



**Virginia Water
Environment Association**

**2012
Industrial Waste and
Pretreatment Seminar**

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Wastewater Reuse Considerations at a Petroleum Refinery

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Refinery Located in Midwestern United States

Owned by three cooperative associations to provide fuel to farmers in the Midwest United States

🏭 Started in 1932 as a 6,000 bpd refinery

🏭 Currently 85,000 bpd

🏭 Receives crude oil by pipeline from North American sources

🏭 Main fuel products are gasoline and diesel



FUN FACTS



What does oil refining have to do with basketball???




Members from the refinery's basketball team won a gold medal at the 1936 Olympics in Berlin!

1936 was the first year basketball was played as an Olympic sport, and was the same year Jesse Owens won his gold medals.

Presentation Overview

Background

-  Water sources and treatment
-  Wastewater sources and characteristics
-  Existing treatment facilities

Refinery wastewater reuse experience

Refinery reuse approach

[illegible]

1 Identify wastewater sources and general characteristics

Collect data to develop a water flow and mass balance around the refinery



Process Water Sources and Treatment

Water Sources

3,100 gpm of water use during summer months

Refinery water sources:

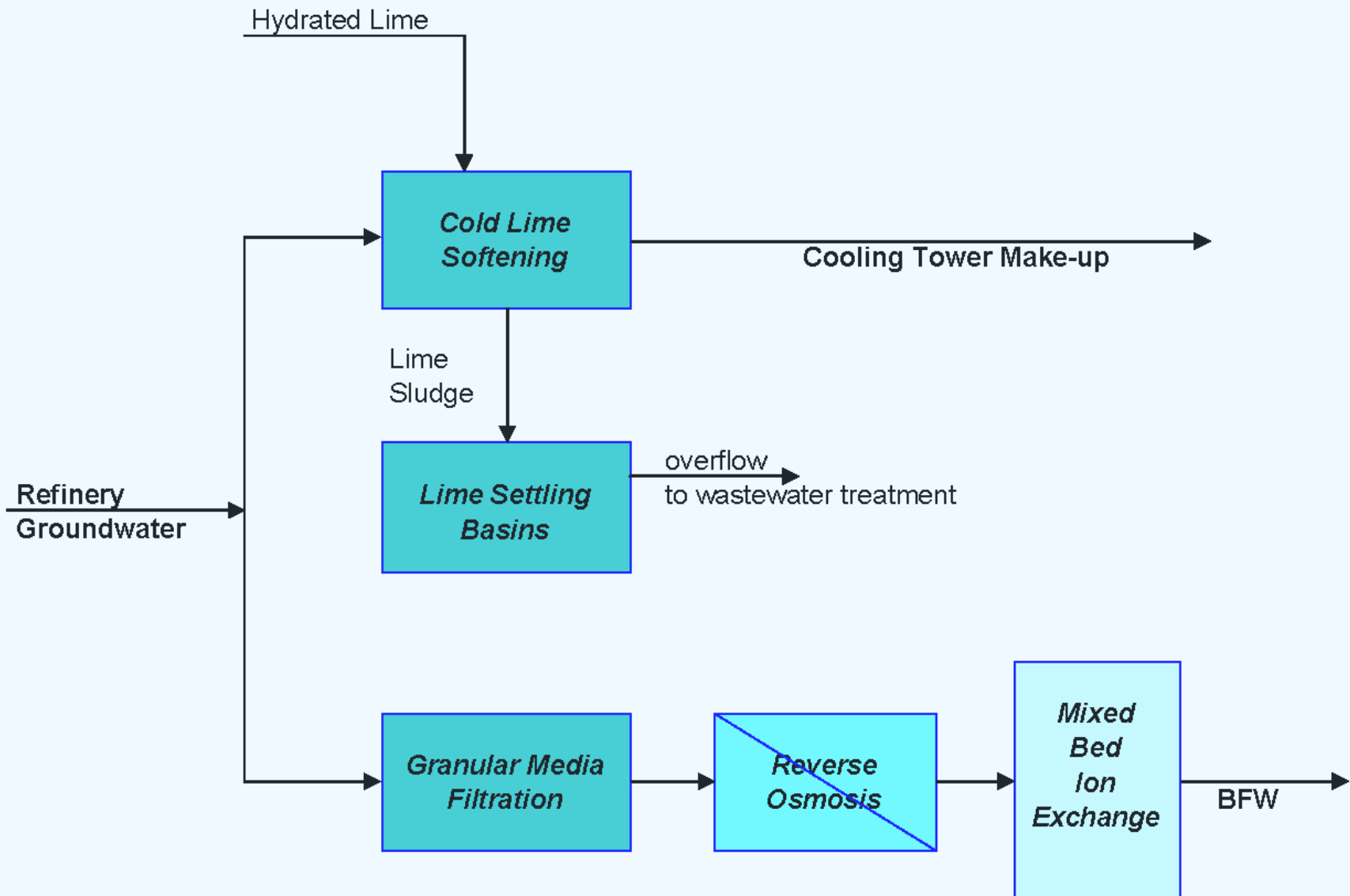
- Groundwater wells
 - High chlorides
 - Medium chlorides
- Purchased municipal water



Current Feed Water Characteristics

Parameter	mg/L	Parameter	mg/L
TDS	798	Calcium as CaCO_3	386
TSS	6	Magnesium as CaCO_3	56
COD	10	Sodium	40
BOD ₅	2	Barium	0.28
TKN	0.2	Iron	0.19
Ammonia-N	0.1	Manganese	0.044
Phosphorus	0.5	Strontium	0.62
Carbonate Alkalinity	20	Chloride	135
Bicarbonate Alkalinity	300	Sulfate	23
Silica	20		

Process Water Treatment





Wastewater Characteristics and Treatment

Wastewater Sources

Desalter Blowdown

- Organic load, O&G
- Inorganic load

Sour Water

- Pretreat to remove H_2S
- Pretreat to remove NH_3
- Organic load

Scrubber Blowdown

- Sulfites
- Dissolved & suspended solids

Spent Caustic

- Sulfur compounds
- Organic load

Oily Sludges

- O&G (from desalters)
- TDS and TSS (scrubbers, etc.)

Process Water Treatment Wastes

- Lime softening sludges
- Ion exchange waste regenerant
- Filter and RO reject/CIP waste

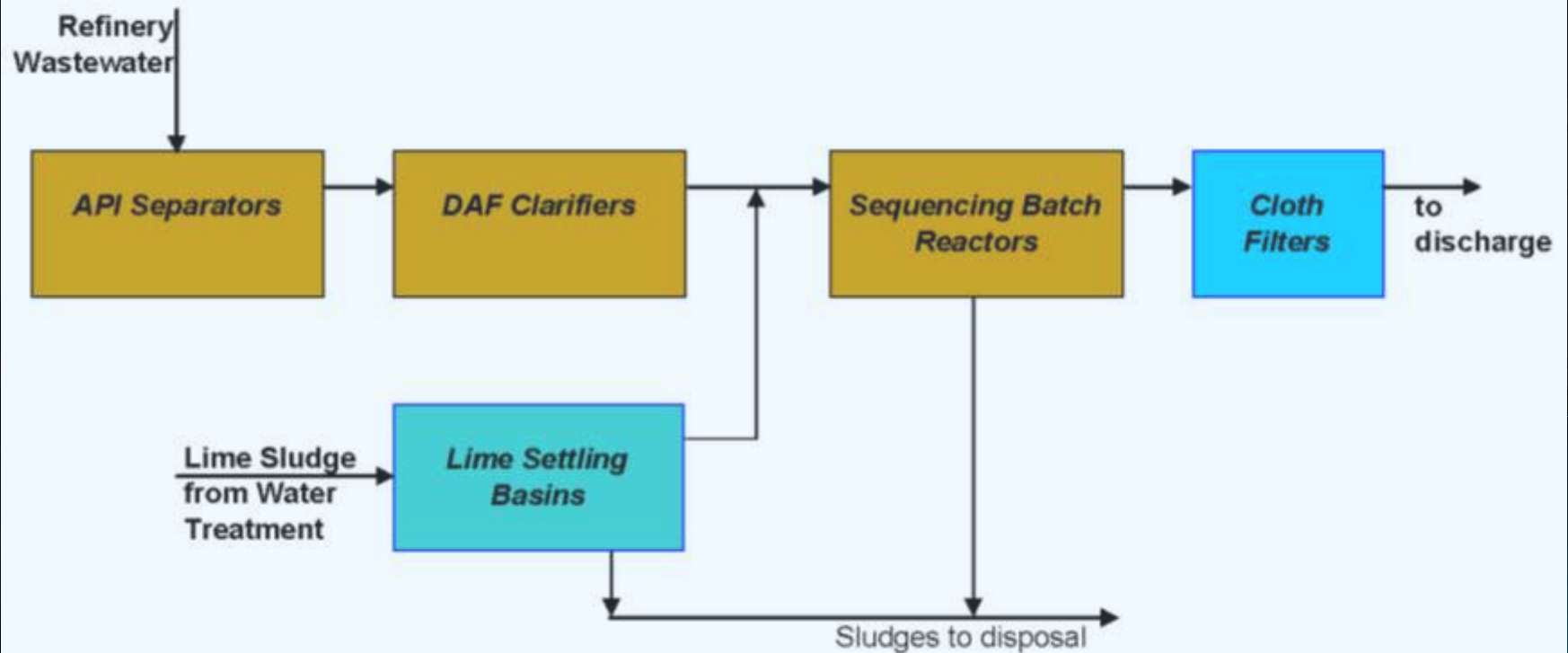
Cooling Tower Blowdown

- Dissolved solids
- Suspended solids

Boiler Blowdown

- Dissolved solids

Current Wastewater Treatment



Water and Wastewater Characterization

- 🏭 Data existed for water sources and wastewater streams, but did not include all the constituents of interest for reuse
- 🏭 Implemented sampling program to characterize individual water sources and wastewater streams
- 🏭 Constructed mass balance
- 🏭 Used mass balance to project future wastewater characteristics
 - 🏭 New sources of crude oils
 - 🏭 Impacts to TDS and SS in raw wastewater
 - 🏭 Re-routing internal wastewater streams
 - 🏭 RO reject will be re-directed to deep wells



Wastewater Treatment Upgrades

Wastewater Treatment Upgrades

- 🏗️ Upgrades implemented to improve treatment system performance in preparation for reuse
- 🏗️ New wastewater collection sump and gravity sewer to new lift station
- 🏗️ Replaced API separator and DAF clarifier
 - 🏗️ Duplicate, 100% capacity parallel trains
 - 🏗️ 230 m³/hr each (1,000 gpm)
- 🏗️ Oil and sludge storage facilities

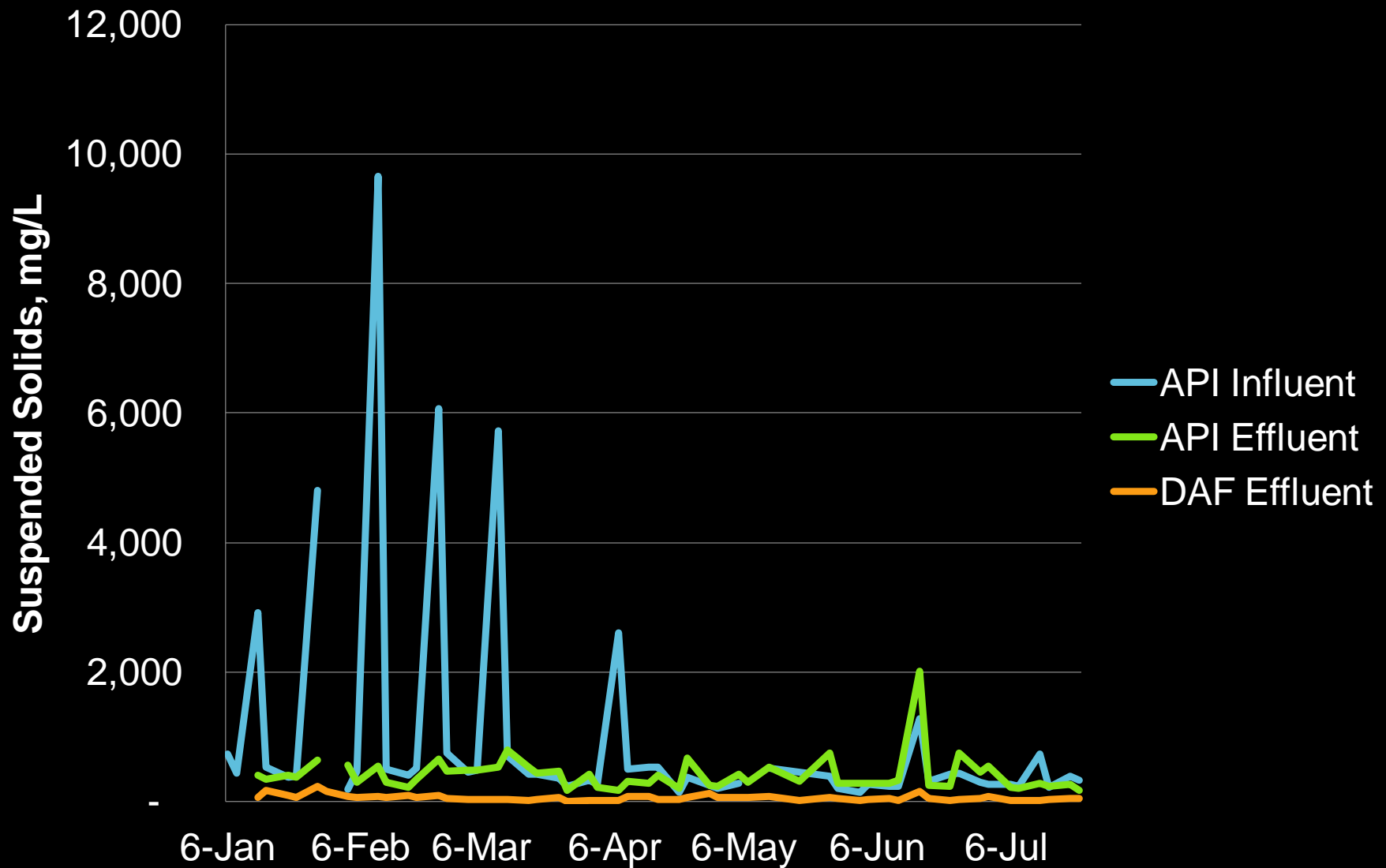
API-DAF Replacement Project



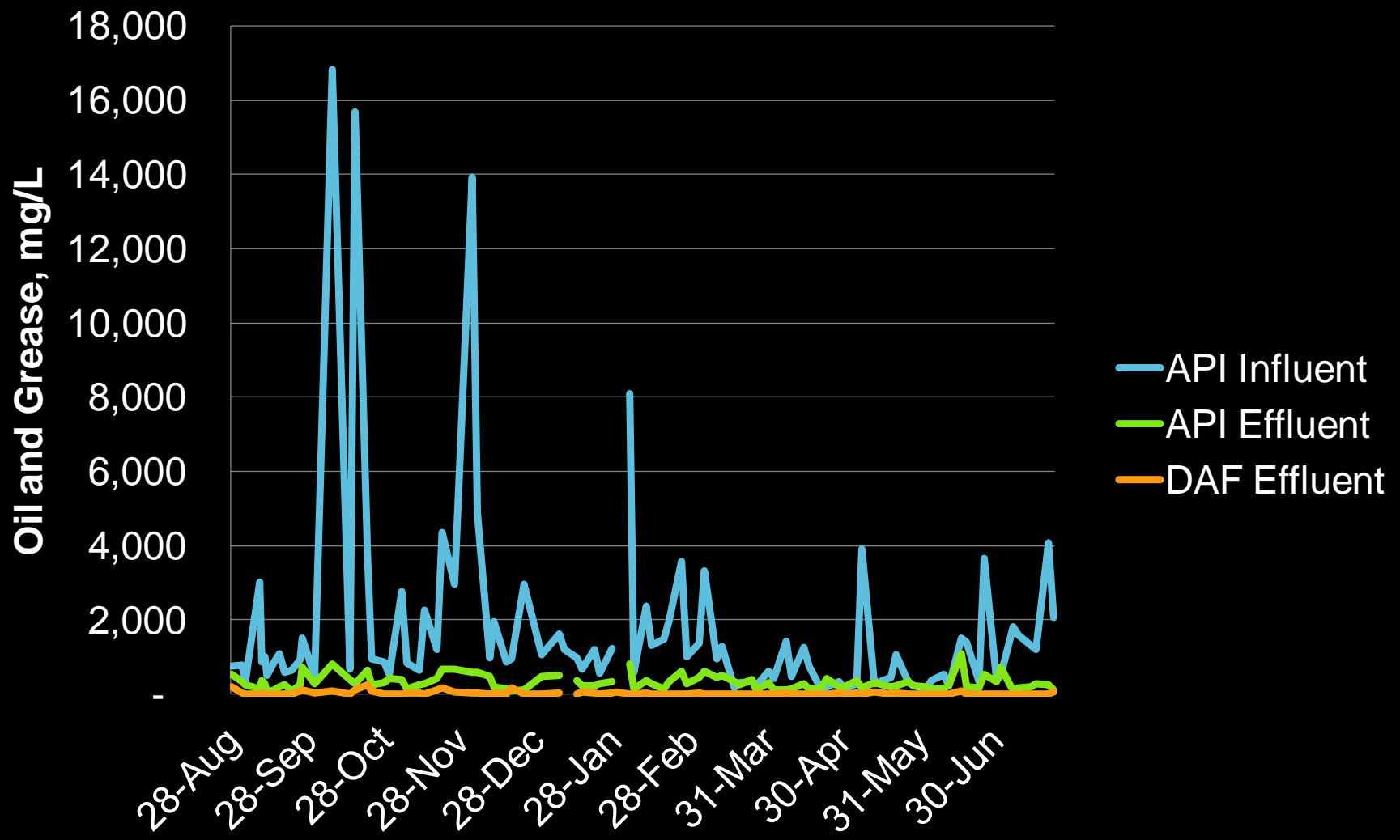
API-DAF Replacement Project



API and DAF Performance – Suspended Solids



API and DAF Performance – Oil and Grease



Refinery Wastewater Effluent Characteristics

Parameter	mg/L	Parameter	mg/L
TDS	2,190	Calcium as CaCO_3	610
TSS	29	Magnesium as CaCO_3	116
COD	100	Sodium	387
TKN	6.8	Barium	0.48
Ammonia-N	2.6	Iron	3.8
Phosphorus	0.97	Manganese	0.11
Carbonate Alkalinity	20	Strontium	2.4
Bicarbonate Alkalinity	323	Chloride	703
Silica	45	Sulfate	228



Previous Refinery Wastewater Reuse Experience

Wastewater Reuse at Pemex Refineries, Mexico



🏭 Documented by Falcón and Romano (2006)

🏭 Pemex objectives:

- 🏭 Preserve limited water resources
- 🏭 Minimize discharge of pollutants to waterways



🏭 Similar, but unique approaches taken at four refineries


Pemex Refinery Wastewater Reuse Features

- DAF and biological treatment**
- Chlorination for control of microbial growth**
- Warm or cold lime softening**
- Granular media filtration and GAC**
- Reverse osmosis**
- Municipal effluent used at two refineries**
- Zero liquid discharge achieved at two refineries**

Low Pressure Membrane Filtration Pilot Testing


 LPMF evaluated for Refinery Four

 Side-by-side testing of four LPMF configurations

 Flat sheet

 Inside-out hollow fiber pressure membranes

 Outside-in hollow fiber vacuum membranes

 Spiral wound

 Outside-in hollow fiber vacuum membranes selected

Lessons Learned

🏭 TDS requires careful control

- 🔧 Scaling
- 🔧 Corrosion



🏭 Combining lime softening and reverse osmosis

- 🔧 Optimizing anti-scalants is critical



Lessons Learned

Oil removal and biological processes must be robust


-  Residual oils and organics can foul downstream processes
-  Contribute to biological growth in tankage, piping, process equipment




Provide disinfection at multiple points in treatment train

Consider compatibility with membrane processes

-  May need to provide residual disinfectant removal

Lessons Learned

 **Low pressure membrane filtration provides effective pretreatment to reverse osmosis**

-  Outside-in hollow fiber vacuum membranes selected based on pilot testing
-  Over ten years of operating experience
-  Superior to granular media filtration and GAC





Wastewater Reuse Approach

Considerations for Wastewater Reuse

⚙️ **Maximize water recovery**

⚙️ **Two-train approach**

🏭 Common processes

🏭 Redundancy

🏭 Reliability

⚙️ **Refinery wastewater and high-chloride well water used for BFW**

⚙️ **Low-chloride well water used for cooling tower make-up**

⚙️ **Deep well disposal of concentrated waste streams**



Train 1 BFW Treatment Requirements

Parameter	Feed, mg/L	Product, mg/L	Parameter	Feed, mg/L	Product, mg/L
TDS	3,508	40	Calcium	683	4.5
TSS	30	5	Magnesium	142	0.5
COD	66	10	Sodium	556	6.5
BOD ₅	10	2	Barium	0.6	0.01
TKN	6	0.2	Iron	3.8	0.3
Ammonia-N	2.3	0.1	Manganese	0.04	0.007
Phosphorus	1.1	0.5	Strontium	3.2	0.01
Carbonate Alk.	33	20	Chloride	1,467	6.1
Bicarbonate Alk.	161	20	Sulfate	212	1.8
Silica	33	2.1	Oil & grease	5	0

Train 2 Cooling Tower Make-up Treatment Requirements




Parameter	Feed, mg/L	Product, mg/L	Parameter	Feed, mg/L	Product, mg/L
TDS	800	800	Calcium	386	101
TSS	6	6	Magnesium	56	8
COD	10	10	Sodium	40	160
BOD ₅	2	2	Barium	0.3	0.06
TKN	0.2	0.2	Iron	0.2	0.05
Ammonia-N	0.1	0.1	Manganese	0.04	0.005
Phosphorus	0.5	0.5	Strontium	0.6	0.21
Carbonate Alk.	20	20	Chloride	135	135
Bicarbonate Alk.	300	52.5	Sulfate	23	21
Silica	20	19	Oil & grease	5	0

Train 1 BFW Process Alternatives

Lime softening and reverse osmosis

-  Lime softening, LPMF, RO
-  Lime softening removes Ca, Mg, Si and Ba
-  Increases RO recovery rate (70 – 80%)

Membrane softening and TDS removal

-  LPMF, RO
-  Increased loading of TSS and hardness/scaling compounds to membranes
-  Reduced RO recovery rate (55 – 65%)

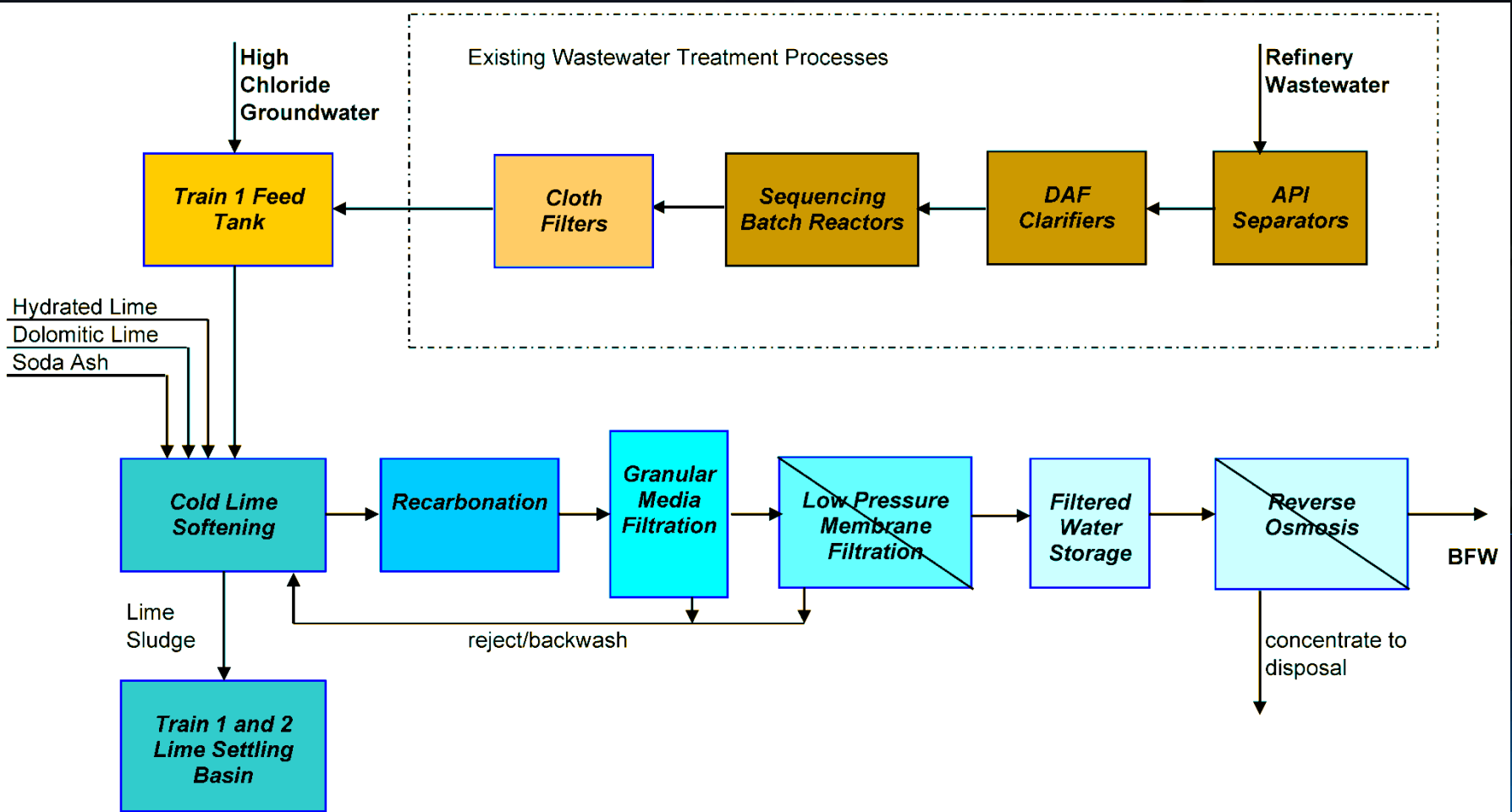
Expected Cold Lime Softening Performance

Parameter	Feed, mg/L	Effluent, mg/L
TSS	<100	<20
TDS	3,500	3,500
Calcium as CaCO_3	690	35
Magnesium as CaCO_3	140	10
Barium	0.5	0.05
Silica	35	<25

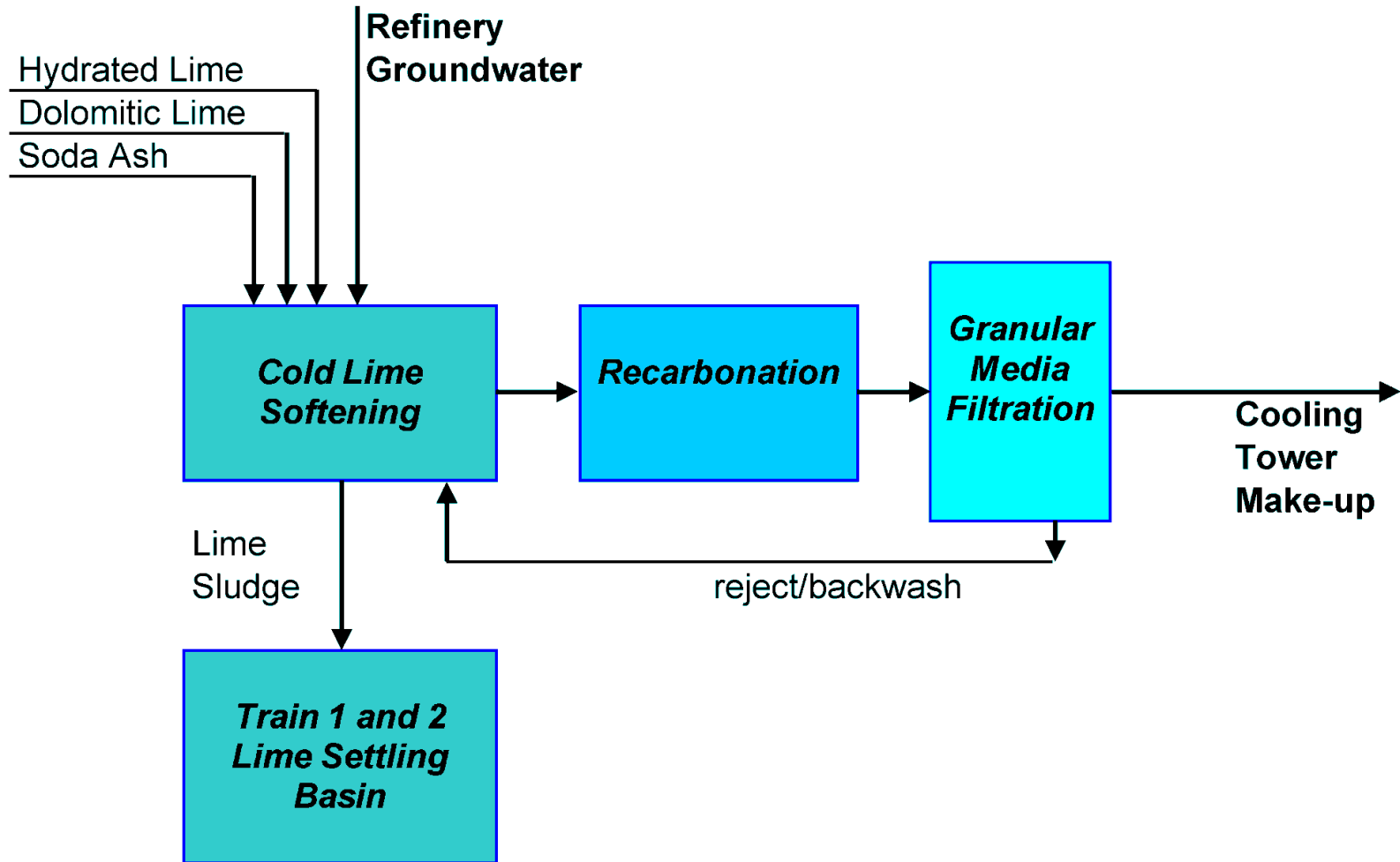
Expected LPMF Performance

Parameter	Feed, mg/L	Effluent, mg/L
COD	80	<30
BOD₅	10	<3
TSS	30	<2
Color	150	<20
Silt density index	Infinite	<3.0
Oil & grease	10	<2
TPH	5	<1


Train 1 BFW Treatment



Train 2 Cooling Tower Make-up Treatment




Conclusions

 **Refinery wastewater reuse is receiving increased focus for minimizing water use and wastewater discharges**

-  Characterize water sources and wastewater streams

-  Optimize existing processes

 -  Oil & grease removal

 -  Suspended solids

 -  Dissolved organics and nutrients

-  Construct mass balance and project future characteristics

-  Build on previous experience

Questions?

