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ULTIMATE EOR
The Ultimate Source for Enhanced Oil Recovery

23RD EUROPEAN SYMPOSIUM ON
IMPROVED OIL RECOVERY

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TOWARDS SUSTAINABLE RESOURCE UTILISATION

CEOR – The Time for Implementation is Now

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Critical Timing for Oil Production

- Energy Transition is an “issue”.
- Stranded assets are a possibility (Annual Reports)
- Offshore Developments are Decade Long Commitments.
- EOR Oil is available on a much shorter time line, can be phased and adjusted. Operating costs are significant and can be titrated to market conditions.
- EOR Oil (polymer especially) is proven technology.
- EOR Oil requires a much smaller capital investment, especially if a water flood is in place.
- It is an advantageous time to implement EOR projects to guarantee increased production with minimal long-term risk.



1. Setting The Scene – Polymer Flooding (1980)

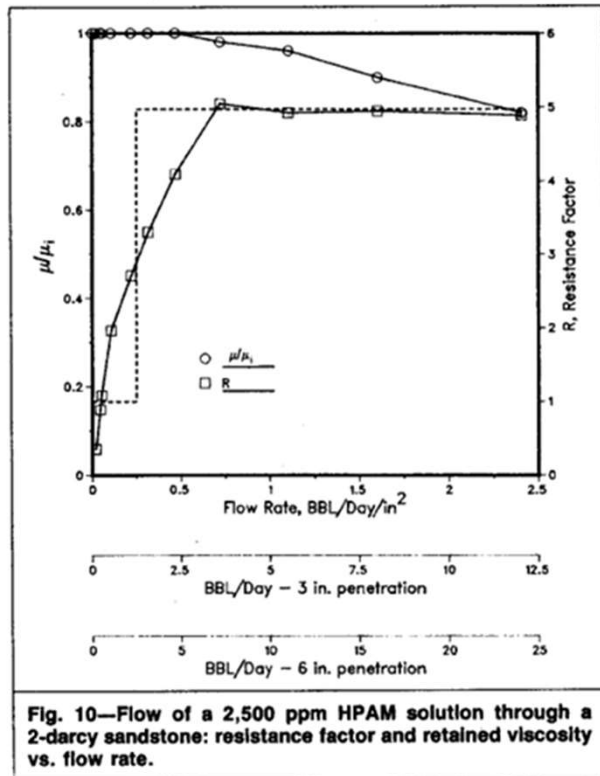
	October 1980	January 2025	October 1980 price in current dollars
Oil Price	\$40 all time high	\$70-80	\$153
Polymer Price	\$1.25	Similar to 1980	\$4.78
Well Technology	Vertical	Vertical/Horizontal	
Field Operations	Unproven	PSU, Proven Reliable	
Injectivity	Hit and Miss	Proven	
Products	2,3 MW's	10+ ATBS, MW, etc.	
Technology	Emerging	Mature	

Significant Progress - Proven Products, Field Handling, and Reliability

Improved Economics



Can We Inject Polymer at Reasonable Rates? Lab Experiments Say No. Radial Flow.



RF = apparent viscosity/low shear viscosity

Near wellbore shows shear thickening.

RF = 5 20 cp low shear injects like 100 cp.

At maximum RF polymer degrades.

Coil Stretch Transition of Flexible Coils.

Xanthan (rigid rod) injects easily, RF = 0.1

Southwick and Manke, SPEJ, 1988



Design Perforated Completion for Polymer Injection

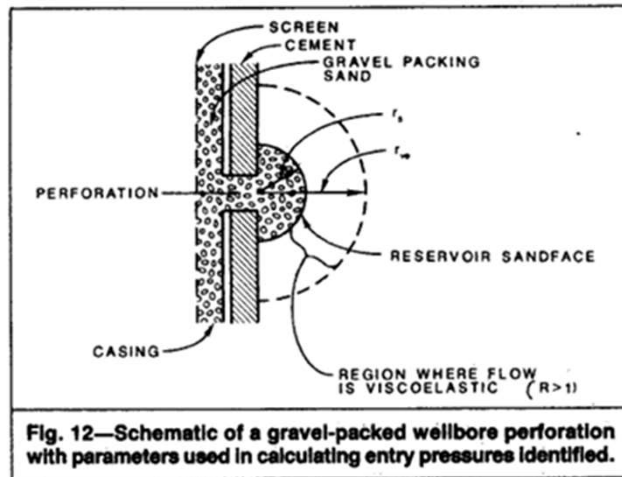


TABLE 3—CALCULATED VISCOELASTIC SHELL DIMENSIONS (r_s and r_{ve}) FOR $\frac{3}{8}$ -in. PERFORATIONS	
Sandface Area Ratio F_A	Radius of Gravel-Filled Cavity, r_s (in.)
10	0.419
25	0.663
50	0.937
Calculated Distance Over Which Enhanced-Resistance Flow Occurs	
Flow Rate (B/D-perforation)	Distance for Enhanced Resistance, r_{ve} (in.)
2.5	1.26
5.0	1.78
10.0	2.52
15.0	3.09

Design enough surface area for injection so flow is not in the shear thickening regime.

8 Shots per foot was the recommendation.

Lack of confidence in polymer injectivity – pilot run as AS in dipping reservoir (gravity stable).

Southwick and Manke, SPEJ, 1988



Injectivity Lab Experiments are Misleading



1) Koning, et al. "Evaluation of a Pilot Polymer Flood in the Marmul Field, Oman", [SPE-18092-MS](#) (1988)

"Injection of the water preflush was at 500 m³/d from the end of May 1986 till the middle of September 1986. Polymer injection followed at 500 m³/d until the middle of August 1987 when the switch-over to water injection took place."

No problem injecting 15 cP polymer at Marmul. Lab Experiments can be misleading.

2) Many commercial polymer floods with no problem with injectivity.

3) Explanation is controlled fractures are formed which reduces flux and prevents "viscoelastic flow", and modified deleterious affects of radial flow.

- In some cases, polymer is injected at lower pressure than water.
- Much supporting literature and field data.





Progress in Polymer Flooding Technology – 1980 to 2025

- 1) Control of Oxidative Degradation – Effect of Iron and Oxygen Scavenging
- 2) Preparation of High-Quality Polymer Solutions in the Field. Mother Solutions. Polymer Slicing Unit. Avoidance of Gels and “Fish-Eyes”.
- 3) Understanding that Fractures are not bad, and enable injectivity.
- 4) Understanding that unit mobility ratio is not an absolute requirement. Significantly enhanced recovery with highly viscous oils with unfavorable mobility ratios.
- 5) Fundamental understanding of viscous fingering and consequences of crossflow.
- 6) **Tremendous economic improvement from polymer suppliers.**
- 7) Many more polymer molecular weights, and products (ATBS) that can function at high temperatures and salinities.
- 8) Experience and success implementing polymer flooding offshore.





Polymer Flooding Projects Have Been Economically Successful

- **It is all about physics (the efficient application of pressure to move oil, not complex chemistry).** Water is inefficient due to poor mobility control. Reliable. Not complex.
- Incremental production from polymer flooding is about 400,000 B/D
- Polymer Flooding:
 - ✓ About 1 bbl of oil for each \$3 spent on the polymer (100 tons of oil per ton of polymer)
 - ✓ Overall **real** polymer costs decreased by a factor of 3 since 1980's

More than **320** projects
in the US

1966 - 1982

- East Coalinga
- Taber - Manville
- West Yellow Creek
- North Burbank

Large success in China

1989 - 2000

- Daqing: world's largest polymer injection: 12% inc. recovery

More than **200** projects

2010 - 2016

- China (Daqing cont'd)
- Oman
- India (Mangala, Bhagyam, Aishwariya)
- Canada (more than 30 polymer floods)
- Europe (North Sea & Eastern Europe)
- South America
- USA (Alaska North Slope, Texas)



Applicable to a Wide Variety of Reservoirs Due to New Products

- When looking at the papers in the 60's, 70's or even 80's, polymer flooding was limited to a narrow range of field conditions...
- What about now? New chemistries, new injection strategies, salt & temperature resistant polymers...

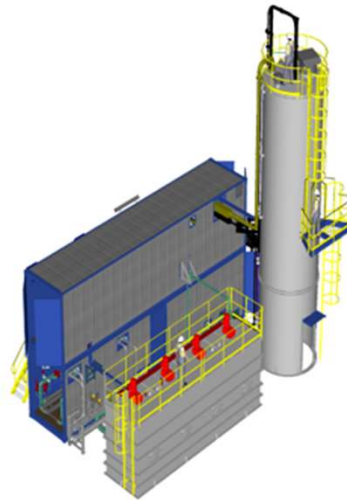
Parameter	Yesterday	Today & Tomorrow	
			Canada
Oil viscosity	<200 cP	<10,000 cP	Brazil, Middle-East...
Temperature	<95° C	<140° C	Middle-East
Permeability	>100 mD	>10 mD	East. Europe
Salinity	Low	<220 g/l TDS	
Cost	4.78 \$/lb	1\$/lb	Higher Mw, improved chemistries

Examples of Deployment Strategies

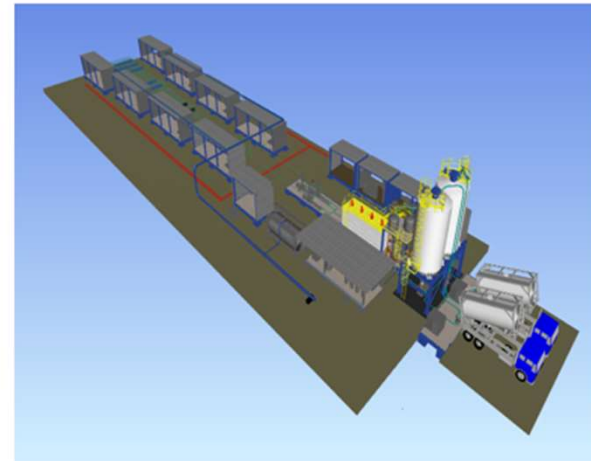
- From pilot to full field with a modular approach: adding skids and modules for expansion
 - Saving on overall costs and project execution lead time
 - Step by step investment to facilitate the decision process
 - Gain on flexibility : modular and progressive deployment of EOR modules, cluster by cluster



7 t/day dry polymer



15 t/day dry polymer

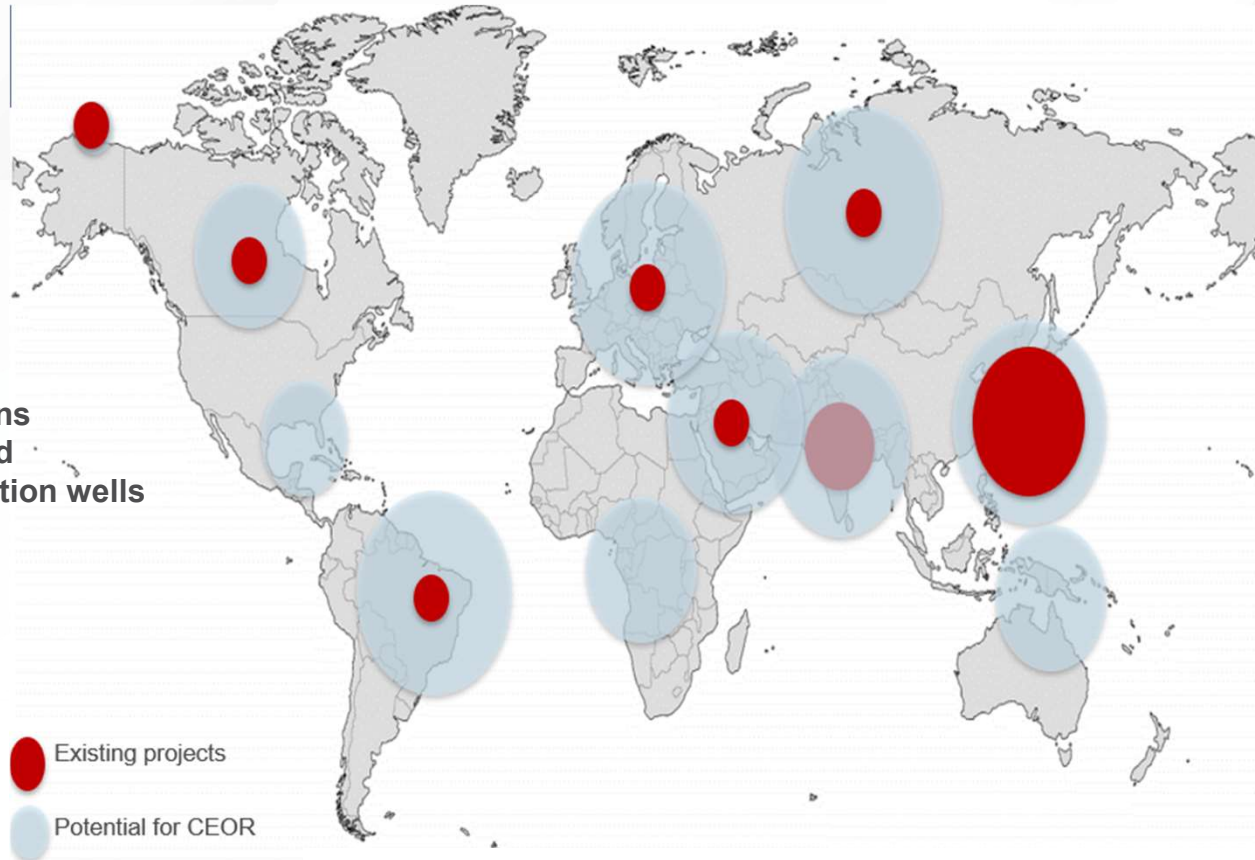


15 t/day dry polymer – 32 wells



Current Projects and Potential Growth of Polymer Flooding

- More than 50 polymer injections
- More than 200 projects studied
- More than 3,000 polymer injection wells



Percentage of PAM used in CEOR is <20% of the worldwide PAM production capacity



2. Setting the Scene (1980) Caustic Flooding with High Acid Number Oils

- Inject Sodium Hydroxide (with Polymer) into reservoirs with high acid number oils. Form low IFT by converting petroleum acids to petroleum soaps. Sodium Hydroxide is preferred as it gives the highest pH at low concentration (strong base).
- Not a good idea. Sodium hydroxide dissolves sandstone quickly forming a sodium silicate solution. Soluble silicates produce intractable silicate scale in production wells. Buffered alkali (sodium carbonate) solves this problem and has become the alkali of choice for ASP. However, NaOH can be used in carbonate formations.

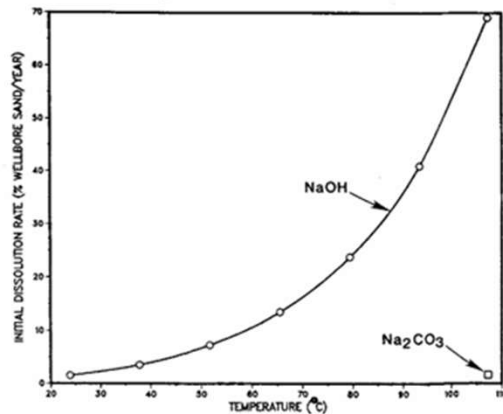


Fig. 7—Calculated initial dissolution rates for quartz, expressed as percent wellbore sand dissolved per year vs. temperature. (—) 1% NaOH, (---) 2.65% Na₂CO₃.

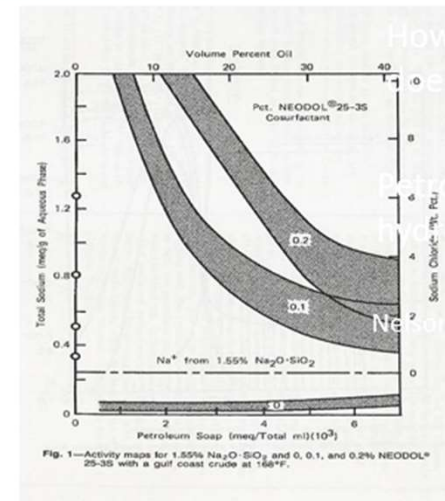
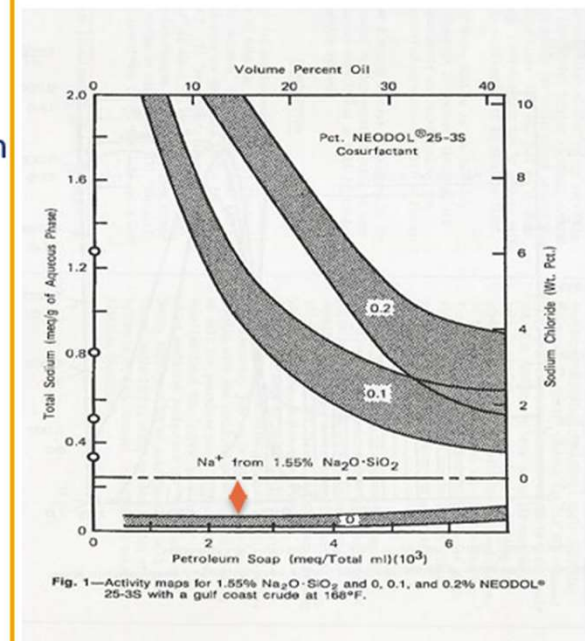


Fig. 1—Activity maps for 1.55% Na₂O-SiO₂ and 0.1, and 0.2% NEODOL® 25-35 with a gulf coast crude at 168°F.



Adding a (Co) Surfactant to An Alkaline Flood Invention of ASP!

- ASP developed from Alkaline flooding (AP).
 - AP uses alkali to form surfactants from the oil. No added surfactant.
 - However, it was determined that **AP flooding has a major flaw**. Petroleum soaps are too hydrophobic for required injection salinity (alkalinity).
 - 1) A certain alkali concentration is needed to propagate a high pH bank through the rock. We cannot control this amount. It depends totally on the rock since the rock neutralizes alkali.
 - 2) The required amount of alkali has salinity which is too high to generate low IFT with the surfactant derived from the oil.
 - 3) A small amount of a 2nd surfactant (co-surfactant) is added to modify the behavior of the oil derived surfactant so that low IFT is obtained with sufficient alkali for propagation through rock.
- Advantage is also much reduced surfactant adsorption due to ionization of rock surfaces.



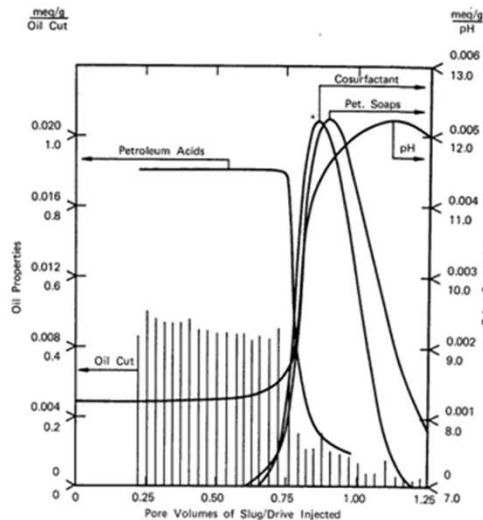
R.C. Nelson et al. SPE 12672 (1984)



ASP – Low IFT attained and Very High Displacement Efficiency Attained with (Co) Surfactant

- Hydrophilic cosurfactant mixes with hydrophobic soap producing low IFT!
- ASP with high TAN oil. Very low surfactant levels (uses natural occurring soaps) and low adsorp on rock. High pH.
80% of the produced oil is never contacted by surfactant or alkali!

Optimum Low IFT Flood



*Peak Cosurfactant Concentration is 45% of Injected Concentration.
 Fig. 4—Composition of liquids produced from a cosurfactant-enhanced alkaline flood.

Fundamental Concept

The oil is banked, not solubilized,

Potentially very little surfactant is needed to produce all the oil.

Very little surfactant is needed to recover all the oil from rock.

It is not an emulsification process. Clean oil bank.

Oil bank is formed and mobilized due to rel. perm effects.

Berg, van Batenburg et al, EAGE 2015, CT scanning of ASP. Inherently stable. Leading polymer front does not finger through oil bank.
 Matsuura, van Batenburg et. al. EAGE 2015, Modelling of ASP displacement.



Commercial Project – Huge Amounts of Alkali Required in Remote Location

LOGISTIC – FROM SALALAH TO MARMUL



- 450 tons of sodium carbonate/day
- Major challenge for commerciality. Scale of operation is challenging.

Logistics - Transport risk					
Name	Trucks/yr	Km/y	Yearly Project Risk Nr of fatalities	Km lifetime project	Risk during lifetime
Alkaline	8.926	4.641.574	0,12	49.510.119	1,28
Surfactants	1.799	935.443	0,02	9.978.057	0,26
Polymer (ASP)	1.252	650.981	0,02	6.943.794	0,18
Polymer (chase)	1.718	893.503	0,02	9.530.698	0,25
Demulsifier	157	81.851	0,01	1.054.597	0,11
Sum	13.853	7.203.351	0,19	77.017.265	2,07

77,017,265 kms traveled by delivery drivers = safety risk



More Efficient Alkali Alternatives (MW/mole)

General observation – the lower MW the better. Liquid ammonia is ideal but is discounted due to *safety concerns*.

Organic amine can be considered to be ammonia with carbons.

The 1 Carbon organic amine (methyl amine) is not a commercial product.

The 2 Carbon commercial organic amines are shown in the table above. Monoethanolamine is preferred, cost and safety.

The second amine group on ethylene diamine is not useful, pKa is too low.

Table 1. Comparison of Monoethanolamine, Ethylene Diamine, and Sod Carbonate

Alkali	Cost \$/ton	M.W.	pH 1%	Cost \$/mole	HSSE*	Bulk Density	M.P.	B.P.	Visc at 20°
MEA	1200	61	11.5	0.073	3,2,0	1.01	10	170	24 cp
EDA	2600	60	11.5	0.156	3,3,0	0.90	8	116	1.8 cp
Na ₂ CO ₃	225	106	11.5	0.024	2,2,0	1.02	100	na	na



Alkali	Dissociation Constant at 25 C	Calc pH - 0.1 Moles
NH ₃	1.8×10^{-5}	11.12
Ethanolamine (MEA)	2.72×10^{-5}	11.21



Surprise #1 Organic Amine (MEA) ionizes Petroleum Acids at Lower pH

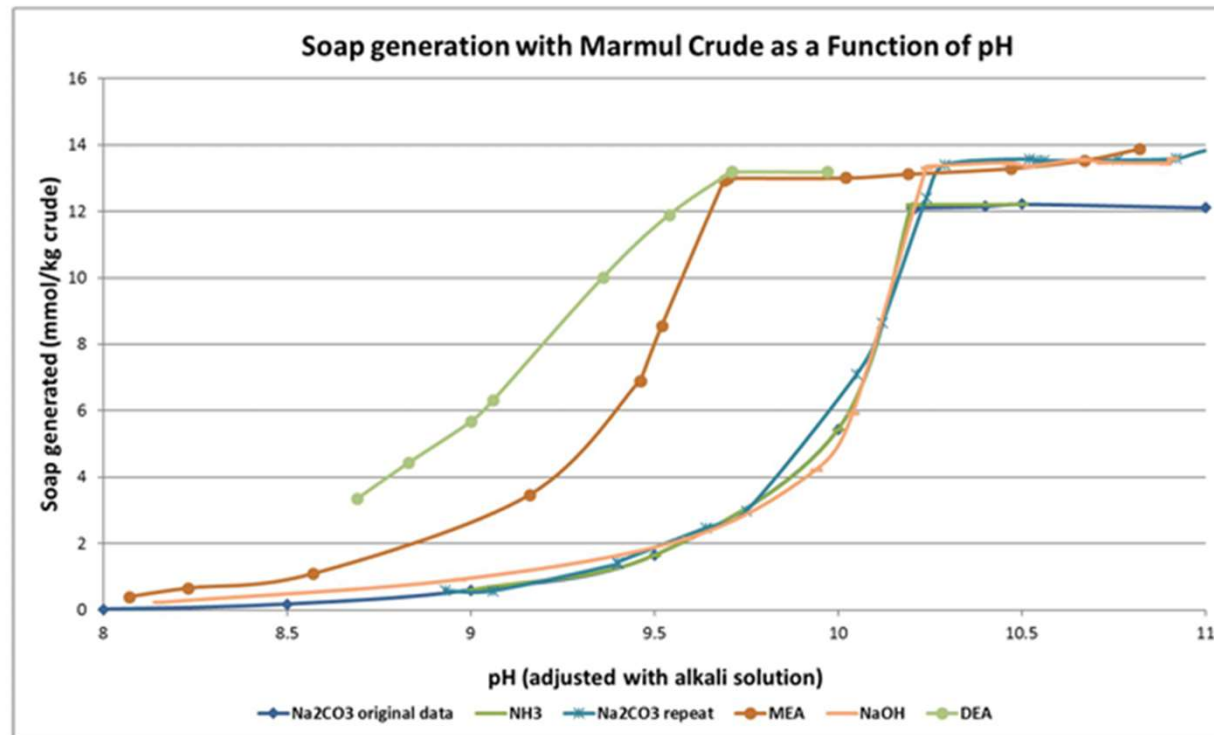
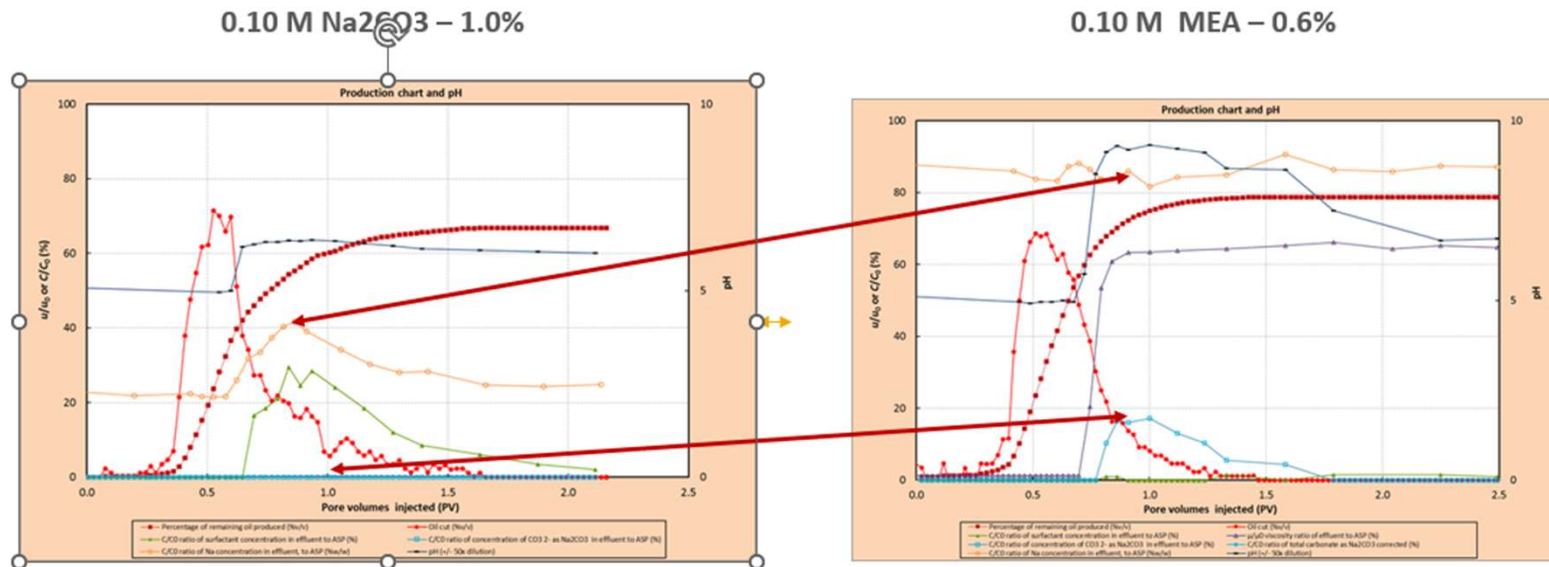


Figure 2. Titration of Marmul crude oil with various alkalis.



Surprise #2 Lower Alkali Consumption by Rock with MEA



Oil Recovery equally good with MEA.

Surprise #2. Similar alkalinity injected, but much more produced with MEA. Sodium Hydrogen Exchange consumes carbonate.

Mahruqi, D. et al. Successful Marmul Pilot with MEA, SPE (2021).



Alaska North Slope Reservoir Rock – 8 Times Less Alkali Loss with MEA

Table 4: MEA & Na₂CO₃ consumption

	MEA	Na ₂ CO ₃
Injected alkali mole	1.9E-02 mol	4.4E-02 mol
Recovered alkali	1.7E-02 mol	3.3E-02 mol
Alkali consumed	2.5E-03 mol	1.2E-02 mol
Alkali consumed, mg	153	1230
% Consumed	12%	26%
mg. cons/g. rock	0.3	2.2

Surprise #2!

Due to equilibrium
Sodium concentration

Significantly less MEA is required for ACP/ASP floods! 8 Times less by weight. Cheaper overall even though MEA is more expensive than sodium carbonate.

Southwick et. al. (2022) SPEJ



Alkali – Cosolvent Liquid Blend - Simplified Logistics

- MEA cosolvent blend – low viscosity. Delivered formulated. Allows for use in cold weather environment or offshore.

Figure 1 below shows an MEA/alkoxylate/co-solvent blend and a typical sulfonate surfactant with MEA. Sulfonate surfactants are aqueous concentrates and at concentrations of 50% solid/50% water are typically viscous pastes.

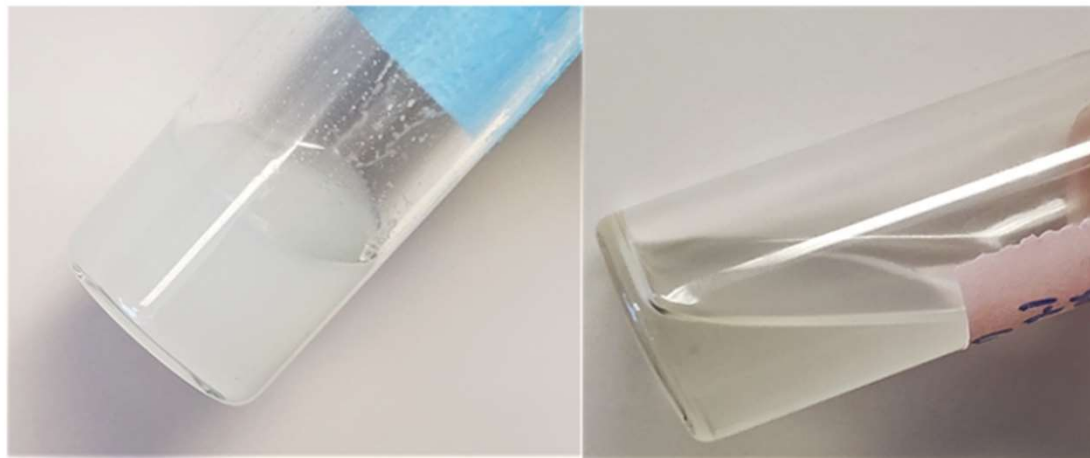
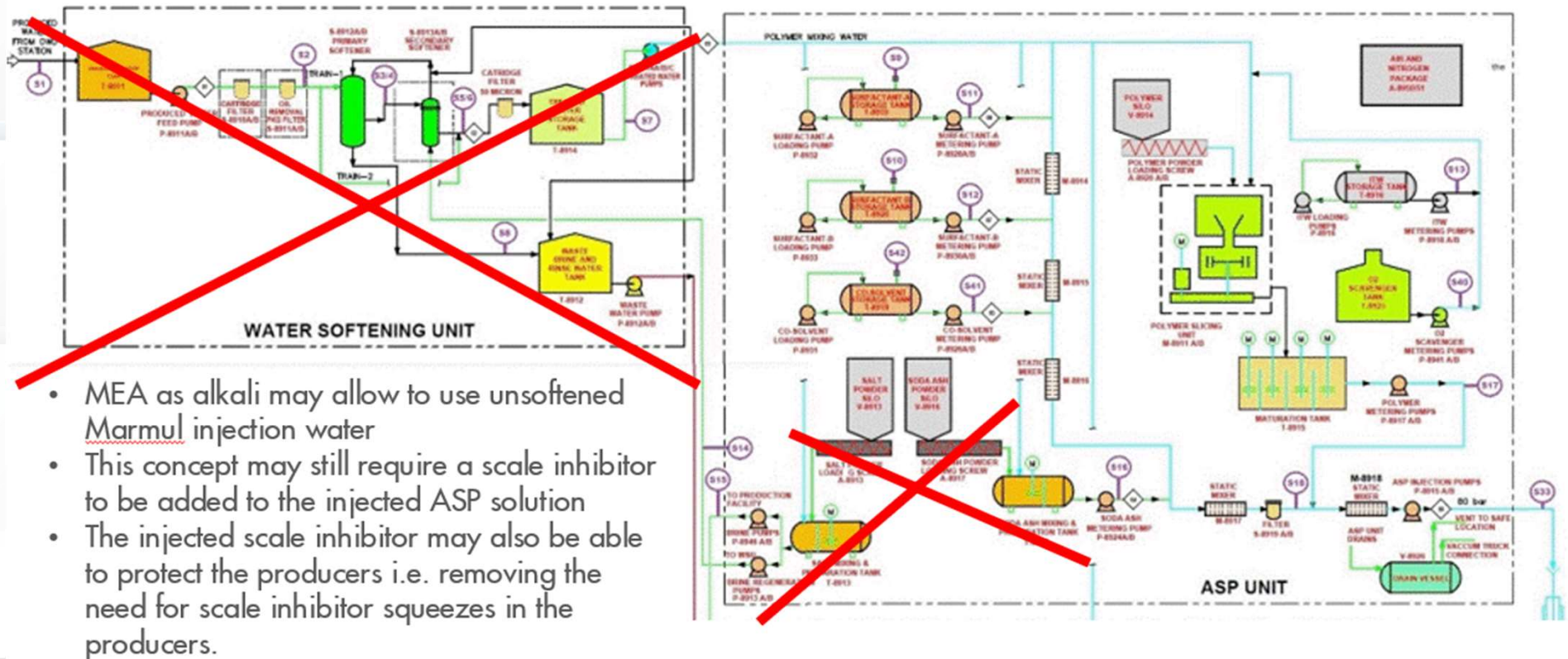


Figure 1. Left- Blend of sulfonate with MEA solid paste. Right-Blend of Glycerin-30PO-35EO with MEA, flowable liquid at 8°C.

Concept of No Water Softening w Marmul Reservoir Brine





3. Setting the Scene – SP Flooding (1980)

- Very Limited Number of Appropriate Surfactants.
- Commercial Surfactants (Laundry, Dishwashing, Shampoo, etc.) are too hydrophilic and do not generate low IFT with crude oil. They are designed to solubilize oil in water not to form low IFT.
- Industry approach, petroleum sulfonates, specialty surfactants with higher molecular weight hydrophobes (alkyl benzene sulfonates (ABS), internal olefin sulfonates (IOS)).
 - not tolerant to divalent cations (Ca, Mg)
 - expensive compared to commercial (laundry, etc.) surfactants.
- Due to limited number of products injection salinity needed to be modified and controlled. Expensive.
- Limited success. Not economically attractive.





Prolific Development of Surfactants for EOR

- Chemical Companies and Academia responded to the challenge of synthesizing surfactants that generate low IFT with crude oil over a range of injection brine conditions.

Improved Aqueous Solubility – Solved a major problem with early surfactants. Low IFT and aqueous stability were mutually exclusive.

- Unique and effective branched hydrophobes
- Branched Guerbet alcohols
- Ethylene oxide (EO) Propylene Oxide (PO) sulfates with a range of hydrophobes. Divalent cation tolerant.
- Blends of cationic/anionic surfactants to control optimal salinity
- Effective and adjustable blend of internal olefin sulfonate and C12-15-7PO-Sulfate. Divalent ion tolerant.
- Development of unique surface-active solvents that are liquid and easy to handle.
- Increased manufacturing capacity and supply of EOR surfactants.

Proliferation of Products affords the possibility to simplify SP flooding.

- **Tailor Surfactant molecule to specific Injection Brine – Not the other way around.** No salinity manipulation.
- Wide range of surfactant molecules available that tolerate high salinity and divalent ion concentrations.
- Formulation Development that does not require a salinity gradient.
- Formulation for Seawater. Implementation Offshore.



Constant Salinity Formulation for Seawater

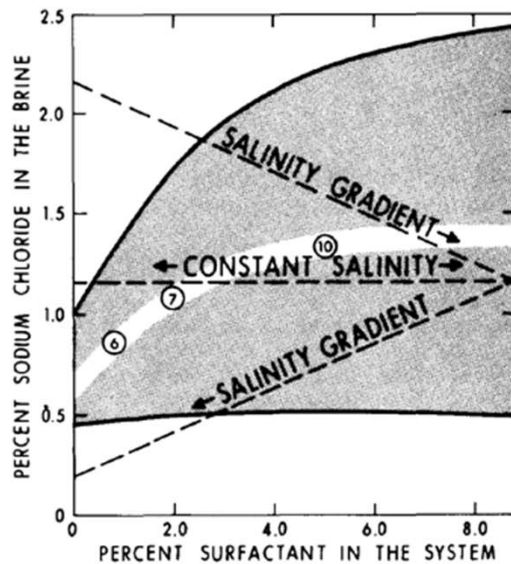


Fig. 3—Comparison of constant-salinity with salinity-gradient designs.

R.C. Nelson, [SPE-8824-PA](#), SPEJ 1982

Modified Salinity Requirement Diagrams

PO Sulfate/IOS

J771 Fraction	O332 Fraction	Phase Behavior Type			
0.8	0.2	2	2	2	3
0.75	0.25	2	2	3	3
0.7	0.3	2	2	3	1
0.65	0.35	3	3	1	1
		0.2	0.4	0.6	1
		surfactant concentration (%)			

PO Sulfate/EO Sulfate

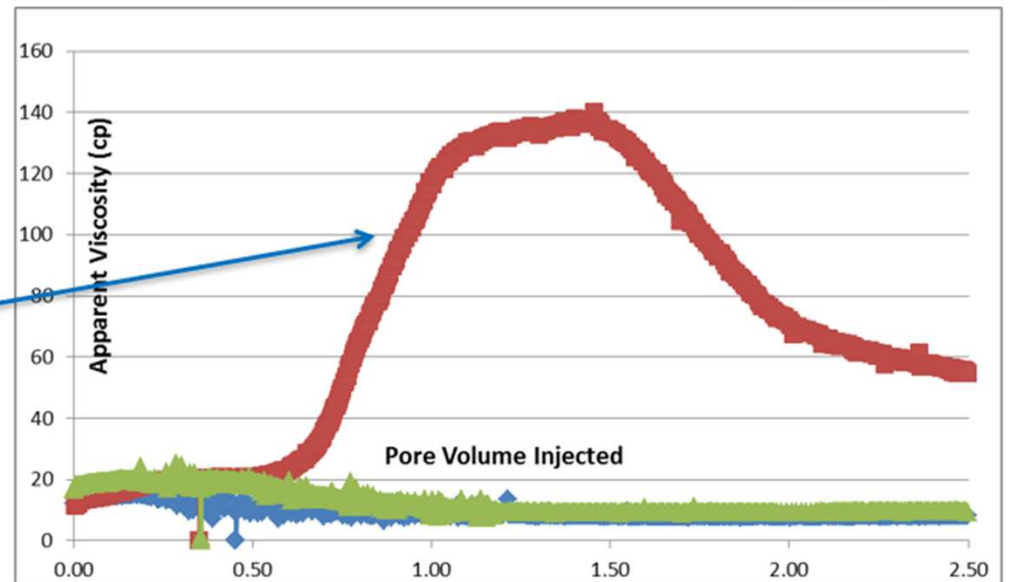
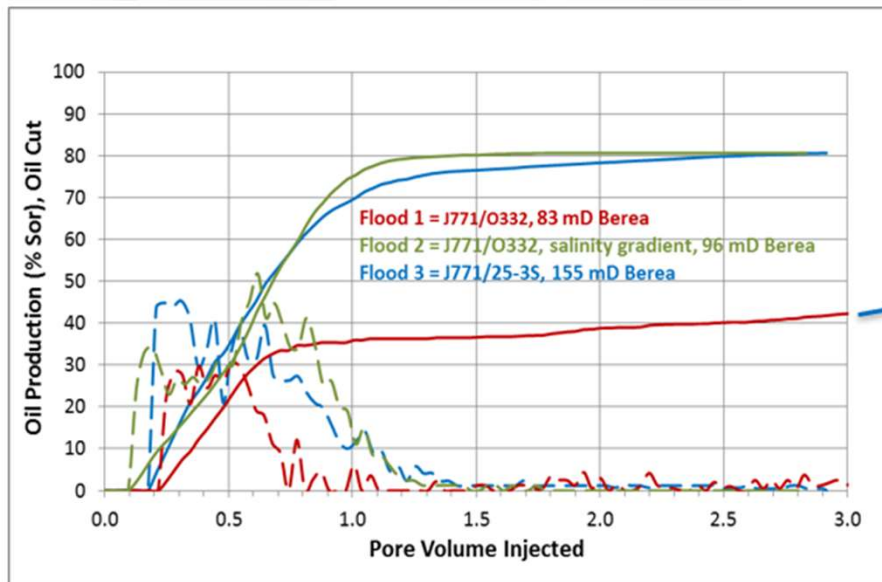
Frac J771	Frac S330	Phase Behavior Type				
0.8	0.2	2	2	2	2	3
0.75	0.25	2	2	2	3	3
0.7	0.3	3	3	3	3	1
0.65	0.35	1	1	1	1	1
0.6	0.4	1	1	1	1	1
0.55	0.45	1	1	1	1	1
		0.06	0.2	0.4	0.6	1
		Surfactant Concentration				

New formulation maintains low IFT as surfactant is adsorbed by rock. Standard formulation does not. Significant simplification.

SPE 179642 • Surfactant Flooding in Offshore Environments • J.G. Southwick et al



Constant Seawater Formulation Verified



PO sulfate/IOS requires a salinity gradient.

PO sulfate/EO sulfate gives high recovery in constant salinity seawater.

Predictions from phase behavior are true.

PO sulfate/IOS goes over-optimum generating viscous emulsions.

SPE 179642 • Surfactant Flooding in Offshore Environments • J.G. Southwick et. al. (2018, SPEJ)



4. Early Injection of Polymer Highly Desirable



Positive Aspects of Early Polymer

- *High chance of success.* Risk principally related to operational issues.
- Gain experience with injectivity, operational issues before utilizing expensive surfactant.
- Gain experience of reservoir response. Can tailor surfactant injection to responsive regions of the reservoir. *Tracer tests. Characterize reservoir!*
- Time to sort out logistics, supply of chemicals, field operations.
- Improved flow of surfactant into lower permeability zones?
- 9-month implementation time frame.
- Higher net present value earnings.

Negative Aspects of Early Polymer

- Less field experience with this scenario.
- *Viscous fluid injection ahead of surfactant bank. Slower propagation of surfactant. Injection pressure limited. 1D corefloods – lower throughput at constant pressure.*
- Reduced oil recovery?
- Why hasn't early injection of polymer been "the norm" to date?
- Reservoir connectivity is unproven, and water is the cheapest injectant.





History Match of Experiment (SPE 190271) ASP following WF or PF

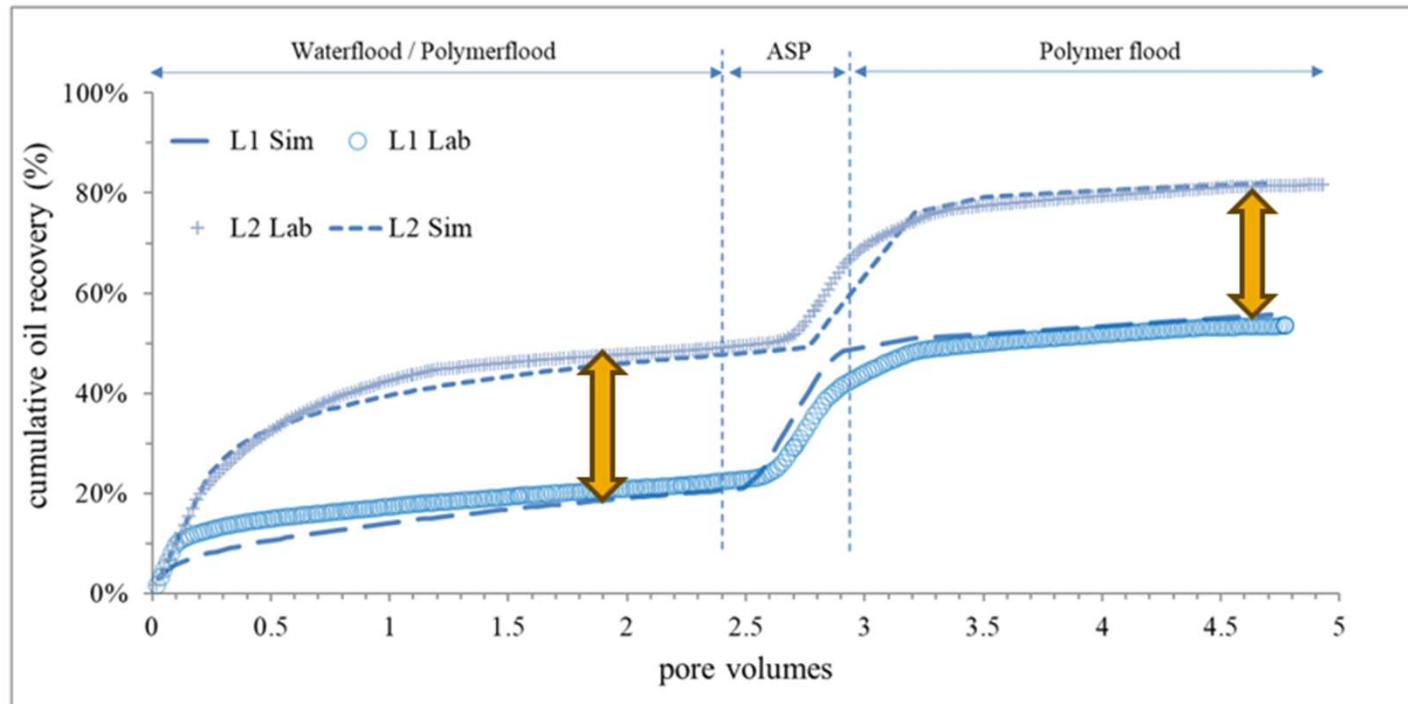


Fig. 4—History match of ASP laboratory experiments with waterflood prior to ASP flood (circles, dashed line) and polymer flood prior to ASP flood (crosses, dash-dot line).

Early Injection of Polymer Produces higher total recovery. It does not plug the reservoir and impede ASP.



Take Away Messages



- 1) Polymer Flooding is reliable and, in many cases, economically attractive.
- 2) Liquid Organic Amine Alkali significantly improves ASP economics for high acid number oils (facilities, logistics. Possibility of using low-cost commodity surfactants.
- 3) New tailor-made surfactants greatly improve the performance and economics of SP floods with available injection brines.
- 4) The time to implement chemical flooding projects is now.





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