

# Pickling Procedures

- Removes mud, rust, scale, and pipe dope from the ID of the tubing and casing below tubing and displaces it from the tubing, not into the formation.
- It is normally done before any stimulation, especially
  - Acid Treatments
  - Sand control.
- Reason: pumping of acid and/or proppant will loosen debris from walls of pipe, and will sweep the materials into the perforations, creating severe damage.

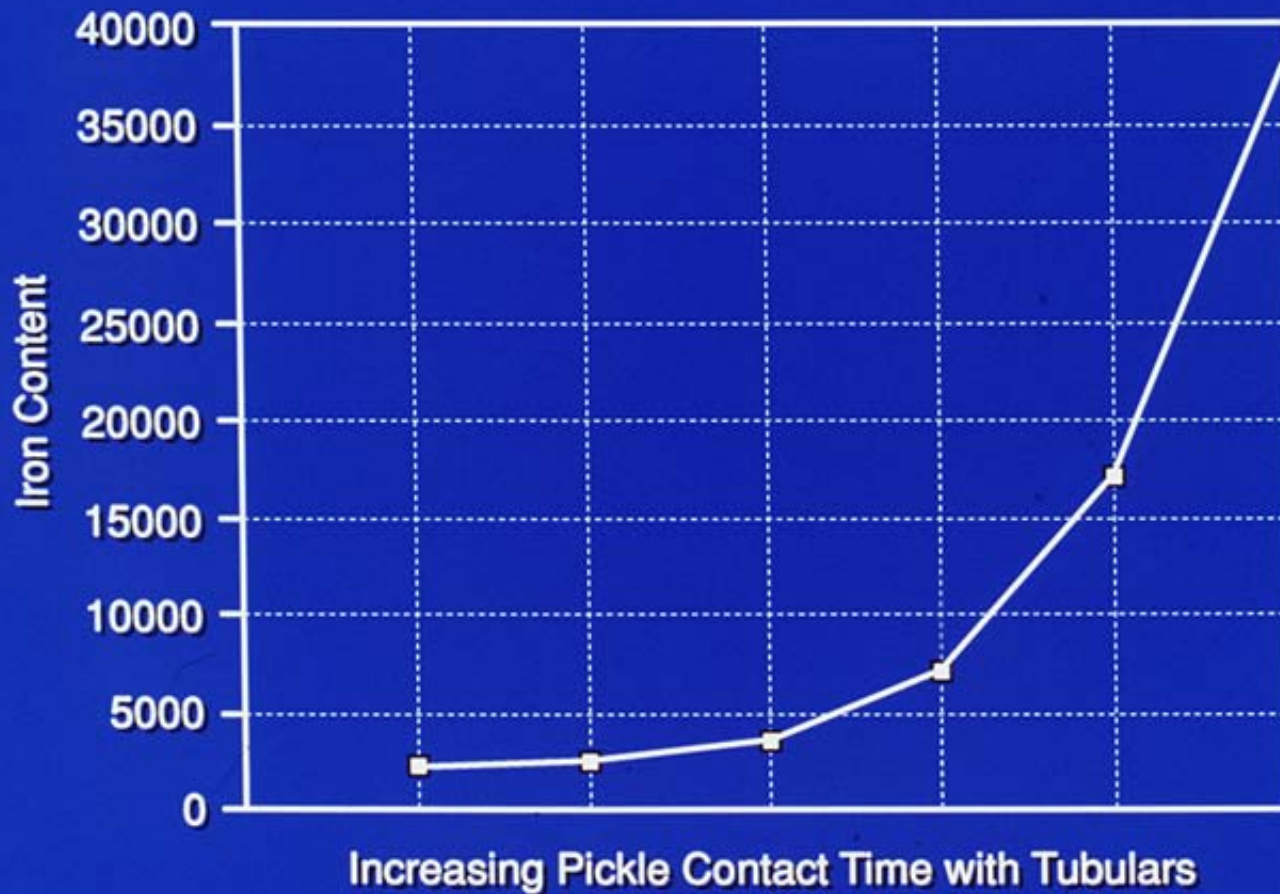
**Debris inside of pipe that was cut and pulled from a well. This debris (pipe dope, mill scale, paraffin, scale, wireline grease, etc.) can be picked up by acid or sand slurries and carried into the perforations.**



**Initial HCl acid samples loaded with various iron contents. You cannot tell the level of iron content from visual exam. The samples must be analyzed. Ideal level of initial iron in the acid is less than 100 ppm. Most iron comes from tank and pipe contact. Returning iron content is typically from 500 to over 20,000 ppm, depending on pipe condition and formation composition.**



# Reactivity of Steel Pipe with HCl During Pickle Job



# Tubing Pickling

- What and Why
- How

# Tubing Pickling

- Pickling removes pipe dope, residual mud, corrosion by-products (rust), mill scale, and other debris.
- Without pickling, the leading edge of the acid or brine sweeps the junk into the perforations and damages the well.
- Failure to effectively pickle or clean the tubing is a leading cause of acid failure.

# Acid Failures?

- An estimated 70% of acid jobs fail to meet the treating objective.
- About 20% of jobs actually lower the production.

# Pickling Operations

- Find the best way to remove the debris:
  - Acid sweeps
  - Abrasive slurry (sand slurry) sweeps
  - Solvent sweeps



# Treating Path

- Clean as much of the tubing as possible without letting the cleaning sweep enter the perforations.
- Alternatives – use coiled tubing to bypass the dirty tubing

# Pickling Procedure to 8,000 ft (without a Packer)

- Set retrievable bp above perfs
- establish circulation w/ water (+ mutual solvent if oily)
- pump acid at 0.5 to 1 bpm
  - new tubing: 200 to 300 gal
  - old tubing: 300 to 500 gal
  - heavily scaled: 500 to 700 gal

# Pickling Procedure to 8,000 ft

- Displace w/ water until first 10% of acid is out of tubing
- Reverse acid out of tubing at 0.5 to 1.0 bpm

# Inhibitors

- All pickle jobs should have a properly selected and blended inhibitor
- An inhibitor will not stop the acid from reacting with iron corrosion (rust), but it will slow the reaction with pipe.

# Problems

- If an acid pickle is left too long in the pipe, the pipe will be attacked by the acid.
- Sand slurry cleaning sweeps need to be pumped at turbulence.
- Solvent cleaning sweeps must be compatible with other fluids and the seals in the system.

# Acid Strength

- Should initially return an acid between about 0.5% and a maximum of 3% HCl.
- pH is not a good measurement to check acid strength. Even 0.2% acid strength has a pH lower than 1.
- If HCl strength is more than 3%, reduce acid strength or acid volume in the next comparable job in the area.

# Sources of Iron

## Most Common

1. Iron and Iron Scale in Tubulars
  - A. Iron Oxide
  - B. Iron Sulfide
    1. Biogenic Corrosion
    2. Inorganic Corrosion
2. Iron Dispersions
  - A. Sludges
  - B. Iron Sulfide in Water
  - C. Iron Fixing Bacteria
3. Iron in Solution
  - A. In the Acid
  - B. In Acidic Waters
4. Iron in the Formation
  - A. Magnetite
  - B. Hematite
  - C. Chlorite Clay
  - D. Iron Carbonates
  - E. Red Beds
  - F. Iron Sulfides

# Iron Sulfide

## Forms

Amorphous FeS  
Mackinawite  $\text{Fe}_9\text{S}_8$   
Greigite  $\text{Fe}_3\text{S}_4$   
Troilite FeS  
Pyrite  $\text{FeS}_2$   
Maracasite  $\text{FeS}_2$   
Smythite  $\text{Fe}_3\text{S}_4$   
Pyrrhotite  $\text{Fe}_7\text{S}_8$

## HCl Acid Solubilities

Amorphous ?  
Mackinawite Fast  
Greigite Moderate  
Troilite Moderate  
Pyrite Slow  
Maracasite Slow  
Smythite ?  
Pyrrhotite Slow



# *Iron Control in Sweet Wells*

## Main Problem

Precipitation of Ferric Iron at a pH of 2  
Precipitation of Ferrous Iron at a pH of 7

## Main Solutions

Cleanouts, Chelating and pH Control

### Products

Acetic Acid	(pH Control)
Citric Acid	(Chelating Agent)
EDTA	(Chelating Agent)
NTA	(Chelating Agent)
Ethorbic Acid	(Reducing Agent)
Hydroxyl Amine	(Reducing Agent)

### Techniques

Tubing Cleanout  
Jobs  
Stringer Acid  
More Acid Volume  
Earlier Backflow

For all around performance, the iron reducing agents are superior to other forms of iron control.

# Acid Corrosion Inhibitor

- Purpose
- Solubility
- Mixing
- Problems

# Corrosion Inhibitor Purpose

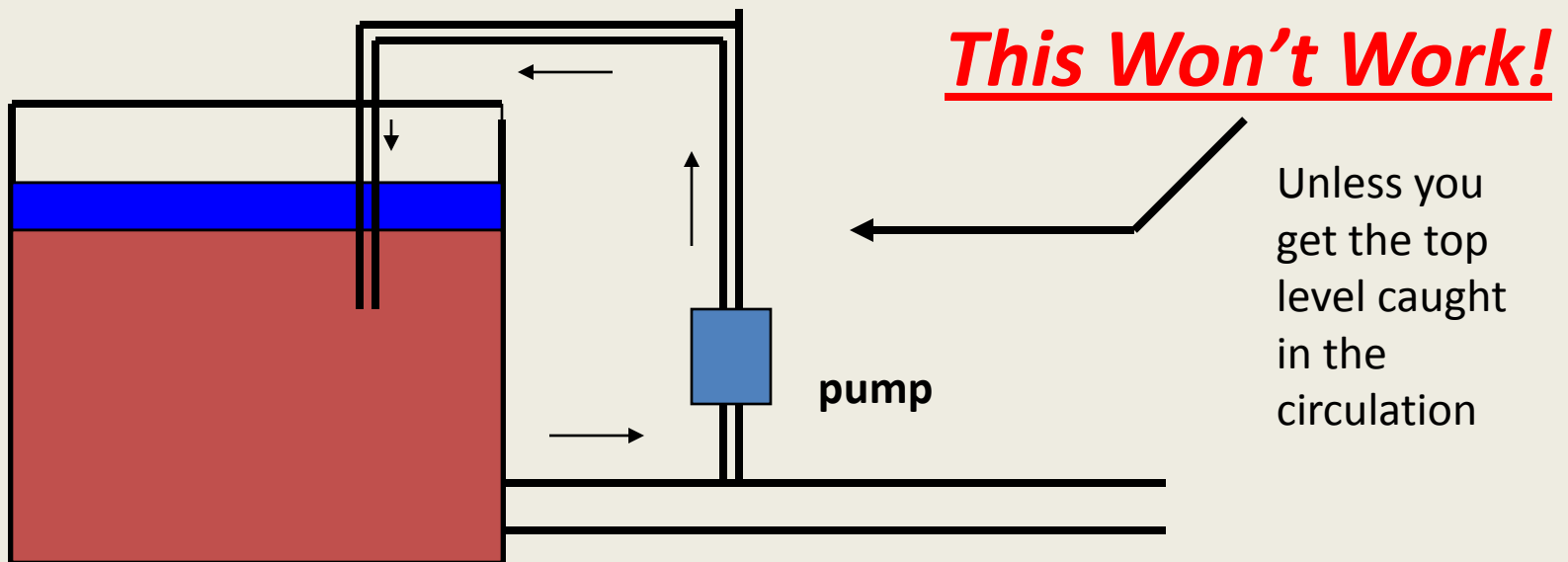
- Inhibitors help protect steel pipe and other equipment
- However:
  - Some inhibitors are much more effective than others
  - Chrome tubulars are severely affected by acid and require special inhibitor packages
  - Inhibitors are time, temperature and acid strength sensitive
  - Inhibitors adsorb in the formation – none on backflow?

# Acid Corrosion Inhibitor

- Work well BUT,
  - their efficiency is time, acid strength temperature, and metal surface dependent.
  - are not soluble in acid! - will separate!
    - separates to top in 30 minutes
    - needs vigorous mixing to disperse - gentle circulation will not work.

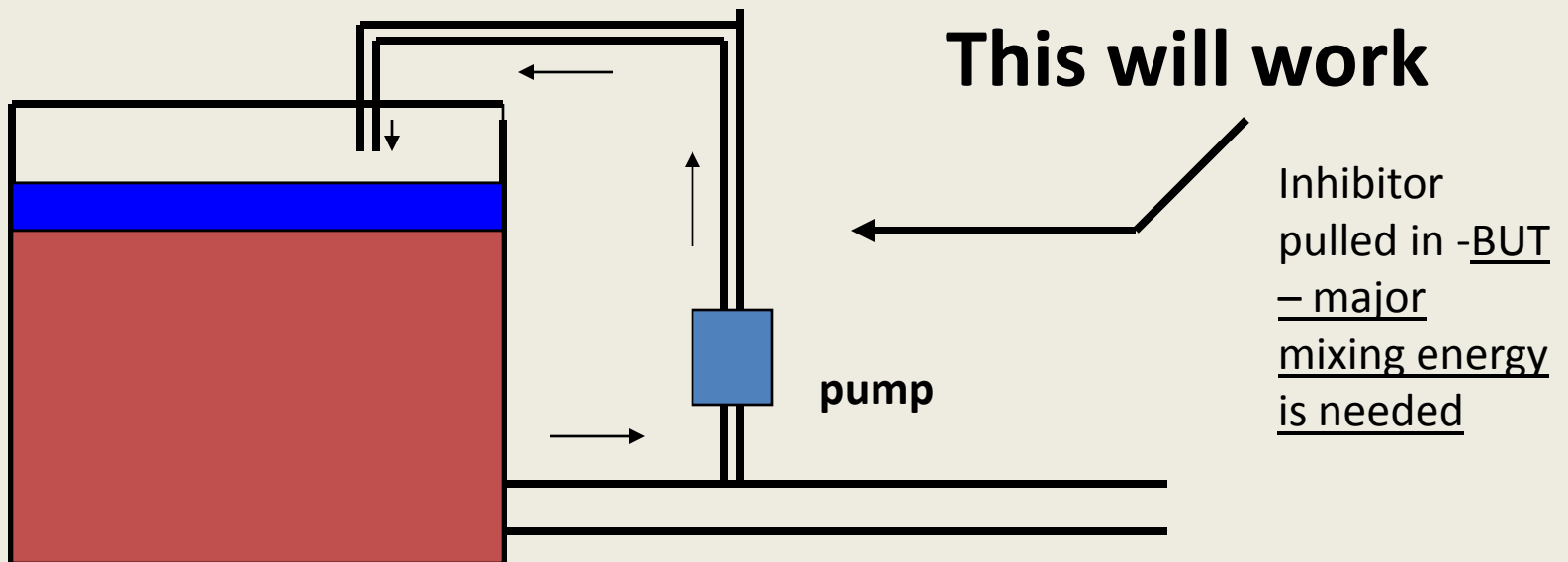
# Acid Inhibitor Mixing

- Set up for “rolling” the tank, not slow circulation - upper layer must be mixed in



# Acid Inhibitor Mixing

- Check the inhibitor layer is possible



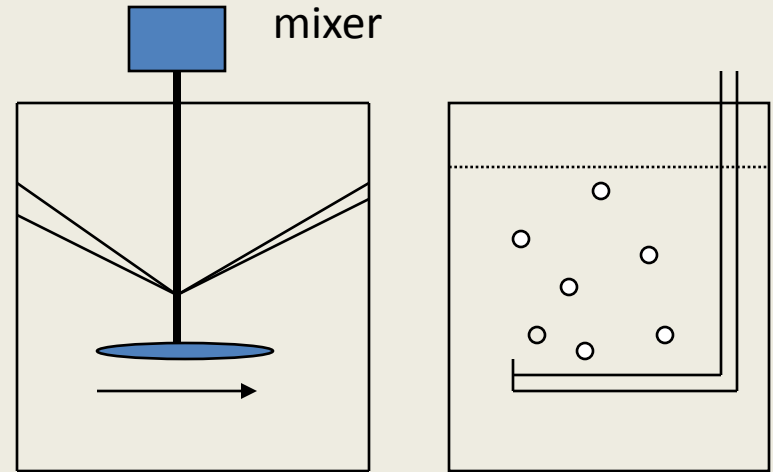
# Inhibitor Mixing

- **What will work?**

- **Air sparging or rolling the tank with gas**
- **paddle mixing that creates a vortex**
- **vigorous rolling**

- **Effect of oxygen in acid -**

- oxygen does increase corrosion
- oxygen saturation in acid is 7 parts per billion, so effect of oxygen is limited (not a major factor)



# Checking the inhibitor presence

- Spectrophotometer
- steel wool test is a presence test – not a quantitative test (placing uncoated 0000 steel wool in uninhibited acid will cause the wool to flow from bubbles of CO<sub>2</sub> gas by-product).
- Remember: inhibitor effectiveness is time and temperature dependent - must be replenished after set time. Samples taken for inhibitor testing must be tested immediately.



# Chrome Pipe Inhibitor Packages

- Check data on any inhibitor packages to determine if it is suitable for Chrome pipe protection.
- Chrome pipe is extremely sensitive to acid – special inhibitors and inhibitor intensifiers are required or the pipe can be ruined with a single acid job.