AAPG HEDBERG CONFERENCE
"NATURAL GAS GEOCHEMISTRY: RECENT DEVELOPMENTS, APPLICATIONS, AND TECHNOLOGIES"
MAY 9-12, 2011 – BEIJING, CHINA

TSR alteration of carbonate reservoirs and gas pools in Sichuan Basin, China

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The northeastern Sichuan Basin is an area where the largest-scaled reserves of natural gases with high H_2S in China have been discovered and high-quality carbonate reservoir beds are developed best. The reservoir beds are mainly composed of Triassic Feixianguan Formation oolitic dolestones with minor gypsolyte. Being once buried over 6000m~8000m, they commonly have a present-day burial depth about 4000m~6000m and good physical properties with porosity of 8~12%. Natural gases from these reservoirs contain dominant methane, less than 0.1% of heavier hydrocarbons, 12~17% of H_2S and 4~10% of CO_2. Studies show that the intensive accumulation of H_2S in deep carbonate reservoir beds is resulted from thermochemical sulfate reduction (TSR), while the formation of a high-quality reservoir bed is closely related with the alteration of carbonates by TSR, which has been further proved by simulation experiments using H_2S flow to alter carbonates. Currently, gas reservoirs with high H_2S in the northeastern Sichuan Basin are characterized by a low-pressure coefficient, presence of edge water and bottom water, and good physical properties. These characters may reflect significant alteration of carbonate hydrocarbon reservoirs by TSR.

1. Geological characteristics of gas reservoirs

The Lower Triassic Feixianguan Formation in the northeastern Sichuan Basin is an evaporate platform-facies deposit, conformably contacting with the underlying Permian Changxing Formation and overlying Triassic Jialingjiang Formation. The deposit consists mainly of oolitic dissolved-pore dolostones intercalated with silty oolitic limestone, mud-silty limestone, argillaceous dolostone and a 15~30m gypsum layer or dolomitic gypsolyte. This suite of deposit has a total thickness of 350~450m, of which a high-quality reservoir bed accounts for 40~150m. Dense carbonates and gypsolytes are well developed on the top of reservoir beds, composing high-quality regional cap rocks with high H_2S. Natural gases of the Feixianguan Formation come mainly from Permian Longtan Formation and underlying Silurian argillaceous source rocks (Zhang et al., 2007), which have been in highly- or over-mature stage. Feixianguan Formation reservoirs experienced a higher paleo-temperature that was over 120°C~160°C in the Middle Jurassic to Cretaceous and lasted for a considerably long period because the homogeneous temperature of inclusions ranges between 120~220°C. Thus, Feixianguan Formation has basic conditions for the occurrence of TSR.

H_2S accounts for 12~17% of natural gases from these reservoirs and CO_2 amounts to 4~10%, moreover, the both have a positive correlation. Heavier hydrocarbons are minor in the natural gases, ethane and propane are all less than 0.1% and butane is almost zero. Natural gases with high H_2S from Feixianguan Formation in the northeastern Sichuan Basin are demonstrated to be a result of thermochemical sulfate reduction (TSR) by geochemical data, such as carbon isotopes of hydrocarbons and carbonates, sulfur isotopes of brenstone, gypsum, H_2S and pyrites (Zhu et al., 2005).

2. Alteration of carbonate reservoirs and its evidence during the formation of H_2S

Oolitic dolostones in Feixianguan Formation have well-developed secondary pores with a permeability over 20%, and they have thick high-quality reservoir beds with a continuous thickness over 300m, being as an abnormal deep high-quality porous reservoir bed. Burial history shows that the burial depth of Feixianguan Formation was as deep as 8000m at the end of Cretaceous and the temperature was over 220°C. It is worth investigating that how pores could be conserved and developed at such a depth of burial. Studies show that a severe alteration of carbonate reservoirs by H_2S is likely the most important cause for the development of deep high-quality gas reservoirs with high H_2S. Erosion by H_2S can accelerate the formation of large-scaled secondary pores and cavities, making reservoirs better in porosity. The present study by simulating erosion at various temperatures and in different solutions for a long period demonstrates that H_2S can erode carbonate reservoirs effectively and improve reservoir quality greatly.

(1) Experimental

Samples were divided into four groups in consideration of the carbonate reservoir erosion by different types of solutions at various temperatures, and consequently, four devices were applied in the simulation experiment, i.e. H_2S solution constant at 50°C, 70°C and 90°C, respectively, and $H_2S + CO_2$ solution constant at 90°C. 39 different carbonate cores sampled from 9 wells of the Feixianguan Formation reservoir in the northeastern Sichuan Basin were dipped in different solutions, respectively, for 100 days. All of these samples were prepared into a cylinder with 5cm in diameter and 5cm in length. Then, routine methods for physical property measurement were used to determine porosity, permeability and rock density of these samples (Table 1). These 39 samples were combined into four groups according to their difference in porosity, and each group contained samples with both high and low porosity. All the samples were dipped in solution at a given constant temperature controlled by a thermostatic controller with an error of ±1°C. The solutions were all kept saturated with H_2S or CO_2. After dipping erosion, all the samples were dried and measured for their porosity, permeability and rock density using the same methods as before (see Table 1).

Table 1 Porosity, permeability and density analyses of rocks before and after erosion

No.	Well No.	Depth/m or sampling order	Lithology	Porosity%		Permeability/md		Group
				Before *	After**	Before	After	
1	Puguang 2	4929.7	oolitic porous dolomite	3.7	5.1	0.038	0.456	Group I, 50°C, H_2S saturated solution
2	Puguang 2	4869.39	oolitic porous dolomite	3.9	4.8	0.121	0.502	
3	Puguang 2	5091.9	oolitic porous dolomite	7.4	9.4	0.142	0.554	
4	Puguang 2	5192	oolitic porous dolomite	9.9	11.4	28.4	31.7	
5	Puguang 2	4537	oolitic porous dolomite	11.0	13.1	1.59	2.33	

6	Puguang 2	4939.7	oolitic porous dolomite	11.4	13.6	15.5	2120	
7	Luojia 2	3256.74	oolitic porous dolomite	12.7	14.0	158	164	
8	Luojia 2	3304	dense limestone	0.9	2.1	0.062	0.746	Group II, 70°C, H_2S saturated solution
9	Wuke 1	19-655	gypsum	3.0	8.1	\	\	
10	Luojia 1	3465.32	gypsolyte	4.7	4.8	0.104	0.378	
11	Po 1	3461.5	vug dolomite	1.4	2.2	0.044	0.659	
12	Luojia 1	3517.27	dense limestone	1.9	2.4	0.057	0.535	
13	Puguang 2	4537	oolitic porous dolomite	13.6	13.6	0.824	1.08	
14	Luojia 2	3263.85	oolitic porous dolomite	11.3	11.3	15.6	16.9	
15	Luojia 6	3969	oolitic porous limestone	2.2	3.0	0.051	0.884	
16	Puguang 2	4872.89	oolitic porous dolomite	6.5	7.0	\	\	
17	Puguang 2	5021.76	oolitic porous dolomite	9.6	9.8	0.830	1.21	
18	Puguang 2	5100	oolitic porous dolomite	11.8	12.3	\	\	
19	Po 1	3461.5	vug dolomite	2.4	4.0	0.041	0.689	Group III, 90°C, H_2S saturated solution
20	Zhujia 1	5578.7	fractured dolomite	4.9	6.5	0.076	0.895	
21	Luojia 2	3285.53	dense limestone	2.1	3.2	0.044	0.589	
22	Luojia 1	3465.32	gypsolyte	3.7	4.7	0.065	0.578	
23	Luojia1	3490.71	oolitic porous limestone	1.5	3.1	0.043	0.921	
24	Luojia 6	3939	oolitic porous limestone	1.4	2.9	0.043	0.788	
25	Puguang 2	5122.7	oolitic porous dolomite	9.8	10.6	0.343	0.772	
26	Puguang 2	5091.9	oolitic porous dolomite	6.4	7.2	3.95	22.7	
27	Luojia 2	3263.85	oolitic porous dolomite	12.1	12.5	18.5	20.5	
28	Puguang 2	5192	oolitic porous dolomite	10.9	11.9	19.6	23.8	
29	Puguang 2	4980.4	oolitic porous dolomite	13.9	15.7	75.5	79.7	
30	Luojia 2	3304	dense limestone	1.2	2.4	0.028	0.207	Group IV, 90°C, H_2S, CO_2 saturated solution
31	Luojia 2	3285.53	dense limestone	2.4	3.0	0.058	0.413	
32	Zi 2	3350.48	gypsum	2.1	6.6	0.142	5.60	
33	Wuke 1	19-655	gypsum	2.6	5.9	0.070	1.67	
34	Luojia 6	3939	oolitic porous limestone	1.5	2.2	0.045	0.226	
35	Puguang 2	4929.7	oolitic porous dolomite	5.3	6.0	\	\	
36	Maoba 3	4369	oolitic porous dolomite	6.1	6.7	0.066	0.226	
37	Puguang 2	5100	oolitic porous dolomite	9.5	9.6	\	\	
38	Puguang 2	4939.7	oolitic porous dolomite	10.0	11.8	11.1	19.5	
39	Luojia 2	3256.74	oolitic porous dolomite	12.5	13.2	223	227	

Before*, before erosion; After**,after erosion.

(2) Results of simulation experiments

The simulation results showed that porosity of all the samples increased apparently after 100-day dipping erosion no matter what primary physical properties they had before the erosion, among which those with originally poor physical properties were greatly improved in physical properties, and differences in fluid property and temperature might affect the erosion effect very much, the higher the temperature, the greater the permeability and the more the pores increased. Moreover, the erosion with the presence of both H_2S and CO_2 was more severe relative to H_2S alone, which is consistent with the natural gas from the Feixianguan Formation gas field where both H_2S and CO_2 are high in the natural gas. Reservoir beds with deeper burial and higher temperature usually have severer erosion.

The Feixianguan Formation reservoir bed is characterized by high porosity and high permeability, 80% of its pores are secondary eroded pores that are distributed along bedding direction and well connected with each other due to bigger aperture. The formation of these eroded pores is related with erosion of H_2S. TSR may produce H_2S that resolves in water to form hydrosulphuric acid, this strong acid may accelerate the burial erosion of carbonate rocks to form a spongy cavity system with well-developed pores distributed along bedding plane. The heat and acidic fluid produced by TSR can only migrate laterally from a high potential area to low potential area due to the overlying dense and thick gypseous cap rocks, i.e. the flowing direction of acidic fluids in subsurface is limited to pressure and energy transfer within reservoirs. This hydrodynamic condition determines a laterally stratified distribution of fluid-rock interaction, i.e. eroded pores develop along bedding plane in a direction of decreasing pressure to form a stratified distribution of eroded pores. The characteristics of well-developed pores in the Feixianguan Formation fully indicate a fluid-rock interaction of deep acidic fluids under the shield of overlying gypseous cap rocks in subsurface. Under scanning electron microscope (SEM), large-scaled eroded pores distinctly show a stratified distribution and a good connection with each other.

3 Alteration of gas reservoirs by TSR

H_2S in natural gases from the northeastern Sichuan Basin is produced by TSR occurring in reservoirs. TSR can alter reservoirs significantly, moreover, during TSR by hydrocarbons with sulfate, reservoir space increases and hydrocarbons are consumed (consumption of hydrocarbons by TSR) with the erosion of gypsum (forming SO_4^{2-} to take part in the reaction), leading to decreasing fluid level and pressure coefficient of reservoirs. Exploration has proved that all the gas pools with high H_2S discovered in China up to now belong to a normal pressure gas reservoir with pressure coefficient ranging between 1.0~1.2, and they are gas reservoirs containing edge water or bottom water. These characters indicate that TSR can alter reservoirs significantly, i.e. consumption of hydrocarbons, space dilatation of reservoir erosion and formation of water by TSR are major factors that result in the decrease of fluid level for gas pools with high H_2S, ubiquitous occurrence of edge water and bottom water, and the hardness of ultra-high pressure formation in reservoirs.