Pergamon

Cement and Concrete Research, Vol. 26, No. 12, pp. 1753-1759, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00176-7

# THE HYDRATION OF SALINE OIL-WELL CEMENT

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(Communicated by Z.W. Wu)
(Received September 12, 1996; in final form October 17, 1996)

## ABSTRACT

The effect of salt content on the properties of the oil-well cement cured at high temperature and high pressure was studied. DTA, TG, XRD and SEM techniques were employed in studying the cement hydration process. An attempt is made to elucidate the change in the properties of fresh and hardened saline cement slurry in terms of the changes in microstructures. The results obtained are helpful in cementing operations with saline oil-well cement slurries. *Copyright © 1996 Elsevier Science Ltd*

## Introduction

In salt layer cementation, using the slurry prepared with fresh water tends to cause well bore collapse due to large amount of salt dissolved into the slurry. Thus, both lower saline slurry and high saline slurry are commonly used in these environments. For the former, the NaCl content is lower than 15% by weight of water (BWOW), while for the latter, the NaCl content can be as high as the saturation level, i.e. 36% (BWOW). The properties of the fresh saline slurry, such as thickening time, rheology, fluid loss, free water etc. differ greatly from those of ordinary slurry. Salts also change the strength of the hardened slurry. This brings about difficulties in selecting technological parameters. R.P.A.R.Van Kleef [1] studied the effect of salt content on the properties of saline slurry and B.J.Whisonant et al [2] discussed the oil well cementation with saline slurry. The present work systematically studies the effect of salt content on the properties of cement slurry, and in addition, the hydration process and products of the saline cement slurry are also discussed.

## Raw Materials and Testing Methods

The chemical composition and the mineral compound (as calculated by the Bogue method ) of the cement are listed in Table 1. Cement—high sulfate-resistant class G cement. NaCl—table salt. Water—local tap water. The water/cement ratio is 0.44 for all the slurries. The NaCl contents are 0%, 5%, 15%, 25% and 36% (BWOW). The thickening time, fluid loss and free water were determined for all slurries according to the API specifications.

Specimens were cast in 3 × 3 × 3 cm molds after hand mixing. The specimens were cured at 93°C, 20.7MPa in a pressurized curing chamber. The salt content of the curing

TABLE 1

Chemical and Mineral Compositions of Class G Cement

| loss | $SiO_2$ | $Al_2O_3$ | CaO | $Fe_2O_3$ | MgO | $SO_3$ | $TiO_2$ | $Na_2O$ | $K_2O$ | other |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.56 | 22.5 | 3.44 | 65.04 | 4.70 | 1.28 | 2.55 | 0.20 | 0.52 | 0.44 | 0.60 |

| $C_3S$ | $C_3A$ | $C_4AF$ | $C_2S$ |
|---|---|---|---|
| 56.5 | 1.17 | 14.29 | 18.06 |

water is the same as that of the mixing water. The temperature was raised to the desired value in 2h and kept there for the curing periods of 4, 8, 12, 24, 48 and 72h respectively. The compressive strengths were then tested. After strength tests the specimens were ground in absolute alcohol, filtered in vacuum, washed with acetone for several times and dried in air for phase identification.

For samples cured at 160°C, 20.7MPa, the proportion of the slurries is cement/sand/water = 1/0.4/0.6. The salt content is the same as that of the specimens cured at 93°C.

The following equipments were used. XRD—Rigaku D/Max-1000. Thermo-analysis—Shimadzu DT-30. SEM—KYKY-1000B manufactured by the China Academy of Sciences.

## Results and Discussions

Effect of Salt Content on the Properties of Cement Slurries. Fig. 1 shows the thickening time of cement slurries at 52°C. The results of fluid-loss and free-water tests are shown in Figs. 2 and 3. At low concentration NaCl exerts accelerating effect, resulting in short thickening time, low fluid loss and low free-water. At higher concentration, 10–15% (BWOW) and above, however, the effect of NaCl on the properties of the fresh slurries is reversed. S.Diamond [3] was of the view that $CaCl_2$, as an accelerator, acceleerates the rate of formation of $Ca(OH)_2$ and C-S-H gel and does not change the hydration products. Kondo et al. [4] suggested that the rate of diffusion of Cl- be three time as rapidly as that of $Ca^+$. Young et al. [5] suggested that NaCl, like $CaCl_2$, bring about the precipitation of insoluble calcium salt, which in turn keeps low calcium concentration in the solution. Thus, the dissolution of $C_3S$ is accelerated.

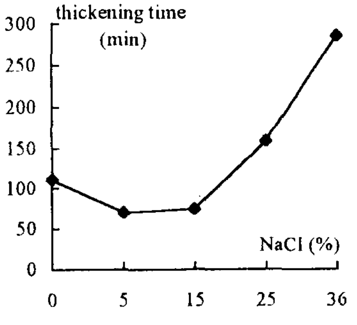

FIG. 1.
The effect of salt content on thickening time of cement slurry.

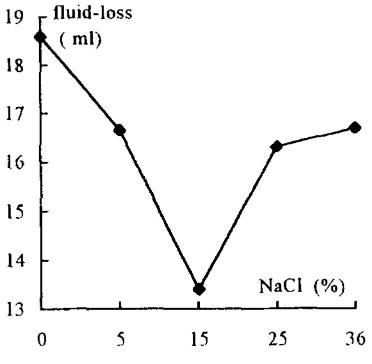

FIG. 2.
The effect of salt content on fluid-loss.

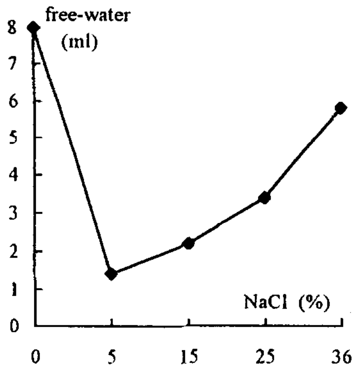

FIG. 3.
The effect of salt content on the free-water.

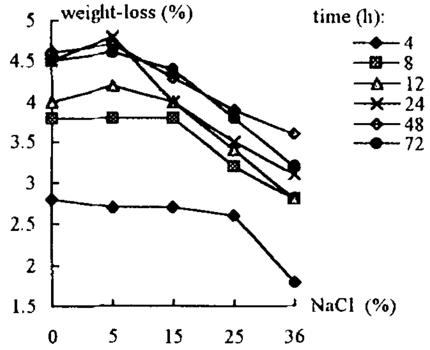

FIG. 4.
The effect of salt content on the weight loss of $Ca(OH)_2$ of pastes cured at 93°C.

The retardation of the cement paste in high NaCl content environment is normally considered to be caused by the mechanical shielding of the precipitated salt.

Effect of Salt Content on the Degree of Hydration. It is presumable that the content of $Ca(OH)_2$ formed should be an indication of the rate of hydration, The authors determined the $Ca(OH)_2$ formed in the oil-well cement during hydration by the weight loss against the weight of hardened slurry on an ignited basis at 800°C, above which NaCl melts and volatizes. The results for cement slurries cured at 93°C are shown in Fig. 4. For samples with 5% of salt content the $Ca(OH)_2$ formed does not differ much from that formed for samples mixed with fresh water. Larger salt content generally brings about a decrease in $Ca(OH)_2$.

Effect of Salt Content on the Strength of Hardened Cement Slurries. The strength of the hardened cement slurry in the annulus is of vital importance in fixing and protecting the casings. The strength of slurries hydrated at 93°C and 160°C under 20.7 MPa are shown in Figs. 5 and 6 respectively. At 93°C, the strength of the 5%(BWOW) saline samples are comparable with those of the samples mixed with fresh water, while for samples with more

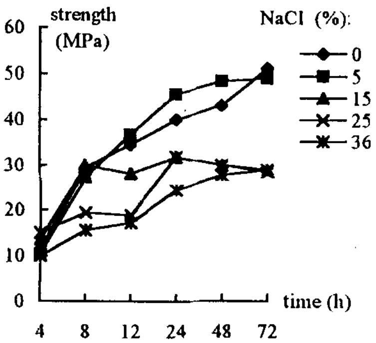

FIG. 5.
Time versus strength (time interval) for samples cured at 93°C.

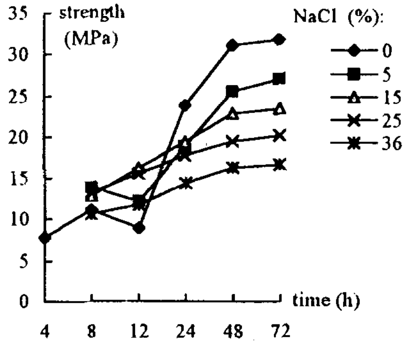

FIG. 6.
Time versus strength (time interval) for samples cured at 160°C.

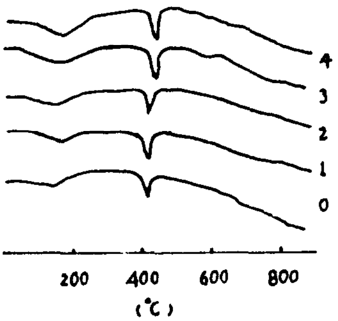

FIG. 7.
The DTA curves of pastes cured at 93°C (0–0%, 1–5%, 2–15%, 3–25%, 4–36%).

than 5% salt contents the strengths are substantially lower. In the case of 160°C and 20.7MPa, the strengths decrease with increasing salt content at long curing periods. The lower strength of saline samples cured at 93°C is the result of lower degree of hydration (as show in TG result of $Ca(OH)_2$ analysis). The lower strength of samples cured at 160°C is caused by new phases formed at elevated temperatures. At high salt concentration, an additional decrease in strength may result from the precipitation of NaCl. Though there is a degradation of strength for applying saline slurries the strength is higher than that required for well cementing, i.e.14MPa.

Influence of Salt Content on Hydrating Products. The salt changes the properties of the cement slurries before and after hardening. This is due to the change in the rate of hydration and the change in the hydration products. The authors studied the influence of salt content on the hydration products with SEM, DTA and XRD.

*a) DTA*. The DTA curves of the samples with various salt contents cured at 93°C for 24hr are shown in Fig. 7. The broad band at 100–200°C originates from adsorbed water and interlayer water in C-S-H. The endothermic peak at 430°C comes from $Ca(OH)_2$. It shows that the area under the endothermic peak increases as the increase of the salt content. At a given curing period the temperature of the endothermic peak decreases as the increase of the NaCl concentration (Table 2). In the case of samples cured at 160°C with silica, the temperature of the endothermic peak is also affected by salt concentration (Fig. 8 and Table 3) with lowering $Ca(OH)_2$ and $C_2SH(A)$ peak temperatures when salt content is increased. The authors point out in another paper [6] the salt content in the hardened slurry is lower than that of the salt added to the mixing water. This implies that part of the NaCl is dispersed in C-S-H and $Ca(OH)_2$ in the form of solid solution or micro-crystallite precipitation. NaCl lowers the activation energy for the decomposition of $Ca(OH)_2$.

TABLE 2

| content | 0 | 5 | 15 | 25 | 36 |
|---|---|---|---|---|---|
| $Ca(OH)_2$. peak-Tem | 435 | 438 | 432 | 428 | 425 |

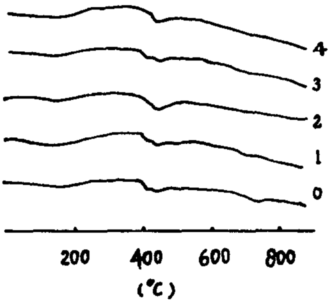

FIG. 8.

The DTA curves of pastes cured at 160°C (0–0%, 1–5%, 2–15%, 3–25%, 4–36%).

K. Susuki et al [7] studied the formation of C-S-H in dilute NaCl solution. The result shows that $Na^+$ in the solution is partly adsorbed on the C-S-H surface and this brings about the decrease of Ca/Si mol ratio. P.Lambert et al [8] studied the ion composition of the pore solution of C54S15AM (Jeffrey's alite) hydrated in dilute NaCl solution. They pointed out that C-S-H does not bond $Cl^-$ and that $Na^+$ is adsorbed partly on the C-S-H surface, while $Cl^-$ remains in the solution. The fact that $Na^+$ remains in the C-S-H phase is in agreement with lowering of the endothermic temperature of C2SH(A) dehydration in DTA analysis.

*b) XRD.* The XRD results for the samples cured at 93°C and 160°C under 20.7MPa for 24hr are shown in Figs. 9 and 10. The hydration products at 93°C consist mostly of $Ca(OH)_2$, CSH(B), $C_2SH_2$ and NaCl peaks enhance as the NaCl content over 15% (BWOW). It should be noted that when NaCl content is over 25% (BWOW), two extra peaks appear at d = 7.915 and d = 2.456, indicating that at high temperature and high pressure cement components may react with NaCl to form calcium chloro-aluminate hydrate, ($C_3A(CaCl_2(10H_2O)$), which seems to be in contrast with the result for reference [3] that no new product is formed under such conditions. The hydration products formed at 160°C are mainly $C_2SH(A)$, CSH(B), $Ca(OH)_2$ and $C_2SH_2$.

*c) SEM.* The morphologies of typical hydration products of cement slurries prepared with fresh water and saline water cement pastes cured at 93°C for 24h are shown in Fig. 11 (a) and (b) where layered $Ca(OH)_2$ and Fibrous C-S-H gel are observed. The effect of salt on the microstructure is shown in the interface between $Ca(OH)_2$ and C-S-H gel. There is an obvious demarcation line in the interface of the two phases in fresh water cement slurry, while there is a transitional zone in the interface of the two phases in saline cement slurry. The hydration product in the transitional zone distinguishes itself from the C-S-H as well as $Ca(OH)_2$.

TABLE 3

| content | 0 | 5 | 15 | 25 | 36 |
|---|---|---|---|---|---|
| $C_2SH(A)$. peak-Tem. | 435 | 419 | 422 | 415 | 420 |
| $Ca(OH)_2$ peak-Tem. | 458 | 451 | 451 | 450 | 447 |

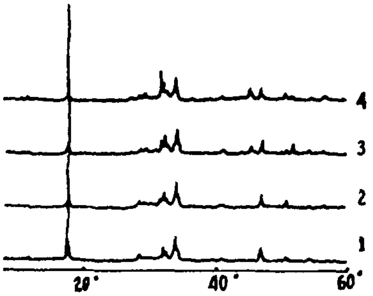

FIG. 9.
(0–0%, 1–5%, 2–15%, 3–25%, 4–36%)

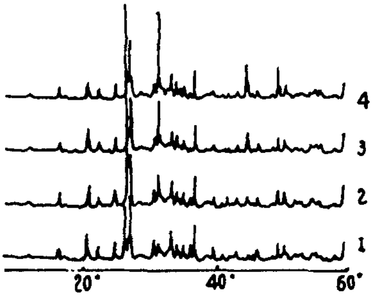

FIG. 10.
(0–0%, 1–5%, 2–15%, 3–25%, 4–36%)

The SEM micrographs of samples cured at 160°C are shown in pictures 12(a) and 12(b). The fibrous and prismatic hydration products are observed in all these photos. However, the hydration product of the slurry with salt is mainly fibrous. Л. Г. ШПЫНОВА et al. [9] indicated that the fibrous product is C2SH2 or CSH(B) and the prismatic product is $C_2SH(A)$.

## Conclusions

1. The thickening time, fluid-loss and free water of saline cement slurries are influenced by salt concentration; low salt concentration accelerates hydration and high salt content retards hydration, which are governed by two mechanisms.

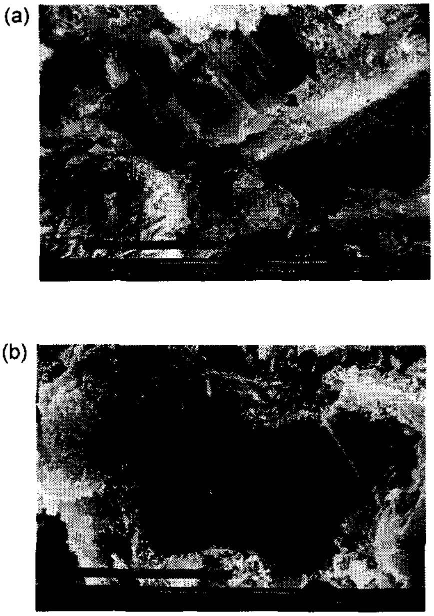

FIG. 11.
SEM micrographs of samples cured at 93 °C. (a) 0% NaCl. (b) 15% NaCl.

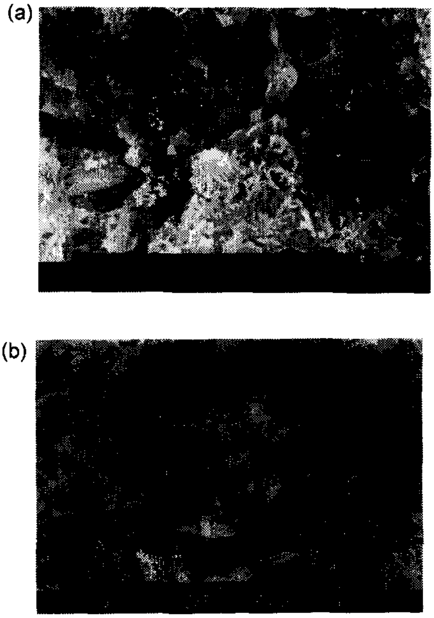

FIG. 12.
SEM micrographs of samples cured at 160°C. (a) 0% NaCl. (b) 36% NaCl.

2. At more than 5% (BWOW) salt, the strengths of saline cement slurries cured at both 90°C and 160°C decrease with increasing salt content. This agrees with the effect of salt content on the degree of hydration.
3. Salt content effects the $Ca(OH)_2$ formation, and also affects the interface between $Ca(OH)_2$ and C-S-H. Salt also changes the endothermic peak of $Ca(OH)_2$ in DTA analysis.
4. The effect of salt on C-S-H is due to the absorptions of NaCl microcrystallites and $Na^+$ on the surface of the fibrous structure.

## Acknowledgment

The authors thank professor Yang Nanru of the Nanjing Institute of Chemical Technology for helpful discussions.

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