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Experimental insights into a novel over-saturated brine cement slurry used in anhydrite formation

L. Xu[1], H. Gao[2], J. Xu[3], M. Xu[4]*, X. Wang[4], F. You[4], Y. Long[1]

[1] *College of Petrochemical and Energetic Engineering, Zhejiang Ocean University, Zhoushan, China*
[2] *Engineering Technology Research Institute of PetroChina Xinjiang Oilfield Company, Karamay, China*
[3] *Institute of exploration techniques, CAGS, Langfang, China*
[4] *Hubei Cooperative Innovation Center of Unconventional Oil and Gas, Yangtze University, Wuhan, China*

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Well cementing properties of anhydrite formation are always challenging, due to the negative impact of anhydrite on the stability of cement slurry. Design and development of certain cement slurry appropriate in anhydrite formation is always essential. In combination to anhydrite properties of Missan Oilfields, herein, systematic experiments were made to develop a special kind of weighted over-saturated brine cement slurry. The density of cement slurry was designed up to 2.36 g/cm^3 to mitigate the plastic deformation of anhydrite formation. Dosages of key additives were optimized by evaluating performance of cement slurry. The results showed that the developed cement slurry had favorable properties such as appropriate rheology, good fluid loss control, short thickening time, right angle consistency, and rapid development of compressive strength. This work not only provides instructive information on a kind of novel weighted over-saturated cement slurry of anhydrite formation, but also extends an important category of cement slurries.

Keywords: Over-saturated brine; Cement slurry; Anhydrite formation; Performance evaluation.

INTRODUCTION

In well cementing operations, an appropriate type of cement slurry is always fundamental, which enables the sustainable, safe and economic production of oil & gas. However, the anhydrite cementing remains a large obstacle to the efficient well operation because of the negative properties of anhydrite rock: (1) cramping behavior caused by the horizontal stress, (2) mirabilite and gypsum swelling, (3) instable rock structure, and (4) abnormal pressures. The common cement slurries appear to be very limited in salt resistance, and some cannot work in the anhydrite formation. It is thus not surprising that various accidents linked with the wellbore shrinkage, pear-shaped profile, casing deformation, or even well collapse, have been encountered in the cementing operation of anhydrite formation.

In recent years, a new kind of cement slurries based on saturated brine (e.g., NaCl and KCl) has been widely reported, which exhibits excellent applicability in anhydrite cementing [1-5]. In 2000, Liu *et al*. [6] proposed a semi-saturated and a saturated brine cementing system to improve the salt resistance of cement slurries. Subsequently, Tao *et al*. [7] further analyzed accidents of anhydrite cementing in Tuha Oilfield, and developed a saturated brine cement slurry which can entirely avoid cementing failure. Simao *et al.* [8] investigated the effect of NaCl and KCl concentration on the properties of the cement slurry, and pointed out that the type and content of salts were the key to the saturated brine cement slurry. In addition to the salt-resistance, the density of the cement slurry is another factor to retard cramping behavior of anhydrite. Recently, Xu *et al.* [9] have developed weighted saturated brine cement slurry. The density of such slurry can be consciously controlled using specific spherical weighting materials.

Despite a wide range of investigations on saturated brine cement slurries, the common results appear to be very limited to the unique anhydrite formation. When the formation environments are varying, the intrinsic characteristics of rock would change. Thus, the cement slurry of anhydrite formation needs to be explored in combination with certain environments, for the purpose of effective implement of cementing operation. In Missan Oilfields, a huge thickness (500 m) of anhydrite formation was detected at 2,000 m, which would readily cause various cementing accidents. According to the in-field cementing project, a double stage cementing technology was designed: at the first stage, the densities of lead and tail slurry were proposed to be 2.36 g/ml and 2.33 g/ml, respectively; at the second stage, the densities of both the lead and tail slurries were proposed to be 2.36 g/ml. To ensure quality of double stage cementing, the thickening times of lead and tail slurry were proposed in the range of 360~480min and 150~180 min, respectively.

*To whom all correspondence should be sent:
E-mail: xuhu_11@yeah.net

Previous studies focused mainly on semi-saturated and saturated cement slurries. In contrast, less attention has been paid to over-saturated systems. In the present work, extensive laboratory tests were carried out to develop a novel kind of over-saturated brine cement slurry well appropriate to the anhydrite formation. As a continuous study on the high performance of cement slurry, this work cannot only provide instructive information on the over-saturated brine cement slurry, but also extend the category of cement slurry system.

METHODOLOGY

Experimental materials

The over-saturated brine cement slurry was constructed with nine functional additives, including weighting agent, filtrate loss reducer, expanding agent, strength stabilizer, dispersant, defoamer, and retarder (see Table 1). Here, several key additives that can significantly affect the performance of cement slurry such as the weighting phase, filtrate loss reducer, proppant, strength stabilizer, and the retarder were typically taken into account.

Testing performance

As for the over-saturated brine cement slurry, several primary performances like those of rheology, filtrate loss, compressive strength, and thickening were examined. Rheological data of the designed cement slurry were measured at six specific shear rates 600, 300, 200, 100, 6 and 3 rpm with the Fann 35 viscometer. Filtration tests were performed at 6.9 MPa and the considered temperature by the fluid-loss cell. The thickening performance was measured at 120oC/110MPa using the HTHP consistometer. The gel strength was examined by a static gel strength analyzer. Using the compressive strength tester, the compressive strength of cement stone was measured at 120oC after 24 h of curing.

Experimental design

With the selected functional additives, the over-saturated brine cement slurry available in Missan Oilfields can be constructed by optimizing the additive dosage. Herein, dosages of key additives such as saturated salt, filtrate loss reducer, strength stabilizer, retarder, and proppant were optimized by a set of one-factor experiments, as shown in Fig. 1. As a consequence, the optimized formula of over-saturated brine cement slurry can be defined.

RESULTS AND DISCUSSION

Content of filtrate loss reducer

As one kind of liquid filtration loss reducer, LATEX contains about 50 wt.% of colloidal particles with a size of 0.05~0.5μm, which can fill the filter cake to reduce its permeability. To optimize the content of LATEX, the performance of cement slurry concerning thickening, compressive strength, filtration, and rheology, was tested in the range of 0~7.5wt.%. The relations between LATEX contents and fluid loss, compressive strength, and thickening time are presented in Fig. 2.

Table 1. Components of the over-saturated brine cement slurry designed here

Additives	Ingredients	Terms
Continuous phase weighting material	Over saturated NaCl solution	NaCl
Filtrate loss reducer-A(FLR-A)	AMPS-polymer	AMPS-P
Filtrate loss reducer-B(FLR-B)	Styrene-butadiene latex	LATEX
Proppant	Silicone fluid	MX
Solid phase weighting material	Hematite	---
Expanding agent(EX)	Metal oxide	EX
High temperature(HT) strength stabilizer	Silica flour	SP
Dispersant	Formaldehyde condensation polymer	CF44L
Defoamer	Anionic surfactant	CX66L
Retarder	Phosphonate	H63L

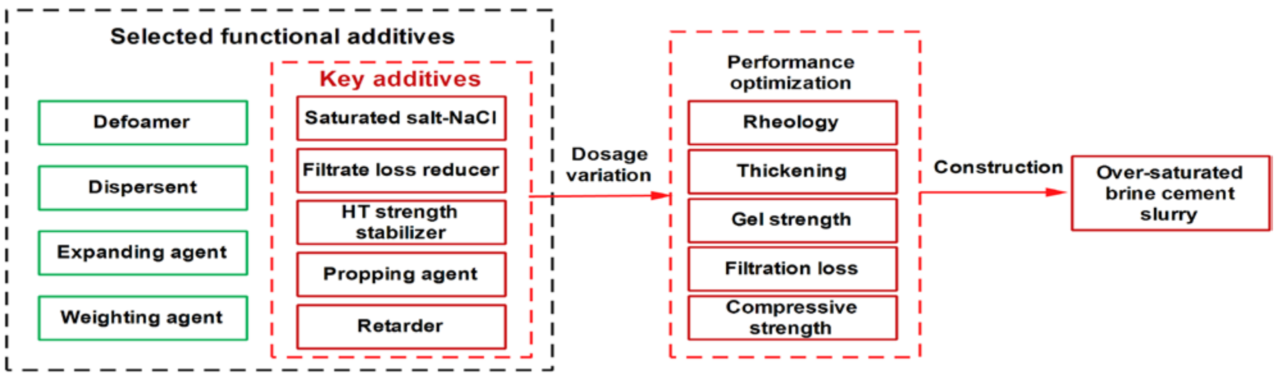

Fig. 1. Experimental design of constructing over-saturated brine cement slurry.

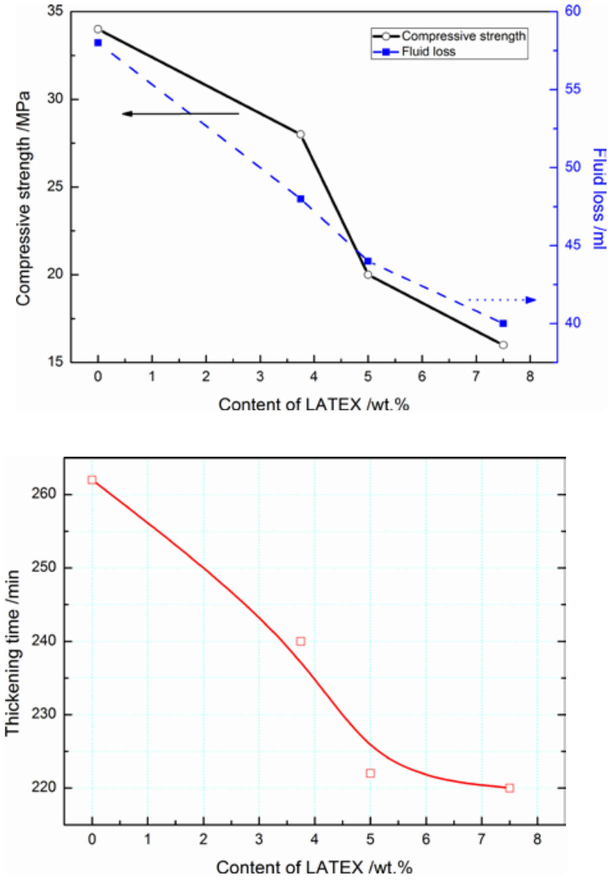

Fig. 2. upper: relation between content of LATEX and compressive strength and fluid loss; lower: curve of content of LATEX *vs.* thickening time.

In Fig. 2, all of the tested data involving the compressive strength, fluid loss, and thickening time declined with a rise of the LATEX content, wherein the fluid loss exhibited a larger decrease than others. For example, the fluid loss was reduced by 31% when LATEX content increased to 7.5wt%. This result disclosed that LATEX performed well as filtrate reducer in the slurry. Due to the special liquid state, LATEX can penetrate the deep formation and form an effective block to prevent fluid loss. Note that the LATEX content should be controlled because this additive can lower the compressive strength of slurry.

Further, Table 2 lists the rheological parameters for the slurry with the considered LATEX content. One can find that for the investigated contents, all rheological readings slightly increased, suggesting that LATEX had a little impact on the slurry rheology. On the basis of the results obtained above, the LATEX content was proposed to be 5 wt.%.

To optimize the content of NaCl, the performance of cement slurry was tested in the content range of 0~60wt.%. Note that, the NaCl content was calculated with respect to fresh water.

Table 2. Rheological readings of the cement slurry at different LATEX contents

Latex content (wt.%)	Rheological readings		
	$\theta_{600}/\theta_{300}$	$\theta_{200}/\theta_{100}$	θ_6/θ_3
0	190/101	72/39	5/3
3.75	225/129	92/50	5/3
5	245/140	101/56	5/3
7.5	255/147	107/60	6/4

Content of NaCl

In Fig. 3, one can observe that with increasing NaCl content, both compressive strength and fluid loss value decreased, but a reverse trend was found for the thickening property. The larger the NaCl content, the longer was the thickening time.

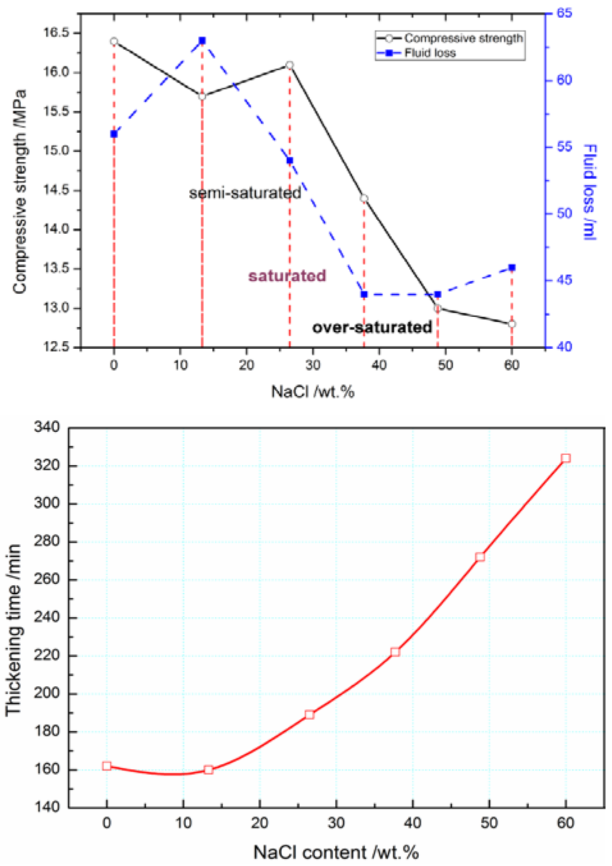

Fig. 3. Upper: relation between content of NaCl and compressive strength and fluid loss; lower: curve of content of LATEX *vs.* thickening time

In particular, thickening time rapidly increased while the NaCl content exceeded 50wt.%, displaying a strong retard property at the high NaCl contents. This phenomenon should be mainly attributed to weak hydration of cement caused by the high NaCl content. In general, the thickening property is closely associated with the compressive strength of cement slurry. The longer the thickening time, the weaker becomes the compressive strength. Here, the compressive strength decreased with an increment of NaCl content.

Table 3. Rheological readings of the cement slurry at different NaCl contents

NaCl content (wt.%)	Rheological characteristic readings		
	$\theta_{600}/\theta_{300}$	$\theta_{200}/\theta_{100}$	θ_6/θ_3
0	—/—	246/150	16/12
13	—/200	149/84	9/5
26	242/138	99/54	5/3
38	245/140	101/56	5/3
49	225/126	91/50	5/3
61	230/129	92/50	5/3

Rheological characteristic readings obtained by a six-speed viscometer are listed in Table 2. The rheological readings decreased with increasing NaCl content, which reflected that NaCl can dilute the cement slurry to some degree. When the NaCl content was 0wt.%, for instance, the θ_{600} and θ_{300} readings exceeded the measurement range of viscometer; when the NaCl content was 49wt.%, the values of high shear rates (i.e., θ_{600} and θ_{300}) were 225 and 126, respectively. Meanwhile, the θ_6 and θ_3 readings tested at 49wt.% NaCl content were separately reduced by 69% and 75%, when compared to those tested at 0wt.% NaCl content. These results showed that in the over-saturated brine system, NaCl should be important to improve the comprehensive performance of the slurry. The NaCl content was determined to be 49wt.% in the over-saturated system.

Content of HT strength stabilizer

The influence of the SP content on the properties is illustrated in Fig. 4. To elucidate the strength of the cement slurry, thickening tests were carried out at 130°C/110MPa and compressive strength tests were performed at 150°C.

As can be seen in Fig. 4, the thickening time ddecreased and the compressive strength ascended with increasing SP contents. In particular, thickening time had a dramatic decrease when the SP content was larger than 35wt.%, suggesting that the compressive strength is significantly reinforced. This result was well consistent with the change trend of compressive strength with increasing SP contents. Such reinforcing behavior can be rationalized by the theory of particle size distribution. The size of SP particles was in the range of about 300 mesh, which can cooperatively work with cement particles to significantly improve compressive strength of cement stone. As a result, the filtration of the slurry can also be effectively reduced. Herein, the SP content was proposed to be 49wt.% on the basis of analyses of the compressive strength and thickening.

Also, Fig. 4 displays the stability of HT compressive strength with exposure time at different SP contents. Two main changes can be observed in the considered time: (1) the compressive strength increased with SP content, and (2) the compressive strength was improved with increasing time. While the SP content was 20wt.%, for instance, the compressive strengths obtained at 3d and 7d were 9.4MPa and 1.4MPa, respectively, and the former was lower by 5MPa than the latter. SP was excellent in enhancing HT strength stabilization, which would be suitable for the over-saturated brine slurry.

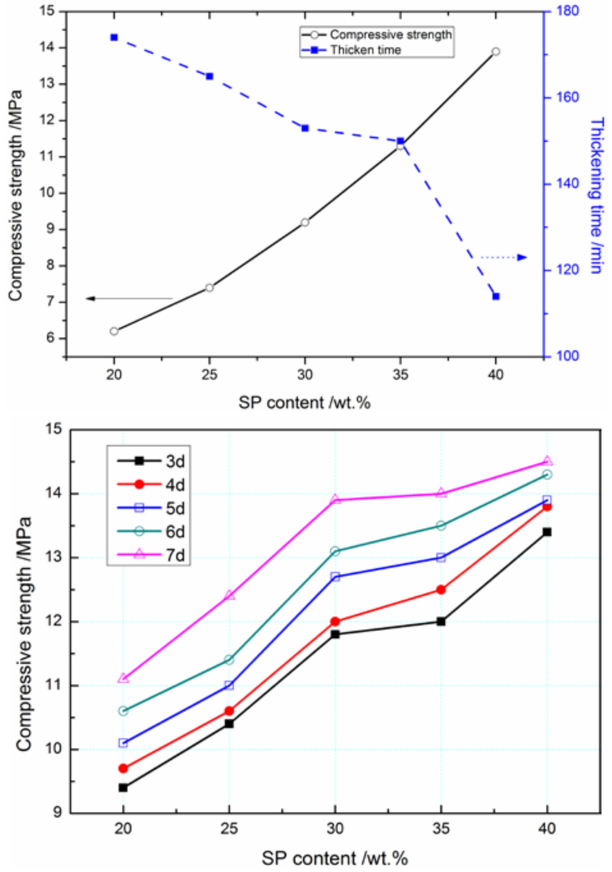

Fig. 4. Upper: relation between SP content and compressive strength and thickening time; lower: relation of SP content and compressive strength after a long-term high temperature.

Content of retarder

Effect of the H63L content on thickening time was investigated and is presented in Fig. 5.

The thickening time dramatically decreased with an increment of the H63L content, which revealed strong retardation capability. The thickening times of the slurry at the considered H63L content spanned over a large range from 186 to 315 min, and the latter was nearly two times larger than the former. It is worth mentioning that the retardation effect of H63L should be attributed to its chemical reaction with Ca^{2+} and OH^- in the cement slurry. The final product can precipitate on the surface of slurry hydration and hinder further cementing action. According to the operation requirements on-site, the thickening time of the slurry was designed in the time range of 180~300 min. According to testing data and cementing standard, H63L content of 1.5wt.% was enough for the cement slurry.

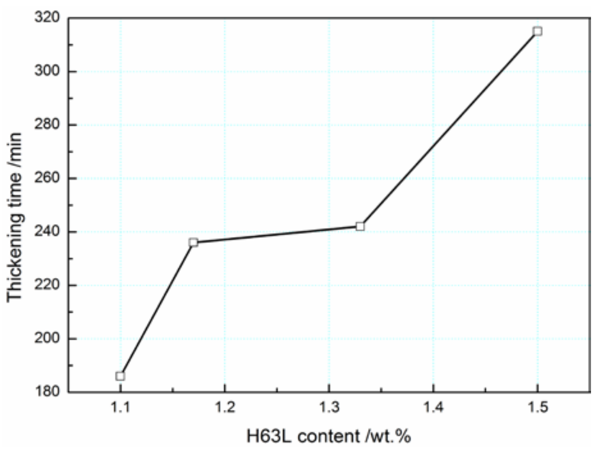

Fig. 5. Relation between H63L content and thickening time.

As follows from the data presented in Figs. 2~5, the major retard contribution to the designed slurry thickening property emerged from the retarder, H63L. In spite of partial retardation caused by brine, its effect appeared to be quite limited. Given the thickening time of 160~320 min, for example, variations of H63L and NaCl contents separately were 1.5wt.% and 61wt.%, and the H63L content was by one order of magnitude lower than that of NaCl, disclosing the dominant retardation by H63L.

Content of proppant

MX was employed as the proppant in the over-saturated brine slurry, and its main component is silicone fluid. Effect of MX on properties is presented in Fig. 6.

One can readily observe that with increasing MX content, the compressive strength was reinforced and the fluid loss declined. As the MX content raised up to 12wt.%, for instance, the compressive strength increased by about 100%, while the fluid loss decreased by almost 45%. These findings showed that MX had an excellent propping capability in the over-saturated slurry. On the other hand, an increment of the MX content can, as expected, greatly decrease the thickening time, which was reverse to the variation of compressive strength. In fact, the propping action of MX should be mainly attributed to its size cooperativity. MX is a particular kind of ultra-fine active nano-particles, which can entirely full the pores (or little fractures) in the cement stone. As a consequence of propping behavior, the stability and strength of the final cement stone can be improved and the gas channels can be effectively removed upon solidification.

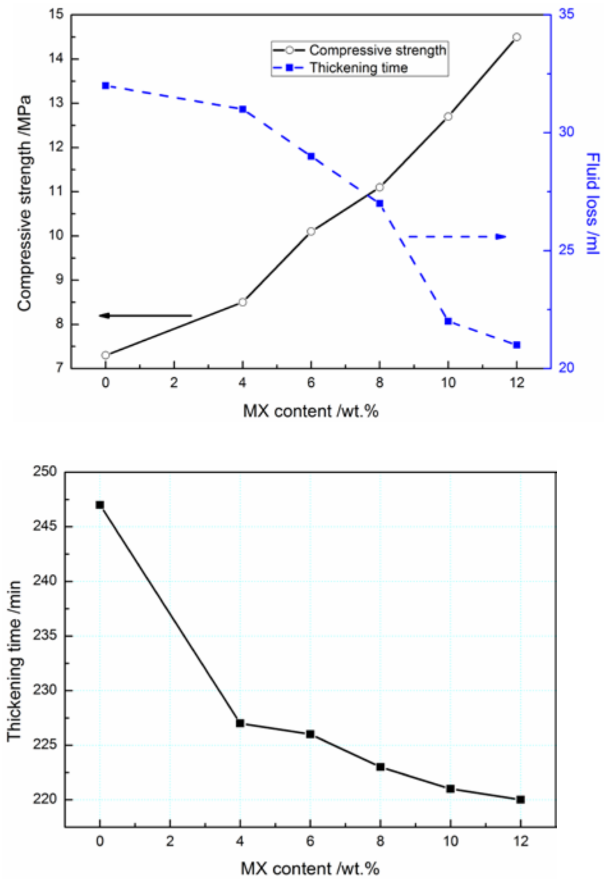

Fig. 6. upper: relation between MX content and compressive strength and fluid loss; lower: relation of MX content *vs.* thickening time.

Evaluation of over-saturated brine cement slurry

On the basis of the results obtained above, the formula of over-saturated brine cement slurry was proposed as:

G class cement + 60wt.% fresh water + 30wt.% NaCl + 10wt.% HT strength stabilizer + 112.5% weighting agent + 5wt.% FLR-B + 10wt.% FLR-A + 2wt.% dispersant + 10wt.% proppant + 0.8wt.% retarder + 1wt.% defoamer + 1.5wt.% EX.

It should be referred that the density of the designed slurry can be controlled by reasonably varying the dosage of weighting agent. Herein, 112.5wt.% of weighting agent was added and the density of the over-saturated brine cement slurry was as high as 2.36 g/ml.

Curves of gel strength and consistency *vs.* time that indicate real-time variation of characters for over-saturated cement slurry are given in Fig. 7. The gel strength increased from 48 Pa to 240 Pa in 30 min, as marked with red lines, which disclosed the strong capability of anti-gas channeling for the designed slurry. In the consistency curve, on one hand, the initial consistency was lower than 20 BC, displaying robust rheology during the course of cement cycle; on the other hand, the consistency quickly increased up to 100 BC in 20 min and, in this regard, a certain right angle consistency occurred, which should be extremely essential to ensure the cementing quality for the double stage cement slurry.

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