A CASE STUDY FOR EFFECTIVE LABORATORY EVALUATION OF MEOR TECHNOLOGY IN SULFIDE CONTAMINATED MATURE OIL FIELDS

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ABSTRACT
This paper describes an extensive MEOR experimental program for sulfide contaminated mature oil fields comprised of a series of core flooding and glass model experiments and measurements of fluid properties using sulfide contaminated reservoir fluids to determine if the selected microbial system could be effective for enhanced oil recovery and potentially effective to inhibit souring. The selected microbial composition demonstrated positive growth in a sulfide contaminated environment, and core flooding tests produced increases in oil recovery 2% to over 10% above waterflooding. Core and sand pack studies confirmed that the MEOR displacement mechanisms were not inhibited by sulfide levels in the Grobla oil field.

INTRODUCTION
The occurrence of poisonous and corrosive hydrogen sulfide in aqueous systems is a major problem in upstream and downstream oil and gas production. In addition to corrosion and iron sulfide plugging it can lead to environmental hazards and reduced oil value. Moreover, it limits the use of standard MEOR technology. Among the Sulfate Reducing Bacteria (SRB) mitigation methods found to be useful in MEOR work, competitive exclusion emerges as the most efficient. This method uses fast growing microbes, both facultative anaerobes (nitrate respiration) and fermentative anaerobes that can out-compete the SRB's sulfate respiration. Since the role microbes play in MEOR is strongly correlated with growth and the production of primary and secondary metabolites, a dual role of enhanced oil recovery and SRB mitigation is conceivably possible.

Grobla, a mature oil field located in the northern part of central Carpathian Foredeep was selected for the current field trials. Two types of reservoir rocks are present and hydrocarbons are accumulated in a structural stratigraphic (the Oxfordian carbonates sealed by the marly Senonian – Turonian deposits) and stratigraphic (the pinching out of the Cenomanian sandstones) type traps [1]. The field produces light oil with gravity 38.36 - 42.97 ºAPI. Production is in decline and undergoing reinjection of production brine in a waterflood configuration. Challenges to effective MEOR treatment in this field arise from the levels of hydrogen sulfide (H_2S) and sulfide in production fluids (43g/m^3

of extracted gas and from 300 to 350 mg/dm^3 of formation water) which could alter or inhibit growth of the microbial composition selected for this field trial. Additionally, we needed to investigate whether the sulfide would diminish other aspects of microbial modes of action requisite to increase Recovery Factors necessary for economic success.

EXPERIMENTAL

The microbial system (MS) selected for the Grobla pilot was similar in composition to the one used earlier for the Plawowice MEOR project. Bacterial strains selected for Grobla were adapted to grow in sulfide free sterile brine that otherwise matched Grobla water analysis both chemically and osmotically. Sugar beet molasses was used as carbohydrate and nitrogen sources. Microbial materials for Grobla were batch produced in 30L and 300L Sartorius fermenters at the BTEC facility in Raleigh, NC, USA. The final 300L batch was concentrated in disc bowl centrifuges to produce the Grobla microbial system inoculum (MSI) which was cryo-protected and air shipped frozen to the INiG-PIB laboratory in Krakow, Poland for laboratory studies and field application.

A novel, but simple closed system using plastic syringes in anaerobic bags was developed to incubate oil and brine with the microbial materials. Multiple tests were conducted; three series contained 5% MSI (microbial system inoculum / bacterial concentrate) and two series each with 2.5% and 0.5% MSI. Tables 2 and 3 show the results of serial analyses of the two liquid phases by LSRV (low shear rate viscosity) and interfacial tension (IFT) measurements. Basically, lab procedures consisted of serial inoculations of oil (Fig.1), followed by 144 hours of anaerobic incubation at reservoir temperature (35ºC). Further examination of inoculated and control oil using full computational rotational viscometer (Anton Paar Physica MCR 301) generated quantitative indexes describing the degree of oil compositional alteration such as: Newtonian Index (NI), the Delta Viscosity Index (DV) and Enhanced Oil Recovery Index (EOR) related only to viscosity (Table 4). Additional experiments using core plugs and sand pack models were conducted to evaluate microbial system performance. All tests were carried out under anaerobic conditions on TEMCO® core flooding system using original reservoir fluids under simulated reservoir conditions (pressure, temperature, flow rate). Five core plugs and 4 sand packs (1 inch in diameter and 11.8 inches in length) were prepared with different grain size and/or layering and marked as Z1-Z4 (Table 1).

After determining the basic petro physical parameters of absolute permeability and porosity, core plugs and sand packs were saturated with Grobla Formation Water (GFW) by vacuum, aged for one month and then evacuated by a displacement method using high pressure gradients, after which they were saturated with reservoir oil until irreducible saturation of GFW (Swi,) was obtained. This allowed for estimation of oil saturation of the cores and packs. Waterflooding and MEOR treatment were then simulated to produce recovery factor (RF) volumes. Core plugs and sand packs were then injected with one pore volume of bio-product and incubated for 4 days at 35°C under anaerobic conditions. Microbial enhanced waterflood simulation displaced additional oil (Table 1).

To confirm microbial activity in plugs cryo-SEM and energy-dispersive X-ray (EDX) mapping were performed. Cores were thin sliced and immediately mounted on microscope stubs without any adhesives. Samples were immersed in liquid nitrogen until they reach its boiling temperature to avoid evaporation of oil remnants. Frozen samples were quickly transferred to the preparation chamber (Quorum) to coat them with platinum. The temperature at the preparation chamber and at the microscope chamber was -140 C. Samples were sputtered with platinum for 80 sec/10uA and then transferred to the cross-beam field-emission scanning electron microscope chamber (Auriga60, Zeiss). Observations were made at 25kV of electron beam voltage using the SE2 and InLens detectors (Pic. 1,2). Cross-sections made with FIB were visualized at 2kV with ESB detector. The SEM-EDX mapping was performed at 25kV and -140 C using the Oxford instrument and Aztec software.

RESULTS AND DISCUSSION

Initial experiments were designed to verify the hypothesis that a dual role of microbial enhanced oil recovery and H_2S mitigation is possible. Laboratory tests of Grobla production fluids show high levels of sulfide and low levels of indigenous SRB's. This suggest that at least some H_2S at Grobla may be due to a combination of biotic and abiotic processes from deeper in the Grobla formation rather than SRB activity in the near well bore and producing formation's water. However, SRB's are present in Grobla brine which has an alkaline pH of 7.6-8.0, and therefore conducive to SRB growth.

The first step in verifying a possible dual role was to confirm that the selected microbial system is capable of displacing additional oil under simulated oil field conditions. One sees from Table 1 that microbial treatment after initial waterflooding recovered additional oil. The average coefficient obtained in the laboratory from simulation microbial waterflooding is 5.2% and per individual cores it range from 2.5% to 10.6%.

A second confirmation step was aimed at mitigating the biotic component of sulfide generation using known SRB mitigating methods judged compatible with MEOR. This step used nitrite and/or a nitrite proxy (nitrate). It it required additional RF testing with using various SRB Mitigants, authentic field samples of Grobla brine and oil and microbial system materials. Shown in Table 2 are increases in reservoir brine viscosity with the addition of MSI (microbial system inoculum), N (Nitrogen) and Mo (Molybdate). This is a very positive factor when assessing the potential effectiveness of the proposed microbial treatment technology.

The best results from waterflooding are obtained when the viscosity of the oil recovery displacement fluid is close to the viscosity of the fluid being displaced [3,4]. Quantitatively, the mobility factor (M) expresses the impact of changes in viscosity of resorvoir fluids as a ratio. Ideally, the value of M should approach unity. All microbially treated samples had lower values of M than the baseline value for crude oil / brine. The incubated sample that included molybdate salt produced the lowest M value of 1.41.

Another means of evaluating MEOR treatability is by oil viscosity analysis [2]. Oil is a very complex liquid that exhibits typical non-Newtonian behavior. Viscosity is shear rate sensitive (pseudo plastic model) and it correlates strongly with the fluid dynamics occurring in the pore space. Specific quantitative lab procedures were conducted to measure the shift in rheological properties in treated (inoculated) and untreated (control) samples. One can see from Table 4 that all obtained indexes for bio-treatability show positive changes in fluid characteristics after microbial treatment. The comparison between control and inoculated oil samples clearly shows microbial cracking in that all EOR values are greater than 1.10. A global change in viscosity is also indicated by DV values greater than 0.10. Cryo-SEM images combined with EDX mapping also confirm positive bacterial growth activity in a sulfide contaminated environment and show clogging of pores by the biofilm produced by the bacteria strains (Pics.1,2).

CONCLUSION

Laboratory studies point to the possibility of a dual role for microbial enhanced oil recovery; 1) increased oil recovery, and 2) inhibition of oil field souring. The selected microbial composition demonstrated positive growth in a sulfide contaminated environment, and core flooding tests produced increases in oil recovery 2% to over 10% above waterflooding. Core and sand pack studies confirmed that the MEOR displacement mechanisms were not inhibited by sulfide levels in the Grobla oil field production fluids. Laboratory studies tested the hypothesis that H_2S mitigation and microbial enhanced oil recovery at Grobla are not mutually exclusive. The Grobla pilot field project which commenced on March 25th may further validate a dual role of microbial EOR and H_2S mitigation.

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REFERENCES

1. Golonka J. and Picha F. J., *Carpathians and their Foreland: Geology and Hydrocarbon Resources*, AAPG Memoir 84 (2006), 351–393, ISBN Number: 0891813659
2. Maure M. A., Dietrich F. L., Diaz V. A., Argañaraz H., "Microbial Enhanced Oil Recovery Pilot Test in Piedras Coloradas Field, Argentina" SPE 53715, 1999, Paper presented at SPE Latin American and Caribbean Petroleum Engineering Conference held in Caracas, Venezuela, 21–23 April 1999.
3. Lake, L. W., Johns R. T., Rossen W. R., Pope G. A, *Fundamentals of enhanced oil recovery*, Society of Petroleum Engineers, 2014.
4. Kantzas A., Bryan J., and Taheri S. *Fundamentals of Fluid Flow in Porous Media*,http://perminc.com/resources/fundamentals-of-fluid-flow-in-porous-media/

Table 1. Core and sand pack test results

Plug/Sand Pack	Initial Recovery Factor (RFi) [%]	volume of displaced oil in MEOR [cm3]	final recovery factor (RF_f) [%]	Increment of recovery factor E_{mwf} [%]
1-C	24.4	0.00	24.4	**0.0**
Gr-5	17.8	0.20	22.2	**4.4**
Gr-8	14.5	0.20	18.2	**3.6**
Gr-9	15.4	0.55	26.0	**10.6**
Gr-10	19.0	0.20	23.8	**4.8**
Gr-11	19.6	0.13	22.2	**2.5**
Z-1	71.0	3.10	76.8	**5.8**
Z-2	81.8	1.50	84.5	**2.7**
Z-3	70.7	1.50	74.4	**3.7**
Z-4	82.2	1.05	84.6	**2.3**

Initial Recovery Factor (RF) from saturated cores and sand pack columns, volume of oil displaced by MEOR, final RF of waterflood and MEOR flood combined, and percent of incremental oil recovered.

Table 2. MEOR viscosity, surface tension and pH alteration

Fluid	Viscosity	Surface tension	pH	Viscosity	Surface tension	pH
	[mPas]	[mN/m]	[-]	[mPas]	[mN/m]	[-]
	Base measurement			After 6 days of incubation		
Oil	3.220	26.00	-	-	-	-
Brine	0.973	59.70	5.60	0.973	59.70	5.60
MSI	1.157	52.77	6.70	1.361	41.20	4.87
MSI+N	1.173	52.45	6.73	1.270	35.00	4.80
MSI+N+Mo	1.128	52.20	6.72	2.035	40.57	4.85

Table shows changes from baseline values for viscosity, surface tension and pH after 6-day incubation period. MSI = Microbial System Inoculum, N = Nitrogen, Mo = Molybdate

Table 3. Percentage change in IFT

Phase	Interfacial tension [mN/m]	Change [%]
Brine/oil	15.4	-
MSI/oil	6.8	55.8
MSI+N/oil	10.7	30.5
MSI+N+Mo/oil	12.4	19.5

MSI = Microbial System Inoculum, N = Nitrogen
Mo = Molybdate

Table 4. MEOR Indexes

Oil after contact with:	MEOR Indexes		
	NI	DV	EOR
MS	3.2	0.17	1.21
MS+N	3.8	0.15	1.18
MS+N+Mo	3.9	0.16	1.19

A positive test for bio-treatability results when the value of NI > 1.10, DV > 0.10, and EOR > 1.15

NI = Newtonian Index

$$NI = \left(\frac{(\mu app^{control})^{minSR} - (\mu app^{control})^{maxSR}}{(\mu app^{inoculated})^{minSR} - (\mu app^{inoculated})^{maxSR}}\right) TMD \quad \text{..... Eq. 1}$$

DV = Delta Viscosity Index

$$DV = \left(\frac{\sum_{i=minSR}^{maxSR}(\mu appi)^{control} - \sum_{i=minSR}^{maxSR}(\mu appi)^{inoculated}}{\sum_{i=minSR}^{maxSR}(\mu appi)^{control}}\right) \quad \text{..... Eq. 2}$$

EOR = Oil Recovery Index

$$EOR = \frac{1}{1-DV} \quad \text{..... Eq. 3}$$

TERMS for Eq. 1-3: Control = original sample (pre-inoculation), minSR = minimum explored shear rate [1/s], maxSR = maximum explored shear rate [1/s], i = data point, spatial reference, TMD = Temperature of maximum discrimination of rheological properties [ºC]

OTHER TERMS: GFW = Grobla Formation Water, SRB = Sulfate Reducing Bacteria, IFT – Interefacial Tension, RF = Recovery Factor, Swi = irreducible saturation, MSN = Microbial System Nutrient, MSI = Microbial System Inoculum, MS = Microbial System

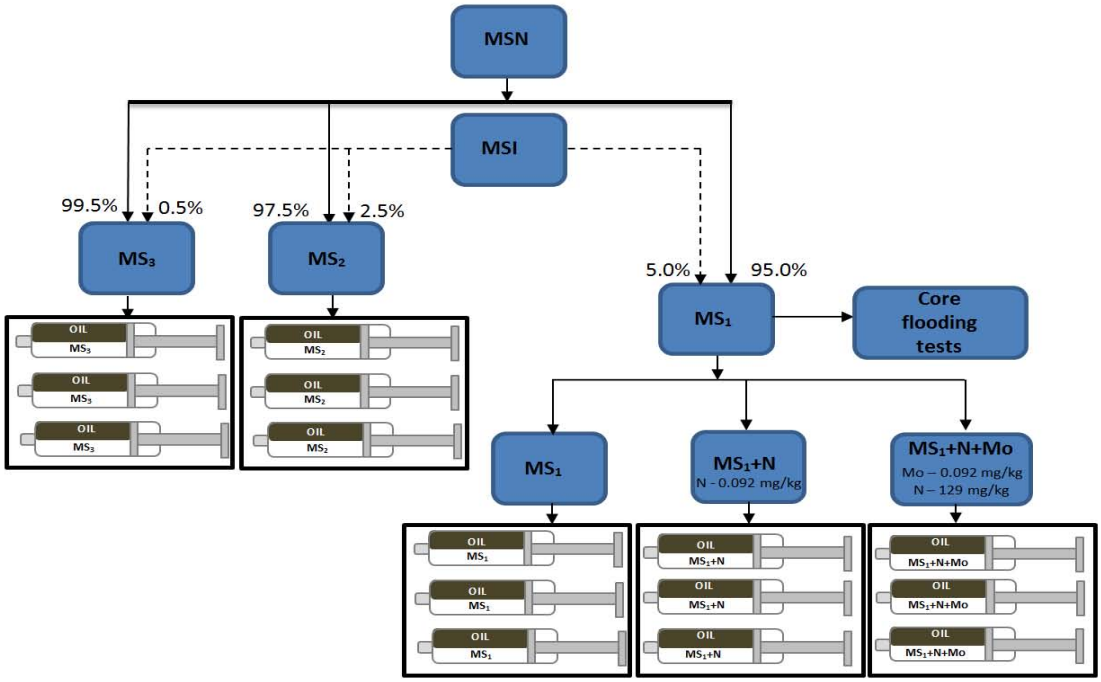
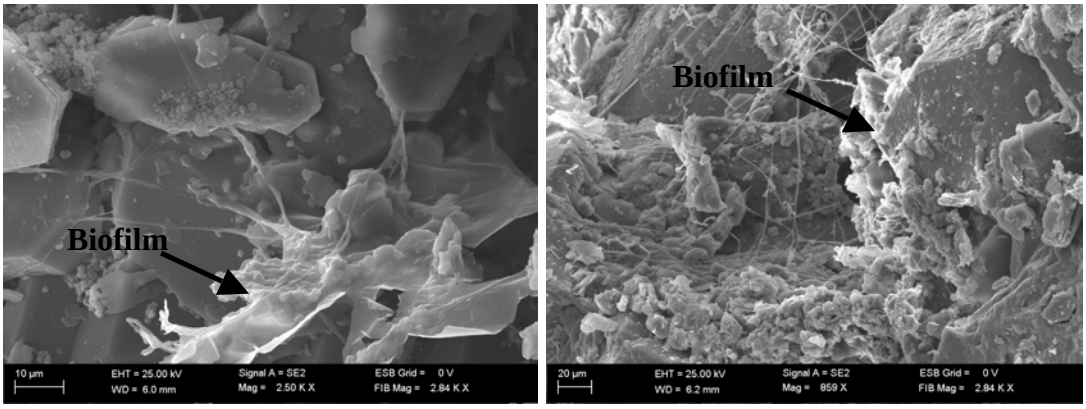


Fig. 1. Scheme of laboratory incubation tests (MS – microbial system, MSN – microbial system nutrient, MSI – microbial system inoculum, N – nitrogen, Mo – molybdate)



Pics. 1 and 2. Cryo-SEM observation made at 25kV using the SE2 and InLens detectors of an Auriga60 Zeiss cross-beam field-emission scanning electron microscope. Image show microbial growth in the core after incubation.