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

CICHA-SZOT R.[1], FALKOWICZ S.[1], LAUNT P.[2], NELSON S.[2], GRZESIAK J.[3]

[1]*Oil and Gas Institute - National Research Institute, Krakow, POLAND*
[2]*RAM Biochemicals, Inc. Research Triangle Park, North Carolina, USA*
[3]*EIT+ Wrocław Research Centre, Poland*

SCA2016-046

## INTRODUCTION

Hydrogen sulfide (H2S) is a major problem in up-stream and down-stream oil and gas production. Sulfate reducing bacteria (SRB's) are identified as a major source of H2S and corrosive acids that precipitate iron sulfide plugging. H2S is also a major environmental concern. Additionally, its presence in oil reservoirs increases production costs and reduces the sales value of oil and gas. Moreover, it limits the use of available MEOR technologies. Among the SRB mitigation methods in use, competitive exclusion emerges as the most efficient method that is compatible with MEOR. Fast growing MEOR organisms injected into the reservoir simply out compete the SRB population disrupting their metabolism and inhibiting growth. Because SRB and MEOR microbes both depend on access to certain essential primary and secondary metabolites, a dual role of microbial enhanced oil recovery and SRB mitigation is conceivably possible.

Grobla, a mature oil field in southern Poland was selected for field trials because of its similarity to earlier lab and field work performed by INiG and RAM Bio for the Plawowice oilfield MEOR project.[1] Grobla and Plawowice produce from the North Central Carpathian Foredeep. Hydrocarbons are accumulated in structural stratigraphic traps of Oxfordian carbonates sealed by marley Senonian-Turonian deposits and the pinching out of Cenomanian sandstones. The Grobla field produces light crude oil 38.36 - 42.97 °API gravity. Oil production is in decline. Produced brine is now being re-injected in a waterflood configuration. H2S in gas extracted from Grobla measured 43g/m$^3$. Sulfide in formation waters measured 300 to 350 mg/dm$^3$. This creates challenges to MEOR treatment. A toxic environment can inhibit growth of MEOR organisms and diminish production of bio-products needed to increase recovery factors (RF). Consequently, an investigation was undertaken to evaluate MEOR growth at Grobla sulfide levels, and make rheological measurements to determine the Enhanced Oil Recovery Index.

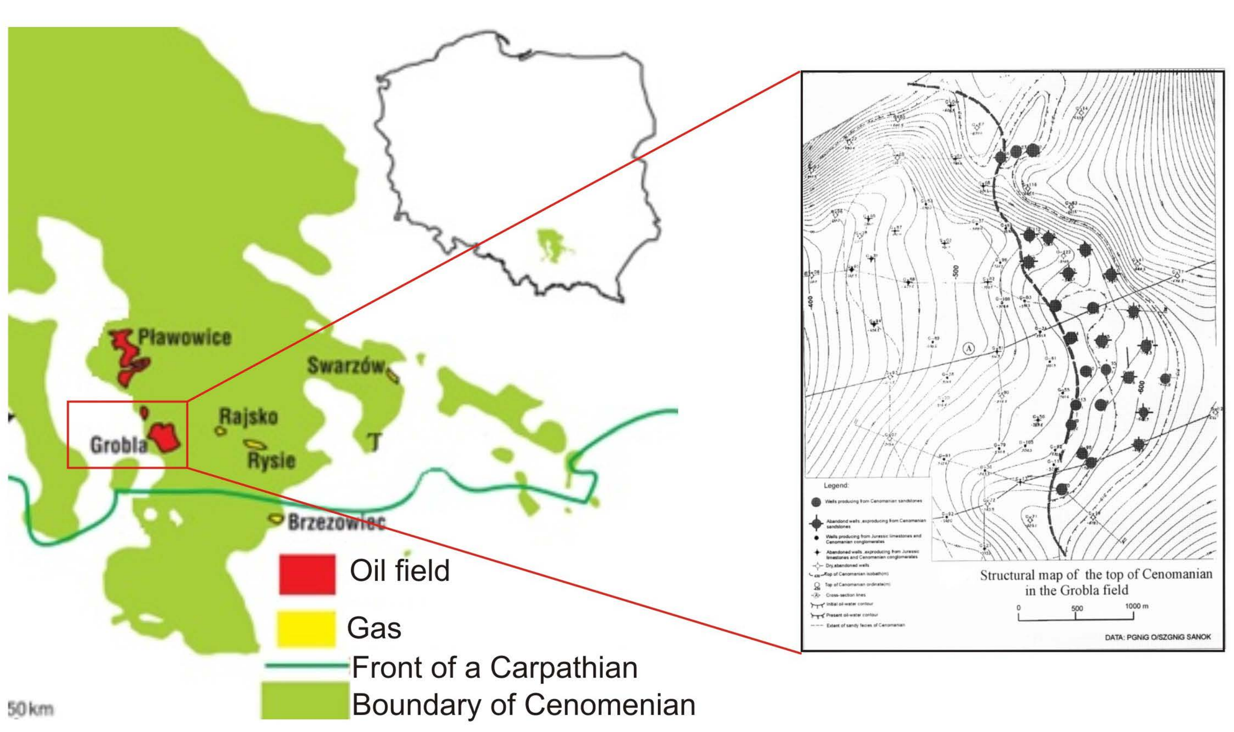



*Fig.1. Grobla Oilfield vicinity map*

## EXPERIMENTAL

### Preparation of Microbial System Inoculum (MSI) at BTEC, USA

Selection of Microbial System → Production of batch 30 mL in Sartorius fermenters → Concentration in disc bowl centrifuge → Cryo protection and shipment of frozen MS to INiG

**Laboratory testing procedure**

- Siringe tests according to protocol → Rheological measurements → Viscosity
  - Delta Viscosity Index: $$EOR = \frac{1}{1 - DV}$$
  - Newtonian Index: $$NI = \left( \frac{(\mu app^{control})^{minSR} - (\mu app^{control})^{maxSR}}{(\mu app^{inoculated})^{minSR} - (\mu app^{inoculated})^{maxSR}} \right)$$
  - Enhanced Oil Recovery Index: $$DV = \left( \frac{\sum_{i=minSR}^{maxSR} (\mu appi)^{control} - \sum_{i=minSR}^{maxSR} (\mu appi)^{inoculated}}{\sum_{i=minSR}^{maxSR} (\mu appi)^{control}} \right)$$
- Core Flooding tests → Cores → SEM+EDX; Sand packs

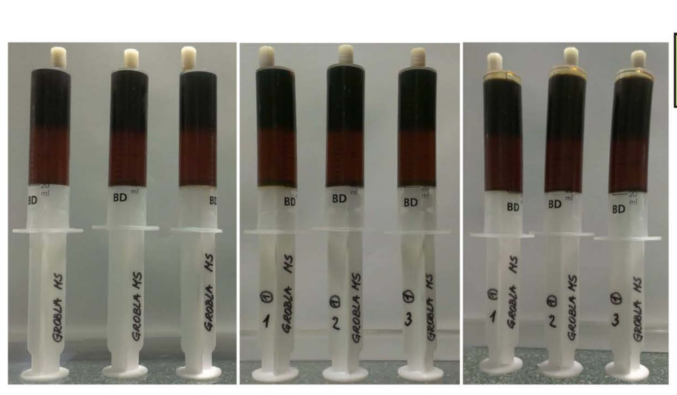
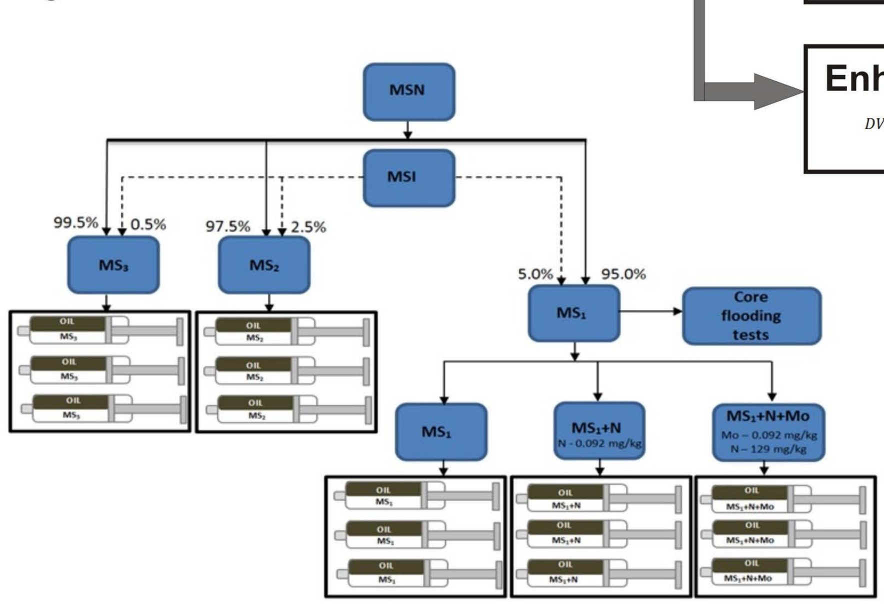


*Fig.2. Incubation tubes with label*




A novel, but simple closed system using plastic syringes in anaerobic bags was developed to incubate oil and brine with the microbial materials.

*Fig.3. Scheme of laboratory incubation tests*
*(MS – microbial system, MSN – microbial system nutrient,*
*MSI – microbial system inoculum, N – nitrogen, Mo –molybdate)*

## RESULTS AND DISCUSSION

Initial experiments were designed to test the hypothesis that a dual role of microbial enhanced oil recovery and H2S mitigation is possible. Grobla production fluids show high levels of sulfide and the produced brine is alkaline (pH 7.6-8.0) and conducive for SRB growth. SRB's are present though at lower levels than indigenous anaerobes in Grobla brine

### Validating a Possible Dual Role of MEOR and SRB Mitigation

Selection of microbial system → Confirmation steps

- step 1 → Confirmation of capability of displacing additional oil under Reservoir Conditions
- step 2 → capability mitigating the biotic component of sulfide generation → nitrite and/or nitrite proxy → Additional RF testing with using :
  - various SRB mitigants
  - Grobla brine and oil
  - microbial system materials

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.

The average coefficient obtained in the laboratory from simulation microbial waterflooding is 5.2%.

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

The results of additional RF tests shown 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 the potential effectiveness of the proposed microbial treatment

Bio-treatability determined by oil viscosity analysis (Table 2) and IFT measurement (Table 3). Oil is complex liquid that exhibits typical non-Newtonian behavior. Viscosity correlates strongly with the fluid dynamics occurring in pore spaces. Specific quantitative lab procedures measured the shift in rheological properties between treated (inoculated) and untreated (control) samples. All bio-treatability indexes showed positive changes (Table 4), and 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 show biofilm produced by the MEOR microbes confirming positive bacterial growth in a sulfide contaminated environment. (Pics.1,2).

Table 3. Percentage change in IFT

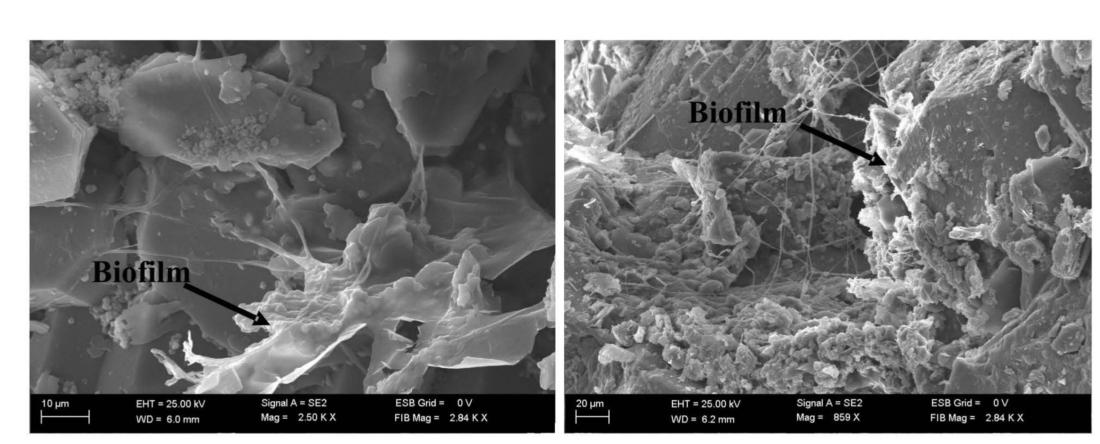
| Phase | Interfacial tension [mN/m] | Change [%] |
|---|---|---|
| Brine/oil | 15.4 | - |
| MSI/oil | 6.8 | 55.8 |
| MSI+N/oil | 10.7 | 30.5 |
| MSI+N+Mo/oil | 12.4 | 19.5 |

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




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

## CONCLUSION

Laboratory studies point to a possible dual role for microbial enhanced oil recovery; 1) increased oil recovery, and 2) inhibition of oil field souring. The microbial composition selected for Grobla demonstrated positive growth in sulfide contaminated brine. Core flooding and sand pack trials show MEOR treatment displaced 2% to over 10% more oil than waterflooding alone. Further laboratory studies confirmed MEOR displacement mechanisms were not inhibited by Grobla sulfide levels. The hypothesis that H2S mitigation and microbial enhanced oil recovery at Grobla are not mutually exclusive has been tested in the laboratory. Field work at Grobla commenced March 25th. Data from Grobla may further validate a dual role of microbial EOR and H2S mitigation.

## ACKNOWLWDGEMENTS

We wish to thank the Biomanufacturing Training and Education Center at North Carolina State University (BTEC-NCSU) and RAM Biochemicals (RAM) for producing Grobla microbial materials, and to RAM for collaboration on laboratory testing and field application protocols. Thanks as well go to the Polish Oil and Gas Company (PGNiG) management for their cooperation and permission to publish this paper.

## REFERENCES

[1] Microbial flooding increases recovery factor of depleted Pławowice oil field - from lab to the field. Falkowicz, S and Cicha-Szot, R., Research Gate Article, Jan 2015, DOI: 10.7494/drill.2015.32.2.345
[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]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/