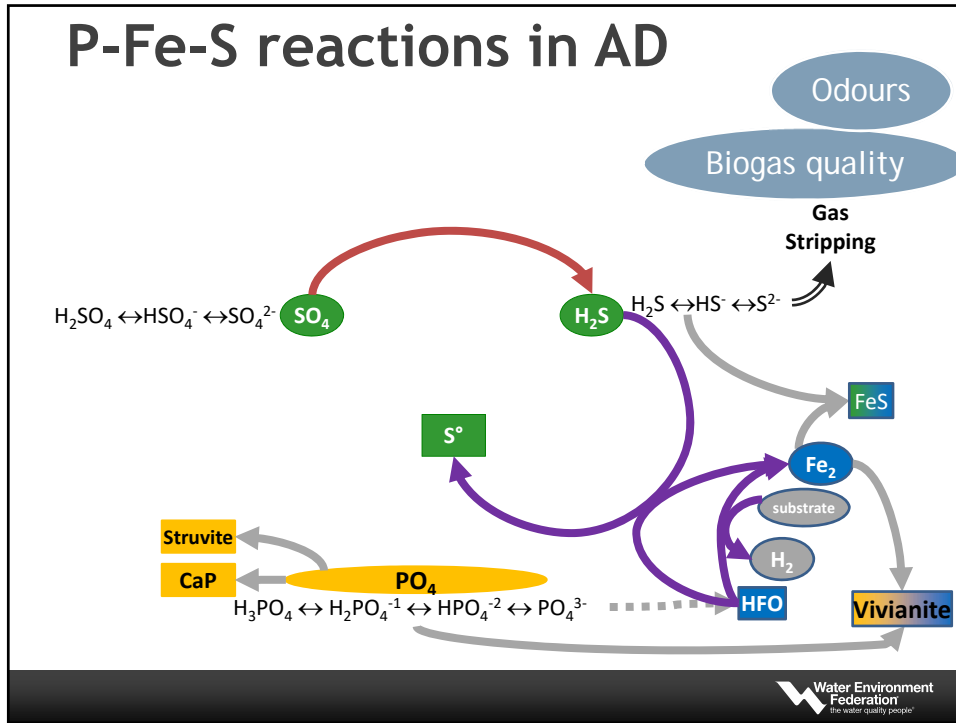


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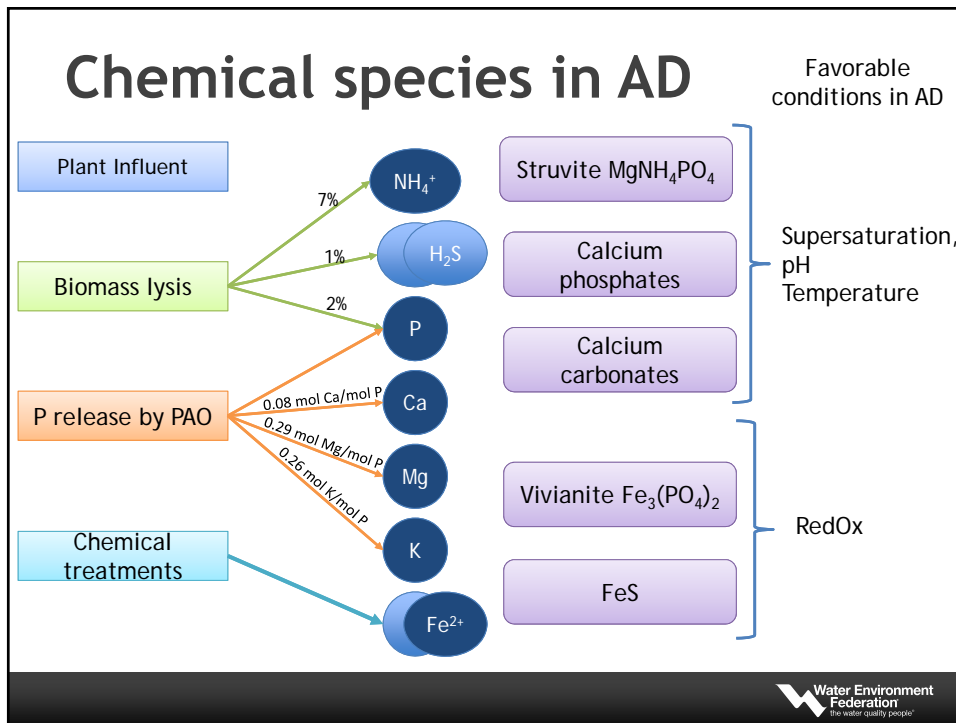
Sulfur reactions in AD



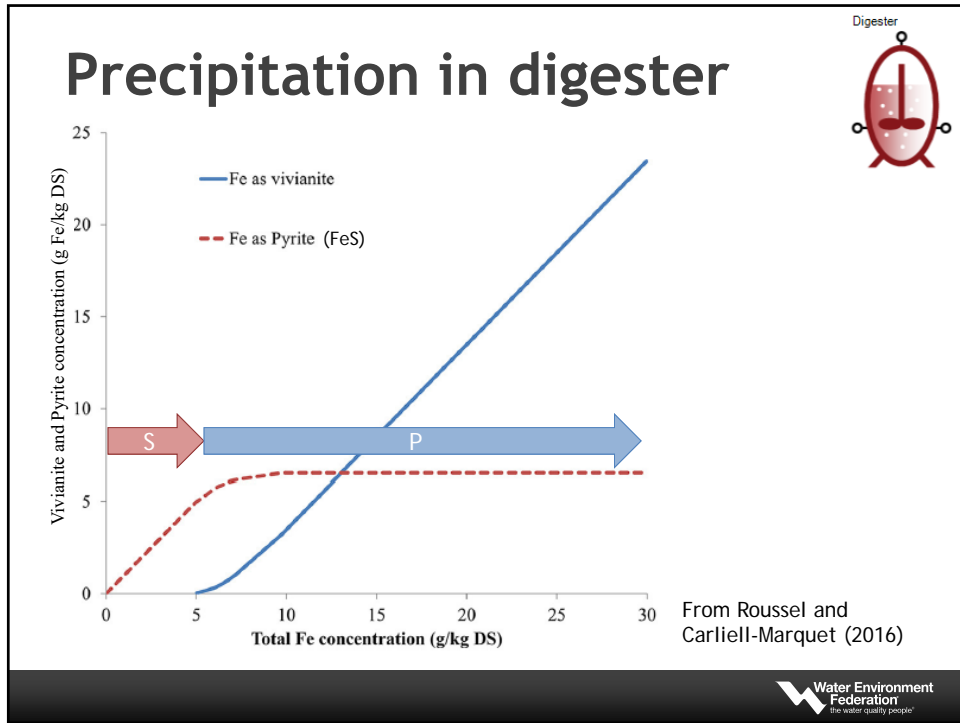
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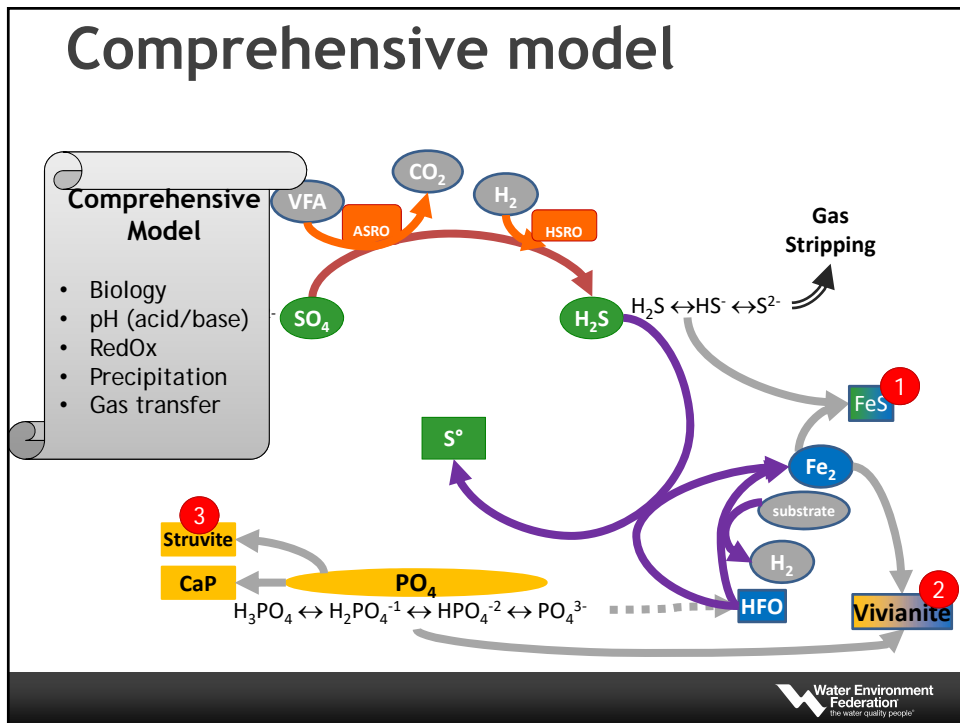
63



64



65



66

Lander Street primary digester Simulation of mitigation strategies



Parameter	Unit	Data	Model	Fe for	Fe for
				H ₂ S control	struvite
				25	100
				g FeCl ₃ /kg VSS	g FeCl ₃ /kg VSS
Digester Total Solids	%	1.70%	2.10%	2.15%	2.24%
Digester VSS	% of TS	67%	66%	65%	62%
Digester pH	-	7.15	7.16	7.07	6.80
Alkalinity as CaCO ₃	mg/L	4100	3544	2939	1762
Gas production	Nm ³ /hr	176	172	174	178
Digester gas H ₂ S	ppm	2125	1926	141	4
Digester ammonia	mg N/L	1169	979	978	1018
Digester phosphate	mg P/L	156	166	113	2
Struvite	mg TSS/L	?	842	827	37
Vivianite	mg TSS/L		0	578	2488
Iron sulfide	mg TSS/L		0	146	163

67

Conclusions on Chemical Processes in Anaerobic Digesters

- AD processes results in nuisances:
 - Struvite precipitation
 - H₂S in biogas
- Fe addition in water line and sludge line as mitigation strategy for P and S control
- Complex interactions of P-S-Fe cycles

68

Conclusions on a comprehensive model

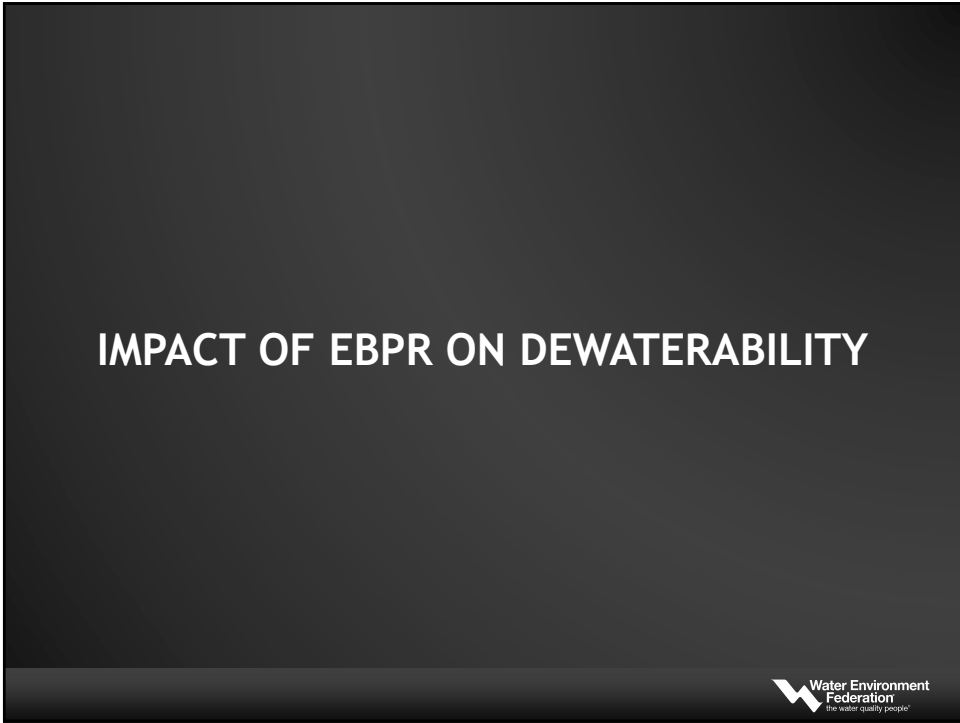
- Optimisation of mitigation strategies
- Impact of mitigation strategies
 - On return streams and mainstream processes
 - On digestate chemical composition

Our Next Speaker



Mario Benisch PE
Senior Process Engineer
Portland, OR





71



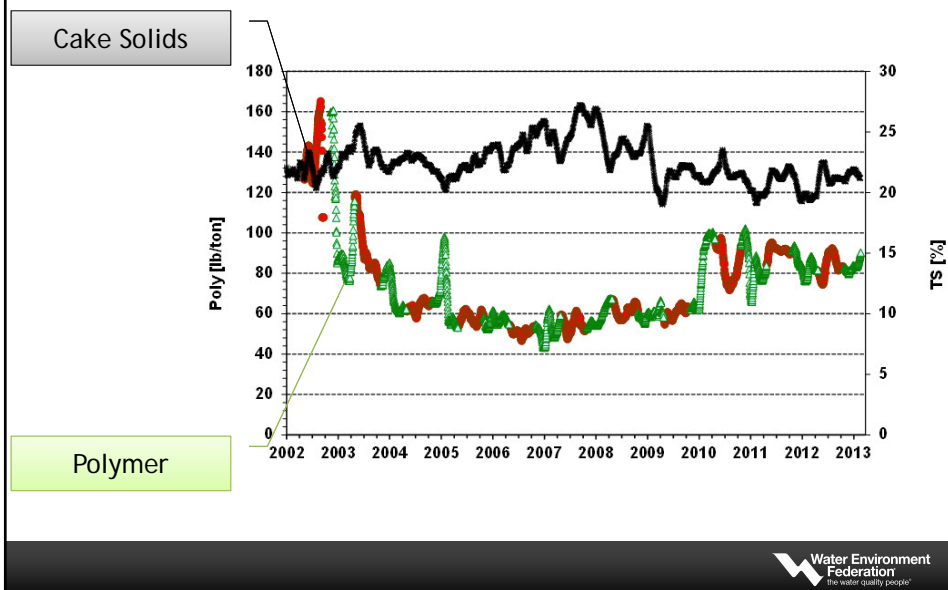
72

Key Takeaways

- EBPR decreases dewaterability
- Often occurs under the radar
- Struvite = indicator for EBPR
- There are mitigation options

73

What do we know



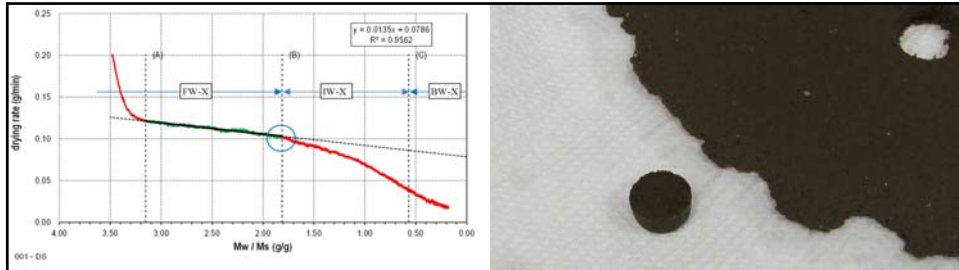
74

What do we know

- Dewatering performance varies in general
- Increase digester $\text{PO}_4\text{-P}$ correlates with decline in dewaterability
- Removal of $\text{PO}_4\text{-P}$ increases dewaterability
- Increase MV/DV ratio correlates with decline in dewaterability
- Ferric (usually) Increases Dewatering Performance

What do we know

- Alum sometimes increases dewatering performance
- Trivalent metal ions can coagulate biopolymers
- EPS holds water and aids flocculation
- Monovalent metal ions block bridging



02 Water Distribution



77

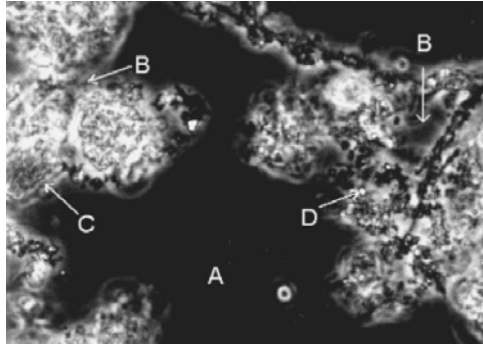
Water distribution

Only free water can be removed with mechanical dewatering

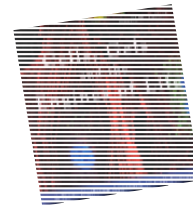
WHY DOES DEWATERING PERFORMANCE VARY?

78

Water distribution



- A: Free
- B: Interstitial
- C: Surface
- D: Intracellular



79

Water distribution

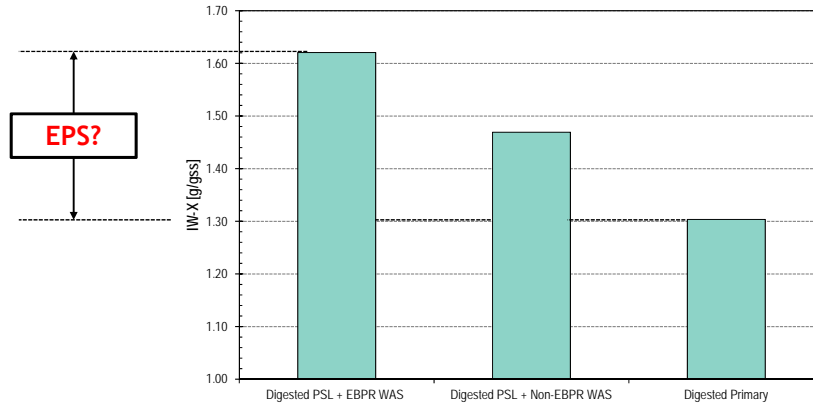
Water distribution in sludge is a function of

- process design
(liquid treatment, solids treatment, etc)
- influent composition
(plant influent, external loads)
- chemical addition
(alkalinity, polymer, coagulants)

80

Water distribution

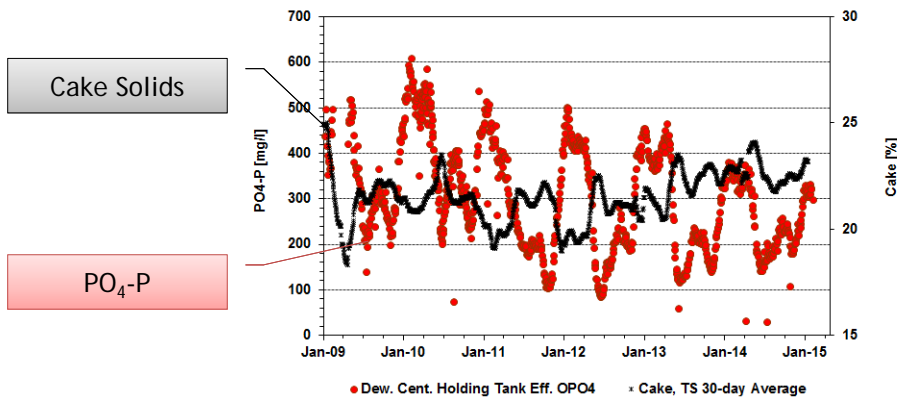
- Thermo-Gravimetric Analysis of Water Fractions



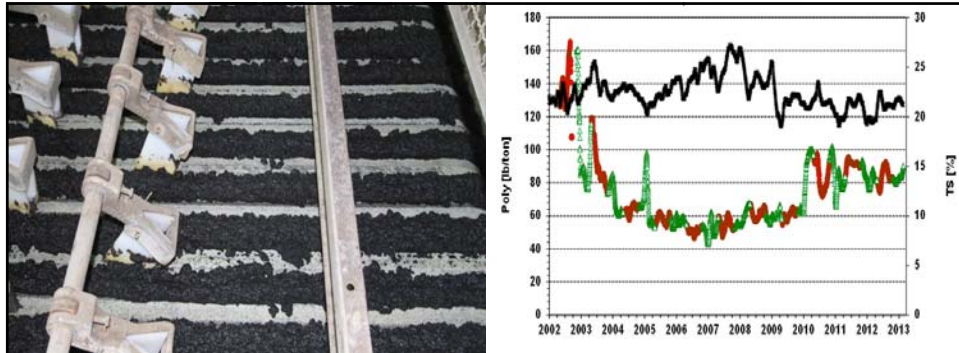
81

Phosphate Concentration


- Dewaterability declines with increasing PO₄-P



82



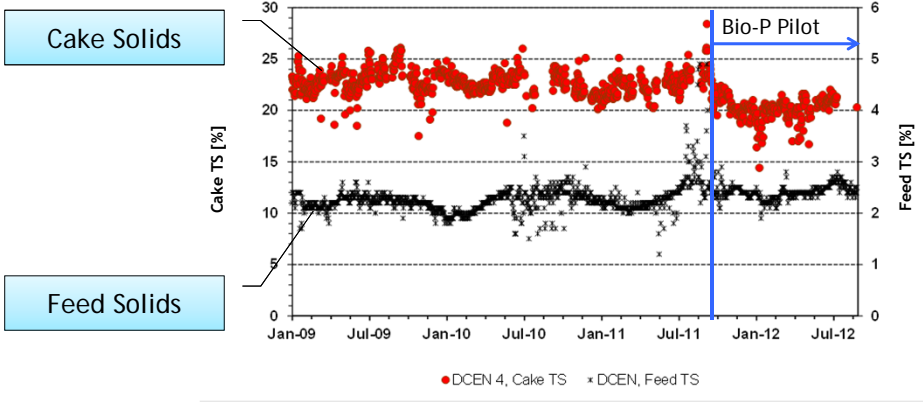
03 Impact of EBPR on Dewatering



83

EBPR and Dewatering

- Denver Hite EBPR Pilot




Cake Solids

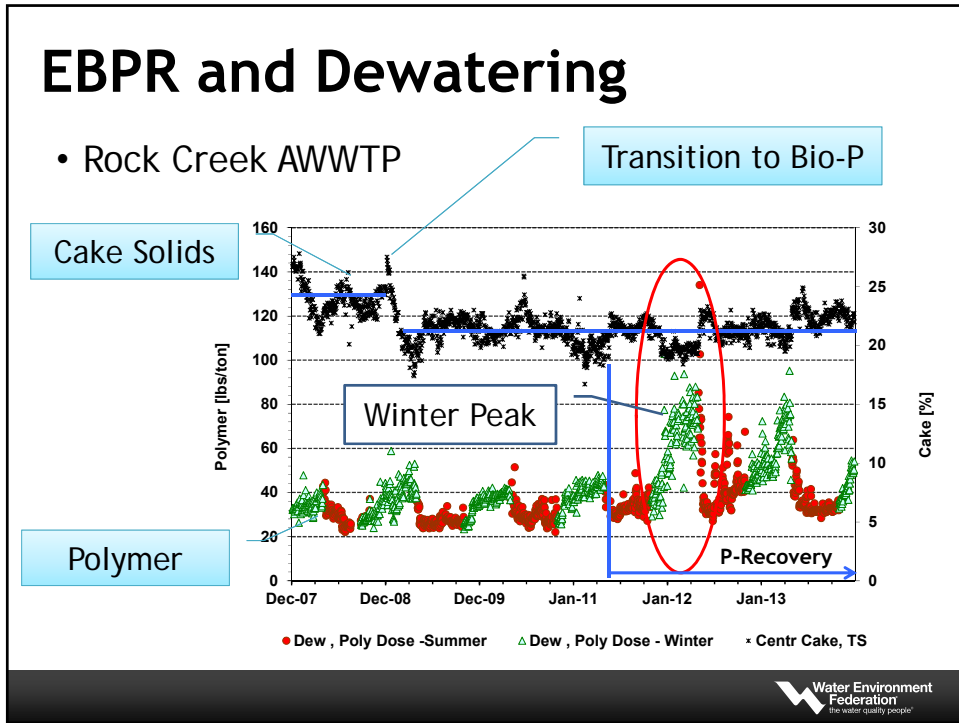
Feed Solids

Bio-Pilot

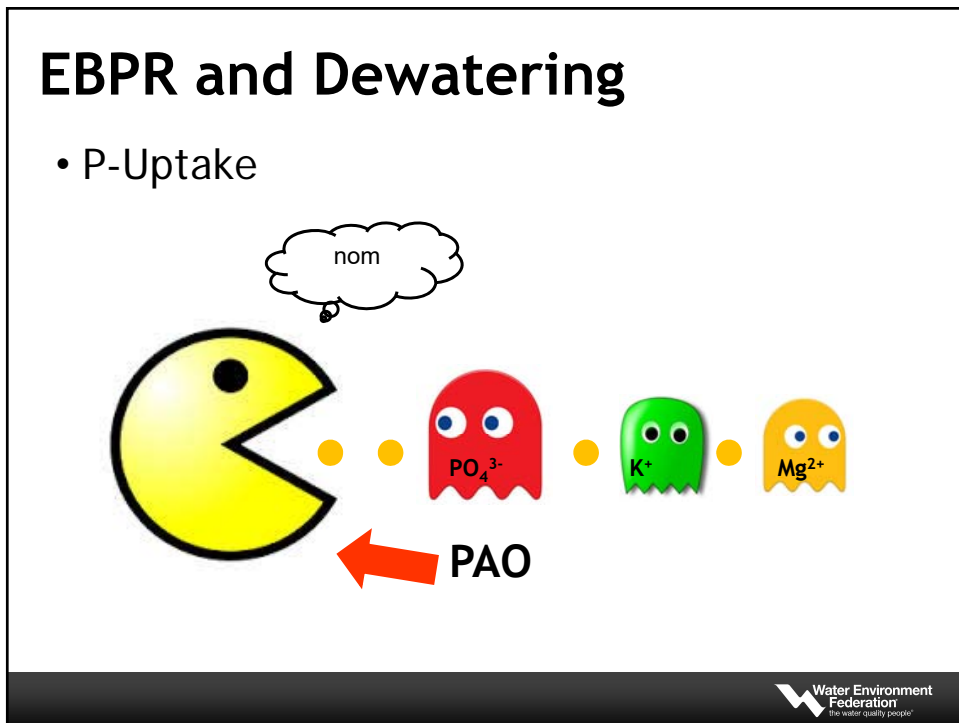
● DCEN 4, Cake TS × DCEN, Feed TS



84



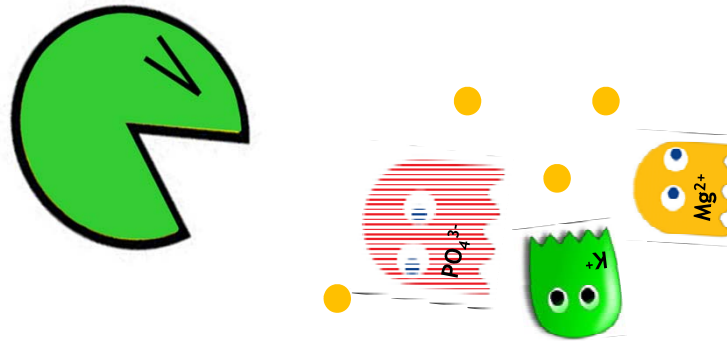
85



86

EBPR and Dewatering

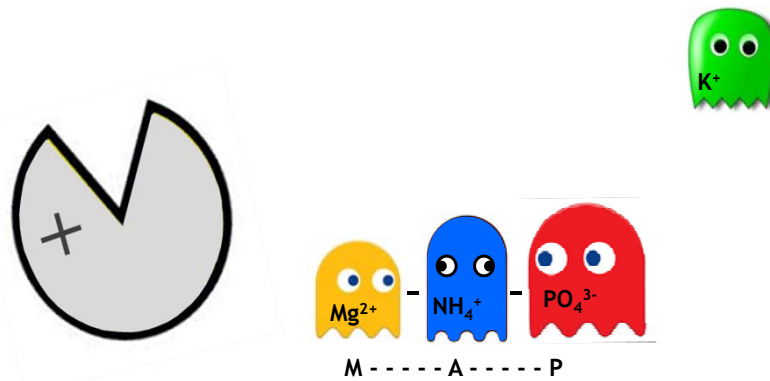
- ANR P-Release



87

EBPR and Dewatering

- Digestion and Struvite Formation



88

EBPR and Dewatering

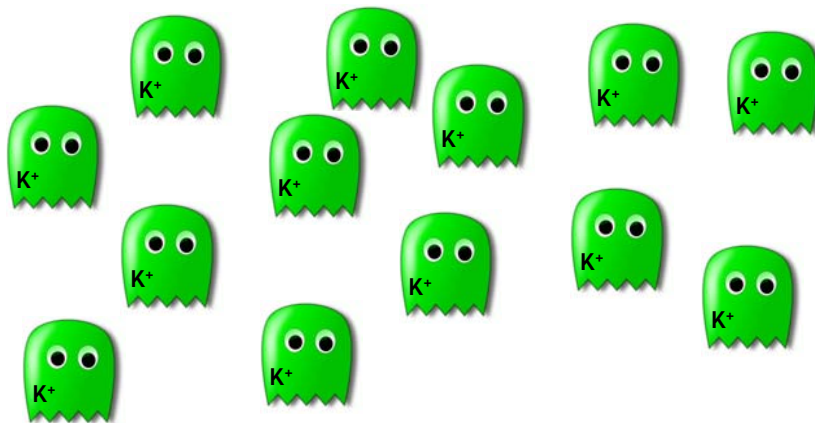
- Bio-P Transfer P to digester and Mg and K
- Mg^{2+} Precipitates out as $MgNH_4PO_4 \cdot 6H_2O$



89

EBPR and Dewatering

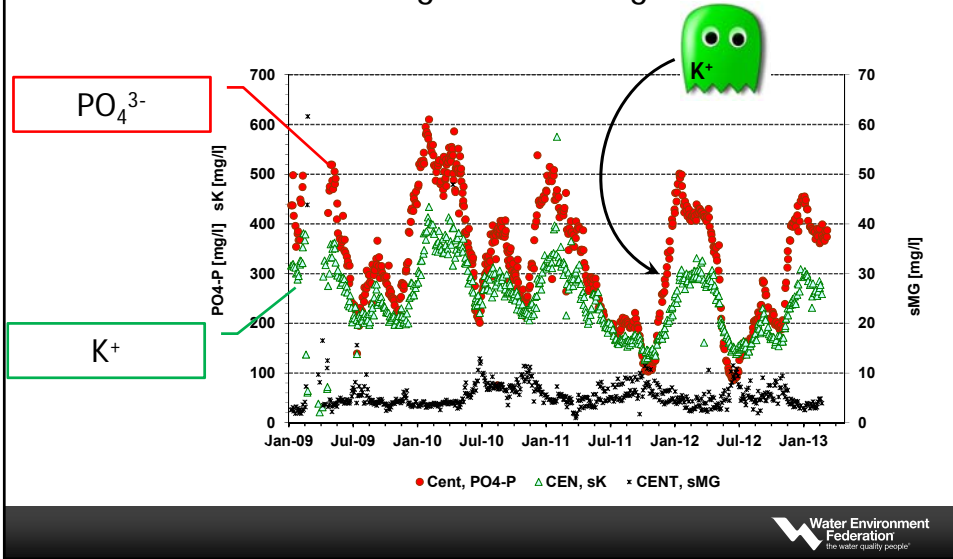
- K^+ Remains



90

EBPR and Dewatering

- Bio-P Transfer P to digester and Mg and K



91

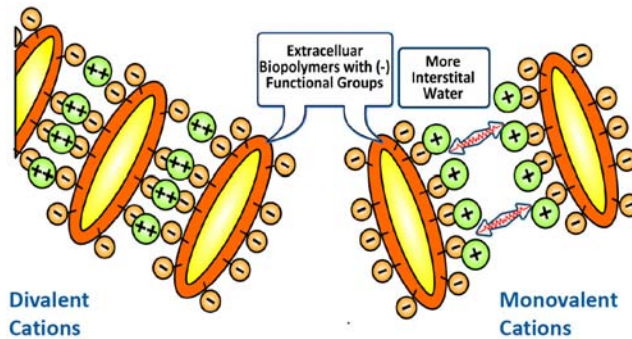
04

PO4-P vs. MV/DV

92

Monovalent/Divalent Cation Ratio (M/D)

- Divalent Cation Bridging



(Source: Nova, Higgins)



93

Monovalent/Divalent Cation Ratio (M/D)

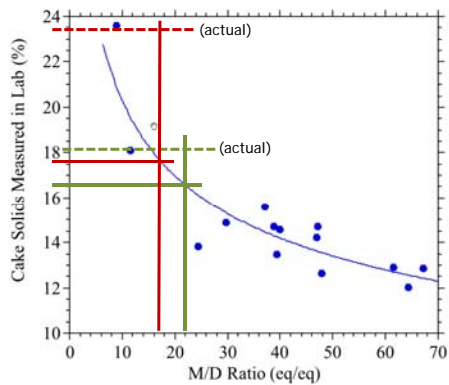


Figure 3. Relationship between cake solids and the M/D ratio for the different samples.

(Source: Higgins)

Summary from Kopp report		Lakota	Redondo
NH4-N	mg/L	1130	1240
PO4-P	mg/L	130	68
Na	mg/L	52	454
K	mg/L	260	304
Mg	mg/L	16	31
Ca	mg/L	52	83
M/D	-	22.8	17.1
pH	-	7.4	7.7
cond	mS/cm	8.8	14.6
Poly	lb/dry ton	48.1	75.0
DS(A)kbkopp	%	18.0	23.4

(Source: City of Lakehaven)



94

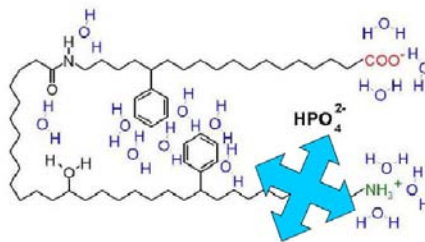
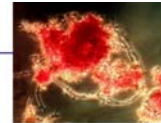
EBPR and Dewatering

- PO₄-P Increase EPS stored Water



Hydrogele – Bio.- P

- EPS = Proteine & Polysaccharide
 = Schutzhülle & Nährstoffreservoir
 = Hydrogele bestehen zu 90% aus Wasser
 = beeinflusst durch pH und Phosphat



Weiterbildungskurs W 17 „Klärschlamm“ 2011/12

(Source: Julia Kopp, PhD)

95

PO₄-P vs. Dewaterability

- Phosphate (anions) in Food Processing
 - Can dissolve proteins
 - Act stabilizing on dispersions, suspensions, and emulsions
 - When phosphate anions enter protein molecules they unfold the protein through electrostatic repulsion and bridge forming which impact its water binding ability
 - Diphosphate have very specific impact on the water storage in muscle protein (casein and actomyosin)

(Source: Yvonne Matthei pp, PhD)

96

PO₄-P vs. Dewaterability

- Use of Phosphate (anions) in Food Processing
 - To reduce growth of gram positive microorganism (extend shelf live of cream cheese with poly-phosphates)
 - pyrophosphate used to restore water content in meat and to slow down auto-oxidation reactions by binding multivalent cations
 - Phosphate is added to milk products to stabilize milk proteins, stabilize the pH, binding of multivalent cations, and to increase viscosity (i.e. for cream)
 - To enrich food products with Ca, Mg, Fe, etc

(Source: Yvonne Matthei pp, PhD)

97



05 Implications

98

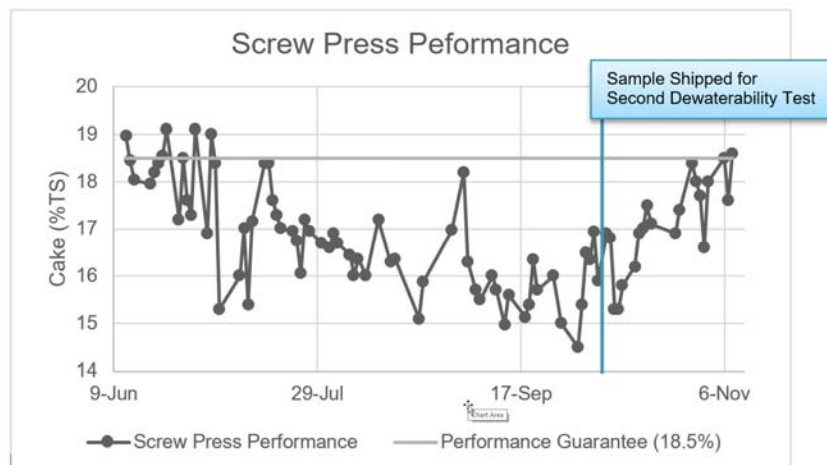
Implications

- Polymer → 100% to 200% more
- Cake TS → 3% - 5% less
- Operating cost → Polymer, Hauling
- Resiliency → Struvite
- Recovery option
- Procurement

(Source: Yvonne Matthei pp, PhD)



Implications





101

Metal Salt Addition

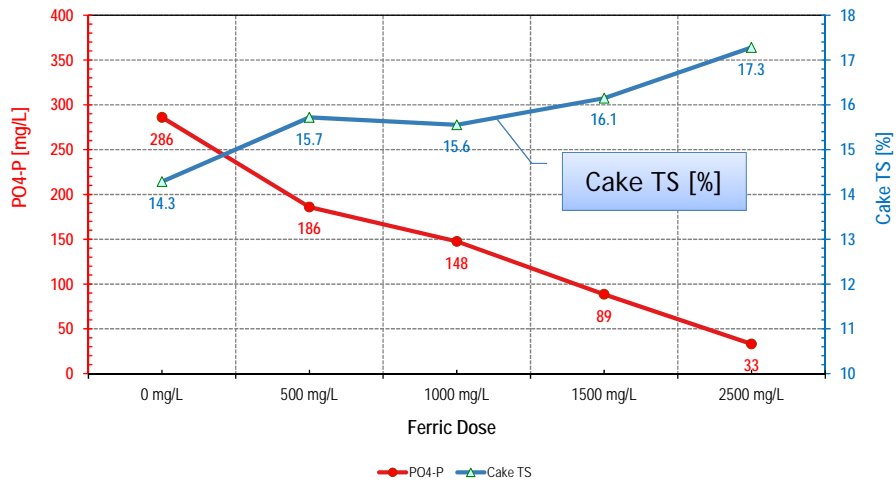
- Simplest Option
- Ferric or Alum
- Recycle P control
- Lower polymer demand
- Dryer cake
- More sludge
- Consumes alkalinity*



Water Environment Federation
the water quality people

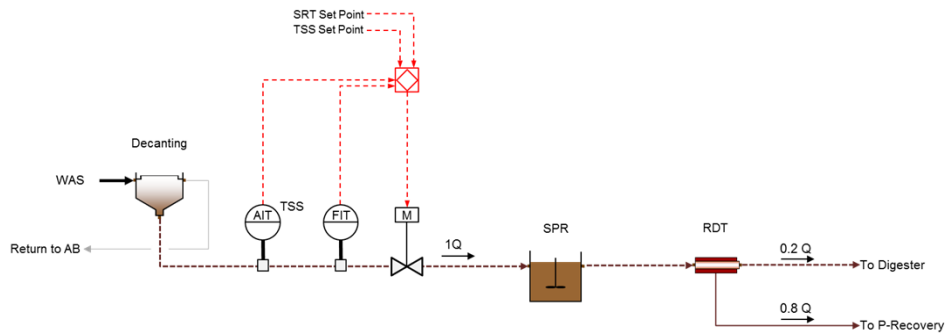
102

Metal Salt Addition



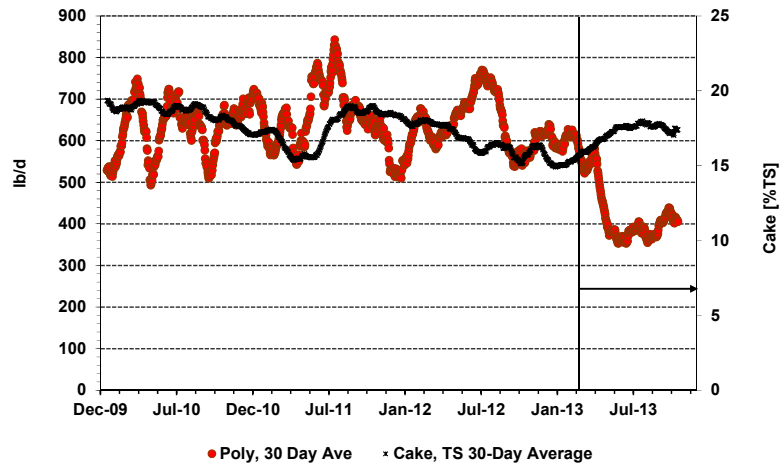
103

Stored Phosphorus release



104

Stored Phosphorus release



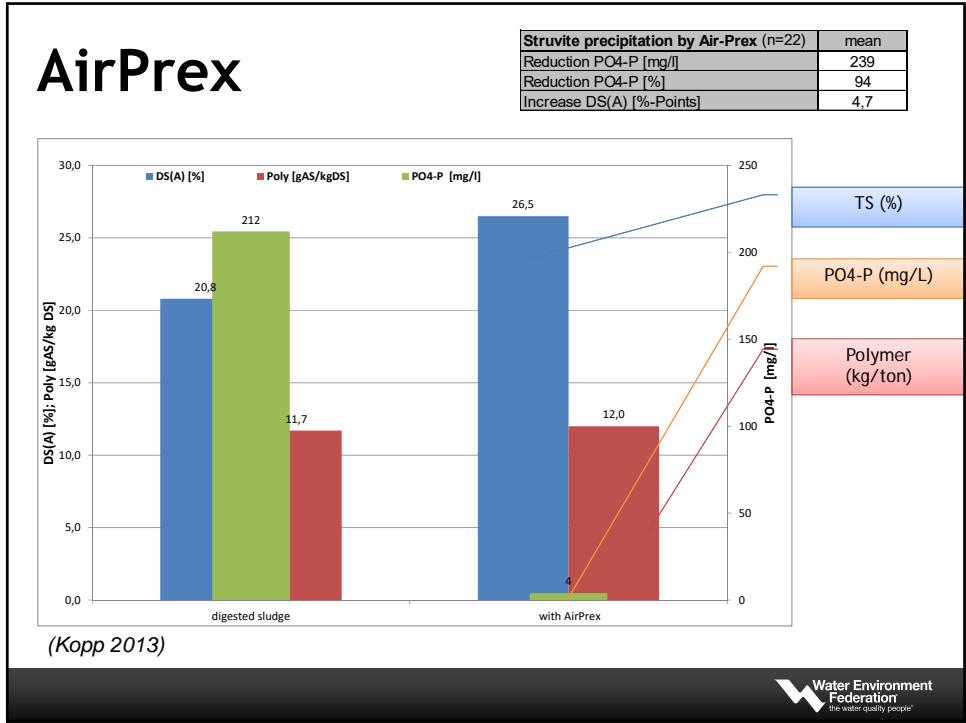
105

AirPrex

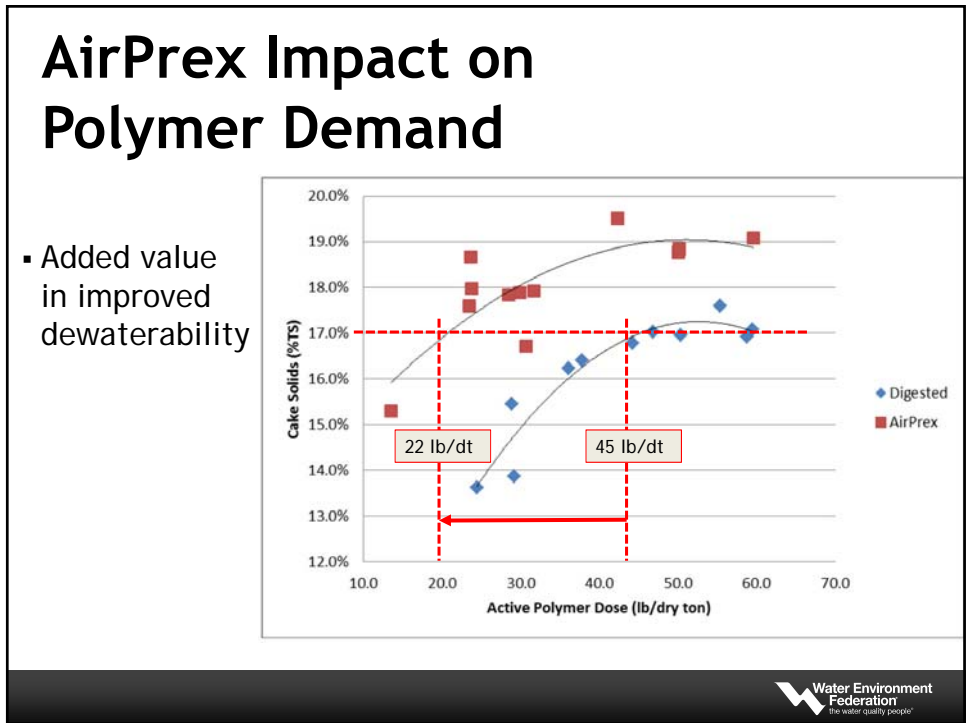
- Post digestion sludge treatment
- Simple process
- Air mixed reactor
- Adding $MgCl_2$ to bind PO_4-P



106



107



108

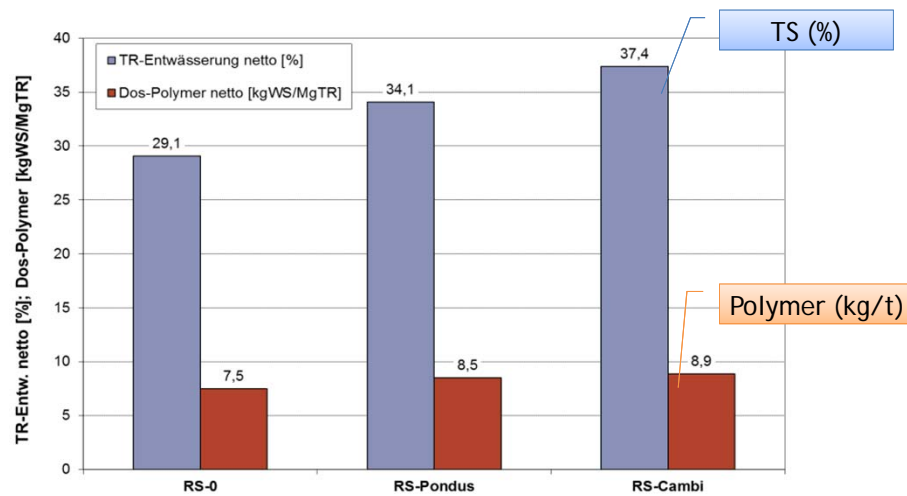
Thermo Hydrolysis

- Pre Digestion Process
- Cell lysis
- High Temperature and Pressure



109

Thermo Hydrolysis



(Kopp 2013)

110

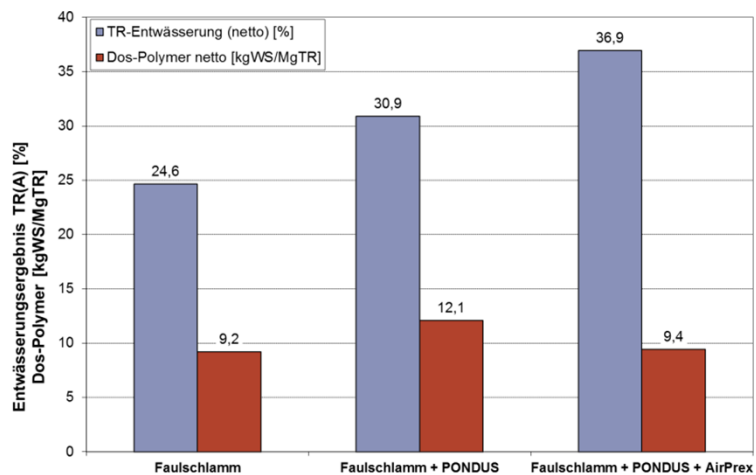
CTHP (PONDUS)

- Chemical/Thermal Hydrolysis
- Simple Process
- 80% - 90% as effective as THP



111

PONDUS



(Kopp 2013)


112

Key Takeaways

- EBPR decreases dewaterability
- Often occurs under the radar
- Struvite = indicator for EBPR
- There are mitigation options




113

A photograph showing the silhouettes of four cowboys on horseback, standing in a line against a bright, glowing sunset sky. The sun is low on the horizon, creating a strong backlight effect.

Closing Slide

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HDR Portland

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The logo for the Water Environment Federation, featuring a stylized 'W' and the text 'Water Environment Federation' with the tagline 'the water quality people' below it.

114

Final Q & A

115

Solids Stream P – Jan. 24, 2019

An MRRDC Short Course

Solids Stream Phosphorus Modeling

- Final Q & A:

Moderator	→ John Copp	Primodal
Basics	→ Patrick Dunlop	Black & Veatch
Nuisance	→ Murthy Kasi	Smith & Loveless
Chemistry	→ Hélène Hauduc	Dynamita
Dewatering	→ Mario Benisch	HDR

116