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Construction and evaluation of synthetic carbonate plugs

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Construction and evaluation of synthetic carbonate plugs

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ABSTRACT

Many of Brazil's pre-salt basins are located in ultra-deep waters, and the high heterogeneities of its offshore carbonate reservoirs make the extraction of representative rock samples difficult, risky and expensive. Synthetic plugs are required to understand oilfield properties and the behavior of oil in reservoirs where natural plugs cannot be extracted. Specifically, in cases where it is necessary to reproduce representative mineralogical and petrophysical characteristics from carbonates reservoir, it is evident that there are a lack of publications focusing on synthetic plug construction. In this work, the construction of synthetic plugs is studied, using a combination of published methodologies to achieve an alternative construction of synthetic carbonate plugs for laboratory scale studies. The obtained plugs used a procedure based on disintegrated rock matrices with known particle sizes and particle size ratio, uniaxial compaction with controlled load force and velocity, CaCO_3 solubility control by changing temperature and pH and bonding material. Consolidation, wettability and petrophysical properties of the synthetic plugs were evaluated to characterize them. Generally, it was observed that the porosity and permeability features of the synthetic plugs were within the range of carbonate reservoirs. However, without reproducing a heterogeneous pore structure normally present in natural samples. On the other hand, wettability properties of the resulted synthetic plugs were similar to the natural carbonate plugs. Further studies are necessary to obtain more similar chemical and petrophysical properties to the natural samples.

Keywords: synthetic, carbonate, plugs, petroleum, petrophysics, wettability, consolidation

RESUMO

A localização em águas ultra profundas das reservas petrolíferas do pré-sal brasileiro e a alta heterogeneidade dos seus reservatórios carbonáticos dificultam a aquisição de uma amostra de rocha representativa, além de ser uma operação de risco e de alto dispêndio. Plugues sintéticos são utilizados para compreensão das propriedades dos campos petrolíferos e para avaliação do comportamento dos hidrocarbonetos em reservatórios onde plugues reais não podem ser adquiridos. Especificamente, nos casos onde são necessários reproduzir características representativas mineralógicas e petrofísicas dos reservatórios carbonáticos, sendo notório a falta de publicações voltada para construção de plugues sintéticos. No presente trabalho, estudou-se a construção de plugues sintéticos empregando metodologias já difundidas, visando a construção de plugues carbonáticos sintéticos para utilização em escala laboratorial. Os plugues obtidos foram construídos utilizando matrizes de rochas desintegradas com tamanhos e proporções de partículas conhecidos, compactação uniaxial com força e velocidades controladas e controle de solubilidade de CaCO_3 , variando apenas temperatura, pH e proporções de material cimentante. Foram avaliadas as propriedades petrofísicas, a molhabilidade e a consolidação dos plugues sintéticos para posterior caracterização dos mesmos. Comumente, observou-se que os valores de porosidade e permeabilidade dos plugues sintéticos se encontravam dentro do intervalo de valores obtidos em reservatórios carbonáticos reais. No entanto, não reproduziram a estrutura heterogênea dos poros, normalmente presente em amostras de rochas naturais. Em contrapartida, as propriedades de molhabilidade dos plugues sintéticos se apresentaram análogas aos plugues de rochas carbonáticas naturais. Estudos complementares são necessários para obtenção de propriedades químicas e petrofísicas mais próximas das amostras reais.

Palavras-chave: sinteticos, carbonatos, plugues, petroleo, petrofisica, molhabilidade, consolidação

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1 INTRODUCTION

The study of petroleum reservoirs from plugs has a long importance dating back to the beginning of the oil and gas industry. Plugs are cylindrical rocks with specific dimensions about 3.8 cm in diameter and a height 1.5 times greater than the diameter, extracted by drilling from reservoirs (CONSENTINO, 2001). Due to the representative in-situ characteristics such as mineralogical composition and petrophysical properties (CONSENTINO, 2001), plugs are used to understand at a laboratory scale the behavior and interaction of the reservoir rocks and fluids in a production system (GAAFAR; TEWARI; ZAIN, 2015; ALOTAIBI; AZMY; NASR-EL-DIN, 2010). For example, Svec and Grigg (2001), used plugs to study the enhance oil recovery during an injection of water alternating gas; Howe et al. (2015) flowed surfactants through plugs to study changes in oil production; Zamirian et al. (2014) reported new techniques for measuring permeabilities under in-situ conditions using plugs.

In cases such as the Brazilian Presalt carbonate reservoirs, heterogeneity and high depths (PIZARRO; BRANCO, 2012; BARBASSA, 2007) make it difficult to obtain reservoir plugs. Due to this challenge, commercial plugs (SANNI, 2013; CHURCHER et al, 1991) or synthetic plugs constructed in the laboratory (TAREK 2014; GREAVES et al, 1996; BERNARD, 1967; FURRE; HOLT, 1995) may be used. Some research works can be found in the literature relating about the construction of this plugs, but in contrast to the sandstone reservoirs (WANG et al, 2008; RAIMONDI; TORCASO, 1964; ANBAH; CHILINGAR; BEESON, 1965), there is a lack of publications that focus on the construction of representative carbonates that consider both mineralogical composition and petrophysical properties such as porosity and permeability.

In this sense, the contribution of this work is to study a methodology to construct synthetic carbonate plugs, using a combination of published methodologies aiming to reproduce the mineralogy and control the petrophysics properties similar to the natural samples, in order to enable the generation of promising studies to understand the oil and gas reservoirs, such as the Brazilian Presalt.

1.1 OBJECTIVE

To study a methodology to construct synthetic carbonate plugs aiming to reproduce the mineralogy and control the petrophysics properties similar to the natural samples.

2 LITERATURE REVIEW

2.1 CARBONATE NATURAL ROCK PROPERTIES

In order to construct synthetic plugs with similar properties to natural rocks, it was necessary to screening properties of natural carbonate samples. Plugs are formed by carbonates or sandstones, which are the main conforming types of rock in oil and gas exploration areas (EHRENBURG; NADEAU, 2005). These two types of rocks have significant differences. The former is the sediment production location, and the latter is the higher chemical reactivity due to the carbonate mineral (PIZARRO; BRANCO, 2012). One of the know carbonate rock found in the Brazilian Presalt is the dolomite rock (JING et al., 2012; BOYD et al., 2015). Due to the rock chemistry, wettability properties of carbonate rocks are different of sandstone rocks. Wettability can be explained as the preference of a solid surface to be in contact with a fluid in the presence of other immiscible fluids (ANDERSON, 1986). Wettability of a solid surface can be preferentially hydrophilic (water-wet) or hydrophobic (oil-wet). Literature reports wettability of natural carbonate rocks to be intermediate and oil-wet (PIZARRO; BRANCO, 2012; MANRIQUE et al., 2004; MASALMEH et al., 2014; AL-DHAHLI et al., 2011; AKKURT et al., 2000), contrary to the known water-wet for sandstone rocks (PENTLAND et al., 2010; CHATZIS et al., 1988).

Petrophysical characteristics are important in the evaluation and characterization of oilfields rocks (QIN et al., 2018). Petrophysics is defined as the study of physical, electrical and mechanical properties and rock-fluid interaction in a petroleum system (CHEN; PAGAN, 2013). In this work, it was studied the physical properties porosity and permeability in the synthetic plugs, in order to understand how to control and reproduce these properties similar to the samples found in oilfield. In this sense, it is important to mention that petrophysic properties of natural carbonate rocks are heterogeneous and highly variable, due to the combination of micro-porosities, intergranular porosities, vuggy porosities and fracture porosities (MURPHY et al., 1996). Table 2.1 presents the petrophysical properties of some carbonate Brazilian Presalt oilfields, in order to evidence

the mentioned highly variable properties. Additionally, it was observed porosities from 6% to 28% and permeabilities from 0.1 mD to 10000 mD.

Table 2.1 – Petrophysical properties of some carbonate Brazilian Presalt oilfields

Brazilian Presalt oilfield	Porosity (%)	Permeability (mD)
Bicudo (ANP, 2018a)	28	10 -10000
Bonito (ANP, 2018b)	-	< 10
Garoupa (ANP, 2018c)	18	10 - 100
Linguado (ANP, 2018d)	22 / 10 / 10	380 / 250 / 50
Pampo (ANP, 2018e)	10 - 25	250 - 1000
Piranema (ANP, 2018f)	19 – 26	-
Siri (ANP, 2018g)	6	0.1 – 15
Badejo (ANP, 2018h)	10	250
Trilha (ANP, 2018i)	10	390

2.2 CONSTRUCTION OF SYNTHETIC PLUGS

A selection of papers was screened by using the following keywords: lithology (carbonate), rock sampling (plug or core) and sample feature (synthetic or artificial). Only papers focused on the use of such samples for the petroleum engineering area, and the ones where the construction methodology could be identified, were considered. In addition, some undergraduate and master's degree works were analyzed.

2.3 MATERIALS AND CONTENTS USED TO CONSTRUCT SYNTHETIC PLUGS

Due to the relationship between the rock chemistry and the material used to construct synthetic plugs, it was important to identify the main materials and their contents which were used to construct such samples, independent of the approach used for their construction, such as uniaxial compression, cementing of materials, sintering and others.

In this way, it was possible to identify 10 different materials and their contents. Table 2.2 presents these materials, their content range and associated publications.

Table 2.2- Main minerals used to construct synthetic plugs

Minerals	Constructed plugs	Content range % (w/w)	References
Sand	9	70-98%	i.e (BERNARD, 1967) i.e (PURNAMA, 2011)
Silica sand	8	80-100%	i.e (RAIMONDI; TORCASO, 1964)
Quartz sand	3	50-85%	i.e (WANG et al, 2008)
Carmel silica sand	2	95%	i.e (ANBAH; CHILINGAR; BEESON, 1965)
Crushed rock*	2	95-100%	i.e (LAKATOS et al, 2003)
Ottawa silica sand	1	90%	(ANBAH; CHILINGAR; BEESON, 1965)
Toyoura silica sand	1	98%	(OYAMA et al, 2016)
CaCO ₃	4	95%	i.e (FEDRIZZI et al., 2018)
Bentonite	1	100%	(OYAMA et al, 2016)
Kaolinite	1	100%	(OYAMA et al, 2016)

* lithology non-identified

Source: from author

From Table 2.2, it is possible to identify the materials content range from 50% to 100% (w/w) of the synthetic plugs. Note that from these 10 materials, 6 correspond to sand matrices, and the rest include crushed formation rock, CaCO₃, bentonites and kaolinites. Most of these selected studies were therefore based on the construction of sandstone plugs. There are two likely reasons for this finding. The first is that constructing a porous media with a naturally granulated material, with known particle size, is fast and easy. The second is that because it is a porous media, it allows studies with no influence of chemical reactivity, due to the simple chemical composition of the sand (silicon and oxygen) (WEINAN et al., 1997).

Regarding the approach for construction of carbonate plugs, it was possible to identify four works that used a carbonate matrix material and its content (ANBAH; CHILINGAR; BEESON, 1965; FEDRIZZI et al., 2018; WANG et al. 2017; LUO et al. 2018). For example, Anbah; Chilingar and Beeson (1965) used calcite flour as its main component material (95% w/w), carbonate plugs were constructed for the application of

electrical current to increase the flow rate of oil and water in a porous media, however petrophysical properties were not reproduced or correlated with the presented methodology. From another approach, Fedrizzi et al. (2018) related the construction of carbonate rocks using calcite, sand, Portland cement and water. In this work, it was investigated the main petrophysical characteristics of these samples and the relationship with the amount of cementing material, however this study did not consider the possible heterogeneous porous structure of natural carbonate rocks. The construction of representative synthetic carbonate plugs requires special pore studies considerations that it was not studied by Fedrizzi et al. (2018).

Wang et al. (2017), during the construction process, embedded NaCl grains of average particle size of 3mm and aluminum foils with radius of 1.5 mm and a thickness of 20 μm into a blend of carbonate drilling cuttings and epoxy resin. Then, the embedded materials were leached out by immersing the consolidated synthetic plug in 75 °C water and 4% NaOH (sodium hydroxide) alkali solution respectively. The use of these materials and procedures simulates vuggy (due to the NaCl) and crack (due to the aluminum foils) pores into the samples. Their observation indicated that secondary pores crack and vuggy are important factors to control the permeability of the synthetic plugs. It was observed that increasing the quantity of NaCl grains the permeability increases with the increase of total porosity, contrary to the observed with aluminum foils which decrease the permeability and increase the porosity, increasing the quantity of aluminum foil used. However, it is necessary to develop a better understand about the pore structure and the influence of the quantity of epoxy resin and particle size drilling cuttings in the petrophysical properties. Additionally, the chemical nature of epoxy resin as bonding material could change the chemical properties of the constructed samples, fact that can affect the fluid-rock interaction tests, such as, wettability measurements.

Therefore, using the same base material, Luo et al. (2018) prepared drill cuttings with toluene as a packing fluid and then, they applied a compression press of 5000 psi for 30 minutes to consolidate the synthetic plugs. As the main objective of this research was the evaluation of formation damage using synthetic plugs, the influence of compression press and drill cuttings particle properties in the petrophysical properties was not identified. In this sense, despite of mineralogical properties of the constructed plugs may

be similar to the found in a specific field, these analog samples not guarantee the reproduction and control of similar petrophysical properties of the natural plugs.

Additional papers were identified that used a non-carbonate matrix material, such as sands, but using cementing procedures to allow the calcium carbonate precipitation on them. Melo, (2012), evaluated a quartz sand (50% w/w) cemented in a medium favorable to precipitation of calcium carbonate to simulate a carbonate medium. The aim was to evaluate the geochemical interactions with a reactive fluid for carbon dioxide geological storage purposes. The findings and discussion about these approaches will be detailed in the following sections.

According to Tiab and Donaldson (2004), petrophysical properties of rocks depend on the particle size, amount of cementation and compaction. For this reason, the next analyses from this literature review will be focused on these parameters.

2.4 PARTICLE SIZE

It is important to mention the importance of the particle size distribution on porosity and permeability. Particle size is defined as the size of each particle which compounds a porous media. Naturally, a rock is composed of different particle sizes, which generates a heterogeneous system. Empty spaces called pores are generated between these particles, and fluids, such as oil and gas, can be stored in these spaces in reservoir rock. The measurement of this empty space, commonly known as porosity, is defined by the relation between the volume of the empty space and the bulk volume of the sample (where pore volume is dependent on the volume of particle, and therefore also dependent on its size) and calculated using equation (1) (TIAB; DONALDSON, 2004; HOLSTEIN, 2007).

$$\phi(\%) = \frac{\text{pore volume}}{\text{bulk volume}} \times 100 = \frac{\text{bulk volume} - \text{solid volume}}{\text{bulk volume}} \times 100 \quad (1)$$

In the case of an ideal system with an arrangement of uniform spheres and a fixed bulk volume, the porosity will be independent of the particle volume, and therefore of the particle size. But in a real system with particles of different sizes, smaller particles enter

the empty spaces between the larger particles, thus decreasing the porosity. This demonstrates the importance of the particle size on the resulting porosity (HOLSTEIN, 2007). Figure 1 presents a schematic of three porous solids with the same dimension and composed by different particle sizes: A. Large uniform particle, B. Uniform smaller particle size and C. Different size particles. For these cases, the porosity will be demonstrated based on Equation 1. The bulk volume of the three solids with dimensions, L , was calculated.

$$\text{bulk volume} = L \times L \times L = L^3 \quad (2)$$

Subsequently, it is necessary to calculate the volume occupied by the particles in each of the examples cited previously. For this, it is necessary to employ the following volume sphere equations: A. $L/2$ radius, B. 8 spheres of $L/4$ radius and C. 8 spheres of $L/4$ radius for larger particles, and 6 spheres of $L/6$ for smaller particles.

$$\text{Grain volume case A} = \frac{4}{3}\pi\left(\frac{L}{2}\right)^3 = \frac{1}{6}\pi L^3 \quad (3)$$

$$\text{Grain volume case B} = 8 \times \left(\frac{4}{3}\pi\left(\frac{L}{4}\right)^3\right) = \frac{1}{6}\pi L^3 \quad (4)$$

$$\text{Grain volume case C} = 8 \times \left(\frac{4}{3}\pi\left(\frac{L}{4}\right)^3\right) + 6 \times \left(\frac{4}{3}\pi\left(\frac{L}{6}\right)^3\right) = \frac{11}{54}\pi L^3 \quad (5)$$

Finally, using Equation 1, the porosity of these volumes was calculated:

$$\phi(\%)A = \frac{L^3 - \frac{1}{6}\pi L^3}{L^3} \times 100 = \frac{6 - \pi}{6} \times 100 = 47.6\% \quad (6)$$

$$\phi(\%)B = \frac{L^3 - \frac{1}{6}\pi L^3}{L^3} \times 100 = \frac{6 - \pi}{6} \times 100 = 47.6\% \quad (7)$$

$$\phi(\%)C = \frac{L^3 - \frac{11}{54}\pi L^3}{L^3} \times 100 = \frac{54 - 11\pi}{54} \times 100 = 36.0\% \quad (8)$$

According to the obtained results, it was shown that in ideal systems with uniform particles, as for cases A and B, the resulting porosity is the same, corroborating the non-relation between particle size and porosity. Otherwise, in the real system, C, that contains particles of different sizes, the presence of smaller particles affects the porous space and decreases the porosity. In the same way, similar reductions for porosity are expected due to the influences of compaction and cementation. This occurs because empty spaces will be filled by particles or cementitious materials, which decreases the percentage of pores in a solid sample. In addition, the ability of the oil stored in the pores to flow through a reservoir rock, known as permeability, has a direct relationship with the particle size, consolidation and cementation of the sample.

In cases where a solid possesses connected pores, the presence of smaller particles occupying the empty spaces, as well as high degrees of compaction and cementation, generally reduce the permeability. This can be corroborated by the mathematical equation by Darcy for the flow of a fluid in a porous medium, by studying the pressure gradients (TIAB; DONALDSON, 2004; HOLSTEIN, 2007).

$$fv = \frac{q}{A_c} = -\frac{k}{\mu} \frac{dp}{dl} \quad (9)$$

where:

fv = fluid velocity, cm/s

q = flow rate, cm³/s

k = permeability of the porous rock, Darcy

A_c = cross-sectional area of the rock, cm²

μ = viscosity of the fluid, cP

l = lenght of the rock sample, cm

$\frac{dp}{dl}$ = pressure gradient in the direction of the flow, atm/cm

Figure 1 presents an interpretation of the flow of a fluid within 3 types of porous solids. From here, it is possible to demonstrate the application of the previous mathematical equation by Darcy. Flow restrictions caused by a decrease of the porous space due to the presence of particles

of different sizes, compaction, or cementation result in a increase in the pressure gradients, and therefore lower permeabilities.

Figure 1 - Porosity and permeability due to A: Uniform particle of large size, B: Smaller uniforms particles and C: Different sized particles.

Source: from author

It is important to mention that only 33 papers described particle sizes, allowing the identification of a range from 0.017 mm to 4.76 mm. To have a better view of the particle sizes used, the times in which these granulometries were used versus particle size was plotted. Figure 2 presents this particle distribution. It should be noted that the thickest and finest particles were less used. This could be explained by causing a weak consolidation of the sample for the former, and a substantial decrease in the porosities and permeabilities for the latter. However, fine particle sizes can improve the consolidation behavior due to the particle agglomeration by compression (CI, 1987). In addition to this, a clear tendency to use particle from 0.841 mm to 0.037 mm sizes and close to 0.149 mm was identified.

Figure 2 - Particle size based on the literature review to construct synthetic plugs.

Source: from author

Table 2.3 presents papers where these particle size materials were used to construct synthetic plugs. For example, in the work of Furre and Holt (1995), two materials with a particle size distribution centered around diameters 0.053 and 0.297 mm, were cemented with epoxy resin to construct a porous medium to study the acoustic behavior, in order to compare the permeability of synthetic sandstone samples.

Table 2.3 - Particle size used to construct synthetic plugs.

Particle size (mm)	Reference
6	(HASHMAT et al., 2016)
2.38	(NARAYAN et al., 2016)
2	(NARAYAN et al., 2016)
1.19	(NARAYAN et al., 2016)
1	(HEATH, 1965)
0.841	(RAIMONDI; TORCASO, 1964; HEATH, 1965; CRAIGHEAD; HOSSAINI; WATSON, 1983)
0.707	(RAIMONDI; TORCASO, 1964)
0.595	(RAIMONDI; TORCASO, 1964; NARAYAN et al., 2016; PEI et al., 2016)
0.5	(HASHMAT et al., 2016; PEI et al., 2016)
0.4	(WANG et al., 2008; KARIZNOVI et al., 2008; PEI et al., 2016)
0.354	(WANG et al., 2008; KARIZNOVI et al., 2008; PEI et al., 2016)
0.297	(FURRE; HOLT, 1995; WANG et al., 2008; KARIZNOVI et al., 2008; NARAYAN et al., 2016; PEI et al., 2016)
0.25	(WANG et al., 2008; PEI et al., 2016)
0.21	(NEMATI; VOORDOUW, 2002; WANG et al., 2008; KAWAMURA et al., 2008; PEI et al., 2016)
0.177	(HOLT et al., 1998; WANG et al., 2008; NARAYAN et al., 2016; PEI et al., 2016)
0.149	(ARIHARA et al., 1976; WANG et al., 2008; ZHAO et al., 2010; NARAYAN et al., 2016; PEI et al., 2016)
0.125	(LU, 1988; WANG et al., 2008; ZHAO et al., 2010; PEI et al., 2016)
0.105	(WILLIAMS; UNDERDOWN, 1981; ZHAO et al., 2010; PEI et al., 2016)
0.088	(WILLIAMS; UNDERDOWN, 1981; ZHAO et al., 2010; PEI et al., 2016)
0.074	(AMBA et al., 1962; CHILINGAR et al., 1970; WILLIAMS; UNDERDOWN, 1981; RANJBAR et al., 1992; NEMATI; VOORDOUW, 2002; NARAYAN et al., 2016; PEI et al., 2016)
0.063	(RANJBAR, 1992)
0.053	(RANJBAR, 1992; FURRE; HOLT, 1995)
0.044	(RANJBAR, 1992)
0.037	(ANBAH, et al., 1965; PEI et al., 2016)
0.023	(ANBAH, et al., 1965; PEI et al., 2016)
0.017	(PEI et al., 2016)

Source: from author

2.5 METHODOLOGIES FOR CONSOLIDATION OF SYNTHETIC PLUGS

The methodology used for consolidation of the plugs was categorized into five groups: Group 1: unconsolidated samples; Group 2: consolidated by compaction; Group 3: consolidated by bonding materials; Group 4: consolidated by material solubility or precipitation; Group 5: consolidated by materials sintering and Group 6: consolidated by 3D-printed. Following items present the mentioned groups.

2.5.1 Group 1 – Unconsolidated samples

A rock plug sample may be unconsolidated, as with unconsolidated sand, depending on the oilfield properties as in the case of Wang et al. (2008). For this reason, after a particle size analysis of reservoir rock particles, the author mixed sands of sizes between 0.4 and 0.125 mm, and this was used to represent the reservoir zone of interest.

Another material conforming to unconsolidated plugs was found (HASHMAT et al., 2016). Here, packed glass beads of different sizes were used to study the chemical interaction of fluids within the porous media. The author justified the control of porosities and permeabilities due to the use of glass beads and its physical standard characteristics. Based on the same packaging principle quartz sand of size 0.595-0.297 mm was used, packed in a stainless-steel tube and sterilized at 165 ° C for 3 hours. The sample was used for a fluid displacement test (XU; LU, 2011).

2.5.2 Group 2 – Consolidation by compaction

Within the consolidated samples, compaction was identified as one of the methodologies with greater application. Here, a load to the plug can be exerted in a uniaxial or triaxial way. For example, by mixing particles of sand with shale in different proportions and applying a uniaxial compaction within a metallic cell. As a result, a consolidated rock sample can be obtained and used to analyze the dielectric constants of the rocks (WEINAN et al., 1997).

In this same way, it was proposed to obtain consolidated synthetic plugs by using unconsolidated reservoir rock samples (LUQUOT et al., 2016). The samples were disintegrated manually to guarantee the same particle size of natural unconsolidated rock. In the mentioned work, the aim was to compare the porosity, particle size and internal structure of unconsolidated and synthetic plugs. It was concluded that both samples had similar properties. In addition, it can be emphasized that in this way, it is possible to guarantee a natural sample reproduction.

2.5.3 Group 3 – Consolidation by bonding materials

One of the first methodologies regarding the consolidation of plugs using bonding materials was reported in 1999 (THOMPSON et al., 1999). This consolidation was achieved by applying a uniaxial force into a mixture of quartz and epoxy resin, during the curing process of the epoxy. These constructed plugs were used to evaluate the compressive strength of the plugs. It is noteworthy that properties such as porosity and permeability of these plugs were not evaluated due to its geophysics application studies.

Subsequently, based on previous methodology by Thompson et al. (1999), sandstone rock plugs were constructed by Tarek (2014) aiming to simulate reservoir conditions and evaluate the xanthan gum effect on water production. Portland cement was used instead as a bonding material. The composition of the sandstone samples was 74% (w/w) sand, with particle sizes of 0.71 mm, 0.5 mm and 0.25 mm. The mixture consisted of 14.8% (w/w) Portland cement and 11.1% (w/w) water.

On the other hand, other authors developed an equipment called EDR - Radial Displacement Equipment, Londoño (2010) apud Celis and Fernandez (2012) and Alarcon and Cavanzo (2013), which allowed them to simulate the physical behaviour of water and steam injection processes in synthetic sandstone rocks. For such, synthetic samples were constructed using sand and polyester resin as a bonding material, however, without control of petrophysical properties.

Based on the previous methodology of Londoño (2010), a methodology for plug construction with controlled petrophysics properties (porosity and permeability) was developed, by mixing different quantities of sand, white kaolin and resin epoxy (CELIS;

FERNANDEZ, 2012). The author concluded that a greater amount of binder material caused lower porosities and permeabilities. Alarcon and Cavanzo (2013) adapted the methodology used by Celis and Fernandez (2012) by using a manual compaction procedure that allowed synthetic plugs with different petrophysics properties to be obtained, although without the control of the manual applied force.

Therefore, using the same homogenized material of Alarcon and Cavanzo (2013), Padron and Lizcano (2014) standardized the compaction process by applying controlled uniaxial torques, resulting in a greater reproducibility and repeatability of the petrophysical properties of the samples.

Caceres and Porras (2015) focused their research on constructing electro-pneumatic equipment that produced a more controlled and higher compaction than those obtained by Padron and Lizcano (2014). In this sense, the authors developed a methodology correlating the applied pressure and mixture composition (sand, white kaolin, epoxy resin and water). It was concluded that samples manufactured with 100 psi, using kaolin and sand with particle size of 0.149-0.074 mm, presented an excellent consolidation. Additionally, porosities between 21 to 33%, and permeabilities between 40 to 470 mD, were observed. Consequently, the authors recommended the construction of high pressure equipment to obtain samples with lower petrophysical properties.

2.5.4 Group 4 – Consolidation by material solubility or precipitation

Within the synthetic plug construction, the consolidation by precipitation of silica and carbonate materials was identified.

Holt et al. (2003) and Brignoli et al. (1998) describe precipitation, and subsequent consolidation, of silica by CO₂ flowing in a homogeneous sand and sodium silicate solution, which was subsequently subjected to uniaxial and confinement pressure. The authors concluded that samples had weak mechanical properties. In turn, they emphasize that due to the particle size distribution and precipitated material quantity, it will be possible to control the petrophysical properties.

From another consolidation perspective by calcium carbonate, two types of methodologies were identified: use of bacteria (biologically induced precipitation) and

enzyme-induced precipitation. A biologically induced precipitation, with a petroleum engineering application, was described in Ferris et al. (1992). This consolidation method employed a flow of solution consisting of *Bacillus pasteurii* NRS 673 bacteria, Difco nutrient, ammonium chloride, sodium bicarbonate, anhydrous calcium chloride and distilled water. Additionally, solvent and water stability precipitation were noted. The authors describe a permeability reduction on porous media, due to the carbonate precipitation. In addition, this paper emphasizes that this carbonate acted like two agents: cementer and obstructor.

Van-paassen et al. (2009) described some of the improvements that are obtained implementing the biologically induced carbonate precipitation. In this sense, regarding construction of experimental plugs, the author used sand with a density of 1560 kg/m^3 added into a suspension solution of ureolytic bacteria "*Sporosarcina pasteurii*", urea and calcium chloride. After the treatment, five sample blocks were extracted by drilling, and cylindrical rock plugs with a fixed porosity value were obtained.

Kucharski et al. (1996 and 1997) apud Al-Shahri et al. (2010), Yasuhara et al. (2012) and Ronan (2005) describe a controlled calcium carbonate precipitation process around silicon sand. This process simulated a natural cementation rock, and used a patented aqueous solution flow at low pressure. This method titled "CIPS - Calcite in-situ precipitation system" allowed synthetic sample permeability control until a given condition.

Ismail et al. (2000), based on the CIPS patent, developed a technique for artificially cemented calcareous soil preparation, looking for a high cementing quality and consistent density of the sample.

Besides, Yasuhara et al. (2012) creates another method, justifying the CIPS unknown patent solutions and the complex management of containment, extinction and generation of bacteria. The author describes a precipitation method using urease, urea and calcium chloride. After testing this method, it was concluded that further studies are needed to understand how permeability and resistance can be restricted, controlling the amount of precipitated calcium carbonate.

Another method based on carbonate precipitation was described by Melo (2012), adapting the Brazilian standard "NBR 7182: Construction of compacted soil samples" ABNT (1986) to construct a synthetic rock plug to study the behaviour of this sample in

the presence of hydrochloric acid, aiming at carbon capture CO₂ storage studies. For this reason, a quartz sand sample was cemented using a homogeneous aqueous calcium hydroxide and calcified green algae (halimeda), using a proportion of 50%, 25% and 25%, respectively. Subsequently, the sample was compacted and carbonated with CO₂. From this work is important to note the author's emphasis on carbonate mineralogical reproduction, despite not reproducing petrophysical properties.

Pei et al. (2016) aiming to study seismic physical modelling, construct synthetic sandstone plugs applying a load force over a blend of quartz sand with controlled particle size (from 0,6 mm to 0,02 mm) and epoxy resin. The authors explain that changes in the porosity of the synthetic plugs, probably, occurs due the described particles size and the applied load force used to consolidate the sample, but, a relationship between these construction parameters and the obtained porosities was not identified.

2.5.5 Group 5 – Consolidation by materials sintering

Manière et al. (2017) describes a sintering process that involves a compacting heat treatment to transform powder into a solid material by the union of its particles. For this, heat treatments are required close to the material melting temperature. Some materials were found as a basis of consolidation by thermal sintering of materials: PTFE (Polytetrafluoroethylene) or Teflon and quartz.

Mccaffery and Bennion (1974) describes the methodology for constructing plugs by using PTFE or Teflon particles previously compressed in a mould, where a temperature of 371°C was applied for a sintering process to occur. Anderson (1986) explains that Teflon guarantees an inert chemical composition and low surface energy, resulting on wettability control.

Weinbrandt et al. (1969) and Farley et al. (1970) apud Mccaffery and Bennion (1974) indicate that porous media and surface of sintering PTFE samples appear like sandstone rocks. They claim this due to its pore structures at microscopic scale, rough and irregular surfaces, and uniform porosities and permeabilities. However, they did not elaborate on the surface chemical composition.

Ranjbar et al. (1992) describes the production of porous models by quartz particle sintering, with particle sizes between 0.04 and 0.07 mm. The author justifies the use of this technique due to the easy cleaning procedure and reuse advantage. No concerns about mineralogical and petrophysical parameters control were considered.

2.5.6 Group 6 – Consolidation by 3D-printed

From another approach, Kong et al. (2018) manufactured synthetic plugs using 3-D printed gypsum rock and evaluated its physical properties through quantitative porosity analyses. Their observation indicated that these manufacture rocks host spherical pores and fewer blade-shaped pores, evidencing a homogeneous pore structure. In contrast, additionally to the mentioned by the authors about the limitation of replicate similar natural rock pore frame due to the printing resolution, it can be noted that the use of gypsum powder may not represent a complex mineralogizes found in plugs from field. In this sense, it can be another limitation of these synthetic samples when submitted to interaction rock-fluid tests.

In a summary, the construction of synthetic carbonate plugs is viable and dependent on the selected materials and methodologies. Therefore, there is a lack of researches focusing both mineralogical composition and petrophysical properties to reproduce a heterogeneous but controlled pore structure and chemical composition characteristics typical of carbonate oilfield rocks. In this way, this research presents a promising approach to obtain such plugs, aiming to contribute to the evidenced research lack.

3 PROPOSAL FOR CARBONATE PLUG CONSTRUCTION

Plug composition has a direct relationship with the rock chemistry, and therefore with the behavior of the sample in the laboratory tests focused on the surface chemistry behavior, such as wettability measurements aimed at enhanced oil recovery studies.

According to Abdallah et al. (2007), wettability refers to the preference of a solid surface to be in contact with a fluid, due to the equilibrium of interstitial forces (fluid-solid). In the case of a petroleum reservoir, these forces will generate a system with preferences to be oil-wet or water-wet due to the behavior between oil, water and reservoir rock. This means that due to the wettability, if reservoir rock is oil-wet, higher amounts of oil can remain retained inside the reservoir rock, resulting in a negative economic situation (ALOTAIBI et al., 2010). For example, in the case of sandstone rocks, preferences to be water-wet (PENTLAND et al., 2010; CHATZIS et al., 1988) were found, and carbonate rocks to be oil-wet (MANRIQUE et al., 2004; MASALMEH et al., 2014; PIZARRO; BRANCO, 2012) or with an intermediate wet behavior (AL-DHAHLI et al., 2011; AKKURT et al., 2000) were found.

Because these plugs can be also used for advanced petrophysics studies, such as flooding or wetting measurements, it is important to choose materials which allow synthetic carbonate samples to be built, guaranteeing their similarity to the natural ones, such as in studies of changing wettabilities due to the application of chemical treatments to the rock-fluid system in order to enhance oil production.

To achieve carbonate reservoir samples that reproduce the proper mineral chemistry composition, materials based on silicas and sand, as well as bonding materials based on epoxy, resins and cements, will not be considered. Therefore, based on the developed methodologies by Lakatos et al. (2003) and Luquot et al. (2016), which used a disintegrated rock material to obtain a core plug, an adaptation is proposed that uses a disintegrated dolomitic carbonate rock. In this way, disintegrated carbonate rock will be the base material of synthetic plugs, guaranteeing a similar natural composition compared to the corresponding reservoir rock. Based on the previously particle size analysis by literature, a particle size control in five intervals around the most used granulometry was

proposed, aiming to obtain plugs with different basic petrophysical parameters. They were: 0.3-0.6 mm, 0.15-0.3 mm, 0.074-0.15 mm, 0.020-0.074 mm and <0.020 mm.

Additionally, it is proposed to use during the construction process some bonding materials in low content and the increasing calcium carbonate solubility followed by precipitation, in order to generate a natural bonding material into the particles used to construct the synthetic plugs. Figure 3 presents the related solubility due to the decreasing of both, pH and temperatures.

Figure 3 - Degree of supersaturation - CaCO_3 formation

Source: Software Frechcreek (2017)

4 MATERIALS AND METHODS

4.1 BASE MATERIAL - DISINTEGRATED DOLOMITIC CARBONATE

The base material used in this work to construct synthetic plugs was a disintegrated dolomitic carbonate rock with controlled particle size. The base material was disintegrated first by a jaw crusher and then by a roller crusher. Chemical analysis of the dolomitic carbonate rock used was carried out by X-ray spectrometry fluorescence in the STD-1 (Standardless) calibration, concerning the analysis of chemical elements between fluorine and uranium. In addition, the loss on ignition (LOI) was carried out at 1020 °C for 2 hours.

Then, to obtain particle size intervals from 0.3-0.6 mm, 0.15-0.3 mm, 0.074-0.15 mm, 0.02-0.074mm, and <0.02 mm, sieves with a known mesh (0.02mm, 0.074mm, 0.15mm, 0.3mm and 0.6mm) were used.

In cases where the quantity of the finest particle size (<0.02 mm) obtained was too low, particle size 0.02-0.074 mm were sampled and pulverized in a Herzog pulverizer to obtain the needed material. To corroborate the true size of the finest particle material resulting from this procedure, a low angle laser light scattering measurement (Malvern Mastersizer) was used to assure particle size.

4.2 METHODOLOGY TO CONSTRUCT SYNTHETIC PLUGS

Two kinds of samples were constructed. One sample was composed of 5g of disintegrated rock and disk geometry of 3.77 cm diameter and 0.2 cm height. It was used to screening of the different parameters before the construction of the real size plugs. The other was composed of 100 g of disintegrated rock with a plug geometry of 3.77 cm diameter and 40 cm height and was used to reproduce the final plugs of real size with the identified better parameters. To study the effect of particle size of the base material on consolidation of the plugs, samples composed by a unique particle size and 1:1, 1:2, and 1:3 ratios (w/w) of particle size (fine:coarse) were used as shown in Table 4.1.

Table 4.1 - Particle size ratios (fine:coarse)

Composed by a unique particle size (mm)	Particle Sizes (mm) ratio 1:1 (Fine:Coarse)	Particle Sizes (mm) ratio 1:2 (Fine:Coarse)	Particle Sizes (mm) ratio 1:3 (Fine:Coarse)
<0.02	<0.02 : 0.020+0.074	<0.02 : 0.020+0.074	<0.02 : 0.020+0.074
0.020+0.074	<0.02 : 0.074+0.15	<0.02 : 0.074+0.15	<0.02 : 0.074+0.15
0.074+0.15	<0.02 : 0.15+0.3	<0.02 : 0.15+0.3	<0.02 : 0.15+0.3
0.15+0.3	<0.02 : 0.3+0.6	<0.02 : 0.3+0.6	<0.02 : 0.3+0.6
0.3+0.6	0.020+0.074 : 0.074+0.15	0.020+0.074 : 0.074+0.15	0.020+0.074 : 0.074+0.15
	0.020+0.074 : 0.15+0.3	0.020+0.074 : 0.15+0.3	0.020+0.074 : 0.15+0.3
	0.020+0.074 : 0.3+0.6	0.020+0.074 : 0.3+0.6	0.020+0.074 : 0.3+0.6
	0.074+0.15 : 0.15+0.3	0.074+0.15 : 0.15+0.3	0.074+0.15 : 0.15+0.3
	0.074+0.15 : 0.3+0.6	0.074+0.15 : 0.3+0.6	0.074+0.15 : 0.3+0.6
	0.15+0.3 : 0.3+0.6	0.15+0.3 : 0.3+0.6	0.15+0.3 : 0.3+0.6

Source: from author

Samples were constructed with and without using water content to study the sample consolidation. In case where water content was used, water content of 2,4,6,8 or 10 w/w relative to the base material with pH 3 or 7 were mixed with the base material. Water content of pH 3 were carried out by and hydrochloric acid solution. Additionally, samples were constructed with and without using bonding materials to study the effect on both consolidation and wettability properties. The proportion used of these bonding materials were 5% w/w and 10% w/w relative to the base material. Table 4.2 reports the

materials used to construct synthetic plugs. On the other hand, To study the effect of temperature on the consolidation of the sample based on CaCO_3 solubility, it was submitted to a drying temperature of 25°C (room temperature) or 100°C (for 1 hour into an oven).

In this way, a base material with known particle size and particle size ratio was placed in a plastic bag, manually mixed with the bonding material (if necessary) and the water content pH 3 or 7 (if necessary) by 1 minute. After this, the resulting blend was placed inside the cylindrical metallic vessel, which had previously been lubricated with an ethyl alcohol solution containing 1% w/w stearic acid powder. The dimensions of this vessel were 3.77 cm internal diameter, 3.00 cm thickness and 13.00 cm height and the dimension of the piston were 3.75 cm diameter and 15.90 cm height. A load (200 kN) was applied with controlled velocity (25mm/min) two times. To study the e

Subsequently, the resulting consolidated sample was placed for 1 hour into an oven at 100°C (if necessary) to guarantee a drier and higher consolidation based on CaCO_3 solubility. After that, samples were exposed to room temperature. Photographic register of the samples was taken at 0, 1 and 120 hours after removing from compression moulding.

Table 4.2 – Materials and contents used to construct synthetic plugs

Function	Description	Content
Base material	Disintegrated dolomitic carbonate rock	5 g or 100g
Sample consolidation	Water pH 7	2,4,6,8 or 10% w/w relative to the base material
Carbonate solubility	pH 3 hydrochloric acid solution	2,4,6,8 or 10% w/w relative to the base material
Bonding materials	Commercial amide wax of type N,N-bis-stearyl ethylenediamine	5% w/w or 10% w/w relative to the base material
	Stearic acid powder	
	Slow setting gypsum powder	
	Fast setting gypsum powder	

Source: from author

After this, the resulting blend was placed inside the cylindrical metallic vessel, which had previously been lubricated with an ethyl alcohol solution containing 1% w/w stearic acid powder. The dimensions of this vessel were 3.77 cm internal diameter, 3.00 cm thickness and 13.00 cm height and the dimension of the piston were 3.75 cm diameter and 15.90 cm height. A load (200 kN) was applied with controlled velocity (25mm/min) two times. Subsequently, the resulting consolidated sample was placed for 1 hour into an oven at 100°C to guarantee a drier and higher consolidation based on CaCO_3 solubility. After that, samples were exposed to room temperature. Photographic register of the samples was taken at 0, 1 and 120 hours after removing from compression moulding.

4.3 METHODOLOGIES TO EVALUATE SYNTHETIC PLUGS

4.3.1 Immersion tests

120 hours after removing from compression moulding, samples were submitted to a water immersion test for 12 hours to evaluate their stability related to consolidation. The main aim was to verify if such samples would not have disintegrated in this medium, which can be used in routine plug tests such as spontaneous imbibition, fluid displacement and saturation tests (GAAFAR et al., 2015). Photographic register of samples was done during, and 1 hour after the test. After the test, the samples were handled to verify their consolidation.

4.3.2 Wettability measurements

Air-water and air-mineral oil contact angle measurements were done using a DSA 100 Kruss drop shape analyzer at room pressure and temperature conditions. Measurements were done on samples with a disk geometry. A drop of distilled water or mineral oil was placed on the flat surface of the sample and the contact angle was measured immediately and after 10 seconds.

4.3.3 Gas porosimetry

Gas porosimetry is a technique based on the gas expansion which allows the measurement of either pore or grain volume, grain density and permeability of a rock sample (DE OLIVEIRA et al., 2016). Before the test, synthetic plugs of full size (Figure 4, the part A) were dried for 24 hours in an oven at 60°C with controlled humidity of 45%. Plugs were submitted to porosity and permeability gas (nitrogen) test with a confinement pressure of 2400 psi in an Ultrapore 300 porosimeter and Ultraperm 500 permeameter. Klinkenberg effect was corrected to obtain porosities and permeabilities results. Grain density is a measure of mass per unit of volume of the elemental composition and internal bonding materials of rocks (Schön, 2011). From this technique grain density can be also obtained.

4.3.4 Mercury injection porosimetry

A Micromeritics AutoPore IV mercury porosimeter was used to estimate the pore size distribution of the synthetic samples, porosity, permeability and grain density. Due to the limitation of sample size of the technique, full size plugs cannot be analyzed. In this sense, from plugs of full size used for the gas porosimetry test, it was necessary to extract a fragment rock to be study. For this reason, plugs were cut in 3 disk of 13.3 ± 0.1 mm height and extracted a fragment rock of 20 ± 0.1 mm width from the central disk. (Figure 4, the part B). Synthetic plugs were cutting off carefully to avoid alterations of the pore space. After this, extracted fragments were dried for 24 hours in an oven at 100°C and weight. This value was used as input data in the porosimeter software. A maximum intrusion mercury pressure of 40000 psi was used in all the tests.

4.3.5 Theoretical porosity calculus

In addition to gas and mercury porosimetry tests, the theoretical porosity value was used as an approximation to the expected porosity and it was used to be compared with the experimental results and calculate the deviation of the measures. It should be noted

that experimental tests only access to the connected pores, in other words, the effective porosity.

Theoretical porosity was calculated as follow:

- a) Calculus of the volume of the synthetic plugs, based on the measured diameters and heights (equation 10).

$$v = \frac{\pi * d^2 * h}{4} \quad (10)$$

v = Volume of the synthetic plug (cm³);

d = Measured diameter of the synthetic plug (cm);

h = Measured height of the synthetic plug, (cm);

- b) Calculus of the mass of the previously calculated volume of the synthetic plugs, considering this as a homogeneous solid without porosity (equation 11).

$$ms = v * \rho \quad (11)$$

ms = Mass of the synthetic plug considered as a homogeneous solid without porosity (g);

v = Volume of the sample (cm³);

ρ = Average grain density of the synthetic plug (g/cm³);

- c) Calculus of the missing mass in the synthetic plug, considered as porous (equation 12).

$$mp = ms - m \quad (12)$$

mp = Missing mass in the synthetic plug, considered as porous (g);

ms = Mass of the synthetic plug considered as a homogenous solid without porosity (g);

m = Measured mass of the synthetic plug (g) ;

d) Calculus of the volume that should be occupied by the missing mass in the synthetic plug, considered as porous volume (equation 13).

$$vp = \frac{mp}{\rho} \quad (13)$$

vp = Porous volume (cm³);

mp = Missing mass in the synthetic plug, considered as porous (g);

ρ = Average grain density of the synthetic plugs (g/cm³);

e) Calculus of the expected porosity of the synthetic plug (equation 14).

$$\phi = \frac{vp}{v} * 100 \quad (14)$$

ϕ = Porosity (%);

vp = Porous volume (cm³);

v = Volume of the synthetic plug (cm³);

4.3.6 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis were conducted to determine the micro-structures and the identification of the surface elements in the samples. Surface images of a fragment plug size of 20 ± 0.1 mm width (Figure 4, the part B), cold-mounted (*embedded*) in epoxy resin were done at magnifications of 21x, 100x, 350x and 1000x by using a Stereoscan 440 LEO.

4.3.7 Micro-computed tomography (micro-CT)

A micro-computed tomography was used as nondestructive method of image acquisition. It was analyzed a sub-sample extracted of the plug of real size Figure 4 the part b, using a micro-CT Xradia versa xrm 510, with objective lens of 4x, 160 kV and 10W to observe the internal distribution of the materials used to construct the synthetic plugs.

Figure 4- Fragments rocks used to characterization analysis. (a) Synthetic plug of full size used to gas porosimetry test; (b) Fragments extracted from the central part of the synthetic plugs, used to MIP and Micro-CT test.

Source: from author

5 RESULTS AND DISCUSSIONS

5.1 MATERIALS CHARACTERIZATION

Firstly, it was corroborated the chemical composition of the dolomitic carbonate rock used to construct the synthetic plugs. Table 5.1 presents the chemical composition of the used dolomitic carbonate, obtained by X-ray spectrometry fluorescence. It is emphasized that according to Souza and Bragança (2013), the high concentration of the compounds MgO (15.5%-17.2%), SiO₂ (4.51%-4.06%) and CaO (36.4%-33.8%) corresponds to dolomitic calcareous samples.

Table 5.1 - Chemical composition of the dolomitic carbonate used to construct synthetic plugs.

Chemical composition	Sample 1	Sample 2
Na ₂ O	<0,001	0,059
MgO	15,5	17,2
Al ₂ O ₃	0,765	0,652
SiO ₂	4,51	4,06
P ₂ O ₅	0,014	0,018
SO ₃	0,033	0,089
Cl	0,021	0,014
K ₂ O	0,064	0,205
CaO	36,4	33,8
TiO ₂	0,043	0,028
Cr ₂ O ₃	0,011	0,012
MnO	0,103	0,046
Fe ₂ O ₃	0,564	0,579
NiO	<0,001	0,006
ZnO	0,024	<0,001
SrO	0,018	0,014
ZrO ₂	0,044	0,002
Nb ₂ O ₅	0,029	0,014
LOI	41,9	43,2

Source: from author

After the corroboration of the chemical composition of the mentioned dolomitic carbonate rock, samples were disintegrated and particle size controlled by a sieve. Figure 5 presents the resulting particle size.

Figure 5 - Particle size ranges used to construct samples with a disk and plug geometry.

Particle Sizes (mm)				
0.3-0.6	0.15-0.3	0.074-0.15	0.02-0.074	<0.02

Source: from author.

In addition, as mentioned previously, it was necessary to pulverize quantities of 0.02-0.074 mm granulometry to obtain higher quantities of the finest particle (<0.020 mm). Figure 6 shows the low angle laser light scattering measurement results of this particle size (percentage of volume versus size of particle, and accumulated percentage of the volume analysed). From this figure, it can be determined that according to the distribution of particle size, the material analysed has a particle size less than 0.020 mm. Therefore, it was concluded that the described procedure of pulverization of the sample is correct to obtain this specific finest particle.

Figure 6 - Particle size distribution of pulverized fraction.

Source: from author.

5.2 CONSTRUCTION AND EVALUATION OF THE SYNTHETIC PLUGS

The first disks geometry samples were constructed using a unique particle size and uniaxial compression, in order to observe the effect of the particle size in the consolidation.

Figure 7 presents this exploratory samples after 120 hours of their construction. From this test, fragile disks with varying consolidation were observed, which was improved with a decrease in the particle sizes. This consolidation behavior can be explained probably due to favorable material agglomeration. This first exploratory test demonstrated a promising preliminary result regarding the construction of real size plugs.

Figure 7 - Resulting disks varying the unique particle size at drying temperature 25°C, without using water content and additional bonding material. Uniaxial compression (200 kN; 25 mm/min). After 120 hours of construction.

Source: from author.

Based on the previous results, the following samples were constructed using the proposed CaCO_3 solubility. Aiming to evaluate the effect of these new parameters on plug consolidation, the pH effect was verified by adding distilled water content with pH values of 3 and 7 (2 to 10 w/w relative to the base material) to the 5 g particle size material, followed by mixing for 1 minute before the compression process. The acidity of the water was achieved by using diluted hydrochloric acid solution.

The mixture was submitted to the same uniaxial compression used on previous exploratory tests. Load force and compression times used were fixed aiming to guarantee an experimental reproducibility, and compare the resulting plugs with exploratory ones. These samples were dried at room temperature (25 °C). Figures from the appendix A present all of the constructed disks, at 0 and 120 hours after the consolidation process. Figure 8 presents some of the resulting disks, in order to illustrate the following analysis.

The consolidation behavior, again, present a tendency to improve with decreasing particle size. Figure 8, the part a and b present a resume of this improved consolidation corresponding to the decrease of particle size for disks with the same number of water content (8% w/w) with a pH value 3 and 7. In addition, it was noted an effect of the time of sample drying on the consolidation behavior, getting worse over time. It is due to temporary sample consolidations caused by the presence of humidity. On the other hand, comparing the Figure 8 the parts a and b, a possible calcium carbonate dissolution when

using acid water content (pH 3), followed by its probable precipitation, led to a more effective consolidation, even after 120 hours. In this way, the use of acid water would be the most beneficial way for the construction of samples, even when using larger particle sizes.

Figure 8 the part c presents a resume of the consolidation sample behavior due to the content of water pH 7. From here, it was observed that few (2 and 4% w/w) or more (8 and 10% w/w) did not generate good material consolidation. This trend may be due to the amount of water not being enough to impregnate all of the particle surface, or the content of water being too much to allow good material handling, turning it into a very weak sample. Therefore, with water content of 6% w/w the material was not excessively humid, and the total impregnation of its particles was possible, causing a homogeneous solubility (in the case of acidic pH) and material consolidation. Finally, water content of 6% w/w, pH=3 and particle size <0.02 mm seemed to generate the best disk consolidations

Figure 8 – The part a and b presents the resulting disks varying the unique particle size at drying temperature 25°C, using 8% w/w of water content at pH 7 (A) and at pH 3 (B); uniaxial compression (200 kN; 25 mm/min); without using bonding material; after 0 and 120 hours of construction. The part c presents the resulting disks from the unique particle size 0.3-0.6 mm; from 2% to 10% w/w of water content at pH 7 and drying temperature 25°C; uniaxial compression (200 kN; 25 mm/min); without using additional bonding material. After 0 and 120 hours of construction.

A.

B.

C.

Source: from author.

Next, the constructions were also performed by using a drying temperature of 100 °C for 1 hour. Figures from the appendix B present all the constructed disks at 0 hours (after removing from compression moulding), 1 hour (after drying process at 100°C) and 120 hours (after the consolidation process).

Figure 9 presents a resume of this figures from appendix B, comparing constructed disks after 120 hours of construction, with particle size (0.074-0.150 mm), water content from 2 to 10 % w/w, pH value 7 and drying temperatures of 25°C and 100°C. From these samples, it was observed a positive influence on the consolidation of the material due to

high drying temperatures. In this sense, samples with high drying temperatures (100 °C) present a tendency to have a better consolidation than those with dried at room temperature (25 °C). In addition, it is believed that due to the high temperature (100 °C), a lower content water was retained within the sample. This made it possible to guarantee a drier and more definitive consolidation.

Figure 9 - Resulting disks from the unique particle size 0.074-0.150 mm; content water from 2 to 10% w/w at pH 7; uniaxial compression (200 kN; 25 mm/min); without using additional bonding material; after 5 days of construction; drying temperature 25°C (A) and 100°C (B).

A.

B.

Source: from author.

Given the previous findings, a sample with a plug geometry were manufactured. For this reason, the construction conditions selected to guarantee a good consolidation were: the finest particle size material (<0,020 mm), 6% w/w of water content at pH 3 and drying temperature of 100°C. The first synthetic plug of real size is presented in Figure 10. Scratches on the lateral surface were observed, which seem to compromise the structure of the material. These samples were sanded (sandpaper N° 600), where it was observed that the scratches were superficial and therefore, did not affect the internal structure of the sample. It is notable that this sample presented a good consolidation

before and after the sanding, confirming a good choice of the construction materials and method.

Aiming to evaluate the basic petrophysical properties, samples were submitted to porosity and permeability gas (nitrogen) test with a confinement pressure of 2400 psi in an Ultrapore 300 porosimeter and Ultraperm 500 permeameter, both from Corelab. For the synthetic plug, a porosity of 25.19% $\pm$ 1% was obtained, and mean absolute permeability was 0.073 mD $\pm$ 0.022 mD. This high porosity and low permeability can be explained as the result of small internal pores in the structure of the sample. On the other hand, due to the undamaged condition of the samples after the application of the high confinement pressure of 2400 psi, it was concluded that sample presented good consolidation. Additionally, grain density of this synthetic plug was calculated in order to compare the dolomite rocks value of 2.84 g/cm³ from literature (D.M.D., 2018). In this sense, it was found a grain density for this synthetic plug of 2.87 g/cm³, corroborating the similarity of the synthetic sample with the natural ones.

Figure 10 – Resulting synthetic carbonate plug of real size, using the unique particle size <0,020 mm; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100 °C for 1 hour; without using additional bonding material.

Source: from author.

Based on the observed consolidation behavior of the samples due to the use of a unique particle size, it was studied the consolidation behavior of the samples due to the use of a combination of particle sizes. In this sense, samples with disk geometry was constructed with the proposed particle size ratios (1:1, 1:2 and 1:3 w/w), the finest (<0.02:0.02-0.074 mm) and thickest (0.15-0.3:0.3-0.6 mm) particle sizes, 6% w/w of water content at pH 3 and drying temperature 100°C for 1 hour, using a uniaxial compression (200 kN; 25 mm/min) and without using additional bonding material. Figure 11 presents these resulting disks.

From here, considering the same particle size mixture, it was evident that a higher proportion of fines led to a tendency to obtain better consolidated disks, seen with the ratio 1:1 (w/w) shown in Figure 11, 120 hours after removing from compression moulding. The use of a higher fine particle content favors material agglomeration, improving the consolidation of samples. Figures from appendix C presents all these constructed disks, demonstrating the same tendency.

Figure 11 - Resulting disks with the finest (<0.02 : 0.02-0.074 mm) and thickest (0.15-0.3 : 0.3-0.6 mm) particle sizes, using the particle size ratios 1:1, 1:2 and 1:3% w/w; 6 % w/w of water content at pH 3; drying temperature 100°C for 1 hour; uniaxial compression (200 kN; 25 mm/min); without using additional bonding material. After 120 hours of construction.

Source: from author.

To evaluate the wettability behavior due to different particle size ratios of these first disk samples, air-water and air-mineral oil contact angle measurements were carried out at times 0 and 10 seconds of the drop deposition. An example of these measurements is presented in Figure 12 for the disks with the finest (<0.02 : 0.02-0.074 mm) and thickest (0.15-0.3 : 0.3-0.6 mm) particle sizes, using the particle size ratio 1:2, 6% w/w of water content at pH 3 and drying temperature 100°C, uniaxial compression (200 kN; 25 mm/min) without using additional bonding material and after 120 hours of the sample construction.

For both water and oil drops, disks constructed with the finest particle size present a tendency to obtain higher contact angles at 0 seconds and decrease with the time. In contrast, disks constructed with the thickest particles, show water contact angle value of zero over time. Oil drops present greater contact angles and a slower contact angle decrease with time.

Figure 12 Resulting air-water and air-mineral oil contact angle measurement at times 0 and 10 seconds of the disks with the finest (<0.02 : 0.02-0.074 mm) and thickest (0.15-0.3 : 0.3-0.6 mm) particle sizes; particle size ratio 1:2; 6% w/w of water content at pH 3; drying temperature 100°C for 1 hour; uniaxial compression (200 kN; 25 mm/min); without using additional bonding material; measurements obtained after 120 hours of the sample construction.

		Particle Sizes (mm) at Ratio 1:2			
		<0.02 : 0.02-0.074		0.150-0.3 : 0.3-0.6	
		Water drop	Oil drop	Water drop	Oil drop

Contact Angle Measurement at Time (s)	t = 0	8.6°	10.0°	0°	11.8°
	t = 10
	t = 10	0°	0°	0°	10.6°

Source: from author.

Probably, absorption of water by the sample influenced the measurement. A contact angle of zero was caused by this absorption instead of the spreading of the water drop. This is in contrast to the oil drop behavior in which no absorption was observed. From these preliminary results, such samples are not indicated as suitable to represent the wettability behavior of carbonate samples based on contact angle measurements, from a known intermediate to oil-wet behavior (PIZARRO; BRANCO, 2012; MANRIQUE et al., 2004; MASALMEH et al., 2014; AL-DHAHLI et al., 2011; AKKURT et al., 2000). It based to the known air-water contact angles, where a value lower than 55° is relative to a water-wet surface (GRATE et al., 2012). Figure from appendix D, presents all the contact angle measurements, showing this same tendency

Subsequently to the contact angle measurements, water immersion tests were carried out on the preliminary disk samples. To this end, based on the presented results from Figure 11, the better consolidated disks were selected (particle sizes $<0.02\text{mm}$: 0.02 - 0.074mm , ratio 1:1, 6% w/w of water content at pH 3, drying temperature 100°C for 1 hour, uniaxial compression (200 kN; 25 mm/min), without using additional bonding material). The disks were placed into a glass flask which was then filled with water. From there, as presented in Figure 13, it was noted that the previous proposed methodology to construct the samples does not guarantee the consolidation of the samples when immersed in a water medium, probably due to the lack of cementing of the particles. Due to this challenge, it was necessary to improve this consolidation methodology aiming for both better consolidation and stability in a water medium and wettability behavior closer to natural carbonates from a reservoir.

Figure 13- Photograph register obtained during and after water immersion on disks constructed with particle size $<0.02:0.02-0.074$ mm; particle size ratio 1:1 w/w; 6% w/w of water content at pH 3; drying temperature 100°C for 1 hour; uniaxial compression (200 kN; 25 mm/min); Without additional bonding material. The test was carried out after 120 hours of construction.

Source: from author

To this end, some bonding materials were selected to construct other disks using the same previously parameters (particle sizes $<0.02\text{mm}:0.02-0.074\text{mm}$, ratio 1:1, 6% w/w of water content at pH 3, drying temperature 100°C for 1 hour, uniaxial compression (200 kN; 25 mm/min), using additional bonding material with content of 5% and 10% w/w relative to the base material). The bonding materials used were slow setting gypsum powder, fast setting gypsum powder, amide wax of type N,N-bis-stearyl ethylenediamine powder and Stearic acid powder, following the content given in Table 4.2. Figure 14 shows the photographic register of these samples 120 hours after removing from compression moulding, where it was possible to observe a good consolidation, even during handling for all samples, except when using the two kinds of gypsum powder at 5% w/w content relative to the base material.

Figure 14- Resulting disks with the finest particle sizes $<0.02 : 0.02-0.074$ mm; particle size ratio 1:1 w/w; 6% w/w of water content at pH 3; uniaxial compression (200 kN; 25 mm/min); drying temperature 100°C for 1 hour; using different bonding materials and varying content of 5% and 10% w/w relative to the base material; after 120 hours of construction.

Source: from author.

Water immersion and contact angle measurements were also carried out on the disk samples constructed using bonding materials. Figure 15 shows a summary of these samples 1 hour after the 12-hour water immersion test where only the ones constructed using stearic acid powder and commercial amide wax powder were stable, even under handling.

Figure 15 – Photograph register obtained 1 hour after 12 hours of water immersion on disks constructed with particle size <0.02:0.02-0.074 mm; particle size ratio 1:1 w/w; 6 % w/w of water content at pH 3; drying temperature 100°C for 1 hour; uniaxial compression (200 kN; 25 mm/min). Different bonding materials and varying content of 5% and 10% w/w relative to the base material; the test was carried out after 120 hours of construction.

Source: from author.

Disks constructed with Stearic acid and commercial amide wax were chosen to evaluate wettability. Results are presented in Figure 16. A tendency to generate higher contact angles for water was observed with both bonding materials, and not changes was observed to the oil. For commercial amide wax, higher water contact angles were obtained when using the higher (10%) content of bonding materials. To interpret these results, it is considered that an intermediate wettability is relative to air-water contact angles in the range of approximately 55° to 80°, while values lower than 55° or higher than 80° are relative to water-wet and oil-wet, respectively, as shown by Grate et al. (2012). In this sense, the obtained sample disks show an intermediate wetting behavior which is closer to the known intermediate and oil-wet carbonates from oilfields (PIZARRO; BRANCO, 2012; MANRIQUE et al., 2004; MASALMEH et al., 2014; AL-DHAHLI et al., 2011; AKKURT et al., 2000).

Figure 16- Resulting air-water and air-mineral oil contact angle measurement at times 0 and 10 seconds of the disks constructed with the finest <0.02:0.02-0.074 mm particle size; particle size ratio 1:1 w/w; 6 % w/w of water content at pH 3; drying temperature 100°C for 1 hour; uniaxial compression (200 kN; 25 mm/min); different bonding materials and varying content of 5% and 10% w/w relative to the base material; measurements obtained after 120 hours of the sample construction.

		Commercial amide wax 5% w/w		Commercial amide wax 10% w/w	
		Water drop	Oil drop	Water drop	Oil drop
Contact Angle Measurement at Time (s)	t = 0 sec.
		63.1°	6.8°	75.8°	7.3°
	t = 10 sec.
		52.6.°	0°	70.4°	4.9°
	Stearic acid powder 5% w/w		Stearic acid powder 10% w/w		
		Water drop	Oil drop	Water drop	Oil drop
		t = 0 sec.
	113.1°		2.1°	118.45°	8.4°
	t = 10 sec.
		112.5°	0.0°	116.6°	7.1°

Source: from author.

That fact, in addition with the better consolidation of the samples observed in the previous step, justifies the use of bonding materials to construct synthetic plugs to reproduce wettability properties. Therefore, in order to use a minimum content of bonding material while keeping an intermediate wettability of the synthetic plug, commercial amide wax powder at 5% w/w was selected to construct real size plugs.

Figure 17 presents a summary of the constructed plugs, using the finest (mm) $<0.02:0.02-0.074$ and the thickest (mm) $0.150-0.3:0.3-0.6$ particles sizes, particle sizes ratios 1:1, 1:2 and 1:3 w/w, commercial amide wax powder at 5% w/w as a bonding material relative to the base material, 6% w/w of water content at pH 3, uniaxial compression (load 200 kN; 25 mm/min) and drying temperature 100 °C for 1 hour. From these plugs was observed good consolidation for all the cases (3 ratios using thickest and finest particles sizes). In addition, samples did not present visual lateral surface scratches were not observed.

Figure 17- Resulting synthetic carbonate plug of real size, using the finest (mm) $<0.02:0.02-0.074$ and the thickest (mm) $0.150-0.3:0.3-0.6$ particles sizes; particle sizes ratios 1:1, 1:2 and 1:3 w/w; using commercial amide wax powder at 5% w/w as a bonding material relative to the base material; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100 °C for 1 hour; after 120 hours of construction.

Source: from author.

Given the previous findings, a final wettability study was developed in the samples obtained in the Figure 17 to observe contact angle changes due to the mixture of particle size and commercial amide wax powder. Figure 18 presents these results. A tendency to obtain greater contact angles from water drops compared with oil drops was observed, probably due to the presence of the organic character of the bonding material. In addition, in comparison with the plugs constructed without bonding material, water contact angles for both particle mixtures decreased slowly with time, indicating slower water absorption due to the presence of the commercial amide wax powder.

Plugs constructed with the thickest particles show water contact angle greater than ones with the finest particles. In this study, different visual surface roughness was observed relative to the particle size used to construct them, i.e. the more roughness was observed when using the thickest particles sizes. Alotaibi (2010) explains that solid surface will affect the contact angle due to the roughness and heterogeneity of the solid surface. In this sense, further studies relating surface roughness of the constructed plugs and contact angles need to be developed.

Figure 18- Resulting air-water and air-mineral oil contact angle measurement at times 0 and 10 seconds of the synthetic carbonate plug of real size with the finest (mm) <0.02:0.02-0.074 and the thickest (mm) 0.150-0.3:0.3-0.6 particles sizes; particle sizes ratios 1:1, 1:2 and 1:3 w/w; commercial amide wax powder at 5% w/w as a bonding material relative to the base material; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100°C for 1 hour; measurements obtained after 120 hours of the sample construction.

		Particle Size <0.02:0.02 - 0.074 at ratio 1:1		Particle Size 0.150 - 0.3 : 0.3 -0.6 at ratio 1:1	
		Water drop	Oil drop	Water drop	Oil drop
Contact Angle Measurement at Time (s)	t = 0
		63.1°	6.8°	87.6°	0°
	t = 10
		52.6°	0°	70.35°	0°
		Particle Size <0.02:0.02 - 0.074 at ratio 1:2		Particle Size 0.150 - 0.3 : 0.3 -0.6 at ratio 1:2	
	t = 0
		58.1°	6.5°	84.8°	9.6°
	t = 10
		33.2°	0°	57.8°	9.1°
		Particle Size <0.02:0.02 - 0.074 at ratio 1:3		Particle Size 0.150 - 0.3 : 0.3 -0.6 at ratio 1:3	
	t = 0
		57.3°	7.2°	87.9°	10.2°
	t = 10
		40.5°	6.4°	27.1°	9.7°

Source: from author.

Regarding the petrophysical properties, as will be shown later (Figure 19 and Table 5.2), it was selected 8 of the 30 synthetic plugs construction condition, based on the particle size and particle size ratio. These plugs were analyzed in duplicate in order to study the reproducibility of the petrophysical properties. Additionally, one of the selected samples were constructed without using commercial amide wax as bonding material to study its influence on petrophysical measurements.

Figure 19 presents these synthetic plugs, and the geometry of these plugs (diameter and height) and mass were measured in triplicate and resultant values presented in the Table 5.2.

Figure 19- Resulting synthetic carbonate plug of real size; using particle sizes (mm) <0.02:0.02-0.074, 0.02-0.074:0.074-0.15, 0.074-0.15:0.15-0.3, 0.15-0.3:0.3-0.6; particle size ratios 1:1 and 1:3 w/w; commercial amide wax powder at 5% w/w as a bonding material relative to the base material; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100 °C for 1 hour; after 120 hours of construction.

Source: from author.

Table 5.2 - Diameters and heights of the constructed synthetic plugs presented in the Figure 19.

Sample	Diameter (cm)	Height (cm)	Mass (g)
P1	3.77	4.43	105.0371
P2	3.77	4.43	104.2059
P3	3.77	4.23	105.0045
P4	3.77	4.22	104.1730
P5	3.77	4.15	105.2482
P6	3.77	4.15	104.7904
P7	3.77	4.10	104.7259
P8	3.77	4.11	104.9851
P9	3.77	4.40	105.5181
P10	3.77	4.11	99.4521
P11	3.77	4.20	105.6383
P12	3.77	4.19	104.4206
P13	3.77	4.15	104.7029
P14	3.77	4.15	104.3889
P15	3.77	4.06	104.4053
P16	3.77	4.07	104.4175

Source: from author

Grain density of the synthetic plugs were measured by gas and mercury porosimetry and are presented in the Table 5.3. It is expected that the main contribution to the grain density of the synthetic plugs corresponded to the base material used to construction. Thus, the expected grain density corresponds to the related in the literature for dolomite rocks $2,84 \text{ g/cm}^3$ (D.M.D., 2018). Due to the low density of the wax, synthetic plugs using bonding material showed lower grain density in comparison with the one constructed without it. This expected behavior was confirmed with the resultant grain densities by gas and mercury porosimetry, where samples with bonding material shows an average of $2,64$ and $2,62 \text{ g/cm}^3$, and sample without bonding material (P10) of $2,87$ and $2,84 \text{ g/cm}^3$, respectively.

Table 5.3 presents the theoretical (item 4.3.5) and experimental petrophysics results obtained by gas and mercury porosimetry and its relative error, based on the theoretical value. From here, based on the theoretical porosity calculated for synthetic plugs with bonding material, it was observed expected values from 12.99% to 19.88% for particle size ratio 1:1 and 12.41% to 18.31% for particle size ratio 1:3. In this sense, it was not observed evidences of relationship between porosity and the particle size ratios.

Subsequently, a tendency to the decreasing of porosity with the decrease of particle sizes used to construct the synthetic plugs was observed. Considering the previously explained calculus, theoretical porosity has a direct relationship with the volume of the sample and grain density. In this sense, considering that all the constructed synthetic plugs have a similar grain density, the calculated porosity was influenced by the observed decreasing heights (Table 5.2) with the increasing of the particle size. It due to the packing of the particles used to construct the synthetic plugs. In this way, the largest the particle size, the higher the difference of size between particles. It causes a better pack of the smaller particles into the empty spaces between the larger particles, thus reducing the bulk volume occupied by the particles. Additionally, it is important to mention that comparing the synthetic plugs with and without (P10) bonding material, it was observed that maximum porosities are obtained in the absence of the commercial amide wax, with a value of 19,71%, probably because the bonding material is not entering into the pore spaces of the plug.

To generate a better understand of the pore structure and therefor porosities and permeabilities, the correlation between experimental tests were discussed following.

Based in the observed tendency of theoretical porosity, it was analyzed the experimental petrophysical results obtained from gas and mercury porosimetry. The same tendency to decrease porosity with the decreasing of particle sizes used to construct the synthetic plugs was observed for the experimental test. In this way, porosities of the constructed plugs with bonding materials was found from 10.43% to 17.23% and 10.32% to 14.67% for particle size ratio 1:1 and 1:3 w/w respectively, based on the gas porosimetry and values from 11.27% to 19.96% and 11.39% to 15.36% for particles size ratios 1:1 and 1:3 w/w respectively, based on the mercury porosimetry. Additionally, it was observed higher relative errors from the gas porosimetry compared to the mercury porosimetry. It can be due probably to the higher intrusion pressure applied by the mercury porosimetry than gas porosimetry, allowing the identification of smaller pore sizes.

On the other hand, based on the permeability results obtained by the two experimental techniques, it was observed a tendency to increase permeabilities with the

increasing of particle size, contrary to the found for the porosity. To explain these behaviors, pore size distribution was studied.

Table 5.3 – Grain density, theoretical and measured porosities and permeabilities of the constructed synthetic plugs presented in the the Figure 19.

Particle size ratio	Sample	Theoretical porosity (%)	Gas porosimetry				Mercury porosimetry			
			Grain density (g/cm ³)	Porosity (%)	% Rel. Error	Permeability (mD)	Grain density (g/cm ³)	Porosity (%)	% Rel. Error	Permeability (mD)
1:1	P1	19.24	2.63	17.07	11,28	0.073	2.6019	19.96	3,74	0.021
	P2	19.88	2.63	17.23	13,33	0.093				
	P3	15.45	2.64	13.18	14,69	0.461	2.5915	13.77	10,87	0.077
	P4	15.92	2.61	13.77	13,51	0.450				
	P5	13.62	2.65	11.72	13,95	0.600	2.6044	12.77	6,24	0.140
	P6	13.99	2.61	12.11	13,44	0.578				
	P7	13.00	2.63	10.66	18,00	0.671	2.6466	11.27	13,31	0.274
	P8	12.99	2.64	10.43	19,71	0.723				
1:3	P9	18.31	2.64	14.67	19,88	0.131	2.6354	15.36	16,11	0.038
	P10	19.71	2.87	22.19	12,58	1.112	2.843	25.62	29,98	0.317
	P11	14.33	2.65	12.04	15,98	0.423	2.6317	14.21	0,84	0.099
	P12	15.11	2.62	13.27	12,18	0.397				
	P13	14.06	2.66	10.85	22,83	0.656	2.6781	14.78	5,12	0.353
	P14	14.32	2.63	11.40	20,39	0.524				
	P15	12.41	2.64	10.47	15,63	0.717	2.6065	11.39	8,22	0.289
	P16	12.61	2.64	10.32	18,16	0.683				

Source: from author

Pore size distribution was studied using the mercury porosimetry by cumulative mercury injection volume with gradual increasing pressures. Figure 20 presents the resulted pore size distribution of samples constructed using bonding materials and particle size ratios of 1:1 and 1:3 w/w. It demonstrates that most pore size lay in the in the micro-range of 0.01-10 μm . From this result, it was observed in the two particle size ratios increases of the pore size distribution with the increasing of the particles size used to construct the synthetic plugs. This pore size behavior, in addition with the found porosities and permeabilities, can be explained by: the previously mentioned packing of the particles and the accessibility to previously closed pores into the particles due to the reduction of the particle size. In this sense, these two factors may be causing the increasing of porosity, decreasing of pore size distribution and therefore, decreasing of permeability of the synthetic plugs with the decreasing of the particle size used to construct the synthetic plugs.

Figure 20 - Pore size distribution of the synthetic plug constructed presented in the Figure 19 with particle size ratio 1:1 (a) and 1:3 (b); measurements obtained after 120 hours of the sample construction.

Source: from author

On the other hand, in order to get detailed understanding of the internal distribution of the bonding material in the synthetic plugs, one sample were examined by SEM. In this way, it was selected a plug from Figure 19 with the thickest particle size 0.15-0.3:0.3-0.6 mm, particle size ratio 1:1 w/w, commercial amide wax powder at 5% w/w as a bonding material relative to the base material, 6% w/w of water content at pH 3, uniaxial compression (load 200 kN; 25 mm/min) and drying temperature 100 °C for 1 hour. From this sample, a sub sample were extracted as shown in Figure 4 to acquire the SEM images.

The microchemical analyses of the acquired images by backscattered electron and secondary electron are presented in the Figure 21. From this analyzes, in the part a of the Figure 21, it was selected four points based on different density and atomic number.

The lower the density and atomic number, the higher the gray-black color in the acquired image. As expected, from points 1, 2 and 4 selected in the part a of the Figure 21, it was observed higher content of calcium, magnesium and oxygen, fact that represent the nature of the dolomitic carbonate used as base material to construct the synthetic plugs. Additionally, the point 3 presented the material with lower atomic number. The higher content of carbon on this point, may be due to the nature of the commercial amide wax used to construct the plugs, in addition to the epoxy resin in a porous area. In addition, it was focusing the area where probably bonding material is located. Figure 21 the part b, present this characterization. From here, it was observed the presence of chlorine at point 2, which may be related to the epoxy resin where the sample as embedded, whereas in the point 1 it was not identified, corroborating the presence of the wax and epoxy resin in a porous area. Additionally, based on the acquired image it was observed the probably presence of voids in this same porous area that may represent porous into the bonding material.

Figure 21- Microchemical analysis of acquired image by the SEM analysis using backscattered electron (a) and secondary electron (b) of sub-samples extracted from the synthetic carbonate plug of real size presented in the Figure 19 with the thickest 0.15-0.3:0.3-0.6 mm particle size; particle size ratio 1:1 w/w; commercial amide wax powder at 5% w/w as a bonding material relative to the base material; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100 °C for 1 hour; measurements obtained after 120 hours of the sample construction.

a.

b.

Source: from author.

Acquisition images from micro tomography were carried out in order to observe the internal distribution of the particle rocks and bonding material into the samples. Two samples were selected from the manufactured in the Figure 19: samples constructed with the finest ($<0.02:0.02-0.074$ mm) and the thickest ($0.15-0.3:0.3-0.6$ mm) particle sizes, particle size ratio 1:1 w/w, commercial amide wax powder at 5% w/w as a bonding material relative to the base material, 6% w/w of water content at pH 3, uniaxial compression (load 200 kN; 25 mm/min) and drying temperature 100 °C for 1 hour. From these samples, sub samples were extracted as shown in the Figure 4 to acquire the micro-CT images.

The acquired images from this technique are presented in the Figure 22. From the processing of the acquired images from the micro-CT, it was separated the two conformant elements of the synthetic plugs: the disintegrated rock and the bonding material. Based on the previous SEM analyses, it was adopted that the first is in grayscale and the latter in color blue. From here, it was observed homogeneous distribution of the bonding material in the samples with coarse particles size and larger conglomerates in the samples with the finest particle. Probably, it occurs due to the packing of the rock particles causing different distributions of the bonding material. From another approach, this evidence may be caused due to a poor mixture of the used elements to construct the

synthetic plugs. In this sense, it could be improved with the enhancing of the preparing methodology to construct synthetic plugs, specifically when used finest particle sizes.

Figure 22 - Acquired micro-CT images of sub-samples extracted from the synthetic carbonate plug of real size presented in the Figure 19 with the finest $<0.02:0.02-0.074$ mm (a) and the thickest $0.15-0.3:0.3-0.6$ mm (b) particle sizes; particle size ratio 1:1 w/w; commercial amide wax powder at 5% w/w as a bonding material relative to the base material; 6% w/w of water content at pH 3; uniaxial compression (load 200 kN; 25 mm/min); drying temperature 100 °C for 1 hour; measurements obtained after 120 hours of the sample construction.

Source: from author.

This study demonstrates the promising construction of carbonate synthetic plugs as an alternative to the well-known difficulty of obtaining reservoir plugs samples as well as the importance of synthetic plugs to understand reservoir behavior. The following approach was made to contribute to the construction of further samples.

Gas porosimetry results were selected to be plotted versus a combination of particle size, represented by the numbers 1 to 4: **1.** <0.02 mm : $0.02-0.074$ mm; **2.** $0.02-$

0.074 mm : 0.074 – 0.15 mm; **3.** 0.074-0.15 mm : 0.15-0.3 mm; **4.** 0.15-0.3 mm : 0.3-0.6 mm and particle size ratio 1:1 w/w (Figure 23) and 1:3 w/w (Figure 24). These petrophysical results were chosen because it allows to evaluate the synthetic plug of real size. In this sense, the obtained petrophysical results by gas porosimetry may represent a more faithful measurement of the whole volume.

The following procedure was constructed to use Figure 23 and Figure 24, in order to manufacture the synthetic carbonate plugs:

1. Select a petrophysical property to be reproduced by the synthetic plugs: porosity or permeability.
2. Select a value of porosity or permeability value to be reproduced.
3. Identify the selected porosity or permeability value in the graphs of particle size of ratio 1:1 w/w or 1:3 w/w.
4. Once the value is identified on the y axis, observe the associated value corresponding to the x axis.
5. Use the Table 5.4 to obtain the combination of particles size to be used in the construction of the synthetic plugs.

Table 5.4 – Identification of the particle size based on the identified number on the x axis from Figure 23 and Figure 24.

Identified number on the x axis	Particle size (mm)
1	<0.02 : 0.02-0.074
2	0.02-0.074 : 0.074 – 0.15
3	0.074-0.15 : 0.15-0.3
4	0.15-0.3 : 0.3-0.6

Source: from author.

6. Use the proposed combination of particle size in the construction of synthetic plugs. Note: The ratio to combine this particle size is relative to the graph used in the step 3.

7. Construct the synthetic plugs using the disintegrated carbonate rock matrix with the particle sizes and particle size ratios, water content of pH 3 (6% w/w relative to the base material), commercial amide wax as bonding material (5% w/w relative to the

base material), drying temperature of 100C for 1 hour, and uniaxial compaction with controlled load force (200kN) and velocity (25 mm/min).

Figure 23 – Proposed particle size combination to obtain specific petrophysical properties in the constructed synthetic plugs. Particle size ratio 1:1 w/w.

Source: from author

Figure 24 – Proposed particle size combination to obtain specific petrophysical properties in the constructed synthetic plugs. Particle size ratio 1:3 w/w.

Source: from author

6 CONCLUSIONS

In this study, consolidated synthetic carbonate plugs were obtained using disintegrated carbonate rock matrix with controlled particle sizes and particle size ratios, water content of pH 3 (6% w/w relative to the base material), commercial amide wax as bonding material (5% w/w relative to the base material), drying temperature of 100°C for 1 hour, and uniaxial compaction with controlled load force (200kN) and velocity (25 mm/min). The approach of construct disk samples was useful for the screening of the different parameters before the construction of the real size plugs.

Generally, it was observed that the porosity and permeability features of the synthetic plugs were within the range of carbonate reservoirs. However, without reproducing a heterogeneous pore structure normally present in natural samples. On the other hand, wettability properties of the resulted synthetic plugs were similar to the natural carbonate plugs.

Regardless the porous heterogeneous structure of natural carbonate samples, an attempt to relate particle size and petrophysical characteristics of the synthetic plugs was presented. In this sense, synthetic carbonate plugs can be reproduced correlating a disintegrated carbonate rock matrix.

Considering the limitations of the existing methodologies to construct synthetic carbonate plugs, the presented methodology demonstrates a promising way to be explored in order to generate further studies to understand carbonate oilfields. This promising result makes viable the construction of synthetic carbonate plugs and the use of this samples in laboratory tests where petrophysical properties of the sample are not a concern, which is not the case of core flooding tests.

7 FUTURE WORKS

With the purpose of construct a more representative plug similar to the natural ones, a combination of methodologies to generate heterogeneous pore structures and higher petrophysics properties should be explored. Additionally, it is suggested to use drilling cuttings from carbonate reservoirs as base material to construct synthetic plugs.

On the other hand, the constructed carbonate plugs should be compared with natural samples to evaluate the behavior of this synthetic samples in tests such as advanced petrophysics studies such as core flooding.

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APPENDIX A – Resulting disks varying the unique particle size (0.3-0.6 mm, 0.150-0.3 mm, 0.074-0.15 mm, 0.02-0.074 mm, <0.02 mm), ph (3, 7) and water content w/w (2,4,6,8,10) at drying temperature 25°C; uniaxial compression (200 kn; 25 mm/min). Without using bonding material. After 0 and 120 hours of construction. Source: from author. (5 pages)

		Particle size 0.3-0.6 mm with water content (w/w)				
		2	4	6	8	10
		pH 7				
Drying time (h)	t = 0
	t = 120
	pH 3					
	t = 0
	t = 120

		Particle size 0.150-0.3 mm with water content (w/w)				
		2	4	6	8	10
		pH 7				
Drying time (h)	t = 0
	t = 120
	pH 3					
	t = 0
	t = 120

		Particle size 0.020-0.074 mm with water content (w/w)				
		2	4	6	8	10
		pH 7				
Drying time (h)	t = 0
	t = 120
	pH 3					
	t = 0
	t = 120

		Particle size <0.020 mm with water content (w/w)				
		2	4	6	8	10
		pH 7				
Drying time (h)	t = 0
	t = 120
	pH 3					
	t = 0
t = 120

APENDIX B – resulting disks varying the unique particle size (0.3-0.6 mm, 0.150-0.3 mm, 0.074-0.15 mm, 0.02-0.074 mm, <0.02 mm), ph (3, 7) and water content w/w (2,4,6,8,10) at drying temperature 100°C; uniaxial compression (200 kn; 25 mm/min). Without using bonding material. After 0, 1 and 120 hours of construction. Source: from author. (5 pages)

APENDIX C – resulting disks varying the particle size (0.3-0.6 mm, 0.150-0.3 mm, 0.074-0.15 mm, 0.02-0.074 mm, <0.02 mm), particle size ratio (1:1, 1:2, 1:3); using ph 3 and water content 6 w/w at drying temperature 100°C; uniaxial compression (200 kn; 25 mm/min). Without using bonding material. After 0 ,1 and 120 hours of construction. Source: from author. (3 pages)

		Particle size (mm)					
		<0.02:0.3-0.6	<0.02:0.15-0.3	<0.02:0.074-0.15	<0.02:0.02-0.074	0.02-0.074:0.3-0.6	
Drying Time (h)	t = 0
	t = 1
	t = 120
			0.02-0.074:0.15-0.3	0.02-0.074:0.074-0.15	0.074-0.15:0.3-0.6	0.074-0.15:0.15-0.3	0.15-0.3:0.3-0.6
	t = 0
	t = 1
	t = 120

APENDIX D – resulting air-water and air-mineral oil contact angle measurement at times 0 and 10 seconds of the disks with the finest (<0.02 : $0.02-0.074$ mm) and thickest ($0.15-0.3$: $0.3-0.6$ mm) particle sizes; particle size ratio 1:1, 1:2, 1:3; water content 6 w/w; pH 3; drying temperature 100°C ; uniaxial compression (200 kN; 25 mm/min); without bonding material. Measurements obtained after 120 hours of construction. Source: from author. (1 page)

		Particle Size (mm) <0.02:0.02-0.074		Particle Size (mm) 0.150-0.3:0.3-0.6	
		Water drop	Oil drop	Water drop	Oil drop
Ratio 1:1					
Contact Angle Measurement at Time (s)	t = 0
		10.0°	0°	0°	17.6°
	t = 10
		0°	0°	0°	9.9°
	Ratio 1:2				
	t = 0
		8.6°	10.0°	0°	11.8°
	t = 10
		0°	0°	0°	10.6°
	Ratio 1:3				
	t = 0
		6.8°	10.1°	0°	9.1°
	t = 10
		0°	0°	0°	8.7°