

# Polymer-Acid Solutions: Their Use for the Enhancement of Oil Reservoir Stimulation

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**ABSTRACT:** A reduction in permeability occurring around the wellbore resulting from drilling, completion and/or workover fluids increases the flow resistance to the petroleum reservoir fluids and is defined as formation damage. Acidizing process removes near-wellbore damage and enhances hydrocarbon production from producing wells. This study investigates the effect of adding polymer as a retarding agent to acid solutions to slow and control the reaction in matrix acidizing treatment of carbonate rocks. Two different polymers, polyacrylamide (PAA) and polysaccharide (xanthan) and two different acids, acetic acid and formic acid, were used through this study. The results revealed that the presence of PAA did not change the viscosity of the acid solution significantly, while the viscosity of xanthan-acid solutions was decreased with increasing the acid concentration. Additionally, the reaction of polymer-acid solutions with the rock material was monitored under microscope. Original rock samples

obtained from Saudi reservoirs containing mainly carbonate were used in the reaction. The PAA-acid solution did not show any decrease in the reaction rate compared to that of acid solution. Thus, the PAA solution applied in this study is not recommended as a retarder. However, xanthan-acid solutions showed a significant decrease in the reaction time. Therefore, xanthan was selected to perform further investigations in Rotating Disk Reactor at different pressures. Scanning electronic microscopy (SEM) was conducted on pretreated and posttreated rock samples. This provides the opportunity to perform a detailed description of the rock surface and facilitates the identification of the changes occurring due to polymer-acid treatment. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1382–1387, 2008

**Key words:** damage zone; compatibility; viscosity; polysaccharides; rheology

## INTRODUCTION

Various forms of acidizing are used in the petroleum industry such as matrix acidizing and acid fracturing to stimulate oil and gas wells. The main objective of acid fracturing is to enhance the productivity or injectivity of the reservoir considerably depending on the length of the etched fractures into the formation. In this respect the goal of the petroleum engineer is to increase the penetration depth and the propagation of the fractures by slowing and controlling the reaction between the acid solution and the formation. Therefore, special efforts are required to achieve deep penetration depth into the formation before the acid spends. While matrix acidizing enhances well productivity by reducing the skin factor through either removing near wellbore damage or superimposing a highly conductive structure into the formation. In carbonates, acids react with flow channel sand pores and can create long wormholes,

effectively increasing permeability for several feet in the reservoir. In contrast, acid treatments in sandstones remove only the damage within the formation and do not actually stimulate the reservoir. Carbonates, which tend to be less homogeneous than sandstones, often contain natural fractures. Acid can open natural fractures by reacting more quickly with fracture infilling material, causing unexpected high production rates after matrix acidizing treatments.<sup>1–4</sup>

There is also “*in situ* gelled acid” as acid diversion, which consists of acid-soluble polymers, crosslinker, and other additives. The main aims of the gelled acid are to retard the acid reaction with the formation and to improve the treatment efficiency in terms of acid penetration. This type of acid treatment was the subject of several lab studies. However, this system has some limitations and disadvantages due to higher viscosities and scale precipitations.<sup>2,5–8</sup>

The present work deals with polymer-acid solution without crosslinker. Polymer-acid solution provides a better control of the viscosity, which can be varied depending on the polymer concentration in the solution. Thus, the pumping and the injectivity of the polymer-acid into the formation will be verified.

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In this study, polymer-acid solutions are investigated as a suggested method to increase the penetration depth by reducing fluid loss and slowing the reaction rate. Acid-soluble polymers and different core samples representing Saudi reservoirs consisting mainly of carbonate are investigated using rotating disk reactor.

Therefore, the main objectives of this study are:

- Investigation on the ability of polymer as a retarder and the compatibility of polymer-acid solutions at different acid concentrations by measuring the apparent viscosity,
- Determination of carbonate dissolution in presence of acid and polymer-acid solutions at different pressures and shear rate, and
- Identification of the main mechanisms leading to an increase in the acid spending time in presence of polymer using the scanning electron microscopy (SEM).

To achieve the objectives of this work, intensive experimental work in rotating disk reactor (RDR) was performed with different acids, polymer-acid solutions, and formation rock types. Moreover, viscosity measurements of polymer-acid solutions are conducted prior to the RDR-experiments.

## MATERIALS AND METHODS

### Polymer-acid solution

The polymer-acid solutions were prepared by mixing gently 1000 ppm of polymer-powder with distilled water using magnetic stirrer. The solution was stirred for 1 day, after that it was mixed again with salts containing 83 wt % sodium chloride (NaCl) and 17 wt % calcium chloride dehydrate ( $\text{CaCl}_2$ ) from Winlab, UK. A salt concentration of 5 wt % and two different commercial polymer types are applied in this study, polysaccharides (xanthan) with an average molecular weight of  $5 \times 10^6$  Da and polyacrylamide (PAA) with an average molecular weight of  $0.9 \times 10^6$  Da. Both polymers were purchased from Sigma-Aldrich, Germany with a purity of 99%. These types of polymers are acid-soluble over a wide range of acid concentrations and are soluble in sodium magnesium and calcium chloride and they have been used successfully to reduce the mobility of injected fluids to enhance oil recovery from oil fields and for water control operations.<sup>9-11</sup>

Biocide (formaldehyde) from Carlo Erba, Italy with a concentration of 37% was added at 100 ppm to all solutions to prevent a bacterial degradation of the polymer.

Three types of acid were used to prepare the polymer-acid solutions. Namely, two organic acids (glac-

ial acetic acid, and formic acid with a concentration of 98–100%) and one inorganic (hydrochloric acid with a concentration of 35.4%) were AnalaR grade from BDH, UK. The acids were added to the prepared polymer solution at different concentrations. The organic acids were added at 3, 6, 9, and 18 wt %, while the HCl concentration was adjusted at 1.1–3.3 wt % to avoid severe corrosivity on some parts of the experimental system.

The viscosity of the solutions under different conditions was measured using a calibrated viscometer of the model DV-III from Brookfield, USA, equipped with thermal jacket, which allowed conducting the measurements at different temperatures and shearing rates up to  $73.43 \text{ s}^{-1}$  with an accuracy of  $\pm 1\%$  of the viscosity value.

### Core samples

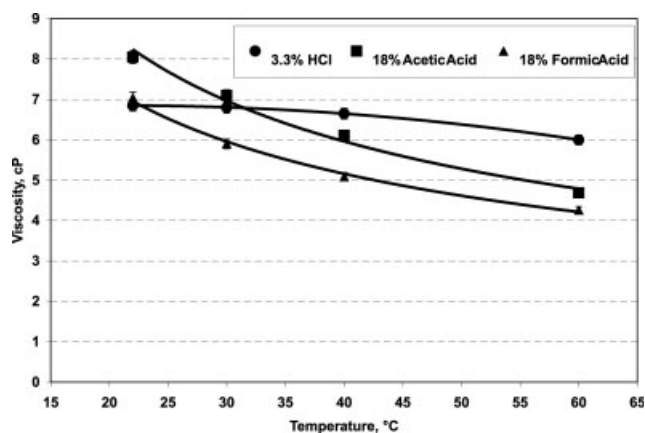
Core samples in diameter 1.5 in. and a length of nearly 4 in. were obtained from Saudi reservoirs. The composition of the core sample was investigated using X-ray diffraction (XRD) analysis and showed that the samples are composed mainly of calcium carbonate (96.7%). The average porosity of the received rock samples is 18 vol %, whereas the permeability varies from 3 to 8 mD, representing very tight carbonate reservoir. In addition and, in terms of mechanical property, the unconfined compressive strength of the rock samples was measured yielding values around 1800 psi.

Core samples were cut from original reservoir samples in slices in a diameter of 1.2 in. and a length of  $\sim 0.25$  in. The core samples were weighed before (initial weight) and after each experiment.

### High pressure/high temperature rotating disk reactor

HP/HT RDR used in this study was Stirred Reactor 4570 manufactured by Parr Instrument Company, USA, to examine the reaction rate of polymer-acid solution with the reservoir rock samples under high pressure and shear rate. The experimental procedure used in the stirred reactor is explained later.

The core samples were installed on Teflon-tube designed for this purpose, which was connected to the internal stirring system in the reactor. The reactor was closed and the stirrer motor was adjusted to provide a rotation of 60 rpm. The vessel temperature was set at  $35^\circ\text{C}$ . The prepared polymer-acid solution of  $500 \text{ cm}^3$  was injected into the vessel at different pressures varying from atmospheric up to 1600 psi. The reaction time was adjusted to 30 min. The core sample was then removed from the Teflon-tube after cooling and pressure reduction and washed with distilled water and left to dry and was finally



**Figure 1** Effect of temperature on the viscosity of 1000 ppm xanthan-acid solutions at shear rate of  $73.42 \text{ s}^{-1}$ .

weighed again. Weights of the core samples pre-treatment and post treatment were recorded for different solutions and conditions. In addition, photographs were taken by the use of microscopy (Model SteReo Discovery.V12 of Carl Zeiss, Germany), and SEM analysis was conducted using JEOL, JSM-6360, Japan, to check the 3D original minerals prior to their treatment by polymer-acid solutions and post treatment.

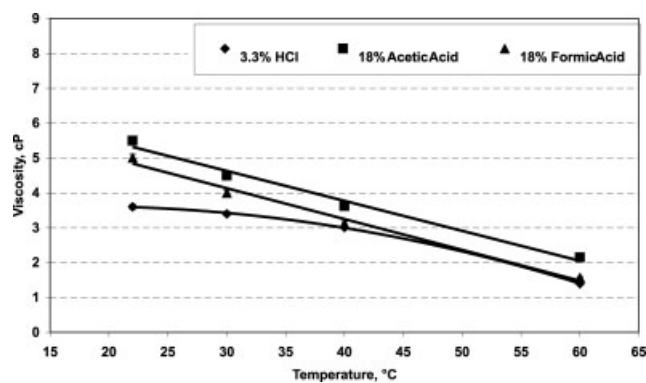
The same experimental procedure was repeated in presence of pure acid and the results were compared with those of polymer-acid solutions.

## RESULTS AND DISCUSSION

### Viscosity measurements

The viscosities of polymer-acid solutions were determined to evaluate the compatibility of the polymers with the acids. It is important to measure the viscosity of the polymer-acid solutions to identify the pumpability of the solutions into the formation and the pressure required to maintain the injectivity of the prepared solution. The injectivity is the description of fluid transport by pumping it through the porous media. This generally can be identified by measuring and monitoring the injection pressure. In case of an increase in injection pressure, the resistivity of fluid flow through the porous media will be increased leading to low injectivity. Therefore, it is desirable to have an adequate range of viscosity to allow easy pumping of the fluid into the formation. To examine the effect of temperature on the viscosity of polymer-acid solutions, the measurements were conducted at  $22^\circ\text{C}$  (room temperature), 30, 40, and  $60^\circ\text{C}$  and as a function of shear rate.

The measurements of the viscosity behavior of xanthan-acid and PAA-acid solutions at 5% salinity are illustrated in Figures 1 and 2 as a function of temperature at constant shear rate of  $73.42 \text{ s}^{-1}$ .



**Figure 2** Effect of temperature on the viscosity of 1000 ppm PAA-acid solutions at shear rate of  $73.42 \text{ s}^{-1}$ .

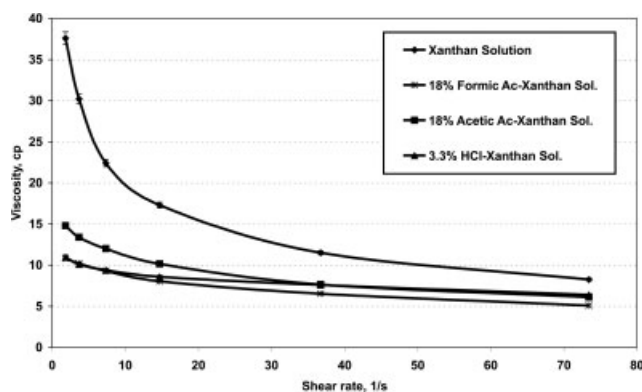
It is clear, that the viscosity of acid-polymer solutions decrease as the temperature is increased.

Figure 1 shows that the viscosity of xanthan-acid solution is reduced at higher temperature for all types of polymer-acid solutions. In presence of 18% acetic acid the viscosity of xanthan solution decreased from 8.05 cp at  $22^\circ\text{C}$  to 4.7 cp at  $60^\circ\text{C}$ , while the viscosity of solution in presence of 18% formic acid dropped from 7 cp at  $22^\circ\text{C}$  to 4.3 cp at  $60^\circ\text{C}$ . The viscosity of xanthan solution in presence of HCl decreased from 6.85 cp at  $22^\circ\text{C}$  to 6 cp at  $60^\circ\text{C}$ . This reduction is less than that observed in xanthan solution in presence of organic acids, which can be explained by the low HCl concentration (3.3%). However, the viscosity of PAA-acid solution at different temperatures is much more drastic and becomes around 2.15 cp in presence of acetic acid, and 1.4 cp in presence of formic acid at  $60^\circ\text{C}$  and HCl as shown in Figure 2.

Figures 1 and 2, demonstrate that the viscosity of both polymer solutions decreases with an increase of temperature. This reduction is ascribed to acid-type dependency; a behavior might be due to weakening or breaking of intermolecular bonds in polymers. More information regarding the xanthan and PAA properties is provided by Mohammed et al.<sup>12</sup> and Yan Li et al.,<sup>13</sup> which are only related to general rheological behavior. Hence, the present results contained in this experimental investigation can be considered as original in this specific field.

However, as shown in Figure 2, PAA is more sensitive at high temperature and in presence of strong acids, noting that the obtained values of viscosity are below the threshold required for the concerned acid stimulation. Therefore, PAA was not considered for further investigations.

The effect of shear rate on the viscosity behavior of xanthan-acid solutions has also assessed. The relationship is established in Figure 3 which presents the obtained viscosity values at a constant temperature of  $40^\circ\text{C}$ . The figure shows that the viscosity



**Figure 3** Effect of shear rate on the viscosity of 1000 ppm xanthan solutions with different acids at temperature of 40°C.

decreases as shear rate increases till a minimum value, e.g., the viscosity of pure xanthan solution drops from 37.6 cp at a shear rate of  $1.83 \text{ s}^{-1}$  to 8.3 cp at shear rate of  $73.4 \text{ s}^{-1}$ . It is noticed that the viscosity decreases further, when acids are added to the solutions. In presence of 18% acetic acid the viscosity of polymer solution decreases from 14.8 cp at shear rate of  $1.83 \text{ s}^{-1}$  to 6.1 cp at shear rate of  $73.4 \text{ s}^{-1}$ .

However, variation in minimum values depends on the type of acid and its concentration.

In addition, Figure 3 shows that the studied polymer solutions are non-Newtonian fluids with viscosity that decreases with shear rate (shear thinning behavior). This behavior is essential for drilling operations and enhanced oil recovery in the oil industry. Measurements of viscosity in case of HCl-polymer solutions at high temperatures were difficult and time consuming due to development of bubbles.

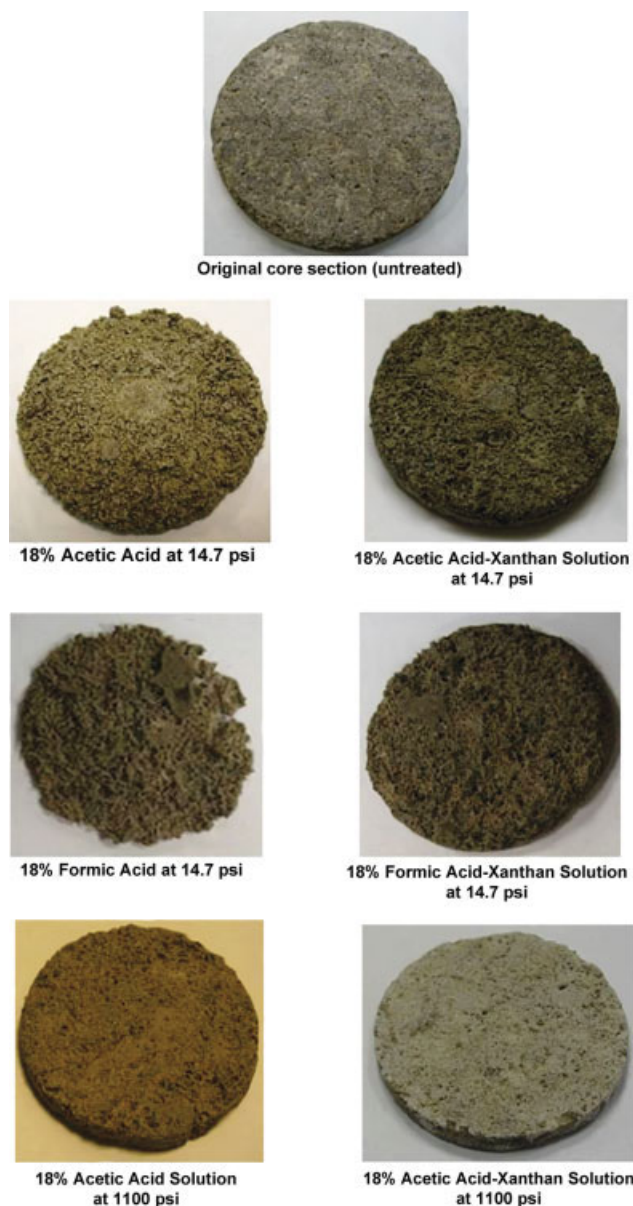
### Rotating disk reactor

Rotating disk tests were performed with organic acid diluted in 5% brine in the absence of polymer and with polymer-acid solution to investigate the intensity of acid reaction with the rock samples. In addition, the experiments were conducted at atmospheric pressure, 500, 1100, and 1600 psi to study the effect of pressure on the reaction rate with the core samples. HCl was not used in the following investigations due to the corrosion sensitivity of the equipment.

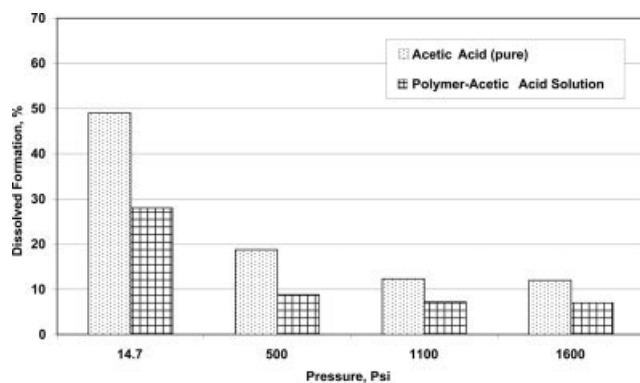
The unconfined compressive strength was measured after acidizing. It shows a reduction of 10–80%, but this rate depends on the type of treatment. This is due to the higher porosity and permeability created after acidizing. Accurate values of porosity and permeability post treatment could not be measured due to the low compressive strength of the rock samples. Thus, images were taken showing dissolution pattern.

The dissolution pattern shows more pitting on the sample face in presence of acid solution, whereas with gelled acid the number of pitting is less.

Photographs of the core sections were taken to compare the core surfaces pretreatment and post treatment to clarify the function of the polymer as a retarder. Figure 4 shows images of different core samples run in the rotating disk at 14.7 and 1100 psi. For instance, the treatment of the core sample using 18% acetic acid at 14.7 psi without polymer solution resulted in weight reduction of 49%, while the treatment under the same conditions in presence of polymer solution showed that the core sample lost 28% of original matrix. Similar trend was obtained



**Figure 4** Images of core sections treated at various conditions. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]



**Figure 5** Effect of the pressure on the dissolution rate in presence of xanthan-acetic acid solution.

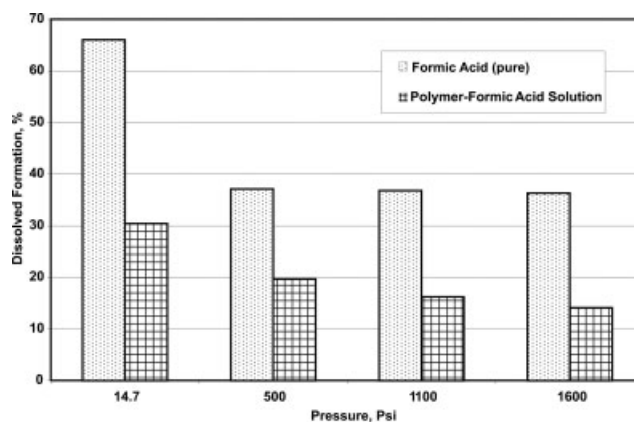
using 18% formic acid. The core sample lost 66% of its original material, while the presence of polymer solutions in the 18% formic acid has reduced the dissolved matrix to 30.4%. In addition, core samples, which were treated at a pressure of 1100 psi, in 18% acetic acid and, in presence of xanthan solution respectively, are also shown in the same Figure (Fig. 4). It is also found that the core sample treated with acid solution lost 12% of its original matrix, while the application of 18% acetic acid-xanthan solution lead to lower rock dissolution (7%). Thus, the rock dissolution in presence of polymer-acid solution is clearly lower with regard to the case of acid solution in the absence of polymer.

Moreover, polymer concentration was reduced to 500 ppm to investigate its influence on the reaction rate in presence of both organic acid solutions. More dissolution of the rock material is found when decreasing the polymer concentration. Therefore, the dissolution rate can be controlled by the amount of added polymer to the solution.

It is of interest to note that the reaction of the polymer-acid solutions with rock material was also monitored under the microscope and it was found, that the presence of PAA did not change the spending time of PAA-acid solution compared to pure acid. Thus, PAA is not effective as a retarder, while the presence of xanthan in the polymer-acid solution indicates a significant delay in the reaction time.

To clarify the differences between all runs made in the rotating disk, overall results were plotted in Figures 5 and 6, which show the effect of pressure on the dissolution of the core material in presence of xanthan-acetic acid solution and xanthan-formic acid solution, respectively.

Figures 5 and 6 clearly show that the amount of dissolved rocks decreased in presence of xanthan using both organic acid solutions. This indicates that the spending time of the acids will increase due to the retarding effect created in presence of xanthan. Certainly, the presence of polymer decreases the dis-



**Figure 6** Effect of the pressure on the dissolution rate in presence of xanthan-formic acid solution.

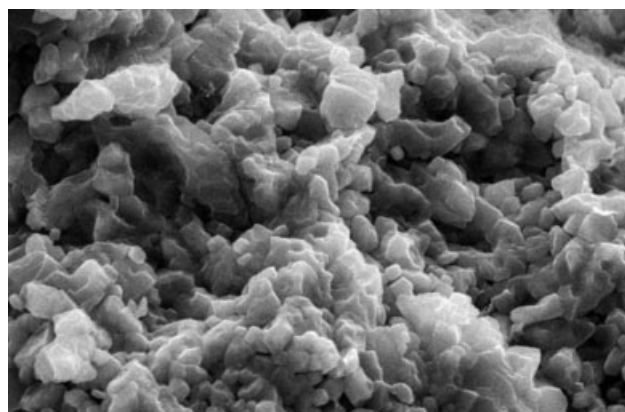
solution of carbonate compared to acid solution in absence of polymer at any pressure.

Moreover, the dissolution of the carbonate material under atmospheric pressure is high and it drops rapidly with increasing the pressure. Similar trend is found in case of formic acid (Fig. 6); thus, it can be inferred that acid reaction rate decreases significantly with increasing the pressure.

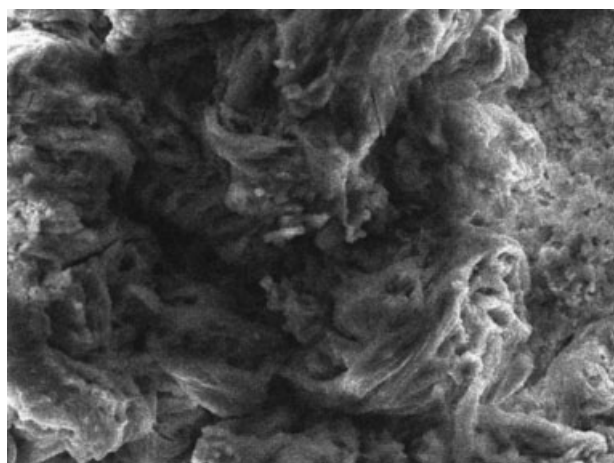
It is worth to mention that several repeat runs were made to ensure the reproducibility of the obtained results. It is found that all points are only slightly scattered around the main values. In addition, it is noticed that the deviation of the weight loss results was less than 2%; this reveals a good reproducibility.

### SEM analysis

SEM provides the opportunity to perform a detailed description of the rock surface and facilitates the identification of the changes occurring after the treatment. Figures 7 and 8 illustrate examples of



**Figure 7** SEM photo showing the general texture of the original sample, which consists of fine-rounded oolites grains with some intergranular pores (Magnification  $\times 1500$ ).



**Figure 8** SEM photo shows the effect of xanthan-acetic acid solution on the sample post treatment at atmospheric pressure. The core sample lost 28% of its original matrix (Magnification  $\times 2000$ ).

the SEM analysis of the samples pretreatment and post treatment.

Figure 7 shows SEM image of the general texture of the original sample. Figure 8 illustrates SEM image of the rock sample post treatment and it shows the presence of polymer in elongated form covering the mineral surface, which decelerates the reaction.

It can be noted that the sample in Figure 8 has lost part (28%) of its original matrix due to carbonate dissolution. Thus, the function of the polymer in this case is in retarding further reaction and not stopping the reaction. The presence of large holes and the reduction of the original matrix resulted from carbonate dissolution are evidence of acid reaction with the rock samples even in presence of polymer solution. Therefore, the dissolution of the carbonate would continue until the acid in the polymer solution is spent. Thus, the spending time is increased in presence of polymer allowing the polymer-acid solution to penetrate deeper into the formation. Moreover, it is important to note that SEM photos show increased pore volume post treatment with pure acid as well as with xanthan-acid solutions in all cases.

## CONCLUSIONS AND RECOMMENDATIONS

It should be emphasized that the ultimate aim of this research is to develop a method to predict acid spending time and to find the suitable additives as retarders in the matrix acidizing. Such method is desirable to achieve an extended matrix acidizing in the reservoir. A rotating disk is the most convenient apparatus to evaluate such additives under simulated reservoir conditions.

Based on this research the following conclusions can be drawn:

1. Adding acid to the polymer solutions reduces the viscosity. A desired viscosity of the polymer-acid solution can be adjusted by the variation of the polymer concentration.
2. the acid reaction with the rock samples decreased significantly with increasing the pressure.
3. The presence of xanthan in the acid solution leads to a reduction of dissolution rate and therefore, an increase in the spending time can be achieved.
4. PAA-polymer solution was found to be incompatible with the selected acid concentrations, therefore, PAA is not recommended as a retarder in matrix acidizing.
5. Xanthan showed high compatibility in presence of acid under reservoir conditions concerning salinity, temperature, pressure and shear rate.
6. To compensate the reduction of reaction rate due to high-pressure, higher acid concentration or lower polymer concentration should be selected.
7. SEM studies allowed to glean a better understanding of the reaction between polymer-acid solution and rock samples and to identify the retarding mechanisms of dissolution of carbonate in presence of polymer.

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