



Multiscale pore structure evolution of shale induced by dilute acid

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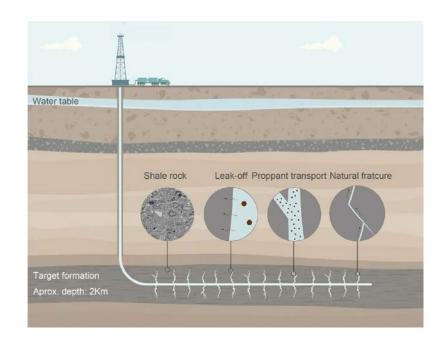
Outline

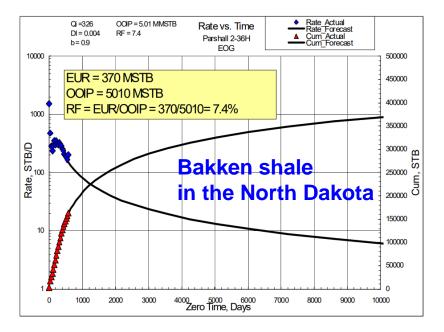
- 1. Background
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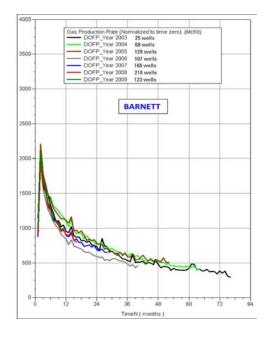
Background

- Hydraulic fracturing to generate complex fracture networks is the most effective stimulation method to develop unconventional reservoirs, such as shale oil and gas.
- The recovery of shale oil and gas is still low, and the production of fractured wells usually suffer a sharp decline in the first few years.

limited stimulated reservoir volume (SRV)







(Chen et al., 2021) (Clark, 2009) (Baihly et al., 2010)

Background

Methods of EOR in shale reservoirs:

- Surfactant injection
- □ Gas flooding
- □ Acid treatment

Matrix acidizing

(Injection pressure below breakdown pressure)

Acid fracturing

(Injection pressure exceeding breakdown pressure)

Calcite: $CaCO_3 + 2H^+ = Ca^{2+} + H_2O + CO_2 \uparrow$

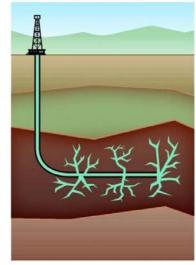
Dolomite: $CaMg(CO_3)_2 + 4H^+ = Ca^{2+} + Mg^{2+} + 2H_2O + 2CO_2 \uparrow$

'Acidizing' for oil

In states such as North Dakota and Texas, shale formations that contain oil lie in flat lavers that can be tapped by a combination of horizontal drilling and hydraulic fracturing. But California's Monterey Shale formation. folded by seismic forces, may respond better to acid pumped into a vertical well. The acid opens tiny pores in the rock.

Source: Next Generation

Typical shale deposit



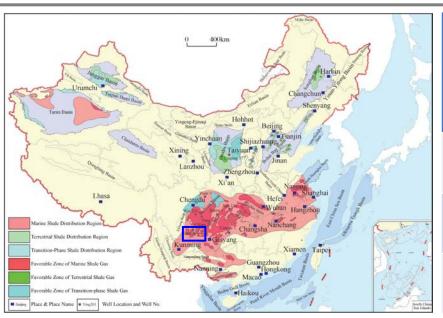
Monterey Shale



Todd Trumbull / The Chronicle



Materials and experiments



Sample	TOC (%)	Mineral composition (%)							
		Quartz	K-Feldspar	Plagioclase	Calcite	Dolomite	Pyrite	Clay	
Y107-1	0.86	34.8	2.2	10.3	12.2	9.8	2.1	28.6	
Y107-22	3.26	50.6	1	2.9	12.3	5	4.6	23.6	
Y107-25	3.54	38.3	_	2.3	25.1	13.8	4.5	16	

(Dong et al., 2016)



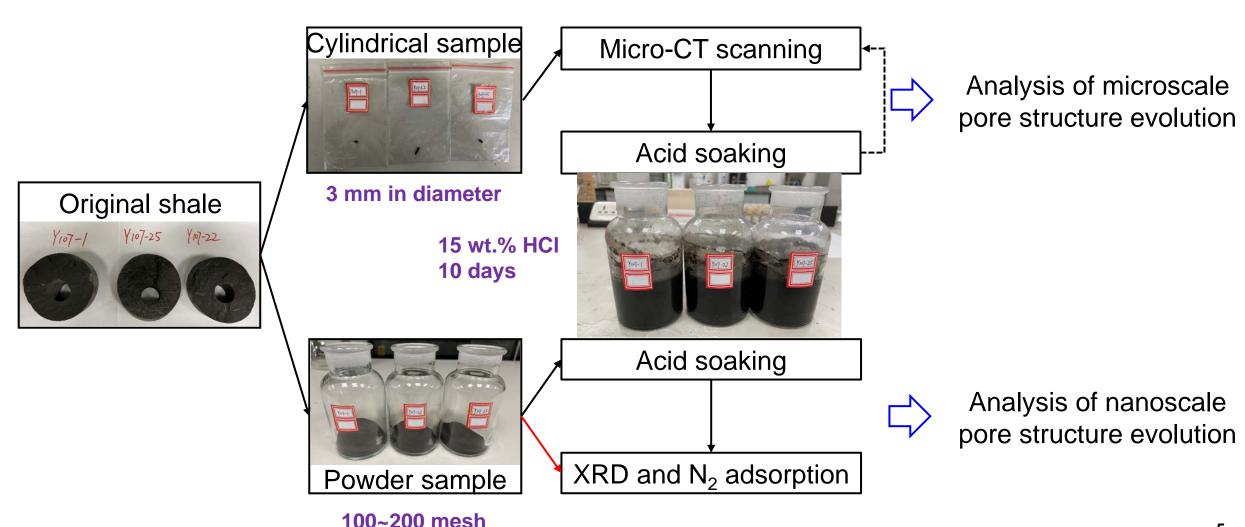
Longmaxi black shale from Zhaotong shale gas demonstration area

☐ Clay-rich shale: Y107-1, Y107-22

☐ Carbonate-rich shale: Y107-25

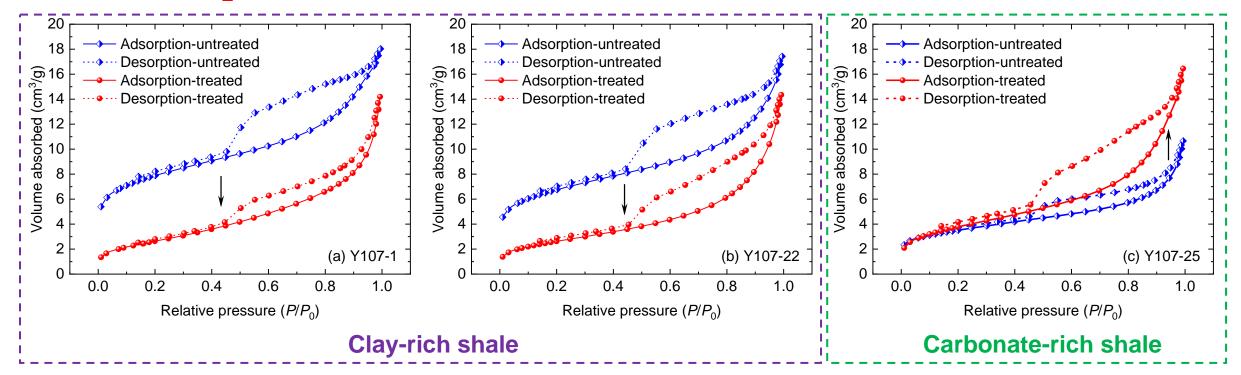
Materials and experiments

Experimental workflow



Nanoscale pore structure evolution

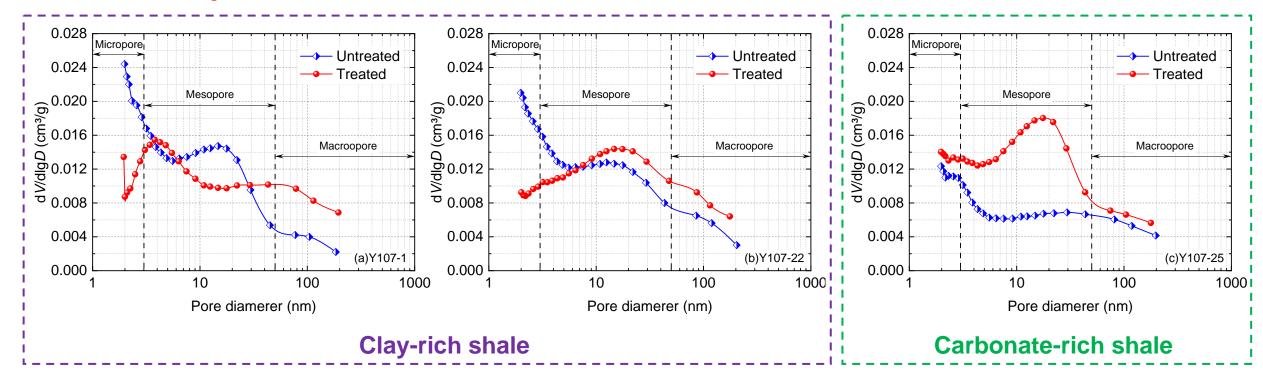
Variations in N₂ adsorption-desorption isotherms



- For clay-rich shale, the shape of isotherms barely changed, while the locations obviously shifted downward.
- For Carbonate-rich shale, the shape of isotherms changed a lot. At relative pressure lower than 0.45, the isotherms almost coincided. When relative pressure exceeded 0.45, much more quantity of N₂ was adsorbed, with a more obvious hysteresis loop.

Nanoscale pore structure evolution

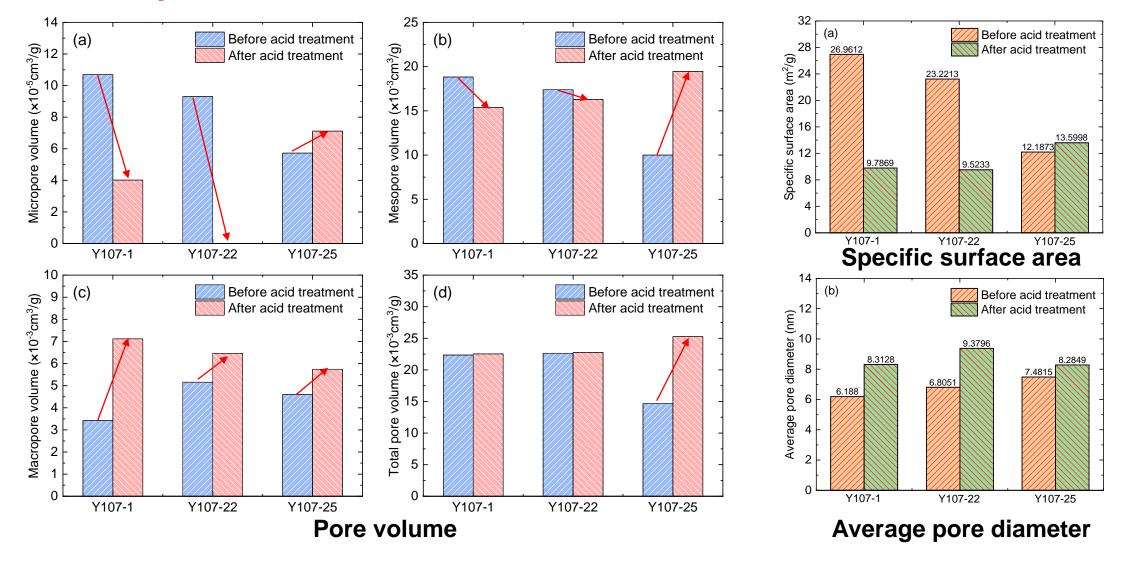
Variations in pore size distribution



- In clay-rich shale, some micropores and mesopores decreased, while macropores increased.
- In carbonate-rich shale, all the nanopores increased.

Nanoscale pore structure evolution

Variations in pore structure

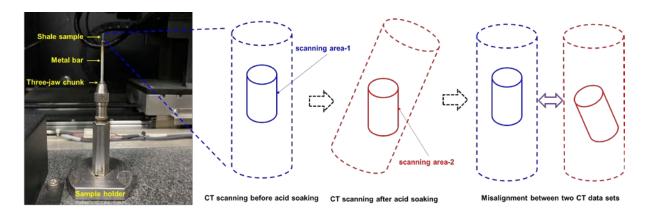


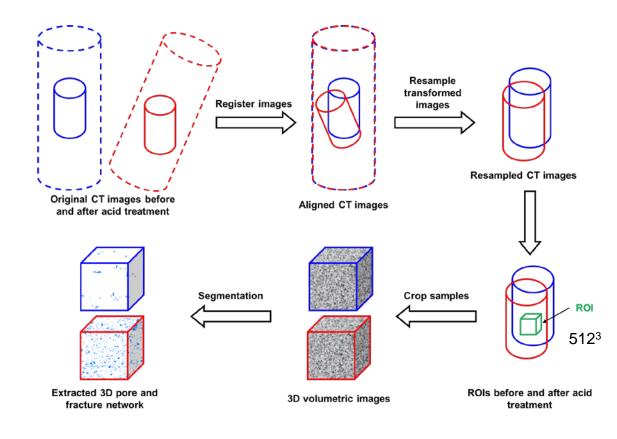
CT scanning and image processing



961 sheets of CT slices with a resolution of 1.78 µm were acquired for each sample

Zeiss Versa XRM-500 CT Scanner

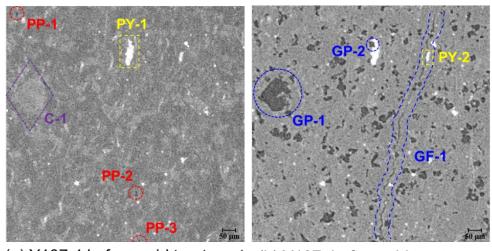




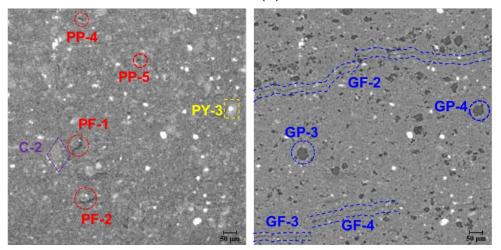
Workflow followed for processing CT images

Misalignment of CT images

Variation in minerals, pores and fractures from 2D CT images



(a) Y107-1 before acid treatment (b) Y107-1 after acid treatment

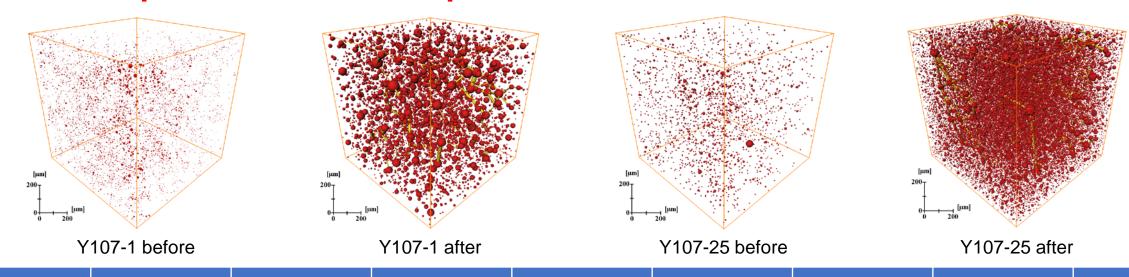


- Massive dissolution of Calcite (C-1, GP-1)
- Partial dissolution of pyrite adjacent to carbonate (PY-1, PY-3)
- Generation of pores and fractures
 (GP-1, GP-2, GP-3, GF-1, and GF-2)
- Shrinkage of pre-existing pores and fractures (PP-2, PF-1 and PF-2)

Variation in pore structure from 3D

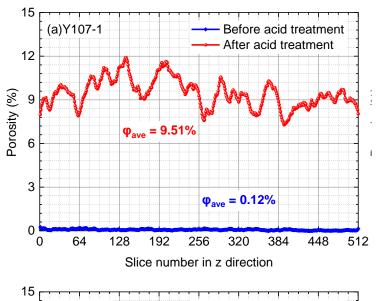
	Untreated Y107-1	Treated Y107-1	Untreated Y107-25	Treated Y107-25
2D slices in x, y, and z directions	[jm] 200 0 200	[ma] 200 0 0 200	200 [ma] 0 200	[jum] 200 0 200
3D grayscale images	[jim] 208 0 200 100	[jun] 200 0 0 200	[jun] 200 0 200	[Jum] 200 0 200
3D color-labeled pores and fractures	200 jum)	200 (ium)	200 [nm]	200 0 200

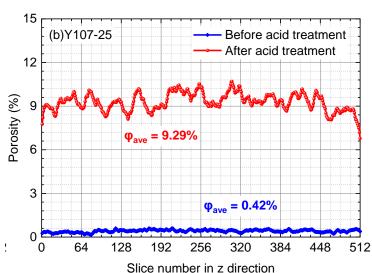
Variation in pore structure from pore network models

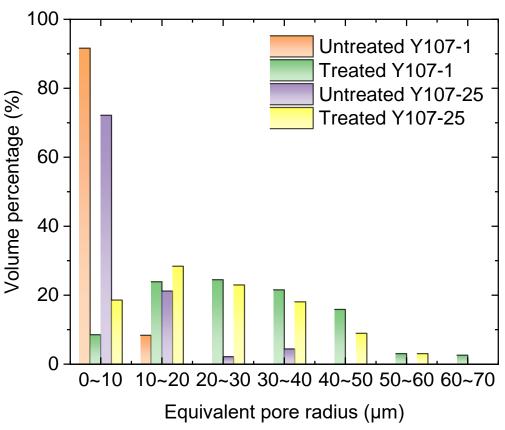


Sample	V _{total} (μm³)	V _{max} (μm³)	V _{ave} (μm³)	S _{max} (µm²)	S _{ave} (µm²)	R _{max} (μm)	R _{ave} (µm)	F _c (%)
Untreated Y107-1	939329.82	13873.46	126.95	7011.41	107.62	14.91	2.48	0
Treated Y107-1	72096260.58	956760.38	13711.74	211412.66	4832.77	61.13	10.79	32.21
Untreated Y107-25	3150698.14	138740.25	1498.90	64222.07	1062.67	32.11	6.53	0
Treated Y107-25	70389090.03	796309.50	7113.60	409407.56	3080.10	57.50	9.13	36.78

Variation in pore structure from pore network models







This significant increase in porosity and pore size could substantially improve permeability

Summary

- 1. An experimental workflow combining CT and N₂ adsorption is developed to study the multiscale pore structure evolution of shale induced by acid treatment.
- 2. Clay-rich and carbonate-rich shales show differences in variation of pore structure.
- 3. Acid treatment results in an increase of about 9% in porosity.
- 4. Acid treatment is a promising strategy to develop Longmaxi shale reservoirs by improving petrophysical properties and SRV.