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Perspective

# Evolution of rock pore structure and physical properties due to acidification: Recent advances and future perspectives

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**Abstract:**
Acidification is crucial to oil and gas development, which effectively improves reservoir development by reacting acid with some minerals in the rock. There are a large number of minerals that react with acid in carbonate and shale reservoirs. Acidification has a good effect in these two reservoirs, so it is necessary to conduct multi-scale research on the acidification process. This work briefly introduces the evolution characteristics and factors affecting acidification on reservoir pore structure and physical properties, and also analyzes their similarities and differences. Meanwhile, the application status of the acidification method is also discussed. Finally, the challenges and opportunities faced by shale acidification are discussed, aiming to provide new insights into the development of acidizing technology.

## 1. Introduction

As conventional oil and gas resources gradually deplete, the development of unconventional reservoirs has attracted widespread attention in the petroleum industry. Unconventional reservoirs with poor physical properties are mainly composed of micro-nano pores, and have a complex pore structure. These reservoirs are difficult to develop, and conventional methods are inefficient for extracting oil and gas. Acidification is a commonly used reservoir stimulation technique in the developmet of tight oil and gas reservoirs. The minerals in the rock react with the injected acid, changing the pore structure, improving its physical properties and ultimately enhancing its flow capacity.

The minerals that react with acid are mainly calcite, dolomite, pyrite and clay. Therefore, acidification is primarily used in carbonate reservoirs and some sandstone reservoirs with high carbonate mineral content. In addition, with the advancement of unconventional reservoir development technology, acidification is also used to improve shale reservoir conditions and the flow capacity. Acidification can be divided into matrix acidification and acid fracturing. Matrix acidification refers to the injection of acid into the formation at a pressure lower than the formation fracture pressure, which is suitable for reservoirs with high permeability. Acid fracturing referring to the acid injection pressure is higher than the formation fracture pressure, commonly used in unconventional reservoirs (Li et al., 2016). In recent years, acidification has been gradually used in shale. Compared with carbonate reservoirs, shale has more complex mineral compositions, pore structures and physical properties. There are relatively few studies on

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the influence of acidification on shale. Acidification for shale draws on the experience of acidification of carbonate reservoir, but it should also be appropriately modified according to the reservoir characteristics.

This work discusses the transformation effect of acidification on the two types of reservoirs, introducing the factors affecting the pore structure and physical properties evolution. Additionally, exploring the experience of acidification in carbonate reservoirs provides a new perspective that promote the advancement of shale acidification.

## 2. Acidification in carbonate reservoirs

The content of calcite and dolomite in carbonate reservoirs is high, and the reaction with acid is more intense. In the process of acidizing the carbonate reservoir, the acid system must have good dissolution ability and a fast dissolution rate for minerals. Furthermore, the acid should have good corrosion inhibition ability to ensure that it deeply penetrates the reservoir and forms an effective flow channel (Liu et al., 2017). The type of acid and the way of acid injection have diverse effects on the pore structure and physical properties of carbonate rocks. Therefore, specific acid and different injection conditions should be adopted for the characteristics of carbonate reservoirs.

The pore structure of carbonate rocks before and after acidification can be quite different. The effectiveness of the acid-rock reaction is controlled by the rock pore structure. When the rock has larger pore sizes and better connectivity, the reaction with acid is faster. After acidification, the radius of many tiny pores increases and some fractures are produced. Most of the new pores and fractures exist on the surface of the sample (Xu et al., 2022). The heterogeneity of rock affects the evolution of pore structure. The area with higher carbonate mineral content has a better dissolution effect, more pores and larger size. In addition, factors such as temperature, acid concentration, acid type and acid injection rate have significant effects on the expansion of wormholes in carbonate rocks (Ghommem et al., 2015). Among these factors, temperature positively correlates with acidification efficiency. However, the acid injection rate and concentration are not simply positively correlated with the acidification effect. As the injection rate and concentration increase, the acidification effect initially rises and then falls (Qi et al., 2017; Kiani et al., 2021). At the optimal injection rate and concentration, the pore volume in carbonate rock increases the most, along with the fracture width and length.

The physical properties of carbonate rocks have been significantly improved after acidification. The porosity and permeability of the carbonate reservoir will increase due to mineral dissolution during acidification, and the corresponding mechanical properties will also change. Since more pores and fractures are generated between particles after acidification, both the uniaxial compressive strength and elastic modulus decrease (Huang et al., 2022). Controlling the acid flow rate and concentration allows deeper penetration into the reservoir, significantly enhancing the rock permeability. In order to prevent the closure of fractures caused by acid fracturing under closure pressure and avoid a decrease in productivity, the two methods of acid fracturing and proppant fracturing can be combined to effectively improve the fracture conductivity (Gou et al., 2024).

## 3. Acidification in shale reservoirs

Compared with carbonate reservoirs, shale reservoirs usually have less calcite and dolomite mineral content, but more clay mineral content. In addition, shale reservoirs have a large number of micro-nano pores and a small number of microfractures, and have strong heterogeneity (Khalil et al., 2020). Hence, the acidification mechanism of shale is more complicated.

The evolution of pore structures of shale under acidification is complex. The differences in mineral composition between carbonate rocks and shale lead to distinct changes in their pore structures after dissolution. Shale contains relatively small amounts of carbonate minerals but is richer in clay. Numerous dissolved pores and fractures are generated in shale after acidification, and the variances in mineral composition can reslt in the differences in shale pore structures (Sheng et al., 2021). The shale rich in clay minerals mainly produces stress-induced fractures and shrinkage fractures after acidification, while the carbonate-rich shale mainly produces dissolution fractures (Khalil et al., 2020). After acidification, the nanopore surface fractal dimension of shale decreases and the micropore fractal diension of shale increases (Xu et al., 2023). It shows that the pore surface becomes smoother, but the distribution of micropores becomes more irregular.

Acidification has a great influence on the physical properties of shale. Through shale imbibition experiments, it was found that the dissolution of carbonate rock minerals effectively improved the connectivity of matrix pores and increased the permeability dozens of times (Teklu et al., 2017). Computed tomography and core flooding experiments quantitatively characterize the evolution of shale physical properties before and after acidification (Singh et al., 2019). The reactive mineral content in shale has a positive effect on the increase of porosity and permeability. Furthermore, the mechanical properties of shale deteriorate after acidification, which leads to a decrease in the hardness and elastic modulus of the shale fracture surface (Wu and Sharma, 2016). Acidification increases the brittleness of shale, and under high pressure, fracturing further enhances rock flow capacity.

## 4. Evaluation of acidification of two reservoirs

The acidification process of carbonate rock and shale reservoir is similar. The soluble minerals in both reservoirs will form a large number of pores and fractures after being dissolved. After acidification, the pore structure improves significantly: the number of pores increases, along with the pore radius and volume, and the connectivity is enhanced. Acidification significantly enhances the physical properties: porosity and permeability increase, leading to an improved flow capacity of the reservoir (Xu et al., 2024). As the rock skeleton is partially dissolved, its brittleness will also increase.

There are also many differences in the acidification effects of the two reservoirs. Carbonate rocks are primarily characterized by the formation of pores, followed by fractures. The acidification of shale mainly generates fractures, accompanied by dissolution micropores. The factors affecting the pore structure and physical properties changes of the two reservoirs due to acidification are also different. Carbonate rock minerals are mainly calcite and dolomite, and the acidification reaction is relatively intense. Excessive acid injection rate and concentration lead to reactions limited to the rock contact surface, preventing effective penetration into the reservoir. An increase in acid injection rate, concentration, and temperature positively influences the acidification of shale.

Additionally, the acidizing methods for the two reservoirs are different. The application of acidification in carbonate reservoirs is mature. For carbonate reservoirs with good physical properties, the matrix acidizing method can be used. For tight carbonate rocks, acid fracturing is generally used. However, the development of shale reservoirs is still in the exploratory stage, and many conventional development methods are not applicable. Due to the high heterogeneity and poor physical properties of shale, the effect of acid fracturing in shale development is not ideal. Currently, acid is often added to the pre-fluid of the fracturing fluid to improve the reservoir. The acidification of shale needs to be further explored.

## 5. Conclusion and perspective

Acidification has a positive significance for reservoir transformation. The pore structure and physical properties of carbonate rock and shale reservoirs are significantly improved after acidification. However, due to variations in mineral composition, physical properties and other factors, the acidizing effects on the two reservoirs are different. Acidification has been widely used in carbonate reservoirs, while acid-rock interaction in shales is still being explored. As the research on shale acidification mechanism deepens, the theory should be combined with engineering development. The effectiveness of shale reservoir acidification measures can be verified through field tests, thereby increasing the reservoir transformation volume and oil and gas recovery rate.

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## Conflict of interest

The authors declare no competing interest.



## References

Ghommem, M., Zhao, W., Dyer, S., et al. Carbonate acidizing: Modeling, analysis, and characterization of wormhole formation and propagation. Journal of Petroleum Science and Engineering, 2015, 131: 18-33.

Gou, B., Xu, K., Wang, C., et al. Experimental and modeling investigation on artificial fracture conductivity for hybrid fracturing in a deep carbonate reservoir using an acid and a proppant. Energy & Fuels, 2024, 38(9): 7801-7816.

Huang, B., Hou, M., Zhao, X., et al. Experimental investigation on the reformation and strength weakening of hard limestone by acidizing. International Journal of Mining Science and Technology, 2022, 32(5): 965-979.

Khalil, R., Emadi, H., Altawati, F. Investigating the effect of matrix acidizing injection pressure on carbonate-rich marcellus shale core samples: An experimental study. Journal of Petroleum Exploration and Production Technology, 2020, 11(2): 725-734.

Kiani, S., Jafari, S., Apourvari, S. N., et al. Simulation study of wormhole formation and propagation during matrix acidizing of carbonate reservoirs using a novel in-situ generated hydrochloric acid. Advances in Geo-Energy Research, 2021, 5(1): 64-74.

Li, N., Dai, J., Li, J., et al. Application status and research progress of shale reservoirs acid treatment technology. Natural Gas Industry B, 2016, 3(2): 165-172.

Liu, P., Yao, J., Couples, G. D., et al. Modeling and simulation of wormhole formation during acidization of fractured carbonate rocks. Journal of Petroleum Science and Engineering, 2017, 154: 284-301.

Qi, N., Li, B., Chen, G., et al. Optimum fluid injection rate in carbonate acidizing based on acid dissolution morphology analysis. Energy & Fuels, 2017, 31(12): 13448-13453.

Sheng, M., Khan, W. A., Cheng, S., et al. Characteristics of micro-fracturing in shales induced by dilute acid. Journal of Natural Gas Science and Engineering, 2021, 88: 103855.

Singh, R., Tong, S., Panthi, K., et al. Stimulation of calcite-rich shales using nanoparticle-microencapsulated acids. SPE Journal, 2019, 24(6): 2671-2680.

Teklu, T. W., Abass, H. H., Hanashmooni, R., et al. Experimental investigation of acid imbibition on matrix and fractured carbonate rich shales. Journal of Natural Gas Science and Engineering, 2017, 45: 706-725.

Wu, W., Sharma, M. M. Acid fracturing in shales: Effect of dilute acid on properties and pore structure of shale. SPE Production & Operations, 2016, 32(1): 51-63.

Xu, P., Sheng, M., Lin, T., et al. Influences of rock microstructure on acid dissolution at a dolomite surface. Geothermics, 2022, 100: 102324.

Xu, S., Xia, Y., Lu, M., et al. Fractal perspective on the effects of the acid–rock interaction on the shale pore structure. Energy & Fuels, 2023, 37(9): 6610-6618.

Xu, S., Zhou, S., Zhou, J., et al. Multiscale pore structure evolution of Longmaxi shale induced by acid treatment. SPE Journal, 2024, 28(2): 831-844.