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The use of chemical tracers to water injection processes applied on Romanian reservoirs

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Abstract. The hydrocarbon reservoirs are extremely complex, each reservoir having its own identity. Reservoirs heterogeneity (mainly regarding the layered ones) frequently results in low recovery efficiencies, both under the primary regime and when different agents are injected from the surface. EOR processes efficiency depends on how detailed the reservoir is known and on the information related to fluids flow through reservoir. There are certain analyzes, investigations and tests providing good knowledge about the reservoir. The tracer tests are among them, being frequently used to water injection processes. Depending on the method used, IWTT (Interwell tracer test), SWTT (Single-Well Tracer Test), TWTT (Two-Well Tracer Test), information are obtained as related to: the setting of the preferential flow path of the injected fluid, the identification of water channels, evidencing the geological barriers, determining the residual oil saturation, around the well bore or along the tracer's path between two wells. This paper is focused on ICPT Câmpina efforts related to the use of the chemical tracers to the water injection processes applied to the oil reservoirs of Romania. It describes the usual tracers and the methods used to detect them in the reaction wells. Up to now, more than 50 tests with IWTT tracers have been performed on-site and this work presents some of their results.

1. INTRODUCTION

The main part of the problems encountered while producing an oil reservoir are due to the heterogeneity, some times quite significant, of that reservoir. This heterogeneity, related both to lithology and to flow properties, results in low displacement efficiency, considering both the pores level and the entire reservoir. The tracer tests belong to that category of tests which give us valuable information on fluids flow through reservoir.

Depending on the information we need, several tracer tests can be applied:

- Interwell Tracer Test to evidence the communication between the injection well and the producers.
- Single-Well Tracer Test to set the residual oil saturation around the well bore.
- Two-Well Tracer Test to set the residual oil saturation along the tracer path between two wells.

The IWTT has only been applied initially to water injection and EOR processes; later on SWTT and TWTT implementation helped us in setting the residual oil saturation around a single well or between two wells.

2. TRACER TYPES

The tracers used in IWTT are water soluble substances, injected into an injection well and afterwards monitored in the reaction wells by collecting samples according to a well pre-established schedule. Because there is no ideal tracer to monitor fluids flow through oil reservoirs, tracer selection is always done by laboratory tests aiming to screen the optimum tracer for each single reservoir.

In order to be used with good results, the tracer must meet the following conditions:

- to travel at the speed of the injected water;
- not to be present or found in very low concentrations in the reservoir water;
- to be stable: the reservoir fluids or bacteria should not decompose it;
- not to be adsorbed on the rock;
- detectable even as very small quantities;
- to be injected and produced under secure conditions;
- to be cheap and readily available.

The tracers used by petroleum industry can be divided in three categories: radioactive, chemical and dye tracers, each presenting specific advantages and disadvantages.

The radioactive tracers are the most frequently used, especially the tritium [1–11]. First of all, they have the advantage of being detectable even at very low concentrations, of several ppt's (parts per trillion), which means very small quantities injected into the formation, implying low cost equipment to prepare the solution and inject it. Also, they are not influenced by the reservoir conditions (rock nature, pH, temperature), are not adsorbed on rock's surface and do not pre-exist in the reservoir. Nevertheless, the risk of contaminating the environment and the operating personnel is present. This is why the radioactive materials can only be handled by authorized personnel.

The chemical tracers, best known and most used, are: halogens, thiocyanates, nitrates and alcohols. These tracers can be identified using chromatography.

Although the halogens (chlorides, bromides, iodides) are contained by most reservoir waters, their use as tracers is well-known. They are not environment hazardous. The disadvantage is that because sometimes the reservoir waters contain quite big quantities of these (mainly chlorides), the chemicals consumption is significant and implicitly the test is expensive.

Thiocyanates is one of the most used chemical tracers. Its advantage is that it is not present in reservoir waters, opposite to the halogens. In spite of that, it must be handled with care, avoiding the disposal of high concentrations on the soil or other places from where it might reach the underground waters.

Ammonium nitrate is used by agriculture as a fertilizer, to enhance and maintain soil fertility. The use of nitrites is not environment hazardous; but the disposal of high concentrations in places from where it might reach the underground waters must be avoided. Also the solid ammonium nitrate must be carefully handled because under certain conditions it may become explosive.

The most frequently used alcohols are the ones having a low molecular weight (methanol and ethanol). They are water soluble and not oil soluble. Being biodegradable, they are nor environment hazardous. Although methanol does not naturally exist in reservoir waters, it may appear after treating the wells (stimulation treatments) with solutions containing methyl alcohol. In these cases the use of this tracer is not recommended.

The dye tracers represent the third tracer category. The petroleum industry most frequently uses the fluorescein and the B rhodamin. Their advantage is that they can be detected as very low concentrations using a spectrofluorimeter; the disadvantage is their consistent adsorption on the rock. This is why they are only used when the injector-producer communication is thought to be fast (fractured reservoir).

The tracers used for SWTT are the alkyl esters of fatty acids and alcohols. The ester selection depends on reservoir's characteristics. The most frequently used ester is the ethyl acetate which hydrolyzes and forms ethylic alcohol (a new tracer) and acetic acid. The tracer (the ester) is injected into the reservoir, in a single well, up to a certain distance depending on the injected tracer quantity. The well is then shut in to allow the ester react with the reservoir water and get partly hydrolyzed. This results in the presence of a new tracer in the reservoir. The new tracer, together with the non-hydrolyzed ester, forms a pair of tracers at a certain distance in the reservoir. The well starts again to produce and both tracers are detected in the produced water. Because they have difference in water and in oil distribution coefficients, they will reach the well bore at different times. This time difference is the basis in calculating the residual oil saturation around the well bore [1,6–8].

For TWTT, two tracers with different distribution coefficients to water and to oil are used. The two tracers, one only soluble in water and the other soluble both in water and in oil, are injected into the reservoir through an injector and monitored in the producers. The difference in time between the arrivals of the two tracers, due to the chromatographic separation, is used to calculate the residual oil along the tracer's path between the two wells [1,5,6,9,10].

The oil and water soluble tracers are characterized by the partition coefficient, K_d. This coefficient is specific to each tracer and only stays as valid under its determination conditions. K_d is the ratio of the two immiscible phases tracer concentrations. Examples of such tracers: alcohols (isopropanol, n-propanol, n-butanol, pentanol), acetones, aldehydes with 2-6 carbon atoms, phenols etc. Only convenient Kd values are considered in selecting the SWTT and TWTT tracers.

3. LABORATORY TESTS

The on-site tracer test is preceded by laboratory works consisting in:

- selecting the tracers and setting the methods to detect them;
- flow tests under reservoir conditions to determine the moment of tracer's arrival, its adsorption on the rock and the partition coefficient.

3.1. Tracers selection and setting the detection methods

Different chemical and dye tracers have been tested in the laboratory and, up to present, the ICPT Câmpina on-site applied tests used the following tracers: thiocyanate, ammonium nitrate, methanol, sodium chloride, methyl tertiary butyl ether (MTBE) and n-butanol.

Concerning the methods of detecting these tracers, in the beginning we used the colorimetric methods; later on these have been successfully replaced by the chromatographic methods, enlarging this way the range of usable tracers. The nitrate ions, the thiocyanate, the halogens (chlorides, bromides, iodides) and the acetate ions are presently identified by ion-chromatography as concentrations of tens of ppb (parts per billion). The detection limit is given by: the detector performance, the column type and the type of water used for the determination (reservoir water chlorides content). Alcohols (methanol, ethanol, n-butanol), ethyl acetate and MTBE are identified by gas-chromatography (GC-MS), and the detection limit may go to hundreds or tens of ppb, even lower for MTBE.

Finding more sensitive detection methods has been our permanent objective because it is the only way we can decrease the tracer quantity used for tests, which results in making the tests cheaper and easier to perform.

3.2. Flow through core tests performing

The FRT Chandler (Formation Response Tester) equipment was used to perform several dynamic tests on sandstone and limestone cores, with reservoir fluids, under reservoir pressure and temperature conditions.

As an example, Figure 1 presents the results of a test consisting of the injection of a mixture of number of tracers (0.33 of the pores volume), the solution mixture containing 1,000 ppm of each tracer. The concentration of each tracer was identified and measured by collecting the effluent, also determining their recovery degree (Table 1).

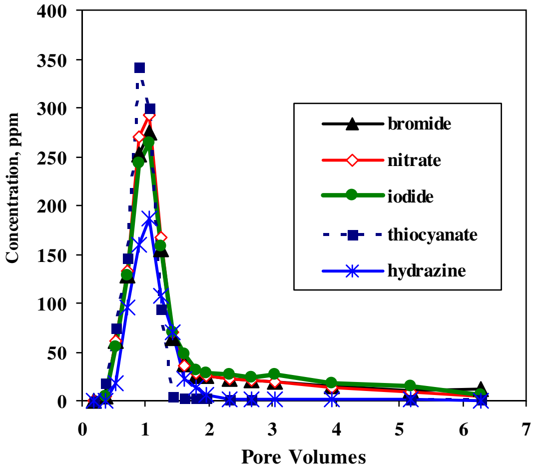

Figure 1. Tracers' arrival in a flow-through-core (carbonate) test.

Table 1. Tracers recovery degree.

Tracer	Maximum concentration, ppm	Recovery, %
Thiocyanate	342	99.00
Nitrate	291	98.70
Bromide	274	97.80
Iodide	264	95.40
Hydrazine	186	67.90

Table 2. Adsorption of methanol.

Rock type	Sandstone	Carbonate
Concentration of injected methanol, ppm	100	100
Adsorption, mg/100g rock	2.87	4.36
Methanol recovery degree, %	88.27	82.6

Adsorption was determined by passing the same tracer type through sandstone and then through carbonate. Table 2 shows the results of methanol.

In the case of SWTT and TWTT, the calculus of oil saturation needs the value of the partition coefficient, K_d. For most of the water-and-oil soluble tracers, this coefficient depends on oil and water compositions, tracer concentration and temperature. This is why K_d has to be determined under reservoir conditions (rock, fluids, temperature, pressure), several methods having been developed for this [1,2,5].

The method used in the laboratory consisted in injecting a plug containing a tracer soluble both in water and in oil and another tracer only soluble in water through a porous space brought to the residual oil saturation, S_{or}. Tracers are injected in the water phase which flows through the porous space. The arrival time of each tracer is measured, Figure 2, and then the partition coefficient is calculated with the following equation [1]:

$$K_d = \frac{(t_p - t_w)}{t_w}\frac{(1 - S_{or})}{S_{or}} \qquad (1)$$

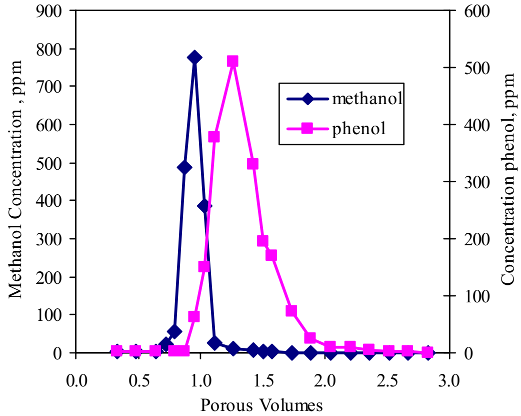

Figure 2. Arrivals of different Kd tracers, for a porous space with 28.1% Sor.

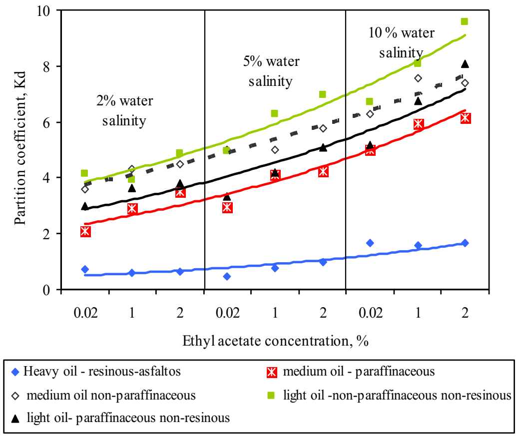

Figure 3. Setting the partition coefficient of ethyl acetate for different oil types, at 22°C.

t_p = residence time of partitioning tracer
t_w = residence time of non partitioning tracer
S_{0r} = residual oil saturation
K_d = partition coefficient.

For correct results, it is important that the arrivals are significantly different.

The results of the laboratory tests performed to set the Kd of ethyl acetate, under different conditions, are presented as a graph in Figures 3 and 4. Kd was measured for 5 types of oil, from a heavy oil containing resins and asphaltenes to a light one, all coming from different Romanian reservoirs. The tests considered 3 different concentrations of ethyl acetate (0.02%, 1% and 2%) prepared in water with different salinity (2%, 5% and 10% NaCl) and two temperatures (22°C and 50°C). The tests showed that the partition coefficient increases with temperature, with water salinity and with the ethyl acetate concentration. Oil type influence is also noticeable, regarding both its density and the resins, asphaltenes and paraffins content.

4. PERFORMING THE ON-SITE TRACER TESTS

Romania made the first tracer tests in the 80's, when radioactive tracers were used in monitoring a polymer

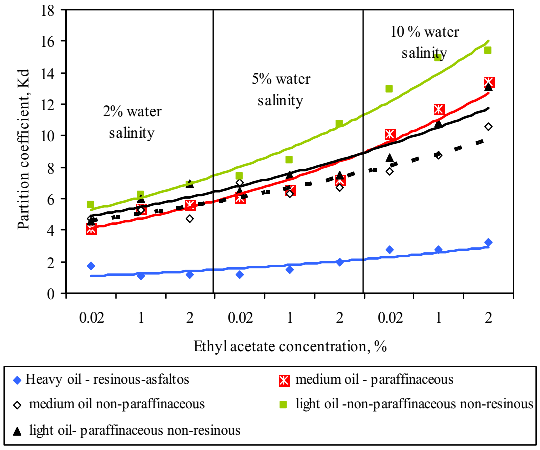

Figure 4. Setting the partition coefficient of ethyl acetate for different oil types, at 50°C.

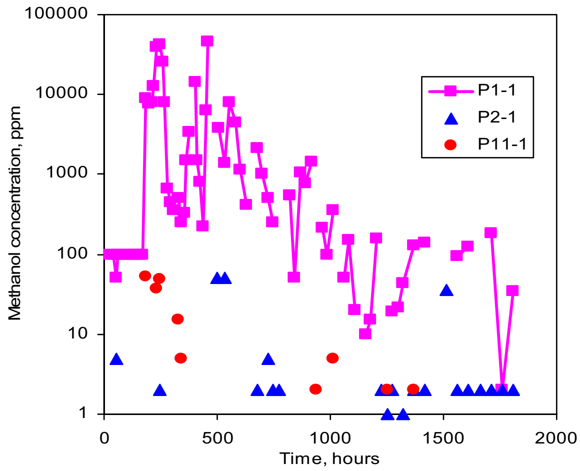

Figure 6. Tracer arrivals in wells P1-1, P2-1 and P11-1 Tazlau.

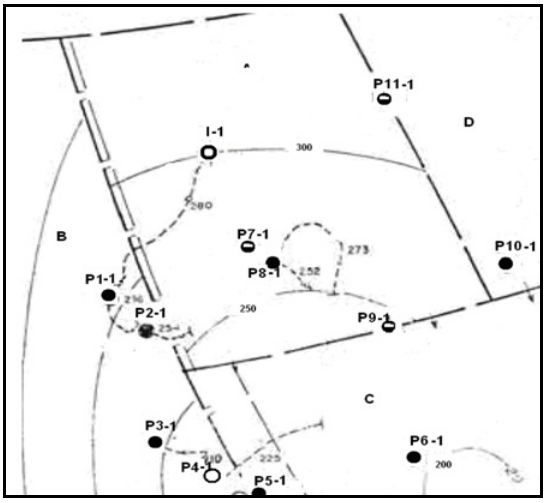

Figure 5. Area of Tazlau reservoir on which the tracer test was applied.

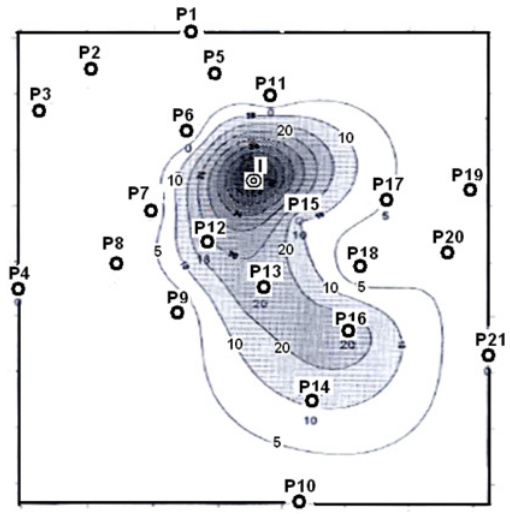

Figure 7. Evidencing the preferential flow direction of the injected water (Turnu Nord reservoir).

injection process. Starting with 1997, only chemical tracers are being used. Thus, the last 13 years counted 50 IWTT with chemical tracers on 23 reservoirs, and 2 TWTT, the near future scheduling 2 tests for setting the oil saturation (SWTT and TWTT).

The IWTT were performed on oil reservoirs where water injection is applied, the most frequently tracers used being the thiocyanate, methanol and nitrate [3,4]. These tests have:

1) *Identified the injected water channeling.* We take for example the test applied on Tazlau reservoir, situated in the Paleogene flish of the Oriental Carpathians. The oil accumulations are trapped in the Oligocene, the collector rock being mainly the Kliwa siliceous sandstone. The reservoir is water injected since 1953. The chemical tracer test was done through the injector I-1 Tazlau, Figure 5, the tracer (methanol) being soon identified in the producer P1-1 Tazlau, after 29 hours from its injection. The methanol concentration increased to very high values, of approx. 40,000 ppm measured after 245, respectively 461 hours from injection, Figure 6. The tracer was also identified in other 6 observation wells (P2-1, P6-1, P9-1, P10-1, P11-1, P12-1), but in much less significant concentrations than in well P1-1 Tazlau. The arrival of methanol in wells P2-1 and P11-1 is also represented in Figure 6. Also, the way the tracer arrives in well I-1 evidences the communication between the 4 blocks: A, B, C and D as being separated by non-sealing faults.

2) *Set the preferential flow paths of the injected fluid.* The Turnu Nord reservoir, situated in the northern sector of the Pannonian Depression, has oil accumulations in Pannonian, which mainly comprises sandstone, sand and marl limestone, with marl and shale intercalations. The structure was first produced in 1975, and in 1992 a water injection process was initiated aiming to increase the recovery. A chemical tracer (thiocyanate) test was performed in injector I, showing that the injected water flows mainly towards the southern part of the structure. For better evidencing this aspect, tracer concentration maps were drawn at different times after injection, by measuring concentration in the observation wells. The thiocyanate ion was identified in concentrations up to 70 ppm. Thus, Figure 7 presents the tracer arrival in the reaction wells, after approx. 72 hours from its injection.

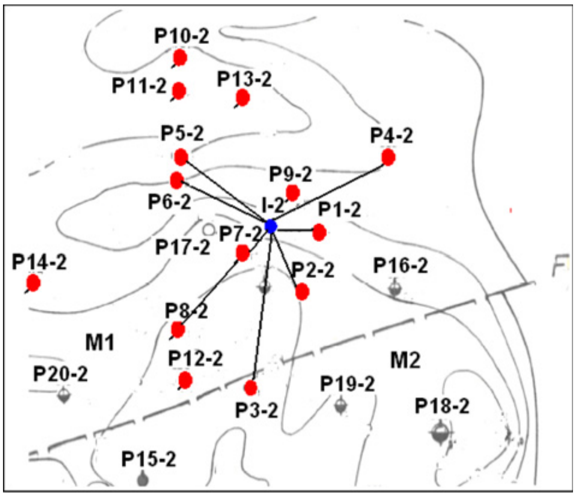

Figure 8. Moinesti reservoir area of applying the tracer test.

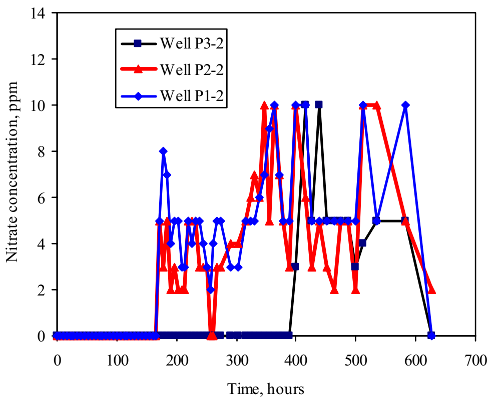

Figure 9. Tracer arrival in wells P1-2, P2-2 and P3-2 Moinesti.

3) *Checked faults sealing character.* The test performed in the injection well I-2 of Moinesti reservoir, also situated in the Paleogene flish of the Oriental Carpathians, showed the non-sealing character of the fault separating 2 blocks, Figure 8. The tracer, ammonium nitrate, was first identified after approx. 7 days from injection, in wells P1-2 and P2-2 Moinesti, situated 58 m respectively 103 m from the injector, in concentrations up to 10 ppm, Figure 9. Tracer was identified in wells P3-2, P4-2, P5-2 and P6-2, after 8, 11, 13 and respectively 17 days after the injection, in concentrations between 3 and 10 ppm. The tracer was identified in most of the observation wells, but the moments of its arrival and the concentrations differ from well to well, depending on the distance to the injector.

4) *Evaluated the efficiency of water shut-off treatments.* The applying of gelling systems is one of the methods used to reduce water in the production wells. This method works both for injectors and for producers, when the injected water channels towards one of the producers. The efficiency of such a treatment can be assessed by performing a tracer test before and after applying the water blocking treatment. The injector I3 Strambu was treated that way. Figure 10 shows the difference between the tracer (methanol) arrival in producer P3 before and after the treatment using a gelling system.

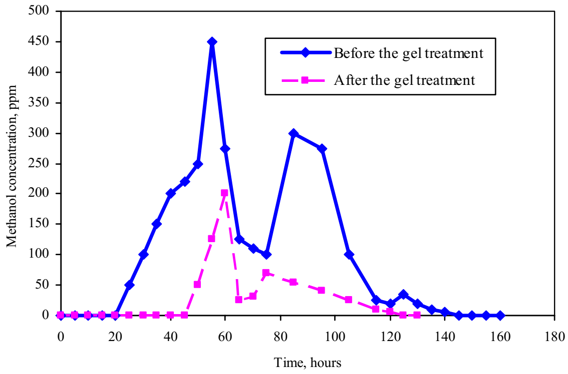

Figure 10. Difference between tracer arrivals in well P3 before and after applying the gelling system treatment.

After the treatment, the tracer arrived later and in a lower concentration, which indicates a decrease of the flow capacity towards the producer.

5. CONCLUSIONS

1. The tracer tests provide information on the injected fluids flow through reservoir related to different recovery processes, information also valuable for setting the oil residual saturation.
2. Tracers selection and setting the detection methods are done with the help of laboratory tests. Finding the most sensitive tracer detection methods is the only way of decreasing the tracer quantity used in a test, which results in cheaper and easier/safer to apply tests.
3. The displacement tests are performed in the laboratory on natural cores and by trying to restore the reservoir conditions (pressure, temperature, rock and fluids).
4. Up to the present day, Romania performed 50 IWTT with chemical tracers on 23 reservoirs and 2 TWTT. The most frequently used tracers were thiocyanate, methanol and nitrate. Those tests evidenced: preferential flow directions of the injected water and its channeling towards one of the producers, the non-sealing character of certain faults, as well as the efficiency of a water blocking treatment.

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