# On the Estimation Possibilities of the Temperature Reached in Reservoirs Exploited by In-Situ Combustion Based on the Mineralogical Transformation

### Gheorghe Brănoiu, Octavian Georgescu

Universitatea Petrol-Gaze din Ploiești, B-dul București 39, Ploiești, Romania e-mail: gbranoiu@yahoo.com

### Abstract

The maximum temperature reached in reservoirs exploitation by thermal methods, especially the in-situ combustion method, is an important parameter when evaluating the results of field or laboratory studies of oil production. Mineralogical transformations often occur in reservoir rocks on heating, and these may serve as indicators of combustion zones temperature. The usefulness of the method of estimating reached temperature in reservoirs exploitation by in-situ combustion depends on the mineralogical composition of the deposit, as minerals that undergo suitable transformations in the required temperature range must be present. The paper makes an attempt at identifying the transformations likely to serve as useful temperature indicators of in-situ combustion; the precision of the method is necessary to be tested in laboratory experiments.

Key words: mineralogical transformations, in-situ combustion, combustion zone temperature.

### Introduction

In-situ exploitation thermal processes rely on some means of heating the oil to cause the reduction in viscosity necessary for it to be displaced. Thus, an important parameter at evaluating the performance of laboratory or field tests is the maximum temperature experienced throughout the test area. In laboratory tests, this temperature can often be determined satisfactorily by installing thermocouples, although uncertainty may exist in regions of hightemperature gradients, or when data points are widely spaced. In the field, additional techniques are desirable because the optimum location of observation wells is often difficult to foresee. Cores frequently are taken after field tests to determine residual oil saturations and to estimate sweep efficiencies. During the field testing of an in-situ combustion process at the Sloss Field in Nebraska (USA), the determination of mineral changes that had taken place in core specimens was used to estimate the maximum temperature experienced [11]. The methods have also been used in a more limited manner in other field trials in the United States [13,15]. In none of these instances, however, has the reliability of the transformations under in-situ combustion conditions been checked. The feasibility of using the method of estimating the reached temperature during in-situ combustion process in the field tests involving the Alberta oil sand (Canada) was investigated by firetube experiments [25]. A good agreement between observed and estimated temperatures was noticed.

In order to obtain information on temperature from combustion zones there were made experiments based on heating in certain conditions of some cores from the reservoir and then they were investigated with instrumental methods of physical-chemical analysis for identifying modifications which might appear [6,26]. These attempts are useful at determining the temperatures from combustion zones, on interpreting mineralogical modification, being necessary to consider many factors that influence minerals behavior at thermal treatment [18,24,29]. Using some information concerning the behavior of clay-minerals under the influence of thermal processes in laboratory conditions requires a certain judgement imposed both by the conditions in which this process developed and by its duration.

### **Argumentation of the Possibilities of Identifying and Using Mineralogical Transformations**

Mineralogical transformations often occur in reservoir rocks on heating, and these may serve as indicators of combustion zone temperature. Previous experiments carried out both in laboratory and in the field reveal that a number of common minerals which occur in rocks of reservoirs exploitation by thermal methods may be potentially constrained to useful transformations. These minerals experimentally investigated include: smectite, kaolinite, chlorite, illite, mixed-layers I/S or C/S, calcite, dolomite and siderite, and their transformations occur at temperatures estimated over the range 200-700°C. The concordance between the observed and the estimated temperatures was generally good, provided that certain interfering factors were taken into account. These factors contain the production of acids during in-situ combustion, the effects of combustion-gas concentrations on some of the transformation temperatures, and the reaction of certain minerals under hydrothermal conditions.

Mixed-layer clay structures have proved useful mineral geothermometers in the study of many geothermal systems around the world [20-30]. The proportion of illite layers in mixed-layer illite/smectite (I/S) and the ordering of I/S are effective geothermometers [19-22]. Steiner [28] at Wairakei (New Zealand) was the first to point out the progressive transformation of dioctahedral smectite to illite in geothermal systems. He included clay minerals within host mineral alteration studies, and reported a predominance of smectite-like spacings at between 11 and 14Å at shallow depths and the dominance of the 10 to 11Å above 150°C. Steiner focused not only on the clays but his studies also included recognizing many zeolites as useful mineral geothermometers (including wairakite).

The studies concerning the dehydration transformation of Ca-montmorillonite within the temperature range 30-500°C revealed that samples underwent transformations from hydrated phase to dehydrated phase at 200°C, and as a consequence, their basal spacing collapsed from 16.02Å (30°C) to around 10Å (200°C) [1] (figure 1). This transformation occurs within a wide range of temperature (120-200°C). The crystallite size decreases along with increasing temperature in the hydrated phase, whereas size increased with increasing temperature for the dehydrated phase (figure 2). The interlayer spacing and the proportion of the planes which were affected in hydrated and dehydrated phases increase and respectively decrease along with increasing the temperature.

The thermal dehydration of Ca-montmorillonite has also been studied by in-situ X-ray diffraction at temperatures between the range 60-120°C [6]. The time-temperature dependence of the position of the basal (001) reflection reveals that interlayer water loss on isothermal dehydration occurs in two stages: after an initial rapid decrease in interlayer spacing (on shock heating to an isothermal soak temperature) the reaction proceeds towards equilibrium more slowly. The water driven off at more advanced stages of dehydration is more firmly held, being believed to be involved in water-cation interactions. The end of dehydration is marked by a breakdown of the interlayer after reaching a *d*-spacing of 10.3Å. After dehydration, migration of

the exchangeable cations begins, and they become associated with the outer tetrahedral sheet (in the case of  $Ca^{2+}$ ) or enter vacant octahedral sites (in the case of  $Mg^{2+}$ ) [6].

During the forward combustion process, a point in the reservoir will be exposed to the following conditions as the heated zone moves through [3,10,12,27]: (1) Downstream hydrothermal zone: the reservoir is heated ahead of the combustion zone by the passage of hot gases, particularly water vapour. The latter originates: (a) from the formation (connate water); (b) as a product of combustion; and (c) from injected water (wet process only). As it cools, the water vapours condense and a hydrothermal zone of approximately constant temperature occurs. Its temperature depends mainly on injection pressure and is commonly in the region of 200-300°C. Combustion gases moving through this zone contain high level of carbon dioxide but normally no oxygen. In the field situation, these conditions may exist for several weeks or, in some cases, several months, but in laboratory experiments they often last only a few hours. (2) Combustion zone: the temperature reached in the combustion zone depends on many factors but, typically, it is within the range 400-800°C in both laboratory studies and in field studies. Normally, no liquid phase is present and the gases contain water vapours, carbon dioxide and oxygen. In laboratory experiments, maximum temperatures are maintained for one to two hours, but in the field they may last for several weeks. (3) Upstream zone: the temperature drops behind the combustion zone, mainly because of heat transfer forwarded by the injected fluids. In the wet combustion process, a hydrothermal zone is established similarly to the one on the downstream side but of much shorter duration. No carbon dioxide is present in the gas stream unless complex flow patterns occur.



**Fig. 1**. Variation of interplanar spacing (*d*) for Ca-montmorillonite as function of temperature [1].



**Fig. 2.** Plot of the crystallite size obtained by the Fourier method versus the temperature at which Ca-montmorillonite samples were heated [1].

Normally, no aqueous phase is present in the combustion zone, and peak temperatures are attained for relatively short periods. Consequently, reactions between minerals are unlikely to be significant unless peak temperatures are unusually high. Hence, there may be used only transformations that the minerals undergo on heating up to a maximum temperature of 1000°C.

Usually, the mineralogical composition of rocks varies considerably; the main minerals and their overall modes of occurrence are listed in table 1. Only the minerals detectable by the X-ray diffraction method are included, being necessary to be verified by other methods of mineralogical investigations: optical microscopy, thermal analyses, electronic microscopy etc. The approximate transformation temperatures included in table 1 were obtained from specialty literature. They have guiding purpose, because they depend on many factors and preliminary heating tests are needed to determine suitable values for each sample rock. In table 1 there are also comments regarding the prediction of the transformations as temperature indicators.

Mineral	Occurrence	Transformation	Temperature range (°C)	Comment on transformation	Prediction of estimation
Quartz	common major	(1) $\alpha$ - $\beta$ quartz	573	reversible	unsuitable
	component	(2) to tridymite	870	very slowly	unsuitable
Orthoclase feldspar	common minor component	order-disorder	500-700	slowly	unsuitable
Plagioclase feldspar	sporadically component in variable amounts	order-disorder	850-1100	slowly	unsuitable
Calcite	sporadically component in variable amounts	dissociation	> 550	reversible in CO <sub>2</sub> depends on p <sub>CO2</sub> decomposed by acid	limited
Dolomite	sporadically component in variable amounts	(1) decomposition + dissociation of MgCO <sub>3</sub>	550-800	decomposed by acid	suitable
		(2) dissociation of CaCO <sub>3</sub>	500-850	reversible in CO <sub>2</sub> depends on p <sub>CO2</sub> decomposed by acid	limited
Siderite	sporadically component in variable amounts	decomposition	400-550	decomposed by acid may depends on po2	suitable
Pyrite	sporadically component in variable amounts	decomposition	350-450	may depends on po2	suitable
Chloritoide	common component in trace amounts	decomposition	550	decomposed by acid	suitable
Muscovite	common minor component	(1) dehydroxylation	700-900	heavy detectable by X-ray diffraction (XRD)	unsuitable
		(2) decomposition	900-1000		suitable
Biotite	sporadically component in variable amounts	(1) dehydroxylation	900-1000	heavy detectable by XRD	unsuitable
		(2) decomposition	> 1000	decomposed by acid	suitable
Kaolinite	common minor component	(1) dehydroxylation	500-600	depends on p <sub>H2O</sub>	suitable
		(2) decomposition	900-1000		unsuitable
Illite	common minor component	(1) dehydroxylation	500-600	heavy detectable by XRD	limited
		(2) decomposition	750-950		suitable
Chlorite	sporadically component in variable amounts	(1) brucite dehydroxylation	250-600		suitable
		(2) dehydroxylation and decomposition	450-800	decomposed by acid	suitable
Smectite	sporadically component in variable amounts	(1) irreversible collapse	300-700		suitable
		(2) dehydroxylation	500-750	heavy detectable by XRD	limited
		(3) decomposition	650-950	some species decomposed by acid	suitable

**Table 1**. Occurrence and individual transformations of minerals from the reservoirs exploited by thermal methods (according to [26], modified).

Mineral	Occurrence	Transformation	Temperature range (°C)	Comment on transformation	Prediction of estimation
Degraded illite	sporadically component in variable amounts	irreversible collapse	250-300		suitable
Halloysite	sporadically component in variable amounts	(1) dehydration	150		suitable
		(2) dehydroxylation	450-520		suitable
Mixed- layers illite- smectite (I/S)	sporadically component in variable amounts	(1) to illite	200-350	heavy detectable by XRD	limited
Mixed- layers chlorite- smectite (C/S)	sporadically component in variable amounts	(1) to chlorite	200-350	heavy detectable by XRD	limited
Aragonite	sporadically component in variable amounts	(1) to calcite	400-500	irreversible decomposed by acid	suitable
Ankerite	sporadically component in variable amounts	(1) decomposition + dissociation of FeCO <sub>3</sub>	750	decomposed by acid	suitable
		(2) dissociation of CaCO <sub>3</sub>	930-950	reversible in CO <sub>2</sub> depends on p <sub>CO2</sub> decomposed by acid	limited
Glauconite	sporadically	(1) dehydration	100-200		suitable
	component in variable amounts	(2) dehydroxylation	550-625		suitable

The temperature at which the dissociation of calcite takes place considerably varies with carbon dioxide pressure and may be increased by several hundred degrees centigrade under in-situ combustion conditions. Consequently, the transformation is of limited value, as the carbon dioxide pressure varies in a complex manner in the combustion zone and only approximate values can be estimated. Also, the calcite reforms readily in the presence of carbon dioxide, although the gas has not been reported behind the combustion zone in laboratory studies [10]. The exact temperature at which dissociation of calcite occurred would depend on the carbon dioxide pressure in the combustion zone, and additional heating tests under analogous conditions with reservoir conditions are necessary in order to determine if the transformation may be used for estimation with precision of the temperature. When dolomite is heated, it first decomposes into its component carbonates (calcite and magnesite). The temperature at which this occurs is not significantly affected by carbon dioxide pressure [24] and the transformation is irreversible. At higher carbon dioxide pressures, which are likely during in-situ combustion, calcite rather than calcium oxide would be formed and the former mineral would dissociate at higher temperatures. In experiments using the firetube, decomposition of the siderite was reported to occur at 195°C [4]. This value is considerably lower than the value given in table 1, and it is possible to occur either acid decomposition or oxidation at relatively low temperatures.

Another factor that influences the usefulness of carbonate transformation and of other acidsoluble minerals is the production of dilute acids during in-situ combustion. When analyzed rocks contain a sufficient quantity of carbonatic minerals for neutralizing the acids produced, the decomposition transformations of acid-sensitive minerals may be certainly used. Uncertainty arises, however, with regard only to decomposition of the minerals and not to the transformation of one species or another. Many of the clay-mineral transformations given in table 1 involve loss of water, and the temperature at which they occur are likely to be influenced to some degree by the partial pressure of water vapour in the gas stream. Data are available concerning the dexydroxylation of kaolinite [30], and under in-situ combustion conditions, the variation in dehydroxylation temperature is expected to be small. When water is injected, hydrothermal conditions exist for a relatively short period behind the combustion zone, and it is possible that some of the transformations could be reversed. In the case of kaolinite, tests conducted by [26] indicate that only a limited amount of rehydration takes place and, in fact, kaolinite may not be the equilibrium product [5]. Similarly, unusually high temperatures may be required to collapse smectite irreversibly, because of the severe rehydration conditions behind the combustion zone and the dependence of the transformation temperature on rehydration conditions [18,26]. Hydrothermal reactions are likely to be more problematic in field tests than in short-term laboratory experiments [26].

When rock samples are treated hydrothermally under neutral or basic conditions, kaolinite, quartz and dolomite can react to form smectite and analcime [5]. Similar reactions have been observed in field tests involving steam injection. A number of reactions are possible under such conditions, and calcite and illite may also participate [2]. Hence decomposition of certain minerals could occur ahead of the combustion zone and, in the case of wet forward combustion, synthesis of others could occur behind the combustion zone. The pH and the composition of fluid phase may be important factors, and such reactions are likely to be more significant in field trials where the hydrothermal zones are of much longer duration.

The temperatures at which many of the transformations listed in table 1 take place vary, depending on the heating conditions and such mineral properties as composition, particle size and crystallinity. Therefore, for each rock sample it is necessary to determine with precision the transformation temperatures in preliminary heating tests carried out under appropriate conditions. The standard method of analysis used for determining of minerals present in rock samples unaffected and affected by combustion and for tracking their transformations is X-ray diffraction verified by optical microscopy and thermal analysis.

#### Conclusions

The usefulness of the method of estimating reached temperature in reservoirs exploitation by insitu combustion on the based of mineralogical transformations depends on the mineralogical composition of the deposit, as minerals that undergo suitable transformations in the required temperature range must be present. It is necessary to identify the transformations likely to serve as useful temperature indicators of in-situ combustion and testing the precision of the method in laboratory experiments.

Using mineralogical transformations allows temperatures to be estimated over the range 200-700°C with a precision of about  $\pm$  50°C. In the laboratory experiments there has been observed a good concordance between measured and estimated temperatures, and it appears that few of the factors identified earlier had seriously influenced the reliability of mineralogical transformations from rocks of the reservoirs exploited by in-situ combustion. Possible complicating factors could be: (a) the production of acids during in-situ combustion; (b) the influence of  $p_{CO2}$ ,  $p_{H2O}$  and  $p_{O2}$  on transformation temperatures; (c) the reversal of transformations involving loss of water; (d) hydrothermal reaction in front of and behind the combustion zone.

The hydrothermal-type conditions that are found in the reservoirs exploited by this method, conditions which presuppose the increase of the reaction rates and the existence of sources of primary material create the premises of the formation of the neoformation minerals. At 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 prior to the formation of the new minerals.

#### References

- 1. Bala, P., Samantaray, B.K., Srivastava, S.K., Dehydratation transformation in Camontmorillonite, Bulletin of Material Science, v. 23, no. 1 (Feb. 2000), p. 61-67, 2000
- 2. Bayliss, P., Levinson, A.A., Low temperature hydrothermal synthesis from dolomite or calcite, quartz and kaolinite, Clay and Clay Minerals, v. 9, p. 109-114, 1971
- Bennion, D.W., Donnelly, J.K., Moore, R.G., A laboratory investigation of wet combustion in the Athabasca oil sands. In: CIM Special Volume 17, The Oil Sands of Canada-Venezuela, Canadian Institute of Mining and Metallurgy, p. 334–342, 1978
- Bennion, D.W., Donnelly, J.K., Moore, R.G., *Effect of fireflooding temperature on mineral composition and bitumen properties*. In: CIM Special Volume 17, The Oil Sands of Canada-Venezuela, Canadian Institute of Mining and Metallurgy, p. 139–143, 1978
- Boon, J.A., An experimental-statistical study of mineral transformations during in-situ recovery of bitumen from various oil sand deposits in Alberta, Canada, 3rd International Symposium, Water-Rock Interaction, Edmonton, p. 97-99, 1980
- 6. Bray, J.H, Redfern, A.T.S., Clark, M.S., *The kinetics in Ca-montmorillonite an in situ X-ray diffraction study*, Mineralogical Magazine, October 1998, v. 62 (5), p. 647-656, 1998
- Brănoiu, G., Investigații mineralogice pe probe de roci prelevate înainte şi după inițierea proceselor de exploatare secundară, Referat pregătire doctorat, Universitatea Petrol-Gaze din Ploieşti, 81 p., 2003
- Brănoiu, G., On the mineralogical transformations caused by underground combustion process in reservoir rocks from Suplacu de Barcau field, Buletinul Universității Petrol-Gaze din Ploiești, Seria Tehnică, v. 57, nr. 2, p. 33–43, 2005
- Brănoiu, G., Georgescu, O., On the calcium silicates hydrated forming in-situ combustion of petroleum deposits, Proceedings of XVIIIth Congress of Carpathian-Balkan Geological Association, Special Volume, September 3-6, Belgrade, Serbia, p. 41-45, 2006
- Burger, J.G., Sahuquet, B.C., Laboratory research on wet combustion, Journal of Petroleum Technology, v. 25, no. 10, p. 1137-1146, 1973
- 11. Buxton, T.S., Pollock, C.B., *The Sloss COFCAW project further evaluation of performance during and after air injection*, Journal of Petroleum Technology, v. 26, no. 12, p. 1439-1448, 1974
- Castanier, L., *In-situ combustion*, In: Research on Oil Recovery Mechanisms in Heavy Oil Reservoirs, Final Report June 1999, p. 105-108, Stanford University – Petroleum Research Institute, Stanford, California, 1999
- 13. Craig, F.F., Parrish, D.R., A multipilot evaluation of the COFCAW process, Journal of Petroleum Technology, v. 26, no. 6, p. 659-666, 1974
- 14. Crăciun, C., Zamfir, M., Teișanu, E., Purdel, V., *Transformările mineralelor argiloase ca indicatori ai temperaturii atinse în zonele combustionate*, a V-a Conferință Națională a Grupului Român pentru studiul argilelor, București, 1992
- 15. Emery, L.W., *Results from a multi-well thermal-recovery test in southeastern Kansas*, Journal of Petroleum Technology, v. 14, no. 6, p. 671-678, 1962
- 16. Georgescu, O., Cristalochimie, Editura Imprimex, Ploiești, 1997
- 17. Georgescu, O., Brănoiu, G., *Mineralogie descriptivă*, îndrumar de lucrări practice, Editura Universității din Ploiești, 2005
- 18. Grim, E.R., Clay mineralogy, Second edition, McGraw Hill Book Co., New York, 1968
- Hao, F., Li, S., Gong, Z., Yang, J., Thermal regime, interreservoir compositional heterogeneities, and reservoir-filling history of the Dongfang gas field, Yinggehai Basin, South China Sea: Evidence for episodic fluid injections in overpressured basins ?, A.A.P.G. Bulletin, v. 84, no. 5 (may 2000), p. 607-626, 2000
- Harvey, C., Browne, P., Mixed-layer clays in geothermal systems and their effectiveness as mineral geothermometers, Proceedings World Geothermal Congress 2000, Hyushu-Tohoku, Japan, May 28 – June 10, 2000
- Lanson, B., Bouchet, A., Identification des minéraux argileux par diffraction de rayons X apport du traitement numériques, Bulletin Centres Recherches Exploration-Production Elf Aquitaine, v. 19, no. 1, p. 91-118, 1995

- 22. Lanson, B., Meunier, A., La transformation des interstratifiés ordonnés ( $S \ge 1$ ) illite-smectite en illite dans les séries diagénétiques. État des connaissances et perspectives, Bulletin Centres Recherches Exploration-Production Elf Aquitaine, v. 19, no. 1, p. 149-165, 1995
- 23. Lasaga, A.C., *Rate Laws of Chemical Reactions*, In: Reviews in Mineralogy, v. 8, Kinetics of Geochemical Processes, p. 1-68, Mineralogical Society of America, Washington, 1981
- 24. Mackenzie, R.C., Differential Thermal Analysis (DTA), vol. 1 Fundamental Aspects, Academic Press, London and New York, 1970
- 25. Perry, C., Gillott, J.E., The formation and behavior of montmorillonite during the use of wet forward combustion in the Alberta oil sand deposits, Bulletin of Canadian Petroleum Geology, v. 27, p. 314-325, 1979
- Perry, C., Gillott, J.E., Mineralogical transformations as indicators of combustion zone temperature during in situ combustion, Bulletin of Canadian Petroleum Geology, v. 30, no. 1 (March 1982), p. 34-42, 1982
- 27. Prats, M., *Thermal Recovery*, Second Printing S.P.E., Henry L. Doherty Memorial Fund of AIME, New York, Dallas, 1986
- 28. Steiner, A., *Clay minerals in hydrothermally altered rocks at Wairakei, New Zealand*, Clay and Clay Minerals, v. 18, p. 165-177, 1968
- 29. Todor, D.N., Analiza termică a mineralelor, Editura Tehnică, București, 1972
- 30. Weber, J.N., Roy, R., Dehydroxylation of kaolinite, dickite and halloysite: DTA curves under  $pH_2O = 15$  to 10,000 psi, Journal of American Ceramics Society, v. 48, p. 309-311, 1965

## Asupra posibilităților de estimare a temperaturii atinse în zăcămintele exploatate prin combustie subterană pe baza transformărilor mineralogice

#### Rezumat

Temperatura maximă atinsă în zăcămintele exploatate prin metode termice, în special prin combustie subterană, este un parametru important când se evaluează rezultatele testelor de teren sau de laborator asupra producției de țiței. Transformările mineralogice apar frecvent în rocile rezervor la încălzirea acestora, și ele pot să servească ca indicatori ai temperaturii zonei de combustie. Utilitatea metodei de estimare a temperaturii atinse în zăcămintele exploatate prin combustie in-situ depinde de compoziția mineralogică a zăcământului, deoarece trebuie să fie prezente mineralele care sunt supuse transformărilor adecvate intervalului de temperatură cerut. În lucrare se urmărește identificarea transformărilor de natură să servească ca indicatori utili de temperatură în condițiile combustiei in-situ fiind necesară testarea acurateței metodei prin experimente de laborator.