Study of corrosion mechanism of sour gas to cement stone in PUGUANG gas field

Abstract
The gas reservoir of PUGUANG contains high levels of H\textsubscript{2}S and CO\textsubscript{2} with 15\% and 8\% by volume respectively. As to the corrosion of CO\textsubscript{2}/H\textsubscript{2}S mixture to cement, people seldom involve in research. Cement stone samples corroded by H\textsubscript{2}S/CO\textsubscript{2} mixture under different temperature and pressure are tested to probe the change of compressive strength and permeability. Microstructure and corroded products of corroded samples were observed by SEM and XRD. The result shows the corroded products of CO\textsubscript{2}/H\textsubscript{2}S mixture to cement are similar to those by single-component H\textsubscript{2}S or CO\textsubscript{2} gas, except that the amount of expansive crystal produced by H\textsubscript{2}S is reduced. Combination of H\textsubscript{2}S and CO\textsubscript{2} accelerates the corrosion progress, the recession of strength and permeability is more serious than that of single action by H\textsubscript{2}S or CO\textsubscript{2} simultaneously, but CO\textsubscript{2} dominates the whole corrosion process after the long duration. Fly ash and Clay have benefits to resist corrosion of combination of H\textsubscript{2}S and CO\textsubscript{2}.

Keywords: sour gas, cement stone, corrosion, H\textsubscript{2}S, CO\textsubscript{2}, puguang

Introduction
The PUGUANG gas field is the biggest sour gas field in China which contains 15\% and 8\% by volume of H\textsubscript{2}S and CO\textsubscript{2} respectively. Acidic gas and alkaline cement ring will react in wet condition to cause compressive strength reduce and damage seal function of cement ring.\textsuperscript{2,3} Previous studies focused on the single corrosion mechanism of CO\textsubscript{2} or H\textsubscript{2}S to cement stone, as to the corrosion of CO\textsubscript{2}/H\textsubscript{2}S mixture to cement, people seldom involve in research. Such as Yaoxiao\textsuperscript{4} & Zhou Shiming\textsuperscript{5} has studied the change of compressive strength of cement by CO\textsubscript{2}, Ma kaifu\textsuperscript{6} has made systematic studies on the H\textsubscript{2}S corrosion to cement. What will happen on the cement after the combinatorial action by H\textsubscript{2}S and CO\textsubscript{2} mixture? In this paper test methods are established under well whole condition of PUGUANG gas field,\textsuperscript{7} the compressive strength and permeability of cement stone are measured before and after corrosion according to API Spec10B. SEM and XRD are used to study the change of micro structure and reaction product before and after corrosion.

Test procedure and cement composition

Experimental process

Experimental parameter: Test parameters are determined according to well condition of PUGUANG gas field as follows:

i. Experimental temperature: 95\°C, 130\°C, 150\°C.

ii. Corrosive media: xH\textsubscript{2}S = 65.2\% xCO\textsubscript{2} = 34.8\%.

iii. Pressure: 15MPa, the partial pressures of H\textsubscript{2}S and CO\textsubscript{2} are 10MPa and 5MPa respectively.

iv. Conservation Time: 21 days.

v. Test water: Simulated formation water.

Table 1 Slurry compositions of group 1 at 95\°C

| Composition No. | 1 | 2 | 3 | 4 | 5 | 6 |
|----------------|---|---|---|---|---|---|
| API G class cement, g | 500 | 500 | 500 | 500 | 500 | 500 |
| Silica flour, g | - | - | - | - | - | 175 |
| Dispersant, g | - | 7.5 | 17.5 | 15 | 17.5 | - |
| Filtration controller, g | - | 30 | 30 | 30 | 30 | - |
| Latex, g | - | 60 | 60 | - | 60 | - |
| Al\textsubscript{2}O\textsubscript{3}, g | - | - | - | 50 | - | - |
| Clay, g | - | - | 50 | 50 | - | - |
| Fly ash, g | - | - | 90 | 150 | 75 | - |
Table 2 Slurry compositions of group 2 at 130°C and 150°C

| Composition No. | 1   | 2   | 3   | 4   | 5   | 6   |
|-----------------|-----|-----|-----|-----|-----|-----|
| APIG class cement g | 500 | 500 | 500 | 500 | 600 | 500 |
| Silica flour g   | 175 | 175 | 150 | 175 | 175 |
| Dispersant, g    | -   | 7.5 | 17.5| 15  | 17.5| 17.5|
| Filtration controller, g | - | 30  | 30  | 30  | 30  | 30  |
| Latex, g         | -   | 60  | 60  | 60  | 60  | 60  |
| Al₂O₃, g         | -   | -   | 25  | 50  | 25  | 25  |
| Clay, g          | 25  | 25  | -   | 25  | -   | 25  |
| Fly ash, g       | 75  | 75  | 150 | 75  | 75  | 75  |

Result and analysis of test

Change of compressive strengthen and permeability after corrosion

Table 3 shows the change of compressive strengthen and permeability of group 1 cement stone before and after corrosion at 95°C, and Table 4 & 5 show those changes of group 2 at 130°C and 150°C. Table 3–5 shows most of samples present compressive strengthen reduction and permeability increase after corrosion. Sample 3 and 4 show comparatively good corrosion resistance with other samples.

Information in tables also shows that as the temperature rises, the recession of strengthen and permeability is more serious, which presents a complete opposite rule with that of single corrosion by H₂S or CO₂.

Table 3 Change of compressive strengthen and permeability after corrosion at 95°C

| Number of Sample | Compressive Strength (Mpa) | Permeability K/(10⁻³um²) |
|------------------|---------------------------|--------------------------|
|                  | Before Corrosion | After Corrosion | Change | Before Corrosion | After Corrosion | Change |
| 1                | 17.01           | 18.82           | 10.64  | 0.2006           | 0.3317           | 65.35  |
| 2                | 13.83           | 12.13           | -12.29 | 0.2978           | 0.3351           | 12.53  |
| 3                | 13.15           | 11.79           | -10.34 | 0.1903           | 0.3134           | 64.69  |
| 4                | 14.23           | 14.29           | 0.42   | 0.3              | 0.2743           | -8.57  |
| 5                | 18.71           | 14.52           | -22.39 | 0.1677           | 0.2714           | 61.84  |
| 6                | 20.47           | 16.33           | -20.22 | 0.2              | 0.279            | 39.5   |

Table 4 Change of compressive strengthen and permeability after corrosion at 130°C

| Number of Sample | Changes in Strength (Mpa) | Permeability K / K/(10⁻³um²) |
|------------------|---------------------------|-----------------------------|
|                  | Before Corrosion | After Corrosion | Change | Before Corrosion | After Corrosion | Change |
| 1                | 25.6            | 15.2           | -40.63 | 0.623            | 2.731            | 338.36 |
| 2                | 18.48           | 13.38          | -27.6  | 0.621            | 2.745            | 342.03 |
| 3                | 14.86           | 16.22          | 9.15   | 0.439            | 0.362            | -17.54 |
| 4                | 18.37           | 17.69          | -3.7   | 0.417            | 0.522            | 25.18  |
| 5                | 13.5            | 17.46          | 14.07  | 0.2988           | 3.337            | 769.01 |
| 6                | 14.29           | 14.29          | 0      | 0.556            | 2.923            | 425.72 |

Table 5 change of compressive strengthen and permeability after corrosion at 150°C

| Number of sample | Change in strength (Mpa) | Permeability K / K/(10⁻³um²) |
|------------------|--------------------------|-----------------------------|
|                  | before corrosion | after corrosion | Change | before corrosion | After Corrosion | Change |
| 1                | 38.73           | 21.05           | -45.65 | 0.3255           | 0.523            | 60.68  |
| 2                | 32.34           | 13.56           | -58.07 | 0.2969           | 2.755            | 827.92 |
| 3                | 17.18           | 17.46           | 1.63   | 0.2988           | 0.672            | 124.9  |
| 4                | 31.58           | 25.86           | -18.11 | 0.312            | 1.828            | 485.9  |
| 5                | 15.93           | 14.23           | -10.67 | 0.3669           | 0.4561           | 24.31  |
| 6                | 20.58           | 15.52           | -24.59 | -                | -                | -      |
Analysis on reaction products of corroded cement samples

Corroded products analysis at 95°C: Figure 1 is XRD result of sample 1 and Figure 2 is SEM picture of sample 1 and 6 of group 1. Figure 1 shows that there is lots of CaCO₃ crystal in outer layers of sample 1, which are the products of CO₂ reaction. Little CaSO₄ Crystal is founded in the inside of the sample which is the products of H₂S reaction. A large amount of Ca (OH)₂ is founded in the inner of sample 1. Figure 2 shows that there are lots of cracks and pores in both samples of 1 and 6 which verifies the recession of strengthen and permeability. The picture also indicates there is almost no hydrated calcium silicate (CSH) in the cement stone.

Corroded products analysis at 130°C: Figure 3 & 4 are of XRD results of the corroded samples from No.1 to No.6 of group 2 at 130°C. Figure 3 analyzes products in the outer layer of samples and Figure 4 analyzes products of in the core of samples. Figure 3 shows there are large amount of mini-crystal calcium carbonate (CaCO₃ (I)) and calcite (CaCO₃ (II)) and a little gypsum in all the samples. Figure 4 shows almost no Ca(OH)₂ in the core of samples. For lack Ca(OH)₂, CSH lost stability by transforming to C₂SH, which can explain why the recession of strengthen and permeability becoming more serious as the temperature rising. Figure 5 is the SEM pictures of sample 3 and 4. The picture indicates there are lots of cracks and pores in both samples. The picture also indicates There are almost no hydrated calcium silicate (CSH) and Ca(OH)₂ in the cement stone.
Corroded products analysis at 150˚C: Figure 6 & 7 are of XRD results of the corroded samples from No.1 to No.6 of group 2 at 150˚C. Figure 6 analyzes products in the outer layer of samples and Figure 7 analyzes products in the core of samples. Figure 6 shows there are large amount of mini-crystal calcium carbonate (CaCO\(_3\) (I)) and calcite (CaCO\(_3\) (II)) and a little gypsum in all the samples. Figure 7 shows there is CaCO\(_3\) in the core of cement stone which indicates the corroding reaction makes deeper. Figure 8 is the SEM pictures of sample 3 and 5. The picture indicates there are lots of cracks and pores in both samples, and almost no hydrated calcium silicate (CSH and Ca(OH)\(_2\)) in the cement stone. The crystal of CaCO\(_3\) and CaSO\(_4\) is founded in the core of cement which verifies the further corroding reaction with temperature rising.

Corrosion mechanism analysis

**Corrosion mechanism of CO2 to cement**

Corrosion mechanism of CO\(_2\) to cement composes with reaction formula (1) and (2).\(^{1,8}\)

\[\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \] (1)

\[\text{Ca(OH)}_2 + \text{H}^+ + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{2H}_2\text{O} \] (2)

There is almost no CSH gel in the corroded cement stone sample, but there is large volume of C\(_3\)SH, which shows that CSH gel begins to react with CO\(_3\) and produce CaCO\(_3\) and C\(_3\)SH, its reaction composes with the reaction formula (3).\(^{3,9,11}\)

\[\text{CSH} + \text{H}^+ + \text{HCO}_3^- \rightarrow \text{C}_3\text{SH} + \text{CaCO}_3 \] (3)

**Corrosion mechanism of H2S to cement**

Firstly H\(_2\)S reacts with Ca(OH)\(_2\) to produce CaSO\(_4\),2H\(_2\)O (gypsum) and the volume of solid substance expands, producing fractures in cement stone, then it makes corrosion expanding into the cement until all cement gelatin is corroded and collapsed.

The reaction of H\(_2\)S with cement stone is as following.\(^{1,2}\)

\[\text{Ca(OH)}_2(S) + \text{H}_2\text{S}(g) + \text{H}_2\text{O}(1) \rightarrow \text{CaSO}_4 + \text{2H}_2\text{O} (S) \] (4)

The density of Ca(OH)\(_2\) is 2.24 g/cm\(^3\), while the density of CaSO\(_4\),2H\(_2\)O is 2.30 g/cm\(^3\). Therefore, when corroded by H\(_2\)S, the volume cement stone will expand, and producing fractures in it. CSH gel of cement stone also reacts with H\(_2\)S solution to produce CaSO\(_4\),2H\(_2\)O (gypsum).

The reaction formula is as following.\(^6\)

\[\text{CSH} + \text{H}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \text{2H}_2\text{O} + \text{C(m)S(n)H(x)} \] (5)

\[\text{CaSO}_4 \cdot \text{2H}_2\text{O} \text{ will continue to react with C3A to produce Ettringite (AFT) catalyzed by Ca(OH)}_2 \text{.} \]

The reaction formula is as following.\(^{1,2}\)

\[\text{C}_3\text{A} + 3(\text{CaSO}_4 \cdot \text{2H}_2\text{O}) + 2\text{Ca(OH)}_2 + 24\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \] (6)

The density of Ettringite is 1.73 g/cm\(^3\), too much ettringite generate will cause cement stone expanding split.

**Corrosion mechanism of CO2 and H2S mixture to cement**

The products corroded by H\(_2\)S and CO\(_2\) mixture to Cement stone are similar to those by single-component gas.\(^{1,5}\) CO\(_2\) dominates the whole corrosion process in the long duration, because its' corroding products are more than the products by H\(_2\)S. For the small quantity of products by H\(_2\)S, expanding split cannot be founded in whole process by combination of H\(_2\)S and CO\(_2\).

Combination of H\(_2\)S and CO\(_2\) accelerates the corrosion progress, the recession of strengthen and permeability is more serious than that of single action by H\(_2\)S or CO\(_2\) simultaneously. As temperature rises, the recession of strengthen and permeability is more serious, which presents a complete opposite rule with that of single corrosion by H\(_2\)S or CO\(_2\).

**Conclusion**

The temperature of bottom well bore of PUGUANG gas field is 150˚C, and the partial pressures of H\(_2\)S and CO\(_2\) are 10MPa and 5MPa

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respectively, which will bring serious corrosion on cement ring, and damage its’ seal ability. The higher of the temperature rises, the more severe of the recession of strengthen and permeability, which presents a complete opposite rule with that of single corrosion by H_2S or CO_2. The composition of cement slurry is the predominant factor affecting cement corrosion resistance. The introduction of Latex and Fly ash and clay into system will reduce the alkalinity in the cement slurry system and improves the corrosion resistance of set cement. The hydration products are crystallized after corrosion under combination of H_2S and CO_2 and loose arrangement of that crystal is the reason of strength decline and permeability rise. Measures against composite corrosion of H_2S and CO_2 mixture: decline the alkalinity and reduce the porosity of cement slurry.

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**Conflict of interest**

The authors declare no conflict of interest.

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