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MODIFICATION OF THE PETROPHYSICAL PROPERTIES OF ARTIFICIALLY CONSOLIDATED CORE SAMPLES WITH SUPERCRITICAL CO_2 TREATMENT

Gyula Varga
assistant research fellow, Research Institute of Applied Earth Sciences, University of Miskolc
3515 Miskolc, Miskolc-Egyetemváros, e-mail: ***oljvarga@uni-miskolc.hu***

Ákos Pintér-Móricz
assistant research fellow, Research Institute of Applied Earth Sciences, University of Miskolc
3515 Miskolc, Miskolc-Egyetemváros, e-mail: ***afkpiak@uni-miskolc.hu***

Renáta Zákányiné Mészáros
senior research fellow, Research Institute of Applied Earth Sciences, University of Miskolc
3515 Miskolc, Miskolc-Egyetemváros, e-mail: ***afkzmr@uni-miskolc.hu***

Abstract

During the evaluation of certain hydrocarbon fields, for the petroleum engineering tests, natural rock core samples are needed. If there is a shortage of such samples, preparation and development of artificially consolidated rock samples become necessary. These samples can be made of different compositions and by using different technologies. The used model materials can play a role in the exploitation of petroleum and natural gas, and they can also promote the development, selection or application of secondary or tertiary technologies in conventional and non-conventional reservoirs. The process developed and used by us makes it available to construct these rock samples from different raw materials, under different pressure and temperature conditions and by using different post-treatment methods. In this paper, the changes of petrophysical parameters (porosity, permeability) originating from a CO_2-rich environment ensured by a post-treatment (cure) were analyzed.

The authors proposed further investigations of additional important parameters – zeta-potential, wettability – which could alter during different preparation methods of artificially consolidated rock samples, and by this, they could also enhance the research of geological storage of CO_2 and EOR technologies.

Keywords: *artificially consolidated rock samples, porosity, permeability, zeta-potential, wettability.*

1. Introduction

During the life-cycle of petroleum reservoirs, sooner or later, the enhanced recovery (so-called secondary or tertiary) technologies available for them will become determined. In order to match the available methods and technologies with a certain reservoir, a well-constructed decision process is necessary. In order to produce, economically develop and maintain the hydrocarbon reservoirs, different measurements (as data collection) are necessary, which mostly rely on the properties of natural rock samples. The main part of the related information can be provided by laboratory measurements on natural rock samples. However, a natural rock sample can only be used once during the laboratory tests,

due to the specification of the measurements. The natural rock samples are available in limited quantities, which are gradually decreasing. One of its causes is that the number of core drillings is also decreasing as it is a costly well drilling activity. In addition, as a result of the development of the information collection technologies applied in deep drilling environment, some of the measurements can also be conducted at well environment. Therefore, due to the lack of the natural rock samples and their high value the arising needs cannot be covered from these sources alone.

Therefore, our aim was to prepare artificially consolidated rock samples. It can be said that the artificially consolidated rock samples, apart from their limited application, can have numerous advantages. Their preparation is significantly cheaper and faster, their application can for instance facilitate control measurements, planning and implementation of EOR experiments. However, this also requires a description of their behaviour in terms of reservoir mechanics. Another advantage is the variability of the desired geometric shape. As for natural rock samples, preparation of a 1.5" cylindric rock sample is not always available. On the other hand, if artificially consolidated rock samples are used, the desired diameter and length can be varied, thus, special needs of measurement devices or experimental instruments can also be fulfilled.

Furthermore, the prepared artificially consolidated rock samples are also important since their petrophysical properties and their relationships, the correlation are relative unknown, or they are highly dependent on the production technology. The evaluation of the measurement results can provide important information in connection with the replacement of natural rock samples originating from real hydrocarbon reservoirs during measurements where a huge number of samples are required.

Therefore, the aim of our research was to observe the influence of a given particle size composition on the petrophysical parameters of artificially consolidated rock samples. During the process, the rock samples were held in a cell filled up supercritical state carbon dioxide and then in a cell where an atmosphere with high water moisture (RH>98%) was present. Later, the order of the treatments was swapped and the changes were observed. More precisely, after the two rock samples had been taken out of the compressive press, one of them was put into a cell for two weeks where supercritical carbon dioxide was present, while the other one was placed into a moisture rich atmosphere for the same period. After the two weeks interval, the atmosphere of the samples was reversed and the samples were treated in the other environment as well for another two weeks period.

It can be presumed that several petrophysical parameters like porosity and permeability of the rock samples may change by using a different preparation method (for instance, swapping the two steps of the post-treatment). In addition, the wettability of the rock can also be changed by the reaction between supercritical carbon-dioxide and water (Hua et al., 2016), which is another factor which can influence the recovery factor during the enhanced oil recovery (EOR) technology methods. It was proved earlier by Hua et al. (2016) by zeta-potential, XRD and FTIR measurements that the wettability properties of the rock can be considered as a macroscopic manifestation of several microscopic forces (van der Waals-forces, electrostatic forces, hydrogen bonds) caused by the attractive force between the charged and molecular surface chemical groups.

In this paper, as the first stage of a research, the determination and comparison of the porosity and permeability of the prepared samples were in focus.

2. Artificially consolidated rock samples

2.1. Preparation of artificially consolidated rock samples

The first attempts to produce so-called artificially consolidated samples similar to the natural rock samples required by the oil industry were several decades ago (Jishun, 2004). With the development of the technology newer materials and devices have been used depending on the field of research where the rock samples were to be used. Based on the scientific literature it can be said that by using different technologies, artificially consolidated rock samples can be prepared on which even laboratory measurements connected to hydrocarbon reservoirs (basic core tests, flood tests, EOR model experiments etc.) can be performed.

Before all, basic materials are needed, which is a kind of bulk material and a binding agent. Bulk material is generally reported to be quartz grains in most of the technologies (Holt and Kenter, 1992; Den Brok et al., 1997; Al Homadhi and Hamadha, 2003), while others use artificial glass beads (Weinhardt and Heinemann, 1985), waste glass and stone fragments (Lee et al., 2008) or waste stone sludge and waste silt (Chang et al., 2010) to create an artificially consolidated porous medium.

The other essential basic material is a suitable binding agent. Depending on the target application field of the consolidated synthetic sample, different binding agents can be used. Sodium silicate or alkali silica gel can be used for manufacturing fragile cement material with brittle mechanical properties (David et al., 1998; Al Homadhi, 2002). Besides its favorable characteristics it should be noted that the silica gel binder can be devitrificated (Den Brok, 1993), thus, liquid permeability measurements on such samples cannot provide representative data. This was tried to be improved by Tilliston et al. (2012), who improved the sodium silicate based binding agent with kaolinitic clay to create stronger chemical bonds. Other brittle binding agents can also be used like borosilicate glass (Bernabé et al.) or the strongly toxic $SiCl_4$ (Visser, 1988). Similarly, Portland cement or different type of industrial cements can also serve as binding agents (Viksne et al., 1961; Saidi et al., 2003, Younessi et al., 2013; Rios et al., 2014), whose use can also result in a fragile, brittle rock sample.

Other advantage of the cement based binding agents is that they can provide water-wet medium, by which the wettability properties of natural sandstones can well be approached. Brittle rock samples can be also manufactured with firing method, like it was carried out by Maccarini (1987), Hemzi et al. (2009) and Shabdirova et al. (2016).

Unlike the previous methods, by using resin (epoxy adhesive), a mechanically plastic binding agent can be created (Rathmore et al., 1995, Lee et al., 2018). Therefore, the rock samples prepared by this method are not suitable for experiments based on mechanical parameters as the result will not be representative for the natural reservoir medium. On the other hand, they are suitable for the measurements with water-wet medium, if it is considered that this binder mostly behaves oil-wet (Xie et al., 2016).

In accordance with the needs, a rock matrix can be prepared from the selected basic materials by a thorough homogenization. The mixture is then filled into a cylinder or prism shaped cell, using a compaction process. The due compaction of the mixture can be achieved by various devices and equipment operating on vibration and/or compaction principles (Holt and Kenter, 1992; Lee et al., 2008; Chang et al., 2010; Al Homadhi, 2012)., The shaped and compacted mixture should be kept at different pressures and/or temperatures during the curing time, depending on the technology and the basic materials. This can be important because the diagenesis of natural reservoir rocks takes place at deep zones, sometimes thousands of metres below the surface, and therefore at high pressures and temperatures. Therefore, consideration must be given to the extent of the applied pressure and the

method the compaction while the artificially consolidated rock samples are being formed (Holt, 2001). On the other hand, when the artificially consolidated samples are taken out of the core holder, the occurring sudden pressure drop can imitate the removal of the natural rock sample from the sub-surface, ensuring an environment closer to the one which exists when a rock sample is originating from a natural reservoir (Holt, 2001).

2.2. Preparation of synthetic rock samples with the method developed by us

Based on the experiments performed previously it can be said that it was available to manufacture rock samples from natural and non-natural rock base materials, whose porosity and/or permeability value can be pre-selected (Varga and Fiser-Nagy, 2018). The base material originating from deep drilling are considered natural base material, while ground form of river sand, pit sand or rocks from open-cast mines are considered non-natural rock base materials (or bulk materials). In this study a natural base material originating from a Hungarian reservoir was selected, on which several exploration and research data are available. The bulk material was composed of different grain sizes as its particle size distribution shows (Table 1), while for binding agent, a cement based industrial adhesive was chosen.

Table 1. *Particle size distribution of the prepared rock samples*

Distribution of the bulk material	Particle size interval
(mass percentage)	(μm)
15.49	70-100
18.33	100-125
17.64	125-160
14.91	160-200
15.14	200-250
11.52	250-315
6.97	315-400

Manufacturing artificially consolidated rock samples for experiments where CO_2 injection takes place is known in the scientific literature (El Husseiny and Vanorio, 2015). However, publications or research data for the effects of the use of supercritical carbon dioxide on the manufacturing process of porous rock samples are not available. Nevertheless, carbon dioxide storage technics in cement based materials has become an important research topic recently (Panesara and Mo, 2013; Haselback and Thomas, 2014; Siriwardena and Peethamparan, 2015), since it has a beneficial environment friendly effect, it may mitigate the climate change. These scientific papers describe that in case of cement based adhesives, the sequestration of carbon dioxide with carbonation reaction – primarily in types of concrete – follows the same mechanism as mineral 'carbonation': silicate minerals and carbon dioxide react chemically and calcium and/or magnesium carbonates are formed (Huijgen et al., 2005; Olajire, 2013).

Thus, the poroperm data of manufactured synthetic rock samples can be changed, since calcite crystals are formed as a result of the post-treatment (curing) with supercritical state carbon dioxide. To investigate this phenomenon, the following set of measurements were performed. During the experiments, four samples were prepared as shown in Table 2.

Table 2. *Post-treatment of the four rock samples prepared by us with the same method and composition*

Sample number	Post treatment in the first two weeks	Post treatment in the second two weeks
T-299	moisture	supercritical CO_2
T-300	moisture	supercritical CO_2
T-302	supercritical CO_2	moisture
T-303	supercritical CO_2	moisture

The first two samples prepared according to the routine described above, they underwent a curing where in the first two weeks, they were kept in a moist environment (RH > 98%), while in the second half of the post-treatment, they were placed in a pressurized (90 bar) carbon dioxide (min. 96 V/V %) chamber at 45 ^{o}C. The curing of the other two samples took place in reverse order, i.e. the samples were kept in supercritical state carbon dioxide in the first two weeks and then they were put into the moist environment cell.

3. Results

3.1. Results of petrophysical measurements

As the first step of the measurement process aiming at the investigation of the changes of petrophysical parameters resulting from supercritical state carbon dioxide treatment, the determination of the porosity values took place. It was followed by the determination of the absolute permeability values with nitrogen gas. The porosity and absolute permeability values obtained for the rock plugs treated in different environment are summarized in Table 3.

Table 3. *Poroperm data measured on the prepared rock samples*

Sample number	Porosity	Abs. permeability
	(%)	(mD)
T-299 (first two weeks: moisture, second two weeks: supercritical CO_2)	30.30	146
T-300 (first two weeks: moisture, second two weeks: supercritical CO_2)	30.73	165
T-302 (first two weeks: supercritical CO_2, second two weeks: moisture)	29.98	121
T-303 (first two weeks: supercritical CO_2, second two weeks: moisture)	29.62	114

The porosity of the plug size samples was determined by a Quantachrome 1200e type helium pycnometer. Helium gas is used for porosity measurements since it has very small atomic size and great diffusive properties, it can penetrate the smallest size pores, even as small as 0.2 nm. This measurement technique is based on pycnometric volume determination, which is equal to – in this case – the volume of gas displaced by the rock sample (Archimedes law, Boyle-Mariotte gas law). Its disadvantage is that only the volume of the open pores can be measured with this method, since restricted pores or impermeable pores cannot be reached by the helium atoms.

The porosity values of the samples initially treated in moist environment (RH > 98%) were 30.30 and 30.73%. Thus, it can be said that the porosity values of the samples are within a small interval, which is an important attribute of good reproducibility. The porosity of the other group was 29.98 and 29.62 percent. It should be emphasized that there is only a small difference between the values again. The same can be concluded for the permeability values (146 and 146 mD vs. 121 and 114 mD). Based on the experiments it can be stated that the initial carbon dioxide treatment resulted in a decrease of porosity and permeability. The change is small, but it is measurable.

3.2. Results of zeta-potential and wettability measurements

Based on the scientific literature data (Hua et al., 2016) it can be presumed that the carbon dioxide treatment alters the attractive forces between the chemical functional groups and the water molecules on the surface of the rock grains, as it was described for tight natural sandstone samples. It results in the decrease of the absolute value of the zeta potential despite becoming more hydrophilic: the longer the reaction time with carbon dioxide, the greater the change. The increasing hydrophility is caused by the formation of C-O and C=O groups on the surfaces of the grains. The macroscopic manifestation of these forces results in the change (decrease) of the contact angle, which is another important factor in petroleum industry since it can influence the recovery factor in EOR technologies and may also affect the carbon capture storage capacity of the rocks as well. Overall, it would be very interesting and important to perform these wettability and zeta potential measurements on artificially consolidated rock samples cured by carbon dioxide treatment since there are no such data available in the scientific literature.

4. Summary

The aim of this study was to introduce the possible manufacturing methods of artificially consolidated sandstone core samples, and the investigate the effect of different post-treatment (curing) techniques on the synthetized rocks. Two groups of the samples were separated. The post-treatment of the first group was keeping the samples in supercritical state carbon dioxide for two weeks, where the overburden pressure was 90 bar and the temperature was 45 ^{o}C, and then, in the second stage of the curing, the sample was put into a moisture-rich chamber for another two weeks. The post-treatment of the other two samples took place in reverse order: they were kept in moisture-rich environment for two weeks, and then they were put into supercritical state carbon dioxide for the same period.

The porosity and the absolute permeability of the rock sample groups are varying in a relatively narrow interval. Generally, it can be said that the investigated rock samples are well consolidated, they have medium porosity and low permeability. However, there are differences in porosity and absolute permeability of the samples prepared with different post-treatment methods. The samples whose initial post-treatment was water moisture showed higher porosity and permeability values than the samples whose initial curing was at supercritical state carbon dioxide environment.

According to the scientific literature, the supercritical carbon dioxide can influence not only the porosity and the permeability, but also the wettability (contact angle, hydrophility) and the electrochemical (zeta-potential) properties of the rocks. Thus, the scope of future studies would be extended mainly to investigate the effect of the supercritical carbon dioxide treatment of tight sandstone samples on other petrophysical and chemical properties. By such investigations important scientific data could be obtained which could be utilized in enhancing the oil recovery factor and in carbon capture/storage plants, moreover, the relationship between zeta-potential and contact angle could also be clarified.

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