Annales Societatis Geologorum Poloniae (2010), vol. 80: 115–122.

MIXED WETTED CARBONATE RESERVOIR: ORIGINS OF MIXED WETTABILITY AND AFFECTING RESERVOIR PROPERTIES

Irena MATYASIK[1], Grzegorz LEŚNIAK[1], Piotr SUCH[1] & Zbigniew MIKOŁAJEWSKI[2]

[1] *Oil and Gas Institute, ul. Lubicz 25A, 31-503 Kraków, Poland; e-mails: matyasik@inig.pl, lesniak@inig.pl, such@inig.pl,*

[2] *PGNiG S.A. – department Zielona Góra, pl. Staszica 9, 64-920 Piła, Poland; e-mail: gustek@geonafta-pila.com.pl*

Matyasik, I., Leśniak, G., Such, P. & Mikołajewski, Z., 2010. Mixed wetted carbonate reservoir: origins of mixed wettability and affecting reservoir properties. *Annales Societatis Geologorum Poloniae*, 80: 115–122.

Abstract: The greatest Polish oil fields are built of the Main Dolomite. They are mainly created as a single porosity – double permeability reservoir rocks showing mixed wettability. Mixed wettability is a result of differentiated diagenetic processes connected with basin evolution. The Main Dolomite sediments were sealed very quickly between salt and anhydrite sediments within the whole basin. Hence, reservoir rocks were also source ones when carbonate grains were mixed with organic matter. This caused that residual organic matter is still present in the Main Dolomite rocks. Presence of organic matter and way of mixing are factors affecting wettability of rocks. There is no evident correlation between the content of residual organic matter and wettability index. The main role is played by the process of mixing carbonate grains and organic matter. Rock Eval analyses were applied to indicate the type of oil wet parts within pore space. It was shown that oil wet pores occupy the range from the smallest to the greatest pores. Oil and water paths of fluid migration are practically independent. A large part of samples (70) are predominantly oil wet, 17 show predominant water wetting. There was no pure oil or water wet rocks. Such type of wettability produces irreducible oil and water in all samples.

Key words: mixed wettability, saturation, capillary pressure, filtration properties.

Manuscript received 7 April 2009, accepted 16 April 2010

INTRODUCTION

The greatest oil and gas reservoirs in Poland are built by carbonate rocks of the Main Dolomite. It was quickly sealed by salt and anhydrite and finally formed a completely closed basin (Wagner, 1994). Therefore, reservoir rocks were also source ones. It caused that residual organic matter is still present in the Main Dolomite rocks (Lesniak *et al.*, 2006). Carbonate grains are mixed with organic matter and such composition strongly affects reservoir and filtration properties. Investigation of these reservoirs showed inconsistency both between various types of routine analyses and in well log interpretation. The initial diagnosis was simple: mixed wett- ability, but the type of wettability, its range and influence on filtration parameters were unknown. So, several methodical investigations were performed. Additionally, as a by-products, probitumines were found in these rocks.

GEOLOGICAL BACKGROUND

The investigated area is a fragment of the Gorzów block, situated at the boundary of the Szczecin trough and Fore-Sudetic monocline (Dadlez, 1979). Intensive Early Permian volcanic activity was marked in this area. At the turn of the Early and Late Rotliegendes, the intensity of tectonic movements, related with the Saalian phase, distinctly increased. Consequently, the Variscan platform was disintegrated into blocks. Such morphologically diversified surface was submerged by the Zechstein Sea. Due to such diversified morphology, deep- and shallow-water zones were formed. In elevated parts the development of sulphate platforms of the Werra cyclothem (locally more than 300 m thick) started to form. As the result of successive transgressive cycle, they were overlain by platform deposits of the Main Dolomite (Stassfurt cyclothem).

The Grotów peninsula (Fig.1) embraces the northernmost part of the Wielkopolska platform (Wagner, 2004). On the west it is bordering with the Noteć bay whereas on the northern and eastern side with the central basin.

Geological analyzes and interpretations, enhanced by seismic 3D data, have evidenced considerable diversity of structure of this zone. This refers both to facies variability and reservoir properties. The Main Dolomite series, occurring on the western side of the Grotów Peninsula, was formed on the slope and at the toe of the carbonate platform zone and in the area of basinal plane (Jaworowski & Mikołajewski, 2007; Słowakiewicz & Mikołajewski, 2009). The best collector properties were estimated both in shallow-water platform series (Mikołajewski & Słowakiewicz, 2008)

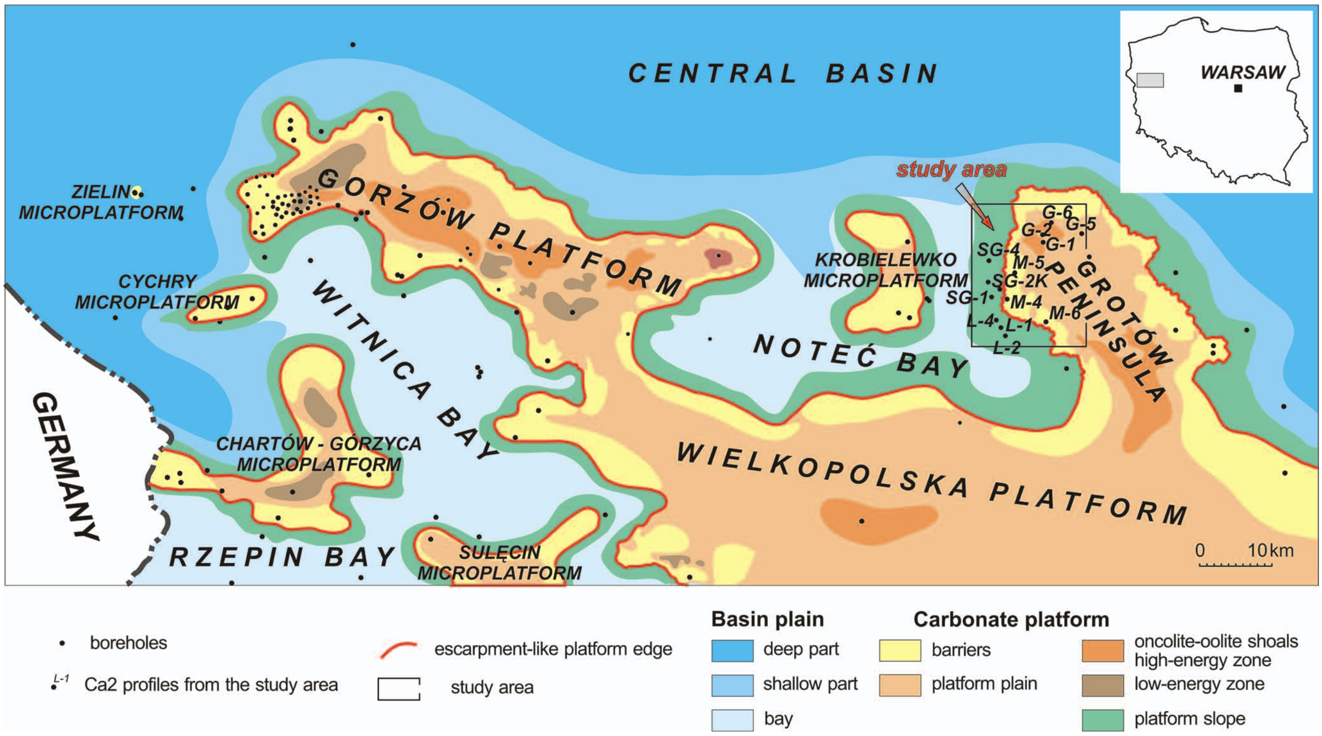

Fig. 1. Palaeogeographic map of the Main Dolomite strata on the Gorzów Platform and on the northern part of the Wielkopolska Platform (Wagner 2004). Boreholes from the study area: L-1 – Lubiatów-1; L-2 – Lubiatów-2; L-4 – Lubiatów-4; SG-1 – Sowia Góra-1; SG-2K – Sowia Góra-2K; SG-4 – Sowia Góra-4; M-4 – Międzychód-4; M-5 – Międzychód-5; M-6 – Międzychód-6; G-1 – Grotów-1; G-2 – Grotów-2; G-5 – Grotów-5; G-6 – Grotów-6

and in deep-water sediments related with its western toe-of-slope (Jaworowski & Mikołajewski, 2007; Słowakiewicz & Mikołajewski, 2009). Detailed geological exploration of this area resulted in the discovery, just in this area, of a rich petroleum and gas deposit Lubiatów–Miedzychód–Grotów (LMG) (Dyjaczyński *et al.*, 2006).

Detailed sedimentological-facies recognition made it possible to reconstruct the sedimentatary environments of the Main Dolomite (Ca2) in the western part of the Grotów Peninsula and at its toe-of-slope (Jaworowski & Mikołajewski 2007). The proposed model (Fig.2) shows the spatial relations of depositional environments during the highstand of sea level (HST). Just in this period, considerable majority of sediments in the areas of carbonate platforms were formed, also on the Grotów Peninsula. The cross-sections of the Main Dolomite (Ca2) are characterized by the diversification of both thickness and facies properties. They represent the zones related with peri-marginal part of the carbon-

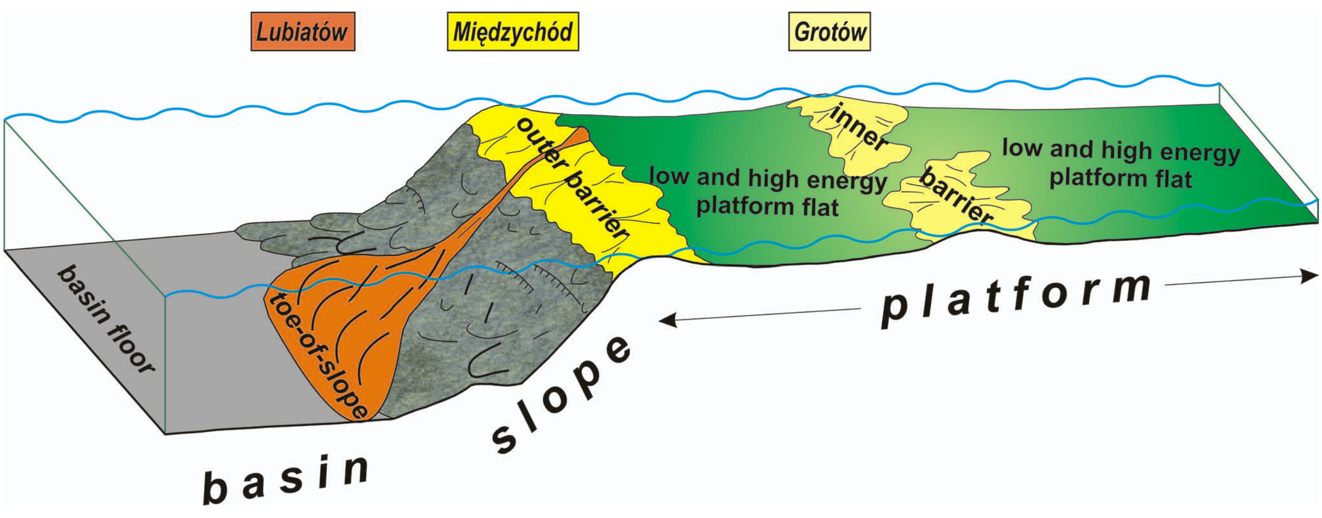

Fig. 2. Depositional model of the Main Dolomite in the western part of the Grotów Peninsula during the sea-level highstand (Jaworowski & Mikołajewski 2007)

ate platform (region of Międzychód gas deposit) with its external part (region of Grotów petroleum deposit), as well as with the slope of the carbonate platform (region of Lubiatów petroleum deposit).

Toe-of-slope of the platform

The characteristic feature of this zone is the co-occurrence of calcareous and arenaceous muds with carbonate sands, containing intercalations of carbonate conglomerates. In lower parts of some cross-sections also anhydrite conglomerates occur. From microfacies viewpoint, these are mudstones and packstones, intercalated with floatstones. Arenaceous-gravelly material was transported from platform and its slope by turbidity currents and debritic flows (Jaworowski & Mikołajewski, 2007). Scarce symptoms of biostabilization in this zone may indicate the periods of release or intervals of sedimentation. Significant content of granular carbonate material at the toe-of-slope of western part of the Grotów peninsula is evidencing high productivity of the platform, causing a progradation of sediments of the platform margin and its slope, characteristic of the HST and FRST conditions (Jaworowski & Mikołajewski, 2007).

Slope of the platform

The nature of sediments depends on their position in the basin. Muds, sands and intercalations of conglomerates dominate in the lower part. On the other hand, sands, conglomerates, breccias and microbial deposits occur in the upper part. From microfacies viewpoint these are: mudstones, wackestones, packstones, grainstones, floatstones, rudstones and bandstones. Deformation structures are often observed (Jaworowski & Mikołajewski, 2007), as well as redeposited fragments of beds composed of consolidated calcareous sands or microbial deposits. These sediments were formed due to rock slides downgoing on the slope of carbonate platform. Some conglomerates, breccias and calcareous sands, containing dispersed rock fragments and showing fractional bedding represent reversed debrites. They are the products of cohesive gravitation slides. The occurrence of fractional bedding indicates the presence of turbidites. Sedimentological features of sediments on platform slope in the western part of the Grotow Peninsula indicate this slope to be accretional in character (Jaworowski & Mikolajewski, 2007).

Barrier

Carbonate barriers occur not only along the margin of the carbonate platform. They form a more or less continuous belt of outer barriers of platform flat, isolating it from the open sea. They are also occurring at the inner zone of the platform, forming external barriers, dividing the area of platform flat into low- and high-energy areas (Jaworowski & Mikolajewski, 2007). The deposits of outer and inner barriers represent the environment of active calcareous sand sedimentation related with highest energy waters. Peri- and sub-littoral calcareous sands dominate in them. Arenaceous muds or calcareous conglomerates are less frequent. From microfacies viewpoint, they represent grainstones and bandstones and less frequently packstones, wackestones, floatstones and rudstones. Calcareous sands are composed predominantly of ooids, pisoids, oncoids, intraclasts and bioclasts, locally also of peloids and other clothed grains. Significant content of mats and microbial structures is an important feature of barrier deposits, including trombolites, characteristic of the Grotow region.

Platform flat

In the zone of platform flat the shallow-water conditions were dominating. Small differences in bathymetry were the cause of the change of depositional conditions and the formation of high- and low-energy zones. ooidic greenstones with bandstone horizons dominate in high-energy zones. Biostabilization of sediments is common. Low-energy zones, related with depressions, are characterized by the occurrence of mudstones, wackestones and peloid packstones with oncoids and bioclasts (worms, ostracods, foraminifers, bivalves). Intraclasts and ooids were supplied to this zone from high-energy area.

INVESTIGATION

Saturation

Totally, 87 samples were prepared for investigations. 83 of them belong to high-energetic carbonate sands.

Plug type samples were prepared for investigation; after extraction and drying, the porosity of all samples was estimated. Samples were weighed, then grain density was measured with the use of helium pycnometer (Such *et al.*, 2007). Bulk volumes were calculated from geometrical measurements. Grain density, bulk volume and mass of dry sample allowed us to calculate open porosity, not very exact, but in the way independent from wettability properties:

$$V_g = m/d$$

$$V_b = 2prh$$

$$Por = ((V_b - V_g)/V_b) \times 100;$$

where: d – grain density, V_b – bulk volume, V_g – grain volume, m – mass of dry sample, Por – porosity (%)

In the next step, samples were sunk in original reservoir water for two weeks. Then additionally, they were saturated under vacuum conditions for 24 hours. The saturated samples were weighed again. Difference between the saturated and dry mass gave the volume of injected water:

$$m_w = m_s - m$$

$$V_d = m_w/d_w$$

saturated part of pore space (%) = $((V_b - V_g) - V_d)/V_b) \times 10$;

where m_w – mass of reservoir water, m_s – mass of saturated sample, d_w – density of reservoir water, V_d volume of saturated pore space

The results are presented in Fig. 3. It is a frequency diagram, showing the degree of water saturation for the collected samples. Even taking into account low accuracy of bulk volume measurements, they showed the scale of mixed wettability and a great impact of the oil wet factor on reser-

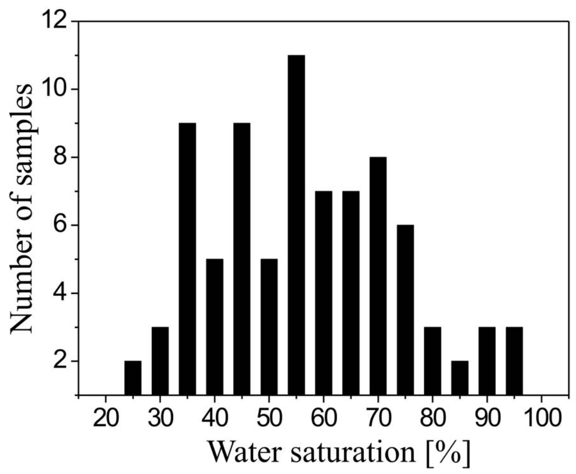

Fig. 3. Degree of pore space saturation (frequency diagram)

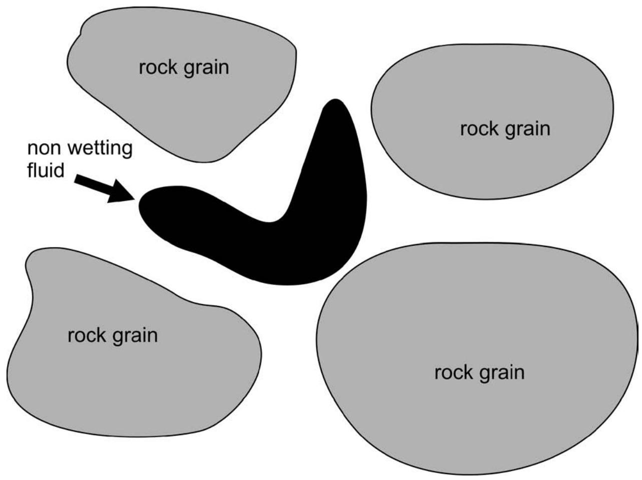

Fig. 4. Space distribution of fluids in a pore space

voir parameters. Values of water saturation vary from 10% to 95 %. Average saturation is equal to 55%.

Mixed wettability investigations

Wettability can be defined as a tendency to adhesion of one fluid to a solid state in the presence of another fluid. This effect is caused by interfacies tension. Wettability depends on the parameters of solid state of both fluids and such parameters, like pressure and temperature. Wettability steers space distribution of fluids in a pore space. This fact defines also parameters of flowing of fluids through porous media. Space distribution of fluids in a pore space is shown in Fig. 4.

Generally, wetting fluid is sticking to the rock grains while non wetting occupied central parts of pore chambers. It implies greater mobility of non wetting fluid in a pore space.

The Amott test is performed in simulated reservoir conditions (pressure, temperature, original reservoir fluids). A sketch of the measuring chamber in shown in Fig 5.

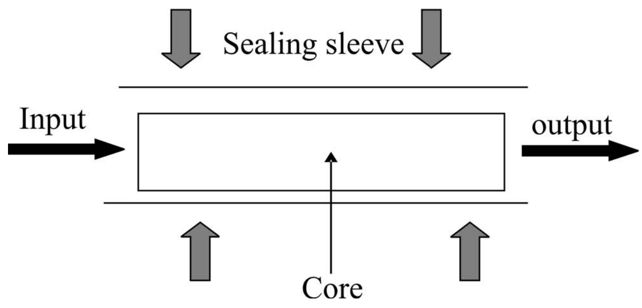

Fig. 5. Sketch of a measuring chamber

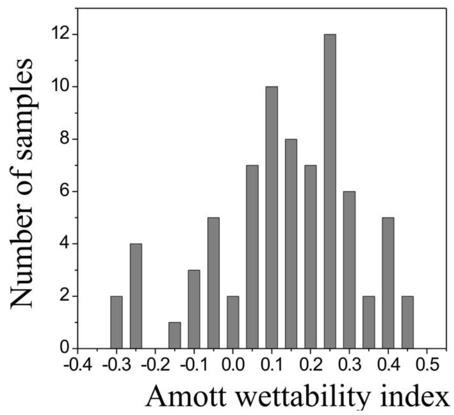

Fig. 6. Calculated Amott wettability index

The Amott test depends on alternate, forced and spontaneous displacement of one fluid with the use of the second one (water, oil) (Donaldson & Tiabb, 1996).

1. Sample is saturated with oil. Then oil is displaced by reservoir water up to residual oil saturation (volume of forced displaced oil is measured).
2. Sample is submerged into oil for 24 hours (volume of spontaneously displaced water is measured).
3. Water is displaced by oil.
4. Sample is submerged into brine for 24 hours (volume of spontaneously displaced oil is measured).
5. Oil is displaced by water up to residual oil saturation (volume of forced displaced oil is measured).

Amott wettability test

The Amott wettability tests were conducted for all samples (Donaldson & Tiabb, 1996). Forced displacement was realized by the use of relative permeability apparatus. Final results are presented in Figs 6–8. Figure 6 shows the obtained values of Amott wettability index. 17 samples share predominantly water wet characteristics. The rest is predominantly oil wet. Frequency diagrams of spontaneously displaced oil and water (respectively presented in Figs 7, 8) confirm that there is no pure oil or water wet samples. All of them are mixed wetted. The results can be treated as typical for carbonate reservoir rocks of the Main Dolomite in the Polish Lowland.

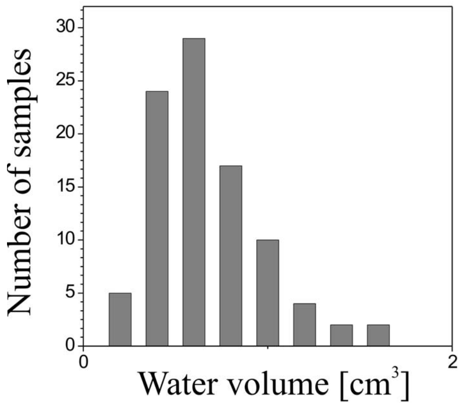

Fig. 7. Spontaneously displaced water

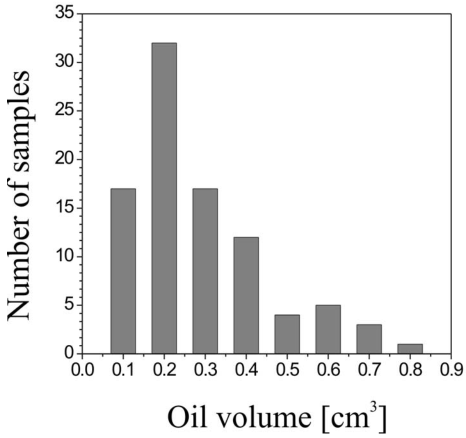

Fig. 8. Spontaneously displaced oil

The Amott wettability index investigations showed the scale and domination of oil wettability in carbonate reservoir rocks of the Main Dolomite in the Polish Lowland. Several investigations were performed to examine micro effects of mixed wettability and the kind of wettability (Donaldson *et al.*, 1969; Skauge *et al.*, 2006). It is obvious that wettability changes in pore scale and that there are oil and water wet paths in each sample. In the first step we tried to check the range of pore diameters connected with mixed wettability (Skauge & Otesen, 2002; Skauge *et al.*, 2006). A series of Rock Eval pyrolysis tests were preformed. They shows that extraction was not complete and some amount of hydrocarbons was non extractable from pore space. Table 1 showed balance of hydrocarbons index. RC is residuum organic carbon and ROM means residuum organic matter. The difference between these two values gives the content of non extractable hydrocarbons

These hydrocarbons became removable when samples were ground to powder before extraction. This was confirmed by the next investigations in which the same, though powdered samples were used. These investigations show that hydrocarbons occupy the smallest pores in pore space and that these pores are oil wet. It means that oil wet pores form a part of pore space from the greatest to the smallest pores and that two pore spaces (oil wet and water wet) existed in each sample (Tiorre-Verdin *et al.*, 2006). This implies that irreducible water and irreducible oil existed in all samples (Skauge *et al.*, 2006).

Table 1

Balance of hydrocarbons index

Sample	RC (%)	ROM (%)
1	0.32	0.38
2	0.25	0.31
3	0.28	0.33
4	0.7	0.77
5	0.26	0.33
6	0.31	0.5
9	0.30	0.32

RC – residuum organic carbon, ROM – residuum organic matter

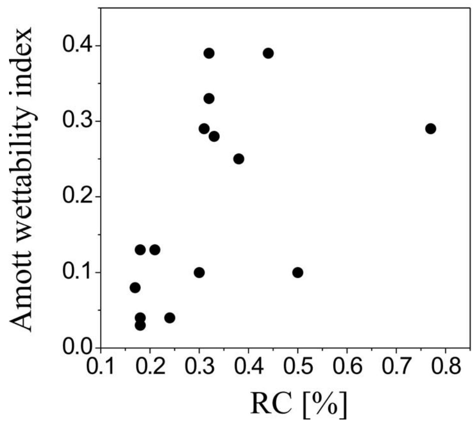

Fig. 9. Correlation of Amott wettability index and content of ROM

FACTORS AFFECTING AMOTT WETTABILITY INDEX

Rock-Eval analyses provided an opportunity to correlate values of the Amott wettability index and the content of residual organic matter in the investigated samples. The results are presented in Fig. 9. They show that it is not a simple dependence and that other factors affecting wettability index play a role there.

There are space distributions of residual organic matter (Kamath *et al.*, 2001; Torre-Verdin *et al.*, 2006). This effect can be called black and white samples or grey samples. Residual organic matter can occupy walls of pores (often mixed with clay minerals). This effect gives characteristic black and white rocks. When grains of carbonate sands and organic matter are homogeneously mixed, only a part of organic matter occupies the walls of pores and its impact is lower. Rocks are grey. Figure 10 presented various type of organic matter distribution.

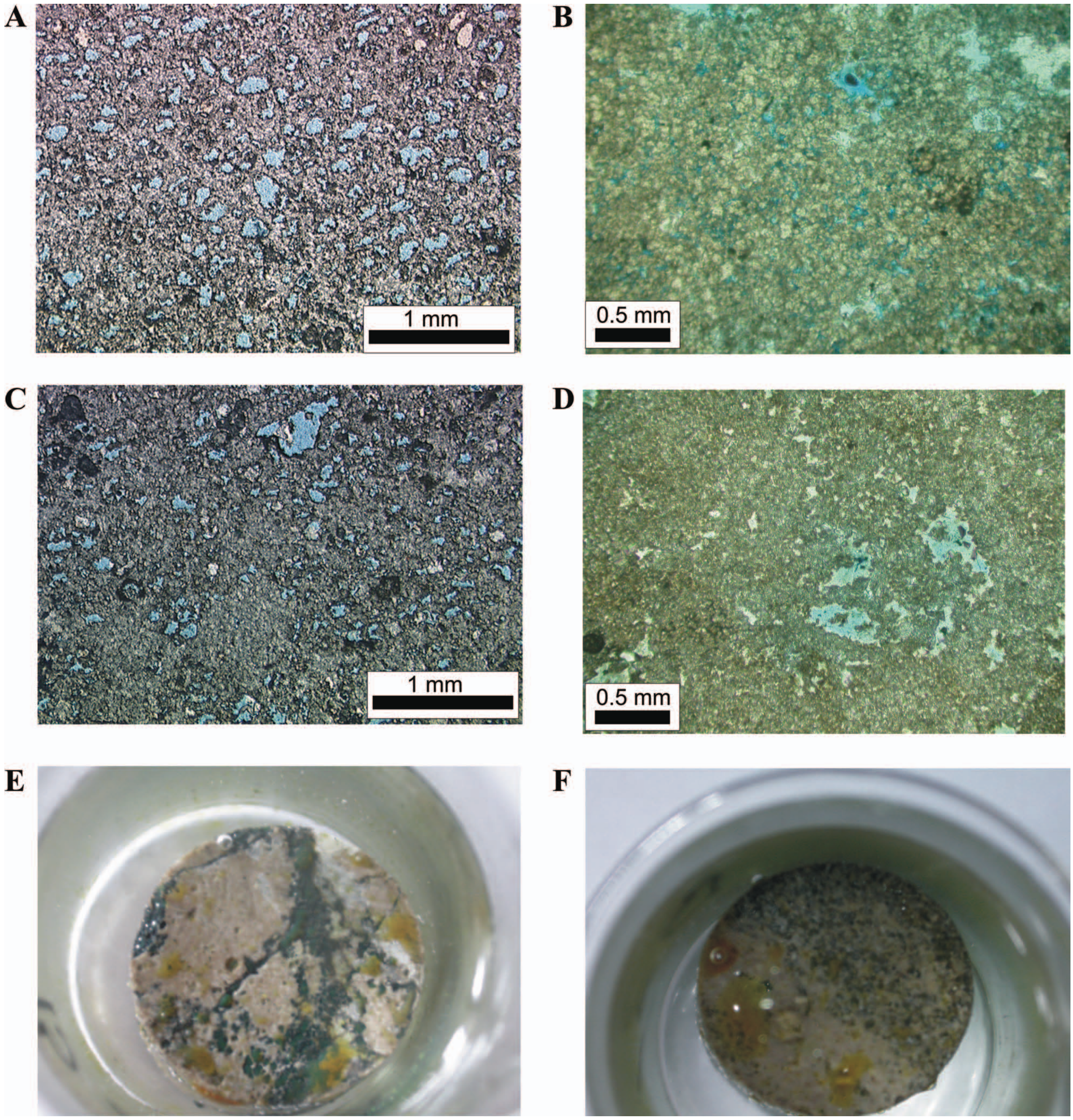

Fig. 10. Various types of mixing ROM and carbonate grains. **A**, **B** – the Main Dolomite – (without analyser) – organic matter covers walls of pores. Small amount of organic matter between grains (blue color – open porosity); **C**, **D** – the Main Dolomite – (without analyser) – organic matter covers walls of pores and is dispersed between grains (blue color – open porosity); **E**, **F** – the Main Dolomite – (plug sample) spontaneous displacement oil by brine. Typical "black and white" sample

PYROBITUMENS

Pyrobitumen in pore space provides the second source of mixed wettability in the Main Dolomite rocks of the Polish Lowland. Solid bitumen generally implies an immovable solid material under reservoir conditions, derived from alteration products of once-liquid petroleum by physical and chemical changes. The occurrence of solid bitumens in petroleum reservoirs is a common phenomenon in many petroliferous basins worldwide (Lomando, 1992; Huc *et al.*, 2000; Marikos *et al.*, 1986). Several natural processes leading to deposition of solid bitumen in a reservoir have been proposed in the literature, often representing tar-mat formation or asphaltene precipitation. Thermal alteration (maturation) of pre-existing liquid hydrocarbons to form hydrogen-depleted carbonaceous residues and associated gases can result in deposition of solid bitumen in the carrier bed and reservoir under elevated temperatures (Mort *et al.*, 2007; Mueller *et al.*, 1995).

Pyrobitumens in pore space affect wettability, permeability and porosity. They can close pore throats and make a rock impermeable. Reservoir rocks filled with pyrobitu-

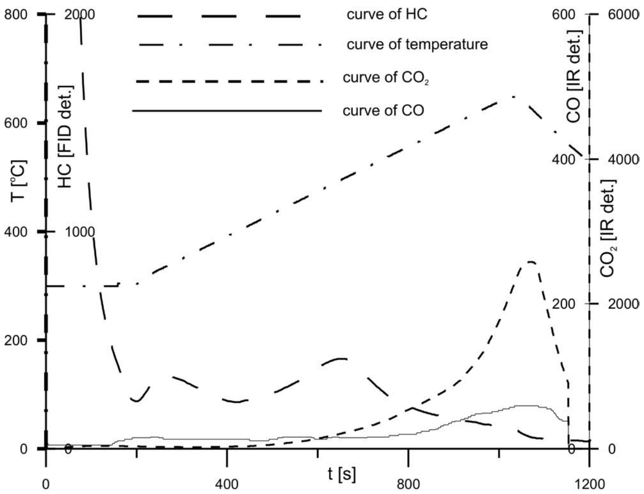

Fig. 11. Pyrolysis curves from Rock-Eval 6 illustrating presence of S_1 peak and double S_2 peak

mens cannot be distinguished with the use of well logs from typical rocks saturated with oil. This is caused by the fact that oil and pyrobitumens show very similar density (Wilson, 2000).

For verification of pyrobitumens presence in the pore space of the investigated rocks, GCMS (gas chromatography-mass spectrometry) and Rock Eval analyses were applied. Samples whose pyrograms suggest presence of pyrobitumens (double peak S_2) were examined.

In dolomite samples vertical variation in total pyrolyzates (S_1+S_2) determined by Rock- Eval 6 analysis was observed. These results tend to exhibit small S_1 peak, a bimodal S_2 peak and significant amounts of CO and CO_2 released during oxidation at high temperature (near 800°C) (Fig. 11). Most of the analyzed samples displayed a high level of maturity suggesting the presence of over mature rocks. It seems that pyrobitumens occupied pore space of reservoirs rocks. Such types of samples were found in several investigated boreholes in carbonate reservoir rocks. Thermal alteration of crude oils in the reservoir is one of the major contributing factors to the formation of solid bitumen Therefore, maturity assessments were necessary to clarify whether or not the formation of the solid bitumen in investigated reservoir was related to thermal degradation of the oil. The bitumens in this reservoir exhibit a wide range of thermal maturity levels based on the MPI-1 and MDR ratios (maturity indexes), corresponding to an equivalent to vitrinite reflectance above 1.3%. In-reservoir oil cracking has been reported as a mechanism responsible for solid bitumens formation, occuring when the reservoir temperature reaches 145°C or higher.

CONCLUSIONS

1. Carbonate rocks of the Main Dolomite generally show mixed wettability. Nomeclature – oil wet or water wet shows only predominant tendency.

2. Residual organic matter and pirobitumes were recognized as a sources of mixed wettability.

3. Oil wet paths in pore space cover the range from smallest to biggest pores.

4. Amott wettability index depend on content of organic matter and its space distribution.

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