

1 **Experimental study of carbonate rock-oil-acid solution in the oil well acidizing**
2 **from a molecular and macroscopic points of view**

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12 **Abstract**

13 This study addresses the rock-fluid interactions in the carbonate rock acidizing from molecular
14 and macroscopic insights. After treating the aged rock slices, the desorbed hydrocarbon
15 chemistry, wettability alteration, and rock dissolution were studied by using the ATR–FTIR
16 technique, contact angle measurement, and weight loss calculation. To investigate the effect of
17 accompanying ions on the acidizing, the acid solutions were prepared with various dissolving salts
18 (NaCl, Na₂SO₄, MgCl₂, and CaCl₂) and HCl concentrations. The acid solutions (concentrations
19 of 0.05% and 0.2%) with a base of distilled water showed a higher rock dissolution respect to the
20 ones with a brine water base. The weakest dissolution was observed in the solution with the

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1 formation water base, showing the inhibition effect of formation water on dissolution. The
2 acidizing of the aged rock slice increased the rock hydrophilicity. Based on the contact angles,
3 the Na₂SO₄ and KCl are prohibiting agents for hydrocarbon desorption. According to ATR-FTIR
4 characteristic indexes, aromatic hydrocarbons have a greater desorption respect to the aliphatic
5 ones. The asphaltenes have a higher potential to be desorbed from the rock surface in the
6 acidizing. It was shown that the NaCl and CaCl₂ were more feasible for desorbing the aromatic
7 hydrocarbons.

8 **Keywords.** Acidizing; Desorption; ATR-FTIR spectroscopy; Wettability alteration; Rock
9 dissolution; contact angle; carbonate reservoir

10 **1. Introduction**

11 It is imperative for each drop of crude oil to traverse the porous medium near the wellbore region
12 before reaching the surface. Therefore, ensuring the smooth flow of fluid in the wellbore region
13 is crucial for achieving optimal production capacity [1]. Regrettably, oil wells face a myriad of
14 challenges, spanning from issues arising during drilling and completion operations to challenges
15 encountered in the production stages [2,3]. In drilling operations with overbalanced conditions,
16 the drilling mud enters the oil zone, leading to wellbore damage [4]. The completion and
17 workover fluids also have the potential to damage the oil zone in a similar way [2]. The damage
18 to the oil well is not restricted to the drilling and completion. The production could damage the
19 oil well region through organic scale, inorganic scale, and fine migration [5–9]. There are some
20 methods for remediation of damage from oil wells, such as acidizing, fracturing, acid fracturing,
21 microwave, and ultrasonic radiations [10–15]. Acidizing the damaged zone, which is not the
22 most common stimulation method, dissolves or bypasses the damaged area by creating new

1 passages for fluid flow[1]. In acidizing the carbonate reservoirs, the hydrochloric acid with a
2 concentration of 15 or 28%, including an anti-sludge agent, anti-corrosion agent, solvent,
3 oxidizers, and scale removal agents, is injected into the oil well region [16,17]. Regarding the
4 complexity of the acid reactions, the injection rate, injection pressure, and acid volume are vital
5 parameters in designing acidizing operations [1,18]. Novikov et al. 2022, suggested a rating
6 matrix to assess the feasibility of acidizing operation based on the experimental studies. The
7 feasibility of the matrix was proven in pilot field tests, where 8-31% improvement was obtained
8 respect to the conventional acidizing [19]. In addition, Derendyaev et al. 2022 developed a
9 statistical approach to anticipate the effectiveness of emulsion acid injections. higher acidizing
10 efficiency (17–23%.) in two pilot injections proved their suggested approach [20].

11 Extensive research has been conducted to tackle the hurdles associated with acidizing operations.
12 In a study by Shafeer et al. 2019, a microemulsion acid solution was proposed as an effective
13 method for eliminating both organic and inorganic scales produced during the acidizing process.
14 The formulated microemulsion demonstrated efficiency in addressing both types of scales [21].
15 Martyushev et al.2021 used a new emulsion acid that was able to dissolve paraffin deposits aside
16 from the rock dissolution, leading to higher well productivity. The advantages of the novel
17 emulsion acid were lower corrosion, more penetration depth, and the ability to diffuse into low
18 permeability formations due to lower interfacial tension [22]. Ibrahim et al. 2020 used a new
19 additive (based on natural resin materials) to reduce the reaction rate of HCl solutions.
20 According to the three-dimensional CT scan, the acid-flooded carbonate core plug showed a
21 single new passage with a few deviation paths [23]. Karimi et al. 2018 investigated the role of
22 pre-flush in acidizing operation to modify rock surface wettability. By employing various pre-
23 flush fluids, they suggested using a cationic surfactant of C16TAB surfactant with a

1 concentration of 0.5 wet% as an efficient agent for improving the water-wetness of the rock
2 surface. Based on their study, the presence of a cationic surfactant (C16TAB) in the pre-flush
3 fluid did not affect the dissolution rate, making the C16TAB a potential additive for acidizing
4 operations [24]. Al Moajil et al. 2019 used a novel commercial acid formulation to retard the
5 acid reactions and lower the breakthrough time. The CT-scan image of the flooded core plugs
6 showed multiple wormholes. While the compatibility tests reported the presence of organic
7 precipitates, the precipitation did not affect the acidizing stimulation [25].

8 Using X-ray tomographic and filtration tests, Martyushev et al. 2022 suggested that the mineral
9 content of carbonate formations (calcium and dolomite) highly influences the performance of
10 acidizing. They showed that the presence of quartz in the carbonate formation leads to an
11 increase in the formation permeability [26].

12 Jafarpour et al. 2019 improved the efficiency of the acidizing operation by introducing a multi-
13 bached acid system. They suggested using a surfactant (GF – 15 MPS) at the 0.5% concentration
14 of 0.5% as an additive to the HCl solution to improve the acidizing performance in multi-layered
15 oil zones. The ability of the multi-bached acid for diversion was confirmed in the coreflooding
16 tests [27].

17 It is well-understood that acidizing of the carbonate rock dissolves the formation matrix, leading
18 to opening new pathways for reservoir fluids. Although many research papers have aimed to
19 improve the rock-fluid interaction in the acidizing operation, it is not fully understood. This
20 research aims to investigate the two poorly addressed aspects of acidizing: 1. desorption of
21 hydrocarbon from the rock surface and 2. the effect of companying dissolved ions on the rock-
22 fluid interactions. In this regard, rock-fluid interactions were studied by examining the rock
23 dissolution, wettability alteration, and desorption of the hydrocarbon from the rock surface.

1 Employing the acid (HCl) solutions with various ion contents enabled us to discuss the effect of
2 accompanying ions on acidizing performance. In addition, aside from wettability alteration and
3 rock dissolution, the ATR-FTIR analysis was employed to address the chemistry of separated
4 hydrocarbons to know whether the desorption is selective or not.

5 **2. Materials and Methods**

6 **2.1 Materials**

7 **2.1.1 Oil sample**

8 The crude oil, which is used in this study was sampled from an oil field in the south of Iran. The
9 physical properties of the oil samples are shown in Table 1. As shown in Table 1, the employed
10 oil sample was an asphaltene-rich oil with low API.

11 **Table 1**

12 **2.1.2 Rock slice**

13 The rock samples, which originated from chemical carbonate rocks in the sea bed of the Persian
14 Gulf Sea, were used to be used for conducting the experiments, including rock dissolution, ATR-
15 FTIR, and contact angle measurement. After extracting tablet-shaped rock slices from the rock
16 sample using the thawing device, they were washed with toluene and methanol using a soxhlet
17 device. The washing process was continued for 10 and 2 days for respectively toluene and
18 methanol washing. After drying the rock slices, regarding their water-wetness wettability
19 condition, it was required to restore the reservoir wettability condition. In this regard, the rock
20 slices were saturated with the synthetic formation water, and then, they were kept at 90°C for 2
21 days. Afterward, the brine water-saturated slices were dynamically saturated by crude oil. After

1 saturating the slices, they were kept at 90°C for 35 days to restore the reservoir wettability
2 condition. The petrophysical properties of the rock slices were obtained using core analysis of
3 the cylindrical core plugs extracted from the rock sample. The petrophysical properties of the
4 rock slices are shown in Table 2.

5 While the reservoir formations typically exhibit lower porosity and permeability than the rock
6 slices analyzed in this study, the experimental rationale necessitated the utilization of rock slices
7 with minimal impurities. The static acid treatment of these rock slices was carried out without
8 external pressure. Given the brief exposure time in static tests, employing rock slices with high
9 permeability proved crucial for expediting the diffusion of acid solution throughout the entire
10 porous medium. Carbonate rock samples, owing to their chemical origin, are known for their
11 high purity. Therefore, their inclusion in this study, which seeks to investigate rock-fluid
12 interactions at a molecular level, was deemed suitable.

13 To investigate the purity of the employed rock sample, the X-ray fluorescence (XRF) analysis
14 was used. Based on the XRF result, which is shown in Fig 1, 94.5% of the employed rock sample
15 is comprised of CaCO_3 (s).

16 **Table 2**

17 **Fig 1**

18 **2.1.3 Acid solutions**

19 To investigate the effect of acid concentration, dissolving ions, and ion concentration, the acid
20 solutions with various HCl concentrations and ion content were prepared. Although the
21 concentration of acids used in the conventional acidizing process is 15-28%, using high acid
22 concentration makes the rock surface uneven. The high roughness of the rock surface makes it

1 impossible to conduct the ATR-FTIR tests. Hence, the acid solutions were prepared at two acid
2 concentrations of 0.5 and 2 g/L. To investigate the effect of accompanying dissolved ions on the
3 rock-fluid interactions, the salts of NaCl, Na₂SO₄, MgCl₂, and CaCl₂ were added to the acid
4 solution at concentrations of 1,000 and 10,000 ppm. It should be mentioned that the performance
5 of salt-rich acid solutions was compared with the acid solution with base water of formation
6 water and distilled water.

7 The employed concentrations were selected according to the trial and error of a wide range of
8 acid concentrations, including 15%. In the high concentrations, the entire rock was dissolved in
9 the acid solutions, making it impossible for further analysis. By lowering the acid concentration
10 to an extent (5%), although some part of the rock remained after spending the acid, the rock
11 surface was completely uneven. Having access to a smooth rock surface is vital for conducting
12 the contact angle, and more importantly, ATR-FTIR tests. It should be mentioned that the larger
13 rock slices were also employed to overcome this problem. Unfortunately, the uneven rock
14 surface was still a serious problem in the static tests with larger rock slices. As a result, using
15 lower acid concentration was the only choice to conduct the static tests in a way that rock-fluid
16 interaction is analyzable.

17 **2.2 Methods**

18 **2.2.1 Rock dissolution**

19 To investigate the effect of dissolving ions on rock dissolution, the treated rock slice profile was
20 obtained. To do so, the aged rock slices with identical weight (10 gr) were immersed in the
21 various acid solutions at a temperature of 90°C. The weight of the treated rock slices was
22 measured using a digital scale every 30 min. To remove the effect of the salt weights, the rock

1 slices were flushed with distilled water and then gently heated to vaporize the water. After
2 measuring the rock slice weight, it was returned to the acid solution for further treatment. This
3 procedure was continued until the rock slice weight was not changed due to treatment. At this
4 point, the rock slice was ready for ATR-FTIR and contact angle measurement.

5 **2.2.2 Contact angle measurement**

6 The wettability is one of the essential parameters controlling fluid flow in the porous medium
7 [28,29]. To investigate the acid treatment effect on the wettability condition of acid-treated rock
8 slices, the contact angle measurement was used. The sessile drop method was used to measure
9 the contact angle. The contact angles were measured when no changes were observed in the
10 weight of rock slices due to the treatment. The contact angles of the acid-treated rock slices were
11 compared with the contact angle of the aged one to investigate the effect of acid treatment on
12 wettability condition.

13 **2.2.3 ATR-FTIR spectroscopy**

14 To study the chemistry of the desorbed hydrocarbon due to acid treatment, ATR-FTIR
15 spectroscopy was used. While the contact angle measurement investigates the rock slice
16 wettability condition, it is blind to the chemistry of the desorbed hydrocarbon. Hence, conducting
17 the ATR-FTIR test is required for studying the changes to the compounds on the rock surface.
18 The ATR-FTIR spectrums were obtained using a refractometer (PerkinElmer, USA). The
19 spectrums were obtained in the absorbance configuration. This action was done to make
20 numerical data extraction possible. The spectrums were obtained in the wavelength range of 600-
21 4000 cm^{-1} with a resolution of 1 cm^{-1} . Using the characteristic indexes, which were suggested by
22 Karami et al 2022, the Carbonyl/Aliphatic, Carbonyl /Aromatic, Aromatic/ Aliphatic, Aliphatic

1 length, Polar/Aliphatic, and Polar/Aromatic indexes were calculated [11]. The indexes were
2 calculated by using the integral area from the start to the end of each peak. It should be
3 mentioned that the integral areas were calculated using Origin software.

4 **3. Results and Discussion**

5 **3.1 Rock dissolution**

6 As mentioned before, to investigate the effect of companying ions on rock dissolution, the profile
7 of weight reduction was obtained. To do so, aged rock slices with identical weights (10 gr) were
8 treated with an acid solution with various ion content and acid concentrations. The slice weight
9 was measured in a time step of 30 min until no weight loss was observed. Tables 3-4 show the
10 weight loss of rock slices treated by acid solutions with time steps of 30 min in terms of
11 percentage.

12 **Table 3**

13 **Table 4**

14 As shown in the weight loss profile in Tables 3-4, the rock dissolution due to acidizing is
15 influenced by the chemistry of base water (ion content and concentration). Both of the acid
16 solutions (concentrations of 0.5 and 2 g/L) had a higher rock dissolution respect to the acid
17 solutions with brine water base. Among the acid solutions with salt-rich base water, the CaCl_2
18 and Na_2SO_4 salts reduce the rock dissolution with more severity. For instance, in the acid
19 solutions with a concentration of 0.5 g/L, while the rock dissolutions were 3.06-3.97 and 3.05-
20 3.49% for acid solutions bearing CaCl_2 and Na_2SO_4 , other solutions dissolved 3.39-4.84% of the
21 carbonate rock. In both acid concentrations, the presence of salts in the acid solutions drastically
22 reduced the rock dissolution, indicating the buffering effect of salts for rock dissolution.

1 3.2 Wettability alteration

2 To study the effect of the acid solution with various accompanying ion types and concentrations,
3 the contact angle of the aged/treated rock slice was measured. The aged rock slice was treated
4 with Hydrochloric acid solutions with two concentrations (0.5 and 2 g/L) and three different salt
5 concentrations (0, 1,000, and 10,000 ppm). The brine acid solutions were synthesized with single
6 salts of NaCl, CaCl₂, MgCl₂, Na₂SO₄, and KCl to evaluate the effect of individual ions. The
7 formation water and distilled water-based acid solutions were also used for comparison. Table 5
8 shows the contact angles of the aged and acid-treated rock slices. As mentioned before,
9 according to the multiple contact angle measurements, the accuracy of the obtained data is $\pm 0.6^\circ$.

10 **Table 5**

11 According to Table 5, the acid treatment of the aged rock slice commonly enhances the rock
12 hydrophilicity. The contact angle of the treated rock slice depends on the accompanying ion type
13 concentration and HCl concentration. Comparing the contact angles of rock slices treated with
14 0.5 and 2 g/L acid solutions, increasing HCl concentration enhances the hydrophilicity of the
15 treated rock slice. As shown in Table 5, among the rock slices treated with identical base waters,
16 the one treated with the acid concentration of 2g/L has a lower contact angle. For example, the
17 contact angles of the rock slices treated by acid solution with the base of formation water are
18 respectively 108 and 67° for HCl concentrations of 0.5 and 2 g/L. Regarding the fact that a lower
19 contact angle indicates less adsorbed hydrocarbon, the HCl solution enhances the hydrocarbon
20 desorption.

21 The ion type and content of the acid solution affect the contact angle of the treated rock slice. In
22 both acid concentrations, the acid solutions with the base of distilled water have a lower contact

1 angle. This observation shows that the presence of ions, regardless of the type and concentration,
2 reduces the ability of acid solution for desorbing the hydrocarbons. In low acid concentration and
3 high salt concentration, where the role of ions is more highlighted, the Na₂SO₄ and KCl salts are
4 prohibiting agents for hydrocarbon desorption. Among the slices treated by acid solution with
5 0.5 g/L concentration, the contact angles of slices treated by Na₂SO₄-rich acid solution are 116
6 and 105°, while the contact angle of other slices lies in the range of 83-110°. According to the
7 contact angles, increasing the accompanying salt concentration, regardless of ion type and
8 concentration, leads to rock hydrophobicity enhancement. In other words, the presence of
9 accompanying ions in an acid solution retards its ability for desorption of the hydrocarbons.

10 **3.3 ATR-FTIR spectroscopy**

11 Although the wettability of the rock slices after the acid treatment was addressed using the
12 contact angle measurements, no information regarding the changes to the surface hydrocarbon
13 chemistry was addressed. The chemistry of the rock surface was addressed by the ATR-FTIR
14 spectrums. To highlight the effect of salt presence in the acid solution, the slices, which were
15 treated with solutions with a salt concentration of 10,000 ppm and acid concentration of 0.5wt%,
16 were selected for the ATR-FTIR tests. The ATR-FTIR spectrums are shown in Fig 2.

17 **Fig 2**

18 The peaks in the ATR-FTIR could be subdivided into three groups: hydrocarbon-assigned, rock
19 mineral-assigned, and peaks common in both hydrocarbons and minerals. Because the presence
20 of mineral-assigned peaks in the ATR-FTIR spectrums is inevitable, the mineral-assigned and
21 common peaks should be excluded from interpretation. The peaks in the range of 2755-3000 cm⁻¹
22 ¹ are standing for the aliphatic hydrocarbons. In addition, the presence of the aromatic

1 hydrocarbons could be captured by 3000-3100 and 1566-1668 cm^{-1} , which are respectively
2 standing for C-H and C-C bonds in aromatic rings. The wide peak in the range of 3100-3500 cm^{-1}
3 indicates the presence of N-H and O-H bonds, representing the polarity of the surface
4 hydrocarbons. It should be mentioned that carbonyl-based functional groups, such as carbocyclic
5 acids, ketones, and aldehydes are captured in the wavelength of 1668-1800 cm^{-1} [10,11,30–39].
6 More information about the ATR-FTIR peak interpretation can be observed in Table 6.

7 **Table 6**

8 After the identification of peaks, which are only assigned to the hydrocarbons, it was necessary
9 to obtain numerical information from the ATR-FTIR spectrums. The integral areas below each,
10 from one valley to another one, were obtained using the Origin software. As mentioned before,
11 the spectrums were obtained in the absorbance mode to facilitate the integral calculation. Using
12 the equation suggested by Karami et al 2022, the chemistry of the rock surface was characterized
13 [11]. The indexes of Carbonyl/Aliphatic, Carbonyl /Aromatic, Aromatic/ Aliphatic, Aliphatic
14 length, Polar/Aliphatic, and Polar/Aromatic were obtained by the corresponding integral areas.
15 Table 7 shows the obtained characteristic indexes from the ATR-FTIR spectrums.

16 **Table 7**

17 According to ATR-FTIR characteristic indexes, the surface hydrocarbon chemistry is highly
18 changed after the acid treatment. Besides, the chemistry of the surface hydrocarbons is greatly
19 influenced by the presence of salts in the acid solution. These observations are consistent with
20 the major difference between the aged and treated rock slices and the minor deviations among
21 the treated slices. As shown in Table 7, the Aromatic/ Aliphatic indexes of the acid-treated slices
22 are lower than the aged one (untreated), indicating more intense desorption of aromatic

1 compounds respect to the aliphatic ones as the result of acid treatment. Hence, the acid treatment
2 of the rock slice led to a reduction of the Aromatic/ Aliphatic index. The Aromatic/Aliphatic
3 index of the hydrocarbons on the rock surface is proportional to the respective concentration of
4 aromatic compounds to the aliphatic ones. As a result, the acid treatment enhances the separation
5 of aromatic compounds from the rock surface. Regarding the fact that during the aging process,
6 the longer aliphatic chains and larger aromatic compounds, such as asphaltenes, are adsorbed
7 onto the rock surface, the respective changes of asphaltene and wax compounds could be
8 deduced from the Aromatic/ Aliphatic index. In this regard, the asphaltene compounds have a
9 higher potential to be desorbed from the rock surface due to acid treatment.

10 Among the acid-treated slices, the Aromatic/Aliphatic index of one treated by acid solution
11 without dissolving ions is higher, representing the contribution of dissolved ions for asphaltene
12 compound desorption. The acid solutions bearing NaCl and CaCl₂ salts were more feasible for
13 oil desorbing the aromatic hydrocarbons. The carbonyl index trends were similar to the
14 Aromatic/Aliphatic index. The acid treatment of rock slices led to the reduction of carbonyl
15 indexes, indicating more feasible desorption of carbonyl-bearing hydrocarbons respect to the
16 aliphatic and aromatic ones. Based on the carbonyl indexes, the presence of the dissolving ions
17 reduces the desorption of aliphatic chains. The NaCl and CaCl₂ salts were more successful in
18 improving the desorption of carbonyl-bearing hydrocarbons. The aliphatic length index, which
19 represents the length of the aliphatic hydrocarbons, was lower in the aged slice. This observation
20 indicates that shorter aliphatic chains have more potential for desorbing from the rock slices. In
21 addition, the lower Aliphatic length index of the slice treated by distilled water-based acid
22 solution showed more affinity of the lighter aliphatic chains for desorption in the absence of
23 dissolving ions. The polar indexes showed that acid treatment of rock slices desorbed the

1 aliphatic chains with more feasibility respect to the aliphatic and aromatic hydrocarbons. Similar
2 to the carbonyl index, the presence of the dissolving ions leads to more desorption of polar
3 hydrocarbons. The acid solution bearing NaCl salts was more efficient for desorption of the polar
4 hydrocarbons (containing O-H and N-H bonds).

5 Based on the ATR-FTIR analysis, the separation of hydrocarbons from the rock surface is not
6 only owing to the dissolution of rock grain as a support surface for adsorbing the hydrocarbons,
7 but the hydrocarbons can also separate from the rock surface due to their chemistry and
8 interactions with HCl molecules.

9 Regarding the conducted tests, the presence of the accompanying ions in the acid solution reduces
10 the ability of the HCl acid for rock dissolution, wettability alteration toward hydrophilicity, and
11 desorption of aromatic compounds, such as asphaltene, from the rock surface. Because all of the
12 mentioned observations reduce acidizing performance, it is recommended to conduct the pre-
13 flush injection in a way that no brine water contacts the acid solution. In addition, using base
14 water with the minimum salinity for providing the acid solution is highly suggested based on the
15 findings of this study.

16 The main limitation of our study is using only static tests to study the rock-fluid interactions. For
17 further investigation, studying the rock-fluid interaction using dynamic tests is highly
18 recommended. Besides, this study addresses the interaction of HCl acid and accompanying ions on
19 the rock-fluid interactions, while other agents, such as anti-sludge and anti-corrosion additives,
20 are commonly involved in the acid solution. Investigating the effects of additives on the rock-
21 fluid interactions from macroscopic and molecular insights is suggested for future studies.

22 **4. Conclusion**

1 1. The rock dissolution due to acidizing is affected by base water composition. Both of the acid
2 solutions (concentrations of 0.5 and 2 g/L) had a higher rock dissolution respect to the acid
3 solutions with brine water base. Among the acid solutions with salt-rich base water, the CaCl_2
4 and Na_2SO_4 salts reduce the rock dissolution with more intensity. The presence of salts in the
5 acid solutions drastically reduced the rock dissolution, indicating the buffering effect of salts for
6 rock dissolution.

7 2. The acid treatment of the aged rock slice increases the rock hydrophilicity. Increasing HCl
8 concentration enhances the hydrophilicity of the treated rock slice. Among the rock slices treated
9 with identical base water, the one treated with higher acid concentration has a lower contact
10 angle. Regarding the fact that a lower contact angle indicates less adsorbed hydrocarbon, the HCl
11 solution enhances hydrocarbon desorption. The ion type and concentration of the acid solution
12 influence the wettability of the treated rock slice. The presence of ions, regardless of the type and
13 concentration, reduces the ability of acid solution for desorbing the hydrocarbons. Regarding the
14 obtained contact angles, the Na_2SO_4 and KCl salts are prohibiting agents for hydrocarbon
15 desorption.

16 3. According to ATR-FTIR characteristic indexes, the desorption of hydrocarbon from rock
17 surfaces is selective. The Aromatic/ Aliphatic index of the aged slice is higher than the treated
18 ones, showing more desorption of aromatic hydrocarbons respect to the aliphatic ones. The
19 asphaltene compounds have a higher potential to be desorbed from the rock surface in the acid
20 treatment. The Aromatic/Aliphatic index of slices treated by acid solution without dissolving
21 ions is higher, indicating the contribution of dissolved ions for asphaltene compound desorption.
22 The acid solutions bearing NaCl and CaCl_2 salts were more feasible for oil desorbing the
23 aromatic hydrocarbons.

1 4. In the end, regarding the negative effects of the accompanying ions on the acidizing
2 performance, it was recommended to prohibit the contact of reservoir brine water with the acid
3 solution using an efficient pre-flush injection. Moreover, selecting a base water with the
4 minimum salinity for preparing the acid solution is suggested to maximize the acidizing
5 feasibility.

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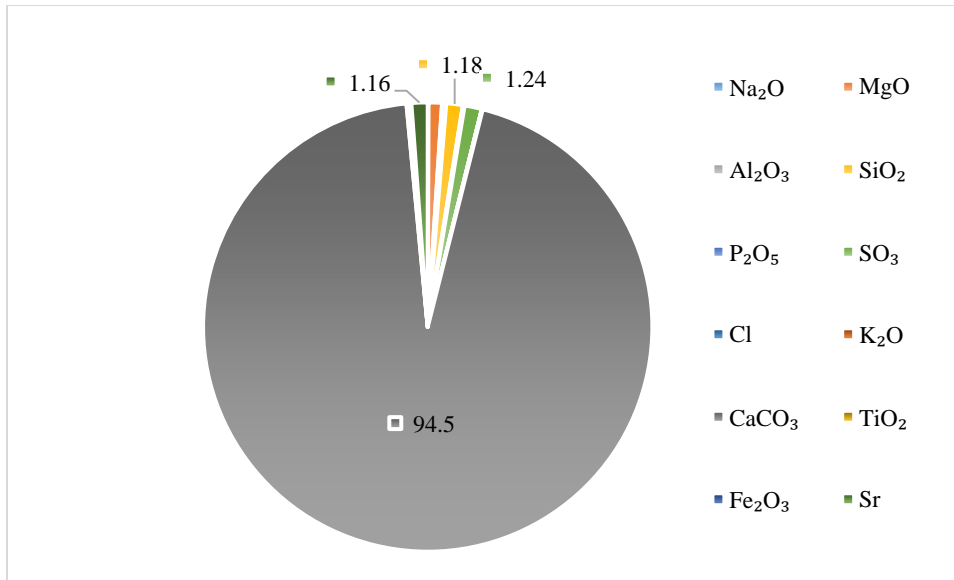


Figure 1. The XRF analysis of employed rock sample.

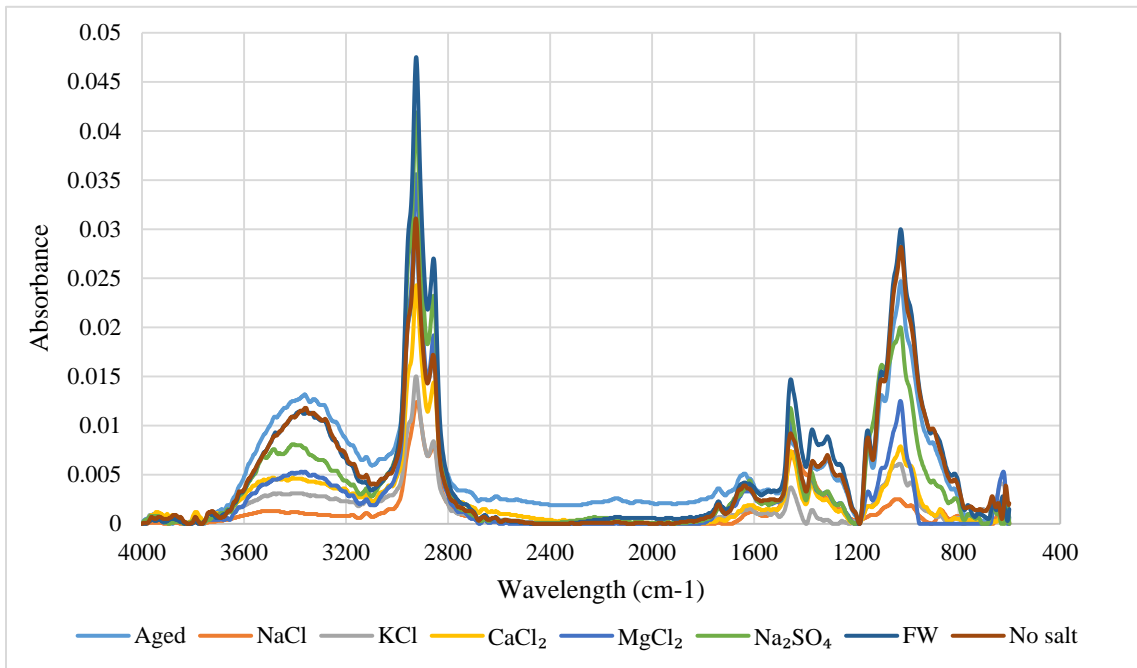


Figure 2. The ATR-FTIR spectrums of the aged and acid-treated rock slices

1 **Tables**

2 **Table 1 .The physical characteristics of the crude oil**

Properties	API (°)	Viscosity (cP) (@ temperature 26°C)	Acid number (mg KOH/g)	Asphaltene content (%)
Values	20.65 °	377	0.6	16

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5 **Table 2. The petrophysical properties of rock sample**

Properties	Porosity (%)	Permeability (D)	Type	Grain density (gr/cm ³)	Thickness (cm)
Rock slice	38.48	3	Carbonate	2.31	0.8

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8 **Table 3. The weight loss of rock slices treated by acid solutions (with various base water) with a concentration**
 9 **of 0.5 g/L with time steps of 30 min in terms of percentage.**

Solutions	Salt Conc (ppm)	Salt Type	30min	60min	90min	120min	150min
#1	1,000	NaCl	1.41	3.43	4.44	4.84	4.84
#2	10,000	NaCl	1.25	2.32	3.04	3.39	3.39
#3	1,000	KCl	1.1	1.76	3.74	4.62	4.62
#4	10,000	KCl	1.86	2.42	3.53	4.65	4.65
#5	1,000	CaCl ₂	1.26	2.34	3.79	3.97	3.97
#6	10,000	CaCl ₂	1.29	1.77	2.58	3.06	3.06
#7	1,000	MgCl ₂	1.3	1.86	2.79	3.73	3.73
#8	10,000	MgCl ₂	2.1	3.15	3.85	4.2	4.2
#9	1,000	Na ₂ SO ₄	0.36	1.65	2.75	3.49	3.49
#10	10,000	Na ₂ SO ₄	2.13	2.74	2.89	3.05	3.05
#11	231,138	FW*	0.89	2.14	2.49	2.67	2.67
#12	0	-	0.92	2.99	4.37	5.52	5.52

*FW stands for formation water.

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1 **Table 4. The weight loss of rock slices treated by acid solutions (with various base water) with a concentration**
 2 **of 2 g/L with time steps of 30 min in terms of percentage.**

Solutions	Salt Conc (ppm)	Salt Type	30min	60min	90min	120min	150min
#13	1,000	NaCl	12.58	13.56	13.89	14.12	14.12
#14	10,000	NaCl	11.53	12.36	12.36	13.04	13.04
#15	1,000	KCl	10.46	11.17	11.73	11.88	11.88
#16	10,000	KCl	11.23	11.81	12.16	12.34	12.34
#17	1,000	CaCl ₂	10.02	10.31	11.34	11.42	11.42
#18	10,000	CaCl ₂	10.65	10.98	11.41	11.78	11.78
#19	1,000	MgCl ₂	12.32	13.71	13.92	14.02	14.02
#20	10,000	MgCl ₂	11.77	12.32	12.89	13.01	13.01
#21	1,000	Na ₂ SO ₄	10.89	11.58	11.72	12.13	12.13
#22	10,000	Na ₂ SO ₄	10.81	12.07	12.35	12.5	12.5
#23	231,138	FW*	11.32	12.36	12.76	12.96	12.96
#24	0	-	15.88	17.12	17.67	17.81	17.81

* FW stands for formation water.

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5 **Table 5. The contact angles of the aged and rock slices treated by acid solutions with various base water**

HCl Concentration: 0.5 %				HCl Concentration: 2 %			
Solutions	Salt Conc (ppm)	Salt Type	Angle (°)	Solutions	Salt Conc (ppm)	Salt Type	Angle (°)
#1	1,000	NaCl	98.23	#13	1,000	NaCl	57.84
#2	10,000	NaCl	113.67	#14	10,000	NaCl	81.61
#3	1,000	KCl	89.59	#15	1,000	KCl	90.4
#4	10,000	KCl	110	#16	10,000	KCl	112.81
#5	1,000	CaCl ₂	86.83	#17	1,000	CaCl ₂	57.34
#6	10,000	CaCl ₂	87.34	#18	10,000	CaCl ₂	78.6
#7	1,000	MgCl ₂	86.48	#19	1,000	MgCl ₂	68.51
#8	10,000	MgCl ₂	93.46	#20	10,000	MgCl ₂	87.07
#9	1,000	Na ₂ SO ₄	105.12	#21	1,000	Na ₂ SO ₄	77.66
#10	10,000	Na ₂ SO ₄	116.7	#22	10,000	Na ₂ SO ₄	84.03
#11	231,138	FW*	108.31	#23	231,138	FW	67.86
#12	0	-	84.4	#24	0	-	54.91
Aged			123.34				

* FW stands for formation water.

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Table 6. The chemical interpretations of the peaks in the ATR-FTIR spectrums [10,11,30–37]

Wavelength (cm ⁻¹)	Assignments
3100-3500	N-H, O-H
3000-3100	C-H stretch in aromatic
2946-3000	C-H ₃ asymmetric stretch
2881-2946	C-H ₂ asymmetric stretch
2755-2881	C-H ₂ symmetric Stretch
1668-1800	Carbonyl-based groups such as ketones, aldehydes, and carboxylic acids
1566-1668	Aromatic C=C stretch

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Table 7. Obtained characteristic indexes from the ATR-FTIR spectrums

Index/slices	Aged	NaCl	KCl	CaCl ₂	MgCl ₂	Na ₂ SO ₄	FW*	No salt
Carbonyl/Aliphatic	0.286	0	0.097	0.042	0.085	0.086	0.092	0.114
Carbonyl /Aromatic	0.953	0	0.583	0.312	0.5	0.531	0.567	0.531
Aromatic/ Aliphatic	0.3	0.138	0.166	0.136	0.17	0.162	0.163	0.216
Aliphatic length	1.811	2.409	2	2.169	2.247	2.141	2.293	2
Polar/Aliphatic	2.923	0.6	1.472	1.333	0.987	1.208	1.515	2.378
Polar/Aromatic	9.721	4.333	8.833	9.75	5.785	7.437	9.297	11

*FW stands for formation water.

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8 **Brief technical biography**

9 **Leili Boustani** is a petroleum engineer with diverse experience in both industry and academia.

10 Her research interests span various areas of petroleum engineering, including acidizing

11 techniques, artificial lifting, petroleum chemistry, and reservoir analysis. Academically, she

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1 **Amir hossein Saeedi Dehaghani** has received his Ph.D. from Tarbiat Modares University. He is
2 now a professor assistant at the chemical engineering department of Tarbiat Modares University.
3 His research interests are Enhanced Oil Recovery and Organic scale in the petroleum industry.
4 He has published more than 80 research papers in peer-reviewed journals.

5 **Saeed Karami** is the head of the Research and development of Petro Atlas Zagros Company,
6 who graduated from Tarbiat Modares University in 2018 in the field of Petroleum Engineering -
7 Reservoirs, one of his areas of expertise is petroleum chemistry and molecular characterization.
8 He is also the author of several international papers in the fields of molecular characterization
9 and microwaves.

10 **Nowzar Salehi** graduated with his Ph.D. from Tarbiat Modares University in 2023. He is an
11 expert in the fields of petroleum management, petroleum engineering, and chemical-enhanced oil
12 recovery. Besides, he published his findings in the field of ion-tuned water in peer-reviewed
13 journals.

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