CHEMICALS TREATMENT FOR PRODUCED WATER

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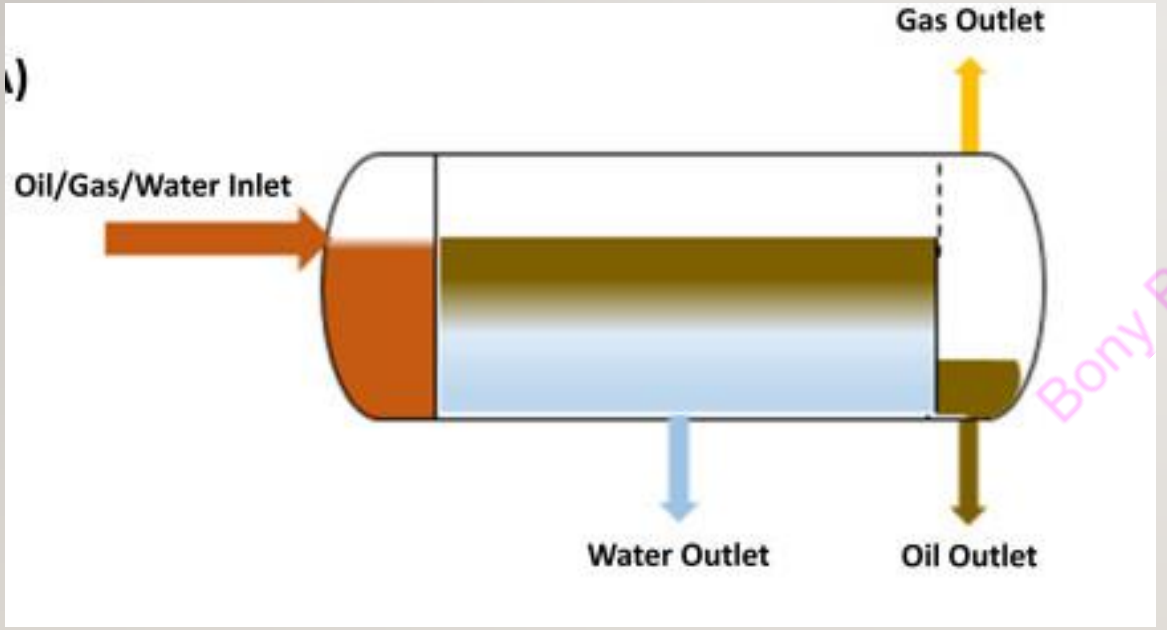
OBJECTIVES

- Introduction produced water
- Knowing problem of produced water
- Sharing method how to treat produced water by chemicals

OUTLINE

- **INTRODUCTION OF PRODUCED WATER**
- **PROBLEM OF PRODUCED WATER**
- **CHEMICALS TREATMENT**
- **FIELD CASE**
- **SUMMARY**

PRODUCED WATER



- Produced water is water trapped in underground formations that is brought to the surface along with oil or gas.
- Produced Water shall be separated from the hydrocarbon phase since it has no financial value

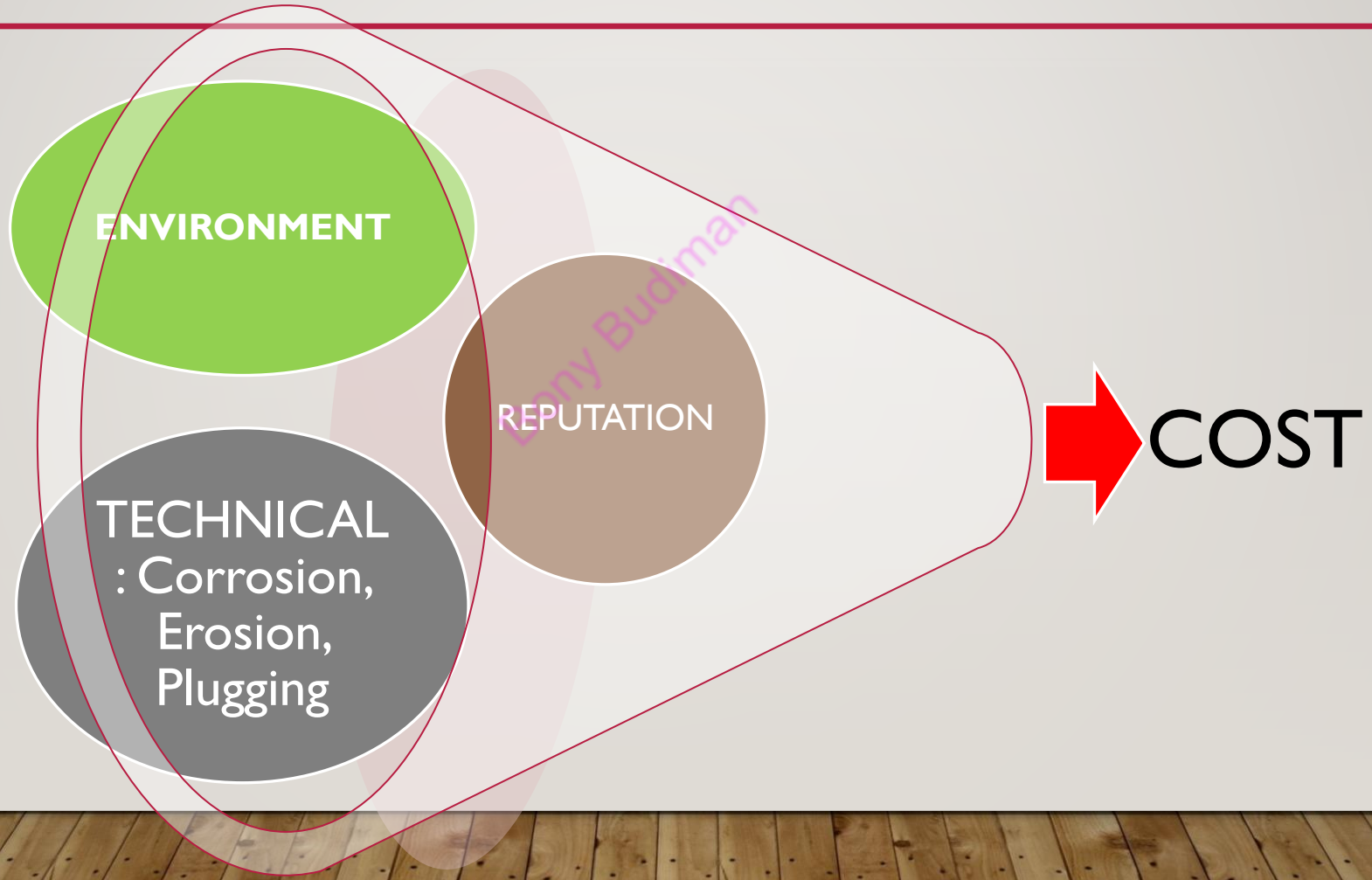
Courtesy Picture :
https://www.google.com/url?sa=i&url=https%3A%2F%2Fwww.sciencedirect.com%2Fscience%2Farticle%2Fpii%2FB9780323993043000145&psig=AOvVaw1gc06HZGsva_3tV8HqnTXE&ust=1703218793851000&source=images&cd=vfe&opi=89978449&ved=0CBIQjRxqFwoTCPDQw-PWn4MDFQAAAAAdAAAAABAR

PRODUCED WATER DISPOSAL

There are two way of produced water disposal :

- Dispose to the river, sea, or lake
  - Limited by amount of water disposal and contaminant concentration
- Re injection to the formation
  - Has minimum issue to environment but shall consideration regarding the reservoir acceptance.

PROBLEMS OF PRODUCED WATER

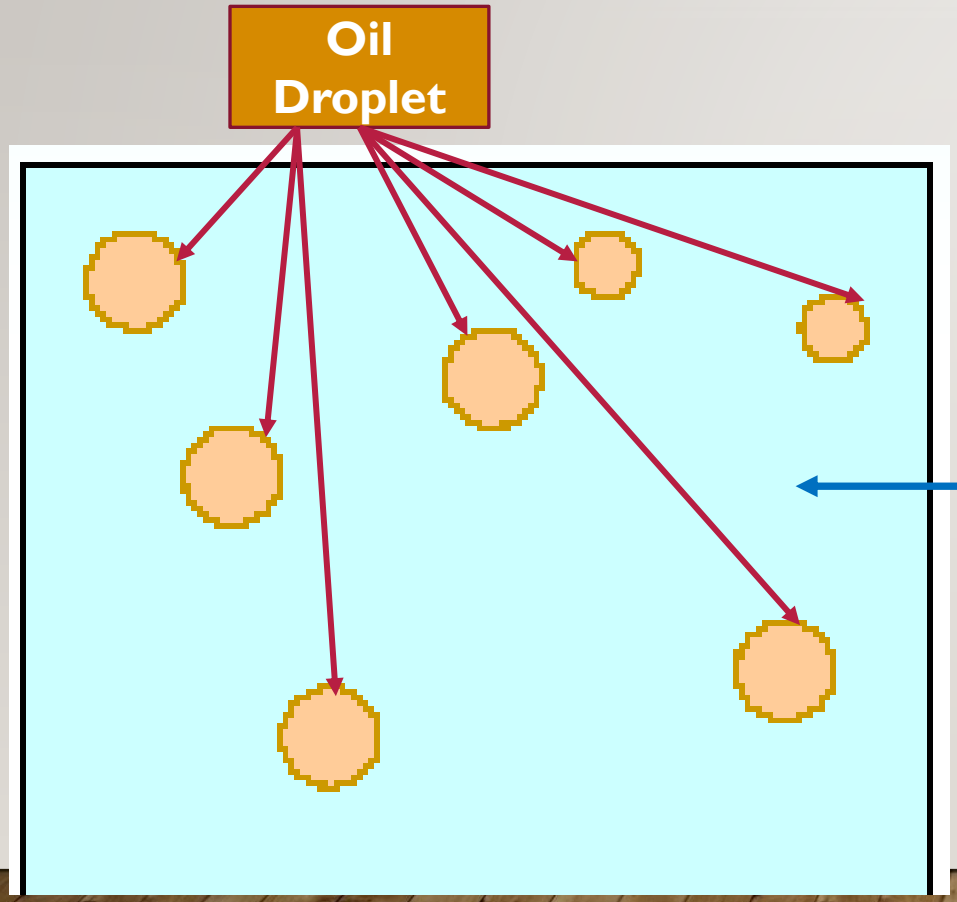


CHEMICALS TREATMENT FOR PRODUCED WATER

- Reduce oil content in water
- Corrosion Control
- Scale Inhibition
- Bacteria Control

Oil Content Reduction

OIL IN WATER EMULSION (OIL CONTENT / OC)



- Separated produced water usually still contain oil emulsion
- Oil in water emulsion is condition when oil droplet dispersed in water phase
- Bear in mind that in oil in water emulsion the oil is minor component (usually less than 1% or 10,000 ppm) and the water is the major component.
- As emulsion, the oil may stay dispersed in water phase for long period and cannot separate instantly.

PROBLEM OF OIW EMULSION / OIL CONTENT

- Production loss
- Plugging especially at water injection well
- Environmental issue

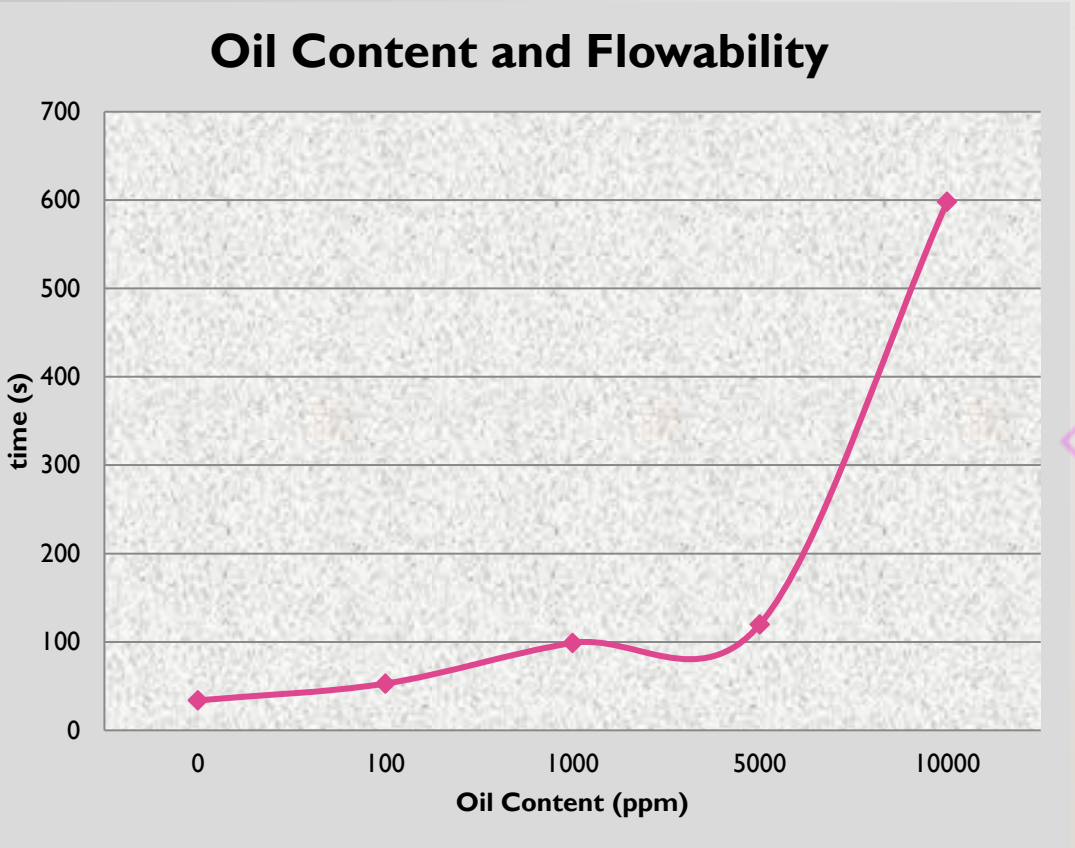
PRODUCTION LOSS

- Glass bottle beside is produced water that contain 20 ppm oil content
- If the water production rate is 100,000 BWPD, lets calculate how much volume of oil that discharged ?
- Volume of oil = concentration of oil content * water production rate

  = (20 * 100,000 BWPD) / 10^6

  = 2 BOPD = 318 LPD = 9,540 liters per month
- How if the oil content is 100 ppm ? The production loss will be 5 times higher

PLUGGING



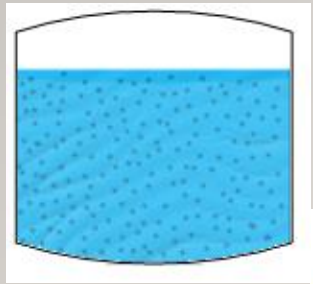
- Water with oil content will affect the flowability when reinjected through water injection well.
- At graph besides, 100 ml water with variation of oil content passed to sand media. When oil content increase, time required to pass 100 ml increase as well

OIL CONTENT REMOVAL FROM PRODUCED WATER

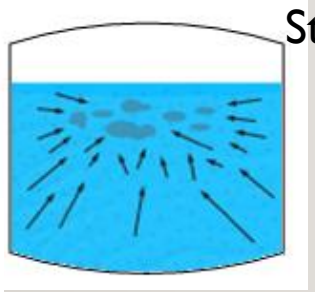
1. **Upstream** stage: Water removal during dehydration of crude oil, FWKO, separator vessels, heater treater, storage tanks
2. **Primary** Water Treatment: Skim Tanks, API separators, plate interceptors
3. **Secondary** Water Treatment: Flotation, hydrocyclones, media filters, Centrifuges, coalescers
4. **Final** Treatment (oil below 10 mg/l): cartridge or dual media filters, membranes

Better Quality

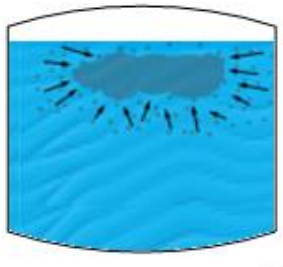
FOUR STAGES OF WATER CLARIFICATION



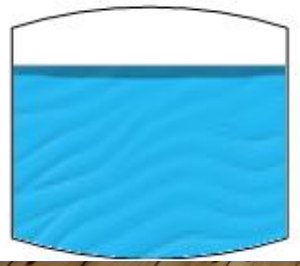
Stage 1: Coagulation



Stage 2: Coalescence



Stage 3: Flocculation



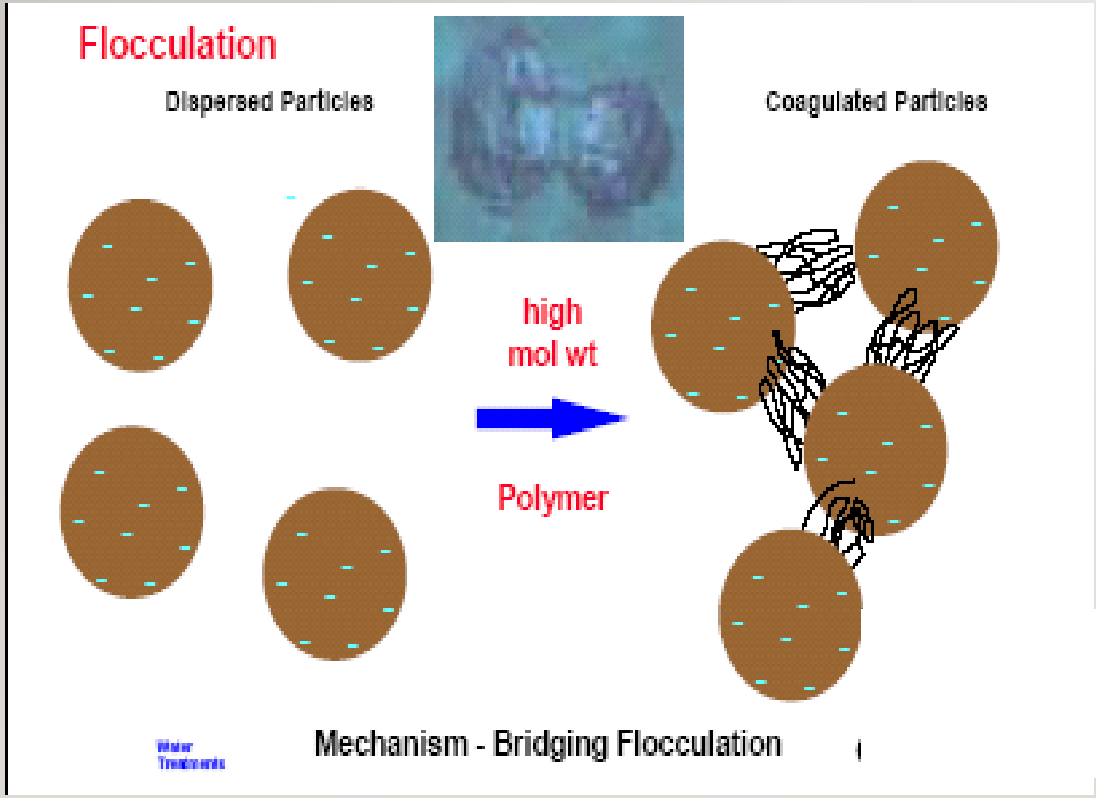
Stage 4: Flotation

- The oil in water separation process involves four stages : coagulation → coalescence → flocculation → floatation
- Coagulation - charge neutralization to bring oil droplets close together
- Coalescence – small oil droplets merge into larger oil droplets.
- Flocculation – using chemical polymer to bring together coagulated or coalesced particles into removable floc
- Flotation – used of induced gas to provide artificial lift for any of the above to the surface of the water

REVERSE DEMULSIFIER (RD)

- Chemicals used to improve the mechanical treatment called as reverse demulsifier or reverse emulsion breaker, polyelectrolite or deoiler
- Reverse demulsifier accelerate the coagulation and coalescence process then the flocculation and floatation process will be improved as well. Or in other words, the RD accelerate the oil droplet join each others form higher oil molecule until it big enough to separate from water phase due to differences in specific gravity
- By the mechanism, there are two type of RD :
  - Flocculants : a nonionic polymer with high molecular weight (> 10^5)
  - Coagulant : an ionic molecule with low molecular weight (<10^5)
    - Organic coagulant
    - Inorganic coagulant

MECHANISM OF FLOCCULANTS



1. The entire flocculants molecule act as a “glue”
2. A part of the “glue” polymer will attach the oil droplet.
3. The next part will attach another oil droplet, the flocculants act as molecule bridge that connect one oil droplet to another
4. The molecule bridge will join with another bridge until create big molecule and separate from the water phase.

FLOCCULANTS

1. Advantages

- Effectively separates uncharged particles such as soil and dust
- Low dosage, 1 – 10 ppm based on water rate.
- Rapid separation (<15 minutes)

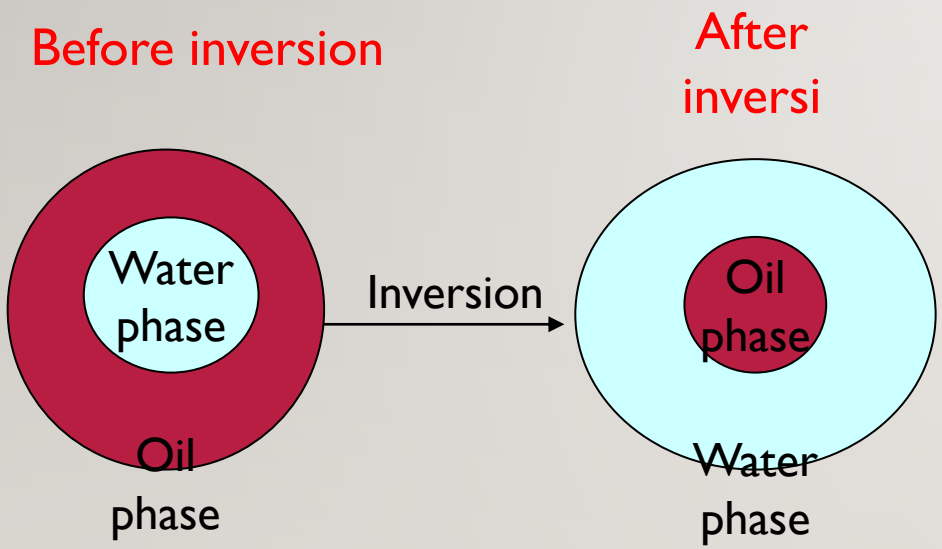
2. Disadvantages

- May broken caused by high agitation
- Shall be well inversed, since it may become jelly if the water too little or separate if the water is too much.
- Sensitive of over treat effect (effect that cause the separation not working well or even the emulsion become tighter)

FLOCCULANTS APPLICATION

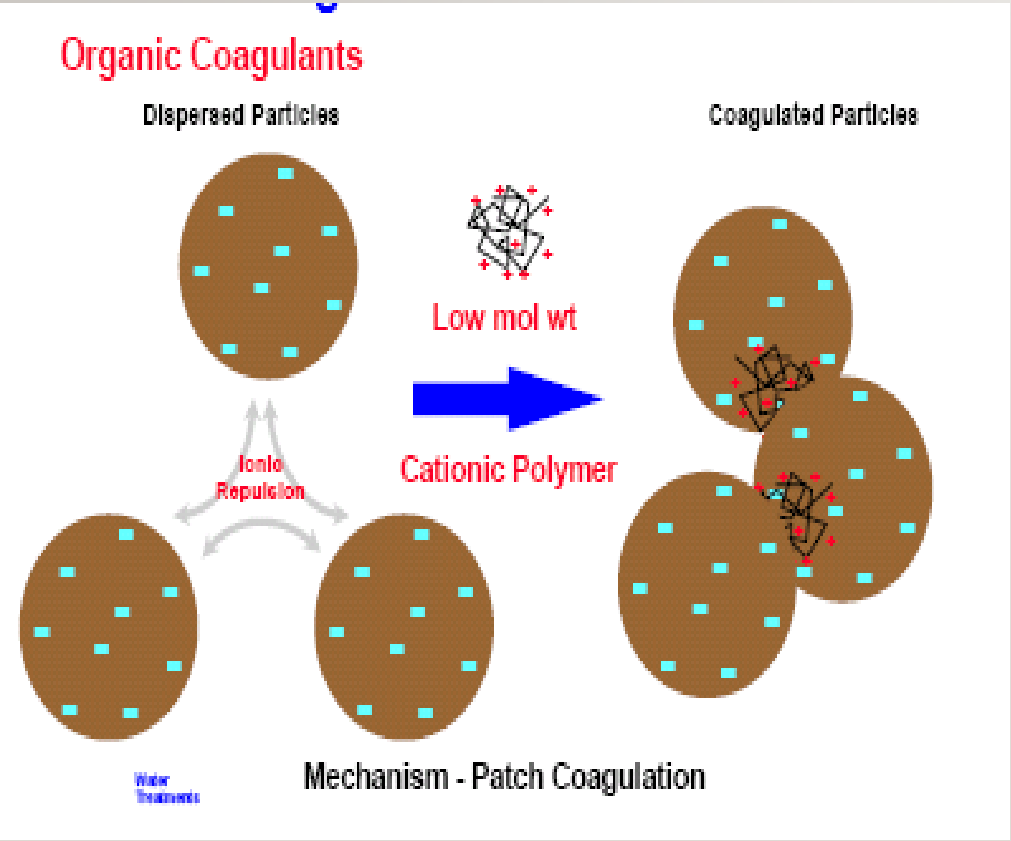
1. Direct concentrate injection (no dilution).
   - This could be applied when the water is quite turbulence
2. Dilution injection
   - The concentrate inverted with water until the concentration 1-1.5%. This solution may stable less than 1 week. If found separation, the solution shall be re-mixing
   - Use in line mixer, flocculants injected to a pre-dilution tank with a mixer prior to inject to the wastewater.

INVERSION



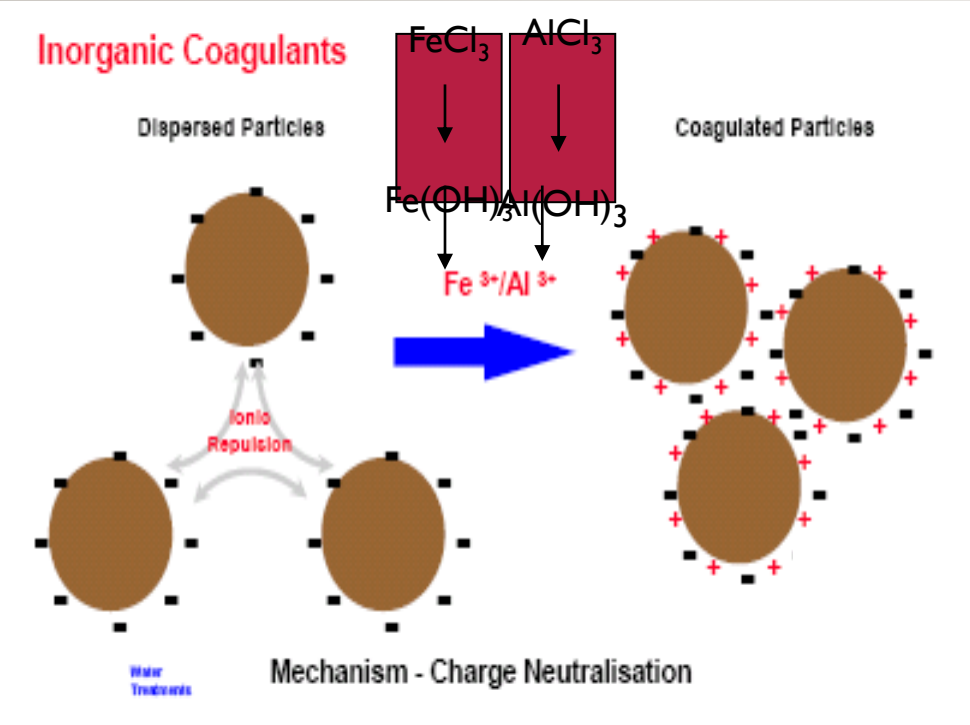
- Inversion is transformation of flocculants molecule from water in oil to oil in water through the addition plenty of water and mixing.
- Flocculants will work at optimum concentration 1,0 – 1,5 %
- If the concentration too high, the flocculent create jelly solution.
- At too low concentration the molecule not sufficient to attach all oil droplet.

ORGANIC COAGULANT MECHANISM



1. Coagulant hydrolyzed to be positive molecule
2. One positive part attach the negative part of oil droplet.
3. The other positive part of coagulant attach another droplet oil
4. The next positive part coagulant attach the next oil droplet then they join each other become larger and larger until big enough to separate from the water phase.
5. The mechanism looks similar with the flocculants, but not that at flocculants the molecule act as “glue” to tie the oil droplet meanwhile the organic coagulant create positive part to attach the negative part of oil droplet

INORGANIC COAGULANT MECHANISM



1. The coagulant hydrolyzed in water to form positive (cationic) and negative (anionic) ion
2. The cations of coagulant neutralize the negative oil droplet.
3. Neutral molecule oil droplet join each other and form bigger and bigger molecule until big enough to separate from the water phase

COAGULANT

1. **Advantages**
   - More resist to agitation.
   - Well diluted at any proportion with water

2. **Disadvantages**
   - May not too effective to separate waste water that contain a lot of suspended solid
   - Not effective for relatively heavy crude oil

COAGULANT VS FLOCCULANTS

No	Parameter	Flocculants	Coagulant
1	Solubility in water	Has specific solubility, usually at 1-1.5 %	Well soluble
2	Aggitation Effect	Sensitive	Resistant
3	Application	Suitable to separate heavy oil and water with suspended solid	Suitable to separate light to medium oil in water emulsion
4	Work Mechanism	Works as glue that sticks to oil droplets	Charge neutralization
5	Injection Point	Before separator that contain relatively low oil content (for example below 200 ppm)	Before separator that content at any variation of content
6	System Requirements	Usually used in high shear system	Require low shear and settling time.
7	Selection Test	Bottle Test	Jar Test

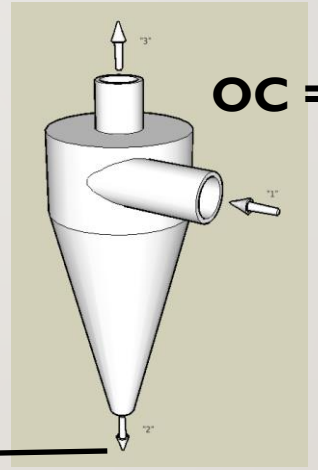
Video Coagulation - Flocculation

SOME REVERSE DEMULSIFIER

COAGULANTS	FLOCCULANTS
Aluminum Sulfate (Alum)	Charged polyamides
Aluminum chloride (pH dependent)	Polyanionics
Polyaluminum chloride (pH dependent)	Polyampholytes
Zinc Chloride	Polymeric surfactants
Sodium aluminate	
Iron salts – (Iron chloride, Iron sulfate)	
Polyferric sulfate	
Mineral acids	

CASE STUDY

- At offshore facility at East Kalimantan , waste water was send to hydrocyclone then to Wemco/DAF.



OC = > 10,000 ppm

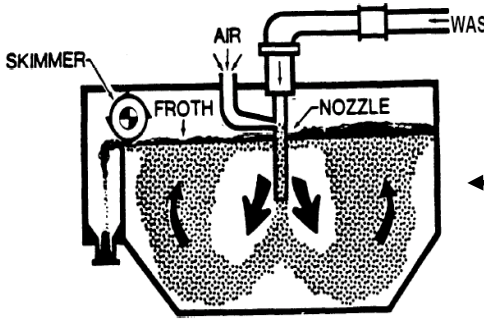


FIGURE 8 / CROSS SECTION OF INDUCED AIR FLOTATION UNIT

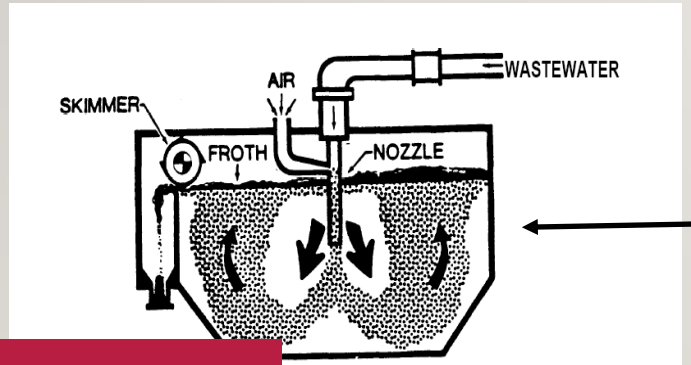
OC = 900 ppm

OC = 150 ppm

Initial Condition

CASE STUDY

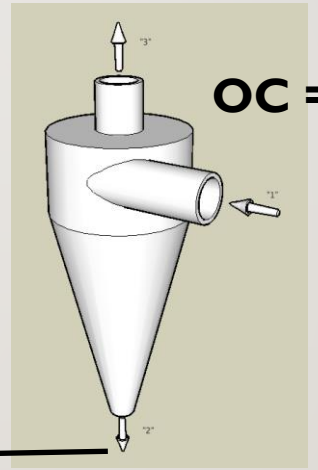
- Since Oil Content at outlet DAF still high, then the Company decide to inject deoiler / water clarifier / reverse demulsifier



ION OF INDUCED AIR FLOTATION UNIT

OC = < 20 ppm

Deoiler



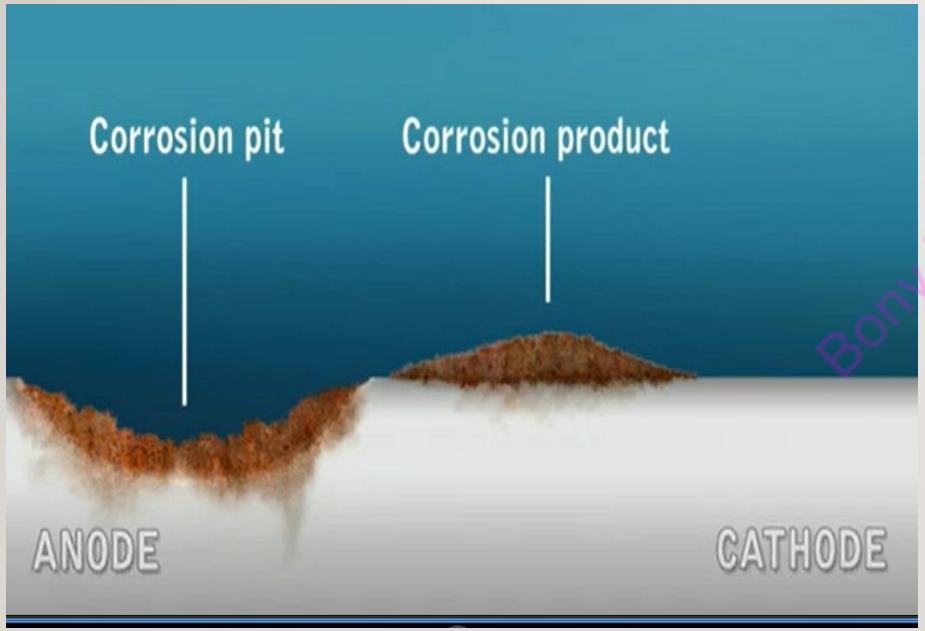
OC = > 10,000 ppm

OC = 900 ppm

Result after Deoiler Treatment

Corrosion Inhibition

CORROSION



- Corrosion is a deterioration material, especially metal, as a result of chemical/ electrochemical reaction to its environment
- Corrosion never sleeps, can't stopped but controllable.

CORROSION ELEMENTS

Cathode Reactions

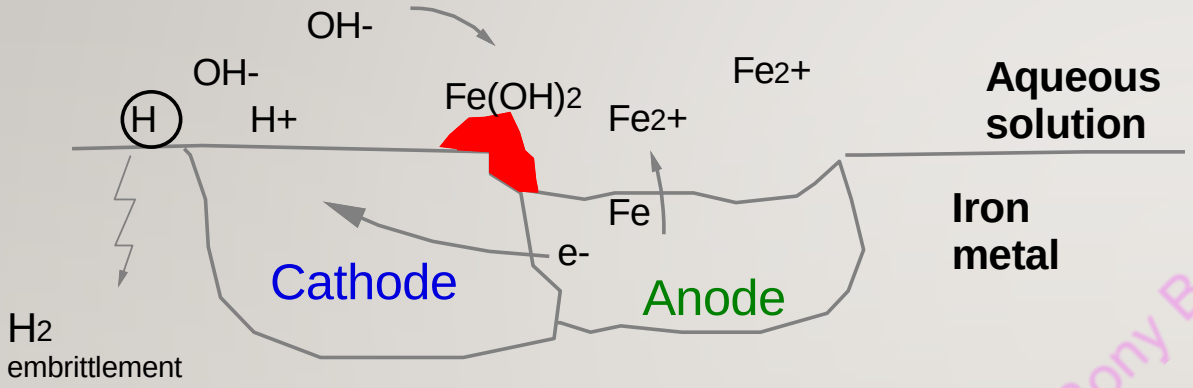
$H_2O \rightarrow H^+ + OH^-$

$H^+ + e^- \rightarrow H$

$2H \rightarrow H_2$

Anode Reaction

$Fe \rightarrow Fe^{2+} + 2e^-$



Corrosion product reactions

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

- There are four elements that caused corrosion :
  - Anode
  - Cathode
  - Electrolyte
  - Connection
- If any of these are missing then there will be no corrosion

CORROSION EFFECTS

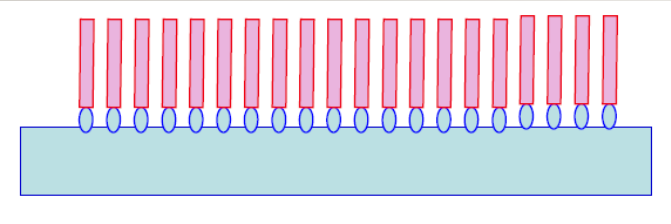
- Fluid loss
- Cost of repair
- HSE issues

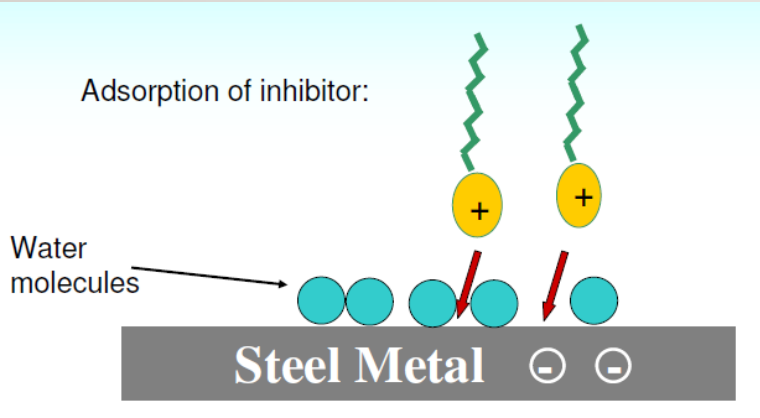
CORROSION CONTROL

Some methods are applicable for corrosion control :

- Design : upgrade material to CRA (Corrosion Resistant Alloy) level
- Coatings
- Electrochemical / cathodic protection : sacrifice anode or impress current
- Chemical :
  - Reduce corrosion agent : oxygen scavenger, H_2S scavenger, biocide
  - Corrosion inhibitor

CORROSION INHIBITOR



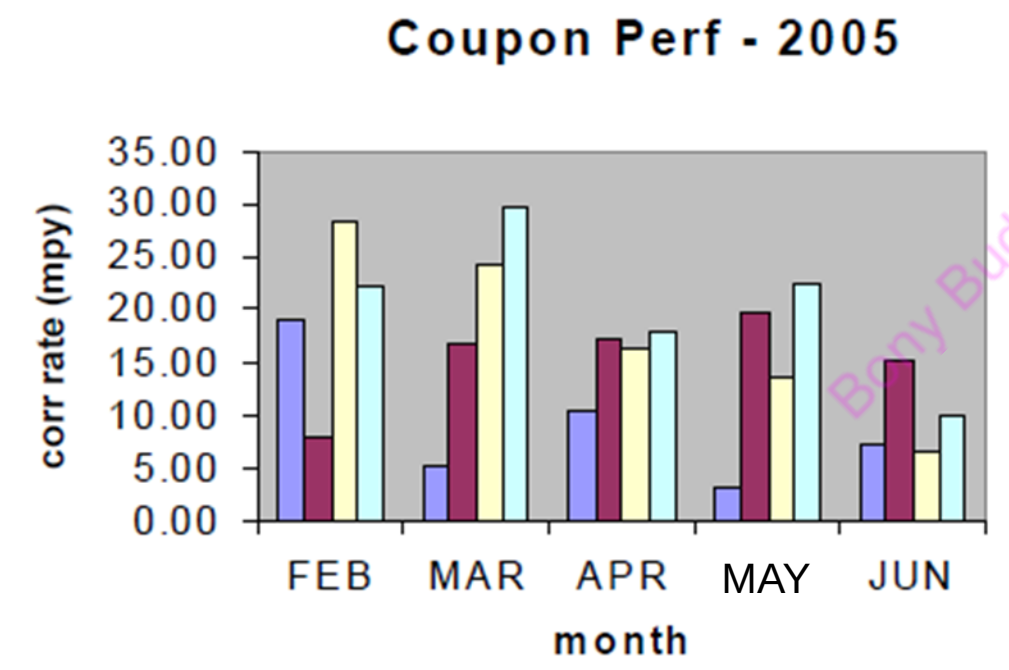


- A chemical that used to control corrosion rate
- CI will filming pipe and prevent contact with corrosive gases
- CI should be :
  - Well transported to the corrosive area
  - High effectiveness
  - Not causing other(s) problem(s) such as foaming and create tight emulsion

CORROSION INHIBITOR

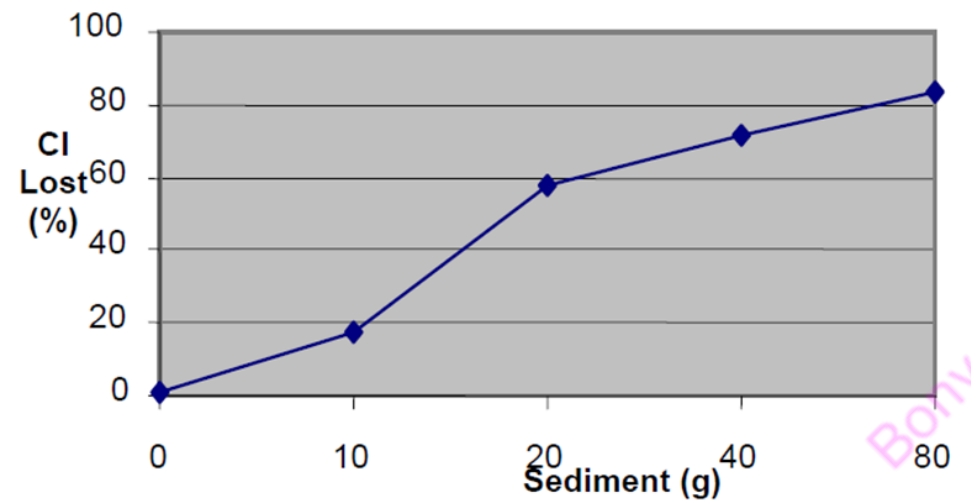
Field Condition	Characteristic	Kind of CI	Treatment Method
A. Wet Gas or oil well with water produced	➢1 bbls water / MMSCF ➢ 10 % water cut	Water soluble- oil dispersible	
	High tendency of corrosion		Dosage 0.5 - 10 ppm based on water
- Low Velovity	< 50 ft/sec		Pigging should be done regularly following with continuous injection
- High Velocity	> 50 ft/sec Possible of erosion	Have high film persistency	Continuous injection
B. Dry Gas or oil well with low water produced	**<** 1 bbls water / MMSCF **<** 10 % water cut	Oil soluble - water dispersible	Continuous injection
	Low corrosion rate		Dosage 1 pint /MMSCF or 0.5 – 5 ppm based on water
- Low Velocity	< 50 ft/sec	Volatile corrosion inhibitor	
- High Velocity	> 50 ft/sec Possible of erosion	Have high film persistency	

FIELD CASE : DEPOSIT EFFECT



- Corrosion rate at some spots of the water pipeline not meet requirement (max 2 mpy)
- Some study and trial :
  - Chemicals : change the type of chemicals → no effect
  - Erosion effect : monitor by SS coupon → low weight loss
  - Chemical injection mode : use nozzle sprayer / atomizer → no significant effect

3. DEPOSIT EFFECT



- During pigging job, it was found a lot of deposit (most likely sand and silt).
- To study the deposit effect, a laboratory test conducted by mix Cl with sand at various weight
- Refer to graph beside, it was found that sand may adsorb the Cl or it may a competition between iron and silica (in sand) to attract the Cl molecule
- Recommendation are : conduct regular pigging then following by batching Corrosion Inhibitor.

Scale Inhibition

SCALE

- Scale is deposition of soluble inorganic salts from aqueous solution
- Scale will reduce inner pipe diameter and causing damage of production facilities
- Causes for scale deposition :
  - Mixing incompatibility water
  - Change in physical-chemical environment such as pH, temperature and pressure

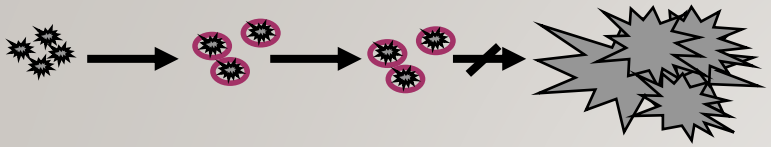
SCALE INHIBITION

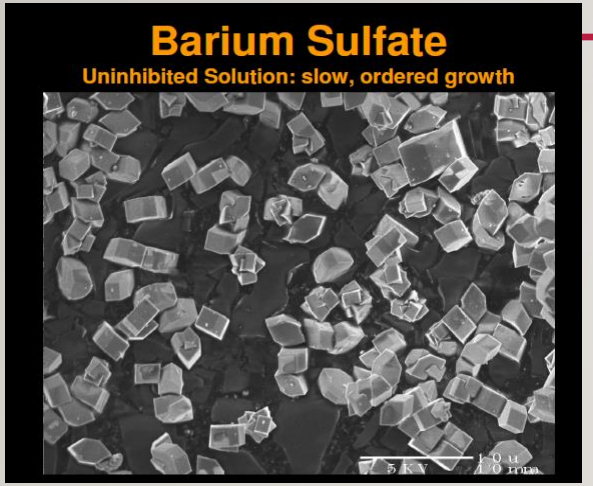
- Mechanical
  - Injecting water which compatible with formation water.
  - Maintain pressure.
  - Lowering pH.
  - Pigging
- Chemical
  - Scale Inhibitor
  - Scale Removal

SCALE REMOVAL

- For removing scale that has been formed (scale build-up).
- Scale removal react chemically with scale (acid-base or dissolving reaction).
- Higher dosage than scale inhibitor .
- Need sufficient contact time for scale removal to dissolve or destroy scale deposit
- Need agitation.
- Can be applied batch or continuous injection.

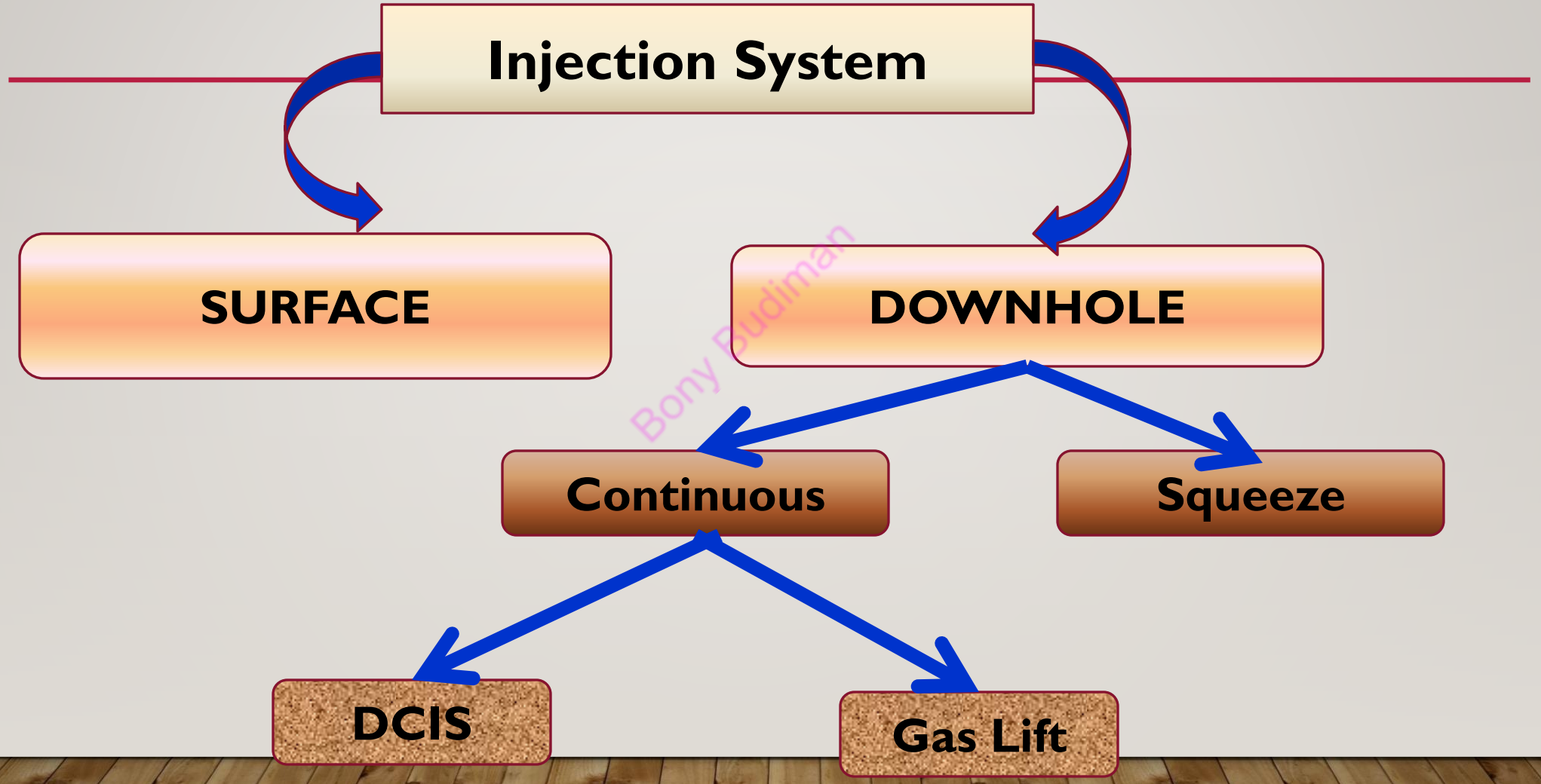
SCALE INHIBITOR





- A chemical that used to prevent scaling
- Could be applied at surface and downhole by continuous injection or squeezing.
- Dosage rate for continuous injection is less than 20 ppm
- SI will :
  - Inhibit crystal growth
  - Modify crystal structure

INJECTION SYSTEM



FIELD CASE : OVERDOSE EFFECT

Dossage 100 mg/l	% Inhibition
3701	64.50

Dossage 2000 mg/l	% Inhibition
3225	10.78

Dossage 20000 mg/l	% Inhibition
3190	6.83

- Scale still found even scale inhibitor has been injected
- A laboratory test refer to NACE TM0374 conducted to check the effectiveness of existing scale inhibitor by mimic the liquid composition.
- The design dosage is 100 ppm. However due to minimum pump flowrate the dosage increase to around 1000 ppm
- The result show that at too high dosage the inhibition performance of scaling inhibitor decrease.

1. OVERDOSE EFFECT

Dossage 60 mg/l	% Inhibition
3614	50.70

Dossage 100 mg/l	% Inhibition
3718	63.43

Dossage 200 mg/l	% Inhibition
3892	84.71

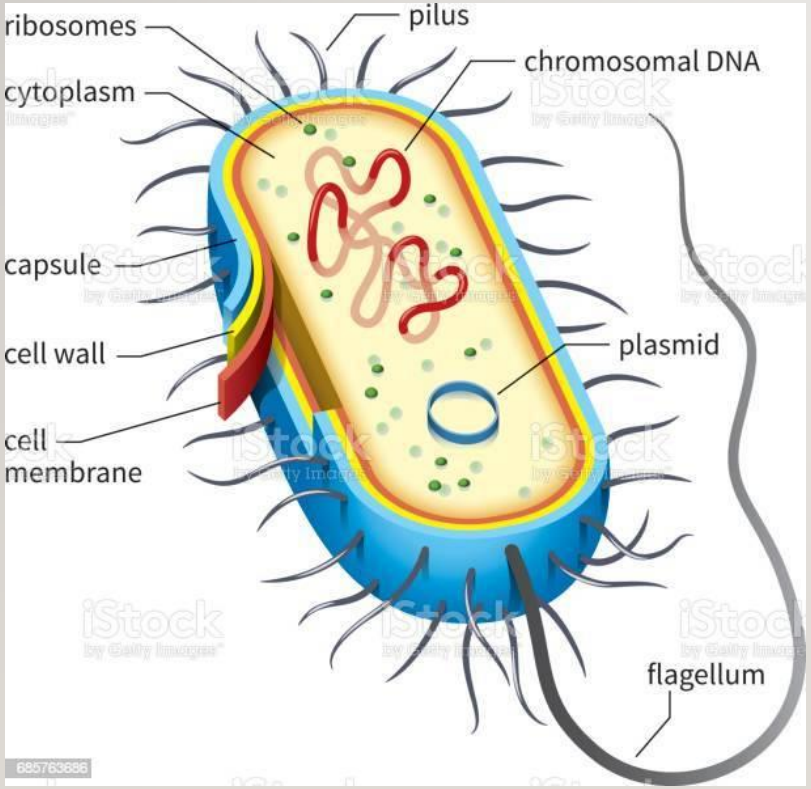
Dossage 600 mg/l	% Inhibition
3888	84.22

Dossage 1000 mg/l	% Inhibition
3700	61.22

- To determine optimum dosage, another test conducted at various dosage below 1000 ppm
- From result above the optimum dosage is between 200 – 600 ppm
- Since injection rate pump cannot be lowered, the solution is ask chemical vendor to dilute the SI until the active content similar with the laboratory test result.

Bacteria Control

DEFINITION



- Bacteria are single celled microbes. The cell structure is simpler than that of other organisms as there is no nucleus or membrane bound organelles
- Bacteria are living organisms that are naturally occurring and can be found in a very wide range of conditions.
- In nature, some types of bacteria can be found at the bottom of 10,000-foot deep trenches in the oceans, near volcanic areas .Bacteria are very resilient!

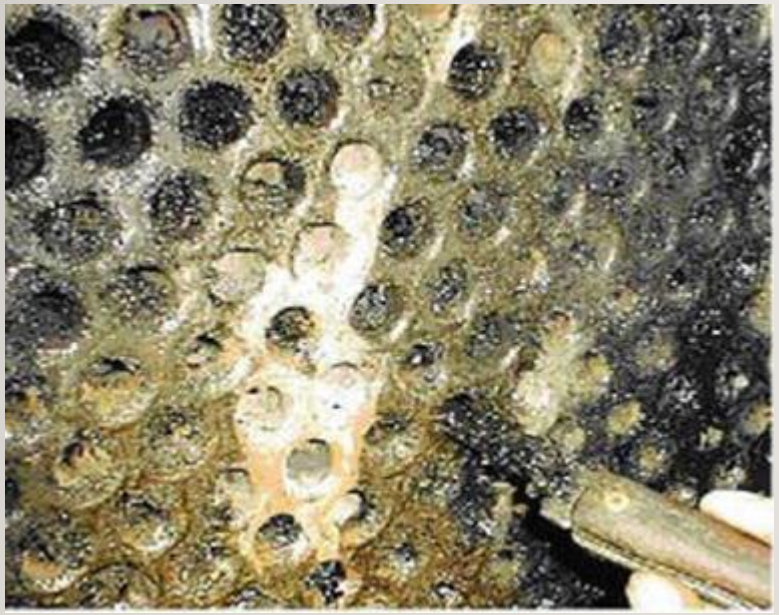
Courtesy Picture : https://media.istockphoto.com/vectors/bacterial-cell-diagram-vector-id685763686?s=612x612

SPECIFIC PROBLEM CAUSED BY BACTERIA

- Plugging in facilities such as at filter
- Reservoir souring
- Corrosion : SRB create corrosive acid H_2S or create slime that cause Microbial Induced Corrosion (MIC)
- MIC is the term used for the phenomenon in which corrosion is initiated and/or accelerated by the activities of micro-organisms (such as SRB). MIC is believed to account for 20 % of the damage caused by corrosion

Courtesy Picture : https://www.ecscorrosion.com/blog/microbiologically-influenced-corrosion-mic

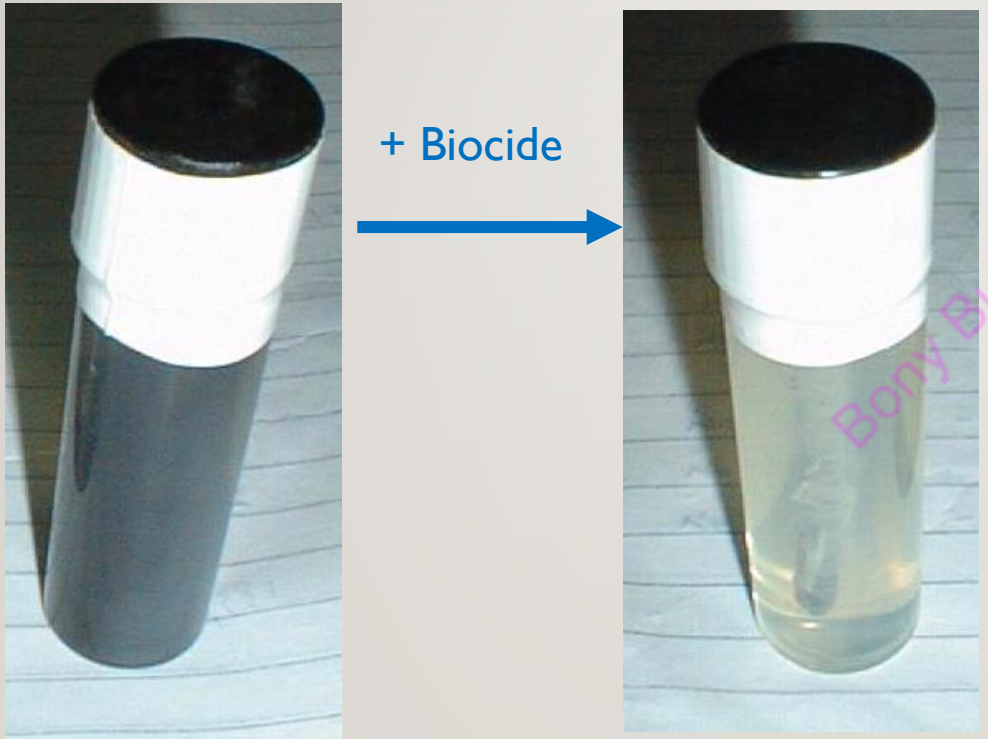
BIOLOGICAL TREATMENT



- Depend on the water source, some chemical treatment are as below
- Chlorine : used to control seawater organism. Chlorine is oxidation biocide but chlorine not too effective for SRB
- Organic biocide : used especially used to control SRB in produced water.

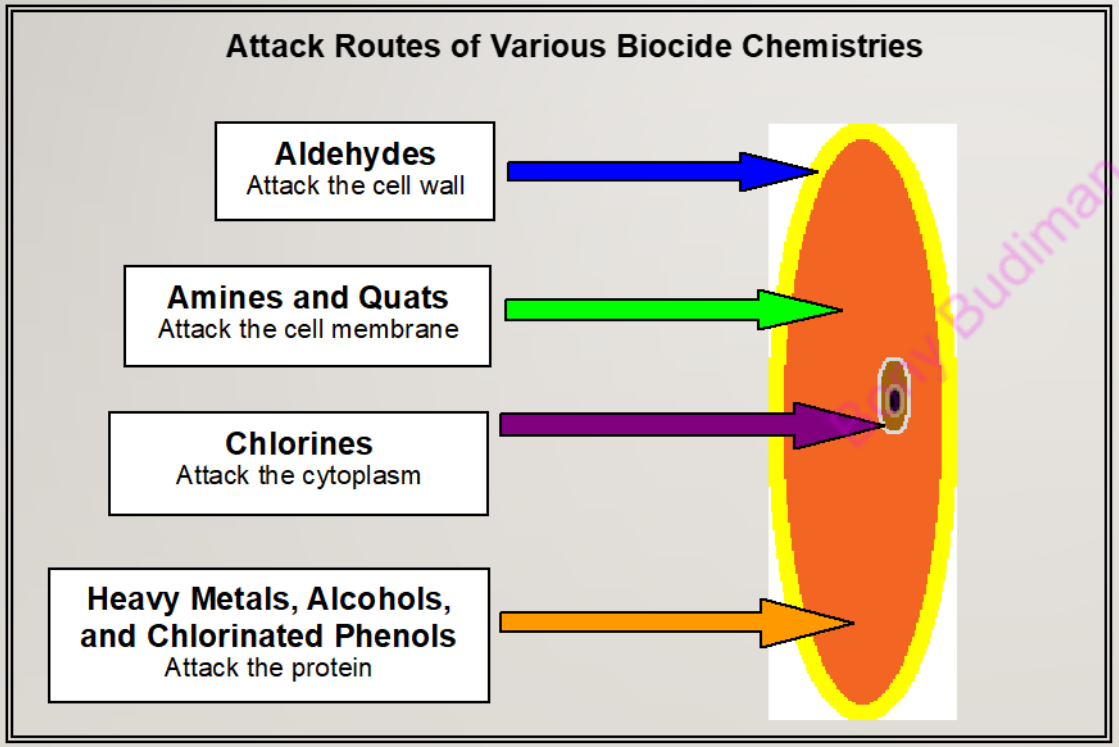
Courtesy picture : https://www.intechopen.com/media/chapter/68149/media/F3.png

BIOCIDE



- Biocides, also called "bactericides" or "antimicrobials," are used in oil and gas production primarily to reduce sulfide production and microbiologically induced corrosion (MIC) and related biofouling.
- The aim of a biocide is to kill microorganisms, especially bacteria, or interfere with their activity

BIOCIDE MECHANISM



- Each type of biocide has specific mechanism to inhibit bacteria growth.
- Picture beside illustrate a simple mechanism of common biocide
- None of biocide that could work for all bacteria, even one type bacteria can mutate to become resistant to certain biocide.

FIELD CASE :VELOCITY EFFECT

Coupon Before Cleaning

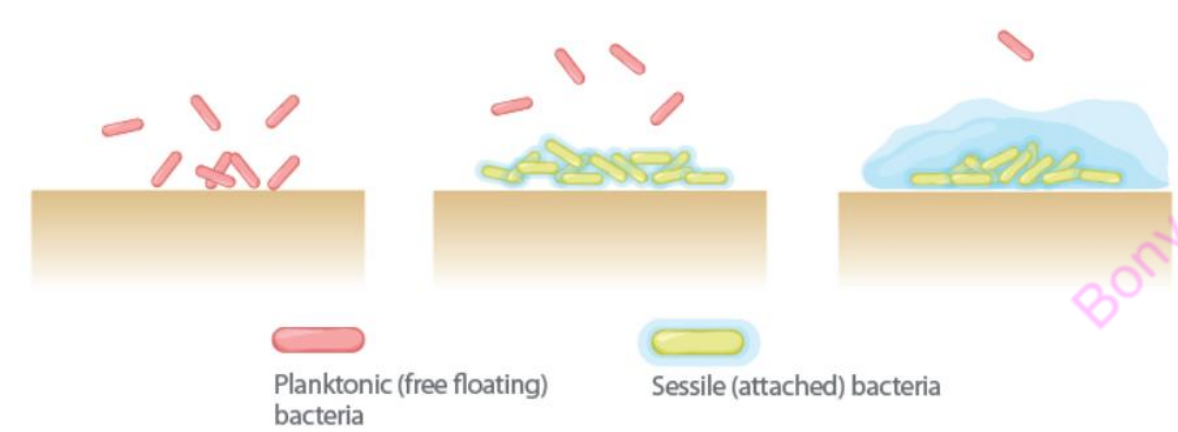
Coupon After Cleaning

- At Kapha Field, one monitoring point near water injection well KP#109 the corrosion rate is 16 mpy. Much higher than specification maximum 5 mpy. Others monitoring points meet specification.
- As shown at picture beside, the corrosion coupon blanketed with black deposit after retrieved, and after cleaning we found a general corrosion form at the coupon
- Dose of corrosion inhibitor has been increased from 8 to 13 ppm for several months with no significant improvement

VELOCITY EFFECT

- Hypothesis : the molecule of corrosion inhibitor cannot form a thin layer film to protect corrosion at inner pipeline due to the black deposit.
- What is the black deposit ? The fluid of water injection shall be a treated water with minimum oil content, so it shall be not crude oil deposit.
- We conduct bacteria rapid test to deposit KP#109 and at near monitoring point, KP#029
- As shown at picture beside, the deposit of KP#109 is bacteria slime.

VELOCITY EFFECT



- Why the bacteria slime deposit found at KP#109 and not found at others while the waters coming from same source ?
- Refer to NACE Paper No.07516 Microbiologically Influenced Corrosion (MIC), the sessile SRB may found when the pipe velocity is ≤ 0.35 m/s or equal to 1.1 ft/s.
- Flow velocity at KP#109 on October 2010 is 0.5 ft/s meanwhile flow velocity at others is more than 2 ft/s

Courtesy Picture : https://www.woundsource.com/blog/biofilm-and-wound-healing

VELOCITY EFFECT

Month	BC Batching (USG)	Surfactant Batching (USG)	BC Continuous (USG)	CI (USG)	Corr Rate (mpy)
Jan	-	-	-	82	14.9
Feb	-	-	-	82	51.0
Mar	-	-	-	82	53.9
Apr	260	208	72	51	4.1
Mei	260	208	72	51	2.2
Jun	104	208	72	51	3.4

- Since the suspect root cause of high corrosion rate is deposited slim SRB, the action objective is how to reduce the slime
- Below are the summary action :
  - Every month, Slug dose / batching mode 260 US Gallon biocide (BC) at the skimmer tank (water source for all Kappa field), continue with slug dose 208 USG surfactant to clean clean the surface
  - Continue injection with Biocide and Corrosion Inhibitor
  - The corrosion rate significantly decrease and meet specificati0n

SUMMARY

- Produced Water is 'unwanted" product in the oil and gas field
- Produced water shall be treated to minimize risks to environmental, technical, reputation and cost as well
- Some chemicals used for produced water :
  - Reverse demulsifier to reduce oil content
  - Corrosion Inhibitor to inhibit corrosion
  - Scale Inhibitor to prevent scale deposition
  - Biocide to control bacteria

REFERENCES

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6. Optimizing Standard And Produced Water Injection Systems Extracted and adapted by Bob Eden of CAPCIS Ltd. from the forthcoming Industry Guidelines: “Disposal of Produced Water by Injection