

CH. R-3

MICROBIAL ENHANCEMENT OF OIL RECOVERY FROM CARBONATE RESERVOIRS WITH COMPLEX FORMATION CHARACTERISTICS

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ABSTRACT

Laboratory experiments with microbes adapted to subsurface conditions of temperature, pressure and salinity using oilfield carbonate rocks showed successful enhancement of oil recovery. Based on the laboratory work, field application of the adapted *Clostridium* species were conducted. A decrease of the percentage of produced water from 80 to 60% and an increase of oil production from an average of 50 tons per day to 150 tons per day occurred after treatment with bacteria.

INTRODUCTION

The German Democratic Republic (GDR) has only limited energy resources; the main source of energy being lignite. The production of natural gas amounts to 10 billion m³ annually, and oil is found in the north and southeast of the GDR with a production of not more than 40,000 tons per year.

The oil reservoirs in this region developed as a result of an intensive generation of biomasses in a relatively shallow Zechstein sea, which covered today's continent about 250 million years ago. Most important reservoir rocks are the dolomites of the Zechstein formation, encountered today at depths from 1200 to 2500 m. The temperatures in our oil reservoirs are accordingly high (from 50 to 90°C), Table 1. As relicts of the Zechstein sea, which dried out later, the pay zones have high-salinity formation waters of NaCl, CaCl₂ and MgCl₂ even the fissures and fractures of the reservoir rocks are partially filled with salt.

Table 1 Reservoir characteristics

<u>Reservoir Beds</u>	
Depth	1240 m
Formation temperature	53 °C
Formation pressure	8 MPa
Type of reservoir	fissured-porous carbonate reservoir
Matrix porosity	1-2%
Fissure porosity	0.1-0.5%
Fissure permeability	10-50 mD

In 1967, we began to investigate the possibility of an application of the molasses-in-situ process in these ecologically unfavorable conditions, since other technologies, such as waterflooding and the use of surfactants or biopolymers in fractured-porous carbonate rocks with a low-viscosity oil has not been effective.

This microbial research work, as in most other countries, was stopped in the 1970's and renewed again in 1982. Now we are engaged in the following research topics:

1. Microbial characteristics of the GDR Zechstein formation
2. Cultivation of anaerobic, halophilic, thermophilic, fermentation bacteria
3. Growth and product Generationes a function of salinity temperature and pressure
4. Analysis of oil desorption on core models
5. Process engineering for the cultivation of the inoculum at injection site
6. Field testing

MICROBIOLOGICAL CHARACTERISTICS OF THE ZECHSTEIN FORMATION

Because of the extremely unfavorable initial conditions for ecology, specifically the combination of high formation temperature and high-salinity formation waters, the GDR oil and gas fields are supposed to be sterile.

Bacteriologic analysis in untreated wells showed no bacteria. Bacteria may have been introduced into the formation with the drilling mud or with well treating agents. After essential changes of the formation environment caused by water flooding, a temperature drop and a decrease of salinity growth of microorganisms occurred in the bottomhole area of the reservoir. As a rule, only sulphate-reducing bacteria survived. The formation waters, however, did not contain bacteria suited for the molasses-in-situ processes such as Clostridia.

To separate appropriate bacteria we carried out an extensive screening program analyzing samples from locations with extreme conditions, such as salt samples from mines, saltgardens, different high-salinity waters from salt lakes and technical units, formation waters from different beds, thermals, hot-water circulation systems, etc.

We selected those microorganisms, which in an anaerobic molasses medium with a salinity of more than 100 g/l, generated gas at a minimum of 100 ml per g molasses. By increasing salinity and temperature stepwise we adapted the bacteria to more unfavorable conditions. Equipment for continuous cultivation of microorganisms was constructed for this purpose. The culture itself controls the nutrient flow in the fermenter by its acid generation through

molasses fermentation. This self-regulation by metabolic activity of the wells prevents a wash-out of the culture, which is destroyed with more severe conditions of cultivation.

First we tried to adapt the bacteria to formation temperature rising it gradually to 55 °C, followed by an increase of salinity. The halophilic cultures quickly became accustomed to a salinity of 150 g salt/l, whereas two critical concentration points occurred at 180 g and 250 g of salt per liter. Especially at these concentrations, we observed the well-known transformations such as filamentous growth of cells, partial autolysis and formation of ghosts.

We did not succeed in adapting all isolated halophilic anaerobic fermentation bacteria to a salinity of 320 g/l. Bacillus polymyxa and Clostridium butyricum developed only up to 180 and 210 g of salt per liter. At higher salinities Clostridium coccoides spec. and Clostridium oroticum spec. dominated.

TOXICITY OF IONS

High-salinity formation waters often are characterized by different ion-contents. We analyzed only waters of the chloride type.

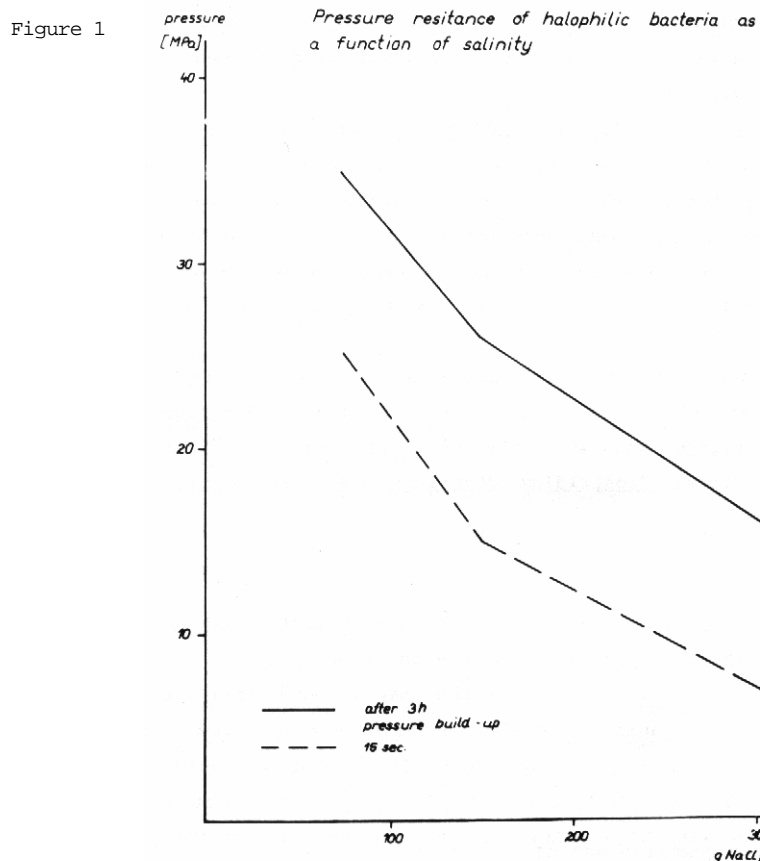
We found that sodium and potassium may be exchanged without impairing the growth of microorganisms. Magnesium has higher toxicity than Na⁺ and K⁺, but microorganisms adapt quite readily to it so that we could cultivate them in presence of 160 g/l NaCl and 160 g/l MgCl₂. The most toxic formation waters were these with high CaCl₂. In the presence of high NaCl (150-200 g/l) adaptation could only be attained with less than 100 g CaCl₂/l.

PRESSURE RESISTANCE OF HALOPHILIC BACTERIA

Microorganisms injected into deep reservoir beds are subject to high pressure. In nearly depleted low-pressured formations the stress results from hydrostatic pressure and the injection pressure at the surface. In our test formation at 1200 m, and with a surface injection pressure of 10 MPa the bottom-hole flow pressure may amount to 25 MPa.

The growth experiments were conducted in 2-l autoclaves at 55°C in molasses media with different concentration of salt (Fig. 1). In general, pressure effects decreased with increasing salinity. Sudden pressure increases (15 s) affected the bacteria more than a gradual rise of pressure (2-3 hrs).

Knowledge of the pressure sensitivity of bacteria is essential for design of the injection technology. In high-salinity media bacteria may be destroyed by the injection pump by a sudden pressure increase to 10 MPa. It is essential to use injection media with a salinity of 75 g/l to 150 g/l. A



minimum salinity of 75 g/l is dictated for the application of halophilic bacteria, which undergo autolytic decomposition at low salt contents. As to temperature resistivity, thermophilic bacteria of the species *Clostridium thermocellum* showed better temperature resistance with increasing pressure. The optimum growth temperature increased from 76°C (in low-salinity molasses media with a NaCl content up to 30 g/l) to 82°C with a pressure minimum 2 MPa.

In spite of long-term adaptation experiments we did not succeed in adapting halophilic bacteria to temperatures of more than 55 °C, or thermophilic microorganisms to a salinity of more than 50 g/l.

CULTURE MEDIUM

The composition of the culture media was minimized to a degree allowing sufficient growth of the organisms and maximum product generation. The following formulation was developed: Sugar-beet molasses, 40 g/l, polyphosphate 0.3 g/l, NH₄Cl 1.0 g/l, CaCO₃ 10 g/l, salinity 75 to 320 g/l,

ion content according to the formation water analysis, pH 7.5.

Fig. 2 shows the characteristic parameters of growth and synthesis. With an extremely unfavorable cultivation environment an initial cell content of $4-5 \cdot 10^7$ bacteria/ml is necessary. The maximum cell content of the culture medium was to $4-5 \cdot 10^8$ bacteria/ml. Generation time was 2 hours. The conversion (that is the anaerobic fermentation) of the molasses sugar (nearly 50%), together with the development of organic acids are demonstrated in Fig. 2. A decrease of the pH of the medium to 4.6-4.8 occurred. The acid generation is most intensive at the stage of logarithmic growth.

Gas generation was 300 ml of gas per g of molasses used. The gas phase consists of 60% CO_2 and 40% H_2 , with a much higher portion of CO_2 in the production-generation phase than in the growth phase. In the presence of carbonate rock (as in our reservoirs) the CO_2 content of the gas rises to 80% due to acid reaction with the carbonates.

Figure 2

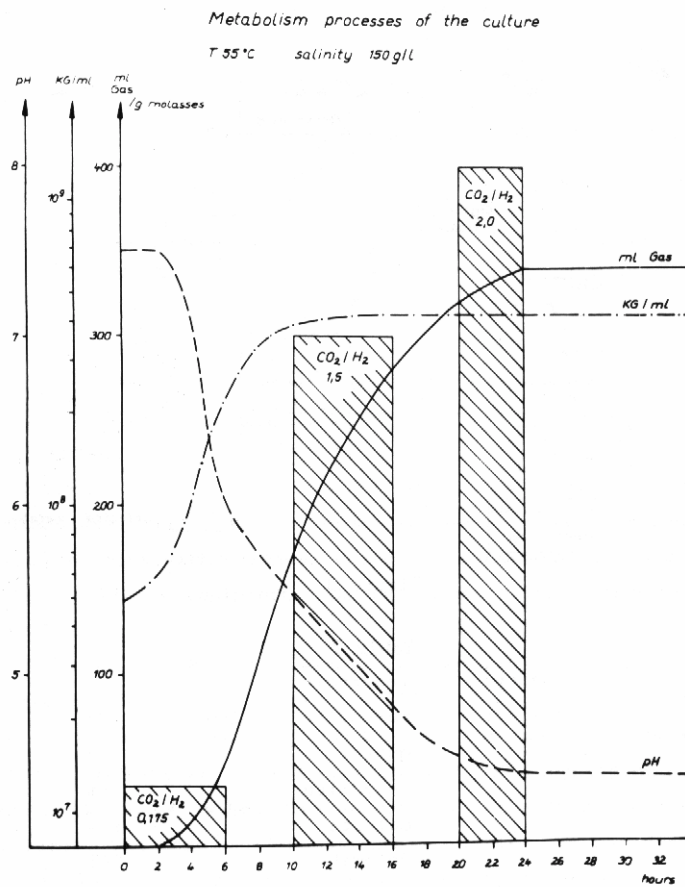


Fig. 3 shows the metabolic products identified in the culture medium during molasses fermentation: CO₂ and H₂, acetic, lactic, propionic, butyric, and valeric acid, acetone, as well as ethanol, propanol, butanol, isopropanol.

SIMULATION OF OIL DESORPTION

Experiments of oil desorption were conducted in static systems (imbibition test) and in flow models under room conditions and under formation pressure.

Six weeks before the beginning of the taste oil-impregnated cores from the Zechstein main dolomite of the Doeborn field were stored in formation water to simulate a primary oil recovery, and then subjected to various tests shown in Table 2. After three weeks of reaction time at 55°C we measured the volume of desorbed oil.

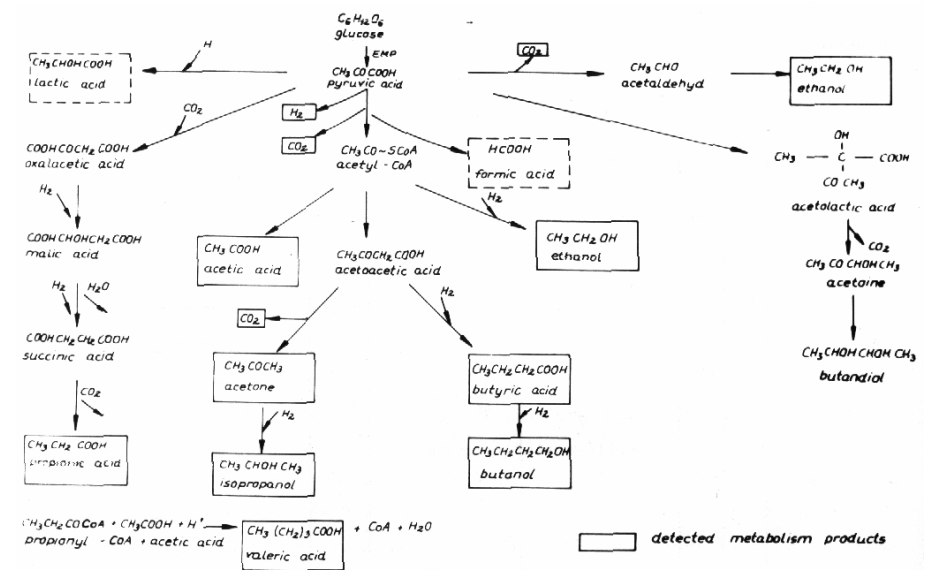


Figure 3

Table 2

Oil:	density:	reservoir rock	
	viscosity:	muscovite lillite	5%
		quartz	3%
		anhydrite	5%
		calcite	67%
		dolomite	20%

The formation water and sterile nutrient solution (Tables 3 and 4) did not affect the core but the sterility filtrated fermented cultural solution had an oil-desorbing effect due to its content of organic acids and alcohols which is caused a change of wettability and rock solution. In the actively growing culture of *Clostridium* this process was intensified, due to the penetration of bacteria into the rock pores and fractures where they produce pressure change by in-situ generation of biogas, and thus stimulate the oil to flow. In the pressure unit, the solution of biogas in the oil lowers the oil viscosity and improves its fluid flow characteristics.

Table 3

Formation water mg/l			
Na ⁺	16.670	Cl ⁻	190.700
K ⁺	102.690	Br ⁻	430
Ca ⁺⁺	3.206	J ⁻	1
Mg ⁺⁺	4.4450	SO ₄ ⁻⁻	1.750
NH ₄ ⁺	101		
Fe ⁺⁺	---		

Table 4 Composition of a molasses nutrient medium
in g/l

sugar-beet molasses	40.0
polyphosphate	0.3
NH ₄ Cl	1.0
CaCO ₃	10.0
salinity	75-320
ion content A in formation-water analysis	

FLOW-MODEL EXPERIMENTS

We conducted various experiments with flow models made of sand, limestone granulate and cores of reservoir beds. Formation conditions are best imitated by tests with original cores and formation pressure carried out in special high-pressure equipment. We used cores which were 6 cm in diameter and 18 cm in length.

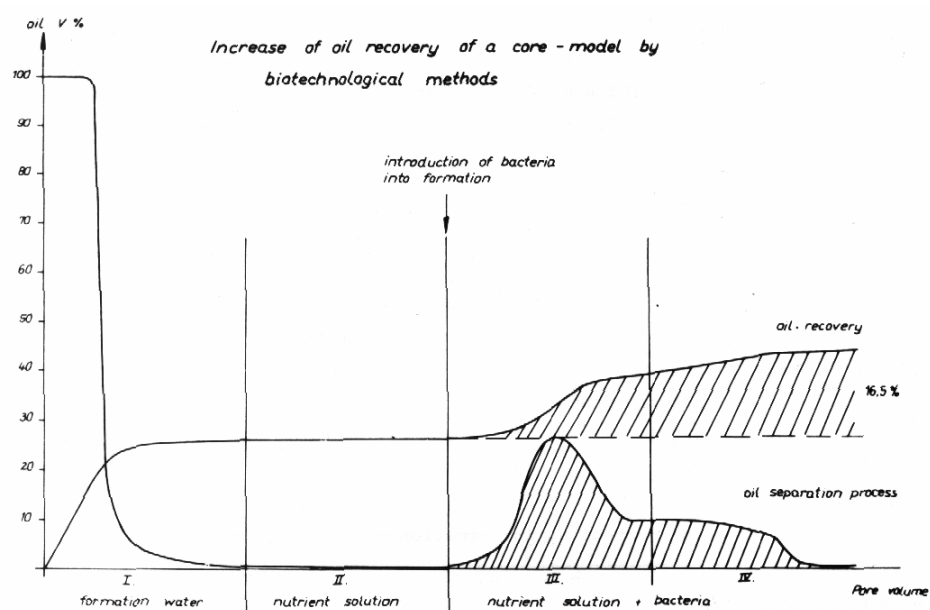
After evacuation, the cores were saturated with oil, applying pressure. The tests were carried out at 15 MPa and 55°C. The core was flooded with one pore volume of formation water followed by two volumes of molasses nutrient solution with a salinity of 150 g/l containing $1 \cdot 10^8$ Clostridia per ml.

As shown in Fig. 4, water break-through was observed after injection of 1/4 pore volume. The core was flooded until no more oil was displaced. The oil desorption was 25%. After the injection of the nutrient solution and

Table 5 Oil separation of a dolomite core after a reaction time of 3 weeks at 55 °C

Type	Preservation medium	ml/desorbed oil
1	formation water	0.0
2	sterile molasses nutrient solution	0.22
3	sterile-filtrated fermented cultural solution	0.6
4	active culture of Clostridia	1.0
5	active culture of Clostridia, 15 MPa	1.6

Figure 4



molasses we observed an increase of the oil in the effluent fluid, to a maximum of 30%, and a longer-lasting effect of microbial metabolism. By application of the molasses-in-situ process, the oil recovery from the core increased by 16.5 to 47.5%.

FIELDTESTS FOR ENHANCED OIL RECOVERY

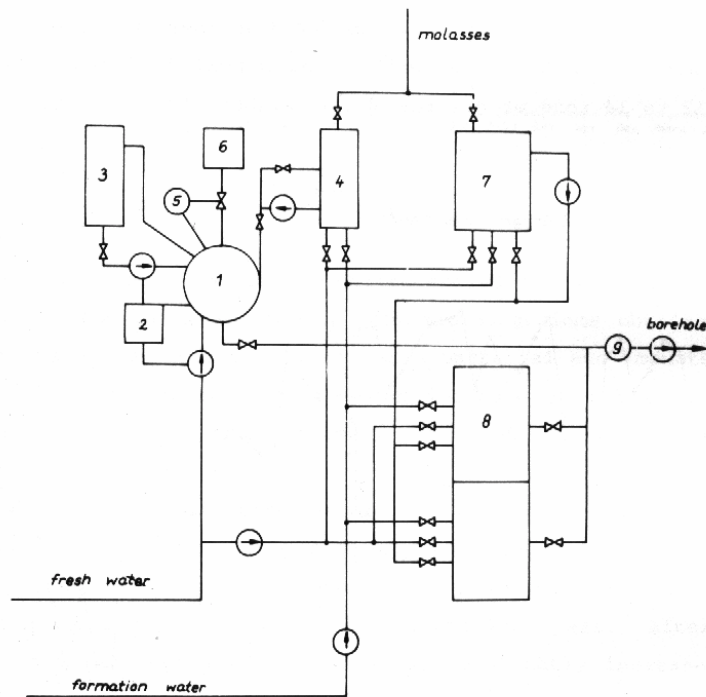
For the direct preparation of the field experiments we conducted small scale lab experiments in a 2.5 liter fermenter. They served to optimize the molasses-based nutrient media, to calculate the requirement of raw materials and to ascertain technical parameters, such as mixing intensity, turnover time, inoculation interval, development pH, alkali dosage, etc. Thus we

obtained the data necessary for the construction and operation of a 2.5 m³ field fermenter for the cultivation of inoculum at the site. The design of the field testing plant is shown in Fig. 5.

The field plant was initially operated discontinuously but in the last few years continuously with flow rates of 0.4 m³/day and a cell content of 4*10⁸ bacteria/ml established at a salinity of 150 g/l.

For example, we injected 2000 m³ of nutrient solution with 50 tone of molasses with polyphosphate and soda as additives, in a mixture of fresh and formation water, followed by inoculation of an adapted cell mixture in a ratio of 1 to 10, using a batch-wise injection program. After injection the well

Fig. 5 Technological diagram of surface equipment for the injection of bacteria and nutrient solution into formations



- 1 - Fermenter for bacterial cultivation
- 2 - Temperature control
- 3 - Water heating
- 4 - Nutrient solution tank for fermenter unit
- 5 - automatic pH-measuring and control unit
- 6 - Alkali tank
- 7 - Mixing unit
- 8 - Nutrient substrate pumping tank
- 9 - Volume measuring device

was closed in, and the effectiveness of the molasses-in-situ technology observed at a production well located 600 m from the injection well by monitoring the production well shut-in pressure. Fig. 6 shows the percent water of the producing well before and after microbial treatment.

Before the MEOR treatment the producing well flowing with 88% water. After injection the water content decreased substantially to a minimum of 34%, and to an average of 60%. The water decrease in the output clearly shows increased oil desorption from reservoir by the activity of the microorganisms (Fig. 7).

Before the beginning of the test the average annual oil production was 50 tons/month. Three months after injection of the nutrient molasses solution and the bacteria we observed an increase of oil production to an average of 150 tons/month and also an increased CO₂ content in the gas, which rose from 0 to 0.2% in the beginning to 4% near the end of the project, despite the considerable distance between the injection well and the producing well. About a year after the injection we observed another increase of oil output to an annual average of 300 tons/month. For a period of four months the daily output of 12 to 14 tons of oil reached an eight-fold increase.

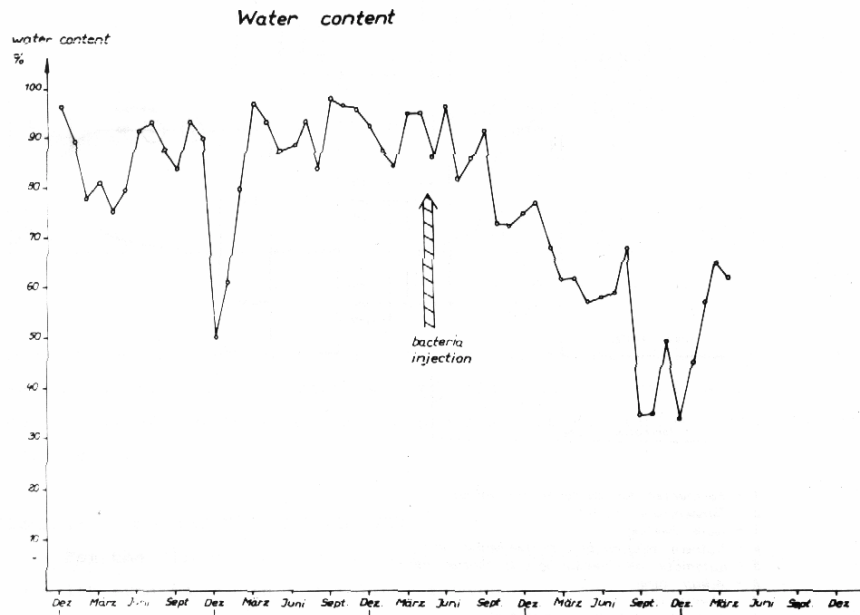


Figure 6

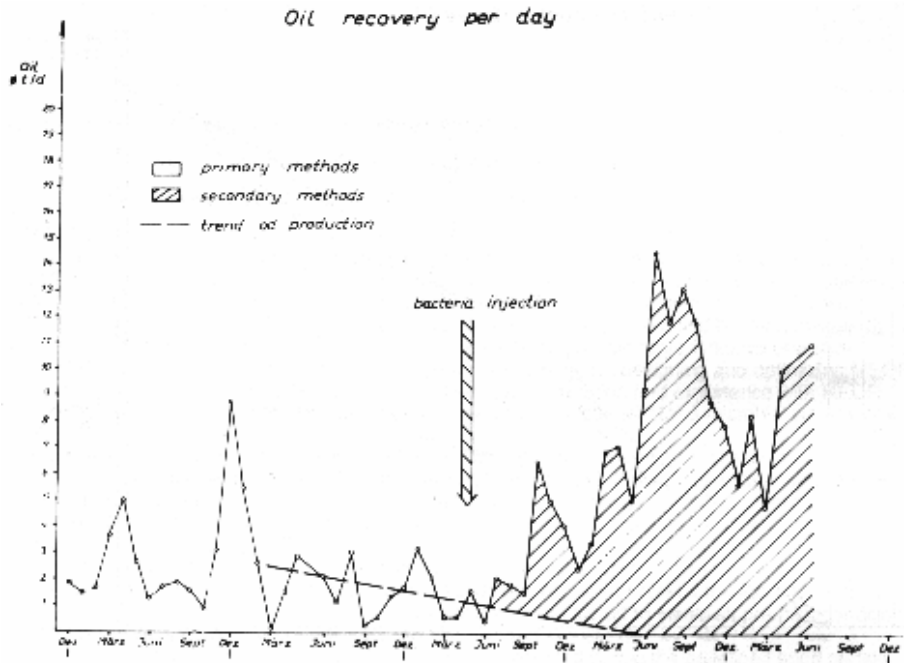


Figure 7

The increase after 12 month is characterized by the first detection of microorganisms at the producing well. The microorganisms obtained from the producing well were identical to the injected bacterial and amounted to $5 \cdot 10^7$ per ml. Therefore we attribute the second increase of oil recovery to the break-through of the injection front. Fig. 8 summarizes the output development of this well.

The oil production increase after the bacteria injection is beyond doubt. we succeeded in increasing not only the prognostic recovery of 2250 tons by 3800 tons of oil, but also the rate of production. The water entrainment did not rise, but dropped during the last year. After microbial treatment the gas production of the reservoir distinctly increased; that is confirmed by observations at the injection well. During the shut-in period the well-head pressure increased from 0.5 to 2.5 MPa. Gas samples taken at the injection well had a biogas component of 60-80% in the natural gas with up to 70% CO_2 and 10% H_2 . In the natural gas component the content of nitrogen and methane substantially decreased, whereas the content of oil-typical components such as ethane, propane, and butane had increased. We interpreted this as a greater participation of dead oil in overall production. Production of hydrogen sulfide did not occur.

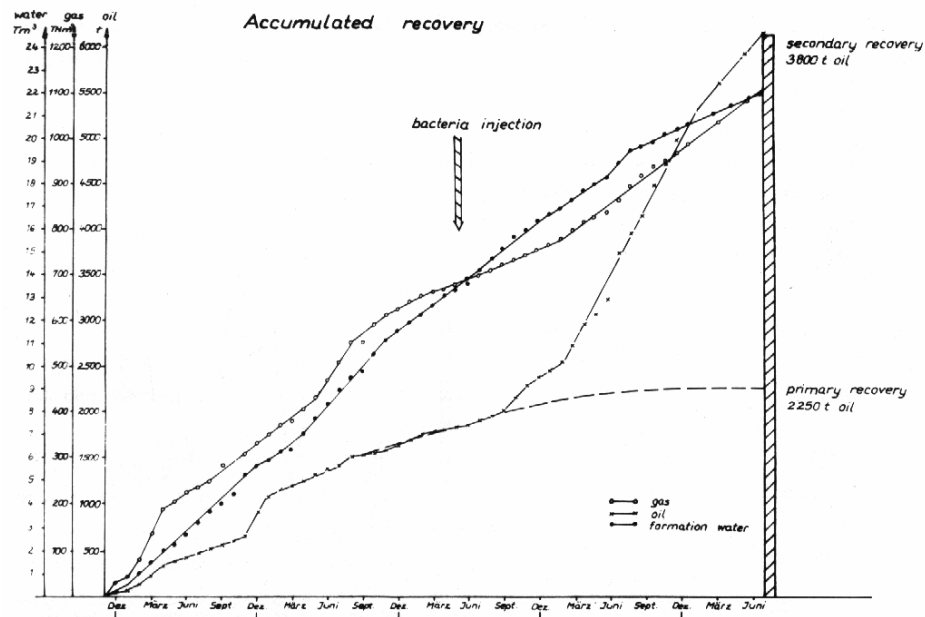


Figure 8

In addition to the current long-time flooding tests we also tested the huff-and-puff method in the carbonate reservoir rocks. After injection of 20 tons of molasses the well production rate increased (without changing the procedure) from 7 m³/d to 14-17 m³/d, and the oil output from 0.5 to 2.5 tons/d with a rise of the wellhead pressure through biogas generation of 2 MPa. The production increase is attributed principally to improvement of flow conditions by microbially enhanced rock solution processes in the formation.

Further development of technologies, extending field application of this method to high-temperature reservoirs, has been successful. The next time we plan to test the microbial reservoir treatment method at a temperature of 82°C with high-salinity waters, using a new technology.

Together with Soviet scientists we have almost completed the development of a technique for flooding the Romashkino field in the USSR with molasses and Clostridia.

As mentioned, earlier, the GDR has only a few oil reservoirs, therefore we are interested in applying our MEOR technology in other countries.