BASIC PROPERTIES OF GELANTS AND GELS

A FEW OF THE HUNDREDS OF GEL SYSTEMS

Cr(III) acetate with high-Mw HPAM (Marcit CT)
Cr(III) acetate with low-Mw HPAM (Maraseal)
Cr(III) propionate HPAM (Aquatrol IV, Matrol III)
Cr(III) lactate/carboxylate HPAM. Cr(III) malonate HPAM
Preformed Particle Gels (PPG)
Nanoparticles (Nanospheres)

Silicates (Injectrol, Zonelock, Pemablock, Siljel V, Silica-Polymer-Initiator)
Sodium silicate + aminopropyltriethoxysilane (Smart Sealant)
In situ polymerization of acrylamides, acrylates, or derivatives (k-Trol, Permseal)
Polyethyleneimine with t-butylacrylate/acrylamide copolymers (H2Zero)

HCHO or HMTA and phenolic/hydroquininone crosslinkers with PAM co- and terpolymers (Phillips and Unocal processes,Unogel, Organoseal, Multigel)

Crosslinked AMPS, NVP, acrylamide/acrylate co & terpolymers (HE)

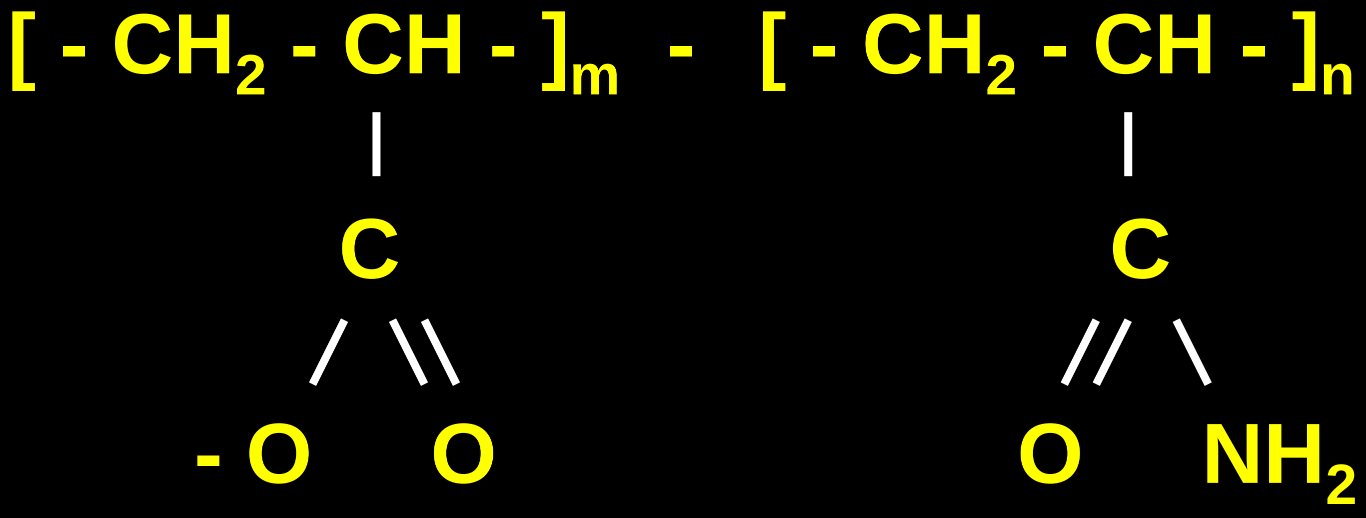
Amphoteric polymers and terpolymers (WOR-Con, Aquatrol I, AquaCon)
Hydrophobically modified polyDMAEMA (WaterWeb, CW-Frac)
Crosslinked expandable polymeric microparticles (Bright Water)

Al-citrate/HPAM (BP North Slope process)
Al-citrate/HPAM/CPAM (Cat-An, colloidal dispersion gel)
$AlCl_3/OH^-$ (DGS or Delayed Gelation System)
$Fe(OH)_3$ (Hungarian precipitation process)

WHY CHOOSE ONE MATERIAL OVER ANOTHER?

- Cost
- Availability
- Sensitivity of performance to condition or composition variations
- Blocking agent set time
- Permeability reduction provided to water
- Permeability reduction provided to oil or gas
- Ability to withstand high-pressure gradients in porous rock
- Ability to withstand high-pressure gradients in fractures or voids
- Rheology and/or filtration properties
- Ability to penetrate into fractures or narrow channels behind pipe
- Stability at elevated temperatures
- Environmental concerns

“Polyacrylamide” or “HPAM” Polymers

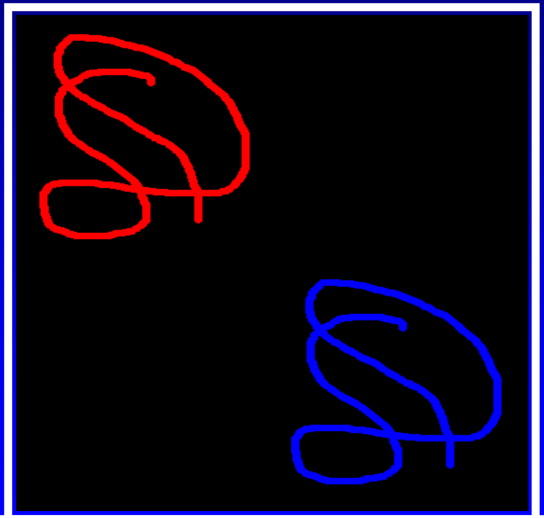


$$[-CH_2-CH-]_m - [-CH_2-CH-]_n$$

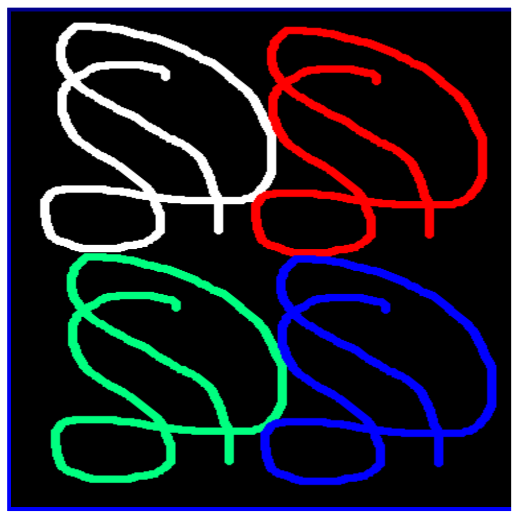
acrylate acrylamide

- “degree of hydrolysis” = m / (n + m)
- For high M_w polymers: n ≈ 90,000, m ≈ 5,000 to 10,000
- Monomers are randomly positioned along the polymer chain

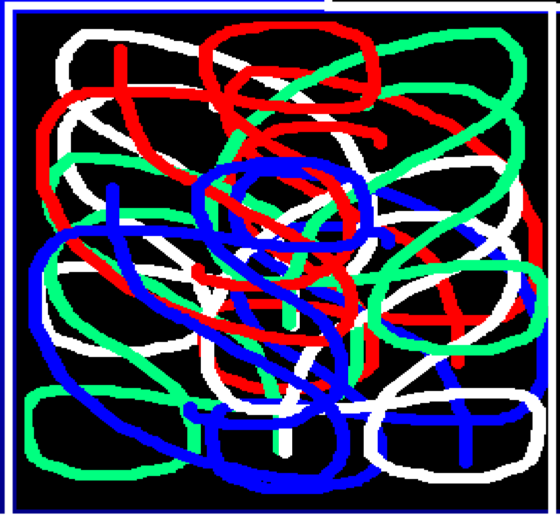
CRITICAL OVERLAP CONCENTRATION – C*



DILUTE SOLUTION: C < C*

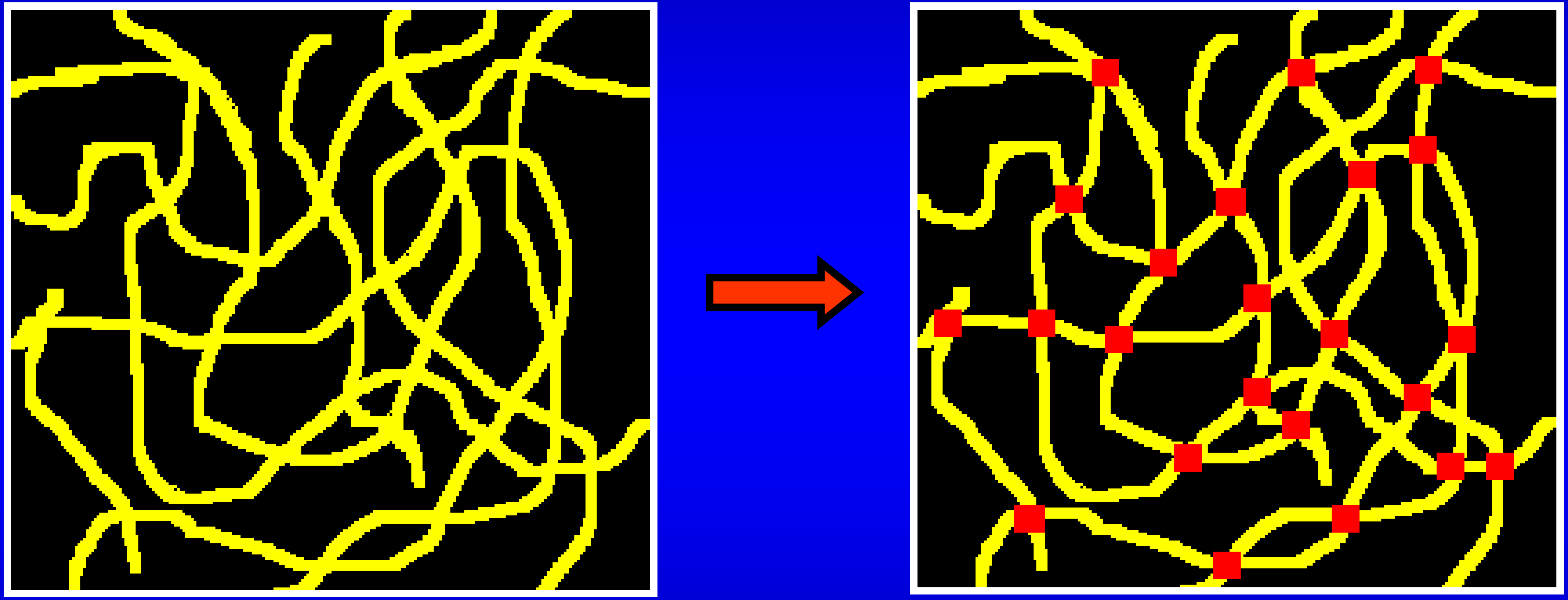


TOTAL POLYMER VOLUME = TOTAL SOLUTION VOLUME: C = C*



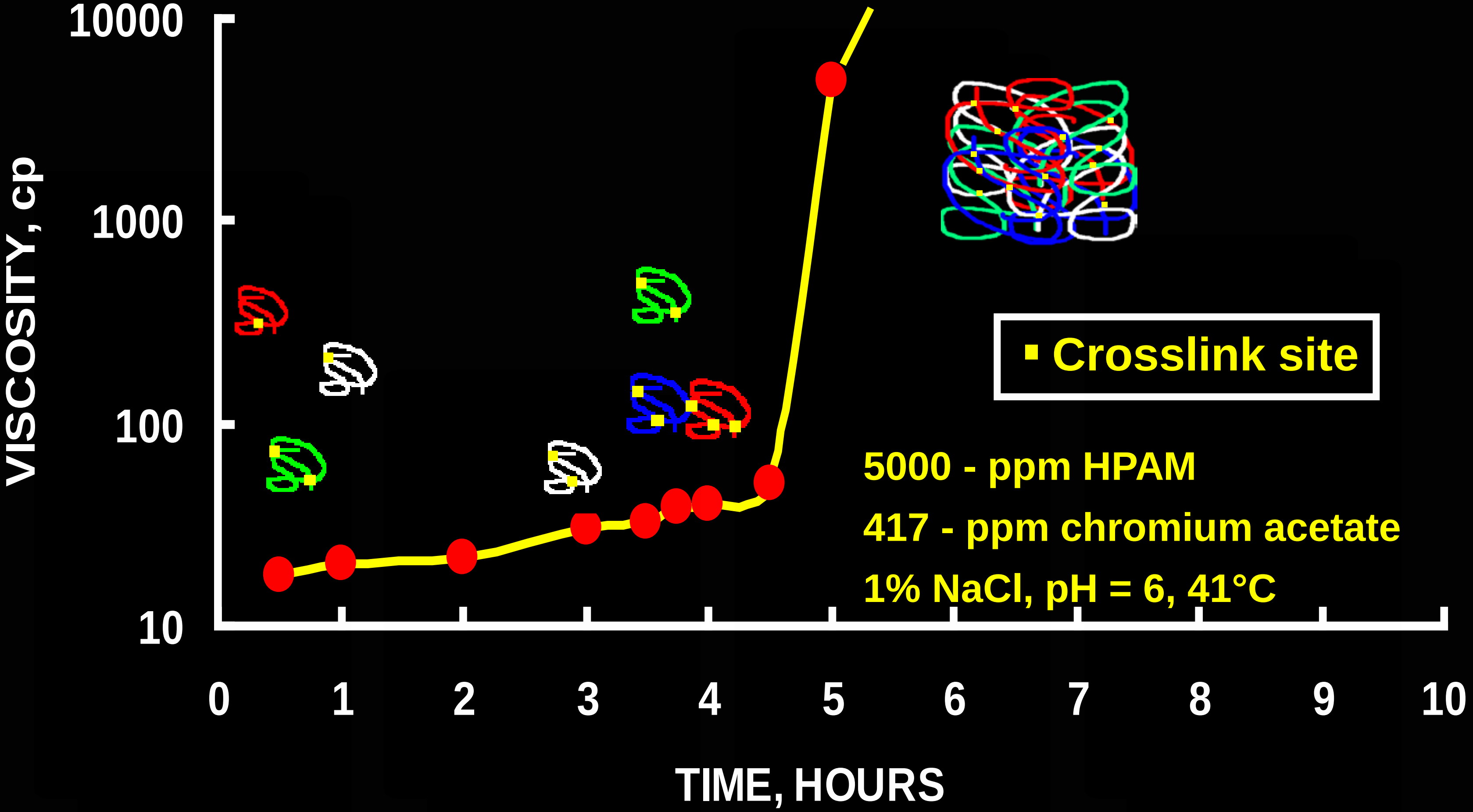
POLYMERS INTERTWINE: C > C*

POLYMER CROSSLINKING



🟥 **Crosslink site**

VISCOSITY VERSUS TIME DURING GELATION



5000 - ppm HPAM

417 - ppm chromium acetate

1% NaCl, pH = 6, 41°C

GELANTS VERSUS GELS

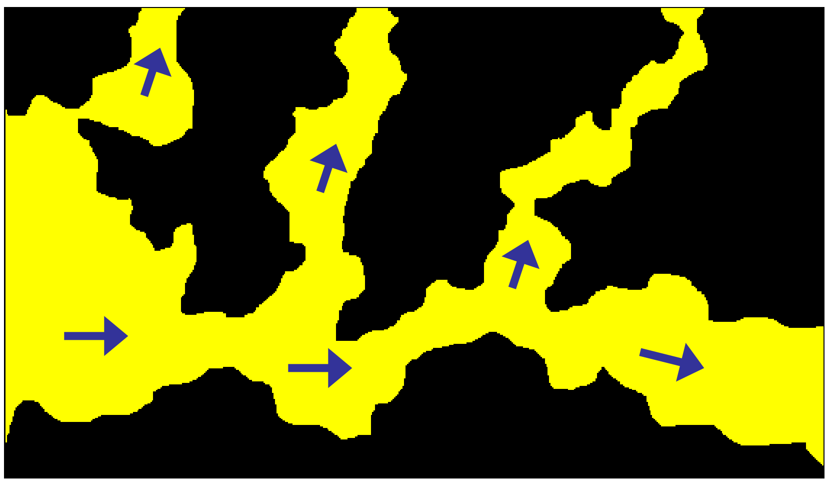
Polymer Solution [e.g., HPAM] + Crosslinking Agent [e.g., Cr(III)] = Gelant

In a gelant, few crosslinks have been made. Gelants can flow into porous rock just like uncrosslinked polymer solutions.

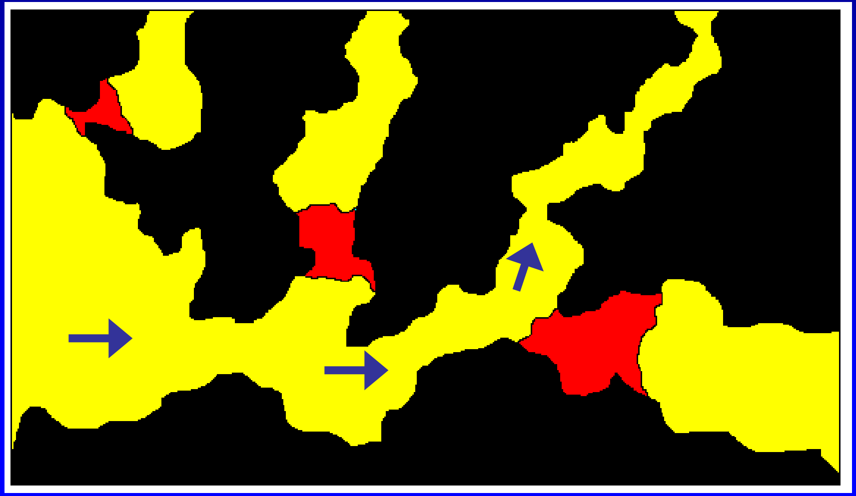
$$\text{Gelant} \xrightarrow[\text{(e.g. } \sim \text{ 5 hrs)}]{\text{time}} \text{Gel}$$

Gels are 3-dimensional crosslinked structures that will not enter or flow through porous rock.

GELANTS FLOW THROUGH POROUS ROCK; GELS DO NOT



Gelant flows freely like a polymer solution

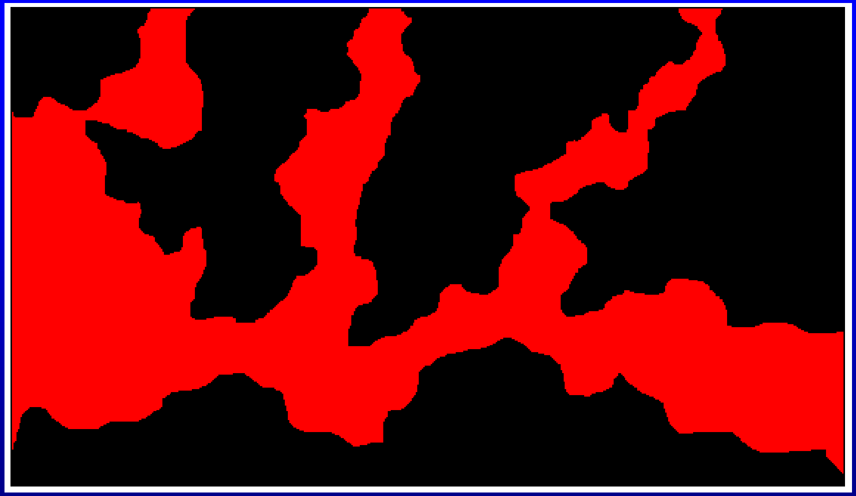


Partial gel formation

🟨 MOBILE GELANT

🟥 IMMOBILE GEL

→ FLOW DIRECTION



Gel filling all aqueous pore space

PROPERTIES OF AVAILABLE GELANTS/GELS

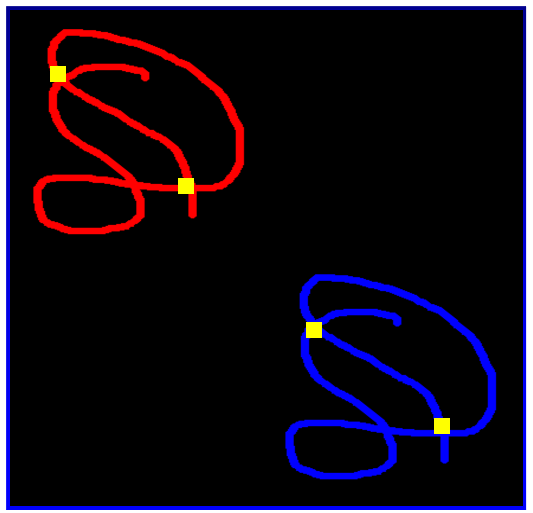
1. Early in the gelation process, gelants penetrate readily into porous rock.

2. After gelation, gel propagation through porous rock is extremely slow or negligible.

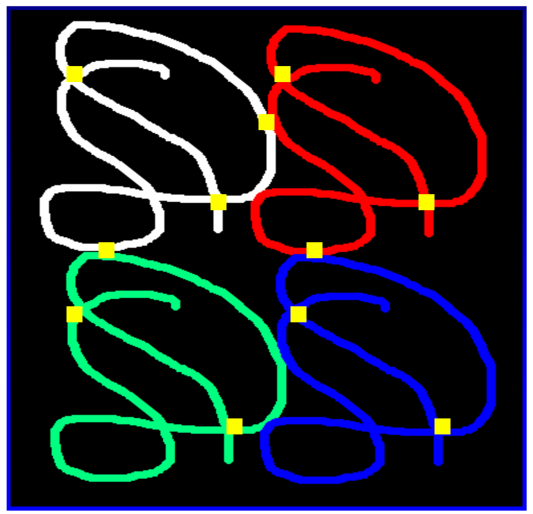
3. The transition between these two conditions is usually of short duration.

SPERE (Nov. 1993) 299-304; *IN SITU* 16(1) (1992) 1-16; and *SPEPF* (Nov. 1995) 241-248.

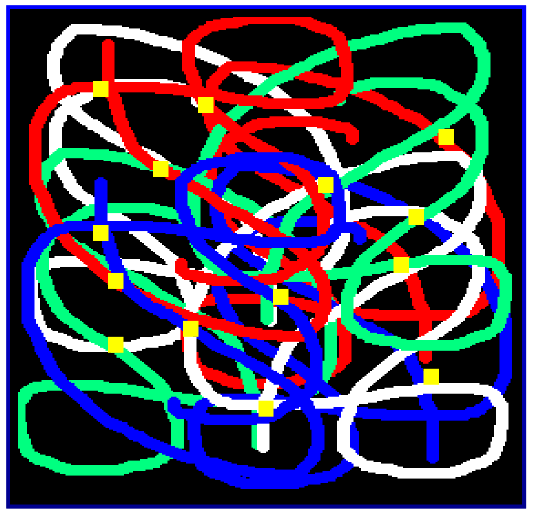
GELATION DEPENDS ON POLYMER CONCENTRATIONS



C < C*: No gelation



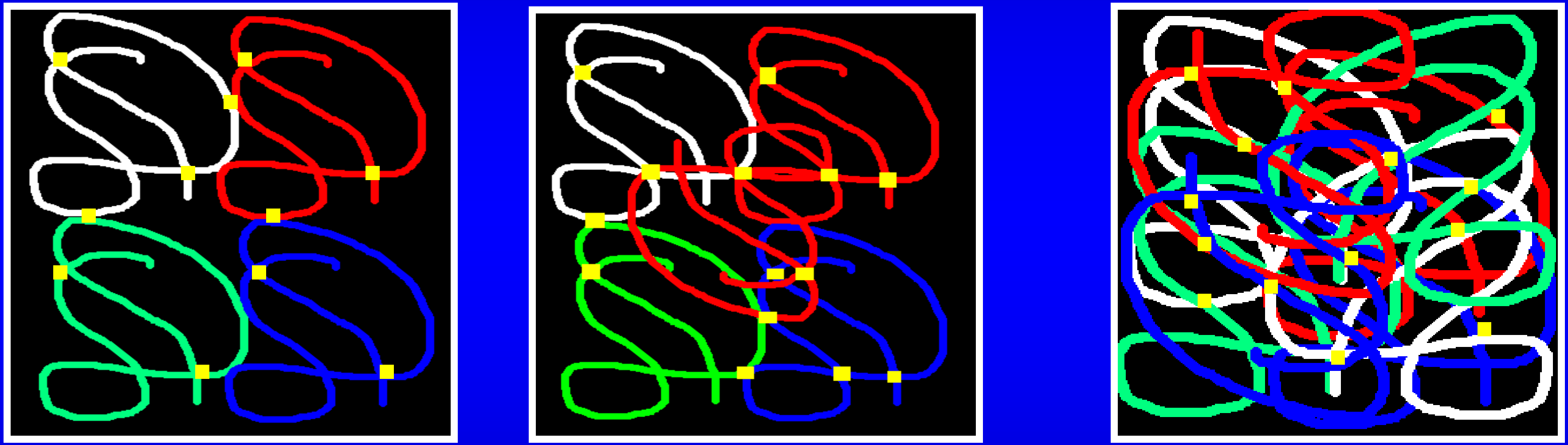
C ≈ C*: Gelation may or may not occur



■ **Crosslink site**

C >> C*: Best opportunity for 3D gel formation

ABOVE C*, HIGHER CONCENTRATIONS OF POLYMER STRENGTHEN THE GEL



Low gel strength

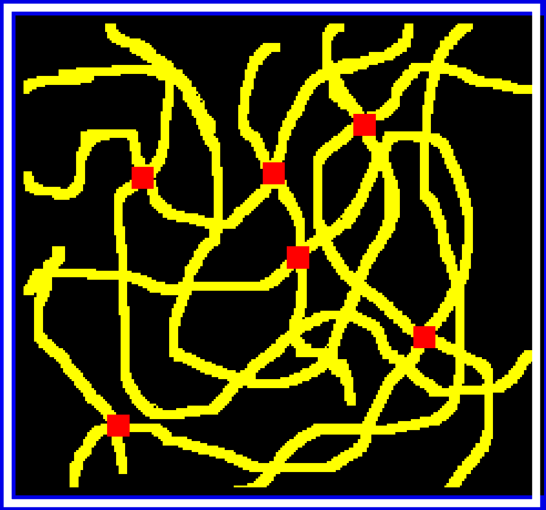
Intermediate gel strength

Strong gel

▪ **Crosslink site**

UP TO A POINT, CROSSLINK DENSITY AFFECTS GEL STRENGTH

Viscous Fluid

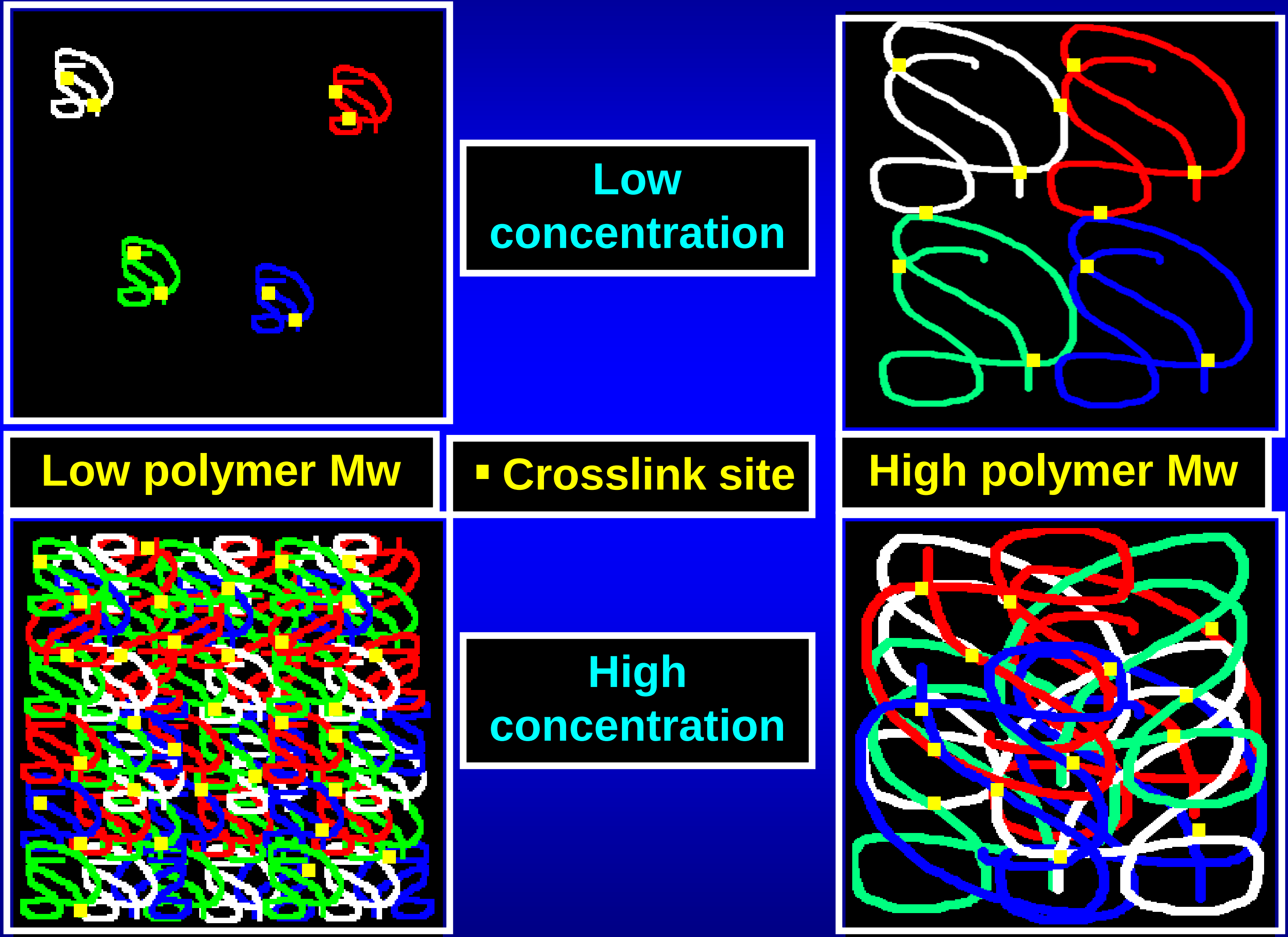


Low gel strength

Strong gel

🟥 **Crosslink site**

HIGHER Mw POLYMERS REQUIRE LOWER CONCENTRATIONS FOR 3D GEL FORMATION



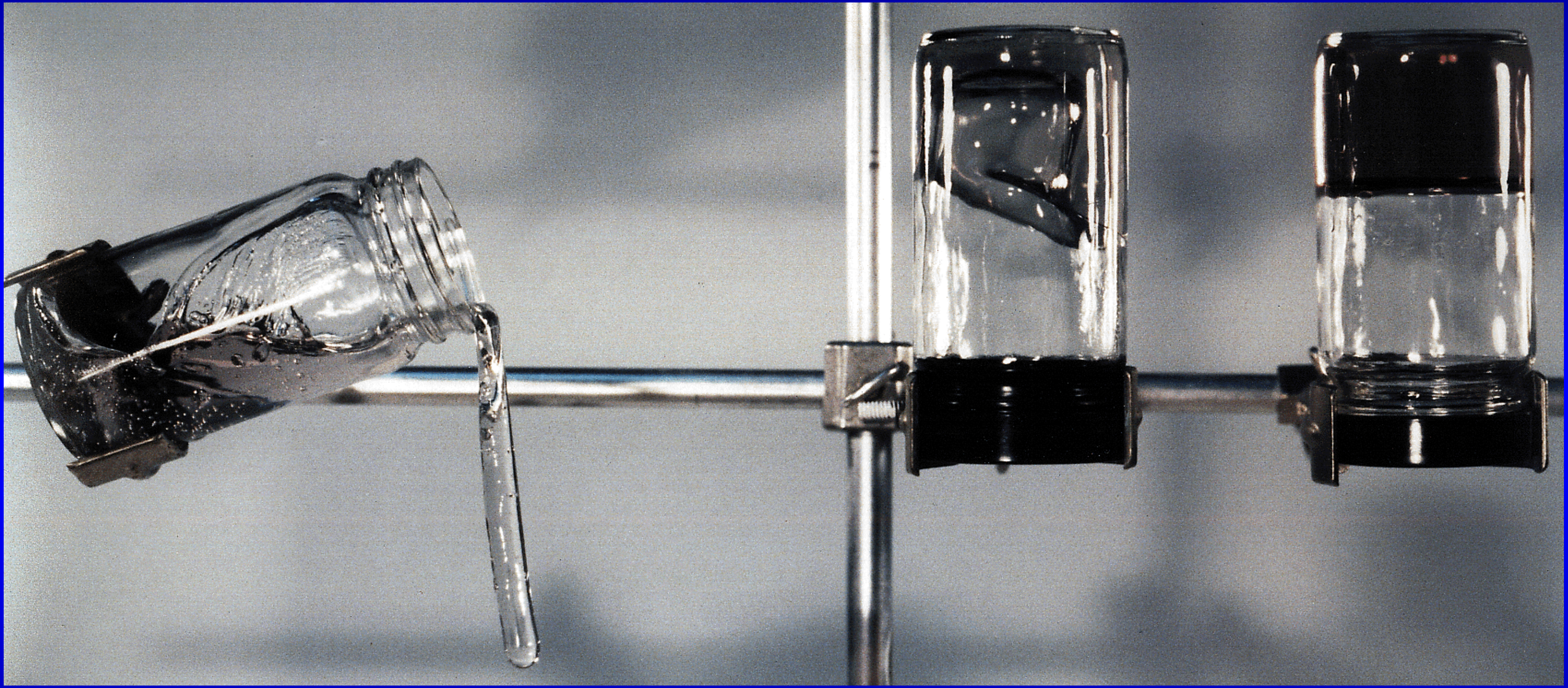
Low concentration

Low polymer Mw

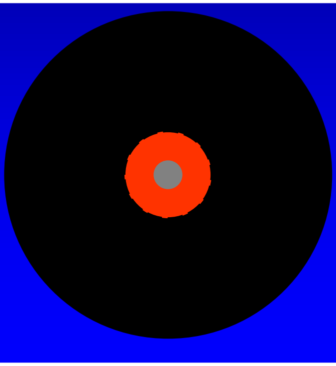
■ **Crosslink site**

High polymer Mw

High concentration

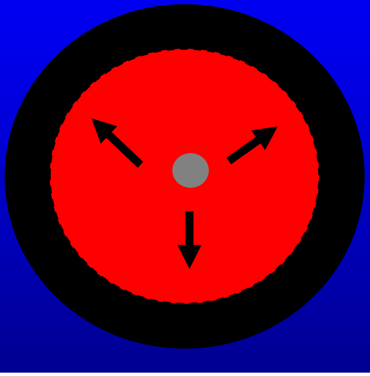


GELATION TIME DETERMINES HOW FAR A GELANT CAN PENETRATE INTO POROUS ROCK

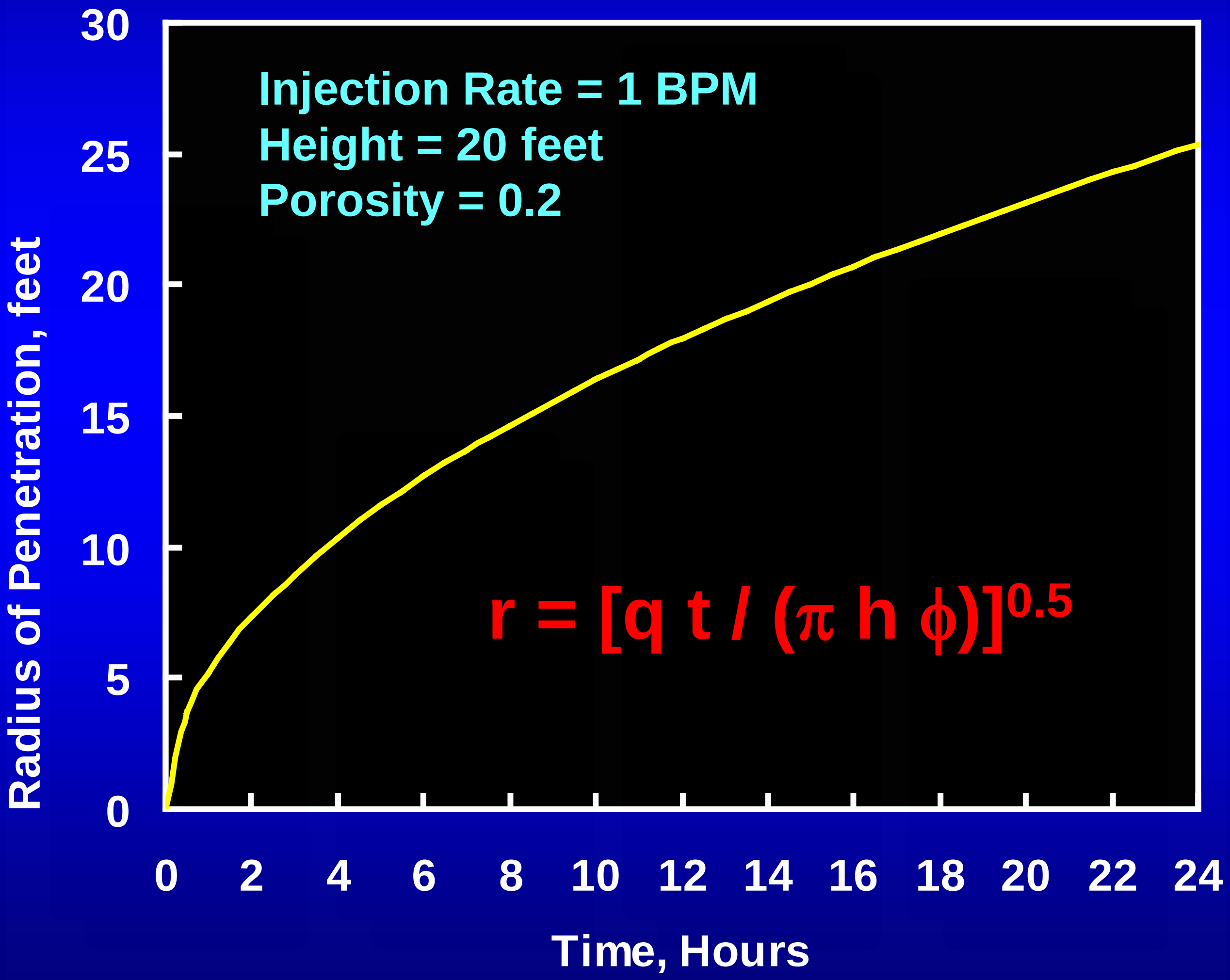


Fast gelation

🟥 **Gelant**



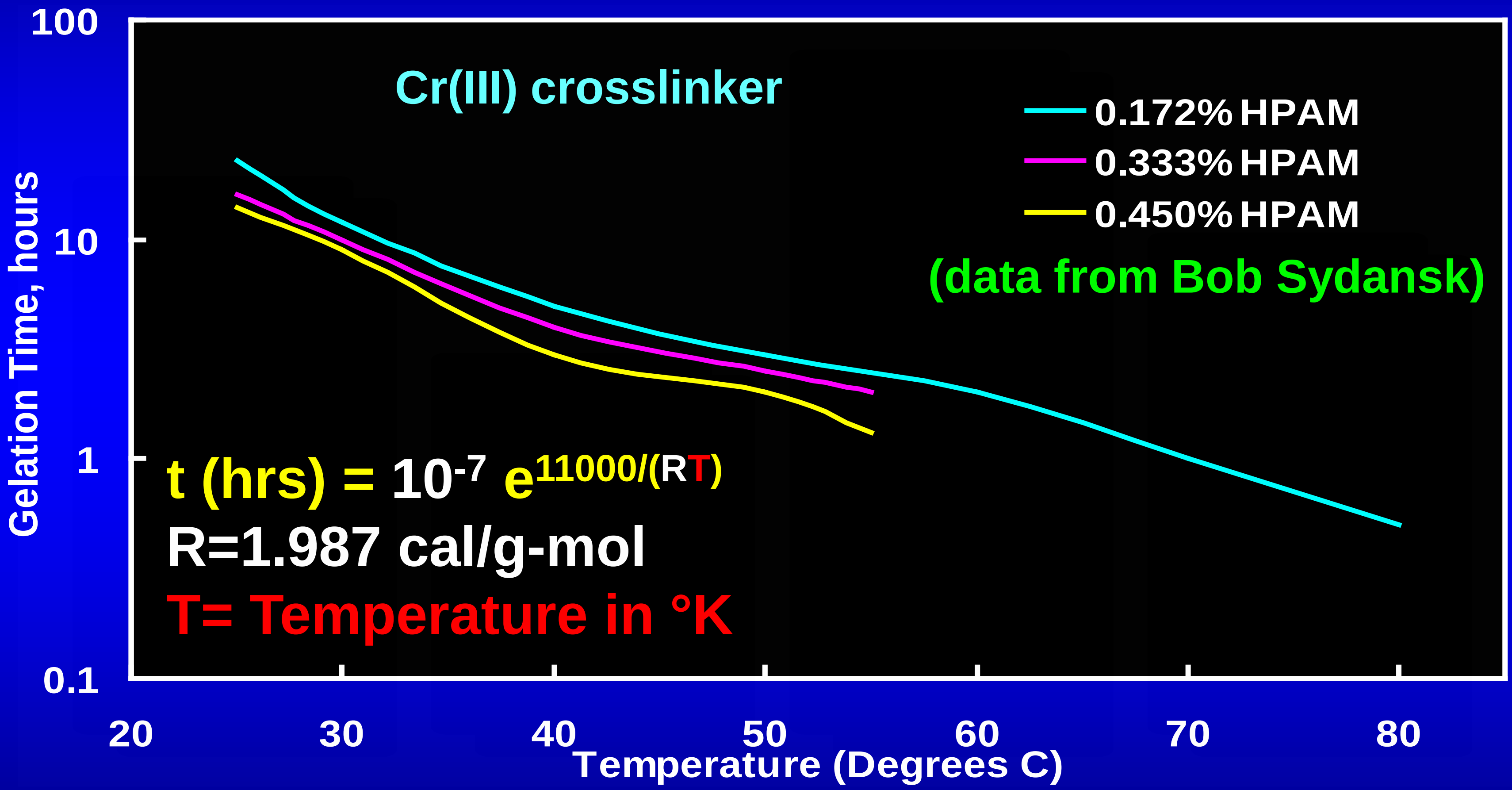
Slow gelation



Injection Rate = 1 BPM
Height = 20 feet
Porosity = 0.2

$$r = [q\ t\ /\ (\pi\ h\ \phi)]^{0.5}$$

GELATION TIME VERSUS TEMPERATURE



$t\ (\text{hrs}) = 10^{-7}\, e^{11000/(RT)}$

R=1.987 cal/g-mol

T= Temperature in °K

Increasing temperature by 10° C halves gelation time.

GELATION TIMES FOR MOST COMMERCIAL GELANTS ARE FAIRLY SHORT EVEN AT MODERATE TEMPERATURES

Some exceptions:

- **BP’s PEI crosslinked/t-butylacrylate-acrylamide polymers.**
- **Unocal’s organically crosslinked polymers. SPE 37246 and *SPEPF* May 1996, 108 - 112.**
- **Phillips’ organically crosslinked polymers. SPE 27826.**
- **Eniricerche’s Cr(III) - malonate crosslinked polymers. *SPEPF* Nov. 1994, 273 - 279.**

Some papers examining gels for elevated temperatures

SPE 190266, 188322, 183558, 179796, 173185, 163110, 129848, 127806, 120966, 104071, 98119, 97530, 90449, 77411, 72119, 50738, 39690, 37246, 27826, 27609.

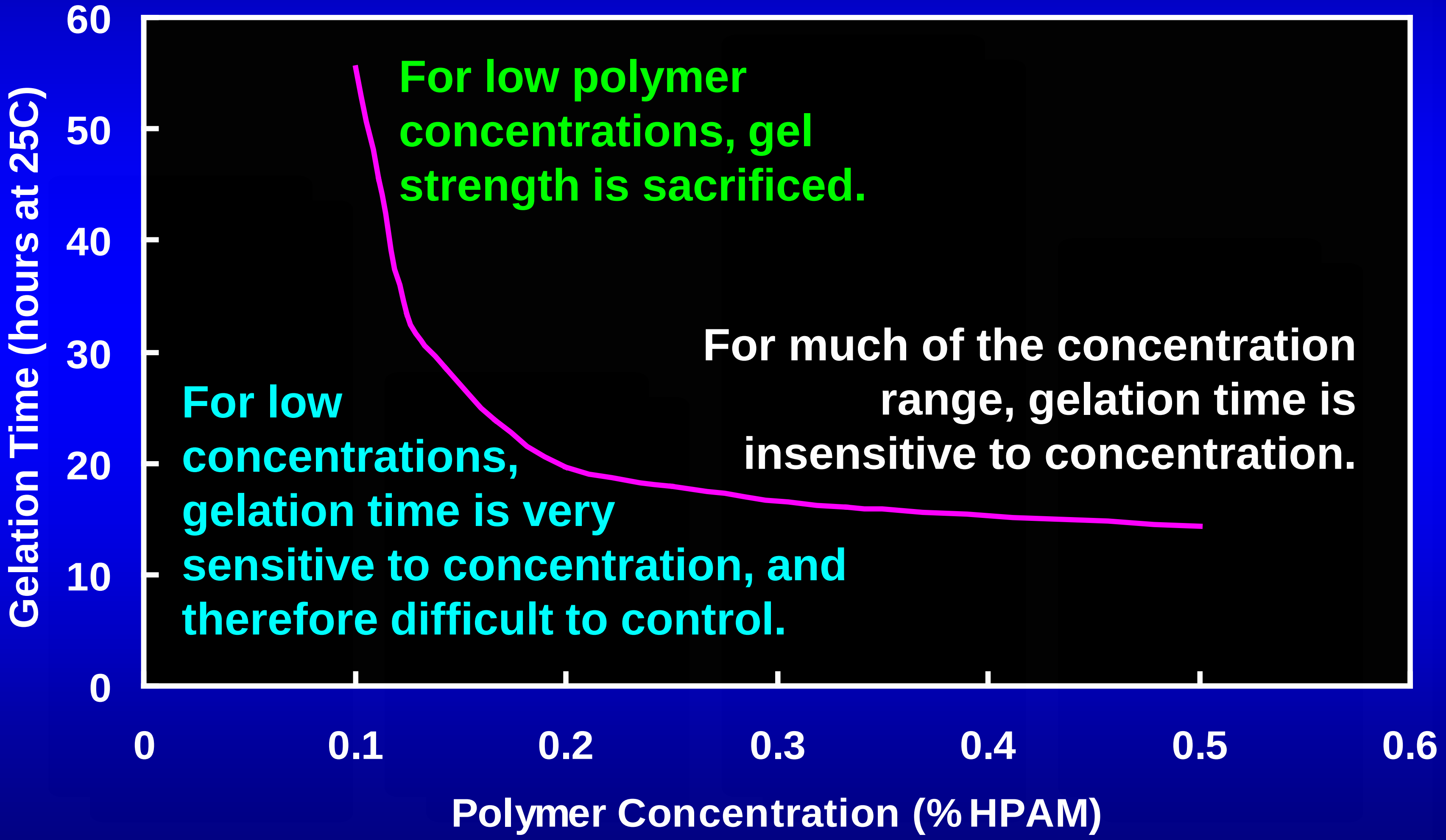
KEY MESSAGES:

1. HPAM polymers will hydrolyze at high temperature—risking gel syneresis if divalent cations are present.
2. Organic crosslinkers delay gelation but do not necessarily improve gel stability.
3. Polymers with high levels of ATBS or NVP promote polymer and gel stability.
4. More concentrated gels have greater stability.
5. Incorporating associative groups does not help stability.

METHODS TO INCREASE GELATION TIMES

- **Vary salinity, pH, or concentrations of chemical additives. SPE 27609.**
- **Use an unhydrolyzed polyacrylamide. With time, hydrolysis at elevated temperatures increases the number of crosslinking sites. SPE 20214.**
- **Cool the near-wellbore region prior to gelant injection. SPE 28502.**
- **Use a chemical retarding agent (e.g., lactate). *SPEPF* (Nov 2000) 270-278.**

GELATION TIME VERSUS POLYMER CONCENTRATION

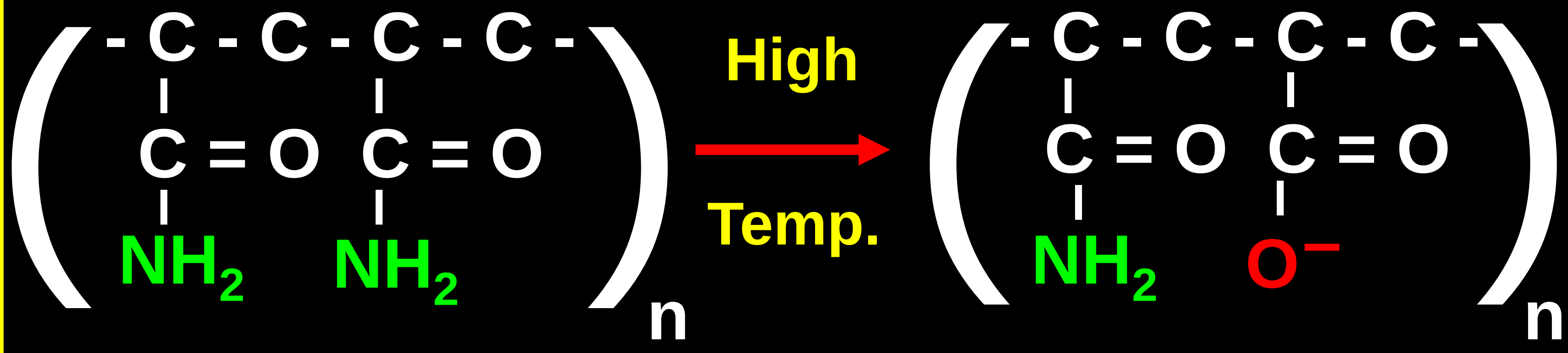


For low polymer concentrations, gel strength is sacrificed.

For much of the concentration range, gelation time is insensitive to concentration.

For low concentrations, gelation time is very sensitive to concentration, and therefore difficult to control.

POLYMER HYDROLYSIS



POLYACRYLAMIDE

HPAM

- Only carboxylate groups react with Cr(III), so Cr(III) crosslinking is delayed until enough COO^- groups form.
- If too many COO^- groups form, polymer precipitates if Ca^{2+} or Mg^{2+} is present.
- Trick only works at high temperatures (~120°C) with low-Mw polyacrylamide polymers.

Gel Stability at Elevated Temperatures

- Some feel that gel stability is no better than the stability of the polymer in the gel.
- Gels can be made using polymers that are more stable than HPAM--e.g., amide/AMPS/NVP copolymers and terpolymers. *SPERE* Nov. 1987, 461-467.
- Some evidence exists that gel stability can be increased by using very rigid gels. SPE 20214.

CC/AP Gel
Aged at 300°F
for 2.5 Years

Gelant Sensitivity to pH

- For most gelants, the gelation reaction is sensitive to pH.
- Clays, carbonates, and other reservoir minerals can change pH -- thus interfering with gelation.
- Need to buffer gelants or develop gelants that are less sensitive to pH changes.

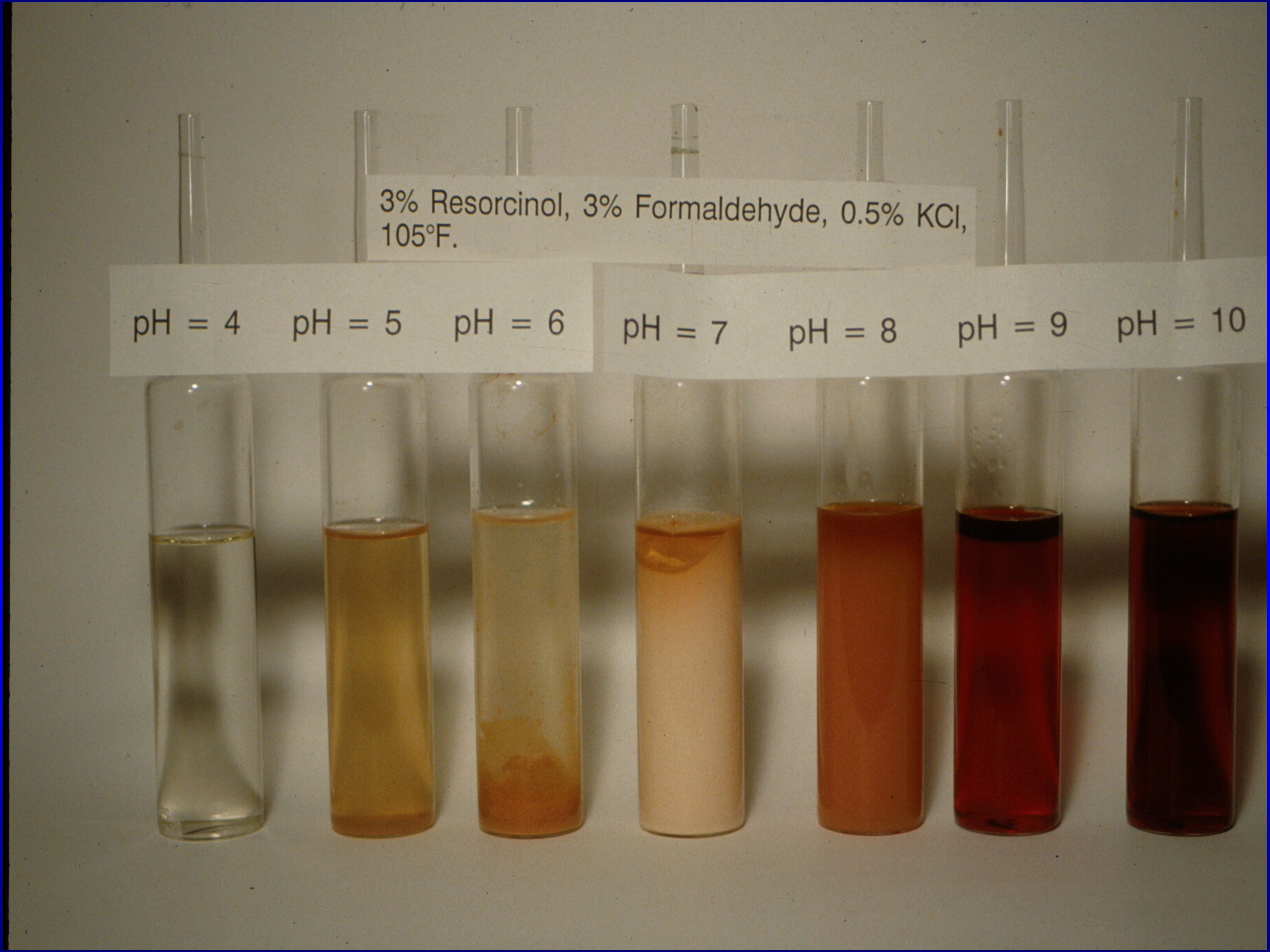
- Marathon: Cr(III)-acetate and lactate crosslinkers. SPE 17329.
- Phillips: Cr(III)-propionate crosslinker. *SPERE* Feb. 1988, 243-250.
- Eniricerche: Cr(III)-malonate and lactate crosslinkers. *SPEPF* Nov. 1994, 273-279.
- IFP: adsorbed polymers. SPE 18085.

Cr(IIII) can bind to:

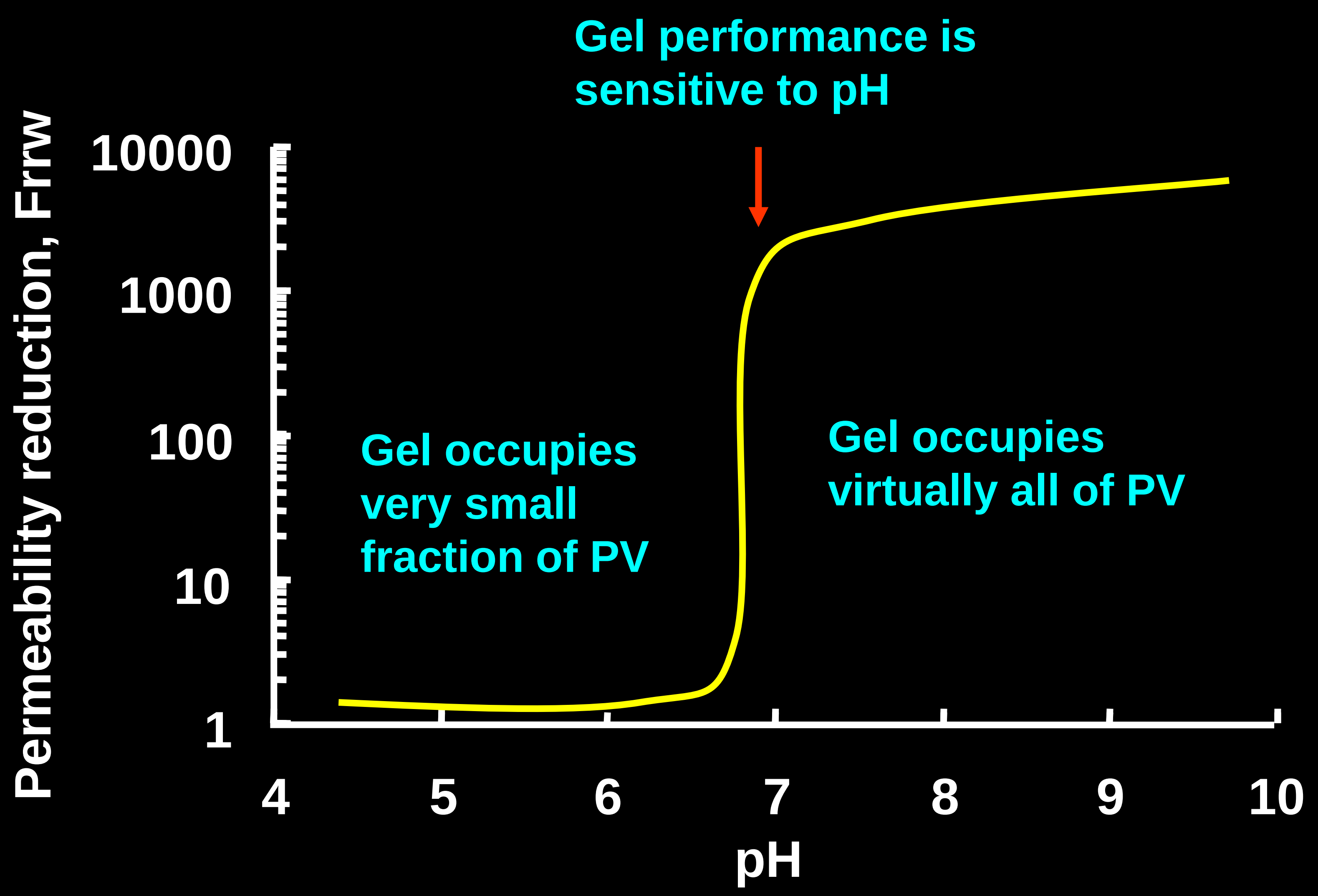
a. Polymer
b. Acetate or other carboxylate
c. Rock

Competition among the above affects gel stability, gel strength, gelant propagation, and gelation time.

Gelation time at high temperatures can be varied by adjusting the ratio of acetate/lactate (or glycolate or malonate).


3% Resorcinol, 3% Formaldehyde, 0.5% KCl, 105°F.
pH = 4
pH = 5
pH = 6
pH = 7
pH = 8
pH = 9
pH = 10

pH OF GELATION AFFECTS PERMEABILITY REDUCTION

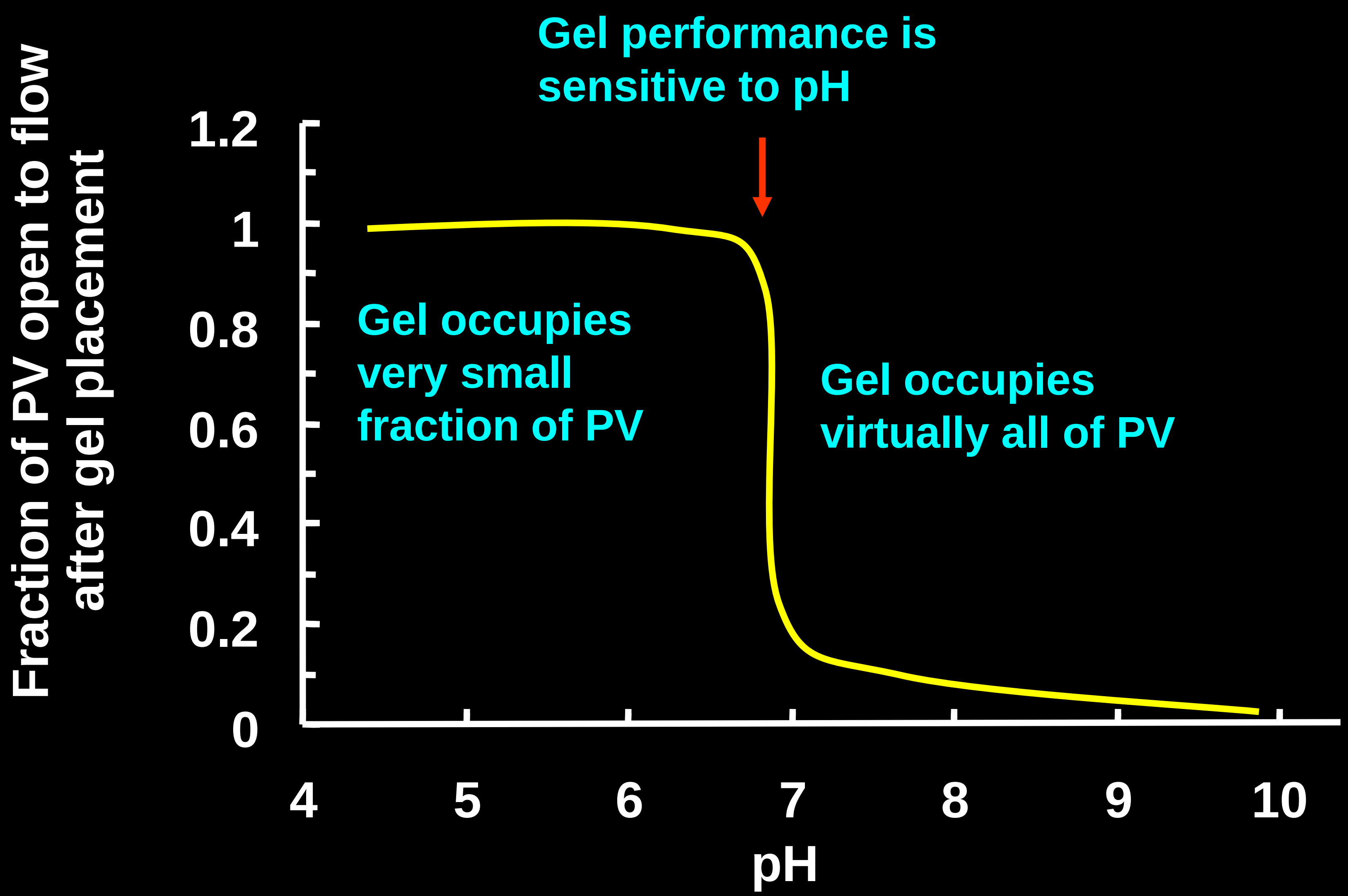


Gel performance is sensitive to pH

Gel occupies very small fraction of PV

Gel occupies virtually all of PV

pH OF GELATION AFFECTS PV OCCUPIED BY GEL



Gel performance is sensitive to pH

Gel occupies very small fraction of PV

Gel occupies virtually all of PV

Resistance factor = Water mobility ÷ Gelant mobility

$F_r = (k/\mu)_{water} / (k/\mu)_{gelant} \approx$ Gelant viscosity relative to water

$$\text{Water residual resistance factor} = \frac{\text{Water mobility before gel placement}}{\text{Water mobility after gel placement}}$$

$F_{rrw} = (k/\mu)_{water\ before\ gel} / (k/\mu)_{water\ after\ gel}$ = permeability reduction

$$\text{Oil residual resistance factor} = \frac{\text{Oil mobility before gel placement}}{\text{Oil mobility after gel placement}}$$

$F_{rro} = (k/\mu)_{oil\ before\ gel} / (k/\mu)_{oil\ after\ gel}$ = permeability reduction

WEAK GELS

- Occupy a very small fraction of the pore volume.
- Usually consist of small gel particles that block pore throats.
- Provide low to moderate permeability reductions.
- Are usually unpredictable in particle size, particle concentration, and permeability reduction provided.

ADSORBED POLYMERS

- Occupy a very small fraction of the pore volume.
- Usually block some fraction of the pore throats.
- Provide low to moderate permeability reductions.
- Because of mineralogical variations, are usually unpredictable in adsorption level and permeability reduction provided.

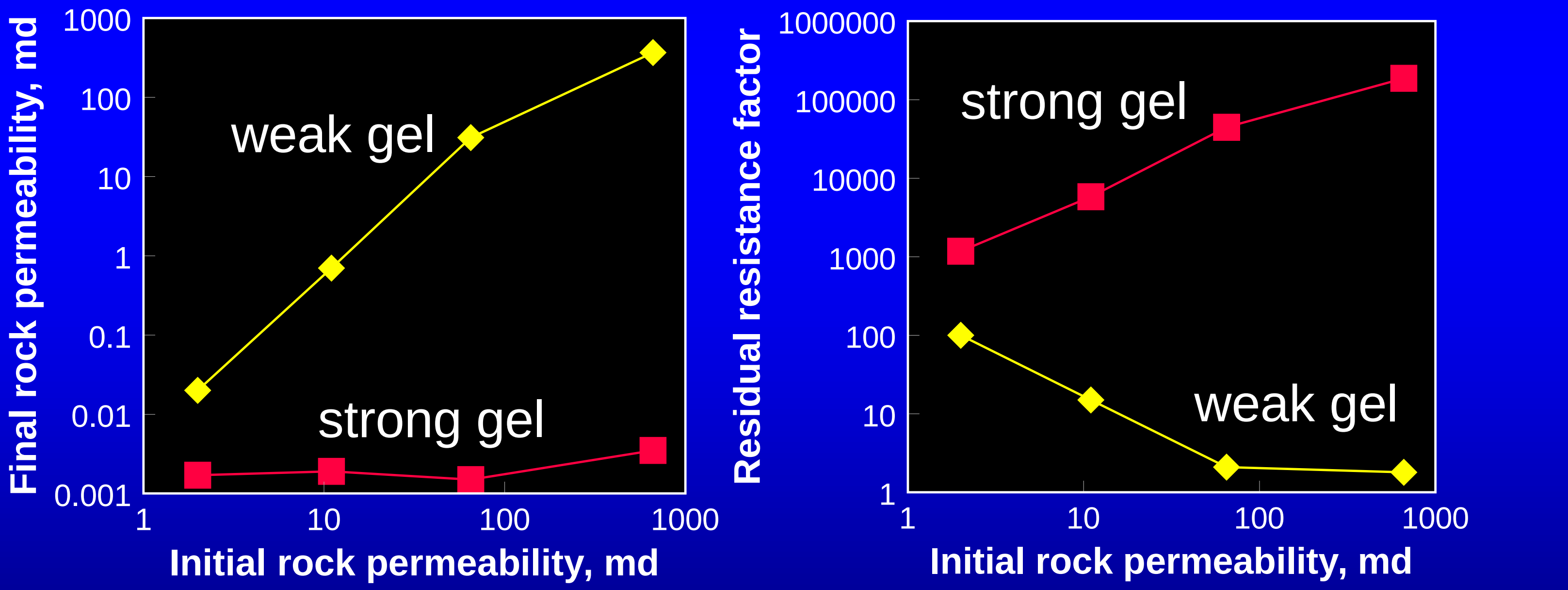
PORE-FILLING GELS

- Occupy most, if not all, of the aqueous pore space.
- Reduce permeabilities to microdarcy levels.
- Water flows through the gel itself.
- Provide high permeability reductions.
- Are much more predictable than weak gels and polymers.

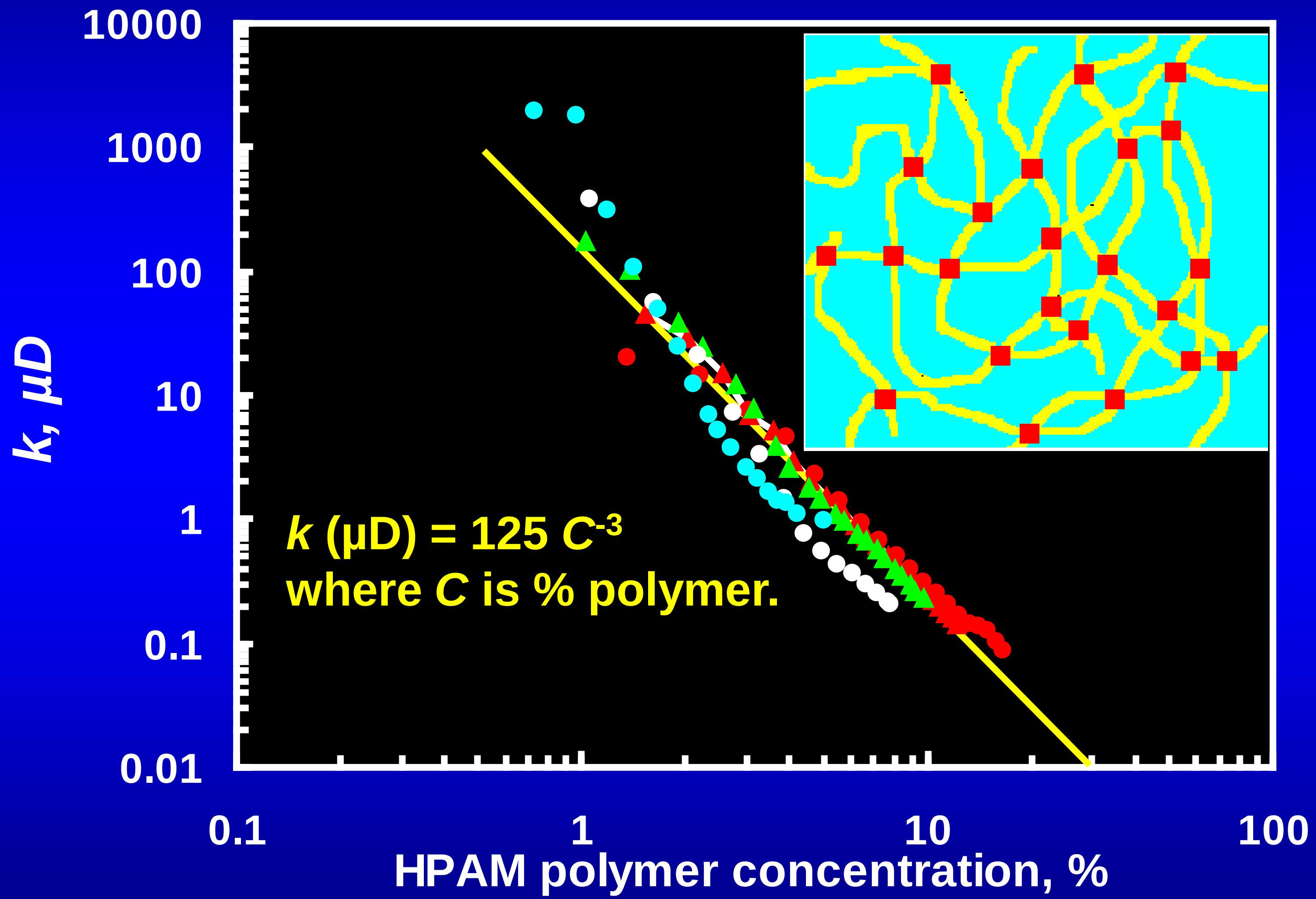
PERMEABILITY REDUCTION BY GELS

"Strong" gels reduce k of all rocks to the same low value.

"Weak" gels restrict flow in low-k rocks by a factor that is the same or greater than that in high-k rock.



Water can flow through gels although gel permeability is very low.



k (µD) = 125 C^{-3}
where C is % polymer.

TREATING FRACTURES WITH GELANTS & GELS

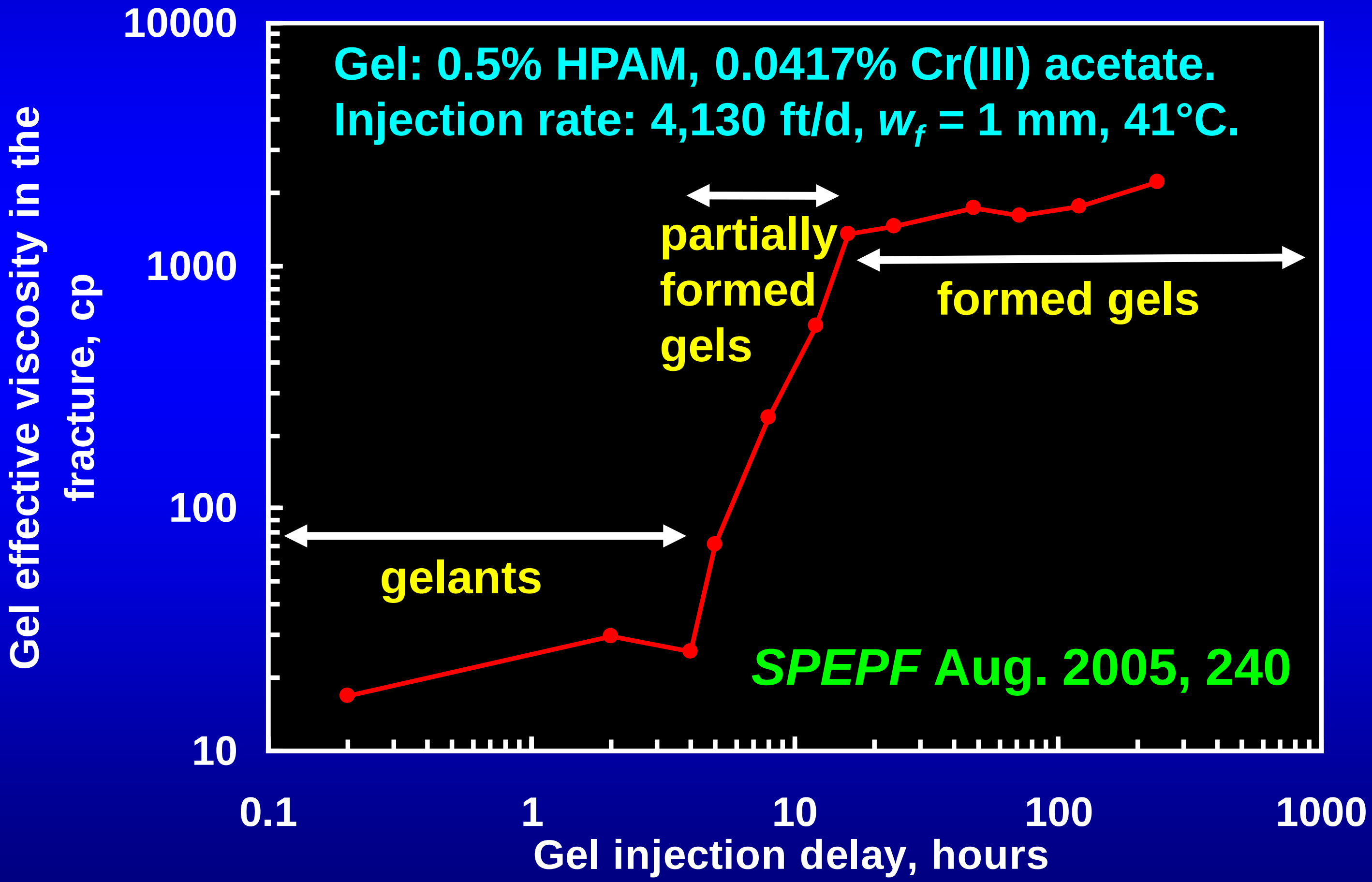
In most field applications, gel formulations:

- Enter the wellhead as gelants (very little crosslinking has occurred).
- Enter the formation as gelants or partially formed gels (i.e., shortly after the gelation time).

In small volume applications, gel formulations exist as fluid gelants or partially formed gels during most of the placement process.

In large volume applications, gel formulations exist as formed gels during most of the placement process.

- **Compared with formed gels, gelants show much lower effective viscosities during placement in fractures.**
- **Low viscosities improve injectivity but often allow gravity segregation during placement in fractures.**



PLACING FORMED GELS IN FRACTURES

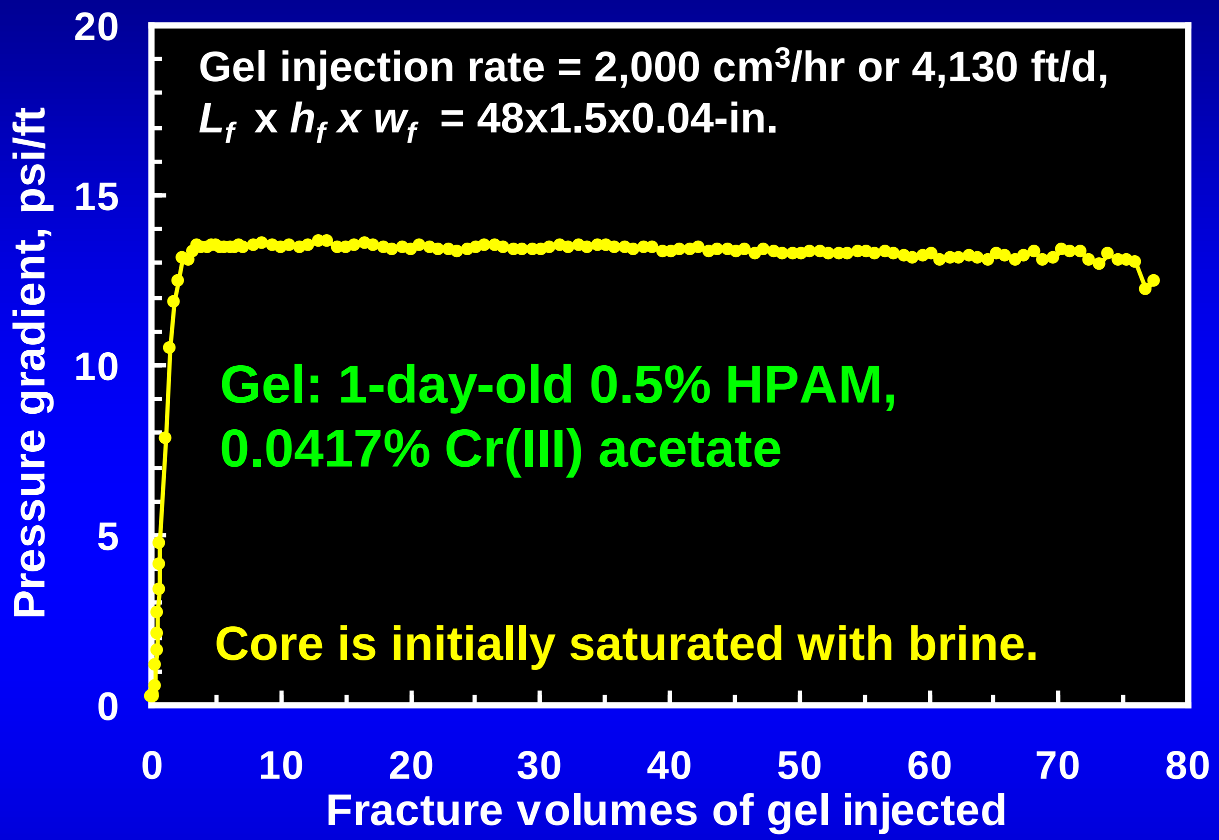
Successful large-volume Cr(III)-acetate-HPAM gel treatments in naturally fractured reservoirs:

- **Typically injected 10,000 to 15,000 bbls gel per injection well.**
- **Injection times greater than gelation time by ~100X.**
- **Gels extruded through fractures during most of the placement process.**

- **What are gel properties during extrusion through fractures?**
- **How far can the gels be expected to propagate?**
- **How will the gels distribute in a fracture system?**
- **How much gel should be injected?**

***SPEPF* (Nov. 2001) 225-232.**

Pressure Behavior in a Fracture During Gel Extrusion



After gel breaks through at the end of a fracture, pressure gradients are stable (no screen out or progressive plugging).

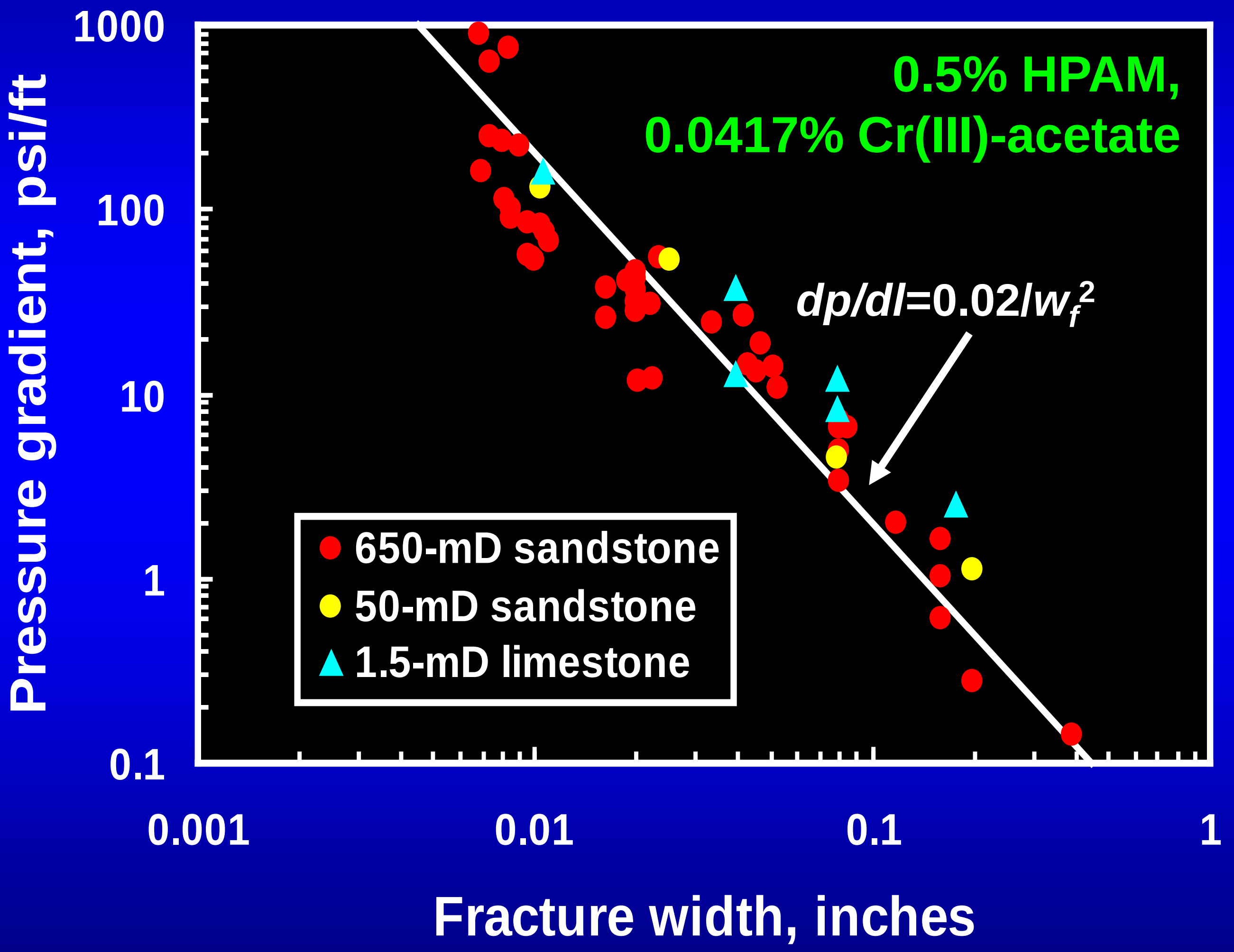
PROPERTIES OF FORMED GELS IN FRACTURES

- A minimum pressure gradient must be met before a formed gel will extrude through a fracture.

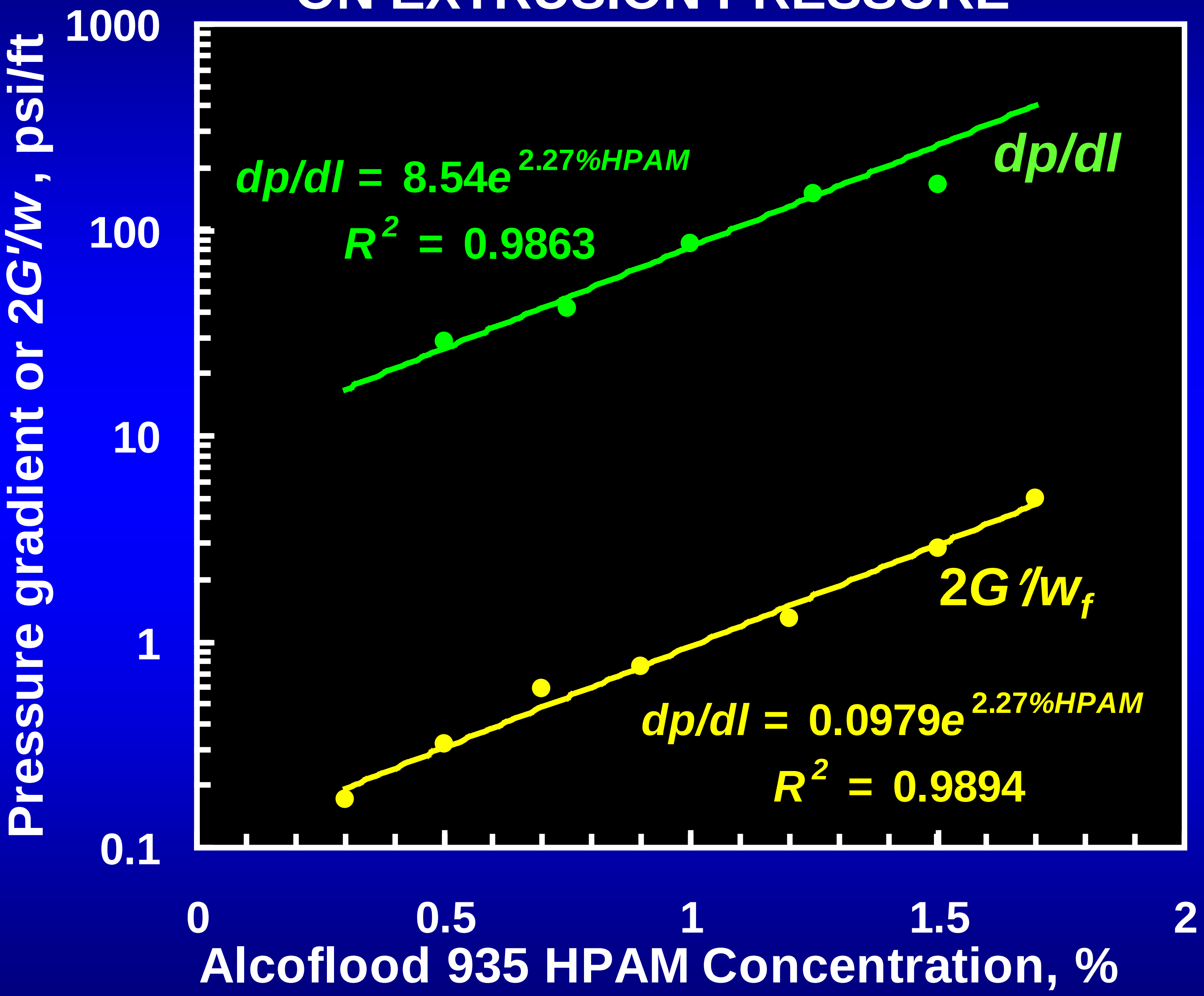
- Once the minimum pressure gradient is met, the pressure gradient during gel extrusion is not sensitive to injection rate.

- The pressure gradient for gel extrusion varies inversely with the square of fracture width.

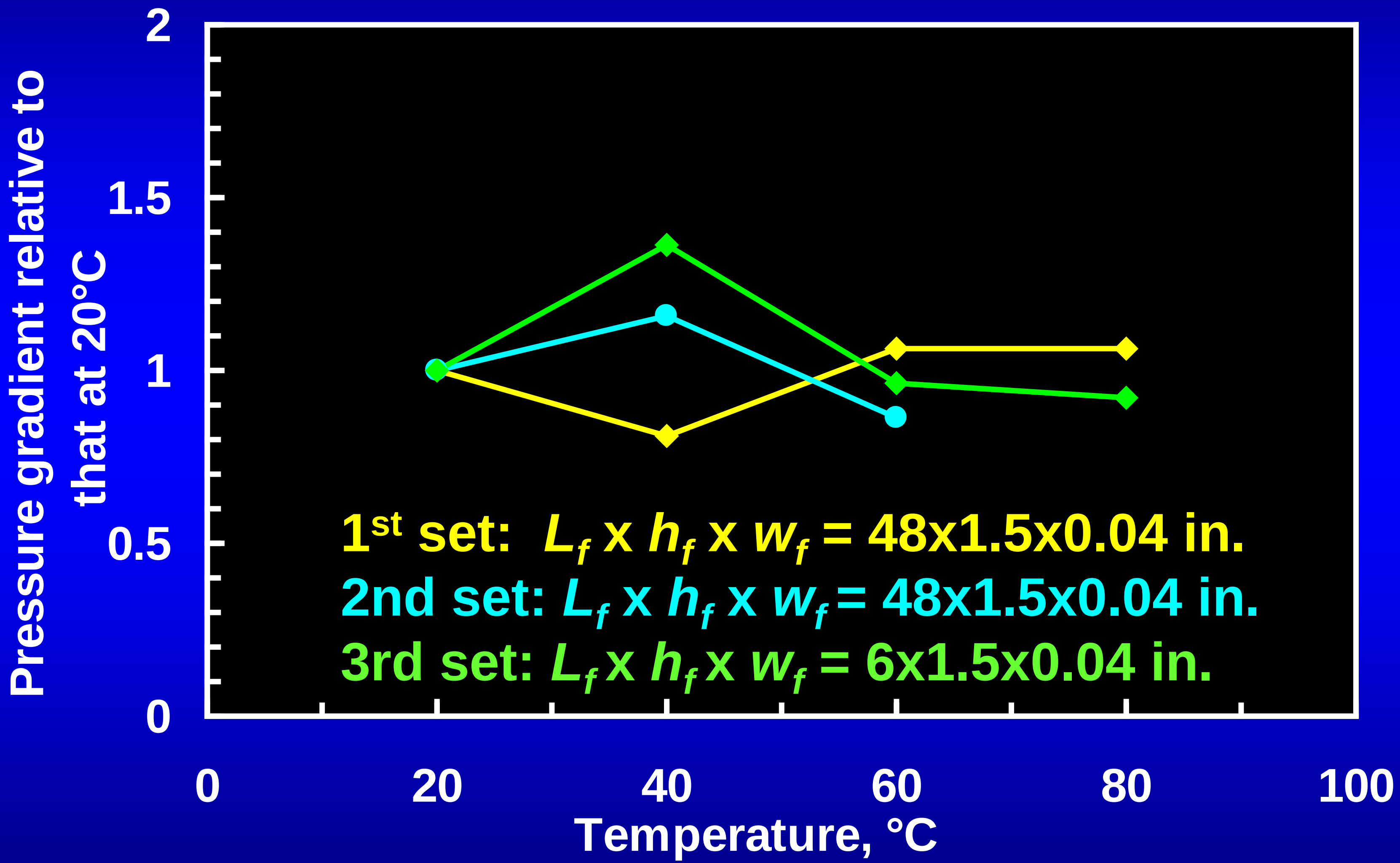
Pressure gradients required to extrude a Cr(III)-acetate-HPAM gel through fractures



EFFECT OF POLYMER CONCENTRATION ON EXTRUSION PRESSURE



PRESSURE GRADIENTS DURING GEL EXTRUSION ARE NOT SENSITIVE TO TEMPERATURE



GELS DEHYDRATE DURING EXTRUSION

Cr(III)-acetate-HPAM gel

Fracture: L_f = 4 ft, h_f = 1.5 in., w_f = 0.04 in.

Injected 80 fracture volumes of gel (~4 liters)

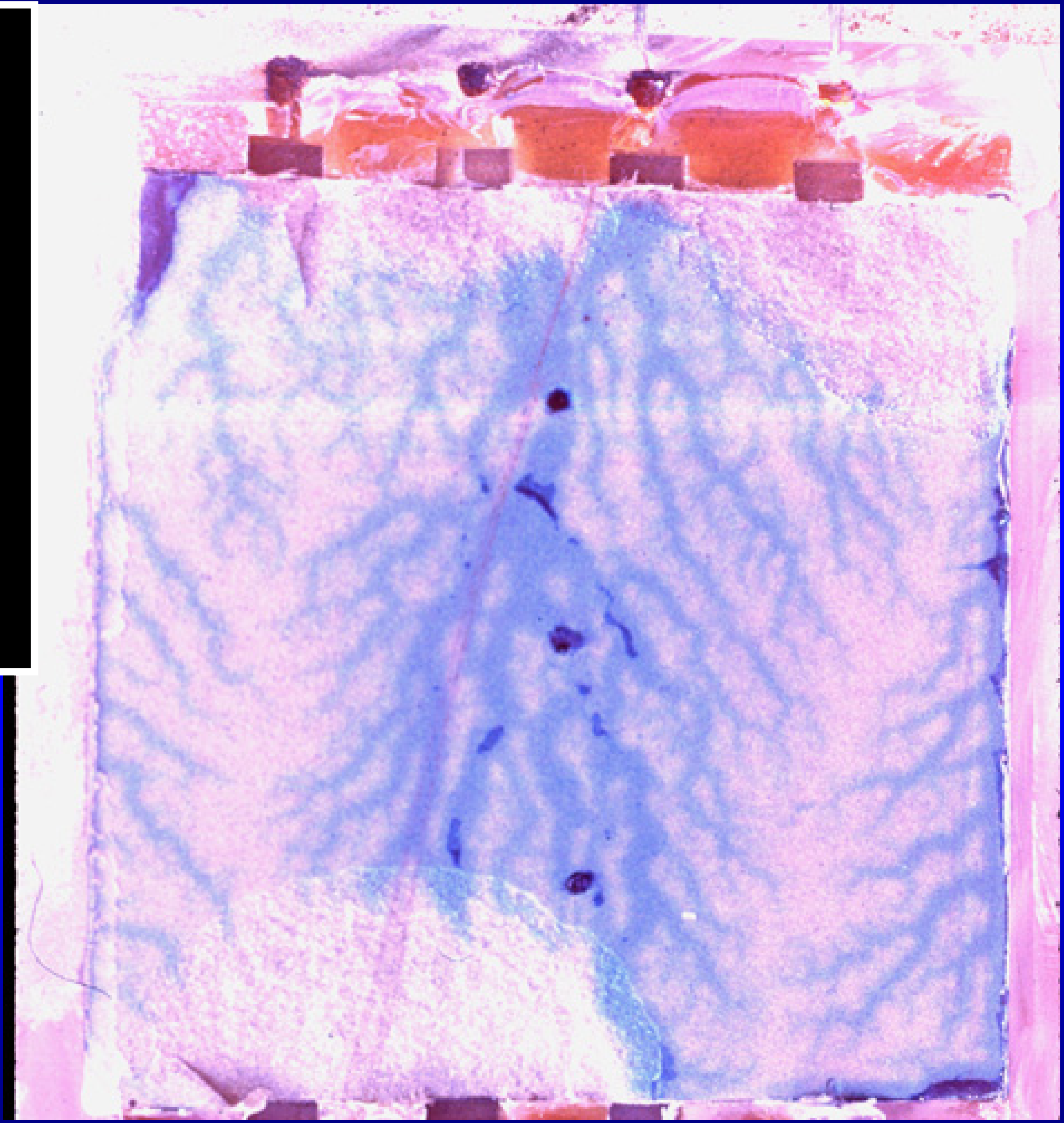
Injection flux, ft/d	413	1,030	4,130	33,100
Average *dp/dl*, psi/ft	28	29	40	18
Gel breakthrough, fracture volumes	15	6.0	4.0	1.7
Average gel dehydration, C/C_o	27	17	11	4

PROPERTIES OF Cr(III)-ACETATE-HPAM GEL DURING EXTRUSION THROUGH FRACTURES

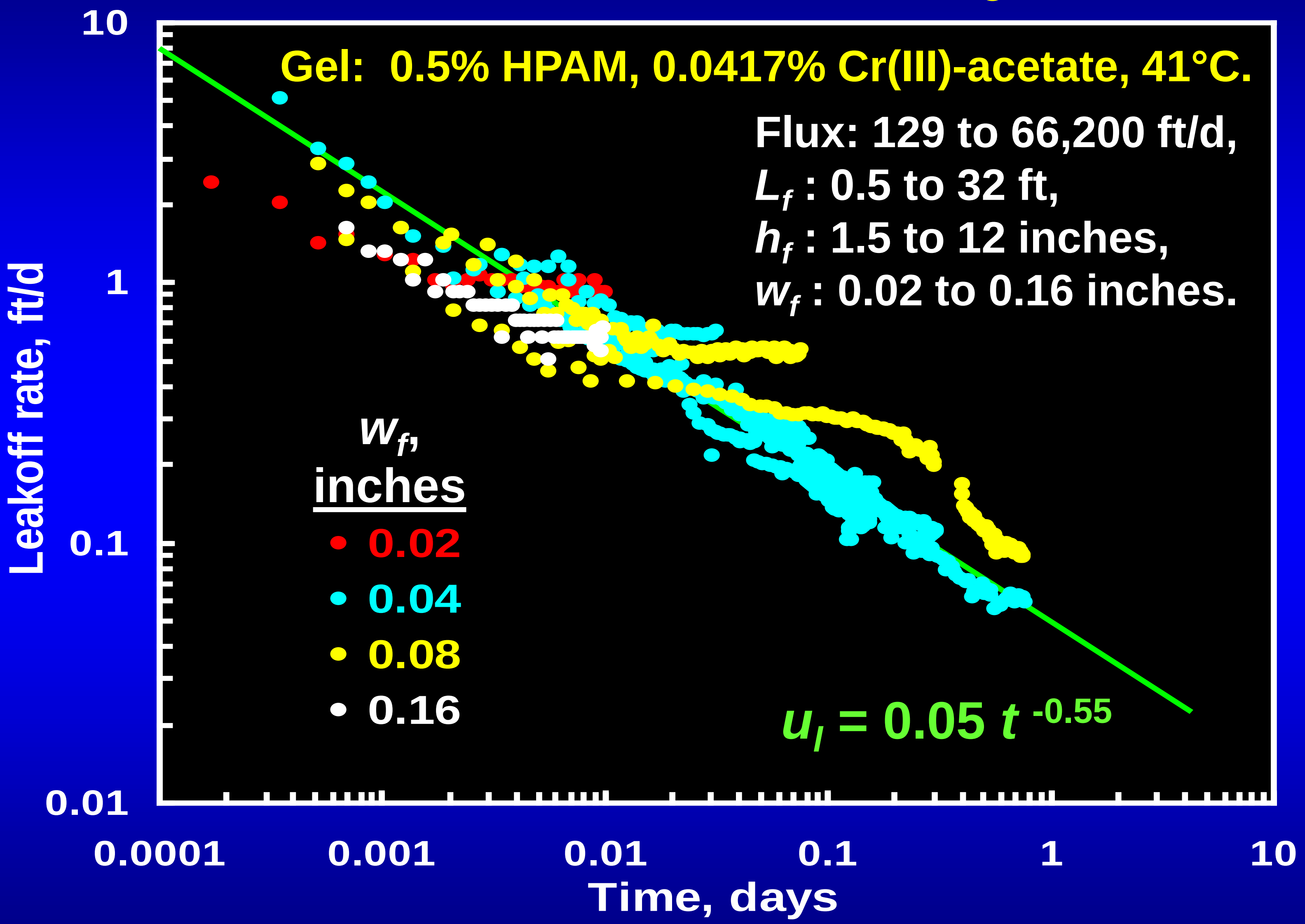
- Gels dehydrate, thus retarding the rate of movement of the gel front.
- Although water leaks off through the fracture faces, crosslinked polymer cannot.
- Dehydrated (concentrated) gel is immobile.
- Mobile gel is the same as the injected gel.
- Mobile gel wormholes through immobile gel.

1-day-old 1X Cr(III)-acetate HPAM gel (in blue) wormholing through dehydrated gel that is 12 times more concentrated.

Fracture dimensions = 15x15x0.1 cm



Water Leakoff Rates From Gel During Extrusion



Gel: 0.5% HPAM, 0.0417% Cr(III)-acetate, 41°C.

Flux: 129 to 66,200 ft/d,
L_f : 0.5 to 32 ft,
h_f : 1.5 to 12 inches,
w_f : 0.02 to 0.16 inches.

$u_l = 0.05\ t^{-0.55}$

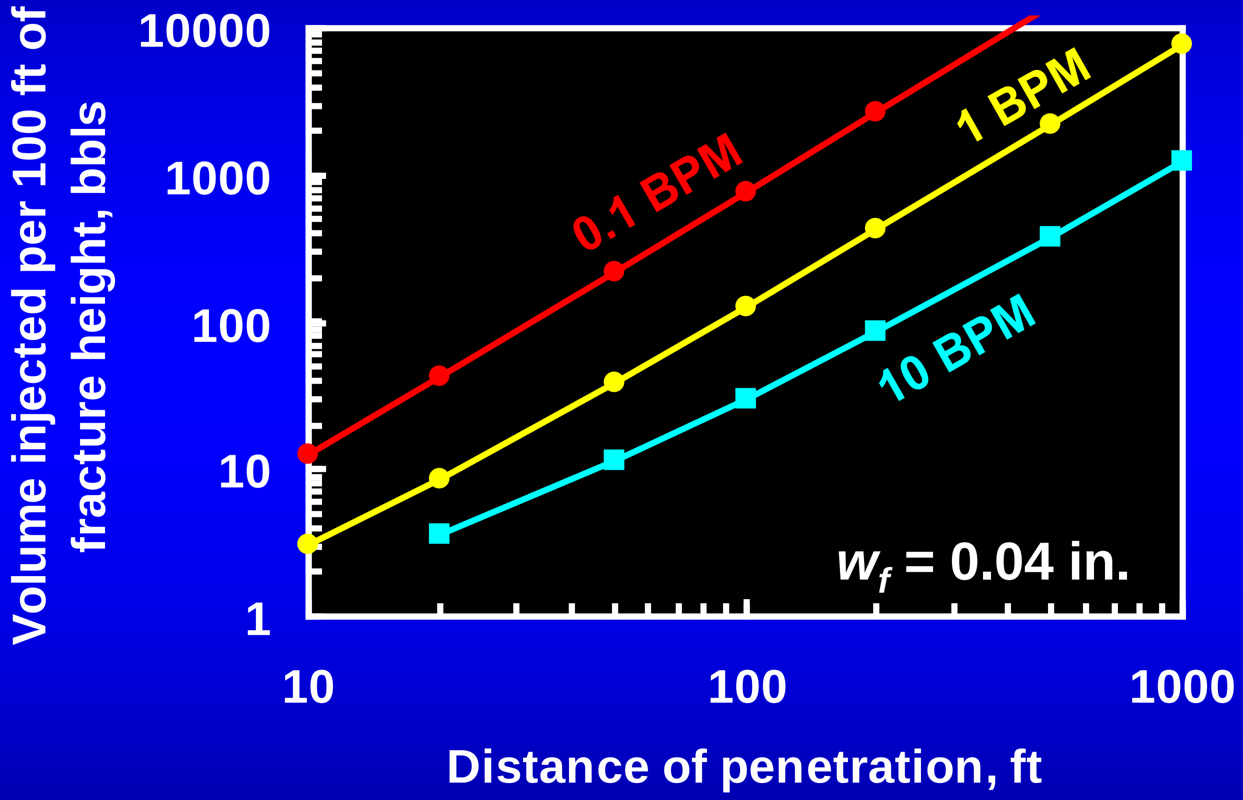
WHAT IS THE RATE OF GEL PROPAGATION THROUGH A FRACTURE?

- The rate of water loss from the gel is given by: $u_l = 0.05\ t^{-0.55}$. Combine with a mass balance.
- Assuming two fracture wings, the rate of gel propagation, dL/dt, is:

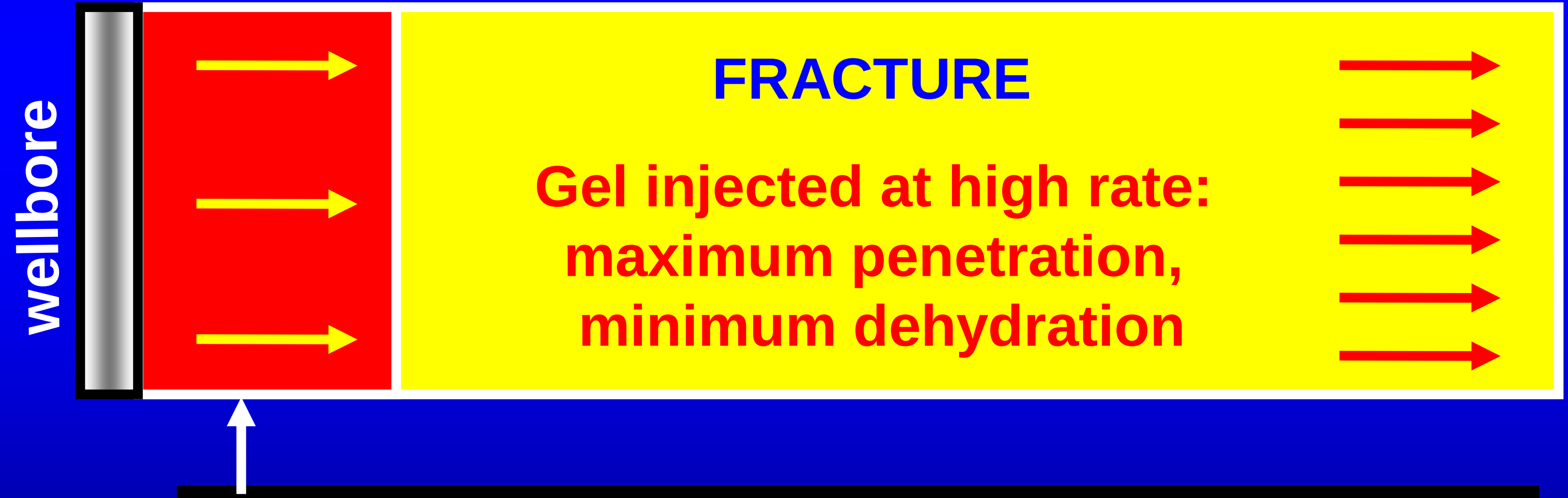
$$dL/dt = [q_{tot} - 4 h_f L\ u_l] / [2\ h_f\ w_f]$$

$$dL/dt = [q_{tot} - 4 h_f L\ 0.05\ t^{-0.55}] / [2\ h_f\ w_f]$$

Predictions in Long Two-Wing Fractures



- The degree of gel dehydration depends on injection rate and time.
- When injecting gel into a fracture, can a more rigid gel plug be formed in the near wellbore portion of the fracture simply by reducing the injection rate?



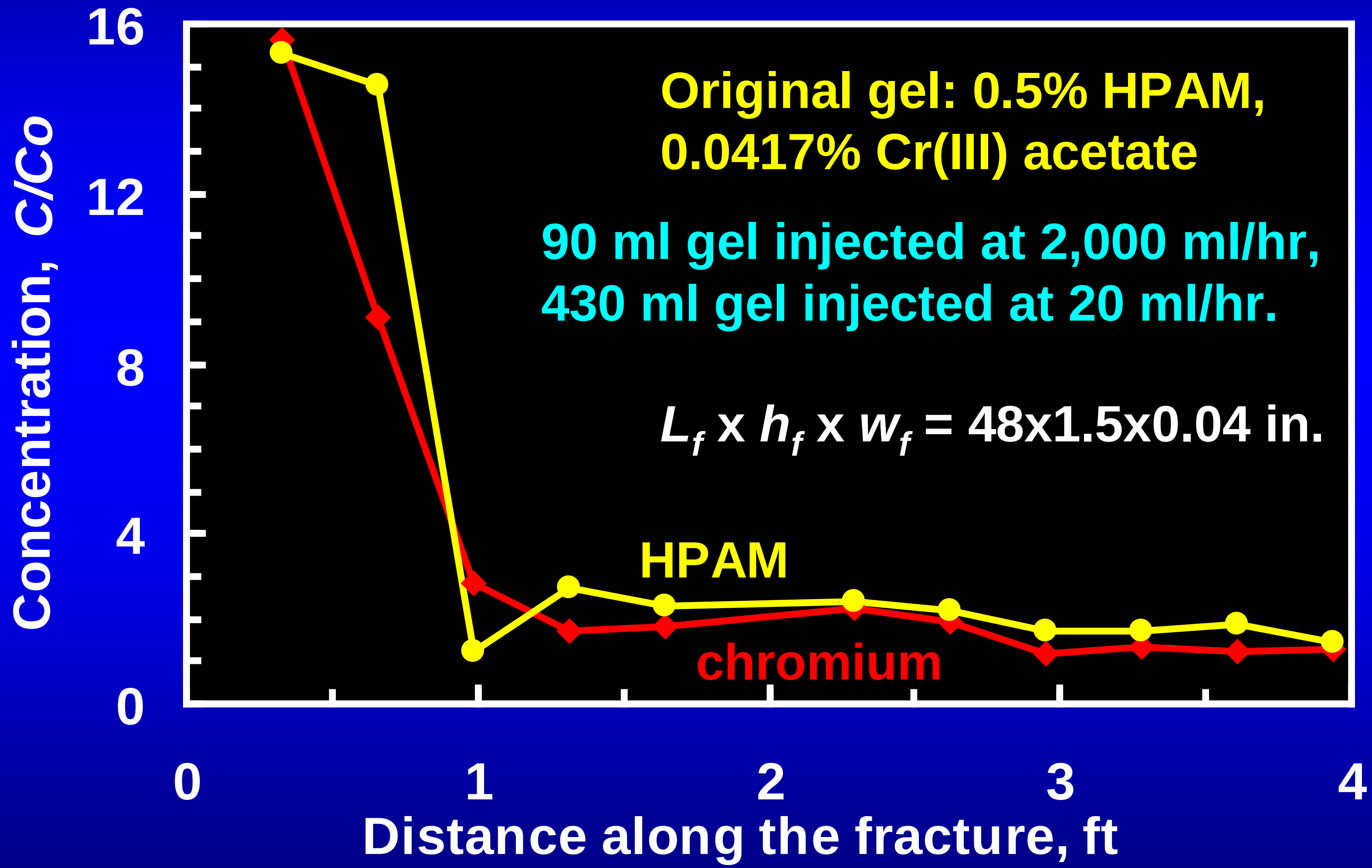
Gel injected at high rate: maximum penetration, minimum dehydration

Gel injected at low rate: maximum dehydration for greater rigidity and strength.

COMPOSITION OF GEL IN THE FRACTURE.

Injection rate = 2,000 ml/hr until fracture filled with gel.

Then the rate was dropped to 20 ml/hr.



PROPERTIES OF FORMED GELS DURING EXTRUSION THROUGH FRACTURES

- **Dehydration limits the distance of GEL penetration along a fracture.**
- **For a given total volume of GEL injection, the distance of gel propagation will be maximized by injecting at the highest practical injection rate.**
- **To double the distance of GEL penetration into a long fracture, the GEL volume must be tripled.**
- **More concentrated, rigid GELS can be formed by injecting slower—decreasing the probability of gel washout.**

Dehydration of Gels in Fractures by Imbibition

(Brattekas: SPE 153118, 169064, 173749, 180051, 190256)

- Water-wet rock can suck water out of gels in fractures—thus collapsing those gels.
- This action could be of value for fractures in oil zones because you want those fractures to remain open to flow.
- For fractures in water zones, if no oil is present, no capillary action occurs so the gels remain intact in the fracture and flow remains restricted.
- Depending on the salinity of the gel and water post-flush, the flow capacity of gel-filled fractures can be varied.

PRE-FORMED PARTICLE GELS (PPGs) (Bai et al.)

- Are crosslinked polymers that are dried and ground to a desired particle size offsite.
- Swell upon contact with water.
- Swell less with more saline brines.
- Dehydrate during extrusion through fractures.
- Are expected to show performance similar to other preformed gels [e.g., extruded Cr(III)-acetate-HPAM].
- Bai references: SPE 190364, 190357, 180388, 188384, 188023, 187152, 182795, 181545, 180386, 179705, 176728, 176429, 175058, 174645, 172352, 171531, 170067, 169159, 169107, 169106, 169078, 164511, 129908, 115678, 113997, 89468, 89389.

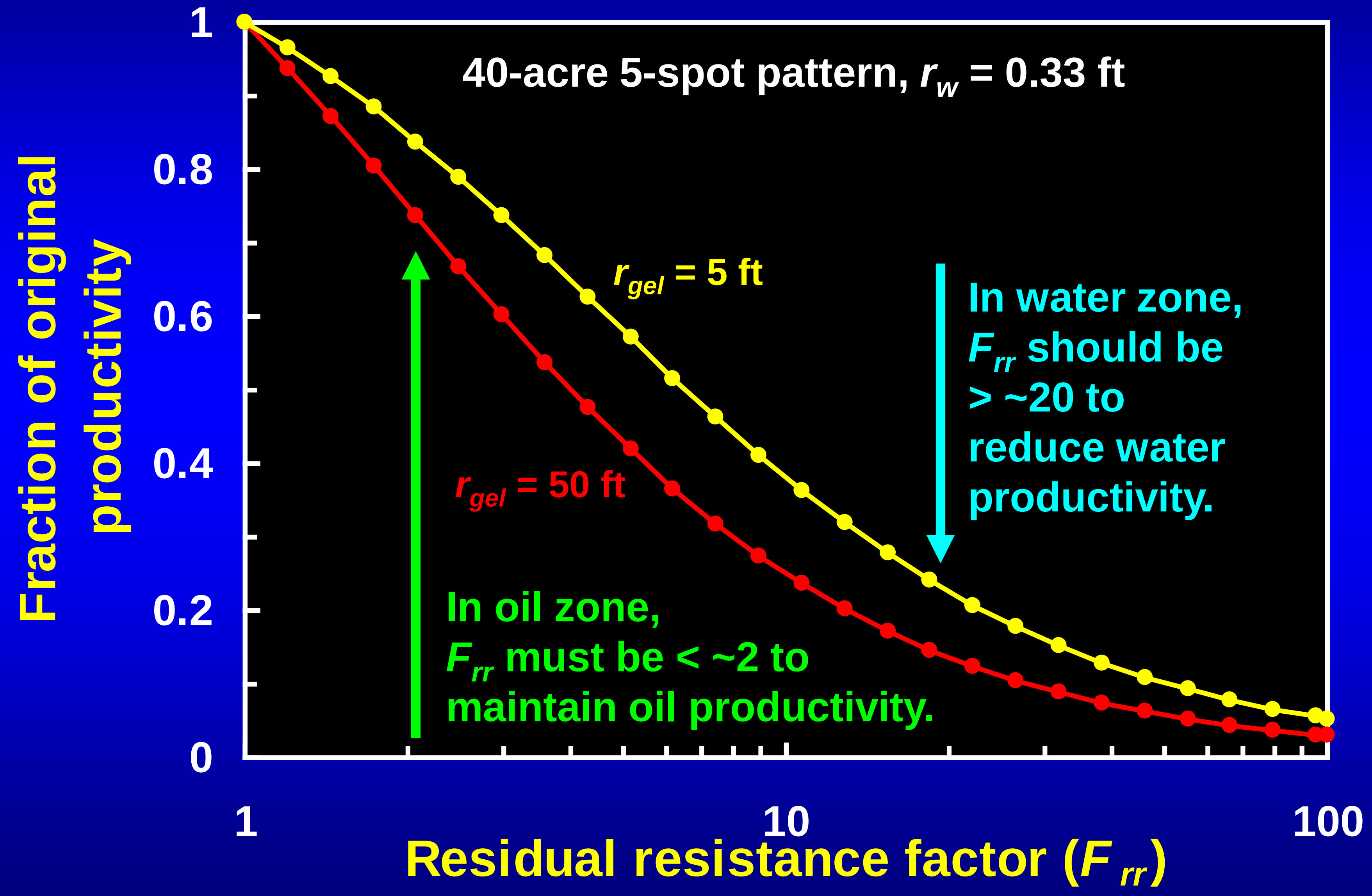
DISPROPORTIONATE PERMEABILITY REDUCTION

- Some gels can reduce k_w more than k_o or k_{gas}.
- Some people call this “disproportionate permeability reduction” or “DPR”. Others call it “relative permeability modification” or “RPM”. It is the same thing!
- This property is only of value in production wells with distinct water and hydrocarbon zones. It has no special value in injection wells!!!
- NO KNOWN polymer or gel will RELIABLY reduce k_w without causing some reduction in k_o !!!

- **IDEALISTIC GOAL OF WATER SHUTOFF TECHNOLOGY: Materials that can be injected into any production well (without zone isolation) and substantially reduce the water productivity without significantly impairing hydrocarbon productivity.**

- **Most previous attempts to achieve this goal have used adsorbed polymers or “weak gels” and most previous attempts have focused on unfractured wells.**

Radial Flow Requires That $F_{rro} < 2$ and $F_{rrw} > 20$



In water zone, F_{rr} should be > ~20 to reduce water productivity.

In oil zone, F_{rr} must be < ~2 to maintain oil productivity.

Problems with adsorbed polymers and weak gels (suspensions of gel particles):

- They show large variations in performance.
- F_{rr} values are greater in low-k rock than in high-k rock.
- F_{rro} values must be reliably less than 2 for radial flow applications.

Why do adsorbed polymers and weak gels show large performance variations?

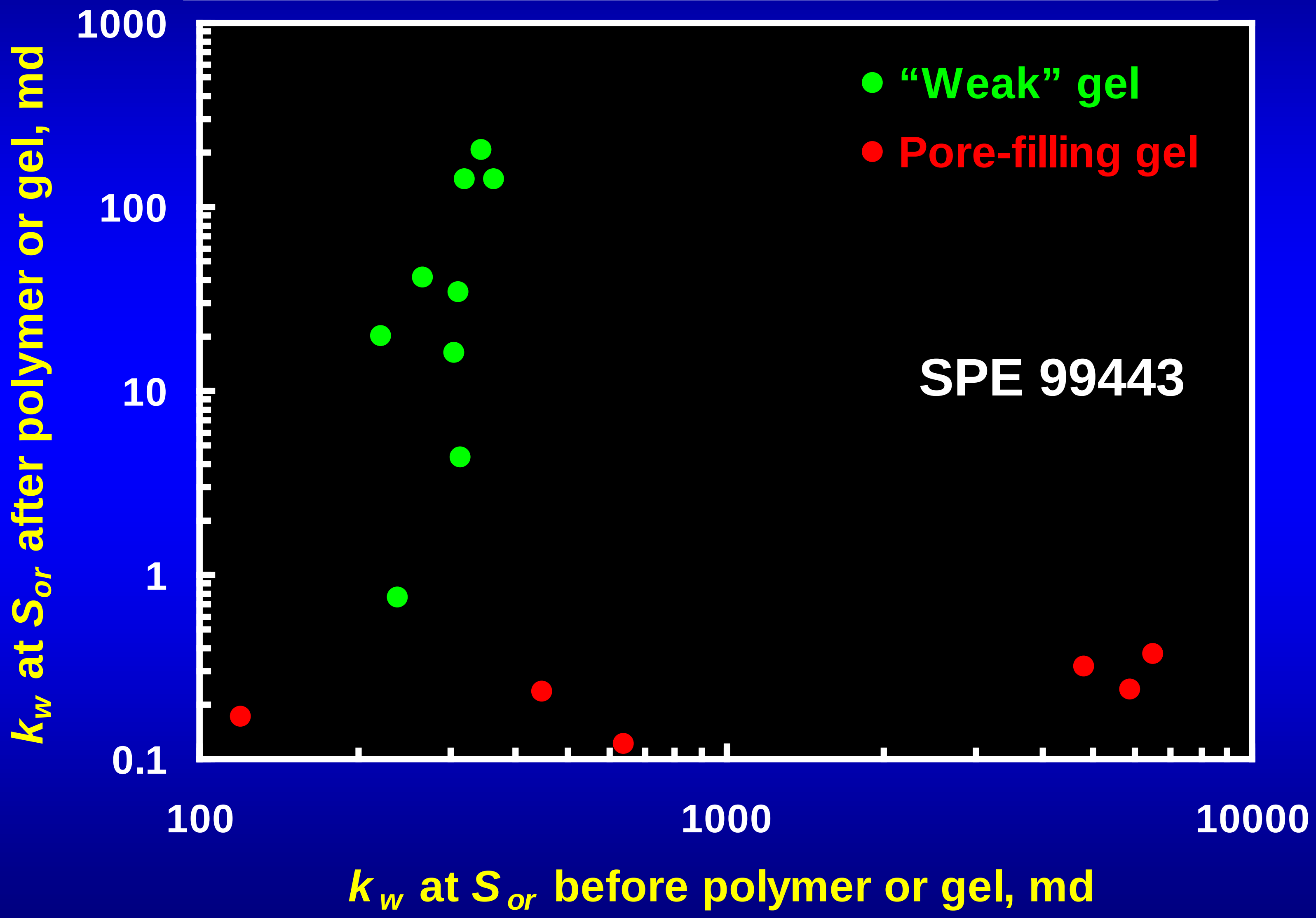
- Mineralogy varies within rock, so the level of adsorption also varies.
- Particle suspensions (e.g., weak gels) often have uncontrolled size distributions.
- Pore size distributions vary in rock.

Conceptual solution to variations and *k*-dependence of gel performance:

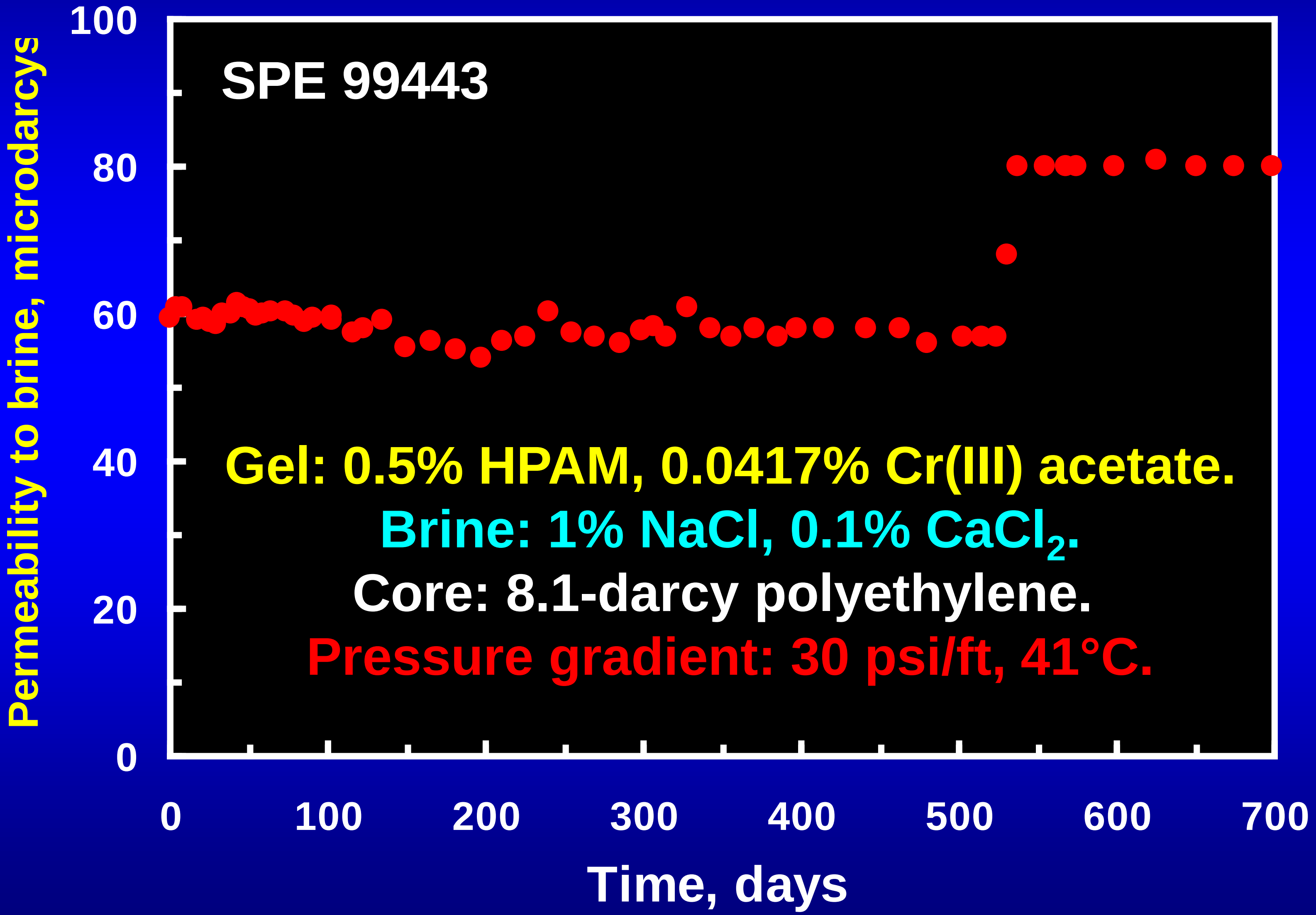
USE A PORE FILLING GEL.

- **Aqueous gels exhibit a finite, but very low permeability to water.**
- **If all aqueous pore space is filled with gel, k_{gel} will dominate k_w .**
- **So, rock with virtually any initial k_w should be reduced to the same final k_w .**

Pore filling gels are more reliable than adsorbing polymers or weak gels.



k_w can be quite stable to brine throughput and time.



SPE 99443

Gel: 0.5% HPAM, 0.0417% Cr(III) acetate.

Brine: 1% NaCl, 0.1% $CaCl_2$.

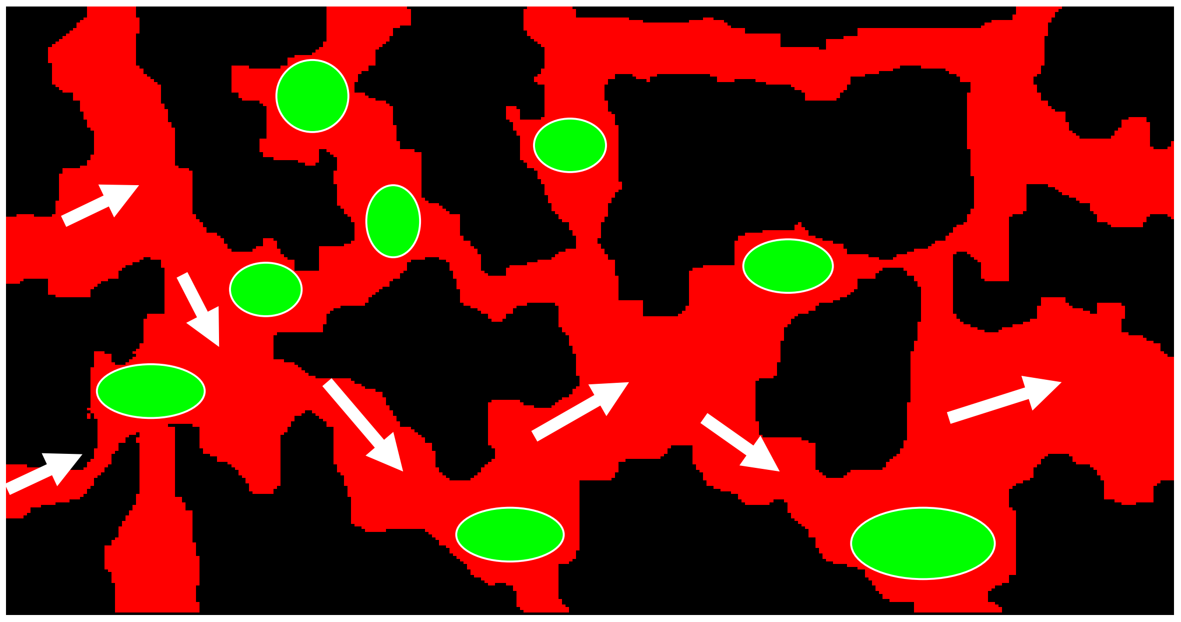
Core: 8.1-darcy polyethylene.

Pressure gradient: 30 psi/ft, 41°C.

WHY DO GELS REDUCE k_w MORE THAN k_o?

FIRST WATER FLOW AFTER GEL PLACEMENT

SPEREE (Oct. 2002) 355–364; *SPEJ* (Jun. 2006)



🟥 IMMOBILE GEL

🟩 OIL

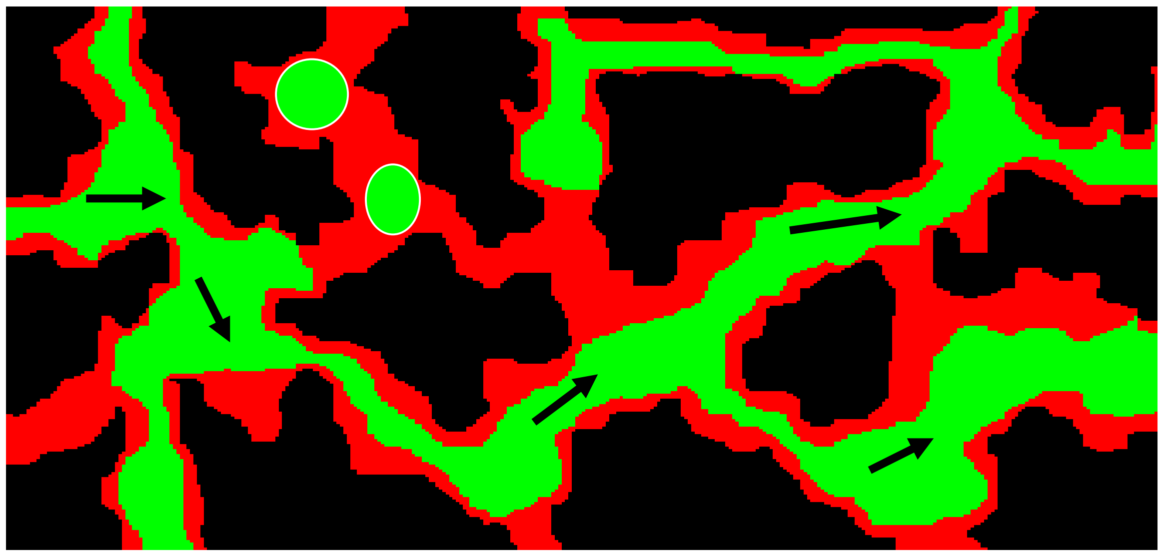
➡ WATER FLOW THROUGH GEL

- Strong gels fill all aqueous pore space.
- Water must flow through the gel itself.
- Gel permeability to water is typically in the µd range.
- Water residual resistance factor (F_{rrw}) is typically > 10,000.

WHY DO GELS REDUCE k_w MORE THAN k_o?

FIRST OIL FLOW AFTER GEL PLACEMENT

SPEREE (Oct. 2002) 355–364; *SPEJ* (Jun. 2006)



🟥 IMMOBILE GEL

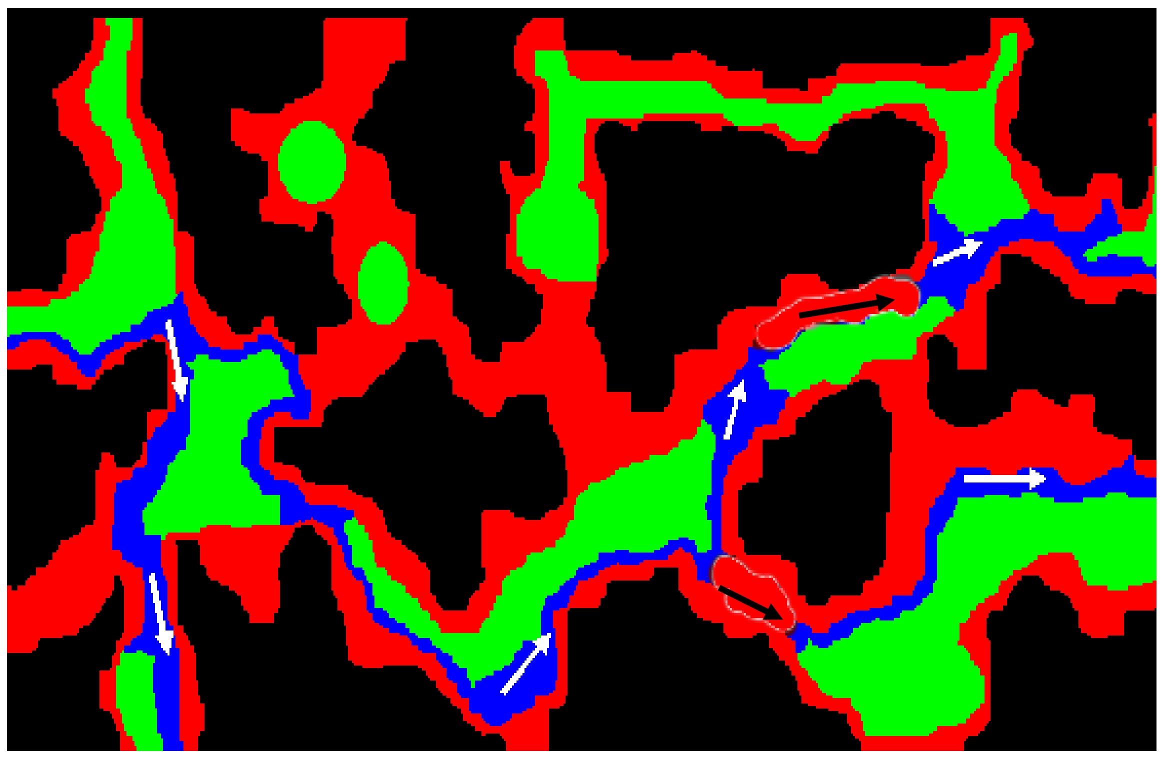
🟩 OIL

➡ OIL FLOW

- Even with low pressure gradients, oil forces pathways through by destroying or dehydrating the gel.
- These oil pathways allow k_o to be much higher than k_w.
- Even so, k_o is lower than before gel placement.

WATER FOLLOWING OIL AFTER GEL PLACEMENT

SPEREE (Oct. 2002) 355–364; *SPEJ* (Jun. 2006)



🟥 IMMOBILE GEL

🟩 OIL

🟦 WATER

🟦→ WATER FLOW

🟥→ WATER FLOW THROUGH GEL

- Gel traps more residual oil.
- Increased S_{or} causes lower k_w ($k_w \approx 1000$ times lower after gel than before gel placement).

A Challenge:

F_{rro} **must be reliably < 2 for radial applications, but** F_{rrw} **must be reliably high (>100) for linear flow applications.**

Can pore-filling gels meet this challenge?

F_{rrw} and final F_{rro} values for pore filling Cr(III)-acetate-HPAM gels in Berea sandstone.

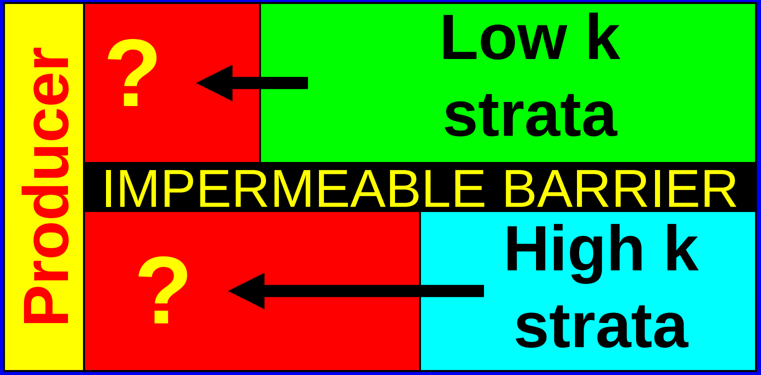
Pre-gel k_w, md	HPAM in gel, %	Post-gel k_w, md	F_{rrw}	Final F_{rro}
356	0.5	0.015	23,700	1.2
389	0.5	0.005	77,800	1.2
31	0.5	0.007	4,430	2.2
40	0.4	0.019	2,110	2.0
270	0.3	0.055	4,980	1.7

SPE 99443

- Polymers and gelants usually enter both oil and water strata when placed.
- Oil must flow or wormhole through the water or gel bank to reach the well.

Gelant Injection

Return to Production

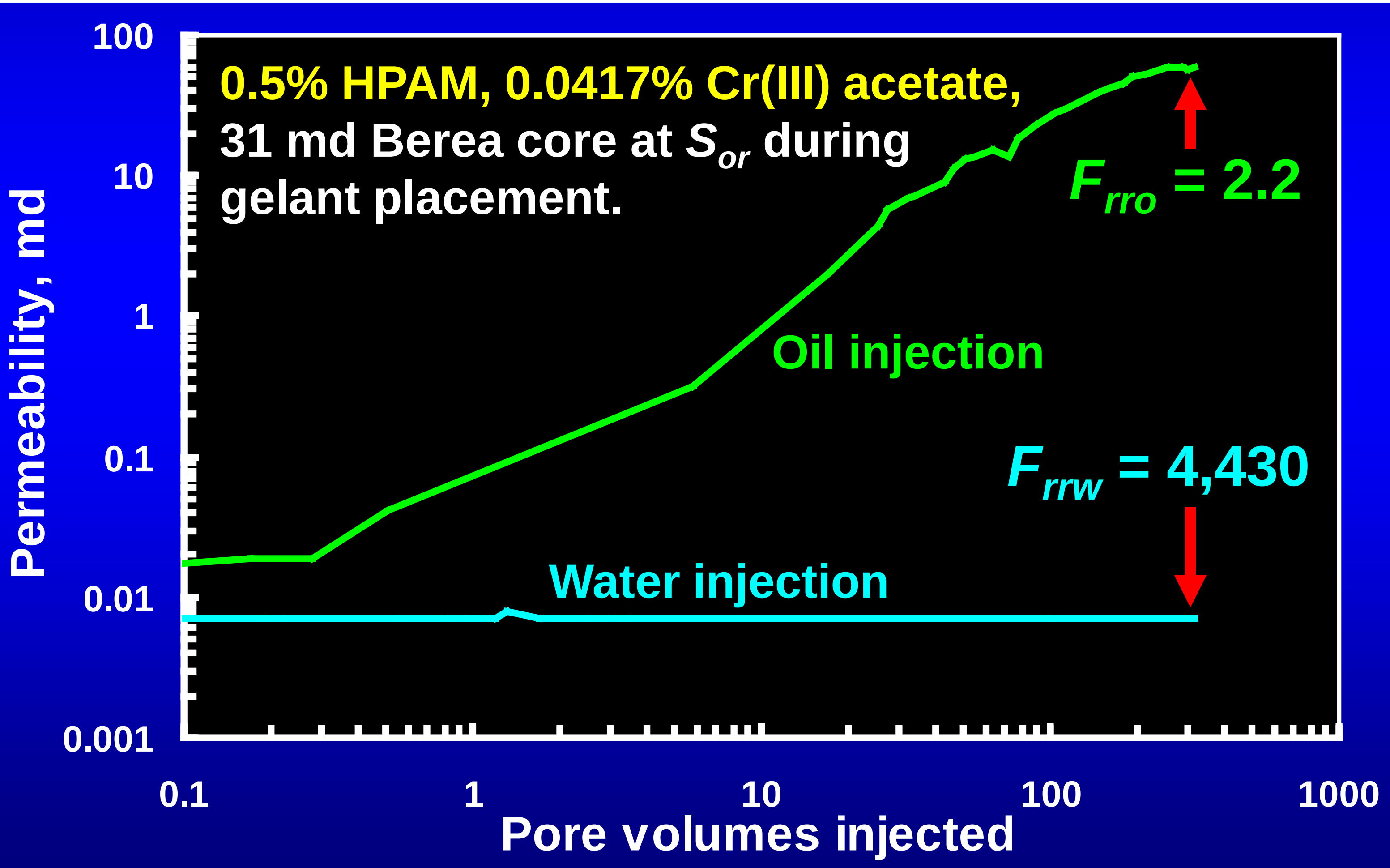


🟦 Water 🟩 Oil 🟨 Gelant 🟥 Gel

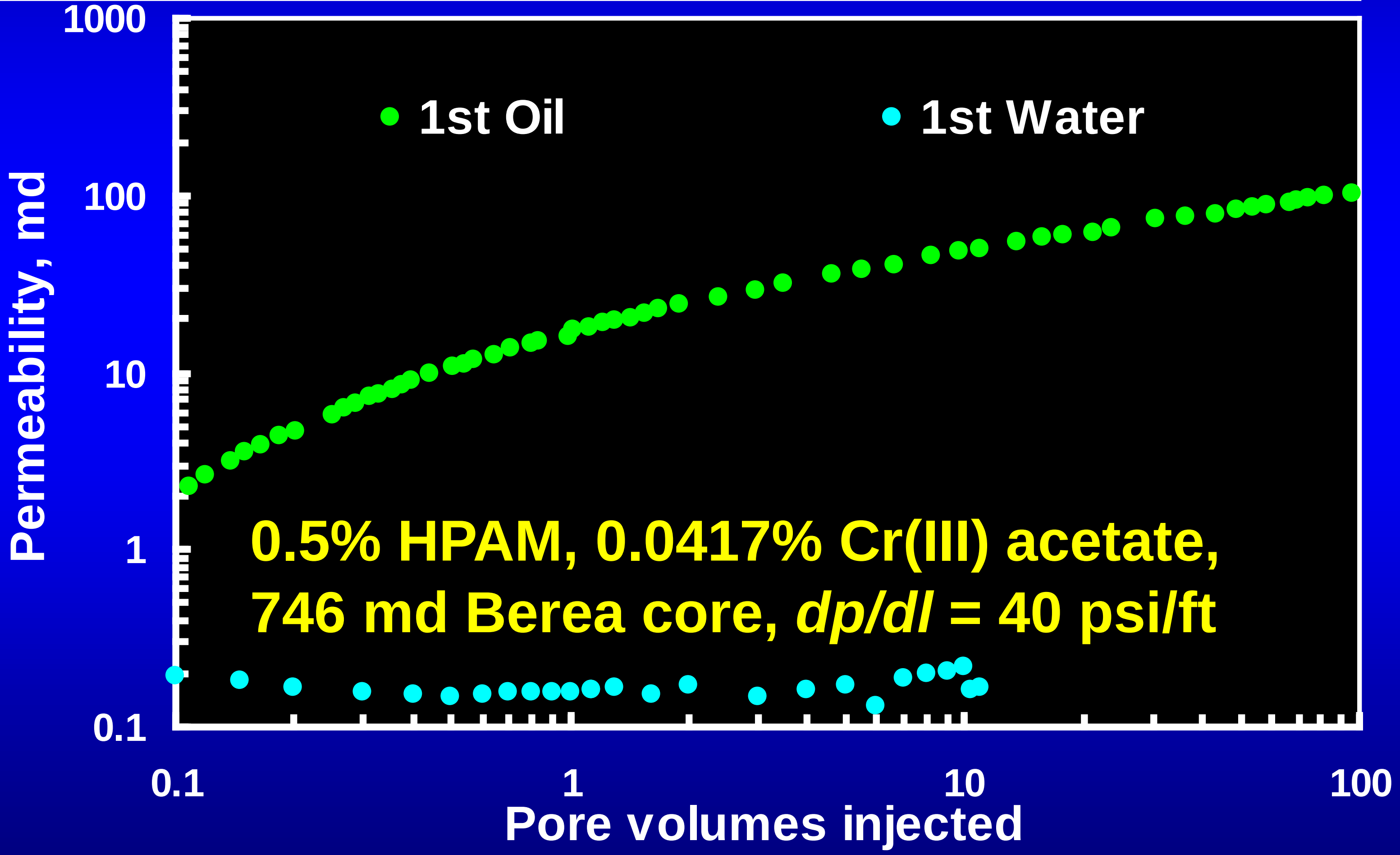
- For some polymers and gels, $k_w \ll k_o$.
- However, some time is needed for oil rates to recover.

After gel placement, during water or oil flow,

- k_w stabilized very quickly at a low value.
- k_o rose gradually to a high value.



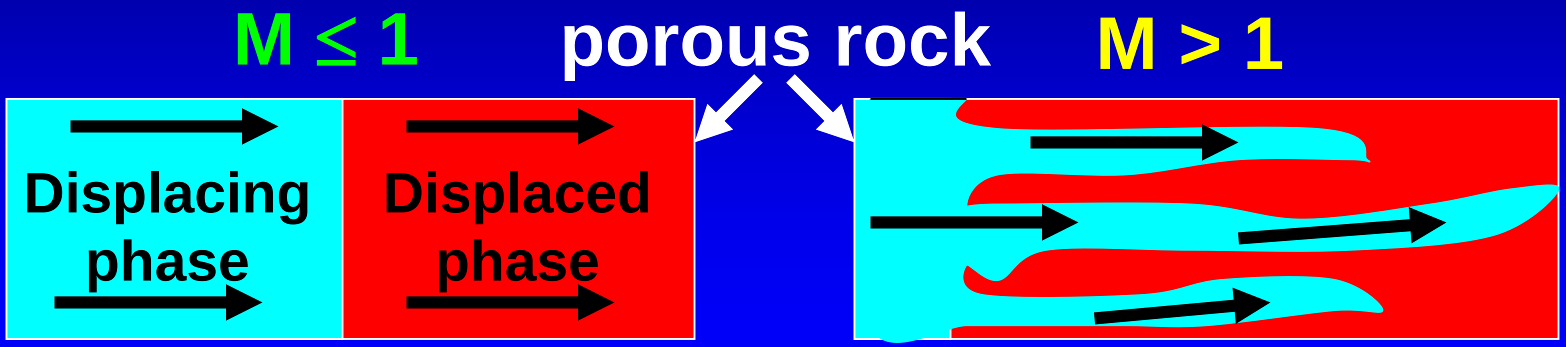
1. After gel placement, k_o rose from 2 to 105 md in 100 PV (F_{rro} = 4.8 @ 100 PV).
2. k_w stabilized at 0.17 md very quickly (F_{rrw} = 706).



0.5% HPAM, 0.0417% Cr(III) acetate, 746 md Berea core, *dp/dl* = 40 psi/ft

MOBILITY RATIO

$$M = (k/\mu)_{\text{displacing phase}} / (k/\mu)_{\text{displaced phase}}$$



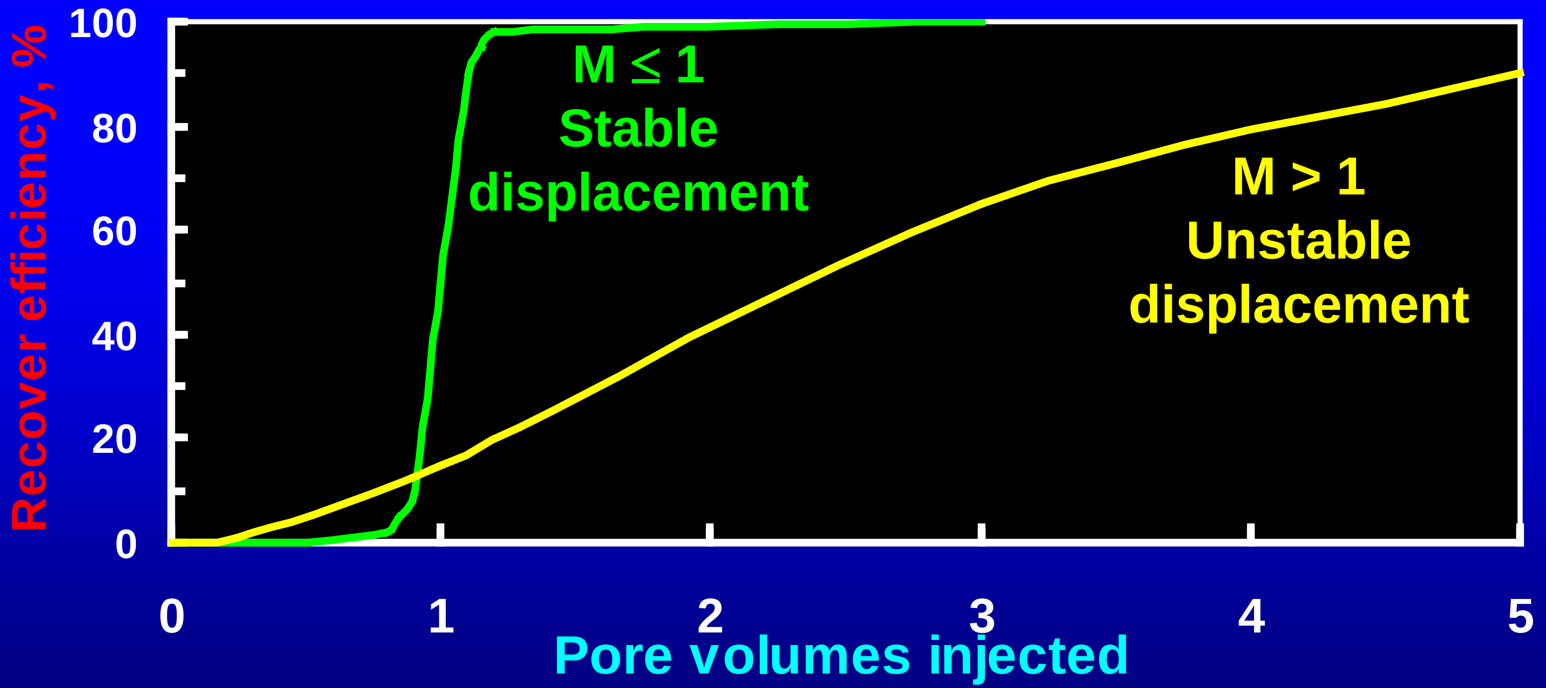
M ≤ 1

porous rock

M > 1

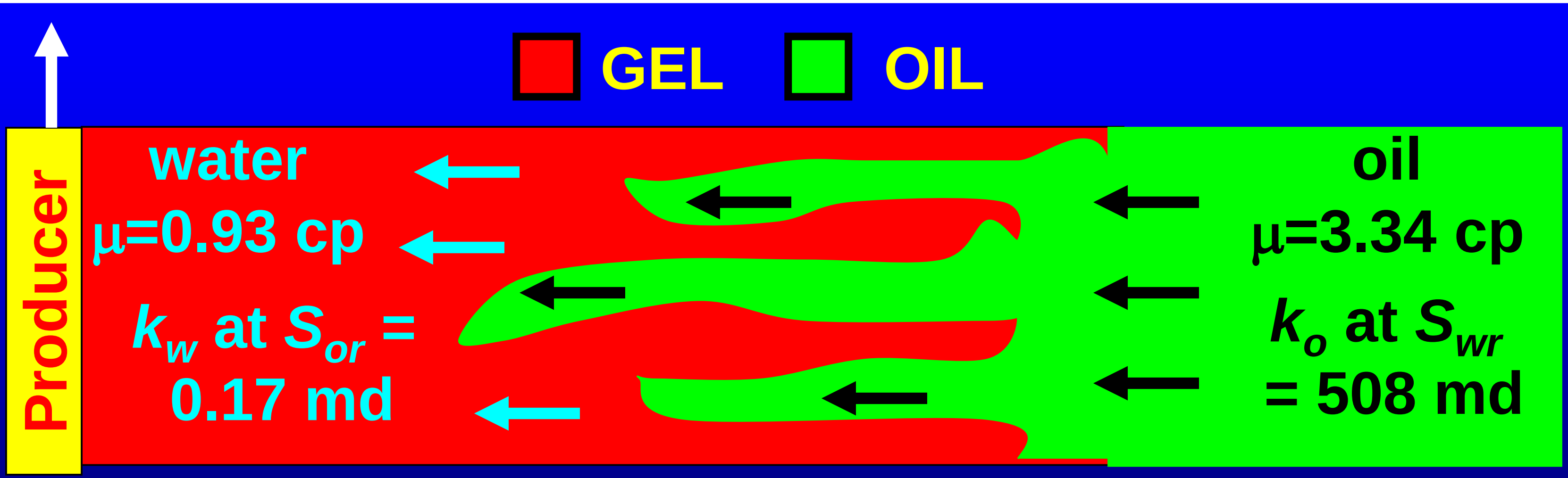
Displacing phase

Displaced phase



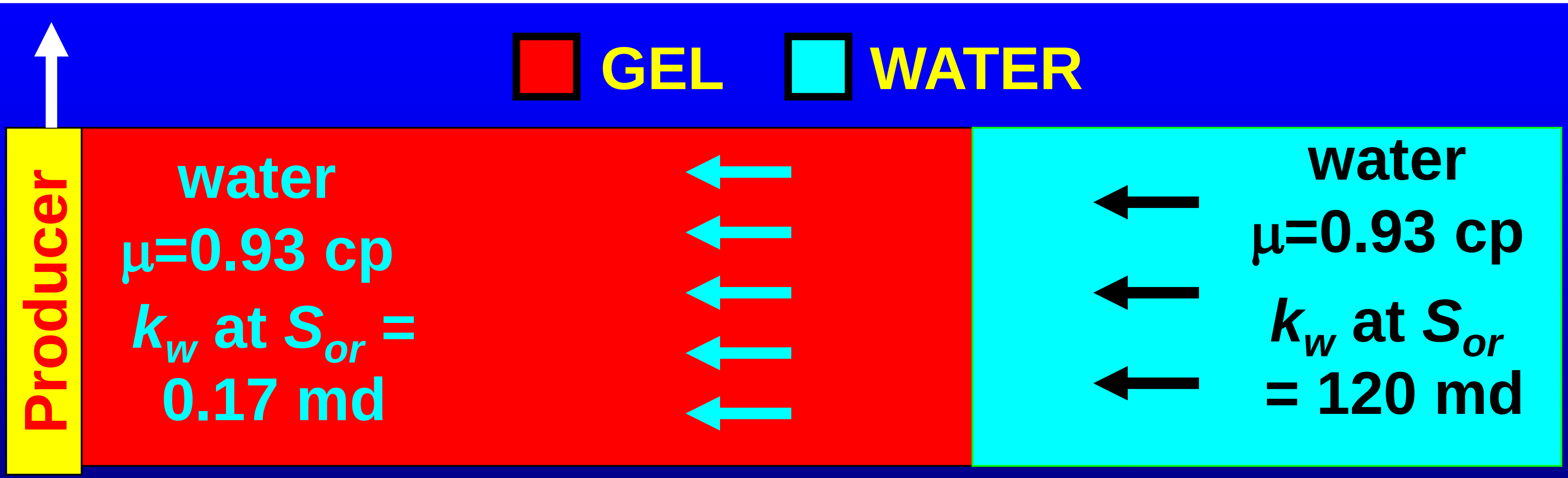
What happens in an oil zone when a well is returned to production AFTER gel placement?

- **Mobility ratio, M = $(k_o/\mu_o)/(k_w/\mu_w)$ = (508/3.34)/(0.17/0.93) = 830**
- **Displacement is very UNFAVORABLE!**



What happens in a water zone when a well is returned to production AFTER gel placement?

- Initially mobility ratio also looks very unfavorable.
- HOWEVER, once the water enters the gel, it becomes part of the gel. So no viscous fingers form, and the displacement remains stable!



DISPROPORTIONATE PERMEABILITY REDUCTION

- **Pore-filling gels show much more reproducible behavior than weak gels or adsorbed polymers.**

- **For pore-filling gels, the first-contact brine residual resistance factor is typically determined by the inherent permeability of the gel to water.**

- **Re-establishing high k_o values requires large oil throughput.**

- **Achieving large throughput values in short times requires small distances of gelant penetration.**

WHY CHOOSE ONE MATERIAL OVER ANOTHER?

- Cost
- Availability
- Sensitivity of performance to condition or composition variations
- Blocking agent set time
- Permeability reduction provided to water
- Permeability reduction provided to oil or gas
- Ability to withstand high-pressure gradients in porous rock
- Ability to withstand high-pressure gradients in fractures or voids
- Rheology and/or filtration properties
- Ability to penetrate into fractures or narrow channels behind pipe
- Stability at elevated temperatures
- Environmental concerns