High density cesium formate brines

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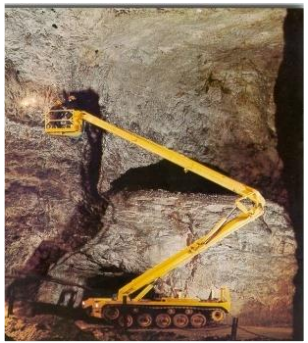
Cabot produces cesium formate brine at Lake Bernic in Canada from pollucite ore

- Pollucite ore: $Cs_{0.7}Na_{0.2}Rb_{0.04}Al_{0.9}Si_{2.1O6}\cdot(H_20)$
- Mined at Bernic Lake, Manitoba
- Processed on site to Cs formate brine
- Cs formate brine production 700 bbl/month



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Cesium formate brines – in use since 1999

>400 applications - mainly deep HPHT gas well constructions, including:

- Reservoir drill-in – 40
- Completion – 207
- Screen-running – 23
- Perforating – 32
- Low-solids OBM – 33
- Gravel packs – 7
- Upper completions - 55
- Workover & Interventions - 24
- Packer and long-term well suspensions - 20

HP = 169
HT = 176
HPHT = 120
Ultra HPHT = 29

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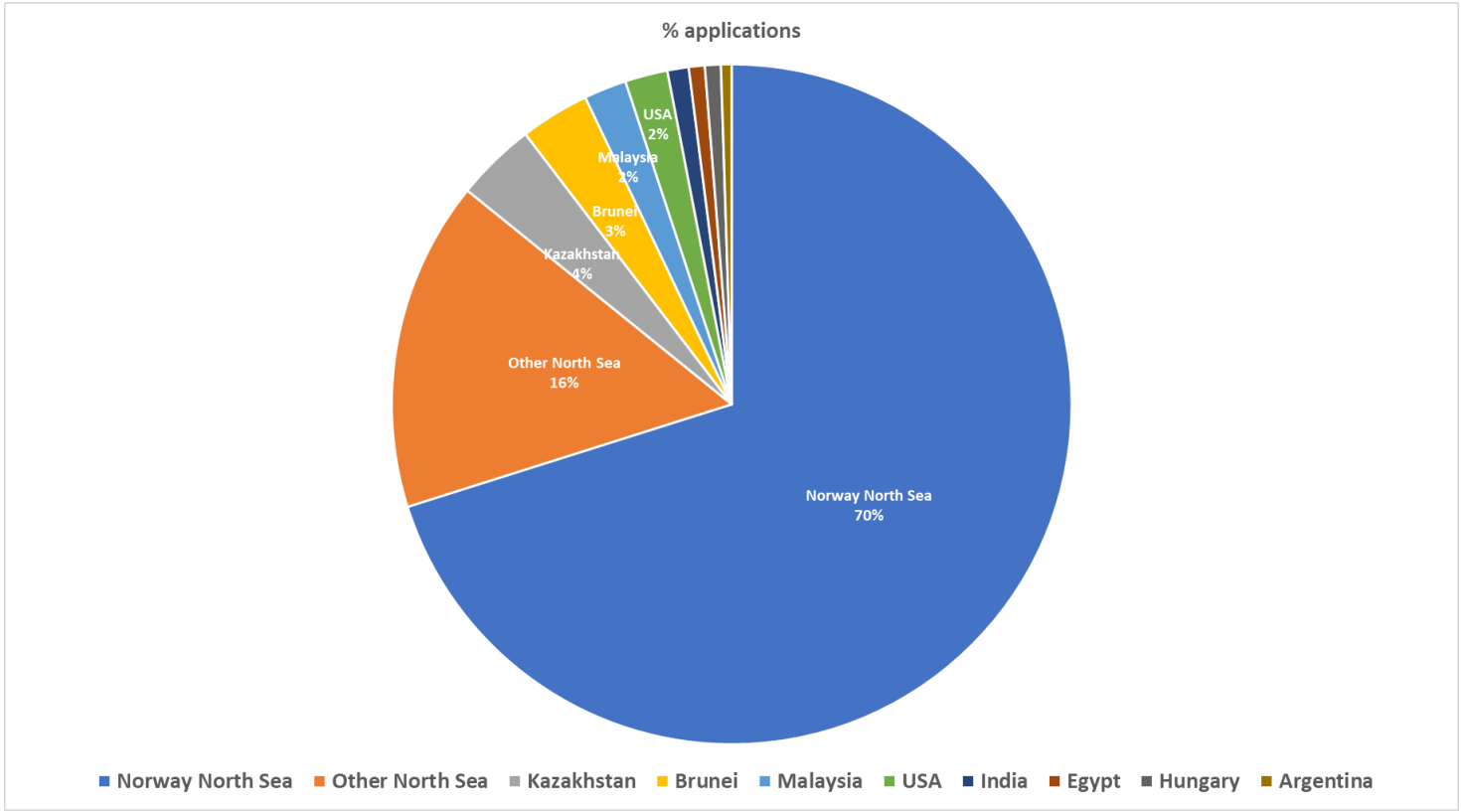
Cs formate applications per geographical area



Cesium formate brines – USA applications

Year	Operator	Field	Application	Density [ppg]	Temp [°F]
2002	BP	High Island	Well intervention	17.6	350
2004	W.O.G	Mobile area 862	Workover	15.9	
2005	W.O.G	Mobile area 862	Barefoot completion	17.2	420
2008	COP	Baker Family Trust	Well kill and OH completion	16.5	
2009	Murphy		Standby	18.4	
2010	Conoco	Malek	Well kill in Eagle Ford shale	16.2	
2011	Conoco	Edith Grey	Well kill in Eagle Ford shale	18.1	
2011	Delta Petroleum	North Vega	Completion	15.1	380

Current application - Deepwater offshore Egypt

- 140 deepwater field in the West Nile Delta
- Drill-in with OBM
- HPHT OHGP completion
- Cs formate:
  - Casing cleaning pill
  - Viscosified pills
  - GP carrier fluid
  - Viscosified suspension pill (solids-free fluid loss pill)
  - Clear brine upper completion fluid
- Three of 7 wells completed with very low skin values

High density Cs formate brine vs halide brines

- HSE:
  - Zinc-free to 19.2 ppg
  - No burns

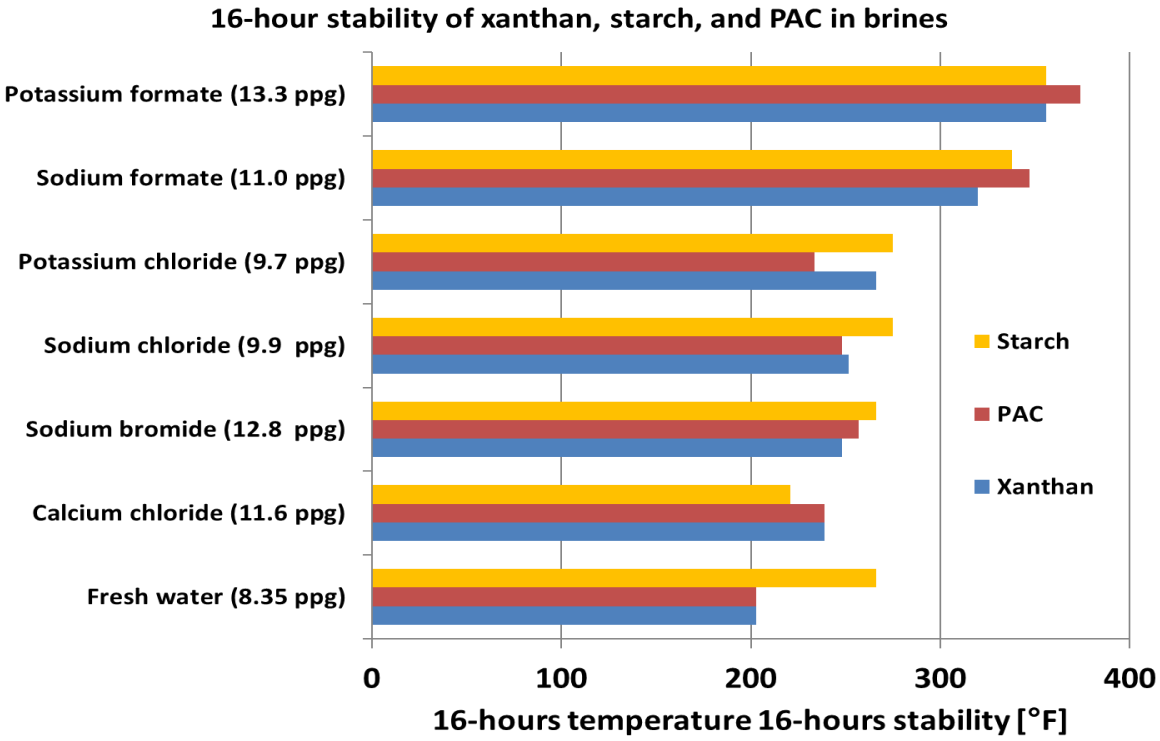
- Reservoir compatibility:
  - Only monovalent ions (Na^+, K^+, Cs^+ $COOH^-$) → compatible with all reservoir water
  - Compatible with biopolymers → damaging synthetic polymers not needed
  - Biopolymer compatibility → Drill-in and complete with same fluid → only one type filtrate
- Metal compatibility
  - Favorable alkaline pH
  - Compatible with carbonate/bicarbonate pH buffer
  - Formate ion is an antioxidant

Reservoir Compatibility

Incompatibility between divalent completion brines and formation water common problem

- Divalent Zn^{2+}, Ca^{2+} cations react with divalent anions (CO_3^{2-}, SO_4^{2-}) and form scales such as $CaCO_3$, $CaSO_4$
- Formate brines have only monovalent ions (Na^+, K^+, Cs^+, $HCOO^-$), which cannot form any scale
- CO_3^{2-} buffer in formate brines can react with formation water with high concentration of divalent cations and form scale, e.g. $CaCO_3$
  - CO_3^{2-} concentration (additive) insignificant compared to Ca^{2+} / Zn^{2+} concentration in high-density halide brines
  - CO_3^{2-} concentration can be reduced in critical applications

Compatibility with biopolymers



The good compatibility with xanthan gum means:

- Non-damaging fluid loss pills, free of synthetic polymers, can be formulated (AADE-NTCE-110)
- Highly pseudoplastic (shear thinning) pills can be formulated
- Fluids with exceptionally good drag reducing properties can be formulated

Formate brines are almost additive-free

High density halide brines can require many additives:

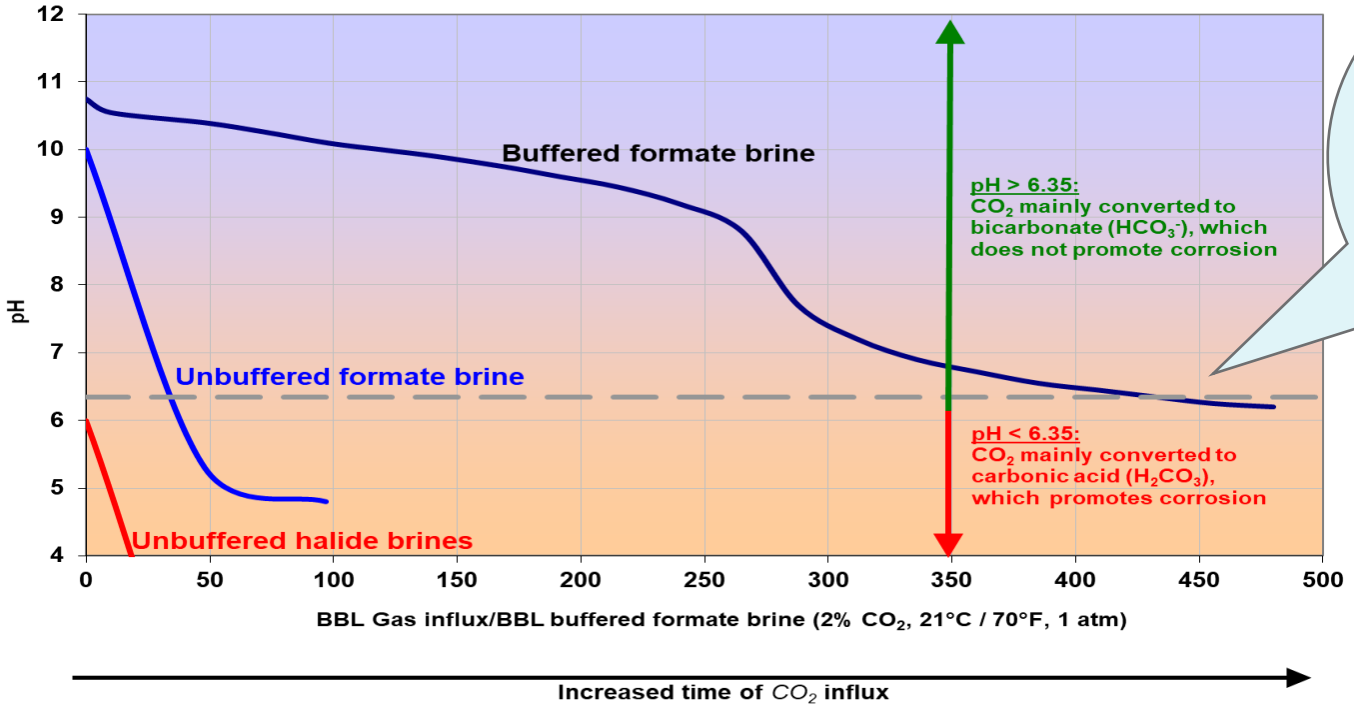
- Biocides
- Corrosion inhibitors
- Oxygen scavengers /antioxidants
- TCT suppressants

Additives can deplete or destabilize**!!**

Formate brines requires only one additive:

- Carbonate/bicarbonate buffer: bicarbonate buffer cannot deplete!!

pH in buffered and unbuffered brines



Final pH after the buffer is overwhelmed with CO_2 depends on the initial buffer concentration.

Typically measured to around 8 in autoclave testing.

Compatibility with metals

Beneficial properties:

- Halide-free
  - Halide brines, and particularly chlorides, are known to promote localized corrosion
  - Corrosion seen in formate brine is mostly general corrosion
- Antioxidant
  - Formate ion is an antioxidant or free radical scavenger – protects against oxidants such as O_2.
  - The use of oxygen scavengers most often not requires.
- Favorable alkaline pH
- Formate salts dissolved in water exhibit a naturally favorable pH (8-10)
- Compatible with carbonate/bicarbonate pH buffer

Natural protection against CO_2 corrosion

- Testing shows that protective iron carbonate layer forms when exposed to large amounts CO_2:
- Small/moderate CO_2 exposures: The carbonate buffer completely resists any effect of the exposure
- Large influx (carbonate buffer overwhelmed): bicarbonate assists in rapid formation of iron carbonate protective layer.
- Iron carbonate layer is self repairing.

Compatibility with metals – field history

Very good track record after 400 (mostly HPHT) applications

- **Pitting** – never experienced in buffered Cs/K formate brines. Not aware of incidents with buffered K/Na formate brines
- **SCC** – never experienced in buffered Cs/K formate brines. No incidents reported in buffered K/Na formate brines
- **HE** – one incident with 25Cr Superduplex tubing. Requires significant cooling (<212°F) after extensive exposure to high temperature. Care should be taken with duplex material - such a situation **can and should be avoided**. HE not unique to formate brine – typical result of galvanic corrosion or poor material production metallurgy (2006 – new API guidelines for production of Alloy 718.

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Formate packer fluid applications

Operator	Location	Type	Density [g/cm³]	Density [ppg]	BHT [°C]	BHT [°F]	Start Date	End Date	Comments
Devon	WC 165 A-7	K	1.03	8.6	149	300	1/2005		
Devon	WC 165 A-8	K	1.03	8.6	149	300	1/2006		
Devon	WC 575 A-3 ST2	K	1.13	10.8	132	270	5/2005		
WO&G/Devon	MO 862 #1	Na/K	1.44	12.0	215	420	4/2005	5/2006	G-3 tubing in excellent condition
BP/Apache	HI A-5 #1	Na/K	1.38	11.5	164	350	2/2002	4/2008	S13CrW in excellent condition
ExxonMobil	MO 822 #7	Na/K	1.44	12.0	215	420	2001		
EPL	ST 42 #1	Na/K	1.38	11.5	133	272	2006		
EPL	ST 41 #F1	Na/K	1.56	13.0	105	222	2006		
EPL	EC 109 A-5	Na/K	1.38	11.5	121	250	2006		
EPL	ST 42 #2	Na/K	1.53	12.8	132	270	2006		
Dominion	WC 72 #3 BP1	Na/K	1.20	10.0	121	250	2006		
EPL	WC 98 A-3 ST1	Na/K	1.52	12.7	153	307	2006		
EPL	WC 98 A-3	Na/K	1.29	10.8	154	310	2007		
BP	Snadd	Cs	1.50	12.5	91	196	2011		

BP High Island Packer Fluid Exposure

- 177°C / 350°F, 14,000 psi
- S13Cr tubing failure from $CaCl_2$ packer fluid
- Well worked over and recompleted with Cs/K formate
- 11.7 ppg Na/K formate left as packer fluid
- Retrieved 6 years later
- Tubing was in excellent condition.

SCC test results – effect of stress-level

18.4 ppg Cs formate tested at 350°F for 90 days with 145 psi CO_2 in headspace

Autoclave #	Test material	Stress level	SCC	Comment
1	13Cr-110 0.5Mo	>100%	YES	API CRA stress level
	13Cr-110 1.9Mo	>100%	YES	API CRA stress level
2	13Cr-110 0.5Mo	60%	NO	
		70%	NO	
		80%	NO	
	13Cr-110 1.9Mo	60%	NO	
		70%	NO	
		80%	NO	
3	13Cr-100 0.5Mo	80%	NO	
		90%	NO	
		100%	NO	
	13Cr-110 1.9Mo	80%	NO	
		90%	NO	
		100%	NO	

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Formate Brines – Thermal Stability

20 years use of formate brines in HPHT applications → Multiple high-temperature suspensions:

- BP Rhum - 250 days at 149°C / 300°F
- Shell Shearwater – 65 days at 182°C / 360°F
- BP Devenick – 90 days at 146°C / 295°F
- Total Elgin/Franklin – 2 years at 204°C / 400°F
- Statoil Huldra – 45 days at 149°C / 300°F
- Statoil Kvitebjørn – 6 months & 15 months at 155°C / 311°F
- Statoil Kristin – 57 days at 171°C / 340°F
- BP High Island – 3 years at 163°C / 325°F
- Devon West Cameron – 1.3 & 1.4 years at 149°C / 300°F
- Walter O&G – 1.5 years at 216°C / 420°F
- TXM Hungary – 38 days, 34 days & 9.5 months at 235°C / 455°F
- Total Kessog – 3 months at 170°C / 305°F

Thermal stability – field case – well A

- BHST = 204°C / 400°F
- Exposure temperature: 180°C / 356°F
- Pressure: 16,700 psi
- Brine: 2.18 g/cm^3 18.2 ppg Cs formate
- Tubing and casing: 25Cr
- Cs formate in annulus and tubing
- Exposure time: 2 years

Well A – Sample analyses after 2 years

Sample #	Temp [°C]	Temp [°F]	Density [g/cm³]	Density [ppg]	pH	Carb. [mol/l]	Bicarb. [mol/l]	Total [mol/l]	Formate conversion [%]	Oxalate [mg/l]	Methanol [%wt]	Acetate [%wt]
Original			2.17	18.1	10.5	0.16	0.07	0.22	0.0	0.09	0.0	0.002
1	5	41	2.17	18.1	10.4	0.16	0.06	0.22	-0.1	0.19	0.0	0.002
2	65	148	2.17	18.1	10.5	0.16	0.06	0.22	-0.1		0.0	0.002
3	80	177	2.17	18.1	10.5	0.16	0.06	0.22	-0.1	0.25	0.0	0.002
4	96	205	2.18	18.2	10.5	0.17	0.07	0.24	0.2	0.19	0.0	0.002
5	112	233	2.18	18.2	10.0	0.17	0.18	0.35	1.3	0.16	0.0	0.002
6	128	261	2.18	18.2	9.8	0.18	0.25	0.43	2.1	0.07	0.0	0.003
7	143	290	2.19	18.3	8.7	0.23	0.32	0.55	3.3	0.07	0.1	0.004
8	153	307	2.19	18.3	9.9	0.42	0.47	0.89	6.7	0.06	1.6	0.005
9	162	324	2.19	18.3	9.9	0.45	0.51	0.96	7.4	0.04	1.6	0.005
10	171	340	2.19	18.3	9.7	0.36	0.61	0.9	7.5	0.28	0.4	0.005
11	180	357	2.19	18.3	9.7	0.36	0.69	1.05	8.3	0.28	0.5	0.005

Thermal stability – field case – well B

- BHST = 235°C / 455°F
- Pressure: 14,000 psi
- Tubing/casing: low alloy steel / carbon steel (no catalyst?)
- CO_2 = 30% / H_2S = 150 ppm

Exposure 1

- Brine: 2.15 g/cm^3 / 17.9 ppg Cc formate brine
- Exposure temperature: 222°C / 432°F
- Exposure time: 38 days

Well A – Sample analyses after 38 days

Sample #	Temp [°C]	Temp [°F]	Density [g/cm³]	Density [ppg]	pH	Carb. [mol/l]	Bicarb. [mol/l]	Total [mol/l]	Formate conversion [%]	Oxalate [mg/l]	Methanol [%wt]	Acetate [%wt]
Original			2.15	17.9	10.9	0.24	0.04	0.29	0.0	0.15	0.00	0.006
1	<130	<266	2.14	17.9	10.5	0.20	0.07	0.27	-0.1		0.00	0.004
2	<130	<266	2.14	17.9	10.6	0.20	0.06	0.26	-0.3	0.14	0.00	0.008
3	<130	<266	2.14	17.9	10.6	0.22	0.06	0.28	-0.1		0.00	0.005
4	<130	<266	2.14	17.9	10.5	0.22	0.06	0.27	-0.1	0.13	0.00	0.005
5	<130	<266	2.14	17.9	10.6	0.23	0.05	0.28	0.0		0.00	0.006
6	134	273	2.14	17.9	10.6	0.22	0.05	0.28	-0.1		0.00	0.006
7	148	298	2.14	17.9	10.6	0.23	0.06	0.29	0.0		0.00	0.006
8	160	320	2.14	17.9	10.6	0.22	0.06	0.28	0.0		0.00	0.005
9	185	365	2.14	17.9	10.4	0.23	0.09	0.32	0.4		0.00	0.006
10	222	432	2.15	17.9	10.0	0.23	0.22	0.45	1.7	0.32	0.00	0.008

Thermal stability – field case – well B

- BHST = 235°C / 455°F Pressure 14,000 psi
- Tubing/casing: low alloy steel / carbon steel
- CO_2 = 30% / H_2S = 150 ppm

Exposure 3

- Brine: 2.21 g/cm^3 / 18.5 ppg Cs formate brine
- Recovered samples exposed to temperature: ~ 201°C / 394°F
- Exposure time 9.5 months
- Cs formate in work string and casing

Well B - Exp. 3 – Sample analyses

Sample #	Temp [°C]	Temp [°F]	Density [g/cm³]	Density [ppg]	pH	Carb. [mol/l]	Bicarb. [mol/l]	Total [mol/l]	Formate Conversion [%]	Oxalate [mg/l]	Methanol [%wt]	Acetate [%wt]
1	23	73	2.20	18.4	10.0	0.16	0.13	0.29	0.0	<0.01	0.00	0.00
3	65	149	2.22	18.5	10.0	0.16	0.12	0.28	0.0	<0.01	0.00	0.03
5	99	210	2.21	18.4	9.9	0.17	0.20	0.37	0.8	<0.01	0.00	0.04
7	171	339	2.11	17.6	9.2	0.21	0.89	1.10	-	0.23	0.00	0.06
8	183	361	2.12	17.7	8.9	0.10	0.86	1.00	-	0.31	0.00	0.05
9	201	394	2.24	18.7	9.4	0.24	0.70	0.94	5.7	0.09	0.00	0.01
10	197	386	2.22	18.5	9.4	0.22	0.69	0.92	5.4	<0.01	0.00	0.04
12	188	370	2.24	18.7	9.3	0.20	0.64	0.84	4.8	<0.01	0.00	0.03
14	143	289	2.23	18.6	9.7	0.16	0.23	0.39	0.9	<0.01	0.00	0.02
16	79	174	2.21	18.4	9.6	0.18	0.24	0.38	0.8	<0.01	0.00	0.02

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Conclusion

- Cs format zinc-free alternative to 19.2
- Cs formate is more than ZnBr replacement:
  - Cs unique natural resource
  - Multiple unique properties → stable fluid without additives
  - Multiple applications :
    - Drilling: well control, shale stability, drilling performance, formation compatibility
    - OH completions: low-solids screen running / GP fluid, also as internal phase in OBM
    - Non-damaging perforating fluid
    - Stable suspension fluid
  - Proven to save rig time and lower overall well construction cost