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FINAL REPORT

FOR CRADA NO. C-14-06

BETWEEN

BROOKHAVEN SCIENCE ASSOCIATES

AND

Schlumberger, Inc.

Project Entitled: Multifunctional cement for geothermal wells

Brookhaven PI: Tatiana Pyatina

Submitted by: Michael J. Furey
Manager, Research Partnerships
Brookhaven National Laboratory

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Submitted by: Ginny Coccorese
Office of Research Partnerships
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DISCLAIMER

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Schlumberger Collaboration
CRADA no C-14-06
Evaluation of Thermal Shock Resistant Cement

Tatiana Pyatina and Toshifumi Sugama

November 2016

CONTENTS

1. INTRODUCTION

This report compiles the work of BNL in support of Thermal Shock Resistant Cement evaluations (TSRC) by Schlumberger. BNL has worked on the formulation of thermal-shock resistant cement since 2011. All the materials on the blend including publications and presentations are in public domain and were sent to Schlumberger for review prior the beginning of the evaluations. Initial efforts focused on achieving long and controlled thickening time of TSRC at 85^{o}C in thickening time tests in a pressurized consistometer. Since the results of BNL set control were not reproduced by Schlumberger technical feedback on Schlumberger testing was among the main efforts of the BNL team in the beginning of the collaboration. When it became clear that the main reason of results deviation was the difference in the mode of retarder addition (dry-blended at BNL and pre-dissolved at Schlumberger) the efforts shifted to the possible decrease in the cost of the formulation by changing concentrations and nature of the alkali activator as well as evaluating performance of more economical formulations with calcium-aluminate cement, Secar #51, Secar #71 and Ciment Fondu, suggested by Schlumberger based on communications with Kerneos (supplier of calcium aluminate cements). Another piece of information obtained by Schlumberger from Kerneos that prompted evaluations of different calcium-aluminate cements in the composition of TSRC was the fact that originally used Secar#80 contains some performance-improving additives that may interfere with the set control and rheological properties of the slurries.
In summary, the report contains the following information:
1. Review of the setting behavior of TSRC slurries prepared by dry-blending TA powder or pre-dissolving it in mix water in calorimetric tests at 85^{o}C;
2. Results of evaluation of different alkali activators for improved compressive strength development and cost reduction;
3. Results of evaluation of Secar #51, 71 and cement Fondu as an alternative to Secar #80 in TSRC formulation – thermal shock tests and phases' analyses of set cement;
4. A brief discussion of early-compressive-strength-development test conditions appropriate for geothermal wells.

List of abbreviations:

CAC- calcium aluminate cement
FAF – fly ash F
OPC – ordinary Portland cement
SMS – sodium metasilicate
SMSP – sodium metasilicate pentahydrate
SS – sodium silicate
TA – tartaric acid
TSRC – Thermal Shock Resistant Cement - a 60/40 mass % blend of calcium-aluminate cement and fly ash F with 6% by weight of the blend sodium-silicate activator
TSRC-Secar – TSRC prepared with a Secar range calcium aluminate cement
TSRC-Fondu – TSRC prepared with Ciment Fondu calcium aluminate cement

2. EXPERIMENTAL

Fly ash F was obtained from Boral Material Technologies, Inc. (San Antonio, TX, USA). A sodium metasilicate granular powder under the trade name "Metso Beads 2048" (SiO_2 46.6% and Na_2O 50.5% by weight), "Metso Pentabead" (SiO_2 28.4%, Na_2O 29.3% and water 41.75% by weight) and SS® (SiO_2 75.7% and Na_2O 23.5% by weight) supplied by the PQ Corporation (Malvern, PA, USA), were used as the alkali activators of FAF in different tests. Secar® #80 and "ciment Fondu", along with Secar® #51 and #71 were supplied by Kerneos Inc., (Chesapeake, VA, USA) and were used as the calcium-aluminate cements (CAC). The X-ray powder diffraction (XRD, Almelo, Netherlands) data showed that the crystalline compounds of FAF consisted mainly of quartz (SiO_2), mullite ($3Al_2O_3{\cdot}2SiO_2$), and hematite (Fe_2O_3), and Secar® #80 included three crystalline phases, i.e., corundum (Al_2O_3), calcium monoaluminate ($CaO{\cdot}Al_2O_3$, CA), and calcium dialuminate ($CaO{\cdot}2Al_2O_3$, CA_2), while #71 had two major phases, namely CA and CA_2, and #51 had CA as the major phase and gehlenite [$Ca_2Al(Al,Si)_2O_7$] and corundum as secondary phases. Ciment Fondu main crystalline phase was calcium monoaluminate (CA), other crystalline phases included mayenite (12 $CaO{\cdot}7Al_2O_3$, $C_{12}A_7$), ferrites ($MgFe_2O_4$), calico-olivine ($CaO{\cdot}SiO_2$, C_2S), brownmillerite (Ca_2FeAlO_5) and hematite (Fe_2O_3).
The blend cement consisted of 60% CAC and 40% FAF (mass fractions). The sodium metasilicates were dry-blended with this mixture at various mass fractions of the cement blend to form the test formulations. The water-to-solid ratio was 0.52. D-(-)-tartaric acid (TA) was supplied by Sigma-Aldrich. The dry blends were hand-mixed with water in all tests but calorimetry where the slurries were mixed in Waring blender following API 10B procedure for mixing speed.
Calorimetric tests were performed on TAM Air isothermal calorimeter (TA, DE, USA) without heating ramp control at the final temperature of 85°C. It took about 40 minutes for the ampules with slurries prepared at room temperature to reach 85°C.
Unless stated otherwise all slurries were prepared in the following manner for compressive strength tests. After mixing the samples were left to set at room temperature overnight in cylindrical molds (25-mm diameter and about 40-mm length), then demolded and cured for 24 hours at 85°C at 100% relative humidity (imitating placement temperature) and finally transferred into an autoclave partially filled with water (20% of volume) at 200°C or 300°C for 24 hours. The compressive strength was evaluated using Instron testing machine (Instron Inc., MA, USA).

3. RESULTS

3.1. Dry-blended vs. pre-dissolved TA, TSRC-Secar #80

The cement blends formulated by Brookhaven National Laboratory targeted applications in geothermal wells; these are on-shore applications. Since for land cementing jobs dry components are dry-blended all the tests on cement retardation were performed with dry-blended retarder. In the tests performed at Schlumberger the retarder was added to the mix water prior to addition of the cement. In Schlumberger tests cement setting times were short both in calorimetric and thickening time tests demonstrating that TA was not effective in set retardation. In response to Schlumberger's feedback BNL reviewed the setting behaviors of TSRC slurries prepared with pre-dissolved or dry-blended retarders using calorimetric tests. The blend formulation tested included 69 g of Secar #80, 46 g of Fly Ash F, 6.9 g of SMS (6%), 2.3 g of tartaric acid (2%) and 53.8 g of water. The dry blend was prepared by hand and the retarder was either added to the mix water or dry blended. Then the slurry was mixed in a Waring blender following API 10B mixing procedure for the speed of blending. The results of calorimetric measurements are shown in Figure 1.

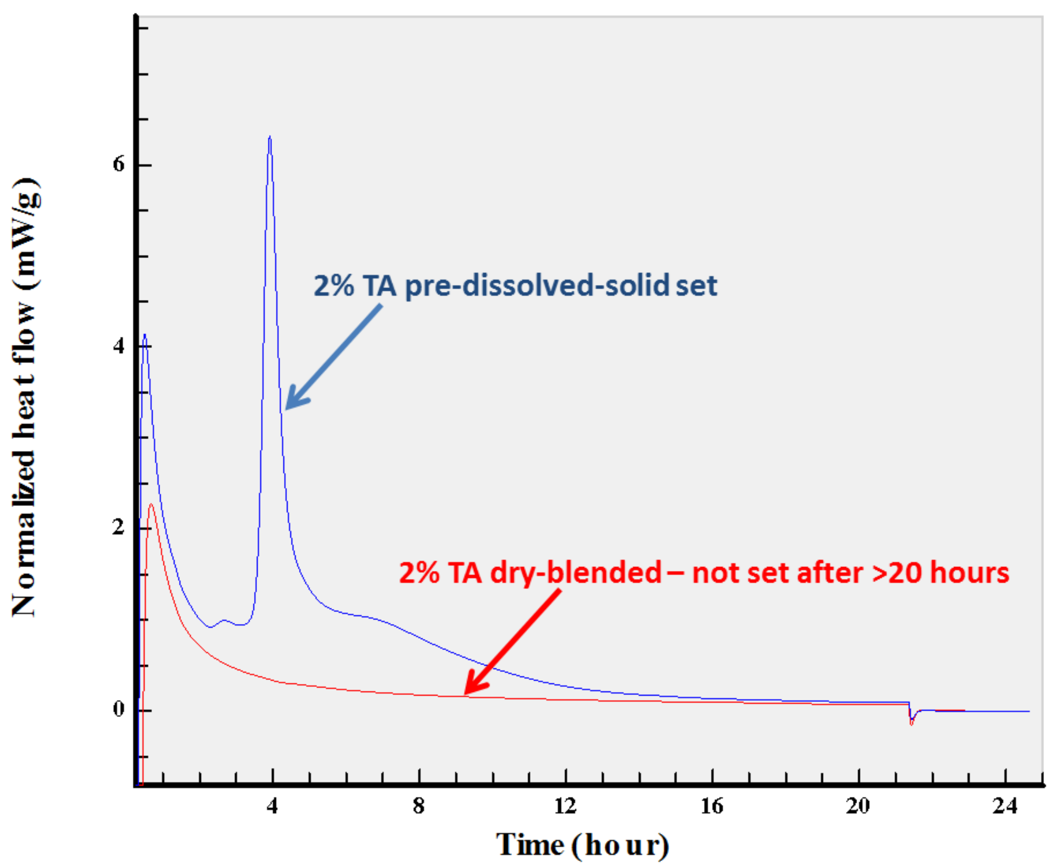

Figure 1. Effect of TA addition mode on the heat release for TSRC slurries prepared with Secar#80/FAF and SMS.

The initial heat-release peak mostly corresponds to the exothermal dissolution of SMS. In the case of pre-dissolved retarder the large sharp peak for the design with pre-dissolved TA corresponds to hydration of calcium-aluminate cement and the wide shoulder on the right of it to the beginning of pozzolanic reaction of FAF. For the dry-blended TA there was no any heat release for more than 20 hours after the initial peak of SMS dissolution, suggesting suppression of the calcium-aluminate hydration and activation of FAF. The ampules with the cement were removed from the calorimetry after 21 hour and tested with a spatula for the set – the cement was fluid (not set) with the dry-blended and solid (set) with pre-dissolved TA .
The result supports earlier tests of BNL that demonstrated effectiveness of the TA as a retarder when dry-blended with TSRC [Pyatina et al., 2016] and points to the sensitivity of the system to the mode of the retarder addition.

3.2. Effect of sodium meta-silicate activator on the mechanical properties of TSRC

Sodium-metasilicate activator in TSRC blend has two separate functions: instigating pozzolanic reactions of fly ash F and retarding fast hydration of calcium-aluminate cement allowing easier blend set control [Pyatina et al., 2016]. Any sodium silicate could be used as an activator in the TSRC blend, however, the higher the sodium content of the silicate the more effective it is in activating fly ash while higher silicon content gives better retardation of calcium aluminate cement. Additionally, to act upon cementitious blend sodium silicate must dissolve, so the solubility plays a role in its performance. Two different sodium silicates were tested along with SMS – Metso Pentabeads (SMSP) and SS® (SS). Based on the specifications of these silicates SMS and SMSP have similar Na_2O/Si_2O mass ratios of 1.08 and 1.03 respectively but SMSP includes 41.75 mass% water, which decreases the actual chemical content per a given mass and improves solubility of the powder. SS, on the other hand, has much high silica content (Na_2O/Si_2O is 0.31) and lower solubility since it is in lumps. Similar FAF activation efficiency could be expected from SMS and SMSP at longer curing periods but likely higher initial reactivity in the case of more soluble SMSP. For the SS with the lower solubility and higher silica content the FAF activation should be lower, which may be reflected in a lower compressive strength at longer curing times.

The blends with different sodium silicates were prepared with Secar #80 and FAF at 60-to-40 mass ratio and silicate added at 6% by the total weight of the blend. The water-to- blend ratio was 0.47, the final curing temperature was 300^{o}C. Figure 2 gives the results of the initial compressive strength development for blends prepared with different sodium silicates.

Addition of SMSP as an alkali activator resulted in the highest early compressive strength development (2700 psi), while strengths of SMS and SS activated blends were similar (31 and 36% below that of the blend with SMSP respectively). Considering that the added amount of the activators was the same for all the silicates, SMSP was actually present at the lowest concentration (2.5%). The high early compressive strength must be a result of the fast dissolution of SMSP that incited faster fly ash F activation.

This result suggests: 1) sodium-metasilicate reacts only partially at early hydration times, non-reacted silicate is still present in the cement blend after the first 24 hours of curing at 300°C; 2) faster activator dissolution allows achieving high compressive strength at early hydration time with lower activator concentrations in the blend.
If the other performance characteristics of TSRC with SMSP are similar to that with SMS using SMSP offers significant economic advantages. The cost of SMS as almost twice as high as for SMSP ($0.204/lb for 11 metric ton minimum order vs. $0.113/lb for 1 metric ton minimum order).

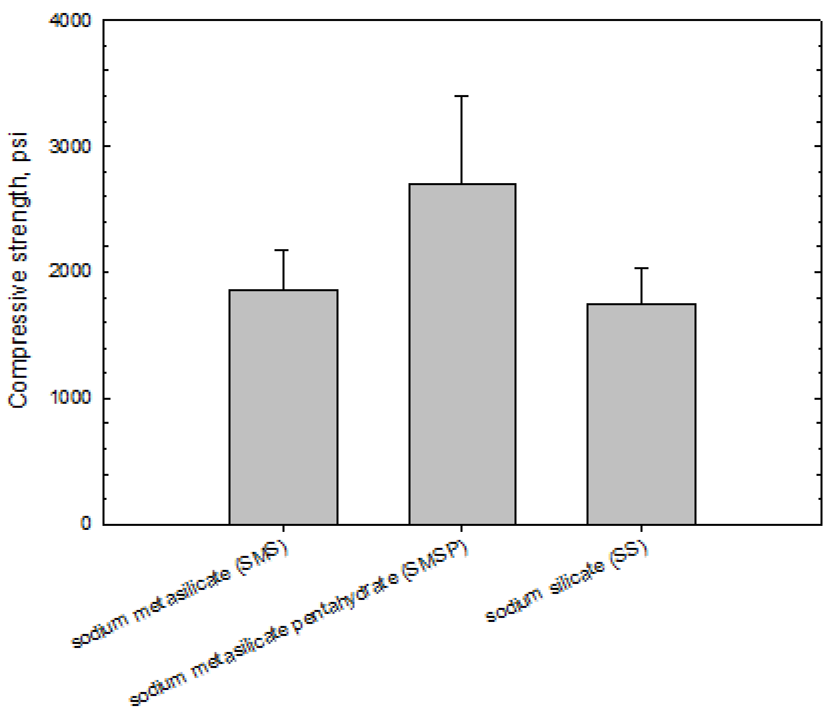

Figure 2. Effect of alkali activator on early compressive strength development in TSRC blends prepared with Secar #80 and cured at 300°C.

The question that arises is whether faster dissolution of smaller amounts of silicate still allows set control of calcium aluminate cement hydration observed with higher silicate concentrations when using SMS. Figure 3 shows calorimetric curves measured at 85°C for two equivalent TSRC formulations (for the test details see section 3.1) in the presence of 1% TA as a retarder. There are several heat release peaks for the blend with SMS within the first 6 hours corresponding to the wetting, SMS dissolution and CAC hydration followed by a wide low heat peak of pozzolanic reactions of fly ash F. In this case the cement is set within these first hours. For the formulation with SMSP the initial low peak of wetting and SMSP dissolution followed by low heat period of more than 24 hours. The cement was not set when the ampule was removed from the calorimeter. It is clear that SMSP-TA combination retards CAC hydration more than does

SMS-TA one at equivalent total concentrations (lower sodium silicate concentrations in the case of SMSP). Although the setting times in calorimetric tests do not correspond to the thickening times measured in pressurized consistometers with sheared slurries they do show relative setting times when the heat peaks that correspond to cement hardening are compared.
In summary, sodium metasilicate pentahydrate (SMSP) was identified as the most effective activator allowing activator's cost decrease of nearly 40% while improving early compressive strength by more than 30% and providing longer setting time in combination with TA retarder compared against that of SMS activator.
The fact of longer calorimetry setting times in the presence of SMSP is further discussed in connection with Ciment Fondu evaluations.

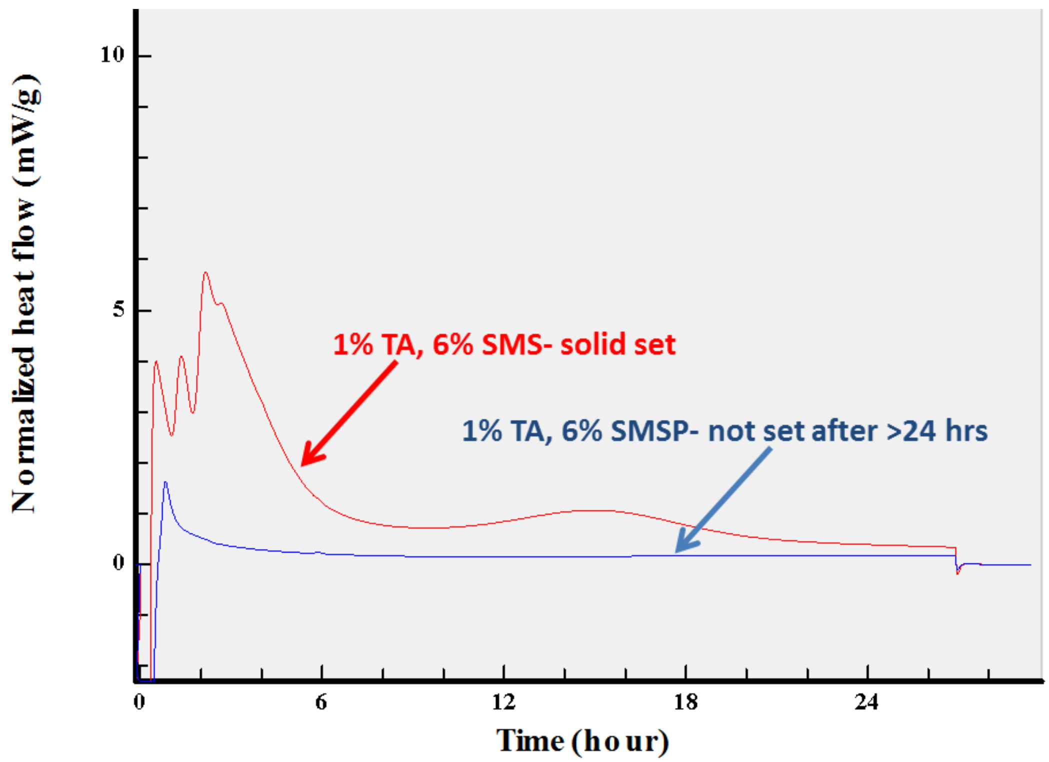

Figure 3. Effect of the activator on the setting time in calorimetric measurements at 85°C

3.3. Performance of TSRC blend with different Calcium Aluminate Cements

3.3.1. Secar range calcium-aluminate cements in TSRC blends

In communications with Schlumberger, Representatives of Kerneos Inc. revealed presence of some proprietary additives accelerating set and compressive strength development of Secar #80. Early set of cement is undesirable for subterranean applications where sufficient pumping time is necessary for cement placement in the annuals. Presence of set-accelerating additives in Secar #80 may require an extra effort to assure its sufficient placement time. This consideration, higher material cost along with the mixing difficulties due to the cement fineness reported by Schlumberger prompted additional experimental work evaluating different grades of Secar range of calcium aluminate cements and "ciment Fondu" of Kerneos Inc. All tested formulations were prepared with calcium-aluminate cement and FAF at 60-to-40 mass ratio and SMS added at 6% by the total weight of the blend. Figures 4 and 5 show the results for samples cured at 200°C and 300°C respectively. Each point is an average of three samples with the exception of Secar #71 formulations (results without error bars), for which some of the samples broke during the testing.

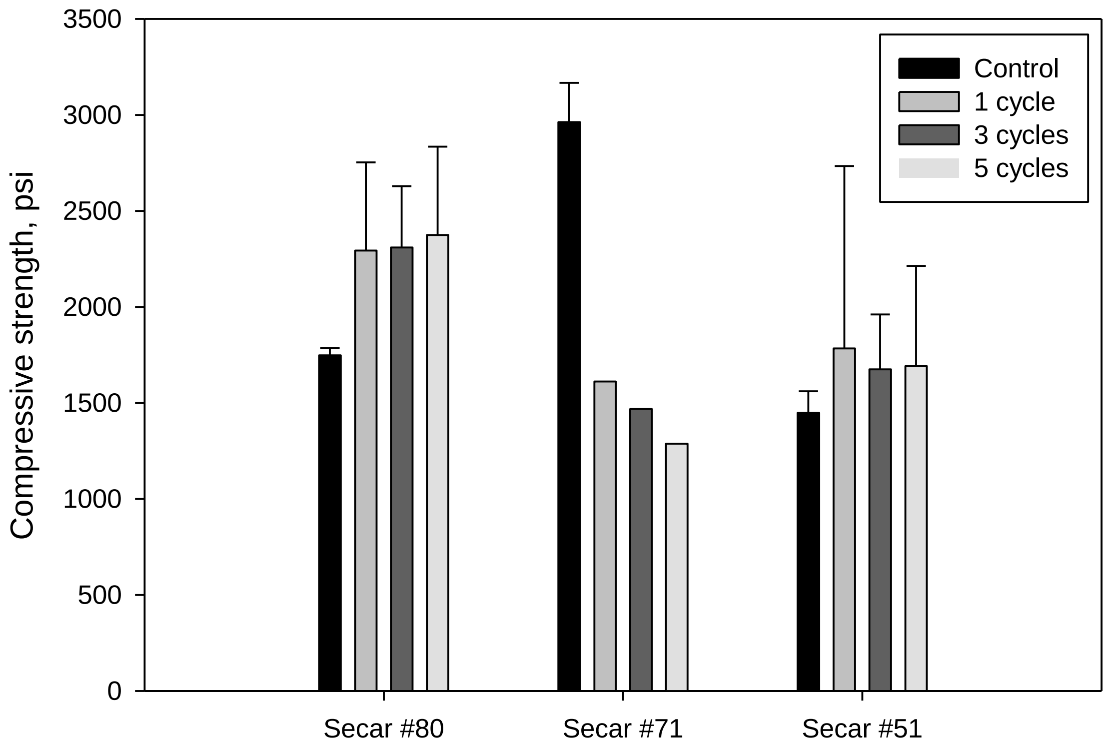

Figure 4. Comparison of performance of different CAC from Secar range as part of TSRC formulation in thermal shock tests after initial curing at 200°C for 24 hours followed by repeated 620°C heat – 25°C water quenching cycles

For both curing temperatures of 200°C and 300°C performance of the blend with Secar #71 was inferior to the blends with Secar #80 and 51. Although TSRC with #71 showed the highest strength of the control samples, the strength dropped after 5 cycles of the thermal shock tests by 56% for both samples cured at 200 and 300°C. On the other hand, TSRC formulations with Secar #80 and 51 demonstrated good thermal shock resistance for both initial curing temperatures. For samples cured at 200°C the strength increased after the first thermal shock cycle by 24 and 19% respectively for #80 and #51-containing formulations. Samples with Secar #80 cured at 300°C lost about 16% of the strength after the first cycle but the strength slightly increased in the following thermal-shock cycles. More surprisingly, TSRC samples with Secar #51 cured at 300°C increased average compressive strength after 5 thermal shock cycles by 27% relative to the control. As a result although the initial strength of the 300°C-cured TSRC samples with #51 was below that of TSRC with #80 the strength after 5 thermal shock cycles was 17% higher for the samples with Secar #51.

In summary, TSRC formulations with Secar #80 and #51 showed good thermal-shock resistance while those with Secar #71 lost 56% of the original compressive strength after 5 thermal-shock cycles. Secar # 51 could be used as a more economical alternative to Secar #80 for environments with high temperature variations.

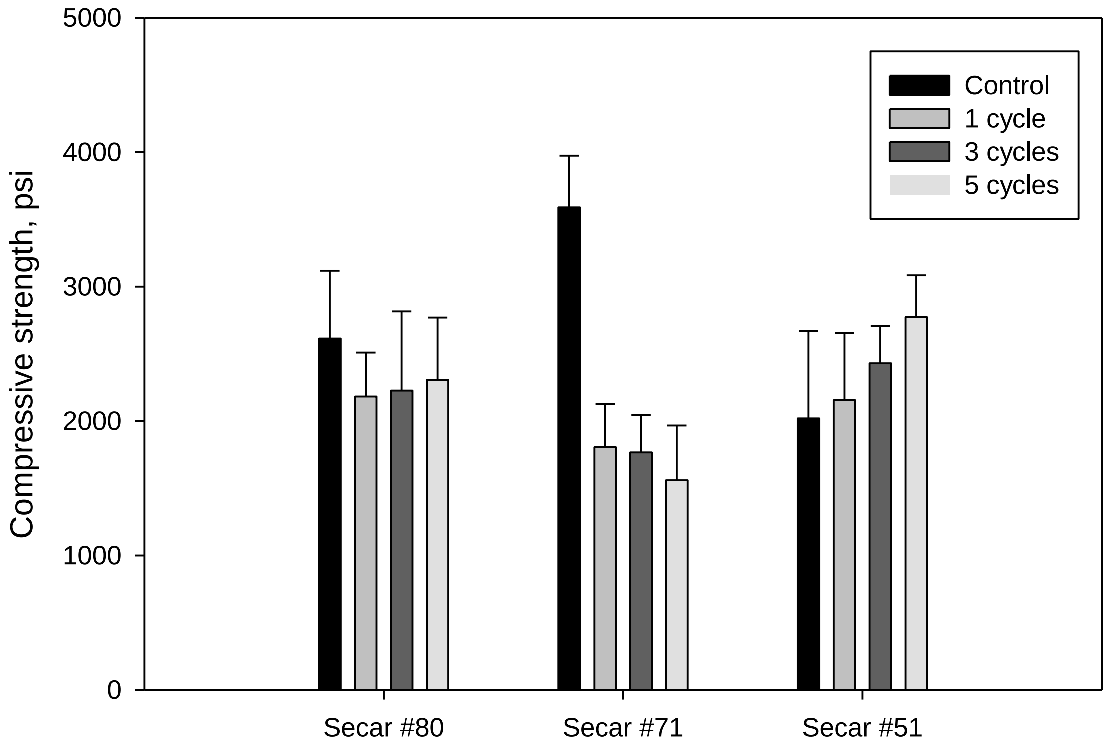

Figure 5. Comparison of performance of different CAC from Secar range as part of TSRC formulation in thermal shock tests after initial curing at 300°C for 24 hours followed by repeated 620°C heat – 25°C water quenching cycles

3.3.2. Ciment Fondu performance in TSRC blends

The cost of Ciment Fondu is about 50% below that of Secar #80, which makes it a desirable replacement in TSRC formulation provided the blend's performance is not compromised. TSRC blends with Ciment Fondu and varied amounts of SMS activator were cured at 300°C and then evaluated in 5 cycles of thermal shock tests (one cycle 600°C, 24 hours heating followed by 25°C water quenching for 15 minutes). For comparison Figure 6 shows performance of TSRC blend with Secar #80. The control samples with Secar #80 displayed excellent thermal shock resistance, showing only 12% reduction of compressive strength from 2600 psi to 2300 psi after 5-cylce testing. Interestingly, the initial strength of TSRC-Fondu reduced as the amount of SMS increased from 1880 psi for the sample without SMS to 1330 psi for 6% SMS, strongly suggesting that SMS delayed hydration of Fondu. The trend of the thermal-shock resistance was opposite to the initial compressive strength: the after-the-shock strength improved with increasing SMS

content of the blend. So the original strength of 6% SMS samples increased by 1.6 fold to 2170 psi after 5-cycle thermal shock testing. SMS provided two benefits to Fondu-based TSRC: it controlled its setting time and enhanced its thermal shock resistance. The formulation without SMS, on the other hand, lost 65% in strength after 5-cycle testing. Figure 7 gives photographs of the TSRC samples with Fondu after five cycles of thermal shock tests for 3 SMS concentrations. It is clear that SMS activation improves thermal-shock resistance of the blend.
An earlier study demonstrated importance of FAF reaction products in cement formulations for thermal-shock resistance [Pyatina and Sugama, 2016]. Since SMS acts as FAF activator better performance of blends with high SMS content in thermal-shock tests may be attributed to faster pozzolanic reactions of FAF at higher SMS concentrations.

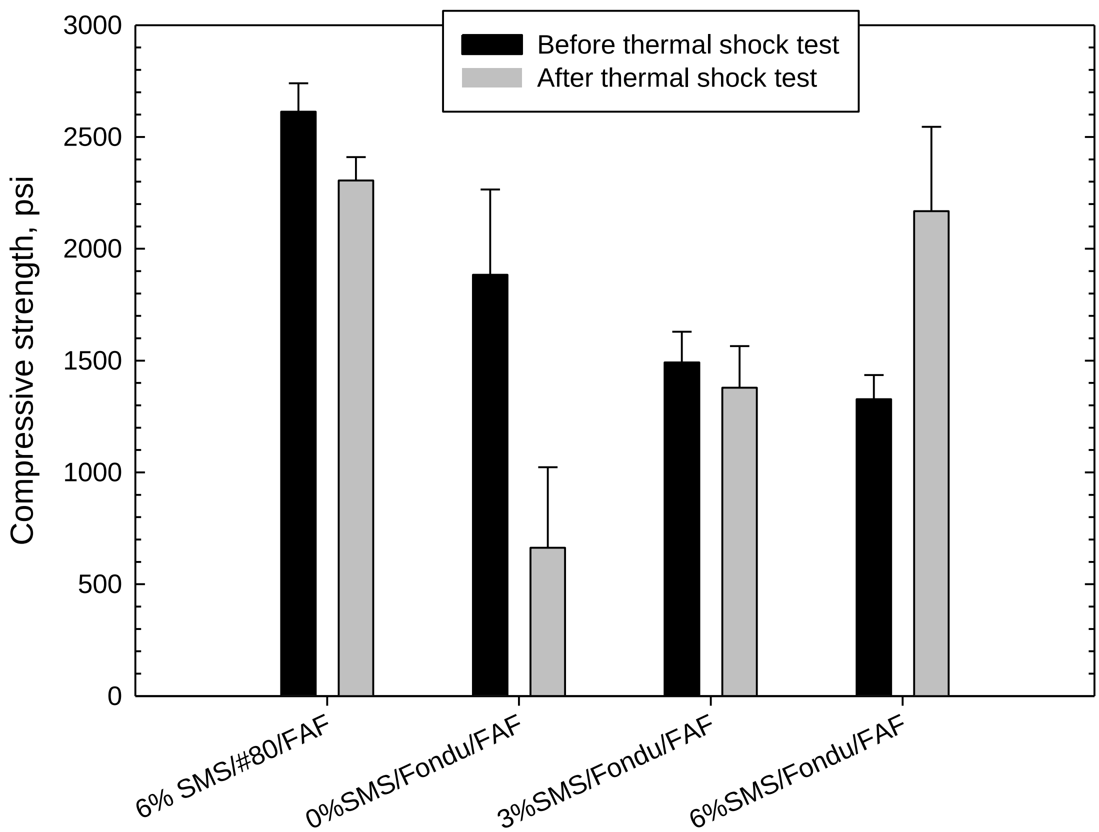

Figure 6. Comparison of Ciment Fondu and Secar #80 performance in TSRC blends with different amount of SMS activator

To understand phase composition responsible for the strength build up in the thermal shock tests XRD analyses of TSRC blends with cement Fondu were performed on samples before and after the thermal shock tests. PDF-4/Minerals 2015 data base of the International Center for Diffraction Data and SIeve+ fitting program were used for the data analyses.

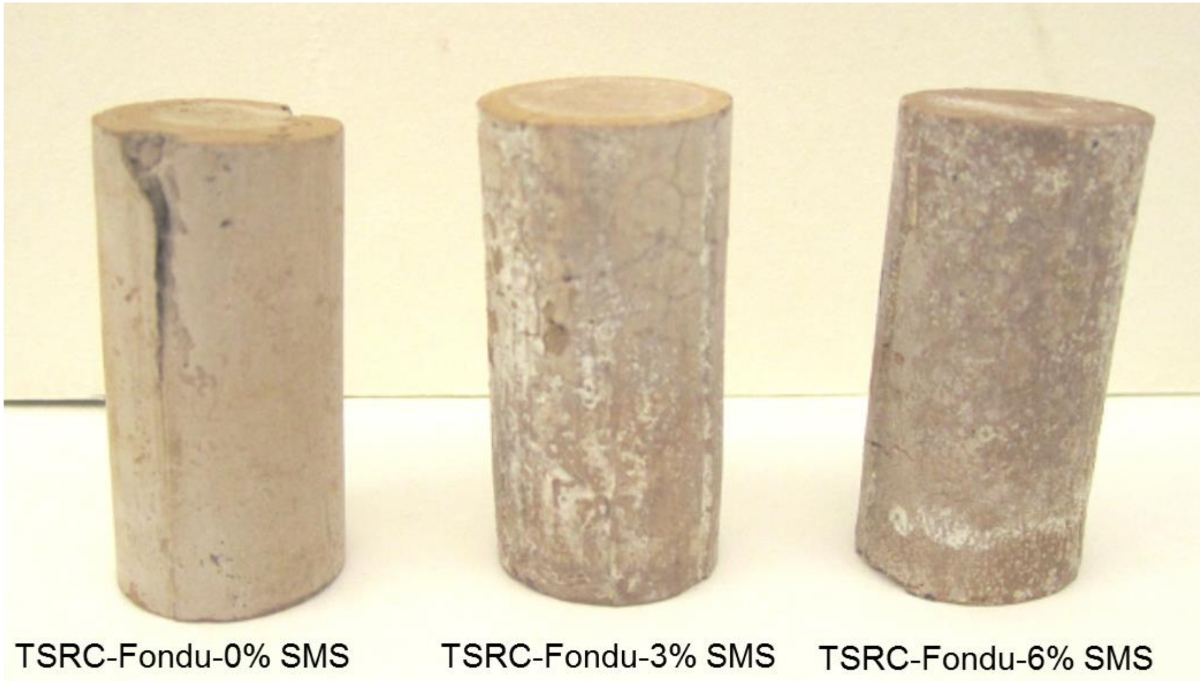

Figure 7. Effect of SMS content on Fondu-based TSRC resistance to thermal shock tests. Samples' images after 5 cycles of 600^{o}C heat-25^{o}C water quenching

Unlike Secar range cements Ciment Fondu has lower aluminum and significantly higher iron content and associated with it crystalline phases (Tables 1 and 2). As a result along with the phases forming in TSRC-Secar, such as dmisteinbergite, katoite, analcime and boehmite, iron-containing crystalline phases, such as andradite, clinoenstatite and chloritoide, formed in TSRC-Fondu after cement hydration at 300^{o}C (Table 3). In fact, a range of Mg-Ca-Fe-Silicate minerals with various proportions of these elements is likely to form as a result of the cement hydration (minerals falling between wollastonite-clinoenstatite and clinoterrosilite; e.g. hedenbergite was detected in the sample). Some non-reacted materials including C_2S, $C_{12}A_7$, gehlenite, hematite and silica still remained in the cement.
After 5 cycles of thermal shock tests among the major crystalline components appears carbonated calcium silicate galuskinite, a mineral that forms in nature in high-temperature skarns in the silicate-carbonate system [Gao et al., 2015]. Its structure is described as calcium and silica polyhedral with CO_3 triangles acting as separators to depolymerize Si-Ca aggregation. Along with spurrite and scawtite it may be expected to form at low Si/Ca ratios in cement systems with carbonate access. This mineral may be predicted to be stable under the environments of geothermal wells. Another mineral chloritoide-2A is likely the one that contributes to the strength increase of the thermal-shock tested cement because of it very high hardness. The calcium(sodium)-aluminum-silicates (dmisteinbergite and analcime) are still present after the thermal-shock tests but the intensity of their peaks decrease. Non-reacted C_2S $C_{12}A_7$, gehlenite, hematite and silica still remained in the cement.

Table 1. Elemental composition measured by EDX in weight %

Element	#80	Fondu	FAF
Na	0.64	-	0.65
Mg	0.25	0.27	1.7
Al	72	30	26
Si	3.2	3.3	47
S	0.27	0.19	0.47
Ca	23	47	8.1
Ti	-	1.3	1.5
Fe	0.40	18	10
K	-	-	4.6

Table 2. Cement Fondu - Crystalline phase composition – semi-quantitative XRD

Phase	ICDD number	Approximate weight %
Krotite (CA) – $Ca(Al_2O_4)$	01-080-3836	77
Mayenite ($C_{12}A_7$) – $Ca_{12}Al_{14}O_{33}$	00-009-0413	5
Ferrites $MgFe_2O_4$	04-014-3715	3
	04-014-3713	2
Calcio-olivine (C_2S)-$CaSiO_3$	04-012-6734	5
Brownmillerite (C_4AF) – Ca_2FeAlO_5	04-011-5939	5
Hematite – Fe_2O_3	00-033-0664	3

In summary, a combination of high-temperature stable calcium(sodium) aluminum silicates, magnesium carbonate and iron-containing hydrates, specifically chloritoide-2A, in crystalline composition of reacted TSRC-Fondu allows withstanding thermal-shock tests.

The change of the calcium-aluminate cement in the composition of TSRC necessarily affects its setting behavior since fast hydration of calcium-aluminates is responsible for the fast set and early compressive strength development of TSRC blends. To verify effect of Ciment Fondu on the setting behavior of the blend calorimetric tests were conducted at 85^{o}C.

Figure 8 gives calorimetric measurements of heat of hydration for TSRC-Fondu, SMS or SMSP activators with or without TA retarder. TSRC-Fondu-SMS heat release times were similar to that of TSRC-Secar #80. Specifically, in the presence of 6 wt.% SMS there was no low heat period between the heat of wetting and dissolution and the heat peaks that resulted in the set of the slurries both for the slurry with and without 1 wt.% TA.

Table 3. TSRC-Fondu (60% Fondu/40% and 6% bwob SMS)

Before Thermal Shock		
New phases	ICDD number	Approximate weight %
Dmisteinbergite $CaAl_2Si_2O_8$	04-011-6236	22
Katoite $Ca_3Al_{3.5}O_{4.5}(OH)_{7.5}$	04-017-1503/04-015-7783	16
Hedenbergite $CaFeSi_2O_6$	04-013-2077	9
Analcime $Na_8Al_8Si_{16}O_{48}(H_2O)_8$	04-011-7963	8
Andradite aluminian $Ca_3Fe_{1.6}Al_{0.4}(SiO_4)_{2.6}(OH)_{1.6}$	04-012-1321	5
Clinoenstatie $FeSiO_3$	04-012-1171	4
Chloritoide-2A $Mg_{0.97}Fe_{1.1}Al_{3.93}Si_2O_{10}(OH)_4$	04-014-7982	3
Bohmite AlOOH	01-074-2900	3
Non-reacted phases		
Calcio-olivine (C_2S)-$CaSiO_3$	04-008-0201	
Mayenite ($C_{12}A_7$) – $Ca_{12}Al_{14}O_{33}$	01-076-5010	
Gehlenite $Ca_2Al_2SiO_7$	04-016-0209	
Iron oxides Fe_2O_3	01-088-2359/01-080-5407/04-	
Silica SiO_2	006-0285/01-077-8624	

After Thermal Shock		
Galuskinite $Ca_7(SiO_4)_3(CO_3)$	04-017-9866	20
Chloritoide-2A $Mg_{0.15}Fe_{1.93}Al_{3.84}Si_2O_{10}(OH)_4$	04-011-6821	10
Dmisteinbergite $CaAl_2Si_2O_8$	04-011-6236	7
Analcime-R $Na_{14.4}Al_{14.4}Si_{33.6}O_{96}(H_2O)_{16}$	04-013-2040	7
Calcium magnesium silicate $CaMgSi_2O_6$	04-015-8344	6
Magnesite $MgCO_3$	04-013-2021	5
Non-reacted phases		
Mayenite ($C_{12}A_7$) – $Ca_{12}Al_{14}O_{33}$	01-076-5010	
Calcio-olivine (C_2S)-$CaSiO_3$	04-008-0201	
Iron oxides Fe_2O_3	04-008-7627	
Silica SiO_2	04-018-0238/04-012-5003	
Gehlenite $Ca_2Al_2SiO_7$	04-016-0209	

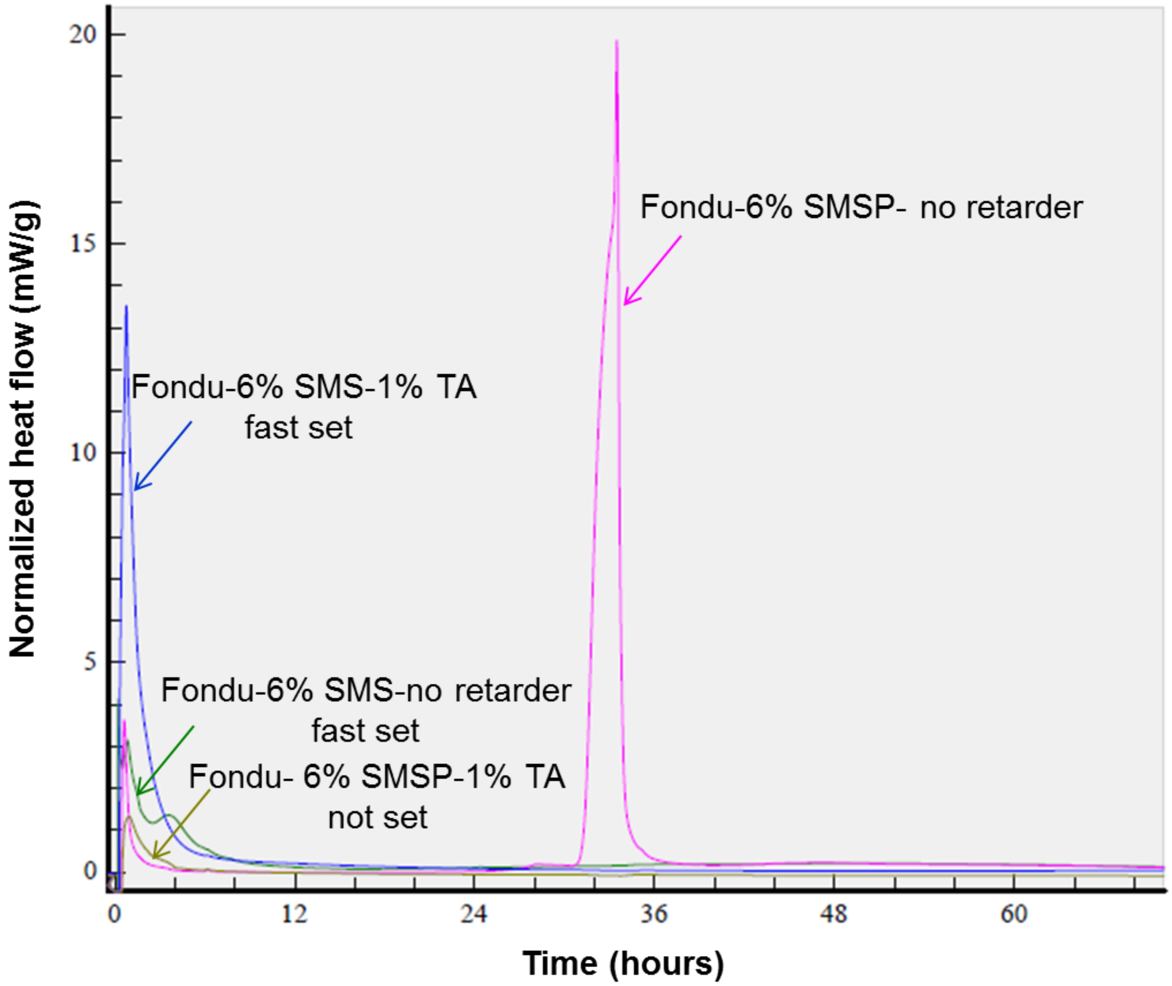

Figure 8. Comparison of setting time of TSRC with Ciment Fondu and SMS or SMSP activators in calorimetric tests at 85°C for slurries with and without TA

On the other hand, with SMSP as an activator and 1 wt.% TA there was no heat release after the initial small peak for more than 60 hours and the slurry was still fluid when the ampule was removed from the calorimeter. Without the retarder the slurry showed a peak of heat corresponding to the set after more than 24 hours at 85°C. These results agreed with the slower set of TSRC-Secar #80 in the blend with SMSP vs. SMS. Lower amount of aluminate in the Ciment Fondu resulted in even longer delay of the TSRC blend set when compared to TSRC-Secar #80 one. Figure 9 shows that TSRC-Fondu with SMSP activator without any retarder set later than TSRC-Secar #80 with SMSP and 1% TA. Provided compressive strength development is not delayed lower reactivity of the TSRC-Fondu may offer a preferable formulation for an easier set control of the blend.

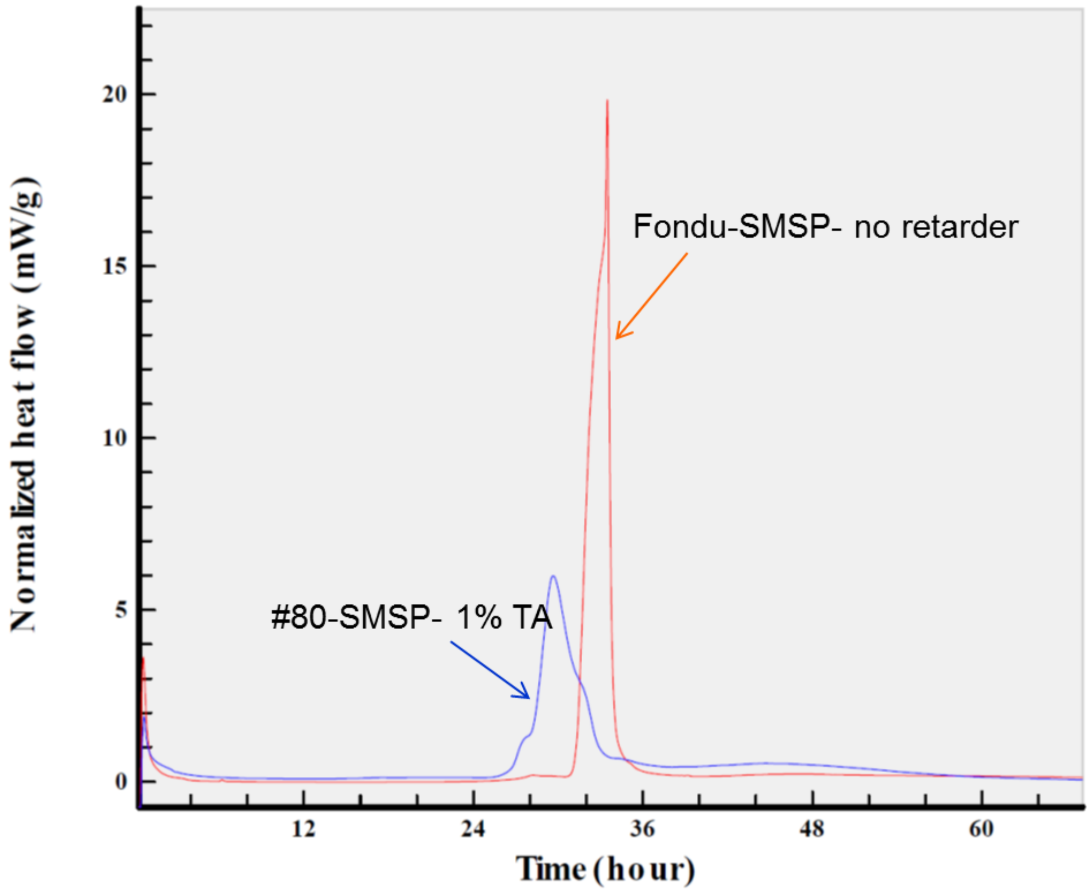

Figure 9. Comparison of SMSP activator effect on the set of TSRC-Secar #80 and TSRC-Fondu in calorimetric tests at 85°C

In summary, there is no doubt that Fondu has a potential as a cost-effective replacement of Secar #80 in TSRC blends.

4. EARLY COMPRESSIVE STRENGTH DEVELOPMENT

In comparison with OPC systems TSRC early compressive strength development is lower. Generally, compressive strength of 500 psi is more than sufficient for all well-construction purposes [di Lullo and Rae, 2000]. TSRC formulations develop above 1000 psi compressive strength in 24 hours when cured at high static temperatures of geothermal wells (>200°C); however in the field it takes some time to reach static temperatures and according to Schlumberger UCA tests at circulating temperature of 85°C with retarded TSRC showed that the compressive strength was not developed for more than 70 hours. (It should be noted that the cement slurry was not sheared to simulate dynamic placement before the tests.)
The question of how long on average it takes for a geothermal well to get to its static temperature after the circulation stops was discussed in personal communications between

BNL group, Bill Rickard, president of Geothermal Resource Group and Hamid Najafi, Operation manager from Resource Cementing, LLC. The following general conclusion was reached as a result of these discussions: "On the whole, except for the permeable zone, it [well] seems to come back near static within a couple of days". For the lost circulation zones Bill added: "With lost circulation, the fluid circulated in the well bore is significantly cooler than recirculated drilling mud and may invade a permeable formation deeper than mud will (mud forms wall cake to minimize fluid loss to the formation), but I believe a couple of days is sufficient to recover a temperature near BHST. The rate in heat up seems to slow as temperature approaches BHST."

Based on this information it is highly unlikely that cement slurry may stay at a constant circulating temperature for any long periods of time. Evaluation of compressive strength development in tests where temperature goes up to static (or near static) in a couple of days seems to be more realistic.

5. CONCLUSIONS

The work done at BNL to support Schlumberger evaluation of TSRC blend focused on evaluation of different addition modes of tartaric acid as a set retarder and evaluation of different calcium-aluminate cements and alkali activators as part of TSRC blend. Based on the results the following general conclusions may be drawn:

Tartaric acid performance as a set retarder of TSRC blend strongly depends on the mode of addition. The acid is much more efficient in delaying cement hardening when dry blended with the rest of the blend as opposed to added to the mix water;

Among the Secar range of calcium aluminate cements Secar #80 and #51 provide good thermal shock resistance of TSRC blend after initial curing at both 200^{o}C and 300^{o}C. Secar #51 is a more economical alternative to Secar #80. TSRC-Secar #71 blend loses compressive strength in repeated thermal-shock cycles so is not suitable for TSRC formulation;

TSRC-Fondu formulation is an economical alternative to TSRC-Secar #80. The formulation with Ciment Fondu and SMS demonstrated good thermal-shock resistance with formation of stable iron-, magnesium-containing and calcium-silica-carbonate phases in thermal shock tests. Higher SMS content (6% vs. 3% by mass of blend) improved thermal-shock resistance of the TSRC-Fondu blend.

Among the three tested sodium-silicate activators sodium-metasilicate pentahydrate was the most efficient in improving the early compressive strength development in TSRC-Secar #80 and delaying the set in TSRC-Secar#80 and TSRC-Fondu formulations. It is also the most cost-effective among the tested activators. However, additional experimental work to ensure resistance of TSRC-Fondu with SMSP to thermal-shock conditions would be necessary to replace SMS with SMSP.

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