Mineralogical Investigations by X-rays Diffraction to Identify the Causes of Blocking Filters in the Injection Process of Connate Water for an Oil Field in Romania

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The paper presents the results of experimental research conducted in order to establish the causes that led to the blocking filters in the circuit of conditioning connate water, for injection into an oil reservoir. Water injection is one of the most widespread conventional methods in the exploitation of the hydrocarbon reservoirs and aims to increase the recovery factor. Water injected into the reservoir must have certain physical-chemical characteristics and to fulfill some quality requirements. We investigated a filter clogged with solids and hydrocarbons coming from a water injection plant which belong to the oil field X, located in Getic Depression (south-western Romania). The filter that is the subject of our research is a filter type glass wool with filtration degree of 20 microns. Were carried out X-ray diffraction analysis, which allowed establishing of mineralogical composition of the solid material causing the blocking filter. As a result has been proposed ways to combat the phenomenon of clogging of the filters and as consequence of blocking of them, and methods of cleaning of the filters.

Keywords: oil reservoir, water injection, blocking of filters, X-rays diffraction

Water injection is one of the most widespread conventional methods in the exploitation of the hydrocarbon reservoirs and aims to increase the recovery factor. Water injected into the reservoir must have certain physico-chemical characteristics and to fulfill some quality requirements. Among the physico-chemical characteristics of water injection we recall:

- content of mechanical suspension and oil;
- total content of salts dissolved;
- *p*H;
- content of gases dissolved;
- content of bacteria;
- temperature;
- viscosity;
- surface tension.

The qualities of water of injection are referring to:

- the degree of purity;
- the degree of aggressiveness;
- stability of the injection water in the reservoir conditions;
- the compatibility of injection water with the fluids in the reservoir rock pores and with the minerals of reservoir rock;
- the content of organic matter.

The water used in the process of injection oil reservoirs can come from:

- salt / fresh waters on the Earth's surface;
- shallow ground waters;
- connate waters from oil reservoirs.

Whatever the origin, it is necessary preconditioning of the injected water. As a result, it requires cleaning and treatment of water before being used in the injection process into reservoir. For this purpose, in oil production units there are treatment plants of injection waters. Conditioning circuit of injection water is performed as:

- open system (in contact with the atmosphere);
- closed system (most appropriate).

Most commonly is used as a fluid injection the connate water, i.e. the water extracted with oil or gas. The connate water includes gas, oil and solids. The solid materials in the suspension are represented by:

- particles of sand, clay, marl, as individual or in the form of slurry;
- various iron salts derived from water or corrosion of the tubular material (pipes, casing, etc.).

The conditioning circuit of connate water for injection back into oil reservoir comprises a series of steps. In parks of separators, tanks and decanters in the oil production unit, occurs the first separation of injection water. Here are separated gas, a part of the larger solids in the suspension and a large part of the oil.

The process is continued into treatment plants, where connate water is separated from the rest of the oil and solid suspensions by:

- decantation (gravitational);
- filtration.

For filtering are used several types of filters such as filters with glass wool or filters with sand. The last operation of cleaning connate water before the injection into the reservoir, occurs in the treatment plant (purge).

In figure 1 is shown a schematic drawing of a circuit of injection water treatment for an oil reservoir.

One of the major difficulties in this circuit is the frequent clogging and blocking of the filters.

In this paper are presented the results of the experimental research on the content of solid suspensions retained in the filter. Also we proposed ways to combat the phenomenon of clogging of the filters and as consequence of blocking of them, and methods of cleaning of the filters [1, 2].

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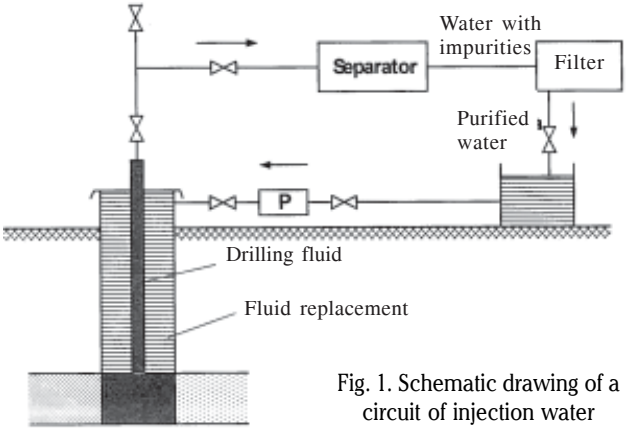

Fig. 1. Schematic drawing of a circuit of injection water treatment for an oil reservoir

Experimental part

We investigated a filter clogged with solids and hydrocarbons (oil) that coming from a water injection plant which belongs to the oil field X, located in Getic Depression (south-western Romania). Clogging (and blocking) frequently and repeated of the filters in the water injection plant was a problem, for which the company which owns the concession of this oil field, requested to the team of researchers from Petroleum-Gas University of Ploiesti studying of the causes that produce this phenomenon.

The filter investigated (fig. 2), is a filter type glass wool with filtration degree of 20 μm.

In the visual inspection the filter looks dirty, being clogged by oil and fine solid material. For discovering the causes that lead to clogging of the filter it was necessary to separate the materials retained into the filter.

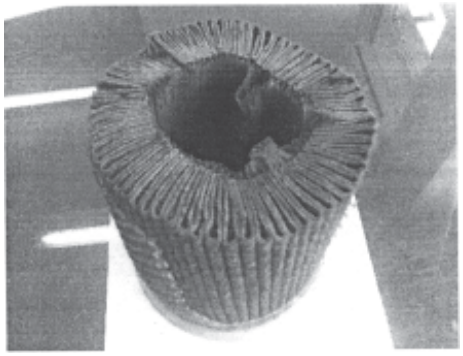

Fig. 2. The investigate filter

In order to separate the solid material from the texture filter we proceed to the washing of the filter for removing the hydrocarbons (using a Soxhlet device type) with a solvent mixture having the following concentration: 50 % toluene, 35% methyl ethyl ketone and 15% isopropyl alcohol.

As a result of washing process we obtained two phases: liquid (solvent plus hydrocarbons) and solid in suspension. After decanting/sedimentation of the solid material, liquid phase was removed and solid material was extracted to be investigated. The solid material resulted after the washing process of the filter was dried into oven and was obtained a quantity of 43.12 g. Visually, the solid material resulted in the washing process is a fine, silty-clay, brown-reddish material. Further, we proceed to sample preparation for analysis by X-ray diffraction.

In this regard the solid material was grinded in an agate mortar to the stage of powder.

Because it supposes the existence of clay minerals, the powder was treated with ethylene glycol in order to expand TOT packages of clay minerals. After a new drying in oven, we proceed to the X-ray diffraction analysis itself.

Measurement conditions: Bruker D8 Advance diffractometer (fig. 3), θ-θ type, Bragg-Brentano geometry, Cu Kα radiation (I=1.54A°, 40 kV; 40 mA°), step 0.1; scan speed 0.1°/5 s., measurement range (2θ) 2-60°. Kβ radiation was eliminated by a Ni filter. Primary and secondary Soller slits were 2.5°. A fixed aperture and divergence slit of 0.6 mm, a 0.6 mm antiscattering slit and 0.1 mm width detector slit were used. The powder was placed into a cavity mount in an attempt to minimize preferred orientation.

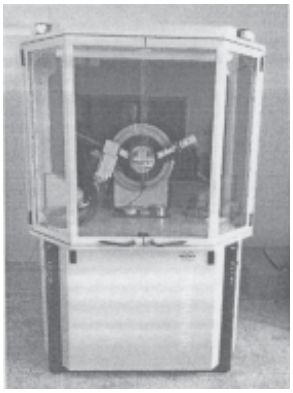

Fig. 3. Bruker D8 Advance diffractometer

Results and discussions

After placing the powder in the sample holder is started the diffractometer. The measurement is done by XRD Commander program. After sweeping the sample surface with a beam of X-rays is obtained a "scan".

A "scan" is the diffractogram, i.e. the measured data set, which is the result of intensity collection by the detector of diffractometer; it is stored in a file with the extension RAW.

The file with the extension .RAW is imported into EVA program and it works as a copy of the data, the original RAW file is never changed. After imported into EVA program, the file with the extension .RAW (i.e. the diffractogram) is subject to specific adjustment procedures such as: background subtraction, Fourier smoothing, removing Ka2 radiation, and is saved as a file with the extension .EVA [3].

A file with the extension .EVA contains a copy of the original data; this copy of data can be adjusted using Toolbox tab depending on the need of the analyst (background subtraction, smoothing, removing Ka2 radiation ...) but the original .RAW files themselves are not modified. The EVA file includes other objects like reference patterns or labels.

X-rays diffraction analysis is usually performed with Ka1/Ka2 radiations doublet. It is extremely useful to get a clean signal only Ka1 radiation in the "scan". Consequently, the EVA program is provided with the possibility of Ka2 radiation removal by stripping method [3].

Qualitative analysis = identification of crystalline phases (minerals) is performed using EVA software with Search/Match tab and PDF-ICDD 2-2008 database (PDF = powder diffraction file; ICDD = International Centre for Diffraction Data). The EVA software use a database that is compiled from the original PDF database called PDF-2. In Search/Match window is defined pattern type, quality marks of the patterns, inorganic/organic/dual character of the minerals, chemical filter (choosing the chemical elements most likely to be found in sample) and number of the patterns that will be listed after ending search.

A pattern is the list of the peaks which can be considered as the signature of a given crystalline phase; is a list of *d*-spacing and of the relative intensity *I* of the corresponding peak [3].

EVA can find a reference pattern by its name or number, or by a search/match process, which tries to identify an

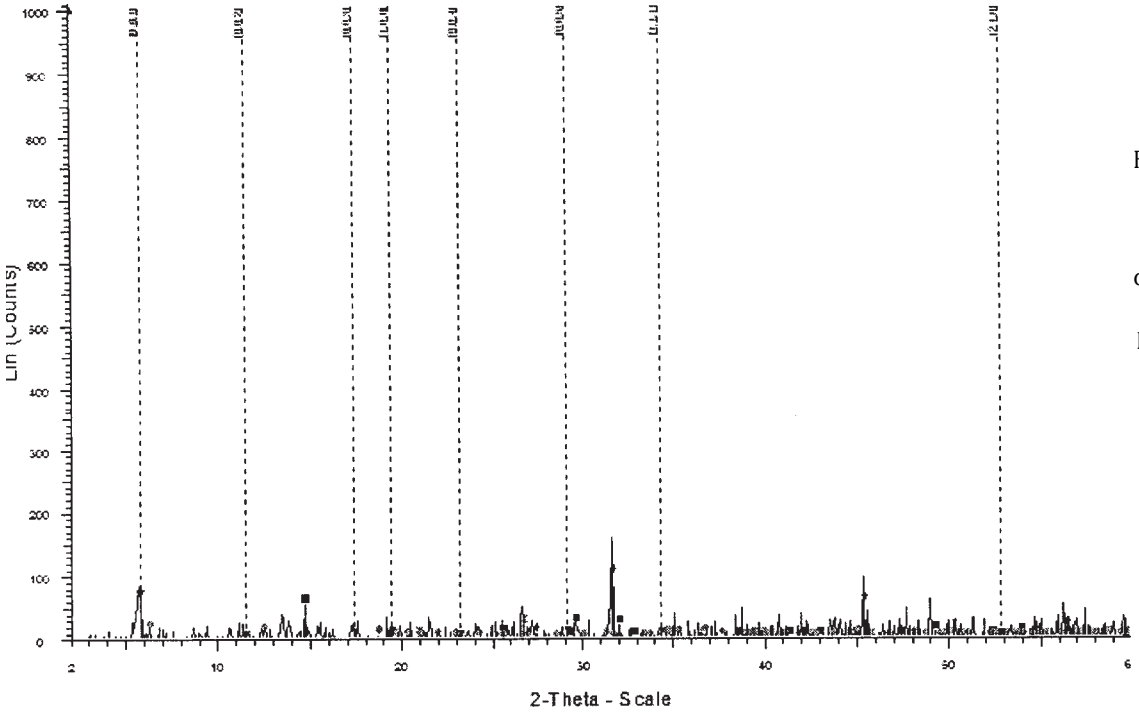

Fig. 4. XRD qualitative analysis of solid phases in the filter (peaks marked with dotted line belongs to saponite – predominant mineral in the sample)

unknown scan using a set of reference patterns. Searching, which is based on pattern recognition techniques, runs automatically in a few seconds and delivers a list of the best results. It is under the user's responsibility to check the patterns in the list, and to decide whether it matches to the scan or not. Matching is an interactive process: the analyst accept or reject each proposed reference pattern based on graphical compatibility between the unknown scan and the reference pattern, and based on compatibility with knowledge of the sample (origin, chemistry, preparation, etc.) [3].

Identification of crystalline phases (minerals) was made using "best quality marks": (* = high quality) and (I = indexed) respectively, after the background subtraction, Fourier smoothing and removing Kα2 radiation. In the footnotes are given sheet number, quality marks, chemical formula, crystal system, lattice parameters, space group, and measurement parameters (table 1).

Were identified the following minerals (fig 4): saponite-15A°, clinochlore (=chlorite), quartz, anhydrite and halite. Saponite (trioctahedral smectite), the prevalent mineral in the solid material obtained by washing the filter, was mentioned in the previous studies on the cores from oil field X [4].

Quantitative analysis was performed using TOPAS 4.1 software by Rietveld method [5]. The Rietveld refinement technique using X-ray powder diffraction data provides a valuable approach for studying structures of minerals that do not form crystals suitable for single-crystal experiments [6]. Basically, the Rietveld method uses analytical profile functions and least-squares algorithms to fit a theoretical to a measured pattern. Nowadays, the Rietveld method is not only used for structure analysis, but also for the quantification of multi-phase mixtures and the determination of the crystallite microstructure which covers size and strain. The method has been successfully used to refine structures for a variety of minerals and compounds [5, 6]. The quantitative analysis by Rietveld method is today commonly used in the industry, from manufacturing of cement to oil industry.

In order to establish the percentage of each component in the solids found in the filter has loaded the file with extension .raw in the Topas 4.1 program. Further, were setting manually or automated: emission profile, background (which uses Chebychev polynomials of superior order), characteristics of the device (primary and secondary goniometer radius, dimensions of the slits, the type of data convolution), were made corrections on the

Symbol	Pattern sheet	Quality marks	Chemical Formula	Intensity, Y	Lattice parameters	Space group
▣	01-083-0437	(*)	Anhydrite III, $Ca(SO_4)$	35.36%	a=12.07; b=6.97; c=6.30; α=90.00; β=90.00; γ=90.00; Z=6	C222 (21)
◈	01-070-2509	(I)	Halite, NaCl	64.74%	a=5.64; b=5.64; c=5.64; α=90.00; β=90.00; γ=90.00; Z=4	Fm-3m (225)
◉	01-083-1365	(*)	Clinochlore, Mg9.8Al1.6Fe0.6(Si6.32Al1.68O20.24)(OH)15.72	9.98%	a=5.32; b=9.23; c=14.39; α=90.00; β=97.16; γ=90.00; Z=1	C-1 (2)
▽	00-029-1491	(I)	Saponite-15Å, Ca0.2Mg3(Si,Al)4O10(OH)24H_2O	40.30%	a=5.28; b=5.28; c=15.35;α=90.00; β=90.00; γ=120.00; Z=1	P (0)
▨	01-070-3755	(*)	Quartz, SiO_2	14.85%	a=4.91; b=4.91; c=5.41; α=90.00; β=90.00; γ=120.00; Z=3	P3121 (152)

Table 1
CHARACTERISTICS OF MINERAL PHASES IDENTIFIED BY QUALITATIVE ANALYSIS OF THE SOLIDS IN THE FILTER

Sample	Saponite	Halite	Quartz	Anhydrite	Clinochlore (chlorite)
Solids in the filter	45.84	38.18	6.23	4.51	5.25

Table 2
MINERALOGICAL COMPOSITION (WT % RIETVELD) RESULTED IN QUANTITATIVE ANALYS

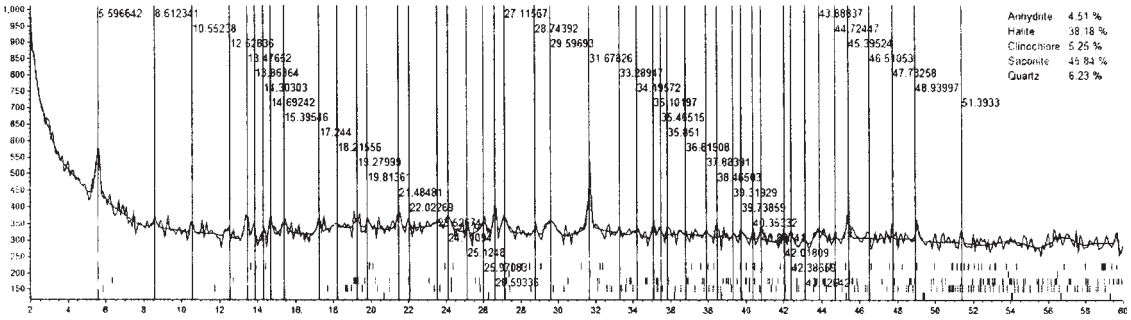

Fig. 5. XRD quantitative analysis of solid phases in the filter

X-ray absorption coefficient and the Lorentz polarization factor.

In the next step were defined mineral structures previously identified by program EVA, as files with extension STR and were loaded into the Topas 4.1 program. Were selected representative peaks (which selection can be done manually or automatically). For the fit of peaks was used pseudo-Voigt profile function.

After all procedures were fulfilled we run Topas 4.1 program in a few hundred iterations and we obtained mineralogical composition given in table 2.

Rietveld refinement quality (fig. 5) is expressed by R-values indices: Rwp, Rexp, GOF si DW [7, 8]. GOF (goodness-of-fit) is the ratio between Rwp (weighted profile R-factor) and Rexp (the best possible value of Rwp that can ever be obtained) and cannot be less than 1. A good Rietveld refinement gives GOF values lower than 1.5. DW indices represent the weighted form of Durbin-Watson "d" statistic. In X-rays diffraction the ideal value of DW indices is 2 [7, 8].

Quantitative analysis of sample analyzed has GOF indices of 1.06 which indicate the good quality of its. Good quality of the quantitative analysis is also revealed by the DW value of 2.11.

Conclusions

Following researches we could establish a procedure containing appropriate steps to establish the causes that led to the blocking of filters.

Clogging and rapid blocking of the filter (20μm) seems to be due to the formation of the clay-oil couple, the molecule with a diameter greater than the sieve mesh of the filter and thus led to flooring of the solid material carried in suspension by the injection water.

In order to avoid clogging and blocking filters can be either preventing the formation of clay-oil couple or reducing the surface tension of clay-oil couple, in both cases using surfactants; either by washing the filters with the solvent mixture (50 % toluene, 35 % methyl ethyl ketone and 15% isopropyl alcohol) used by us to separate the solid material from oil.

The proposed procedure may be applied to any filter (like the one investigated) used in a circuit for treating injection water which occurs similar damages.

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