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## RESEARCH ON THE CORROSION MECHANISM OF CO<sub>2</sub>/H<sub>2</sub>S MIXTURE TO CEMENT STONE

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CO<sub>2</sub> and H<sub>2</sub>S have different corrosion effects on cement stone under wet conditions. Little research has been performed to date on the corrosive effect of CO<sub>2</sub>/H<sub>2</sub>S mixture to cement. However, the mixture usually exists in many sour gas reservoirs. Cement stone samples corroded by H<sub>2</sub>S/CO<sub>2</sub> 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 corrosion products of CO<sub>2</sub>/H<sub>2</sub>S mixture to cement are similar to those by single-component H<sub>2</sub>S or CO<sub>2</sub> gas, except that the formation of expansive crystal is inhibited. Corroded products caused by CO<sub>2</sub> mainly locate at the outer layers of cement, while the corroded products caused by H<sub>2</sub>S mainly exist at the inside the cement. CO<sub>2</sub> dominates the whole corrosion process after a long duration.

**Keywords:** corrosion mechanism, carbon dioxide, hydrogen sulfide, cement stone, well cementing

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### 1. Introduction

China has found rich gas reservoir with high content of sour gas in Sichuan province, such as Puguang gas field [1] has average 15% and 8% percent by volume of H<sub>2</sub>S and CO<sub>2</sub>. Sour gas in wellbore wet condition will enhance corroding reaction on alkaline cement sheath [2-6], but cement sheath is the key to provide sealability and safe for such sour gas wells. Yaoxiao [7] has studied the carbonation corroding mechanical of cement stone. The compression strengthen of cement stone decreased by 80% after 21 days' curing with temperature no more than 110 °C, but the strengthen almost decreased to 0 after 42 days. The compression strengthen of the cement stone decreased and permeably increased evidently with temperature more than 110 °C, which the corroding product Ca<sub>2</sub>CO<sub>3</sub> changed to two kinds of calcite and aragonite crystal with low strengthen and high permeably. Guozhiqin [8] has studied the carbonation of cement and concluded that the main product is a kind of CaSiO<sub>3</sub> stone. There is almost no adhesion of cement on the casing pulled out from abandoned wells corroded by CO<sub>2</sub>, cement is loose and porous [9]. Author [10] and Ma kaiHua [11] has made integrated studies on the CO<sub>2</sub> and H<sub>2</sub>S corrosion respectively in the wet environment. They established test methods of cement stone corrosion. The change of appearance and compression strength and permeability is used to evaluate physical properties of cement stone before and after corrosion. SEM and XRD are used to study the change of micro structure and corroding product. In fact both CO<sub>2</sub> and H<sub>2</sub>S exist in natural gas in many situations. What will happen on the cement after the combinatorial reaction by H<sub>2</sub>S and CO<sub>2</sub> mixture. In this paper the changes of physical and chemical properties of cement stone under combinatorial corroding reaction with both CO<sub>2</sub> and H<sub>2</sub>S are integrated studied and analyzed.

### 2. Experimental method

#### 2.1. Experimental process

Cement slurry is prepared according to API Spec10B and poured into test mold and cured in HTHP cell for 24 hours. The setted samples are removed from molds and numbered and putted into the corroding chamber, then seal the chamber and inject H<sub>2</sub>S and CO<sub>2</sub> mixture curing under high temperature and high pressure, During the test refilling H<sub>2</sub>S and CO<sub>2</sub> in time to keep pressure. Measure the compression strengthen and permeability of the corroded samples and explore corrode outcome and microstructure with X-Ray Diffractometer (XRD) and Scanning Electron Microscope (SEM).

#### 2.2. Experimental parameter and cement composition

Experimental parameters are determined according to gas reservoir of Sichuan province as following:

1. Experimental temperature: 95 °C, 130 °C, 150 °C.
2. Corrosive soul gas concentration: xH<sub>2</sub>S = 65.2% xCO<sub>2</sub> = 34.8%.
3. Curing time: 21 days.
4. Test water: Simulated formation water. Slurry compositions of 95 °C, 130 °C and 150 °C are listed in table1 and table 2.

Composition No.	1	2	3	4	5	6
API G class cement, g	500	500	500	500	600	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 <sub>2</sub> O <sub>3</sub> , g	-	-	-	50	-	-
Al <sub>2</sub> O <sub>3</sub> and clay, g	-	-	50	-	50	-
Fly ash, g	-	-	90	150	75	-

Composition No.	1	2	3	4	5	6
API G class cemen, g	500	500	500	500	600	500
Silica flour, g	175	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
Al <sub>2</sub> O <sub>3</sub> , g	-	-	25	50	25	25
Al <sub>2</sub> O <sub>3</sub> and clay, g		25	25	-	25	-
Fly ash, g		75	75	150	75	75

### 3. Result and analysis of test

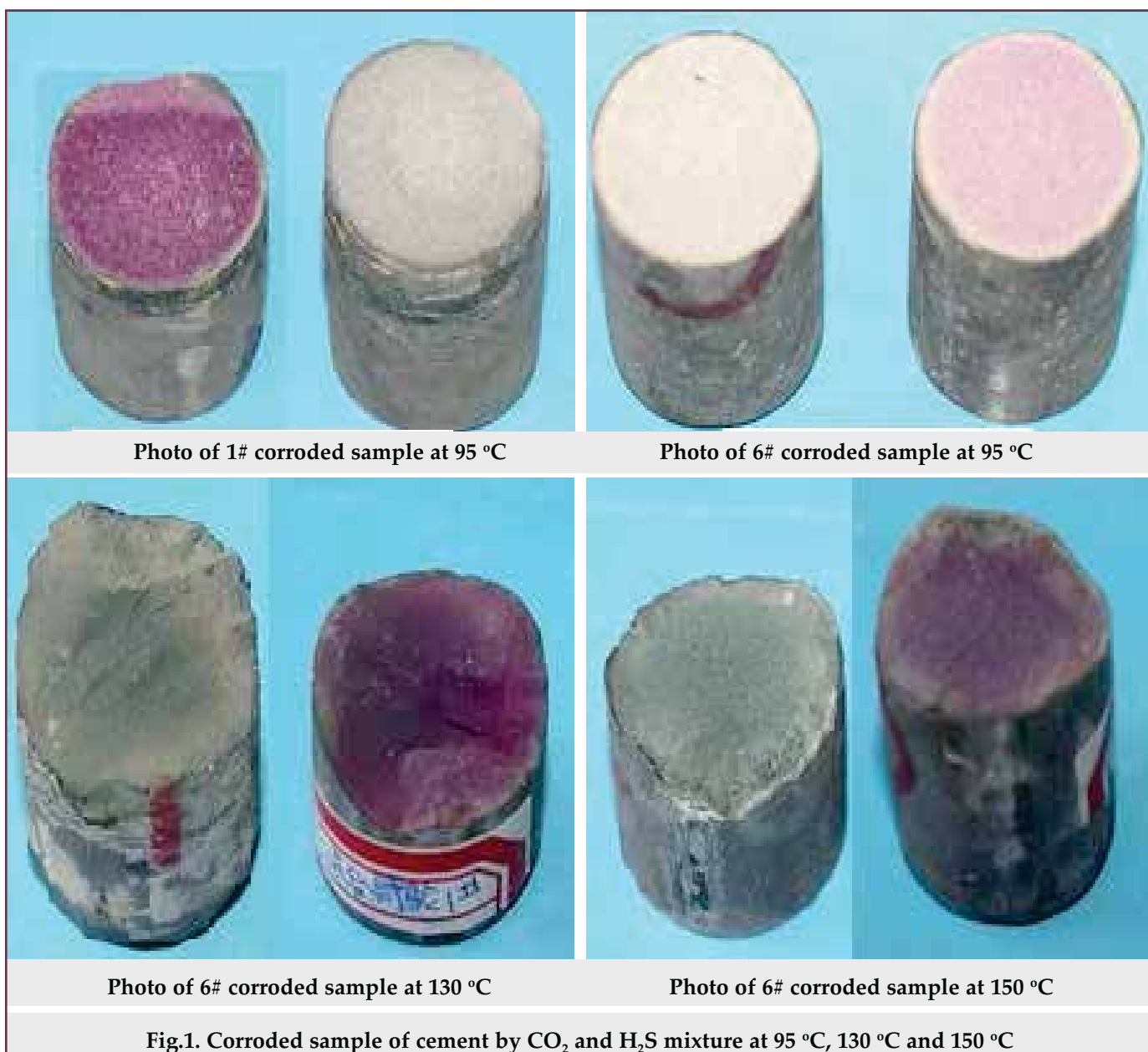
#### 3.1. Description of corroded samples

Figure 1 shows that the corroded samples show two corrosion areas. The outer layer which the phenolphthalein indication is colorless, pH value should be smaller than 7, and the inner layer, which the phenolphthalein indication is red, pH value should be greater than 8.

#### 3.2. Chang of compressive strength and permeability before and after corrosion

Figure 2 and figure 3 show the change of compression strength and permeability before and after corrosion at 95 °C of samples from 1 to 6 in table 2. Test results show compression strength is reduced after corrosion comparing to themselves before corrosion with the maximum reduction rate is 22.39%, except 1# sample. Most samples permeability are reduced after corrosion except sample 4#, and the maximum reduction rate is 39.28%.

But in the high temperature zone, there has been a different result, seeing figure 3 and figure 4. At 130 °C, the permeability of all other samples increase, except sample 4#, the highest growth rate is sample 5# with an increase of 966.92%. At 150 °C, except sample 3, the compressive of all other samples decrease, the largest reduction is sample 2 with 45.7% down. The permeability of all samples improve sharply after corrosion, and sample 3, 4, 5, 6 can not present data in figure 4 because their permeability is too large to be measured.



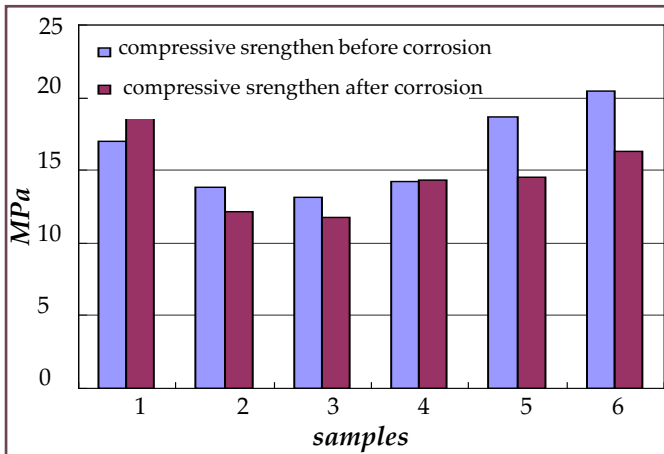


Fig.2. Compressive strength change at 95 °C

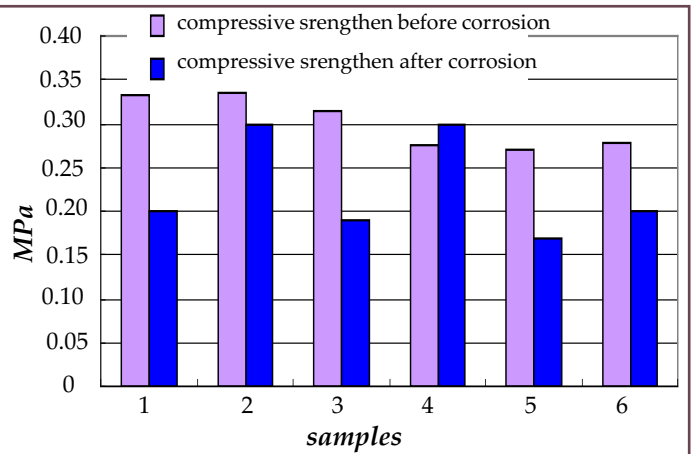


Fig.3. Permeability change at 95 °C

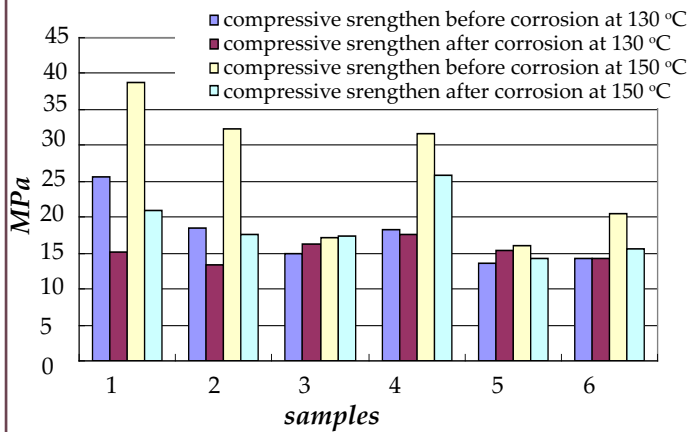


Fig.4. Compressive strength change at 130&150 °C

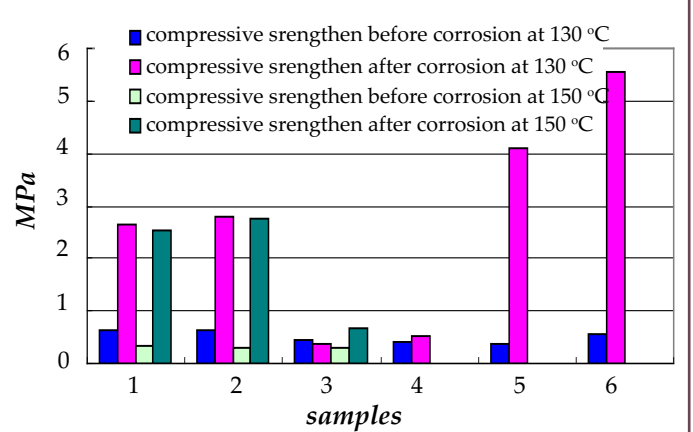


Fig.5. Permeability change at 130&150°C

3.3. Analysis on corroded products of cement

1. Corroded products analysis under 95 °C

Figure 6 and figure 7 are Analysis results by XRD and SEM of 1# to 6# sample.

Figures 1 shows that there are has microcrystalline calcite  $CaCO_3$  and a lot of calcite are produced in middle and outer layers of 1# sample, while a large amount of  $Ca(OH)_2$  is produced in the inner layer.

There is only calcite in the outer layer of 6# sample, and the content of  $Ca(OH)_2$  in the inner layer is much less than that of 1# sample. It indicates that silicon powder can consume  $Ca(OH)_2$  of cement slurry and increase the amount of hydrated calcium silicate. There is a lot of  $Ca(OH)_2$  in 1# sample, indicating that when cement has been corroded by  $CO_2$  and  $H_2S$  together, due to the produced  $CaCO_3$  which has the

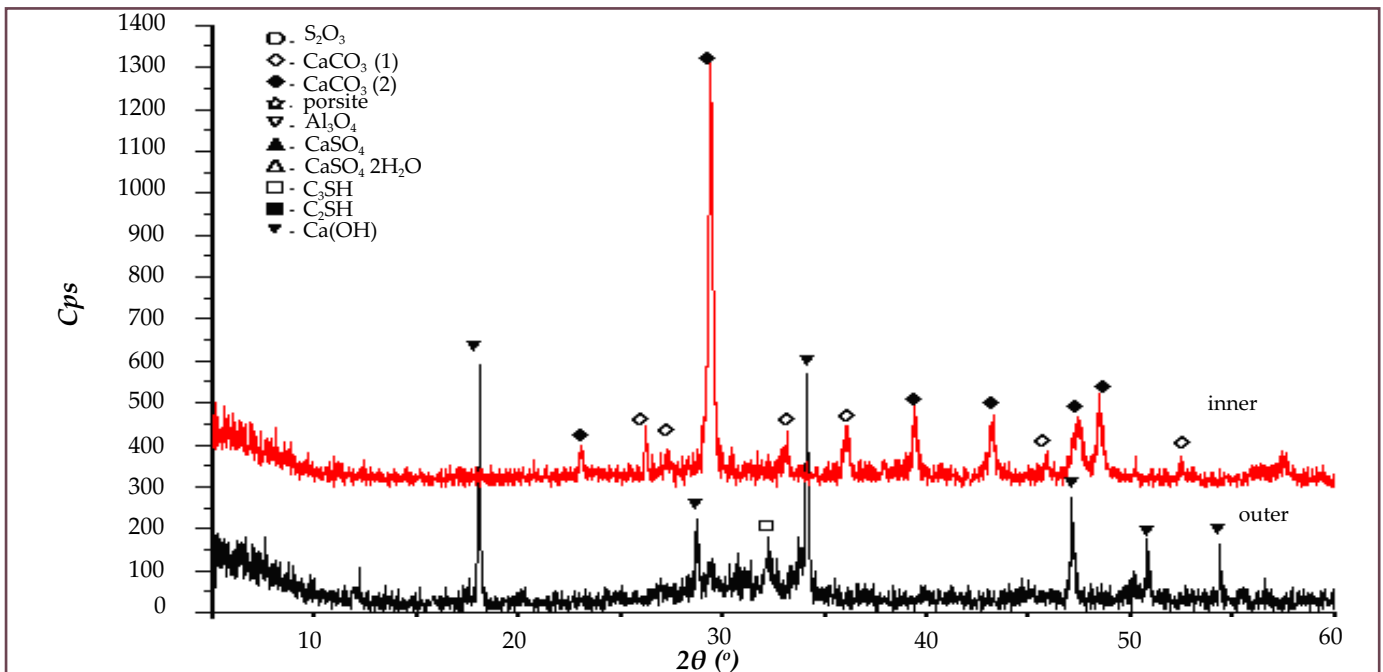


Fig.6. XRD analysis of the inside and superficial of the corrosion sample 1#

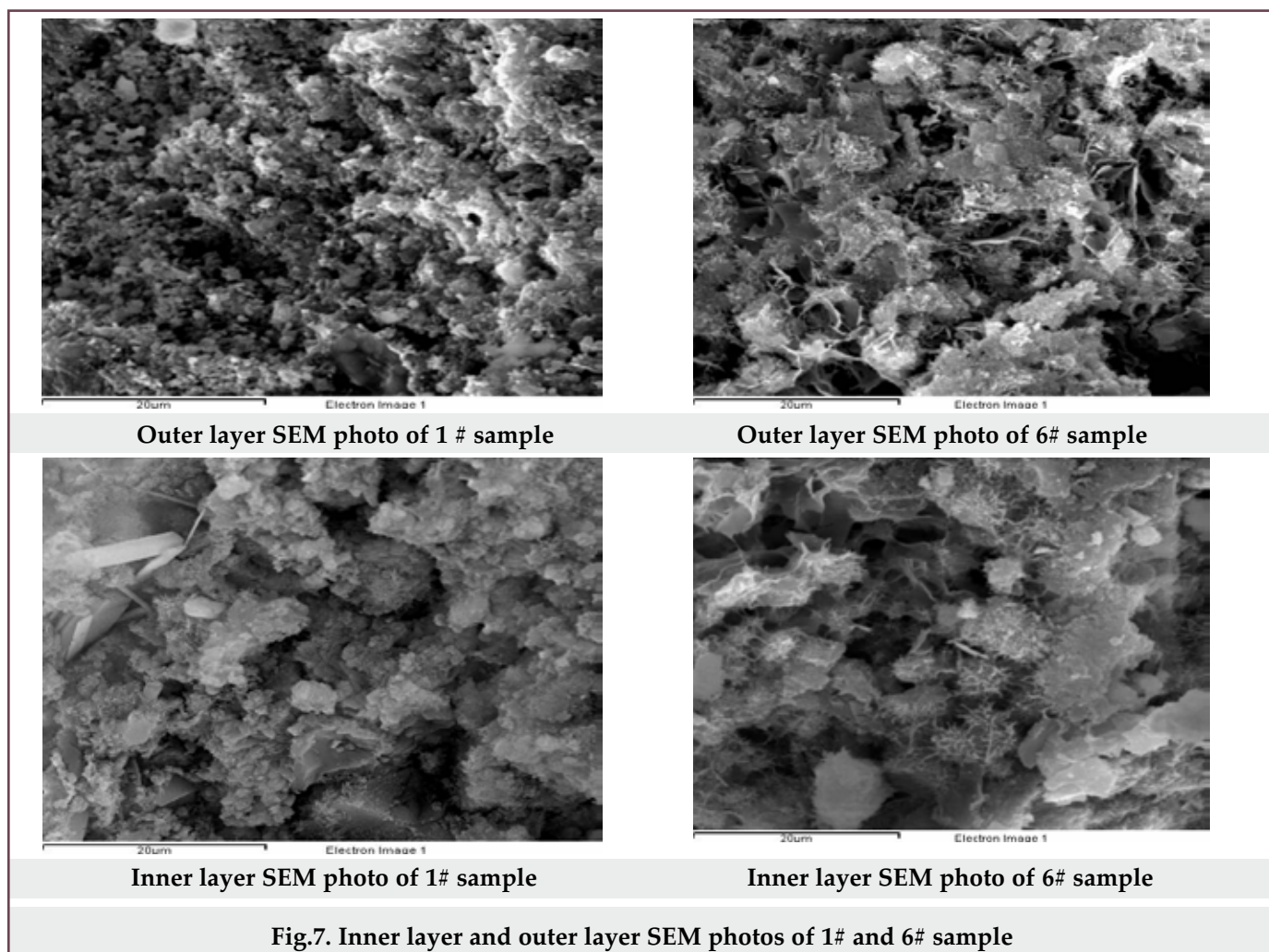


Fig.7. Inner layer and outer layer SEM photos of 1# and 6# sample

effect of blocking pores, soul gasses are prevented from further corroding. The inner layer and outer layer SEM photos of 1# and 6# sample show that there are small crystals of hydration products on the surface of 1# sample. Its structure is compacted, and there is lot of  $\text{Ca}(\text{OH})_2$  inside and pore space is large. There are lots of crystals of hydration products on the surface of 6# sample. There is no  $\text{Ca}(\text{OH})_2$  inside, and

the content of hydrated calcium silicate is increased, and the structure becomes compacted.

## 2. Corroded products analysis under 130 °C

Figure 8, figure 9 and figure 10 are results of XRD and SEM analysis of the corroded samples 1# to 6# at 130 °C.

It shows from the figures that large amount of mini-crystal calcium carbonate ( $\text{CaCO}_3$  (1)) and calcite

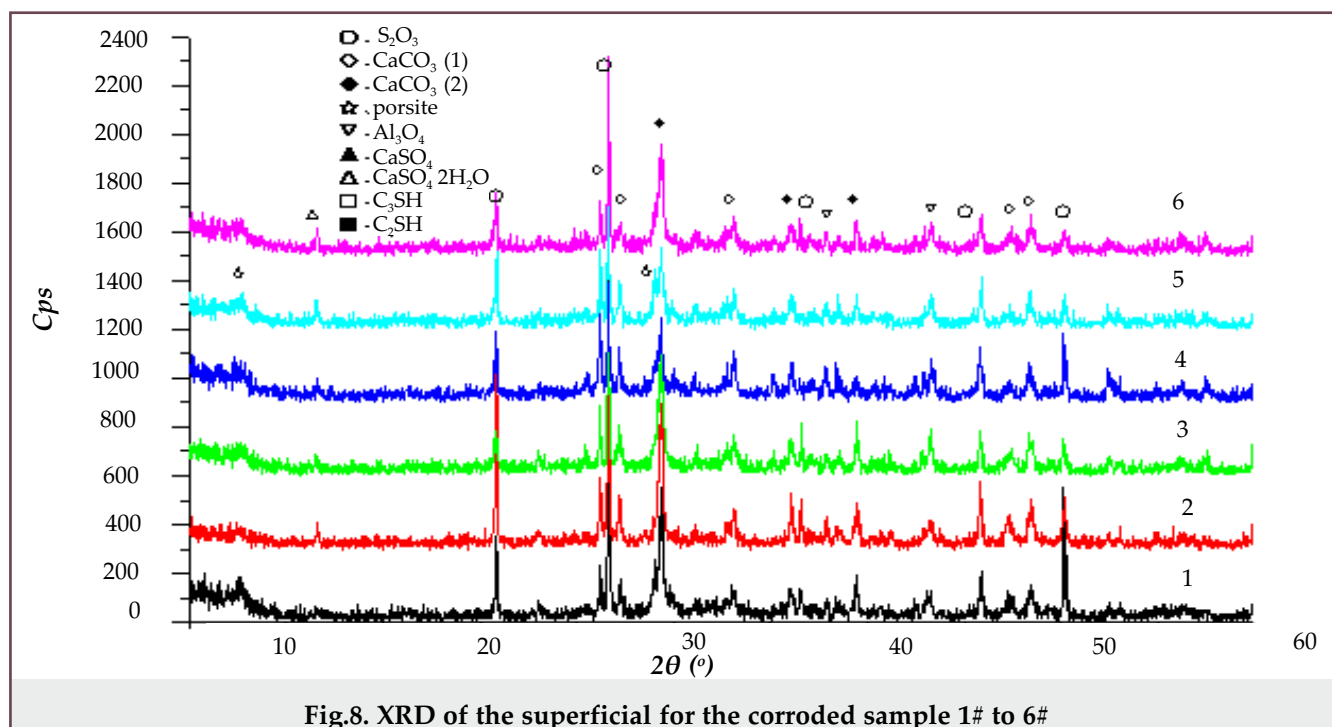


Fig.8. XRD of the superficial for the corroded sample 1# to 6#

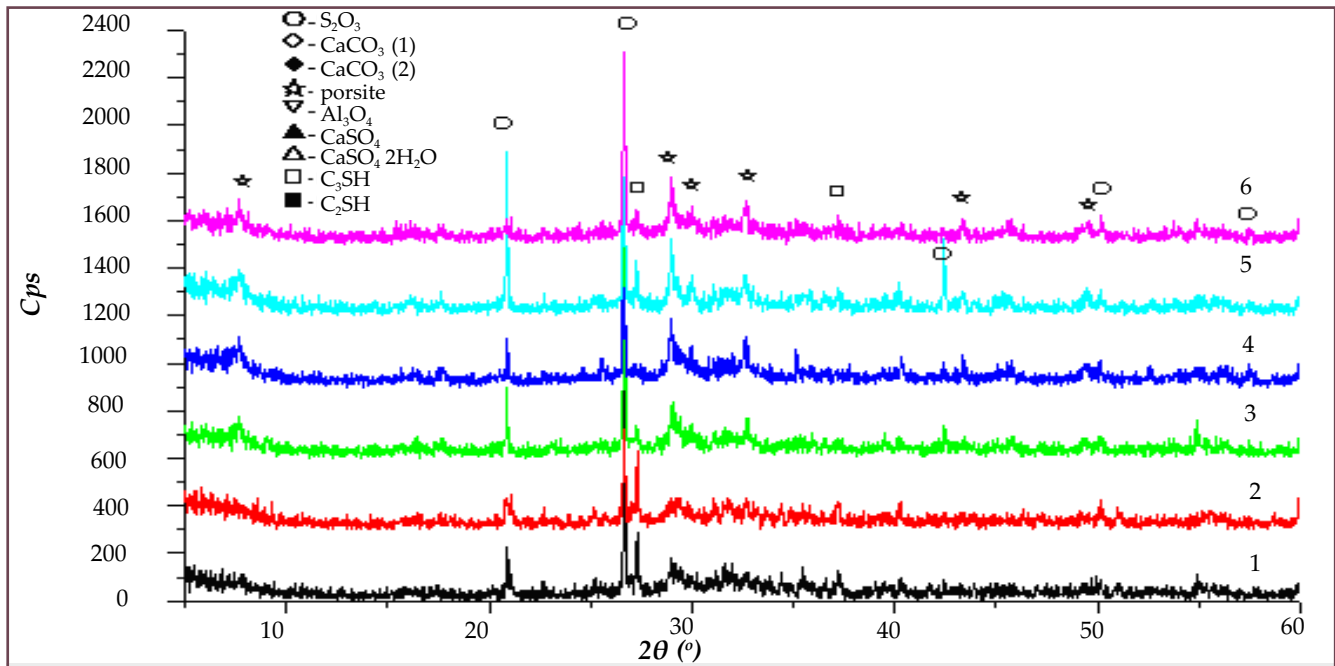
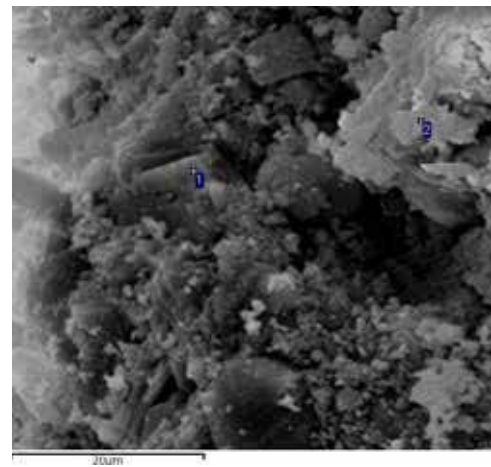
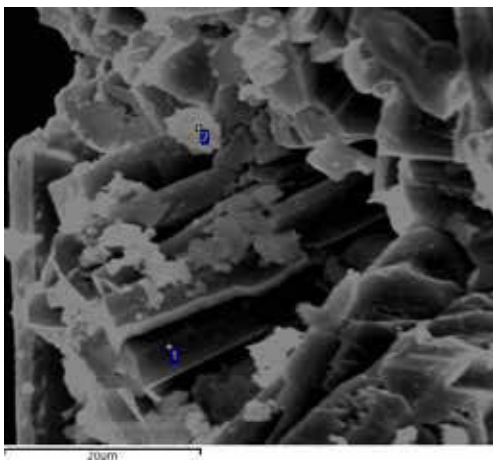


Fig.9. XRD of the inside for the corroded sample 1# to 6#

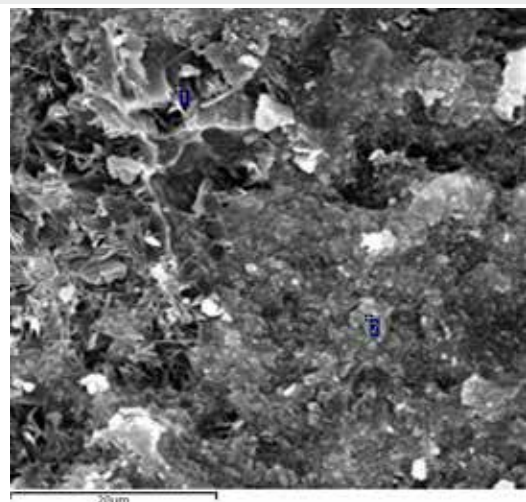
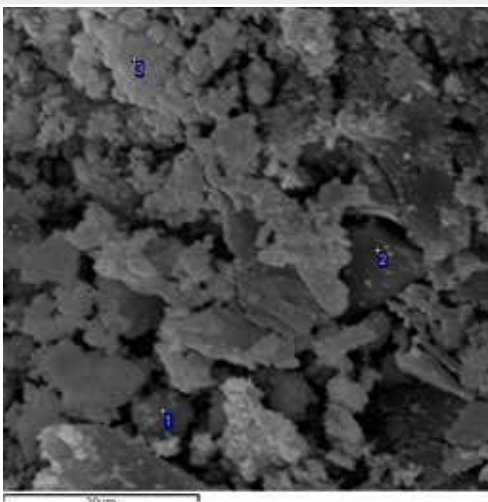
(CaCO<sub>3</sub> (2)) and a little gypsum is produced in outer layers of all the samples. C<sub>2</sub>SH content in inner layers of 1# and 2# corroded sample is higher and in 4# sample C<sub>2</sub>SH content is the least, and in 3# sample C<sub>2</sub>SH content is less. It indicates that in the hardening cement slurry, C<sub>2</sub>SH is an important factor to affect

permeability, and more C<sub>2</sub>SH in samples and the higher permeability of corroded sample.

It indicates from outer layer SEM photos and outer layer material SEM - EDS analysis of 3# and 4# corroded sample that calcite is neatly and tightly arranged in 3# sample; point 1 in 4# sample indicates that calcite is

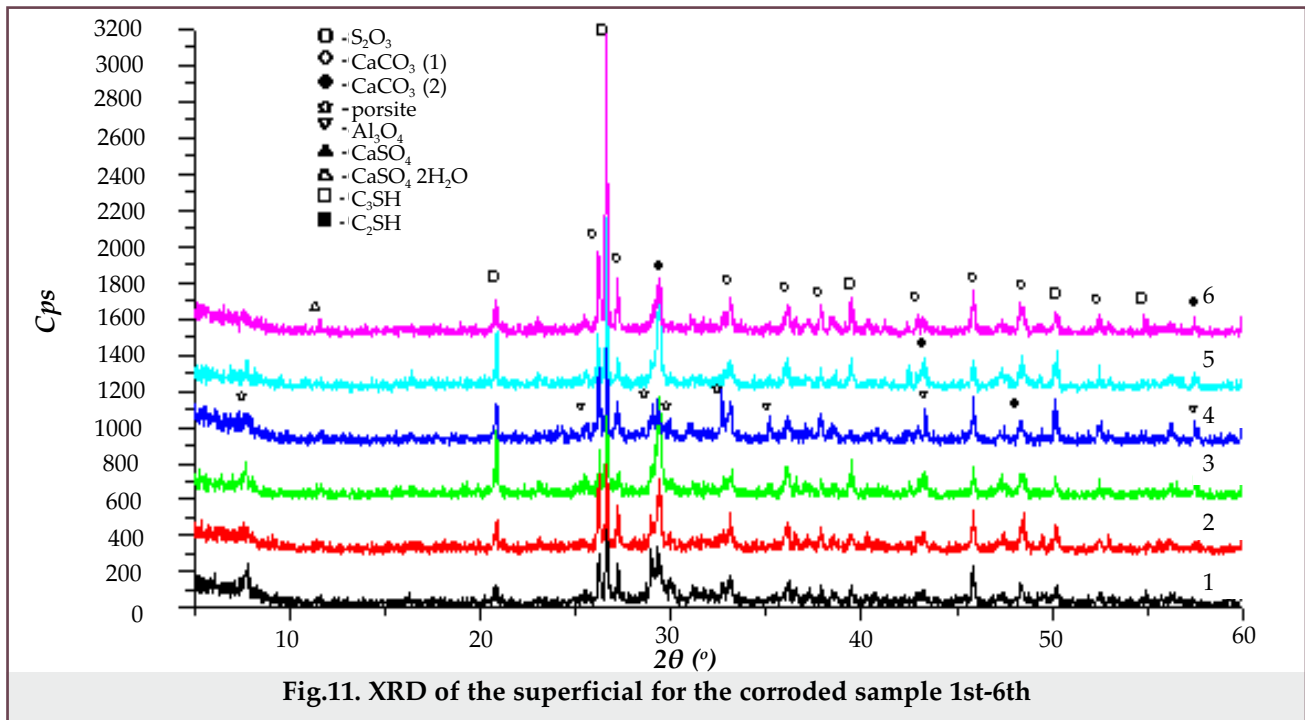


Outer layer SEM photo of 3# and 4# corroded sample (the left is 3#)



Inner layer SEM photo of 3# and 4# corroded sample (the left is 3#)

Fig.10. Inner layer and outer layer SEM photos of No.3 and No.4 sample



buried among the hydrated products with compacted structure. The inner layer SEM photos and SEM-EDS analysis of 3# and 4# corroded sample show that the main phase of the sample is hydrated calcium silicate, and there is a small amount of calcium carbonate. The structure of 4# sample is the most compacted, and pores are evenly distributed in 3# sample.

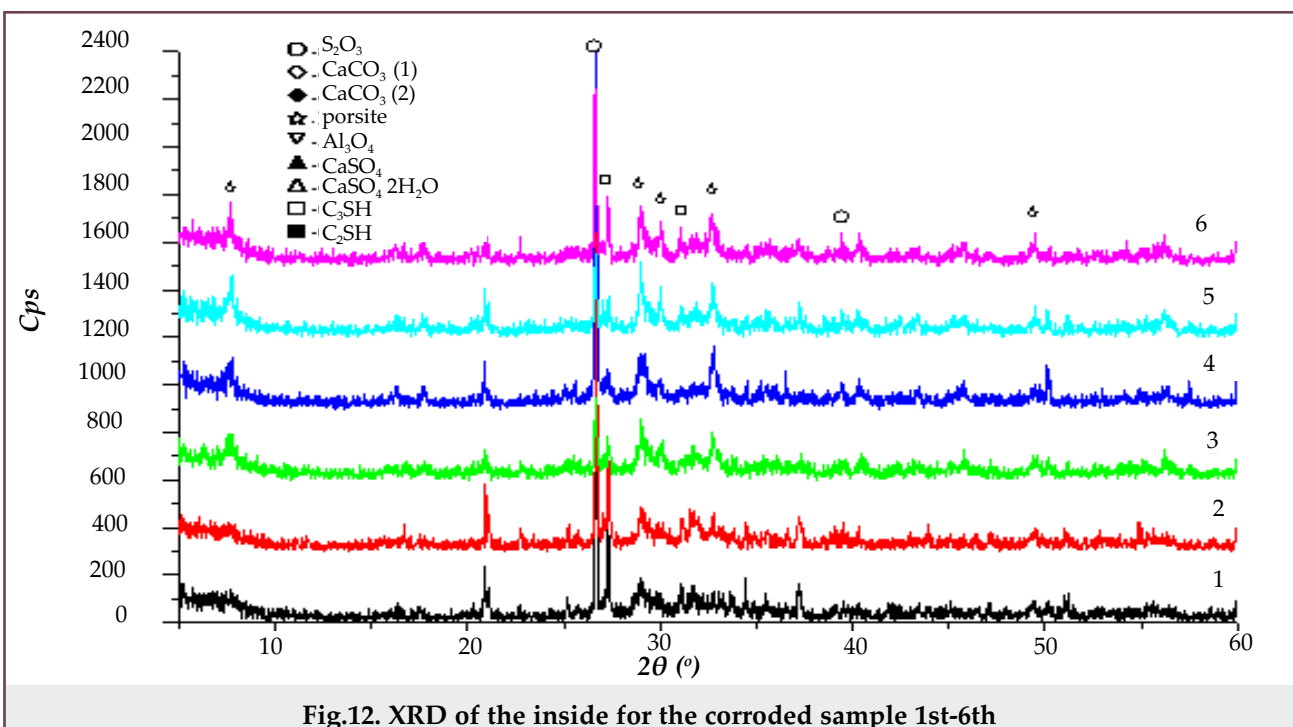
### 3. Corroded products analysis under 150 °C

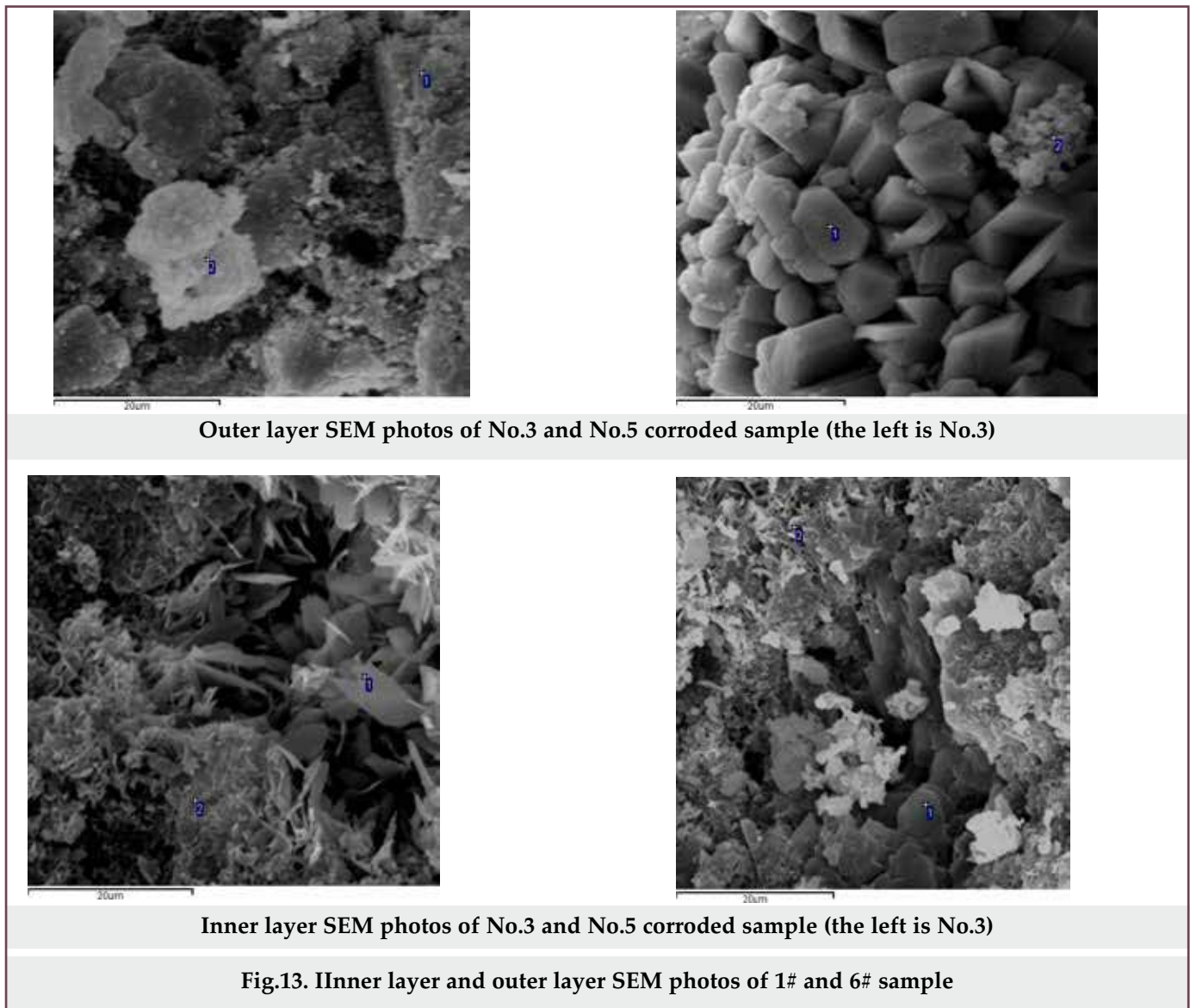
Figure 11, figure 12 and figure 13 are results of XRD and SEM analysis of the corroded samples 1# to 6# at 150 °C.

It indicates from figures that large amount of mini-crystal calcium carbonate ( $\text{CaCO}_3$  (1)) and calcite ( $\text{CaCO}_3$  (2)) are produced in outer layers of all the samples, and  $\text{C}_2\text{SH}$ , the normal hydrated products

(existing in the inner layer) has almost disappeared. Different from corrosion at 130 °C, there is gypsum in 6# sample.  $\text{C}_2\text{SH}$  content in inner layers of 1#, 2# and 6# corroded sample are the highest, and  $\text{C}_2\text{SH}$  content in 3# sample is the least, and  $\text{C}_2\text{SH}$  content in 4# and 4# sample is less. It indicates that  $\text{C}_2\text{SH}$  is an important factor to influence permeability.

It indicates from the outer layer SEM photos of 3# and 5# corroded sample that large amount of calcite is produced in outer layer of the sample, accompanying a small amount of gypsum. The structure near the surface of 3# sample looks like loose, but a compacted layer existed inside. Inner layer SEM photos of 3# and 5# corroded sample indicate that the main phase in the sample is hydrated calcium silicate and a small amount of calcium carbonate. Pores space in 3#



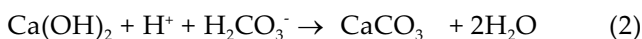
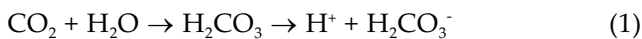


sample is distributed visibly, and the structure of 5# sample is relatively compacted.

#### 4. Corrosion mechanism analyses

##### 4.1. Corrosion mechanism of CO<sub>2</sub> to cement

Corrosion mechanism of CO<sub>2</sub> to cement comply with reaction formula (1) and (2).



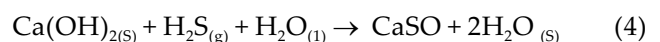
There is almost no CSH gel in the corroded cement stone sample, but there is large volume of C<sub>2</sub>SH, which shows that CSH gel begins to react with CO<sub>2</sub> and produce CaCO<sub>3</sub> and C<sub>2</sub>SH, its reaction complies with the reaction formula (3)[12].



##### 4.2. Corrosion mechanism of H<sub>2</sub>S to cement

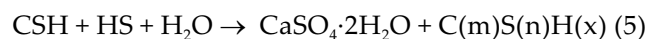
Firstly H<sub>2</sub>S reacts with Ca(OH)<sub>2</sub> to produce CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum) and the volume of solid substance expands, producing fractures in cement stone, then it makes corrosion expanding into the cement until all cement gelatin is corroded and collapsed. The reaction

of H<sub>2</sub>S with cement stone is as following [13]:

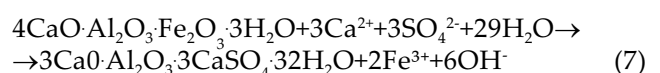
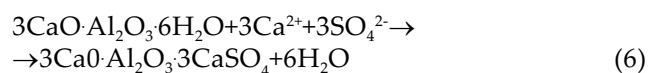


The density of Ca(OH)<sub>2</sub> is 2.24 g/cm<sup>3</sup>, while the density of CaSO<sub>4</sub>·2H<sub>2</sub>O is 2.30 g/cm<sup>3</sup>. Therefore, when corroded by H<sub>2</sub>S, the volume of solid matters in cement gelatin expanded, producing fractures in cement stone;

CSH gel of cement stone also reacts with H<sub>2</sub>S solution to produce CaSO<sub>4</sub>·2H<sub>2</sub>O (gypsum). The reaction formula is as following:



Sulfate radicals (SO<sub>4</sub><sup>2-</sup>) which is dissolved in water can also react with tricalcium aluminate and brown millerite in cement to produce ettringite (AFT). Reaction formulas are as following:



### 4.3. Corrosion mechanism of CO<sub>2</sub> and H<sub>2</sub>S mixture to cement

For the corrosion of H<sub>2</sub>S and CO<sub>2</sub> mixture to set cement, the corrosion of CO<sub>2</sub> is in the leading role and the composite corrosion has more influences on the strength and permeability than single corrosion.

The corrosion products by CO<sub>2</sub>/H<sub>2</sub>S mixture gas are similar to those by single-component gas, except

that the formation of expansive crystal is inhibited. Corroded products by CO<sub>2</sub> mainly locate at the outer layers of cement, while the Corroded products by H<sub>2</sub>S mainly exist at the inner of cement, but CO<sub>2</sub> dominates the whole corrosion process in the long duration.

Temperature rise is not beneficial to the crystallization of calcite and leads to rise of permeability of cement stone.

## 5. Conclusions

1. For the corrosion of H<sub>2</sub>S and CO<sub>2</sub> mixture to set cement, the corrosion of CO<sub>2</sub> is in the leading role and the composite corrosion has more influences on the strength and permeability than single corrosion. Temperature rise is not beneficial to the crystallization of calcite and leads to rise of permeability of cement stone.

2. The composition of cement slurry is the predominant factor affecting cement corrosion resistance. The introduction of Latex and Al<sub>2</sub>O<sub>3</sub> and clay into cement will improve the corrosion resistance of set cement.

3. Measures against composite corrosion of H<sub>2</sub>S and CO<sub>2</sub> mixture: reduce the alkalinity and reduce the porosity of cement slurry, introduction of Pozzolanic Activity materials such as fly ash and slag

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**Исследование механизма коррозии цементного камня  
под действием смеси CO<sub>2</sub>/H<sub>2</sub>S**

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**Реферат**

В статье, с целью изучения механизма коррозии цементного камня под действием смеси агрессивных газов CO<sub>2</sub>/H<sub>2</sub>S, приводящей к изменению прочности на сжатие и проницаемости. Рассматриваются результаты тестирования подвергшихся коррозии под её действием образцов цементного камня при различных температурах и давлениях. Микроструктура и продукты коррозии образцов исследовались сканирующим электронным микроскопом и рентгеновским диффрактомером. Показано, что продукты коррозии цементного камня под действием CO<sub>2</sub>/H<sub>2</sub>S аналогичны продуктам сероводородной коррозии или углекислотной коррозии при их отдельном воздействии. При этом продукты углекислотной коррозии в основном располагаются на внешних слоях, а продукты сероводородной коррозии - внутри цементного камня, но со временем влияние углекислотной коррозии начинает доминировать.

**CO<sub>2</sub>/H<sub>2</sub>S qarışığı korroziyasının sement daşına  
təsiri mexanizminin tədqiqi**

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**Xülasə**

Məqalədə sement daşının sıxılma möhkəmliyinin və keçiriciliyinin dəyişməsinə səbəb olan CO<sub>2</sub>/H<sub>2</sub>S aqressiv qazların qarışığının təsiri altında sement daşının korroziyaya uğrama mexanizmi öyrənilir. Müxtəlif temperatur və təzyiqlərdə qarışığın təsiri altında korroziyaya uğradılmış sement daşlarının təhlilinin nəticələri nəzərdən keçirilir. Nümunələrin mikrostrukturunu və korroziya məhsulları skan edən elektron mikroskop və rentgen diffraktomerlə tədqiq edilmişdir. Göstərilmişdir ki, CO<sub>2</sub>/H<sub>2</sub>S təsiri ilə sement daşının korroziyası məhsulları, ayrı - ayrılıqda hidrogen sulfid korroziyası və ya karbon korroziyası məhsullarına uyğundurlar. Bununla belə karbon korroziyası məhsulları əsasən sement daşının üst qatlarında, hidrogen sulfid korroziyası məhsulları isə daxilində yerləşirlər. Lakin zaman ötdükcə karbon korroziyasının təsiri üstünlük təşkil etməyə başlayır.



## Colored enamels

Enamels PS-1184 and PS-1186 are intended for anticorrosive protection of oil field equipment, pipelines and hydraulic structures. Life time of enamels PS-1184 and PS-1186, applied in 3 layers, is 8 years.



## Epoxy polystyrene enamel

New polystyrene enamel EP - 7105 for anticorrosive protection of steel constructions. Enamel composition is modified by Lacquer - Kors.



## Fire-resisting composition

Is intended for technological equipment inflammation prevention on fixed platforms and fire-hazardous productions. Fire-resisting composition is manufactured in the form of suspension from modified filling agents and fire-retardant. Fire-resisting composition is two-packaged consisting of base and component displacing water. Fire-resisting composition is applied upon protected surface in 3 layers.



## Lacquer - Kors

Lacquer - Kors is utilized as protective coating and, as well, as component of coloured enamels PS-1184 and PS-1186. It is made according to technological regulations. Life time is 5-7 years.



## Bitumen - polymer composition

It is insulating material against corrosive attack and cracking of steel constructions and for underwater pipelines protection. Composition has stable shockproof and thermal insulation properties and, as well, has high electrical resistance.



## Aluminum short circuit galvanic anodes

They are intended for electrical and chemical anticorrosive and microbiological failure of offshore hydraulic structures jackets underwater parts protection. Anodes are installed during new constructions mounting and are manufactured from aluminum alloy.



## Aluminum bracelet galvanic anodes

They are designed for offshore underwater pipelines electrical and chemical anticorrosive and microbiological failure protection. Manufactured from aluminum alloys.



## Plastic composition

Composition is intended for corrosive protection of fixed platforms, piers and other hydraulic structures being in the zone of periodical wetting. It is sea water aggressive attack stable. Plastic composition is mainly manufactured from local raw material.



## Magnesium aluminum binary anodes

They are applied for electrical and chemical anticorrosive and microbiological failure protection of operated offshore hydraulic structures jackets underwater parts, piers, near-pier platforms, shallow water offshore platforms. Anodes are mounted during major (capital) repairs. Manufactured from alloys of aluminum and magnesium.

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