Characterization of Produced Water for Topsides / Surface Water Treatment

- Issues involved
- How to characterize
- How to interpret
- Some examples

Why Characterize Produced Water?

Why characterize produced water?

- **To meet quality required by regulatory environment & ultimate fate (injection, waterflood, overboard discharge)**
- **Troubleshooting – characterization provides a clue to improving system performance.**
- **Design – a produced water treating system that can handle all types of produced water would be large and expensive. Design compromises must be made.**
- **The produced water treating equipment should be designed to handle the specific characteristics of the produced water of a particular field.**
- **To develop specifications for equipment vendors to bid against**
- **To develop specifications for performance agreements**

Observations from Produced Water Society President - Colin Tyrie

- EP Engineers tend to fit the process to the system whereas it should be the reverse.

- Typical oilfield process engineers lack field experience, specific knowledge of produced water flow properties, surface chemistry, and colloidal science. Also, they select generic water treating equipment that may or may not be suitable for the particular fluid characteristics.

- This has resulted in water treatment designs that:

  (1) Are an afterthought

  with too little space available for needed equipment (major problem offshore);

  lack of needed process connections;

  lack of process monitoring equipment for produced water quality.

  (2) Are mismatched to the system

  with too little capacity in one area and too much in another;

  too little capacity for reject streams;

  too little capacity to treat solids, complex emulsions, and recycle streams.

  (3) Are designed to the wrong quality specifications.

  (4) Have bypassed or abandoned equipment.

- Properties of the produced water can change with time. Equipment and processes should be modularized or adaptable to increase or decreases in flow, and changes in produced water properties.

Can we define a 'Standard Oilfield Produced Water Characterization Procedure'?

- **A number of benefits:**
  - **Save time**
  - **Enable sub-contracting of the task**
  - **Reduce mistakes of omission which can cascade into design problems**
  - **Develop a database from which to correlate equipment performance with produced water characteristics.**

- **Are there other EP Industry Standards that we can draw upon?**
  - **Oil and Grease measurements**
  - **Hydrocarbon (liq & gas) analysis for Flow Assurance is well developed**
  - **Water analysis for scaling potential is more or less standard**
  - **Solids analysis is well developed**
  - **New on-line tools available for drop size**
  - **Attitude toward sample system design is improving.**

- **Are there standards from other industries that we can draw upon?**
  - **ASTM**
  - **Handbook of Water Analysis methods**
  - **Municipal water standards**
  - **Navy standards for ballast water**

What is Produced Water?

- **Components Present in Produced Water**
  - Dispersed oil
  - Dissolved oil (HC, BTX, phenols, PAH, etc)
  - Dissolved organic acids (SCFA, naphthenic acids)
  - Dissolved formation minerals (NaCl, $CaCO_3$, $FeCO_3$, FeS_x, $BaSO_4$, etc)
  - Dissolved metals (Fe, Zn, Cr, Mn, etc)
  - Process & Production chemicals (CI, MeOH, glycols)
  - Produced formation solids (clay, sand, carbonate)
  - Precipitated mineral solids ($CaCO_3$, $FeCO_3$, FeS_x, $BaSO_4$, etc)
  - Dissolved and precipitated corrosion products (metal oxides)
  - Dissolved gases (O_2, H_2S, CO_2)
  - **Combinations of the above (e.g. Schmoo)**
  - Various bacteria and by-products (SRB, GHB)

What is Unique about Produced Water?

- **Produced Water is different from other Waste Waters in several important respects:**
  - Having been in contact with an oil phase, it contains dissolved oil components and dispersed oil. Oil floats to the top.
  - The oil drops have a drop size distribution. The drop size distribution puts demands on sampling.
  - Having never been in contact with oxygen, once that occurs, solids will precipitate.
  - Produced water goes through a rapid change in T & P which shifts equilibria and can cause solids to precipitate.
  - Solids can become oil wet and form a conglomerate with a large range of possible densities and a range of surface activity.

What are the gaps in current practice?

- Need an understanding of what to do with results - what design requirements are implied by any given set of characterization results.
- Interpretation of results is a specialized subject and has got to be simplified for application by process engineers.
- Need better understanding of equipment performance (equipment sometimes performs better and sometimes worse than advertised) as a function of characteristics.
- Need more case studies from which to complete the circle of fluid characteristics and equipment performance.

- **Important Analyses in Produced Water Characterization:**
  - **Oil droplet size distribution (on-line and off-line)**
  - **Oil in water concentration**
  - **Oil flow assurance analysis (SARA, wax, paraffin, asphaltenes)**
  - **Gas & oil composition (H_2S, CO_2, BTEX, naphthenates, TAN, biodegradation)**
  - **Water analysis (anions, cations, pH, hardness, alkalinity, dissolved gases , organics, COD, toxicity, etc)**
  - **Suspended solids concentration, PSD, composition and mineralogy**
  - **Desktop settling, visual observations, and optical microscopy**

How to Interpret the Results

Some Examples

Comparison is the key

Typical Oil vs Gas Produced Water Properties:

Table 2.1
Typical hydrocarbon discharges from a selection of North Sea oil and gas production platforms (1989)

		Oil platforms	Gas platforms
Number of platforms measured		12	15
Total oil or gas production	sm^3/d	75,600 (475,500 bopd)	49,100,000 (1,734 MMscfd)
Total produced water	m^3/d	63,713	612
Total hydrocarbon discharge [1]	tonne/y	500	216
Dispersed oil concentration	mg/l	15.3	483.9
Dissolved oil concentration	mg/l	6.2	481.9
Polar hydrocarbon concentration	mg/l	165.9	230.1

[1] Refers to mineral hydrocarbons e.g. aliphatic and aromatics, does not include polar hydrocarbons such as organic acids.

Source: "The composition of produced water from Shell operated oil and gas production in the North Sea", International Produced Water Symposium, Feb. 1992, San Diego, submitted by SIPM/Expro/NAM, ref 1.01.1.b.

Solubility of Oil in Water:

Table 2.2
Solubility of hydrocarbons in water (mg/l at 15°C)

Number of carbon atoms	ALKANES: Normal C_nH_{2n+2}	ALKANES: Cyclo (C_nH_{2n})	AROMATICS: 1 Ring (C_nH_n)	AROMATICS: 2 rings (C_nH_{n-2})
1	25	-------	-------	-------
2	75	-------	-------	-------
3	100	650	-------	-------
4	100	-------	-------	-------
5	60	100	-------	-------
6	12	50	1700	-------
7	2.6	20	500	-------
8	0.6	6	200/350	-------
9	0.1	2	60	-------
10	0.02	-------	15	-------
11	-------	-------	5	24

Notes:

1. These solubilities are for binary systems of a single hydrocarbon and fresh water and are only indicative for produced waters. Solubility levels in produced waters may be different due to factors such as:
   a) The effect of the temperature and pressure in the reservoir where the water is in contact with the hydrocarbons.
   b) The presence of other species dissolved in the water phase such as inorganic salts and soluble organic species such as organic acids.
   c) Preferential partitioning of the hydrocarbons to the hydrocarbon phase when both hydrocarbon and water phases are present.
2. Source: Superseded SIPM Dehydration/Deoiling manual, EP 89-0150

Toxicity of Produced Water Components:

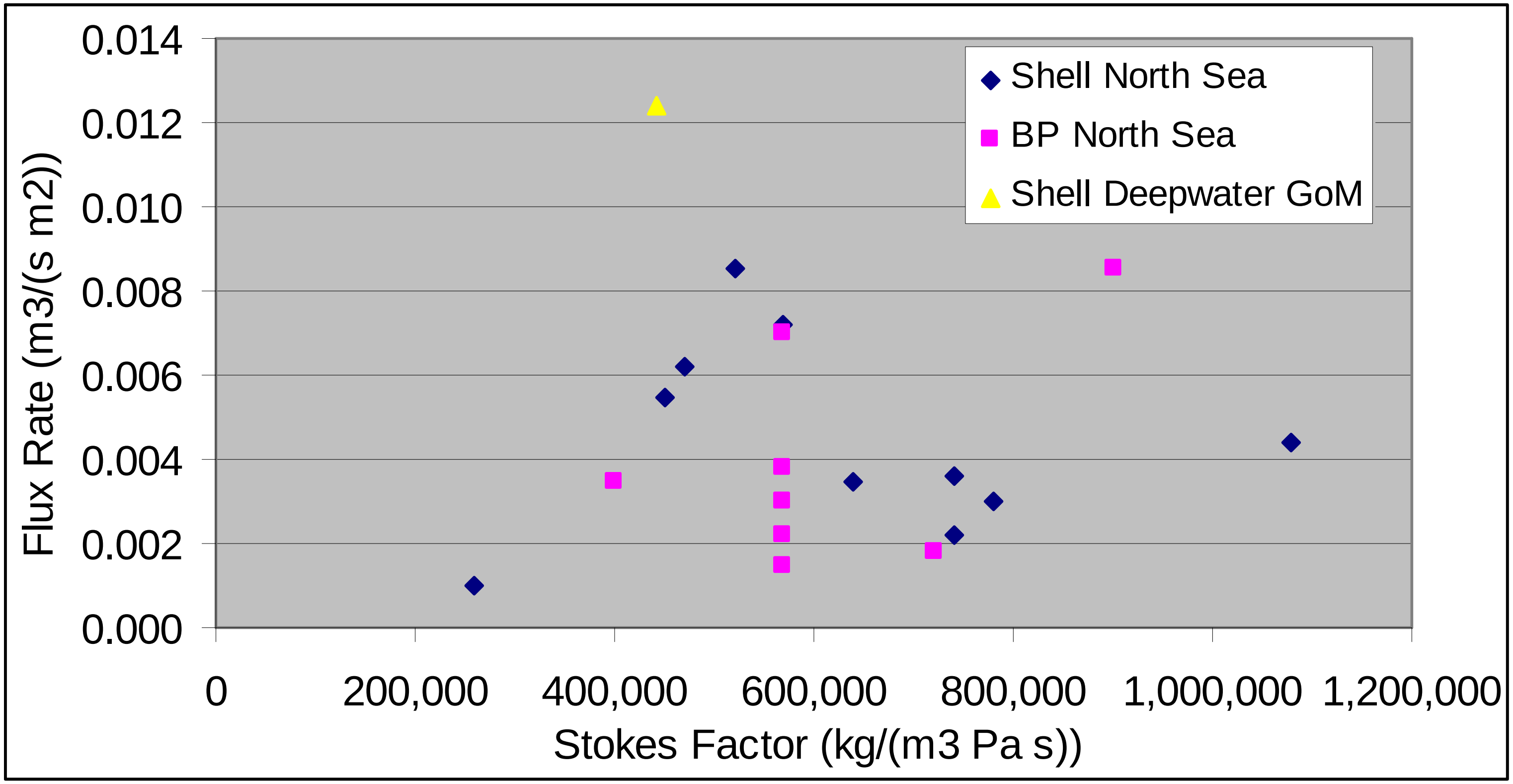
Table 2.3
Relative toxicity of heavy metals and inorganic compounds

Heavy metal or inorganic compound	Environmental Ranking	Heavy metal or inorganic compound	Environmental Ranking
Aluminium	1	Manganese	1
Barium	1	Mercury	3
Boron	~~1~~ 3	Molybdenum	2
Cadmium	3	Nickel	3
Calcium	1	Phosphorus	1
Chromium	3	Potassium	1
Cobalt	1	Silicon	1
Copper	3	Sodium	1
Iron	1	Strontium	1
Lead	3	Sulphate	1
Lithium	1	Vanadium	2
Magnesium	1	Zinc	3

Rankings: 1 ... Not critical
2 ... Toxic, but rare or having low solubility
3 ... Highly toxic and relatively accessible

Source: Shell Expro's Wastes, 1989, Safety and environmental affairs department, ref 1.1.1.i

Stokes Factor for North Sea and Deepwater USA:



Stokes Factor: $S = \frac{\rho_w - \rho_o}{\mu_w}$

North Sea discharge max = 40 ppm
Deepwater discharge max = 29 ppm

North Sea relied on FWKO & hydrocyclones, no flotation
Deepwater required FWKO, hydrocyclones, flotation

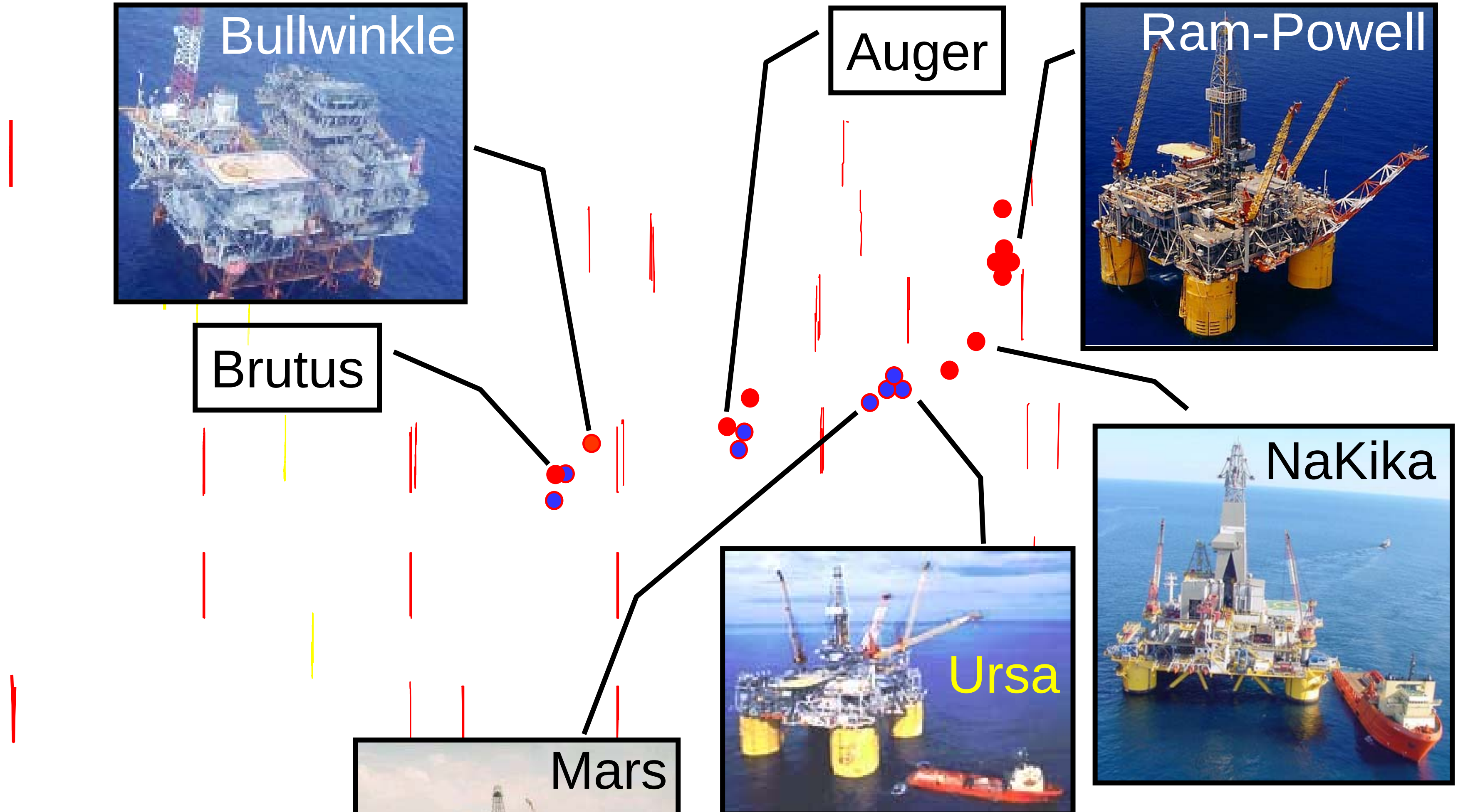
High cost of space and weight in deepwater resulted in high flux rates

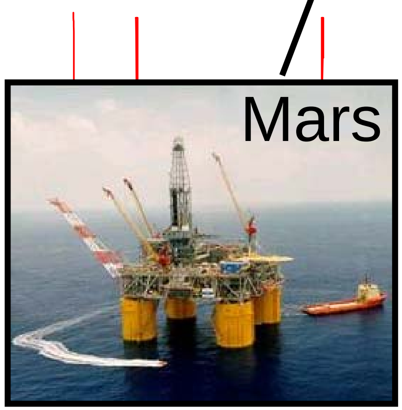
Next Several Slides:

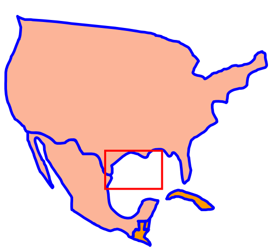
- **Characterization of produced water for: Deepwater Offshore USA**

- **Characterization for a particular project should include a comparison with nearby projects, particularly if similar or analogous equipment is planned to be used**

- **Subsurface setting (depth, T, geochemistry, salt deposits, fines)**
  Possibility of biodegradation







Platform	Oil (BOPD)	Water (BWPD)
Bullwinkle	64,000	24,000
Auger	56,000	30,000
Mars	155,000	20,000
Ram-Powell	80,000	20,000
Ursa	96,000	23,000
Brutus	40,000	8,000

Oil

- **Mostly Miocene age fluids, API: 24 to 40, mostly 27**
- **Mostly deep: 3,500 to 5,500 meters**
  - **Reservoir T: 54 to 80 C**
- **A few waxy wells**
- **Resins & Asphaltenes not a down hole problem, but is a topsides problem: O/W & W/O emulsions**
- **Biodegradation, acids, and naphthenates in a few wells**

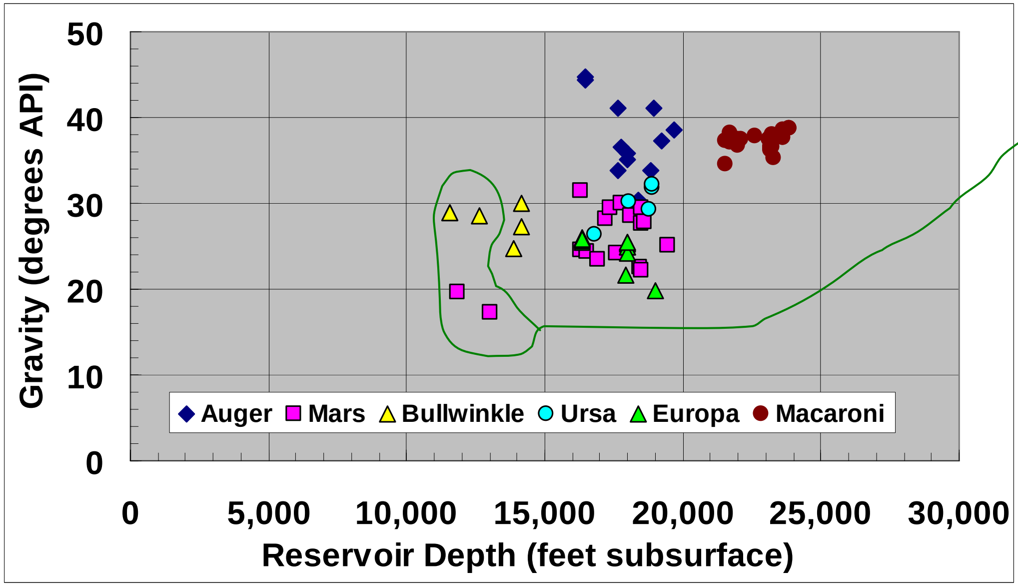
Water

- **Sweet / 0.2 mole % CO_2 / pH around 5.5**
- **Salt domes: 20 to 24 % salt & Barium: 120 to 260 mg / L**

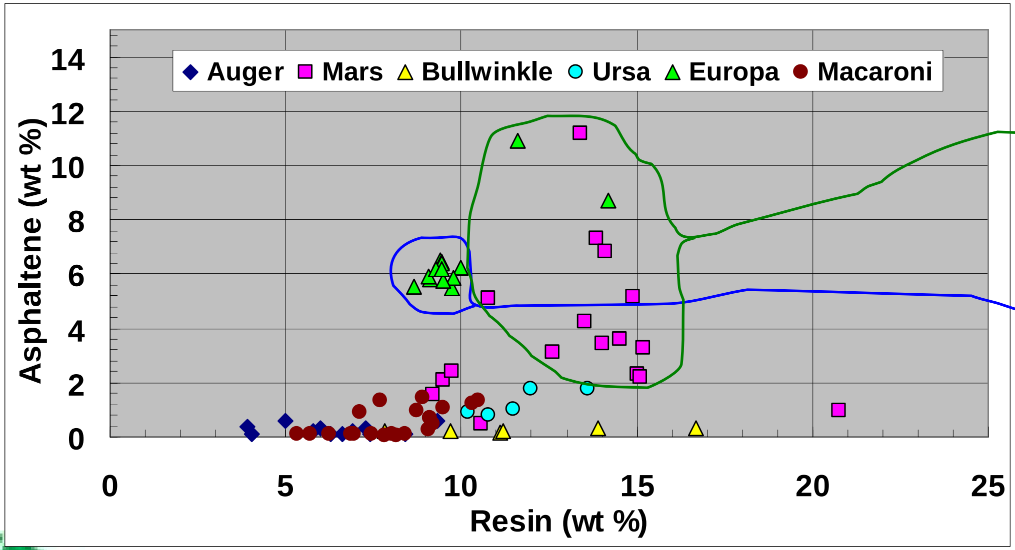
Solids

- **Solids:**
  - **Fines from unconsolidated sands & scale precipitation**
  - **ASTM D-4807: low to 150 to 250 lbs / MBbl**

Subsurface setting & Oil characterization by asset & by region



Biodegradation ceiling around 13,00 ft. Confirmed biodegradation for 2 Mars and 2 Bullwinkle wells - made water treating more difficult. Low API and high Total Acid Number (TAN) are indicative of biodegradation.



High resin + asphaltene content for several wells on Mars and Europa - makes water treating more difficult.

High asphaltene w/o high resin makes water treating even more difficult.

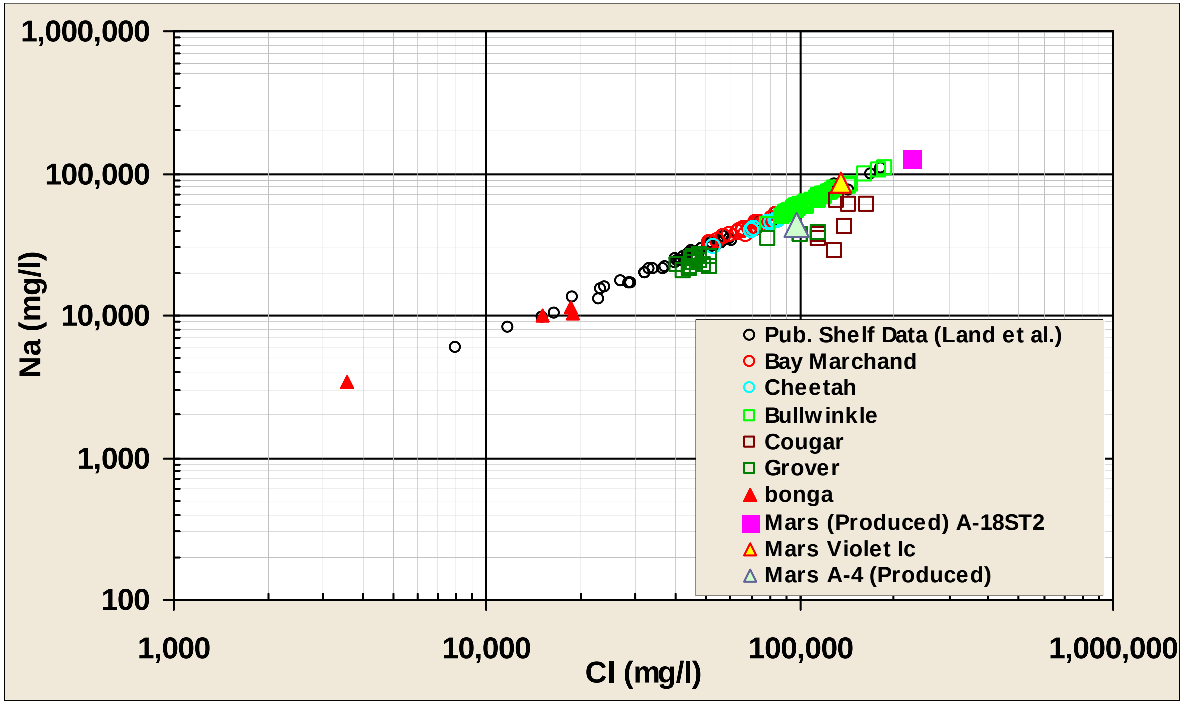
Mars Platform Oil Characterization

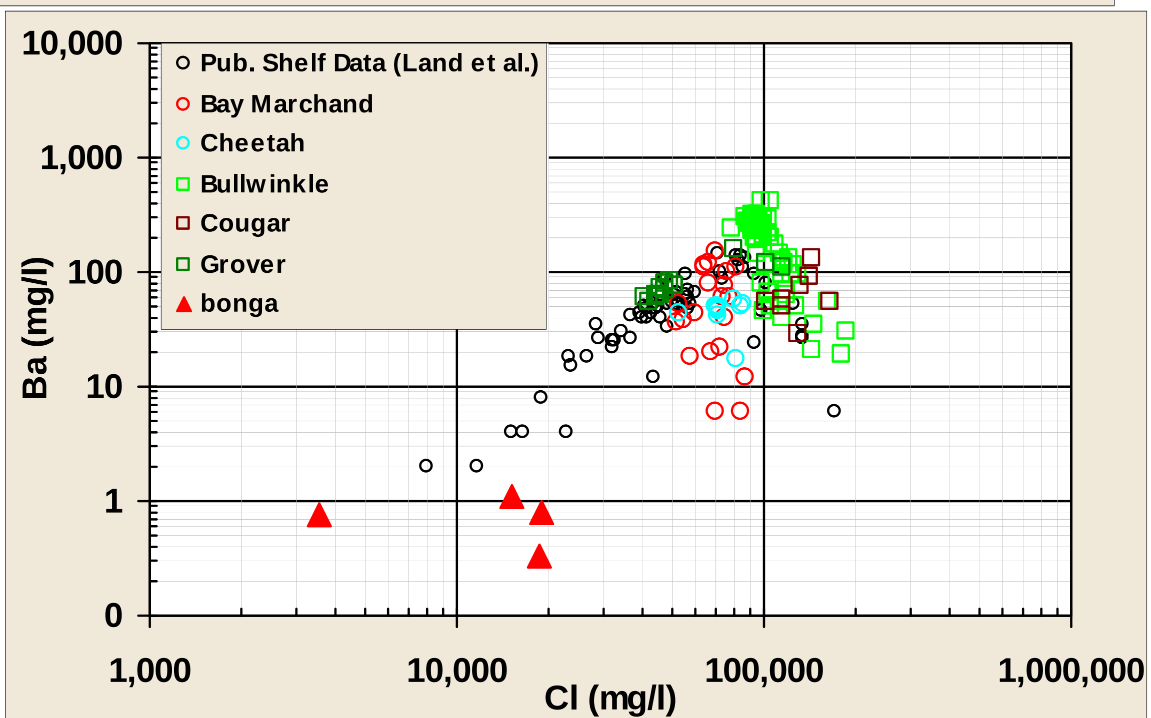
Reservoir	DEPTH	API	Saturates	Aromatics	Resins	Asphaltenes	Atomic S (wt %)	ACID No.
Pink	13,036	17.3	21.0	61.6	14.0	3.4	2.7	4.35
Lower Green	16,287	31.5	40.9	47.6	9.5	2.1	1.8	0.34
Ultra Blue	16,301	24.6	41.3	37.5	13.9	7.3	2.6	
Orange	16,550	24.4	27.4	54.5	14.5	3.6	2.4	1.00
Upper Green	16,910	23.5	24.3	55.6	14.9	5.2	2.6	
Magenta	17,610	24.2	28.1	54.1	13.5	4.3	2.6	0.61
Violet Ic	18,419	22.5	25.0	59.3	12.6	3.1	2.7	1.20
Lower Yellow	18,476	27.6	30.8	51.8	15.1	2.2	2.2	
Terra Cotta	18,476	22.1	25.2	50.2	13.4	11.2	2.8	0.95

Partial characterization of hydrocarbons for Mars TLP.

Shallow reservoir (Pink) above biodegradation ceiling – severe biodegradation.

Moderate API but asphaltenes + resins are high. Given high aromatic & resin concentration, asphaltenes likely to be relatively stable. However, risk of incompatibility with high API fluids from subsea systems through satellite hub concept.





Water chemistry for various shelf and deepwater locations.

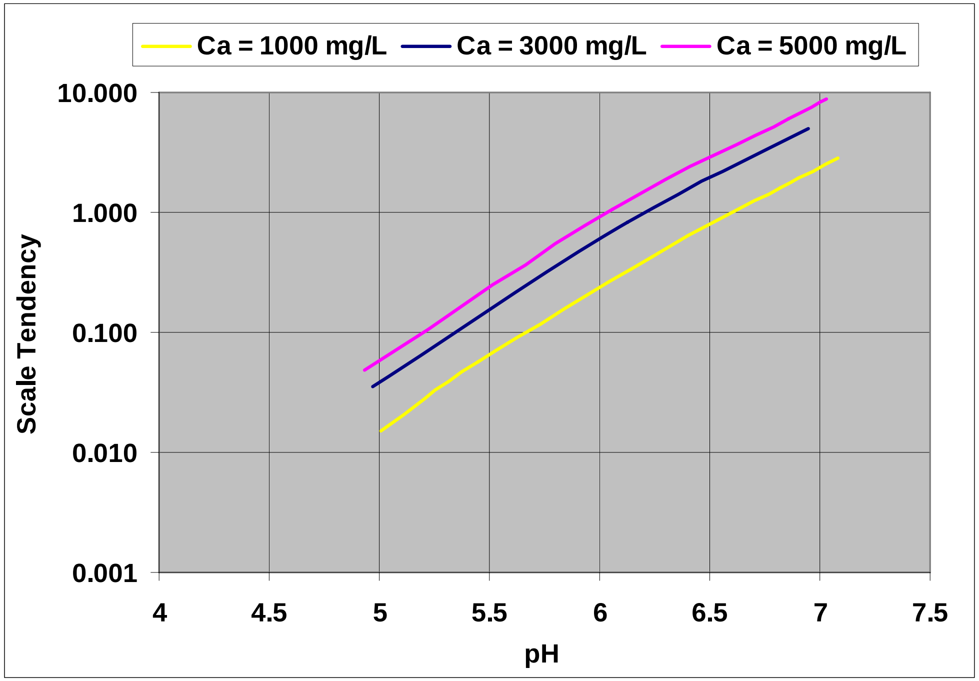
As shown, both shelf and deepwater locations have high salinities.

Deepwater water chemistry analogous to shelf - not a step-out.

High salinity gives a high density difference - good for water treating.

Scaling components present. Scale analysis required.

Scale Tendency Analysis:



Calcium carbonate scale is common in E&P. Calcium comes from the formation water. Carbonate comes from dissolved CO_2, and from bicarbonate in the formation water.

Scale Tendency > 1: thermodynamic possibility of scale formation.
Scale Tendency > 3: mandatory within Shell to mitigate scaling with scale inhibitor.

Specific Water Chemistry – Mars TLP:

Specific Gravity	1.125
pH	6.5
Cations	**mg/L**
Sodium	61,321
Calcium	5400
Magnesium	1626
Barium	159
Iron	20
Anions	**mg/L**
Chloride	109,000
Bicarbonate	122
Sulfate	1
Total Dissolved Solids (TDS)	177,643

Gas phase: no H2S, only 0.1 mol % CO2

High calcium, high magnesium, moderate bicarbonate, low CO2 in the gas, no H2S therefore no alkaline scavengers ➔ no calcium carbonate or magnesium carbonate scaling.

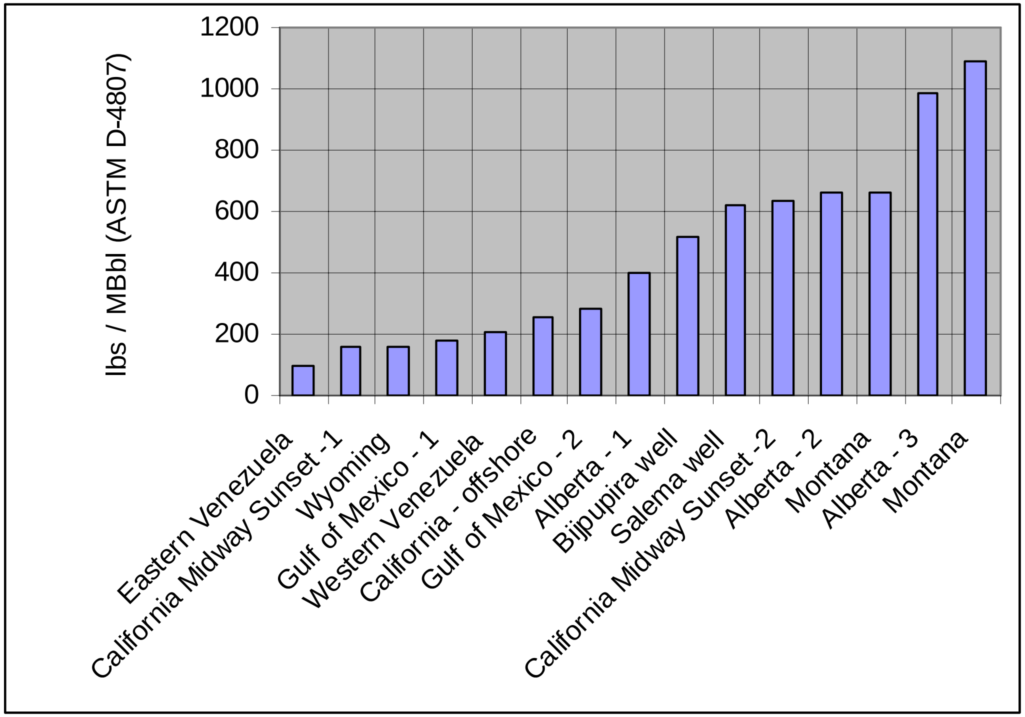
Iron relatively high but no H2S so no iron sulfides.

High barium, and some sulfate, high salinity so barium sulfate relatively stable.

Solids Characterization

- Solids measured using ASTM D-4807, with 0.45 micron filter.
- Results reported as lbs/MBbl.
- High solids levels are likely to cause tight solids-stabilized emulsions.

Proper solids characterization should include mass, size distribution, wetting properties (oil or water), composition.



Solids content of three Shell deepwater facilities compared to global benchmark high solids crude oils - high solids makes water treating very difficult.

Bullwinkle Solids Analysis:

Deionized Water Wash* **19.7%**
(*Includes substances soluble in water such as salts)

Xylene Wash* **9.6%**
(*Includes substances soluble in xylene such as paraffin, oil, and organics)

Acetic Acid Wash* **27.7%** (Iron Carbonate **Pos**
(*Includes substances soluble in dilute acetic acid such as carbonate scale)

Hydrochloric Acid Wash* **27.4%** (Iron Sulfide **Pos**
(*Includes substances soluble in 15% HCl acid such as iron sulfide or iron oxide)

Acid Insolubles* **15.6%**
(*Includes substances insoluble in 15% HCl acid such as sulfate scale, sand, & s

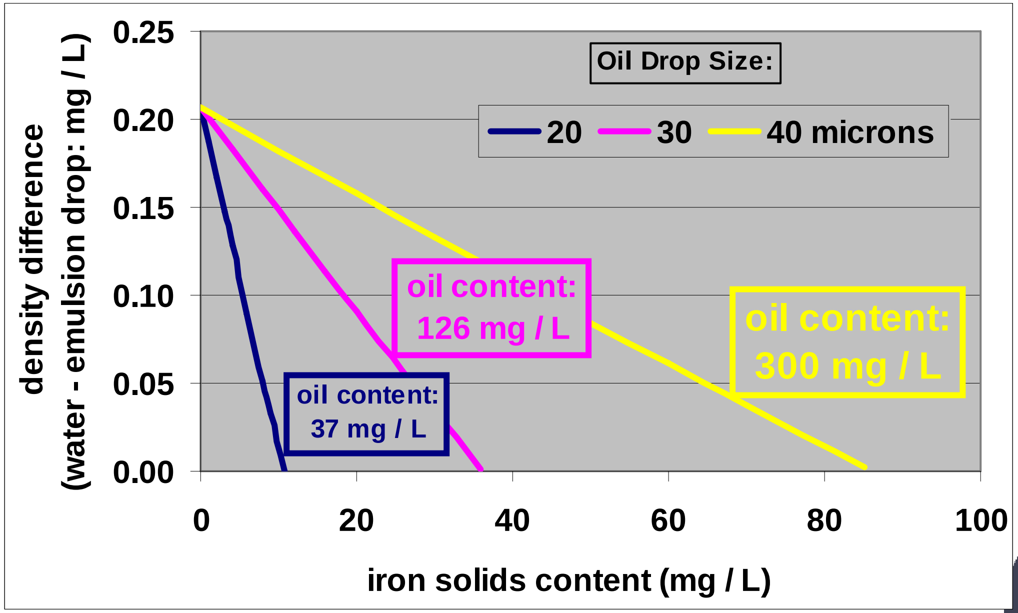
20 % salts
10 % waxes, asphaltenes
28 % carbonate scale
27 % iron compounds
16 % sulfate scale & silica fines

Oil/solids conglomerate are typically a mixture of sticky nasty things

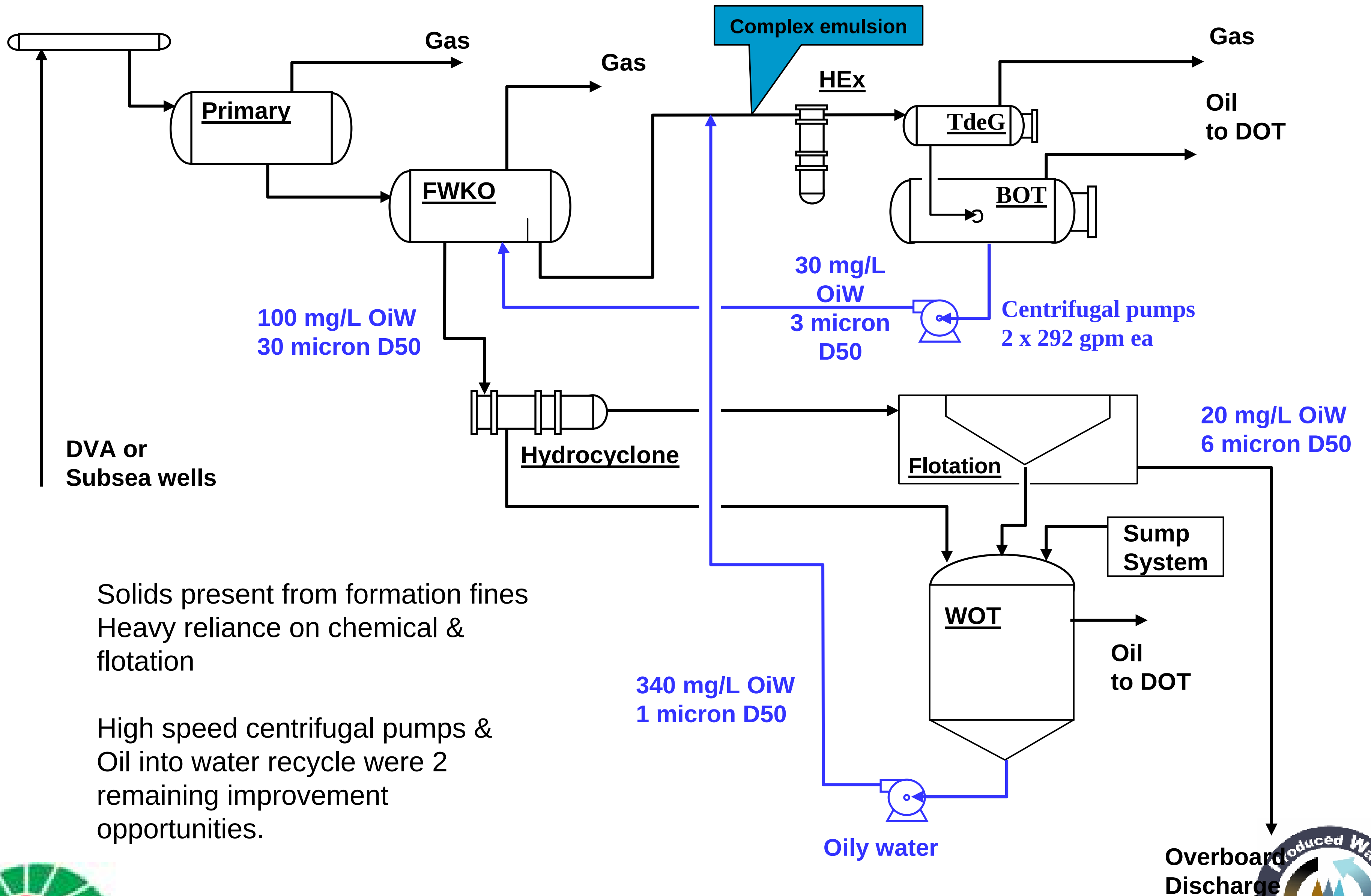
Fine solid particles add stability to oil in water emulsions

Solids also increase the density of the oil drop

When oil drops plus solids are neutrally buoyant they cannot be separated by settling or hydrocyclones



Mars System – OiW and Drop Size Distribution:



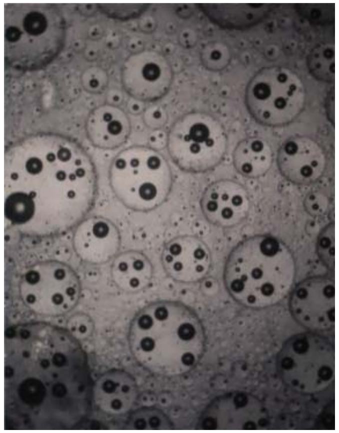
Solids present from formation fines
Heavy reliance on chemical & flotation

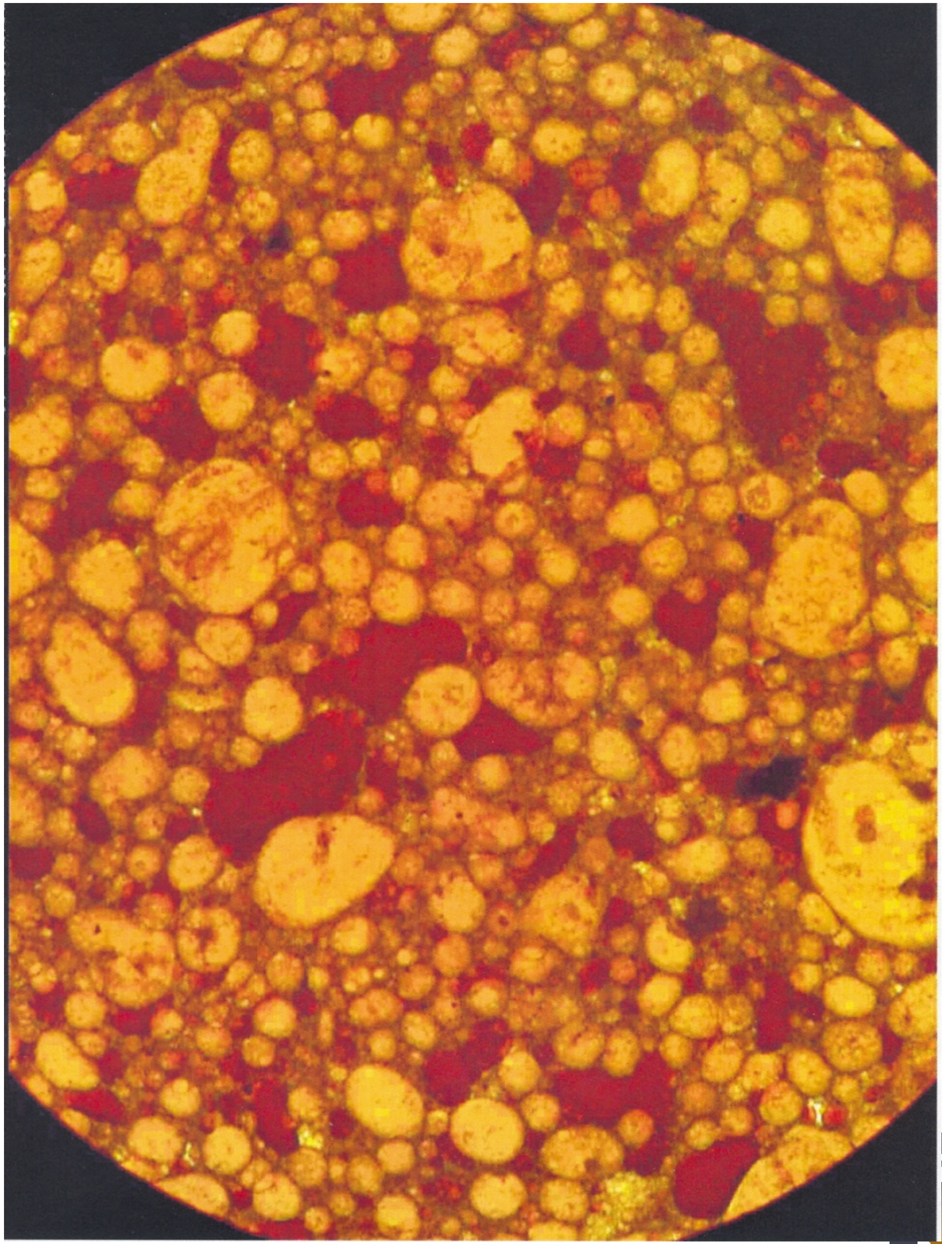
High speed centrifugal pumps & Oil into water recycle were 2 remaining improvement opportunities.

Dark blobs are oil and light blobs are water.

Note that many of the water drops have a coating of oil and that many of them have small drops of oil within. Also notice the very high phase volume of water within the oil.

The origin of this emulsion is shown on the previous slide.





What was learned from Deepwater US characterization:

Characterization of produced water for: Deepwater Offshore United States

Example of all the information that goes into a proper characterization of produced water

Subsurface setting (depth, T, geochemistry, salt deposits)	High salinity seen across the region which gave high density differences, some scale problems addressed with SI, required separate trains to segregate incompatible fluids.
Possibility of biodegradation	Handful of wells caused havoc. Extensive vessel internals modifications, process re-routing and chemical treatment work.
Gas constituents (CO_2, H_2S) & process conditions (T, P)	CO_2 / carbonate equilibria required scale inhibitor at DP locations, but not severe.
Oil characterization	Resins and asphaltenes caused foaming, emulsion, and PWT problems. Had to apply special chemistries, keep PWT equipment clean, develop special acid flow back procedures, change process routing, minimize recycles, avoid condensate mixing w/ oily water, minimize shearing, improve treatment of recycle streams.
Brine analysis by asset & by region	High iron was used to advantage w / DTC chemistry.
Possible solids from reservoir	Cleaned vessels frequently. Auger applied an acid treatment. Solids wetting demulsifiers applied at Mars.

Characteristic	Source	Design Detail	Possible Points	Characteristic	Ranking Points
Stokes Factor	API, temperature, water density	Longer residence time in primary separators	10	< 200,000	10
				400,000 to 800,000	5
				> 800,000	0
Oil flow assurance factors	Wax, paraffin, asphaltene stability, incompatible hydrocarbons	Inhibitors, heating for wax and paraffin	5	No inhibitors or heating required	2
				Inhibitor or heating required and none used	5
				Inhibitor or heating required and is used	0
Biodegradation	TAN, fingerprinting, biomarkers	Secondary separation equipment, optimized chemical treatment	15	0 wells	0
				1 to 2 wells Delta API > 2	10
				> 2 wells Delta API > 2	15
Scaling tendency	Mineral scales e.g. carbonates, sulfates; incompatible water	Water wetting chemicals, filtration / tertiary separation equipment	5	No inhibitors required, or inhibitor required and is used	0
				Inhibitor required and none used	5
Dissolved organics	Acids, naphthenates	Secondary separation equipment, optimized chemical treatment	5	pH > 6, acid < 100 mg/L	0
				4 < pH < 6 100 < acid < 500	3
				pH < 5 acid > 500 mg/L	5
Solids	Formation fines, scale particles,	Water wetting chemicals, filtration / tertiary separation equipment	15	Solids < 100 lb/MBbl	0
				100 < solids < 400	10
				Solids > 400 lb/MBbl	15
Iron sulfide	H2S, iron	Secondary separation equipment, optimized chemical treatment	20	FeSx < 10 mg/L	15
				10 < FeSx < 50	18
				FeSx > 50 mg/L	20
Surface active or shear enhancing chemicals	Corrosion inhibitor, methanol	Secondary separation equipment, optimized chemical treatment	10	No change upon turning off chemical	0
				Moderate water deterioration w/chemical	5
				Severe water quality deterioration w/ chemical	10
Small drops	High shear	Reduce shearing	15	D < 10 micron	15
				10 < D < 50	10
				D > 50 micron	0

Type 1 System: Total points less than 35
No iron sulfide. No biodegradation.
A typical system may consist of primary separation followed by hydrocyclones. Flotation may be required, depending on the Stokes Factor. See the example below.

Type 2a System: Total points between 35 and 55
No iron sulfide. No biodegradation.
A typical system may consist of primary separation, hydrocyclones and flotation. Care should be given to the handling of reject streams from the water treating equipment in order to ensure that a stabilized emulsion is not generated.

Type 2b System: Total points between 35 and 55
Presence of iron sulfide or biodegradation.
For this level of separation challenge, a typical system may consist of primary separation, hydrocyclones, flotation and some means of treating the reject from the water treating equipment. Chemical application will be critical both in terms of demulsifier and deoiler selection and optimization, but also in terms of minimizing the use of methanol and corrosion inhibitor.

Type 3 System: Total points above 55
Presence of iron sulfide and / or biodegradation.
A typical system may consist of primary separation, hydrocyclones, flotation and some means of treating the reject from the water treating equipment. Chemical application will be critical both in terms of demulsifier and deoiler selection and optimization, but also in terms of minimizing the use of methanol and corrosion inhibitor. Some form of tertiary water treating equipment will be required such as filtration, or centrifugation.

Worst Characteristics of Produced Water:

- **Solids (in general) and Iron Sulfides (in particular):**
  - **Water wet or Oil Wet?**
  - **Buoyancy of Conglomerate (oily solids)?**
  - **Organic or Inorganic?**
  - **Particle size distribution?**
  - **Source? (often eliminating the source is the best treatment strategy)**
- **Biodegradation:**
  - **High acid concentration?**
  - **Calcium naphthenate?**
- **Unstable asphaltenes:**
  - **SARA analysis (& stability plot – to be discussed)**
- **Production Chemicals:**
  - **Methanol, AA Hydrate Inhibitors, Corrosion Inhibitors?**
  - **Over-dosing?**

- **Important Analyses in Produced Water Characterization:**
  - **Oil droplet size distribution (on-line and off-line)**
  - **Oil in water concentration**
  - **Oil flow assurance analysis (SARA, wax, paraffin, asphaltenes)**
  - **Gas & oil composition (H_2S, CO_2, BTEX, naphthenates, TAN, biodegradation)**
  - **Water analysis (anions, cations, pH, hardness, alkalinity, dissolved gases , organics, COD, toxicity, etc)**
  - **Suspended solids concentration, PSD, composition and mineralogy**
  - **Desktop settling, visual observations, and optical microscopy**