GEO

Drilling Fluids, Inc.

Brine Fluids

Introduction

Reduced borehole skin damage
Improved permeability
Reduced mechanical problems with completion and production equipment
Solids free fluids

Undissolved solids are a major contributor to formation damage. Use of solids-free fluids for completion and remedial work have resulted in increased production and faster recovery. Fresh water use is avoided to prevent clay hydration in dirty-sand reservoirs. Various salts are used for inhibition of clays. Water with dissolved salts of any species is referred to as a brine. Cost-effective formulations for various densities can be obtained by combining different salts.

The higher initial cost of brine fluids is easily recouped through significant productivity gains for oil and gas wells when compared to fresh water or “mud” completions. When used in drilling applications, the near solids-free nature of clear brine fluids and the controlled high-densities they achieve, contribute to stabilization of sensitive formations. Additionally, when utilized as a Drill-In Fluid the low solids nature of brine fluids contribute to increased penetration rate and lower abrasion for longer bit life.

Completion Methods

Fluid	Density Range ppg	Usable Temperature (°F)	Stability (Static)	Clay Reactions	Corrosion
Gas					
Air/Natural gas	0 to 8.3	all	unlimited	-----	minor
Mist	0 to 8.3	32 to 212	none	minor	variable
Foam	0 to 8.3	32 to 212	limited	minor	variable
Methanol	6.6	-146 to 148	unlimited	minor	variable
Oil					
Diesel	7.03	-12 to 660	very long	----	----
Crude (treated)	7 to 8		very long	----	----
Emulsions	7 to 8.3		long	minor	minor
Weighted Oil	7 to 17		variable	----	----
Weighted Emulsions	8.3 to 17		long	minor	minor
Water					
Fresh	8.3	32 to 212	unlimited	none to extreme	variable
Seawater (treated)	8.5	32 to 212	very long	none to extreme	minor
Brines					
KCl	8.3 to 9.7	-29	very long	none to minor	minor
NaCl	8.3 to 10.0	-29	very long	none to minor	minor
$CaCl_2$	8.3 to 11.6	-51	very long	none to minor	minor
$CaBr_2$	8.3 to 15.2	-12	very long	none to minor	moderate
$ZnBr_2$	8.3 to 19.2	-40	very long	none to moderate	major
Weighted Water/ Brine					
Salt	8.3 to 15		short to very long	none to major	minor
Carbonates	8.3 to 17		short to very long	variable	variable

Maximum Density

The maximum density of a solids-free fluid depends on the type of salt used. Each salt has a maximum concentration before it reaches saturation. The table below indicates the maximum densities of various brines. Thermal expansion of the water effects the density of a clear brine. At elevated temperatures the density decreases. Densities are reported at a specific temperature such as 70°F.
Combinations of salts can be used to economically achieve densities from 8.34 pg to 19.2 ppg.

$D_t=D_0/(1+$ßAT$)$

- **D_t** = density at desired temperature
- **D_0** = density at 70ºF
- **ß** = coefficient of thermal expansion
- **AT** = temperature desired less 70ºF

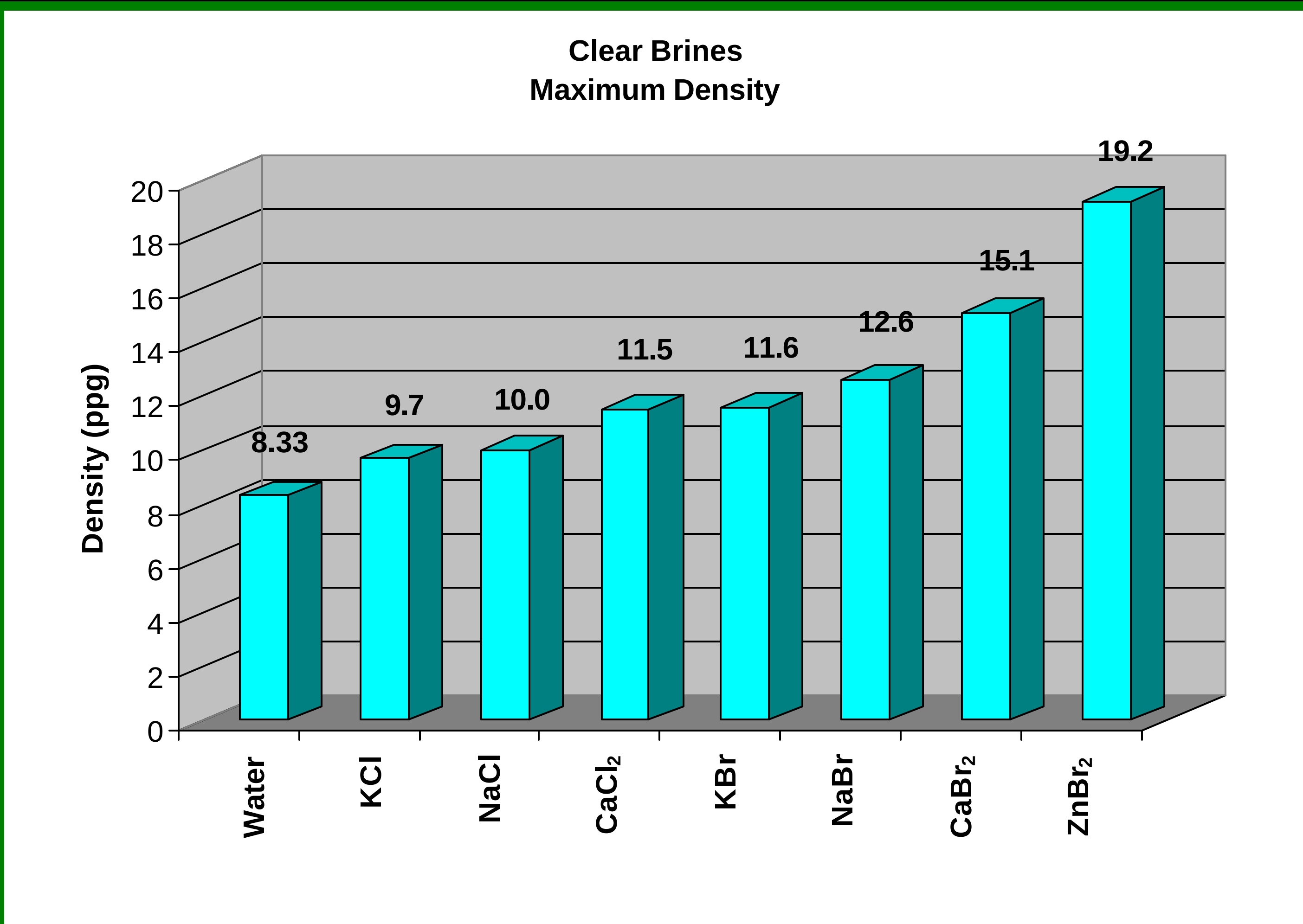
Brine Fluids

Applications

- Drilling Fluids
- Packer Fluids
- Gravel-Pack Fluids
- Perforating Fluids
- Under-reaming Fluids
- Work-over Kill Fluids

Systems

- Potassium Chloride ....KCl
- Sodium Chloride ....NaCl
- Potassium Bromide ....KBr
- Calcium Chloride .... $CaCl_2$
- Sodium Bromide ....NaBr
- Calcium Bromide .... $CaBr_2$
- Zinc Bromide ....$ZnBr_2$

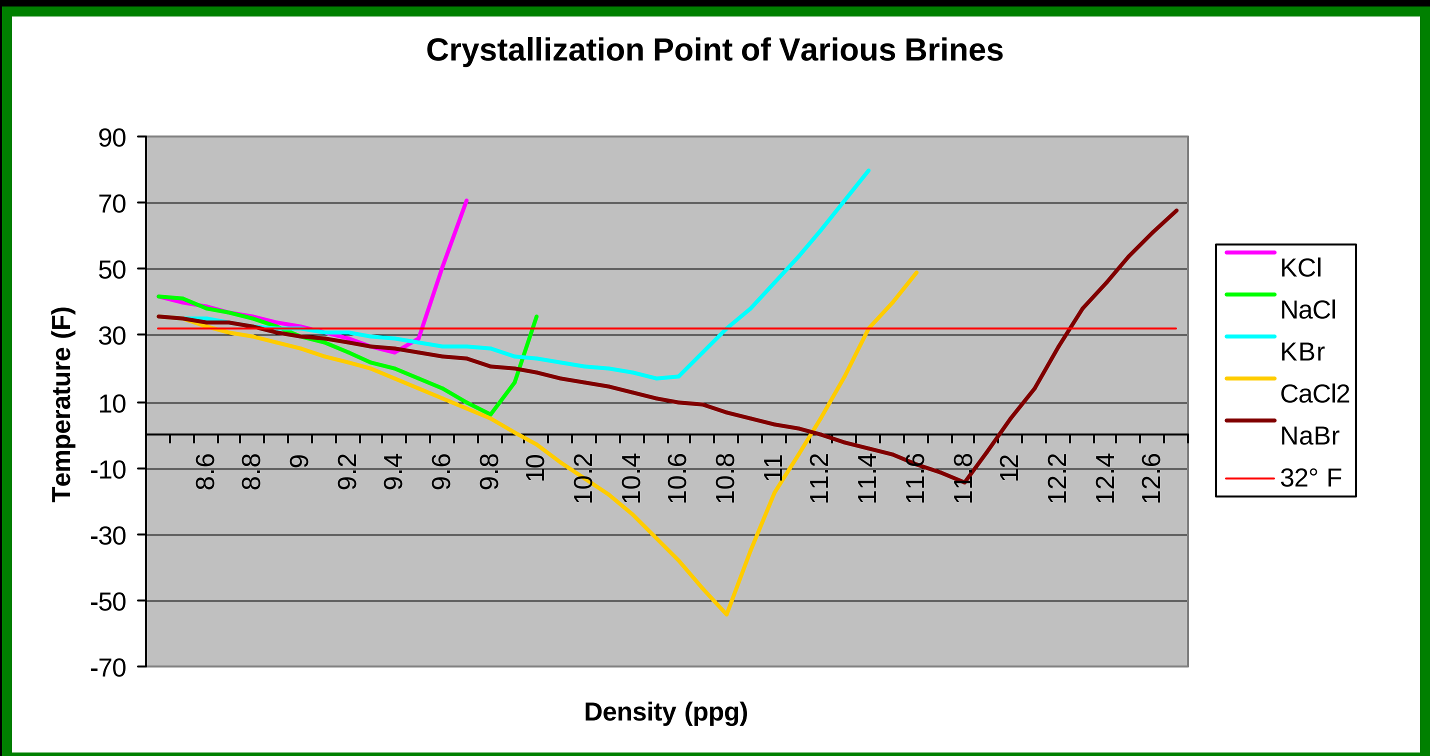


Crystallization

When a saturated brine is heated, the water expands and more salt can be added. As the temperature is lowered saturated brine becomes super saturated and salt begins to crystallize and fall out. The point where precipitation begins in a fluid saturated at 60°F is know as the crystallization point. Cost and formulations of brine fluids vary greatly depending on crystallization points. It is important to determine the maximum crystallization point that can be safely handled in the field. This is particularly true in marine risers.
Calcium chloride and all bromide based brines are more sensitive to the effects of thermal expansion. Coefficients of thermal expansion can be used to calculate density effects using the following formula.

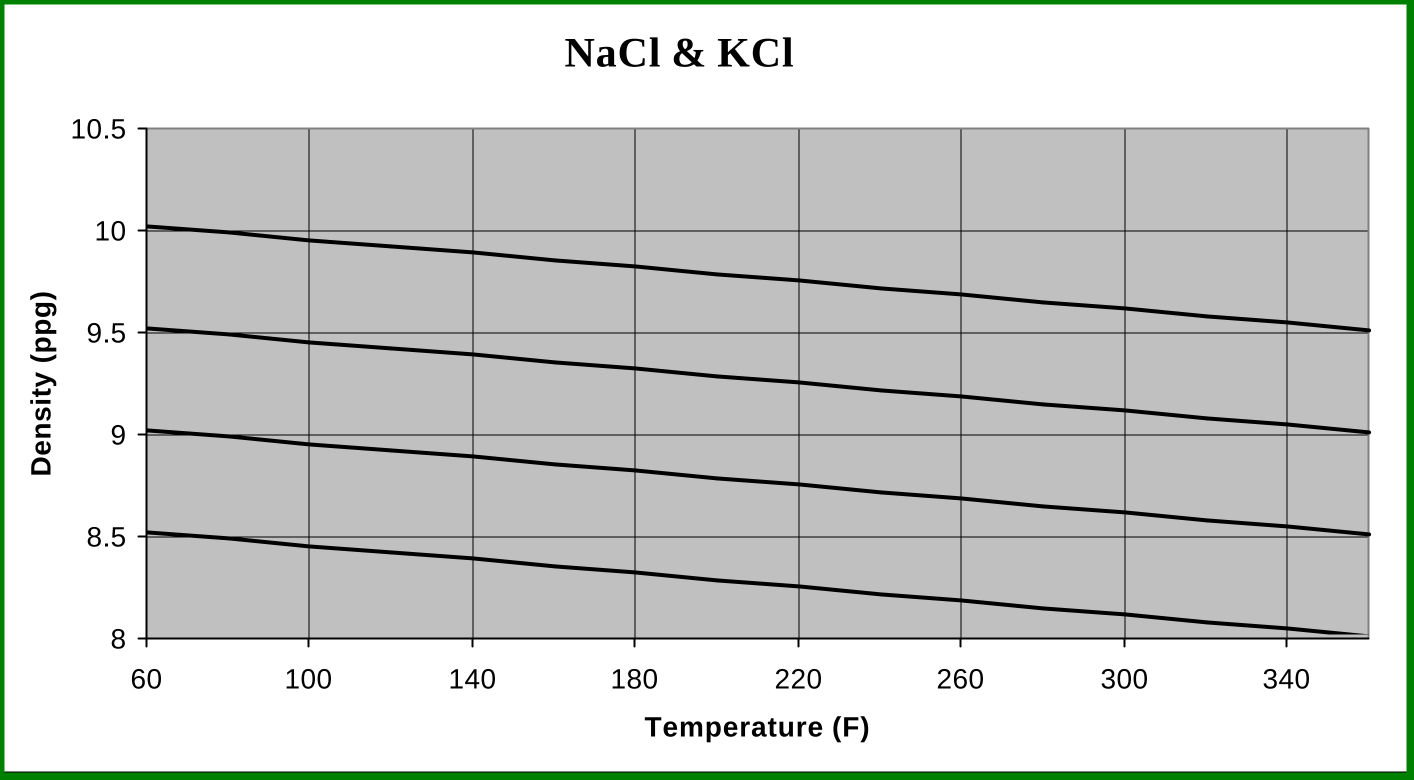
Maintenance

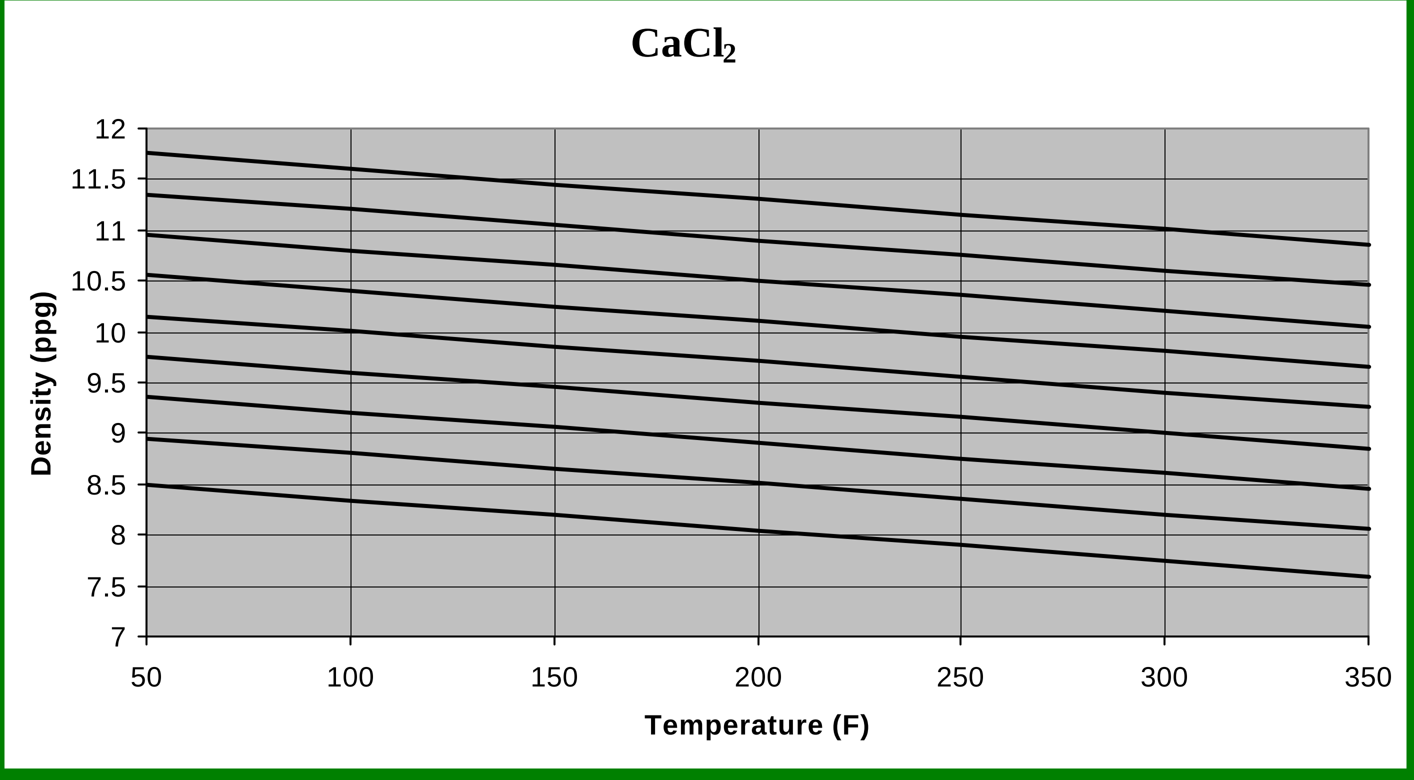
Brine fluids are easier to maintain than mud systems. Many ingredients make up mud systems which must be kept in proper balance. With no solids being added, brine fluids can be properly maintained with routine filtration and pH adjustment. The corrosion rates of brine fluids need to be considered when in use or storage.
Densities higher than saturation can be obtained with produced brine and other sodium chloride (NaCl) based waters by the addition of either sized NaCl , calcium carbonate ($CaCO_3$), or iron carbonate (siderite), in conjunction with polymer viscosifiers. The carbonate materials are considered to be highly acid soluble and can therefore be easily removed from the face of the formation. The sized NaCl crystals can also be easily removed since they are water soluble and will be dissolved by any water less than saturated, such as produced fluids. These materials are usually supplied in graded sizes to assist in controlling the filtrate of the completion fluid.

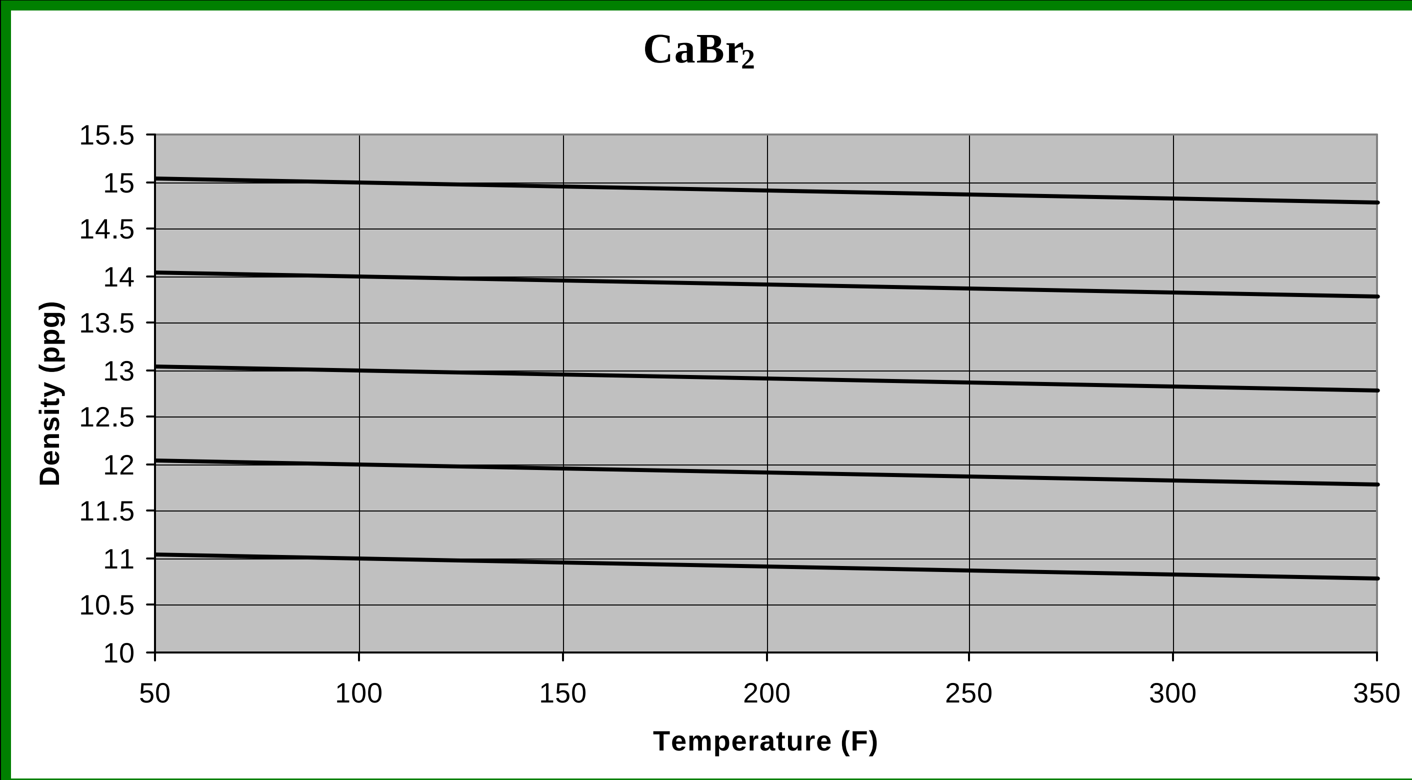


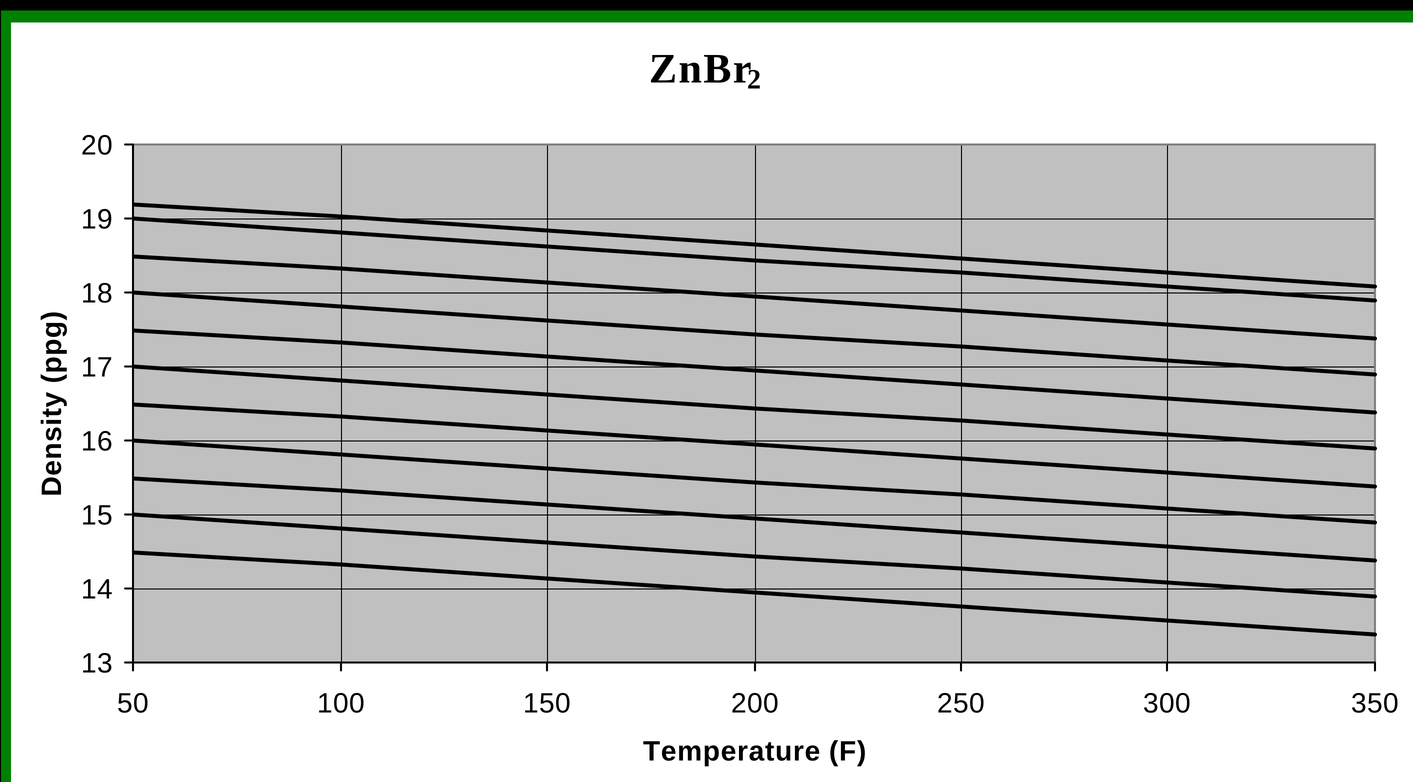
Thermal Expansion

Chloride Brines

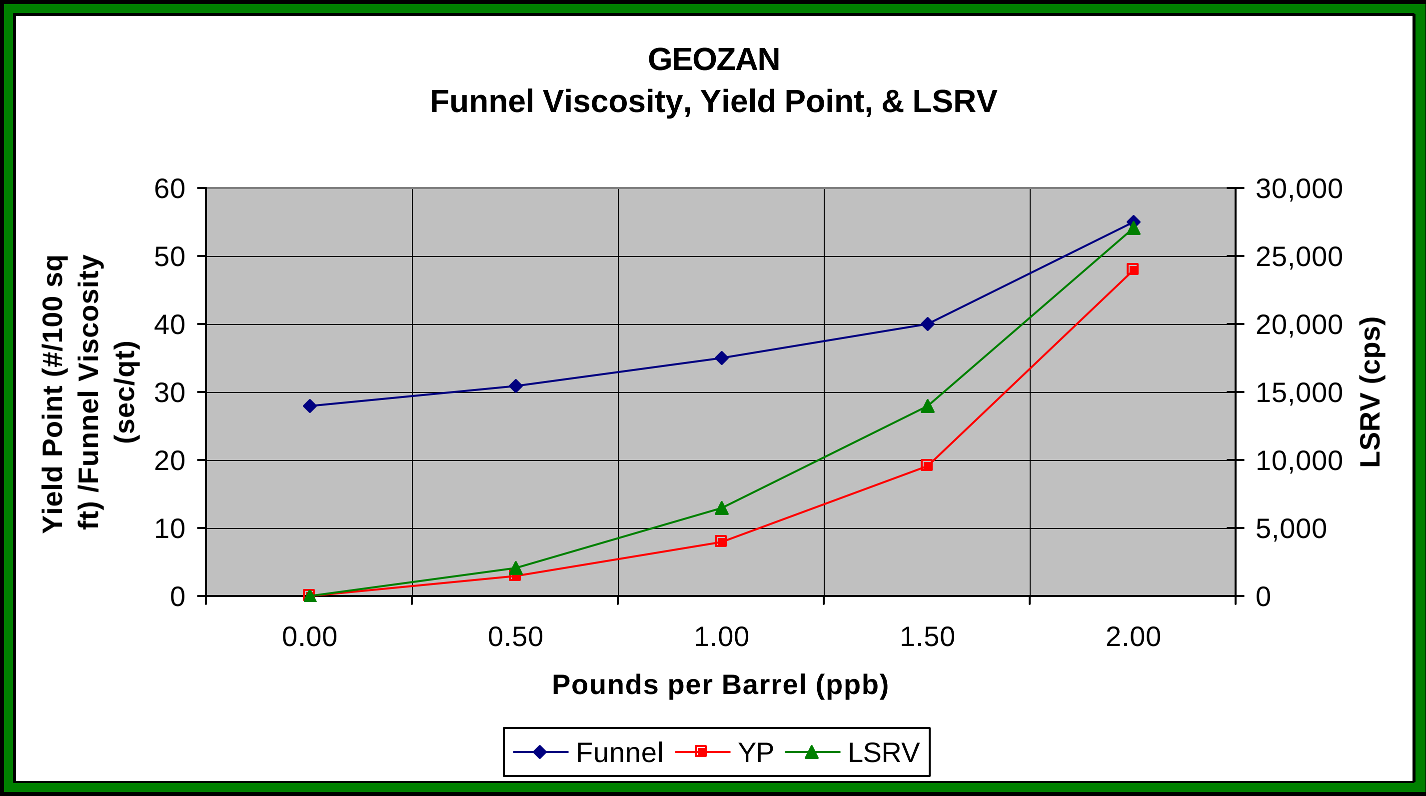


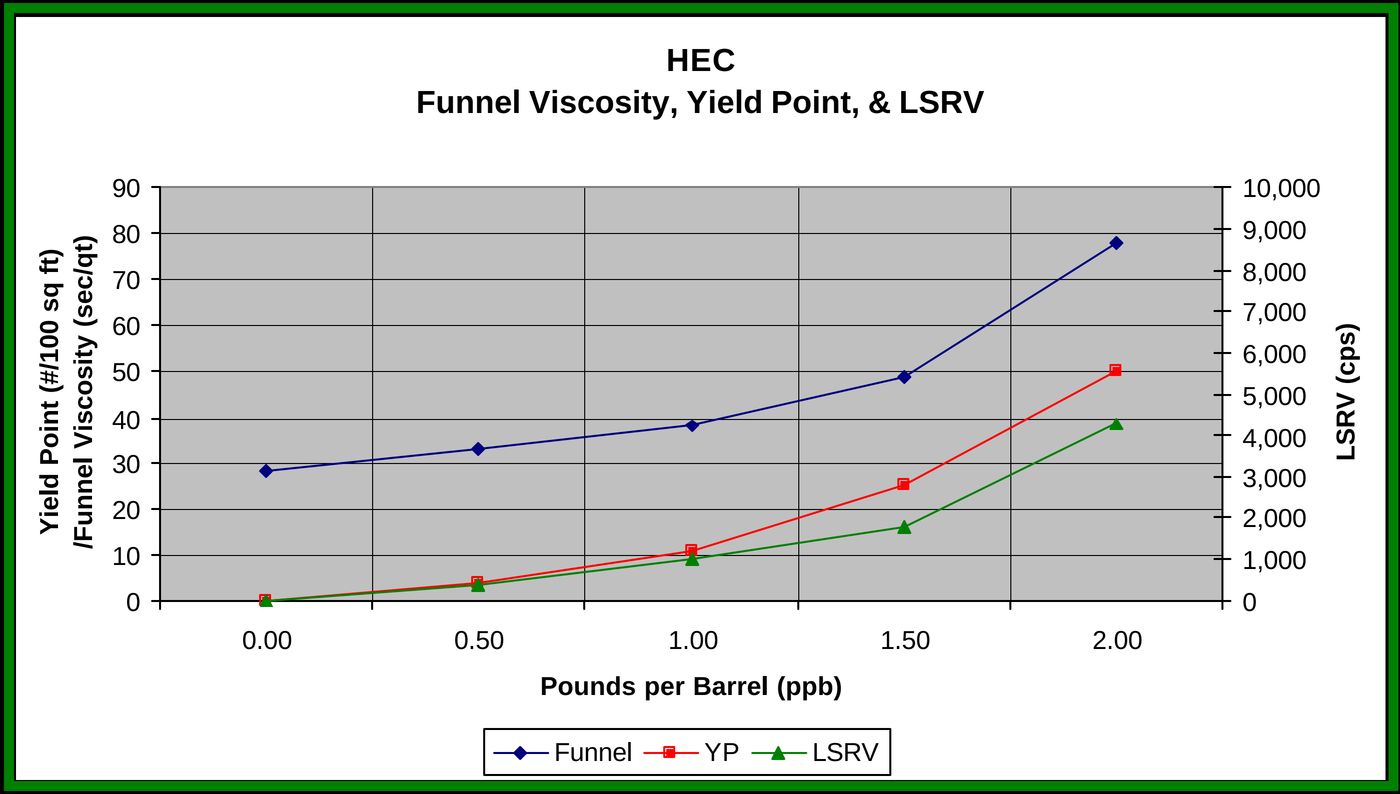



CaBr2
15.5
15
14.5
14
13.5
13
12.5
12
11.5
11
10.5
10
Density (ppg)
50
100
150
200
250
300
350
Temperature (F)


ZnBr2
20
19
18
17
16
15
14
13
Density (ppg)
50
100
150
200
250
300
350
Temperature (F)

Fluid Additives for Controlling Viscosity





HEC vs. GEOZAN

	HEC	GEOZAN
Advantages	High viscosity with very high Yield Point is easily attained with HEC. Viscosity is easily "broken" with either enzymes or Hypochlorite. The product is naturally biodegradable and has been used for years as the completion fluid of choice. The ability to control settling can be advantageous in gravel packs.	Provides a clear fluid with Gel Strengths to suspend cuttings when circulation is interrupted. Exhibits high shear stress at low shear rates for improved cuttings transport in horizontal wells. Provides some filtrate loss control.
Disadvantages	HEC will not provide Gel strengths regardless of concentration. Does not suspend solids well when circulation is stopped. Does not control wellbore slough. Provides no fluid loss control on its own. At temperatures above 125^{o}F viscosity is greatly reduced.	Does not degrade as readily as HEC. Due to its intrinsic viscosity it is potentially more damaging to production unless properly broken.
Polymer Breakers		
Sodium Hypochlorite Solution of Sodium Hypochlorite in water has a pH of 10-12. Break is not as "clean" as with Lithium Hypochlorite.	Effectively degrades the viscosity of HEC by breaking the molecular chain. Reaction time is slow and the resulting by-products have a molecular weight in the 20,000 range. This may cause some formation damage.	Given enough time and temperature the viscosity of GEOZAN is greatly reduced but not degraded. Stability up to 260^{o}F requires no additional treatment. Stability up to 315^{o}F is possible with addition of special salts.
Lithium Hypochlorite Personal safety considerations are more stringent than with Sodium Hypochlorite or SDIC. Solution of Lithium Hypochlorite in water has a pH of 11-12.	Works by a similar mechanism as Sodium Hypochlorite but is somewhat faster. Lithium Hypochlorite provides a cleaner break than Sodium Hypochlorite with smaller residual solids.	Effectively degrades the viscosity of GEOZAN over time. Much faster with increased temperature. Continues to have some residual fluid loss characteristics after breaking but cleaner than Sodium Hypochlorite.
SDIC Solution of SDIC in water has a pH of 5-6. Research shows SDIC to provide a "break" cleaner than Hypochlorite.	Effective breaker for immediate degradation of HEC polymer. Cannot be time delayed like H-Break 100. Cleaner break than Lithium Hypochlorite.	Breaks the viscosity of Xathan Gum polymers more quickly and completely than Lithium Hypochlorite. Exhibits no residual filtrate loss.
H-Break 100 pH is adjusted to suit the drilling fluid. Activation with mild acid. H-Break 100 is not a corrosive product.	An Enzyme Breaker specific to HEC. The enzymes attack the polymer at every molecular branch. They continue to move from site to site until all the HEC has been degraded. The resulting by-products are simple sugars with a molecular weight in the 20 range. Can be controlled with pH so that it is inactive when added but can be activated later. Follows any fluid lost to the formation degrading it to molecules small enough to easily flow through producing formations.	Not applicable. While claims of an enzyme breaker for Xanvis have been made the manufacturer of Xanvis has not seen an example and we have not found such a product.

Brine Properties

Preparing Brines

Brine fluids can be prepared with one salt or a combination of salts. The desired density will determine which salts to use. In many cases Potassium Chloride is the salt of choice because of its superior inhibiting properties.

When preparing a brine solution first select the desired density or the desired concentration (% by Weight). The percentage of fresh water to use is given in each of the tables, Potassium Chloride, Sodium Chloride, and Calcium Chloride, under the heading "Volume to "Pounds per finished Start". The number of pounds to be added for each finished barrel is given under the heading bbl".

Potassium Chloride

KCl % by Weight	Density (ppg)	Pounds per finished bbl	Volume to Start	Cl- (mg/l)	K+ (mg/l)	KCl (mg/l)	Crystallization Point, °F
1%	8.39	3.5	99.46%	4,786	5,278	10,064	37
2%	8.44	7.07	99.08%	9,608	10,596	20,203	36
3%	8.5	10.67	98.69%	14,500	15,991	30,491	35
4%	8.55	14.35	98.29%	19,464	21,465	40,928	34
5%	8.6	18.03	97.88%	24,498	27,017	51,515	34
6%	8.66	21.77	97.47%	29,603	32,647	62,250	33
7%	8.71	25.55	97.04%	34,744	38,316	73,060	32
8%	8.77	29.4	96.60%	39,955	44,064	84,019	31
9%	8.82	33.29	96.16%	45,238	49,889	95,127	31
10%	8.88	37.21	95.70%	50,556	55,754	106,310	29
12%	8.99	45.23	94.76%	61,440	67,757	129,197	28
14%	9.11	53.46	93.78%	72,607	80,073	152,680	26
16%	9.22	61.86	92.77%	84,023	92,663	176,686	24
18%	9.34	70.47	91.71%	95,758	105,605	201,362	22
20%	9.46	79.33	90.62%	107,741	118,820	226,560	24
24%	9.7	97.63	88.33%	120,043	132,387	252,430	66

Sodium Chloride

NaCl % by Weight	Density (ppg)	Pounds per finished bbl	Volume to Start	Cl- (mg/l)	Na+ (mg/l)	NaCl (mg/l)	Crystallization Point, °F
1	8.39	3.54	0.9953	6,098	3,954	10,052	31
2	8.45	7.07	0.9922	12,267	7,954	20,221	29
3	8.51	10.71	0.989	18,542	12,024	30,565	28
4	8.57	14.39	0.9857	24,923	16,162	41,085	27
5	8.63	18.1	0.9823	31,376	20,346	51,722	27
6	8.69	21.98	0.9788	37,899	24,576	62,475	26
7	8.76	25.7	0.9752	44,529	28,875	73,404	25
8	8.82	29.58	0.9714	51,229	33,220	84,449	24
9	8.88	33.5	0.9676	58,036	37,634	95,670	24
10	8.94	37.49	0.9636	64,949	42,117	107,067	22
12	9.07	45.61	0.9554	79,024	51,244	130,268	19
14	9.19	53.95	0.9467	93,489	60,624	154,113	14
16	9.32	62.52	0.9376	108,343	70,257	178,600	12
18	9.45	71.31	0.9281	123,588	80,142	203,730	9
20	9.58	80.38	0.9182	139,258	90,304	229,562	3
22	9.72	89.65	0.9079	155,354	100,741	256,095	0
24	9.86	99.17	0.8971	171,875	111,454	283,329	-5
26	10	108.98	0.8859	188,821	122,444	311,265	25

Calcium Chloride — Using 94%-97% $CaCl_2$

$CaCl_2$ % by weight	Density (ppg)	Pounds per finished bbl	Volume to Start	Ca+ (mg/l)	Cl- (mg/l)	$CaCl_2$ (mg/l)	Crystallization Point, °F
0.9%	8.4	3	0.997	5,485	3,100	8,585	31
2.2%	8.54	10.75	0.9945	14,403	8,141	22,544	30
3.6%	8.6	13	0.992	23,569	13,322	36,891	28
4.6%	8.68	18.2	0.9907	30,070	16,996	47,066	26
5.5%	8.75	22.02	0.9893	36,780	20,789	57,569	25
6.5%	8.8	24	0.988	43,487	24,580	68,067	25
7.4%	8.9	29.86	0.9847	50,132	28,336	78,467	23
8.3%	8.97	33.85	0.9813	56,770	32,088	88,858	22
9.3%	9	35	0.978	63,543	35,916	99,459	21
11.9%	9.2	46	0.971	82,352	46,548	128,901	17
14.7%	9.4	58	0.962	103,379	58,433	161,812	12
16.0%	9.5	63.78	0.956	114,636	64,796	179,431	9
17.4%	9.6	70	0.95	126,246	71,358	197,604	6
19.7%	9.8	81	0.943	145,589	82,291	227,880	0
22.4%	10	94	0.931	168,366	95,166	263,532	-8
24.7%	10.2	106	0.919	189,294	106,995	296,289	-18
27.0%	10.4	118	0.912	210,188	118,805	328,993	-29
29.2%	10.6	130	0.9	231,093	130,621	361,714	-43
30.3%	10.7	134.6	0.8965	243,521	137,646	381,168	-51
31.3%	10.8	142	0.893	256,342	144,892	401,234	-59
33.3%	11	154	0.878	277,537	156,873	434,410	-22
35.5%	11.2	167	0.864	300,724	169,979	470,703	0
37.6%	11.4	180	0.854	323,912	183,085	506,998	27
39.4%	11.6	192	0.843	345,400	195,231	540,632	44

Sodium Chloride & Calcium Chloride — To Make 1 bbl (42 gallons)

Brine Density at 60º F Pounds/Gallon (ppg)	Barrels of 10.0 ppg NaCl	Barrels of 11.6 ppg $CaCl_2$	Barrels of 8.34 ppg Water
10.1	0.808	0.151	0.041
10.2	0.643	0.271	0.087
10.3	0.496	0.375	0.129
10.4	0.376	0.464	0.160
10.5	0.294	0.542	0.165
10.6	0.229	0.604	0.166
10.7	0.184	0.656	0.160
10.8	0.147	0.703	0.150
10.9	0.119	0.750	0.131
11.0	0.092	0.786	0.122
11.1	0.073	0.828	0.098

Viscosifiers in Calcium Chloride

In order to avoid using Bromide fluids, it is often decided to use Calcium Chloride and an acid soluble weight material, usually calcium carbonate. The amount of Calcium carbonate required to reach a given density is much less when starting with a high density fluid making it possible to achieve higher weights then would be possible with fresh water.

Clarizan, GEOXAN, and other Xanthan polymers have yield limitations in divalent cationic fluids such as Calcium Chloride and Calcium Bromide. This is especially true in saturated brine. In that case it is necessary to mix the polymer in a less than saturated brine. After the polymer has yielded, dry salt may be added to bring the fluid up to saturation.

A combination of high pH and high Calcium can destroy the Clarizan viscosity. To prevent this from happening drilling out cement it is essential that sufficient Sodium Bicarbonate be added to precipitate the free calcium ions.

An alternate viscosifier in calcium chloride brine would be Hydroxyethyl-Cellulose (HEC). While the HEC does not provide gel strengths nor is it as temperature stable, it does continue to function in the presence of both high pH and high filtrate calcium levels.

Calcium Bromide / Calcium Chloride — To Make 1 bbl (42 gallons)

Brine Density at 60° F Pounds/Gallon (ppg)	Pressure Gradient (psi/ft)	Specific Gravity	Barrels of 14.2 ppg CaBr	Barrels of 8.34 ppg Water	Pounds of 94%-97% $CaCl_2$
11.7	0.608	1.40	0.0254	0.8106	192.16
11.8	0.613	1.41	0.0507	0.7862	189.80
11.9	0.618	1.43	0.0762	0.7622	187.22
12.0	0.623	1.44	0.1016	0.7381	184.73
12.1	0.629	1.45	0.1269	0.7142	182.20
12.2	0.634	1.46	0.1524	0.6901	179.65
12.3	0.639	1.47	0.1778	0.6660	177.13
12.4	0.644	1.49	0.2032	0.6420	174.59
12.5	0.649	1.50	0.2285	0.6182	172.06
12.6	0.655	1.51	0.2540	0.5940	169.51
12.7	0.660	1.52	0.2794	0.5701	166.97
12.8	0.665	1.53	0.3048	0.5460	164.44
12.9	0.670	1.55	0.3302	0.5220	161.92
13.0	0.675	1.56	0.3556	0.4998	159.37
13.1	0.681	1.57	0.3810	0.4740	156.83
13.2	0.686	1.58	0.4084	0.4466	154.29
13.3	0.691	1.59	0.4318	0.4260	151.76
13.4	0.696	1.61	0.4572	0.4021	149.21
13.5	0.701	1.62	0.4826	0.3780	146.68
13.6	0.706	1.63	0.5080	0.3540	144.15
13.7	0.712	1.64	0.5334	0.3301	141.60
13.8	0.717	1.65	0.5589	0.3059	139.07
13.9	0.722	1.67	0.5842	0.2820	136.54
14.0	0.727	1.68	0.6069	0.2626	133.99
14.1	0.732	1.69	0.6351	0.2339	131.45
14.2	0.738	1.70	0.6604	0.2100	128.94
14.3	0.743	1.71	0.6858	0.1860	126.39
14.4	0.748	1.73	0.7113	0.1618	123.32
14.5	0.753	1.74	0.7366	0.1380	121.32
14.6	0.758	1.75	0.7620	0.1140	118.79
14.7	0.764	1.76	0.7875	0.0998	116.24
14.8	0.769	1.77	0.8128	0.0659	113.78
14.9	0.774	1.79	0.8382	0.0419	111.18
15.0	0.779	1.80	0.8637	0.0179	108.63
15.1	0.784	1.81	0.8891	0.0062	106.10

Calcium Bromide / Zinc Bromide

To Make 1 bbl (42 gallons)

Brine Density at 60º F Pounds/Gallon (ppg))	Barrels of 14.2 ppg $CaBr_2$	Barrels of 19.2 ppg $CaBr_2$ / $ZnBr_2$	Crystallization Point ºF
15.0	0.84	0.16	-22
15.1	0.82	0.18	-25
15.2	0.80	0.20	-27
15.3	0.78	0.22	-29
15.4	0.76	0.24	-32
15.5	0.74	0.26	-34
15.6	0.72	0.28	-35
15.7	0.70	0.30	-38
15.8	0.68	0.32	-40
15.9	0.66	0.34	-37
16.0	0.64	0.36	-33
16.1	0.62	0.38	-30
16.2	0.60	0.40	-26
16.3	0.58	0.42	-23
16.4	0.56	0.44	-20
16.5	0.54	0.46	-16
16.6	0.52	0.48	-11
16.7	0.50	0.50	-8
16.8	0.48	0.52	-6
16.9	0.46	0.54	-4
17.0	0.44	0.56	-4
17.1	0.42	0.58	-2
17.2	0.40	0.60	0
17.3	0.38	0.62	2
17.4	0.36	0.64	4
17.5	0.34	0.66	5
17.6	0.32	0.68	5
17.7	0.30	0.70	6
17.8	0.28	0.72	7
17.9	0.26	0.74	7
18.0	0.24	0.76	9
18.1	0.22	0.78	10
18.2	0.20	0.80	11
18.3	0.18	0.82	13
18.4	0.16	0.84	15
18.5	0.14	0.86	17
18.6	0.12	0.88	19
18.7	0.10	0.90	21
18.8	0.08	0.92	23
18.9	0.06	0.94	20
19.0	0.04	0.96	21
19.1	0.02	0.98	18
19.2	0.00	1.00	16

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