Water Treatment Fundamentals

The Dirty Dozen Revisited

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January 2012

12 COMMON CONTRIBUTORS TO WATER TREATMENT PROBLEMS

The key to successfully designing and operating a water treatment system is to understand the fundamentals of the physics and the chemistry behind the water quality problem. Knowing the source and physical/chemical character of the contaminants is particularly important for selecting water treatment equipment and operating conditions. Without this knowledge, diagnosing and resolving water treatment issues can be problematic.

The more common causes of water treatment challenges can be grouped into the following categories:

- Design and operation of upstream process equipment
- Design and operation of water treatment equipment
- Process conditions (recycle streams, temperature/pressure changes)
- Mixing of Incompatible Fluids
- Presence of fine solids (inorganic or organic) in the produced water
- Chemical treatment programs either upstream of or in support of water treatment

In this presentation, examples of the major contributors to several water treatment problems are given and the manner in which operators resolved their key water treatment issues is discussed. By way of these examples, suggestions are made for identifying the source of and for resolving water quality issues.

Major Contributors to Poor Water Quality - I

1. Inadequate/Improper Design of Upstream Process Equipment
2. Inadequate/Improper Design of Water Treatment Equipment
3. Inadequate control systems on water treatment equipment
4. High shear dispersion of oil droplets in water by Pressure Drops or Pumps

Major Contributors to Poor Water Quality - II

5. Recycling of contaminant and chemical laden emulsions to upstream separators
6. Slug flow of water into/through the water treatment system
7. Solids precipitation as a result of process condition changes: Scale Minerals, FeS
8. Mixing of Incompatible Fluids
   - Incompatible Waters: Scale mineral precipitates
   - Incompatible Oils: Precipitated asphaltenes or wax

Major Contributors to Poor Water Quality - III

9. Formation Fines (e.g., clays) and Neutrally Buoyant, oil-coated solids

10. High concentrations of organic acids or other IFT reducing chemicals in produced water

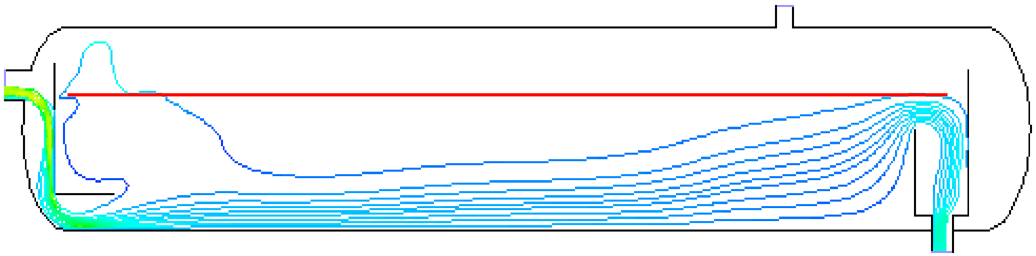
11. Upstream chemical treatment, e.g., water soluble, film-forming corrosion inhibitors

12. The selection and/or injection of water treatment chemicals not optimized

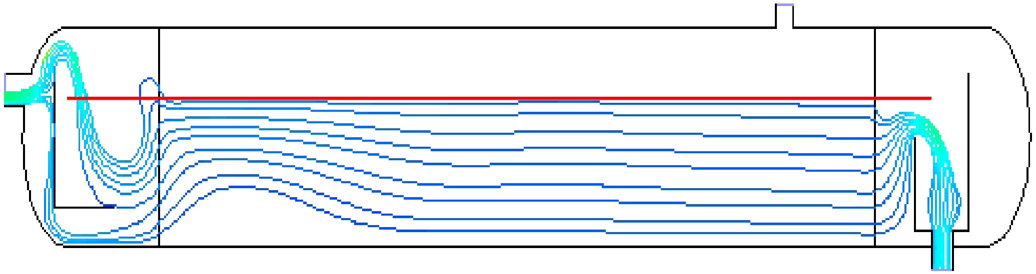
Inadequate/Improper Design or Operation of Upstream Equipment

- **Short fluid residence times**
- **High fluid velocities through a vessel or tank**
- **No control of fluid flow path lines**
- **Low oil/water interface levels**
- **Inability to clear accumulated interface emulsions**
- **Fluid discharges through snap acting valves**
- **Ineffective solids/sand removal from vessels/tanks**
- **Poor designs for inlet and/or outlet nozzles**
- **Dissolved gas evolution/dissolution not considered**

2 Dimensional CFD Illustrates how Flow Path Lines inside a Vessel are Affected by Baffles

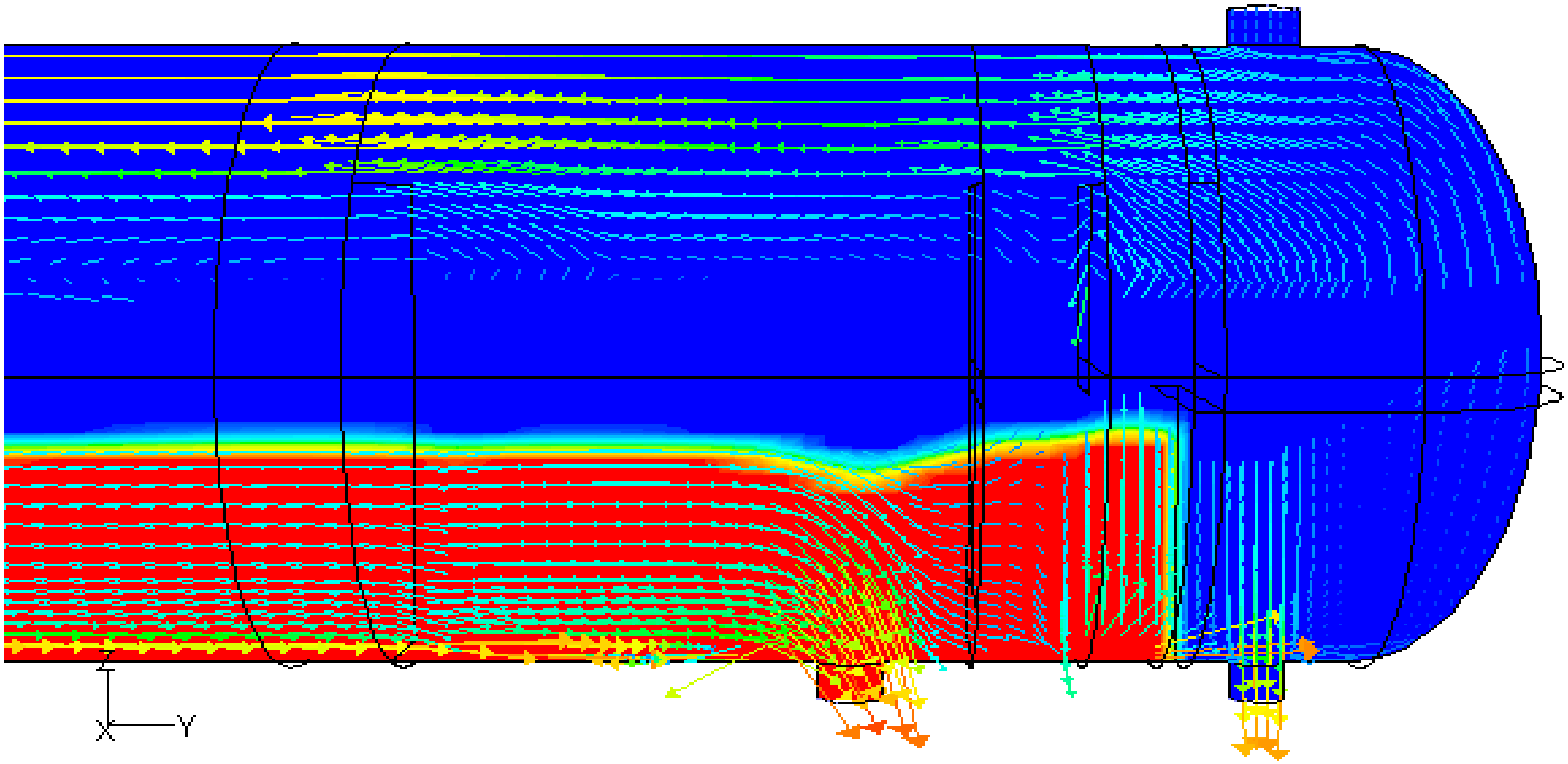


No Baffles for Flow Control



With Baffles for Flow Control

Down-Coning of Water from the Oil Interface Illustrates the Need for Improving Discharge Nozzle Design



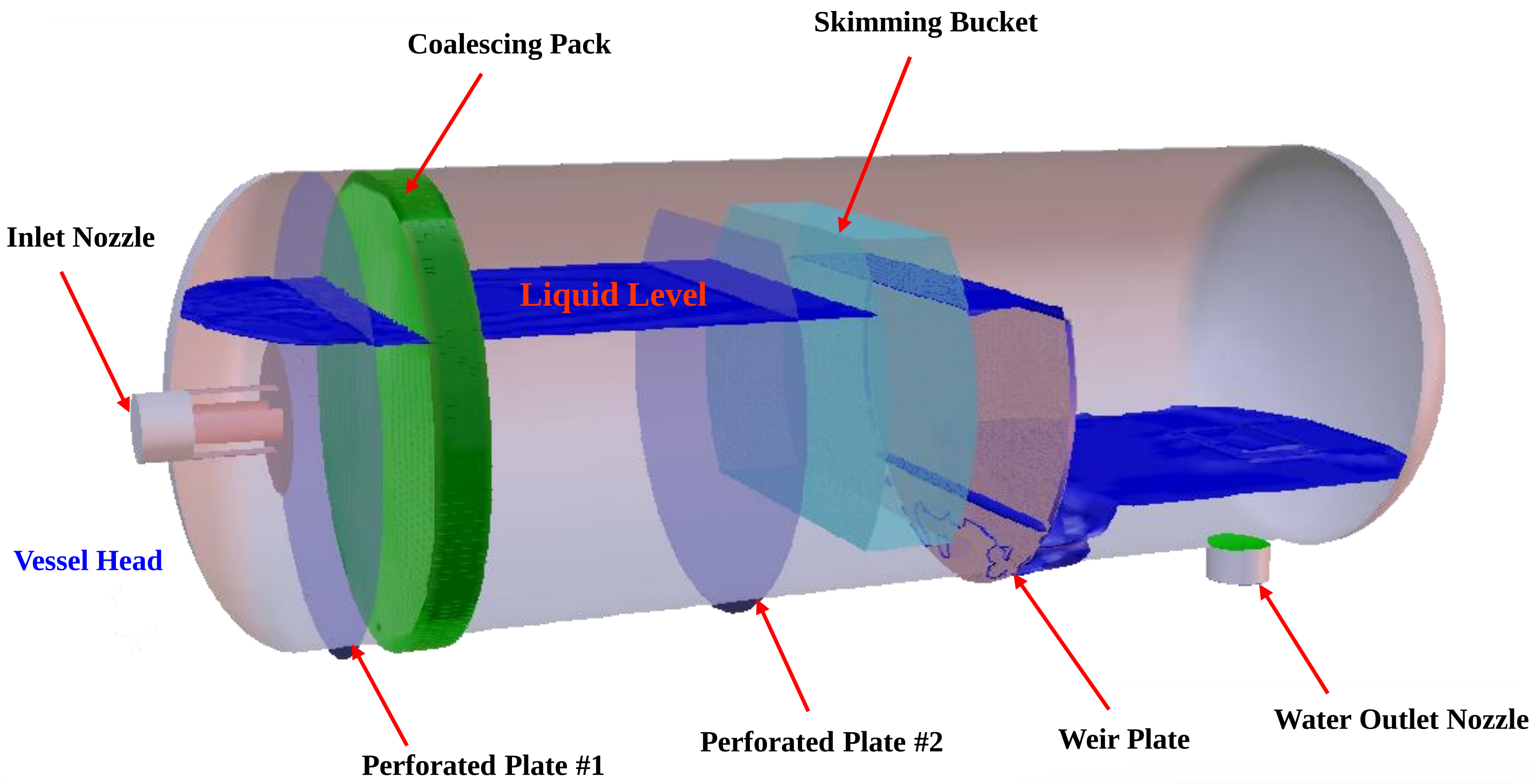
Internals for a 16,000 BBL Tank – Before and After
Design Capacity increased from 20M to 80 MBWPD

Inadequate/Improper Design or Operation of Water Treatment Equipment (The Same list!)

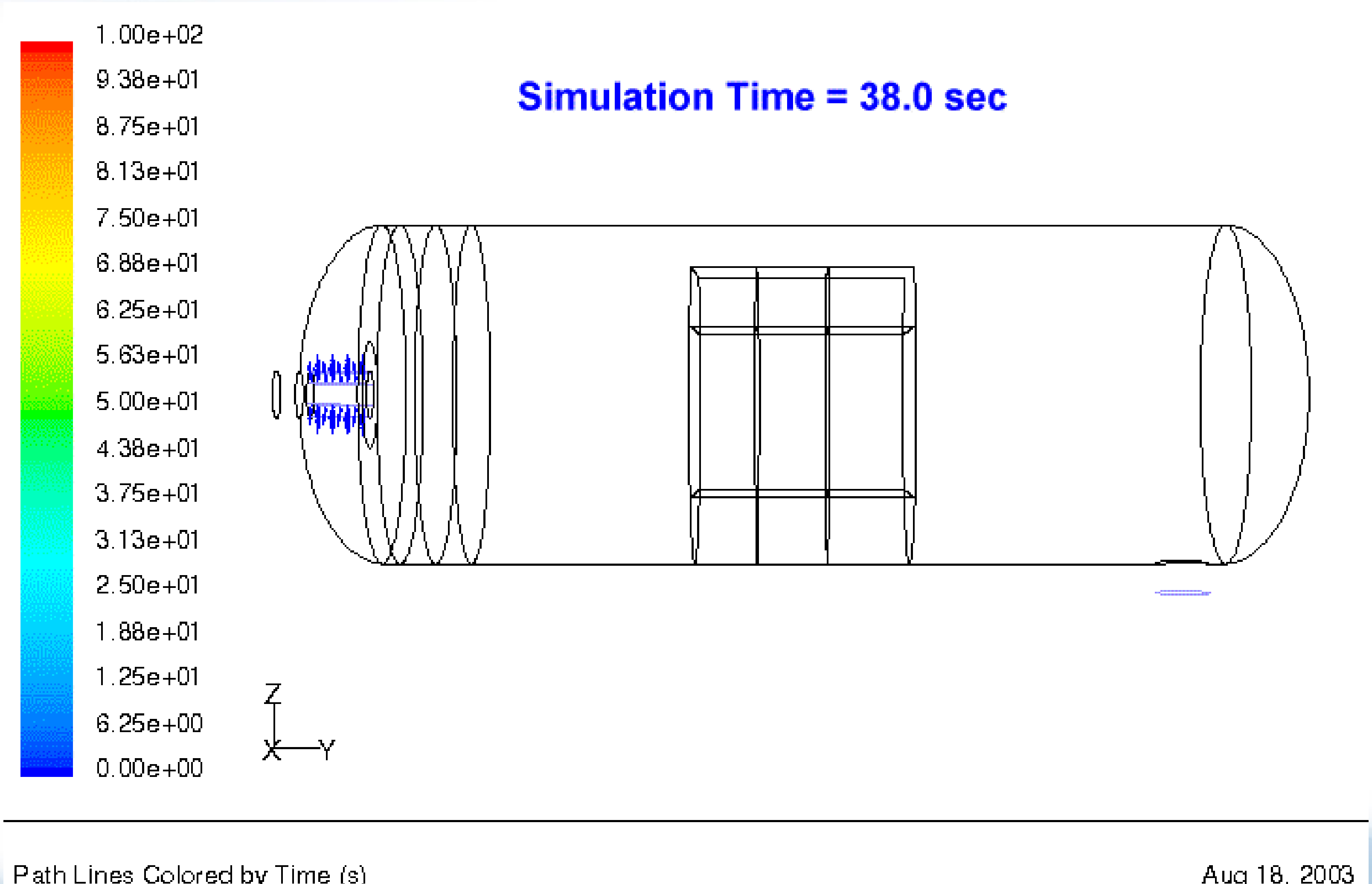
- Short fluid residence times
- High fluid velocities through a vessel or tank
- No control of fluid flow path lines
- Low oil/water interface levels
- Inability to clear accumulated interface emulsions
- Fluid discharges through snap acting valves
- Ineffective solids/sand removal from vessels/tanks
- Poor designs for inlet and/or outlet nozzles
- Dissolved gas evolution/dissolution not considered

Degassing/Skim Vessel with

Perforated Plates for Fluid Flow Control



Animation Shows Uniformity of Flow Through the Vessel



Gas Flotation I

- Three basic Variants on the Technology
  - Mechanical Flotation (e.g., conventional Wemco)
  - Hydraulic Flotation
    - (a.k.a. Induced Static Flotation)
  - Dissolved Gas Flotation
- Captures oil and oily-solids (inorganic TSS)
- Up to 80% of flotation takes place in the first cell
- Balanced skimming is critical for efficient flotation
  - 3 to 5% skim rate preferred; Continuous vs. Periodic?
  - Coherent skim layer or weakly flocculated solids?
- How to compare potential performance efficiency?

"Sweep Factor":
A Flotation Cell Performance Parameter
High Sweep Factor = High Flotation Efficiency

A_{gas} = total cross sectional area of bubbles in a ft^3 of gas (units: ft^2/ft^3)

F_{gas} = gas flow rate (units: ft^3/min)

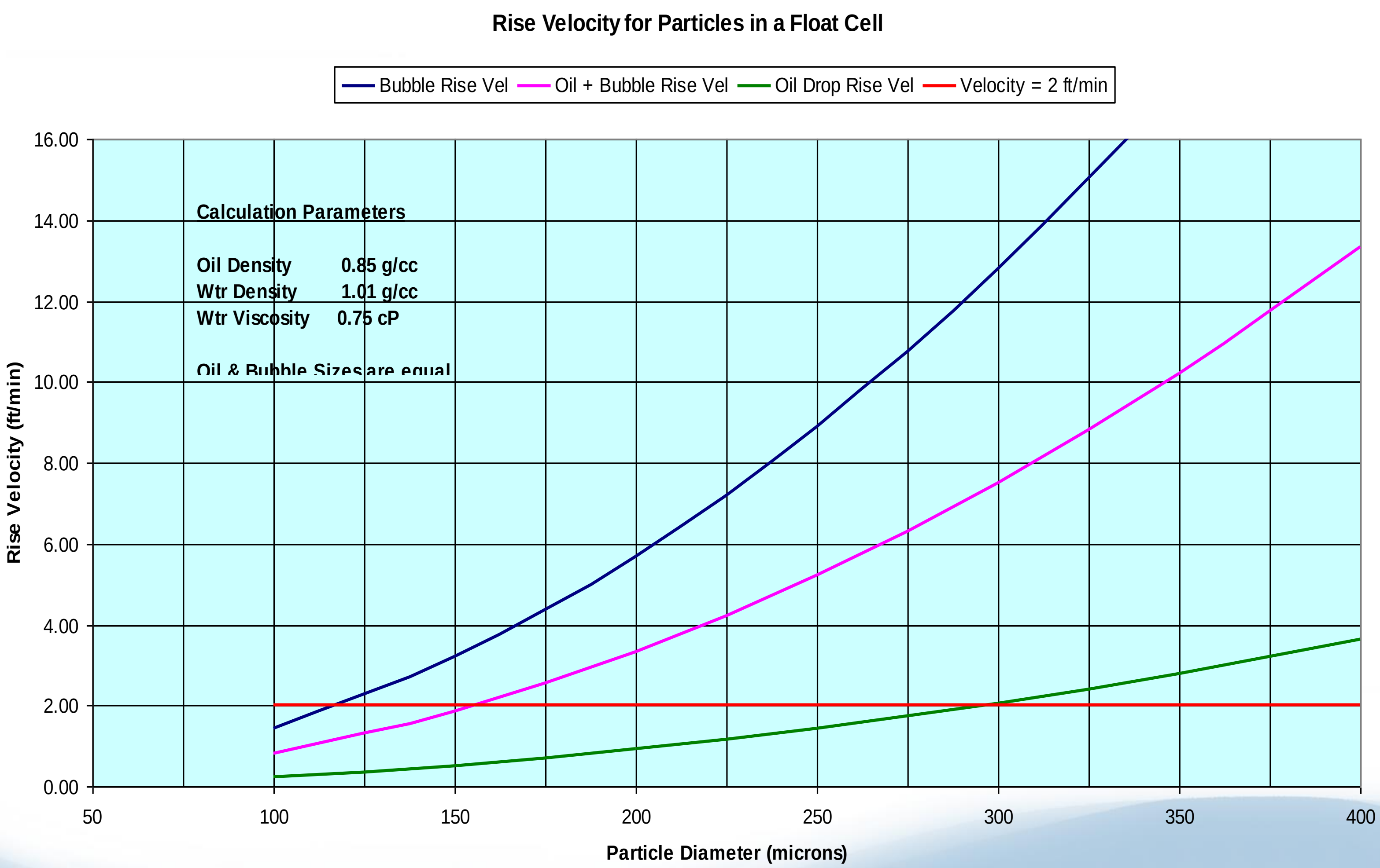
A_{cell} = cross sectional area of flotation cell or chamber (units: ft^2)

$$\text{SWEEP FACTOR } (min^{-1}) = (A_{gas} \times F_{gas}) / A_{cell}$$

For gas flow into an IGF at a rate of 1 SCF/BBL of produced water:

<u>Bubble Diameter:</u>		<u>Sweep Factor:</u>
	100 microns	1634
	120	1362
	200	817
	300	545
	400	408

Rise Velocity for Gas, Oil, and Flotation Particulate



SPEC SERVICES System Planning, Engineering & Coordinating

Dissolved Gas Flotation

- Flotation efficiency increases as bubble size decreases
- Small Bubbles give DGF a potential efficiency advantage
- DGF may require longer retention time for bubble & contaminant separation
- DGF <u>should not</u> be used if water temperatures are high (>160^{o}F or so)
- CO_2 is 20X more soluble in water than is CH_4
- Hydraulics for gas introduction are critical to performance

Mechanical Gas Flotation

- Introduces high volumes of gas into the water
- Typical bubble sizes are large
- May have a problem if oily solids are weakly flocculated or do not adhere to the froth
- Use of skim paddles permits handling of thick flocs
- Continuous skimming with variable water levels is facile (note design of skim paddles)
- Keep skim buckets well drained (all technologies)

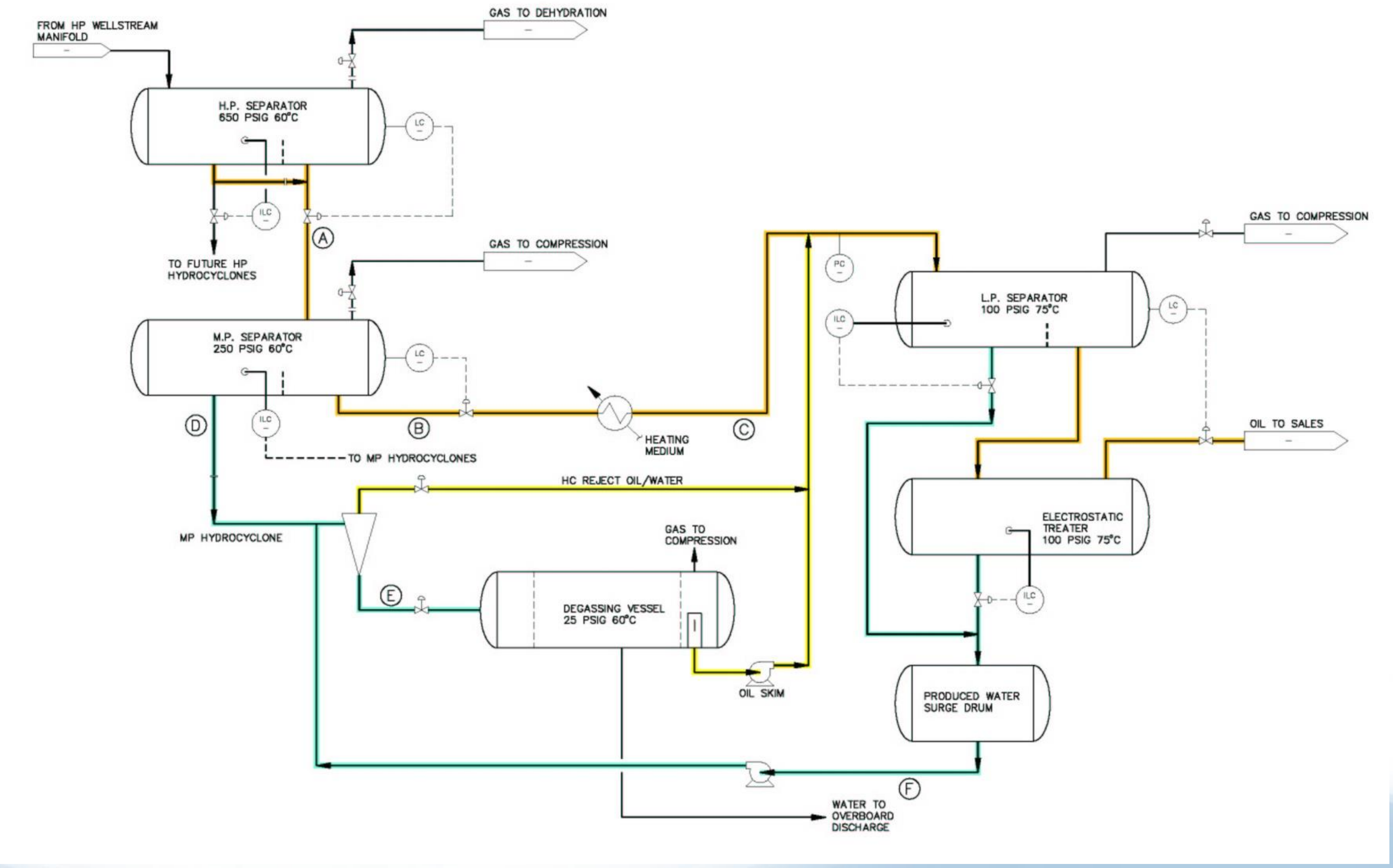
Hydraulic Gas Flotation

- Introduces modest volumes of flotation gas
- Typical bubble sizes are 100 to 300 μ
  - Bubble sizes grow large if GVF in eductor flow exceeds 15 to 20%
- Eductor designs and efficiency varies considerably
- 20 to 50% recycle streams impact capacity
- Pump & eductor shear can reduce polishing efficiency
- Quiescent flotation effective for weakly flocculated contaminants

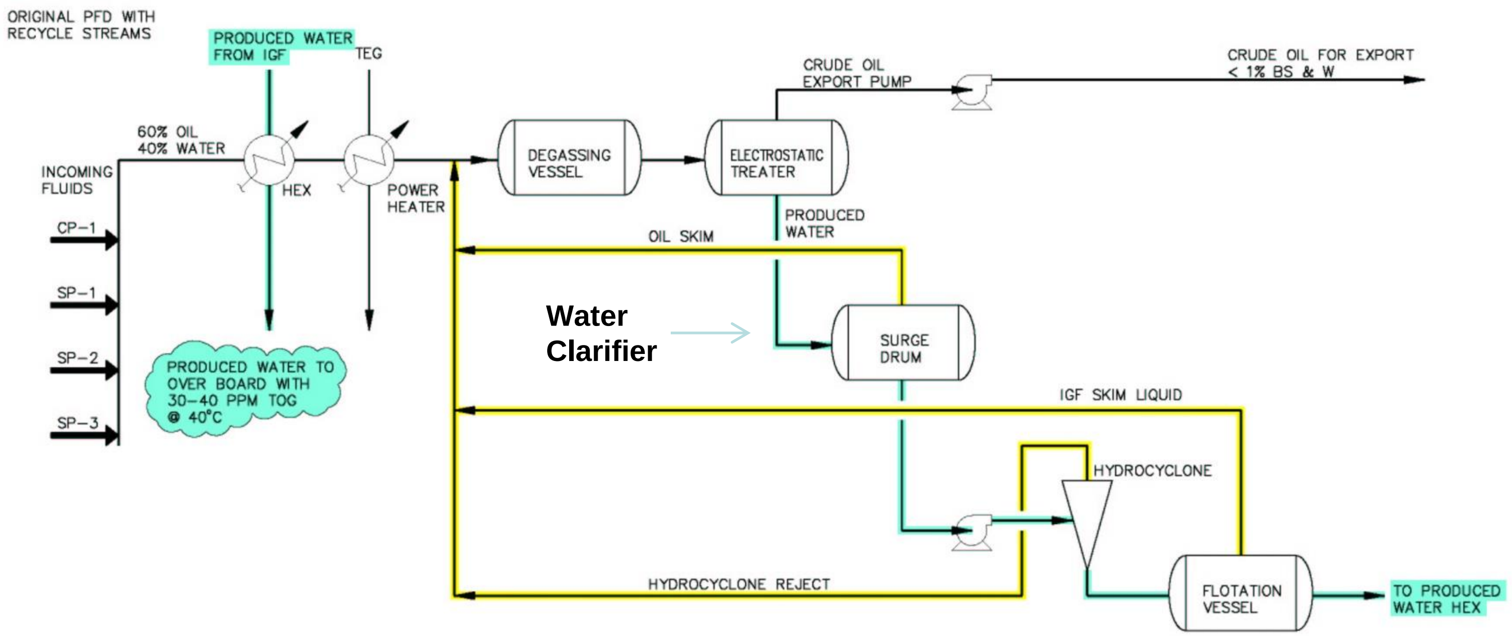
DeOiling Hydrocyclones

- **Use Automatic Control to Maintain the Pressure Drop Ratio between 1.5 and 2.5**
- **Account for Dissolved Gas Break-out in the Design of Reject Control, Piping, and Hydraulics**
- **Scale deposition in reject stream?**
- **Scale mineral precipitates may go with rejects**
- **A simple bench-top centrifuge test can predict the likely performance of a hydrocyclone system**
- **Field droplet size distribution data is helpful**

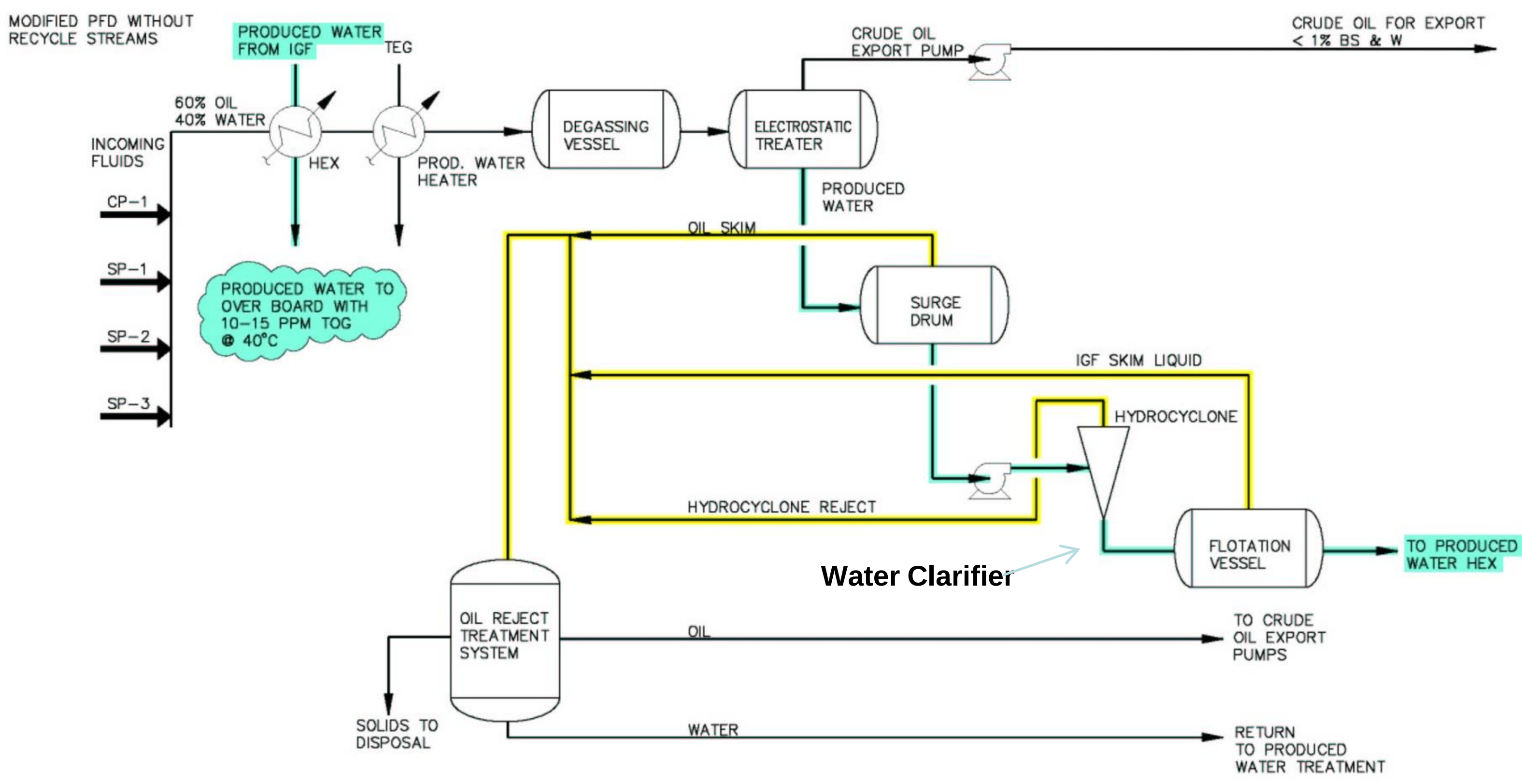
High Shear from a Control Valve Generates Small Oil Droplets (20µ avg) that do not Coalesce



Recycle Streams Send Removed Contaminants Back into the Process, Leading to Upsets and Poor Performance



Eliminating Recycle Streams, reduced TOG to <15 PPM



Slug Flow Sources

- Snap acting valves on upstream equipment
- Slugs can form in flow lines due to gas carry-under from upstream equipment
  - 1 to 5% GVF @ the level control valve is common
- Dissolved gas break-out due to pressure drops across valves or in piping
- Terrain induced slugging
- Software exists for modeling 3-phase flow in piping and predicting slug characteristics

Slug Flow Consequences

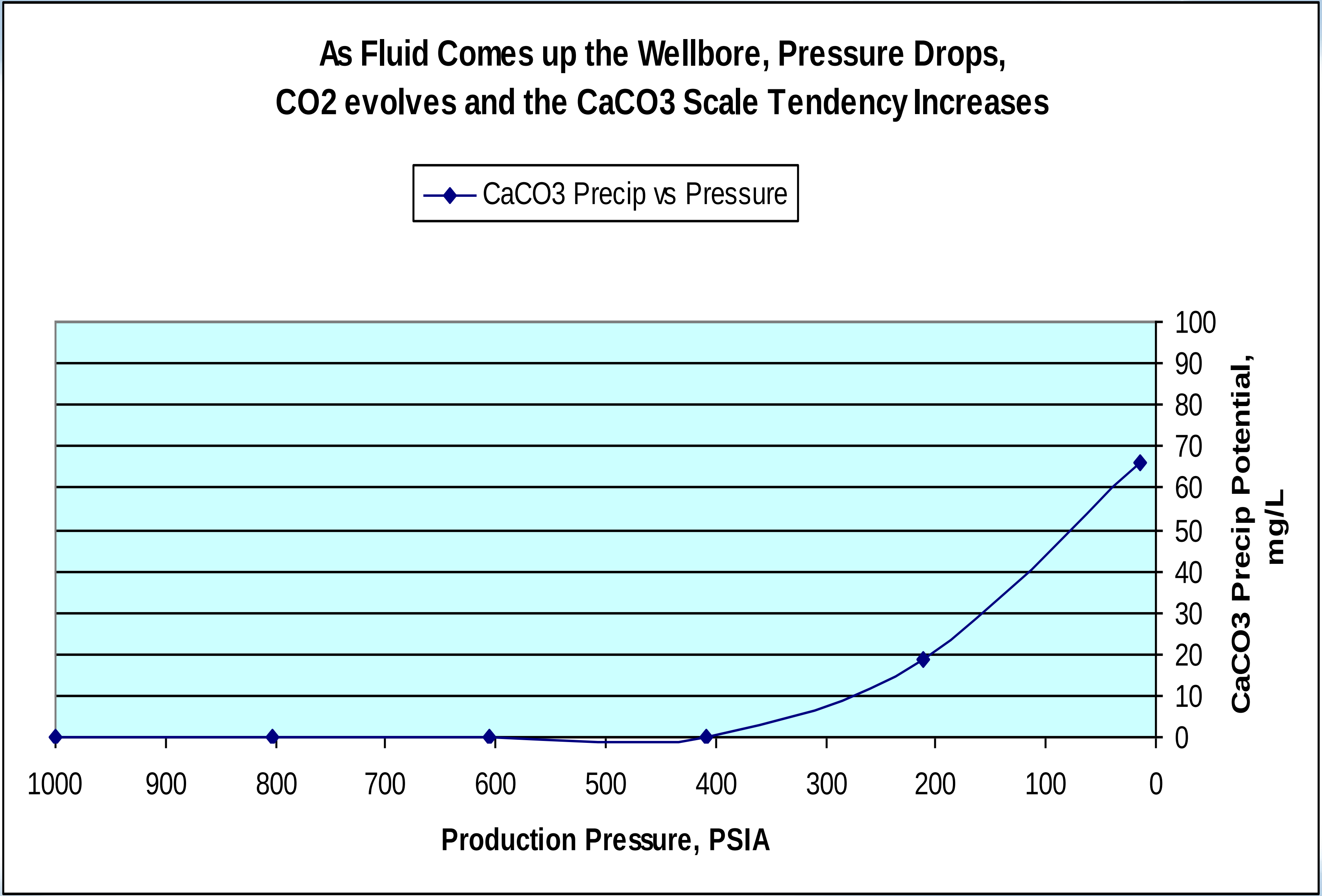
- **Poor performance of hydrocyclones**
- **Uneven, inefficient skimming in flotation cells**
- **Redistribution of weakly flocculated solids in skimmers and float cells**
- **Continuous over-treat/under-treat condition for water clarifiers**
- **Highly variable residence times in tanks/vessels**
- **Level control problems in vessels**

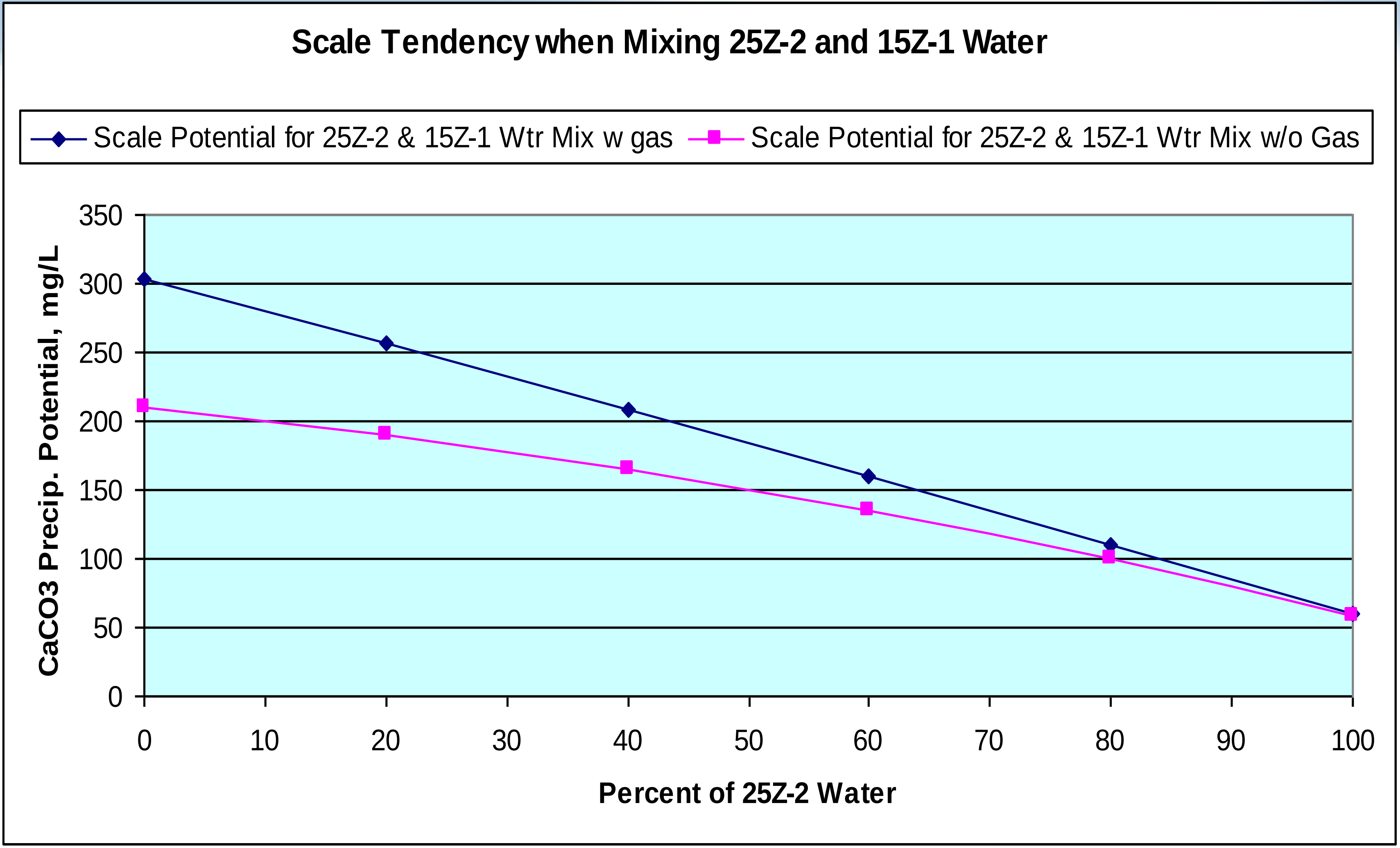
Produced Water Chemistry is a Complex Ionic Balance

- Water chemistry should be assessed because
  - Incompatible waters from several producing zones are often mixed
  - Scale mineral precipitation is dependent on
    - Where waters are mixed
    - Specific Process Conditions
  - Scale inhibitors may delay or slow but not prevent mineral precipitation
- Surface Water Analyses (e.g., a typical Geochem) do not represent water chemistry at Process Conditions.

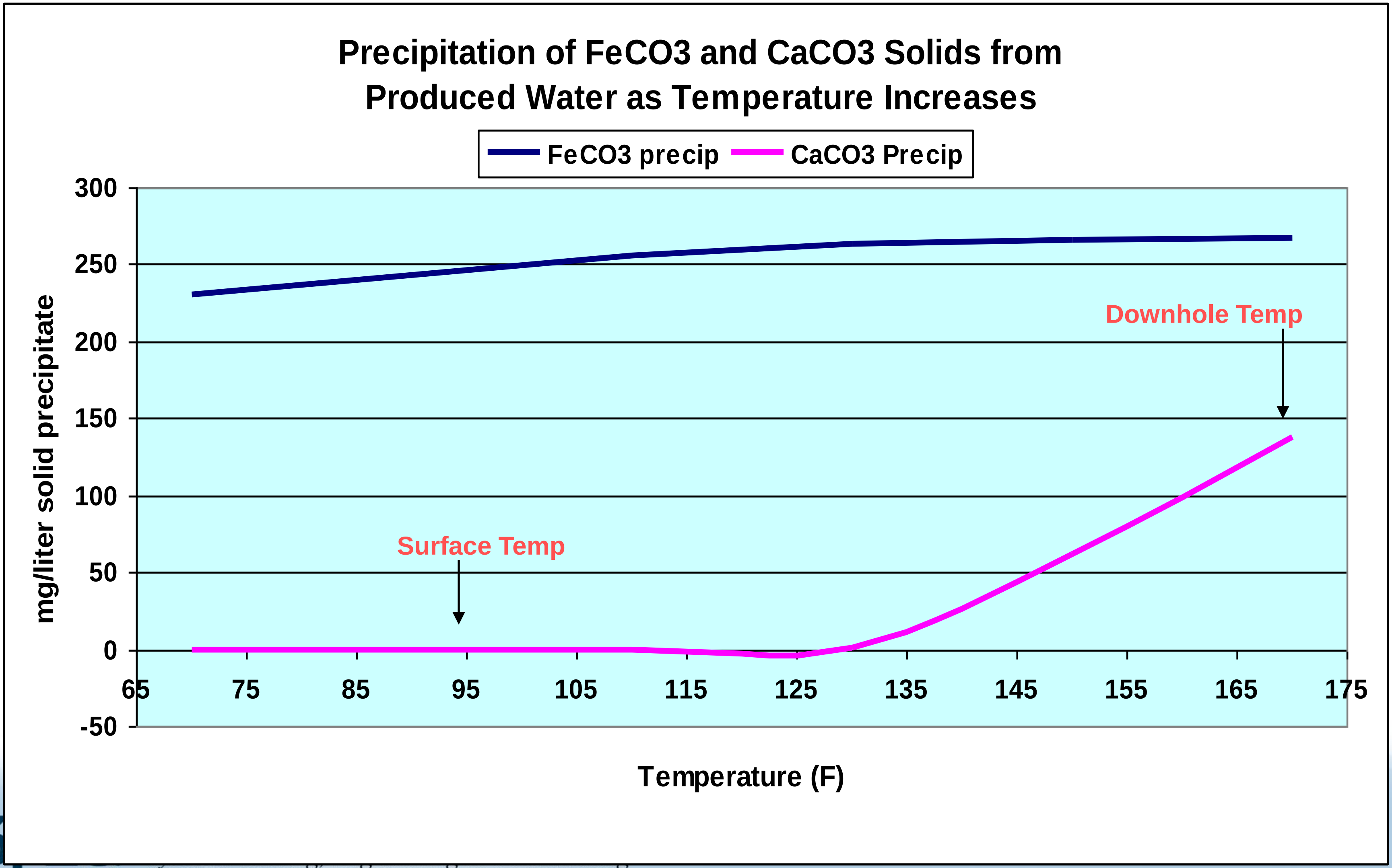
Produced Water Chemistry is a Complex Ionic Balance

- Commercially available thermodynamic water chemistry models are available which can
  - Carry out $CO_2/HCO_3^-/CO_3^=$ balance calculations
  - Gas-saturate water at process temperature and pressure
  - Determine if the solubility of divalent salts are sensitive to
    - Temperature
    - Gas composition and pressure
    - Presence of soluble alcohols, e.g., Methanol


As Fluid Comes up the Wellbore, Pressure Drops,
CO2 evolves and the CaCO3 Scale Tendency Increases
CaCO3 Precip vs Pressure
100
90
80
70
60
50
40
30
20
10
0
1000
900
800
700
600
500
400
300
200
100
0
Production Pressure, PSIA
CaCO3 Precip Potential, mg/L


Scale Tendency when Mixing 25Z-2 and 15Z-1 Water
Scale Potential for 25Z-2 & 15Z-1 Wtr Mix w gas
Scale Potential for 25Z-2 & 15Z-1 Wtr Mix w/o Gas
CaCO3 Precip. Potential, mg/L
350
300
250
200
150
100
50
0
0
10
20
30
40
50
60
70
80
90
100
Percent of 25Z-2 Water

Thermally induced scale mineral precipitation plugs formation near the well bore



SERVICES

Neutrally Buoyant, Oil-Coated Solids

- **Best removed by flocculation and flotation**
- **High MW polymers are effective at collecting solids**
  - **Can be difficult to disperse into water**
  - **Simple systems are available to easily disperse high MW emulsion polymers**
- **Ferric Chloride or Dithiocarbamates are effective solids collectors**
  - **Both chemicals create heavy floc which can clog instrumentation, float cells, or bed filters**

Ultra-Fine Inorganic/Organic Solids

- Precipitated minerals are typically in the 5 - 20 micron size range
- Mineral precipitates tend to be oil-wetted & neutrally buoyant
- Most common precipitates include
  $CaSO_4$ $CaCO_3$ $FeCO_3$ $BaSO_4$
- Formation Fines: Clays, precipitated Silica, …
- Identify precipitated minerals using XRD
- Wax or Asphaltenes dispersed in water

High Concentrations of Organic Acids

- **Common when production is from hot formations or biodegraded oils**
- **Naphthenic acids in crude have some surfactant character**
- **Surface activity enhanced in the presence of low concentrations of divalent ions**
- **Requires specialized analyses to find and identify organic acids**
- **CO_2, acetic acid, phosphorous acid, $AlCl_3$, $FeCl_3$ can reduce the surface activity of organic acids**

Iron Sulfides

- **Major sources of Iron Sulfides**
  - **Sour production**
  - **SRB activity + Long Retention Times**
- **$FeCO_3$ often mistaken for FeS**
- **Iron Sulfides: neutrally buoyant, oil-coated**
- **Dried FeS can be pyrophoric**
- **Best removed by froth flotation**
- **Degradation Products in Dried Solids Sample: Fe_3O_4 and S^o**

Common Chemical Types in the Oil Patch

• Demulsifiers	Excess stabilizes reverse emulsions
• Defoamers	Reduce foam and flotation efficiency
• Hydrate Inhibitors	CH_3OH precipitates divalent salts
• Corrosion Inhibitors	Inhibits floc formation & foaming
• Scale Inhibitors	Limits size of mineral precipitates
• Water Clarifiers	Over-treating degrades water qual.
• Flocculent Polymers	Collect solids; support flotation
• Biocides	Some have surfactant properties
• H_2S Control Agents	May benefit water quality
• TEG	Normally no impact on water qual.
• Various amines	Normally no impact on water qual.

Summary & Conclusions

- **Develop an understanding of the physics and chemistry behind a water treatment problem**
- **Several factors are likely to synergistically combine to degrade water quality**
- **Address mechanical problems first**
  - **Equipment and technology selection**
  - **Process design (recycle streams)**
- **Consider all aspects of process chemistry**
  - **Water, Oil, and Process Chemistries**
  - **Process conditions**