November 1, 2017 - 24th IPEC - Iris Porat and Miguel Pelaez

Chemical Degradation of Polymer Used in Enhanced Oil Recovery (EOR) Produced Water

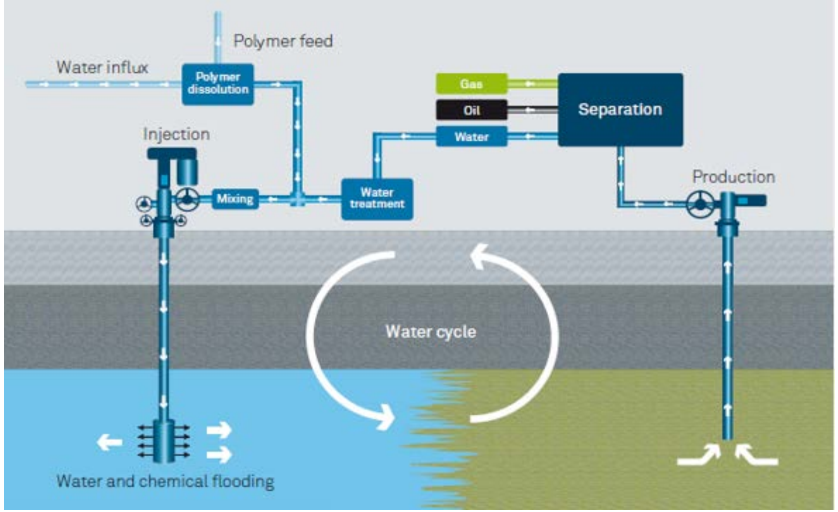
kemira

Background

Produced water with polymer – challenges:

1. Viscosity and viscoelastic properties of produced water - poor performance of water-oil separators
2. Water discharge in sea - polymer (HPAM) is not readily biological degradable and is categorized as red chemical by European regulations.
3. Challenges both offshore and onshore

Optimizing the water cycle



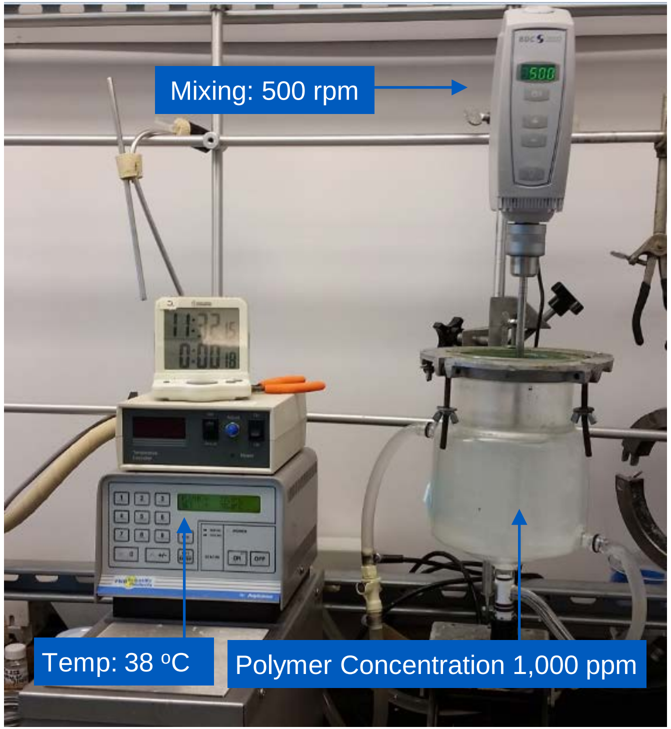
* HPAM – Partially hydrolyzed polyacrylamide

OSPAR and Norwegian Regulations
Classification of chemicals

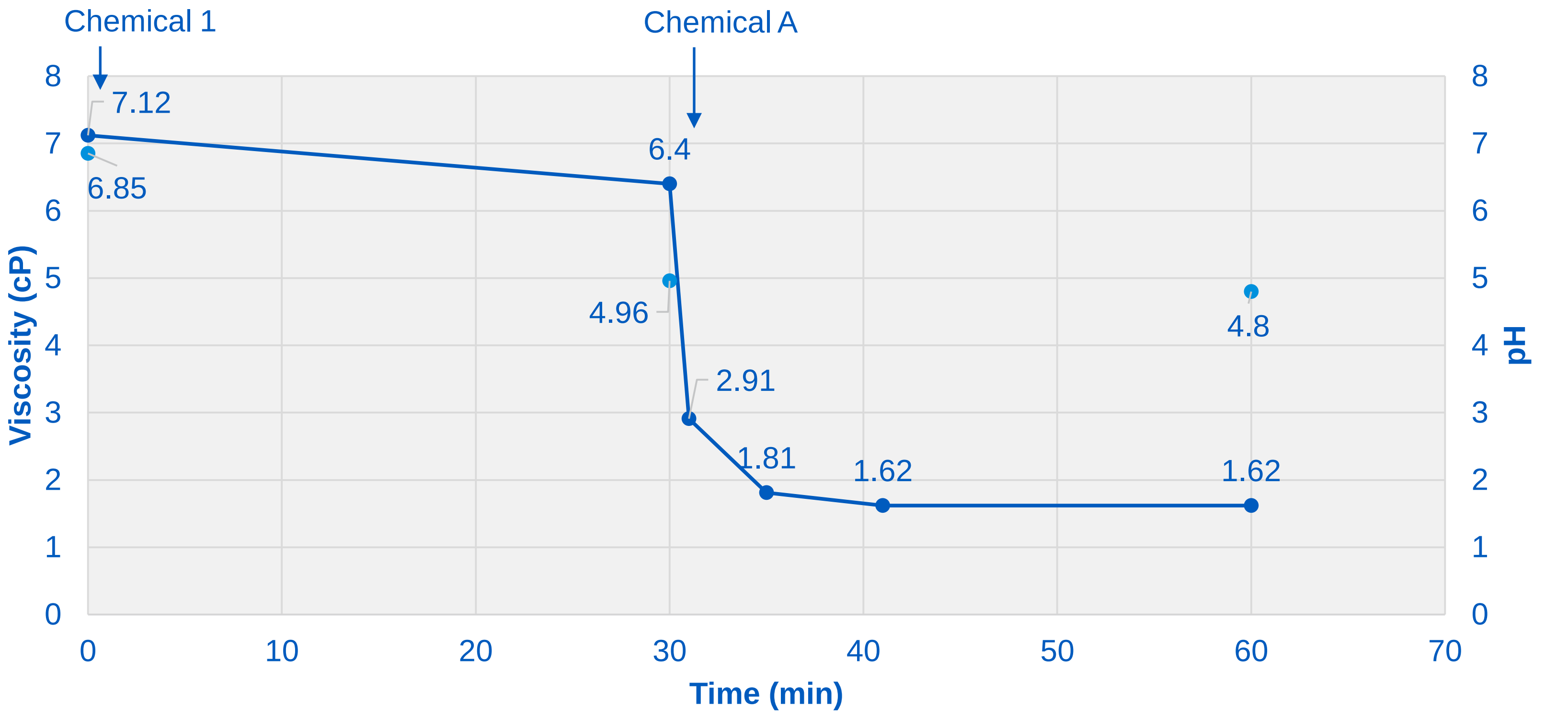
Category	Criteria - toxicity	Actions
Black	• Prioritized list of White Paper No. 21 (2004-2005) • OSPAR List of Chemicals for Priority Action • Low biodegradability + high bioaccumulation (BOD28 <20% and log Pow ≥5) • Low biodegradability + toxic (BOD28<20% and EC50 or LC50≤10 mg/l) • Substances described as carcinogenic/mutagenic or affecting reproductive way	Not discharged
Red	• Inorganic substances with high toxicity (EC50 or LC50≤ 1 mg/l) • Organic substances with low biodegradability (BOD28<20%) • Substances that meet two of the three following criteria: - Biodegradability (BOD28<60%), or - Bioaccumulation potential (Log Pow≥3), or - Toxicity (EC50 or LC50≤10 mg/l)	Not discharged/ exchanged
Yellow	• substances not categorized as red or black • Not on the PLONOR list	Discharge with permits
Green	• Substances on the OSPAR PLONOR list	Discharges permitted – no restrictions

EOR polymers (polyacrylamide) are classified red duo to their biodegradation (BOD28<20%)

Aerobic degradation of HPAM



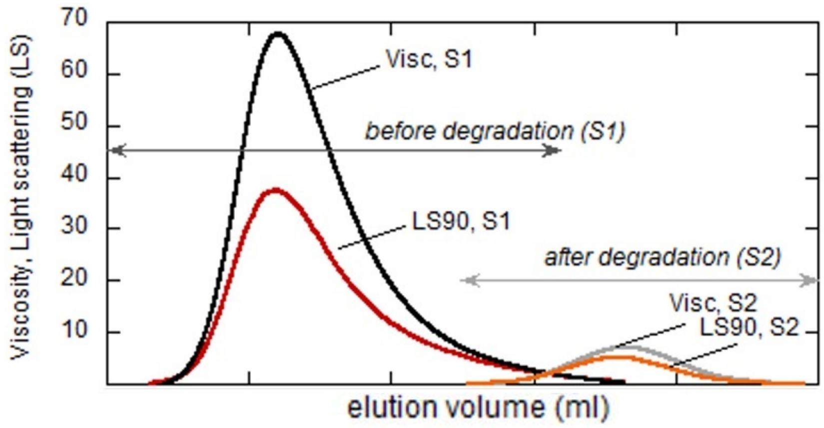
Aerobic degradation of HPAM



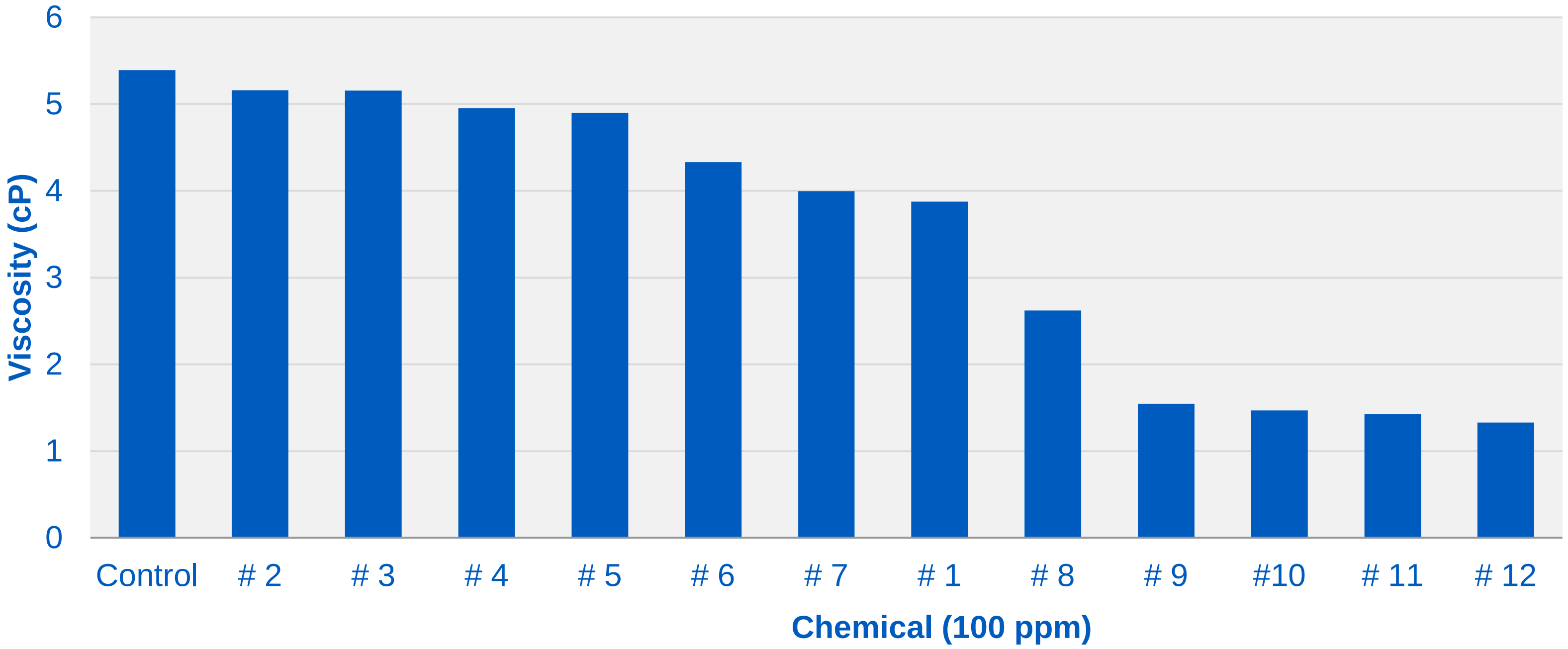
Aerobic degradation of HPAM – GPC results

	S1 (before treatment)	S2 (after treatment)
Viscosity[1]	7.12 cP	1.62 cP
MW[2]	$5.28x10^6$	$1.07x10^5$

1. Using viscometer, at room temp, 60 rpm speed
2. MW using gel permeation chromatography (GPC)

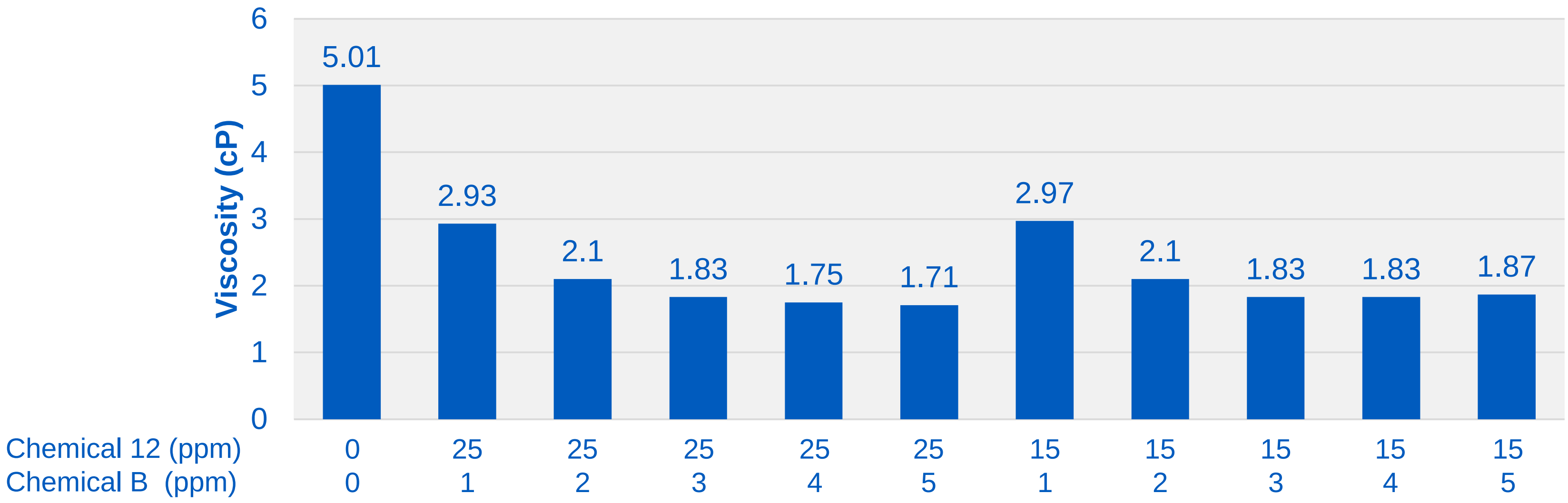


Anaerobic degradation of HPAM (1,000 ppm) in 3% NaCl, using chemical A (100 ppm) and list of chemicals



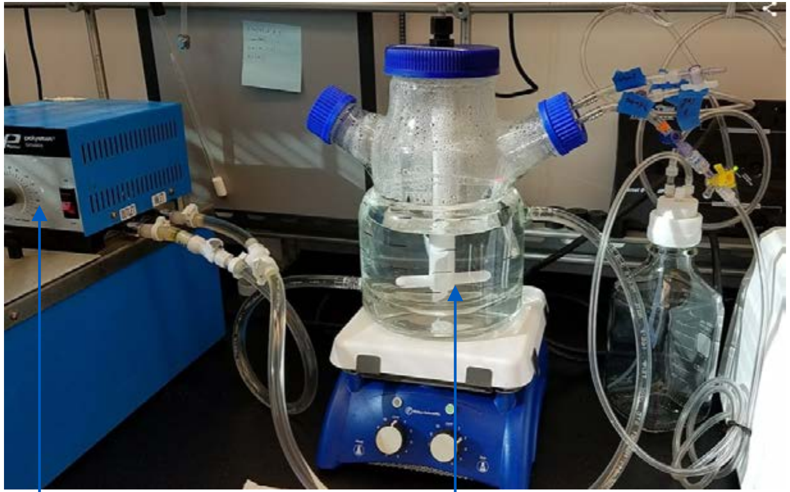
- Small anaerobic bottles incubated in a shaker at 250 rpm, at 40ºC for 2 hours
- 16 chemicals tested replacing #1 and 8 chemicals replacing A

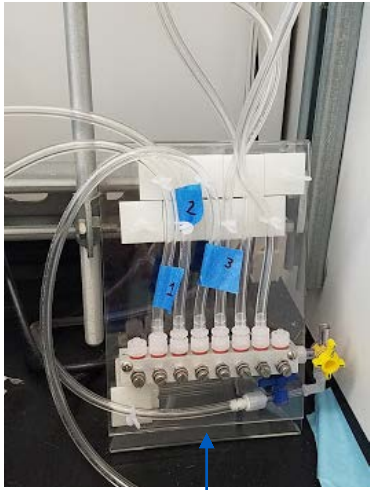
Anaerobic degradation of HPAM (1000 ppm) in 3% NaCl, using concentrations of chemical 12 and chemical B

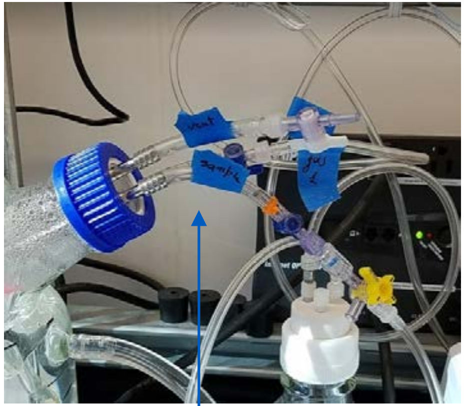


- Small anaerobic bottles incubated in a shaker at 250 rpm, at 40ºC for 30 minutes
- Additional conditions tested included temperatures (room temp to 80 ºC), pH, type of polymers, synthetic water and costumer produced water; in all cases with positive results.

Anaerobic degradation of HPAM in a reactor







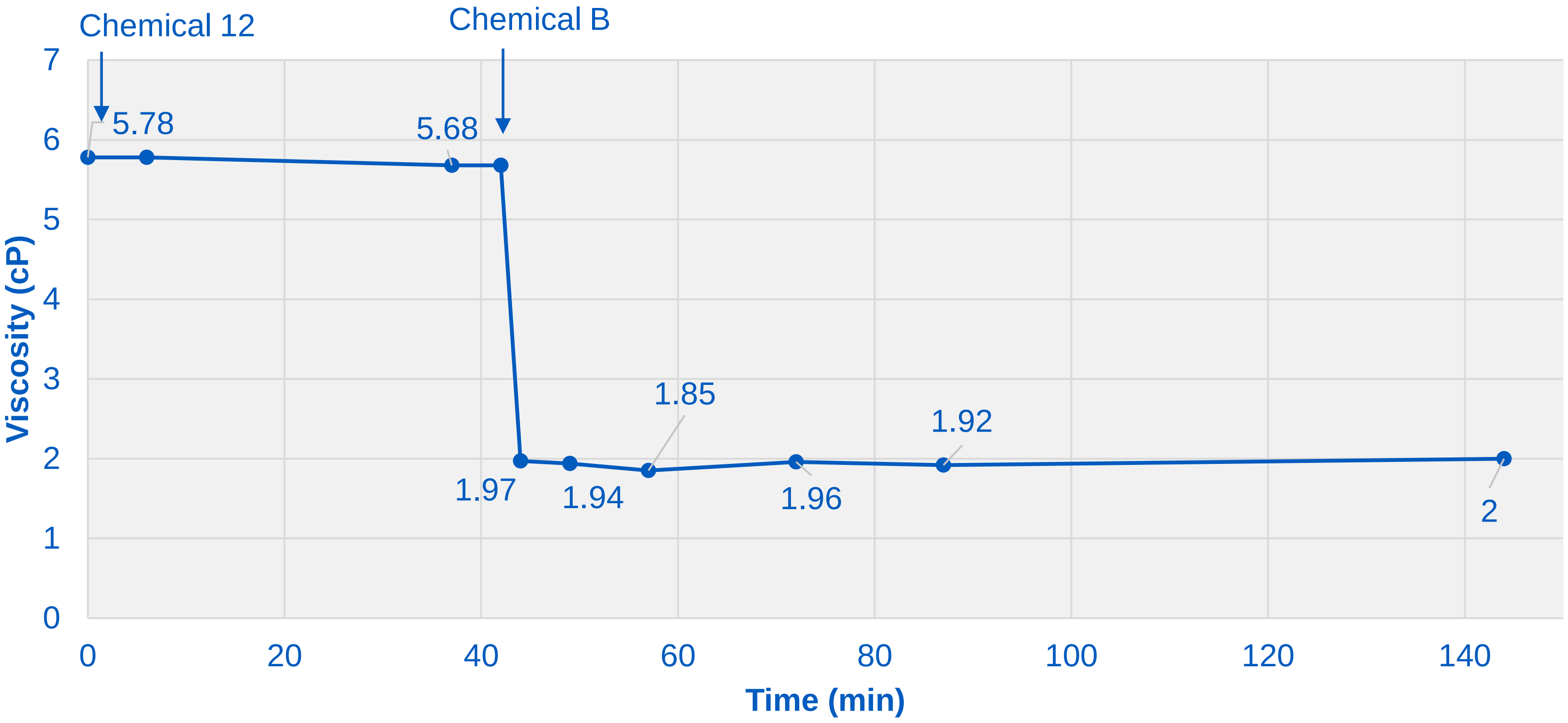
Temp: 40 ºC

Jacket flask for anaerobic degradation, with 1,000 ppm HPAM, by the end of experiment. Magnetic mixing.

Gas manifold to provide N2 gas

Flask ports:
1. Vent
2. Gas supply
3. Sample collection

Anaerobic degradation of HPAM (1,000 ppm) in 3% NaCl, using chemical 12 (25 ppm) and chemical B (5 ppm), at 40 ºC



The chemically degraded polymer (anaerobic conditions) became biodegradable - Internal results

Characteristics of the sea water used for biodegradation test

Microbial content (plating in marine agar):	8.8 * 10^3 cells/ml
Microbial activity (ATP test):	
Free ATP	264 pg
Total ATP	777 pg
Salinity:	2.6 %
pH:	6.9
Total organic carbon (TOC):	5.2 mg/L

Results of biodegradation test

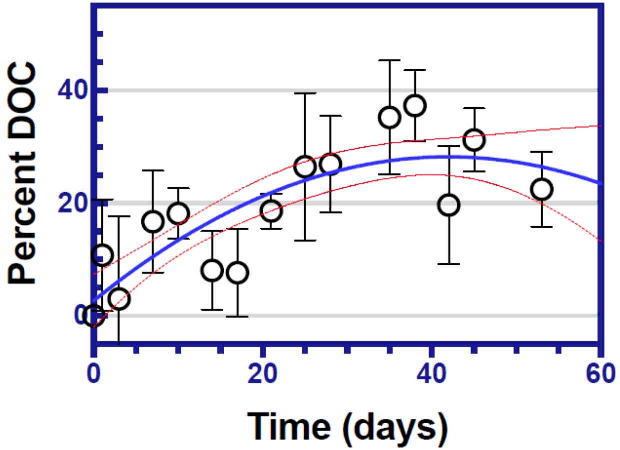
Incubation at room temperature (days)	% TOC biodegradation HPAM (not degraded)	% TOC biodegradation - chemically degraded HPAM with chemical 12 (25 ppm) + chemical B (5 ppm)
25	0	0.26
28	4.16	35.68
33	15.24	60.25
36	93.65	100.52

OECD 306 biodegradability in seawater test using the shake flask method with DOC analysis

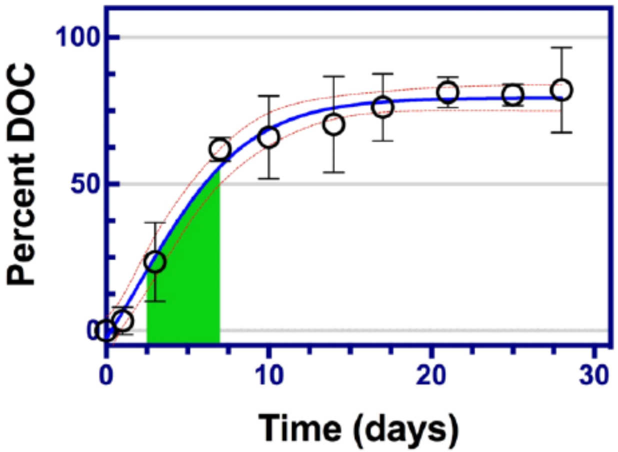
$$D_t = \left[1 - \frac{C_t - C_{bl(t)}}{C_0 - C_{bl(0)}}\right] \times 100$$

The chemically degraded polymer (anaerobic conditions) became biodegradable - External results (Situ Bioscience LLC)

Sample – 1 – Kemira – 487 – 91



Control – Na Acetate



MIC test (minimum inhibitory concentration) didn't show toxicity to bacteria when tested Kemira sample (4 - 500 ppm).

OECD 306 test, showed 26.9% (SD +/-8.5%) biodegradation for the treated polymer following 28 days incubation. The sample achieved a degradation plateau at 45 days. They tested Kemira sample in 6 replicates.

Conclusions

- Following chemical degradation, the viscosity of the polymer solution dropped in a short time.
- Following chemical degradation, the polymer became biodegradable. This would allow oil companies to discharge treated polymer into the sea when is needed.

Acknowledgements

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Thank you!

Questions?

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