IOR: Improving Polymer Selection, Connecting Lab Results with Field Operation*

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Abstract

Polymer injection showed strong growth at the international level as a result of successful implementations at the Daqing Field in China, where polymer is being injected in more than 20,000 wells with an incremental production of 14% over secondary recovery. Taking into account this success and due to the necessity of improving the sweep efficiency and production acceleration in Argentina, YPF has planned the implementation of polymer injection in those reservoirs identified as having potential for this technology.

Laboratory studies became a first and fundamental stage to select the right polymer, as well as determining the target viscosity during flux (resistance factor) and rock adsorption. This information will help to simulate the process and estimate operative costs. Partially hydrolyzed polyacrylamides are the polymers widely used for these applications. One of the most important aspects to consider during injection is controlling chemical and mechanical polymer degradation at the lowest cost. Several chemical degradation processes might occur and the one with greatest relevance is that originated by free radicals. These radicals are generated by redox reactions in the aqueous media, and they attack the polymer chain lowering the molecular weight and viscosity.

In this work, laboratory resistance factor and retention determinations are discussed. During the core flow tests, run with formation plugs, chemical degradation occurred. It was demonstrated this kind of degradation process could be controlled by the addition of a reducing agent, assuring the reduced state by means of ORP (oxidation reduction potential) measurement.

On the other hand, the impact of these results might have during field implementation is discussed, as well as if injection water oxygen content is in the order of ppm. As a main conclusion, chemical degradation will not occur under reservoir reductive conditions. Best practices to avoid degradation in surface facilities and lab experiments are also mentioned.
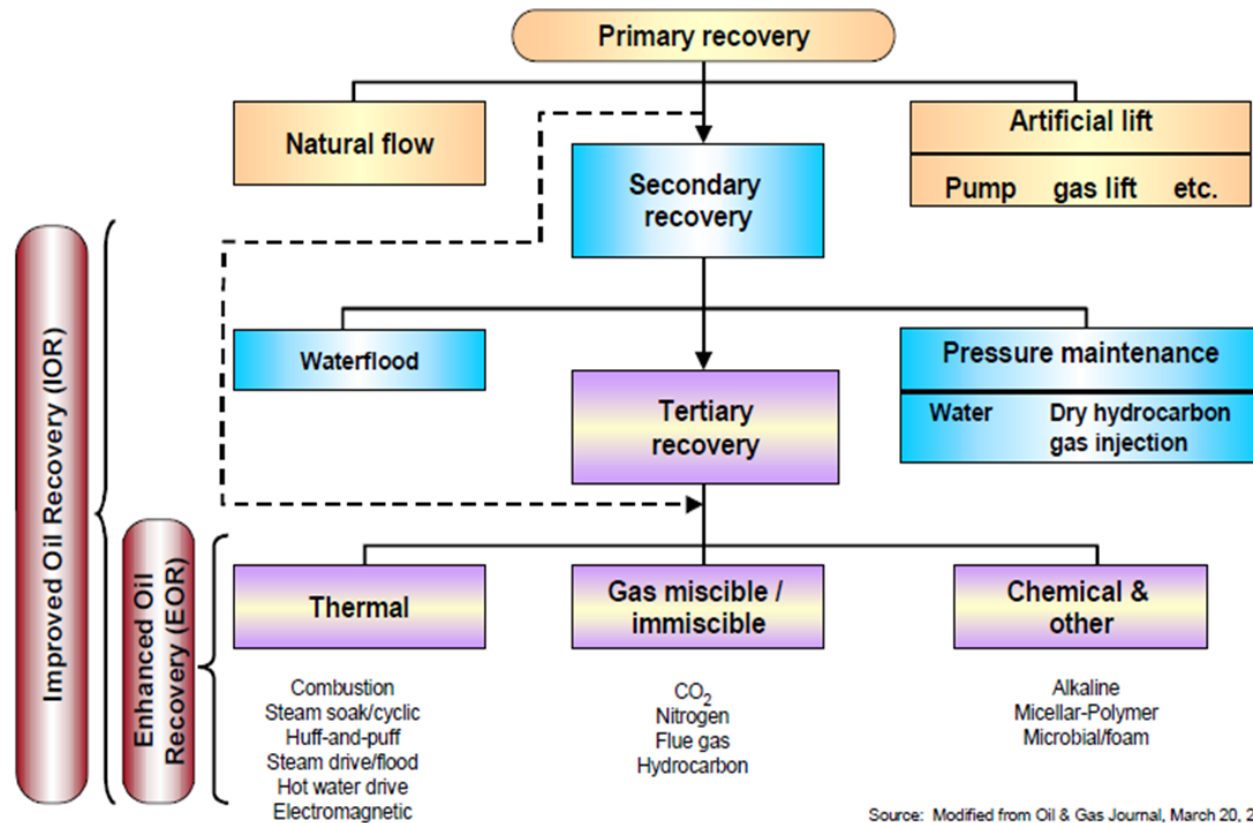
OUTLINE

- **INTRODUCTION**
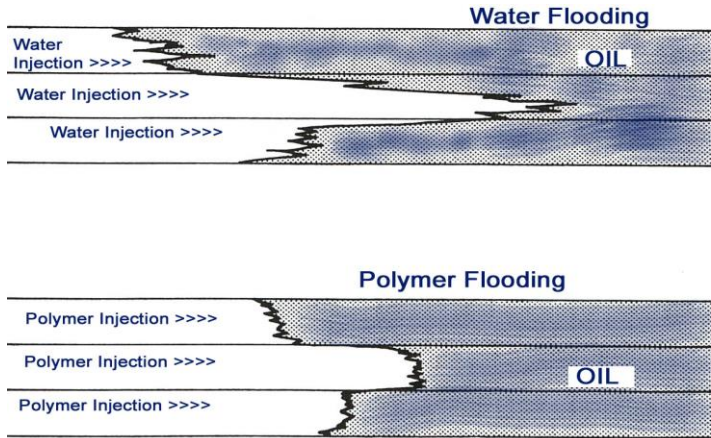
- **EXPERIMENTAL METHODOLOGIES**

- **RESULTS**

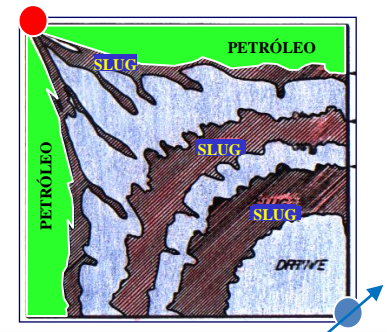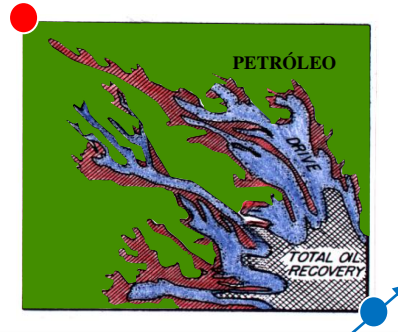- **CONCLUSIONS**

Source: Modified from Oil & Gas Journal, March 20, 2000

- POLYMER FLOODING

After secondary recovery, polymer flooding allows improving oil sweep efficiency by increasing the viscosity of the displacement fluid.

Vertical Efficiency Ev

Areal Efficiency Ea

EXPERIMENTAL METHODOLOGIES

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│        OUTSIDE POROUS MEDIA          │
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┌──────────────────┐   ┌──────────────────┐
│     RHEOLOGY     │   │    STABILITY     │
└──────────────────┘   └──────────────────┘
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- Viscosity vs shear rate
- Rheological model determination

- Chemical Degradation: viscosity changes as function of temperature and time. Turbidity and precipitation
- Mechanical Degradation

INSIDE POROUS MEDIA

RETENTION

INJECTIVITY

- Adsorption/Retention
- FR: viscosity during flow

- Polymer Injection at different rates
- IPM shear rate calculation

CHEMICAL STABILITY
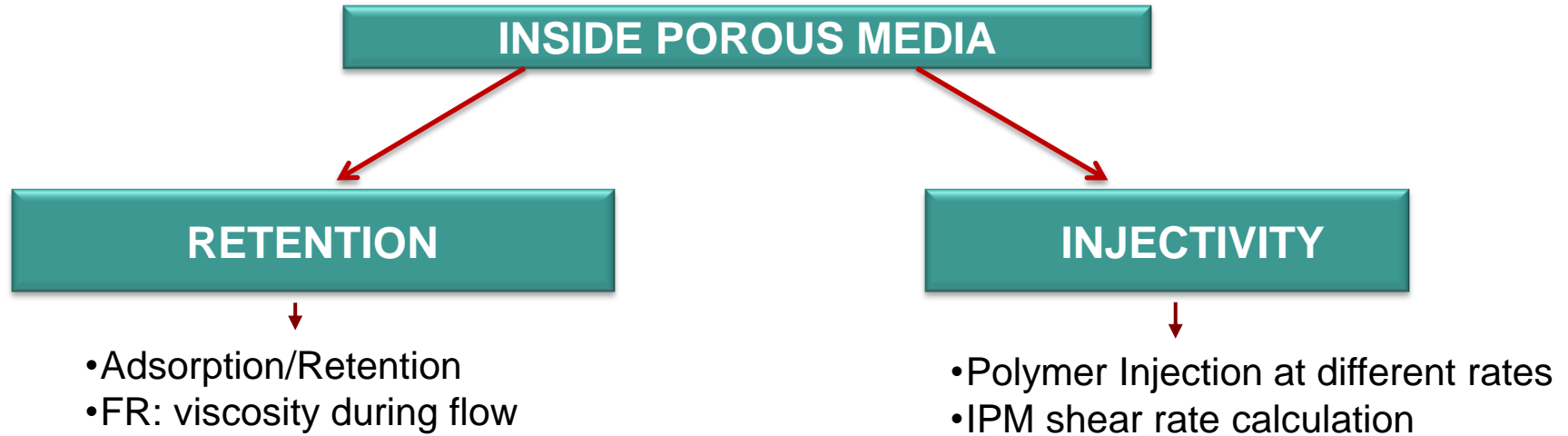
- **HPAM is susceptible to oxidative degradation.**
- **If oxygen or free radicals are absent, C-C bonds in HPAM are very resistant.**
- **HPAM is much more resistant to biodegradation than natural polymers.**

$$-(\, -CH_2 - CH -\,)_n - (\, -CH_2 - CH)_m -$$
$$C = O \qquad\qquad C = O$$
$$NH_2 \qquad\qquad O^-$$
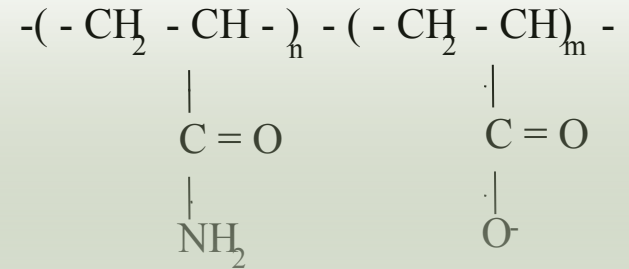
(Partially hydrolyzed Polyacrylamide)

- Fe $^{2+}$ enters into the polymer solution during the flow through the reservoir. This iron does not affect HPAM, if no dissolved oxygen is present. If oxygen is present Fenton reaction occurs:

$$Fe^{2+} + O_2 \longrightarrow Fe^{3+} + O_2^{\cdot -}$$

$$O_2^{\cdot -} + H^+ \longrightarrow HO_2^{\cdot} \xrightarrow{Fe^{3+}} HO_2^{-} \xrightarrow{H^+} H_2O_2$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$$

$$PH \xrightarrow{OH^{\cdot}} P^{\cdot} \xrightarrow{O_2} PO_2^{\cdot} \xrightarrow{PO_2^{\cdot}} PO\text{-}OO\text{-}OP \longrightarrow 2PO^{\cdot}$$

$$PO^{\cdot} \longrightarrow \underbrace{F + F^{\cdot}}$$

Mc Kay *et al.* Polym. Deg. & Stab. Parts I and II   Fragments of lower Mw

1. Setup of 3 core plugs.

2. Water injection. K ef measurement at Sor.

3. Polymer + tracer . FR determination.

4. Polymer and tracer concentrations monitoring.

5. Water injection. Polymer and tracer concentrations monitoring. Polymer retention calculation.
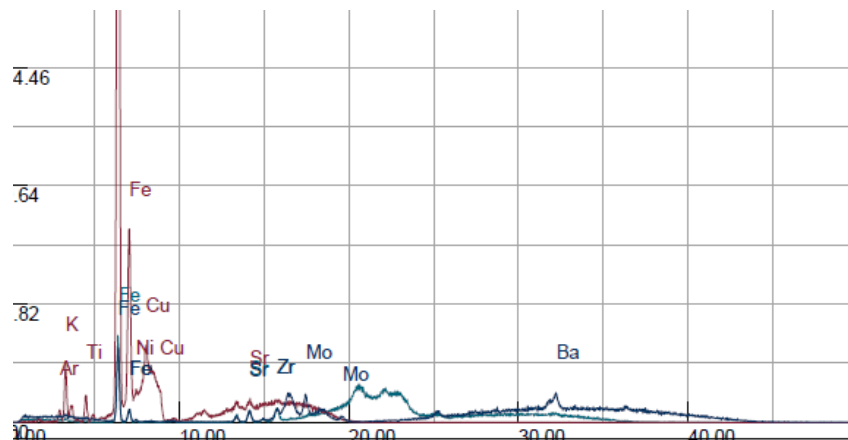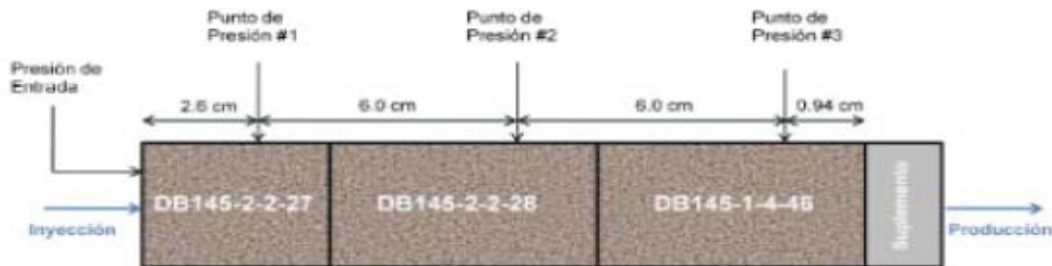
Iron content (FRX): 1-2% (DB-145)

Viscosity loss- Chemical Degradation

Degradación química del polímero en tren de coronas
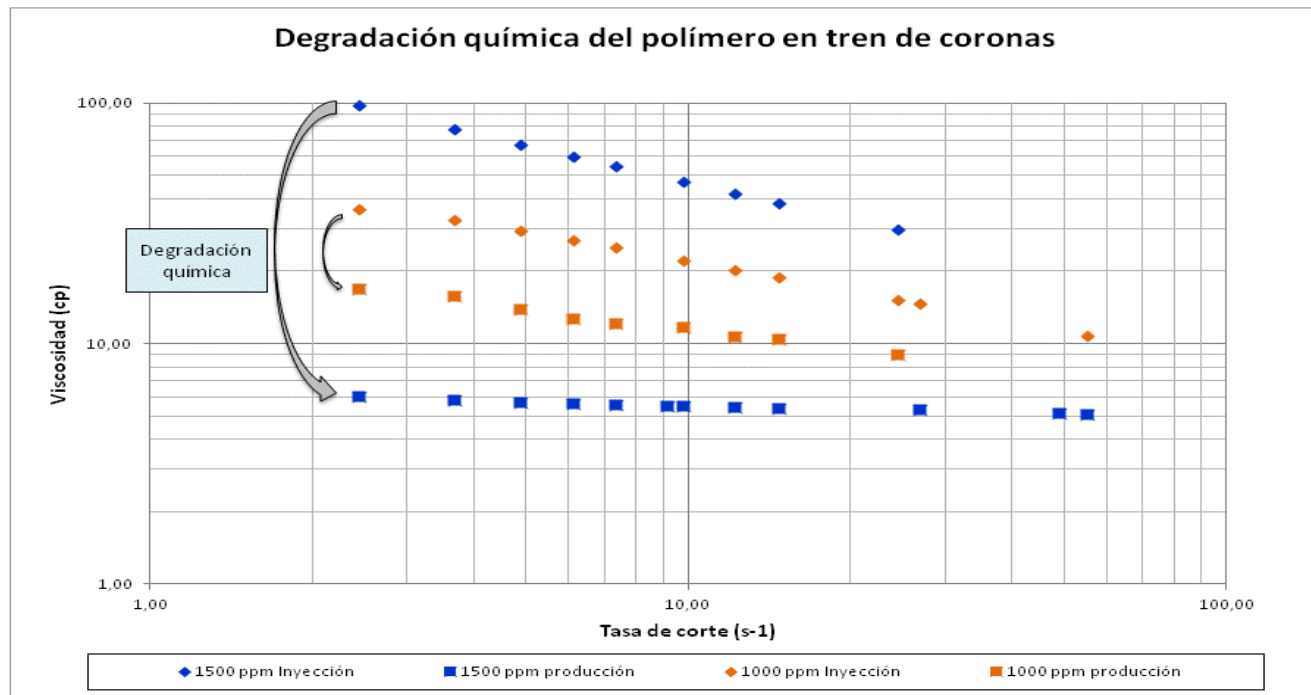
ORP of this study > - 400 mV. This won´t be real reservoir conditions!

POOR PLUG CONSERVATION?

OR

POLYMER ISSUES?

- Stability Tests performed in solutions of 1500 ppm of different commercial polymers:

1. Presence of crushing of new plugs (iron content ca. 1%)
2. Presence of 35 ppm NH_4HSO_3 (used as oxygen scavenger)
3. Presence of $Fe°$
4. Presence of 500 ppm Fe (II)

RESULTS

Vicosity loss (%)	SAMPLE (Preselection)							
	A	B	C	D	E	F	G	H
Rock crushing	6,1	11,1	25,9	7,6	11,3	13,4	10,3	5,3

Vicosity loss (%)	SAMPLE			
	A	D	G	H
Solution Stability	1,5	0,2482	1,2	1,5
35 ppm NH4HSO3	3,4	4,6	9,3	19,1
500 ppm FeSO4	95,2	94,6	95,6	96,4
Fe°	78,9	82,8	76,4	85,5

When Fe (II) is present in solutions with dissolved O_2 , polymers lose great part of their initial viscosity by free radicals attack even at temperatures close to RT.

When reservoir cores were stored under conditions that promote oxidation of iron containing minerals, a coating of ferric ions on the surface would be formed together with ferrous ions in the bulk (Fe° partial oxidation). If oxygen is present, the redox pair $Fe(II)/O_2$ will attack the polymer by Fenton reaction (seen before).


Pope *et al*. SPE-1699887-MS

Reservoirs have reduced conditions coming from the redox reactions between Fe^{3+} and organic reductants such as methane and phenolic compounds in crude oil.

In order to accomplish the same reduced reservoir conditions during core flow tests, a chemical choice is the addition of sodium dithionite to get the ORP < -400 mV.

Pope *et al*. SPE-1699887-MS

AFTER THE ADDITION OF 800 ppm OF DITHIONITE:
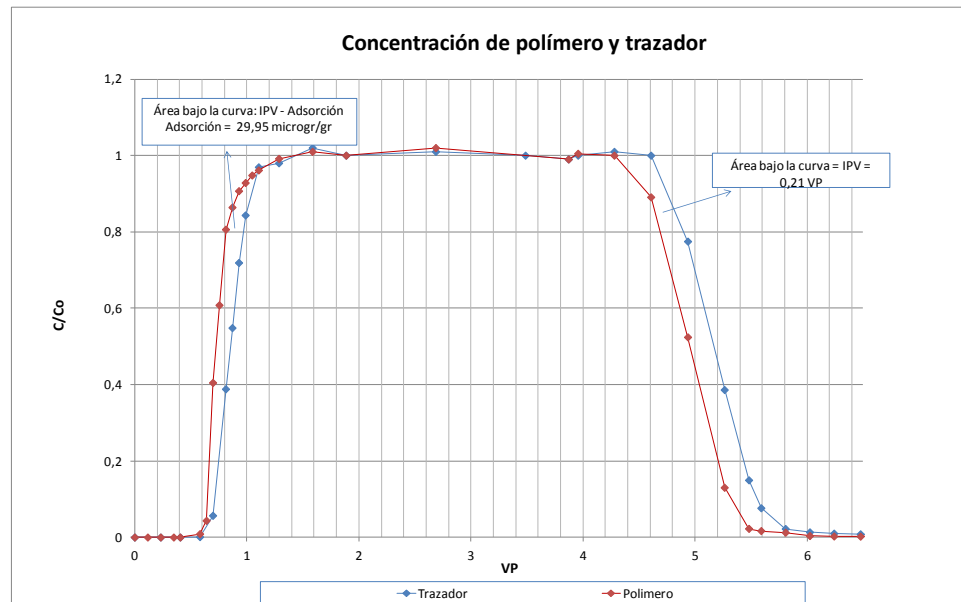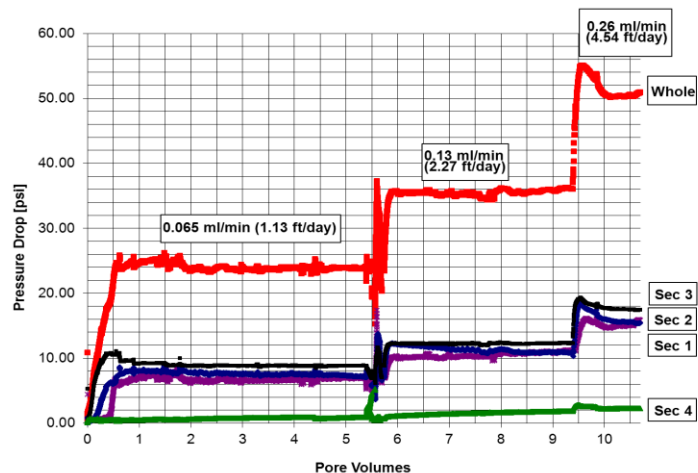
Adsorption/Retention = 30 μg/g rock

Sedimentary rocks contain a variety redox sensitive materials at least in small amounts: such as pyrite, siderite and sedimentary organic matter. Because siderite and pyrite precipitate from solution, they are found at the grain boundaries, thus they have direct contact with fluids of pores.

Pyrite, siderite and organic matter in some cases dramatically lower the oxygen level into the reservoir.

This process is accompanied by the release of Fe(II) to the formation water.

A key message is that dissolved oxygen will be removed fast into the reservoir and will not propagate very far into it, and no significant amounts of iron will be release to the reservoir until all dissolved oxygen is consumed.

✓ Dissolved oxygen that entered the reservoir prior to polymer injection will have been consumed and will not alter polymer stability.

✓ If an oxygen leak, coming from surface facilities or piping, develops during the course of polymer injection, the oxygen will not compromise the stability of the polymer that was injected before or after the leak is fixed.

Seright *et al*. SPE-121460-MS

- If oxygen is present in levels higher than 200 ppb, any presence of iron, oxygen scavenger, polymerization impurities, H2S; HPAM stability could be jeopardized.

- In order to prevent polymer degradation when core flow tests are being run with real core plugs, it is crucial to maintain a reducing environment to simulate the reductive reservoir conditions.

- If oxygen is reintroduced to the system after chemical oxygen scavenger was applied, a redox couple is formed and degrade the polymer.

- **During polymer injection, assuring dissolved oxygen at undetectable levels will help to maximize polymer stability regardless Fe (II) content.**