EPA Workshop on Hydraulic Fracturing, Workshop No. 1, Chemicals

Fracture Fluid Additive and Formation Degradations

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Fracture Additive and Formation Reactions and Degradations

Subsurface Reactive Targets

- Rock (shale, sandstone, limestone, etc.)
  - Matrix
  - Natural Fractures
  - Hydraulic Fractures
  - Fluids (non HC gases, waters, hydrocarbons)
- Tubulars (various alloys)
- Cement
- Drilling components
- Fracture Additives

Chemical & Physical Reaction Controls

- Access (inhibition controls)
  - Permeability (can reactants reach each other?)
  - Area-to-volume ratio (how much diffusion can occur?)
  - Inhibition – (diffusion, viscosity, coatings, form, etc.)
- Reaction variables
  - Flow Rate and Pressure
  - Temperature
  - Pressure
  - **Time** (average frac 3 hrs at pressure, 2 to 4 weeks cleanup)
  - Volumes
  - By-product solubility
  - Re-precipitation

Well Described Shale Reaction/Degradation

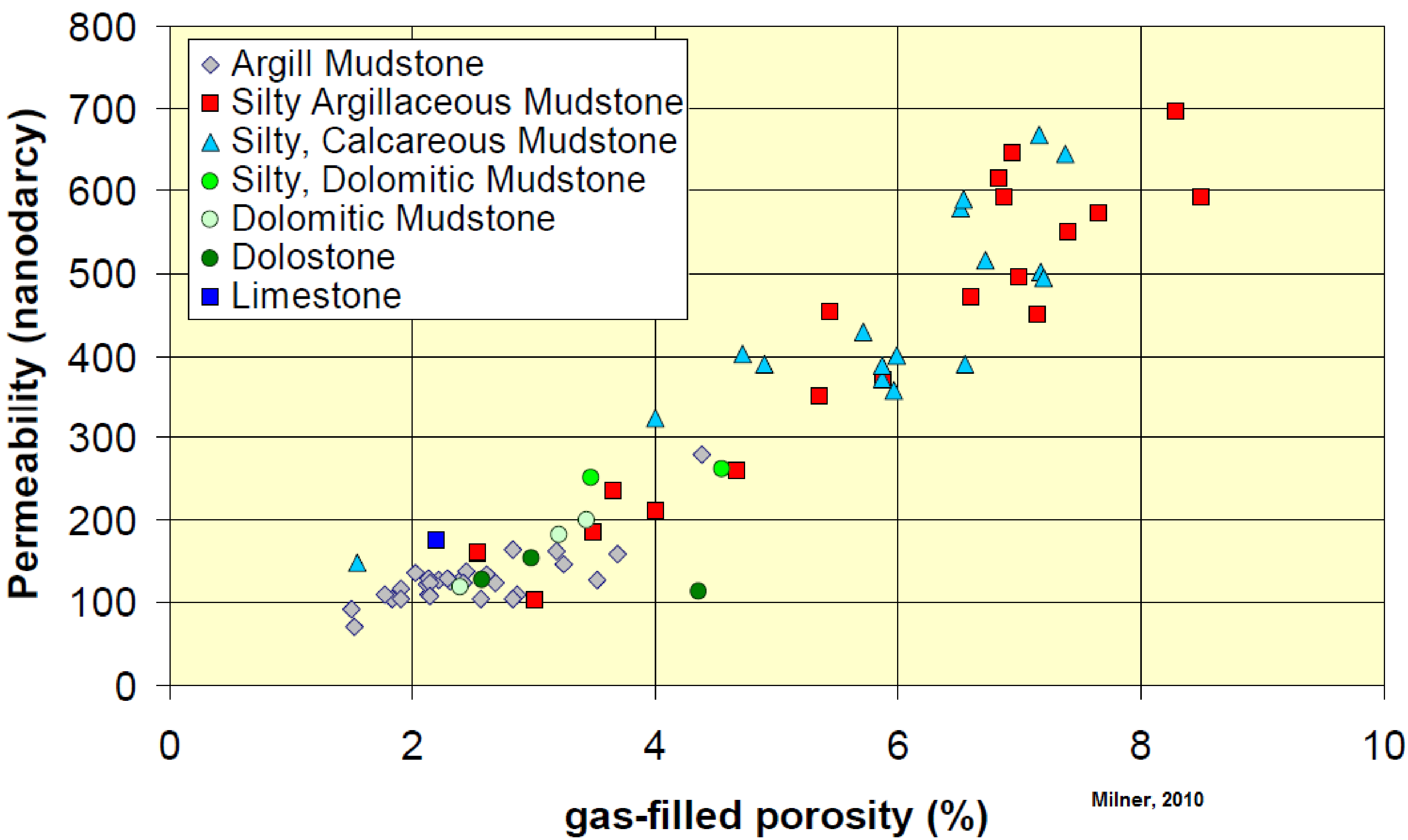
Chemical

- **Ion Transfer**, CEC
- Solution and re-precipitation

Physical

- Creep (Deenadayalu, 2010)
- Osmotic
- Dispersion (breakage)
- **Salt imbalance disaggregation** (drilling)
  - Resolved by more closely matching salinity.

Shale Porosity vs. Permeability



Proppant Diagenesis

SPE 131782, LaFollette and Carman

- Proppants – the conductivity of a propped fracture can decompose in some conditions.
  - Proppant decomposition from prop-fluid reaction
  - Prop embedment into the formation gouges out / liberates small formation particles.

Changes in Recovered Water Composition: Shale + Prop + Fluid

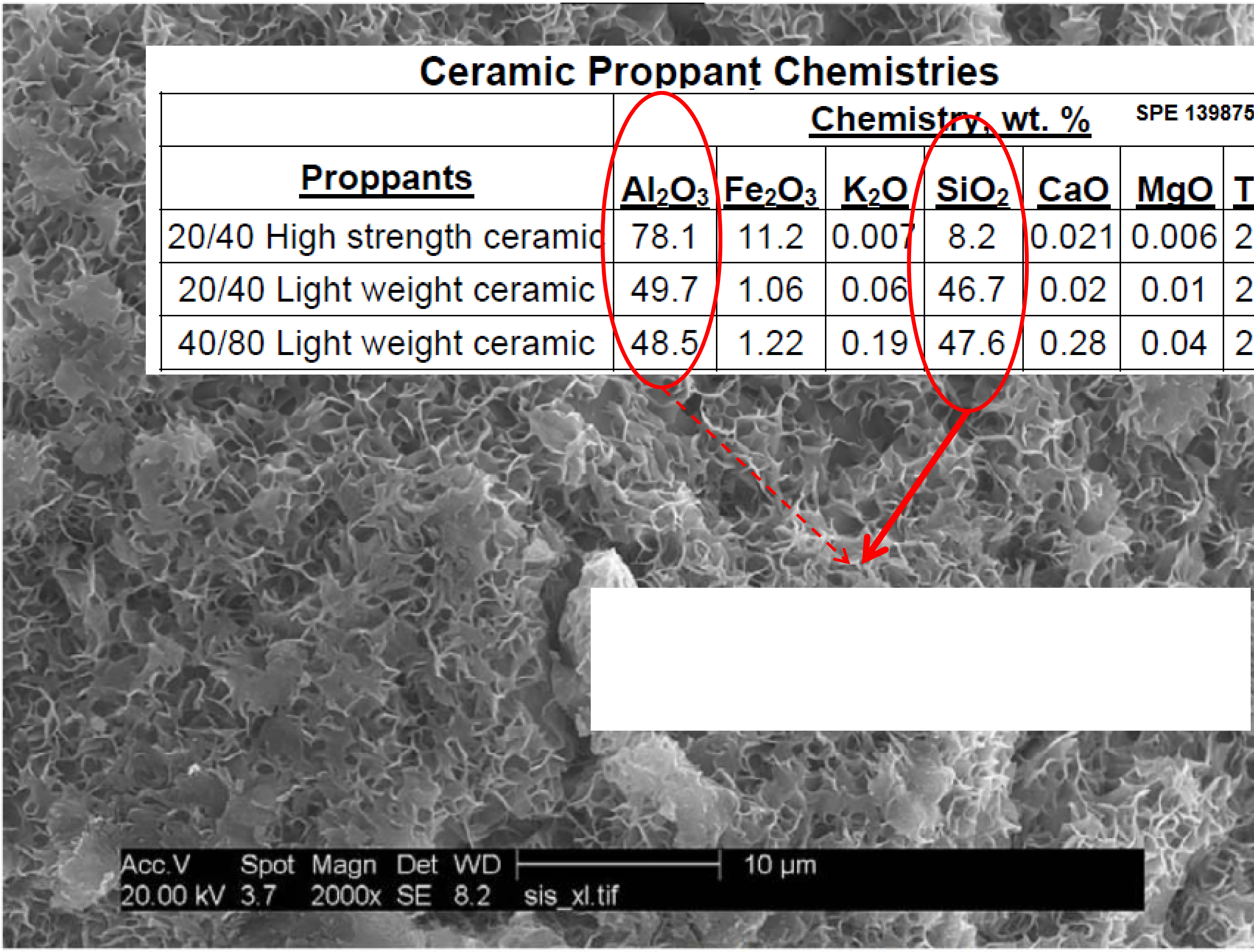
Cations	Baseline	30 days	60 days	120 days	240 days
Sodium	80	870	1400	1400	334
Calcium	29	371	459	312	100
Magnesium	3	10	4	2	1
Barium	1	1	10	1	0
Potassium	984	970	632	660	290
Iron	1	1	1	1	0
Boron	120	130	137	140	60
Silicon	2	40	110	85	20
Anions	**Baseline**	**30 days**	**60 days**	**120 days**	**240 days**
Chloride	30	2200	1591	2031	523
Sulfate	5	5	5	5	5
Carbonate	640	1	1	1	1
Bicarbonate	49	610	721	488	915
Total Dissolved Solids(calc.)	1907	5031	4943	5033	2222
Total Hardness as CaCO3	16	968	1160	787	250
pH	9.73	7.31	7.50	7.19	7.54
Specific Gravity	1.0010	1.0025	1.0025	1.0025	1.0014

water composition of the broken fracturing fluid from baseline through the 240 day test using a mixture of shale, proppant, and fluid.

LaFollette, et. al. SPE 131782

Ceramic Proppant Chemistries

Proppants	Chemistry, wt. %						SPE 139875
	Al_2O_3	Fe_2O_3	K_2O	SiO_2	CaO	MgO	TiO_2
20/40 High strength ceramic	78.1	11.2	0.007	8.2	0.021	0.006	2.24
20/40 Light weight ceramic	49.7	1.06	0.06	46.7	0.02	0.01	2.22
40/80 Light weight ceramic	48.5	1.22	0.19	47.6	0.28	0.04	2.22



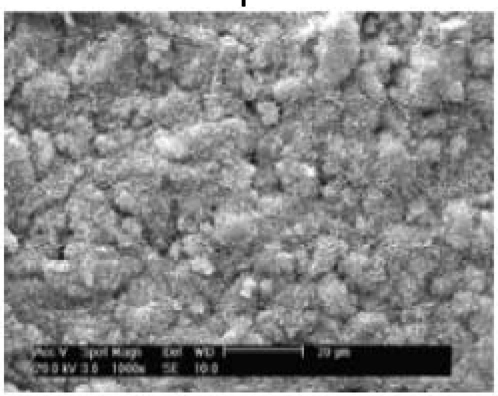
dense mat of honeycomb structure overgrowth. 2000X

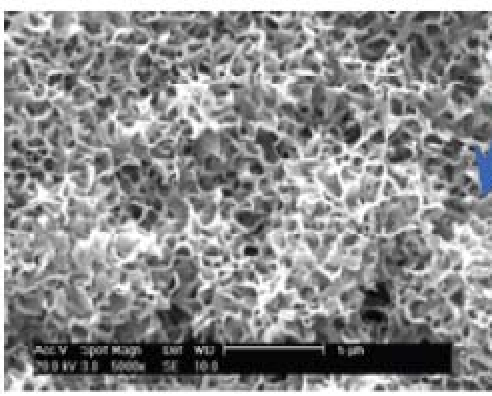
SPE 131782

Zeolites

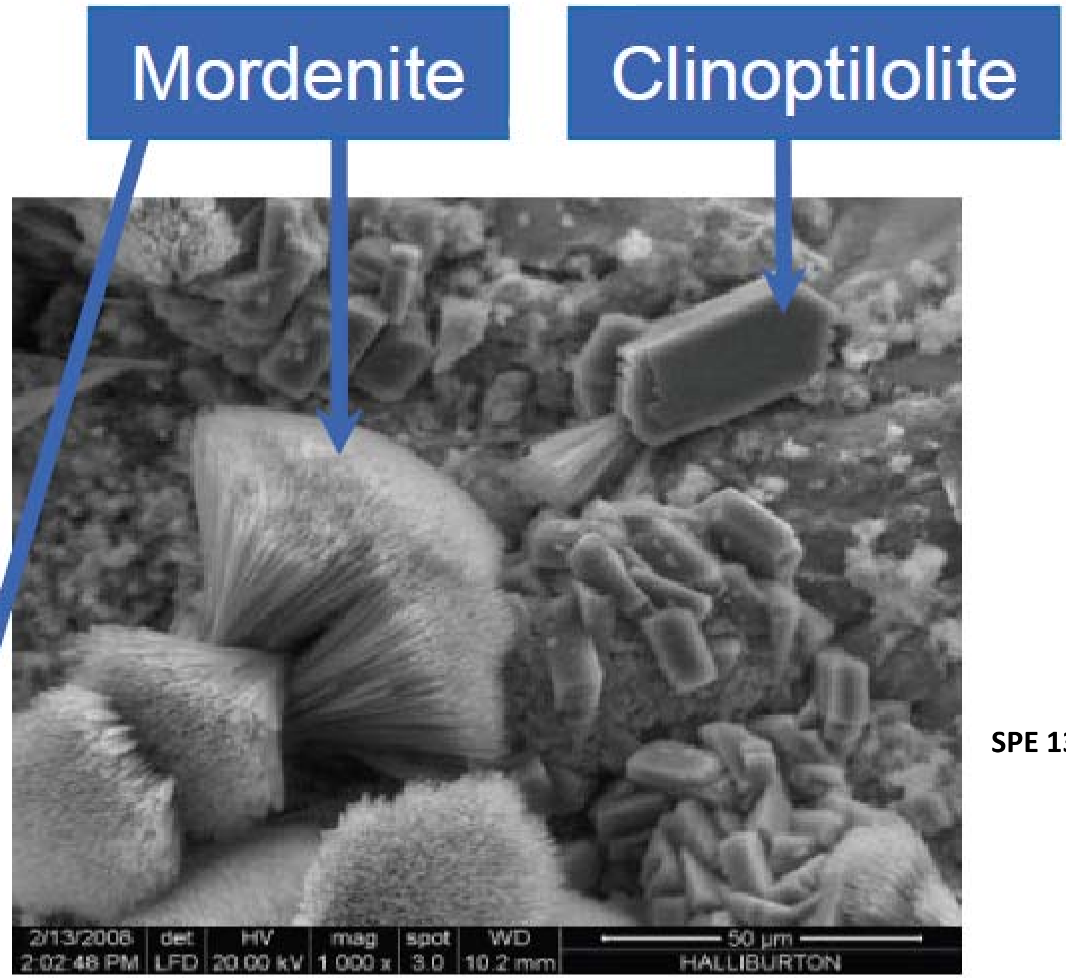
In order to be a zeolite, the ratio (Si + Al)/O must equal ½ and typically have large vacant, interconnected spaces in their structure that form long, wide channels of varying sizes.

The first zeolite formed is often altered to another species.





Common Zeolites



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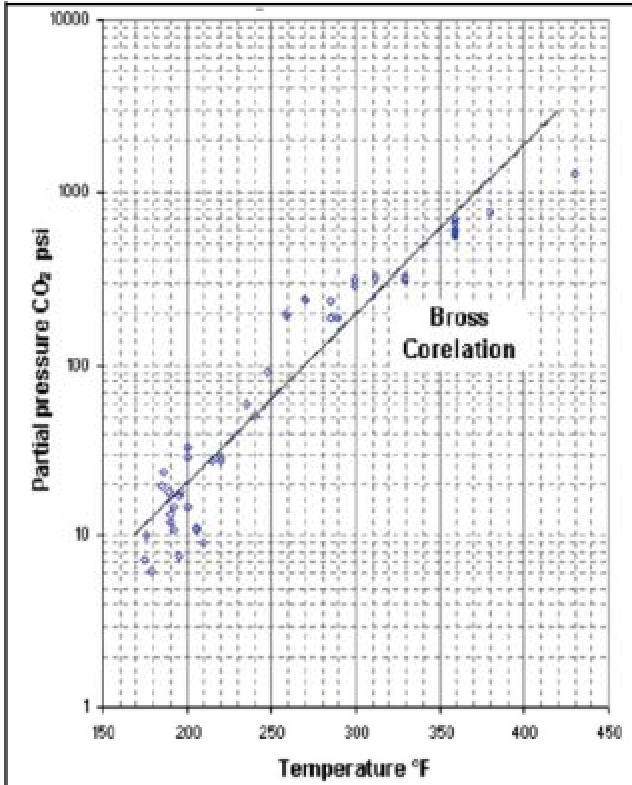
Many Formation Degradations Directly Tied to pH – Low pH Created by CO2 or Mineral Acid



In many reservoirs in the Gulf Coast, it has been determined that CO_2 content is highly correlated with reservoir temperature. [Grimes and McNeil 2005]

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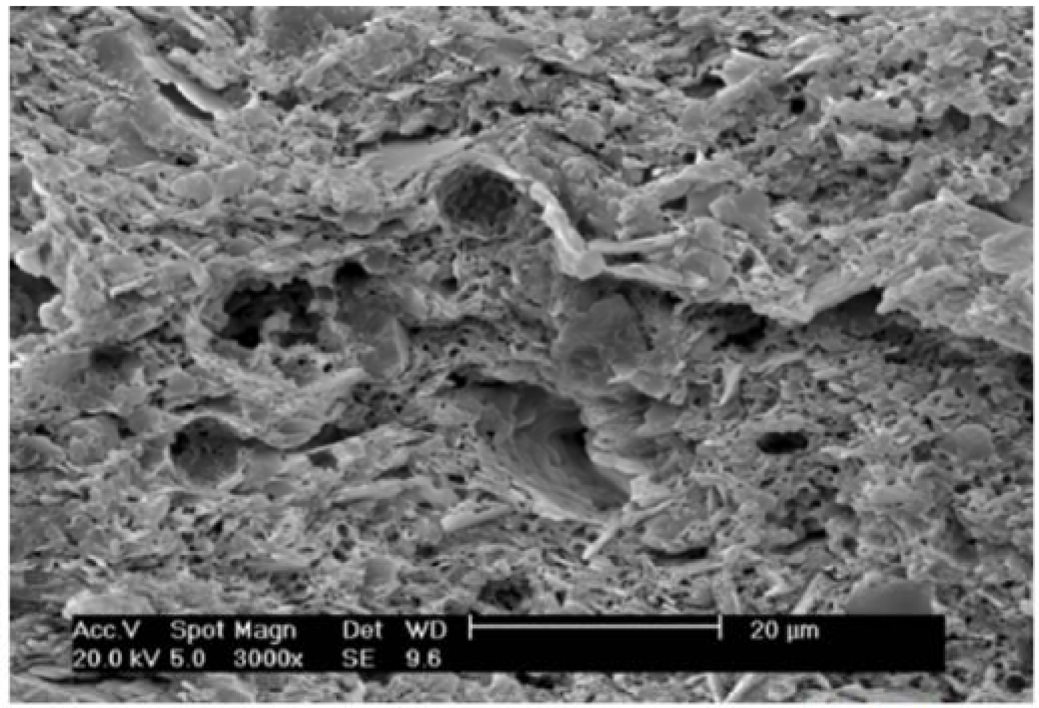
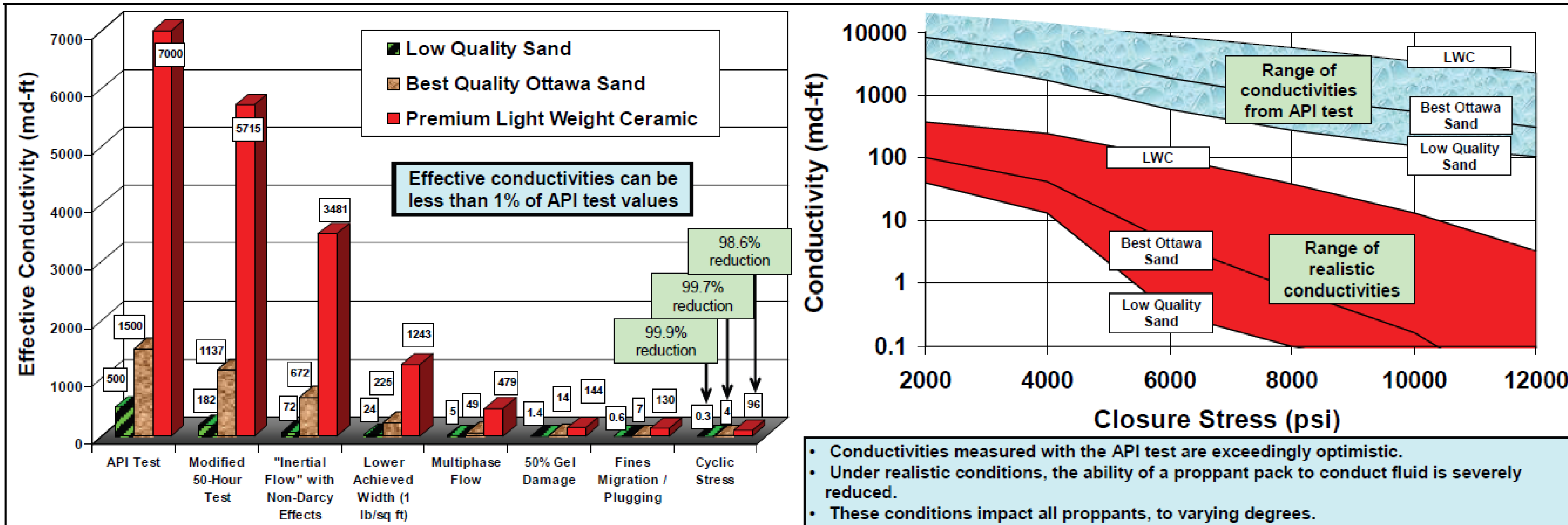


SPE 106815

3000X Closeup of acid-etched shale that showed no detectable amount of calcite or dolomite in XRD analysis.

Reduction of Conductivity with Stress



(a) (b)

Even in simple, planar fracs with uniform proppant distribution, the apparent conductivity is often 50 to 1000 times lower than in published data from standard tests at 6000 psi closure stress (a). Reductions must be applied to all proppant types at all stresses (b). All data shown for 20/40 proppants. [Vincent, 2009] Duenckel, et. al., SPE 139875

Decomposition Reactions of Most-Common Frac Additives (1 of 3)

- Proppant
  - Physical
    - Embedment (pushes up particles of fracture face)
    - Erosive – minor effect with maximum impact on perforations in the casing (large particles, rough surfaces and high velocities)
  - Chemical
    - Diagenesis – solution and common re-precipitation of silica and some aluminum oxides. Strength loss = 20%.

Decomposition Reactions of Most-Common Frac Additives (2 of 3)

- Friction Reducer
  - Physical – lowers friction in pipe by 25 to 35+% (decreases horsepower & resultant emissions)

    Chemical high MW polyacrylamide absorbs in rock
- Surfactants – (flow-back, dispersion, IFT, etc) – most adsorb and are lost.
- Gellants – guar, cellulose derivatives, etc.
  - Physical – increases viscosity & proppant carrying ability, decreases leakoff, absorbs in formation
  - Chemical – breakers & temperature induced degradation leaves partly broken polymer in pores.

Decomposition Reactions of Most-Common Frac Additives (3 of 3)

- Gel Breakers – ammonium persulfate – reduces gel viscosity in lower temperature formations. The materials remain with fluids.
- Biocides – oxidizing biocide vs. metabolic toxin? Best have low bioaccumulation and bio-degradation. Some UV use in clear fluids.
- Scale Inhibitors – phosphonates, phosphate esters, Polymers sorption losses, no degradation of phosphonate or phosphates. Polymer breakdown is common degradation.

Observations

Conventional Rocks

sandstone & carbonates

- Reactions are well described in Literature – 60+ years of data
- Adsorption, absorption & graded release very common.
- Access – the 0.1 to 5000+ mD perm & Area-to-Volume ratios of 20,000 to 30,000 are major chemical & physical reaction controls
- Meaningful work done on core and appears reflective of what happens in the rock.

Unconventional Rocks

shales, mudstones, siltstones, etc.

- Reactions only starting to be described in Literature
- Access is major limiter - all Rx
  - Shale perm 100 to 500 nano-Darcies (0.0001 to 0.0005 mD) limits rate of fluid movement to millimeters/yr.
  - Shale pore size of 0.3 micron bars water entry into the matrix.
  - Area-to-volume ratios reduced into the 100 to 1000:1 range, not the 30,000+:1 of a matrix reaction or the 100,000:1 range of ground up shale particles.
  - **Reaction studies involving ground-up shale are highly suspect and a worst-possible (unachievable?) case.**

Support Slides (for the record)

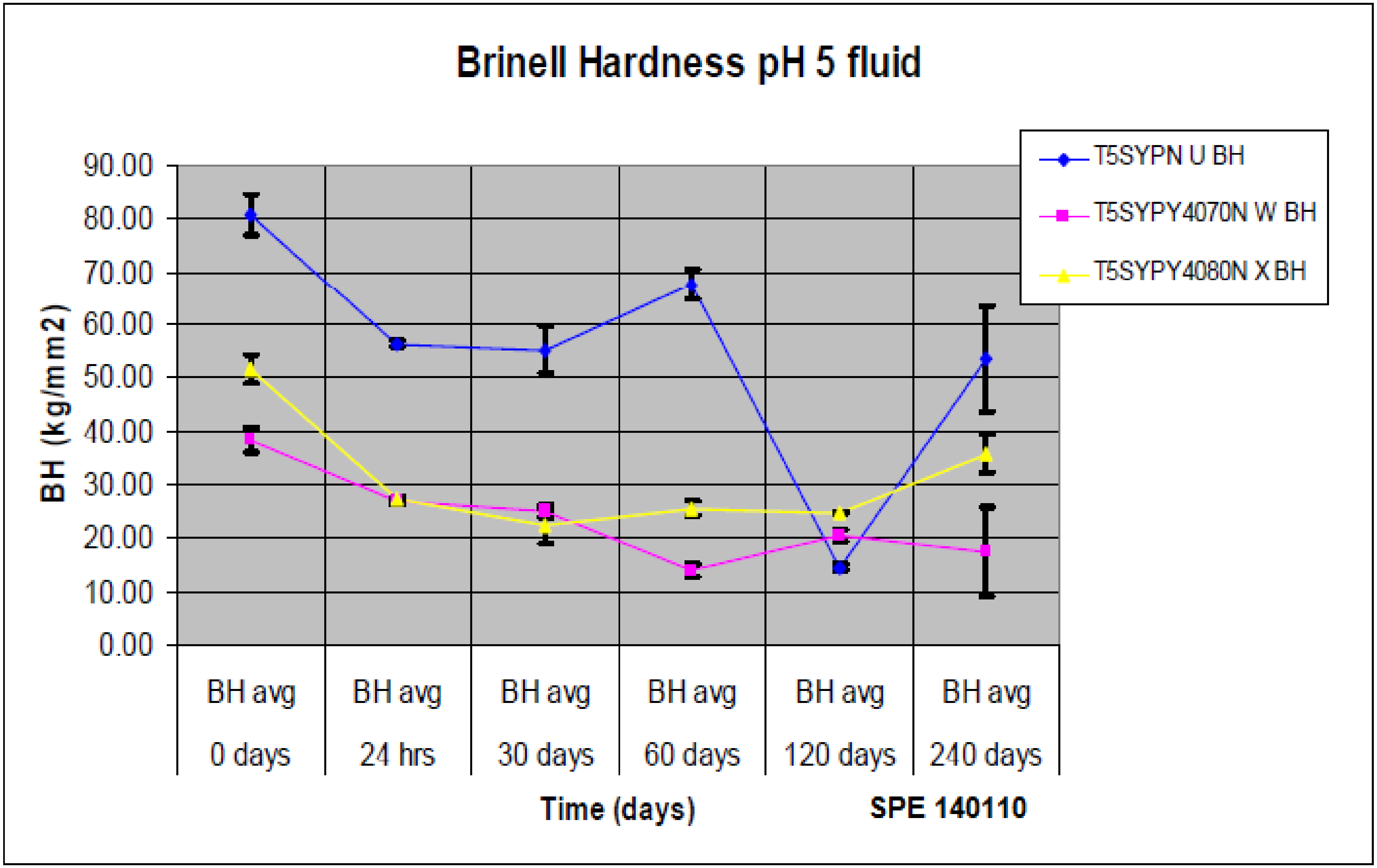
- Shale Characteristics
- References

Molecular Diameter

Gas	Molar Mass M (g/mol)	Kinetic Diameter $d_{kinetic}$ (nm)	Resource for Kinetic Diameter
Methane	16.043	0.38	(Gupta et al. 1995)
Ethane	30.07	0.4	(Sadakane et al. 2008)
Propane	44.082	0.43	(Collins et al. 1996)
Carbon Dioxide	44.01	0.33	(Sadakane et al. 2008)
Water	18.015	0.265	(Ivanova et al. 2007)
Nitrogen	28.014	0.364	(Collins et al. 1996)

Freeman, SPE 141125

pH 5 Fluid Effect on Haynesville Shale



Recognized Mechanisms Affecting Conductivity of Propped Fractures

Category of Damage	Damage Mechanism Causing Higher Pressure Losses
Physical loss of porosity and/or fracture width	Particle crushing, pack rearrangement, compaction Particle embedment into fracture face Spalling of formation material, contaminating proppant pack Cyclic stress loading increasing particle crush and rearrangement Low achieved proppant concentration yielding narrower fracs Gel filter cake at frac face resulting in loss of effective width Dispersed gel residue occupying porosity
Complex fluid flow regimes causing higher pressure losses than reported in low velocity flow tests	Fluid inertia causing non-Darcy pressure losses due to curvilinear flowpath around proppant grains (significant even at modest laminar production rates) Fluid turbulence (significant only at high production rates) Multiphase flow Emulsions, foams, froths, mist flow causing higher pressure losses
Non-linear fracture geometry	Complex fracture geometry would be expected to increase total flowpath length and flowpath tortuosity
Imperfectly uniform proppant distribution	Irregular packing should result in greater proppant crush and embedment and also result in bottlenecks or regions of aperture restriction
Uncertain or multiple mechanisms	Continued degradation over time Thermal degradation of some proppant types
Chemical degradation of proppant	Proppant dissolution causing reduction in particle diameter or strength (especially in acid or steam injection) Stress corrosion, pressure solutioning, static fatigue Deposition of sulfate or carbonate scales Precipitation of waxes or asphaltenes

SPE 139875

pH at Various Points in the Flow Back

pH of Flowback Fluid Recorded by One Operator from Several East Texas and North Louisiana Wells

Deep Bossier - 4% CO2

bbl	% recovery	pH
742	4.5%	6.2
1245	7.5%	6.5
1541	9.3%	6.5
1687	10.2%	6.8
1798	10.9%	6.5
2048	12.4%	6.5
2383	14.4%	6.5
2702	16.4%	6.2
2827	17.1%	6.2
2951	17.9%	6.2
3080	18.7%	6.2
3170	19.2%	6.2
3394	20.6%	6.2
3461	21.0%	6.2
3634	22.0%	6.2
3699	22.4%	6.2
3875	23.5%	6.2
3935	23.8%	6.2
4073	24.7%	6.2
4130	25.0%	6.2
4253	25.8%	6.2
4315	26.1%	6.2
4453	27.0%	6.2
4586	27.8%	6.2
4729	28.7%	6.2
4867	29.5%	6.2
5042	30.5%	6.2

Cotton Valley Lime, Well 1

bbl	% recovery	pH
559	6.6%	7.2
661	7.8%	7.2
726	8.6%	7.2
769	9.1%	7.2
843	10.0%	6.2
865	10.3%	6.2
963	11.4%	6.4

Cotton Valley Lime - 5% CO2

bbl	% recovery	pH
797	4.7%	6.4
1630	9.6%	6.4
1952	11.5%	6.8
2246	13.3%	6.4
2459	14.5%	6.4
2781	16.4%	6.4
2940	17.4%	6.4
3269	19.3%	6.4
3923	23.2%	6.4
3999	23.6%	6.4
4147	24.5%	6.4
4247	25.1%	6.4
4468	26.4%	6.4

Haynesville - 3% CO2

bbl	% recovery	pH
1193	1.2%	6
1313	1.3%	6
1736	1.8%	6
1908	2.0%	6
2259	2.3%	6
2362	2.4%	6
2482	2.5%	6
2777	2.8%	6
2947	3.0%	6

Haynesville - 6% CO2

bbl	% recovery	pH
1172	0.6%	5
1448	0.7%	5
2347	1.2%	5

Deep Bossier - 4% CO2

bbl	% recovery	pH
720	20.7%	6.4
864	24.8%	6.4
1002	28.8%	6.4
1072	30.8%	6.5
1180	33.9%	6.4
1330	38.2%	6.4
1454	41.7%	6.4

James Lime

bbl	% recovery	pH
1096	8.8%	7
1457	11.7%	7
2870	23.1%	7
3807	30.7%	7
4339	34.9%	7
4767	38.4%	7
4877	39.3%	7
5054	40.7%	7

SPE 139875

Proppant Diagenesis Conclusions from SPE 139875

1. Static testing of various proppants at high temperature and in the presence of variable fluids and reservoir rocks shows:
    a. Under some conditions precipitants will form but only when formation material is present.
    b. These precipitants will form on all of the proppant types tested (ceramics, natural sands and RCS) and inert materials.
    c. Chemical makeup of the precipitants and their structure show them to be classified as zeolites.
    d. Chemical makeup of the precipitants always includes alumina and in the case of the sand, RCS and inert materials, the alumina was conclusively sourced from the formation material.
    e. Mechanical properties of proppants post static testing shows strength degradation.
        i. The degradation is related to a stress corrosion or static fatigue phenomena that all oxides undergo upon exposure to water.
        ii. This degradation is unrelated to any sort of "diagenetic" process.
        iii. Static fatigue attacks the silica bonds in both sand and ceramic proppants.
        iv. Resin coatings did not effectively isolate sand particles from static fatigue even in unstressed testing, and it is unlikely that a 100% impermeable resin coating can be achieved in actual fractures.
        v. Water molecules present in the atmosphere are sufficient to induce static fatigue and it does not appear practical to isolate proppants from all moisture given that water is ubiquitous in the atmosphere and in reservoirs.
        vi. This degradation is already incorporated in the reference conductivity testing, and there are no adjustments necessary to account for this phenomenon.
2. Zeolites appear to form only with alkaline pH, and then with poor reproducibility. Hot reservoirs in which zeolite formation was anticipated are typically too acidic to allow deposition.
3. Zeolites did not form under extended conductivity testing under flowing conditions with reservoir shale core at high temperatures and stresses. Under these conditions RCS exhibited a higher loss of conductivity than the ceramic tested.
4. Though only a limited sample set is available for inspection, flow back proppant samples do not indicate the presence of zeolites.
5. While it is recognized that barium sulfate or calcium carbonate scale can significantly impair productivity in some reservoirs, there is not yet evidence that zeolite precipitation poses significant concern in actual propped fractures, or that chemical treatment of the proppant surface is justified or effective at mitigating zeolite precipitation. 139875

Changes in Recovered Water Composition: Prop + Fluid Test

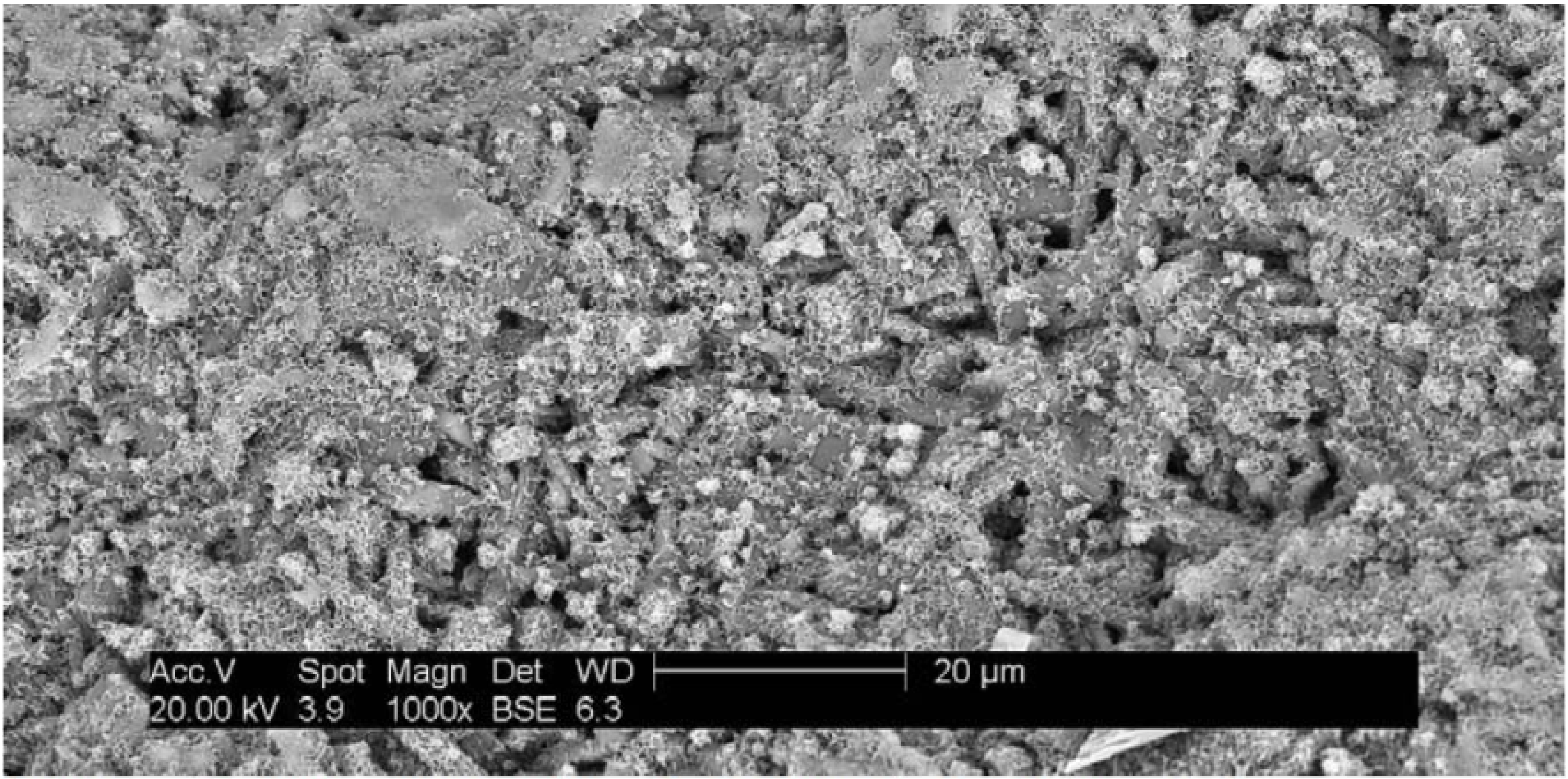
Cations	Baseline	30 days	60 days	120 days
Sodium	80	125	162	85
Calcium	29	84	34	58
Magnesium	3	2	3	1
Barium	1	5	0	1
Potassium	984	1243	1018	827
Iron	1	1	1	1
Boron	120	140	127	90
Silicon	2	95	100	80
Anions	**Baseline**	**30 days**	**60 days**	**120 days**
Chloride	30	219	220	156
Sulfate	5	5	5	5
Carbonate	640	1	1	1
Bicarbonate	49	1092	987	305
Total Dissolved Solids(calc.)	1907	2904	2552	1521
Total Hardness as $CaCO_3$	16	218	97	145
pH	9.73	7.12	5.78	7.27
Specific Gravity	1.0010	1.0015	1.0015	1.0007

water analysis results for the proppant +fluid series tests. SPE 131782

EDS Analyses of Diagenetic Materials from Pinedale Shale Cells

SPE 139875

	Al_2O_3	Fe_2O_3	K_2O	SiO_2	MgO	TiO_2	C
Figure 15A Spot 1 – HSC	63.5	17.5	0.6	15.0	0.4	2.2	0
Figure 15A Spot 2 – Precipitate	35.8	7.0	4.6	45.6	1.8	1.6	0
Figure 15B Spot 1 – Sand	2.6	0	0	97.4	0	0	0
Figure 15B Spot 2 – Precipitate	18.4	7.5	5.0	66.7	2.0	0	0
Figure 15C Spot 1 – RCS	9.0	0	0	19.6	0.7	0	70.7
Figure 15C Spot 2 – Precipitate	23.9	0	4.3	47.4	2.7	1.7	0



honeycomb structure overgrowths on the proppant in the 60 day test of shale +proppant +broken frac fluid. 1000X

SPE 131782

Test of Onset of Proppant Diagenesis – requires formation to be present.

Diagenetic materials formed on all types of proppant – sand, ceramic, glass, resin coated materials, steel balls, etc.

Cell	Proppant	Fluid	Core Present	Time	Diagenesis Present	Crush % Incr	SPC % decr
1	20/40 HSC	Dry	No	7 days	None	0	12
2	20/40 HSC	DI Water	No	7 days	None	34	11
3	20/40 HSC	DI Water	Pinedale Shale	7 days	None	21	12
4	20/40 HSC	Dry	No	14 days	None	11	2
5	20/40 HSC	DI Water	No	14 days	None	21	7
6	20/40 HSC	DI Water	Pinedale Shale	14 days	Extensive	108	5
7	40/80 LWC	Dry	No	14 days	None	16	
8	40/80 LWC	DI Water	No	14 days	None	26	
9	40/80 LWC	DI Water	Pinedale Shale	14 days	Extensive	52	
10	20/40 Sand	Dry	No	7 days	None	0	(6)
11	20/40 Sand	DI Water	No	7 days	None	43	(3)
12	20/40 Sand	Dry	No	14 days	None	30	(5)
13	20/40 Sand	DI Water	No	14 days	None	43	2
14	20/40 Sand	DI Water	Pinedale Shale	14 days	Extensive	209	(4)
15	40/70 RCS	DI Water	Pinedale Shale	14 days	Extensive	158	

SPE 139875

Same Test with Another Shale

Cell	Proppant	Fluid	Core Present	Time	Diagenesis Present	Crush % Incr	SPC % decr
1	20/40 HSC	DI Water	No	14 days	None	37	19
2	20/40 HSC	2% KCl	No	14 days	None	37	8
3	20/40 HSC	DI Water	Steamboat Shale	14 days	Minor	43	
4	20/40 HSC	DI Water	Steamboat Shale	14 days	None	26	1
5	20/40 HSC	DI Water	No	21 days	None	58	6
6	20/40 HSC	2% KCl	No	21 days	None	29	14
7	20/40 HSC	DI Water	Steamboat Shale	21 days	None	16	24
8	20/40 HSC	Hynsvle Water	No	21 days	None	155	18
9	20/40 HSC	Hynsvle Water	Steamboat Shale	21 days	None	55	9
10	20/40 LWC	DI Water	No	14 days	None	61	7
11	20/40 LWC	DI Water	Steamboat Shale	14 days	1 pellet	76	3
12	20/40 LWC	DI Water	No	21 days	None	97	12
13	20/40 LWC	DI Water	Steamboat Shale	21 days	None	97	6
14	20/40 LWC	Hynsvle Water	No	21 days	None	158	12
15	20/40 LWC	Hynsvle Water	Steamboat Shale	21 days	Moderate	121	22
16	20/40 Sand	DI Water	Steamboat Shale	14 days	Moderate	-4	
17	20/40 Sand	DI Water	Steamboat Shale	21 days	None	187	
18	40/70 RCS	DI Water	Steamboat Shale	14 days	Moderate	93	
19	40/70 RCS	Hynsvle Water	Steamboat Shale	14 days	Moderate	417	

SPE 139875

Shale Reactivity

- Shales reactive in the following manners:
  - Chemical Reactivity
    - Shale units are highly laminated and contain acid soluble minerals
    - Acid soluble minerals are homogenized in the shale bulk matrix and natural fractures
    - Reactive fluids may be capable of etching the face of shale fractures.
    - Aluminum oxide, Al2O3

Water Chemistry Changes

- Water chemistry in the presence of shale (Haynesville) changed out to 240 days

  Ca^{++}, $Si^{+/-}$, Cl^{-}, HCO_3^{-} increases sharply and then decreased=>dissolution followed by precipitation

  – The formation initially weakens, then strengthens.

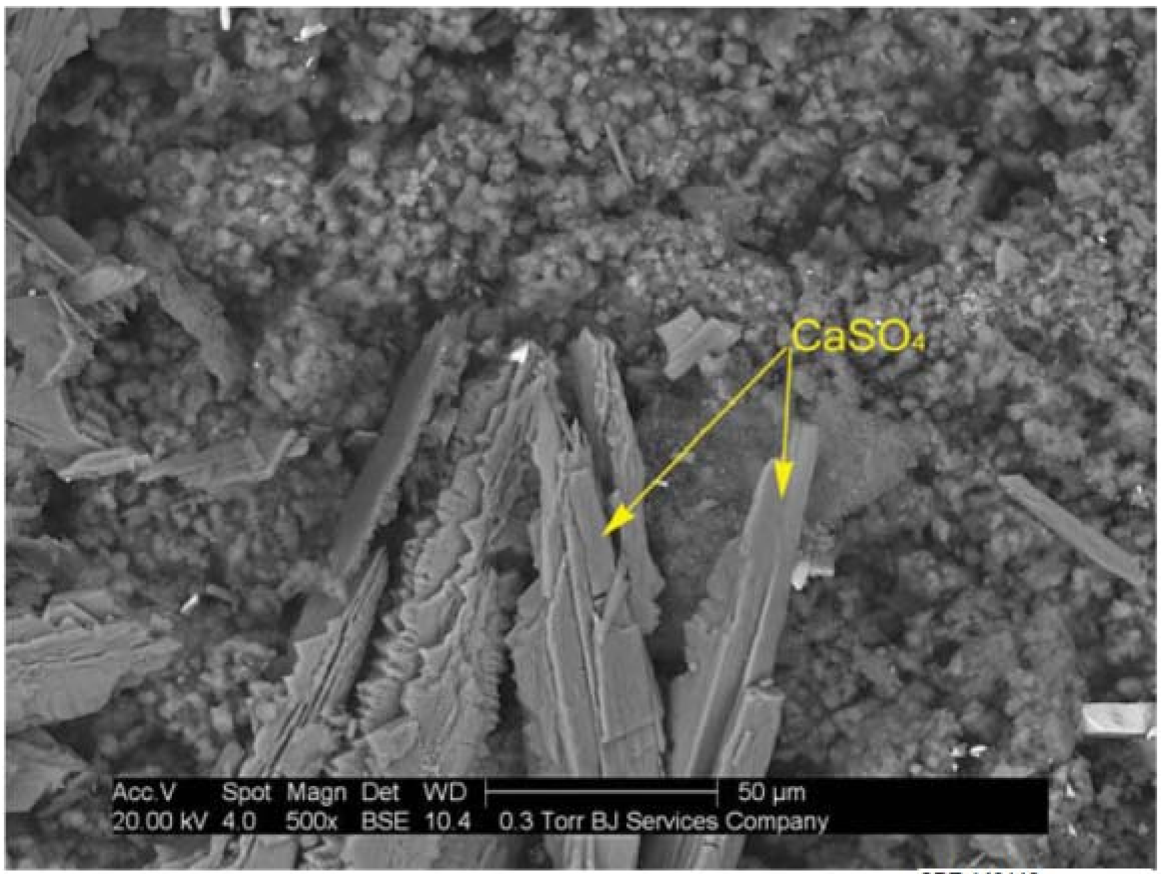
  – There is about a 10% to 20% net strength loss, but that may be due to changes in moisture levels or adjustment of mineral structures to salinity change.

Additive & Formation Degradation Conclusions

- Several chemical and physical actions occuring over time
- Short time tests may be misleading
  - Re-precipitation and Prop/Shale strengthening observed
  - Additives often disappear to absorption, adsorption, precipitation or modification
  - “Lost” additives may or may not come back as extremely dilute solutions.

Proppant Changes

After 120 days of exposure, all the silica in the proppant had been leached out, leaving aluminum oxide behind. Precipitation of minerals on the proppant grains was varied.



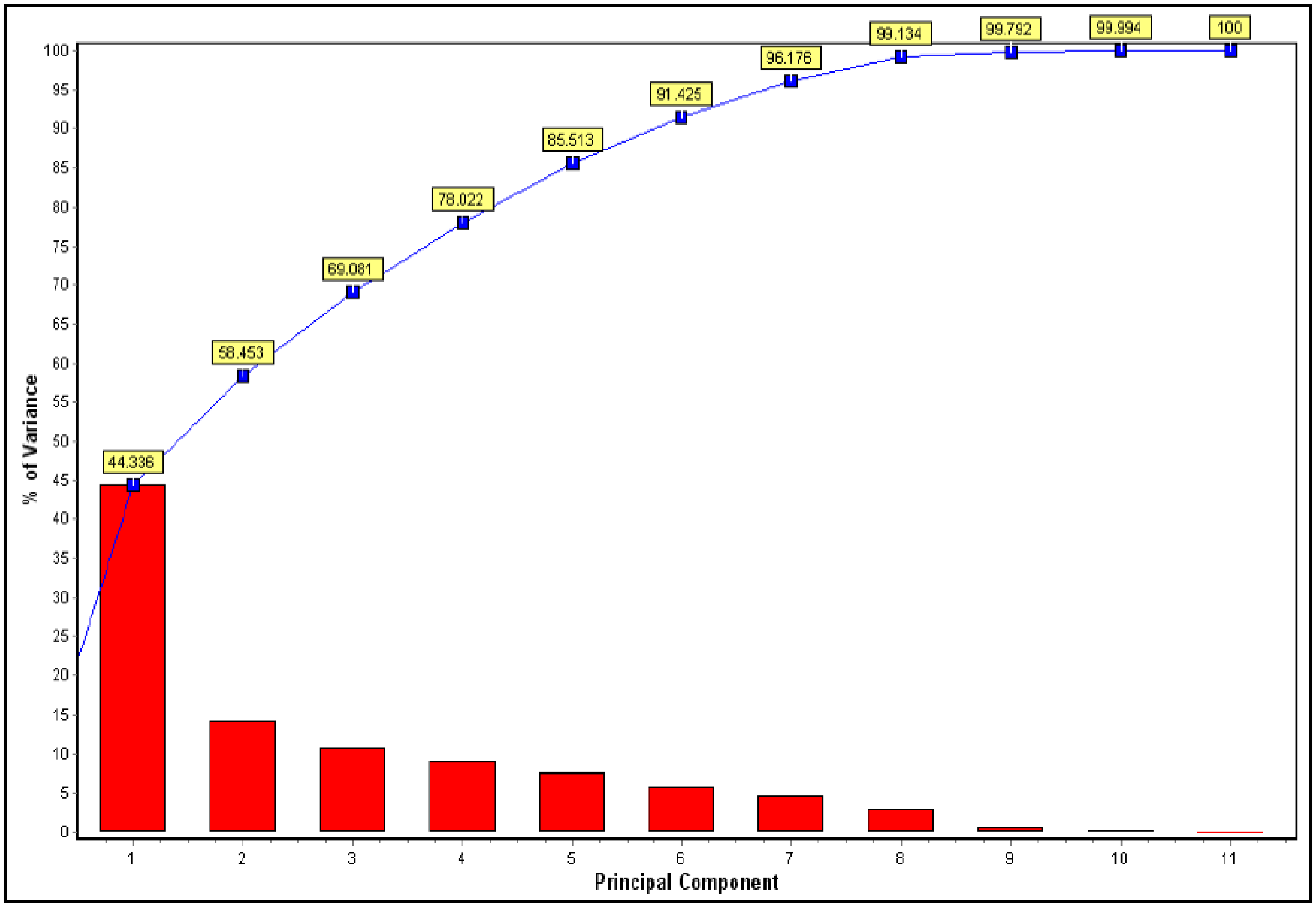
SPE 140110

SEM photo of proppant at 240 days at 500x

Variables that Influence Rock Typing

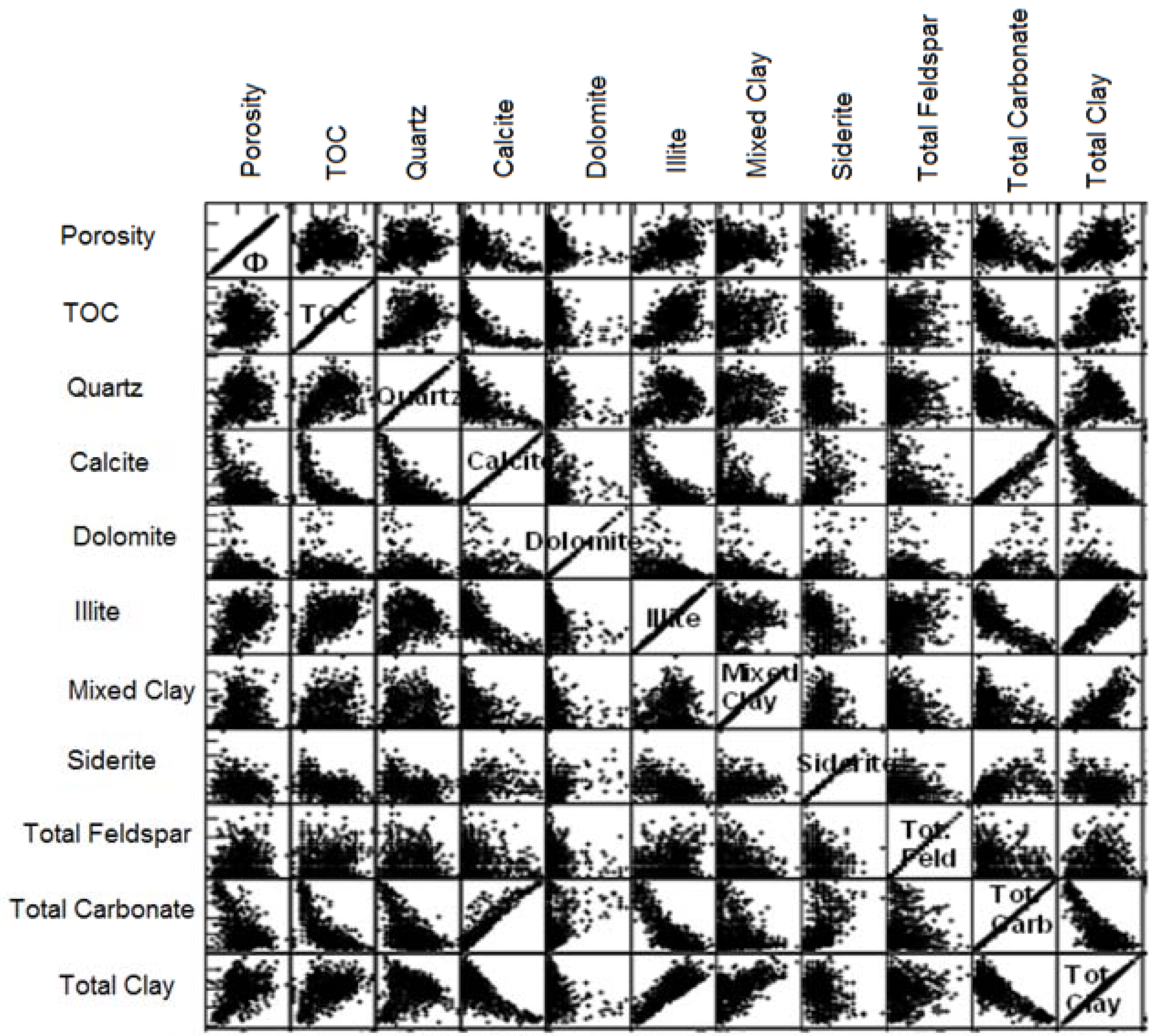
1. Porosity
2. TOC
3. Quartz
4. Calcite
5. Dolomite
6. Illite
7. Mixed Clay
8. Siderite
9. Total feldspar
10. Total Carbonate
11. Total Clay Content

The first three principal components explain almost 70% of the variation in the data set.

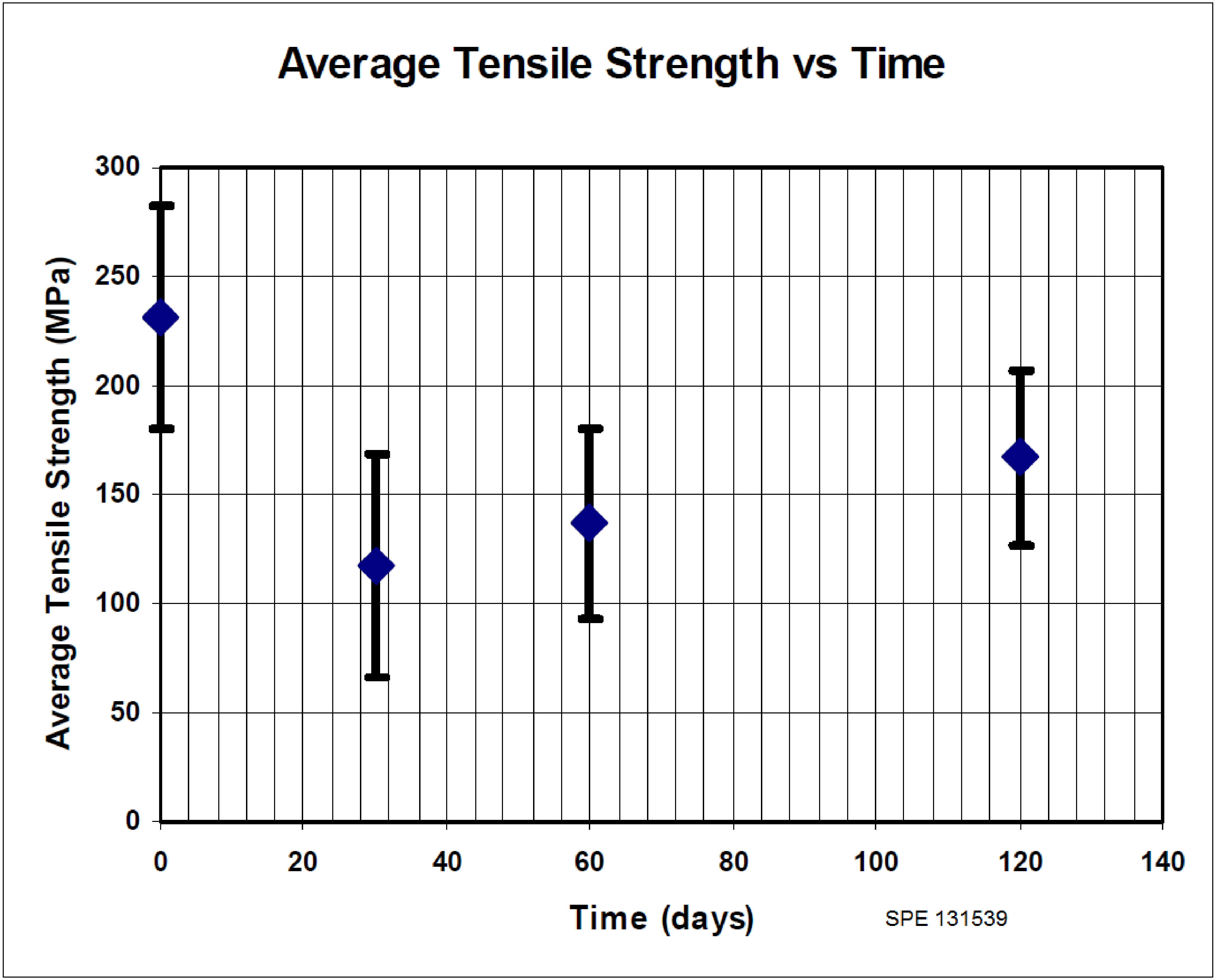


Relationship between the principal components and the variance they explain (11 variables case). SPE 134539

Interactions of Components



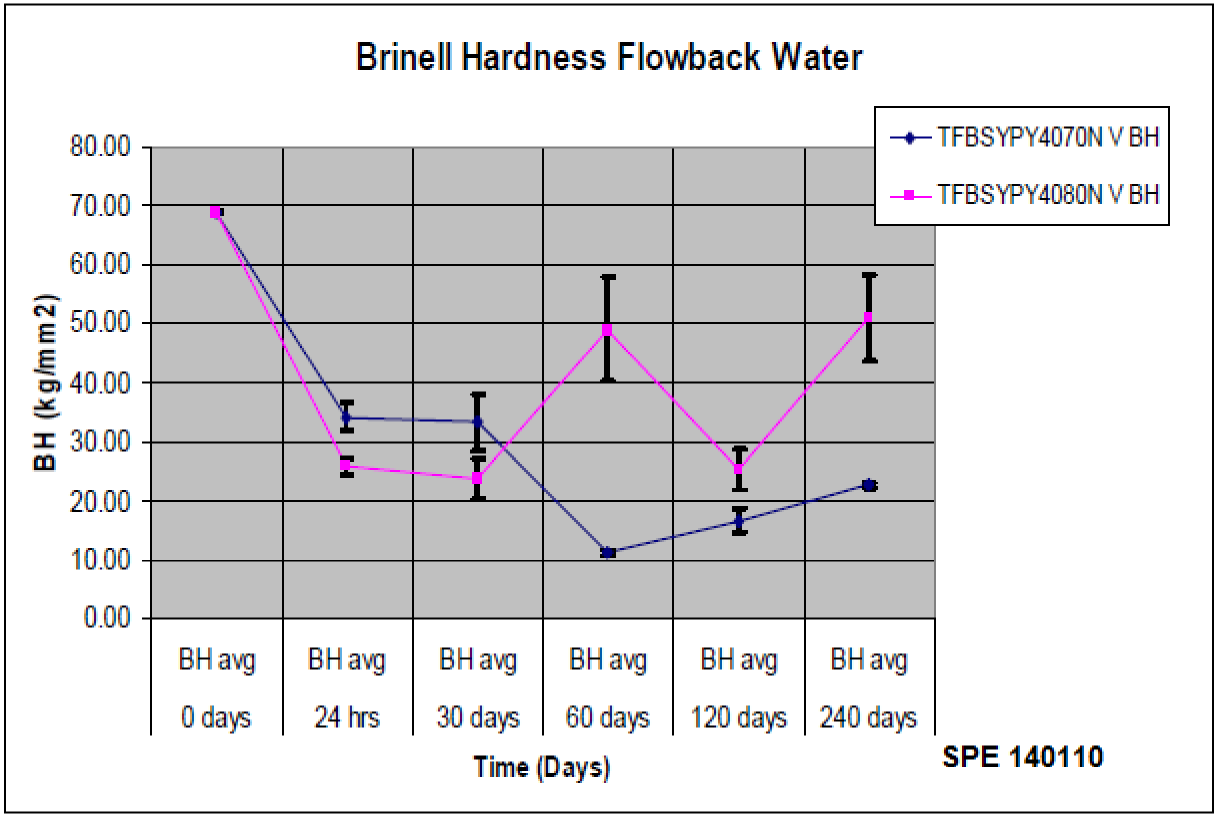
Relationship of Variables -**Modified from Kale, 134539**


Average Tensile Strength vs Time
Average Tensile Strength (MPa)
300
250
200
150
100
50
0
0
20
40
60
80
100
120
140
Time (days)
SPE 131539

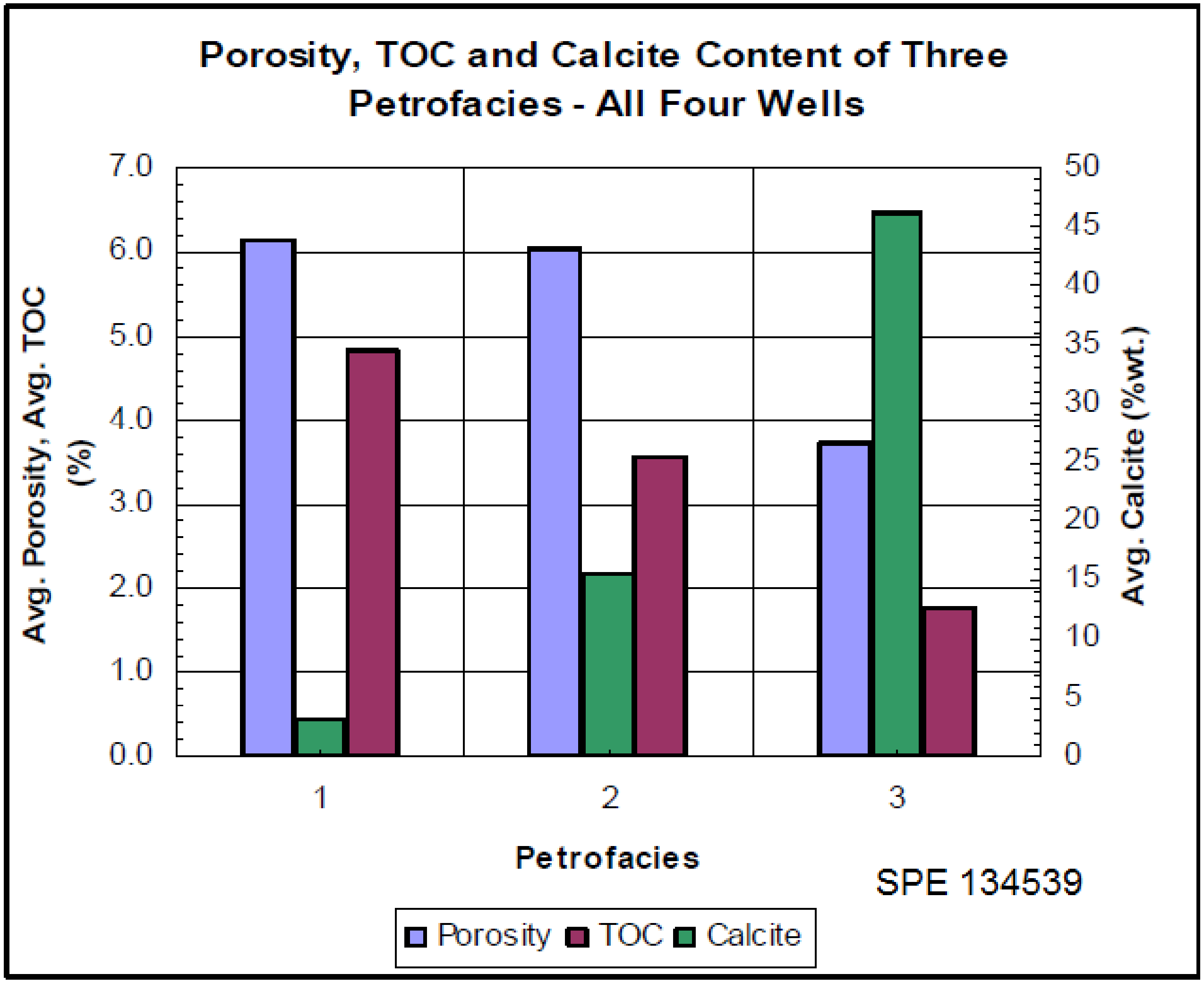
Exposure to Flowback Water

LaFollette, SPE 140110

TDS = 158,000 w/ barium, strontium, sodium and calcium. pH = 5.8.



Petrofacies Variation



Average porosity, TOC and calcite content of three petrofacies in Barnett shale play.

Shales - Composition

- Sedimentary in Nature
  - Seal and gumbo shales high clay content – 40%+ clays, Organic content of 10 to 30+%
  - Gas productive shales – called a shale because of particle size. Actually a siltstone or mudstone. <10 to 30% clay and TOC usually 1% to 8%.
  - Young’s modulus of gas prospective shales plots with tight gas sands – distinctly different from seal and gumbo shales (Britt, 2009)

Core Chemistry / Mineralogy

Core Chemistries

	Chemistry, wt. %				
Shale	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**K_2O+Na_2O**	**$CaO+MgO$**
Pinedale	66.2	20.0	3.2	5.3	3.8
Steamboat	77.0	13.9	2.1	3.0	3.1
Hnysvl/Bssr 1	57.5	20.3	4.9	5.9	10.2
Hnysvl/Bssr 2	61.4	15.5	4.6	5.1	12.7

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Core Mineralogy

	Mineralogy, wt. %				
Shale	**Illite**	**Quartz**	**Kaolinite**	**Calcite**	**Muscovite**
Pinedale	48.6	34.9	11.0	--	--
Steamboat	26.1	56.5	9.3	--	--
Hnysvl/Bssr 1	34.2	25.2	1.5	16.6	17.4
Hnysvl/Bssr 2	29.1	33.4	4.9	14.0	14.9

References

- Al-Bazali, T. M., et.al.: “An experimental Investigation on the Impact of Capillary Pressure, Diffusion Osmosis, and Chemical Osmosis on the Stability and Reservoir Hydrocarbon Capacity of Shales,” SPE 121451 paper and presentation, SPE Offshore Europe Oil and Gas Conference and Exhibition, Aberdeen, UK, 8-11 September 2009.
- Beihoffer, T.W., Dorrough, D.S., Schmidt, D.D.: “The Separation of Electrolyte Effects from Rheological Effects in Studies of Inhibition of Shales with Natural Moisture Content,” SPE 18032, 63rd Annual Conference and Technical Exhibition, Houston, 2-5 October 1988.
- Britt, L.K., Shoeffler, J.: “The Geomechanics of a Shale Play: What makes a Shale Prospective!” SPE 125525, Presented at 2009 SPE Eastern Regional Meeting, Charleston, WV, USA, 23-25 September 2009.
- Dacy, J.M.: “Core Tests for Relative Permeability of Unconventional Gas Reservoirs,” SPE 135427 paper and presentation, SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September 2010.
- Deenadayalu, C., Suarez-Rivera, R.: “The Effect of Horizontal Completions on the Breakdown Pressures of Anisotropic Gas Shale,” ARMA 10-477, Salt Lake City Utah, 27-30 June 2010.
- Duenckel, R., et. Al.: “Proppant Diagenesis – Integrated Analysis Provide New Insights into Origin, Occurrence, and Implications for Proppant Performance,” SPE 139875 paper and presentation, SPE Hydraulic Fracturing Technology Conference and Exhibition, The Woodlands, TX, USA, 24-26
- Freeman, C.M.: A Numerical Study of Microscale Flow Behavior in Tight Gas and Shale Gas Reservoir Systems,” SPE 141125 paper and presentation, SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September 2010.
- Grieser, B., Wheaton, B., Magness, B., Blauch, M., Loghry, R.: “Surface Reactive Fluid’s Effect on Shale,” SPE 106815, 2007 SPE Production and Operations Symposium, Oklahoma City, OK, USA, 31 March – 3 April 2007.
- Kale, S., Rai, C.S., Sondergeld, C.H.: “Rock Typing in Gas Shales,” SPE 134539 paper and presentation, SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September 2010.
- King, G.E.: “Thirty Years of Gas Shale Fracturing: What Have We Learned?, SPE 133456 paper and presentation, SPE Annual Technical Conference and Exhibition, Florence, Italy, 19-22 September 2010.
- King, G.E., Lee, R.M.: “Adsorption and Chlorination of Mutual Solvents Used in Acidizing,” SPE 14432, SPE Production Engineering, May 1988, p205-
- LaFollette, R. F., Carman, P. S.: “Proppant Diagenesis: Results So Far,” SPE 131782 presentation and Paper, SPE Unconventional Gas Conference, Pittsburgh, PA, 23-25 February 2010.
- LaFollette, R. F., Carman, P. S.: “Long Term Stability of Proppants Exposed to Harsh Shale Reservoir Conditions,” SPE 140110 paper and presentation, SPE Hydraulic Fracturing Technology Conference and Exhibition, The Woodlands, TX, USA, 24-26
- Milner, M., Petriello, J., McLin, R., Gathogo, P: “Imaging Texture and Porosity in Mudstone and Shale: Findings from Petrographic, Secondary, and Ion-Milled Backscatter, SEM Methods,” 4th B.C. Unconventional Gas Technical Forum, April 2010.
- Muniz, E.S., da Fontoura, S. A. B., Lomba, R.F.T.: “Development of Equipment and Testing Methodilogy to Evaluate Rock-Drilling Fluid Interaction,” ARMA/NARMS 04-599, 2004 6th North America Rock Mechanics Symposium, Houston, TX, 5-9 June 2004.
- Muniz, E.S., da Fontoura, S. A. B., Durate, R.G., Lomba, R.F.T.: “Evaluation of the Shale-Drilling Interaction for Studies of Wellbore Stability,” ARMA/USRMS 05-816, Alaskan Rocks 2005, Anchorage, Alaska, 25-29 June 2005.
- Sarwar, M.U.: “Gel Degradation Studies of Oxidative and Enzyme Breakers to Optimize Breaker Type and Concentration for Effective Break Profiles at Low and Medium Temperature Ranges,” SPE 140520 paper and presentation, SPE Hydraulic Fracturing Technology Conference and Exhibition, The Woodlands, TX, USA, 24-26 January 2011.
- Tutuncu, A.N.: “Anisotrophy, Compaction and Dispersion Characteristics of Reservoir and Seal Shales,” ARMA 10-344, Salt Lake City City, UT, 27-30 June 2010.
- Van Oort, E., Hale, A.H., Mody, F.K.: “Manipulation of Coupled Osmotic Flows for Stabilization of Shales Exposed to Water-Based Fluids,” SPE 20499. Annual Technical Conference and Exhibition, 22-25 October 1995.

Fracture Fluid Additive and Formation Degradations

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The focus of this presentation is on reactions that describe the degradation of fracturing fluids and formations during the hydraulic fracturing process and the clean-up period of 2 to 6 weeks following the fracturing application. A description of the primary chemical reaction controls, namely permeability and area-to-volume ratio, precedes a discussion of the better known and more common degradation reactions. Although shale formations will be highlighted because of media attention, other formations will be covered as well.

Reactions in wells are subject to most normal catalytic and restriction influences, but also have a set of specific limiters that are found in few other places in chemical industry. Reaction influences of temperature and pressure are reasonably predictable, but other reaction controls such as reaction rate are strongly influenced by the area and mixing constraints described by location of the reaction, the area-to-volume ratio and the behavior and stability of the by-products. The reaction zones include:

- Open wellbore - a zone of high energy but small area in which reactions are possible but segregation of sequenced reactants can be enforced by turbulence during their one-time passage through the wellbore where area-to-volume ratio is sub 1:1.
- Hydraulic fracture – mostly singular in a vertical well and usually narrow (~3mm to 25mm) slit where chemical reactions that depend on diffusion are limited by the pump rate and reactants may be quickly lost to the natural fractures or matrix through leak-off generated by pressure differential and controlled by the permeability to those side connections. Area-to-volume ratio is 8 to 50 for normal fracture widths.
- Natural fractures – very narrow (~0.01mm to 1mm) but numerous slits that may or may not be continuous in even a small area. Area-to-Volume ratios range from 100:1 to over 1000:1.
- Matrix or interstitial porosity – a potentially highly reactive zone because of the ratio of the very large surface area-to-volume of fluid ratio (order of 20,000:1 to 30,000:1).

Reactive target potential in the previously described zones include rock and minerals, metal, cement and a typically short-list of chemical additives used in the wells to facilitate control of natural mineral reactions, transport of solids (e.g., cuttings and proppant), and permit physical reactions (i.e., fracturing) that can create, widen and/or stabilize a flow path of improved permeability to allow the formation fluids to flow to the wellbore.

The primary down-hole limit to any chemical or physical reaction is access. Permeability (a measure of ability to flow a fluid through a rock) is the fundamental restriction to fluid flow.

Once the potential reactant has reached the zone of reaction, the area-to-volume ratio is a primary influence on most reactions. Diffusion, the ability to get reactants to the site and move products away, is controlled by area-to-volume ratio, the permeability of routes to and from the reaction and the type and behavior of by-products themselves.

Degradation reactions involving well construction and operation issues include pipe stability and cement stability, which are mostly chemical concerns. Although physical reactions such as pipe collapse, burst, tension failures and erosion are known to occur, their behavior has been well described and adequate controls appear to be in place based on the population of 50+ year old wells still producing and passing mechanical integrity tests.

Cementing stability and degradation have been addressed in the petroleum engineering literature by more than eleven thousand general papers and over six hundred that comment directly on cement degradation reactions and blocking mechanisms. This discussion has covered mineral and organic acids, CO_2, H_2S, thermal, low pH waters, sulfate effects, cyclic pressure behavior, long term performance and other issues. Reactions that deteriorate cement are easily demonstrated in the laboratory in beakers but are reduced exponentially when issues of access are considered. All reactions depend on access and the low permeability of the formations surrounding the numerous formation barrier seal areas, coupled with the extremely low permeability of the cement itself make significant deterioration reactions unlikely if not practically impossible. Added to this are instability and quick precipitation of common reaction by-products that form an impenetrable barrier on most reaction surfaces. Additives that reduce cement degradation include those for sulfate resistant cement, special thermal compositions for very high temperature wells, a variety of additives that reduce cement permeability, improve strength and chemical and physical treatment to improve bonding. Problems with cement almost universally are traced to poor application during well construction.

Pipe reactions are mostly corrosion and erosion-corrosion. These reactions are also well known with over two thousand papers in petroleum engineering literature of direct application of wells and pipelines. These reactions are most common in long term production with acid gases (CO_2 and H_2S) and the short term contact of mineral and organic acids during acid stimulation. Because of the short duration of the frac and the very small amount of weak mineral acid used as a breakdown stage, the effect of corrosion or erosion-corrosion during a fracturing job is negligible.

Formation degradation during fracturing is possible, but sharply limited by access. Higher permeability conventional formations, sandstones and carbonates with permeability over about 1 mD, are largely inert to reactions with waters used in fracturing except for the limited swelling reactions of smectite and a few mixed layer clays. Reactions in shale are still being researched, but access is still the dominant control. Examples of reactions in the accessible zone of fracture between proppant, shale formation and waters are being researched and results of two recent papers are presented.

Chemical additive reactions resulting in degradation or disappearance of the chemicals are presented. These reactions include gel breaking, adsorption, absorption, capillary trapping and precipitation. Examples of each of these mechanisms will be discussed. Nearly fourteen thousand papers in the petroleum engineering literature deal with subjects of sorption, gel breaking and capillary effects.