RESERVOIR CONFORMANCE ENHANCEMENT IN GAS FIELDS USING MICROEMULSIONS

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Abstract
The primary aim of the research project was to develop such chemical systems, which triggered by mixing with water will form the blocking phase. As a novelty water sensitive homogeneous solutions and water external microemulsions were developed, which are stable until they are diluted with water forming thus stable macroemulsions. Transformation of different metastable systems to stable ones in reservoir space having high water saturation may radically restrict the water flow through their high viscosity and entrapment of the dispersed particles by the pores. As dispersed phases organic silicon compounds, tensides and natural crude oil fractions were tested. The transformation and structure of phases and size of particles were analyzed by photon correlation spectrometry, rheometry, while the flow properties were studied in natural sandstone systems.

The core studies confirmed that all metastable systems reduce the flow of water by 80–90% in water-saturated sandstone. Using chemical-free postflush the flow resistance remains substantial against water in case of silicones; meanwhile the permeability deterioration against oil or gas is negligible. The metastable systems are effective and single step disproportional permeability modifying fluids.

The metastable systems may offer an excellent opportunity for water shut-off in matured oil and gas fields and gas storage facilities. The unique properties of the techniques are that flow resistance may occur only in water saturated reservoir space and in case of technical failure; the flow barrier can be eliminated by oil and gas injection.

1. Introduction and background of R&D activity

Identification, prediction and understanding of conformance problems are fundamental in optimal design of production technology in both oil and gas fields. Appropriate application of reservoir conformance control, particularly in depleted fields, can significantly lead to improved and enhanced oil and gas recovery (IOR/EOR), and hence the profitability of operations. The term “conformance” in its original form is defined as the measure of the volumetric sweep efficiency during the recovery and the forced intervention into the reservoir [1]. The term also refers to a measure of and the treatment of excess water (rarely gas) production. Excess water production usually imparts indirectly a negative influence on volumetric sweep efficiency and as a result deteriorates the profitability of production operations [2]

The idea of water shut-off treatments has arisen already in 1922 when injection of silicate solutions into oil producing wells with the aim at in-situ gelation to form a blocking phase was patented. However as far as the hydrocarbon industry is concerned, a real necessity to control flow profile around wells became known only in the middle of the sixties. Since that time a great variety of polymer methods using polymer solutions, rigid and weak gels as diverting/blocking agents and disproportional permeability modifiers have been developed. The most frequently reported methods form three main groups: injection of
polymer solution, in-situ cross-linking of chain like polymers and in-situ polymerization of monomers. Their general feature is that they are based on application of macromolecular materials. Such a common denominator cannot be found as far the blocking mechanism is concerned. Since the philosophy of profile correction methods is that deliberate formation damage or a drastic mobility reducing effect must be developed in a right reservoir space and in a proper stage of production, the different known techniques, in a wider sense, can be classified as follows:

Mobility control by modification of rheological properties
- Injection of polymer solutions;
- In-situ cross-linking of linear polymer;
- In-situ polymerization of monomers;
- Combined, multifunctional methods;
- Precipitation of gel-like inorganic compounds;
- Precipitation of crystalline inorganic compounds.

Mobility control by modification of pore structure

Theoretically the reservoir engineering concept of the profile correction or in-situ barrier formation is invariant to the factors whether the viscosity of fluids, pore structure the reservoir or simultaneously both of them are modified in the target area. Positive and negative arguments may aptly be listed beside all solutions. Despite the fact that “chemical safety of gelation” under laboratory condition is close to 100% though, the field results often fall short of expectation. Reason of unsuccessful treatments might be that the flow resistance against water flow often develops not in the right time and reservoir space. Analyzing the reasons of unsuccessful well treatments, we may conclude that placement of gel-forming liquids and timing of gelation is controlled by great variety of techniques but the presence of water is rarely considered directly as factor triggering the build-up flow resistance against of water.

Surprisingly polymers were used in majority of routine well treatment jobs; meanwhile other materials, e.g. inorganic compounds were almost completely neglected as barrier-forming agents. Therefore the focus of the Hungarian research projects in the past, comprising more than two decades, was to analyze the silicate, silicate/polymer, alcoholic polymer solutions, metal hydroxides, silicone microemulsions and alcoholic polysiloxane solutions as alternatives and to evaluate the potential of such methods under field conditions [3–11]. Study of the mechanism of the last two methods [10, 11] it was recognized that the flow resistance developed against the water flow could be traced back to transformation of the microemulsion and the ideal polysiloxane solution to high viscosity macroemulsion when mixing with water. Therefore the primary aim of the recent research projects was to develop similar chemical systems, which will form the blocking phase contacting with water.
2. Thermodynamic consideration and concept of methods

Any thermodynamic system is in equilibrium (state of rest) when none of its properties change in time. However many systems have apparently stable states that show no change with time, and thus can be regarded for practical purposes as equilibrium state, even though they are not representing minimum internal energy. Such condition is called metastable state. Transition from metastable state to real stable state needs excess energy to overcome the threshold potential. That excess energy can be provided or introduce into the systems with different ways. When this surplus energy gets into the system, different processes are induced and taking place: chemical reactions, phase transition, etc. and these processes may radically change the physical and chemical properties of systems.

Surveying the most frequently applied well treatment techniques we have to point out that transition of metastable to stable state is in the background of barrier-forming processes. For instance, mixing of stable polymer and cross-linking solution in the mixing zone triggers in-situ bulk phase gelation of polymer/Cr³⁺ systems at elevated temperature. However it is clear that contact between the formation water and the treating fluid is not an active triggering factor in the mentioned cases, and hence, we cannot be certain that the selective flow resistance develops exactly in the highly water saturated reservoir space what we want to isolate. These weak points of the routine well treatment technologies encourages us to study and develop such chemical systems, which may work exactly on transition mechanism of metastable state to stable one initiated by in-situ mixing of homogeneous and microheterogeneous treating fluids with formation water.

3. Experimental conditions, materials, and procedures

The laboratory studies comprised complex colloid chemical, rheological and hydrodynamic studies using untreated and the treated reservoir cores. Primary aim of the measurements was to determine the changes of all parameters, which may influence the selective flow of water and gas, respectively. Details of the laboratory studies are summarized in the following subchapters.

Fluids. The fluids used for saturation of cores and flow measurements were selected according to the target field conditions where the method was expected to be tested.

- Gas phase: natural gas with 95% CH₄ content, nitrogen
- Formation water:
  - 2.6 g/l NaHCO₃
  - 2.6 g/l Na-acetate
  - 0.5 g/l NaCl
- Crude oil:
  - light paraffinic (Algyó field, Hungary)
  - light hydrocarbon cut (petroleum)
- Treating solutions:
  - silicone ME with 33.0% polysiloxane content
  - silicone solution in methyl alcohol with 33.0% amino functional polysiloxane
  - gemini tenside No.1 in IPA containing solution with 10 g/l active content
  - gemini tenside No.2 in IPA containing solution with 10 g/l active content
gemiini tenside No.3 in IPA containing solution with 10 g/l active content
petroleum (light and medium) external microemulsion
lubricant oil external microemulsion
alcohol/keton external microemulsion

Abbreviations: The Wacker-Chemie GmbH, Germany provided the silicone oligomers in form of micro- and macroemulsion and pure chemical compounds. The microemulsions were stabilized by two (anionic and ionic) surfactants in aqueous carrier phase. The Gemini tensides were ethoxylated and alkoxyalted diols manufacturers by the Air Products Chemicals BV (USA) in form of pure compounds (No. 1 and No. 3) and mixtures of two components (No. 2). These materials are characterized by limited solubility in water and hence, their ideal, homogeneous solution could only be made by addition of different amount of IPA to aqueous phase. Because their flow properties in porous media were unfavorable, and their application for conformance improvement was out of question, data of laboratory studies are not included hereafter. The petroleum external microemulsions contained less than 15% fatty acid/ester and 15% water.

Core material. Both synthetic and natural cores were used for flow measurements. The former ones served for serial measurements, while the later ones were used to control the results and predict the real effects under field conditions. The cores were characterized by He- and Hg-porosimetry, and determination of the absolute, effective and relative permeability, capillary pressure and wettabilty. The following data are relevant to the synthetic and formation cores:

Synthetic cores:

Special laboratory technique developed by the institute was use for preparation of the synthetic porous cores. Those cores were prepared from formation rocks using the whole crushed material and adding less 5% thermoplastic resins. Setting the size fractions appropriately cores with 180–210 mD permeability were prepared. The artificial consolidation was carried out by thermal treatment of the pressurized cores. The core porosity and pore size distribution were close to each other within 10 rel. percentage. The wettability however was shifted from the water wet character toward the intermediier range because of partial coverage of the rock surface by the melted and then solidified resins.

Formation cores

The formation rocks derived from different sources. Most of the cores represented the Algyő field, Hungary. In majority of cases the natural Fontainebleau sandstone cores were used. Its properties measured by high pressure Hg-porosimetry (Thermo Finnigen Pascal 440) are listed in Table 1. The natural formation rocks were cut in horizontal direction from the original drilled cores. Since their properties were remarkably different, those pieces were selected for lab studies that had similar physical and hydrodynamic characteristics. Average data of cores were as follows
Table 1

Characteristic data of the Fontainebleau sandstone cores

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Average pore radius</td>
<td>19.45 µm</td>
</tr>
<tr>
<td>Most frequent pore radius</td>
<td>17.72 µm</td>
</tr>
<tr>
<td>Total porosity</td>
<td>12.43%</td>
</tr>
<tr>
<td>Bulk density</td>
<td>2.32 g/cm³</td>
</tr>
<tr>
<td>Apparent density</td>
<td>2.64 g/cm³</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>0.26 m²/g</td>
</tr>
<tr>
<td>Gas permeability</td>
<td>400–600 mD</td>
</tr>
<tr>
<td>Water permeability</td>
<td>250–400 mD</td>
</tr>
</tbody>
</table>

Procedures. The rheological measurements were carried out with Contraves Low Shear 30 rheometer in range of $10^{-3}$–$10^{2}$ 1/s shear rate range at ambient temperature. The structure of microheterogeneous systems and determination of particle (droplet) size were studied by photon correlation spectrometry using transmission and back scattering laser techniques (Malvern Zeta and NanoSizer). Standard linear flow tests were used to demonstrate the effect of different barrier forming media. For correct comparison of the experimental results, those data will be presented here that were obtained for Fontainebleau sandstone cores. The tests were performed with identical injection protocol. First 10 PV formation water was injected into the core with aim at determining the basic data (water permeability and mobility). The water preflush was followed by injection of 10 PV treating agent. In the final phase of the flow tests, injection of 10 PV formation water served to drive the treating fluids out from the cores. In certain cases organic phase, light hydrocarbons (petroleum) was injected after the water postflush to study the permeability reconstruction. The fluids were injected at constant flow rate and measuring the differential pressure the mobility was calculated. Because of numerous data were obtained, only those diagrams will be shown here, which are representative for change of the mobility through the flow tests.

4. Characterization of treating fluids

General feature of all tested treating fluids is that contacting or mixing with water their structure fundamentally changes. The radical change of fluid character can be often visualized by naked eye in case of light, medium and heavy hydrocarbon external microemulsions shown in Figures 1–3. The appropriate microemulsions were diluted by formation water in different ratios and it is clearly seen that phase inversion and microemulsion$^5$ macroemulsion type transformation is immediately taking place in the system when relatively small amount of water (less than 20%) is added to the microheterogeneous colloids. Unfortunately similar change could not be observed in case of alcohol/keton external microemulsion because of its poor stability (Figure 4.).
As a consequence of the mentioned changes, the viscosity of emulsions as a function of water content steeply increases in range of 5–20% water content, and then it drops down above 50–60% (Figure 5).

*Figure 1: Effect of water content on phase behaviour of petroleum (medium) external microemulsion ($c_w = 0\Rightarrow95\%$)*

*Figure 2: Effect of water content on phase behaviour of petroleum (light) external microemulsion ($c_w = 0\Rightarrow95\%$)*
The region shown in Figure 5 as discontinuity of the curves representing extremely high viscosity can be interpreted as phase inversion, viz, at the left-hand side curve represents the microemulsion; meanwhile the right-hand side belongs to macroemulsion phase. Between these two limits, depending on the type of systems, the viscosity can be higher than 10,000 mPa s and these materials are cream like in nature and not mobile even at high deformation forces (Figure 6). Practical importance of that fact is, that such systems form immobile barrier against flow in any porous or fractured systems when the microemulsion penetrates high water-saturated zones and layers. Not surprisingly the water containing macroemulsions show strong Non-Newtonian flow behaviour and the dependence of the viscosity on shear rate becomes more pronounced as the water content approaches the range of 20–40% (Figure 7).
Figure 5: Effect of water on viscosity of different microemulsions

Figure 6: Consistency of water-containing microemulsion at phase inversion

Figure 7: Non-Newtonian viscosity of water-containing microemulsion
It is needless to say that structural modification of the original treating fluids is in the background of the rheological changes. Determination of the particle (droplet) size of the dispersed phase definitely proved that the fine microstructure of the original materials transformed to a coarse macroheterogeneous colloids. According to the shape of the curves shown in Figures 8 and 9, the trend of the $Z$ average droplet diameter is in full convergence with the viscosity changes illustrated in Figure 2. In addition, it deserves attention that the single-peak like size distribution curve became composite in character indicating thus a strong aggregation of the dispersed microdomains in the macroemulsions (Figure 10).

**Figure 8: Size distribution of undiluted silicon microemulsion (c$_w$ = 0%)**

**Figure 9: Size distribution of diluted silicon microemulsion (c$_w$ = 30%)**
aggregates and network of domains formed in-situ jointly result in a stable impediment against water and only in highly water-saturated reservoir space. Now the answer for such microheterogeneous systems transform to a more stable (lower internal energy) state and substantial flow resistance will develop in those zones, layers or even capillaries and pores.

5. Study of flow phenomena in porous media

It is worth mentioning, however, that using water external macroemulsions as treating fluid as suggested by Sobanova et al. [12], Romero at al. [13] and Stavland et al. [14] such unique phenomena cannot be observed. Dilution of any macroemulsions with water is followed by gradual decrease in viscosity and usually constant droplet size until a critical phase ratio of the induced coalescence. In contrast the silicone microemulsions suggested first for treatment of gas wells by Pusch et al. [15] and studied earlier in detail [10] proved to be an excellent model to demonstrate the general features of metastable, water sensitive chemical systems.

Based on the results of the laboratory experiments we may notify in advance that substantial flow resistance will develop in those zones, layers or even capillaries and pores where the water saturation is high and the water contact and mixing induce a structural modification in the potential treating fluids. The phenomena are selective and nothing may happen if water is absent, and the fluids remain unchanged until they get into water containing reservoir space. From chemical point of view the metastable ideal solutions or microheterogeneous systems transform to a more stable (lower internal energy) state and that change initiated just by the presence of water. From reservoir and production engineering point of view the important consequence is that the flow resistance ensues only against water and only in highly water-saturated reservoir space. Now the answer for such questions is that both the high viscosity of water containing emulsions and the large droplet aggregates and network of domains formed in-situ jointly result in a stable impediment against the propagation and flow of water in water-saturated porous systems; meanwhile in oil- and gas-saturated flow path no flow resistance build-up.

As mentioned earlier, numerous flow tests have been carried out in the frame of the project. Although the results of the laboratory studies were convergent, the extents of changes were different depending on the core materials used as porous media. Extensive study of silicone microemulsions and stabilized ideal silicon solutions were reported in two
SPE preprints [10, 11]. Despite that fact the results of their flow tests is repeated here to compare and evaluate the new chemical options. Identical experimental conditions and similar porous cores were used and only the treating fluid was different. In Figures 11–16, the effect of potential treating fluids on mobility is shown as a function of injected pore volume. Basically 100–100 cm$^3$ preflush water, chemical system and postflush water were continuously injected into the cores. In case of the last two tests the experiment was finished by injecting 100 cm$^3$ petroleum to study the barrier breaking effect.

Figure 11: Effect of diluted silicon microemulsion on mobility in porous media

Figure 12: Effect of diluted silicon solution on mobility in porous media
Figure 13: Effect of diluted light petroleum microemulsion on mobility in porous media

Figure 14: Effect of diluted medium petroleum microemulsion on mobility in porous media
The results of the flow tests can be summarized as follows.

1. Both silicone fluids (microemulsion and IPA solution) resulted in a significant mobility modification in cores.

2. The mobility reduction is extreme and permanent in case of diluted, water-containing silicon systems. Sweeping out the silicone fluids from the cores the mobility increased slightly, however it stabilized at level about 50% of the original. It is characteristic also for both treating systems that the residual mobility reduction remained constant through 20 PV water injection.

3. Stunning and peculiar phenomena are that injecting highly diluted silicone fluids, independently of whether the silicone is present as a dispersed phase in water or dissolved in i-propanol.

4. Comparing the efficiencies of the mobility reducing effects, the silicone microemulsion is obviously more effective. Using this treating system the mobility gradually decreases not only through the slug injections, but also in the water post-injection phase.

5. The hydrocarbon external microemulsions are also very effective mobility controlling and reducing agents. Except a few cases the mobility was practically reduced to zero during their injection of these fluids.

6. The experiments however took an unexpected turn when the microemulsions prepared with ultra light, medium and high viscosity carrier or external phases were tested. Contrary to all expectation the least effective mobility reduction during the postflush was obtained with the microemulsion having the highest viscosity (Figure 15); meanwhile the best results were observed when the ultra light microemulsion was injected.

7. Surprisingly, the application of the ultra light microemulsion had residual “memory” effect, but that favorable effect was completely absent in case of heavy oil external microemulsion (Figures 13–15).

8. The post-injected petroleum decreased the partially reconstructed mobility in all cases (Figure 16). These phenomena are attributed to secondary emulsification promoted by the stabilizer (fatty acids and esters) retarded (adsorbed and entrapped) by rock surface and pores. It is characteristic however that this effect was also more pronounced in case of the ultra light microemulsions than of heavy hydrocarbon emulsion.

The results of the flow tests clearly proved that microemulsions, whatever they are might be considered as selective and effective barrier forming agents. Injection of these water sensitive and metastable fluids may develop substantial resistance against the flow of water and that beneficial effect may build-up only in those reservoir spaces and zones where the mobile content or the residual water saturation is high. Since the possibility of a secondary in-situ emulsification cannot be completely excluded when oil starts to flow through the treated porous media, and there is a little chance for similar phenomena in gas/water systems, the microemulsions as treating agents are primarily recommended for water shutoff in gas producing wells.
Figure 15: Effect of diluted lube (heavy) microemulsion on mobility in porous media

Figure 16: Effect of petroleum post-injection on mobility modification in porous media using light petroleum microemulsion
6. Field application of microemulsions

The pilot test was performed in the Algyő field, Hungary. The target area was the Szőreg-2 layer in the stacked field. The depth of the layer (perforation) is between 1803 and 1807 m. Prior to treatments the production characteristics of the well were unfavorable: the gas production was less than 8,000 m$^3$/d accompanied by a stable 120–130 m$^3$/d water production. After appropriate preliminary actions (bottomhole clean-up, analysis of log data and production history) 225 m$^3$ diluted microemulsion containing 0.2 g/l siloxane and 5 g/l KCl was injected, which was followed by injection of 5,000 Nm$^3$ nitrogen to disperse the silicon fluid and to reach deep penetration in the reservoir. The microemulsion injection was carried out at zero well-head pressure. Technical problems or failures have not arisen during the treating period. Opening the well, observation production data lasted 10 months and the gas production is illustrated on Figure 17. The main field experiences make possible the following conclusions to draw:

1. The gas production gradually increased right after the treatment and reached 25,000 m$^3$/d on average through more than a half year. Thus the job tripled the gas output and the operation could not be suspended during this period.

2. The gas/water ratio changed according to the enhanced gas production.

3. The cumulative surplus gas production is estimated to be 2.5–2.9 M m$^3$. Taking this result into account the job was close to the profitability.

![Figure 17: Gas production prior and after microemulsion treatment of Alg. 529 well](image-url)
Figure 18: Gas production of Psz-20 well

Figure 19: Water production of Psz-20 well
Since restriction of water production in gas wells is vital for the operator – just tens of wells might be a target in Hungary – and the field experiment was encouraging for the Hungarian experts, the R&D activity continued in search for more efficient, long lasting in positive response and more profitable treating techniques utilizing different microemulsions. Recently the main efforts were focused on development of cheap, but efficient microemulsions, which may replace the expensive silicon fluids. The successful R&D activity entitled us to recommend appropriate technology to enhance production efficiency at gas fields. The preliminary overview of well candidates has shown that several wells definitely have poor performance, which can be traced back to high water encroachment and production. The well candidates for the field campaign are listed in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>Well</th>
<th>Perforation, m</th>
<th>Form. pressure, bar</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pf-1</td>
<td>1682–1688</td>
<td>152.4</td>
<td>124</td>
</tr>
<tr>
<td>Psz-20</td>
<td>943–946</td>
<td>89.6</td>
<td>78</td>
</tr>
<tr>
<td>Alg.-97</td>
<td>1794–1798</td>
<td>103.6</td>
<td>92</td>
</tr>
<tr>
<td>Hpi-D-6</td>
<td>1872–1884</td>
<td>187.6</td>
<td>107</td>
</tr>
</tbody>
</table>

As an example the gas and water production in Psz-20 well are illustrated in Figures 18 and 12. Although the gas production is relatively constant in the monitored period, the water production after breakthrough steeply increased and 18 m³/d. That value is not really high; however its liquidation at the well site was impossible. Therefore the operator decided to shut-in the well loosing 14 Km³/d gas production. Using similar well selection concept, at the end of 2011 two gas producing wells were assigned for pilot test in the Algyő-2 and the Szeged-3 formation. The Alg.-1007 well has 6–7 Km³/d gas rate with 40–60 m³/d water production; meanwhile the Alg.-588 has relative high, but declining gas rate (40–60 Km³/d), but the accompanying water production is 60–80 m³/d jeopardizing the stable and profitable gas production. Based on the evaluation of the production history, the well were selected as good candidates for water shutoff treatments to be carried out in 2012 using the petroleum external microemulsions.

7. Conclusions

1. Different metastable water sensitive chemical systems were developed, which may be used as water shutoff agents in gas producing wells.
2. Their mechanism is based on transformation of a microheterogeneous system to a more stable macroheterogeneous barrier-forming phase and that process is exclusively induced by contacting and mixing with water.
3. The most effective treating fluids are the water external silicone and the hydrocarbon external fatty acid containing microemulsions.
4. Designing the composition of microemulsions (through concentration of tenside stabilizers and water content), the microemulsions can be easily tailored to specific field and well conditions.
5. The metastable and water sensitive chemical systems having unique barrier-forming mechanism may open new vistas in water control and shutoff at matured oil and gas fields.
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