DEVELOPMENT AND APPLICATION OF A NOVEL ZINC FREE CLEAR BRINE COMPLETION FLUID

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CONTENT

- Industry Needs
- Development Timeline
- Qualification Testing
  - Crystallization
  - Corrosion
  - Elastomers
- First Field Applications
- First Applications Results
- Summary

INDUSTRY NEEDS
CHALLENGE

Zinc Classified as Marine Pollutant

- GOM discharges limited to trace levels of priority pollutants, posing major challenge for fields produced through FPSOs (Floating Production Facilities)
- North Sea has restricted zinc use
- Brazil regulators reluctant to sanction its use
- Low pH risks to personnel and metals

Market for Environmentally Benign Fluids (>14.2ppg) Dominated by Cesium Formate for the Past 19 Years

- Cesium prices reflect depletion of sole commercially viable reserves
- Diminishing cesium ore reserves restricts availability for large UDW wells
- High cost
- Require high pH to minimize corrosion
- Might release Hydrogen under HPHT conditions

INDUSTRY NEEDS
CLEAR SOLUTION

Global Environmental Acceptability

- Zinc-free and no priority pollutants
- Neutral pH – low risk to personnel
- Low corrosivity to metals
- Enables discharge of produced water
- Eliminates cause of damage to refinery catalysts

Cost-Effective Alternative

- Cost savings over cesium formate
- Based on renewable Chemistry with no supply/availability/pricing issues
- Uses Standard CBF mixing equipment

Stable at Elevated Temperatures

Elastomer Compatibility Similar to $CaBr_2$

Can Be Formulated as a Low-Solids RDF (Reservoir Drill-in Fluid)

DEVELOPMENT TIMELINE

- Establish fluid qualification scope and requirements for first application December 2013
- Development approach (ISO9001-derived design process, BOD)
- Novel analytical methods developed to design and maintain fluid
- Design verification conducted in-house and by third-party labs
- Onshore plant trial conducted December 2014
- Design validated in GOM in May 2015

QUALIFICATION TESTING

Physicochemical Properties	Compatibility	Chemical Compliance	Operational Requirement
Density/PCT	Metals	GOM	Filtration & Additives
pH	Elastomers	North Sea	Wellbore Cleanup
Thermal stability	Other Working Fluids		LCM Pills
Hydrate inhibition	Reservoir		Reclamation
	Contaminants		New Testing Procedures
			Extensive Data Base

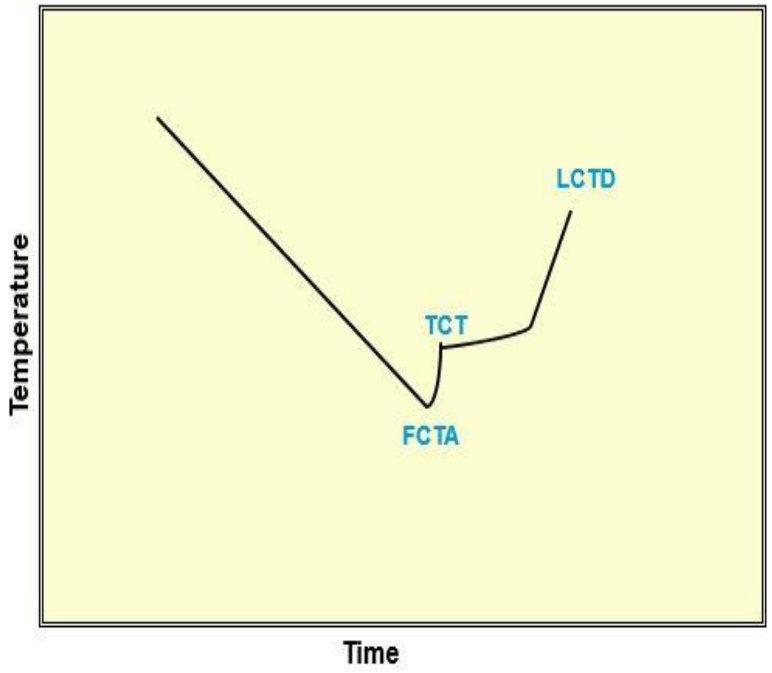
- **Over 50 Unique Tests**
- **Over 280 Testing Scenarios**
- **Developed New Tests for PCT and Special Additives**

MEASUREMENT OF CRYSTALLIZATION TEMPERATURE

- High densities needed for HPHT projects achieved by increasing the fluids salt content
- Increasing salt content above the eutectic point typically increases crystallization temperature
- High pressures and low temperatures experienced near seabed in deepwater operations or during BOP pressure testing can cause brine crystallization
- API RP 13J specifies manual method for TCT measurement, but there is currently no standard method for PCT

HALIDE BRINE CRYSTALLIZATION CHART

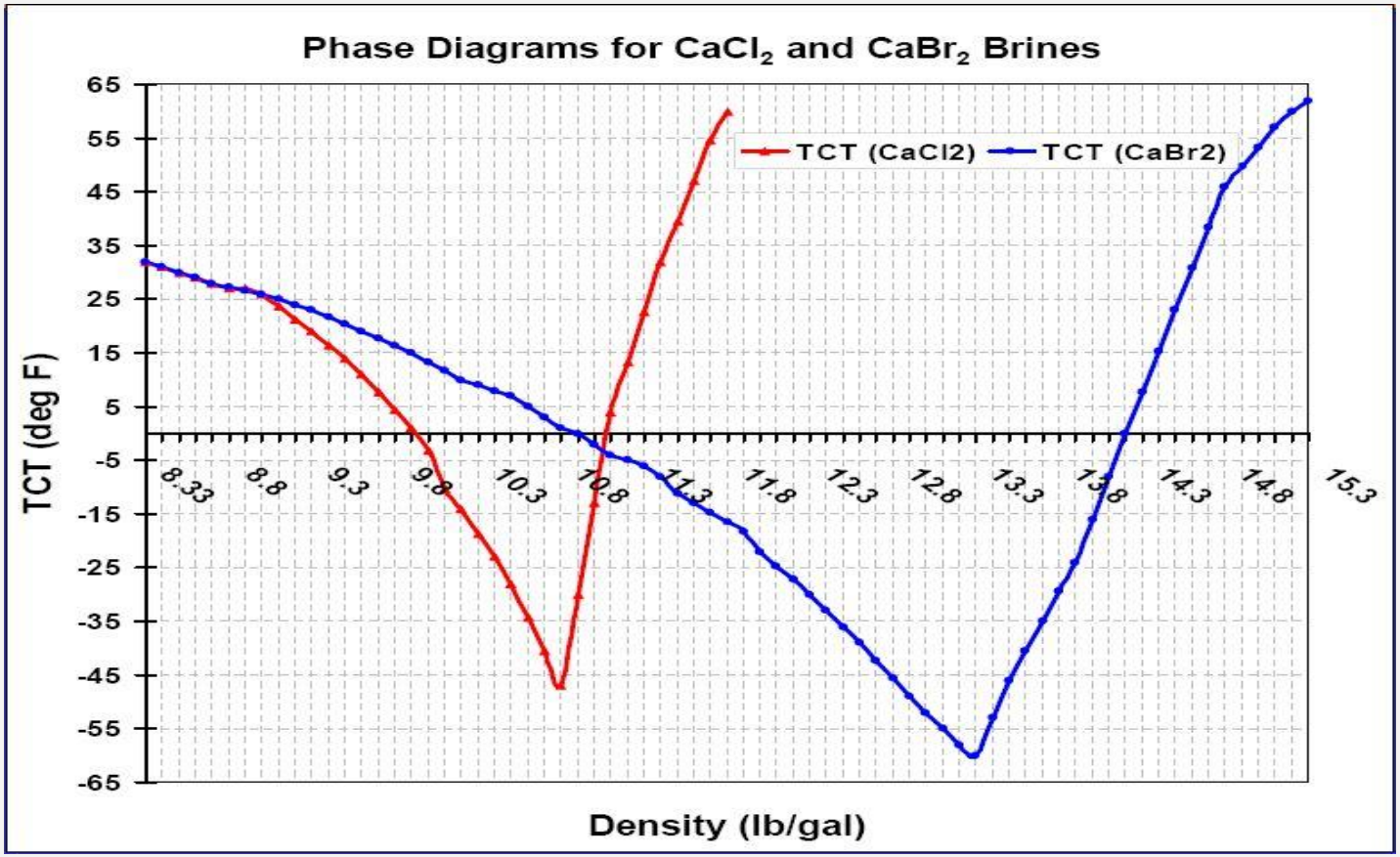
- **True Crystallization Temperature (TCT)**
  - **Maximum temperature following super-cooling minimum or inflection point with no super-cooling**
  - **Temperature at which a brine will naturally crystallize in pumps, lines, filtration units, and tanks**
- **Pressure Crystallization Temperature (PCT)**
  - **Resulting TCT at a specified pressure above ambient**



*FCTA – First Crystal to Appear

*LCTD – Last Crystal to Dissolve

PHASE DIAGRAMS



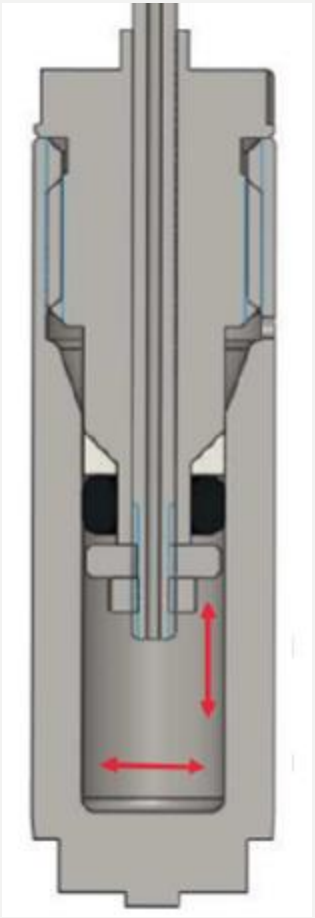
For brines above their eutectic point, crystallization temperature can increase as a result of downhole pressure. This is due to the compressibility of the water phase.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

- **Widely used analysis technique able to detect minute energy changes in sample over a programmed temperature range**
- **Crystallization of halide brines is exothermic and so can be detected by DSC**
- **Performs measurements at high pressures and is extensively utilized to test our novel HPHT completion fluid**

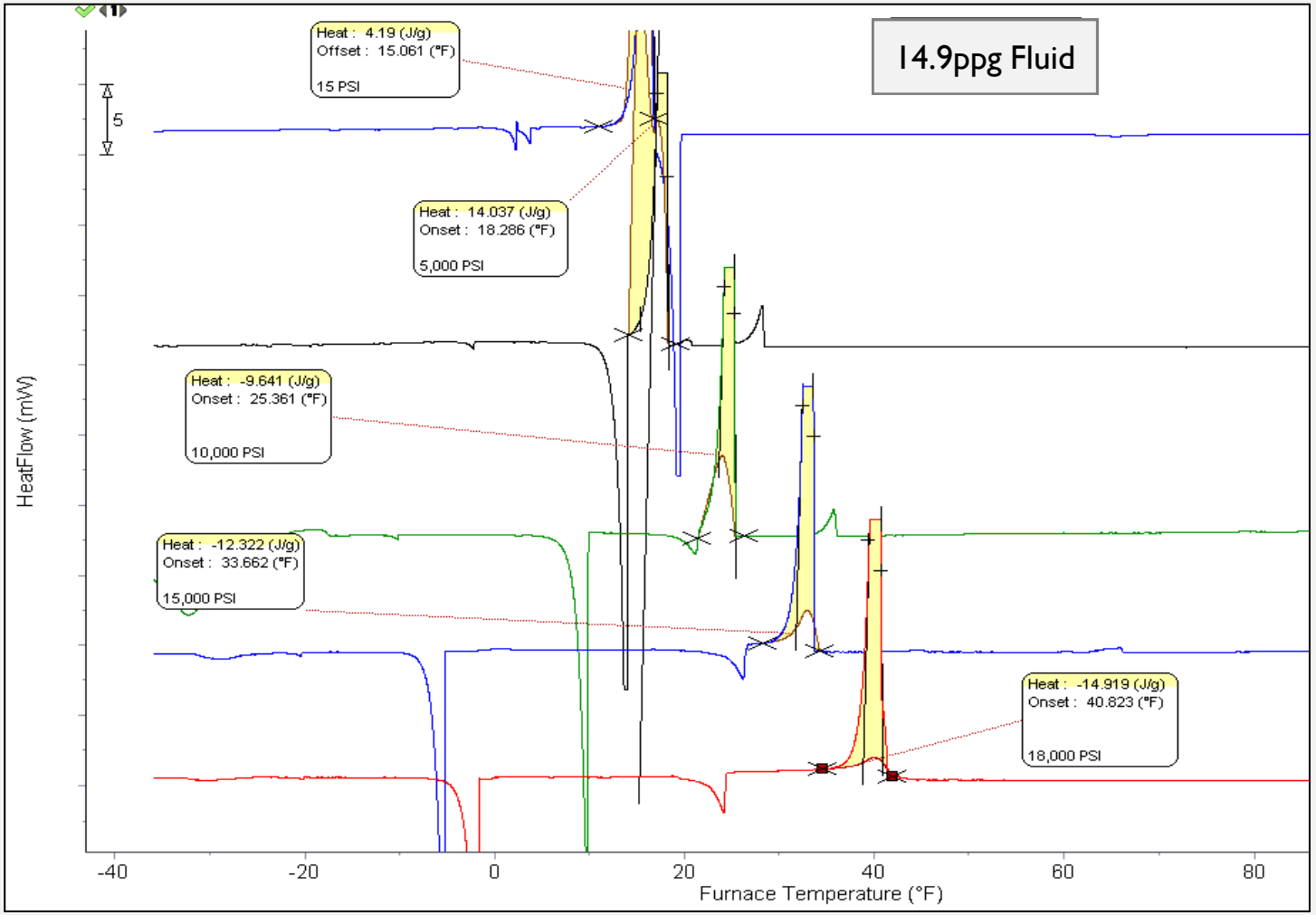
HIGH PRESSURE DSC

Dimensions	Dia. 9mm / 0.35 in Height 30.5mm / 1.2 in
Type	Uncaterorized /V <0.1 L
Test pressure	1859 bar / 26963 psi
Maximum permisssible pressure	1300 bar / 18855 psi
Operating pressure	1000 bar / 14504 psi
Operating Temperature	-40 C to +120 C / -40 F to +248 F
Volume	0.19 ml / 0.34 oz

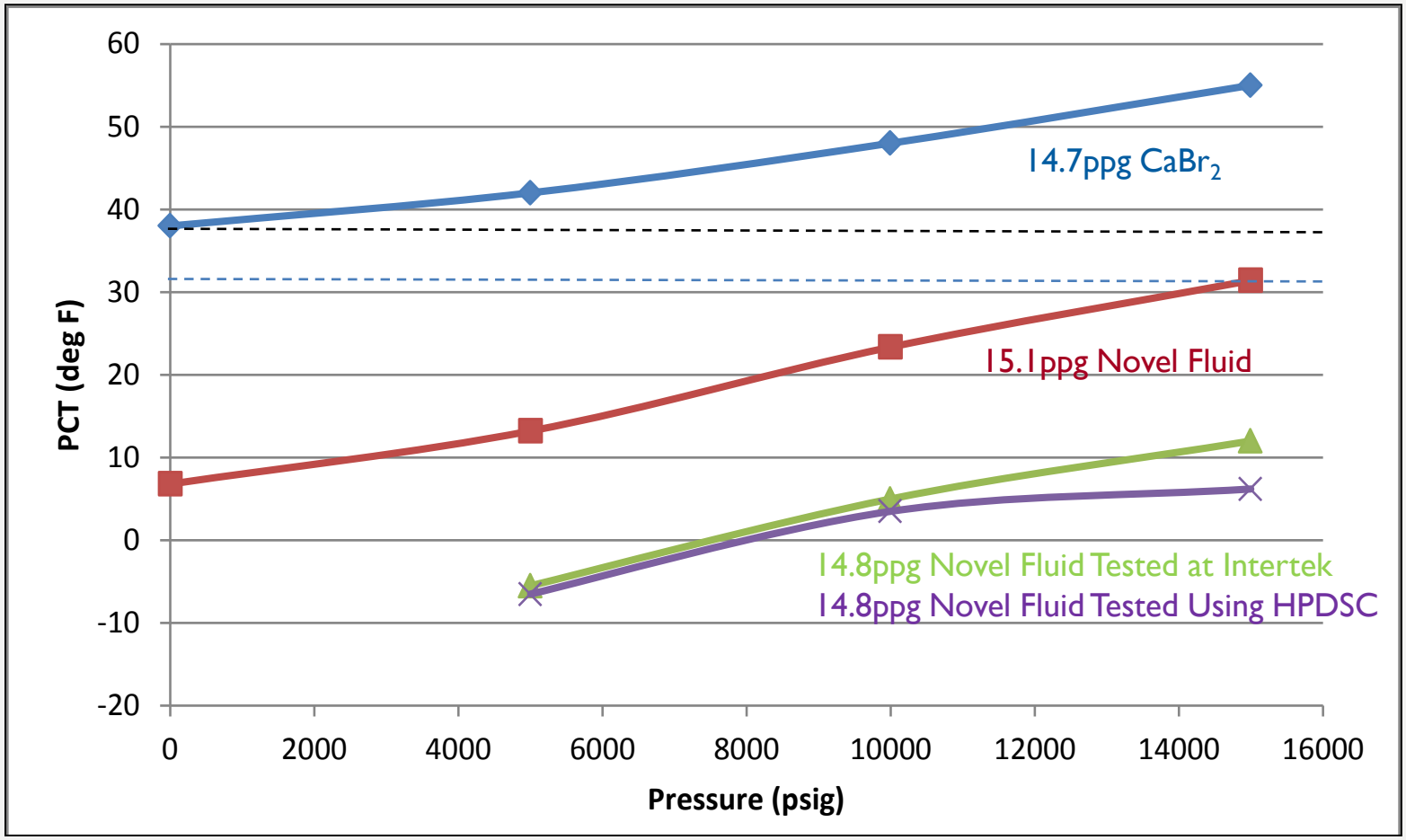


Max Sample	
Height	6mm / 0.24 in
Diameter	5mm / 0.2 in

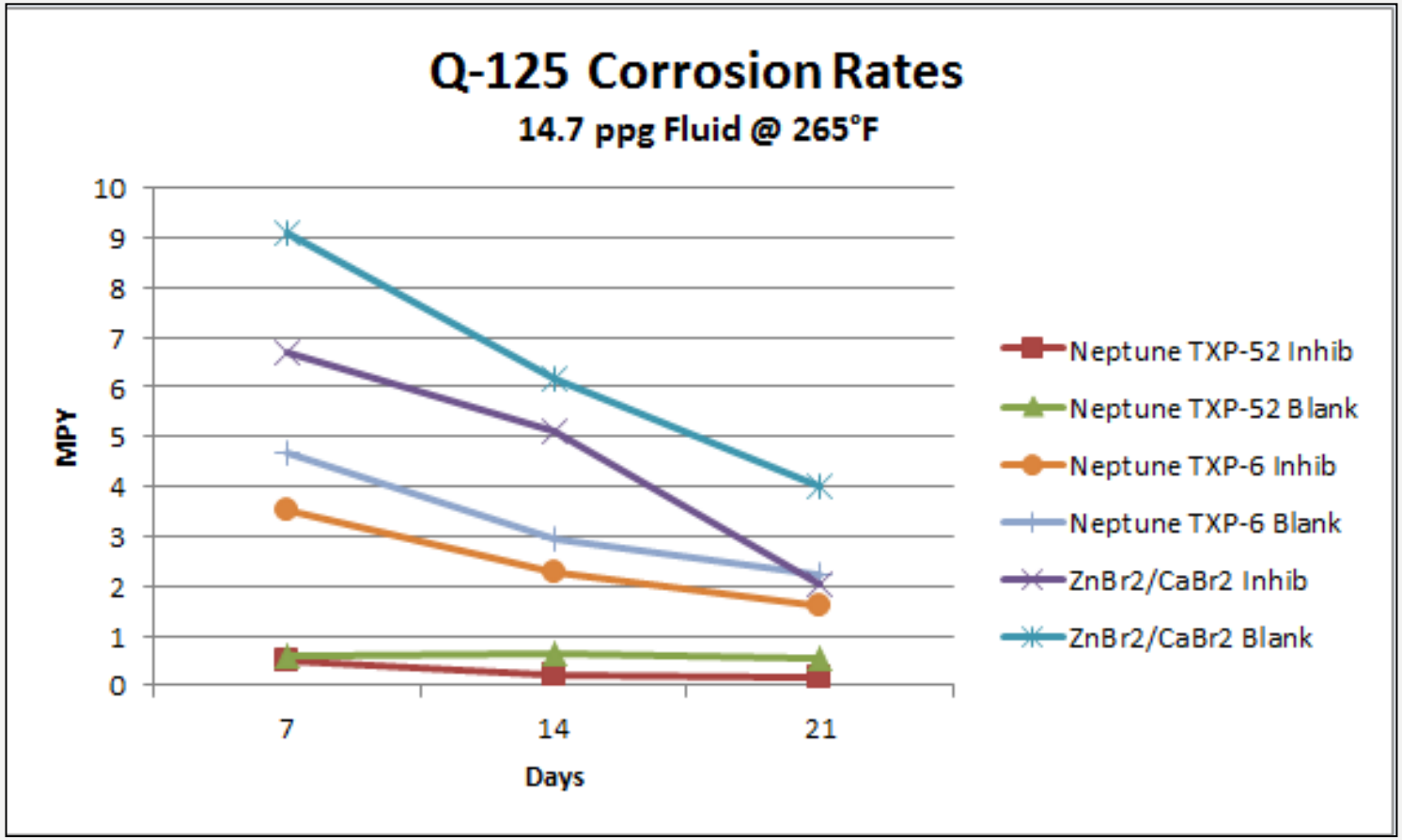
HPDSC - EFFECT OF PRESSURE ON PCT



VALIDATION OF HPDSC TECHNIQUE



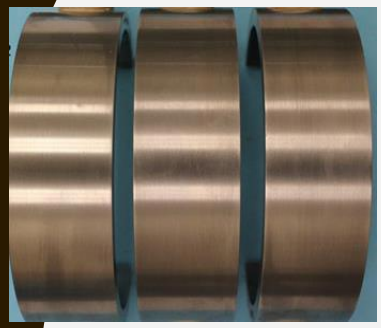
GENERAL CORROSION



- TETRA CS Neptune™ TXP-52 is pre-treated with TETRA®CO_2X
- TETRA CS Neptune™ general corrosion data very low

CORROSION TESTING EXAMPLE

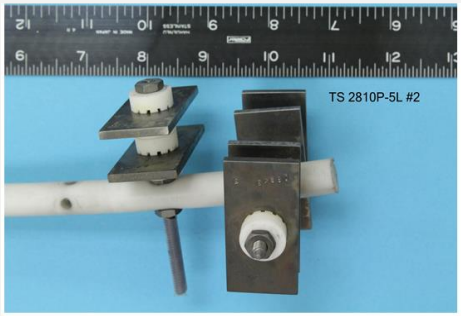
- CRAs 13Cr110, 15Cr125 , Alloy 718, and Q125 Steel
- CO_2-rich environment
- C-Rings, Tensile Bars, and Crevice Coupons Tested
- 30 days at 265°F
- All CRAs and Steel Specimens Tested Passed



13Cr110
C-Rings

NACE TM0177
Method C
C-ring ready to test

Q125 Steel
Tensile Bars



15Cr125
Crevice Coupons

ELASTOMERS COMPATIBILITY

- **Broad Range of Elastomers Tested (3rd party UK)**
  - **NBR, XNBR, HNBR, FKM, and FEPM rubber, GRE1 and Polyamide2**
  - **BOP, Topside and Tool Elastomers were tested**
  - **Temperatures 120oF (49oC), 212oF (100oC), 265oF (129oC)**

- **In all cases, 14.7ppg novel clear brine performed equivalent to or better than Zn/CaBr2 and CaBr2**

[1]GRE was only tested at 265°F (129°C)

[2]Polyamide was only tested at 212°F (100°C)

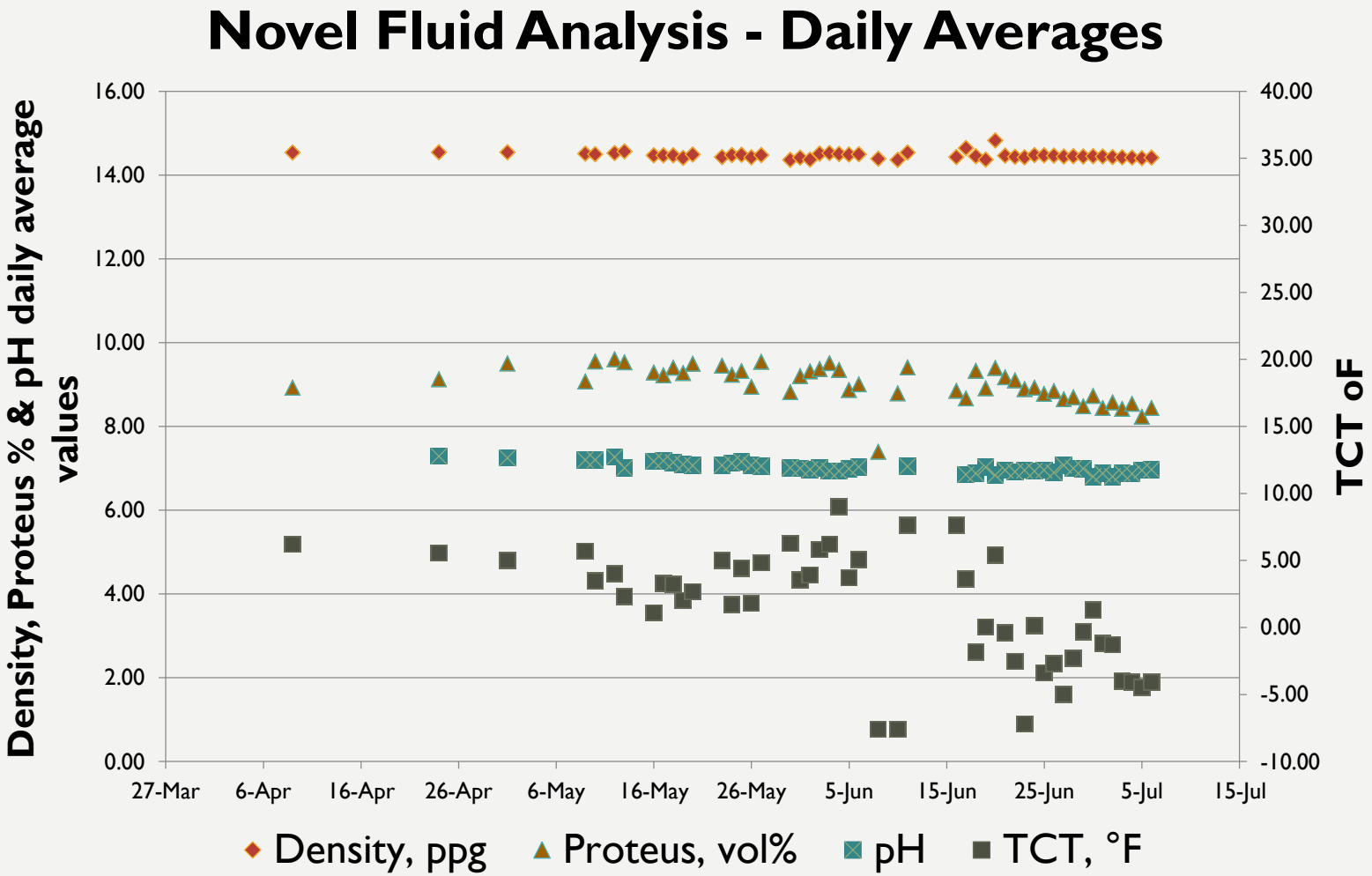
FIRST FIELD APPLICATIONS

- GOM – Ultra deepwater wells with TVDs > 30,000’
- Water depth > 7,000’ with a seabed temp of 39oF
- Fluid densities of 14.5, 14.6, 14.75 and 14.85 lb/gal
- Four- and five-zone smart lower completions installed
- Base fluid for displacement spacers and LCM pills
- Fluid also used as a packer fluid

FIRST APPLICATION RESULTS

- Fluid properties stable from shipping until offloading from the rig after ninety-four (94) days
- 15,000 psi BOP with no PCT or TCT issues throughout well completions
- Tolerated contaminants from SOBM & sea water without deterioration of PCT
- No Iron issues - Iron less than 8 mg/l throughout entire well
- Excellent fluid clarity - NTUs less than 5
- No attrition to surfaces or during filtration
- Additives had no impact on oil and grease

FIRST APPLICATION RESULTS



TETRA CS NEPTUNE ™

- **TETRA CS Neptune™ is a new innovative, high-density, solids-free, completion fluid. TETRA's new zinc and formate free completion fluid is the clear solution to the industry's quest for an environmentally friendly, cost effective alternative to traditional zinc bromides and cesium formate high-density completion fluids.**

- **Features**
  - **Can be formulated to a density of up to 15.4 ppg, 1.85 g/ml (efforts are underway to extend the limits)**
  - **Exhibits significantly lower crystallization temperatures (TCT & PCT) than equivalent density calcium bromide brines**
  - **Stable at elevated temperatures and during storage**
  - **Can be mixed with standard CBF mixing equipment**
  - **Compatible with most downhole elastomers and metallurgies**
  - **Exhibits compatibility similar to that of calcium bromide with other working and reservoir fluids**
- **Benefits**
  - **Zinc Free and hence does not require zero-discharge system to work**
  - **Global Environmental acceptability**
  - **Formulated from renewable products, ensuring continuity of supply**
  - **Neutral pH - poses lower health and safety risks to rigsite and plant personnel**
  - **Significantly lower unit cost than alternative fluid chemistries**
  - **Requires no special mixing, handling or storage equipment at the rigsite**
  - **Can be formulated as a low solids, reservoir drill-in fluid**
  - **Can be reclaimed for reuse, using standard technology**

SUMMARY

- A viable alternative to Cesium Formate and Zinc Halides has been developed
- Novel fluid addresses shortcomings of existing high-density brines technologies
- Work is ongoing to extend density range
- HPDSC provides an accurate, repeatable, and automated method for measurement of crystallization temperature at pressures up to 19,000psi