SPE 164121

Effective Propagation of HPAM Solutions through the Tambaredjo Reservoir during a Polymer Flood

In many polymer floods, the produced HPAM polymer was severely degraded, even in low-temperature applications:

Daqing, 45°C: 92% loss of Mw.
Shengli, 70°C: 77% loss of Mw.
Shuanghe (Henan) 70°C: 85% loss of Mw.
Courtenay, 30°C: 50% loss of Mw.
Tambaredjo, 38°C: 83% loss of Mw.

WHY?

Laboratory results indicate HPAM should be stable at low temperatures (Shupe 1981, Yang & Treiber 1985, Moradi & Doe 1987, Seright 2010).

Where does the degradation occur? If polymer degradation occurs during the first part of the flood, the polymer flood could be jeopardized.

Our hypothesis:

1. Iron minerals strip any dissolved oxygen from solution soon after injection (Seright 2010).
2. Fe^{2+} enters the polymer solution during transit through the reservoir.
3. Dissolved Fe^{2+} does not harm HPAM effectiveness if no dissolved O_2 is present.
4. Degradation occurs when HPAM solutions mix with air during sampling at the producer.
5. Better sampling methods are needed.

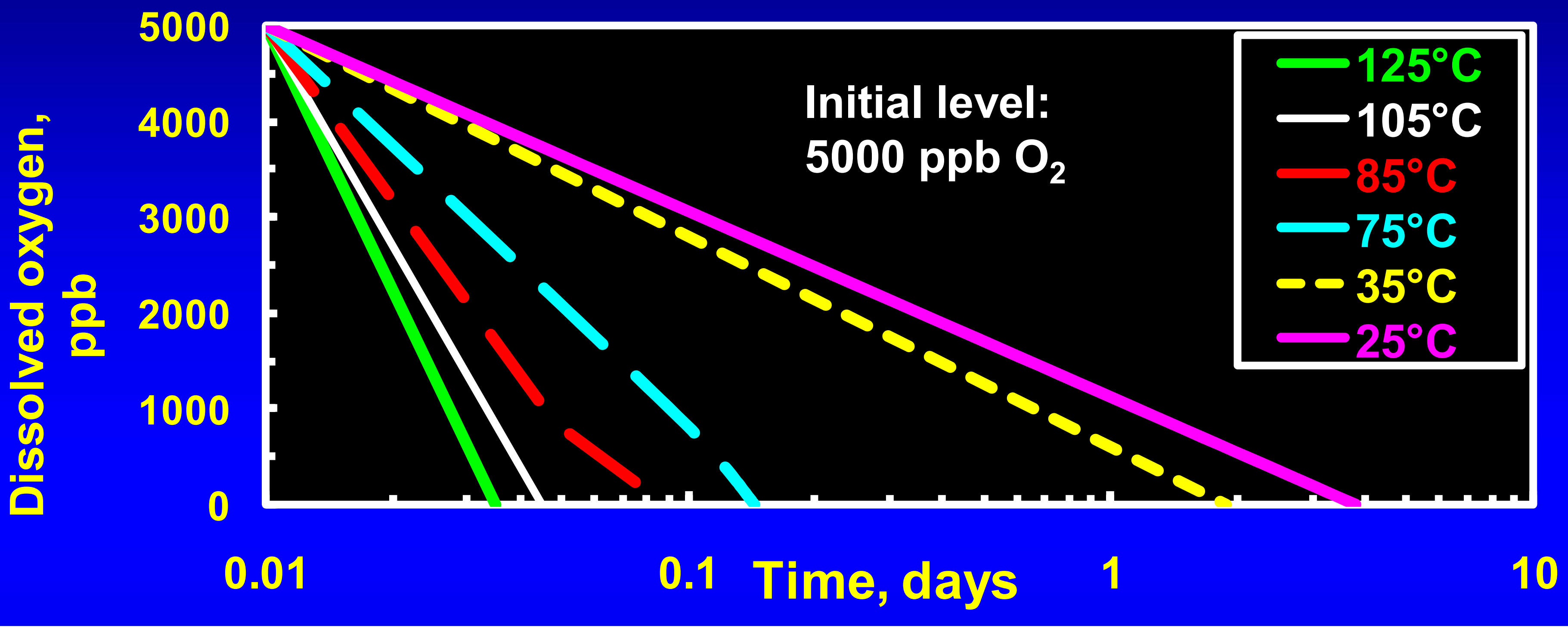
If both dissolved oxygen and iron are present, severe polymer degradation can occur.

$$Fe^{2+} + O_2 + \text{HPAM}$$

$$\downarrow$$

$$Fe^{3+} + H_2O + \text{degraded HPAM}$$

Depletion of dissolved oxygen by reaction with sand containing 1% pyrite



Dissolved O_2 that entered the reservoir prior to polymer injection will have been consumed and will not aggravate polymer degradation.

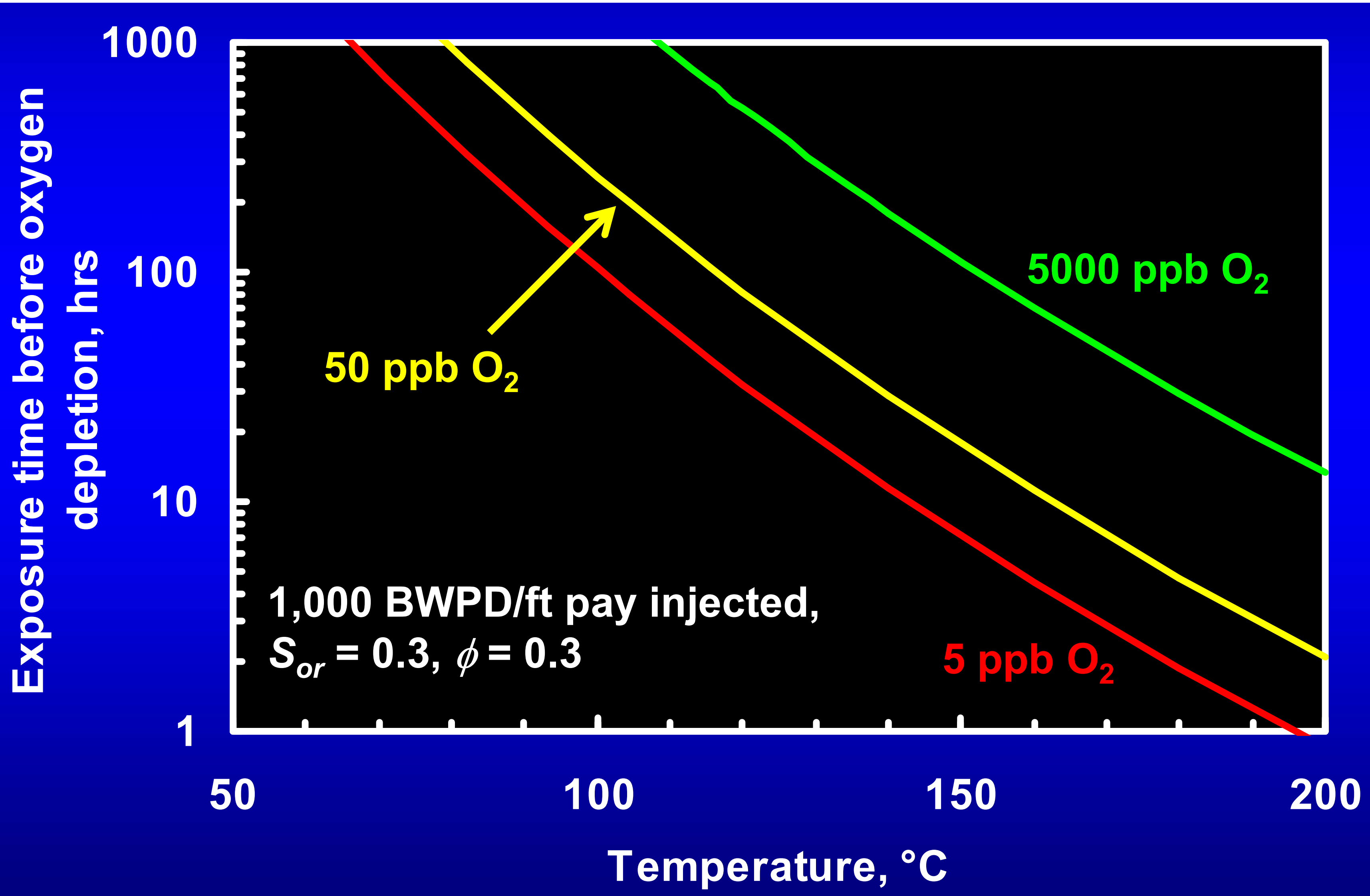
If an O_2 leak develops during the course of polymer injection, that O_2 will not compromise the stability of the polymer that was injected before the leak developed or after the leak is fixed.

Polymer that is injected while the leak is active will be susceptible to oxidative degradation. OXYGEN REMOVAL IS NECESSARY!

(But O_2 can be removed without use of expensive chemicals).

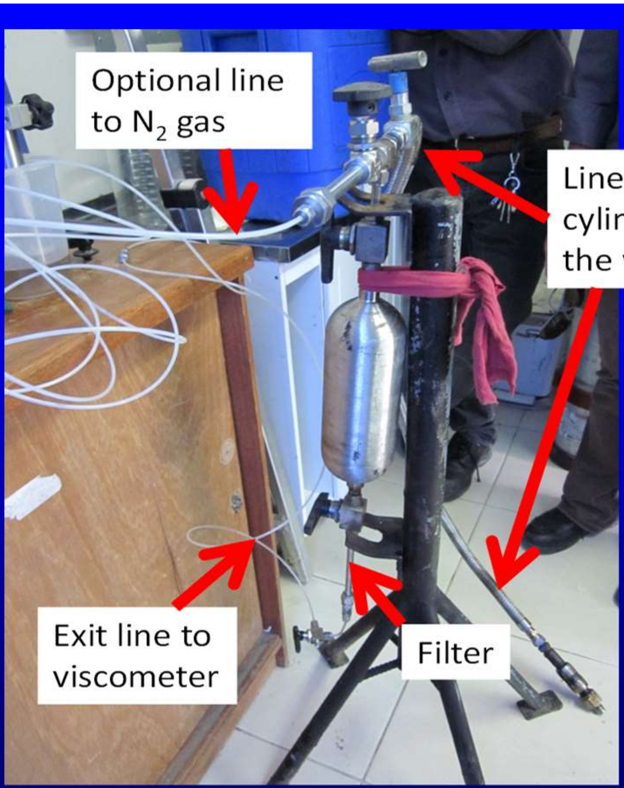
MODELING O_2 TRANSPORT THROUGH A RESERVOIR

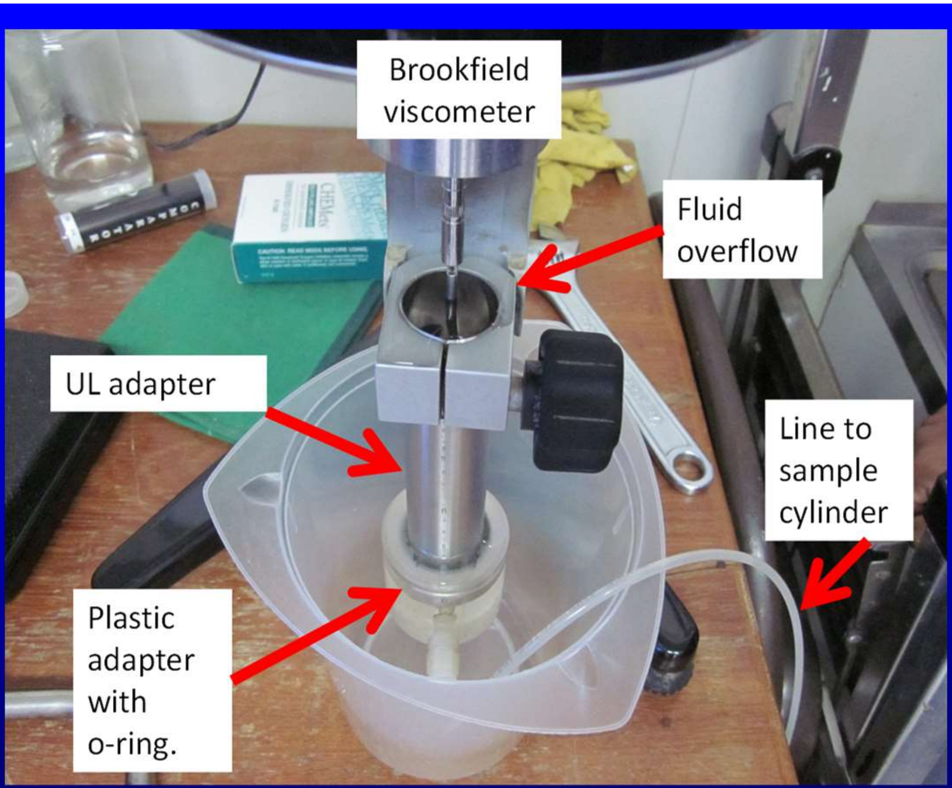
What if some O_2 is present? How long will it take for reaction with the oil to deplete the O_2?



New Anaerobic Sampling Method

1. Point the outlet end of the sample cylinder up during collection at the wellhead.
2. In the lab, if needed, pressurize the sample cylinder with N_2.
3. Flow anaerobic solution into the bottom of the viscometer cup (and overflow out the top).





Improved Sampling Method Results

Well	1N11	1N06
Polymer, ppm	896	465
	cp @ 7.3 s^{-1}	
Direct aerobic sampling	6	5
New method	32	14

KEY POINT: Minimum HPAM degradation after flowing >300 feet through the reservoir.

CONCLUSION (SPE 164121)

1. A new method was developed for anaerobically sampling polymer solutions from production wells in the Sarah Maria polymer flood pilot project in Suriname. Whereas previous methods indicated severe polymer degradation, the improved methods revealed that the polymer propagated intact over 300 ft through the Tambaredjo formation. This finding substantially reduces concerns about HPAM stability and propagation through low- and moderate-temperature reservoirs.

Why bother worrying about degradation?

- How much are you spending on polymer? $10 million? $100 million?
- In polymer flooding, viscosity is money. The volume of oil you get is directly related to the viscosity of your polymer in the reservoir.
- If you lose 50%-90% of your viscosity, you are wasting 50%-90% of your investment. Is it ok to throw away $5-90 million? Wouldn’t it be better to spend a small fraction of that to remove O_2 from the make-up water or prevent O_2 from entering the flow stream?

OXIDATIVE DEGRADATION OF HPAM

- If O_2 is present, HPAM degradation depends on T, pH, E_H, and concentrations of Fe^{2+}, O_2 scavenger, polymerization impurities, and carbonate.
- If O_2 is not present (and divalent cations are not present), HPAM stability is good, regardless of the above impurities.
- If O_2 is re-introduced after a chemical oxygen scavenger is applied, a redox couple can form and degrade the polymer.

APPROACHES TO MINIMIZE OXIDATIVE DEGRADATION IN FIELD APPLICATIONS

1. Do nothing if the temperature is low and no iron is present in the injection water.
2. Remove any existing O_2; don’t let O_2 enter the flow stream.
3. Use an anti-oxidant package, including O_2 scavenger.
4. Intentionally oxygenate the water to precipitate iron. Then try to balance E_H, pH, and water composition to prevent formation of a redox couple.

WHAT IS THE BEST APPROACH?

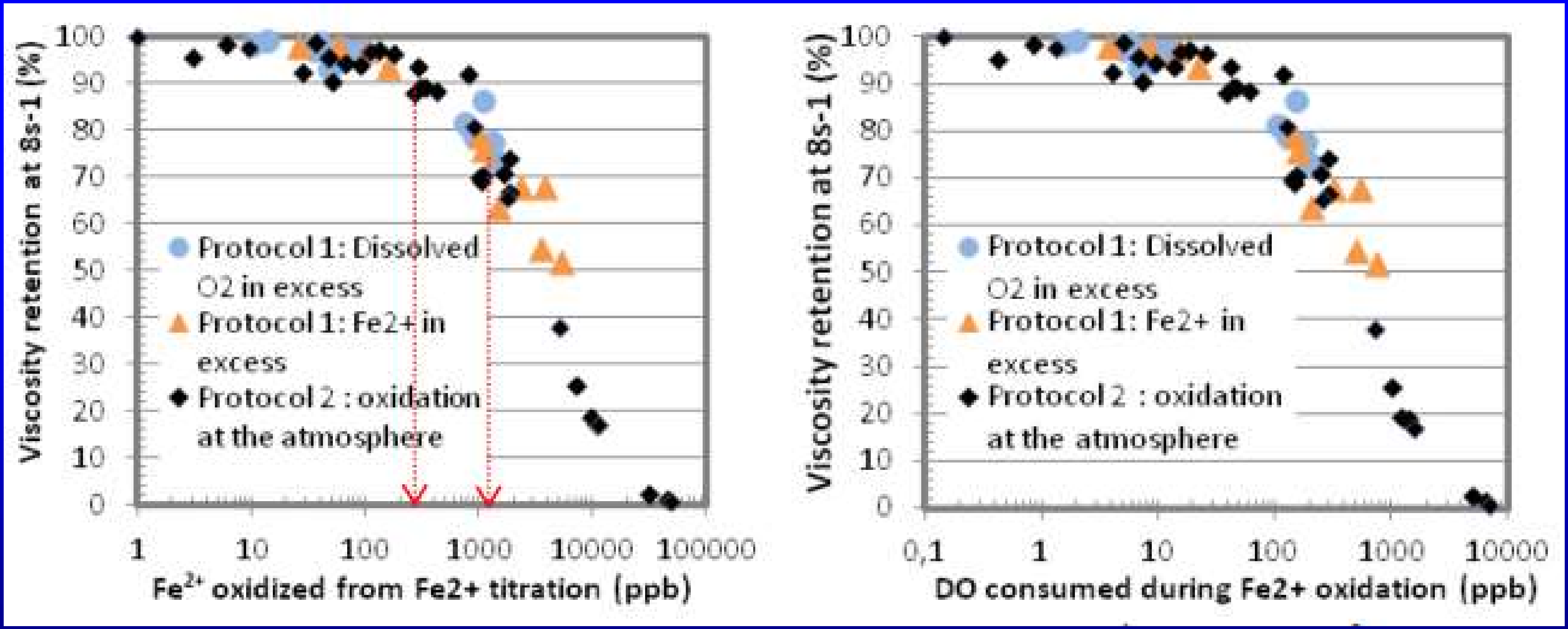
If iron is present, how much dissolved O_2 is acceptable?

Jouenne et al. (SPE 179614)

1. For temperatures below 50°C and if iron is present, dissolved oxygen should be < 40 ppb.
2. Iron-oxygen stoichiometry is governed by:

$$Fe^{2+} + \tfrac{1}{4}\, O_2 + H^+ \longrightarrow Fe^{3+} + \tfrac{1}{2}\, H_2O$$

$$[Fe^{2+}\ \text{(in ppm)}]\ /\ [O_2\ \text{(in ppm)}] = 7.$$



How destructive are free radicals?

1. Wellington (SPE 9296) suggested that one free radical could degrade MANY HPAM molecules.

2. In contrast, data from Shupe (SPE 9299), Yang & Treiber (SPE 14232) and Seright et al. (SPE 121460, SPE 169030) reveals that once the O_2 is consumed, no more HPAM degradation occurs.

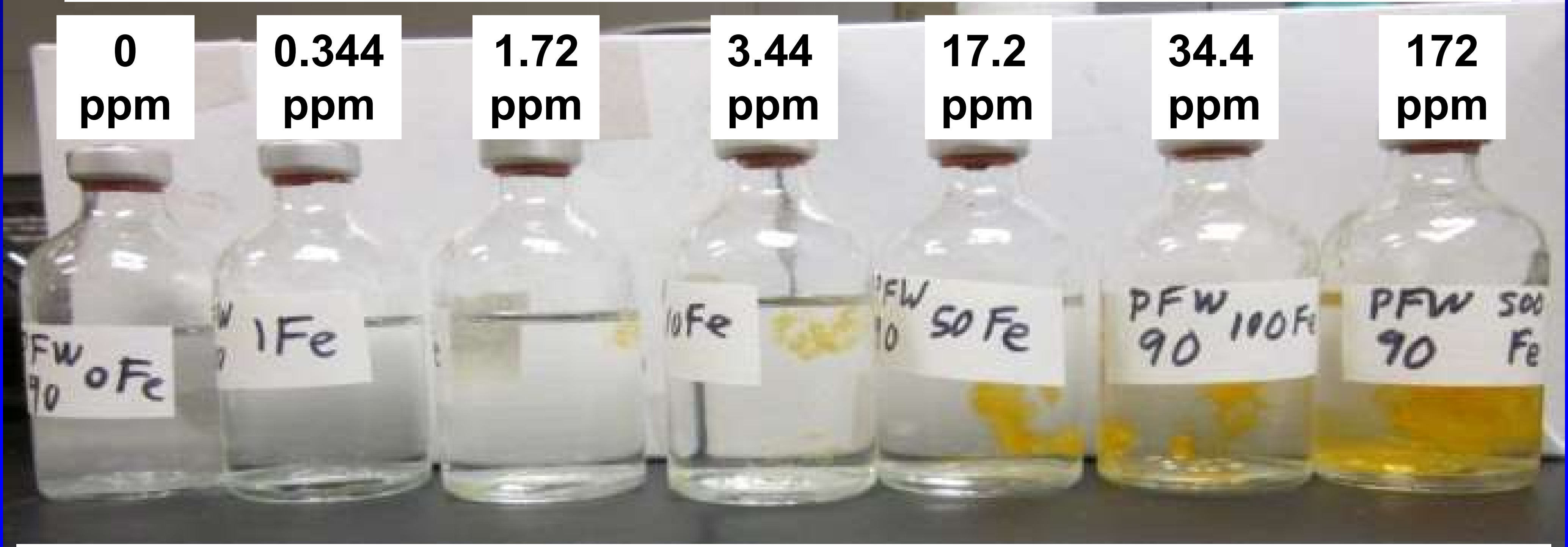
3. The data of Jouenne et al. (SPE 179614) indicates that over 400 free radicals are need to break the central bond in one HPAM molecule. 1 O_2 generates 1 free radical. 600 ppb O_2 halves the viscosity of 800 ppm 18×10^6 Mw HPAM. $[(6 \times 10^{-7})/32][(8 \times 10^{-4})/(18 \times 10^6)] = 422$.

Implications for Field Applications

1. If temperature is low and the water contains no Fe^{2+}, no oxygen removal is needed. Iron minerals in the formation will quickly (days) remove the oxygen.

2. If Fe^{2+} is present in the polymer make-up water, the water is probably oxygen-free at its source. Keeping the water oxygen free is the recommended approach—by preventing O_2 leaks, better design of fluid transfer, gas blanketing, gas stripping.

Concentration (in ppm) of Fe^{3+} added to 2000-ppm HPAM-ATBS in 11%-TDS brine, 10-ppb dissolved oxygen.



- Addition any concentration of Fe^{3+} to a polymer solution forms a gel.
- No gels formed during any of our studies with polymer and Fe^{2+}.
- Therefore, no Fe^{3+} formed during our studies with polymer and Fe^{2+}.

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$

$$Fe \rightarrow Fe^{2+} + 2e^-$$

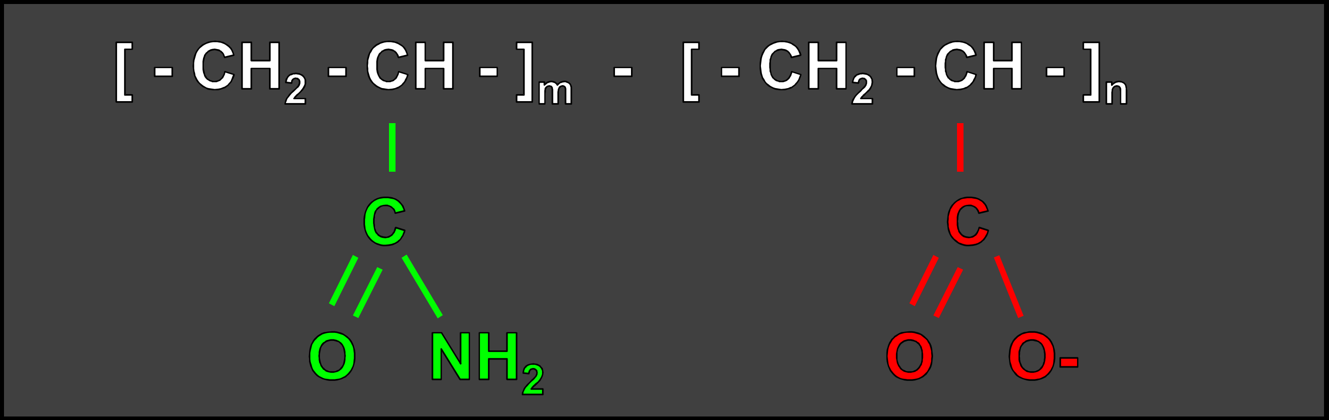
$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$

$$Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$$
$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$$

$$Fe(OH)_2 = FeO + H_2O$$
$$Fe(OH)_3 = FeO(OH) + H_2O$$
$$2FeO(OH) = Fe_2O_3 + H_2O$$

UPPER LIMIT OF TEMPERATURE STABILITY FOR POLYMERS (IF NO OXYGEN IS PRESENT)

What is the upper temperature limit for HPAM use in chemical EOR?



$$[-CH_2-\underset{\underset{O\quad NH_2}{\overset{|}{C}\,\,/\!/\ \backslash}}{CH}-]_m - [-CH_2-\underset{\underset{O\quad O^-}{\overset{|}{C}\,\,/\!/\ \backslash}}{CH}-]_n$$

- Above 60°C, acrylamide groups hydrolyze to form acrylate groups.
- If the degree of hydrolysis is too high and too much Ca^{2+} or Mg^{2+} is present, HPAM polymers precipitate.

Temperature, °C:	75	88	96	204
Max $Ca^{2+} + Mg^{2+}$, mg/L:	2000	500	270	20

(from Moradi-Araghi and Doe, 1987)

You can't stop hydrolysis of PAM or HPAM. At 80°C, hydrolysis will rise to ~60% after 100 days. (Moradi and Doe, Phillips, *SPERE* May 1987). Preventing >50% hydrolysis could be done by incorporating at least 50% AMPS or NVP (SPE 14233).

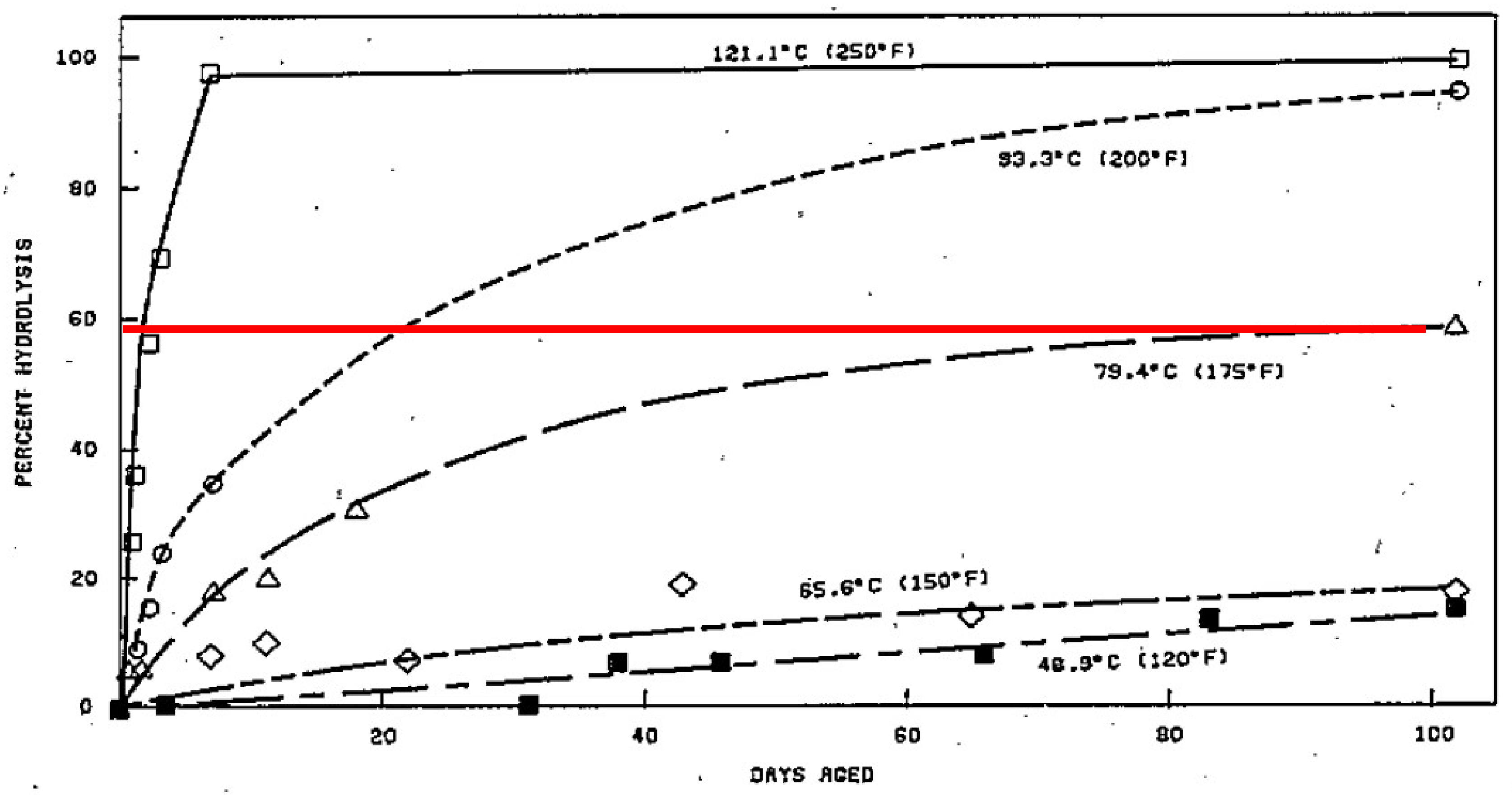


Fig. 13—The effect of temperature on the hydrolysis of 1,000-ppm originally unhydrolyzed Polyacrylamide A in 5% NaCl solution.

Recent paper on hydrolysis of HPAM: SPE 179558.

Approaches to mitigating HPAM precipitation:

1. A few hot reservoirs exist with low hardness.
2. Hydrolysis-resistant monomers (AMPS, NVP) can be incorporated into PAM polymers (Moradi-Araghi, Doe 1987). Need >50% NVP or AMPS. They tend to be expensive and less effective as viscosifiers.
3. Fresh water or low-hardness HPAM solutions can provide efficient sweep with minimum mixing with saline brines if polymer mobility is sufficiently low (Maitin 1992). Requires that mixing and cation exchange be understood and controlled.
4. Complex the hardness with chelating agents (Albonico and Lockhart, ENI, SPE 25220). Expensive. Must still prevent mixing with the formation water. May not provide any benefit over just using seawater.

WILL A CO/TER-POLYMER WITH AMPS OR NVP BE MORE STABLE THAN HPAM?

AMPS or NVP copolymers are more expensive, give lower Mw, and are less effective viscosifiers than HPAM.

However, some stability improvements can be expected, depending on composition: SPE 177073 (Gaillard et al.), SPE 141497 (Vermolen et al.).

AMPS or NVP copolymers with <45% AMPS/NVP will not be more stable (to O_2) than HPAM. [Doe, *SPERE* Nov. 1987; Parker and Lezzi, *Polymer* 34(23) 1993; Seright *SPEJ* June 2010].

Sandegen et al. *J. Petr. Sci. & Eng*. 158: 680-692.

1. Rise in pH seen during storage of HPAM/ATBS solutions is due to imide formation, not hydrolysis.
2. Hydrolysis reactions occur faster at lower pH values—so lab studies using unbuffered solutions may give overly optimistic estimates of hydrolysis rates in the field.

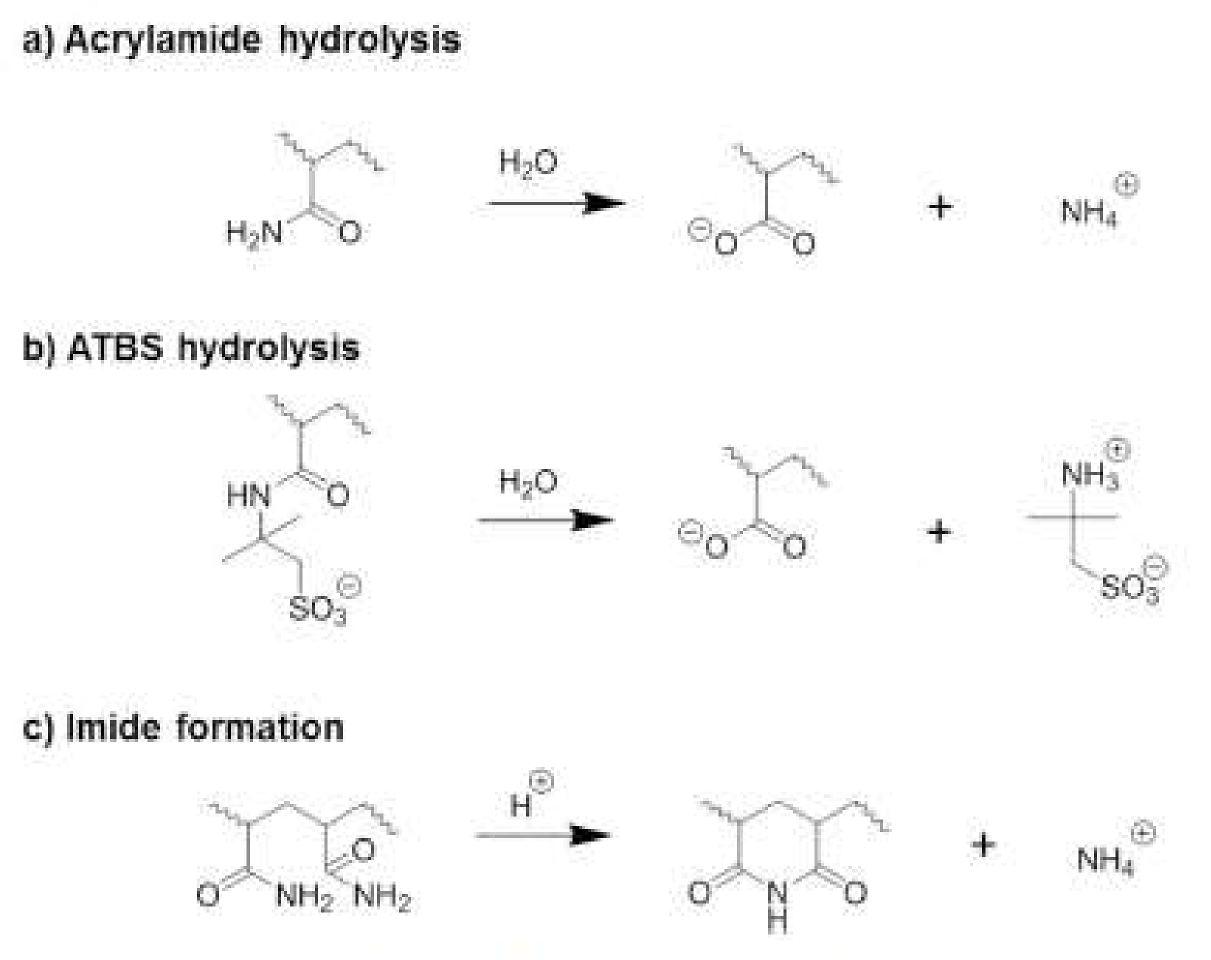


Fig. 1. Schematic of AM and ATBS conversion.

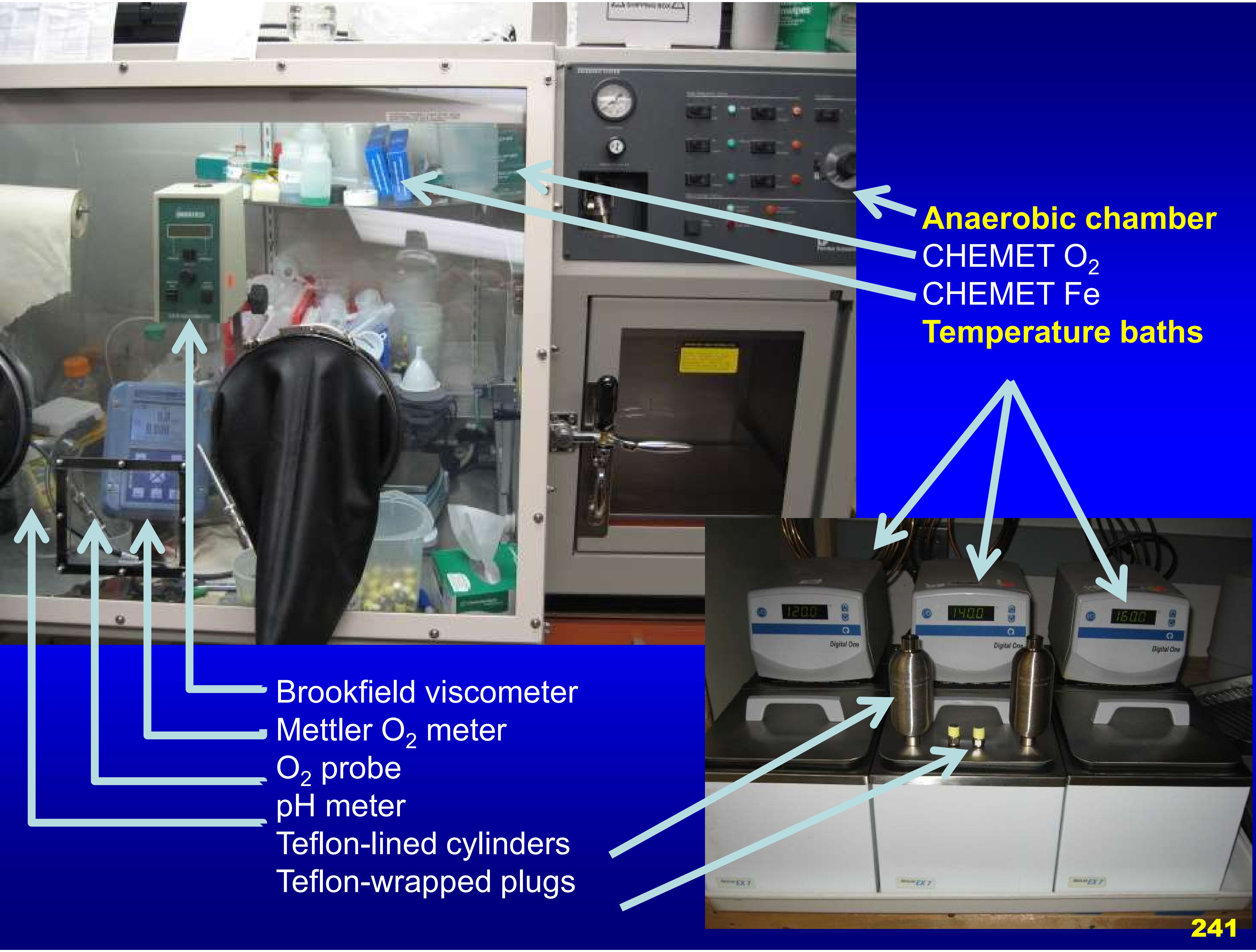
If divalent cations are not a problem, what is the upper temperature limit for HPAM use in EOR?

- Maximizing polymer stability requires minimizing oxygen contact.
- Most reservoirs produce water with no detectable dissolved oxygen.
- Oxygen-free EOR solutions can readily be prepared in the field by (1) preventing leaks, (2) gas blanketing tanks and mixing facilities, (3) gas stripping if necessary, (4) adding chemical oxygen scavengers if necessary.

Lab record to date: Shupe (1981) reported a 13% viscosity loss after 250 days at 105°C when a chemical oxygen scavenger was used.

Preparing, Storing, and Studying O_2-Free Polymer Solutions in the Laboratory. Our Method:

- Prepare solutions in an anaerobic chamber with 10% H_2 + 90% N_2 circulated through Pd catalyst.
- O_2 levels measured to <0.001% in the chamber atmosphere and to <0.1 ppb in solution.
- Brine reduced to <0.1 ppb O_2 by bubbling chamber gas into the brine (requires ~ 1 hour).
- Polymer stored and mixed in the chamber.
- Solutions sealed in 150 ml teflon-lined cylinders.
- Solutions stored in 120°C-180°C baths outside the anaerobic chamber.
- Viscosity at 7.3 s^{-1}, O_2, and pH measured inside the anaerobic chamber (at 25°C).



Anaerobic chamber

CHEMET O_2

CHEMET Fe

Temperature baths

Brookfield viscometer

Mettler O_2 meter

O_2 probe

pH meter

Teflon-lined cylinders

Teflon-wrapped plugs

New Features of Our Method:

- Uses a new oxygen meter that measures to 0.1 parts per billion (ppb) in solution.
- Confirmed that our solutions were prepared with <0.1 ppb O_2 and maintained at this level throughout the study.
- No need for chemical oxygen scavengers.

Advantage of our method over previous methods:

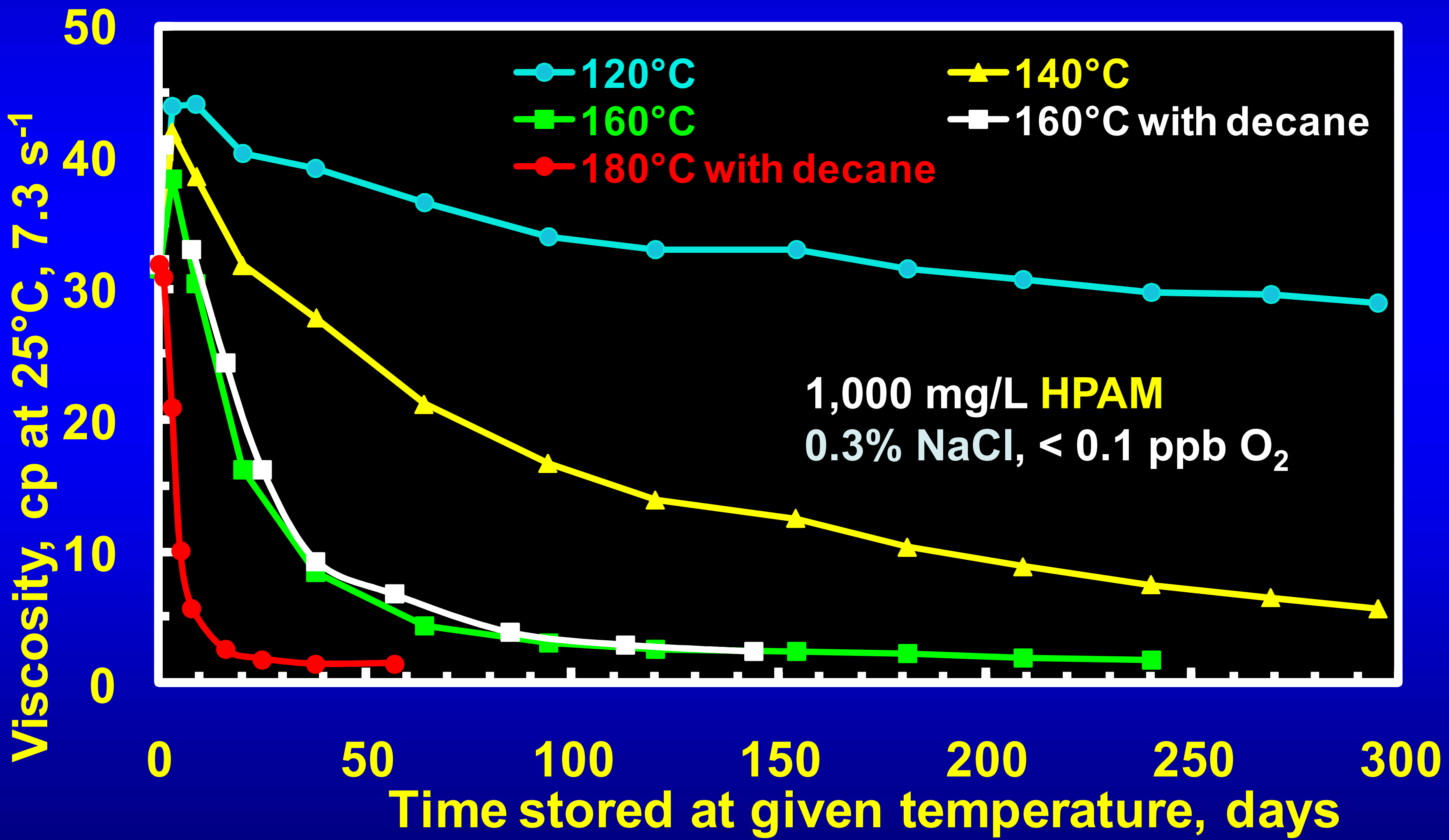
- Measure viscosity, dissolved O_2, and pH on the SAME sample throughout the study.

Disadvantage:

- If the storage cylinder leaks, the sample is lost.

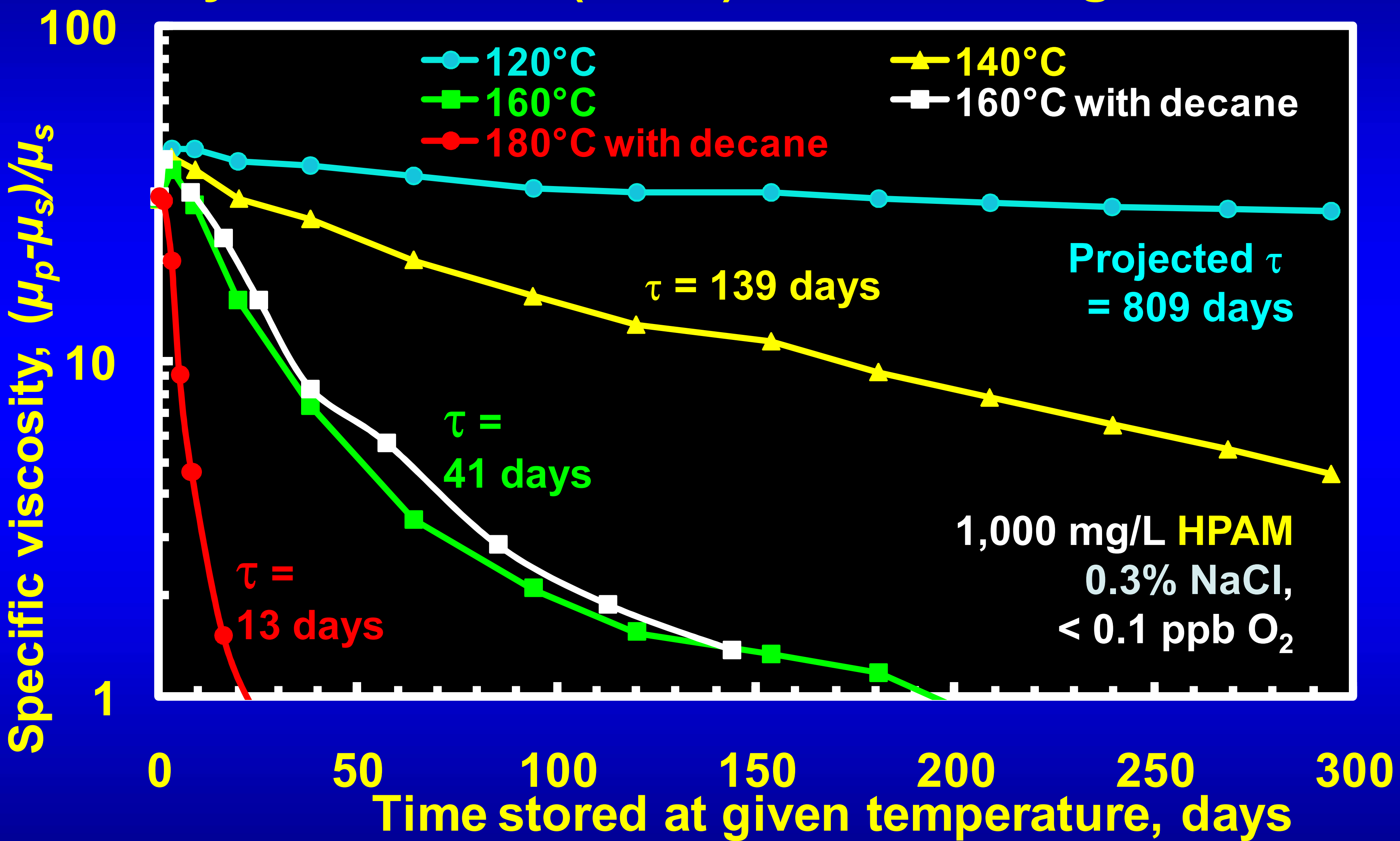
Time/Temperature Behavior of Polymer Stability

- Stability must be studied EITHER at reservoir temperature for MANY years OR at several temperatures and use an Arrhenius analysis.

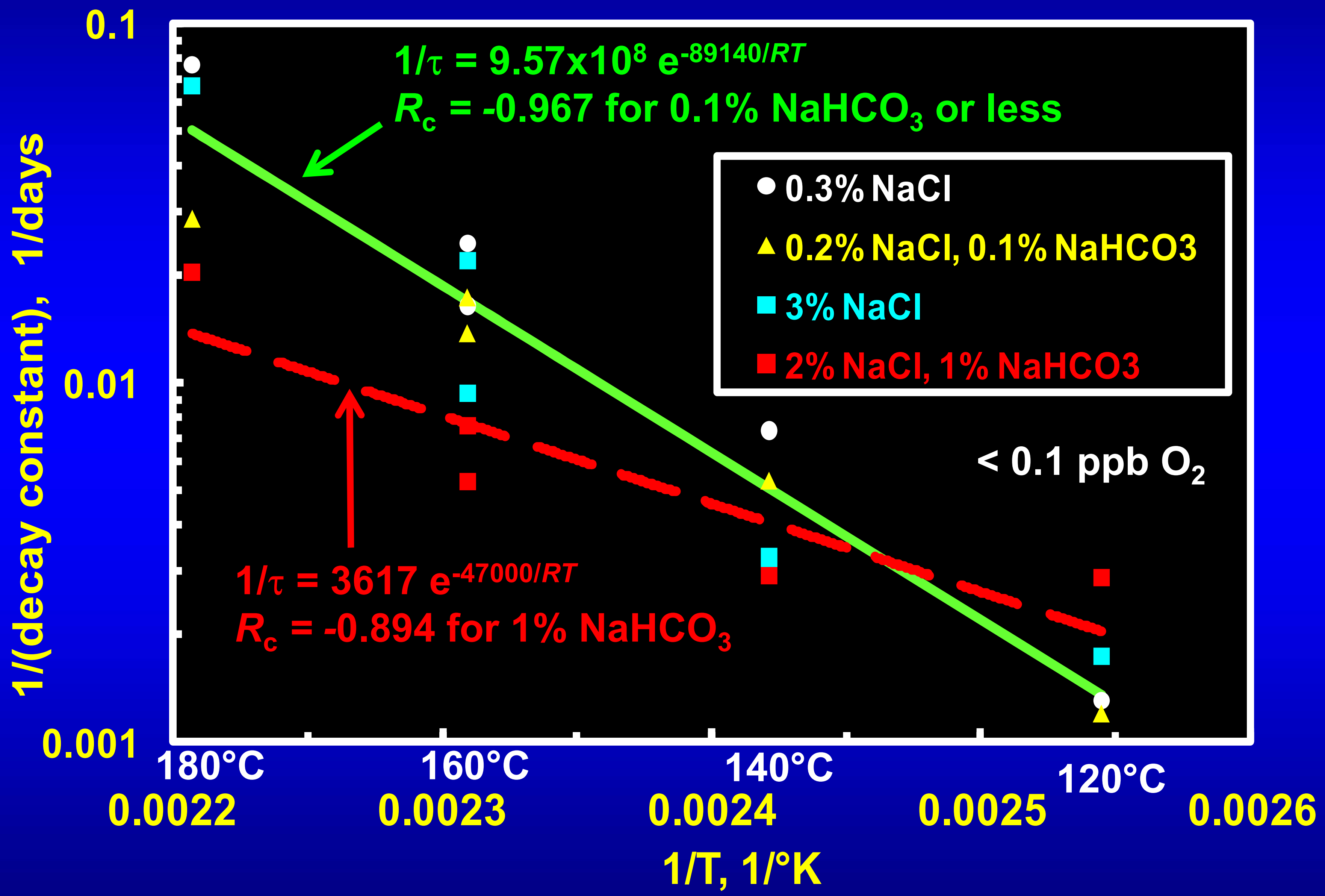


1,000 mg/L HPAM
0.3% NaCl, < 0.1 ppb O_2

Viscosity decay constant, τ, is the time for the specific viscosity to fall to 1/*e* (0.368) times the original value.



Arrhenius Analysis for HPAM



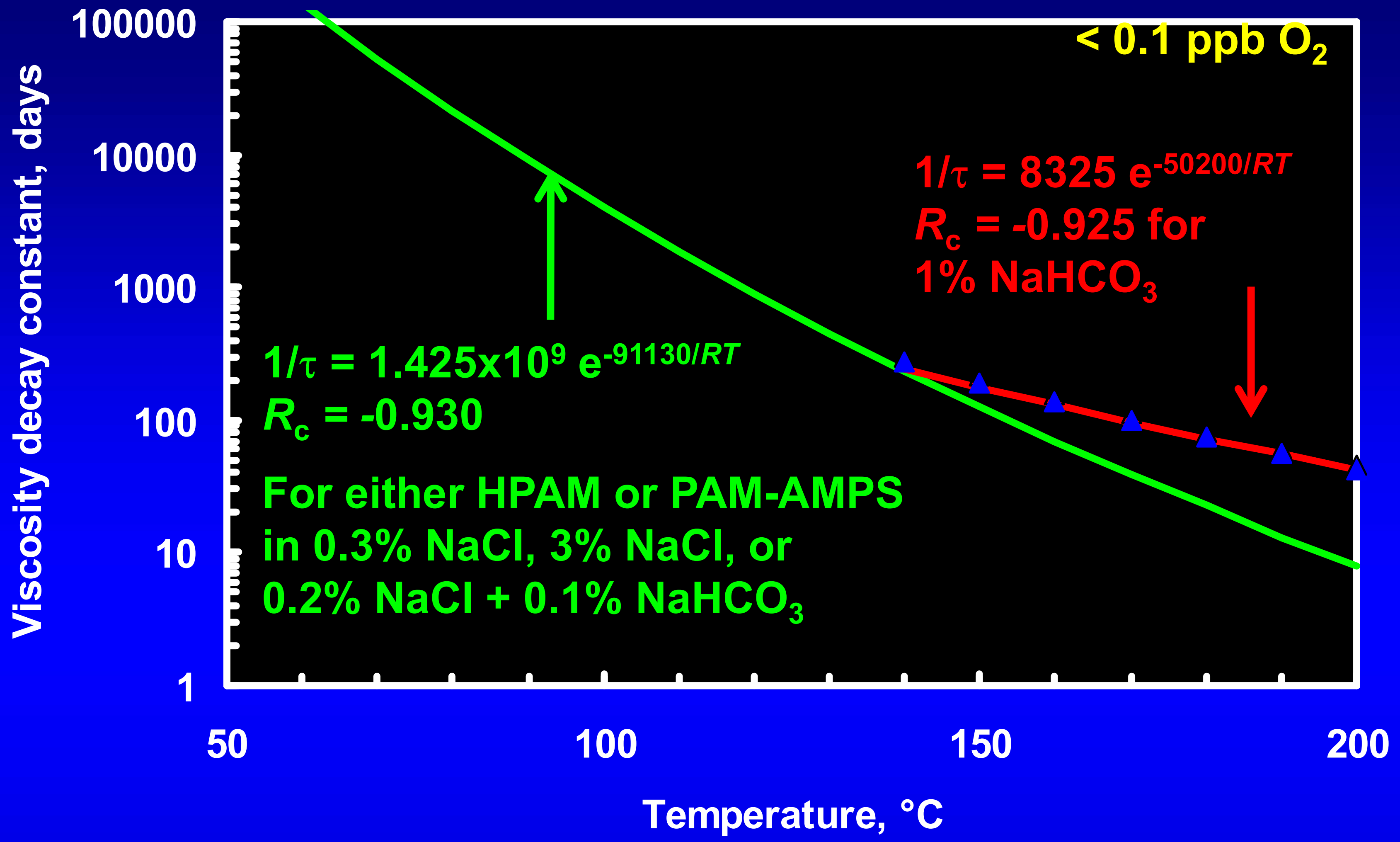
$1/\tau = 9.57\times10^{8}\ e^{-89140/RT}$

R_c = -0.967 for 0.1% $NaHCO_3$ or less

$1/\tau = 3617\ e^{-47000/RT}$

R_c = -0.894 for 1% $NaHCO_3$

< 0.1 ppb O_2



< 0.1 ppb O_2

$1/\tau = 8325\ e^{-50200/RT}$
$R_c = -0.925$ for
1% $NaHCO_3$

$1/\tau = 1.425\times10^9\ e^{-91130/RT}$
$R_c = -0.930$

For either HPAM or PAM-AMPS
in 0.3% NaCl, 3% NaCl, or
0.2% NaCl + 0.1% $NaHCO_3$

- A given viscosity level can be predicted using: $\mu/\mu_o = e^{-t/\tau}$
- Viscosity half-lives for HPAM and PAM-AMPS solutions projected to be ~8 yrs at 100°C and ~2 yrs at 120°C.

CONCLUSIONS (SPE 121460)

By reaction with oil and pyrite, dissolved O_2 will be removed quickly from injected waters and will not propagate very far into the porous rock of a reservoir. Any dissolved O_2 that entered the reservoir prior to polymer injection will have been consumed and will not aggravate polymer degradation. If an O_2 leak develops during the course of polymer injection, that O_2 will not compromise the stability of the polymer that was injected before the leak developed or the polymer that is injected after the leak is fixed. Polymer that is injected while the leak is active will be susceptible to oxidative degradation. Maintaining dissolved oxygen at undetectable levels is necessary to maximize polymer stability. This can readily be accomplished without the use of chemical oxygen scavengers or antioxidants.

THERMAL, CHEMICAL, & BIO-DEGRADATION

- **Both HPAM and xanthan are very susceptible to oxidative degradation. Fortunately, most reservoirs contain no free oxygen.**
- **HPAM's C-C main chain is very resistant to thermal breaking if O_2 or free radicals are absent.**
- **Xanthan's C-O main chain is susceptible to hydrolysis above 70°C.**
- **HPAM's amide groups are susceptible to hydrolysis above 60°C, leading to polymer precipitation if Ca^{2+} or Mg^{2+} are present.**
- **HPAM is much more resistant to bio-degradation than xanthan.**

At 80°C, xanthan may have sufficient stability if the pH = 7-9, and O_2 = 0. (Seright & Henrici *SPERE* 1990).

TABLE 2—EFFECT OF DISSOLVED OXYGEN ON XANTHAN STABILITY*

Temperature (°C)	Viscosity Half-Life (days) <2 ppb O_2	Viscosity Half-Life (days) 50 ppb O_2
64	> 1,000	225
80	500	33
96	70	15
120	5	1

*1,500 ppm Xanthan B, 3% NaCl, 0.3% $CaCl_2$, $\overline{pH}$ = 5, stored in glass.

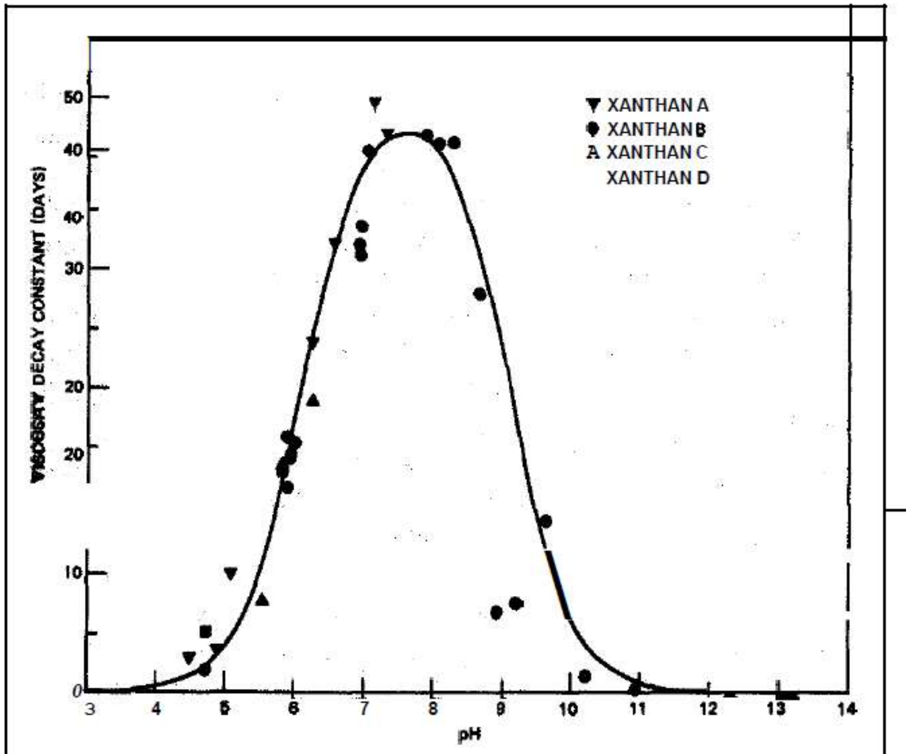


Fig. 4—Effect of pH on xanthan stability at 120°C: 1,500 ppm xanthan, 500 ppm $Na_2S_2O_4$, <2 ppb O_2, salt normality = 0.567 eq/L. Solid curve assumes that $\tau = 1/(0.02 + 25{,}000 [H^+] + 1{,}500 [OH^-])$.

Xanthan stability at pH = 7-9 is much better than a pH=5.

Xanthan may be worth considering because you don't have to worry about mixing in the reservoir.

SPE-200324

Stability and Behavior in Carbonate Cores for New EOR Polymers at Elevated Temperatures in Hard Saline Brines

Target Formation for a Potential Polymer Flood

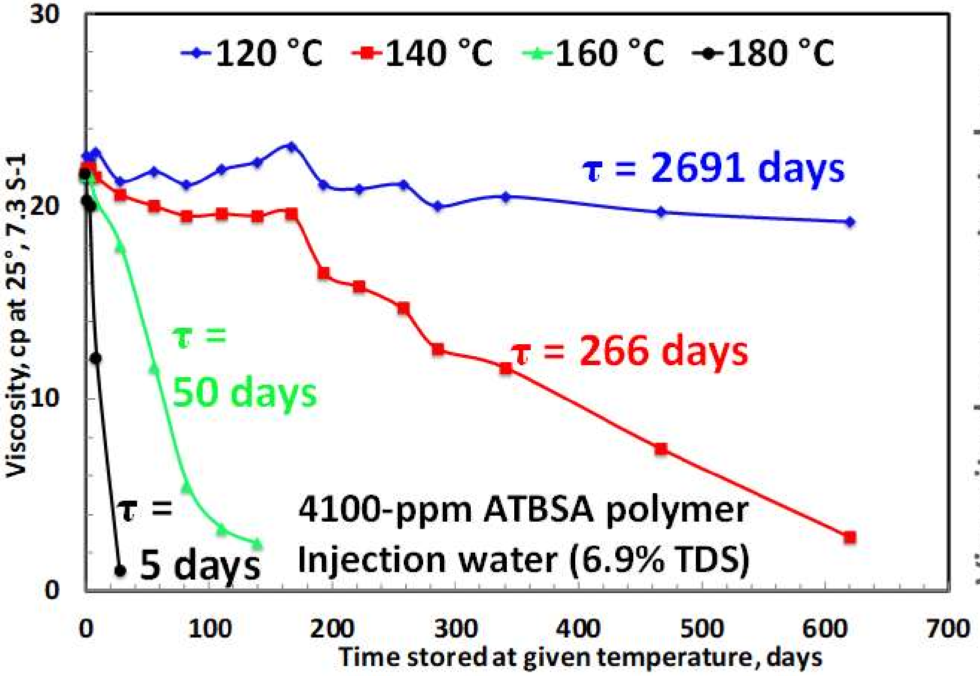
- 99˚C. Carbonate rock.
- 1-2 km well spacing: 17-34-year inter-well transit time.
- Formation water: 24.36% TDS, 2.16% hardness.
- Injection water: 6.90% TDS, 0.34% hardness.
- Smart water: 0.69% TDS, 0.034% hardness.

Will polymers be stable for 17 years at 99°C?

Will polymers provide acceptable retention, injectivity, rheology, and resistance to degradation in carbonate cores at 99°C?

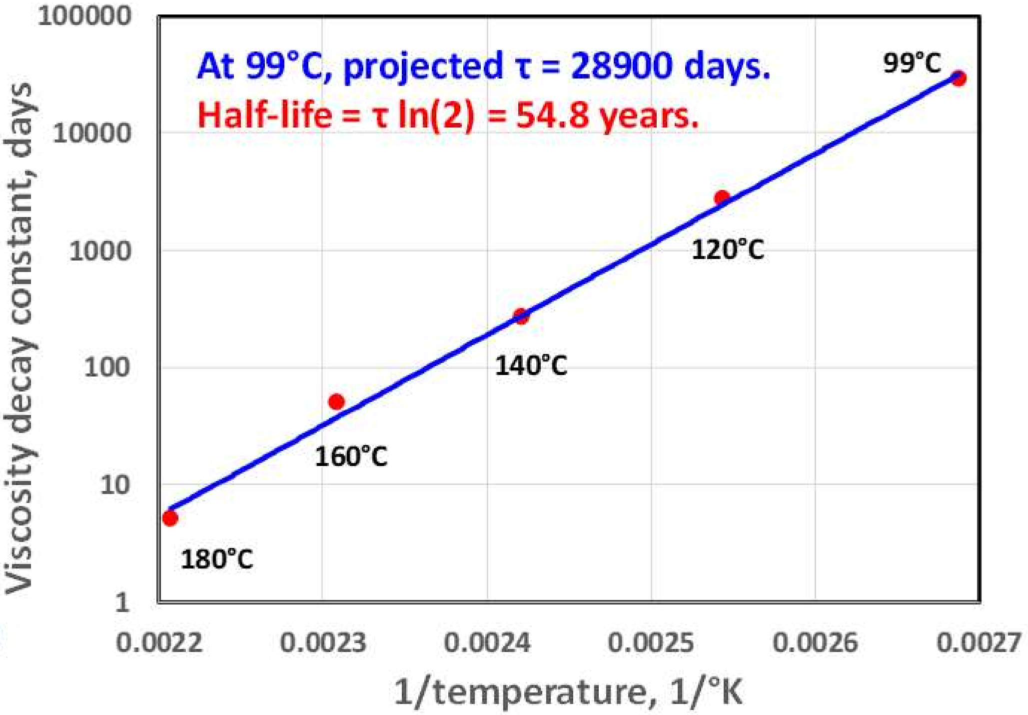
Arrhenius Analysis:

$(\mu-\mu_s)/(\mu_o-\mu_s) = A_1 \exp(-t/\tau)$



4100-ppm ATBSA polymer
Injection water (6.9% TDS)

$1/\tau = A_2 \exp[-E/(RT)]$



At 99°C, projected τ = 28900 days.
Half-life = τ ln(2) = 54.8 years.

Three ATBS Polymers

Average projected half-life at 99°C: 79 years ± 30 years.

Average projected half-life at 120°C: 5.6 years ± 1.7 years.

Stability fairly insensitive to salinity and hardness.

Polymer	Water TDS, %	120ºC τ, days	140ºC τ, days	160ºC τ, days	180ºC τ, days	Projected half-life at 99°C, years
ATBSA	0.69	2595	266	40	5	61
ATBSA	6.9	2691	266	50	5	55
ATBSA	24.3	1947	400	37	9	67
ATBSB	0.69	3942	350	30	6	63
ATBSB	6.9	3990	462	16	7	133
ATBSB	24.3	4359	200	18	1	127
ATBST	0.69	2097	113	17	6	68
ATBST	6.9	2583	292	20	8	58
ATBST	24.3	2390	420	12	6	82

Three other polymers with lower ATBS content.

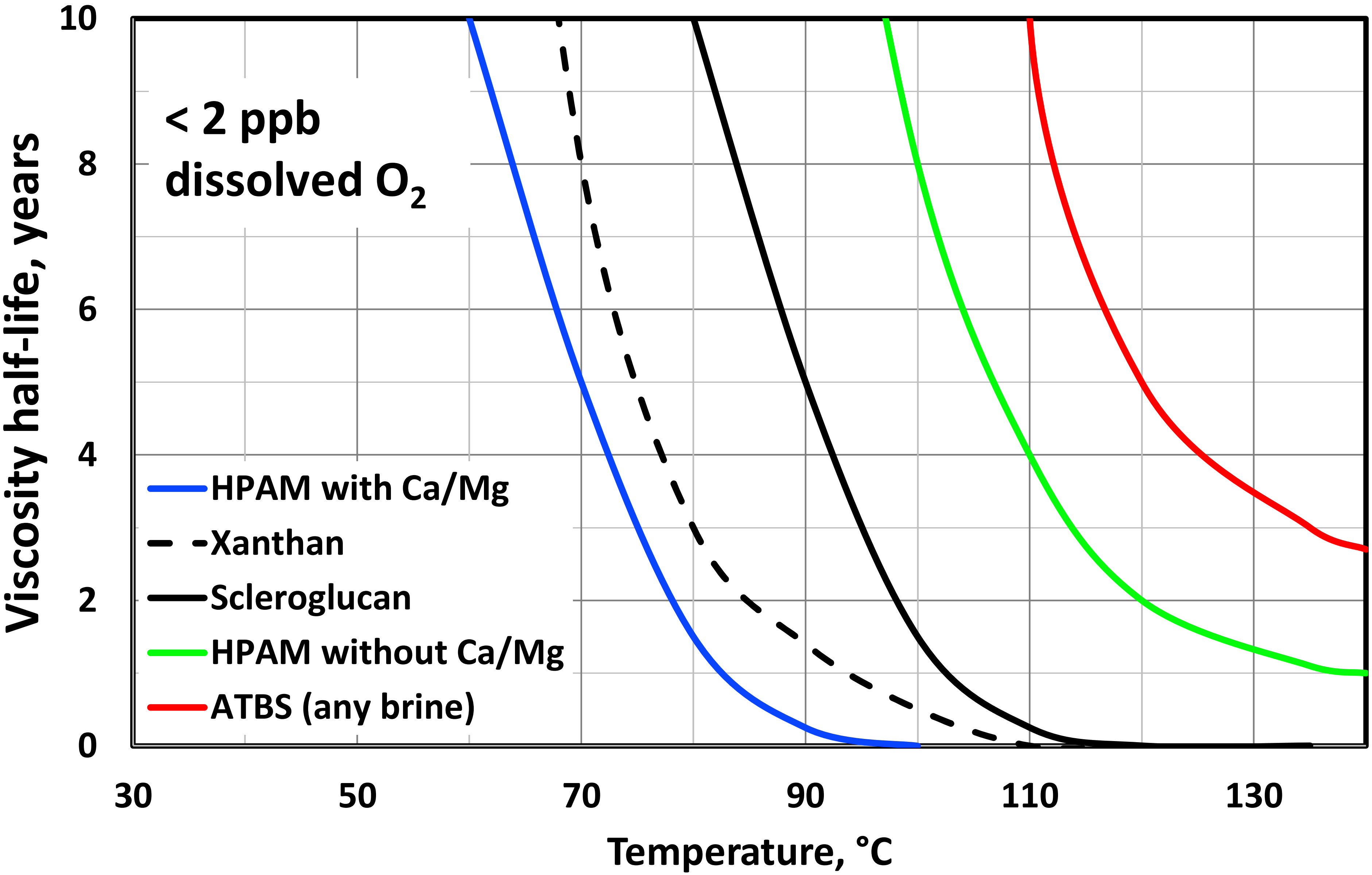
Stability is much less and is more sensitive to salinity.

Polymer	Water TDS, %	120°C τ, days	140°C τ, days	160°C τ, days	180°C τ, days	Projected half-life at 99°C, years
ATBS8A	0.69%	306	49	12	3	4.1
ATBS8A	6.9%	265	42	10	3	3.6
ATBS8A	24.4%	287	55	11	5	4.5
ATBS8B	0.69%	209	30	5	2	3.6
ATBS8B	6.9%	124	15	5	3	1.4
ATBS8B	24.4%	36	23	3	2	0.4
AMNVPATBS1	0.69%	438	410	238	3	1.3
AMNVPATBS1	6.9%	17.4	3.2	1.0	0.7	0.1
AMNVPATBS1	24.4%	8.6	3.1	0.9	0.7	0.1

NVP-based polymer, hydrophobic-associative polymers and scleroglucan were also less stable.

Polymer	Water TDS, %	120ºC τ, days	140ºC τ, days	160ºC τ, days	180ºC τ, days	Projected half-life at 99°C, years
NVP1	0.69%	864	633	368	186	3.5
NVP1	6.9%	839	570	350	149	3.7
NVP1	24.4%	689	197	68	31	5.0
HYASA	0.69%	635	436	247	126	2.6
HYASA	6.9%	633	371	236	23	2.2
HYASA	24.4%	634	157	59	19	5.4
HYASB	0.69%	519	432	258	57.5	3.3
HYASB	6.9%	90.1	56.0	25.0	5.0	0.8
HYASB	24.4%	21.0	4.6	2.2	0.8	0.3
SG1	0.69%	50	0.3	0.2	0.2	2
SG1	6.9%	20	2	0.2	0.2	1
SG1	24.4%	20	2	0.2	0.2	1

New EOR Polymer (ATBS) Could Allow EOR at 120°C



SPE 146087

A COMPARISON OF POLYMER FLOODING WITH IN-DEPTH PROFILE MODIFICATION