On Some Chemico-Mineralogical Transformations in a Petroleum Reservoir Exploited by *In-situ* Combustion

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In-situ combustion is a thermal recovery technique in which a part of the heavy oil in place is burnt to generate heat. This heat brings about a reduction in viscosity of the crude oil to lead to the improvement of the mobility and hence oil production rate and recovery. Typical combustion front moves slow (some cm/day) through reservoir matrix (pores) by consuming the fuel as it moves ahead. The combustion zone is often a few centimeters in thickness and it has a temperature up to 700-800ºC. The hydrothermal conditions that occur in front of and behind the combustion zone may generate chemico-mineralogical transformations following or not from a new minerals forming. In the paper the authors emphasize for the first time calcium silicates hydrate forming in the matrix of siliciclastic rocks from oil reservoirs exploited by in-situ combustion.

Keywords: in-situ combustion, calcium silicates hydrate, X-rays diffraction, Suplacu de Barcau reservoir

Heavy oil deposits from Suplacu de Barcau (Romania) have geological resources estimated by the volumetric method of 46.90 million m3 (295 million barrels) of oil. [1]. This oil field has been exploited since 1961 and it is known as Pannonian – Suplacu de Barcau. Currently it represents the most important oil reservoir in the world that is being exploited by in-situ combustion. The productive formation (sands weak consolidated) lies at shallow depths varying between 70–100 m, reservoir temperatures being 17 °C at 80 m depth. Heavy oil deposits are of naphtenic-aromatic type (unwax-asphaltic-unsulphurous group) and oil viscosity in the reservoir conditions is very large (1800–2500 cP). At starting production of Suplacu de Barcau reservoir, the solution gas drive was the main production mechanism and an ultimate oil recovery of 9% was predicted. Initial oil rates were in the range of 2 to 5 m³/day/well but they decreased very quickly to 0.3 to 1 m³/day/well. Within Suplacu de Barcau reservoir two in-situ processes have been tested, meaning steam injection drive and dry in-situ combustion (initially in a panel-type system in five points with an area of 0.5 ha and with a central injection well, which was then expended with a panel of nine points on an area of 2 ha), with the purpose of an efficient selection of the exploitation method. The better performance of the in-situ combustion determined the design of the exploitation of the whole reservoir by means of this method. Thus was replaced the system of panel with a continuous combustion front that is going to sweep the reservoir step by step from the superior side to the inferior one, approximately parallel with the isobaths [1, 2].

Suplacu de Barcau structure is situated in the north of the Romanian part of Pannonian Basin, around the village that has the same name. It was formed by covering of the crystalline paleorelief by the Pliocene sedimentary covertures and it looks like a slightly-bowed monocline (fig. 1), that is East-West oriented, affected by a longitudinal axial fault. The wells that are drilled on the structure crossed reservoirs that belong to the crystalline basement, Sarmatian, Pannonian (Pliocene) and Quaternary [1, 2].
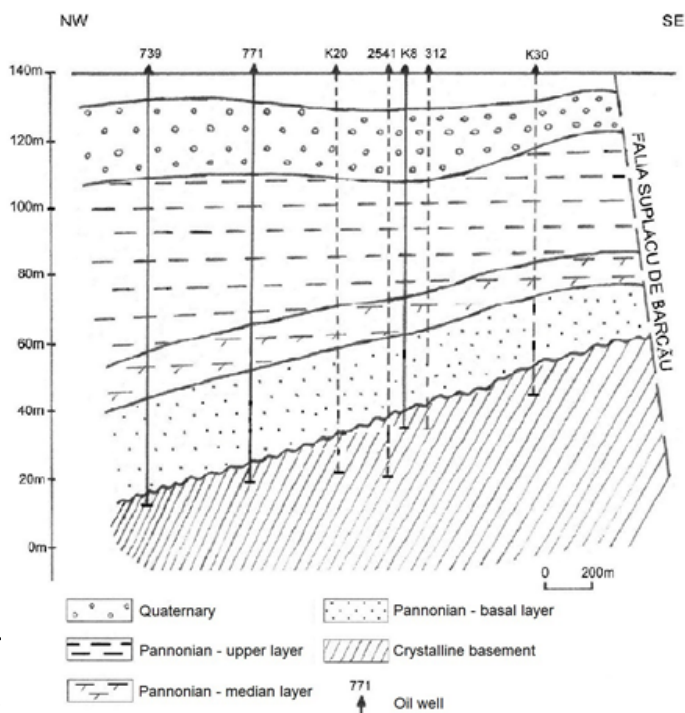

Fig. 1. Geological cross-section in Suplacu de Barcau structure [2]

Hydrocarbon accumulations that consist in heavy oil are deposited in Pannonian, which transgressively overlying the Sarmatian or the crystalline basement, and which has been divided in three complexes: basal (productive), median and superior. The basal complex, that represents the productive formation, is developed in a siliciclastic facies, ebbing made up of slightly consolidates sands, saturated with heavy and viscous oil. It has a total thickness that varies between 5–7 m in the East side and 25–30 m in the North-West side. The reservoir rocks present variation of facies both vertically and laterally [1, 2].

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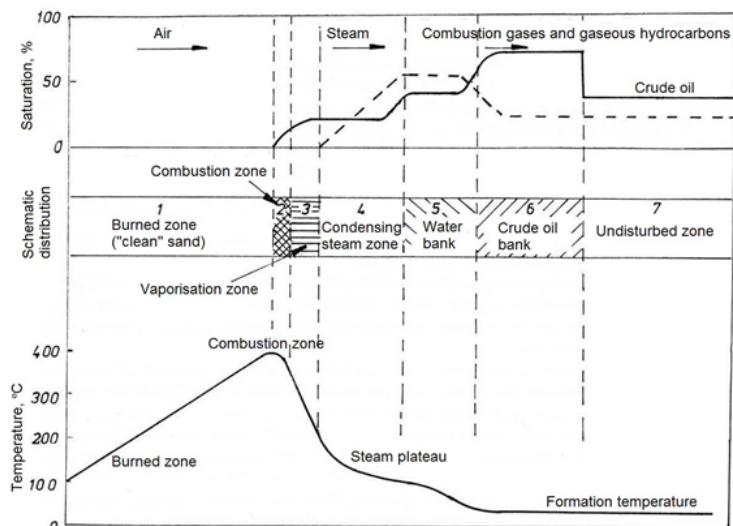* email: gbranoiu@yahoo.com; Phone: 0763662593

Fig. 2. Illustrating of Forward In-Situ Combustion process [6]

oil production rate and recovery. A typical combustion front moves slowly (some cm/day) through the reservoir matrix (pores) by consuming the fuel as it moves ahead. During the Forward In-Situ Combustion process (fig. 2), a point in the reservoir will experience the following conditions as the heated zone moves through [3- 6]:

The downstream hydrothermal zone: the reservoir is heated ahead of the combustion zone by the passage of hot gases and water vapors. The latter originates: (a) from the formation (connate water), (b) as the product of combustion, and (c) from injected water (wet forward combustion process only). As it cools down, the water vapors condense and a hydrothermal zone of approximately constant temperature occurs. Its temperature mainly depends on injection pressure and it is commonly of 200–300°C. Combustion gases moving through this zone contain high levels of carbon dioxide, but normally they do not contain oxygen. In the field situation, these conditions may exist for several weeks or, in some cases, several months.

The combustion zone: has often only a few centimeters in thickness, and the temperature reached in the combustion zone depends on many factors but, typically, it is in the range 400–800°C in both laboratory studies [3, 7, 8] and in field studies [9-11]. Normally, no liquid phase is present and the gases contain water vapors, carbon dioxide and oxygen.

The upstream zone: the temperature drops behind the combustion zone, mainly because of the transfer of heat forward by the injected fluids. In the wet combustion process, a hydrothermal zone is established similar to the one on the downstream side but of much shorter duration. No carbon dioxide is present in the gas stream with the exception of the case in which the complex flow pattern appears [4-6].

The hydrothermal-type conditions that are present in front and behind the combustion zone can produce mineralogical transformations that are accompanied or not by the formation of new minerals. In the paper are noticed for the first time forming of calcium silicates hydrate (C-S-H) in the matrix of arenitic reservoir rocks from oil fields exploited by in-situ combustion.

Experimental part

To evidence the mineralogical transformations and to estimate the temperatures which rocks had been exposed, were performed investigations on thin sections using the polarized optical microscope and X-rays diffraction studies on rock samples taken from the unaffected area (non-combustioned rocks) and from the affected area by the in-

situ combustion (combustioned rocks). Mineralogical studies consist of simultaneous observations upon twelve sample pairs taken from the productive formation or from subjacent crystalline basement, from closely to each other wells, situated in front of and behind the in-situ combustion front.

Observations on the polarizing optical microscope were performed with a Zeiss Amplival-type microscope (fig. 3) belonging to the Petroleum-Gas University Ploiesti.

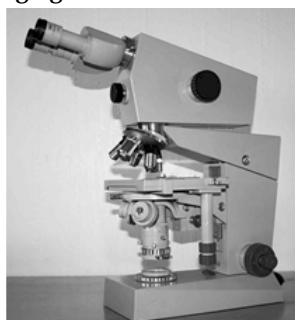
Fig. 3. Zeiss Amplival microscope

Fig.4. HZG 4 diffractometer

X-Rays diffraction analyses (powders method) were performed at Prospectiuni S.A. Bucharest, Geological Analyzes Laboratory Division, using an HZG 4/A-type diffractometer (fig. 4) with following parameters: CuKα radiation, Ni filter, $I = 1.54$Å, 25 kV/15 mA, scanspeed 1°/min, measurement range (2θ) 0-70°.

The standard method of analysis to determine the present minerals in the samples of unaffected and respectively affected rocks by the in-situ combustion and by the surveys of their transformations is X-ray diffraction (verified by optical microscopy and thermal analyses). From the cores of affected rocks by the in-situ combustion we made polished sections that were treated with chemical reactives (distilled water, alcoholic solution of 1% nitric acid, solution of oxalic acid in ethylic alcohol, acetic acid in alcohol) specific to the study in reflected light of the components of clinker of Portland cement (calcium silicates hydrate, dicalcium silicate, tricalcium silicate, tricalcium aluminate, etc.). The treatment of the

polished sections with the mentioned reactives reveal the presence of lime (CaO) in a color of greenish to red-pink, the presence of dicalcium silicate ($2CaO . SiO_2$ or C2S) in a brown color, and also the presence of tricalcium aluminate ($3CaO. Al_2O_3$ or C3A) in the reddish-brown color when treated with oxalic acid, and less of the tricalcium silicate ($3CaO . SiO_2$ or C3S) in the color blue or red-brown.

Results and discussions

The hydrothermal-type conditions that are present in front and behind the combustion zone can produce mineralogical transformations that are accompanied or not by the formation of new minerals [12]. Even *passive* minerals such as quartz and feldspar may become reactive under hydrothermal treatment.

Underlining the mineralogical transformations and the formation of new minerals that appear as a result of the exploitation process by in-situ combustion of petroleum reservoirs cannot be achieved but by specific mineralogical-petrographic studies (optical microscopy and X-rays diffraction) that should be reported to the same reference system. These studies must be achieved on the same types of rocks that are prelevated from wells that are drilled before and after the initiation of, ideally speaking, the secondary and tertiary exploitations or on cores of rocks from the same layer from wells that are close by but situated in the affected or unaffected area through the initiation of the secondary or tertiary exploitation processes. By means of comparing the information obtained from these studies

Sample code	Sampling point	Rock diagnosis
1A	312 well	Lithic Graywacke
2A	771 well	Quartzitic sand
3A	312 well	Subgraywacke
4A	97 well	Quartzitic-micaceous schist
5A	2541 well	Quartzitic-micaceous schist
6A	771 well	Quartzitic sandstone with calcareous cement
7A	771 well	Quartzitic sandstone with calcareous cement
8A	771 well	Lithic Subgraywacke
9A	262 well	Lithic Graywacke
10A	262 well	Graywacke
11A	473 well	Micaceous sand
12A	482 well	Micaceous sand

Table 1
DIAGNOSIS OF THE ROCKS FROM NON-COMBUSTIONED AREA OBTAINED FROM OPTICAL MICROSCOPY STUDY OF THIN SECTIONS [2]

Sample code	Sampling point	Rock diagnosis
1B	K30 well	Lithic Graywacke
2B	K20 well	Quartz sand poorly compacted
3B	K30 well	Lithic Subgraywacke
4B	K20 well	Quartzitic-micaceous-chloritic schist
5B	K20 well	Quartzitic-micaceous-chloritic schist
6B	K8 well	Lithic sandstone with carbonate cement
7B	K30 well	Lithic Graywacke
8B	K40 well	Lithic Subgraywacke
9B	K30 well	Lithic Graywacke
10B	K8 well	Lithic Graywacke
11B	K40 well	Lithic sand
12B	K30 well	Quartz-lithic sand

Table 2
DIAGNOSIS OF THE ROCKS FROM COMBUSTIONED AREA OBTAINED FROM OPTICAL MICROSCOPY STUDY OF THIN SECTIONS [2]

Mineral	Approximate percentage (by weight of mineral fraction)	Transformation	Transformation temperature (°C)
Quartz	30–65	–	–
Plagioclase feldspar	1–15	–	–
Orthoclase feldspar	1–15	–	–
Calcite	5–25	Dissociation (reversible in CO_2)	> 550
Dolomite	1–5	Decomposition	550–600
Siderite	1–10	Decomposition	400–600
Micas	5–25	–	-
Kaolinite	1–10	Dehydroxylation	525–550
Illite	1–5	Dehydroxylation	500–600
Smectite	1–10	Irreversible collapse of crystal lattice	300–700
		Decomposition	> 700
Chlorite	1–15	Brucite-layer dehydroxylation	250–600
		Decomposition	600–700
Chlorite/smectite or illite/smectite interstratifications	0–10	Chloritisation	200–350
		Illitisation	200–350

we may underline the transformations of the minerals in the reservoir rocks or the formation of new minerals.

The diagnosis of rocks from Suplacu de Barcau oil field obtained from optical microscopy study of thin sections is presented in tables 1 and 2. Except the samples from crystalline basement (4A, 4B, 5A, 5B) it is noticed the prevalence of the siliciclastic rocks with carbonate cement.

In order to determine mineralogical composition, rock samples collected from non-combustioned and combustioned areas were investigated by X-rays diffraction. Interpreting of the measurements of X-rays diffraction was made in relation with observations performed on polarizing optical microscope. On the basis of diffraction peaks (fig. 5) characteristic for each mineral was estimate the frequency of main minerals that composed the samples investigated and was established the percentage of them. As shown in table 3, the minerals identified in the sample are quartz, feldspars, carbonates (calcite, dolomite, siderite) and phyllosilicates (micas, kaolinite, illite, chlorite, chlorite/smectite and illite/smectite interstratifications). On the diffractograms of the combustioned samples were identified new minerals namely calcium silicates hydrate (tobermorite and dicalcium silicate) on which we will discuss further.

The diffractogram of core 2A (fig.5) indicates the presence of kaolinite through a peak of low intensity of basal reflection (001) from 7,1Å, followed by reflections of a lower intensity (020), (131), (131) and (204). The intensity increase of the basal reflection peak (001) from 7.1Å as well as of the other reflections (020), (110), (002), (130), (131), that can be noticed on the diffractogram of core 2B (affected by combustion) indicates an increase of the kaolinite crystallinity as a result of the exposure to high temperatures (over 300ºC). Yet the temperature conditions do not exceed the moment in which dehydroxylation (525ºC). Over 525ºC, the kaolinite also dehydroxylates and the height of the peak considerably decreases [12, 13].

The tobermorite is present on the diffractogram of core 2B through the modifications of 12.5Å and respectively of 10Å. The modification of 12.5Å presents the basal reflection (002), followed by reflections of a lower intensity (202),

(206), (204). The tobermorite of 10Å has a basal reflection (002), followed by reflections of a lower intensity (040), (220), (620), (400).

On the diffractogram of core 7B one can notice reflections that may be attributed to the tobermorite of 14Å and respectively of 10Å. The tobermorite of 14Å presents a basal reflection (002) of an intensity that is comparable to the one of the tobermorite of 10Å, yet the fact that the reflections are more numerous and of a lower intensity (220), (400), (208), (040), (620) of the tobermorite of 10Å suggests the formation of a bigger quantity of this product.

On the diffractogram of core 8A (unaffected by combustion) we have identified the chlorite through the basal reflection (001) of high intensity and through the reflections of lower intensity (002), (003), (004), (005) and (006). On the diffractogram of core 8B (affected by combustion) we have noticed that the reflections that are characteristic to chlorite do not appear anymore, which suggests the transformation of the chlorite through the dehydroxylation of the brucitic layer as a result of the exposure of rocks to temperatures higher than 250–300ºC. The tobermorite of 14Å presents the characteristic basal reflection (002), followed by reflections of a lower intensity (201), (006), (207), (220), (222), (400), (012).

The diffractogram of core 9A indicates the presence of chlorite on the characteristic peak (001) from 14.2Å that is followed by the other reflections of a lower intensity (002), (003), (004), (005). On the diffractogram of core 9B, the peaks which are lower in intensity of reflections (001) and then (002) and (003) suggest that the dehydroxylation of the brucitic layer took place and it indicates temperatures over 250-300ºC. On the diffractogram of core 9B the basal reflection (002) appears; it is characteristic to the tobermorite of 14Å followed by the more blurred reflections (201) and (222) from 5.53Å and respectively 2.98Å.

On the diffractogram of core 10B we can notice the basal reflection (002) of the tobermorite of 12.5Å, followed by reflections of a lower intensity (220), (400), (040) and (620). We can also notice the presence of the tobermorite
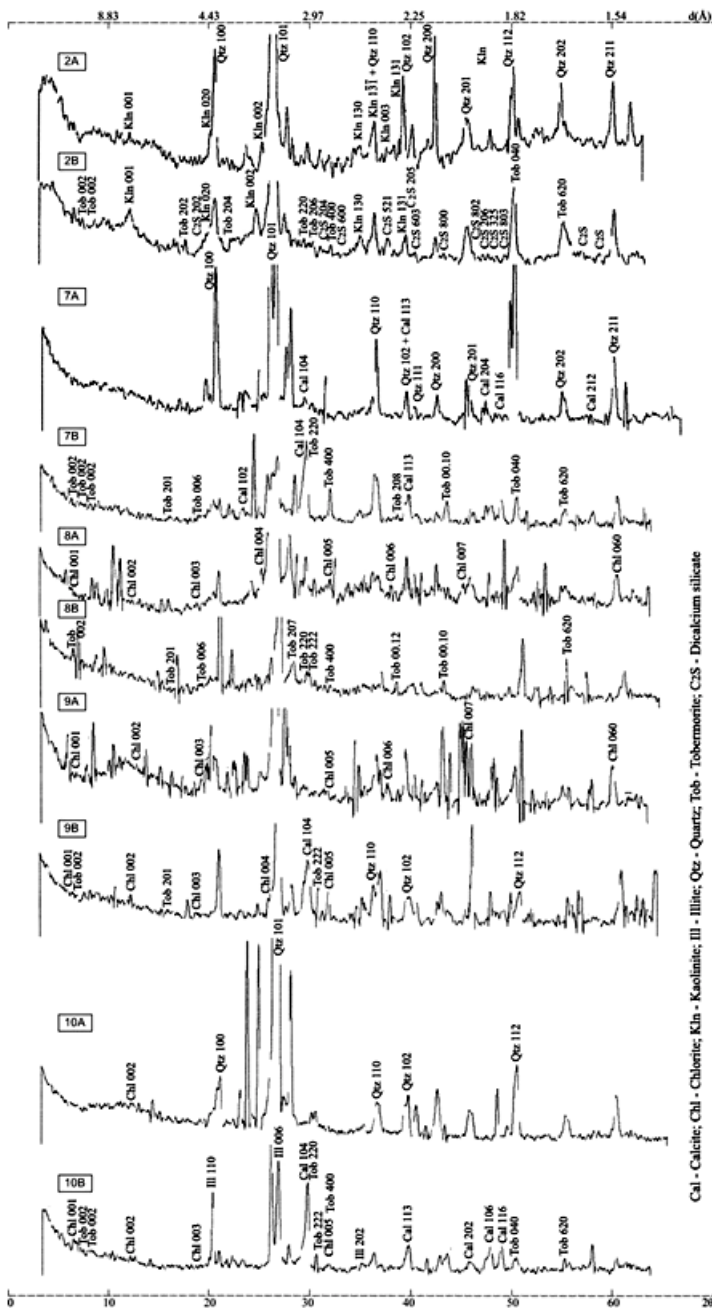
Fig. 5. Diffractograms of the non-combustioned and combustioned rock samples [2]

of 11,5Å through the characteristic peaks of (002), (220), (222), (400), (040).

Calcium silicates hydrate (C-S-H) occurs in both natural environments and hydrated products of Portland cement. Natural deposits are rare, and their occurrence in cements is by far the most important. Calcium silicates hydrate represents a large family of minerals very interesting for the variety of their structural arrangement, among these standing out the tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O$, dicalcium silicate ($Ca_2SiO_4$) and tricalcium silicate (Ca_3SiO_5) respectively.

In the conditions applying to oil fields operated by thermal methods, particularly in-situ combustion, conditions analogous to the hydrothermal ones and reservoir rocks can be sources of lime (CaO) and silica (SiO_2) it is expected to take place the chemical reactions of type 1 and 2:

$$2CaCO_3 + SiO_2 \rightarrow Ca_2SiO_4 + CO_2 \qquad (1)$$
$$Ca_2SiO_4 + H_2O \rightarrow 5CaO \cdot 6SiO_2 \cdot 5H2O \qquad (2)$$
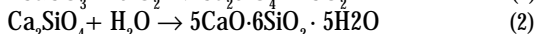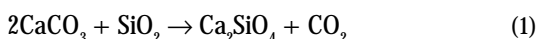
The tobermorite forming it is facilitated by the pH conditions in which the process takes place, the equilibrium pH of the calcium silicates hydrate (C-S-H) hydration being basic. Generally, hydrothermal conditions facilitate direct reactions between calcium silicates hydrate and water, without their decomposition.

Conclusions

The researches carried out are expensive and require specialized and authorized equipments. The collecting and selecting of the rock samples, sample preparation for investigation by X-rays diffraction, processing and interpretation of the X-rays diffraction measurements can be performed only by qualified personnel.

The rocks of Suplacu de Barcau oil field (Romania) which is exploited by in-situ combustion are exposed to variable temperatures, between 200–500°C, which is proved by the mineralogical transformations that were noticed as a result of a comparative study of the cores through X-ray diffraction and optical microscopy.

X-rays diffraction analysis and investigations by optical microscopy shows decreasing of clay minerals content in the combustioned samples from K30, K20, K40 and K8 wells, and suggest that chemico-mineralogical transformations are accompanied by granulometrical changes,

which have influence further on the porosity and permeability of the reservoir rocks.

The hydrothermal-type conditions that are found in the oil reservoirs exploited by in-situ combustion, conditions which involving the increase of the reaction rates, the existence of sources of primary material and the conditions of forming calcium silicates hydrated that are similar to the conditions from Portland-type cements, create the premises of the formation of calcium silicates hydrated tobermoritic-type.

In the same time, the circulation of hot fluids through the rock pores as a result of air or/and water injection facilitates the dissolution and the transport in solution of the material that was primary to the formation of calcium silicates hydrated and further on of the tobermoritic minerals.

Forming of new mineralogical compounds (especially in the rock cement) may have implications on the physical parameters of the rocks modifying the porosity and the permeability, this having important consequence on the exploitation of the oil reservoir.

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