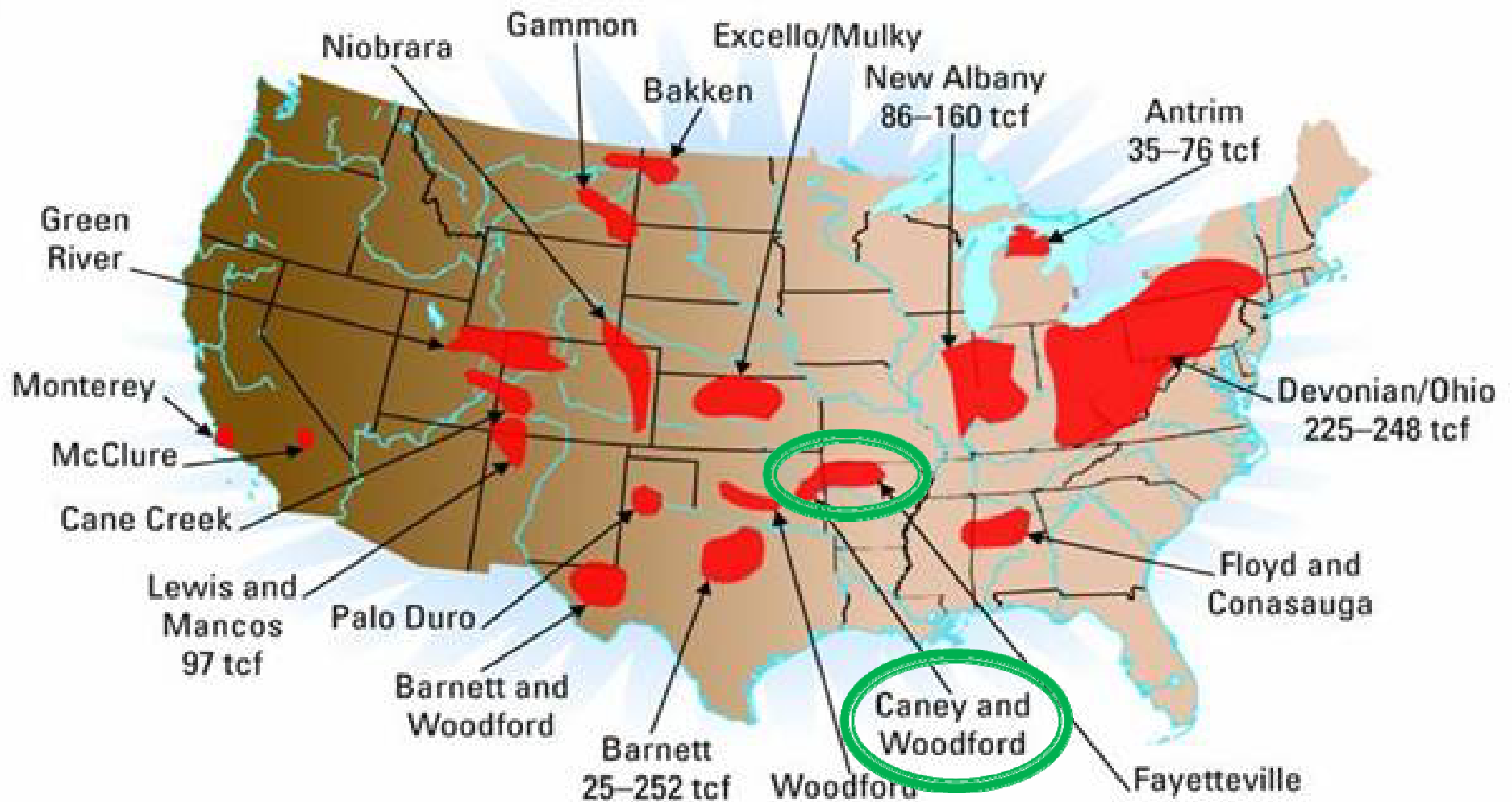


# **Fluid Issues for Unconventional Reservoirs: Shale Gas Drilling**

**H.A. Nasr-El-Din  
Texas A & M University**

**March 24, 2009**



**North America: 3,842 Tcf**  
**World: 16,112 Tcf**

Slide prepared by N. Pascal

Source: USGS and Rodger

# What is a shale? (2)

- WHAT ARE THE PROPORTIONS OF THE MINERALS?
- Caney Shale:

Sample No.	1	2	3	4	5	6	7	8	9	10
Quartz, %	26	34	31	35	36	20	12	25	8	39
K-feldspar, %	1	1	1	2	1	2	2	1		1
Na feldspar, %	3	1	5	6	6	4	1	1	1	6
Calcite, %	22	1	—	—	—	50	4	30	72	—
Dolomite, %	1	—	—	—	—	4	67	1	—	—
Siderite, %	—	—	8	2	2	—	—	1	1	4
Pyrite, %	5	9	9	2	2	—	—	5	7	6
Kaolinite, %	5	6	6	6	8	5	2	7	4	12
Chlorite, %	1	2	1	—	1	—	—	2	—	1
Illite/mica, %	10	14	13	21	16	5	4	8	3	15
Mixed layer, %	26	29	26	26	28	12	6	19	5	21

OFTEN, THE PROPORTION OF QUARTZ IS A lot of quartz!!!

CLAY MINERALS IS < 50% Much more carbonates than clay minerals!!!

SHALE = VERY FINE-GRANULAR GENEOUS

COMPOSITION!!! < 40% clay minerals

# Main Characteristics of Shales

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- Porosity: 1 to 8 vol%
- Permeability: 0.0001 to 0.1 mD
- Organic material, a sources of produced gases
- Clays, tight formation cause problems

# Removal of $\text{Mn}_3\text{O}_4$ -based Filter Cake

A. Al Moajil & H.A. Nasr-El-Din  
A. Al-Yami

## **Mn<sub>3</sub>O<sub>4</sub> Particles**

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- Spherical shape, 1-2  $\mu\text{m}$  in diameter, & SG = 4.8 g/cm<sup>3</sup>
- Introduced to K-formate drilling fluid (Sevendsen et al., 1995)
- Then, to OBM (Franks et al., 2004)
- Finally, to WBM (Al-Yami et al., 2007)
- No study on FCR of Mn<sub>3</sub>O<sub>4</sub>-based DIF

# Current FC Breakers

1. HCl

2. Organic acids

3. Chelating agents

4. *In-situ* organic acids

5. Oxidizers

6. Enzymes

Dissolve  
 $\text{CaCO}_3$   
particles

Degrade  
polymers

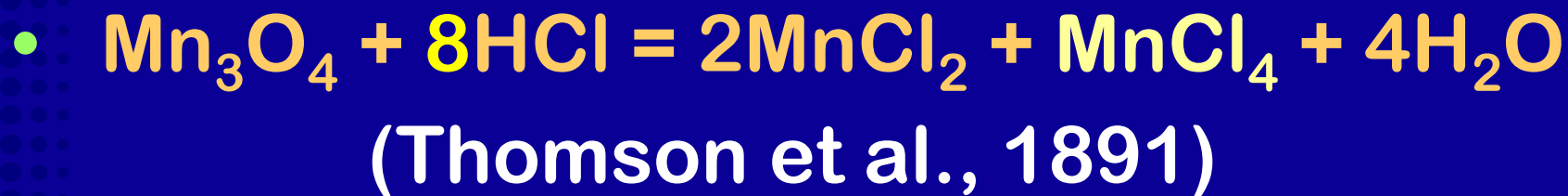
7. Combination of These Chemicals

# Manganese Oxides Reactions

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- Factors affect the reaction of Mn(oxides) with organic acids (Kemmitt et al., 2001)

1. Stoichiometry of Mn (oxide) to the acid
2. Structure of the acid
3. Ability to chelate





# Objectives

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- Examine reaction of various acids with  $\text{Mn}_3\text{O}_4$
- Measure the solubility of  $\text{Mn}_3\text{O}_4$  in various fluids
- Determine the thermal stability of the cleaning fluid systems
- Evaluate and design the filter cake removal cleaning fluid system

# Experimental Studies

# Mn<sub>3</sub>O<sub>4</sub>-based Drilling Fluids\*

Additive	Function	Field Unit ( Per bbl)	
		Quantity	Unit
Water	Base	0.822	bbl
Defoamer	Prohibit foaming	0.01	gal
XC-polymer	Viscosifier	1	lb
Starch	Fluid loss control agent	6	lb
PAC-R	Viscosifier\ fluid loss	0.75	lb
KCl	Density and shale inhibition	41	lb
KOH	pH control	0.5	lb
Ca(OH) <sub>2</sub>		0.25	lb
CaCO <sub>3</sub> (fine)	Weighting materials	3.5	lb
CaCO <sub>3</sub> (medium)		1.5	lb
Mn <sub>3</sub> O <sub>4</sub>		202	lb
Na <sub>2</sub> SO <sub>3</sub>	Oxygen scavenger	0.75	lb

**\* Lab Sample**

# Dynamic HPHT Filter Press

- Tests up to 300°F & 200 psi

## Procedure:

1. Brine Filtration Test
2. Mud Cake Generation
3. Cleaning test
4. Brine Filtration Test

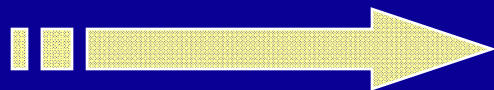




# HPHT See-through Cell

## Objectives:

- Solubility tests
- Stability of cleaning fluids at HPHT
- Collect samples



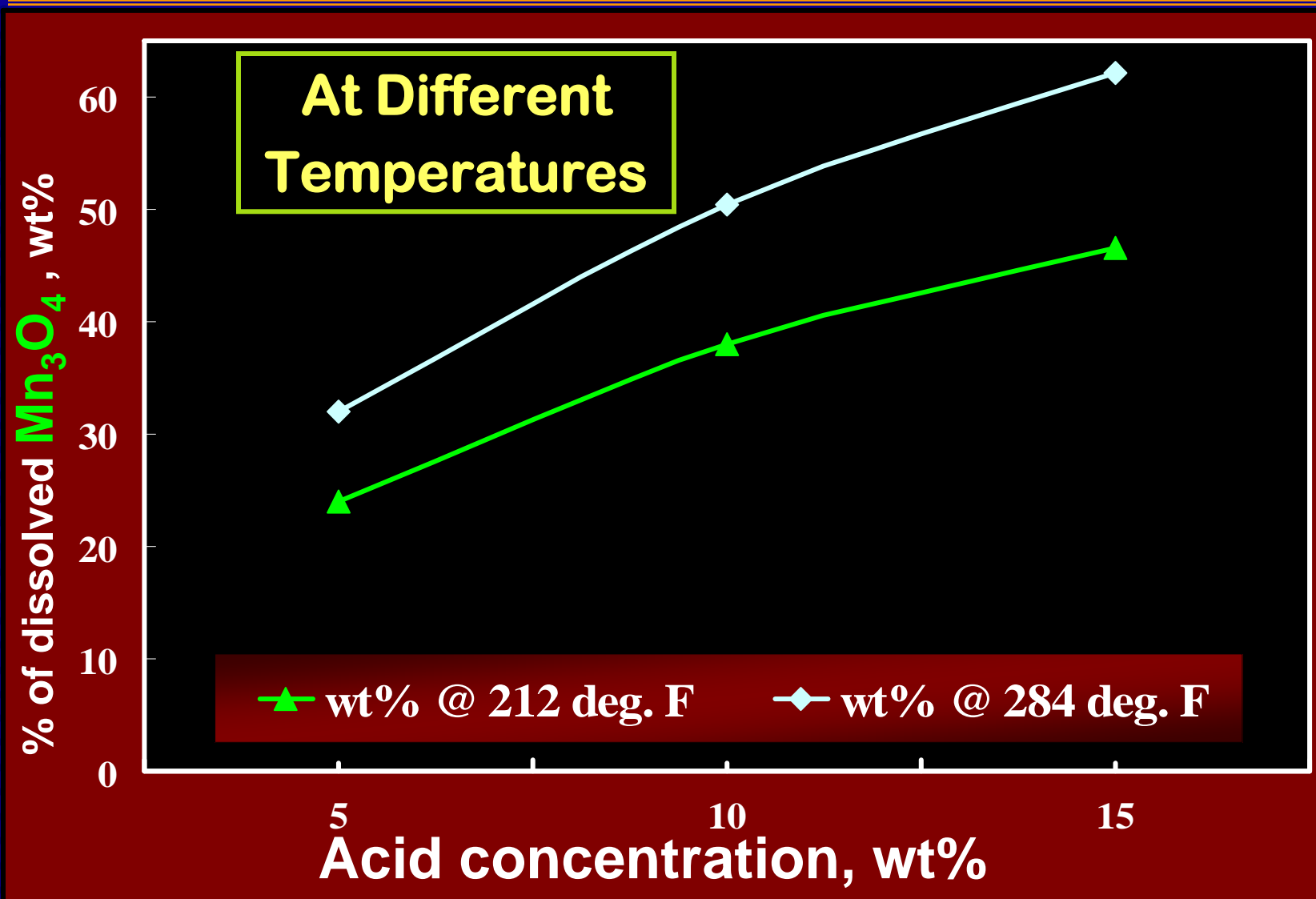
GCMS  
Technique



# Results

# I. Solubility of $\text{Mn}_3\text{O}_4$

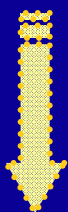
# Solubility of $\text{Mn}_3\text{O}_4$ in HCl Acid





# Analysis of Gases Evolved (1)

$\text{HCl} + \text{Mn}_3\text{O}_4$

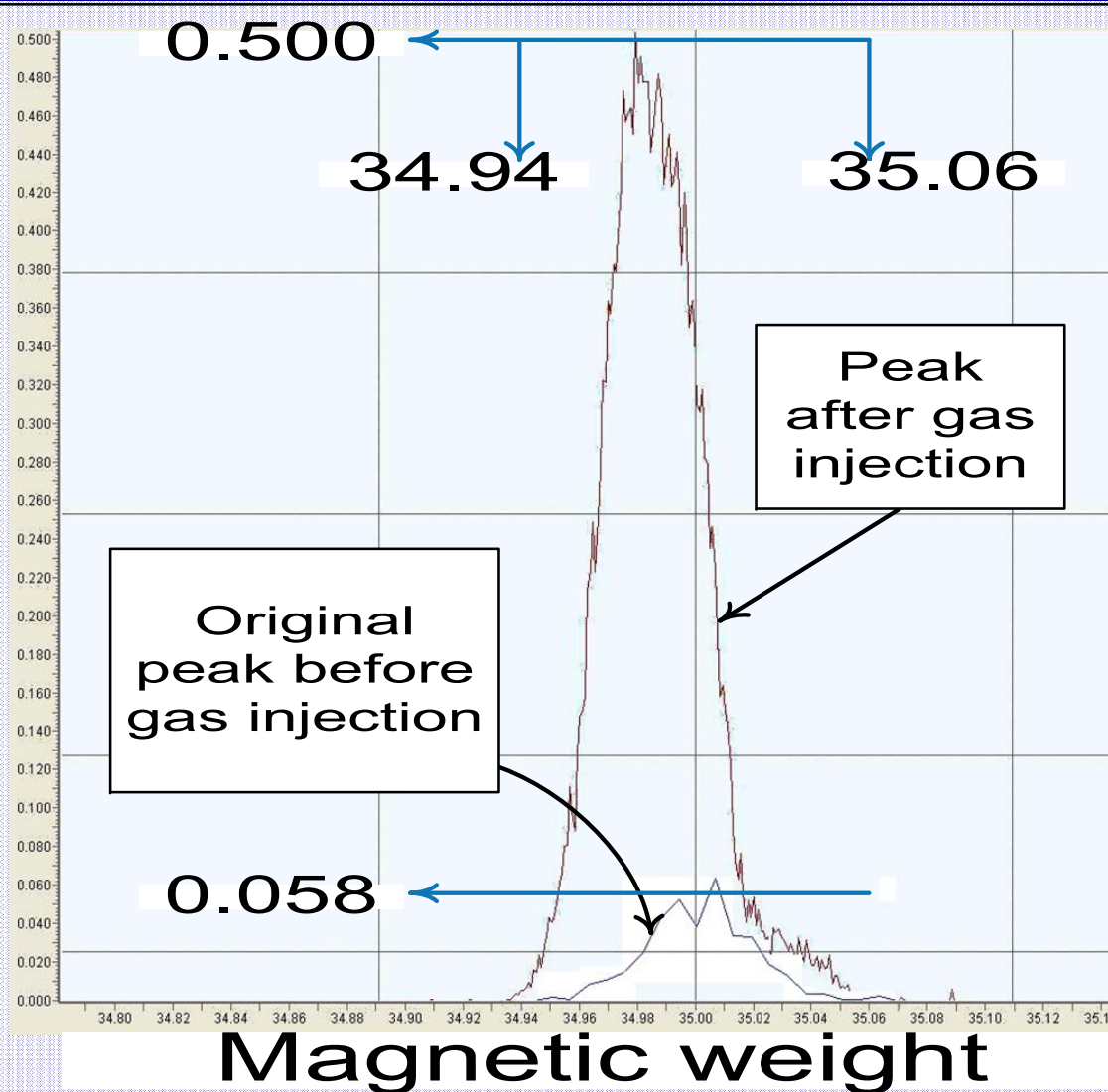


Chlorine...?

15 wt% HCl

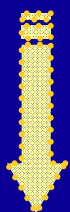
@ 284 °F

Amplitude



# Analysis of Gases Evolved (3)

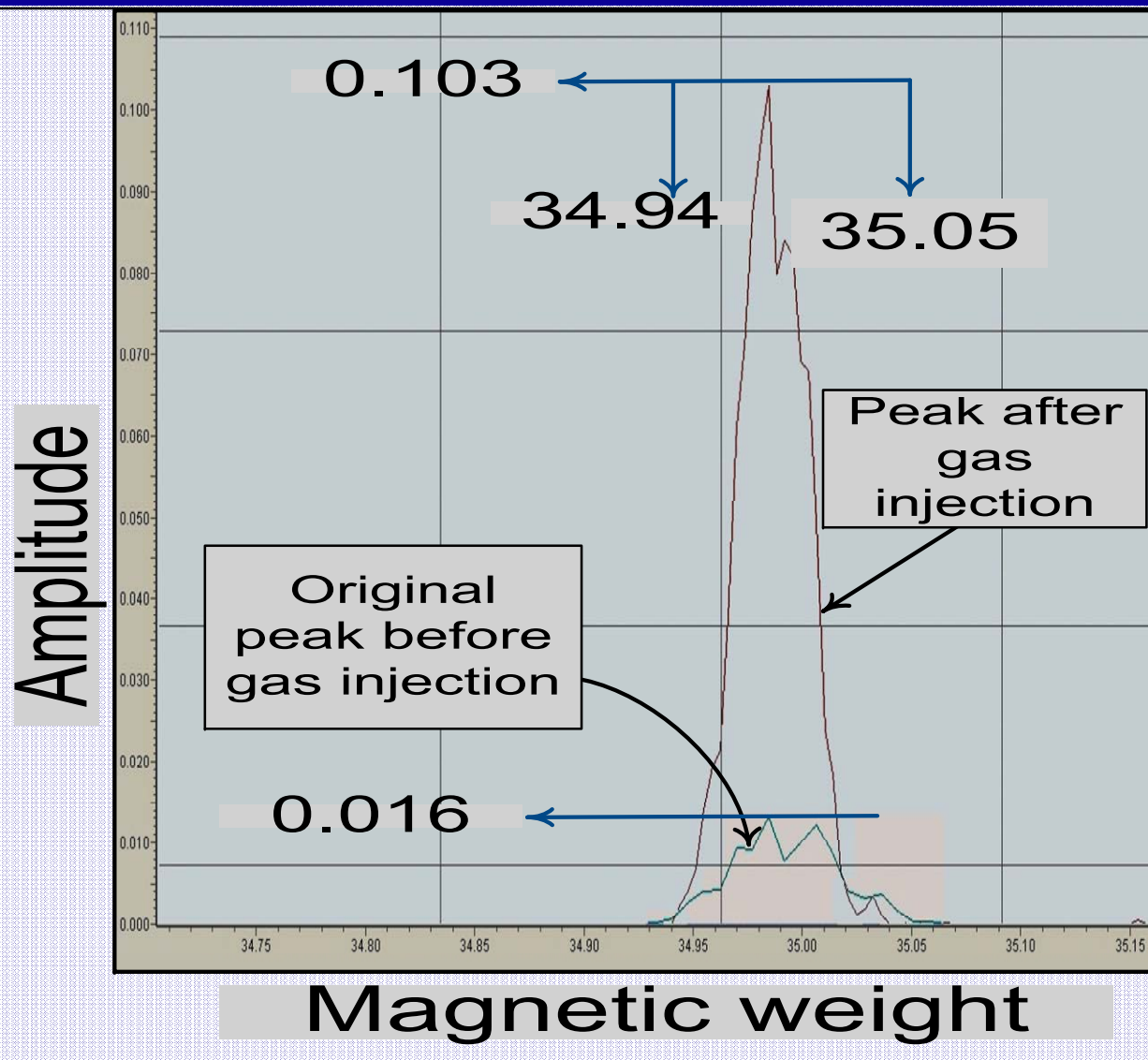
$\text{HCl} + \text{Mn}_3\text{O}_4$



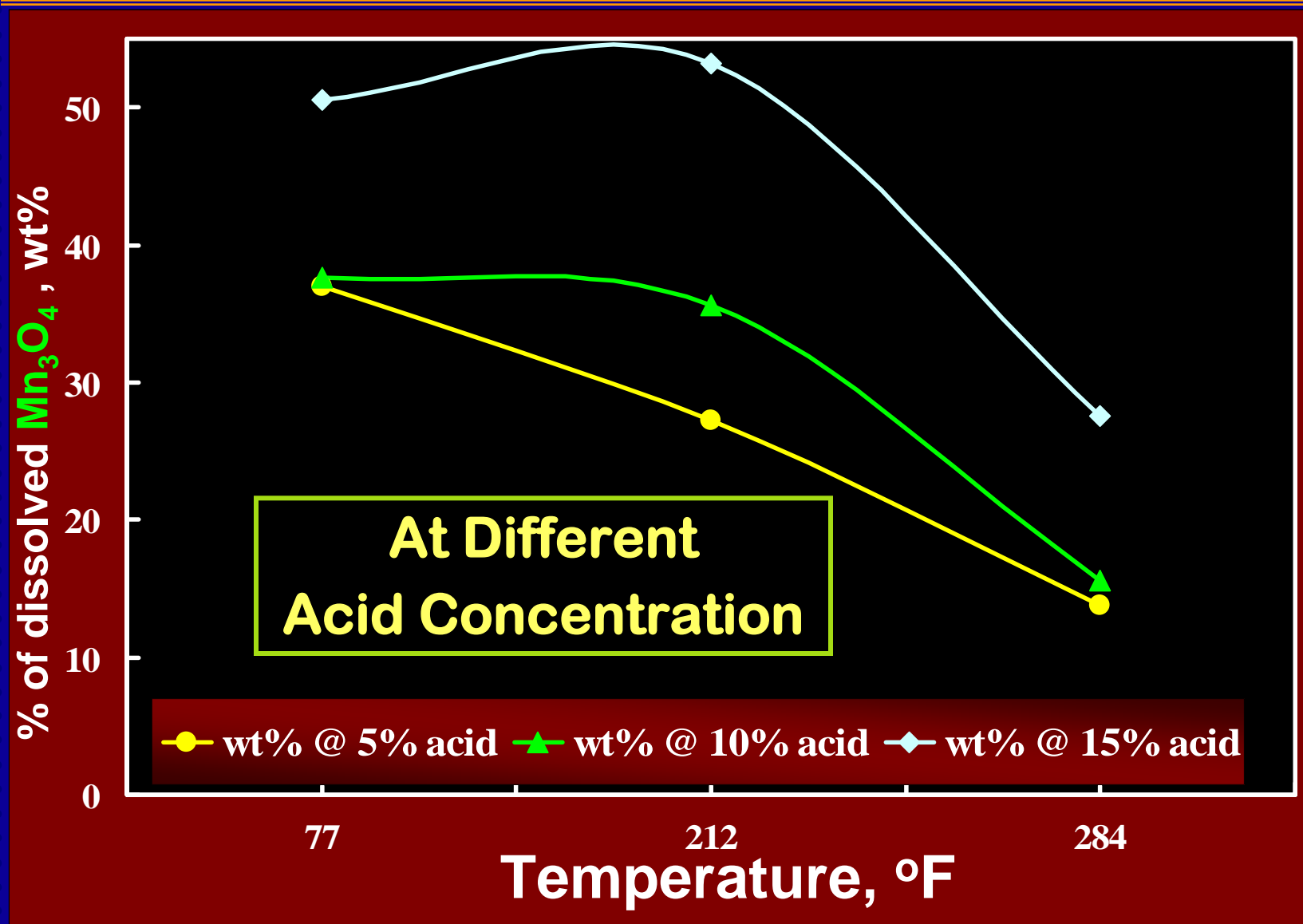
Chlorine...?

5 wt% HCl

@ 284 °F



# Solubility of $\text{Mn}_3\text{O}_4$ in Citric Acid



## Reaction of 15 wt% citric acid solutions with $\text{Mn}_3\text{O}_4$

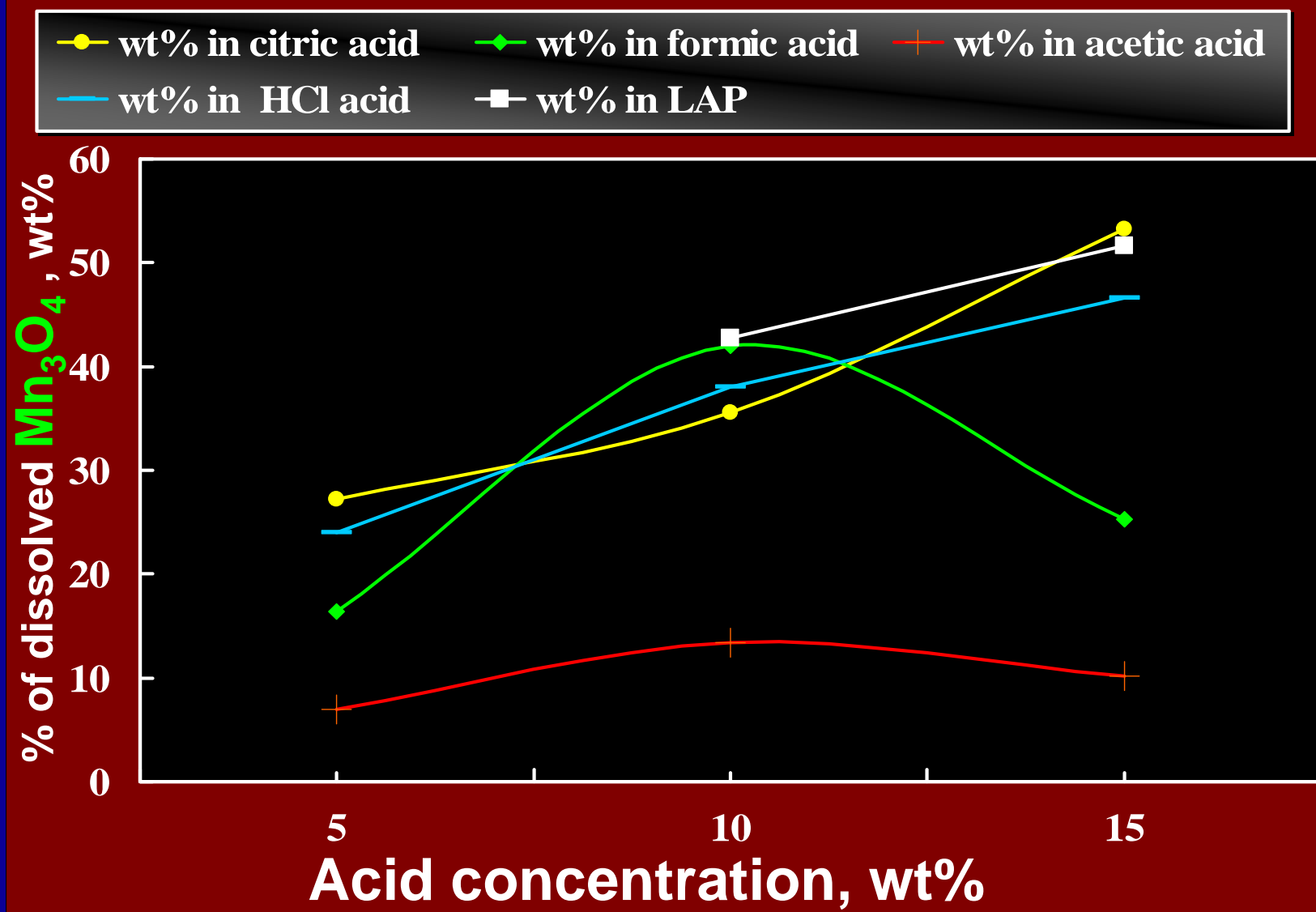
White precipitation  
formed



Spent citric acid  
@ 212 °F & 200 psi  
Acid soaking  
time = 24 hrs

Spent citric acid  
@ 284 °F & 200 psi  
Acid soaking  
time = 24 hrs

# Solubility of $\text{Mn}_3\text{O}_4$ in Acid Solutions at 212 °F





# **11. HPHT Filter Press**

# One Stage Treatment without Enzyme



10 vol% LAP  
T= 250 °F  
ST= 15 hr



15 vol% LAP  
T= 250 °F  
ST= 15 hr



15 vol% LAP  
T= 250 °F  
ST= 46 hr

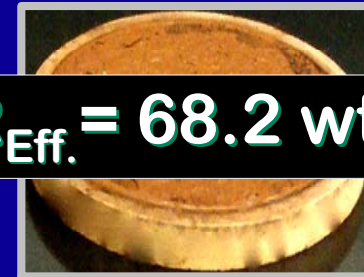


15 vol% FAP  
T= 300 °F  
ST= 46 hr



10 wt% HCl  
T=250  
ST= 28 hrs

Before



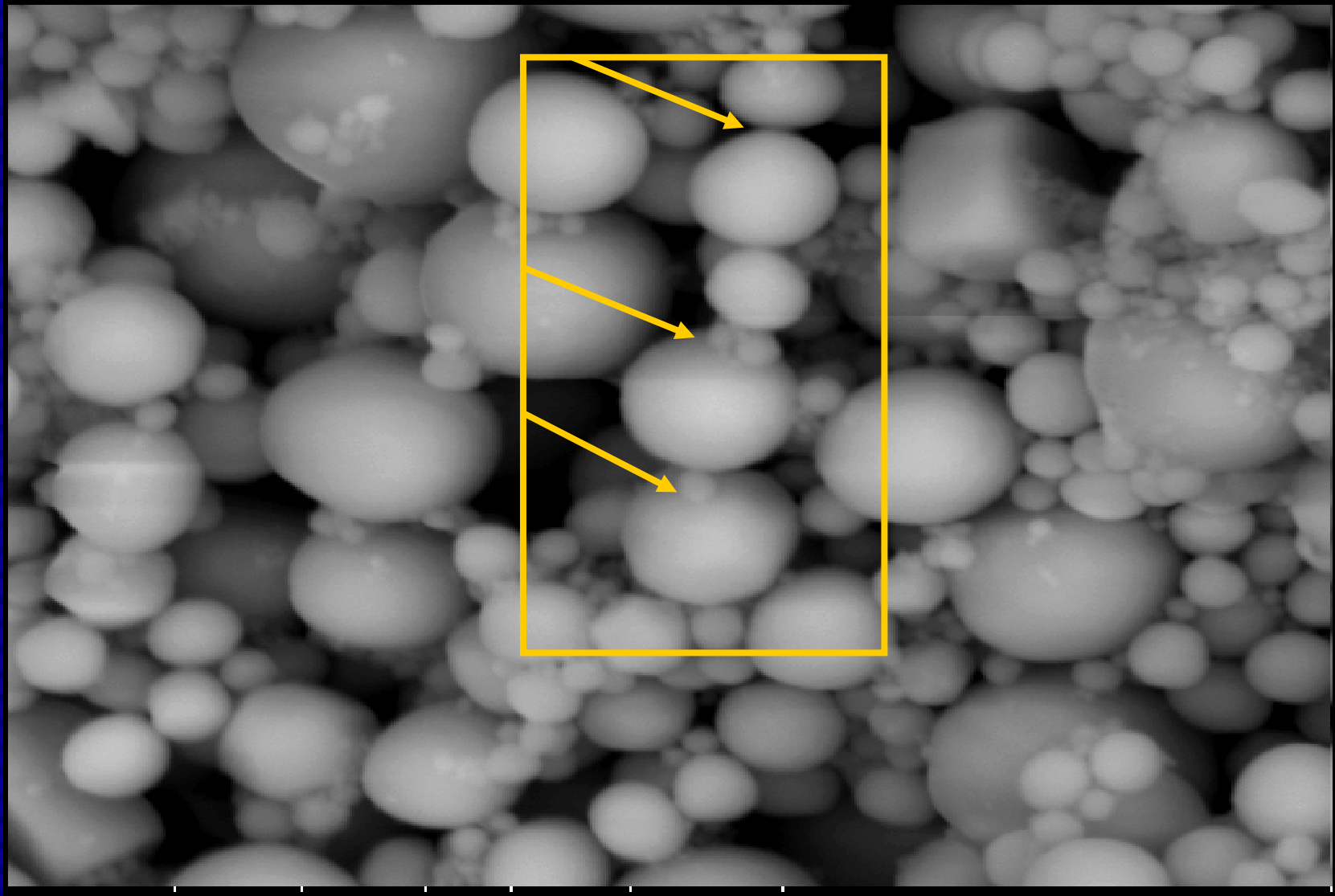
$R_{\text{Eff.}} = 68.2 \text{ wt\%}$

After

\*\*LAP: Lactic acid precursor, FAP: Formic acid precursor, ST: Soaking time

Filter cake before & after soaking  
in acid solution, P = 200 psi

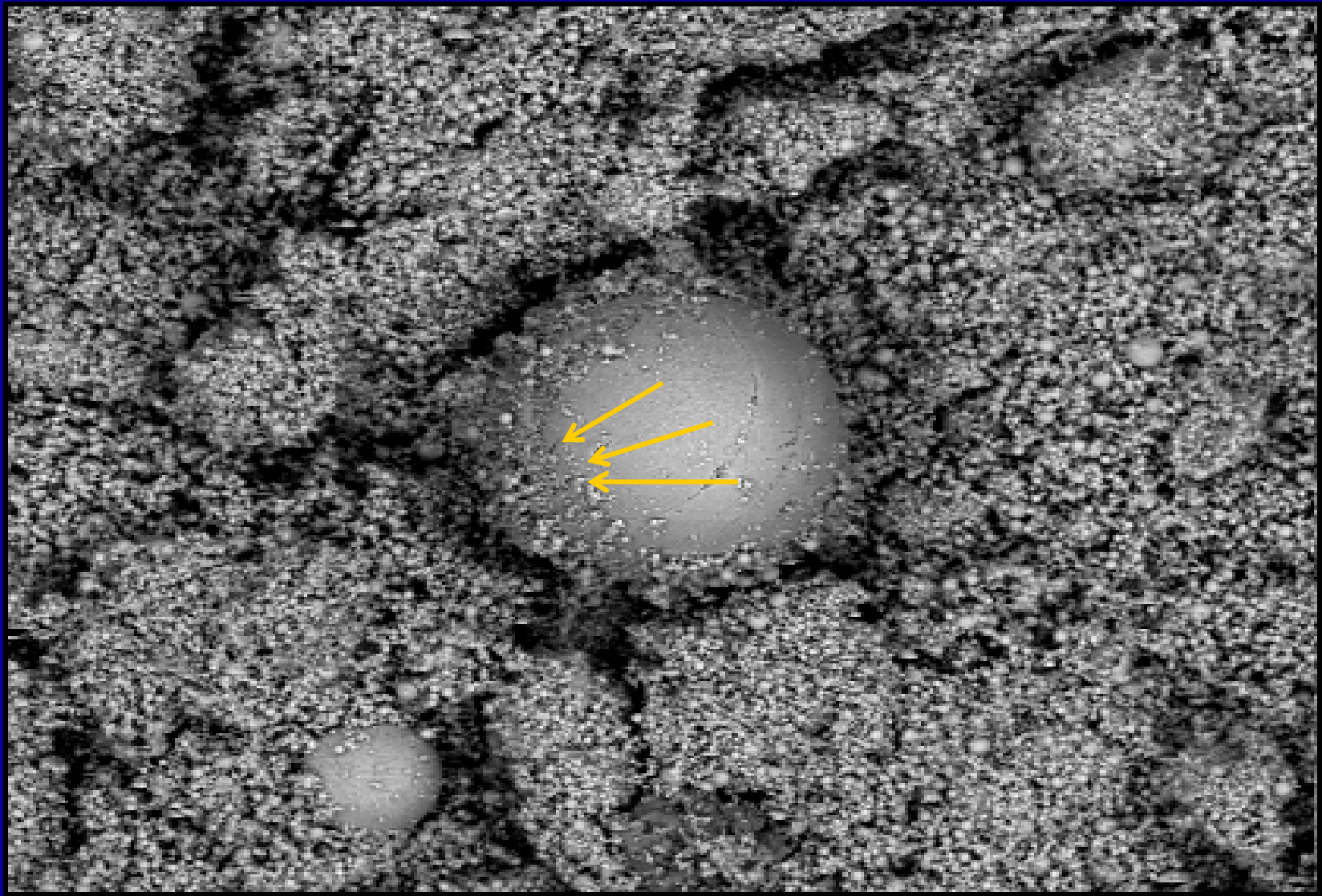
# SEM Analysis on Untreated FC





# SEM Analysis on FC after acid treatment

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# One stage Treatment with Enzyme

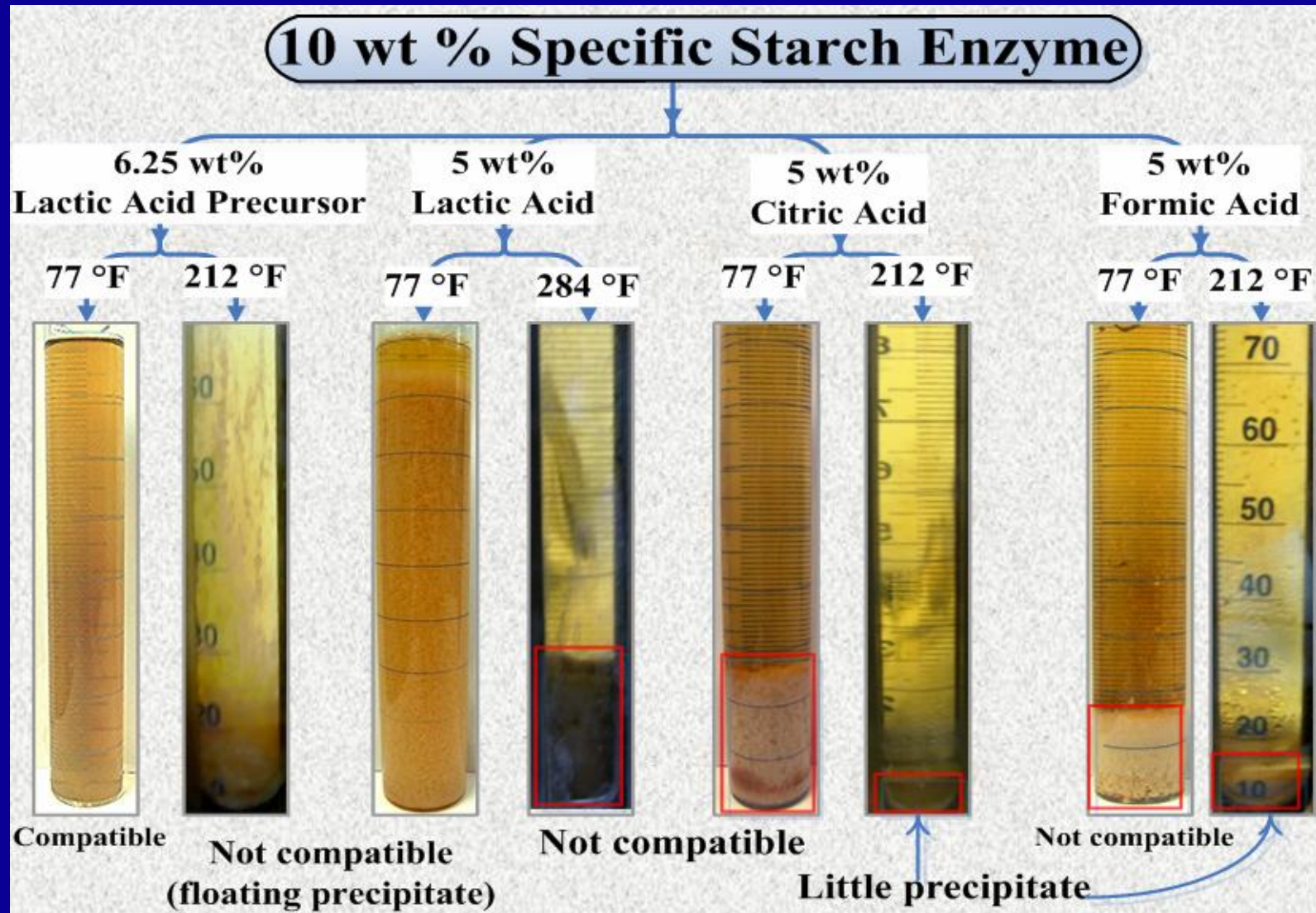
**Filter cake before & after soaking in cleaning solution**



**10 wt% Lactic acid precursor  
+  
10 wt% Specific starch enzyme**

**T = 253 °F  
P = 200 psi  
Soaking time = 18 hr**

# Compatibility of enzyme-A with organic acids





# Two-Stage Treatment (1)

24 hrs enzyme soaking time

Filter cake before & after soaking in  
cleaning solution



**Before**



**After**



**After + Iodine test**

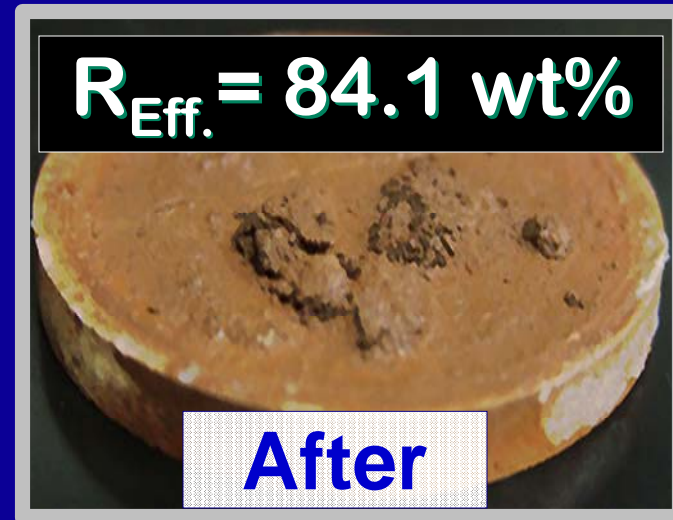
10 wt% Lactic acid precursor  
+  
10 wt% Specific starch enzyme

T = 253 °F  
P = 200 psi  
Acid soaking  
time = 18 hr

# Two-Stage Treatment (2)

4 days enzyme soaking time

Filter cake before & after soaking in cleaning solution



10 wt% In-situ Lactic acid  
+  
10 wt% Specific starch enzyme

T = 244 °F, P = 200 psi  
Acid soaking  
time = 24 hr

# Characteristics and Removal of Filter Cake Formed by Formate-based Drilling Mud

Mohammed B. Al Otaibi, Hisham A. Nasr-El-Din



# Background

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## Formate Brines

- Range of clear fluid densities (11.1-19.2 ppg)
- Stabilize polymers to 350°F
- Stabilize shale
- Easily recycled
- Corrosion, ????
- Compatible with formation fluids...???
- Removal of filter cake ...???

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# Potassium Formate Brine (PFB) Mixed with Unyazah Formation Brine (UFB)

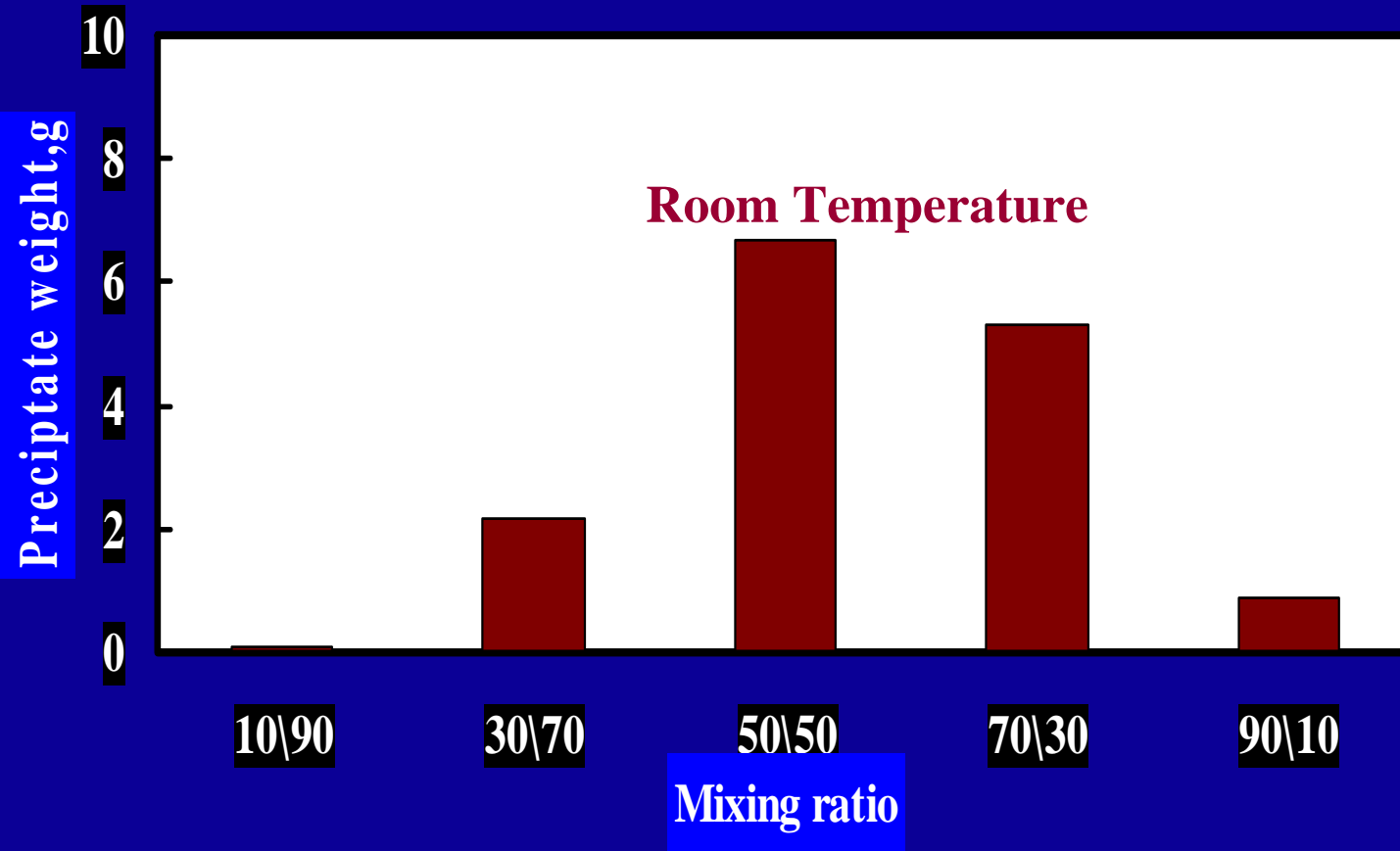


# Brine Sample Composition

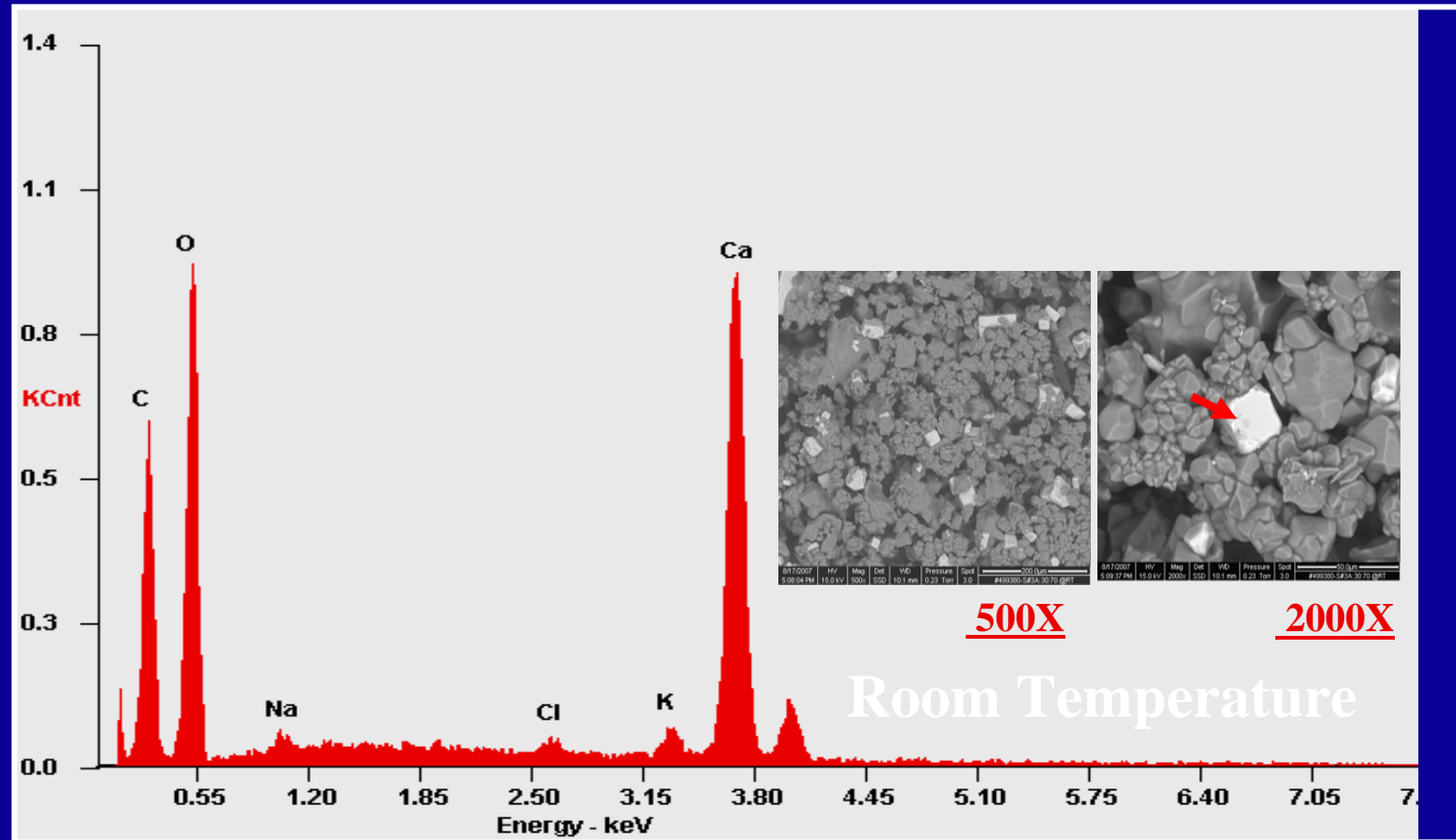
Compound	Concentration, g/l
NaCl	142.57
CaCl <sub>2</sub> ·2H <sub>2</sub> O	76.759
MgCl <sub>2</sub> ·6H <sub>2</sub> O	9.8259
Na <sub>2</sub> SO <sub>4</sub>	0.1479
NaHCO <sub>3</sub>	0.7889

Ions, mg/l								pH	Density, ppg
Na	Ca	Mg	SO <sub>4</sub>	Cl	CO <sub>3</sub>	HCO <sub>3</sub>	TDS		
56,356	20,926	1,175	100	126,935	0	573	206,065	6.031	9.5

## Compatibility Tests between PFB and UFB



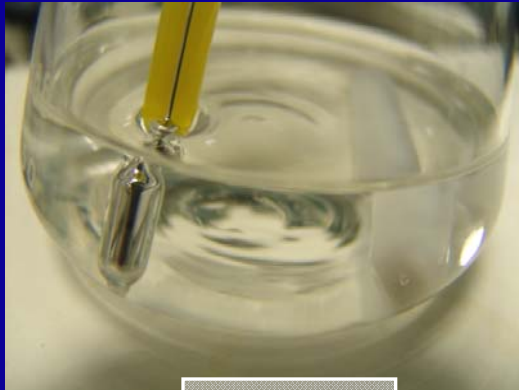
## Backscattered Electron Images and EDS X-ray Spectra



70:30 (PFB/UFB)

# Compatibility of PFB with UFB

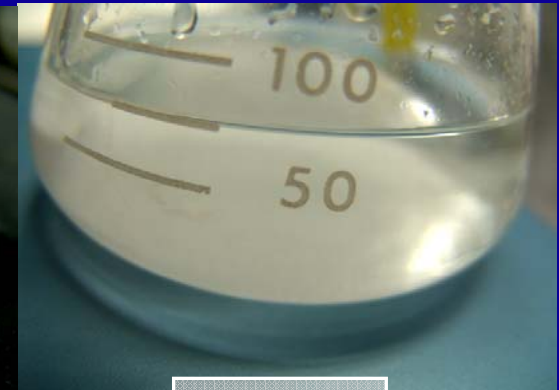
Temperature: 113-127°F



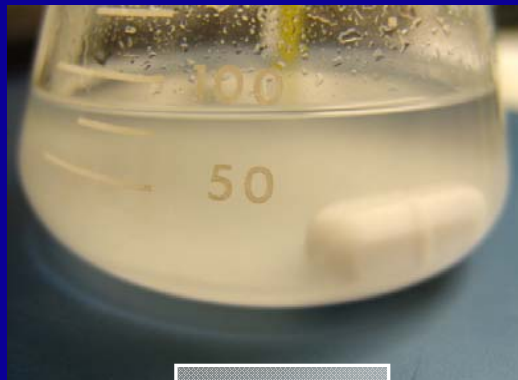
10:90



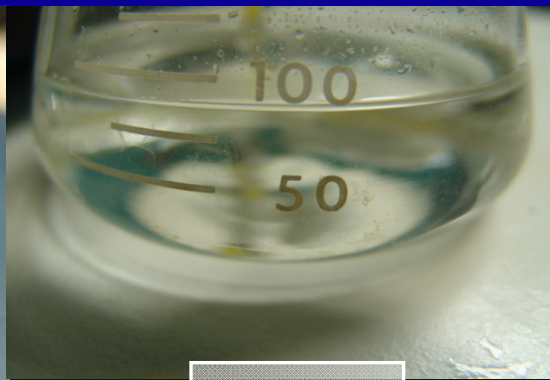
30:70



50:50

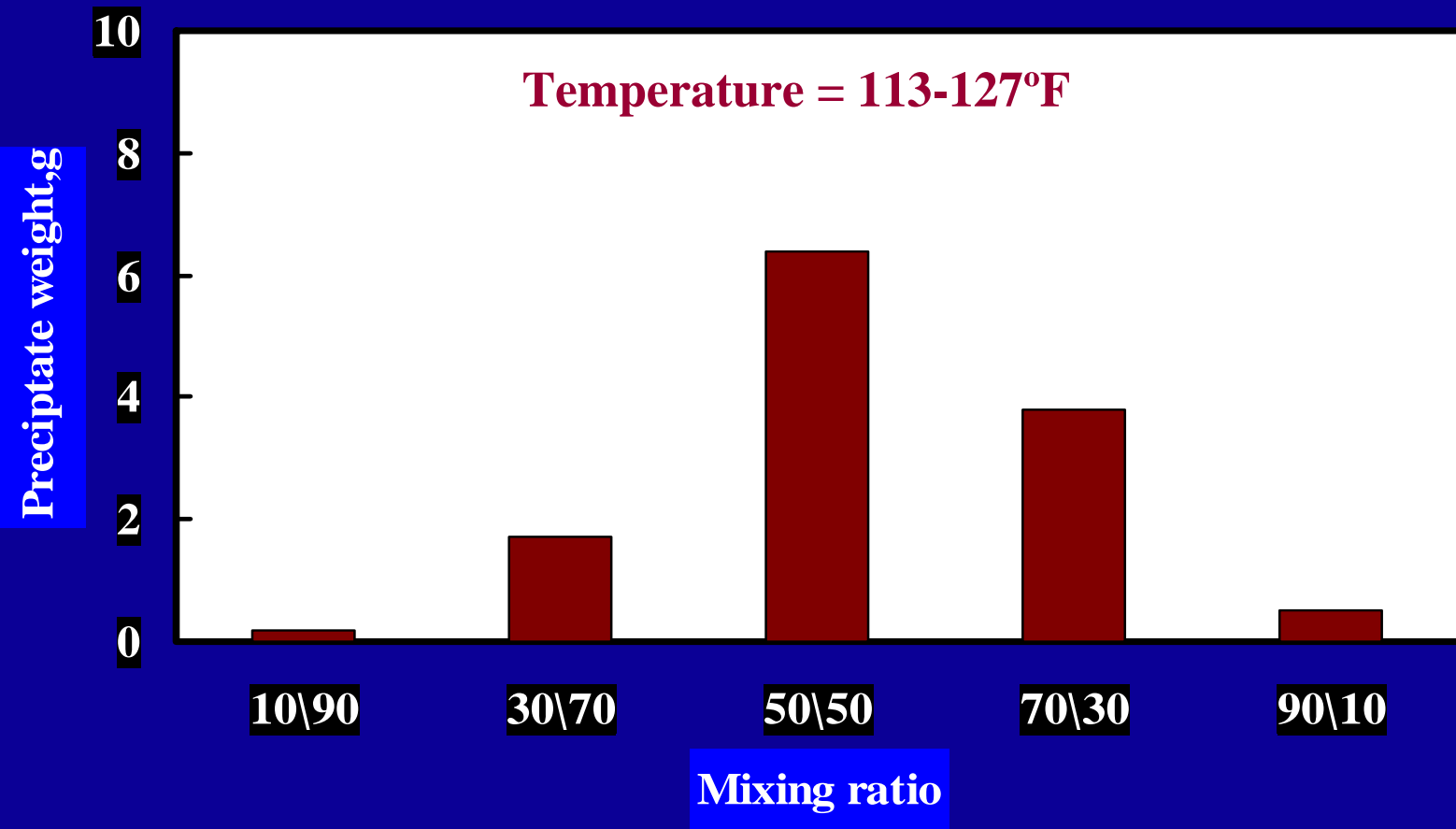


70:30

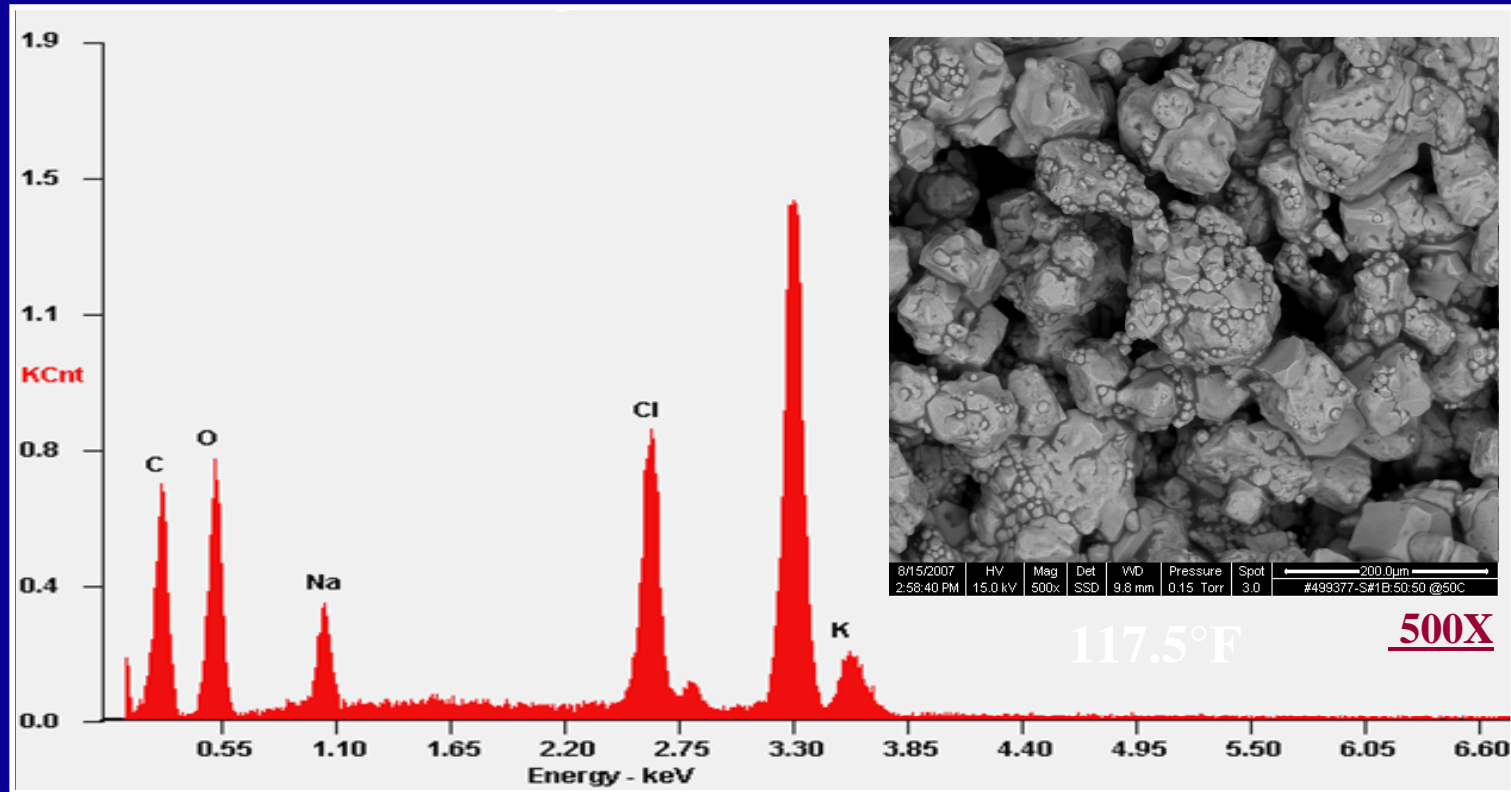


90:10

# Compatibility Tests between PFB and UFB



# Backscattered Electron Images.....



50:50 (PFB/UFB)



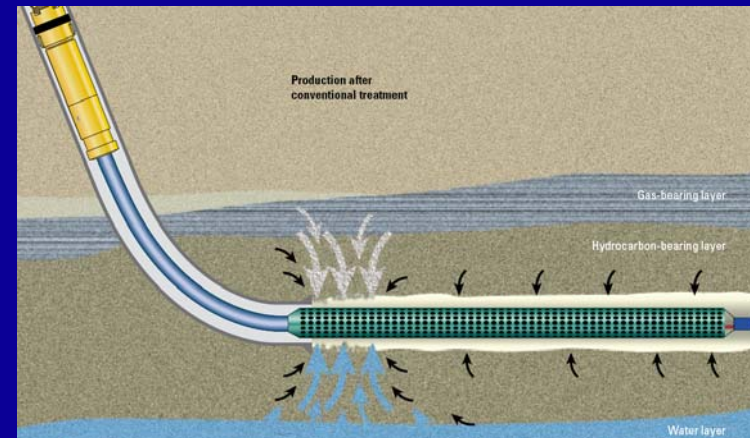
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## **Potassium Formate Brine (PFB) Mixed with Cleaning Solution**

## Cleaning Fluids

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- ❑ HCl (strong acid)
- ❑ Organic acids
- ❑ Esters
- ❑ Oxidizers
- ❑ Chelating agent
- ❑ Enzymes
- ❑ Jetting



[www.slb.com](http://www.slb.com)



# 10 wt% Citric Acid in PFB

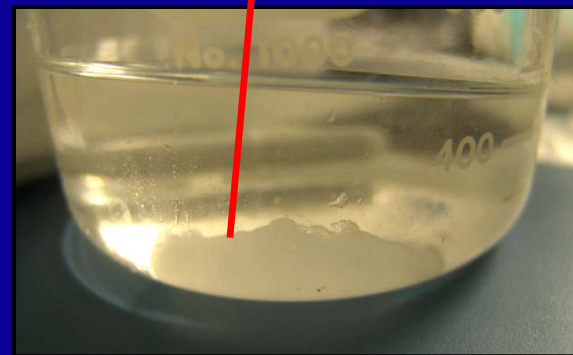
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At room temperature



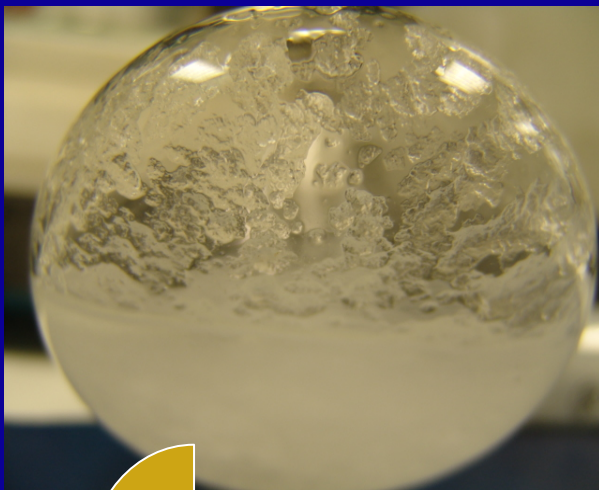
After heating at  
158°F



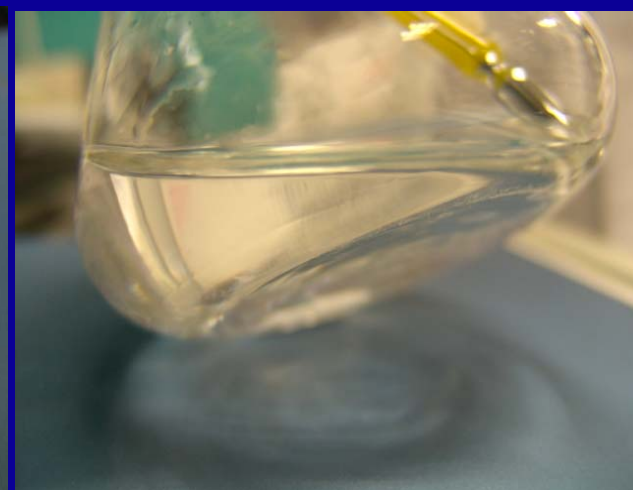
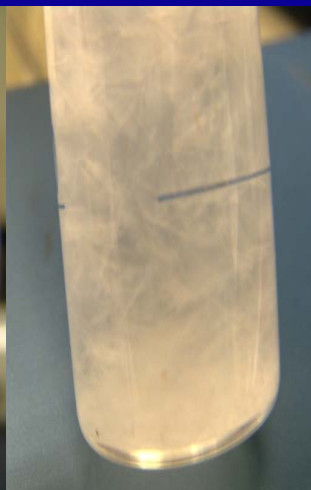
Potassium hydrogen citrate

# 10 wt% Formic Acid in PFB

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Gel fluid at room temperature



Solution prepared at 140°F

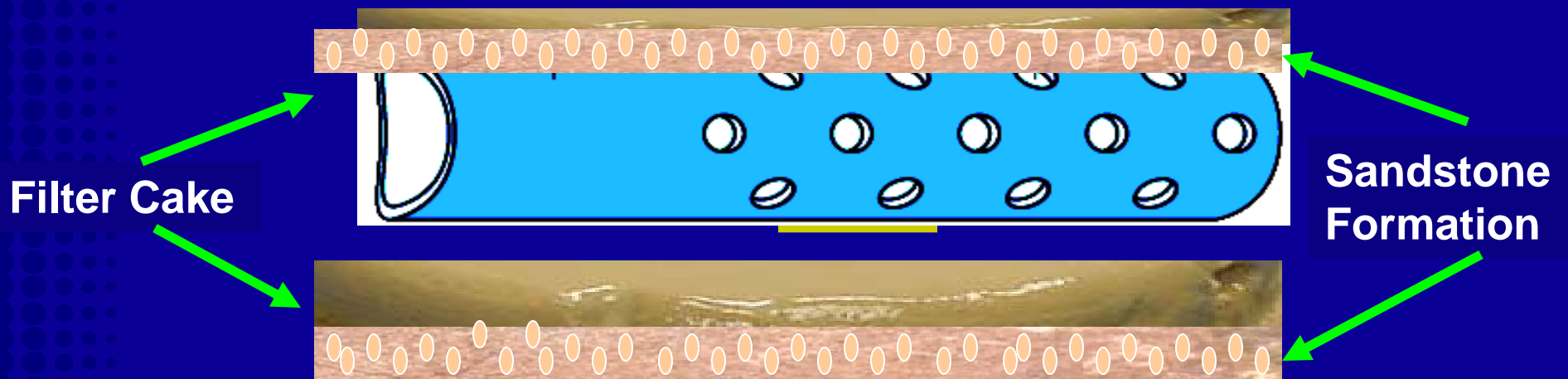


Potassium hydrogen formate

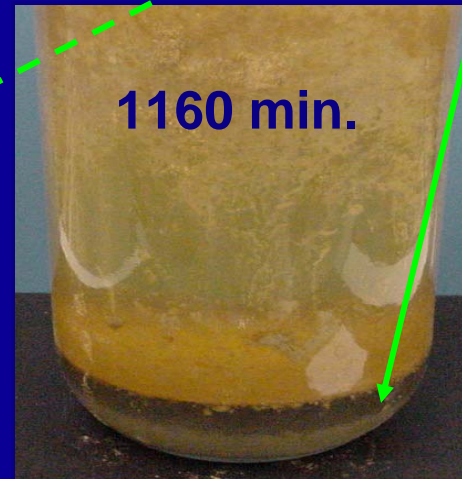
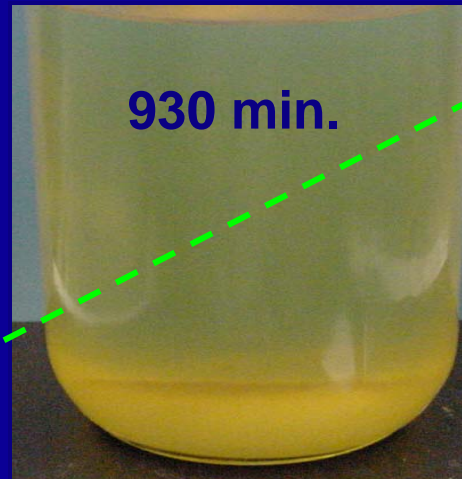
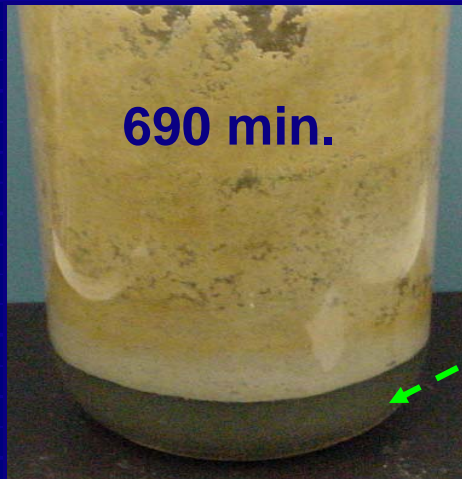
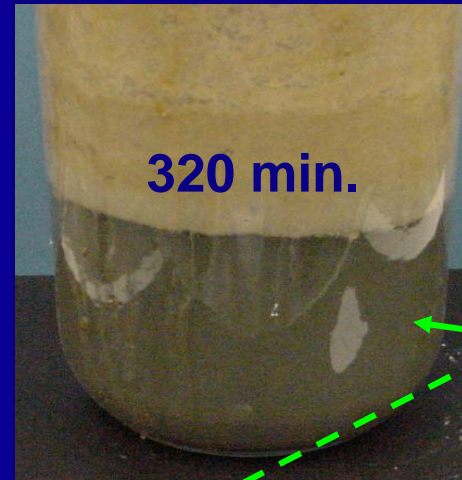
# Pre-Drilled Liner, Well H

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- Low-carbon steel
- 98 wt% Fe, 1.5 wt% Mn
- Poor resistance to CO<sub>2</sub> corrosion

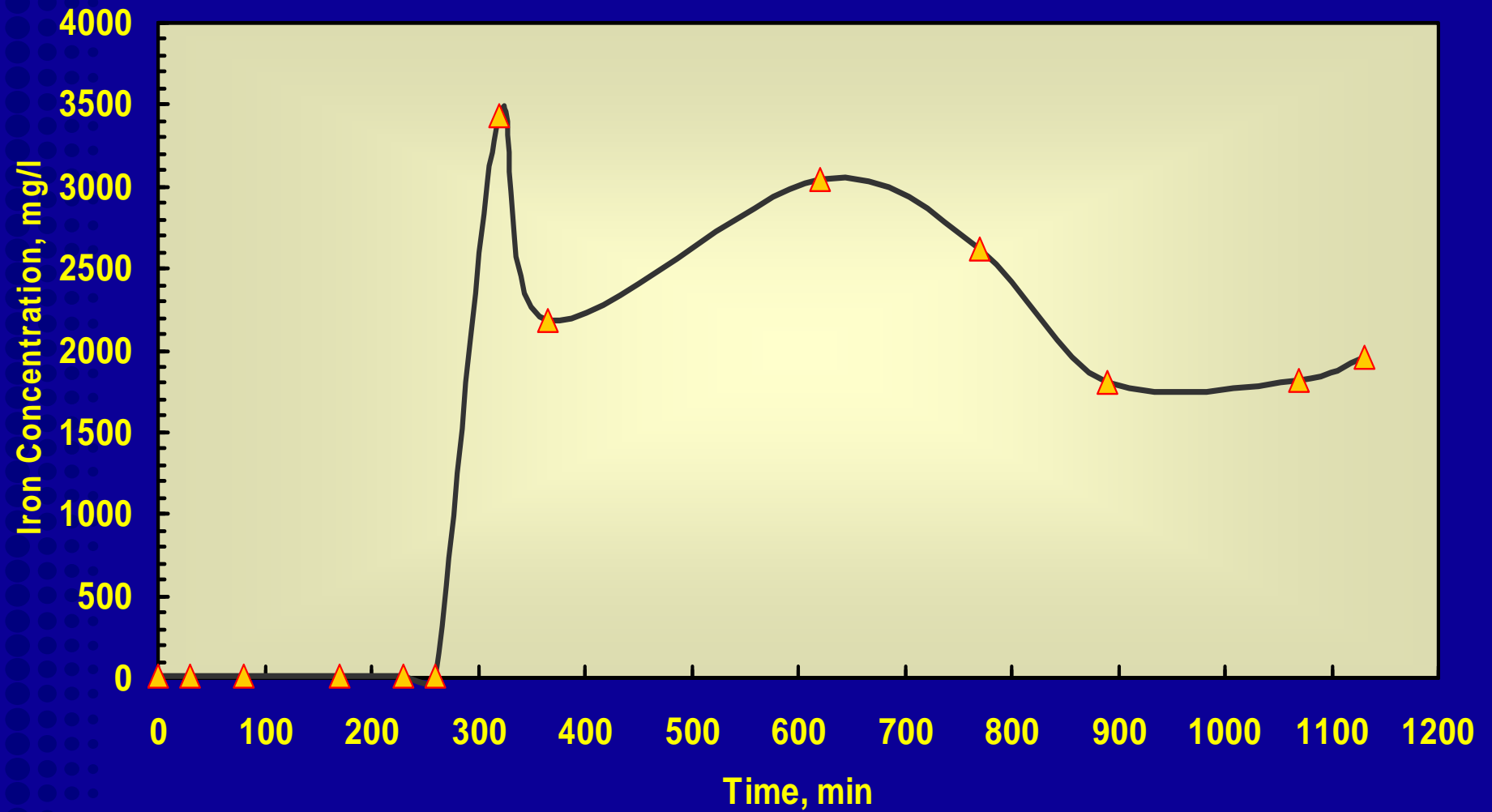


# Samples Collected from Well H



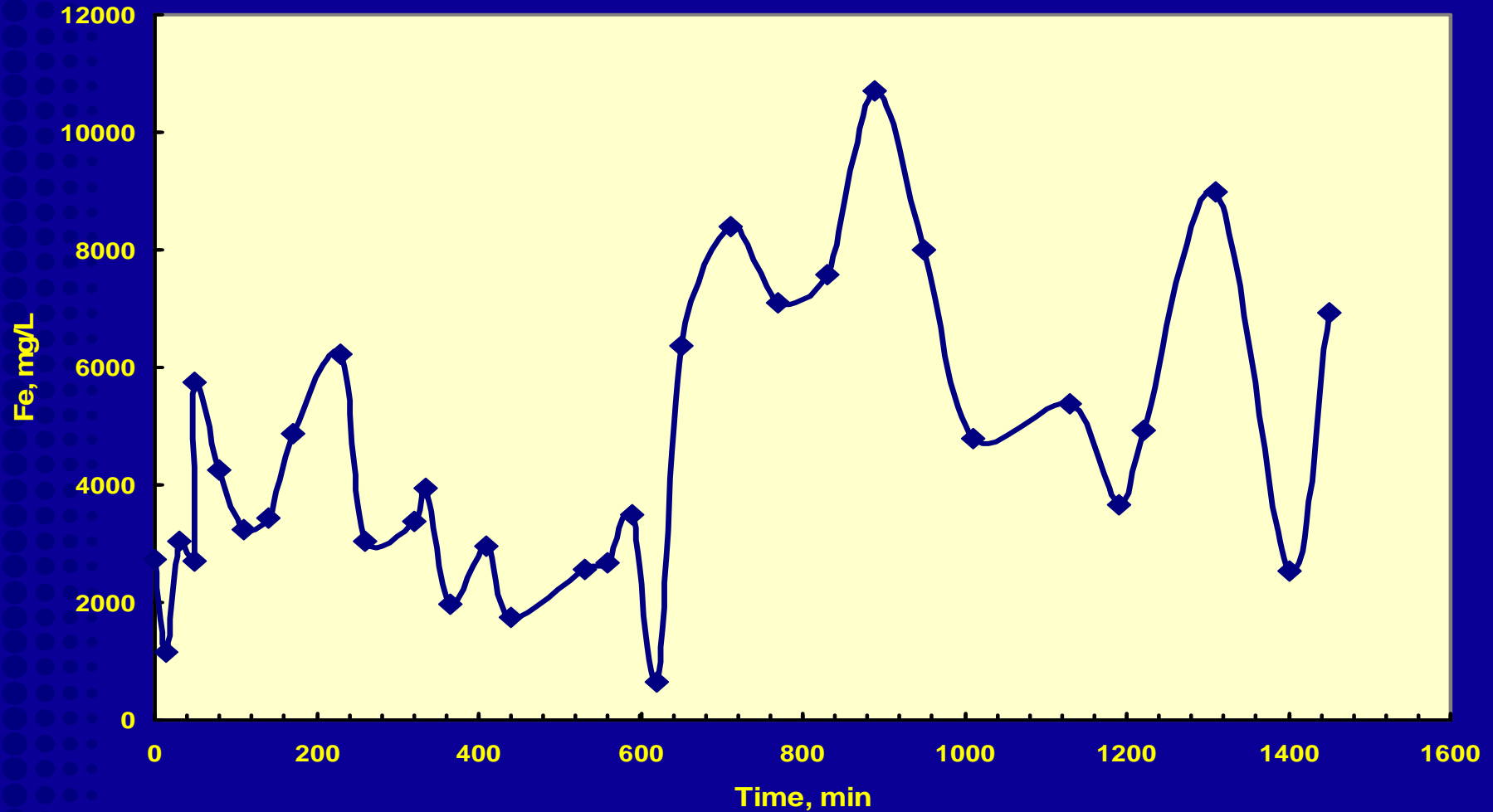
(Green  
Color)  
Iron

# Total Iron, Well H



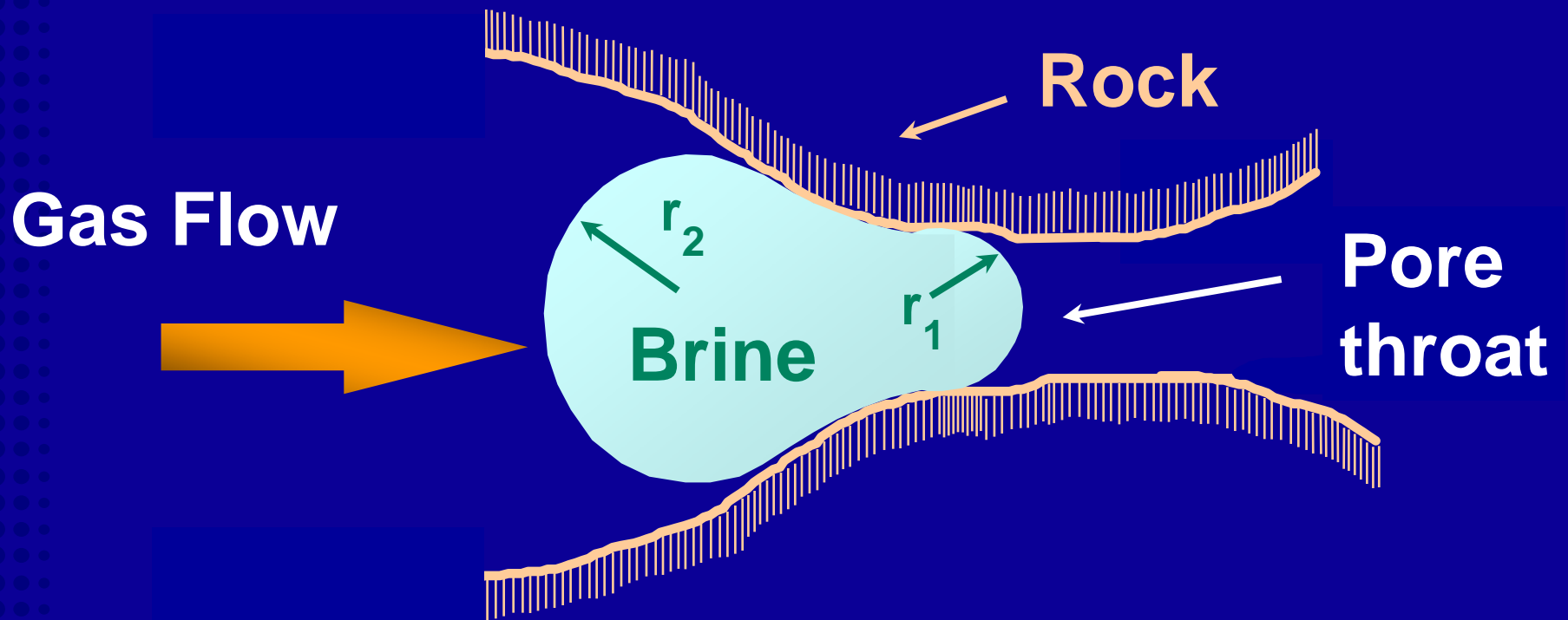


# Total Iron in Supernatant, Well H





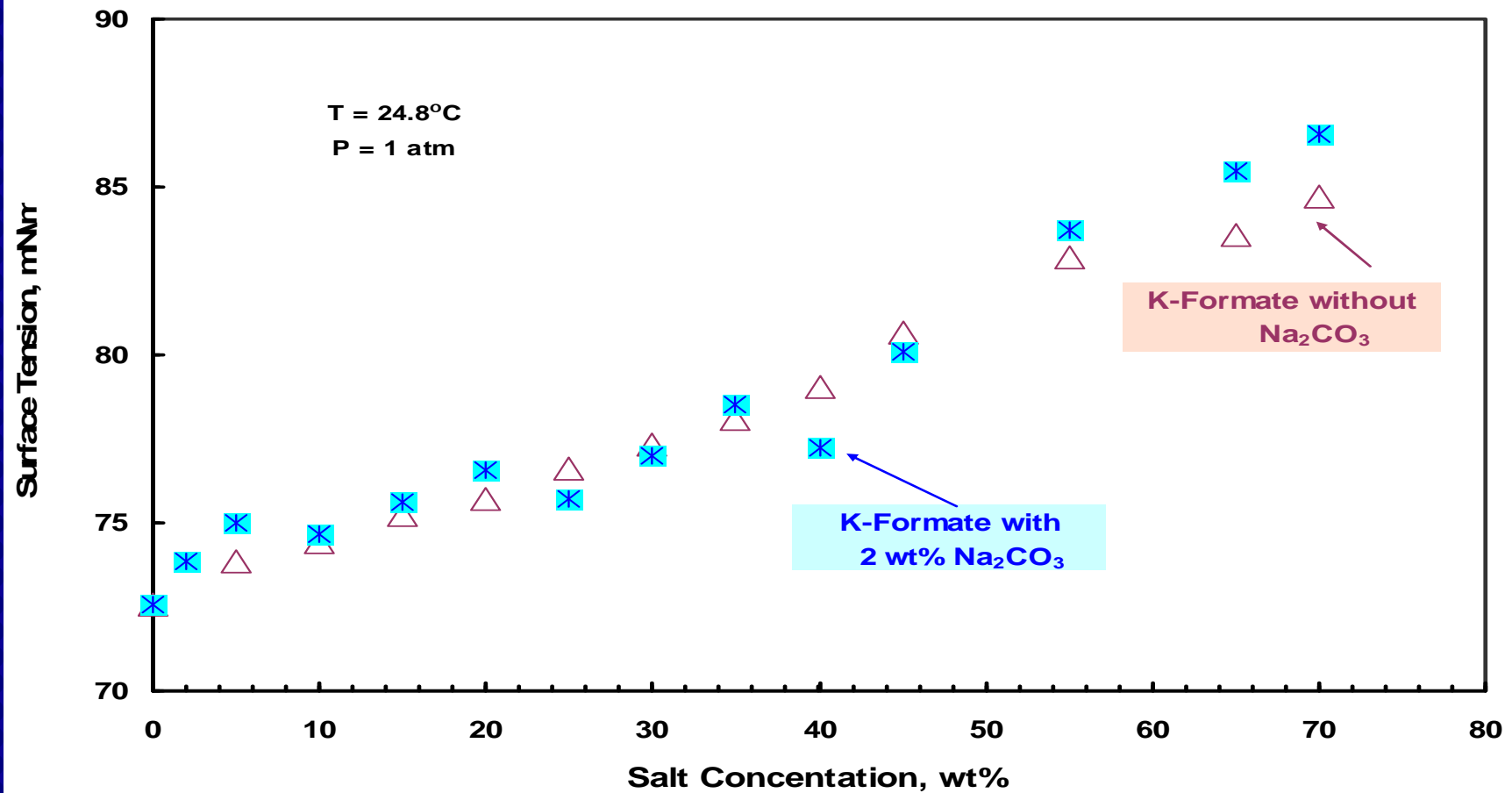
# Trapping of Aqueous Solutions



Laplace Equation:

$$\Delta p = 2\sigma \left[ \frac{1}{r_1} - \frac{1}{r_2} \right]$$

# Surface Tension of K-Formate Solutions



# The Bottomline

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- New fluids and weighing materials were introduced
- There is a need to examine filter cake generated by these fluids
- Also more work is needed to find methods to remove filter cake
- Watch for filtrate, and how to recover it