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Non-damaging Matrix and Fracturing Acids.
Some Key Considerations.

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Society of Petroleum Engineers
Distinguished Lecturer Program
www.spe.org/dl
Do Your Acid jobs live up to expectations?

Have you acidized an oil well to have this happen?

500 BOPD DST

130 BOPD Production
The Power of Formation Damage

Loss of production can only mean one thing – damage to the formation in the near well bore region.

Formation damage best described by a “Skin” effect around well bore

Underbalanced drill – 10,000 psi BHP - gas inflow held back by 2 mm layer of crushed rock.
Matrix Acidizing in Carbonates

5 ft

Creates a Region of Enlarged Pore Spaces and/or Wormholes around the Wellbore
Acid Fracturing

Pad fluid creates fracture - acid then dissolves area around fracture wall - fracture closes - path of increased permeability results

300 ft or more
This lecture summarizes Acidizing in Canada from the 1960’s to the present day

- A summary of the history of non-damaging acids.

- Selected formation damaging mechanisms that may occur while acidizing.

- Acid additives.

- Acid blend formulation and QC testing.

- Global applicability of non-damaging acids.
Acidizing in Canada during the 1970’s

- Very little science or applied technology.
- Almost no acid testing.
- Pumped “bare-bones” acid packages.
Bare Bones Acid stimulation results often only 10 – 30% of DST and sometimes ZERO.

How much formation damage did we do to oil and gas wells while acidizing?
Acidizing in the 1980’s

The light goes on. Technology applied to acidizing - found that many of the acid packages pumped could cause formation damage such as sludge and viscous emulsions.
Canada – 1980

- Major international oil company initiates study to determine why acid jobs were failing to produce expected results.
- Two Alberta oilfields targeted for study: Goose River and Swan Hills.
- Study took about two years to produce conclusive results.
Most noticeable acidizing failures were at Swan Hills, Alberta, Canada, where oil is produced from the Beaverhill Lake formation – a clean limestone.
1981 - Development work on non-damaging oil well acids began at Swan Hills.
1982 - Determined that damage was caused by a combination of Asphaltic Sludge and Spent Acid Emulsion.
Swan Hills 1983 - 1987

- Newly developed non-damaging acid stimulations ramp up production. New life to 30 year old oil field.
1986 – Canadian producers began to demand non-damaging stimulation acids – they wanted ….

- Acids that are non-emulsifying, thermally stable, water wetting and devoid of all sludges and precipitates.

- On lease QC acid testing to verify acid package.
Today the Matrix and Fracturing Acids pumped in Canada are NON-DAMAGING and incorporate many of the acid package design features presented in this lecture.

(Question to ponder - Are these problems unique just only to Canadian crude oils?)
Some formation damaging mechanisms that may occur while acidizing.

1. Acid and ferric iron-induced asphaltic sludges.
2. Emulsion blocks.
3. Fines liberation and precipitates.
4. Formation oil wetting.
5. Acid additive separation.
6. Particulates from tubing.
7. Load fluid and drilling mud additive compatibility.
Damaging Mechanism 1. Acid-induced and Ferric Iron-induced Asphaltic Sludges

- Acid in contact with crude oil can destabilize asphaltenes.
- Exposed reactive sites on asphaltenes cross-link to form acid-induced sludge.
- Relatively small amounts formed.
Acid Induced Asphaltic Sludge
What we saw in acid flow back samples was more sludge than in our acid test bottles.

Spent acid flow back sample - note the amount of asphaltic sludge.

How much sludge is left in the formation?
This was evidence that there had to be another mechanism by which the asphaltic sludge was being formed.

- Post-stimulation analysis of sludge revealed one common thread of evidence – the presence of both Ferric (Fe$^{3+}$) Ions and Ferrous (Fe$^{2+}$) Ions.
So we began to experiment .......

- Ferrous ions added to test acid/crude oils – no increased levels of sludge.
- Ferric ions added to test acid/crude oils – greatly increased levels of sludge.

Sludge formed from 100 ppm Fe$^{3+}$/ BHL$^2$ Oil
Two basic types of ferric iron-induced asphaltic sludge

Oil # 1 – Crystalline form. Oil # 2 – Plastic form.
When produced in the formation iron induced asphaltic sludge will plug almost every formation.

Asphaltic Sludge from Acid + 5000 ppm Fe\textsuperscript{3+} and BHL oil
For 95% of crude oils tested

Acid + Fe$^{3+}$ + Asphaltenes (waxes?)

FERRIC IRON-INDUCED SLUDGE

RISK OF FORMATION DAMAGE
How much Asphaltic Sludge can be produced?

In 1982, 1 bbl of 15% HCl containing 4000 ppm Fe$^{3+}$ when mixed with 1 bbl of SSHU BHL crude oil could produce 26 lbs of asphaltic sludge.

In 2007, this amount is now 47 lbs of asphaltic sludge (about a 5 gall pail).

PRODUCED OILS CHANGE OVER TIME!
So where does the ferric iron come from to contaminate the acid?

RUST!
Some Sources of Ferric Iron Compound Contamination

- Storage tanks
- Pumping equipment and lines
- Tank trucks
- Rusty production and coil tubing
- Acid and mix water
- Formation minerals
How can we eliminate acid-induced and ferric iron-induced sludges?

Solution – (a) by performing a tubing pickle, and (b) by adding functionally specific chemical additives to the acid blend.

1. Acid antisludge agents
   and
2. Iron control agents
Acid Antisludge Agents

- **Anionic Surfactants**
  - an example is DDBSA
  - migrates from acid to oil phase
  - envelopes asphaltenes

- **Cationic Surfactants**
  - do not generally work effectively
Iron Control Agents

- pH control additives.
- Iron sequesterants.
- Reducing agents - converts Fe $^{3+}$ to Fe $^{2+}$
  
  Sodium erythorbate  
  Stannous chloride  
  Organo thio-compounds
Acid Strength, Temperature and Sludge

- As the acid strength and the formation temperature increases, the more difficult it becomes to control sludge.

- 15 to 20% HCl – the range in which most iron control and acid antisludge agents function perfectly.
Levels of ferric iron control (mg/l) required in stimulation acids

From analysis of tubing pickle acid flow back samples -

- Down tubing without pickle - 10000 +.
- Down tubing with pickle - 4000 to 5000.
- Coil tubing (pickled) and acid fracturing - initial acid at 5000, and thereafter 500 to 1000.
Emulsions are formed by shearing two immiscible fluids.

A very stable live acid / crude oil emulsion.

What’s its viscosity? How stable?
Stable Emulsions

A very stable spent acid / crude oil emulsion.

Breaking spent acid emulsions is very important because this is one of the final products of an acid job.
Preventing Acid and Oil Emulsions

- Solution – add a suitable non-emulsifier to the acid blend.
- Must break live and spent acid mixes
- Oil / acid interface – must be active and “knife edged”.
Damaging Mechanism 3. Fines Liberation and Precipitates

Know your formation rock!
.
Fines Liberation and Precipitates

(example for carbonate)

- Acid insolubles and acid filtrate

Pyrobitumens

Pyrites, Clays,

Silicates, etc.

Chemical Analysis

Sulphate Ion

SEM
Fines Liberation and Precipitates

Scanning Electron Microscope (SEM) is a very useful tool for mineral identification.

Here we see Chlorite, an iron rich, acid sensitive, migrating clay.
Fines Liberation and Precipitates

- Spent acid rich in Ca$^{2+}$ / formation water rich in SO$_4$ interaction.
- 28% HCl, Dolomite and Tachyhydrites.
- Anhydrite (calcium sulphate).
Anhydrite (CaSO₄) Bearing Formations

- 15% Hydrochloric Acid dissolves more anhydrite than Spent Acid (0.0% HCl) can hold in solution.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Live Acid Dissolves</th>
<th>Spent Acid Holds</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>6 lbs/bbl of acid</td>
<td>¼ lb / bbl of acid</td>
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- The precipitated CaSO₄ is an excellent well plugging agent.
Spent Acid

Precipitated Calcium Sulphate
Preventing Anhydrite Precipitation

Add Calcium Chloride to Acid Blend
Damaging Mechanism 4. Formation Oil Wetting

Formations are charged.

Sandstone Particles

Carbonate Particles

Charges are under normal oilfield conditions.
Many of the acid additives used today are surface active agents or surfactants. Surfactants are usually charged molecules.

**Simplified Surfactant Molecule**

**Water-soluble Grouping**
- Charged
  - ve, +ve, both, none

**Oil-soluble Hydrocarbon Grouping**
Surfactant / Formation Rock Interactions

Sandstone Particles

Oil Wet by Strongly Cationic Surfactants

Carbonate Particles

Oil Wet by Strongly Anionic Surfactants
Changing the wettability of a formation usually has severe consequences!

- An oil wet formation reduces productivity by increasing effective radius of particles.

- A water wet formation allows hydrocarbons and solids to “slide” through the formation.

- Acid packages that are poorly designed may leave the formation oil wet.
Damaging Mechanism 5. Acid Additive Separation

- Acid additives are typically insoluble or only slightly dispersible in acid.
- Easily separate out from the acid, especially when the acid is heated to BHT.
- Anionic / Cationic surfactant interactions.
Imagine what happens!

First barrel of acid pumped must be same as last barrel pumped.
Acid Additive Coupling

- A coupling agent added to form a stable dispersion or a solution of the acid additives.
- Class 1 and Class 2 Acids.
- Stability tested at ambient and BHT.
Before an acid squeeze or frac, an acid wash or pickle should be performed on the production tubing.

- Removes mill scale, rust, calcium scales, and other debris.
- Reduces the amount of RUST injected into the formation.
Damaging Mechanism 7A. Load Fluids

- Water
  - Should be filtered to 5 microns or less just prior to use, and on the lease.
  - Check for precipitate formation and emulsion tendency with hydrocarbon formation fluids.

- Oil
  - Oil from bottom suction – is it clean? BS&W?
  - Has the stimulation acid been tested against the load oil?
If you plan to acidize after drilling do not use acid reactive mud additives such as PHPA (partially hydrolized polyacrylamides). Use mud additives that are unreactive to acid.
Damaging Mechanism 8. Aqueous Phase Trapping
Damaging Mechanism 8. Aqueous Phase Trapping – Can this happen while acidizing?

YES!

- Acid mix water may cause aqueous phase trapping in very tight sandstone and carbonate reservoirs.

- Acid mix water must be changed to methanol.
Acid / Oil Compatibility Testing

Six simple, but important bench tests

• Live acid emulsion test.
• Spent acid emulsion test.
• Live and spent acid sludge tests.
• Dispersion/Stability test.
• Live and spent acid wetting action.
• Reaction with drilling muds (if required).

Acid blend must pass all required tests before pumping.
Testing Acids - Set up for acid testing at oil company lease shack
Acid / Oil Test Ratios

1. 50:50 acid and oil only

2. 25:75, 50:50 and 75:25 acid to oil ratios
Test the acid blend before its pumped – you may be surprised at the results.

- Customer declines lease testing of acid - Acid plugs formation – blend plant problem

- Dolomitic oil zone with 5% anhydrite – customer declines anhydrite protection as too costly – well plugs off
Customer insists on 1000 ppm ferric iron control – acid tested on lease but well plugs off.

Refused to do acid job because well drilled with PHPA – suggested energized pre-treatment – advice not taken - another pumping company acidized and well plugs off.

28% acid with inhibitor only pumped into BHL horizontal well – well plugs off solid.
Formulating acids - An example
The well conditions

- Oil from carbonate formation with BHT = 225°F.

- 4.9% anhydrite, 3.4% fines.

- Acid stored in lease tank for 1 day prior to pumping.

- 200 ft of pay – foam diverted acid job.

- Formation water high in sulphate ions.
A Typically Pumped Acid

- 15% hydrochloric acid
- Acid corrosion inhibitor
- A non-emulsifier
- Iron sequesterant
- Maybe some acid antisludge agent

No Science – No Testing – Canada 1970’s?
Non-Damaging Oil Well Acid

- 15% hydrochloric acid
- 4 gpt acid corrosion inhibitor
- 12 gpt iron control agent
- 10 % bw calcium chloride
- 1 gpt scale inhibitor
- 22 gpt acid antisludge agent
- 2 gpt non-emulsifier
- 13 gpt coupling agent
- 2 gpt fines suspending agent

(gpt = gallons per thousand)
Are damaging acids robbing you of production and profits?

- Ferric iron induced sludges and/or spent acid emulsion blocks can plug formations solid.
- Forgetting to check simple things such as the possibility of any adverse reaction between acid and the drilling mud can cost you the well.
- Although more costly, non-damaging acids can increase profits by maximizing production.
Swan Hills – 25 years of pumping non-damaging acids.

- Now on CO$_2$ flood. Asphaltenes to the near well bore.

- Oil now has increased sensitivity to ferric iron contamination. Loading levels of acid additives has increased over the years.

- Pumping non damaging acids has extended the life and profitability of this oilfield – ongoing drilling program with 3 to 5 rigs.
Global Applications - can this knowledge be applied elsewhere?

YES!

Crude oils from the world over contain the same basic constituents - paraffins, cycloparaffins, aromatics, asphaltenes, etc.

Oils from Russia, USA and South America have been examined - not unlike those of Canada and show varying degrees of ferric iron sensitivity.
Thank you for listening to my thoughts and ideas.