

Acid Backflow

- When is acid backflow over?
- What flows back?
- What does it mean?
- Will precipitation be a problem?
- What will be left in the formation?
- Will it cause corrosion or upset problems in treaters and surface equipment?
- What information is captured for future acid job design?

HCl Acid Byproducts

- calcium chloride salt (dissolved)
- CO₂ gas

Other common byproducts

- emulsions, sludges, foams and froths
- solids from nonreactive parts of formation
- biomass, polymer mass, mud, etc., flowed back with the acid backflow.

Capturing Information

- Before the job:
 - What was the delivered acid concentration – by field test?
 - Testing by hydrometer can help catch mixing errors, but the hydrometer is fooled by alcohol additives (shows lower acid concentration) and by addition of salt (shows higher acid concentration).
 - Testing by titration (in the field or take a sample to a lab) can pinpoint the acid concentration if the additive levels are known.

Capturing Information

- Before the job:
 - Additives are more difficult to check once in the acid, but additive use can be tracked if mixed on site.
 - Inhibitor tests usually require sampling and quick lab testing. Inhibitors slow the acid reaction of acid on steel, they do not stop it.
 - Acid impurity limits on sulfates, sulfites, iron, HF contamination, total dissolved solids (TDS) and chlorinated hydrocarbons do exist and are best checked by lot by the service company.
 - Don't put problems down the hole and there will be less problems coming back.

Capturing Information

- During the job:
 - Breakdown and/or treating pressures.
 - A step-rate test will confirm breakdown pressure and whether open natural fractures are widening by pressure.
 - What is the effect of acid when it hits the formation? (assuming constant rate injection)
 - Fast pressure reduction indicates shallow, acid soluble damage.
 - Slower pressure reduction indicates low permeability rather than damage, slow acid reaction with the damage, or deeper or more extensive damage.
 - Increasing pressure when the acid hits indicates debris in the acid that is plugging the perfs (the tubing pickling job was insufficient) or an adverse damage reaction of acid is occurring in the formation. Most detrimental reactions are from liberating of potentially plugging particles in the pores or natural fractures that are not completely dissolved.

Capturing Information

- After the job – take a sample every 25 to 50 barrels in a few jobs and have it analyzed:
 - What is the concentration of the acid returning? (Putting 15% acid in the well and flowing back 12% acid creates significant problems)
 - What is the iron content?
 - Are emulsions present (that take longer than a few minutes to break)?
 - What and how much solids are in the return fluids?
 - Are precipitates (including iron) seen after the samples reaches the surface?

General estimate of acid strength and ion ranges

- Acid strength – 1% to 3% - need enough to keep the pH sensitive ions and minerals in solution (iron, calcium, silicates, etc.), but not so much as to create corrosion problems. Corrosion inhibitor is quickly adsorbed in the formation and uninhibited acid flows back.
- No precipitates until after the acid is exposed to oxygen in the flow back tanks. Iron will precipitate over time.
- High undissolved solids content – if the rock is 90% acid soluble, the 10% insoluble material needs to be recovered or it can seed scale and emulsions.
- Emulsion should break within 5 minutes of reaching the surface. Very stable emulsions may indicate a problem with the de-emulsifier or non-emulsifier additive package.
- High iron contents may indicate corrosion problems

When is it over?

- Track acid flowback by comparison of key ions and ion ratios.
- Key indicators:
 - Chloride content from spent acid – concentration dependent, may range from 30,000 to over 70,000 ppm.
 - Iron ion level - Iron ranges from <500 ppm for sweet wells with no corrosion to over 20,000 ppm for sour gas well acid flow back. Watch trend of iron level.
 - Potassium or other unusual ions from base fluids
 - pH – as pH goes over about 6 to 6.5, the backflow is nearing an end.
 - Specific ions and ion ratios may be useful in generating information about where and how the acid is reacting.

Chlorides (Cl⁻)

- Chlorides may peak at 50,000 to 70,000 ppm in acid flow back and then fall as the well cleans up. Compare the chlorides to the acid flowback chlorides to see if this ion can help track the acid.
- Chlorides are usually stable up to the limit of chloride solubility (depends on temperature and acid concentration).

Calcium (Ca⁺⁺)

- Calcium ion concentration in the flowback is dictated by how much carbonate the acid consumes (1000 gal (150 m³) of 15% HCl can consume about 1840 lb (836 kilos) of limestone)
- However, as pH rises, less calcium is stable in the acid and the excess can precipitate or in some cases form Calcium scales uphole.

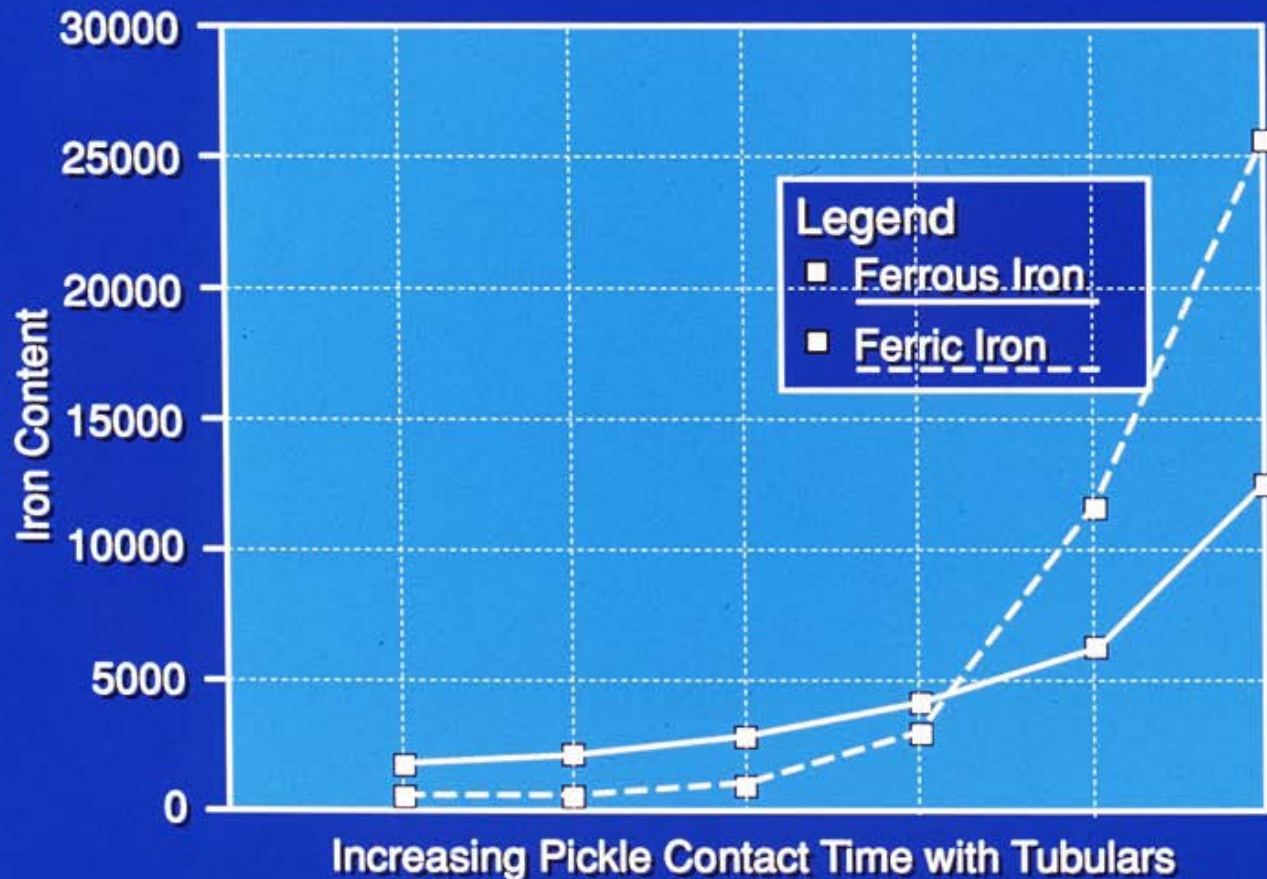
Iron (Fe^{++})

- Bare iron metal has moderately fast reaction with acid and the iron stays in solution up to 70,000 ppm if the acid concentration is still high.
- As acid strength is decreased by spending, the iron will start to precipitate. Iron reducing agents (e.g., stannous chloride), chelating agents (e.g., citric acid) and pH control additives (such as acetic acid) are used for control. The best approach will depend on the well conditions and if there is potential for forming asphaltic sludges.

Iron Problems

- Precipitates - usually with acid spending - not typically a problem – forms iron hydroxide which is usually swept out of the well by efficient gas-propelled flow back.
- Sludges - more of a problem than we realize - can be controlled with iron reducer and anti-sludge – test to find the right additives.
- Solid particles - multiple problems – pay attention to downhole problems in cleanup after and acid job.

Recovered Ferrous and Ferric Iron Concentrations





Chrome

- Normal is 2 ppm
- Additional levels coming from pipe, watch for corrosion.
- (Chrome pipe requires special inhibitors and inhibitor boosters when acidizing. Chrome pipe can be destroyed very quickly by acid.)

HCl on Cr-13 Tubing

- Contact time of acid w/metal should be roughly max 6 hours depending on conditions.
- Continual surface tank mixing of inhibitor required as it separates easily and quickly.
- Test the inhibitor to be used on metal coupons from the pipe in the well at the extremes of well conditions.
- Is the inhibitor affected by CO₂ or H₂S?

HCl on Cr-13 Tubing

- Likely need sulfide scavengers for sour conditions to prevent stress cracking.
- Need to look for all potential isolated area or "dead zones" where acid may become trapped and accelerate corrosion as the inhibitor deteriorates.
- Stimulation acid corrosion control chemicals may adversely affect performance of pipeline inhibitors. Consider pigging surface lines and adding additional pipeline corrosion inhibitor at wellhead as soon as possible after flowing back spent acid. In severe cases, neutralize acid before pipelining.

HCL on Cr-13 Tubing

- Consider using organic acids or 7% HCL if they are adequate to achieve the objective.
- Use spot treatments w/CT to minimize acid volume where possible.

References for Iron Control During Acidizing

- Taylor, K.C., Nasr-El-Din, H.A., Al-Alawi, M.J.: “Systematic Study of Iron Control Chemicals Used During Well Stimulation,” SPE 54602 (see also SPE 50772, 50780, 39419 and 73747).
- Collins, I.R., Jordan, M.M.: “Occurrence, Prediction and Prevention of Zinc Sulfide Scale within Gulf Coast and North Sea High Temperature and High Salinity Fields,” SPE 84963, 2003.
- Smith, C.F., Crowe, C.W., Nolan, T.J.: “Secondary Deposition of Iron Compounds Following Acidizing Treatments, “ SPE 2358, 1969.
- Curtis, J., Kalfayan, L.: “Improving Wellbore and Formation Cleaning Efficiencies with Environmental Solvents and Pickling Solutions,” SPE 81138, 2003.
- Hebert, P.B., et. al.: “Novel Filtration Process Eliminates System Upset Following Acid Stimulation Treatment,” SPE 36601, 1996.

Paraffin

- Although acid has little or no reaction with paraffin, injecting cool fluids into an oil reservoir that is close to the cloud point (paraffin precipitation point), can cool the oil sufficiently to precipitate paraffin.
- This type of damage cleans up slowly as the reservoir warms but return to maximum flow potential may take a long time (months) since the produced oil is near the saturation point with paraffin and cannot redissolve much more.
- In severe cases, the acid can be heated at the surface to prevent the problem. Be careful with this approach, there are multiple safety issues, corrosion challenges and heat transfer problems to work through.



An old picture (circa 1960's) of nitrified treatment flow back to an open pit. Note the energy. Use of high energy flowback helps clean wells of the undissolved solids that can seed emulsions and scale if left in the well.

Acid Jobs that DON'T Work

- Acidizing non-damaged sandstones
- Acidizing non-soluble damage
- Poor water/fluid quality
- Using too much acid or too little acid
- Shutting in acid jobs (precipitate formation)
- Excessive corrosion products liberated
- Failure to clean up the well
- Failure to unload the flowback

Monitoring the Acid Backflow

- Reasons:
 - know when and how well is cleaning up
 - know when emulsions/upsets may be expected
- What to watch
 - pH
 - iron
 - calcium
 - water volumes
 - chlorides,
 - ions and ratios, etc.

Special Case – Acid Reaction with Oil Base Mud (OBM)

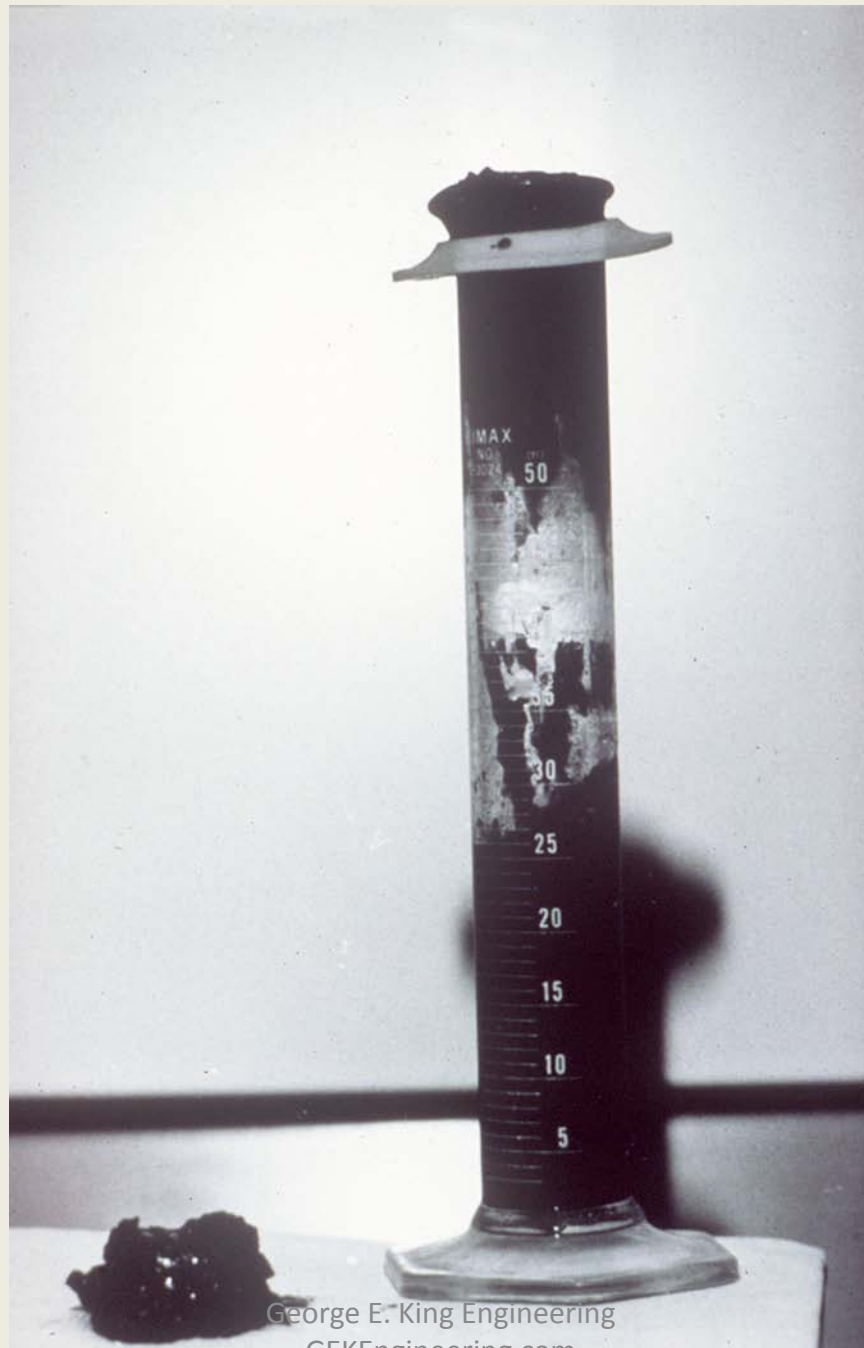
- Rarely occurs on laboratory samples of OBM (no drill cuttings)
- Once formed, this type of sludge is very difficult to break.
- Flushing with a diluting solvent and getting the well as clean as possible minimizes problems with acid.
- Always test “used” field samples of OBM, not lab samples.

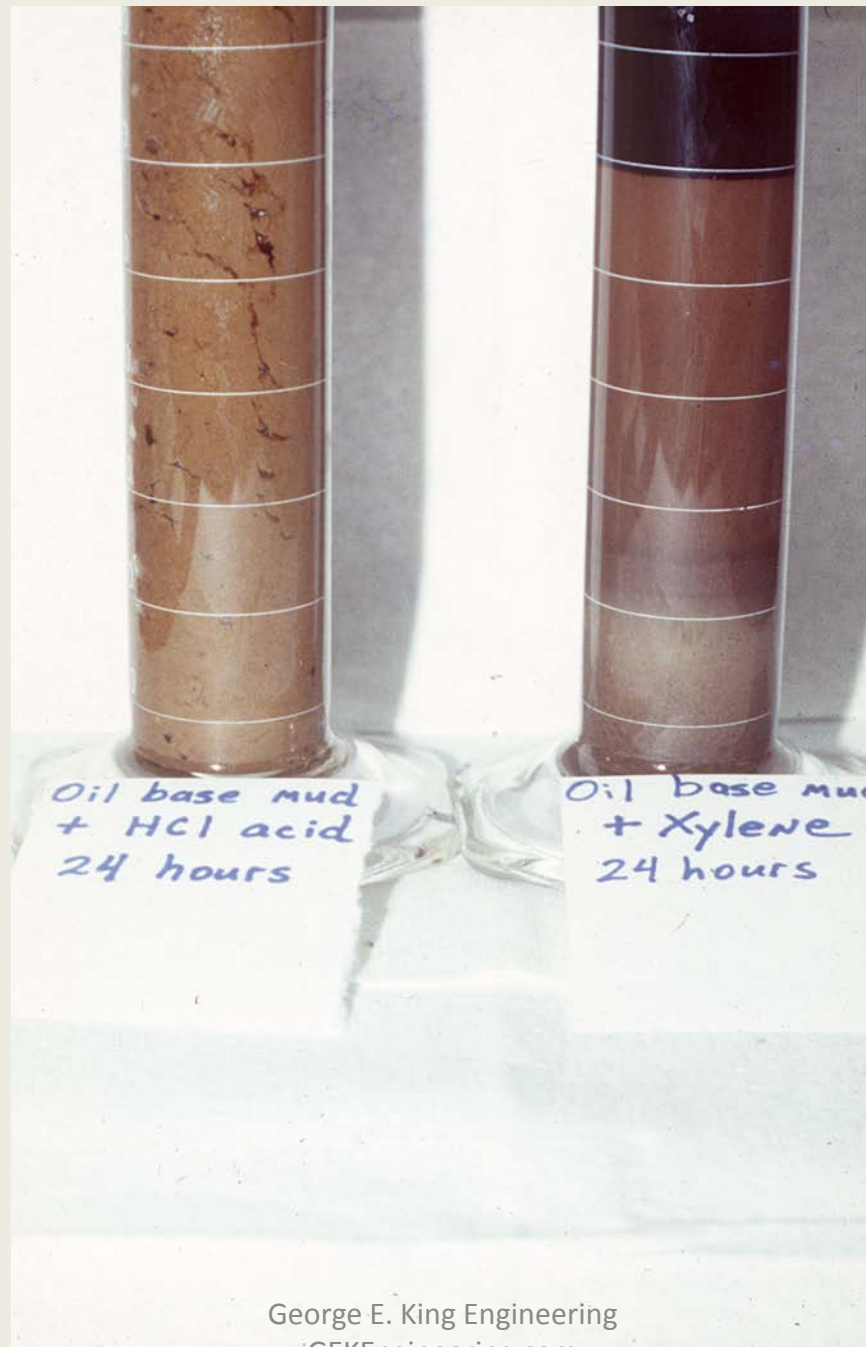
Oil based mud cleanup is a special case, requiring dispersal of the OBM emulsifying agents and wetting of the particles to prevent damage. Contact with acid, as shown in the following slides, will produce some severe sludges that are very difficult to break.



A 50-50 mix of 14 ppg OBM and 15% HCl.
The resultant sludge formed immediately
and was stable for months.







Sampling and Testing Back Flow

- Acid Content
- Iron Content
- Emulsion Presence
- Solids Cleanup
- Precipitates (besides iron)

Starting Point - Initial Acid Specifications (Impurities)

- Iron - 500 ppm or less (preferably less)
- Sulfate - less than 50 ppm
- Gases - probably not a factor
- HF traces in HCl?
- Chlorinated hydrocarbons - **WATCH OUT!**
 - These ruin refinery catalysts.
 - Come from poor quality acid supplies.

Quantity of Solids

- For each 1000 gal of 15% HCl
 - dissolves 1840 lb (836 kilos) of calcium carbonate
 - could possible free up to 280 to 550 lb (127 to 250 kilos) of fines (non acid soluble particles) in a typical range of acid solubilities for carbonates.

Ions in the Backflow

- Frac Fluid
 - KCl, but most debris is organic
- Acids
 - Fe, Ca, Si, Mg, Cr, Cl,
- Ion Ratios may give a clue on what the acid is spending.

Fe:Mg Ratio in Spent Acid

- Normal is around 10:1 to 15:1.
- The ratio can be higher when iron scale is heavy and reactive with acid. Certain reactive iron minerals in the formation or H₂S corrosion can also increase the ratio.
- Very low ratios, e.g., 2:1 are an indication of limited acid reactivity, minimum iron scale, dolomite, low iron content formations and an effective inhibitor design (non corroded pipe)

Fe:Ca Ratio

- For sandstones, 30:1 to 50:1 is normal.
- In sandstones, lower ratios are caused by:
 - High calcium content sandstones (various)
 - Carbonate scale (may be as low as 7:1)
- For carbonates, the ratio swings down to 1:100 or lower. Limestones usually have very little or no iron naturally. Most iron in the spent acid, however, comes from reaction with the pipe or corrosion products on the pipe – Reference SPE 2358.

Aluminum and Silicon

- Both Al and Si come from clay dissolution
- Usually higher in acid backflows when using HCl/HF
- HF reacts very fast with high surface area minerals like authogenic clay and extremely slowly with chert, sand grains, etc.
- Alumino-silicate precipitation can occur if $\text{pH} > 2.5$. Higher HCl contents are needed when acidizing with HCl/HF, especially where clay content in the formation is high.

Al:Si Ratio

- Normal ratio is 1:1 to 2:1
- lower ratios indicate higher concentration HF component and/or more reaction with sand (lower clay content)
- Higher ratios (15:1) indicate silica precipitation or large amounts of authogenic clay and very little acid. (Silica precipitation does not necessarily mean damage.) Silica precipitation can be controlled with more HCl in the acid design.
- A low Aluminum level (<30 ppm) may mean no clays or that precipitation occurred down hole.

Al:K Ratio

- Normal ranges from 3:1 to >5:1.
- Higher ranges may indicate large amounts of kaolinite or other high surface area clay.
- Lower ratios may signal other clays or mixing with KCl from fluids

Fe:Mn Ratio

- Corrosion indication?
- Normal is 100:1, but can vary widely.
- Look at initial pipe surface condition – heavy iron scaling (not protected by inhibitor) will result in very high iron content. Coated or lined pipe will likely generate very low iron contents.