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Well Stimulation and Sand Production Management (PGE 489)

Carbonates Acidizing

By
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15-02-2016

Carbonates Acidizing

- Carbonate formations generally have a low permeability and can be highly fissured.
- HCL is used as basic rock dissolution agent.
- Wormholes form in the process of dissolution of rock.
- Other additives are used as per compatibility with rock minerals.

Acid for Carbonates

- Hydrochloric acid (5 to 28 wt%)
- HCl + organic acids (15/9 HCl/formic acid)
- Acetic &/or formic acid (< 13, 9 wt%)
- Emulsified acids (up to 28 wt% HCl)
- In-situ gelled acids (~ 5 wt% HCl)
- In-situ generated acids

Acid reaction with Carbonates

- **Calcite** $2HCL + CaCO_3 \longrightarrow CaCl_2 + CO_2 + H_2O$

- **Dolomite** $4HCL + CaMg(CO_3)_2 \longrightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O$

- **Siderite** $2HCL + FeCO_3 \longrightarrow FeCl_2 + CO_2 + H_2O$

Carbonates Acidizing

- For effective stimulation, deep wormholes are necessary to maximize conductivity between the reservoir and the well-bore for enhancement of production.
- Generally, the reaction rate between conventional plain HCL and carbonates is very fast at reservoir temp.

Carbonates Acidizing

- For effective stimulation of carbonate reservoirs the following acid systems are used;
  - Emulsified acid system
    - Acid emulsified with hydrocarbon (diesel)
  - Gelled acid system
    - Acid modified with gelling agent (polymer/viscoelastic surfactants)
      - To achieve deep penetration
      - Compatible at reservoir temp.

Carbonates Acidizing

General Acidization steps

- Pre-flush stage (5% - 10% HCl)
  - 50-100 gal/ft of formation
  - To remove carbonates
  - To push Nacl or KCl away from well-bore
- Acid stage
  - HF to dissolve clay/sand
  - HCl to dissolve carbonates
- After-flush stage (10% EGMBE): Ethylene Glycol MonoButyl Ether
  - To make the formation water wet
  - To displace acid away from well-bore

Carbonates Acidizing

Acid additives

- Corrosion inhibitor
- Surfactant
- Non-Emulsifier
- Anti-sludge agent
- Iron Controller
- Mutual solvent
- Friction reducer
- Clay stabilizer
- Diverting agent

Viscous Diversion

- Viscosity ratio of acid to gas is high
- Viscous fluid creates large pressure gradient in formation
- Magnitude of resulting diversion to low perm layers is investigated

Diversion Techniques

- Chemical Means:
  - In the formation
  - In-situ Gelled Acids (Polymers)
  - In-situ Gelled Acids (VES)
  - Foam

Chemical Means

- A chemical is added to live acids
- As the acid reacts with carbonate, pH rises + Ca and Mg ions increase in solution
- These changes will trigger this chemical build a structure in solution
- This is accompanied by a significant increase in viscosity, which will divert the acid into low permeability or damaged zones

Chemical Means

- The chemical can be a special polymer or surfactant
- Gel must break in spent acid to clean up the well
- Breaker depends on the type of chemical used
- High viscosity will reduce fluid loss

Chemical Means

- Chemical + breaker are added to live acid
- No reaction in live acid
- Reaction occurs in the rock
- Gel (structure) forms in the rock
- Gel must break in spent acid to cleanup the well

In-situ Gelled Acids "Polymers"

- HCl (3 - 28 wt%)
- Acid - soluble polymer
- Cross-linker (Fe(III) or Zr)
- Gel breaker
- Other additives
- Known as Self-diverting Acid (SDA)

Mechanism

- Polyacrylamide-based polymer
- Polymer contains COOH groups
- At pH 2, COO- ,which cross-links with Fe(III) or Zr(VI) and forms a gel
- At pH 4, a reducer will convert Fe(III) to Fe(II) = breaking the gel
- Another mechanism is also available for Zr

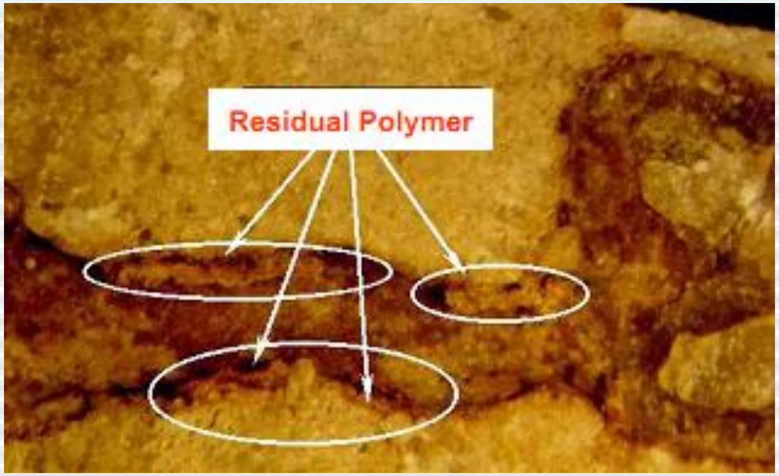
Polymer Residue @ Core Face

In-site gelled acid containing 5 wt% HCl

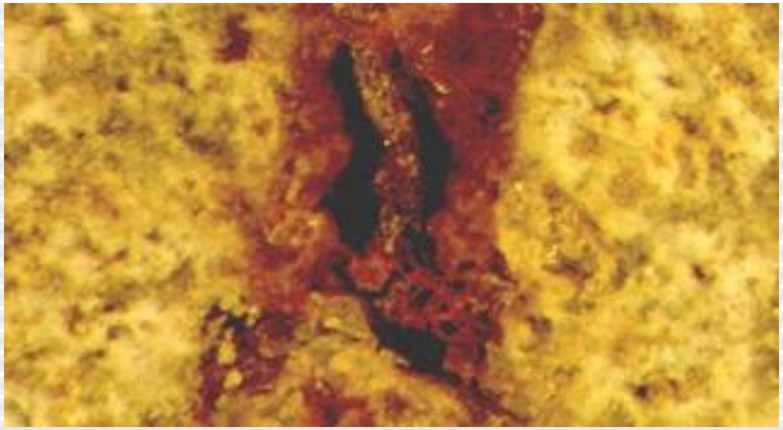
Inlet before

Inlet after

Damage



Polymer trapped in the wormhole



Precipitation of Fe(III) in the wormhole

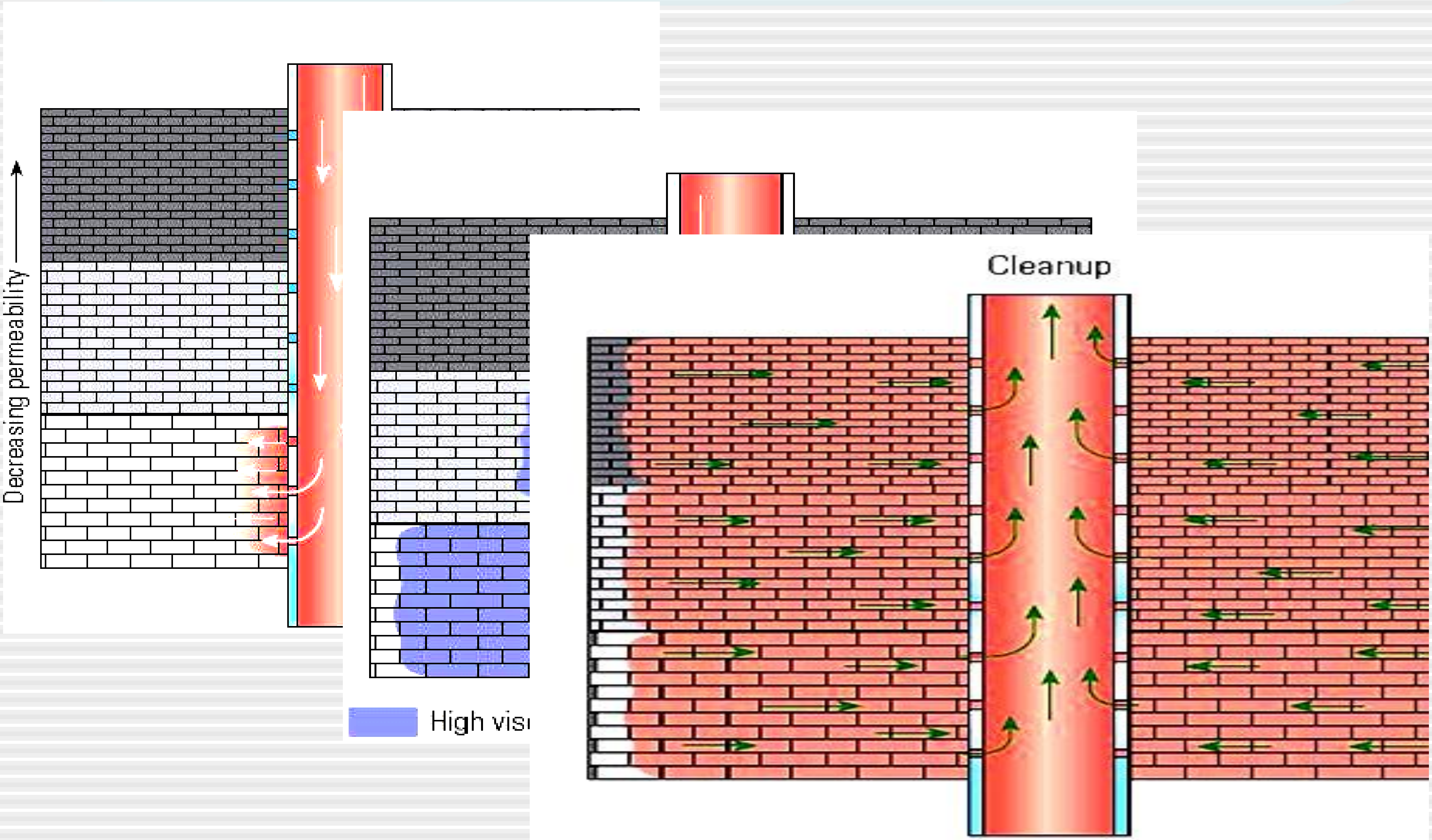
Limitations

- Low HCl concentration and contains Fe(III)
- Polymer residue
- Ppt of the cross-linker
- Cross-linker ppts in the presence of H_2S
- H_2S scavengers don't stop ppt of cross-linker
- Iron contamination may affect the performance of the acid

Recommendations

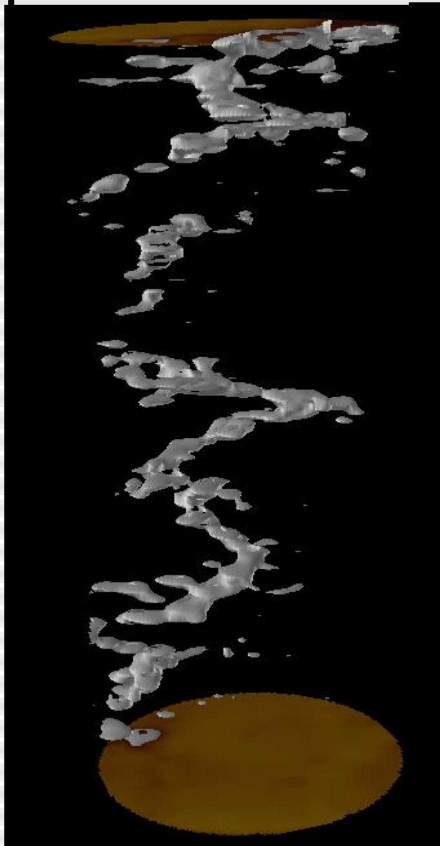
- Acid concentration ~ 3 - 5 wt%
- 25 - 30% of the total acids used
- Not recommended for tight formations
- Not recommended for sour wells
- Flow Well back after acid treatments

Polymer Viscosity Controls Acid Placement



In-Situ Gelled Acid

Polymer Viscosity Controls Acid Placement

Permeability Enhancement	Permeability Reduction
 	 

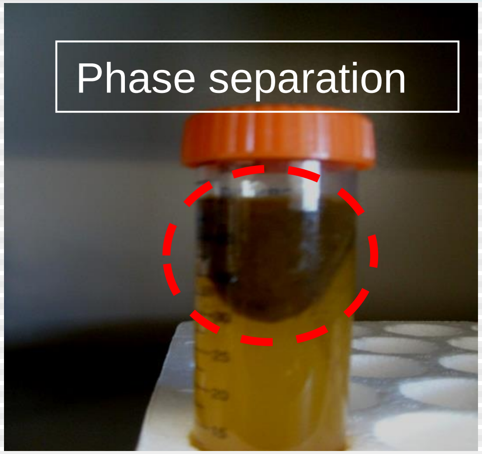
In-Situ Gelled Acid

In-Situ Gelled Acid Formula

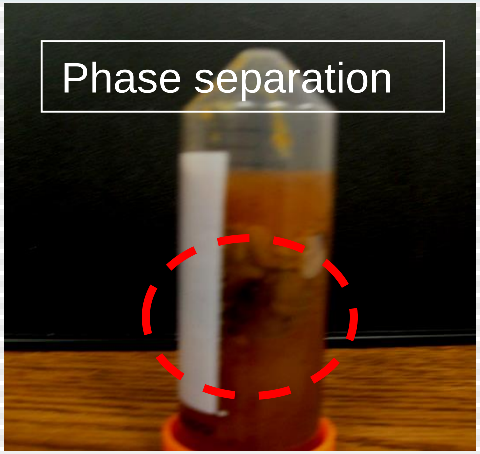
Component	**Concentration**
Hydrochloric acid	5 wt% HCl
Acid gelling agent: a co-polymer of polyacrylamide emulsified in hydrotreated light petroleum distillates	20 gpt
Corrosion inhibitor: Methanol (30-60 wt%), Propargyl alcohol (5-10 wt%)	4 gpt
Cross-linker: Ferric chloride (37-45 wt%)	4.5 gpt
Breaker: Sodium erythorbate (60 to 100 wt%)	20 lb/Mgal
Buffer: Surfactant material	2 gpt

It is important to note that this is the formulaion that is typically used in the field

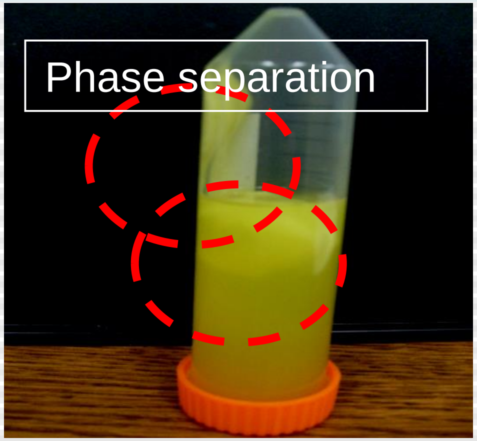
Iron Contamination



Acid A
(1 wt% $FeCl_3$)



Acid B
(1 wt% $FeCl_3$)

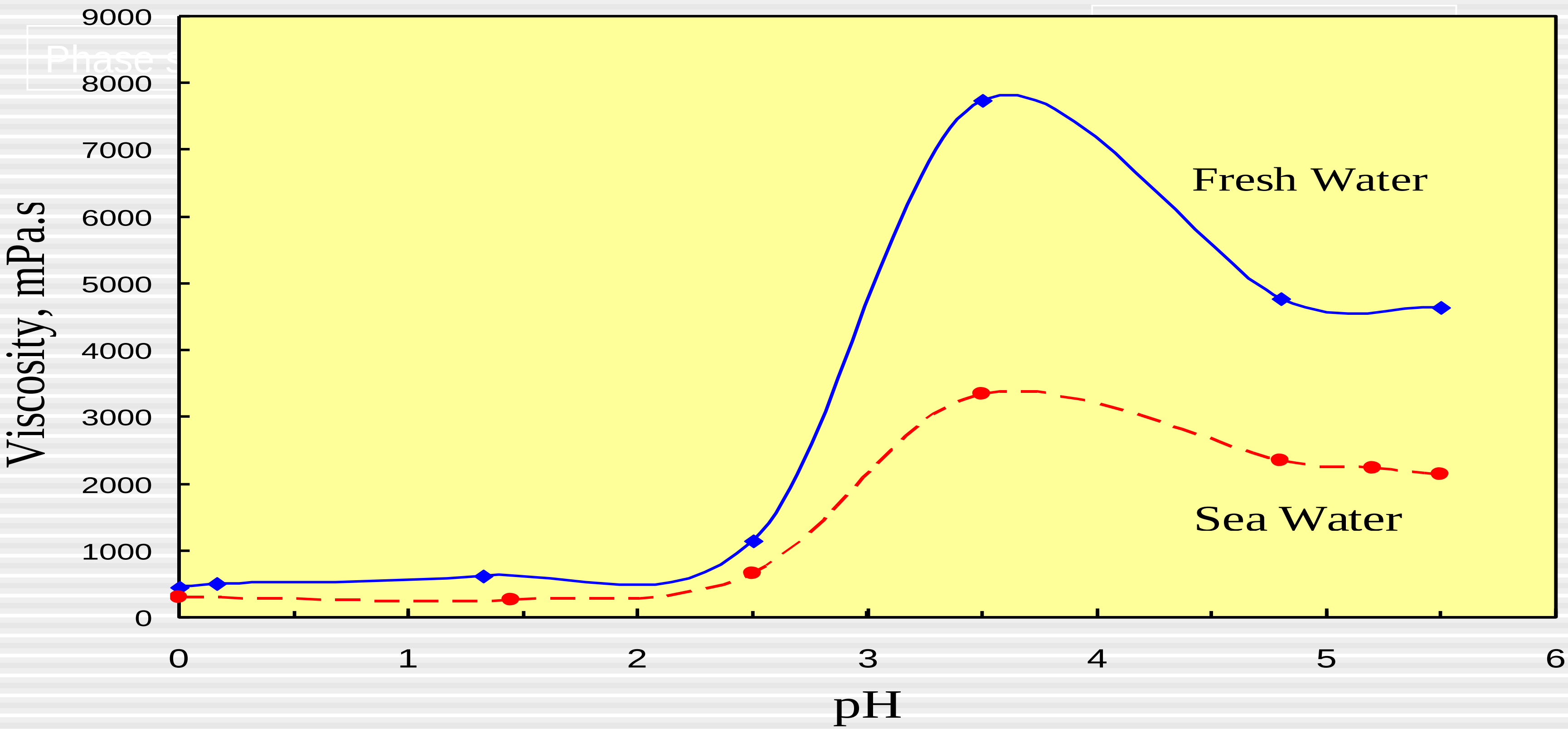


Acid C
(1 wt% $FeCl_3$)

In the field, it is a must to minimize the iron contamination in live acids by

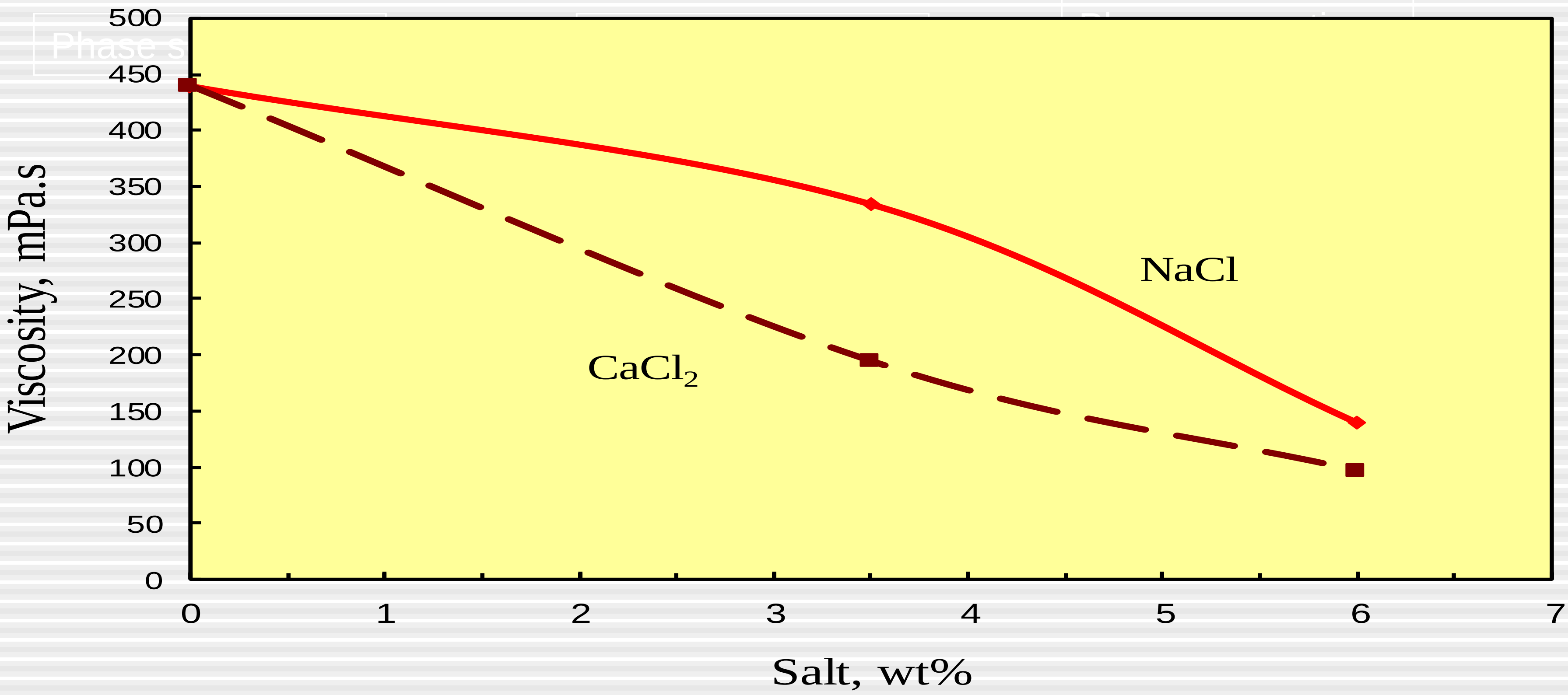
- Cleaning the mixing tank
- Pickling well tubulars or coiled tubing before pumping the acid.

Preparing Acid with Salt Water



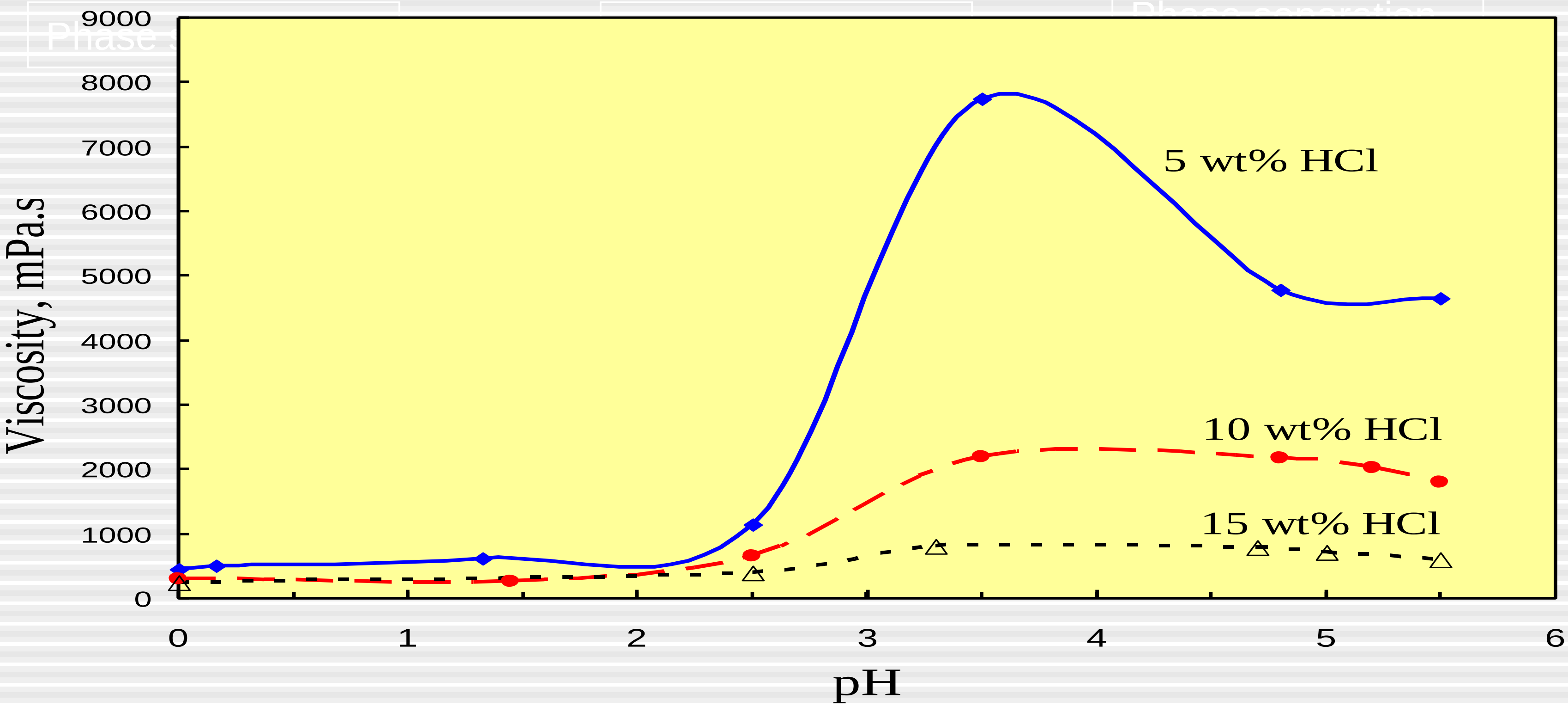
In the field, don’t prepare in-situ gelled acid using aquifer or seawater

Effect of Salt



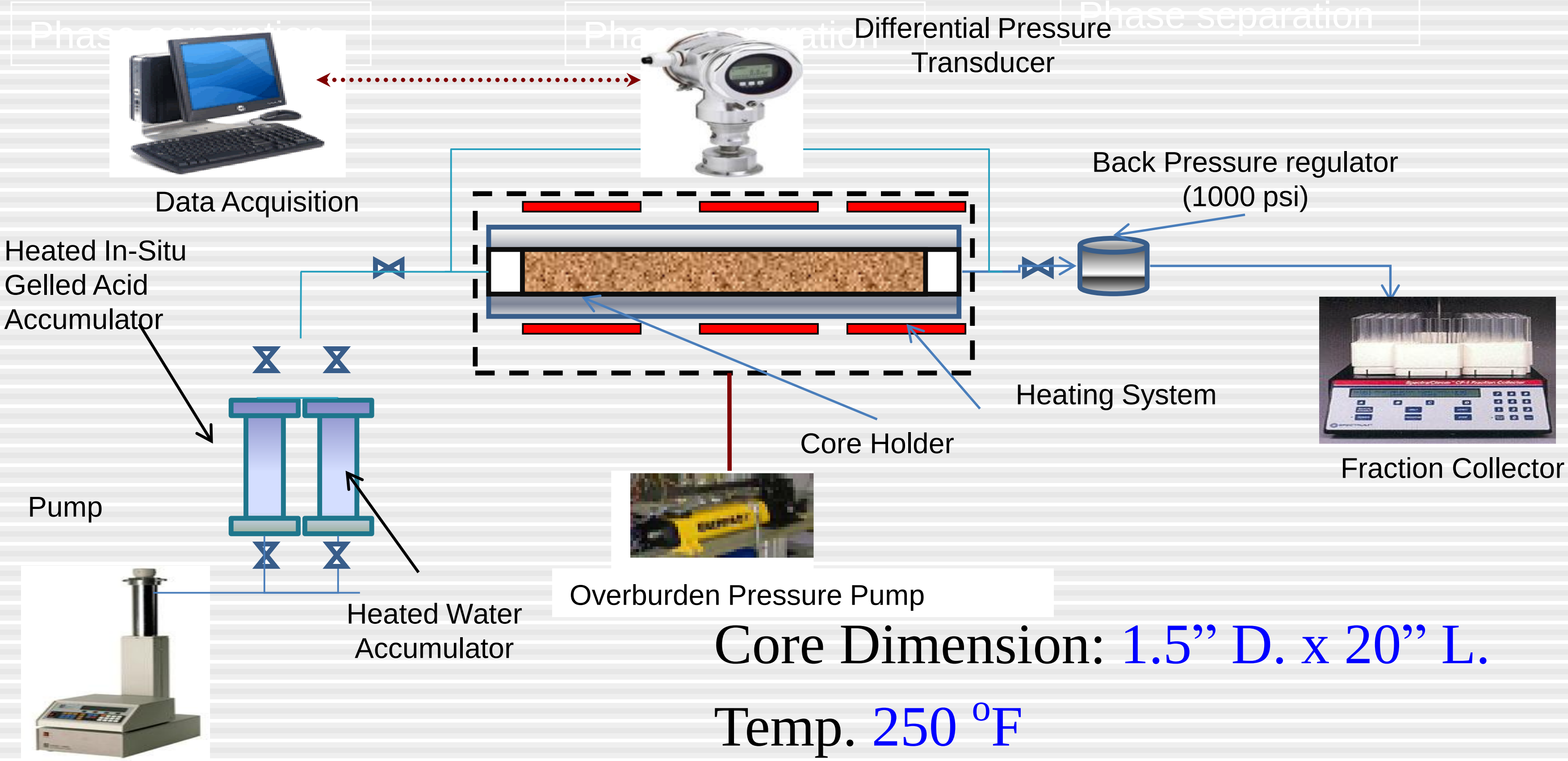
$CaCl_2$ is the reaction product

Acid Concentration



In the field, it is strongly recommended to use polymer-based in-situ gelled acids with 5 wt% HCl

Single Coreflood Setup

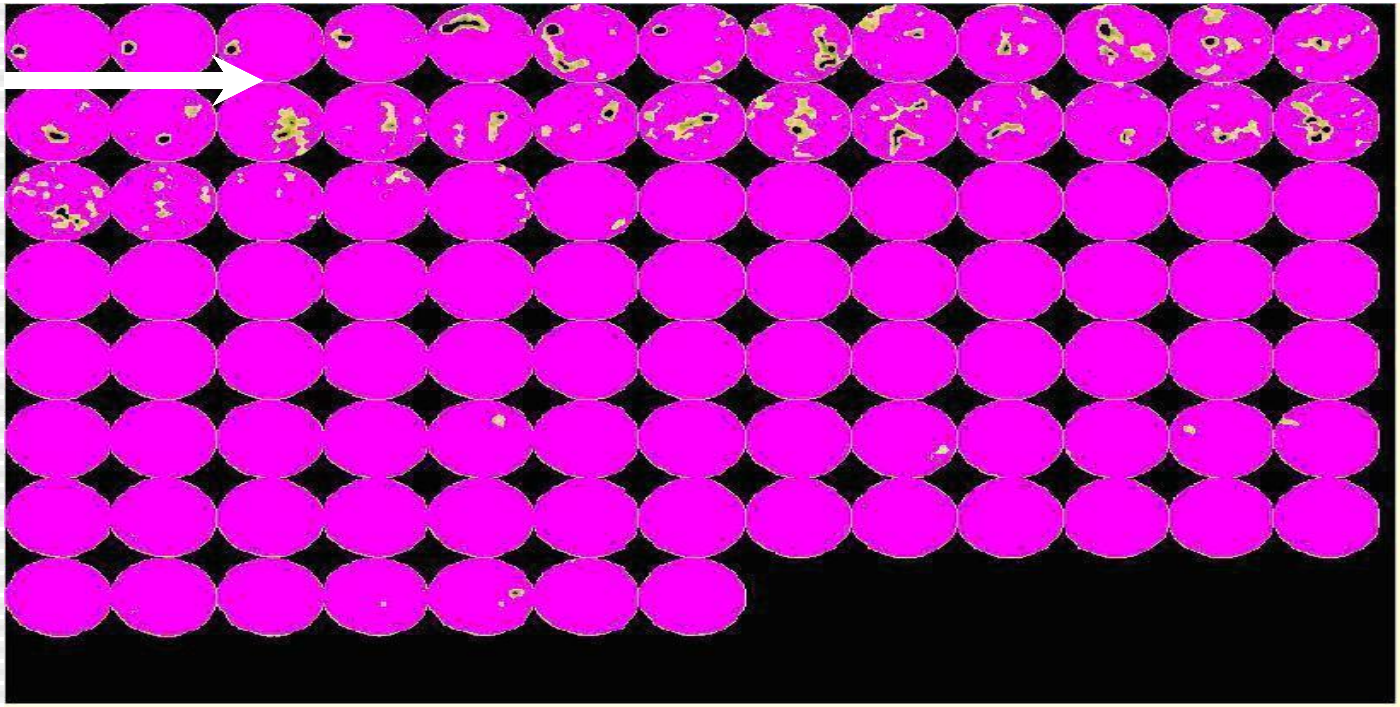


Core Dimension: 1.5" D. x 20" L.

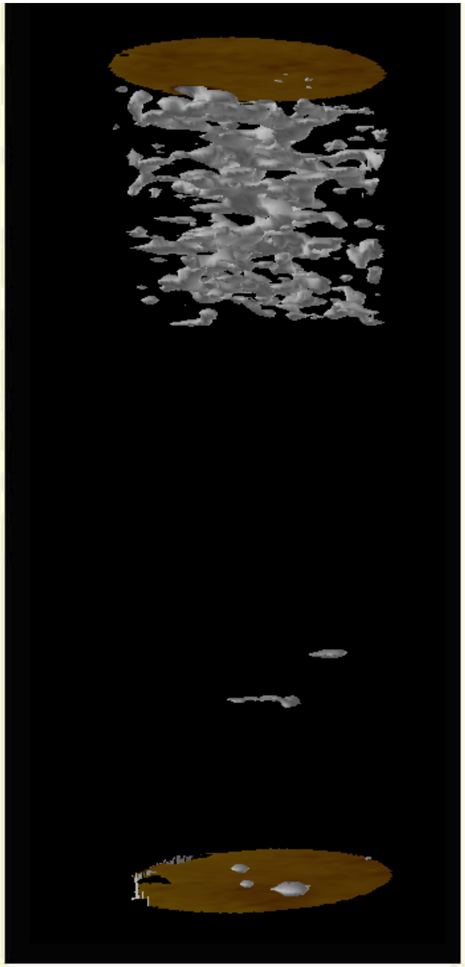
Temp. 250 ^{o}F

Measuring: pH, Density, Ca, and Fe

Core# 1: low injection rate 5 ml/min



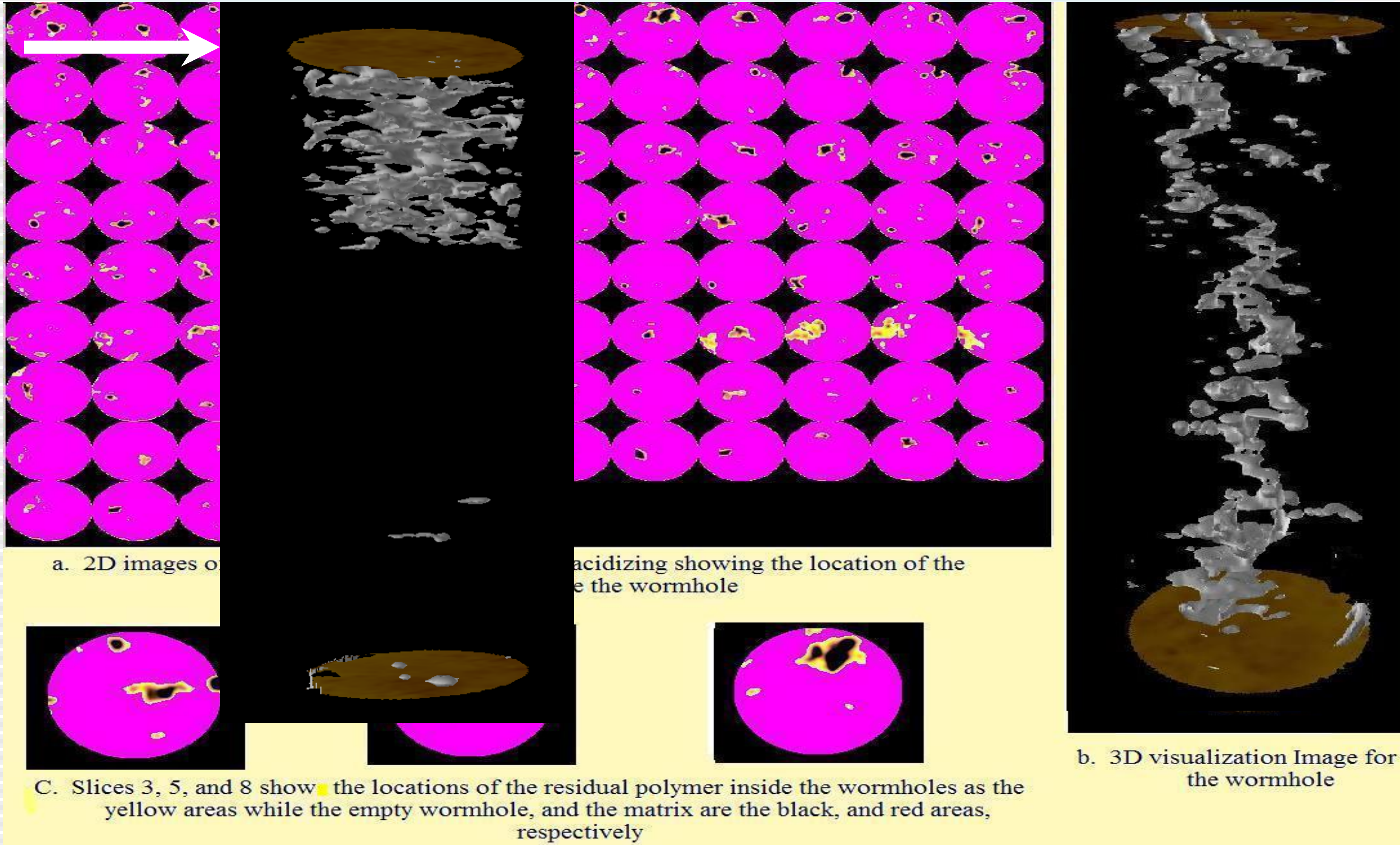
a. 2D images of slices taken along the core after acidizing showing the location of the residual polymer inside the wormhole



b. 3D visualization Image for the wormhole

C. Slices 1, 5, and 8 show the locations of the residual polymer inside the wormholes as the yellow areas while the empty wormhole, and the matrix are the black, and red areas, respectively

Core# 1: high injection rate 20 ml/min

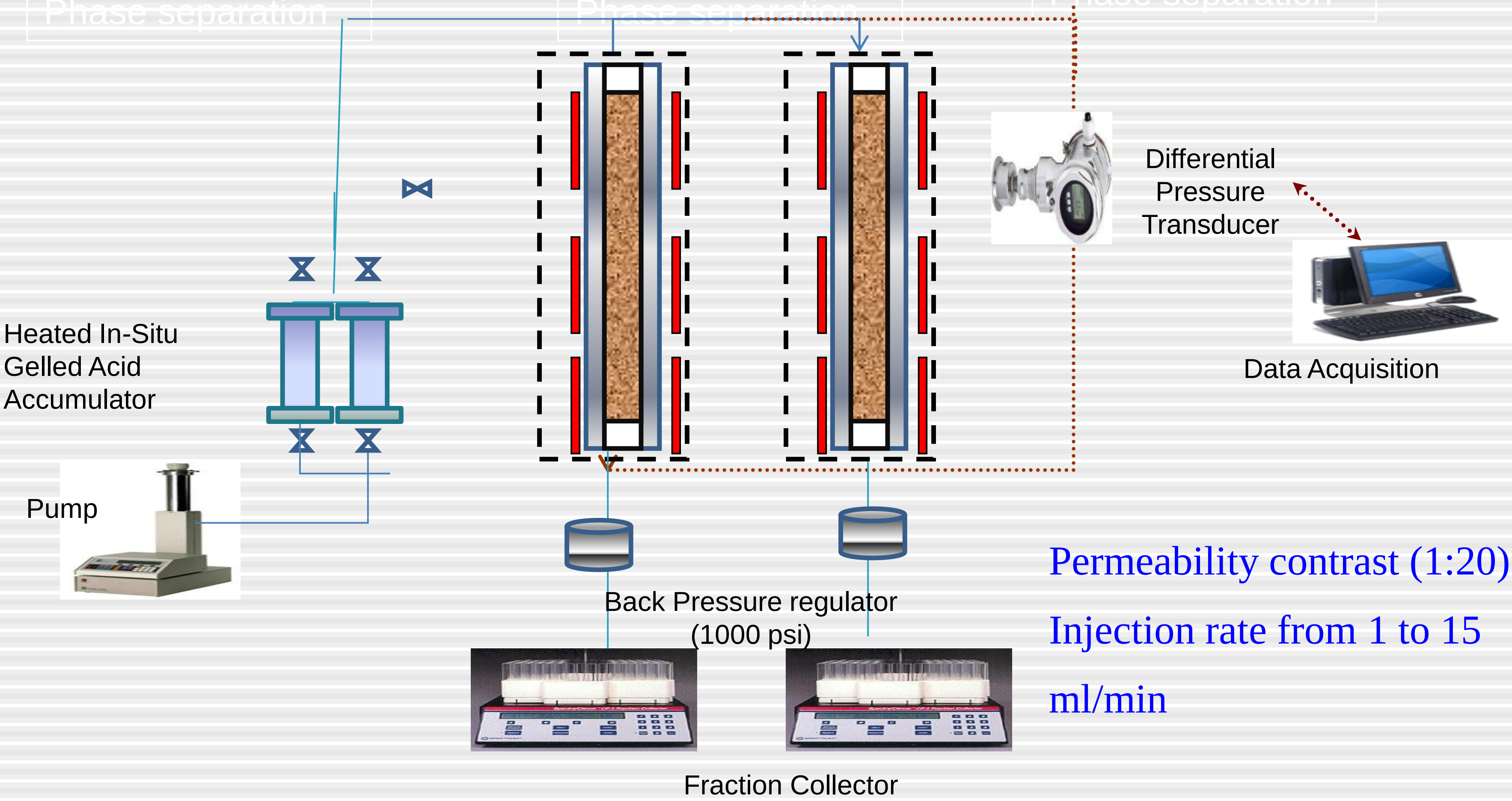


a. 2D images o acidizing showing the location of the
e the wormhole

b. 3D visualization Image for the wormhole

C. Slices 3, 5, and 8 show the locations of the residual polymer inside the wormholes as the yellow areas while the empty wormhole, and the matrix are the black, and red areas, respectively

Parallel Coreflood Setup

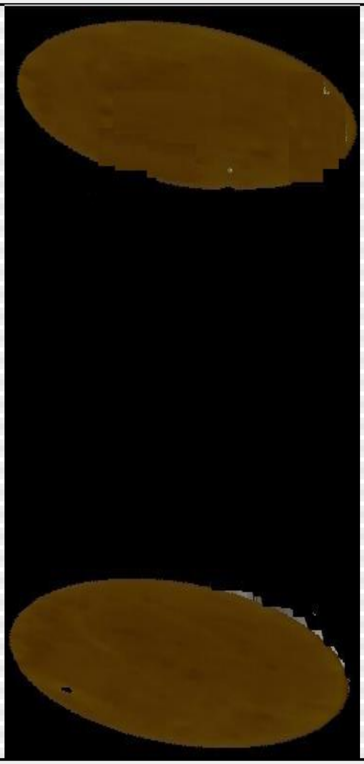
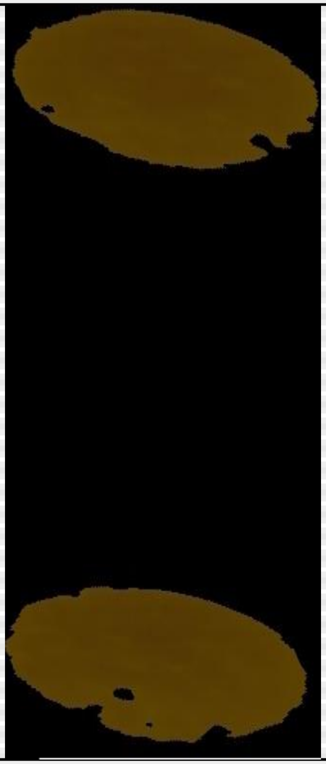


Permeability contrast (1:20)

Injection rate from 1 to 15 ml/min

In-Situ Gelled Acid

No Diversion at Low Rate: 1ml/min

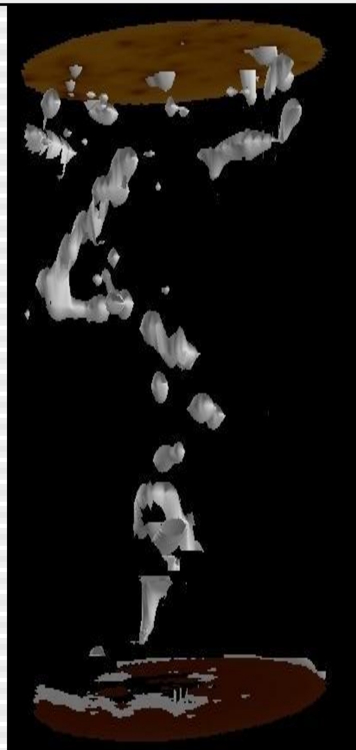
High permeability core	Low permeability core
	

Diversion at Rate: 2.5 ml/min

High permeability core	Low permeability core
	

In-Situ Gelled Acid

No diversion at high rate: 15 ml/min

High permeability core	Low permeability core
	

Need for Alternative Fluids

- Problems associated with HCl:
  - Corrosion of well tubulars at high temperatures (>200^{o}F)
  - Needs numerous additives to reduce corrosion problems
  - HCl cannot be used in wells completed with Cr-13 tubings
  - Corrosion inhibitors may cause alteration of formation wettability
  - Face dissolution is a common problem with HCl at low injection rates
  - Iron precipitation during stimulation with HCl is a common problem, iron control agents should be used

Coiled Tubing Corrosion after Acid Treatment

Need for Alternative Fluids

- HCl causes fines migration in illitic-sandstone reservoirs
- Illite and chlorite are attacked by HCl to produce an amorphous silica (SiO_2) gel residue i.e. the aluminum layer extracted
- The following precipitations may occur during stimulation of sandstone reservoirs if mud acid was used:
  - K_2SiF_6 (potassium fluosilicate)& K_3AlF_6 (fluoaluminate)
  - Na_2SiF_6 (sodium fluosilicate))& Na_3AlF_6
  - $CaSiF_6$ (calcium fluosilicate) &)& $Ca_3(AlF_6)_2$
  - CaF_2 (Calcium fluoride) in high calcite content sandstone
  - $Fe(OH)_3$ may precipitate in spent acid (source of iron is chlorite, siderite, hematite, and tubing rust)

Objectives of Ideal Stimulation Fluids

- The ideal stimulation fluid will remove near-wellbore damage without depositing precipitates in the formation
- Eliminate production decline resulting from solids movement
- The ideal fluid would also exhibit very low corrosion rates at high temperature
- The ideal fluid should penetrate deep inside the formation to avoid face dissolution problems

Chelating Agents

- Alternatives to HCl in deep reservoirs and shallow reservoirs.
- No need for iron control agents because they act as stimulation fluid and iron control agent in the same time
- No need for the corrosion inhibitors at high and medium pH
- Can be used to remove different scale types (sulfate)

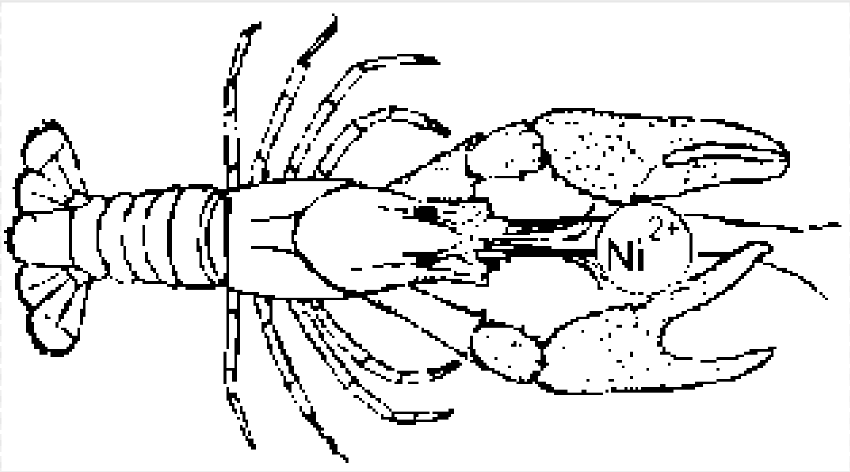
Alternatives (Chelates)

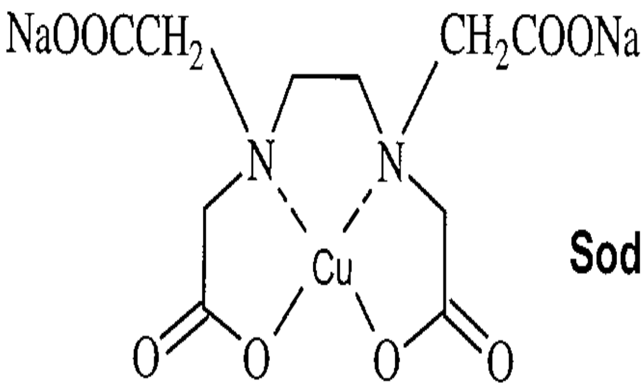
- Chelates are chemicals that complex with metal ions, thus changing the chemical property of the metal ion.
- Virtually all multi-valent cations such as Ca^{2+} and Fe^{3+} can be chelated.
- Usually allows for greater solubility of the metal ion.

Alternatives (Chelates)

- Chelating agents are materials used to control undesirable reactions of metal ions. Also, chelating agents are added to the stimulation fluids to prevent the precipitation of solid after acid treatment .
- Chelating agents applications are
    - Iron control agents in the acidizing process
    - Scale removal
    - Stimulate high temperature deep reservoirs

Chelating Agents



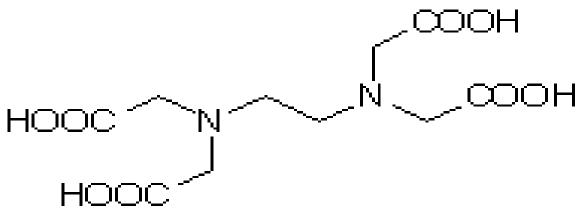
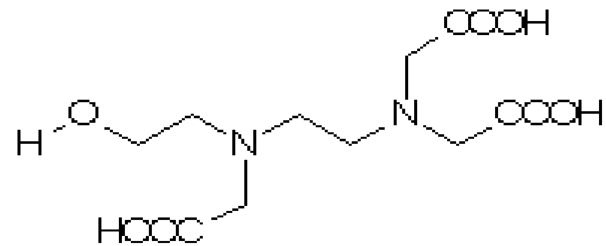
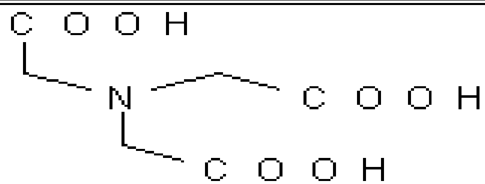
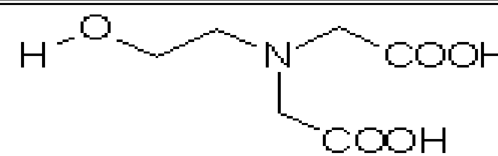
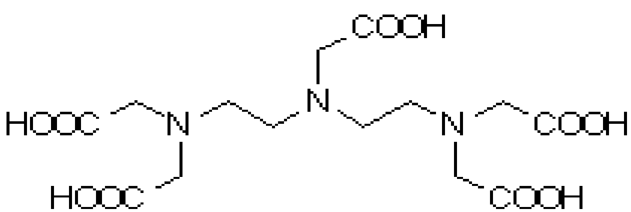
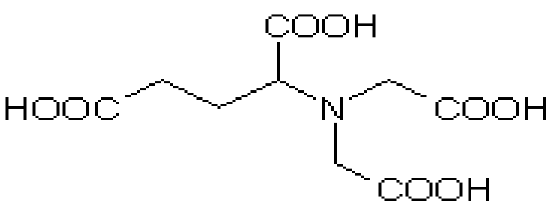


Sodium Copper EDTA

Chelating Agents

- Citric Acid
- Lactic Acid
  - Believed to be not effective Above 100°F
  - Recently being used again but still no successful case history
- Nitrilotriacetic Acid (NTA)
- Ethylenediaminetetraacetic Acid (EDTA)
- Diethylenetriaminepentaacetic Acid (DTPA)
- Hydroxyaminopolycarboxylic (HACA)
  - HEDTA
  - HEIDA
- GLDA

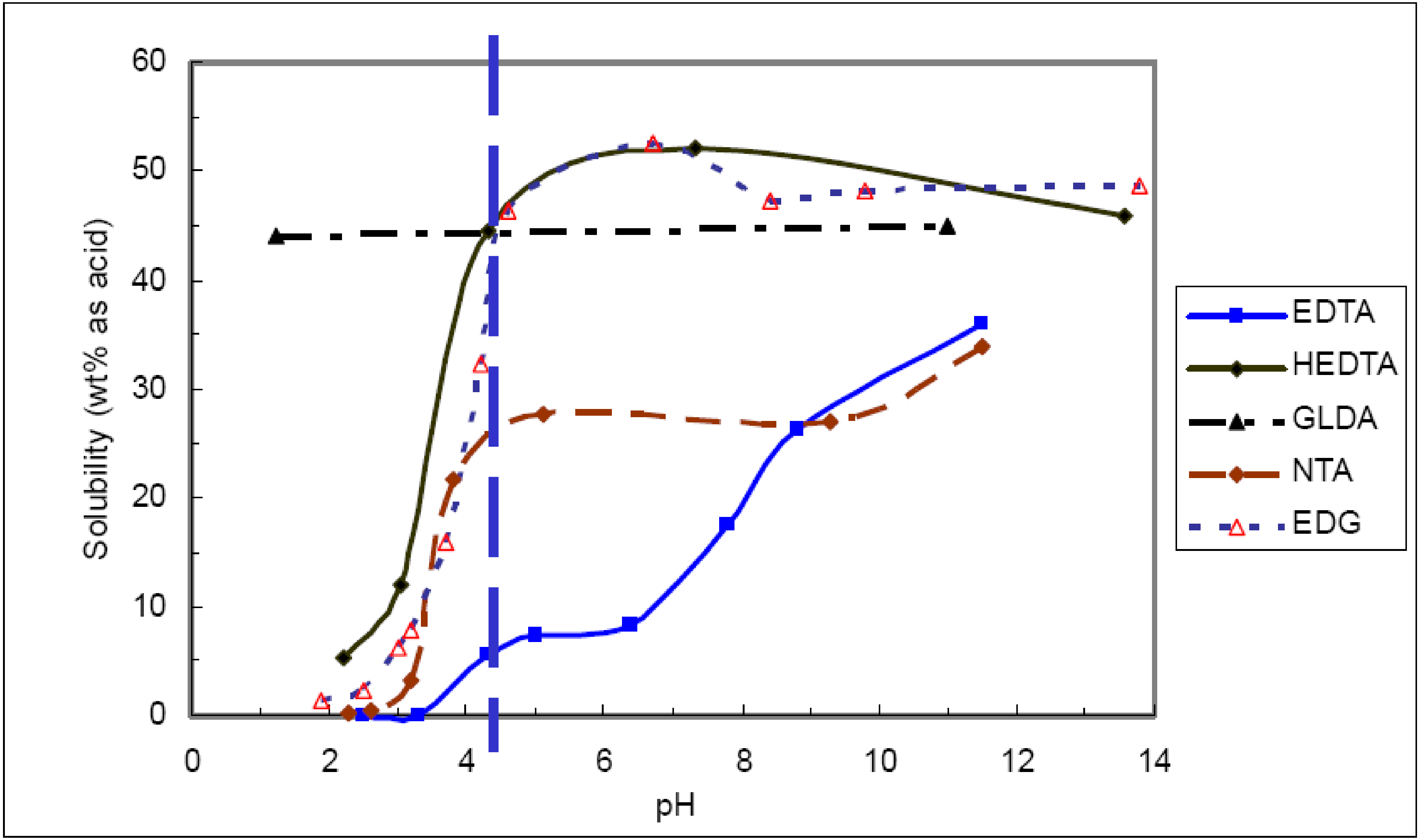
Structures of Chelating agents commonly used in oil industry

 Ethylenediaminetetraacetic acid (**EDTA**)	 Hydroxyethylethylenediaminetriacetic acid (**HEDTA**)
 Nitrilotriacetic acid (**NTA**)	 Ethanoldiglycinic acid (**EDG**) or Hydroxyethyliminodiacetic acid (**HEIDA**)
 Diethylenetriaminepentaacetic acid (**DTPA**)	 L-Glutamic acid, N, N-diacetic acid (**GLDA**)

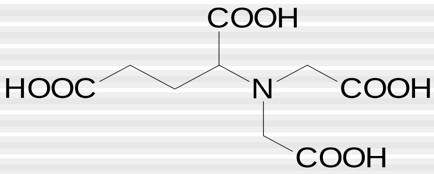
Chelating Agents

- Alternative Stimulation Fluids
  - Several alternative fluids have been tested as alternative to HCl
  - Fredd and Fogler (1998) used EDTA to stimulate calcium carbonate cores (SPE 37212)
  - Frenier et al.(2001) used Na_3HEDTA to stimulate calcium carbonate cores (SPE 68924)
- Problems with current chelates
  - Low biodegradability
  - Low solubility at low pH values
  - Low thermal stability at low pH values
  - EDTA exhibited the same problem of face dissolution at low injection rates

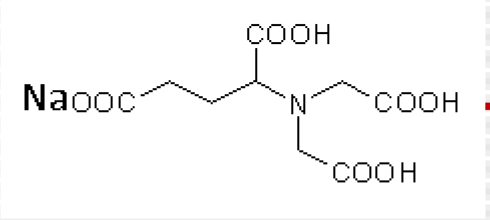
Different Chelates Solubility



Structure of GLDA at Different pH Values

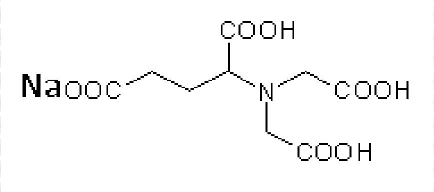


H_4GLDA, pH = 1.7, MW = 263

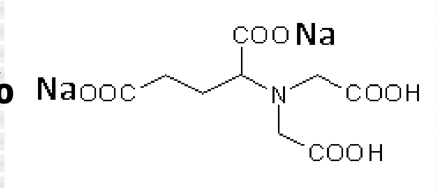


$H_3NaGLDA$, pH = 3, MW = 285

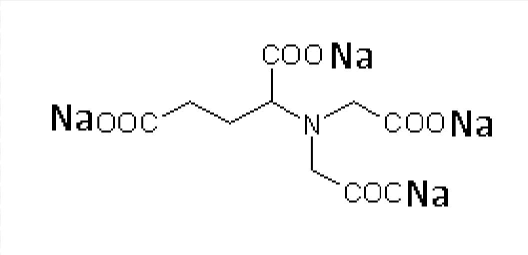
20 wt%



+ 80 wt%



pH = 3.8,
MW = 303

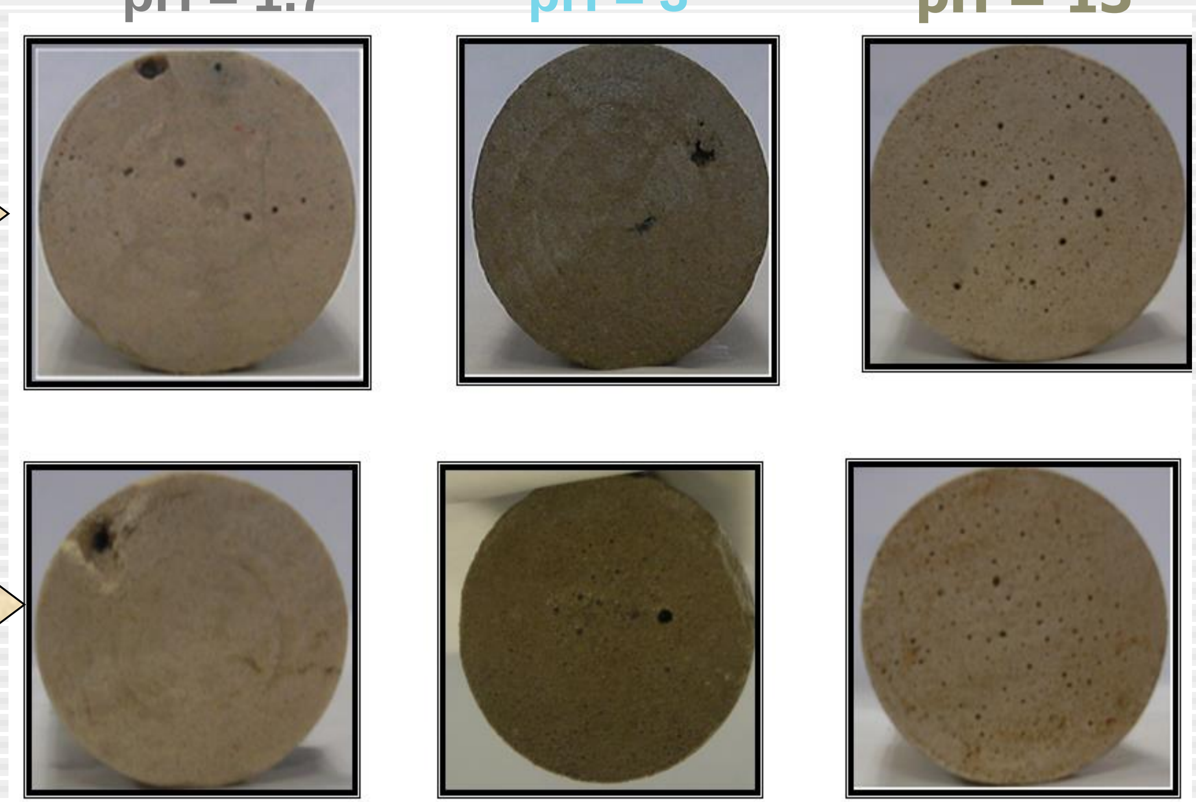


Na_4GLDA, pH = 13, MW = 351

Wormholes formed by Chelating Agents

Inlet and outlet core faces after the core flood experiments with 20 wt% GLDA at 2 cm^3/min and 300^oF, 6-in. cores

pH = 1.7 | pH = 3 | pH = 13



Inlet face

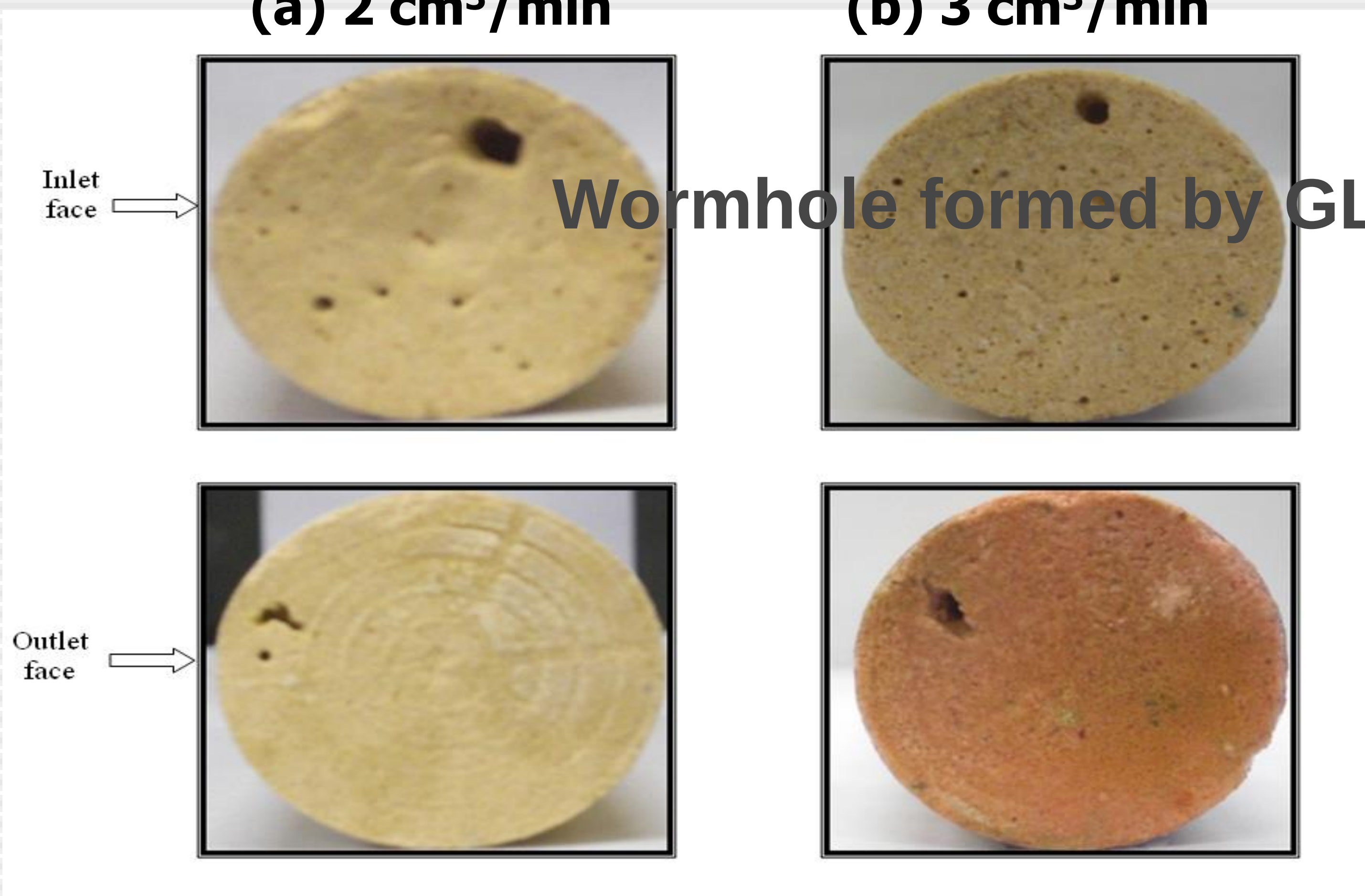
Outlet face

no face dissolution

Wormholes formed by GLDA, 20-in cores

Inlet and outlet core faces after the core flood experiments with 20 wt% GLDA of pH = 1.7 at 300°F

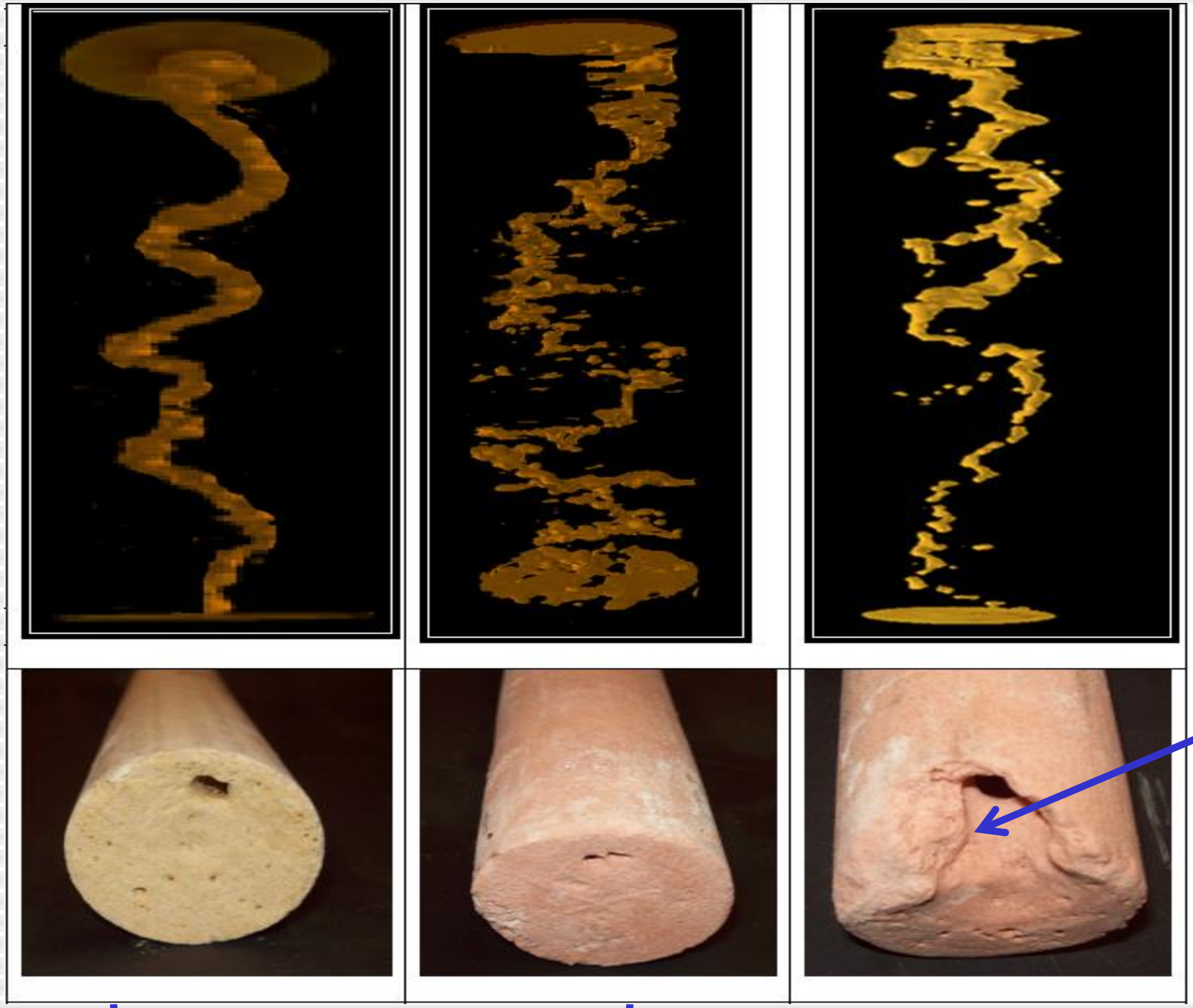
(a) 2 cm^3/min **(b) 3 cm^3/min**



Wormhole formed by GLDA, 20-in

no face dissolution

GLDA and HCl



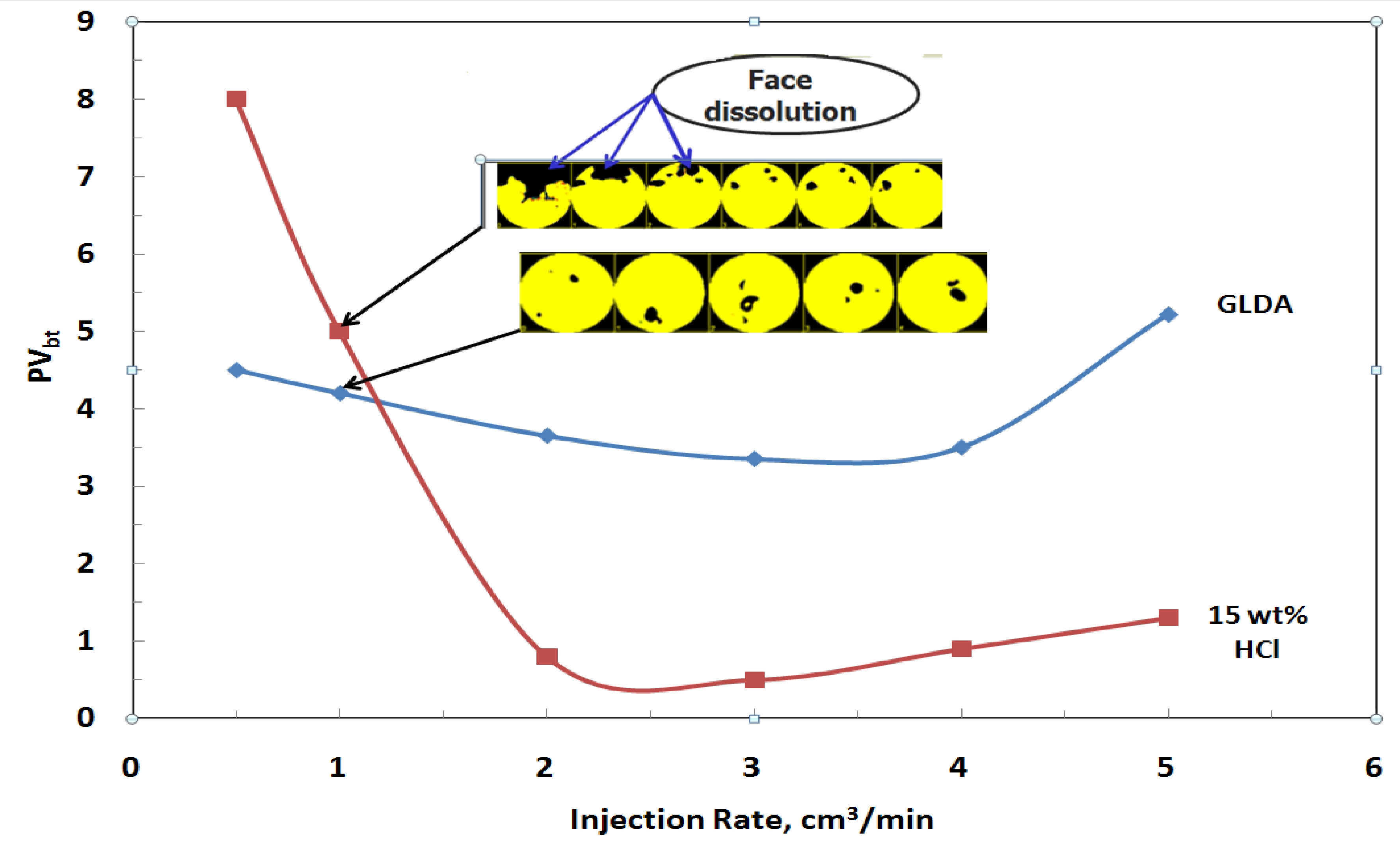
Core inlet face

Core outlet face

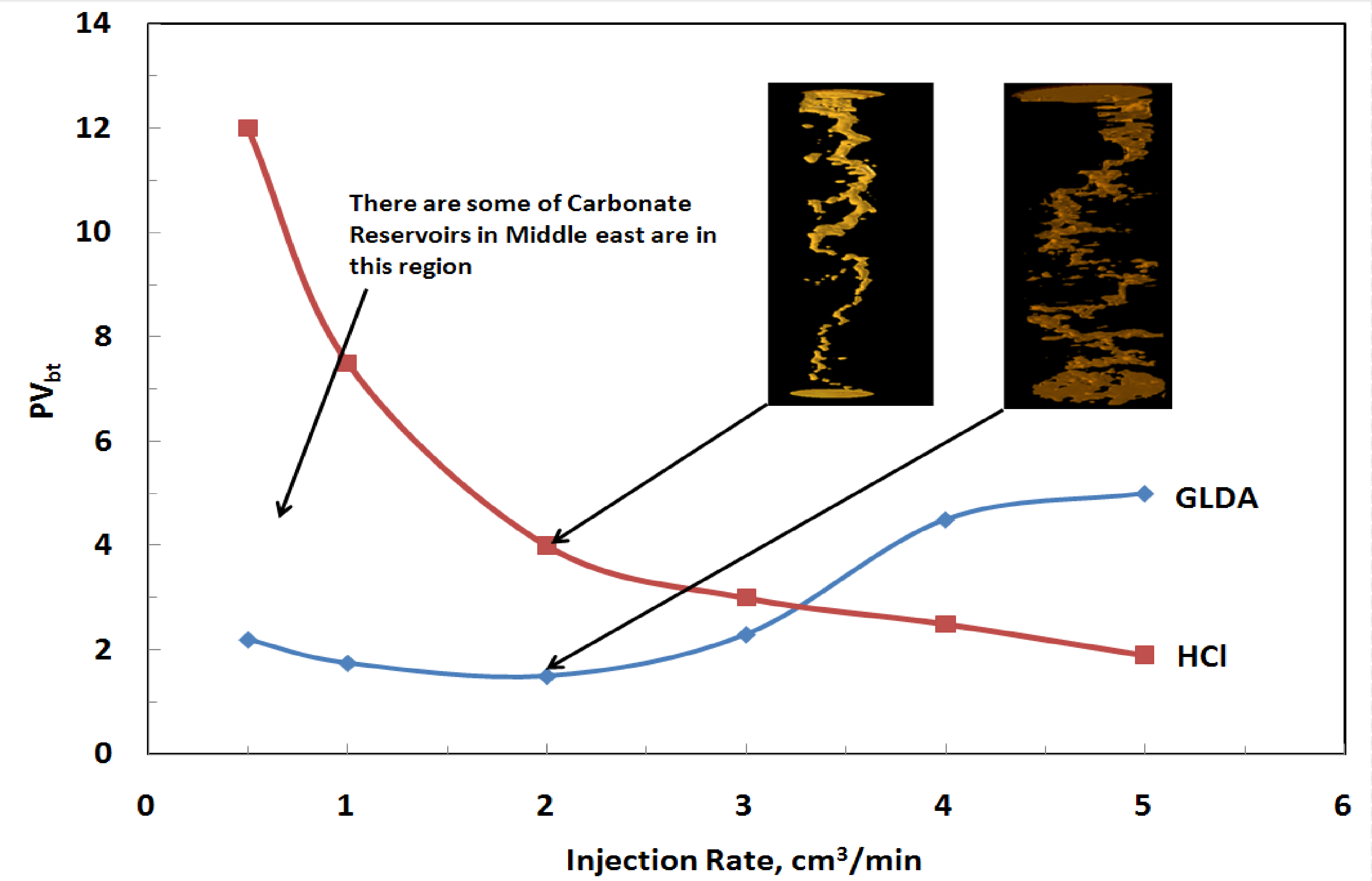
15 wt% HCl at 2 cm^3/min

20 wt% GLDA at 1 and 2 cm^3/min at 300ºF

Short 6-in Cores



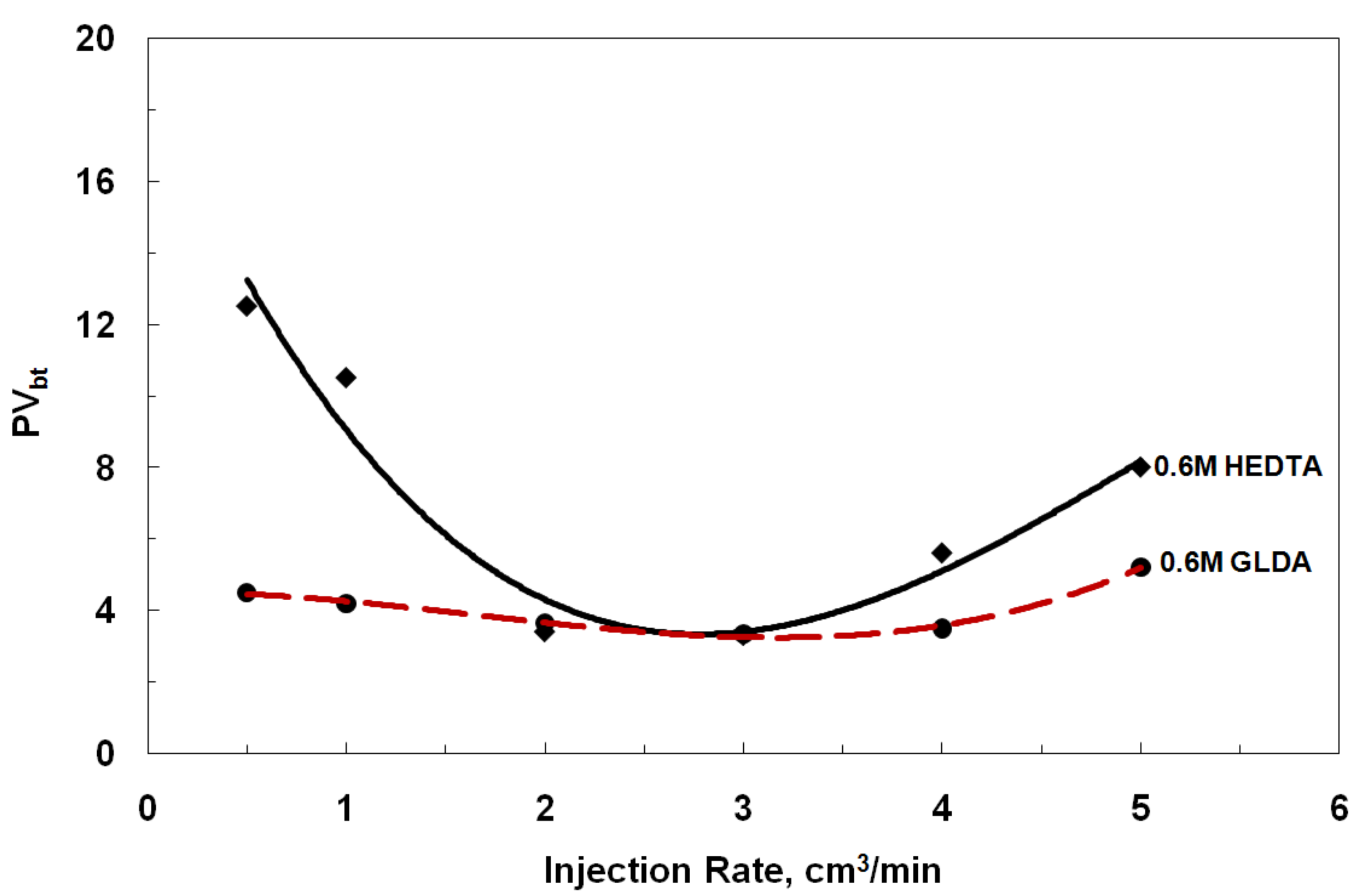
Long 20-in Cores



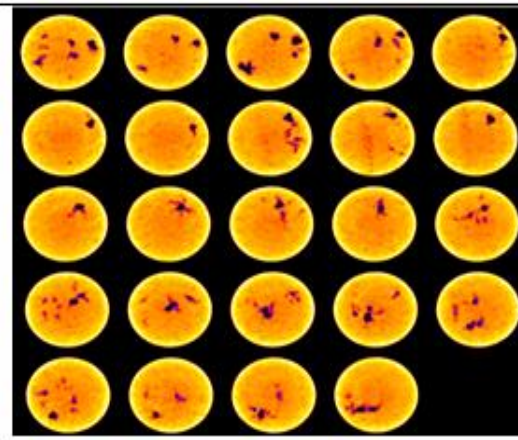
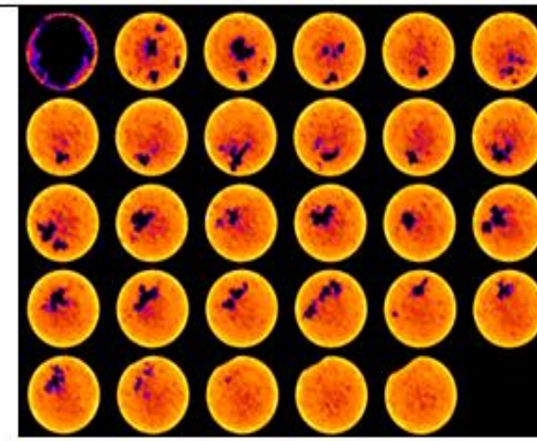
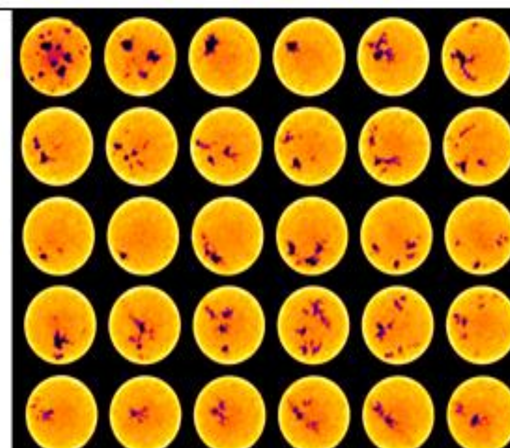
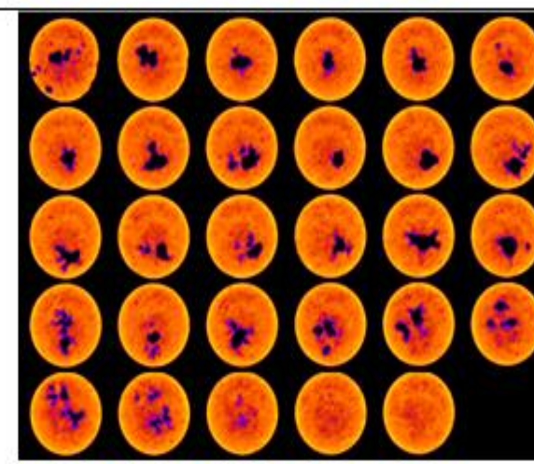
Case Histories on Carbonates

- Tight (k <1 md) carbonate reservoir: HCl had to be injected at low rates to avoid the fracture of the formation because the formation depth is shallow (3000 ft & 135^{o}F).
- One of the HCl criteria, it should be injected at the maximum possible injection rate otherwise it will cause face dissolution.
- Western Desert in Egypt has some shallow depths carbonate reservoirs.
- Coiled tubing availability sometimes force the service companies to inject at low rates

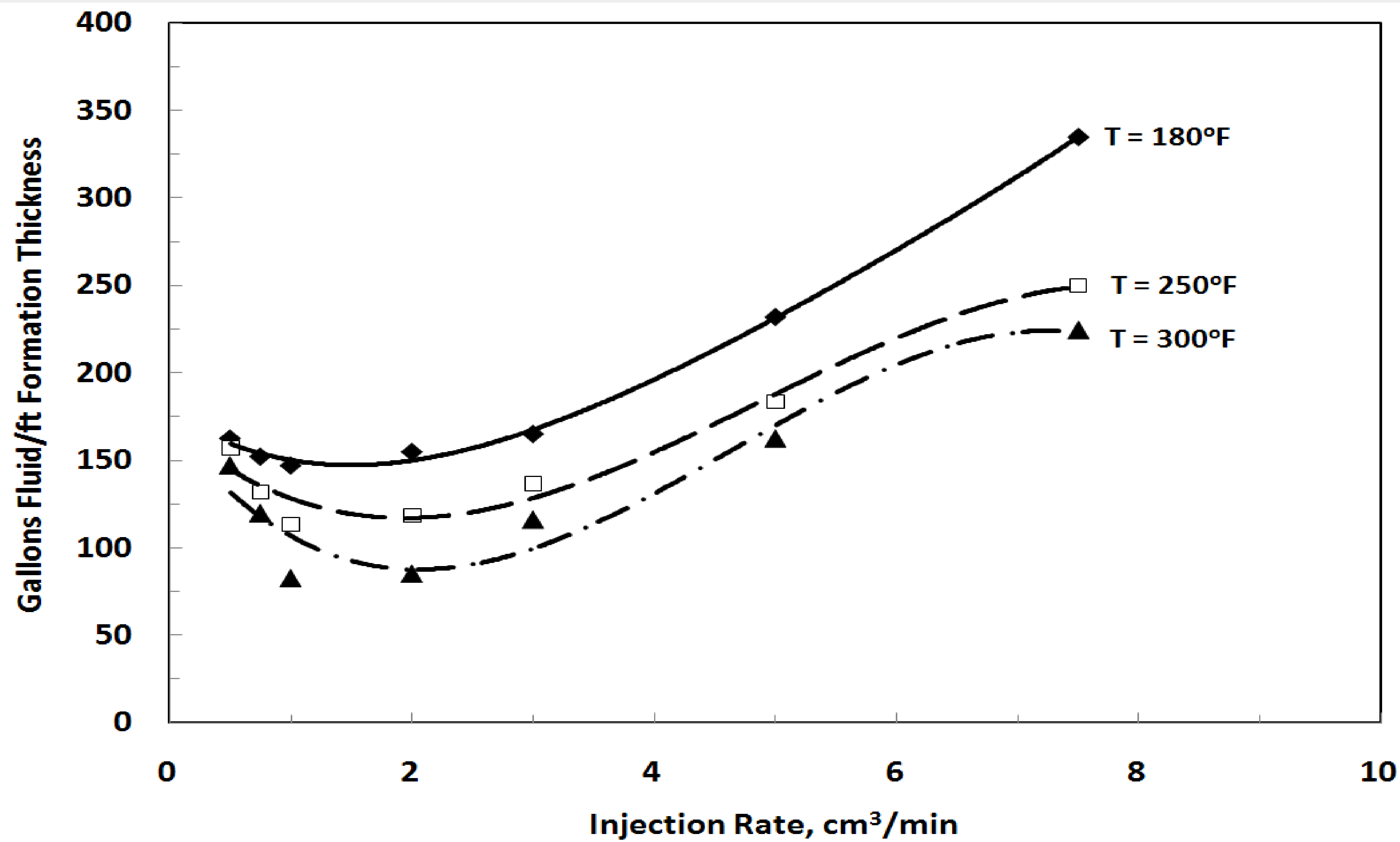
GLDA and HEDTA



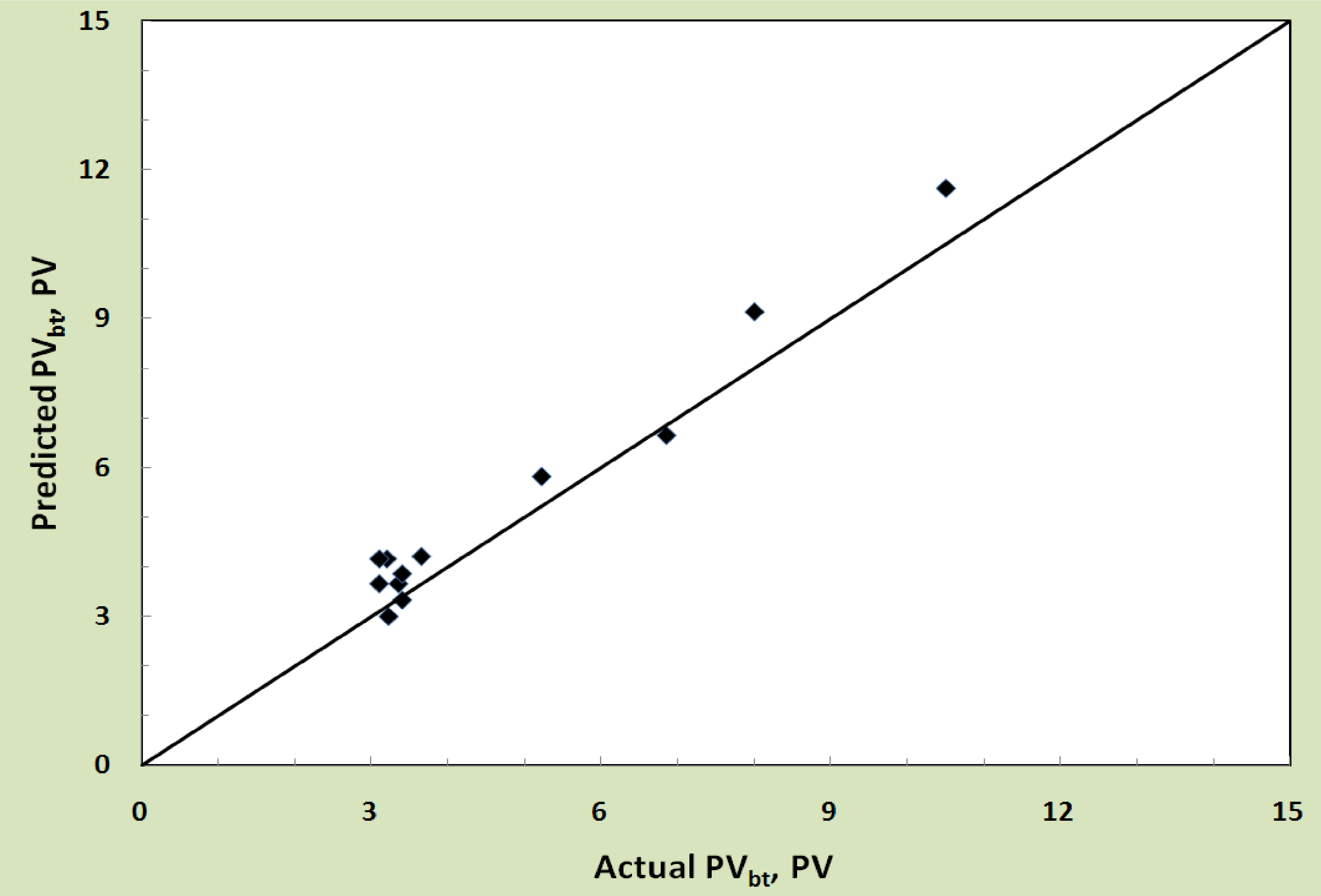
GLDA and HEDTA

Q, cm^3/min	PV_{bt}, GLDA	PV_{bt}, HEDTA	2D CT Scan Images GLDA	2D CT Scan Images HEDTA
0.5	4.5	12.5		
1	4.2	10.50		

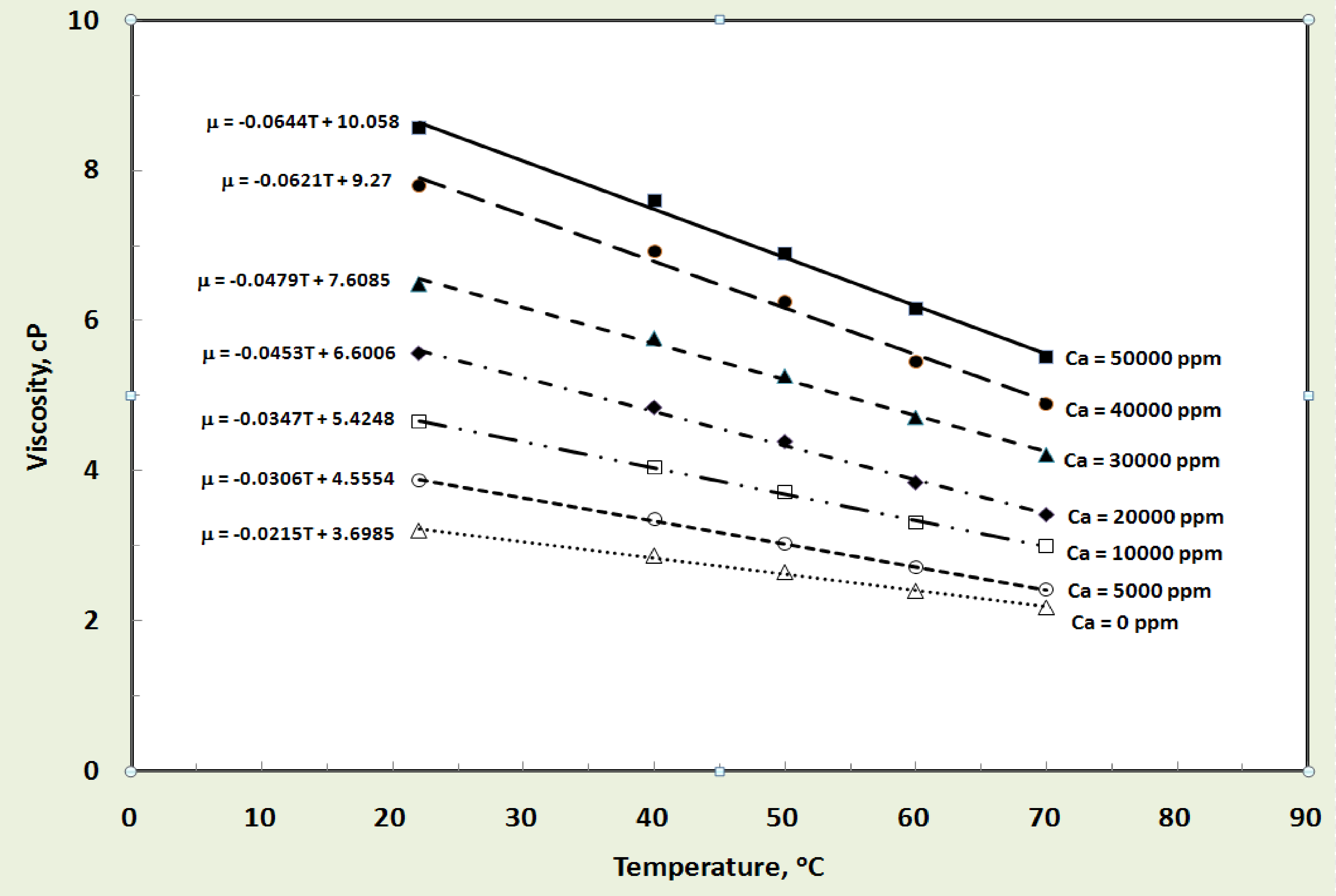
Analytical Model



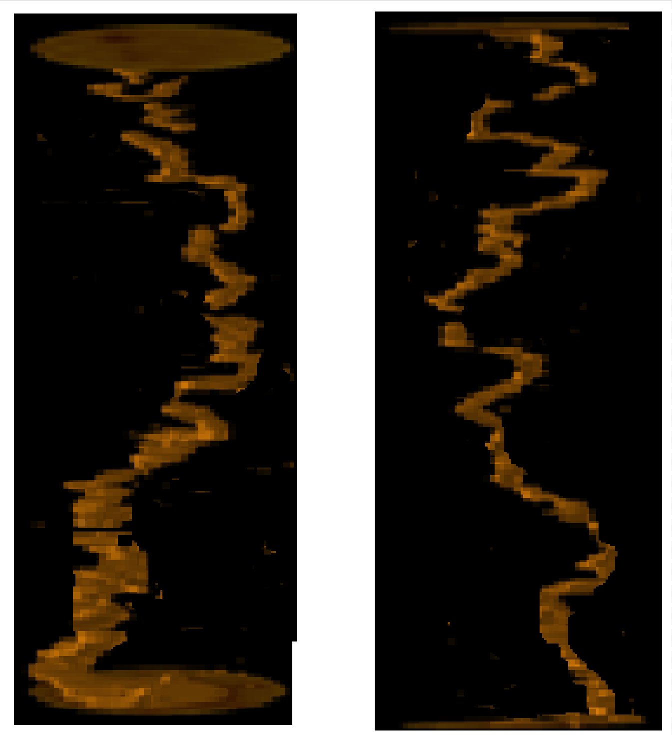
Analytical Model



Analytical Model



Parallel Core Flood

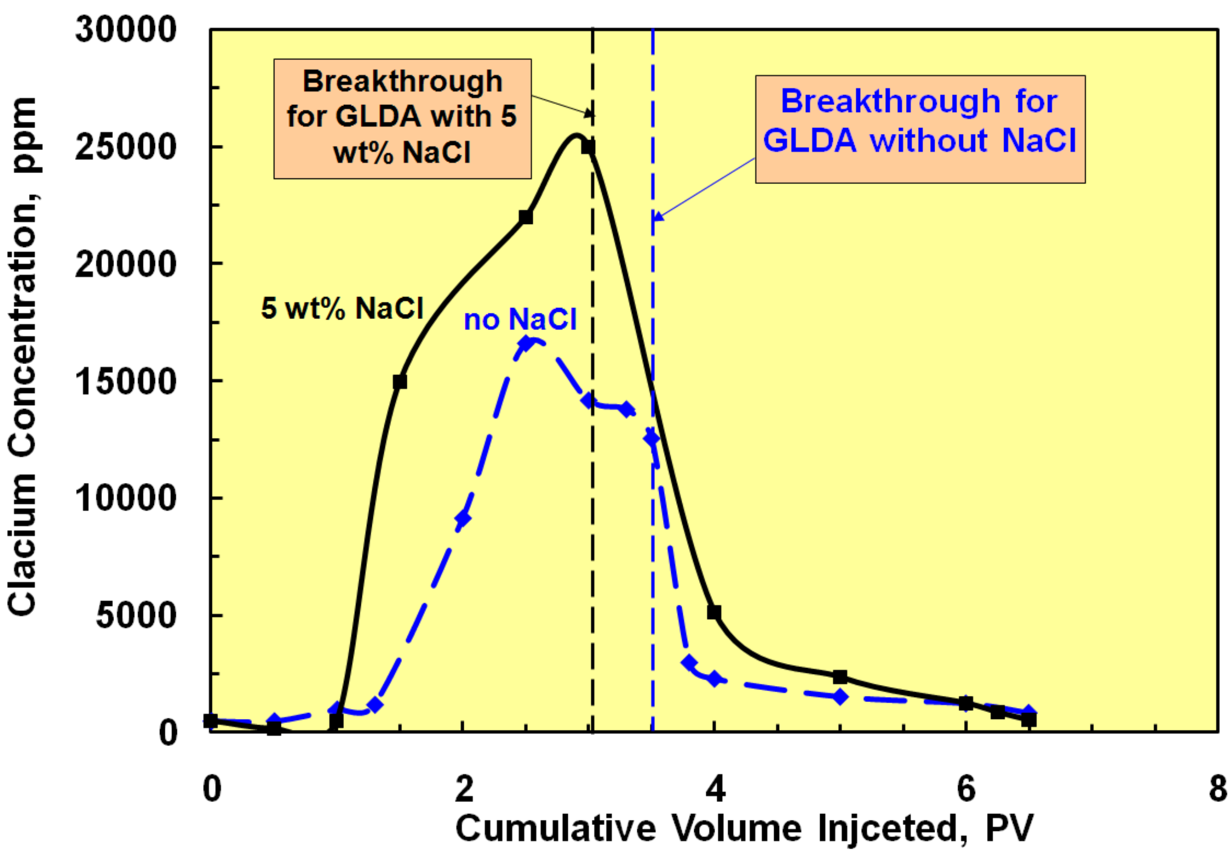


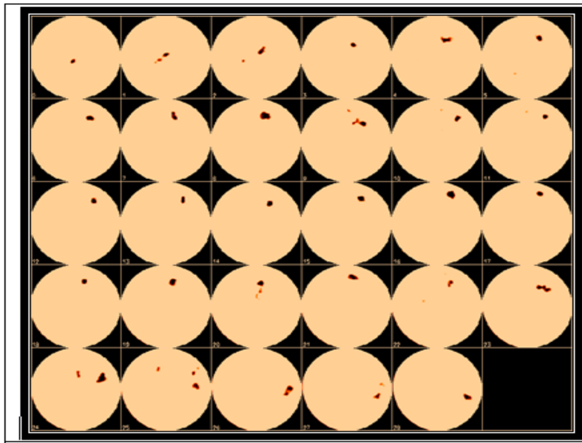
k = 50 md

k = 15 md

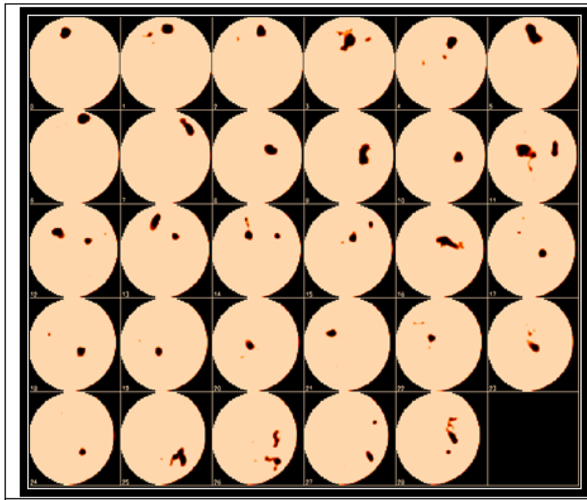
Effect of Salt (NaCl)

Flow rate = 2 cm^3/min, pH = 3.8, T = 300°F





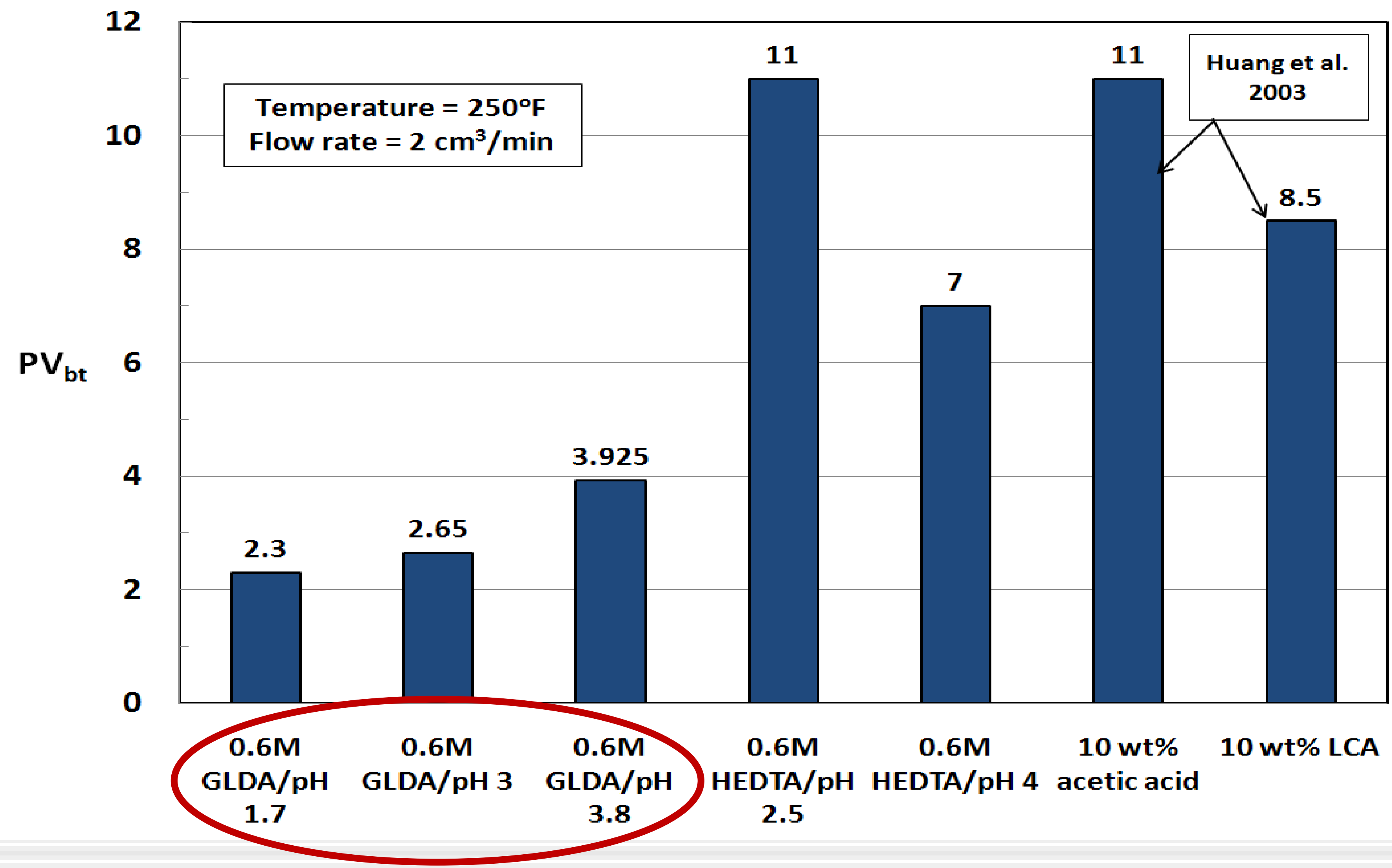
20 wt% GLDA, pH =3.8



20 wt% GLDA, pH =3.8 + 5 wt% NaCl

Adding 5 wt% NaCl to EDTA decreased the reaction rate by 25% (Fredd and Fogler 1998)

Comparing GLDA with other Chemicals



Comparing GLDA with other Chemicals

Pore volumes to breakthrough vs. injection rate at 250ºF