SUMMARY OF CEMENT FORMULATIONS TESTED BY BNL FOR SELF-HEALING ABILITY, TESTS CONDITIONS AND DATA REPORTING: 2016-2017

Types of samples:

1. Cement matrix samples (cylinders 20x40 mm)

2. Lap-shear samples (cement layer of 0.9 mm between two carbon steel (CS) plates: 32x100 mm; the area of cement – 1280 mm^2, cement layer on a single plate – type samples were used for electrochemical measurements of corrosion rate and corrosion protection of CS by cement.

3. Cement sheath samples (cement sheath, 14x74 mm, around a carbon steel tube)

Curing conditions: 300^oC in one of the following three environments – water, alkali carbonate (0.05M sodium carbonate), geothermal brine (Sugama et al., 2015)

Types of tests:

1. Compressive strength (imposing controlled damage) on the control samples and samples after healing (unless specified otherwise samples were crushed and healed twice after the original damage was imposed; in most of the experiments the original curing was done for 1 day at 270-300^oC followed by crush test →5 day healing at 270-300^oC→crush test→5 more days of healing at 270-300^oC, noted as 5+5-day healing in the table). Unless specified otherwise the healing was performed in three environments (see above).

2. Lap-shear and cement sheath bond tests were performed on samples of cement with CS interface after 1 day curing at 300^oC in water, followed by bond strength test. The lap-shear samples had very little cement between the CS plates so were not retested after healing for bond strength recovery. The samples were used to measure corrosion protection and cement coverage after repeated curing for 5 days at 300^oC (3 point average). The cement sheath samples were healed for 5 (or 15) days in water at 300^oC and retested for the bond strength. The bond-strength tests were unconfined.

3. Bond durability was tested on lap-shear samples for acid (pH 0.6, sulfuric acid and NaCl brine for 30 days) and scCO_2 (30 days). The original samples were cured for 1 day at 300^oC before the exposure tests that were performed at 90^oC. Thermal shock tests were done on cement-sheath samples – 6 cycles of 350^oC dry heat followed by ~25^oC water going through the casing tube. The bond durability data are reported in proceedings of 41st GRC Annual Meeting, Oct 1-4, 2017, Salt Lake City, UT.

1. ***Alkali activated cement***: Thermal-shock-resistant cement based formulations (SMS – sodium-meta-silicate)

N	Composite Name	Cement	Pozzolanic additive	Activator	Additives	Tests performed (300C)	References
1	TSRC	CAC #80	Fly Ash F	SMS	None	All	GRC Vol.40[1]; *Materials* [2]
2	TSRC-TA	CAC #80	Fly Ash F	SMS	Tartaric acid	Matrix-water, repeated damage, 5+5-day healing	*Materials*[2]
3	TSRC-Clin	CAC #80	Fly Ash F/Zeolite Clinoptilolite	SMS	None	Matrix, interface, 3 environments, 5-day-, 15-day (re-adherence)	San Diego SPE-GRC meeting[3]
4	TSRC-bentonite	CAC #80	Fly Ash F/Bentonite	SMS	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
5	TSRC-Metakaoline-5%	CAC #80	Fly Ash F/Metakaoline-5%	SMS	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
6	TSRC-Metakaoline-10%	CAC #80	Fly Ash F/Metakaoline-10%	SMS	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
7	TSRC-Montmorillonite	CAC #80	Fly Ash F/Montmorillonite	SMS	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
8	TSRC-MGF	CAC #80	Fly Ash F	SMS	Micro Glass	All	California Geothermal

[1]Pyatina T., Sugama T., Ronne A. "Self-repairing geothermal well cement composites," In *GRC Transaction*, Vol. 40 (2016) 235-243.

[2] Pyatina T. and Sugama T. "Role of tartaric acid in chemical, mechanical and self-healing behaviors of a calcium-aluminate cement blend with fly ash F under steam and alkali carbonate environments at 270°C," *Materials*, 10 (2017) 342-362 doi:10.3390/ma10040342

[3] SPE/GRC Workshop, entitled "High-temperature self-healing geothermal cement composites", March 21-22, 2017, San Diego, CA (*Invited talk*) – presentation submitted to geothermal data repository

					Fibers (MGF) 10%		forum presentation, SPE-GRC[3]; Geothermal Data Repository
9	TSRC-MGF	CAC #80	Fly Ash F	SMS	MGF, 5%	All	Geothermal Data Repository
10	TSRC-MgO	CAC #80	Fly Ash F	SMS	MgO	Matrix, repeated damage, 5+5-day healing, 3 environments	Geothermal Data Repository
11	TSRC-Slag	CAC #80	Fly Ash F/Slag	SMS	None	Matrix, repeated damage, 5+5-day healing, 3 environments	Geothermal Data Repository
12	TSRC-Fondu	Fondu	Fly Ash F	SMS	None	Matrix, Interface, 5-day healing	Geothermal Data Repository
13	TSRC-Fondu-MGF-5%	Fondu	Fly Ash F	SMS	MGF, 5%	Matrix, Interface, 5-day healing	SPE-GRC[3],Geothermal Data Repository
14	TSRC-Fondu-MGF	Fondu	Fly Ash F	SMS	MGF, 10%	Matrix, Interface, 5-day healing	SPE-GRC[3]

2. ***Chemical cement***: Calcium-phosphate based cement (CAP) (Calcium Aluminate Cement/Flay Ash F/Sodium Hexaphosphate Activator, SP)

N	Composite Name	Cement	Pozzolanic additive	Activator	Additives	Tests performed (300C)	References
15	CAP	CAC#51 (50%)	Fly Ash F (50%)	SP	None	All	SPE-GRC[3]
16	CAP-MGF-5%	CAC#51 (50%)	Fly Ash F (50%)	SP	MGF, 5%	All	SPE-GRC[3]
17	CAP-MGF	CAC#51 (50%)	Fly Ash F (50%)	SP	MGF, 10%	All	SPE-GRC[3]
18	CAP-Fondu	Fondu (50%)	Fly Ash F (50%)	SP	None	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
19	Fondu-FAF (10-90)	Fondu (10%)	Fly Ash F (90%)	SP	None	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
20	Fondu-FAF-MGF (10-90)	Fondu (10%)	Fly Ash F (90%)	SP	MGF	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
21	Fondu-FAF (20-80)	Fondu (30%)	Fly Ash F (70%)	SP	None	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
22	Fondu-FAF (20-80)	Fondu (30%)	Fly Ash F (70%)	SP	MGF	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
23	Fondu-FAF (30-70)	Fondu (30%)	Fly Ash F (70%)	SP	None	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
24	Fondu-FAF (30-70)	Fondu (30%)	Fly Ash F (70%)	SP	MGF	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
25	Fondu-FAF (60-40)	Fondu (60%)	Fly Ash F (40%)	SP	None	One-time damage, 5-day healing, water, interface bond strength, corrosion	Geothermal Data Repository
26	Fondu-FAF-MGF (60-40)	Fondu (60%)	Fly Ash F (40%)	SP	MGF	Matrix, interface 5-day healing, corrosion	Geothermal Data Repository
27	Fondu-FAF (60-	Fondu (60%)	Fly Ash F (40%)	None	None	Matrix, interface 5-day	Geothermal Data

	40)					healing, corrosion	Repository
28	Fondu-FAF (60-40)	Fondu (60%)	Fly Ash F (40%)	None	MGF	Matrix, interface 5-day healing, corrosion	Geothermal Data Repository
29	CAP-Clin	CAC #51	Fly Ash F/zeolite Clinoptilolite	SP	None	Interface 5-day healing, 3 environments	SPE-GRC[3]

3. ***Portland-cement-based formulations***: Class G oil-field cement modified with silica flour and FlexCem (Flex) from Trabits Enc.

N	Composite Name	Cement	Pozzolanic additive	Activator	Additives	Tests performed (300C)	References
30	G-SiO_2	Class G	SiO_2	None	None	All	ACR paper[4], Geothermal data repository
31	G-SiO_2-MGF-5%	Class G	SiO_2/MGF	None	MGF, 5%	All	SPE-GRC[3], Geothermal Data Repository
32	G-SiO_2-MGF	Class G	SiO_2/MGF	None	MGF, 10%	All	Geothermal Data Repository
33	G-SiO_2-Clin	Class G	SiO_2/zeolite Clinoptilolite	None	None	All	SPE-GRC[3]
34	G-SiO_2-bentonite	Class G	SiO_2/Bentonite (5%)	None	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
35	G-SiO_2-Metakaoline-5%	Class G	SiO_2/Metakaoline (5%)	None	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
36	G-SiO_2-Metakaoline-10%	Class G	SiO_2/Metakaoline (10%)	None	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
37	G-SiO_2-Montmorillonite	Class G	SiO_2/Montmorillonite	None	None	Matrix, repeated damage, 5+5-day healing, water, carbonate	Geothermal Data Repository
38	G-SiO_2-MgO	Class G	SiO_2	None	MgO, 5%	Matrix, repeated damage, 5+5 day healing, 3 environments	Geothermal Data Repository
39	G-SiO_2-Slag	Class G	SiO_2/Slag (5%)	None	None	Matrix, repeated damage, 5+5 day healing, 3 environments	Geothermal Data Repository

[4] Pyatina T., Sugama T., Ronne A., Trabits G. "Self-repairing properties of OPC clinker-natural zeolite blend in water and alkali carbonate environments at 270°C," *Advances in Cement Research*, http://dx.doi.org/10.1680/jadcr.16.00136 (2017)

40	Flex	Type II OPC	Zeolite Ferrierite	None	None	All	ACR paper[4]
41	Flex-SMS	Type II OPC	Zeolite Ferrierite	SMS	None	All	ACR paper[4]

4. ***Pozzolanic cement***: Slag and fly ash C-based formulations

N	Composite Name	Cement	Pozzolanic additive	Activator	Additives	Tests performed (300C)	References
42	GBFS/FAC	None	Ground Granulated blast Furnace Slag (GBFS)Fly Ash C	SMS	None	Matrix, interface 5-day healing 3 environments	SPE-GRC[3]
43	GBFS/FAC-MGF	None	GBFS/Fly Ash C	SMS	MGF	Matrix, interface 5-day healing 3 environments	SPE-GRC[3]
44	GBFS/SiO_2/MGF -5%	None	GBFS/SiO_2	SMS	MGF, 5%	Matrix, interface 5-day healing 3 environments	Geothermal Data Repository
45	GBFS/SiO_2/MGF	None	GBFS/SiO_2	SMS	MGF, 10%	Matrix, interface 5-day healing 3 environments	SPE-GRC[3]
46	GBFS/FAC-Clin	None	Ground Granulated blast Furnace Slag (GBFS)Fly Ash C/ Zeolite Clinoptilolite	SMS	None	Matrix, interface 5-day healing 3 environments	SPE-GRC meeting
47	FAC/FAF	None	FAC/FAF	SMS	None	Matrix, interface 5-day healing 3 environments	SPE-GRC[3]
48	FAC/FAF-MGF	None	FAC/FAF	SMS	MGF	Matrix, interface 5-day healing 3 environments	SPE-GRC[3]