

Aegis Tech Line

Aegis Chemical Solutions

Technical Newsletter

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SCALE IN OIL & GAS PRODUCTION

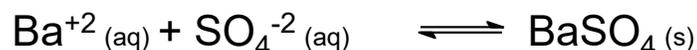
Presented below are some definitions that apply to scale in oil & gas production.

- **Scale:** is the inorganic mineral constituents of water that precipitate to form hard, adherent deposits.
- **Saturation:** is the limit where one constituent can be dissolved in another.
- **Supersaturation:** is the state when a constituent is dissolved more than the capacity of the solvent.
- **Equilibrium:** is the concept that some chemical processes may stop, resulting in a situation where reactants, products and intermediates might be present.
- **Le Chatelier's Principle:** when a system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established.
- **pH: $-\log_{10}[\text{H}^+]$:** As pH value gets lower, more H^+ is present and the solution is more acidic. Higher pH (i.e., generally greater than 7) favors calcium carbonate formation. When a pressure drop releases CO_2 from brine to the gas phase or atmosphere, pH increases and so does the tendency for the formation of calcium carbonate scale.

BRINE IN FORMATION

Brine spends eons in equilibrium in the formation, becoming saturated with ions available from the formation rock. The formation brine is produced with the oil and gas production. The brine undergoes changes in temperature and pressure while being produced. There is sometimes mixture with other brines of a different water chemistry as the production flows up the well. These changes in conditions and composition can cause some

components to become supersaturated (equilibrium shift). Chemically, the following can be occurring:



OILFIELD SCALES

The following are the types of scales that form during oilfield production operations. These must be dealt with for production to continue. Listed are the type of scale, the chemical name and the common name also used in the oilfield (in italics).

Carbonates

- Calcium Carbonate (CaCO_3): *Calcite (Aragonite, Vaterite)*
- Iron Carbonate (FeCO_3): *Siderite*

Sulfates

- Calcium Sulfate (CaSO_4): *Gypsum (Hemihydrate, Anhydrite)*
- Barium Sulfate (BaSO_4): *Barite*
- Strontium Sulfate (SrSO_4): *Celestite*

Sulfides

- Iron Sulfide (FeS)
- Lead Sulfide (PbS)
- Zinc Sulfide (ZnS)

Evaporites

- Sodium Chloride (NaCl): *Halite*
- Sodium Sesquicarbonate ($\text{Na}_3\text{H}(\text{CO}_3)_2$): *Trona*

CALCITE: PRESSURE DROP

A pressure drop allows CO_2 to be released from the liquid (water / oil) and into the gas phase. The resulting loss of CO_2

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dissolved in water shifts the equilibrium towards increased calcite formation.

- Solids
- Corrosion products
- Locations with turbulent flow

SULFATE SCALES

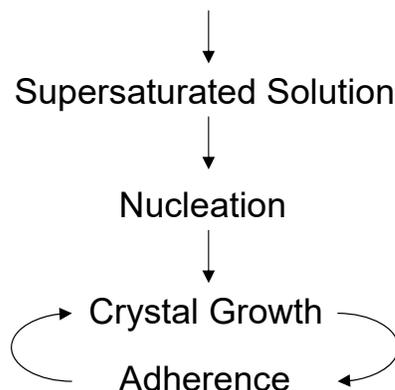
The formation of sulfate scales shows little dependence on pH. More commonly the formation of sulfate scales is due to mixing of incompatible waters. Incompatible waters usually have significant amounts of cation in one brine and of anion in the other. The other major factor in the formation of sulfate scale is temperature change.

Another issue of concern in the production of oil & gas is NORM (Naturally Occurring Radioactive Materials) scale. NORM usually occurs due to ²²⁶Ra occlusion in a barite scale.

Calcium sulfate can occur as gypsum, hemihydrate, or anhydrite. Gypsum is thermodynamically (energetically) more stable, so hemihydrate and anhydrite eventually change to gypsum.

STEPS IN SCALE FORMATION

Equilibrium Solution + External Disturbance



Common nucleation sites – the sites where nucleation commonly occurs include:

- Already present scale
- Sand
- Pipe surfaces

RESOLVING SCALE PROBLEMS

Resolving scale problems in oil & gas production follows a series of steps as follows:

Step 1: Collect Field Samples/Information

Water: Sample and preserve correctly; run appropriate field analyses

Scale: Can perform some field analyses

Conditions: Record temperature and pressure with every water sample; if possible, obtain bottom hole conditions

Historical Information: gather information from everyone from the field superintendent to the pumpers

Step 2: Analyze Samples

Typical Water Analysis (for Scale Work)

Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺, Cl⁻, SO₄²⁻ from lab.

pH, HCO₃⁻, CO₂ (gas and/or brine) from field.

Quality of the water analysis is dependent not only on lab work, but also correct field analyses, sampling, and information.

Scale Analysis

Step 3: Calculations / Analyses

Calculate scaling tendencies using information from water analysis.

Compare scaling tendency results to scale sample analysis, historical information.

Consider possibilities if things don't match up, play detective.

Step 4: Potential Product Selection

Based on scale location(s) select product application.

Based on scale type and product application select product candidates.

Step 5: Perform Laboratory Testing

Compatibility Testing

Performance Testing

Step 6: Select Product

Solubility

Performance

Cost Effectiveness

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Step 7: Apply Product and Monitor Results

Squeeze: Monitor chemical return (residual), production rates, downhole pressure.

Surface: Monitor chemical (residual), use scale coupons, watch system pressure.

WATER SAMPLING

Water sampling is the first step. If it is not done properly, then errors propagate through the process.

- Improper analyses may result.
- Real problems may be overlooked.
- Non-existent problems may be imagined.

Do not collect water sample from “end-run.” Purge sampling port to remove stagnant water. Filter the sample to remove particulates such as rust or sand. Filter may be as crude as a paper towel. Take appropriate field measurements.

It is important to prevent solids formation prior to laboratory water analysis. Preserve the water sample to prevent calcium carbonate or iron oxide solids – acidify to pH <2. Preservation of sulfate scales (barium, strontium, calcium) are not so easy.

Strategy 1: Dilution

Reduces scaling tendency but may dilute some components below detection levels; may not be enough.

Strategy 2: Chelant

Holds cations bound in a complex; ok but may not be the best method.

Strategy 3: Add Preservative

Preservative is a scale inhibitor; add in range of 1000 to 10,000 ppm. Best if screened in lab first.

Strategy 4: Combination

Combining the above strategies, especially dilution with any other, is likely to be most effective.

The container used to collect/transport the water sample is important. Plastic containers are best. Glass containers are good if they do not use metal lids, and clearly glass is breakable. Metal containers are generally not a good idea, but are sometimes necessary (e.g., large samples). Consider the value of sample.

Oxidized Sample



Supersaturated at the Surface



ANALYSES - FIELD

Some analyses should be performed in the field since the results can change during transportation.

- **pH:** this can be measured on collected sample, or with the proper equipment in-line. Measure pH on the collected sample(s) as quickly as possible. The sample will tend to degas CO₂, yielding a higher pH; temperature change will also have a small pH effect. Record temperature and pressure of the sample point.
- **Bicarbonate (Alkalinity):** There is no way to get true bicarbonate value. Perform an alkalinity titration. Interferences in the results include hydrogen sulfide. Bicarbonate is destroyed by acid preservation of the water sample. Sometimes, can get away with not performing in the field, but not recommended.

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- **CO₂:** Dissolved CO₂ can be measured by titration, but the same precautions apply as for pH. CO₂ in the gas can be measured by Dräger or GasTec tubes. An alternative is any a gas analysis the customer may have for their sales gas.
- **Other Components: Iron** - Can be analyzed in the field, or in the lab on a preserved sample. Lab analysis can either be wet or by AA / ICP. **H₂S** - Same analyses and cautions as with CO₂.
- **Field Scale Analysis:** Acid soluble and fizzes: calcium carbonate. Acid soluble but does not fizz, likely to be iron. If sour odor is released, likely to be iron sulfide, otherwise iron oxide. Not acid soluble, but changes form with calcium sulfate converter, then most likely calcium sulfate. If none of the results listed above, then most likely to be barium sulfate or strontium sulfate. Confirm with laboratory analysis.

ANALYSES - LABORATORY

Laboratory analysis of the water sample will quantify the following components using the equipment listed in the tables below:

Component	Instrumental	Wet
Calcium	AA/ ICP	Yes
Magnesium	AA/ ICP	Yes
Strontium	AA/ ICP	No
Barium	AA/ ICP	Yes
Iron	AA/ ICP	Yes
Chloride	IC	Yes
Sulfate	IC	Yes

Component	Instrumental	Wet
Manganese	AA/ ICP	No
Lithium	AA/ ICP	No
Boron	AA/ ICP	No
Aluminum	AA/ ICP	No
Phosphorous	ICP	Yes
Acetate	IC	
Propionate	IC	Yes

Proper preservation of field water sample is critical. Barium analysis by turbidity is inferior. Interference by high levels of

calcium and / or strontium can impact the results. Results should be questioned and verified. If the results do not match the observed problems, attempt to determine the discrepancies. If one component is high and the other low the results can be deceptive. As an example, high sulfate and very low barium could indicate that all the barium has been precipitated out before the water was sampled.

Laboratory scale analysis can include:

- Wet methods
- X-Ray: Fluorescence (XRF) - returns information about elemental composition. Diffraction (XRD) - if a known crystal pattern, returns exact crystal type (i.e. gypsum, hemihydrate, or anhydrite for calcium sulfate).

CALCULATING SCALING TENDENCY

Saturation Index (SI) is the logarithmic degrees of supersaturation.

Saturation Index, SI	Result
<0	Undersaturated
0	Equilibrium
1	10 times (10 ¹) supersaturated
2	100 times (10 ²) supersaturated

Interpret the SI Values as follows:

Saturation Index, SI	Result
0.0 – 0.5	Slightly supersaturated The likelihood for scale is minimal
0.5 – 1.0	Scale is likely to occur, but should not be severe
> 1.0	Scale is almost certain to form, likely to be severe

SI gives indication of how likely scale is to occur.

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PTB is a metric of Pounds of scale per Thousand Barrels of brine produced. PTB reflects how much scale could theoretically form. Determine the amount of scale required to return SI to zero.

Use SI to get a feel for how likely scale is to occur. Use PTB with daily brine production to get a feel for how much scale can form.

- 10 PTB on a 100 BWPD well is not a big problem.
- 10 PTB on a 10,000 BWPD well is a big problem.

This analysis has limitations. It does not provide information about where scale will occur. It also gives no indication of rate of scale formation.

$$SI = \log\left(\frac{(Ca^{2+})(HCO_3^-)^2}{P_{yg}CO_2 \cdot \rho_g^{CO_2}}\right) + 5.85 + 15.19 \cdot 10^{-3} \cdot T - 1.64 \cdot 10^{-6} \cdot T^2 - 5.27 \cdot 10^{-5} \cdot P - 3.334 \sqrt{IS} + 1.431$$

Calcite by CO₂ in Gas

$$SI = \log\left(\frac{(Ca^{2+})(HCO_3^-)^2}{C_{aq}^{CO_2}}\right) + 3.63 + 8.68 \cdot 10^{-3} \cdot T - 8.55 \cdot 10^{-6} \cdot T^2 - 6.56 \cdot 10^{-5} \cdot P - 3.42 \sqrt{IS} + 1.373$$

Calcite by CO₂ in Brine

$$SI = \log((Ca^{2+})(HCO_3^-)^2) + pH - 2.76 + 9.88 \cdot 10^{-3} \cdot T + 0.61 \cdot 10^{-6} \cdot T^2 - 3.03 \cdot 10^{-5} \cdot P - 2.348 \sqrt{IS} + 0.770$$

Calcite by pH

APPLICATION SELECTION

In selecting the application methods, the following need to be considered:

- Location of scale problem
 - Calculated scaling tendency
 - Observed scale
- Equipment to be protected
- Field operations
- Type of inhibitor
- Logistics

The application technique should consider the following:

- Continuous application
 - Can provide a regulated, constant amount
 - Dependent on externally powered source for operation
- Squeeze
 - Return is regulated by squeeze and formation type

- Independent of power source

Continuous treatment should consider the following:

- Surface
 - Continuous Injection
- Downhole
 - Treat String
 - Side Stream
 - Gas Lift

For continuous surface treatment, the following should be considered:

- Inhibitor should be applied as far upstream as possible from the scale problem.
- Always inject inhibitor at a point of good mixing, and never into a static line or tank.
- Never inject scale inhibitor in the same line with neat corrosion inhibitor.

Downhole scale squeeze jobs have the follow:

- **Advantages:** unpowered continuous flowback and treats near wellbore. The general procedures usually are simple to perform.
- **Disadvantages:** well must be squeezed periodically. There is limited control of flowback concentrations. It can be difficult to monitor low levels of inhibitor return. The procedures may difficult to design and perform.

The process for a generic scale squeeze job are:

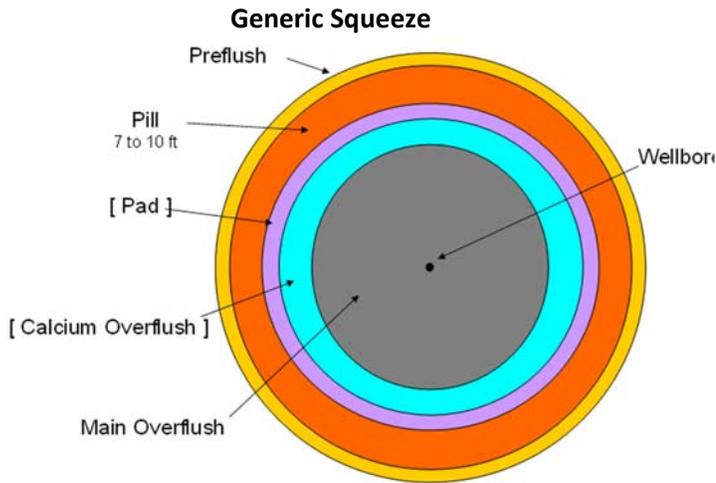
- Select inhibitor
- Evaluate inhibitor / brine compatibility
- Determine MED (minimum effective dosage)
- Perform remedial well clean-out if necessary
- Pre-flush to water wet the formation
- Inhibitor pill, typically 0.5-2.0% inhibitor (evaluate in lab before field use)
- Overflush to push into the formation
- Shut in a minimum of 24 hours

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The following information is needed for scale squeeze design:

- Production Rates/ Volumes
- Formation Type
- Porosity
- Permeability
- Tubing Size
- Casing Size
- Bottomhole Temperature
- Bottom Hole Pressure
- Type of Completion
- Depth of Well
- Length of Pay Zone
- Multiple Zones
- Fractured/ Propped

The criteria for scale squeeze success are:

- Inhibitor is compatible with formation water at bottomhole conditions.
- Inhibitor is compatible with water used for the pill.
- Thermally and hydrolytically stable at bottomhole conditions.
- Prevent scale deposition at low concentrations.
- Be cost effective.
- Good adsorption/desorption characteristics.
- Residuals can be monitored accurately at low inhibitor concentrations.
- Compatible with other treatment chemicals.
- Does not damage the formation.

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Aegis Facilities Locations

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<p>Permian Basin <i>Breckenridge</i> 566 FM 2231 Breckenridge, TX 76424 Tel: (254) 477-3418</p>	<p>Permian Basin <i>Forsan</i> 300 1st St. Forsan, TX 79720 Tel: (432) 634-1967</p>	<p>Permian Basin <i>Lubbock</i> 13622 Hwy 87 S. Slaton, TX 79423 Tel: (806) 329-4609</p>
<p>Permian Basin <i>Monahans</i> 1332 PR Thrasher Ln. Monahans, TX 79756 Tel: (432) 242-0502 x1080</p>	<p>East Texas <i>Kilgore</i> 4524 State Hwy 42 N. Kilgore, TX 75662 Tel: (903) 218-0058</p>	<p>East Texas <i>Raywood</i> 203904 Hwy 90E Raywood, TX 77582 Tel: (409) 550-5211</p>
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