

Correlation of Cement Performance Property Measurements with C₃S/C₂S Ratio Determined by Solid State ²⁹Si NMR Measurements

Christopher L. Edwards,^{a,b} Rickey Morgan,^b Lewis Norman,^b Gary P. Funkhouser,^b
and Andrew R. Barron^{a,c,d*}

^a *Department of Chemistry, Rice University, Houston, Texas 77005, USA*

^b *Halliburton Energy Services, Duncan, OK 73536, USA*

^c *Department of Mechanical Engineering and Materials Science, Rice University, Houston,
Texas 77005, USA*

^d *Energy and Environmental Systems Institute, Rice University, Houston, Texas 77005, USA*

Supplementary Materials

Table S1. Processed deconvolution data from CAP saturation recovery experiments.^a

τ^b	Aliquot	C ₃ S area ^c	C ₂ S area ^c	C ₃ S/C ₂ S area ratio
100 μ s	1	202290037.4	9265950.67	21.83154698
300 μ s	1	611906609.3	58015759.08	10.54724818
700 μ s	1	1332946612	104992819.6	12.69559782
1 ms	1	1770911561	164778021.7	10.74725588
1 ms	2	10535829174	893374367.6	11.79329692
3 ms	1	4468713517	327496167	13.64508647
3 ms	2	25683154738	2482057772	10.34752496
7 ms	1	9552959170	858812883.4	11.12344651
7 ms	2	47182092925	4443310535	10.61868005
10 ms	1	9552959170	858812883.4	11.12344651
10 ms	2	58114533149	6010770237	9.668400364
30 ms	1	16012957734	1695664777	9.443468989
70 ms	1	20539462783	2634809641	7.795425698
100 ms	1	21930141454	3207932589	6.836222659
300 ms	1	25264567156	4156251695	6.078690371
1 s	1	25708504866	5011852595	5.129541299
1 s	2	2031695637	397032550.5	5.117201688
3 s	1	25731329115	5192454848	4.95552294
3 s	2	1993516859	420325357.5	4.742794656
7 s	2	2005679975	420353390.4	4.771413816
10 s	2	2065699229	420717131.5	4.909947978
30 s	2	2033206930	407086244.9	4.994536061
70 s	2	2007320582	435101172.2	4.613457078

^a Edwards, C. L.; Alemany, L. B.; Barron, A. R. Solid state ²⁹Si NMR analysis of cements: comparing different methods of relaxation analysis for determining spin-lattice relaxation times to enable determination of the C₃S/C₂S ratio. *Ind. Eng. Chem. Res.* **2007**, *46*, 5122-5130. ^b First aliquot with central τ values, second aliquot with extreme τ values. ^cArea calculated by

multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

Table S2. Processed deconvolution data from ELT saturation recovery experiments.

τ^a	Aliquot	C ₃ S area ^b	C ₂ S area ^b	C ₃ S/C ₂ S area ratio
300 μ s	1	277427948.1	3732507.341	74.32750232
300 μ s	2	4336136371	75272026.62	57.60621264
700 μ s	1	970213555.6	74995050.14	12.93703456
700 μ s	2	10294523606	647879895	15.88955559
1 ms	1	1400499201	106858980.7	13.10605053
1 ms	2	14697401014	1055194487	13.92861809
3 ms	1	3769041703	256924920.8	14.66981752
3 ms	2	36312418929	2895386078	12.54147735
7 ms	1	6717303905	462372573	14.52790303
7 ms	2	64188409382	5221254945	12.29367462
10 ms	1	8407801991	687539825.4	12.22882178
10 ms	2	79072397166	6619454408	11.94545536
30 ms	1	13459293633	1372340042	9.807550037
70 ms	1	16795668669	2067379462	8.124134433
100 ms	1	18030281847	2309542696	7.80686232
300 ms	1	19997407286	2836874597	7.049098084
1 s	1	20264210192	3356697082	6.036949328
1 s	2	2395258863	385755171.1	6.209272207
3 s	1	20594050996	3518909855	5.852395158
3 s	2	2388943844	430322307.7	5.551522198
7 s	2	2450843012	413394230.6	5.92858543
10 s	2	2403079865	426675983.4	5.632095451
30 s	2	2417933279	432721235.9	5.587738891
70 s	2	2427642161	431492497.4	5.626151499

^a First aliquot with central τ values, second aliquot with extreme τ values. ^bArea calculated by multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

Table S3. Processed deconvolution data from RUS saturation recovery experiments.

τ^a	Aliquot	C ₃ S area ^b	C ₂ S area ^b	C ₃ S/C ₂ S area ratio
1 ms	1	1217031466	203281844	5.986916699
1 ms	2	7872536165	805579398.3	9.772514269
3 ms	1	3346245346	406462657.1	8.232602154
3 ms	2	29551958978	3251557042	9.08855622
7 ms	1	6522577476	810687026.9	8.045740537
7 ms	2	50833052890	5463047081	9.304890135
10 ms	1	8266365004	878205029.5	9.412796246
10 ms	2	66109511407	7132484403	9.268791584
30 ms	1	14249640812	1511334575	9.428515068
70 ms	1	18196848312	1982310683	9.179614714
100 ms	1	20160573377	2372017975	8.499334148
300 ms	1	23181408425	3147425731	7.365196325
1 s	1	24061325967	3662932122	6.568870284
1 s	2	2428677883	372495448.4	6.520020293
3 s	1	24190259828	3810073460	6.349027146
3 s	2	2459091132	408261364.4	6.02332561
7 s	2	2447985517	394160577.6	6.210630023
10 s	2	2432246798	399737008	6.08461751
30 s	2	2422714988	383122870.2	6.323597926

^a First aliquot with central τ values, second aliquot with extreme τ values. ^bArea calculated by multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

Table S4. Processed deconvolution data from SDN saturation recovery experiments.

τ^a	Aliquot	C ₃ S area ^b	C ₂ S area ^b	C ₃ S/C ₂ S area ratio
1 ms	1	1522028060	352253718.2	4.320828941
1 ms	2	7019115703	942160222.7	7.450023398
3 ms	1	3913182045	763805200.4	5.123272324
3 ms	2	9799473820	1182131030	8.289668044
7 ms	1	7151126064	1236888243	5.781545829
7 ms	2	28672700416	3533999021	8.113386633
10 ms	1	9039019930	1321658626	6.839148741
10 ms	2	52733512692	6471791127	8.148209925
30 ms	1	14534552559	2453629436	5.923695056
70 ms	1	17952746559	3383784791	5.305522564
100 ms	1	19113675718	3786686879	5.047598687
300 ms	1	21395860646	4058763397	5.271522026
1 s	1	22303631419	4511532769	4.943692656
1 s	2	1991385571	401293869.3	4.962412147
3 s	1	22346486839	4462667931	5.007427661
3 s	2	1973427181	398012635.6	4.95820234
7s	2	1956724801	390448547	5.011479275
10 s	2	1930807907	402258152.4	4.799922378
30 s	2	1901487655	377267339.2	5.040159741
70 s	2	1979591848	338516467.2	5.847845053

^a First aliquot with central τ values, second aliquot with extreme τ values. ^bArea calculated by multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

Table S5. Processed deconvolution data from THA saturation recovery experiments.

τ^a	Aliquot	C ₃ S area ^b	C ₂ S area ^b	C ₃ S/C ₂ S area ratio
1 ms	1	1760770941	115087585.6	15.2993994
1 ms	2	12854254373	570317889.4	22.5387536
3 ms	1	4163448065	366667539.7	11.3548313
3 ms	2	28949060289	2741882831	10.5580953
7 ms	1	7290172162	971400342.4	7.50480707
7 ms	2	53373936400	5331137711	10.0117347
10 ms	1	8983451975	1130162832	7.94881208
10 ms	2	64466909028	6257465622	10.3023992
30 ms	1	14834718540	2021235696	7.33943032
70 ms	1	19061159485	2449978281	7.78013407
100 ms	1	20024170464	2720638031	7.36010092
300 ms	1	21617701723	3727505757	5.79950861
1 s	1	22346468089	3950864090	5.65609638
1 s	2	2061699553	355440055	5.80041423
3 s	1	22139151016	4117270048	5.37714329
3 s	2	2066855161	345021364.5	5.99051356
7 s	2	2143670770	318558399.2	6.72928661
10 s	2	2093857090	336844364.6	6.21609654
30 s	2	2095346660	393152524.2	5.32960246
70 s	2	2193951345	402956169.8	5.44464016

^a First aliquot with central τ values, second aliquot with extreme τ values. ^bArea calculated by multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

Table S6. Processed deconvolution data from TXI saturation recovery experiments.

τ^a	Aliquot	C ₃ S area ^b	C ₂ S area ^b	C ₃ S/C ₂ S area ratio
1 ms	2	9593377244	1053406360	9.10700524
3 ms	2	25480134750	2067831458	12.32215259
7 ms	1	5972105050	900959314.7	6.628606811
7 ms	2	47616808858	6800188236	7.002278056
10 ms	1	7273731463	1113303485	6.533466896
10 ms	2	60713041928	7871929203	7.712600096
30 ms	1	12734009876	2301889946	5.531980319
70 ms	1	17450127110	3607119078	4.837690891
100 ms	1	18789523252	4223506575	4.44879697
300 ms	1	24703416705	6563149012	3.76395792
1 s	1	24256303331	7701256535	3.149655283
1 s	2	2567415522	717811273.6	3.576727779
3 s	1	24947024554	8112670181	3.07506949
3 s	2	2595416645	797205558.5	3.255642936
7 s	2	2681297489	722376180.4	3.711774504
10 s	2	2701026343	675202654.4	4.000319497
30 s	2	2691042579	719788831.6	3.738655645
70 s	2	2721050244	702758733.9	3.871955072

^a First aliquot with central τ values, second aliquot with extreme τ values. ^bArea calculated by multiplying peak intensity (arbitrary units) by peak half-width (Hz) without rescaling to connect intermediate and extreme τ regimes.

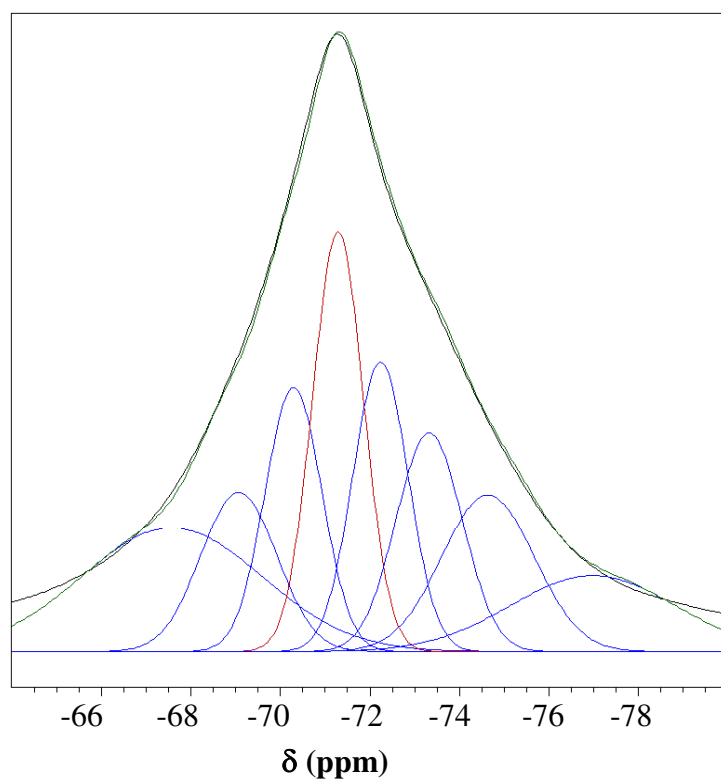


Figure S1. Representative sub-spectra of the saturation recovery data for sample CAP at τ of 3 s, illustrating the superposition of the fitted peaks forming the C_3S (blue) and C_2S (red) contributions resulting from deconvolution (summation in green).

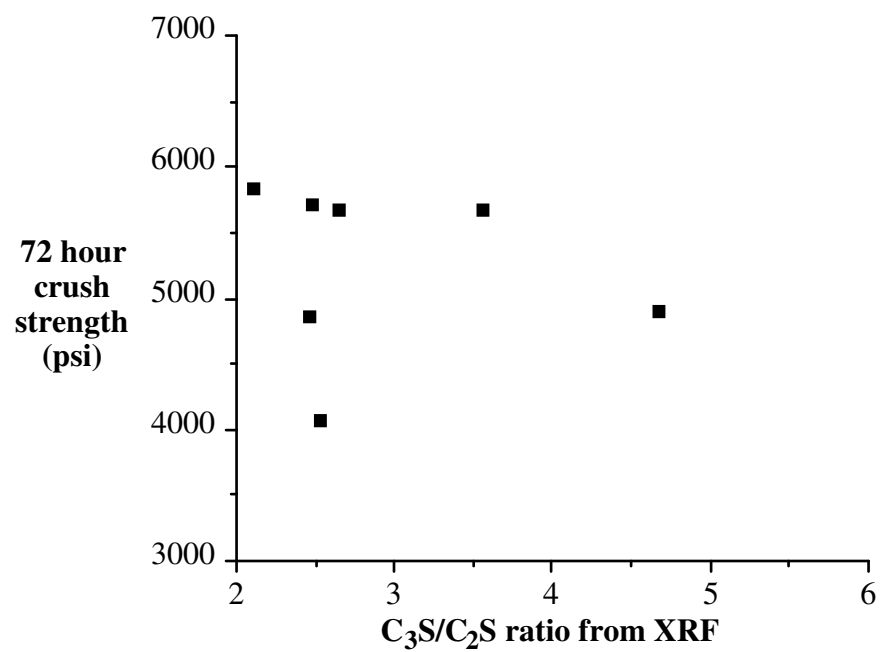


Figure S2. Plot of time for 72-hour crush strength (psi) as a function of C₃S/C₂S ratio as determined from XRF for Portland cements without additives.

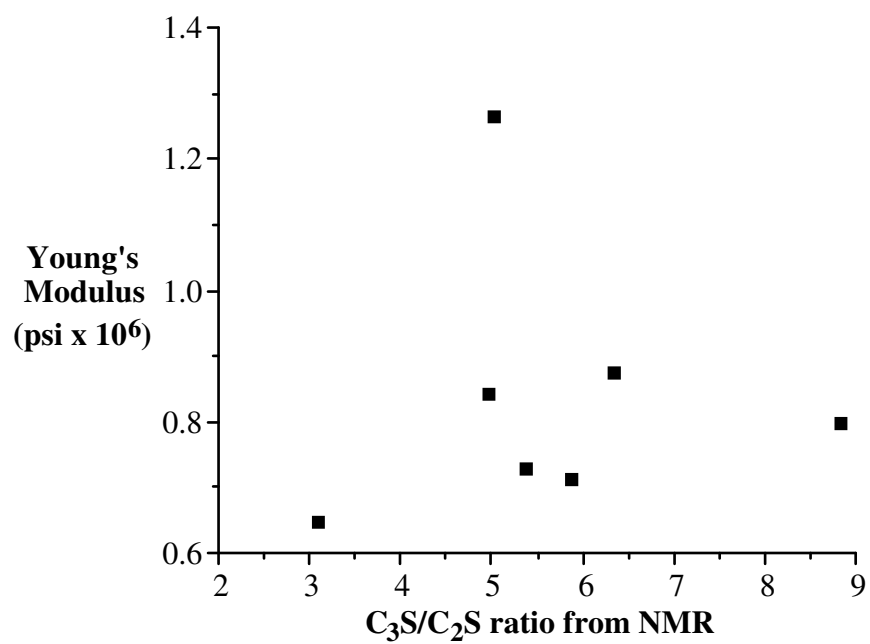


Figure S3. Plot of Young's Modulus (psi) as a function of C₃S/C₂S ratio as determined from MAS ²⁹Si NMR for Portland cements without additives.

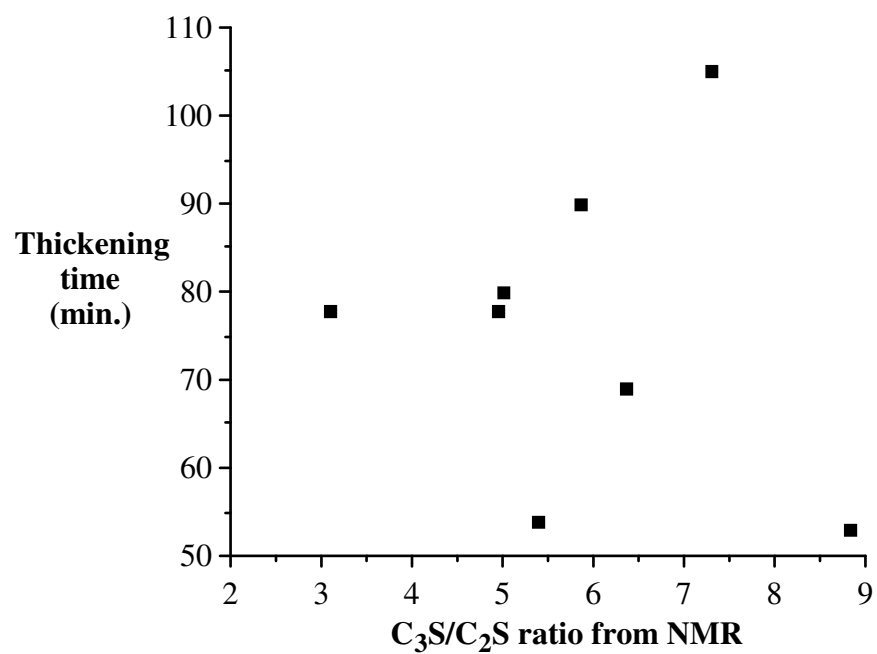


Figure S4. Thickening time to reach an apparent viscosity of 50 Bc as a function of C₃S/C₂S ratio as determined from MAS ²⁹Si NMR for Portland cements without additives

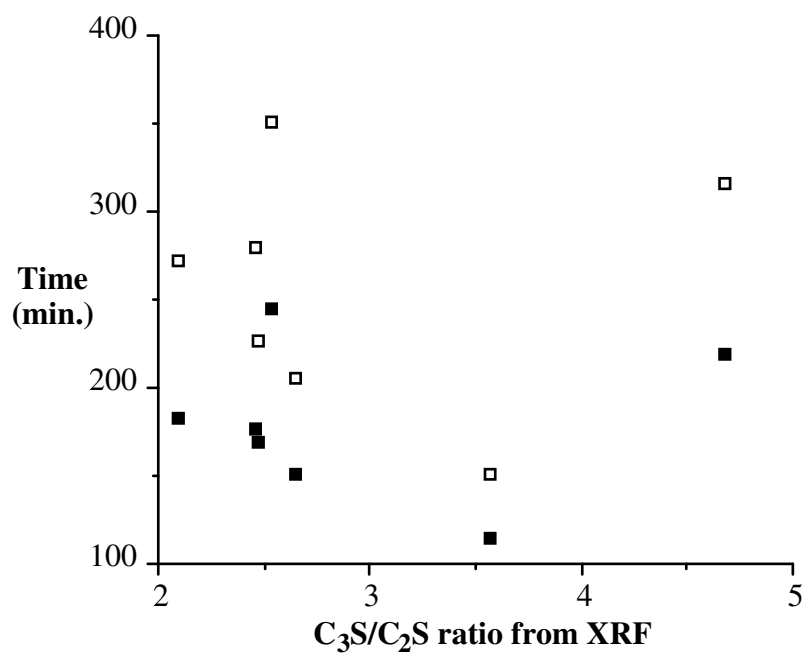


Figure S5. Plot of time for strength development (min.) for Portland cements in the presence of 0.5% lignosulfonate retarder bwoc as a function of C₃S/C₂S ratio as determined from XRF for 50 psi (■) and 500 psi (□).

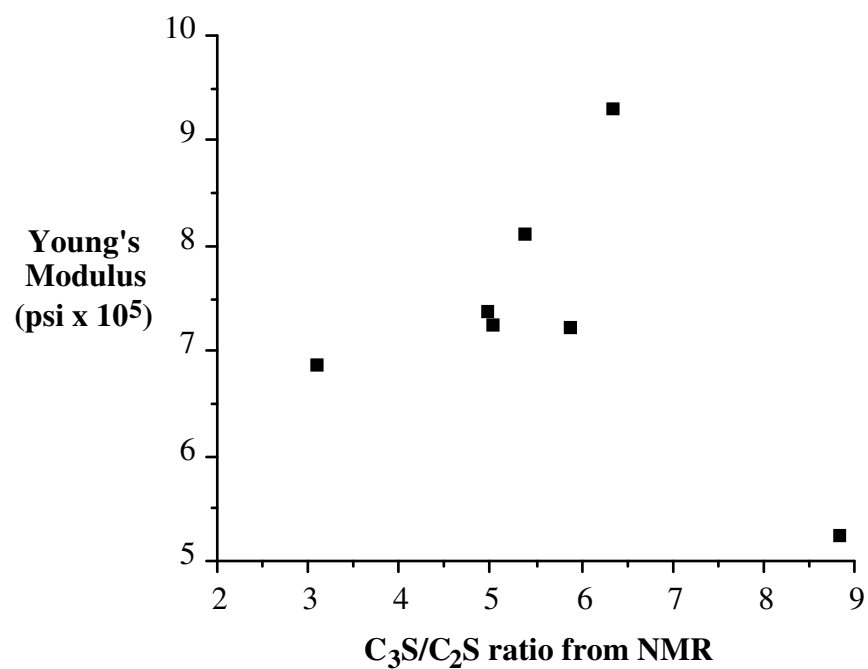


Figure S6. Plot of Young's Modulus (psi) as a function of C₃S/C₂S ratio as determined from MAS ²⁹Si NMR for Portland cements in the presence of 0.5% lignosulfonate retarder bwoc.

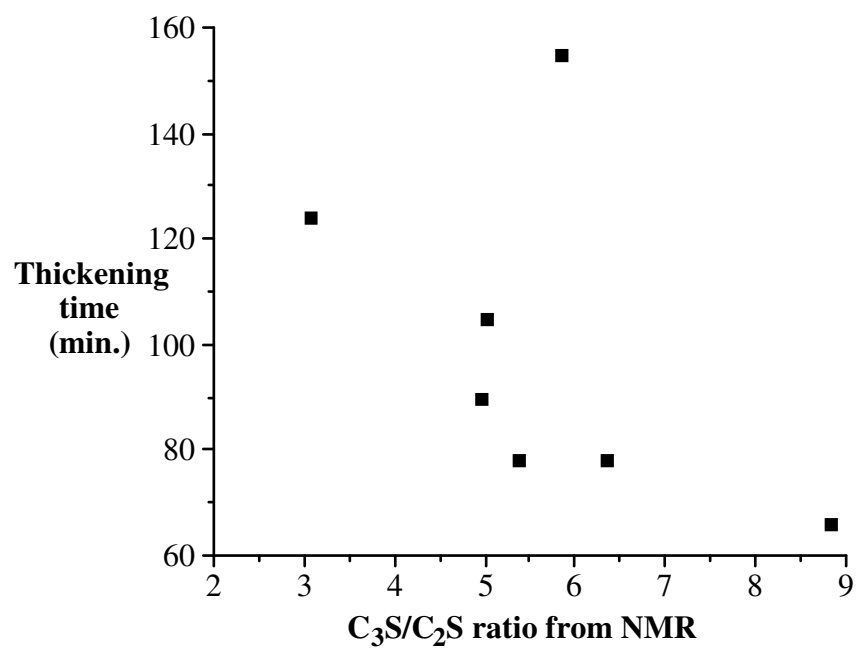


Figure S7. Thickening time to reach an apparent viscosity of 50 Bc as a function of C_3S/C_2S ratio as determined from MAS ^{29}Si NMR for Portland cements in the presence of 0.5% lignosulfonate retarder bwoc.

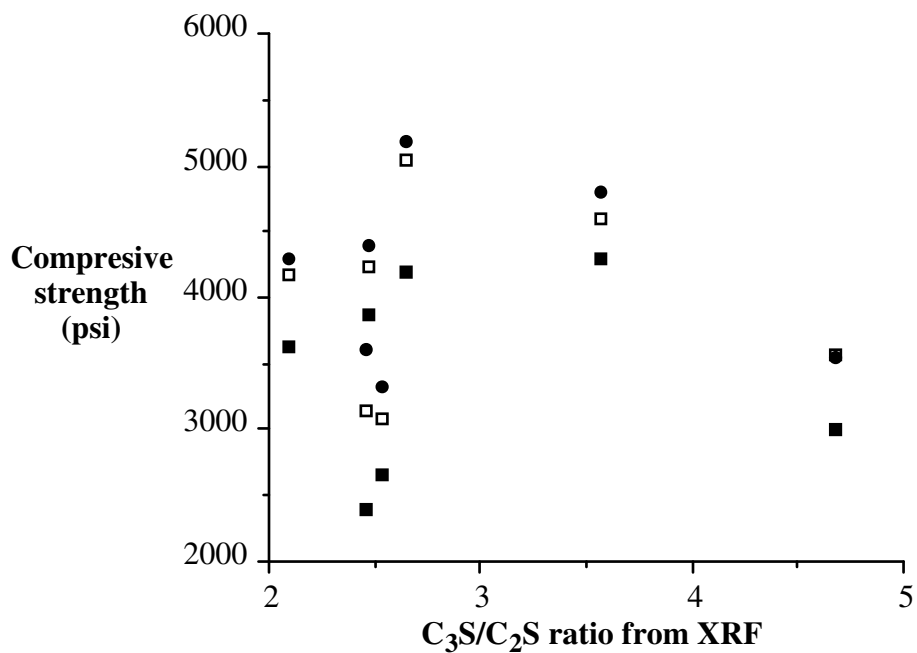


Figure S8. Plot of time for compressive strength (psi) as a function of C_3S/C_2S ratio as determined from XRF for 24 h (■), 48 h (□, $R = 0.381$), and 72 h (●) for Portland cements in the presence of 0.15% fluid loss additive bwoc.

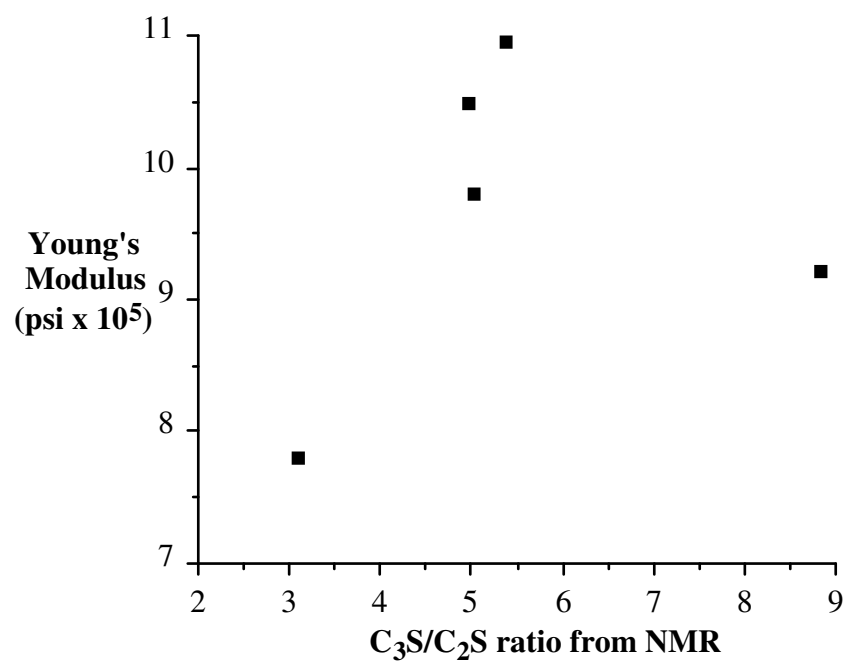


Figure S9. Plot of Young's Modulus (psi) as a function of C₃S/C₂S ratio as determined from MAS ²⁹Si NMR for Portland cements in the presence of 0.15% fluid loss additive bwoc.

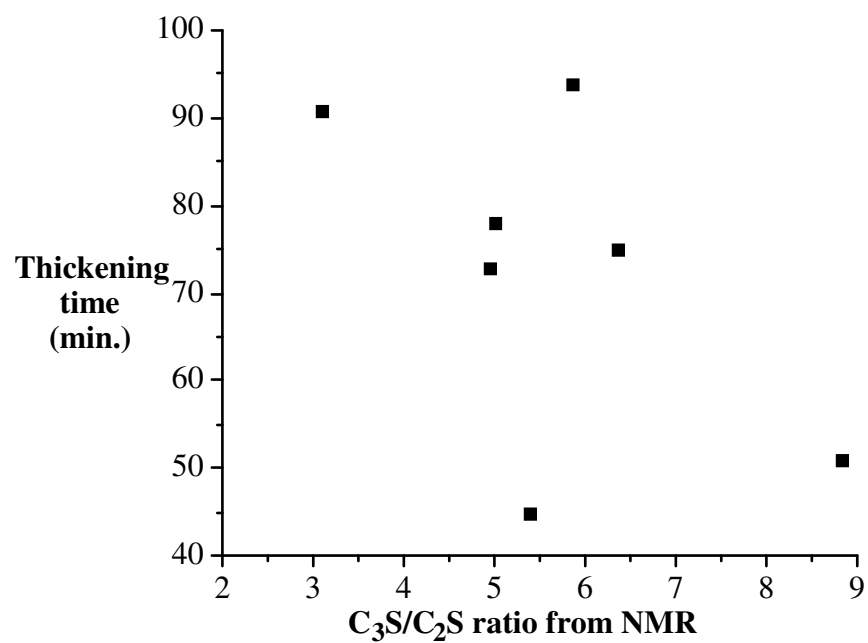


Figure S10. Thickening time to reach an apparent viscosity of 50 Bc as a function of C₃S/C₂S ratio as determined from MAS ²⁹Si NMR for Portland cements in the presence of 0.15% fluid loss additive bwoc.