

Novel Hydrate Prediction Methods for Drilling Fluids

Phase 2

(Progress report 15 April, 1997)

1.0 Overview

In phase 1 of this project, which was completed in June 1996, we developed¹ a novel method to predict the hydrate temperature suppression using the resistivity and density of the drilling fluid filtrate. The method has the following features: (1) useful tool for rapid, on-site determination of gas hydrate temperature suppression in drilling muds; (2) input parameters can be easily measured on site (filtrate resistivity and density at ambient pressure and temperature); (3) valid for drilling fluids inhibited by salts and/or mixtures of salts and glycols; (4) valid for temperature suppression of up to 40°F; (5) except for the type of glycol, no information is needed about the mud composition; (6) valid for glycols and salts concentrations of (0-30 wt%) and (5-26 wt%), respectively.

Phase 2 of this JIP is mainly focused on developing a state-of-the-art hydrate prediction model, specifically tailored for drilling and completion fluids.

The new model, which we called WHyP (Westport Hydrate Prediction Model) is based on the statistical thermodynamic theory of van der Waals and Platteeuw², and incorporates the hydrate temperature suppression methods developed in Phase 1 as well as other available methods. The computer model is Windows 95[®] Compatible and linked to an Excel interface for user friendly data input/output.

2.0 Deliverable

1. All data generated under phase 1 of the project.
2. A user-friendly, IBM-PC Windows 95[®], based, menu-driven hydrate prediction model specifically tailored for drilling and completion fluids. The model will accept either set of the following input parameters:
 - (a) For drilling fluids of known composition
 - Input weight fraction of each inhibitor
 - (b) For drilling fluids of unknown composition
 - Input the following measured filtrate properties :
Resistivity, Density, Temperature, Glycol density, & molecular weight
3. Measurements of solution activity & hydrate equilibrium for:
 - Na-Formate (10, 20, 40 wt%)
 - K-Formate(15, 30, 50 wt%)
 - ZnBr (3 conc.)
 - CaBr₂ (3 conc.)

2.1 Additional deliverables

To take advantage of the increased funding resulting from the additions of two new members to the JIP, we added the following deliverables to the original work program:

4. Measurement and compilation of solution activity, resistivity, density, and hydrate temperature suppression data for over 120 drilling fluids.
5. Developing activity model/correlation for mixed solutions in terms of molarity or wt% of ingredients.
6. Enhance resistivity model to include solutions of bromides and formate salts.

3.0 Accomplishments to-date

1. The computer code is 85% complete. A running version is currently being tested.
2. The hydrate equilibrium and activity measurements for the following solutions are completed:

- Na-Formate (10, 20, 40 wt%)
- K-Formate(15, 30, 50 wt%)
- ZnBr (3 conc.)
- CaBr₂ (3 conc.)

Tables 1 and 2 present a complete listing of these measurements. Figures 1 through 11 show the hydrate equilibrium measurements for these solutions.

3. Measurement and compilation of solution activity, resistivity, density, and hydrate temperature suppression data for over 120 drilling fluids (50% complete).

4.0 Features of the hydrate prediction model, WHyP:

4.1 Input data

The computer program requires the characterization of both the hydrocarbon phase (the gas kick fluid) and the aqueous phase (drilling fluid).

4.1.1 Gas kick fluid

The program accepts both the composition of the fluid or its specific gravity.

4.1.2 Drilling fluid

The drilling fluid can be characterized using one of the following:

1. The weight fraction (or %) of salts and glycols present in the drilling fluid
2. The resistivity and density of the mud filtrate
3. The solution activity

4.2 Hydrate Prediction Methods

4.2.1 *Statistical thermodynamic model*

The statistical thermodynamic theory of van der Waals and Platteeuw² represents the basis for this model. Classical thermodynamics require energy (fugacity) balance at equilibrium of all components in the present phases. This is used to calculate the gas hydrate equilibrium temperature or pressure using the composition of the kick fluid. The code treats mixtures of up to 21 components. These are: C1, C2, C2ene, C3, i-C4, n-C4, i-C5, n-C5, c-C5,n-C6, n-C7, n-C8, n-C9, H₂, CO₂, O₂, N₂, H₂S, SF₆, cis-2-Butene, and Trans-2-Butene.

4.2.2 *Specific gravity model*

This simple model uses only the specific gravity of the kick fluid to predict the hydrate equilibrium temperature at a given pressure. This method is less accurate, and does not consider the effect of hydrate inhibitors. It is only to be used as a first estimate of the hydrate equilibrium temperature when the gas composition data are not available.

4.2.3 *Temperature suppression models*

These models which have been developed in Phase 1 of the project are used to determine the effect of mixed inhibitors on the hydrate temperature suppression. The user can chose to input the weight fraction of each inhibitor present in the drilling fluid or the mud filtrate resistivity and density.

The effect of the inhibitors can also be expressed in terms of the solution activity. A direct input of the measured or calculated solution activity can be selected by the user.

5.0 Remaining Tasks

- Enhance resistivity model to include solutions of bromides and formate salts.
- Completing the Excel interface to make the program more user friendly. The input will be made to self-explanatory screens. Output will be both to the screen and data files.
- Improving the accuracy of the model in the 3-4 phase region to handle kick fluids with liquid hydrocarbon phase. The flash routine in this region still needs further refinement to resolve the convergence problem when the methane content is in the range of 90-93%.
- Finalize the measurement and compilation of solution activity, resistivity, density, and hydrate temperature suppression data for over 120 drilling fluids.
- Attempt to develop activity model/correlation for mixed solutions in terms of molarity or wt% of ingredients.

References

1. Novel hydrate prediction methods for drilling fluids, Westport report no. WTCI-96-133., June 24, 1996.
2. van der Waals, J.H. and Platteeuw, J.C. , Adv. Chem. Phys., 2, 1-55 (1959).

Table 1- Activity and hydrate temperature suppression of tested aqueous solutions.

Na-Formate wt%(m*)	K-Formate wt%(m)	CaBr ₂ wt%(m)	ZnBr wt%(m)	Humidity %	Temp., (°F)	Activity	Hyd. Temp. Suppression (°F)	Density (g/mL)
		10(0.545)		55.3	69.4	0.8917	3.2	1.09
		20(1.13)		50	69.9	0.8435	13.9	1.13
		30(1.79)		45.8	69.8	0.8053	25.2	1.19
			10(0.747)	58.3	69.9	0.9190	2.4	1.09
			20(1.64)	53.5	69.8	0.8754	8	1.20
			30(2.71)	50	69.9	0.8435	15.2	1.32
10(1.57)				50.3	69.8	0.8462	7.7	1.07
20(3.32)				46.4	69.8	0.8107	17	1.13
30(5.29)				42.5	69.5	0.7753	32.9	1.20
	15(1.95)			51.8	69.7	0.8599	9.8	1.09
	30(4.25)			43.5	69.4	0.7844	25.5	1.19
	50(7.98)			30.9	69.5	0.6697	No hydrates	1.34
m*: molarity (mol/liter of soln)								

Table 2- Summary of hydrate equilibrium data.			
Solution	Run ID	Temp., °F	Press., psia
10 wt% Calcium Bromide*	CBRR1P5500	81.5	5600
	CBRR2P4000	78.5	3800
	CBRR3P3000	75	2800
	CBRR4P1500	69	1330
20 wt% Calcium Bromide*	CABR1P5500	73	5080
	CABR2P4000	70.5	3820
	CABR3P3000	67.5	2840
	CABR4P1500	62.2	1363
30 wt% Calcium Bromide*	CARR1P5500	58	4850
	CARR2P4000	56.2	3785
	CARR3P3000	53.1	2855
	CARR4P1500	49.7	1525
10 wt% Sodium Formate*	NAFR1P5500	75.6	5130
	NAFR2P4000	73	3680
	NAFR3P3000	71	2800
	NAFR4P1500	66	1280
20 wt% Sodium Formate	NFAR1P5500	65.8	5000
	NFAR2P4000	64.5	3825
	NFAR3P3000	62.2	2980
	NFAR4P1500	57.2	1480
30% Sodium Formate*	NFMR1P5500	50	4545
	NFMR2P4000	47.4	3595
	NFMR3P3000	44.8	2660
	NFMR4P1500	40.95	1264
10 wt% Zinc Bromide	ZBRR1P5500	81.95	5230
	ZBRR2P4000	79.2	3972
	ZBRR3P3000	76.4	3010
	ZBRR4P1500	71.3	1503
20 wt% Zinc Bromide	ZNBR1P5500	75.85	5085
	ZNBR2P4000	73.4	3955
	ZNBR3P3000	70.6	2985
	ZNBR4P1500	65.3	1430
30 wt% Zinc Bromide*	ZNRR1P5500	67.45	4820
	ZNRR2P4000	66	3817
	ZNRR3P3000	63.1	2825
	ZNRR4P1500	59.1	1465
15 wt% Potasium Formate	KFMR1P5500	74	5065
	KFMR2P4000	71.5	3890
	KFMR3P3000	68.5	2980
	KFMR4P1500	64.3	1480
30 wt% Potasium Formate*	KFAR1P5500	57.1	4596
	KFAR2P4000	55.8	3870
	KFAR3P3000	53.1	2812
	KFAR4P1500	48.9	1532

Figure 1- Hydrate phase equilibrium and pressure-temperature-trace of 10wt% CaBr₂ aqueous solution.

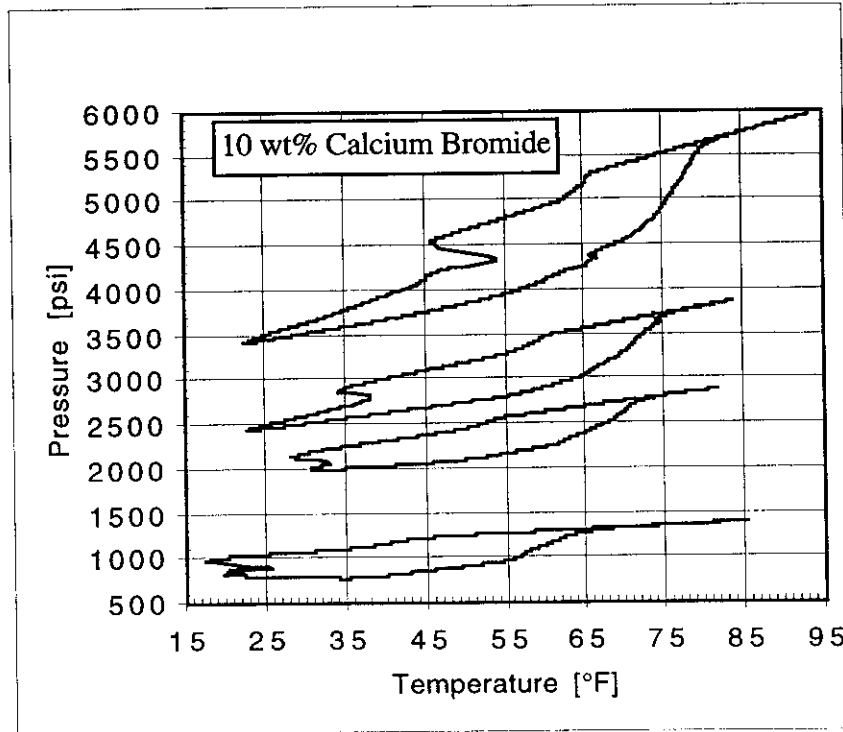
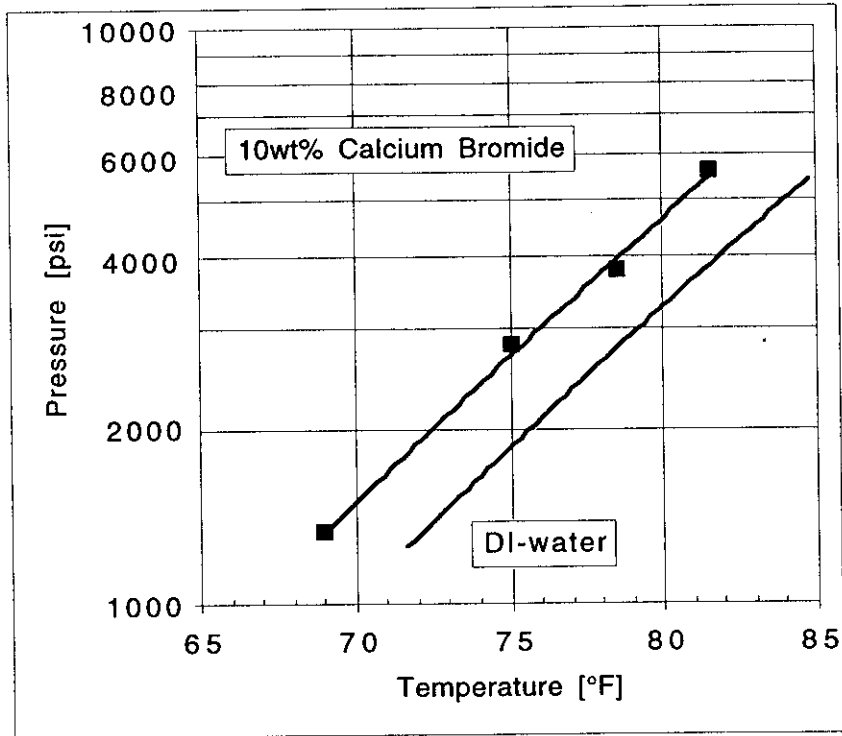


Figure 2— Hydrate phase equilibrium and pressure-temperature-trace of 20wt% CaBr₂ aqueous solution.

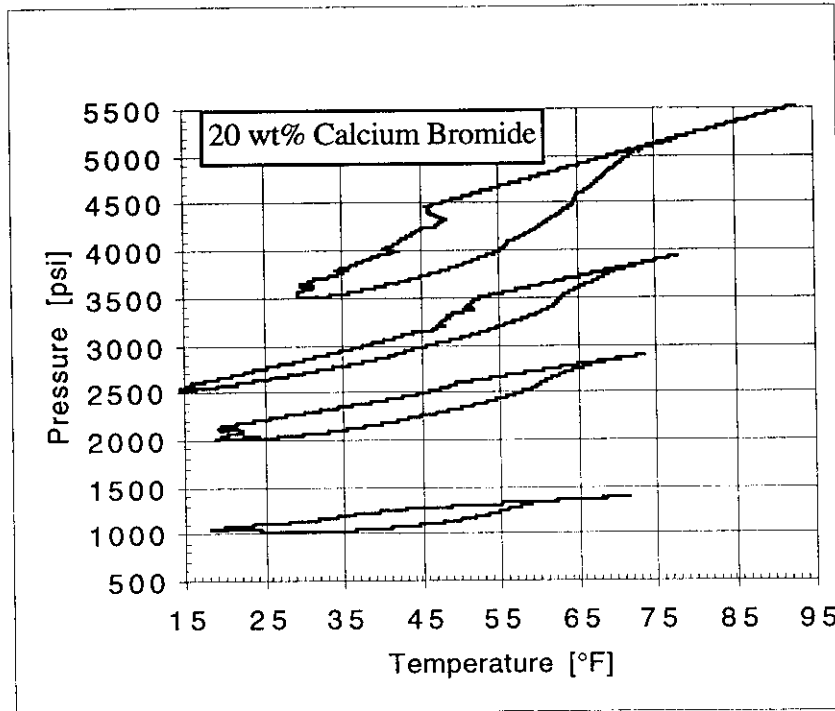
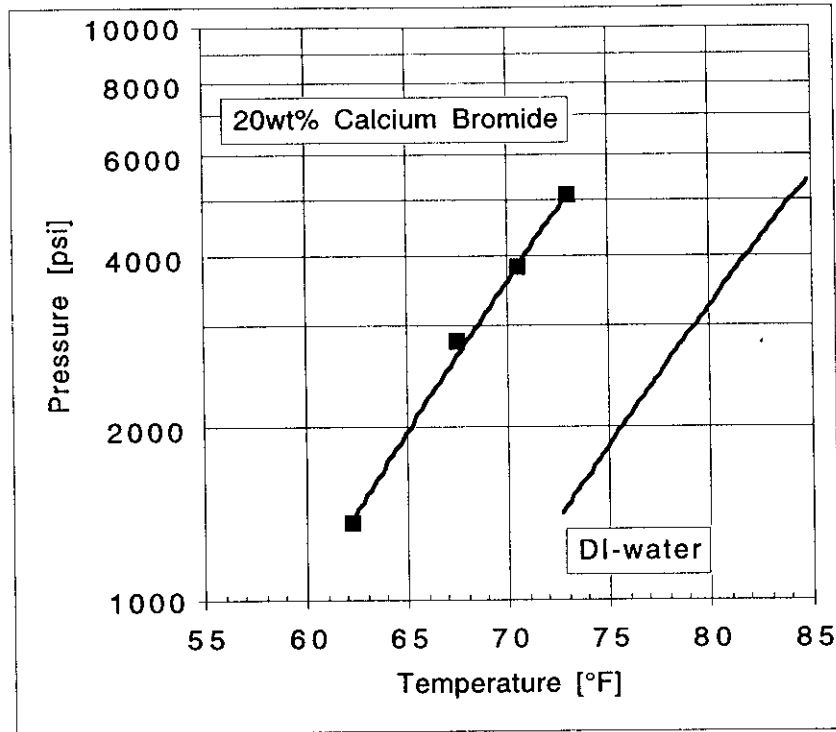


Figure 3— Hydrate phase equilibrium and pressure-temperature trace of 30wt% CaBr₂ aqueous solution.

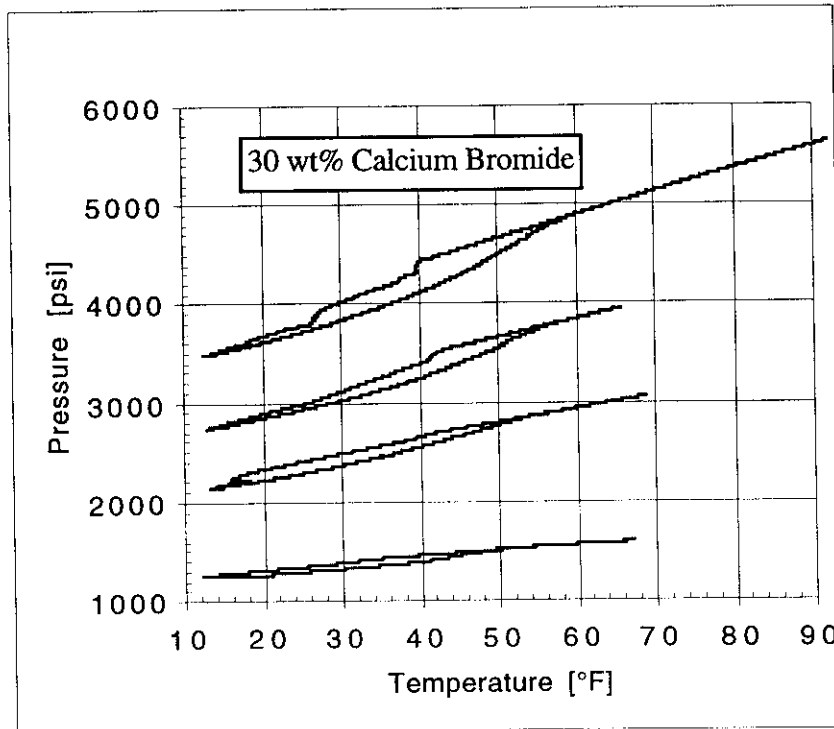
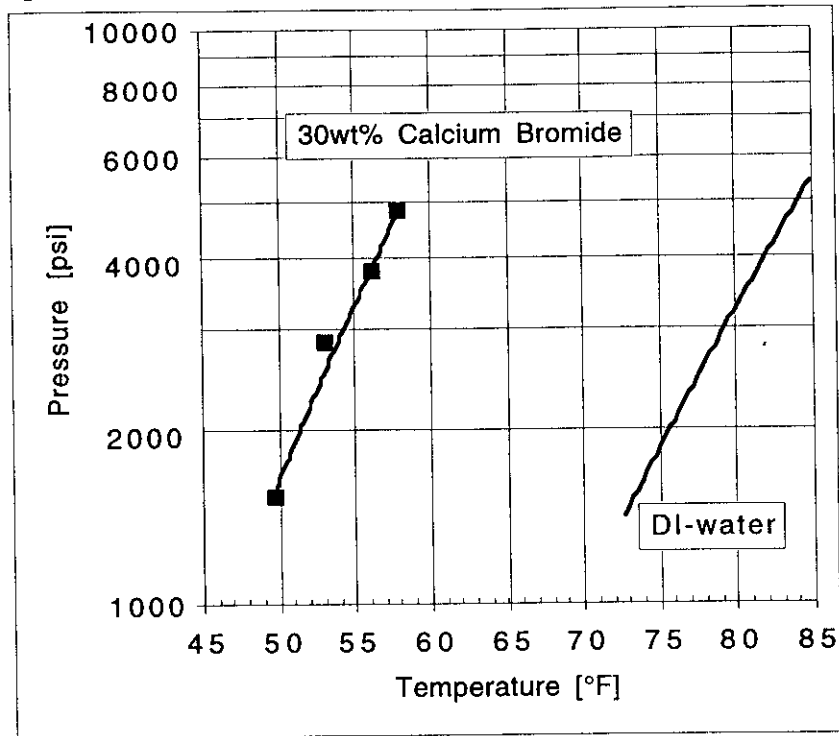


Figure 4— Hydrate phase equilibrium and pressure-temperature trace of 10wt% ZnBr aqueous solution.

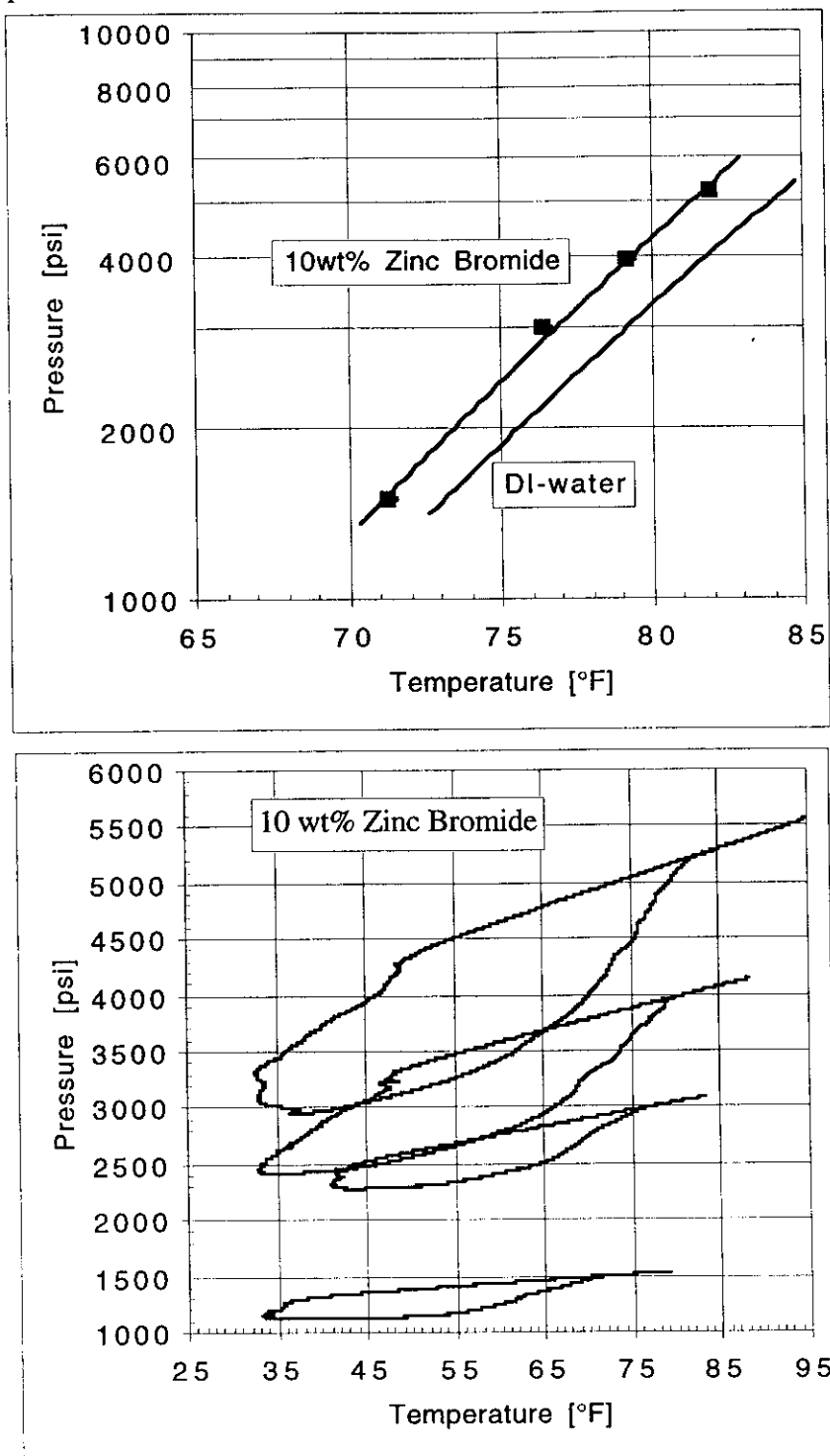


Figure 5- Hydrate phase equilibrium and pressure-temperature trace of 20wt% ZnBr aqueous solution.

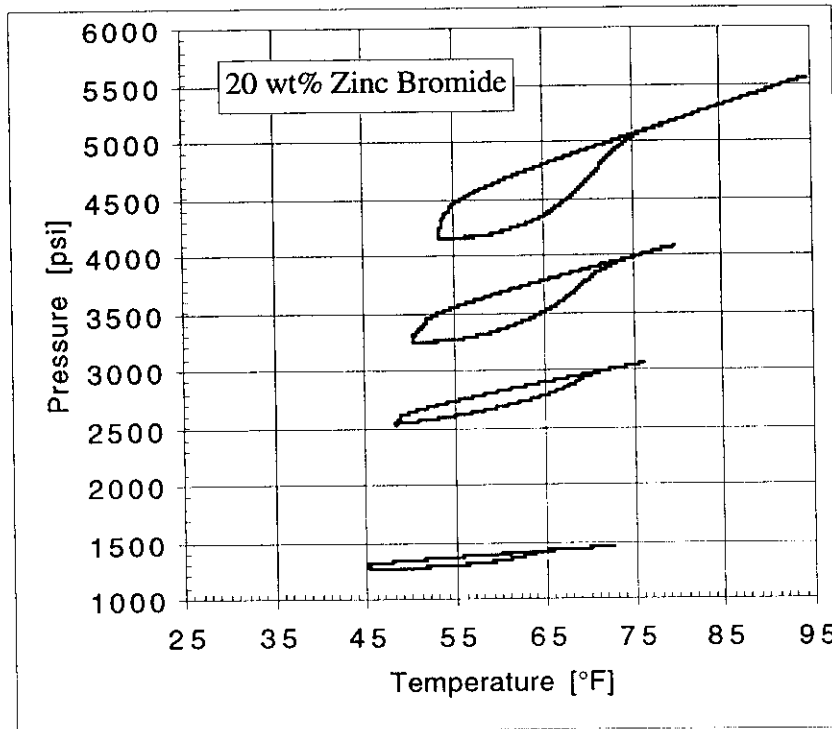
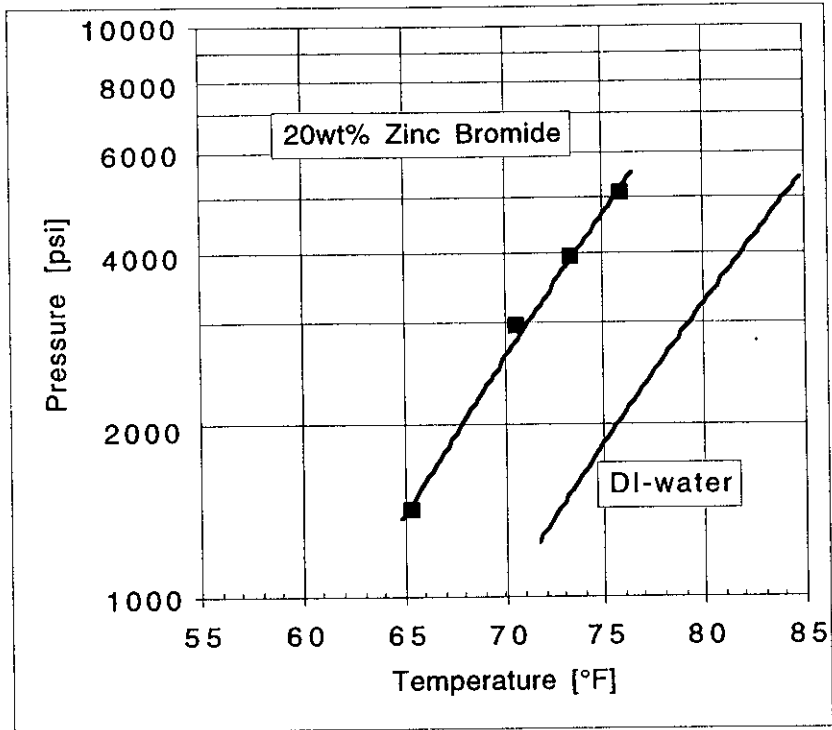


Figure 6– Hydrate phase equilibrium and pressure-temperature trace of 30wt% ZnBr aqueous solution.

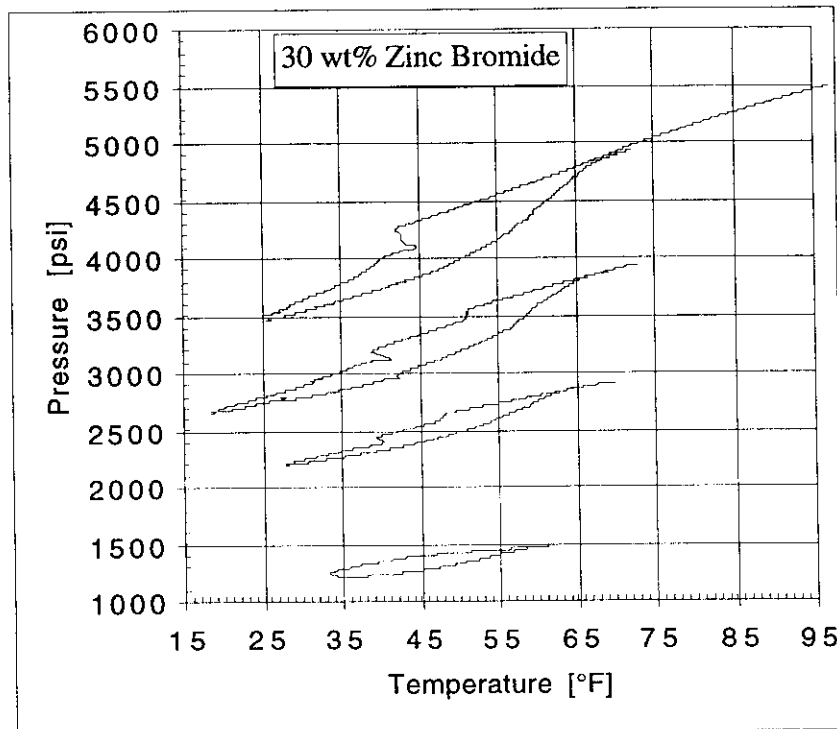
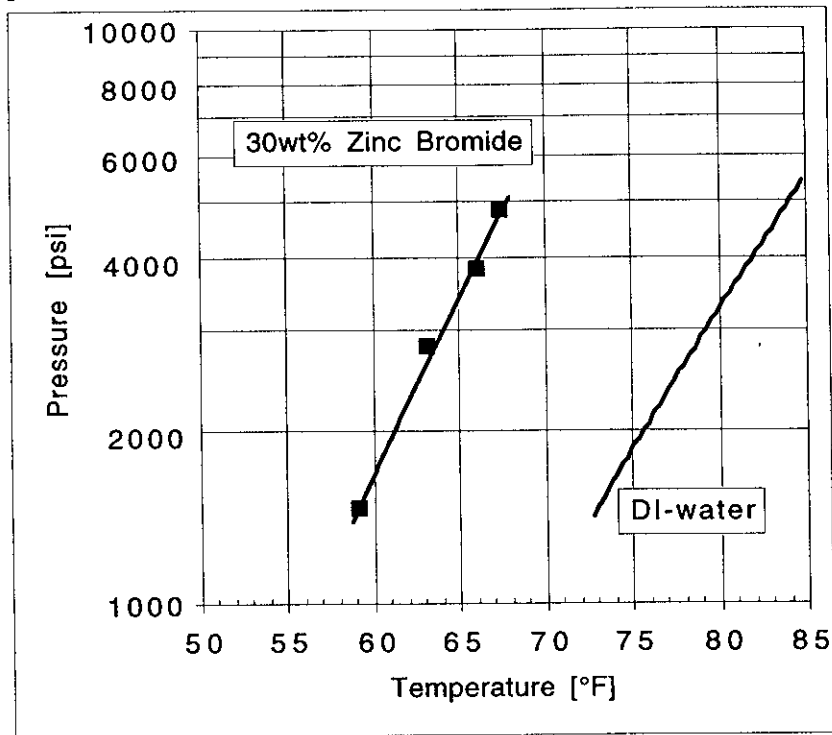


Figure 7- Hydrate phase equilibrium and pressure-temperature trace of 10wt% Na-Formate aqueous solution.

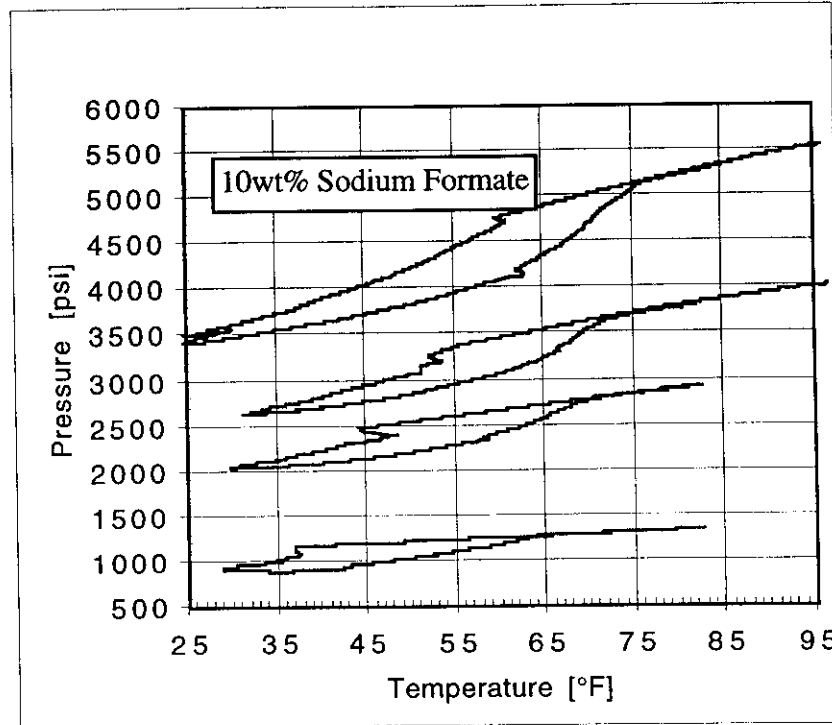
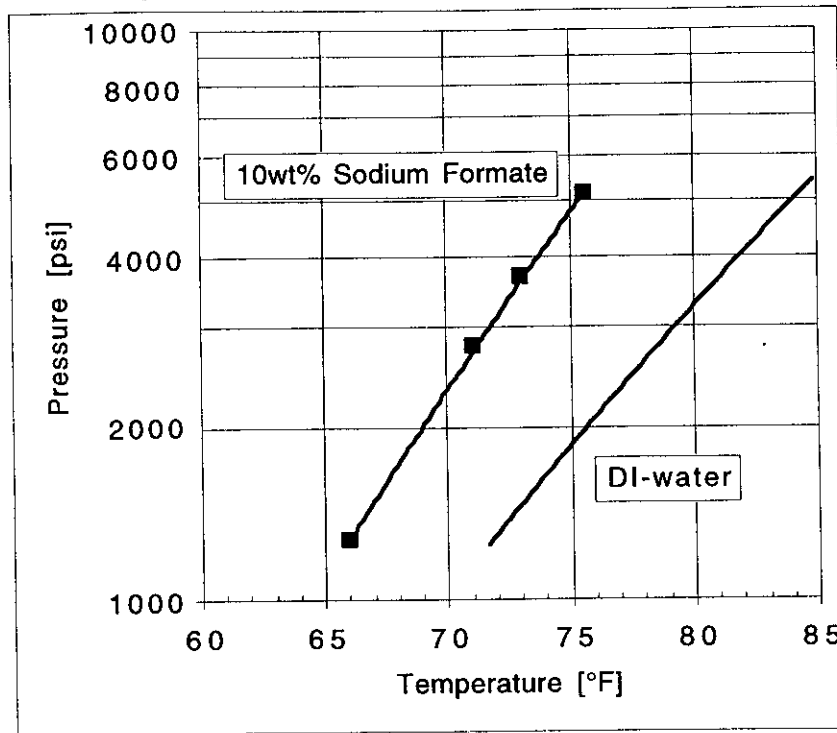


Figure 8- Hydrate phase equilibrium and pressure-temperature trace of 20wt% Na-Formate aqueous solution.

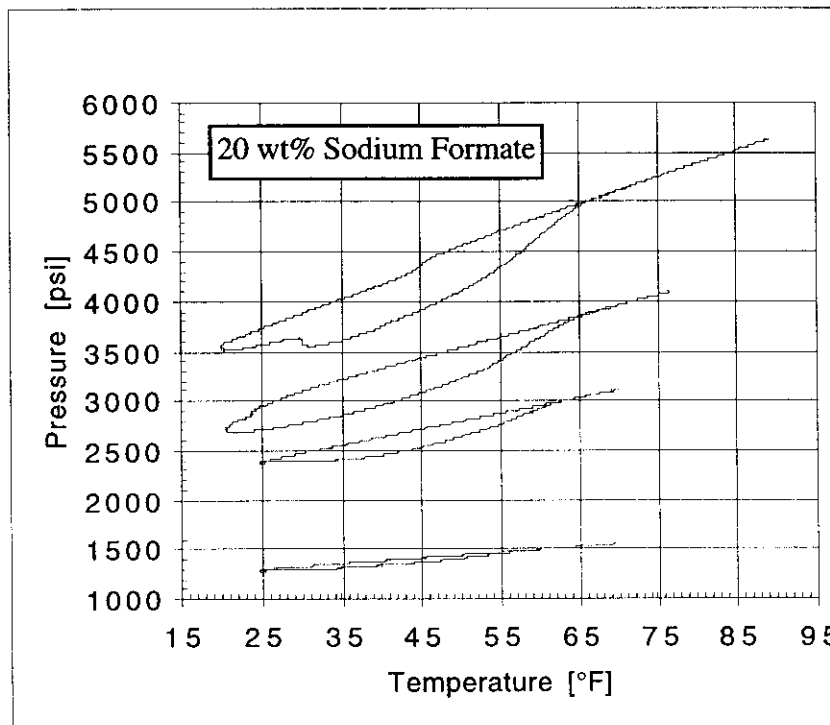
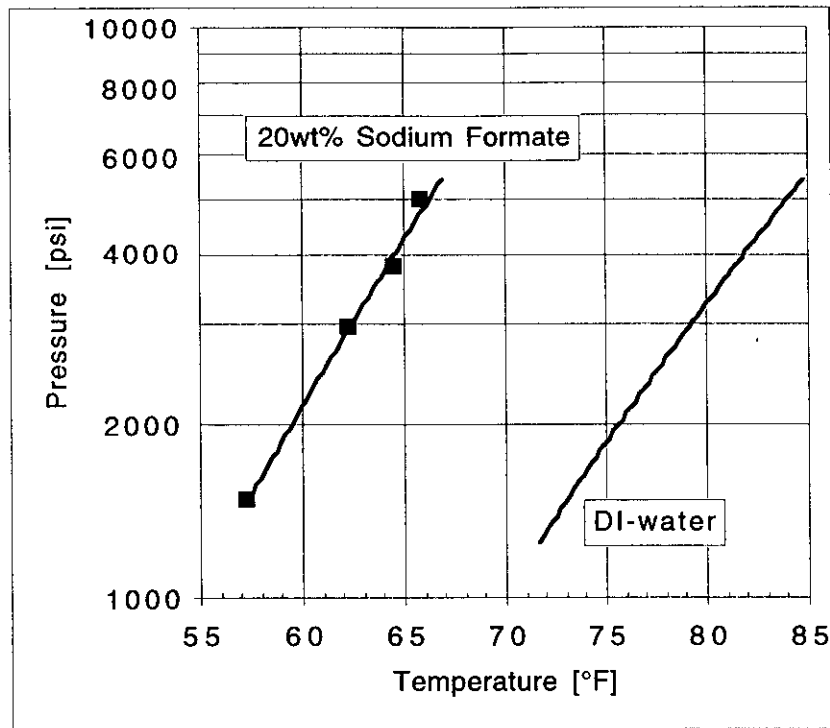


Figure 9- Hydrate phase equilibrium and pressure-temperature trace of 30wt% Na-Formate aqueous solution.

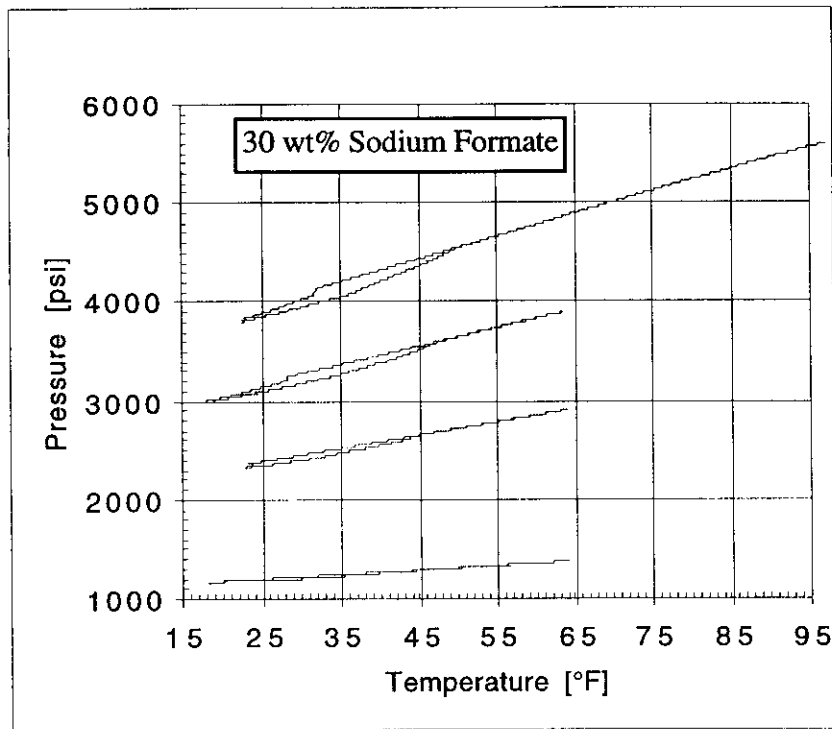
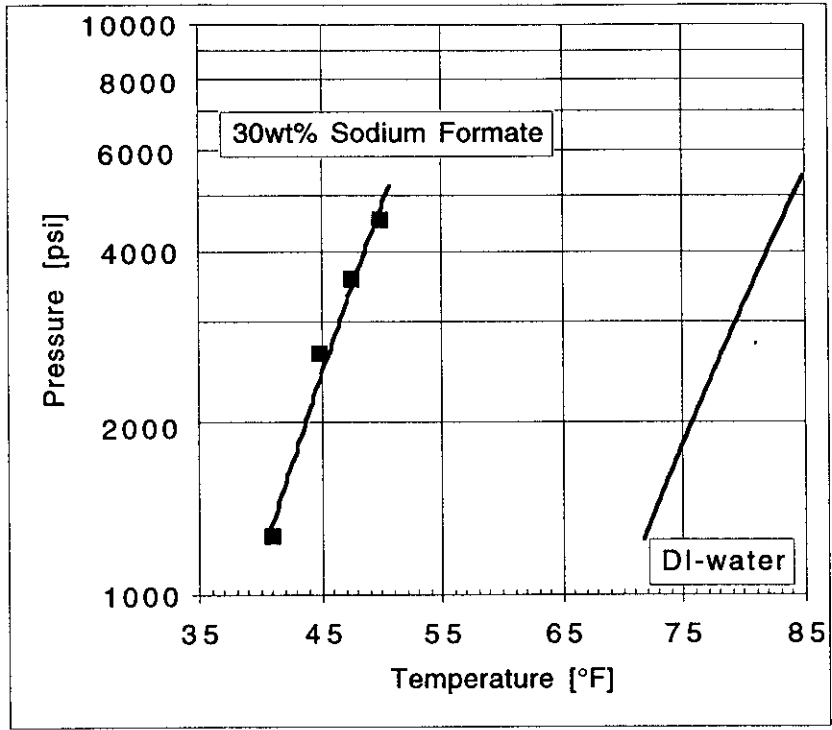


Figure 10- Hydrate phase equilibrium and pressure-temperature trace of 15wt% K-Formate aqueous solution.

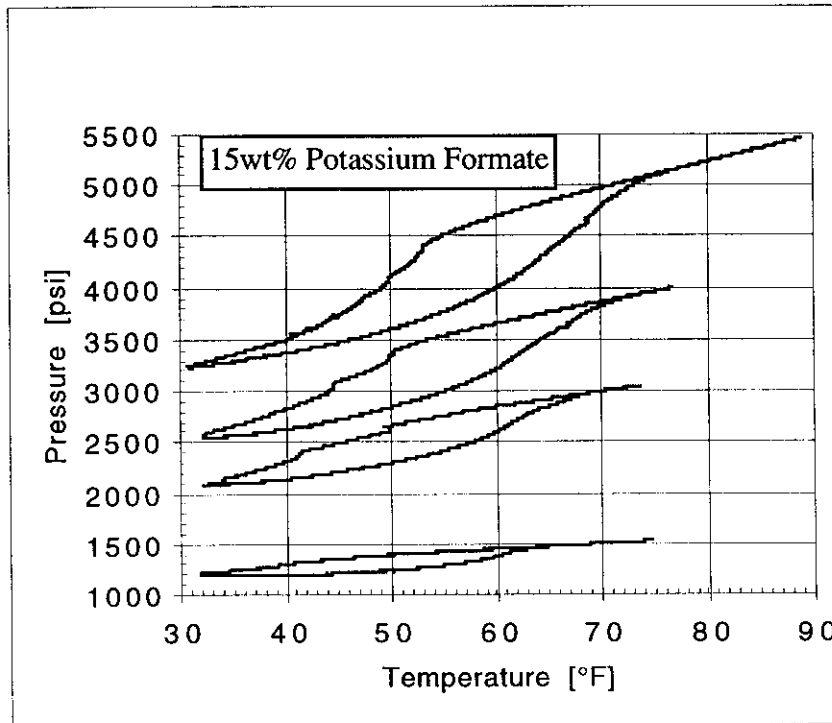
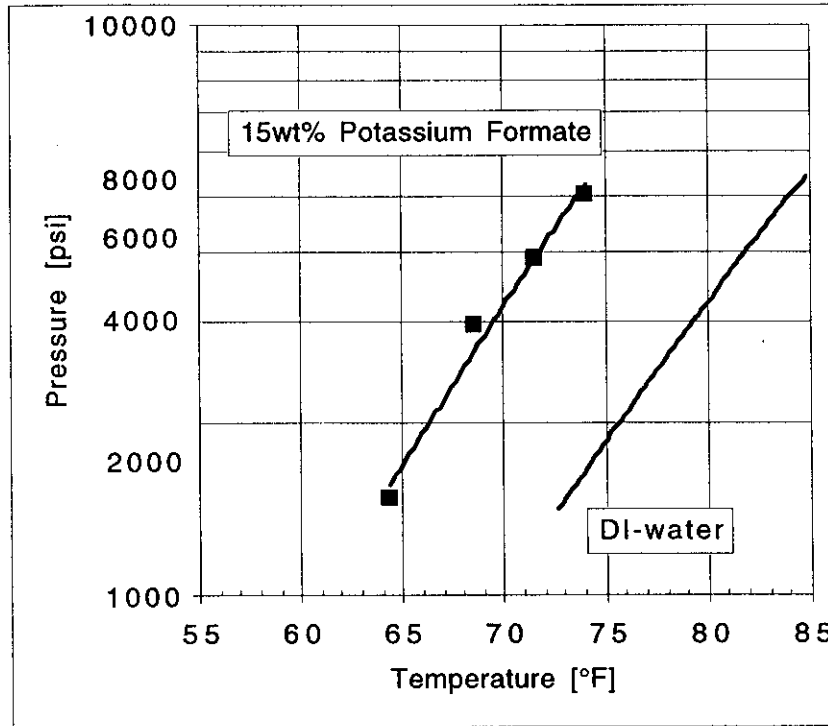


Figure 11- Hydrate phase equilibrium and pressure-temperature trace of 30wt% K-Formate aqueous solution.

