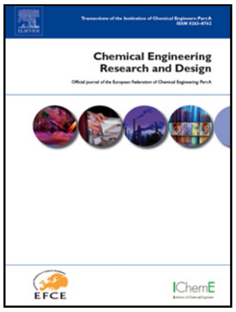

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# Wettability alteration in gas-condensate carbonate reservoir using anionic fluorinated treatment

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## Research Highlights

- Wettability alteration to gas wetness is proposed to Sarkhun rock.
- The treatment is consisted of an anionic fluoro-surfactant with an optimized solvent.
- The effect of this method is evaluated by various tests.
- Brine and condensate imbibition decrease after treatment.
- The relative permeability increase by a factor of 1.7.

During gas production from gas condensate reservoirs, as the bottom hole pressure drops below the dew point pressure, the liquids drop out and form condensate banking resulting

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in significant loss of gas and condensate productivity. A new method for stimulating gas-condensate wells, is changing the rock wettability in near well-bore regions by chemical treatments. In this study, a new chemical treatment was developed to alter the wettability of carbonate rocks from water-wet to intermediate gas-wet in order to enhance gas relative permeability. The treatment involves the use of an anionic fluoro-surfactant mixture with an optimized concentration and a solvent. Contact angle and spontaneous imbibition experiments were run to measure the wettability alterations. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDAX) and adsorption isotherms were also performed to monitor the amounts of surfactant solutions which were adsorbed on the rock surface. The increase in gas relative permeability was quantified by comparing the permeability before and after chemical treatments. The contact angles were increased and water and oil imbibitions were reduced significantly after the treatments. Finally, core flood tests revealed that the optimized treatment could enhance the gas relative permeability by a factor of 1.7 which demonstrated the ability in wettability alteration at reservoir conditions.

**Keywords:** Gas-condensate reservoir, Wettability alteration, Fluorinated surfactant, Imbibition, Permeability

## 1. Introduction

In gas-condensate reservoirs as the bottom hole pressure drops below the dew point pressure of the reservoir fluid, liquids drop out from the gas phase and form condensate banking near the well bore resulting in lower gas productivity (Alfidick et al., 1994; Barnum et al., 1995). Today, several methods have been proposed to improve gas production from the gas-condensate reservoirs after condensate build-up. Gas recycling (Hoier et al., 2004), hydraulic fracturing

(Kumar, 2000) and methanol injection (Al-Anazi et al., 2005) methods have been developed to confront such problem, however their success is limited and they can only remedy the condensate banking for a short period of time. Today, there are a number of research attempts available on use of various surfactants to improve productivity of gas wells. At first, Li and Firoozabadi (2000a, 2000b) proposed to enhance the gas-condensate deliverability by altering the wettability of near wellbore region from liquid-wet to intermediate gas-wet. They concluded that critical condensate saturation could be reduced by altering the wettability of the reservoir rocks, which would result in gas relative permeability enhancement. They also succeeded to alter the wettability of Berea sandstone and Kansas chalk from water-wet to intermediate gas-wet by various chemicals at room temperature. Tang and Firoozabadi (2002) tested the effect of chemical treatment on the oil and water relative permeability of Berea sandstone. However, they did not use gas-condensate fluids in reservoir conditions. Fahes and Firoozabadi (2002) followed the earlier work up to 140 ºC but their chemical treatment process was less successful on the gas and oil relative permeabilities.  Kumar also reported improvements in the gas and condensate relative permeabilities of Berea and reservoir sandstone cores by factor of 2 and 3, which were treated with non-ionic surfactants soluble in water/methanol mixture (Kumar, 2006; Kumar et al., 2006a, 2006b). Bang (2007) and Bang et al. (2010) showed their successful application of a fluorinated surfactant in two different treatment solutions, namely, 2-butoxyethanol/ethanol and glycol/isopropyl alcohol. These solutions proved to be effective at harsh reservoir conditions such as high temperature and pressure.  Ahmadi et al. (2010) modified the method by flooding an amine primer followed by the fluorinated surfactant solution into the carbonate cores and improved the gas relative permeability up to 80%. They employed different chemicals and performed contact angle and imbibition experiments to find the best fluorinated surfactant having maximum stability and compatibility towards brine and reservoir fluids. They showed that these experiments were useful for early detection of appropriate chemicals. Gilani et al. (2011) performed similar experiments on sandstone and limestone cores. They also concluded that the early detection tests such as contact angle and imbibition could be useful to find the optimal and effective chemicals for reduction of number of core flood tests. Later, Asgari et al. (2013) investigated the effect of methanol on limestone cores using experimental core flooding to restore the gas relative permeability in gas condensate reservoir. They also performed modeling study using Cubic-Plus-Association (CPA) equation of state which achieved good agreement between the experimental and modeling results.

As we know, many gas fields in Iran are composed of carbonates. In this project, the samples were collected from Sarkhun, one of the carbonate (limestone) gas-condensate reservoirs located in Hormozgan, south of Iran. Sarkhun has low permeability and is predicted that it may undergo condensate blockage in near future (Sharifzadeh et al., 2012, Mousavi et al. 2013).

Based on previous research works, the significant degrees of fluoro-surfactants adsorbed on different surfaces had led to innovative applications of various materials as hydrophobes, protective, conditioners, anti-foaming agents, oleophobes and anticorrosive agents (McNatt et al., 2003; Kisa, 1994). Since a fluoro-chain is not only hydrophobic but oleophobic, fluorinated surfactants can serve as water and condensate repellents when adsorbed on limestone and sandstone reservoirs.

In the present work, we tried to use a cost-effective “anionic fluoro-surfactant” mixture and select an optimized surfactant concentration and solvent mixture to make the carbonate reservoir rocks hydrophobic/oleophobic, i.e., amphiphobic. Static contact angle and spontaneous imbibition measurements were employed to verify the degree of wettability alteration as an early detection for various surfactant solutions. The microstructure and chemical composition of the surfactant treated surfaces were also examined by scanning electron microscopy (SEM), and electron dispersive analysis of X-ray (EDAX). Adsorption isotherms were also determined in our study. Finally, the increase in the gas relative permeability was quantified by performing core flood experiments before and after the most effective solution at reservoir conditions; leading us to summarize our observations in the last section.

## 2. Experimental

### 2.1. Fluids and Rocks

In our work, normal-decane (DAE JUNG, Korea), with 0.73 specific gravity and 0.92 cp viscosity at 20 ºC, was used as a condensate. Methanol, ethanol and IPA were also obtained from Merck Company to prepare synthetic gas mixture. Air and 2% (by wt) NaCl synthesized with distilled water were used as gas and liquid phases, respectively. Distilled water was self-made in PVT laboratory, Shiraz University, Iran. Carbonate rocks which were selected from Sarkhun reservoir fields, were used in all the experiments. In this study, we used cores with approximately 1.5 inch diameter and the average porosity of around 28.3%, measured by helium porosimeter (Vinci Technologies, France). All the samples were initially dried by $N_2$ gas (purity 99.99%) which was purchased from Abughaddare Gas Company Shiraz, Iran.

### 2.2. Chemicals and Surfactants

Zonyl® UR, a mixture of anionic phosphate fluoro-surfactants, was used for the wettability alteration of Sarkhun carbonate rocks from water-wet to intermediate gas-wet (**Fig. 1**). This was prepared from ABCR Manufacturing Company (Germany). As we know, such surfactant has great wetting characteristics and is stable in harsh conditions under both different thermal and chemical conditions. It also consists of a phosphate hydrophilic head and a fluorocarbon hydrophobic tail. The fluorocarbon portions of these molecules give the surfactant an extreme tendency to orient at air interfaces and reduced the surface energy. Zonyl® UR is an un-neutralized solid, soluble in isopropanol (IPA) and ethanol which requires neutralization with a base to make it water and methanol soluble. The solubility of this chemical is less than 2% (wt) in their solvents. Therefore, we classified our wettability alteration treatments in two groups as follows: group 1 which consisted of an un-neutralized surfactant in IPA and ethanol; group 2 composed of a neutralized surfactant in water and methanol solvents. Details of the neutralization process were as follows: first, 1% (wt) Zonyl® UR in IPA and 1% (wt) NaOH in water were prepared. The Zonyl® UR sample was neutralized by drop-wise addition of a base using burette at room temperature. This process was performed by a pH meter as an indicator until it was neutralizes at pH~7. The sample was then dried at 60 ºC for 24 h. The obtained solid was water and methanol soluble. **Fig.2** depicts pH variation by addition of NaOH solution into Zonyl® UR during neutralization process. In this article, we have abbreviated the un-neutralized Zonyl® UR as "Z" and neutralized Zonyl® UR as "N.Z". In the next steps, we compared both groups with each other for wettability alteration of the rocks.

**Fig. 1.**

**Fig. 2.**

### .2.3 Contact Angle Measurements

The effect of surfactant solutions on the wettability alteration was first examined by a static contact angle analyzer. DSA100 goniometry (Germany) was used to measure the contact angles of treated and untreated surfaces. First, thin sections with 2 mm in height were cut from carbonate cores of each 1.5 inch diameter. Drops of 5µl brine and normal decane (approximately 1 mm apart) were put on the untreated surfaces and the static contact angles of liquid/air/limestone were measured. The samples were then aged in the surfactant solutions, containing both groups 1 and 2 for 24 h, after the primary contact angle determinations. The thin sections were completely dried by dry air to remove the excess liquids and then again the brine and normal decane contact angles of the treated surfaces were measured again. All the results in this section were average values of at least three measurements at different points of samples at ambient temperature.

### 2.4. Spontaneous Imbibition Studies

The air-saturated cores, either untreated or treated, were immersed in 2% (by wt) brine or normal decane to perform the spontaneous imbibition tests by using the experimental setup shown in **Fig. 3**. The cores were hung under an electronic balance and immersed in the liquids while the weight alterations of the cores vs. time were recorded. The untreated cores were first examined and then they were aged in surfactant solutions for 24 h. After pulling out the core samples from the solutions they were completely dried by dry air and the same imbibition tests were repeated on the treated samples. The increase in weight with time was recorded regularly until no change was detected. All the tests were conducted at room temperature with the zero initial water saturation. The reduction by spontaneous imbibition after chemical treatments was an indication of the wettability alteration to intermediate gas-wetting.

**Fig. 3**

## 2.5. SEM and EDAX Analysis

The qualitative and quantitative elemental composition of the treated samples were acquired by means of energy dispersive X-ray (EDAX, model Seron AIS 2300, Korea). As it was expected the surface with higher atomic or weight ratio of fluorine and phosphate elements displayed more surfactant adsorption. Scanning electron microscopy (SEM, Philips XI30, The Netherlands) with excellent resolution was also employed on treated samples at room temperature to assess their morphology structures. The combination of X-ray with SEM detection consequently yielded high elemental information and structural characterization of the samples.

## 2.6. Adsorption Isotherms

The amount of surfactant adsorption is likely to be an influential value for well injection and the durability of the treatment. The more the surfactant is adsorbed on the rock surface, the longer the treatment is expected to last (Bang 2007). Adsorption isotherms can be characterized by the amount of surfactant adsorbed per 1 gram of stone as a function of equilibrium concentration, at constant temperature and pressure. In this section, we have used static adsorption method employing spectrophotometer to analyze the quantitative amount of adsorbed surfactant onto the reservoir samples. First, 50 g carbonate rock was crushed and mixed with surfactant solution in a flask by shaking at ambient temperature. The concentration of aqueous solution were analyzed every 2 h until no significant fluorocarbon concentration change was detected. From the difference between the initial surfactant concentration and the equilibrium values, the amount of surfactant adsorbed on the rock surface was determined. A detailed result of surfactants adsorption is given in discussion section.

## 2.7. Core Flood

### 2.7.1. Core Flood Apparatus

In previous stages we examined the wettability of the surfaces, thin sections and imbibition cores. Our final evaluation was on the core flood system by measuring the gas permeability of the most effective chemical treatment which had been detected from the previous experiments. The schematic of core flood experimental setup for the gas-condensate relative permeability determinations in steady state and reservoir conditions is shown in **Fig. 4**. A positive displacement pump (Vinci, BTSP-500) was used to inject the fluid at constant velocity and two back pressure regulators (BPR) were used to control the upstream (BPR-1) and downstream (BPR-2) core pressures. Other apparatuses such as accumulators, liquid trap, core holder and pressure transducers were placed in a temperature-controlled oven.

**Fig. 4**

### 2.7.2. Gas-condensate Mixture

The components of the synthetic gas-condensate mixture used in core flood tests are presented in **Table 1**. The phase envelope and liquid-dropout vs. pressure of the mixture, which have been calculated by Peng-Robinson equation of state, are also shown in **Figs. 5** and **6**.

**Table 1**

**Fig. 5.**

**Fig. 6.**

### 2.7.3. Core Flood Procedure

In order to evaluate the effect of chemical treatment on the wettability alteration under reservoir pressure and temperature conditions, the gas relative permeability of the treated and untreated cores was determined and compared with each other. The following procedure was used in the core flooding experiments: first, dry gas permeability of the core was determined by methane at room temperature. Initial brine saturation was established by synthetic brine of 2% (by wt) NaCl. Synthetic gas-condensate mixture was then flooded into the core by adjusting the upstream pressure of the core (BPR-1) above and the downstream pressure of the core (BPR-2) below the dew point pressure of the fluids. In such a manner, single phase gas fluid was flushed into the gas and condensate phases through the first back pressure regulator. The steady state pressure drop was then determined and finally the gas-condensate relative permeability was calculated. The treatment solution was then injected into the core with 5 pore volumes and was shut-in for 24 h to allow the surfactant to be adsorbed onto the carbonate. Finally, post-treatment gas relative permeability was then determined by the same method of pre-treatment process.

## 3. Results and Discussion

Zero point charge (ZPC) of calcite was in the range of $8 < pH < 9.5$, thus there existed excess of $Ca^{++}$, $CaHCO_3^+$ and $CaOH^+$ ions on the surfaces at the pH below the ZPC (Samasundaran and Agar, 1967). Anionic surfactants contained negative charge in their head group and therefore they were attracted and adsorbed on positive charge surfaces towards electrostatic interactions at surfactant-solid interfaces (Samasundaran and Krishnakumar, 1997). Whereas, all of the treatment solutions which were used in this study were below pH 8, therefore based on the given theory the condensation reactions could have occurred and formed covalent bonds between the carbonate surfaces and the anionic surfactant on the mineral grains.

### 3.1. Contact Angle Measurements

Our initial assessment to measure the effective wettability alteration was based on contact angles of different solutions. We estimated the contact angle of water (brine) and condensate (n-decane) for various samples. These samples and their corresponding values are shown in **Table 2** and **Table 3**. Before the treatments because of high hydrophilicity/oleophilicity of the carbonate rock, brine and n-decane drops penetrated into the samples as soon as when they were applied onto the surface. Therefore, the angles were approximately zero before the treatments. For comparison, the water and condensate contact angles on different treatment solutions are compared and presented in **Table 2**. One can see from these results that surfactant N.Z in water having 134˚ brine and 83˚ n-decane contact angles and also surfactant Z in ethanol with 121˚

brine and 70.3˚ n-decane contact angles, show maximum values. It is obvious that the treated samples are changed to hydrophobes/oleophobes with excellent water/oil repellency. Since it is important to perform cost-effective surfactant concentration in the field, thus in this work we have also tried to optimize the consumption values of the surfactants. For this purpose, the contact angles of two other concentrations for both Z in ethanol and N.Z in water were measured and the results are shown in **Table 3**. As we can see in this table, all the treatment solutions are successful in wettability alteration of carbonate rock surfaces from water-wet to intermediate gas-wet. Although the measured contact angles are slightly higher for 1.5% concentration of the surfactants, they may be still ignored because of less surfactants consumption in 1% concentration. Finally, we can select 1% (by wt) of Z and N.Z as an optimized concentration for both surfactants. Water and condensate images which were obtained in order to measure the contact angles after chemical with 1% Z in ethanol and 1% N.Z in water are shown in **Figs. 7** and **8**, respectively. **Fig. 9** also provides a clear depiction of brine droplets on the surface of air-saturated samples before and after treatment with 1% Z in ethanol.

**Table 2**

**Table 3**

**Fig. 7**

**Fig. 8**

**Fig. 9**

### 3.2. Spontaneous Imbibition

After the wettability alteration evaluations on the surface of the carbonate, the optimized treatments with maximum contact angles were examined by core spontaneous imbibition to demonstrate effective wettability alteration in larger scale. The main factor that affected gas production by spontaneous imbibition was wettability. In gas condensate reservoirs, the change in capillary force could control spontaneous imbibition (Sharifzadeh et al., 2012). In this stage, the spontaneous imbibition results before and after the treatments were shown to ascertain that whether the treatments could alter the wettability of Sarkhun cores.

As we can see in **Fig. 10**, the gas recovery of the untreated cores by spontaneous brine imbibition which accounts for about 64% of original gas in place (OGIP) is an indication of water-wetting characteristics of the samples. This value is decreased to 38.3% OGIP and 8.5% OGIP for Z in ethanol and N.Z in water after 3 h of imbibition time, respectively. As compared with the initial brine imbibition, it can be deduced that about 40% reductions in the gas recovery or brine imbibition occurs by using N.Z as chemical treatment. This reduction is more significant for surfactant Z in ethanol which about 86%; demonstrating that it can provide greater alteration from water-wetness to gas-wetness. The gas recovery results by normal decane spontaneous imbibition before and after treatments are displayed in **Fig. 11**. From this Figure, it may be observed that the condensate imbibition without any chemical treatment is about 69% OGIP. The same as in brine imbibition results, Z in ethanol is also a more effective treatment in alteration, as compared to N.Z, as it can decrease gas recovery by condensate imbibition to 12.3% OGIP. This figure reveals that Z surfactant in ethanol is also able to reduce an oil imbibition by 82% of its initial imbibition, while N.Z can only decrease this value to 36%.

From the contact angle and spontaneous imbibition results, it seems that 1% surfactant Z in ethanol can be effective in wettability alteration for carbonate surface and its core. Although, 1% surfactant N.Z in water is successful in the surface wettability alteration, it does not have sufficient effect in core scale by imbibition tests. This phenomenon can be attributed to less penetration of the N.Z surfactant into the core pores due to their aggregated shape particles which are obtained from the EDAX and SEM analysis in the next section.

**Fig. 10**

**Fig. 11**

In order to evaluate the surfactant stability against reservoir brines, we have also placed a treated core with surfactant Z in a 0.2% (by wt) NaCl brine for 30 days. After aging time, the spontaneous brine imbibition was repeated again (**Fig. 12**). This observation suggested that initial gas recovery was about 9% OGIP which showed negligible difference as compared with the initial gas recovery by brine imbibition of around 8.5% OGIP.

**Fig. 12**

### 3.3. SEM and EDAX Analysis

Scanning electron microscopy (SEM) which was recorded from Z in ethanol and N.Z in water treated surfaces coupled with the energy dispersive X-ray results are depicted in **Fig.13** and **Table 4**, respectively. Furthermore, we can also observe the EDAX results in **Fig. 14** which have been acquired by surfactant Z in ethanol at region No. 4. EDAX has been of assistance in identifying principal chemical elements on the treated carbonate. As we can see in **Table 4**, the fluorine content percentages on the treated surface with surfactant Z are higher than N.Z treated sample, while their distribution range is lower. This can be an obvious indication for more Z adsorption as compared with N.Z on the carbonate samples. In addition, the phosphate content percentages seem to be close for both treated samples; however, the distribution range average obtained from treated sample with Z is lower than the N.Z. Homogeneous fluorine and phosphate weight percentage values on different Z treated areas of smooth and also rough regions observed with microscopic pore space have been detected in SEM-EDAX results. These values are different in various surface spots for treated N.Z surfactant. It seems that as the carbonate surfaces become porous, the surfactant N.Z penetrates with difficulty, therefore fluorine and phosphate adsorptions and concentrations on the samples are reduced.

The morphology of treated coatings has been examined by SEM micrographs (×1000), depicted **Figs. 15 (a)** and **15 (b)**. **Fig. 15 (a)** indicates that the surfactant Z has covered the sample successfully and the coating is quite uniform on all its surface area. However, the coating prepared by surfactant N.Z is changed to spherical shape particles, as shown in **Fig. 15 (b)**. We speculate that this extremely large size may be the main reason for less penetration of N.Z molecules into the pore spaces. The results obtained from SEM and EDAX reveal that Z shows more adsorption and uniform treatment which can provide better changes in wettability alteration of Sarkhun samples, as compared to N.Z. We may also deduce that lower pH of Z surfactant solution (pH~ 2) compared to N.Z (pH 7 to 8) supplies more positive charges on the carbonate surface. Such behavior can be considered as another reason for favorable wettability alteration on the Z treated surface.

If in the chemical formulation (**Fig. 1**) x value is taken as seven with one fluorocarbon tail (it can be the average value for our estimation), thus the calculated atomic ratio of phosphate (P) to fluorine (F) would be 1/29= 0.0345. Based on this assumption, it is found that there is no significant difference between this value and the P/F=0.0335 obtained from EDAX results. Consequently, such coatings involve a large amount of fluorocarbon groups which can lead to sufficient water and oil repellency characteristics and wettability improvement. It can be also deduced from the contact angle, spontaneous imbibition and including the above results the outermost layer of Z in ethanol coating is almost fully enriched by fluoro groups. Finally, such most effective treatment is selected for next experimental tests.

**Fig. 13**

**Table 4**

**Fig. 14**

**Fig. 15**

### 3.4. Adsorption isotherms

This section reports the results from laboratory investigations of the adsorption in Z solutions on the limestone crushed rock. The investigation includes the data at equilibrium concentrations which are presented in **Table 5**. The initial concentrations have used were 1200, 2400, 4800, 7200 ppm. Our laboratory results show that it takes about 20-25 hours to achieve equilibrium concentrations. After recording equilibrium concentrations and amounts of Z adsorbed by crushed core, $(q_e)$ were calculated as follows:

$$q_e = \frac{C_i - C_e}{Gram\ crushed\ core} \qquad (1)$$

$q_e$: Amount of Z adsorbed per gram of crushed rock

$C_i$: Initial Z concentration

$C_e$: Equilibrium Z concentration

**Table 5** suggests that the amount of surfactant adsorbed onto the rock increases with its equilibrium concentration increase and the maximum value is 2.55 mg/g. Low pH of Zonyl surfactant solution (pH~2) can results in good affinity for fluorine adsorption during its steady state conditions. Equilibrium data which presented in this table demonstrates sharp increase of adsorption up to 4800 ppm and then increases slightly with further Zonyl concentrations. This maybe attribute to active cites and adsorption capacity decline. The adsorption data has been drawn by linear regression of isotherm model equation Viz. Langmuir and Freundlich isotherms in **Fig. 16**. Slopes and intercepts of the respective linear plots are also presented in this figure. The combination of adsorption data with our pervious experiments for Z in ethanol treatment, provide evidence of surfactant ability in surfactant adsorbed and the wettability alteration.

**Table 5**

**Fig. 16**

### 3.5. Core Flood

The core flood experiments were conducted on Sarkhun carbonate cores under conditions which are described in **Table 6**. The gas-condensate mixture was injected at a pressure above the dew point and left the core below the dew point pressure all the time. Therefore, its temperature and pressure ranges were placed at retrograde condensation zone during the test. The synthetic gas-condensate mixture with dew point pressure of 4128 psi was injected at a flow rate of 420 cc/h through the carbonate cores. The temperature and outlet pressure were also set at 80 ºC and 3000 psi, respectively and the liquid dropout was 14.57% of total volume in this temperature and pressure condition.

**Table 6**

The results of the core flood experiments are summarized in **Table 7**. The gas relative permeability of pre- and post-treated cores has been determined followed by improvement factor (IF) estimation. IF was taken as a ratio of after/before treatment of the calculated gas relative permeability, which illustrates the effect of chemical treatment on the condensate blockage remediation and the gas productivity enhancement.

**Table 7**

As it is evident in this table, the improvement factor range varies from 1.49 to 1.70 for the four selected core flood results. As we described earlier, the experiments were handled at high temperature and pressure conditions similar to typical reservoirs. These findings confirm that the treatment with Z can be effective on the wettability alteration and relative permeability improvement under a very harsh condition. In addition, since many gas and gas-condensate reservoirs have high initial brine saturation and brine salinity, hence durability of the treatment solution against brine minerals plays an important role in the wettability alteration. As we know, brine can cause surfactant precipitation on the rock surface and also provides undesirable effects in the chemical treatment. Thus, the durability of the treatment solution with the initial brine saturation in the reservoir has also been examined by various brine saturations experiments as presented in **Table 7**. It can be seen from the results that the surfactant and its solution show stability using synthetic brine and can be effective on permeability improvement. Besides that, the enhancement in relative permeability proves that there has been no precipitation occurred to block the flow paths of the fluid.

Furthermore, **Figs. 17** and **18** depict a pressure drop comparison between the pre-treated and post-treated cores corresponding to Exp#7 and 11, respectively. As we can see in these figures, after the treatment the pressure drop through the core is reduced, resulting in relative permeability enhancement. We can also observe an increase in the pressure drop after the condensate banking occurred in both pre- and post-treatment during flooding. However, it is obvious that pressure drop increment before the treatment is higher than after solution treatment, an indication that the chemical treatment could successfully affect the wettability alteration of the core followed by gas permeability improvement.

**Fig. 17**

**Fig. 18**

## 4. Conclusions

Water and condensate blocking are causes of gas recovery reductions in gas-condensate reservoirs. It has been demonstrated that the wettability alteration is an appropriate method for reducing the liquid blockage and increasing the gas permeability. To date, several compounds have been used to alter the wettability of the reservoir rocks. In our current work, we have used an anionic fluorinated surfactant and optimized the solvent and surfactant concentration for condensate blockage remediation by various various detection methods. Some of the concluding remarks of the current study are as follows:

- Wettability of the carbonate rocks could be altered from strongly water-wet to intermediate gas-wet, resulting in productivity enhancement of the wells which are blocked by the condensate banking around the wellbore.
- Contact angle and spontaneous imbibition experiments were useful to evaluate the wettability alteration caused by the chemical treatment. These methods were so beneficial to optimize solvent and concentration of the components.
- To ensure the adsorption of the fluorinated surfactant onto the carbonate rocks, EDAX, SEM and adsorption isotherms analysis were also performed. These experiments provided good evidence to determine the adsorbed surfactant compositions onto the rock.
- The core flood tests were handled on Sarkhun carbonate cores before and after treatment with the best surfactant solution under the reservoir conditions. These experiments indicated that the chemical treatment was able to increase the gas relative permeability by a factor of up to 1.7.

Finally, we have also recommended performing more durability tests under reservoir conditions before any field applications.

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# Table captions

**Table 1.** Fluid composition of the synthetic gas mixture

**Table 2.** Brine and n-decane contact angles for different treatment solutions after

**Table 3.** Brine and n-decane contact angles for different surfactant concentrations

**Table 4.** Fluorine and Phosphate average concentrations on treated carbonate surfaces by EDX analysis

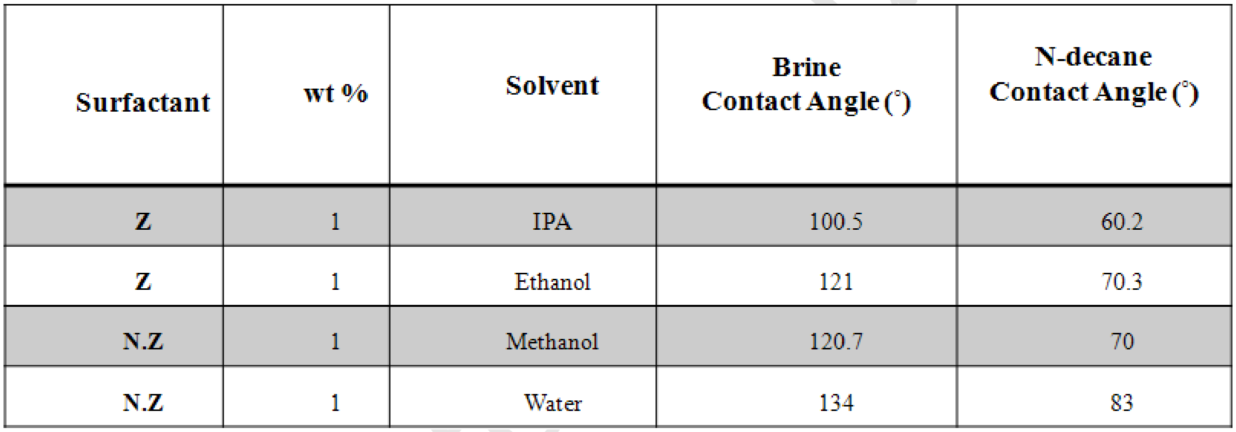
**Table 5.** Adsorption Isotherm values for Z in Ethanol onto crushed core

**Table 6.** Coreflood experiment conditions and gas-condensate mixture properties

**Table 7.** Coreflood conditions and improvements in the relative permeability

| **Component** | **Mole %** |
|---|---|
| Methane | **90** |
| N-Heptane | **8** |
| N-Decane | **2** |

**Table 1.**

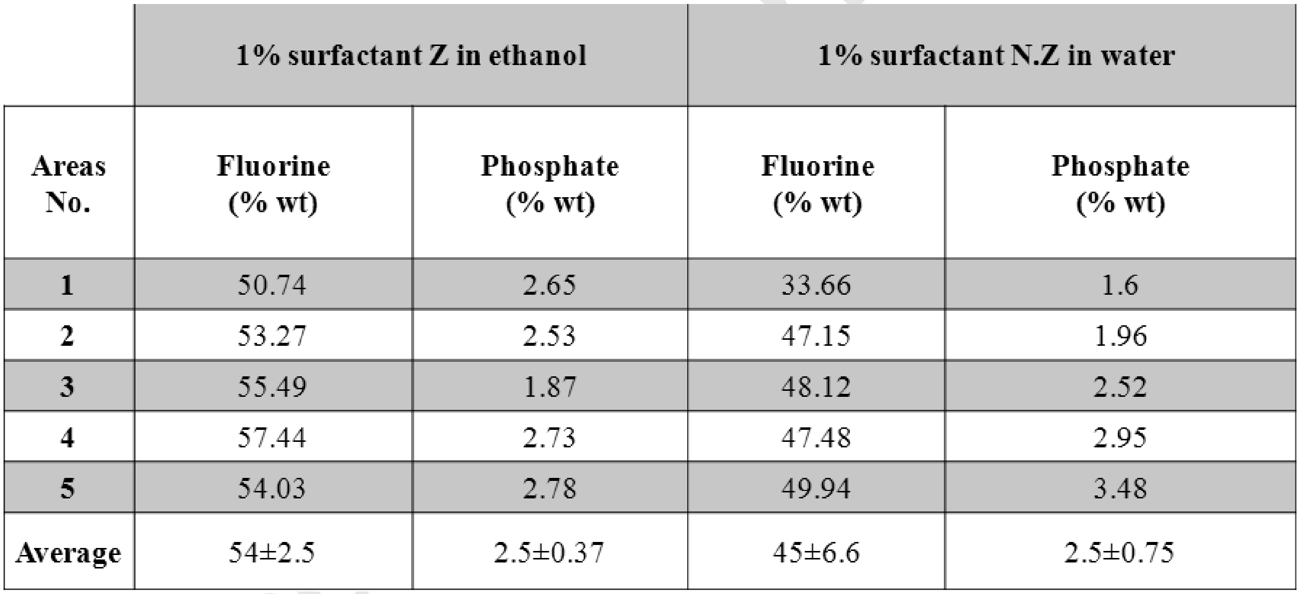


| Surfactant | wt % | Solvent | Brine Contact Angle (˚) | N-decane Contact Angle (˚) |
|---|---|---|---|---|
| **Z** | 1 | IPA | 100.5 | 60.2 |
| **Z** | 1 | Ethanol | 121 | 70.3 |
| **N.Z** | 1 | Methanol | 120.7 | 70 |
| **N.Z** | 1 | Water | 134 | 83 |

**Table 2.**

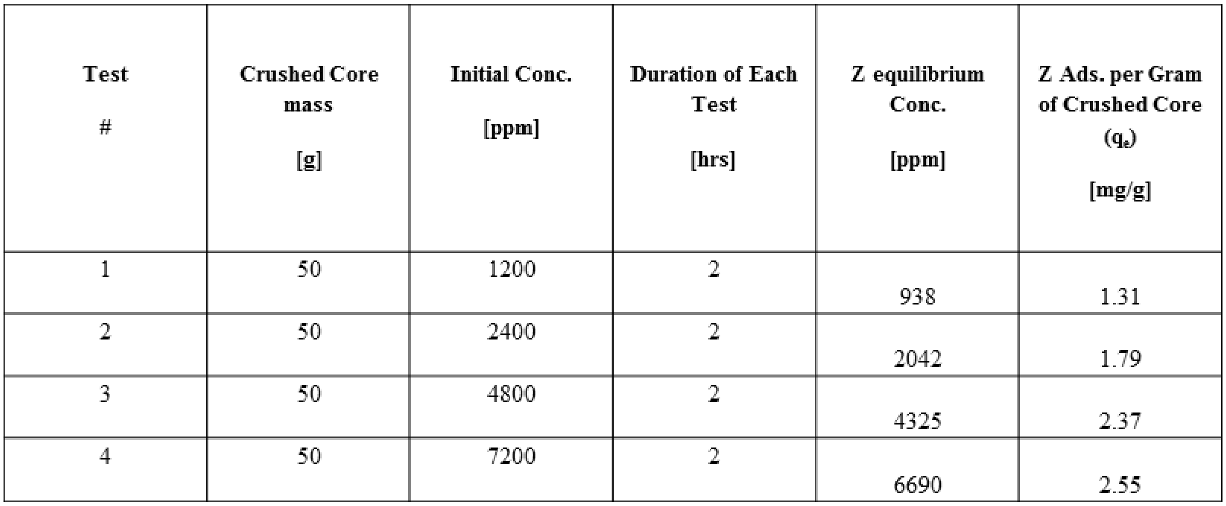
| Surfactant | wt % | Solvent | Brine Contact Angle (˚) | N-decane Contact Angle (˚) |
|---|---|---|---|---|
| Z | 0.5 | Ethanol | 104 | 63.1 |
| Z | 1.5 | Ethanol | 121.5 | 70.4 |
| N.Z | 0.5 | Water | 125 | 72.6 |
| N.Z | 1.5 | Water | 134.8 | 83.3 |

**Table 3.**



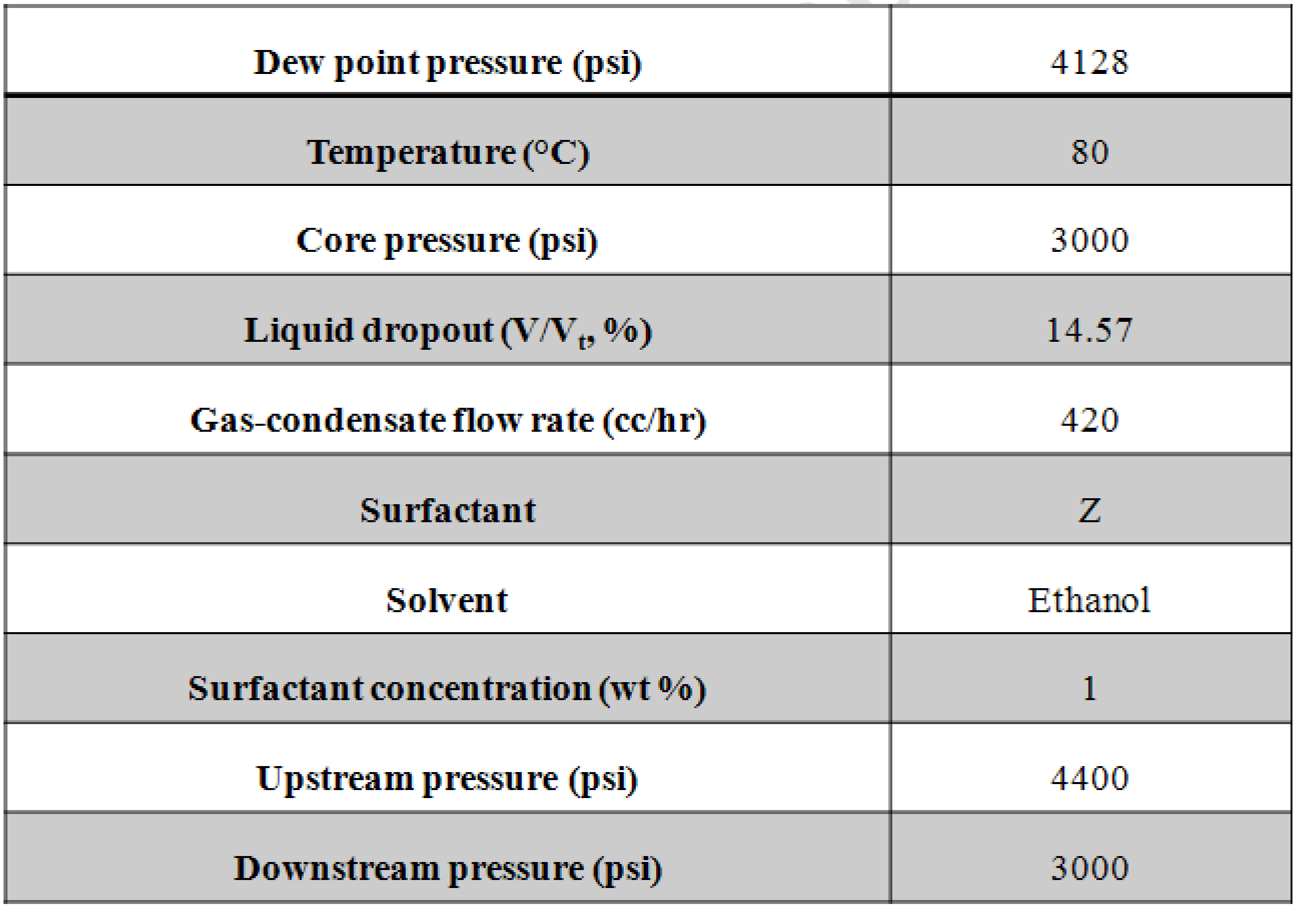
| | 1% surfactant Z in ethanol | | 1% surfactant N.Z in water | |
|---|---|---|---|---|
| **Areas No.** | **Fluorine (% wt)** | **Phosphate (% wt)** | **Fluorine (% wt)** | **Phosphate (% wt)** |
| **1** | 50.74 | 2.65 | 33.66 | 1.6 |
| **2** | 53.27 | 2.53 | 47.15 | 1.96 |
| **3** | 55.49 | 1.87 | 48.12 | 2.52 |
| **4** | 57.44 | 2.73 | 47.48 | 2.95 |
| **5** | 54.03 | 2.78 | 49.94 | 3.48 |
| **Average** | 54±2.5 | 2.5±0.37 | 45±6.6 | 2.5±0.75 |

**Table 4.**



| Test<br>#<br> | Crushed Core mass<br>[g] | Initial Conc.<br>[ppm] | Duration of Each Test<br>[hrs] | Z equilibrium Conc.<br>[ppm] | Z Ads. per Gram of Crushed Core ($q_e$)<br>[mg/g] |
|---|---|---|---|---|---|
| 1 | 50 | 1200 | 2 | 938 | 1.31 |
| 2 | 50 | 2400 | 2 | 2042 | 1.79 |
| 3 | 50 | 4800 | 2 | 4325 | 2.37 |
| 4 | 50 | 7200 | 2 | 6690 | 2.55 |

**Table 5.**

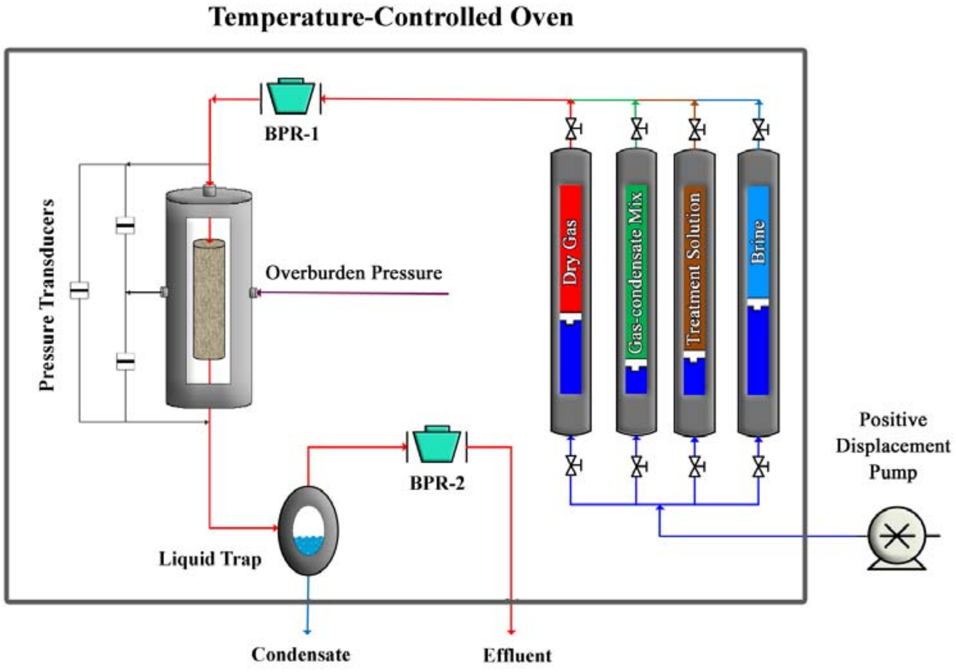


| **Dew point pressure (psi)** | 4128 |
|---|---|
| **Temperature (°C)** | 80 |
| **Core pressure (psi)** | 3000 |
| **Liquid dropout ($V/V_t$, %)** | 14.57 |
| **Gas-condensate flow rate (cc/hr)** | 420 |
| **Surfactant** | Z |
| **Solvent** | Ethanol |
| **Surfactant concentration (wt %)** | 1 |
| **Upstream pressure (psi)** | 4400 |
| **Downstream pressure (psi)** | 3000 |

**Table 6.**

| | Exp#3 | Exp#7 | Exp#11 | Exp#12 |
|---|---|---|---|---|
| **K, md** | 5.26 | 6.45 | 3.53 | 3.12 |
| **Porosity, %** | 28.3 | 27.9 | 28.5 | 28.3 |
| **$S_{wi}$, %** | 0 | 43 | 0 | 30 |
| **$K_{rg}$ Pre-treatment** | 0.203 | 0.133 | 0.155 | 0.151 |
| **$K_{rg}$ Post-treatment** | 0.302 | 0.124 | 0.262 | 0.231 |
| **IF** | 1.49 | 1.61 | 1.70 | 1.53 |

**Table 7.**


Temperature-Controlled Oven
BPR-1
Pressure Transducers
Overburden Pressure
Dry Gas
Gas-condensate Mix
Treatment Solution
Brine
Positive Displacement Pump
BPR-2
Liquid Trap
Condensate
Effluent

# Figure captions

Fig. 1. Molecular structure of Zonyl® UR

Fig. 2. Neutralization curve for Zonyl® UR

Fig. 3. Schematic of the spontaneous imbibition setup

Fig. 4. Schematic of the experimental setup for Coreflood experiments

Fig. 5. Phase envelope for the synthetic gas-condensate

Fig. 6. Liquid dropout during constant composition expansion at 80˚C

Fig. 7. Contact angle of (a) n-decane and (b) brine after treatment with 1% surfactant Z in ethanol

Fig. 8. Contact angle of (a) n-decane and (b) brine after treatment with 1% surfactant N.Z in water

Fig. 9. Brine droplets on the surface of the air saturated (a) before and (b) after Z treatment

Fig. 10. Gas recovery by spontaneous brine imbibition

Fig. 11. Gas recovery by spontaneous n-decane imbibition

Fig. 12. The comparison of %OGIP for initial and after 30 days brine imbibition with 1% surfactant Z in ethanol

Fig. 13. Areas analysis by SEM-EDAX for Surfactant (a) Z and (b) N.Z

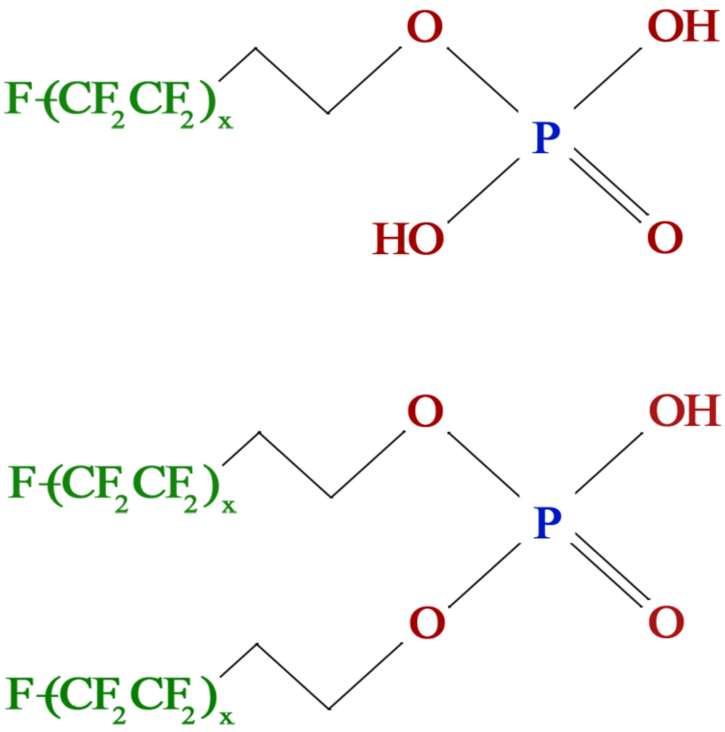
Fig. 14. EDAX spectrum of area No. 4 on treated surface with surfactant Z in ethanol

Fig. 15. SEM images of treated surfaces with surfactant (a) Z in ethanol and (b) N.Z in water

Fig.16. Langmuir and Freundlich isotherms obtained by using linear method for Z onto crushed core

Fig. 17. Pressure drop for pre- and post-treatment at $S_{wi}$=43, Exp #7

Fig. 18. Pressure drop for pre- and post-treatment at $S_{wi}$=0, Exp #11



(x = 1 to 7)

Fig. 1.

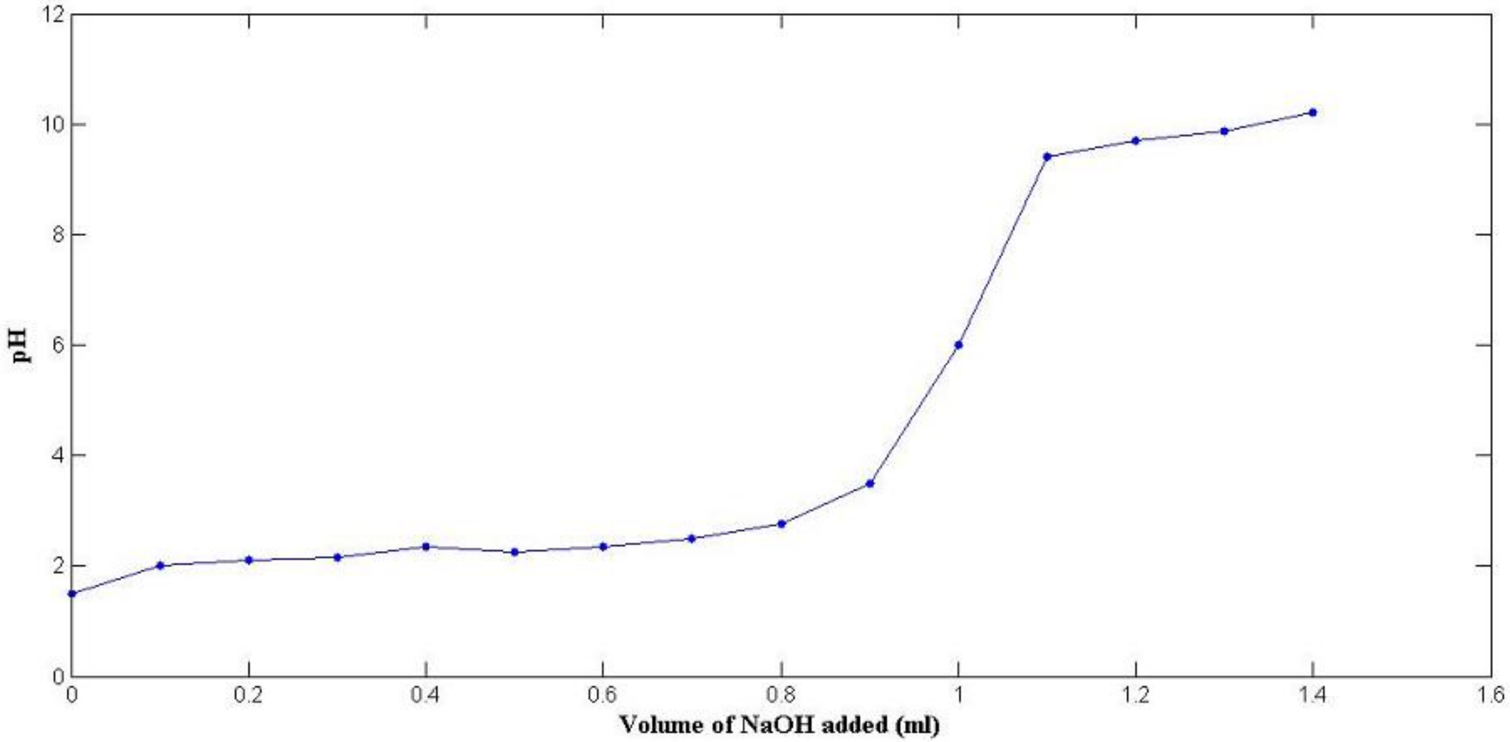


Fig. 2.

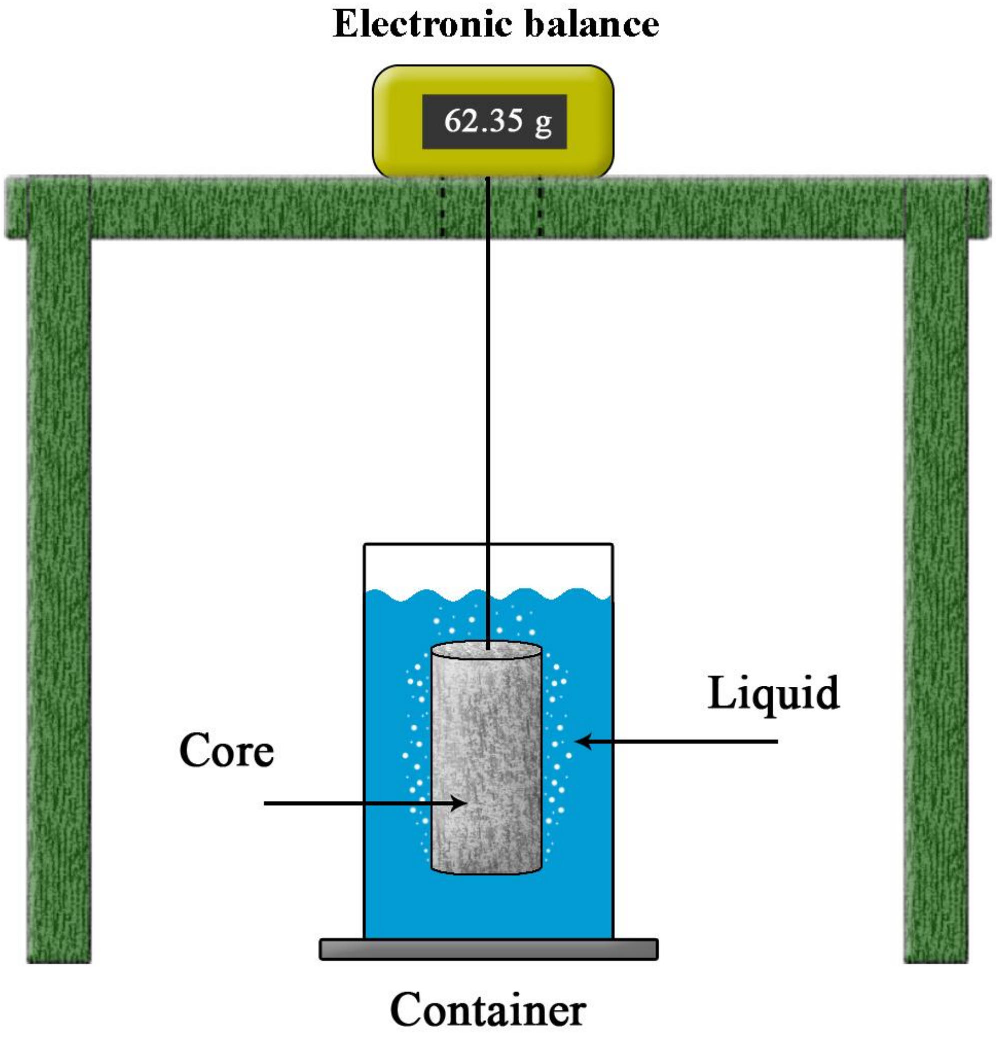


**Fig. 3.**

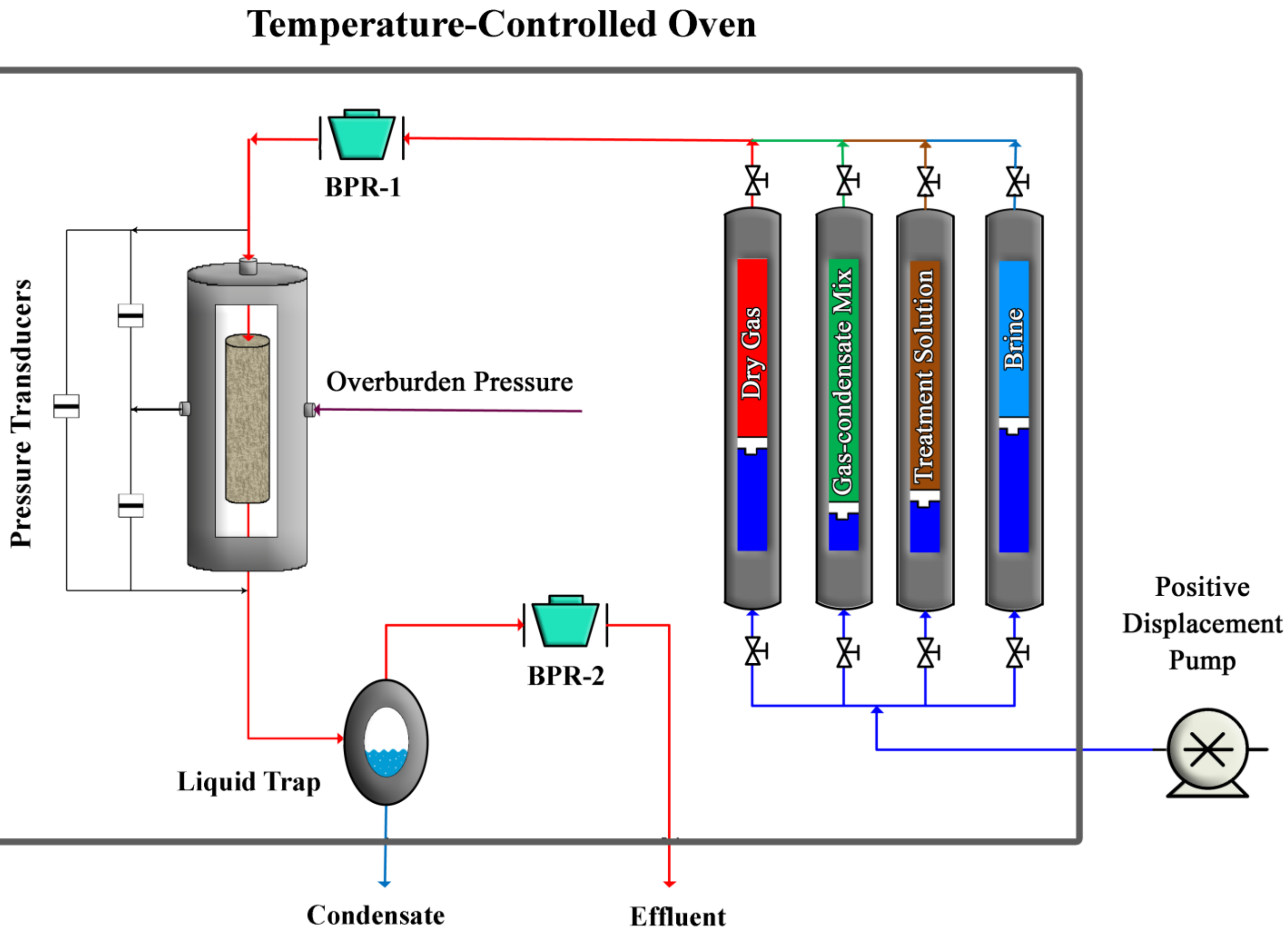
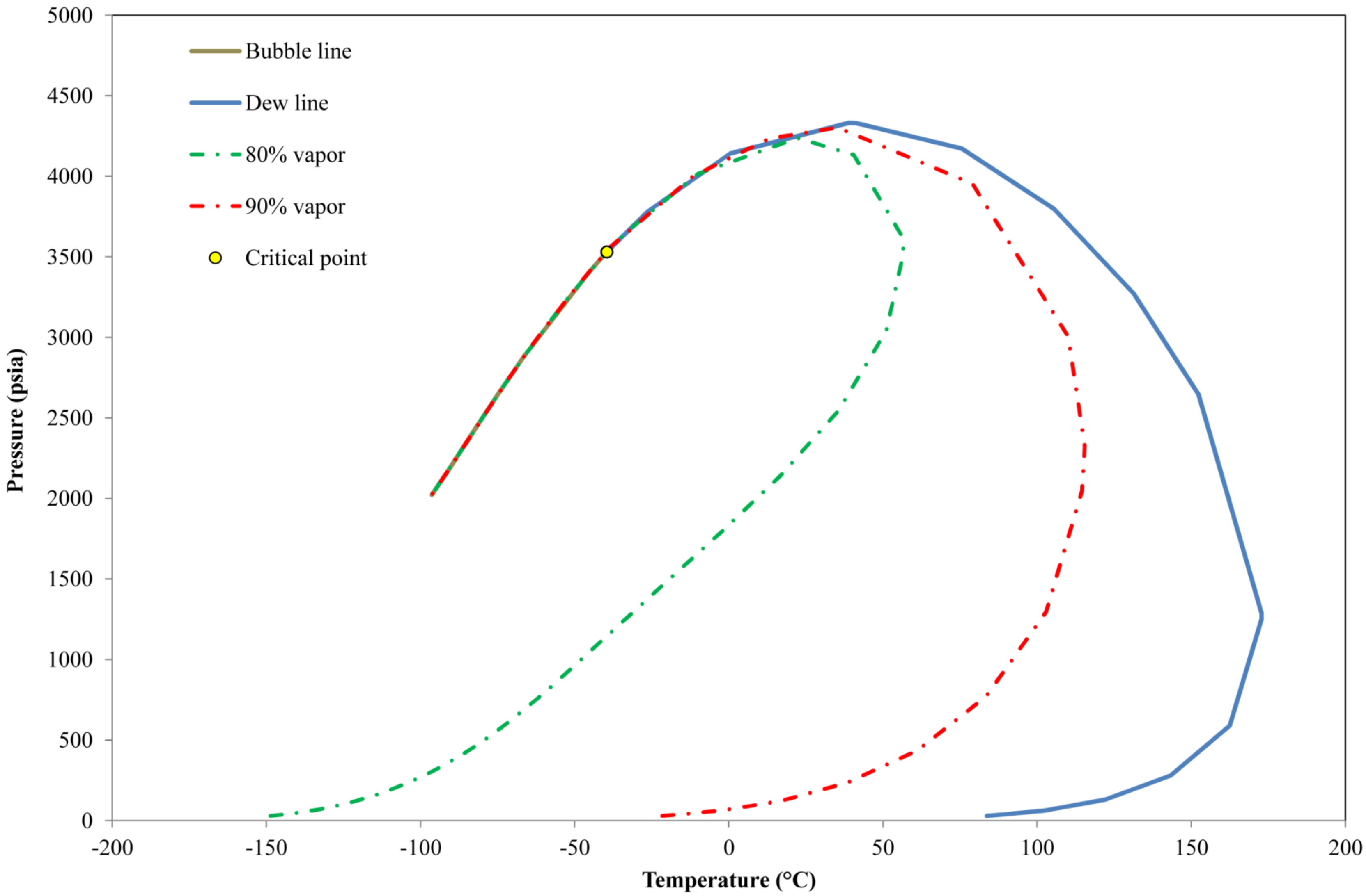
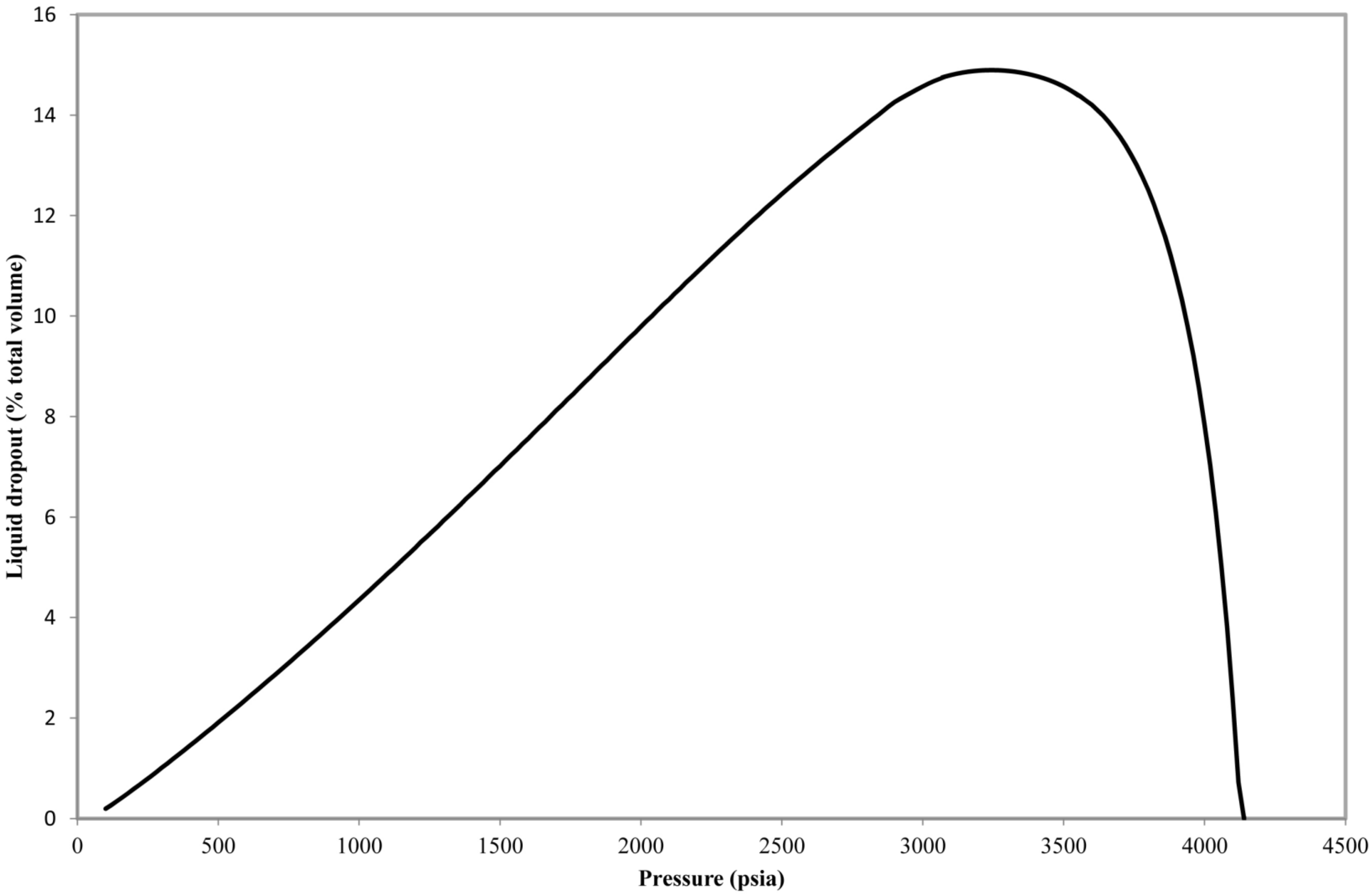

Temperature-Controlled Oven
BPR-1
Pressure Transducers
Overburden Pressure
Dry Gas
Gas-condensate Mix
Treatment Solution
Brine
Positive Displacement Pump
BPR-2
Liquid Trap
Condensate
Effluent

Fig. 4.



5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Pressure (psia)
-200
-150
-100
-50
0
50
100
150
200
Temperature (°C)
Bubble line
Dew line
80% vapor
90% vapor
Critical point

**Fig. 5.**



Liquid dropout (% total volume)
0
2
4
6
8
10
12
14
16
Pressure (psia)
0
500
1000
1500
2000
2500
3000
3500
4000
4500

**Fig. 6.**

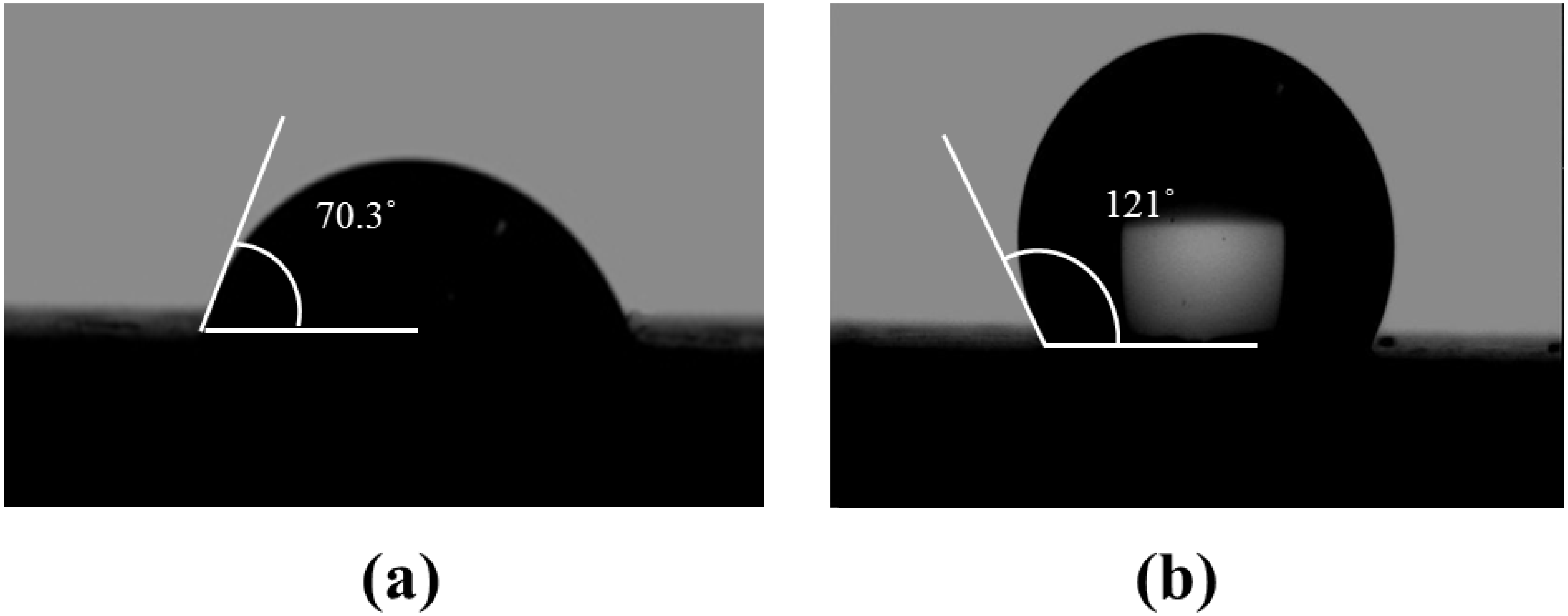


Fig. 7.

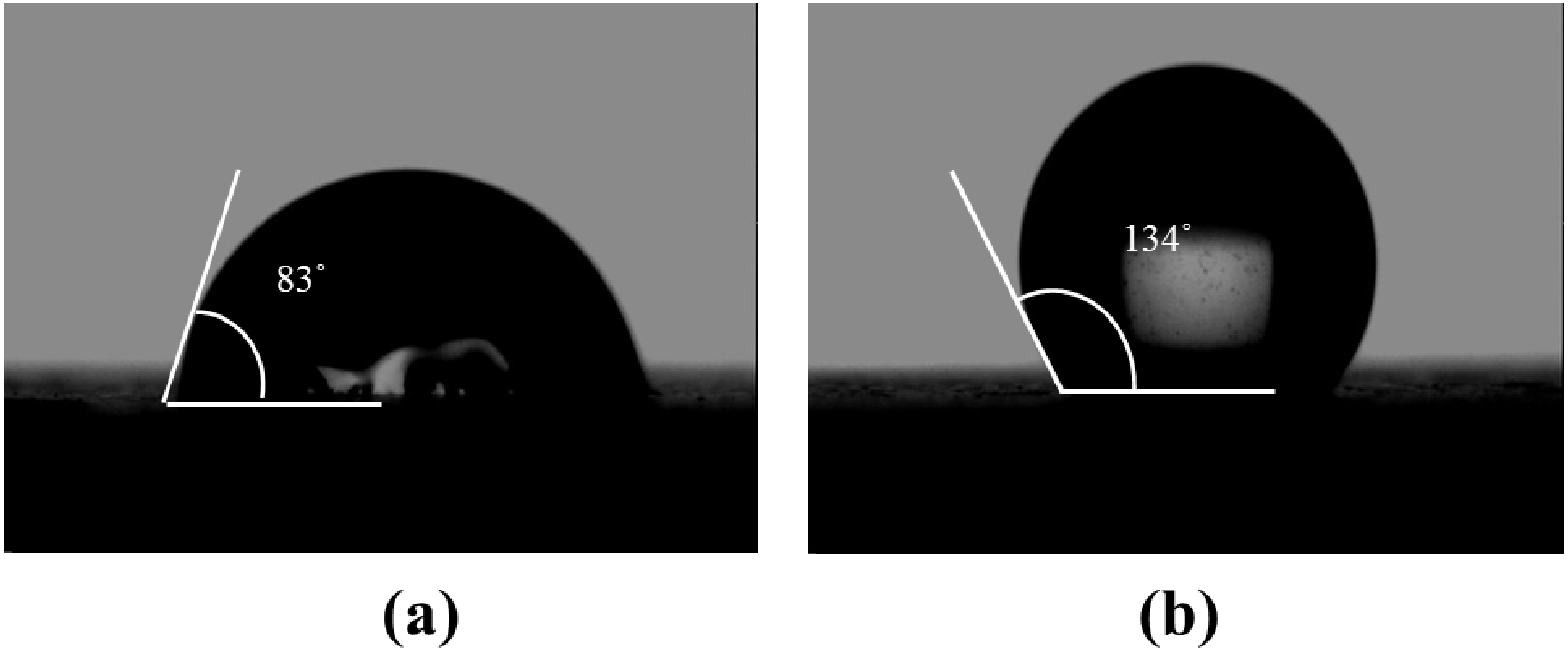


Fig. 8.

**Fig. 9**.

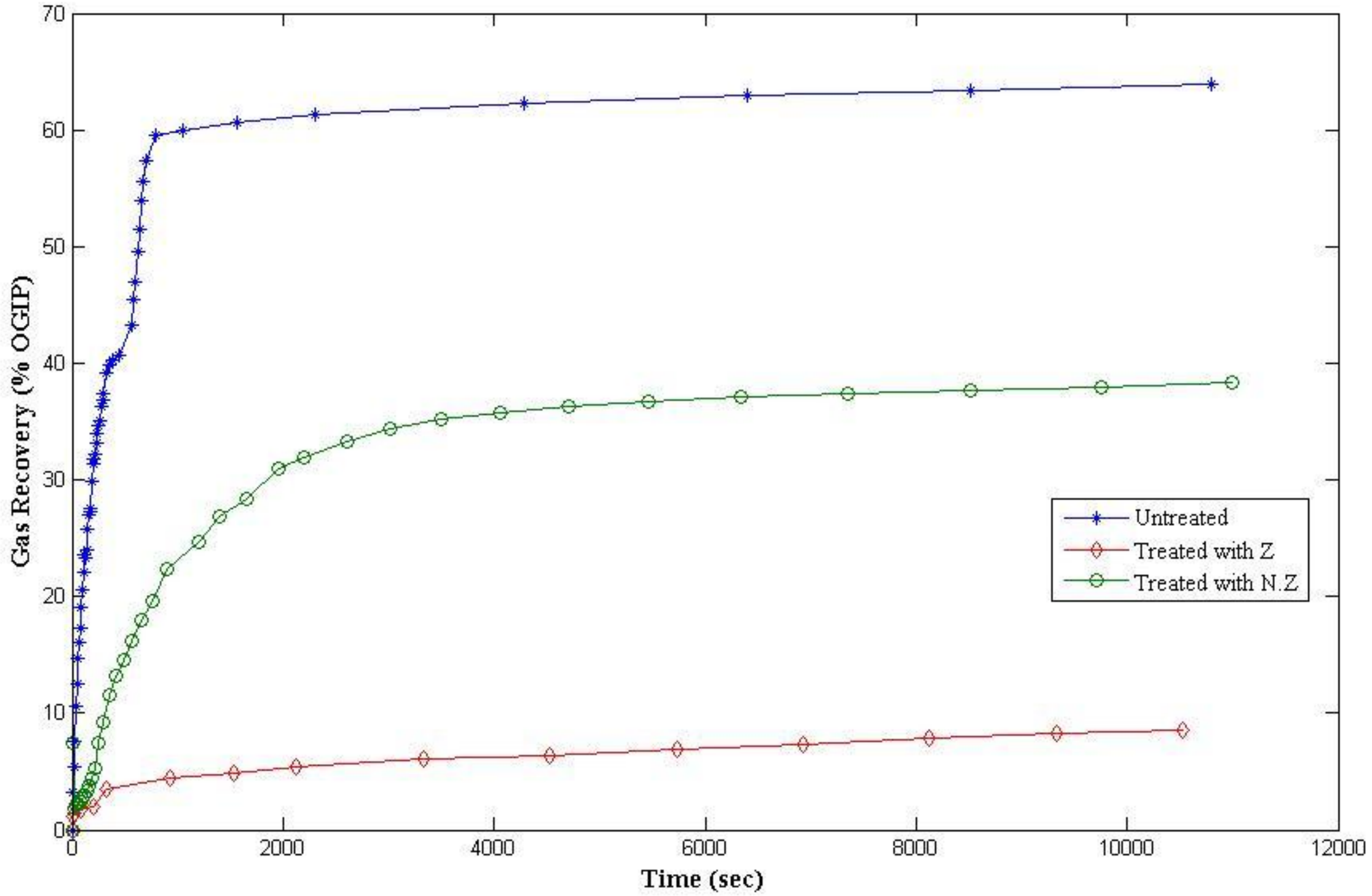

70
60
50
40
30
20
10
0
Gas Recovery (% OGIP)
0
2000
4000
6000
8000
10000
12000
Time (sec)
Untreated
Treated with Z
Treated with N.Z

**Fig. 10**.

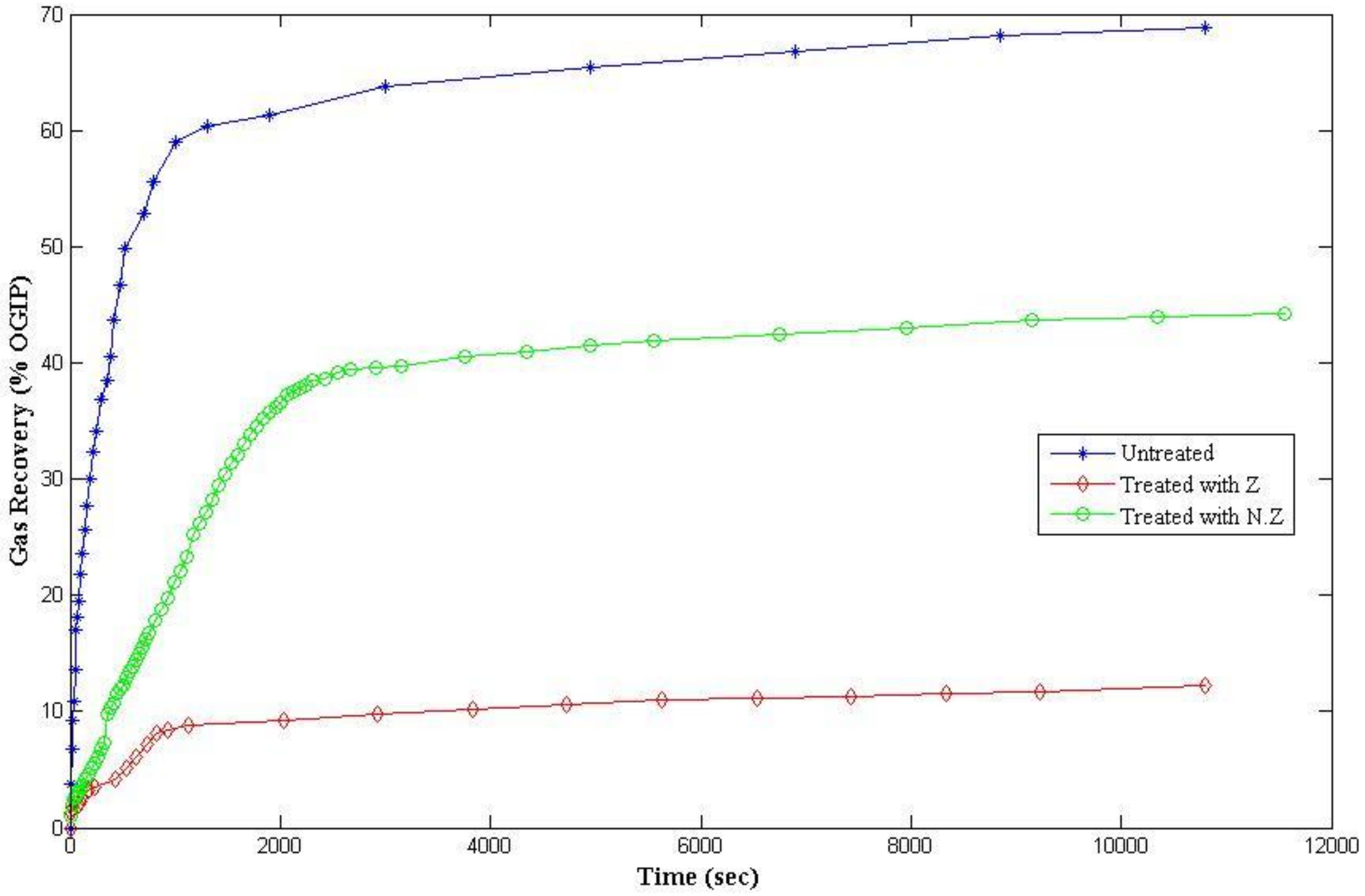

Gas Recovery (% OGIP)
0
10
20
30
40
50
60
70
Time (sec)
0
2000
4000
6000
8000
10000
12000
Untreated
Treated with Z
Treated with N.Z

**Fig. 11.**

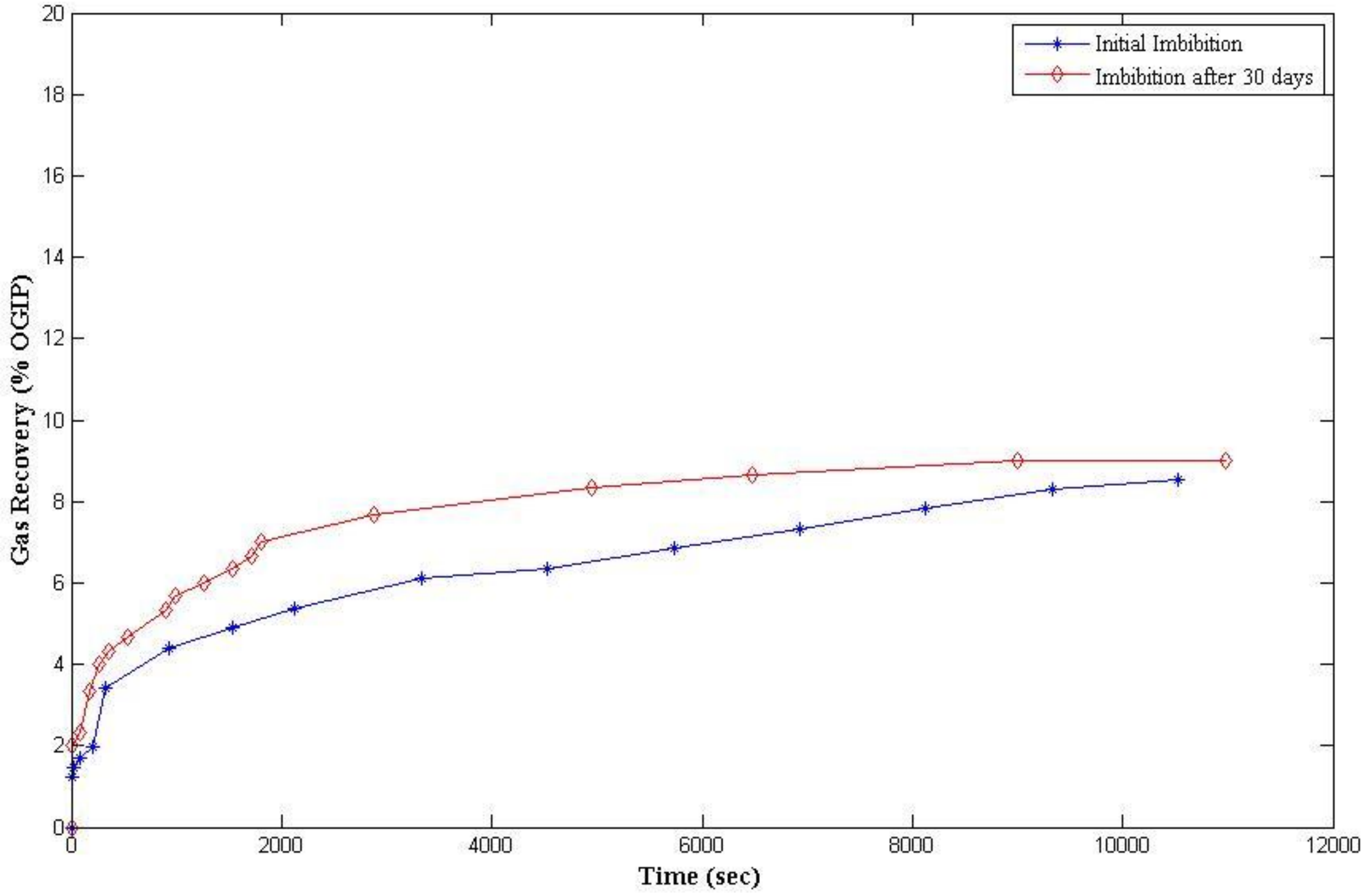

Initial Imbibition
Imbibition after 30 days
Gas Recovery (% OGIP)
Time (sec)
0
2
4
6
8
10
12
14
16
18
20
0
2000
4000
6000
8000
10000
12000

**Fig. 12.**

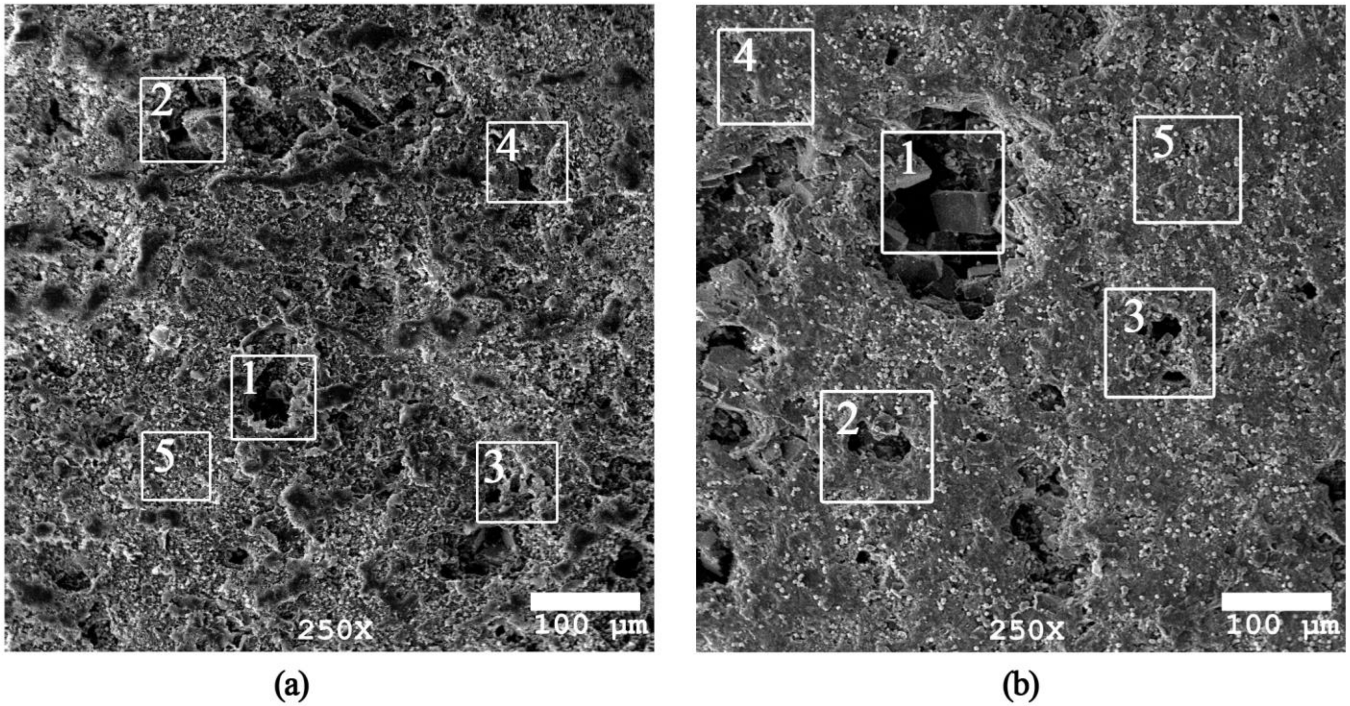


**Fig. 13.**

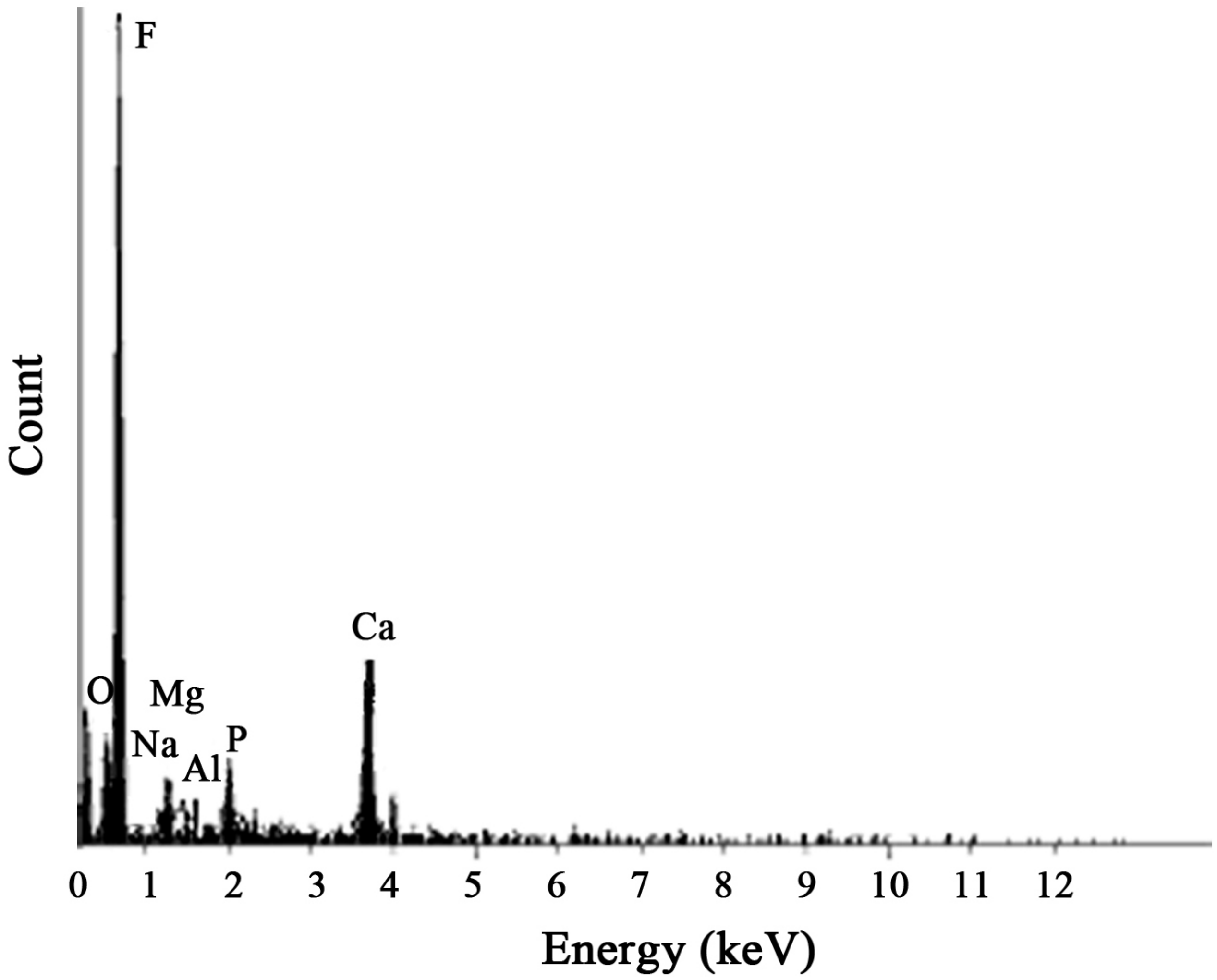


**Fig. 14**.

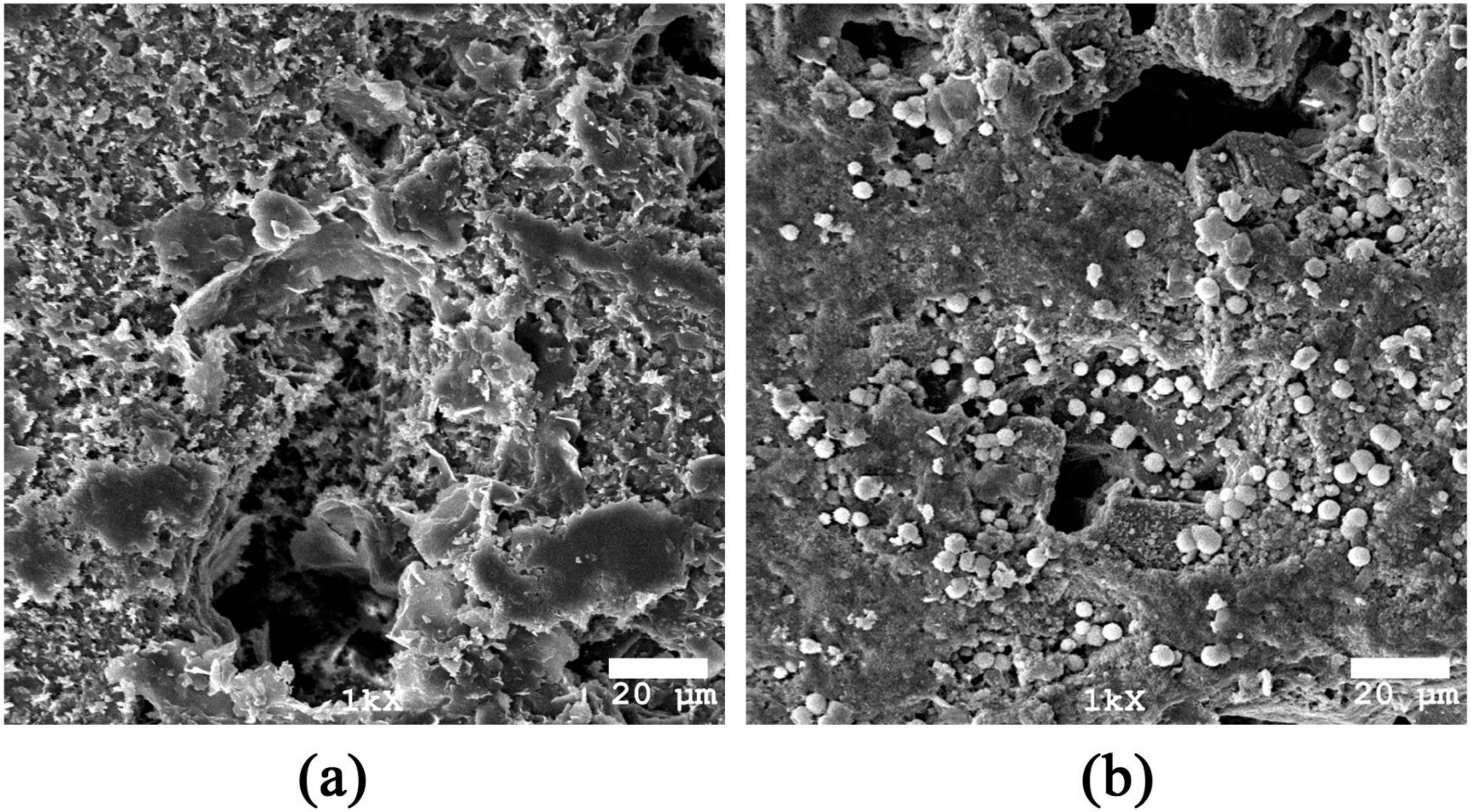


Fig. 15.

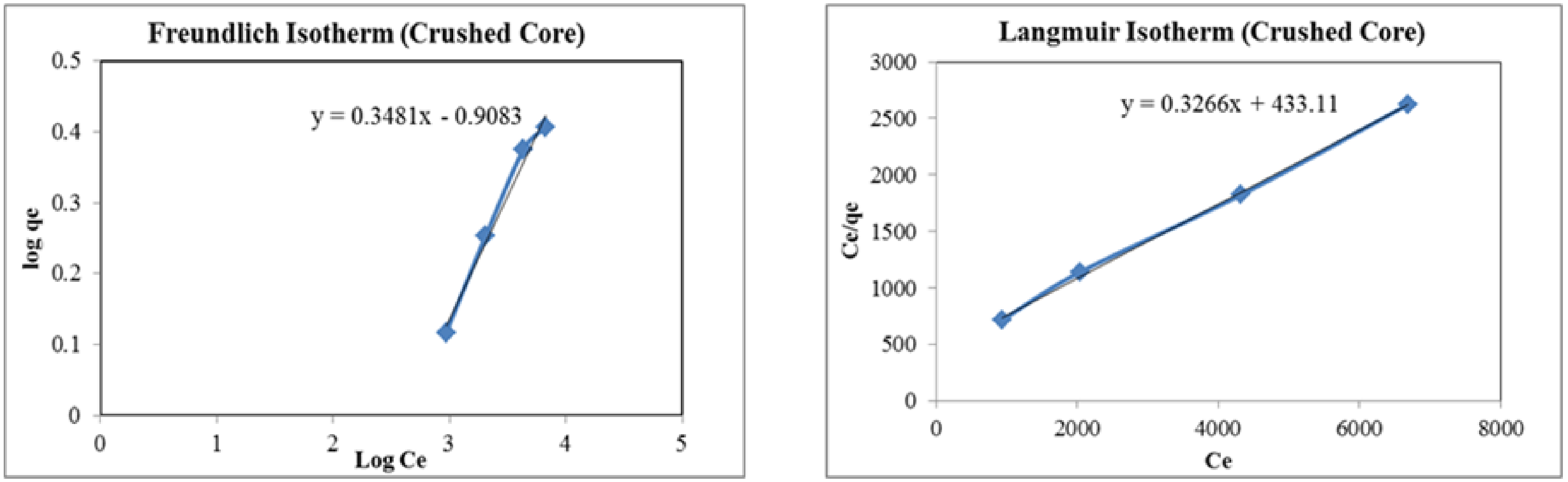

Freundlich Isotherm (Crushed Core)
y = 0.3481x - 0.9083
log qe
Log Ce
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
Langmuir Isotherm (Crushed Core)
y = 0.3266x + 433.11
Ce/qe
Ce
3000
2500
2000
1500
1000
500
0
0
2000
4000
6000
8000

**Fig. 16.**

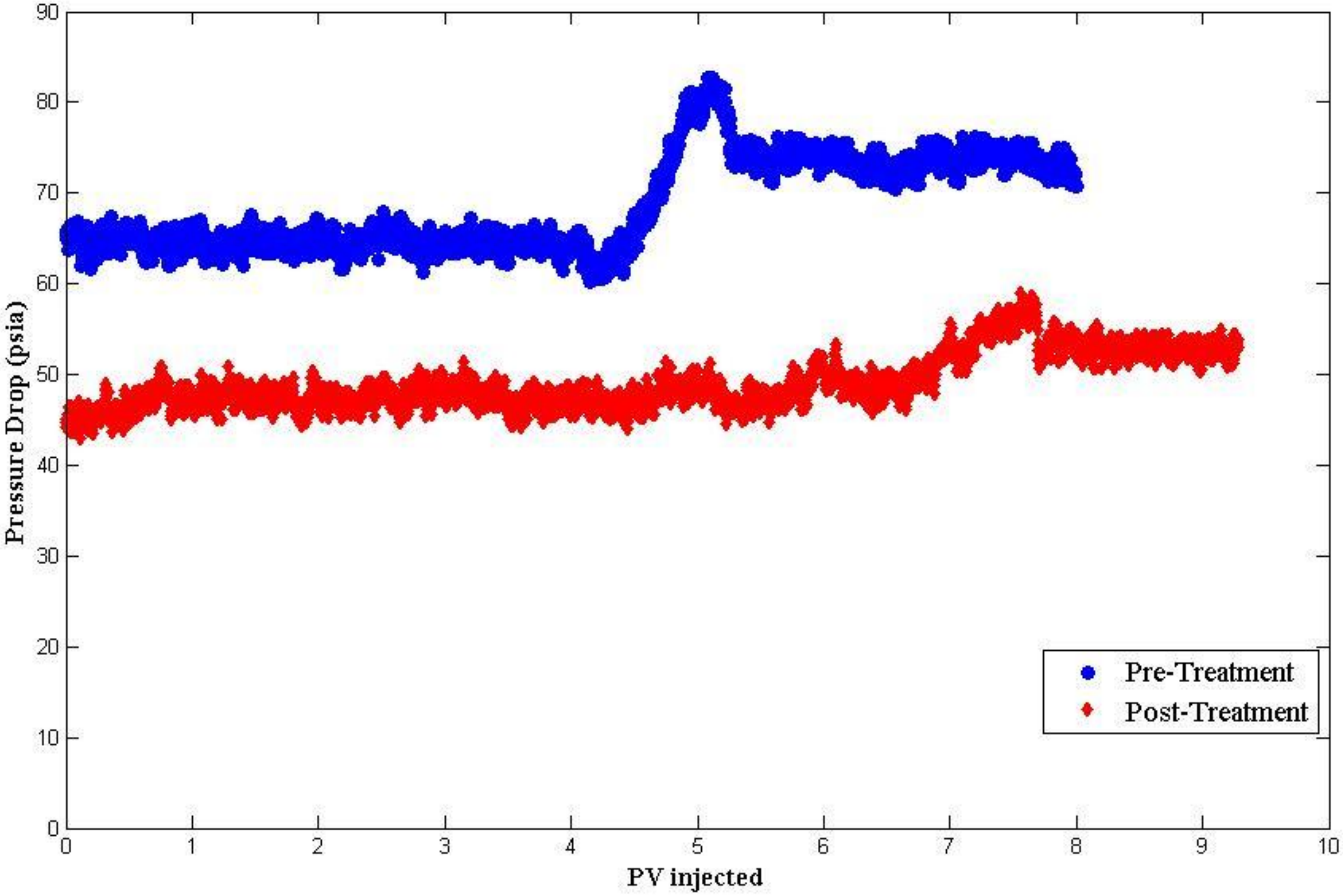
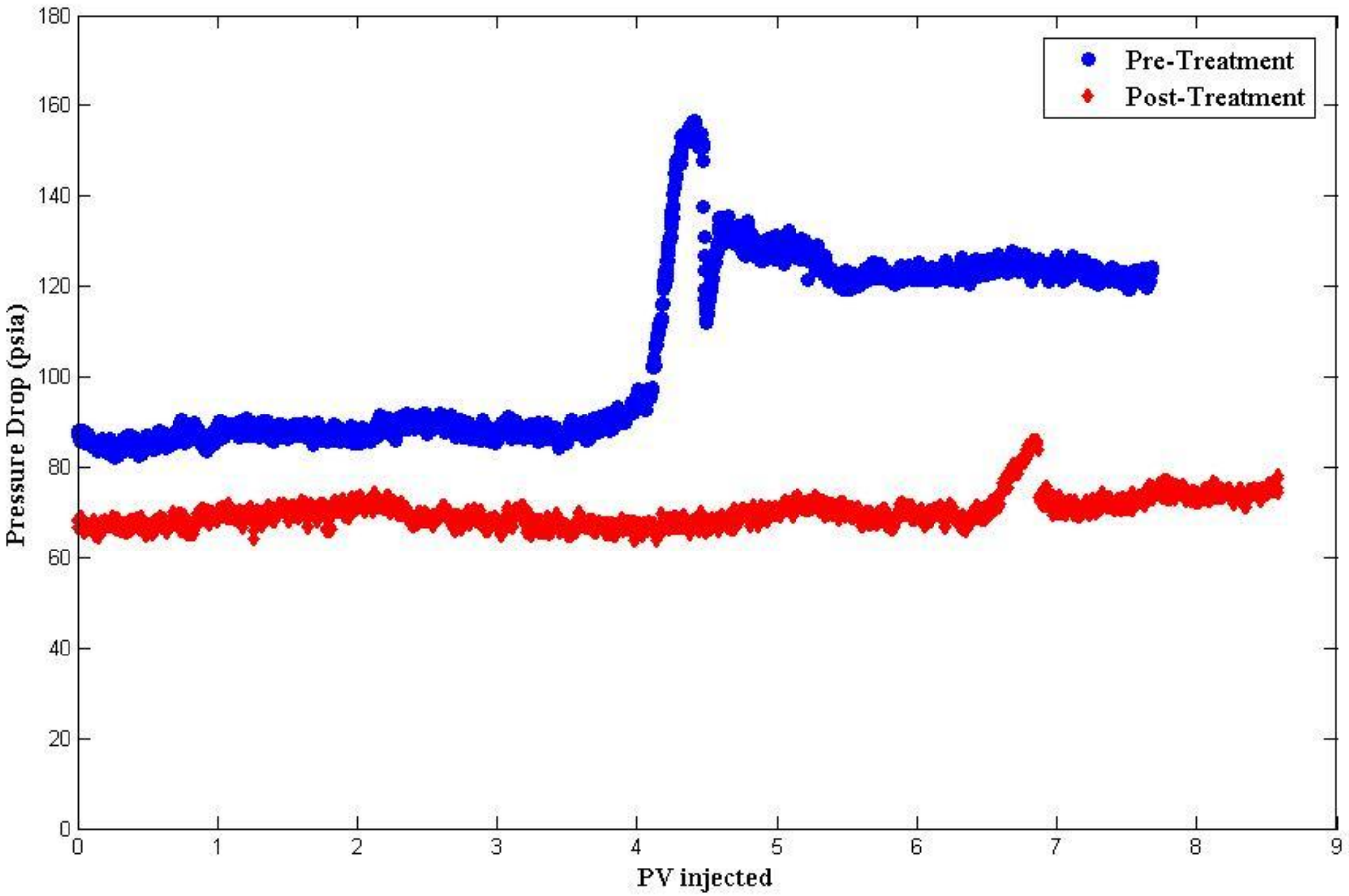

Pressure Drop (psia)
PV injected
0
10
20
30
40
50
60
70
80
90
0
1
2
3
4
5
6
7
8
9
10
● Pre-Treatment
♦ Post-Treatment

Fig. 17.



180
160
140
120
100
80
60
40
20
0
Pressure Drop (psia)
0
1
2
3
4
5
6
7
8
9
PV injected
● Pre-Treatment
♦ Post-Treatment

**Fig. 18.**