INVESTIGATION OF NANO-POROSITY IN CARBONATE RESERVOIRS AND ITS ROLE IN UNDERSTANDING HYDROCARBON RESERVES AND RECOVERY ECONOMICS

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ABSTRACT

This study examines a Kuwaiti carbonate reservoir that is classified as a tight reservoir. In one core sample, the total porosity is reported to be 14%, of which 60% of its total porosity is estimated to be nano-pores. The objective of this study is to establish existence of these nano-pores and their whereabouts, and then investigates their nano-size role in hydrocarbon storage, economics and recovery mechanism.

Characterizing nano-pores available in tight carbonate reservoirs starts with examining the constituents of the rock such as, mineral type and composition of grain, pore-size, and pore-size distribution. Nano-pore characterization has integrated several tools such as X-Ray Diffraction (XRD), Scattered Electron Microscopy (SEM), and mercury-Washburn Pore Size Distribution (PSD). The XRD will examine the rock-fabric minerals associated with the nano-pores. The SEM analysis, which is a 2-dimensional scale technique, is associated with the study of the pore morphology as well as the study of the grain morphology; while the PSD is a 3-dimensional technique associated in measuring the total pore size distributions. As a result of integrating these tools, findings and subsequent inquiries are raised.

INTRODUCTION

The geological genesis, in this reservoir, has naturally fabricated some nano-systems. According to *Chmielewski (2006)* Nanotechnology focuses on manipulating arrangements between nano-features to form nano-systems – with unique physical, chemical and maybe biological properties. Nanotechnology deals with nano-materials (nano-systems) commonly smaller than 100 nano-meters in size (0.1 nm < nano-system <100 nm). The nano-system available in this reservoir is the nano-pores. As the definition suggests, nano-pores is a new system with different set of physical, chemical properties when compared with the conventional micrometer pore. The amazing fact is that nano-world exists around us for a long time, but it has not been recognized until the discovery of the powerful microscopes that enable scientists to study this natural phenomenon carefully, *Xing (2002)*.

Characterizing nano-pores available in tight carbonate reservoirs, at the pore level, starts with examining the components of the rock such as, mineral type and composition, pore-size, and pore-size distribution, *Al-Bazzaz and Engler (2001)*. Therefore, the effort of the characterizing has integrated several tools to achieve the nano-characterizations such as XRD, SEM, and PSD. The XRD investigates the mineral type responsible for hosting these nano-pores. The SEM investigates the pore and the grain fabrics including their sizes and their sizes distribution. The PSD only measures the intrusion volume of mercury, from which the pore and pore-throat sizes and their distribution are calculated using mathematical correlations. The SEM analysis is usually a 2-dimensional scale technique, *Al-Bazzaz and Al-Mehanna (2007)*; while the PSD is a 3-dimensional technique.

PROBLEM DEFINITION

The matrix permeability is very tight, whilst the core porosity is relatively good, *Al-Bazzaz (2001)*. As a result of integrating these tools, important findings and subsequent questions are raised. The findings are the availability of calcium silicates as a major component of the rock fabric; the reservoir is a very competent rock. Four samples are selected for the analysis Samples #4, #12, #19 and #24, of which maximum core porosity is measured at 16% and maximum air permeability is measured at 1.17 md. The minimum core porosity is 7% and minimum core permeability is 0.011 md. XRD analyses confirmed the availability of calcium silicates (Table 1). The subsequent questions are:
(1) Do nano-pores exist? (2) Are they myth or a fact? (3) If they exist, where are they located? (4) Do they contain hydrocarbons? (5) If they serve as hydrocarbon storage, can hydrocarbons be produced from these nano-spaces? (6) Is nano-porosity an economical source of hydrocarbons?

RESULTS & DISCUSSIONS

In this study, some of these questions have been answered (e.g. questions 1, 2 and 3), the answers are: indeed they do exist and they are no myth. Also they are located at a special fabric available in the carbonate rock, the calcium silicate component of the matrix.

Calcium silicate was found in enormous quantities inside this reservoir. Why this mineral is found next to calcium carbonate grain? The answer is metamorphism. Metamorphic rocks are generated by recrystallization of either igneous or sedimentary rocks by the action of pressure, temperature (P/ T) *Al-Bazzaz (2001), (Figure 1).*

In our samples several calcium silicates were identified by XRD such as (Table 1):

(1) Wollastonite-2M (2) Wollastonite-1A (3) Pseudowollasonite-Syn [NR] (4) Ingersonite, Syn. (5) Larinite, Syn. (6) Haturite (7) Rankinite (8) Kilchoalinite.

Wollastonite will be the illustrating example for this group of calcium silicates. Wollastonite is a common calcium silicate mineral found in the carbonate reservoir used in this study. Wollastonite belongs to skarns or contact metamorphic rocks. Skarns, which descended from carbonate rocks, can sometimes produce some wonderfully rare and exotic minerals with very unusual chemistries. Wollastonite forms from the interaction of limestones, that contain calcite, $CaCO_3$, with the silica, SiO_2, in hot fluids. This happens when hot magmas intrude into and/or around limestones. It forms by the following formula:

$$\mathbf{CaCO3 + SiO2 \xrightarrow{\Delta} CaSiO3 + CO2} \quad \uparrow$$

How do calcium silicates impact upon our study? This unconventional texture mineral happens to have tiny pore structure in the order of nano-meter. This nano-porosity can account for almost 60% and 25% of the total porosity (found in samples #12 and #24 respectively of this study). This component of porosity can complicate the carbonate pore morphology and increases its anisotropy. These tiny pore sizes are smaller than the clay mineral particle size 2 μm, as it is classified in the geological Wentworth scale of grain sizes. Usually clay minerals are the smallest feature identified in the rock matrix and they exist attached to the surface of the grain mineral. Nano-pores, however, can be a thousand times smaller than the smallest clay particle, such as montmorilinite.

Question number 4, is intriguing: Do these nano-pores contain hydrocarbon in them? Mercury porosimitery has successfully penetrated inside these nano-pores to make the porosity profile (Tables 3 & 4) and (Figure 4). This analysis is designed to determine the pore geometry. Mercury porosimeter is used to do this analysis. Mercury is intruded into the pores of a given sample over a range of pressures and the volume forced into the sample is measured. Samples #12 and 24 have 100% successful mercury intrusion. Mercury is a non-wetting fluid, and the size of the pore intruded is inversely proportional to the applied pressure. Equation (1-5) calculates the pore diameter in nanometers for each pressure applied in psia (Table 2). The instrument systematically records mean pressures, in this sample pressures were recorded from 6.8 psia (the largest pore size) to 32,938 psia (the smallest pore size). Each mean pressure indicates a range of pore diameters. For example, 32,938 psia mean pressure will yield a mean diameter of 3.25 nm or a range of pores between 0 and 3.25 nm.

The porosity profile technique of mercury has been correlated with other technologies such as Electron Probe Micro-Analysis (EPMA) to match the results, (Figure 2 & 3). This part of the study discusses the use of mercury penetration as a tool to investigate the nano-pore size and its distribution in these reservoirs.

One argument is raised, is mercury small enough to penetrate the nano-pore space? The answer lies in the physical property of mercury, *ChemGlobe (2000)*. The atomic radius of mercury is 1.76 Å, which is small enough to reside in a nano-pore space. In a same analogy another just question is raised: is hydrocarbon molecule small enough to reside inside the nano-pore? And the answer is also lies in the size of the hydrocarbon molecule situated inside these pores. Unfortunately, the hydrocarbon analysis is not available to this study, but some production data has pointed out for the hydrocarbon to be a condensate-like to a gas-like reservoir. Unlike mercury, hydrocarbons molecules vary in their sizes and such data of the size of oil molecules for this particular reservoir was unavailable during the study. However, in theory, some hydrocarbons' sizes are small enough to reside in these nano-pores. As a result, more work is needed to investigate and/ or to confirm this valid argument.

In abstract, since mercury has penetrated inside these pores, it can be concluded that fluids can reside inside these pores, so the following question is raised: can 3-phases of water, oil and gas be found in these pores? The answer will definitely need further investigations. Let us consider that these nano-pores do have hydrocarbon in them; then let us also assume that only the gas phase is available in these spaces. Question number 5 also needs to be answered: can gas be produced out of these tiny pores? Several inquiries will also be raised: can gas move from these pores? Does it need external help/ force to extract it out? And how can this external force be applied/ transferred to these tiny pores?

Question number 6 need the confirmation of question number 5. But with the hypothetical conditions of availability of hydrocarbons, two hypothetical life-time of the reservoir is been conducted, once for only conventional pore system 40% of the storage, and one for the entire pore system. The first case of 10 TCF to be produced at 10,000 mcf/d. Only 40% will be produced conventionally so 5.1 years is estimated for the life of the reservoir. The second case of the same quantity and to be produced at the same daily rate, it is found the life of the reservoir increased to 12.74 years (Figure 5). These two scenarios proof that the role of these nano-pore reserves can improve our perception of reservoir storage and hence increasing hydrocarbon estimations and the life-time of these reservoirs.

CONCLUSION

Nano-porosity is found in carbonates reservoirs. And they may play an important role for future hydrocarbon estimations and hydrocarbon production. In this reservoir the mineral contributing to this phenomenon is calcium silicate, which is a product of metamorphism. Mercury has successfully penetrated these pores to complement the Backscattered images and elemental mapping; therefore, it is believed that hydrocarbon molecule can have the same ability to reside in this nano-space.

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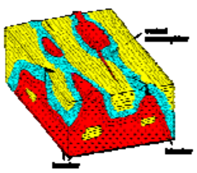


Figure 1 Regional and Contact Metamorphism Subject to P / T Conditions

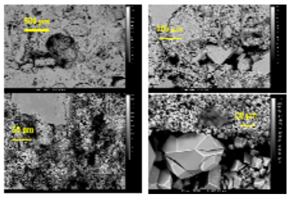


Figure 2 Backscattered Electron (BSE) Image of Plug 24, Resolution of 500 µm, 100 µm, 50 µm and 20 µm

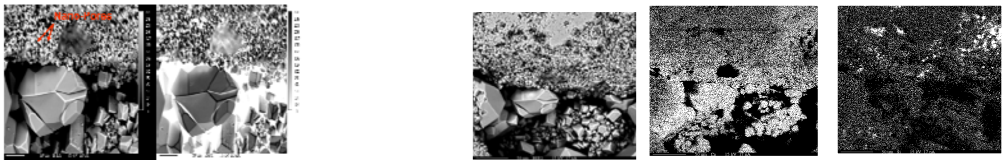


Figure 3 (left) Nano-porosity Available in the Calcium Silicate Grain Fabric Shown in a BSE image Plug #24. (Right) Plug 24 Elemental Calcium-Silicate Mapping Shows Maps of Calcium And Silicon.

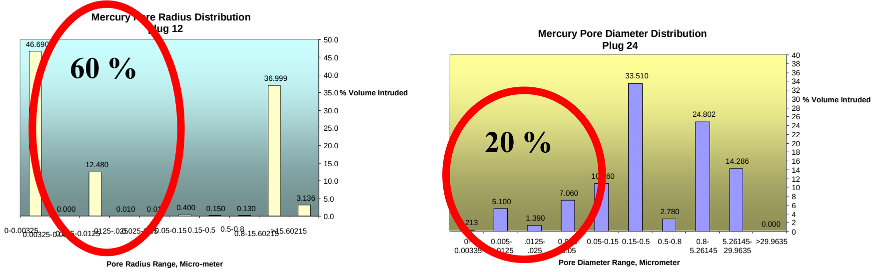


Figure 4 Mercury Pore Size Distribution Showing (Left) Plug #12 the Nano-porosity as 60% of the Total Porosity and (Right) Plug #24 the Nano-Porosity as 20% of the Total Porosity.

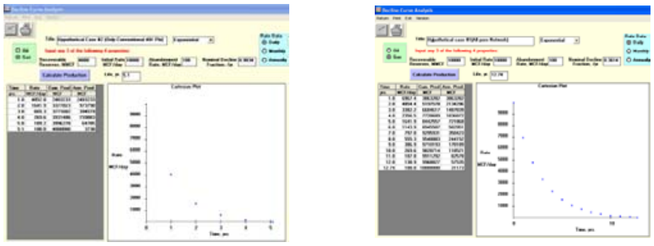
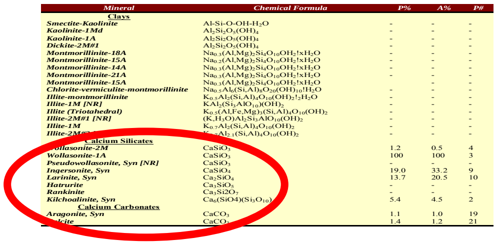


Figure 5 Sensitivity Analysis of Reservoir Life Time when Only Conventional Pore is considered in the Reservoir Estimation (a). The Reservoir Life Time when Difficult Nano-Pores are Considered in the Estimation.



Mineral	Chemical Formula	P%	A%	P#
Clays				
Smectite-Kaolinite	$Al\text{-}Si\text{-}O\text{-}OH\text{-}H_2O$	-	-	-
Kaolinite-1Md	$Al_2Si_2O_5(OH)_4$	-	-	-
Kaolinite-1A	$Al_2Si_2O_5(OH)_4$	-	-	-
Dickite-2M#1	$Al_2Si_2O_5(OH)_4$	-	-	-
Montmorillinite-18A	$Na_{0.3}(Al,Mg)_2Si_4O_{10}OH_2!xH_2O$	-	-	-
Montmorillinite-15A	$Na_{0.2}(Al,Mg)_2Si_4O_{10}OH_2!xH_2O$	-	-	-
Montmorillinite-14A	$Na_{0.3}(Al,Mg)_2Si_4O_{10}OH_2!xH_2O$	-	-	-
Montmorillinite-21A	$Na_{0.3}(Al,Mg)_2Si_4O_{10}OH_2!xH_2O$	-	-	-
Montmorillinite-15A	$Na_{0.3}(Al,Mg)_2Si_4O_{10}OH_2!xH_2O$		-	-
Chlorite-vermiculite-montmorillinite	$Na_{0.5}Al_6(Si,Al)_8O_{20}(OH)_{10}!H_2O$	-	-	-
Illite-montmorillinite	$K_{0.5}Al_2(Si,Al)_4O_{10}(OH)_2!_2H_2O$	-	-	-
Illite-1M [NR]	$KAl_2(Si_3AlO_{10})(OH)_2$	-	-	-
Illite (Triotahedral)	$K_{0.5}(Al,Fe,Mg)_3(Si,Al)_4O_{10}(OH)_2$	-	-	-
Illite-2M#1 [NR]	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$	-	-	-
Illite-1M	$K_{0.7}Al_2(Si,Al)_4O_{10}(OH)_2$	-	-	-
Illite-2M#[illegible]	[illegible]$Al_{2.1}(Si,Al)_4O_{10}(OH)_2$	-	-	-
Calcium Silicates				
[illegible]ollasonite-2M	$CaSiO_3$	1.2	0.5	4
Wollasonite-1A	$CaSiO_3$	100	100	3
Pseudowollasonite, Syn [NR]	$CaSiO_3$	-	-	-
Ingersonite, Syn	$CaSiO_4$	19.0	33.2	9
Larinite, Syn	Ca_2SiO_4	13.7	20.5	10
Hatrurite	Ca_3SiO_5	-	-	-
Rankinite	Ca_3Si2O_7	-	-	-
Kilchoalinite, Syn	$Ca_6(SiO4)(Si_3O_{10})$	5.4	4.5	2
Calcium Carbonates				
Aragonite, Syn	$CaCO_3$	1.1	1.0	19
[illegible]lcite	$CaCO_3$	1.4	1.2	21

Table 1 Plug #12-XRD Mineral Content. This Carbonate Rock has a Mix of Calcium Silicates and Calcium Carbonates

Table 2 Core sample 12 pore size distributions in diameters and radii, measured in angstrom and nanometer, showing ranges 3-7 and rage 9 with no intrusion; as a result no strong pore size is recognized in the distributions of figure 4.

Range Interpolated Intrusion Data	% Vol. Intruded For each Interval	Mean Pressure Psia	Pore Diameter nm	Pore Radius nm
Range 1 (Largest)	**3.136**	**6.836**	**>31,204.3**	**>15,602.15**
Range 2	**36.999**	**Missing data**	**1,600.0-31,204.3**	**800 – 15,602.15**
Range 3	0.130	164.094	1,000.0 - 1,600.0	500 - 800
Range 4	0.150	328.188	300.0 - 1,000.0	150 - 500
Range 5	0.400	1,066.611	100.0 - 300.0	50 - 150
Range 6	0.010	2,844.296	50.0 - 100.0	25 - 50
Range 7	0.010	5,688.592	25.0 - 50.0	12.5 - 25
Range 8	**12.480**	**12,189.840**	**10.0 - 25.0**	**5 - 12.5**
Range 9	0.000	21,319.000	6.5 - 10.0	3.25 - 5
Range 10 (Smallest)	**46.690**	**32,938.000**	**0 - 6.5**	**0 - 3.25**

Σ Intrusions 100.005

Table 3 Plug #12 Pore Geometry Distributions Using Mercury Pore Sizer. Two Ranges of Nano-Pores Are Identified – Range 8 About 12.5 nm, and Range 10 about 3.25 nm.

Pore Range Type	Size According to Amaefule and Kersey Classification, µm	Distribution Percentage From the Total Porosity	Comments
1	>15.6	3.14%	Large pore
2	1.5 < AMHR < 15.6	37%	Macro Pore throat
	0.8< AMHR < 1.5		Meso Pore throat
8	0.005 < AMHR < 0.0125	12.5%	Nano-porosity
10	0 < AMHR < 0.00325	46.7%	Nano-porosity

Table 4 Plug #24 Pore Geometry Distributions Using Mercury Pore Sizer. Four Ranges of Nano-Pores Are Identified – Range 6 About 100 nm, and Range 7 about 50 nm. Range 8 About 25 nm, and Range 9 about 12.5 nm.

Pore Range Type	Size According to Amaefule and Kersey Classification, µm	Distribution Percentage From the Total porosity	Comments
2	5.3 < large pore < 30	14.3%	Large pore

3	1.5 < AMHR < 5.3	24.8%	Macro Pore throat
	0.8< AMHR < 1.5		Meso Pore throat
4	0.5 < AMHR < 0.8	2.8%	Meso Pore throat
5	0.15 < AMHR < 0.5	33.5%	Micro Pore throat
6	0.05 < AMHR < 0.15	10.9%	Micro/ Pore throat
7	0.025 < AMHR < 0.05	7.1%	Nano-porosity
8	0.0125 < AMHR < 0.025	1.4%	Nano-porosity
9	0.005 < AMHR < 0.0125	5.1%	Micro/Nano porosity

The Washburn Equation

This analysis is designed to determine the pore geometry. Quantachrome Mercury porosimeter is used to do this analysis. Mercury is intruded into the pores of a given sample over a range of pressures and the volume forced into the sample is measured. Mercury is a non-wetting fluid, and the size of the pore intruded is inversely proportional to the applied pressure. The sample analyzed in this experiment is a small fragment of the original core sample to fit the high-pressure cell stem tube; usually the sample weighs less than 1 gram. The contact angle of mercury is 140° and surface tension of 480 dyne/cm. The maximum pressure allowed in this instrument is 60,000, which is equivalent to 0.00178 µm or 1.78 nm. However, above 30,000 psia, no appreciable additional intrusion takes place indicating little pore volume exists in pores of radii smaller than 0.0035 micrometers or 3.5 nanometers. Surface tension, γ, has the dimension of force per unit length, or of energy per unit area. The two are equivalent. Surface tension in this analysis is therefore measured in forces per unit length. Its SI unit is Newton per meter but the cgs unit of dynes per cm is most commonly used. One dyne/cm corresponds to 0.001 N/m. Mercury porosimetry was always a part of the routine core analysis to measure bulk and pores volume. The theory of mercury porosimetry is modeled by the Washburn equation, which allows the non-wetting liquid mercury to penetrate cylindrical pores when sufficient pressure is applied. The capillarity forces have an inverse relationship between the pore diameter and the pressure introduced.

$$r = \frac{-2 \cdot \gamma \cdot \cos(\theta)}{P} \quad \text{Where,} \qquad (1\text{-}1)$$

r = Pore radius, microns
P = Applied pressure, psia
γ = Surface tension, 480 dynes/cm
θ = Mercury contact angle, 140°

$$\gamma = 480 \; {}^{dynes}\!/\!_{cm}$$

$$\theta = 140^{\circ}$$

$$D = \frac{-4 \cdot \gamma \cdot \cos(\theta)}{P} \qquad (1\text{-}2)$$

$$1 \; lb_f = 444822.16 \text{ dynes}$$

$$D = \frac{\left[-(4)\cdot\gamma\cdot\left(\frac{dyne}{cm}\right)\cdot\left[\frac{1\cdot lb_f}{(444822.16\cdot dyne)}\right]\cdot\cos(\theta)\right]\cdot\left(\frac{10^7\cdot nm}{1\cdot cm}\right)}{P\cdot(psi)\cdot\left[\frac{{}^{1\cdot lb_f}\!/\!_{in^2}}{psi}\right]\cdot\left[\frac{in^2}{(2.54\cdot cm)^2}\right]} \qquad (1\text{-}3)$$

$$\cos\left(\left(\frac{140^{\circ}}{360^{\circ}}\right)\cdot 2\cdot\pi\right) = -0.766 \qquad (1\text{-}4)$$

$$D = \frac{-4\cdot(480)\cdot(-0.766)\cdot(2.54)^2\cdot 10^7}{444822.16}$$

$$D = \frac{2.133\cdot 10^5}{P} \qquad (1\text{-}5)$$

Where,
D = Pore diameter, nanometer
P = Applied pressure, psia