


Virginia Water Environment Association

2012 Industrial Waste and Pretreatment Seminar

Charlottesville, Virginia

March 5, 2012

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

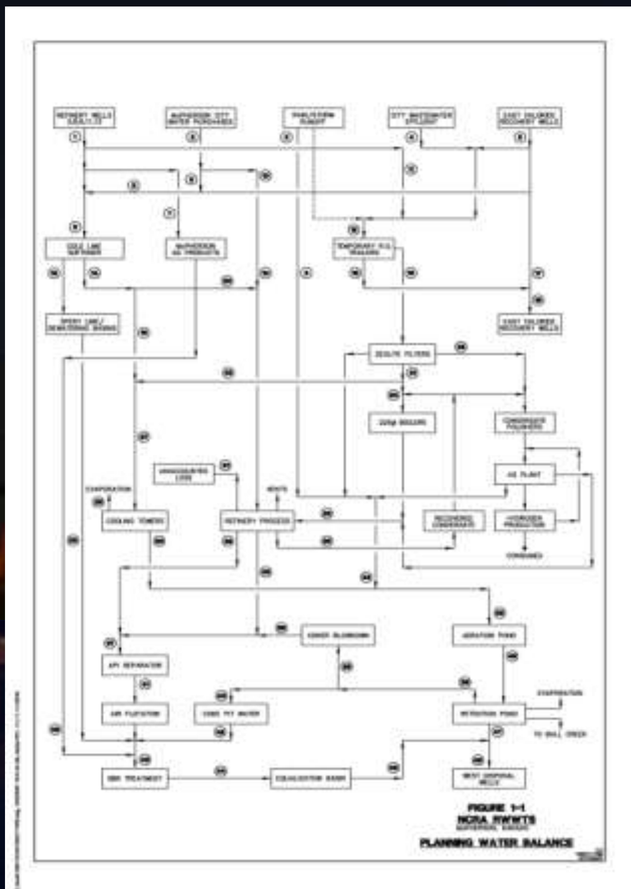
What does oil refining have to do with basketball???

- 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**

First Step – Water and Mass Balance



- Identify water sources and points of entry to process
- Identify wastewater sources and general characteristics
- Collect data to develop a water flow and mass balance around the refinery

Process Water Sources and Treatment

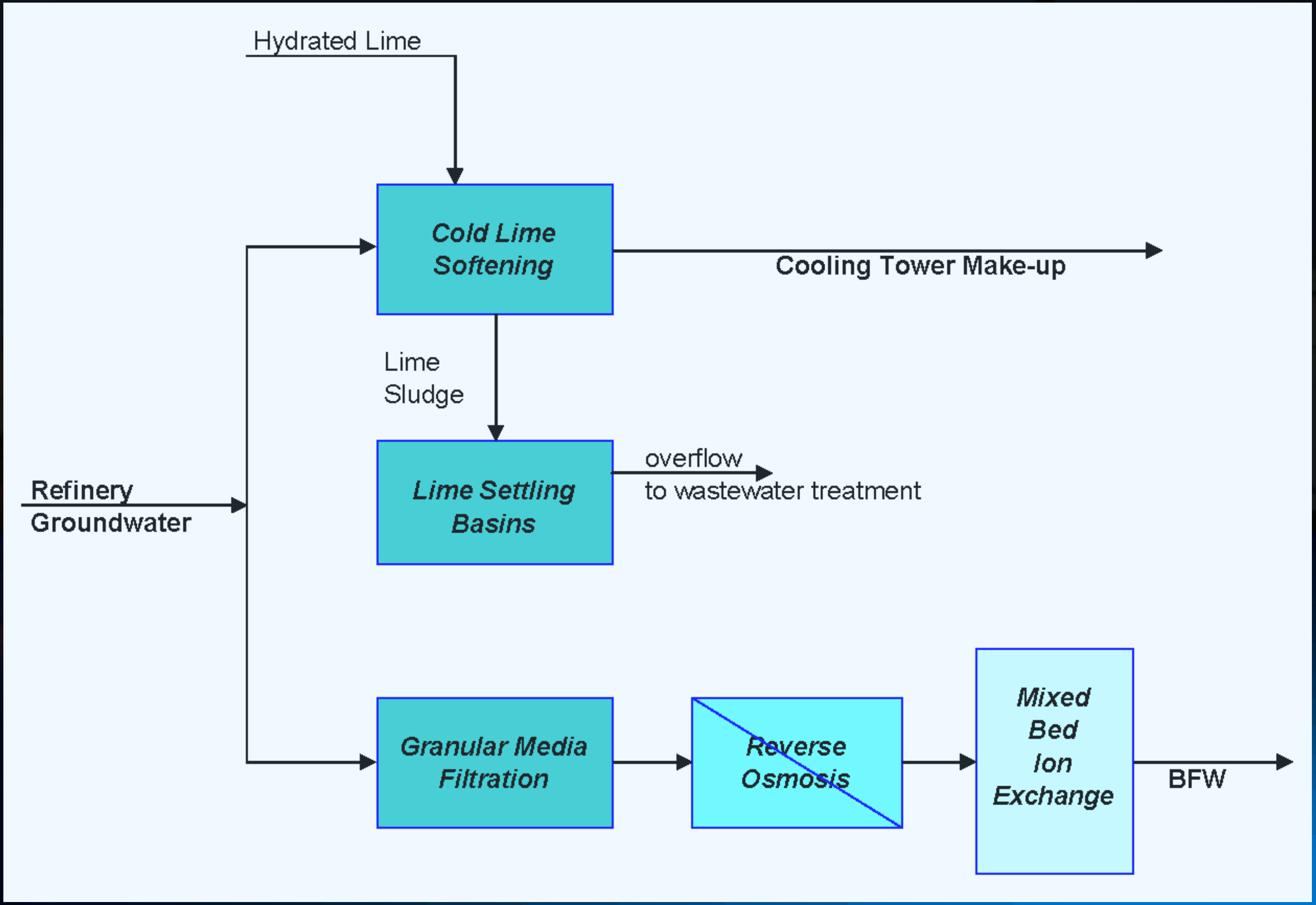
Water Sources

- **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

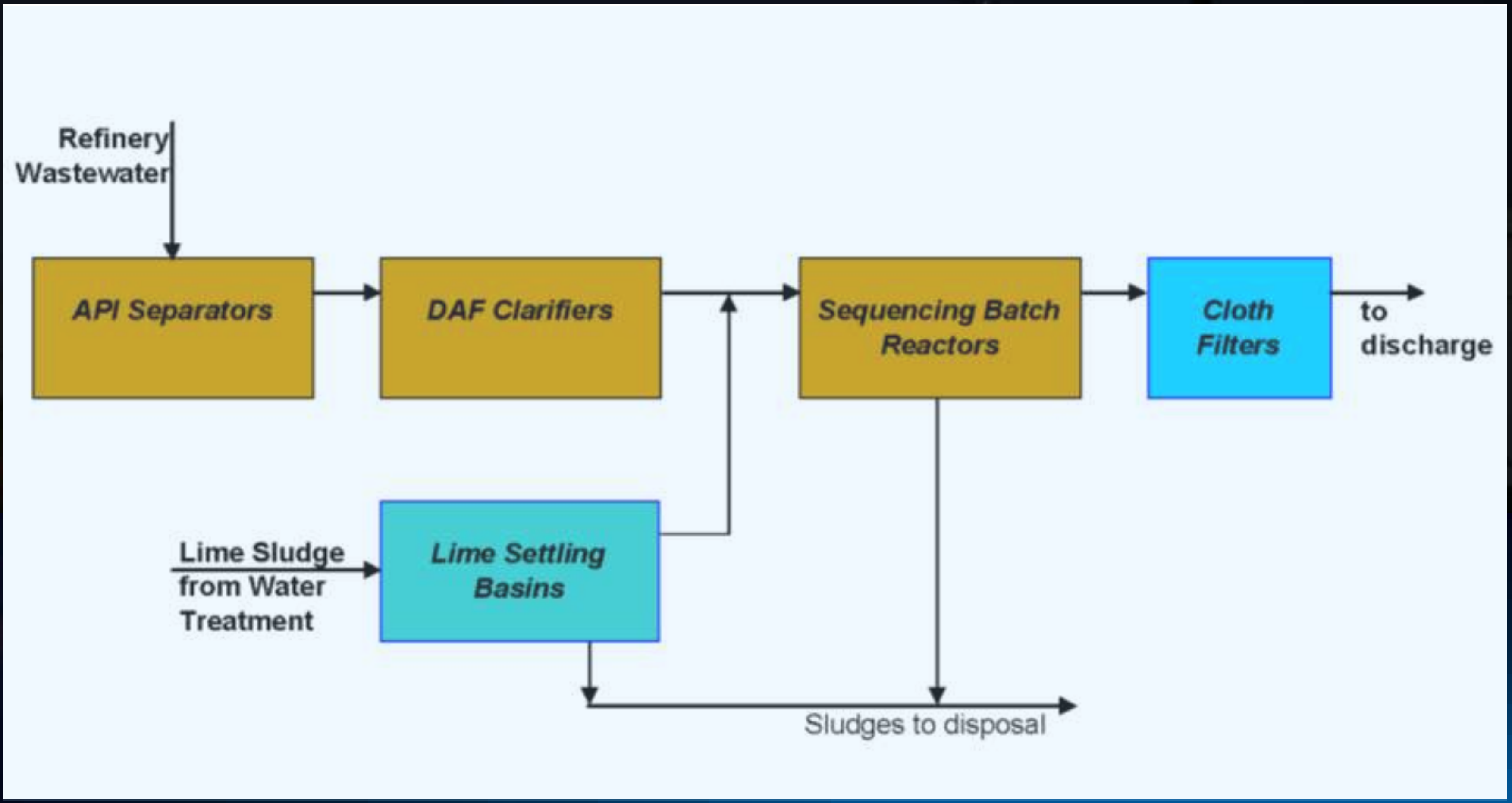
-Dissolved solids

-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 m^3/hr each (1,000 gpm)
- **Oil and sludge storage facilities**

API-DAF Replacement Project

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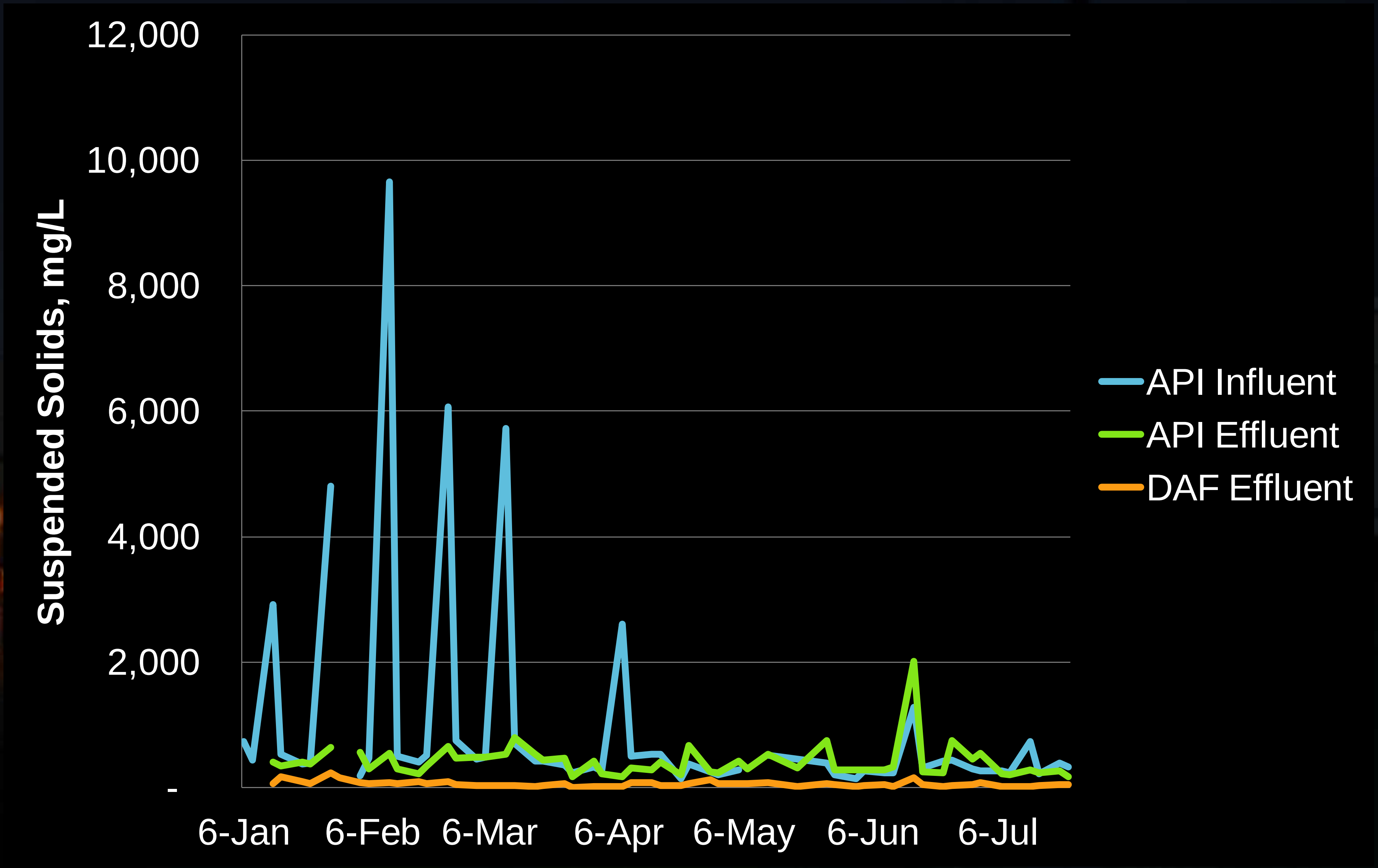
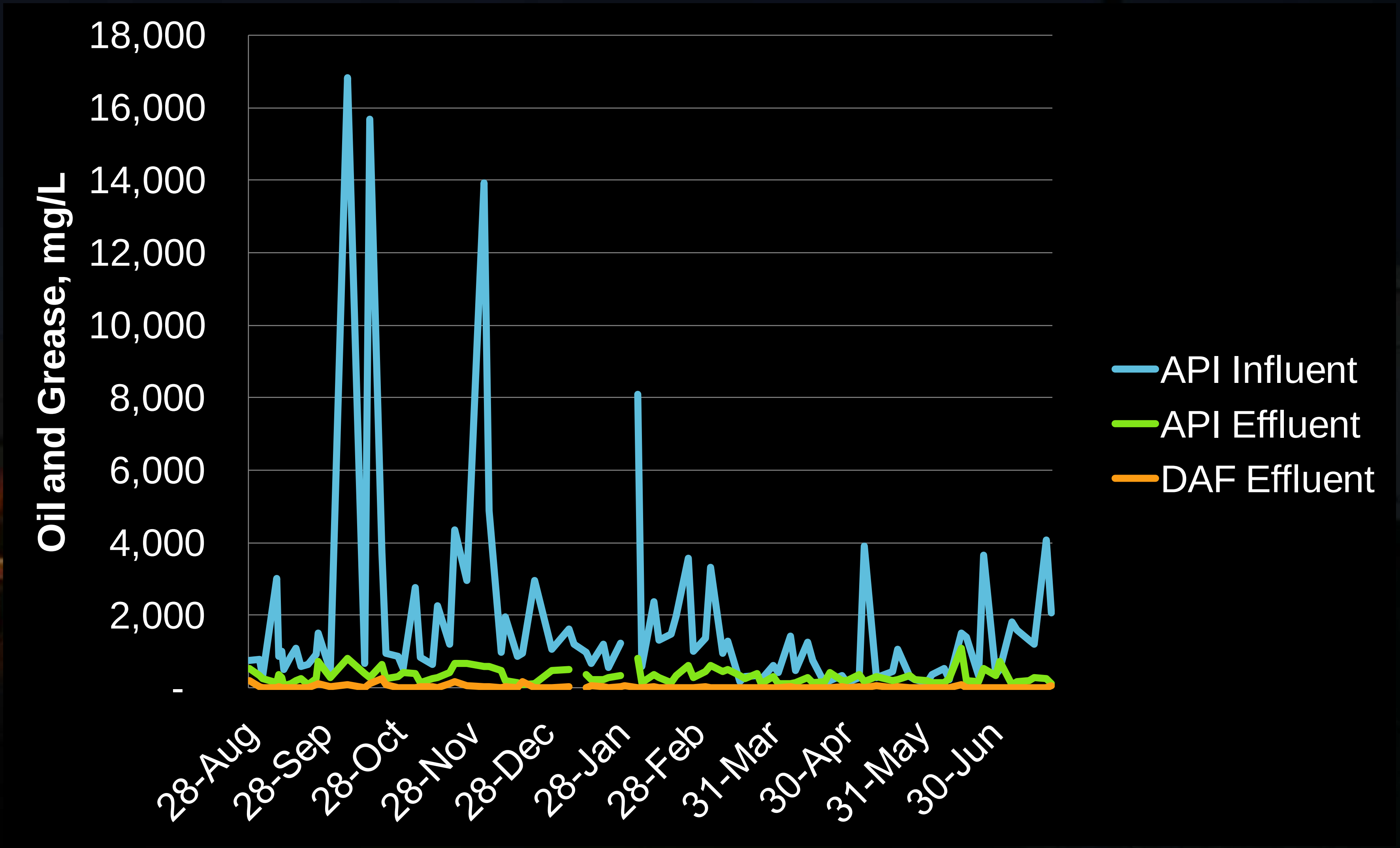
API and DAF Performance – Suspended Solids



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%)

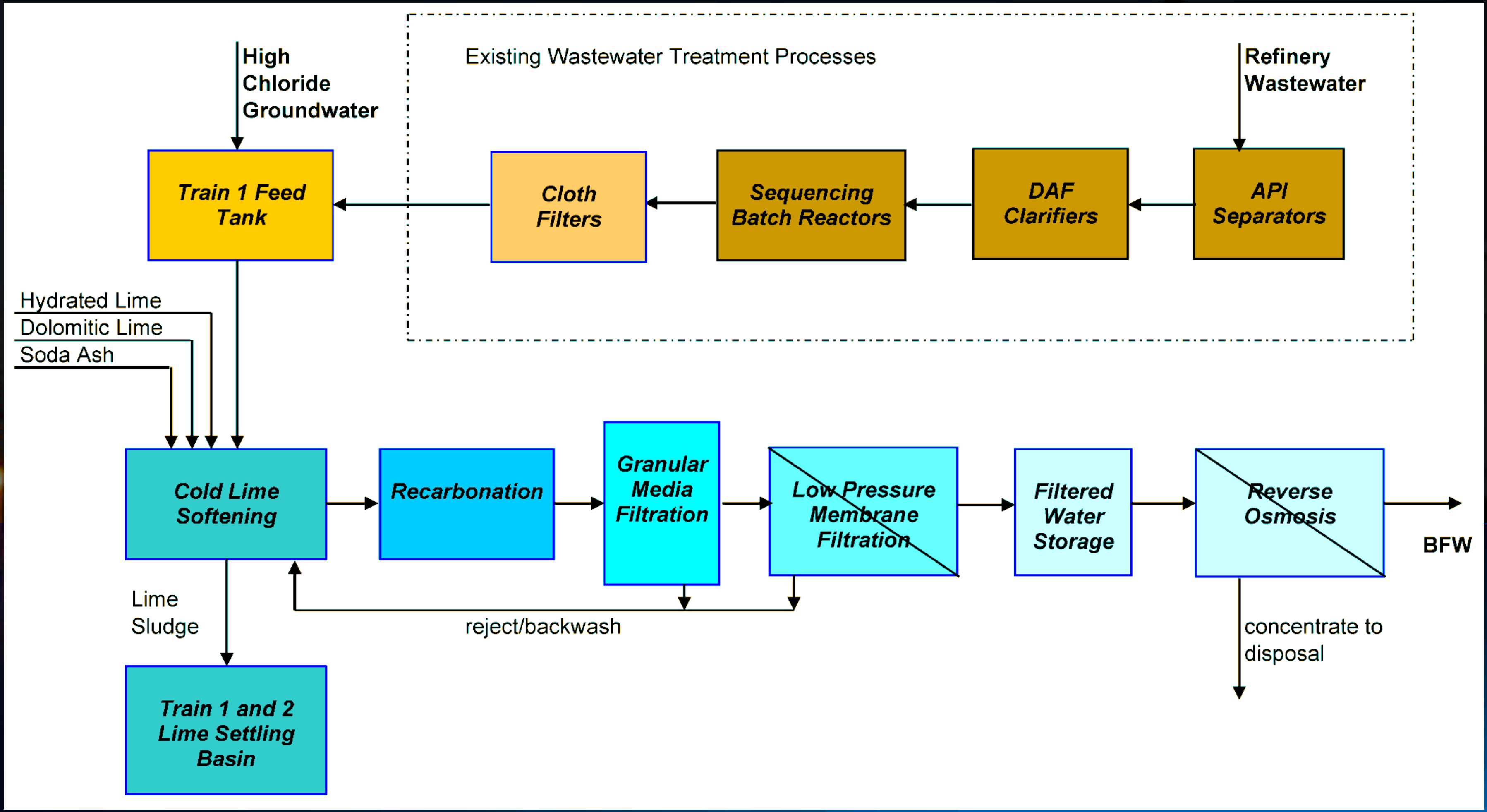
Expected Cold Lime Softening Performance

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**

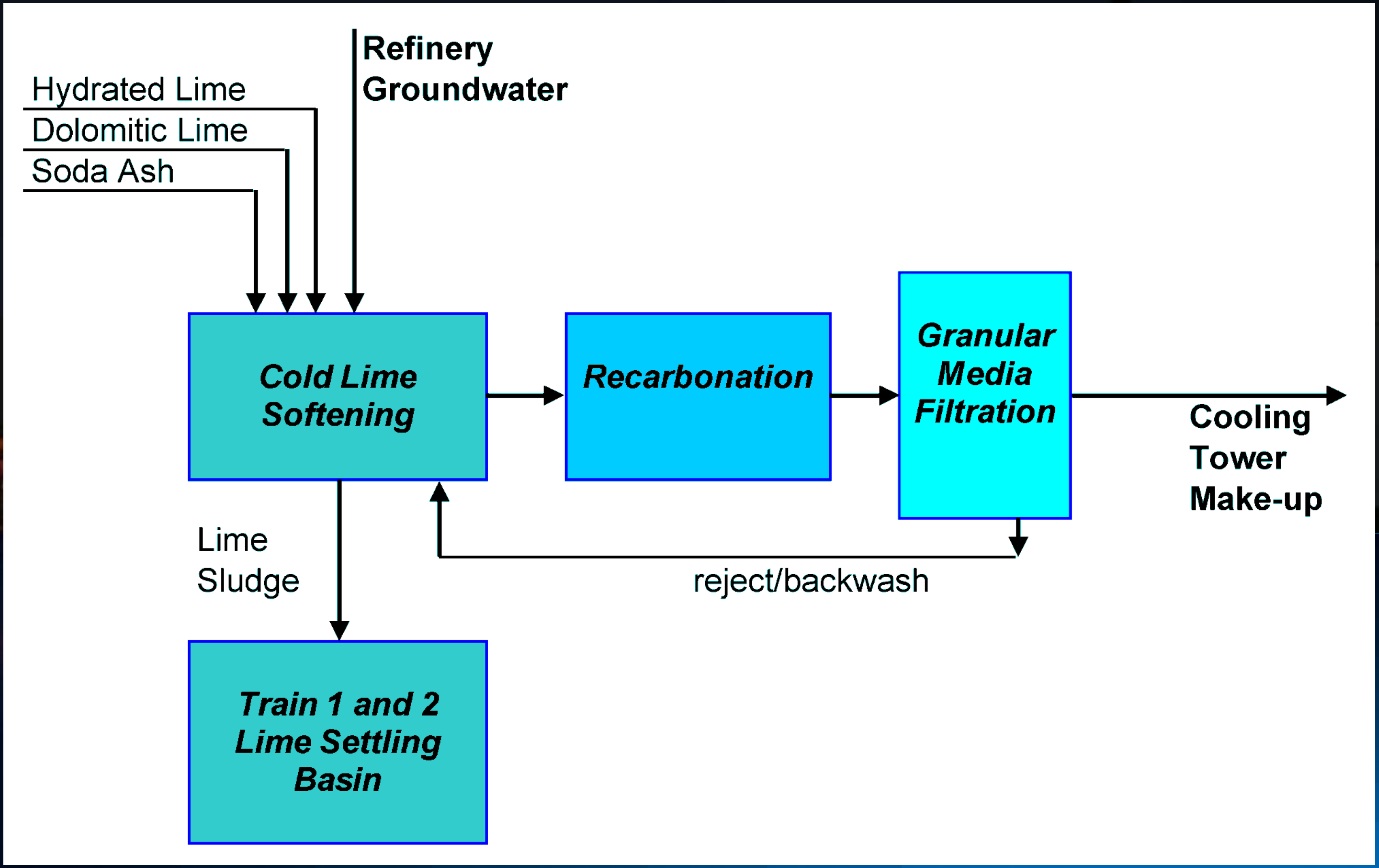
Expected LPMF Performance

Parameter	Feed, mg/L	Effluent, mg/L
COD	**80**	**<30**
BOD_5	**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?