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.
• 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**  
  \[ 2\text{HCL} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \]

- **Dolomite**  
  \[ 4\text{HCL} + \text{CaMg(CO}_3)_{2} \rightarrow \text{CaCl}_2 + \text{MgCl}_2 + 2\text{CO}_2 + 2\text{H}_2\text{O} \]

- **Siderite**  
  \[ 2\text{HCL} + \text{FeCO}_3 \rightarrow \text{FeCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \]
For effective stimulation, deep wormholes are necessary to maximize conductivity between the reservoir and the wellbore for enhancement of production.

Generally, the reaction rate between conventional plain HCL and carbonates is very fast at reservoir temp.
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.
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 + 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 H₂S
• H₂S 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
<table>
<thead>
<tr>
<th>Permeability Enhancement</th>
<th>Permeability Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.jpg" alt="Image 1" /></td>
<td><img src="image2.jpg" alt="Image 2" /></td>
</tr>
<tr>
<td><img src="image3.jpg" alt="Image 3" /></td>
<td><img src="image4.jpg" alt="Image 4" /></td>
</tr>
</tbody>
</table>

**Polymer Viscosity Controls Acid Placement**
In-Situ Gelled Acid Formula

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

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

Phase separation

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

**Phase separation**

In-Situ Gelled Acid

CaCl$_2$ is the reaction product
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 °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 of the acidizing showing the location of 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

- Phase separation
- In-Situ Gelled Acid

- Heated In-Situ Gelled Acid Accumulator
- Pump
- Back Pressure regulator (1000 psi)
- Fraction Collector
- Differential Pressure Transducer
- Data Acquisition

Permeability contrast (1:20)
Injection rate from 1 to 15 ml/min
No Diversion at Low Rate: 1ml/min

<table>
<thead>
<tr>
<th>High permeability core</th>
<th>Low permeability core</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="High permeability core image" /></td>
<td><img src="image2.png" alt="Low permeability core image" /></td>
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</tbody>
</table>

In-Situ Gelled Acid
**Diversion at Rate:** 2.5 ml/min

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<th>Low permeability core</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image of high permeability core" /></td>
<td><img src="image2.png" alt="Image of low permeability core" /></td>
</tr>
</tbody>
</table>

*In-Situ Gelled Acid*
No diversion at high rate: 15 ml/min

<table>
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<tr>
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<tbody>
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<td><img src="image1" alt="Image of high permeability core" /></td>
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</table>

In-Situ Gelled Acid
Need for Alternative Fluids

• Problems associated with HCl:
  - Corrosion of well tubulars at high temperatures (>200°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
- 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) & $K_3AlF_6$ (fluooaluminate)
  - $Na_2SiF_6$ (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).
• Chelates are chemicals that complex with metal ions, thus changing the chemical property of the metal ion.

• Virtually all multi-valent cations such as \( \text{Ca}^{2+} \) and \( \text{Fe}^{3+} \) can be chelated.

• Usually allows for greater solubility of the metal ion.
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

Ni²⁺

NaOOCCH₂

CH₂COONa

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

<table>
<thead>
<tr>
<th>Chelating Agent</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ethylenediaminetetraacetic acid (EDTA)</strong></td>
<td><img src="image" alt="EDTA Structure" /></td>
</tr>
<tr>
<td><strong>Hydroxyethylethlenediaminetetraacetic acid (HEDTA)</strong></td>
<td><img src="image" alt="HEDTA Structure" /></td>
</tr>
<tr>
<td><strong>Nitrilotriacetic acid (NTA)</strong></td>
<td><img src="image" alt="NTA Structure" /></td>
</tr>
<tr>
<td><strong>Ethanol diglycine (EDG) or Hydroxyethyliminodiacetic acid (HEIDA)</strong></td>
<td><img src="image" alt="EDG Structure" /></td>
</tr>
<tr>
<td><strong>Diethylenetriaminepentaacetic acid (DTPA)</strong></td>
<td><img src="image" alt="DTPA Structure" /></td>
</tr>
<tr>
<td><strong>L-Glutamic acid, N, N-diacetic acid (GLDA)</strong></td>
<td><img src="image" alt="GLDA Structure" /></td>
</tr>
</tbody>
</table>
• 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$_3$HEDTA 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

- EDTA
- HEDTA
- GLDA
- NTA
- EDG

Solubility (wt% as acid) vs pH

Graph showing solubility of different chelates (EDTA, HEDTA, GLDA, NTA, EDG) at various pH levels.
Structure of GLDA at Different pH Values

- **H$_4$GLDA**, pH = 1.7, MW = 263
- **H$_3$NaGLDA**, pH = 3, MW = 285
- **Na$_4$GLDA**, 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 cm³/min and 300°F, 6-in. cores

pH = 1.7  pH = 3  pH = 13

Inlet face

Outlet face

no face dissolution
Inlet and outlet core faces after the core flood experiments with 20 wt% GLDA of pH = 1.7 at 300°F

(a) 2 cm³/min
(b) 3 cm³/min

Wormholes formed by GLDA, 20-in cores

Wormhole formed by GLDA, 20-in cores
GLDA and HCl

15 wt% HCl at 2 cm³/min

20 wt% GLDA at 1 and 2 cm³/min at 300°F

Core inlet face

Core outlet face

15 wt% HCl at 2 cm³/min
Short 6-in Cores

Graph showing the relationship between Injection Rate (cm$^3$/min) and $P/V_{bt}$ for different concentrations:

- GLDA
- 15 wt% HCl

The graph indicates the effect of injection rate on $P/V_{bt}$, with a decrease in $P/V_{bt}$ as the injection rate increases.
Long 20-in Cores

There are some of Carbonate Reservoirs in Middle east are in this region.

- GLDA
- HCl
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°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

![Graph showing the relationship between PV_{bt} and Injection Rate (cm^3/min) for 0.6M HEDTA and 0.6M GLDA.](image)
<table>
<thead>
<tr>
<th>$Q$, cm³/min</th>
<th>$PV_{bt}$, GLDA</th>
<th>$PV_{bt}$, HEDTA</th>
<th>2D CT Scan Images GLDA</th>
<th>2D CT Scan Images HEDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4.5</td>
<td>12.5</td>
<td><img src="GLDA05HEDTA12.5.png" alt="GLDA Image" /></td>
<td><img src="HEDTA05HEDTA12.5.png" alt="HEDTA Image" /></td>
</tr>
<tr>
<td>1</td>
<td>4.2</td>
<td>10.50</td>
<td><img src="GLDA1HEDTA10.5.png" alt="GLDA Image" /></td>
<td><img src="HEDTA1HEDTA10.5.png" alt="HEDTA Image" /></td>
</tr>
</tbody>
</table>
Analytical Model
Analytical Model

Viscosity, cP

Temperature, °C

$$\mu = -0.0644T + 10.058$$

$$\mu = -0.0621T + 9.27$$

$$\mu = -0.0479T + 7.6085$$

$$\mu = -0.0453T + 6.6006$$

$$\mu = -0.0347T + 5.4248$$

$$\mu = -0.0306T + 4.5554$$

$$\mu = -0.0215T + 3.6985$$

Ca = 50000 ppm

Ca = 40000 ppm

Ca = 30000 ppm

Ca = 20000 ppm

Ca = 10000 ppm

Ca = 5000 ppm

Ca = 0 ppm
Parallel Core Flood

\[ k = 50 \text{ md} \quad k = 15 \text{ md} \]
Effect of Salt (NaCl)

Flow rate = 2 cm³/min, pH = 3.8, T = 300°F

Adding 5 wt% NaCl to EDTA decreased the reaction rate by 25% (Fredd and Fogler 1998)
Comparing GLDA with other Chemicals

Temperature = 250°F
Flow rate = 2 cm³/min

PV_{bt}

<table>
<thead>
<tr>
<th></th>
<th>0.6M GLDA/pH 1.7</th>
<th>0.6M GLDA/pH 3</th>
<th>0.6M GLDA/pH 3.8</th>
<th>0.6M HEDTA/pH 2.5</th>
<th>0.6M HEDTA/pH 4</th>
<th>10 wt% acetic acid</th>
<th>10 wt% LCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV_{bt}</td>
<td>2.3</td>
<td>2.65</td>
<td>3.925</td>
<td>11</td>
<td>7</td>
<td>11</td>
<td>8.5</td>
</tr>
</tbody>
</table>
Comparing GLDA with other Chemicals

Pore volumes to breakthrough vs. injection rate at 250°F

LCA: Long chain Carboxylic Acid

Huang et al. 2003

10 wt% acetic acid

10 wt% LCA

20 wt% GLDA, pH = 3

Flow Rate, cm$^3$/min

$PV_{bt}$