

**Novel Hydrate Prediction Methods
for Drilling Fluids - Phase 2
Final Report**

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Phase 2**

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Table of Contents

- 1. Executive Summary**
- 2. Project Deliverables**
- 3. The Experimental work and results**
- 4. Features of the hydrate prediction model, WHyP**
 - 4.1 WHyP input and output**
 - 4.2 Prediction of the Hydrate Phase Line - identifying the gas kick fluid**
 - 4.2.1 Statistical thermodynamic method**
 - 4.2.2 Gas specific gravity method**
 - 4.3 Prediction of the Hydrate Temperature Suppression, ΔT - Identifying the drilling fluid**
 - 4.3.1 Mud Activity Method**
 - 4.3.2 Drilling Fluid Composition Method**
 - 4.3.3 Resistivity and Density Method**
- 5. Results - the model calculations compared to experimental data**
 - 5.1 Prediction of the hydrate phase line of a gas mixture with no inhibitor in the drilling fluid**
 - 5.2 Prediction of the hydrate temperature suppression, ΔT using the measured water activity**
 - 5.3 Prediction of the hydrate temperature suppression, ΔT using the inhibitor concentration (wt%)**
 - 5.4 Prediction of the hydrate temperature suppression, ΔT using the measured mud filtrate resistivity and density**
- 6. References**

1. Executive Summary

The main objective for this two-phase Joint Industry Project (JIP) was to develop methods and computer software (model) to predict the hydrate equilibrium conditions of drilling fluids.

In phase 1 of this project, which was completed in June 1996, we developed 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 55°F; (5) except for the type of glycol, no information is needed about the mud composition; (6) valid for glycols and chloride salts concentrations of (0-30 wt%) and (5-30 wt%), respectively.

In phase 2 of this JIP we developed a new hydrate prediction model that is specifically tailored for use by drilling personnel. The model is named **WHyP** for **Westport Hydrate Prediction Program for Drilling Fluids**. **WHyP** is based on the statistical thermodynamic theory of van der Waals and Platteeuw, and incorporates the hydrate temperature suppression methods developed in Phase 1 as well as other available methods. **WHyP** is Windows 95[®] compatible and is linked to an Excel interface for user friendly data input/output. The model is designed to be simple and easy to run while at the same time, maintaining high flexibility to accept a wide range of input data.

WHyP can be run in a **prediction mode** or a **design mode**. The **design mode** is a unique feature added to allow an interactive execution of the program. With the design mode, the user can determine the appropriate amount of a selected inhibitor to suppress hydrate formation at a given mudline pressure and temperature conditions.

A trial version of the software was mailed to the sponsors in July, 1997 for testing. Since then, this version was revised based on the comments received from Patrick Shuler (Chevron) and Richard Chambers (BPX), as well as our in-house testing. A final version of the software is attached to this report. Ultimately, since no software product can be considered complete, Westport Technology will continue to maintain the software with upgrades distributed to the sponsors annually.

To assess the accuracy of the model predictions, we compared the predictions of the model to measured gas hydrate temperature suppression of 101 solutions of mixed salts and glycols. The measured hydrate temperature suppression, ΔT was in the range of 0 to 47°F. The accuracy of the model in predicting the hydrate equilibrium temperature is within 1.75°F when using the drilling fluid composition, 3.34°F when using the mud filtrate resistivity and density, and within 8.46°F when using the measured activity.

This report also provides the background for the model development and the experimental measurements obtained as part of phase 1 and 2 of this JIP.

2. Project Deliverables

- All data generated under phase 1 of the project
- 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 of the following parameters :
 - For drilling fluids of known composition input weight fraction of each inhibitor
 - For drilling fluids of unknown composition input the following measured filtrate properties : Resistivity, density, temperature, glycol density and glycol molecular weight
- Measurements of solution activity and hydrate equilibrium for :
 - Na-Formate (10, 20, 40 wt%)
 - K-Formate (15, 30, 50 wt%)
 - ZnBr₂ (10, 20, 30 wt%)
 - CaBr₂ (10, 20, 30 wt%)

3. The experimental work and results

Table 1 contains selected properties of 101 different solutions inhibited for hydrate temperature suppression. All these data have been measured at Westport. Some of the hydrate temperature suppression data were obtained previous to this project. In chapter 5 the (composition, activity or density/resistivity data are used in the WHyP model to calculate temperature suppression, and the results are compared to the measured temperature suppression.

Table 2 contains the gas hydrate equilibrium data of the 12 solutions, measured in this project. These data are used to determine hydrate temperature suppression.

Table 1
Measured Temperature Suppression, Water Activity, Density And Resistivity
of tested aqueous solutions

No.	Solution	molarity	Water Activity	Density at 60°F [ppg]	Temp [°F]	Resistivity [ohm-m]	ΔT [°F]	Ref.
1	5 wt% NaCl + 5 wt% MeOH	0.88/1.60	0.957	8.563	72.9	0.1459	8.60	a
2	10 wt% NaCl + 10 wt% MeOH	1.80/3.29	0.897	8.786	71.8	0.0777	21.00	a
3	2.8 wt% KCl + 29.4 wt% MeOH	0.36/8.89	0.947	8.088	72.1	0.4148	35.00	
4	5 wt% NaCl + 5 wt% Ethylene Glycol	0.89/0.84	0.902	8.698	69.6	0.1218	6.60	a
4	5 wt% NaCl + 5 wt% Ethylene Glycol				72.0	0.1301	6.60	a
5	10 wt% NaCl + 10 wt% Ethylene Glycol	1.86/1.75	0.929	9.052	72.9	0.1049	16.80	a
6	20 wt% NaCl + 10 wt% Ethylene Glycol	n.a.	0.796		71.6	0.0447	39.70	d
7	10 wt% NaCl + 10 wt% Propylene Glycol ^(*)	1.84/1.41		8.983	77.0	0.1005	18.04	b
8	5 wt% NaCl + 5 wt% Glycerol	0.89/0.57		8.702	77.0	0.1390	5.12	b
9	10 wt% NaCl + 10 wt% Glycerol ^(*)	1.87/1.19		9.138	72.7	0.1131	12.68	b
10	10 wt% NaCl + 20 wt% Glycerol ^(*)	1.92/2.43		9.355	73.0	0.1259	19.50	b
11	10 wt% NaCl + 30 wt% Glycerol ^(*)	1.97/3.74		9.592	77.0	0.1559	26.61	b
12	20 wt% NaCl + 10 wt% Glycerol	4.01/1.27	0.802	9.774	72.1	0.0642	35.70	a
13	20 wt% NaCl + 20 wt% Glycerol	4.13/2.62	0.796	10.072	72.3	0.0614	42.10	a
14	20 wt% NaCl + 20 wt% Glycerol	n.a.			71.6	0.0802	46.91	a
15	23.4 wt% NaCl + 10 wt% Glycerol	4.85/1.32	0.632	10.112	73.0	0.0683	40.30	a
16	22.1 wt% NaCl + 15 wt% Glycerol	4.60/1.98	0.680	10.144	72.9	0.0602	43.50	a
17	20.8 wt% NaCl + 20 wt% Glycerol	n.a.					45.90	a
18	3 wt% NaCl + 5 wt% KCl + 5 wt% Glycerol	0.55/0.72/0.58	0.947	8.901	72.0	0.1189	7.60	a
19	5 wt% NaCl + 5 wt% KCl + 15 wt% Glycerol	0.95/0.74/1.83	0.921	9.251	73.8	0.1195	15.90	a
20	10 wt% NaCl + 10 wt% KCl + 10 wt% Glycerol	1.99/1.56/1.26	0.744	9.708	72.0	0.0466	23.20	a
21	5 wt% KCl + 5 wt% Glycerol	0.70/0.57	0.967	8.721	69.8	0.1057	3.35	a
22	5 wt% KCl + 10 wt% Glycerol ^(*)	0.71/1.14		8.795	77.0	0.1505	5.66	b
23	10 wt% KCl + 10 wt% Glycerol	1.46/1.18	0.958	9.095	72.9	0.1066	9.10	a
24	5 wt% CaCl ₂ + 5 wt% Glycerol	0.47/0.57	0.976	8.787	72.1	0.1388	4.00	a
25	5 wt% CaCl ₂ + 20 wt% Glycerol ^(*)	0.49/2.35		9.035	77.0	0.2151	8.23	b
26	10 wt% CaCl ₂ + 10 wt% Glycerol	1.00/1.20	0.962	9.243	73.0	0.1204	10.10	a
27	20 wt% NaCl + 20 wt% GEO MEG	n.a.	0.813	10.264			36.50	d
28	5.3 wt% NaCl + 12.8 wt% AquaCol-S ^(*)	0.96/0.23		8.805	77.0	0.1932	7.40	b
29	20 wt% NaCl + 10 wt% AquaCol-S	3.97/0.19	0.777	9.680	71.4	0.0785	36.50	d
30	10 wt% KCl + 10 wt% AquaCol-S	1.46/0.18	0.883	9.096	72.0	0.0730	11.60	d
31	10 wt% NaCl + 10 wt% KCl + 10 wt% AquaCol-S	1.98/1.56/0.19	0.814	9.680	72.3	0.0492	30.50	d
32	20 wt% Na-Formate + 10 wt% AquaCol-S	3.35/0.19	0.803	9.513	72.0	0.0929	30.20	d
33	20 wt% NaCl + 10 wt% HF100N	n.a.	0.789	9.847			36.40	d
34	15 wt% KCl + 30wt% HF100N	n.a.	0.827	9.931			29.90	d
35	30 wt% CaCl ₂ + 70 SynTec	n.a.	0.800				n.h.	d
36	5 wt% NaCl ^(*)	0.88	0.915	8.617	74.1	0.1325	3.75	b
36	5 wt% NaCl ^(*)				73.9	0.1321	3.75	b
37	10 wt% NaCl ^(*)	1.83	0.899	8.918	73.9	0.0594	8.42	b
37	10 wt% NaCl ^(*)				73.4	0.0753	8.42	b
38	12.5 wt% NaCl	2.33	0.886	9.105	74.5	0.0635	10.50	a
39	20 wt% NaCl	3.93	0.820	9.584	73.4	0.0516	28.23	a
39	20 wt% NaCl				74.5	0.0414	28.23	a
40	20.44 wt% NaCl	4.02	0.833	9.585	71.8	0.0446	27.00	a
41	26 wt% NaCl	5.32	0.728	9.983			35.20	a
42	10 wt% NaCl + 10 wt% KCl	1.95/1.53	0.834	9.513	71.8	0.0217	20.90	d

Table 1 (continued)

No.	Solution	molarity	Water Activity	Density at 60°F [ppg]	Temp [°F]	Resistivity [ohm-m]	ΔT [°F]	Ref.
43	5 wt% KCl ⁽¹⁾	0.69		8.588	77.0	0.1316	1.62	b
44	10 wt% KCl ⁽¹⁾	1.42		8.862	77.0	0.0672	6.92	b
45	20 wt% KCl	3.06	0.835	9.513	72.1	0.0259	17.00	d
46	5 wt% CaCl ₂ ⁽¹⁾	0.47		8.680	71.6	0.1259	2.34	b
47	5 wt% CaCl ₂				77.0	0.1449	2.34	b
48	14.42 wt% CaCl ₂	n.a.	0.989				14.00	a
49	15 wt% CaCl ₂	1.53	0.921	9.452	74.1	0.0649	15.20	a
50	19.22 wt% CaCl ₂	n.a.	0.908		72.1	0.0489	21.90	a
51	21 wt% CaCl ₂	n.a.					23.00	
52	26 wt% CaCl ₂	n.a.			71.6	0.0492	39.00	
53	10 wt% Na-Formate	1.57	0.846	8.903	72.7	0.1140	6.17	c
54	15 wt% Na-Formate	2.41	0.962	9.130	72.5	0.0993		
55	10 ppg (17.6 wt%) Na-formate	3.13	0.740	10.068				
56	11 ppg (19.4 wt%) Na-formate	3.74	0.676	10.944				
57	20 wt% Na-Formate	3.31	0.811	9.395	72.5	0.0829	14.93	c
58	30 wt% Na-Formate	5.3	0.775	10.021	73.4	0.0752	29.93	c
59	40 wt% Na-Formate	7.59	0.757	10.765	71.8	0.0981	39.20	d
59	40 wt% Na-Formate	7.62	0.938	10.806			39.20	d
60	5 wt% K-Formate	0.61	0.986	8.581	73.2	0.2602		
61	10 wt% K-Formate	1.25	0.970	8.806	73.4	0.1781		
62	15 wt% K-Formate	1.94	0.860	9.089			8.73	d
63	12 ppg (17.1 wt%) K-formate	2.93	0.584	12.033				
64	13.1 ppg (18.7 wt%) K-formate	3.47	0.562	13.052				
65	20 wt% K-Formate	2.64	0.957	9.255	72.7	0.0759		
66	30 wt% K-Formate	4.23	0.784	9.901	73.6	0.0341	23.95	c
67	40 wt% K-Formate	5.95	0.733	10.444	73.4	0.0380		
68	50 wt% K-Formate	7.94	0.670	11.149			n.h.	
69	21 wt% Ca-Nitrate	2.83	0.869	9.430	72.1	0.0848	7.40	d
70	15 wt% NaBr	1.52	0.944	8.689	70.0	0.0807		
71	20 wt% NaBr	2.29	0.888	9.830	71.8	0.0556	16.72	a
72	30 wt% NaBr	3.75	0.783	10.743	69.8	0.0401	29.80	a
73	5 wt% CaBr ₂	0.26	0.991	8.674	72.0	0.2144		
74	10 wt% Ca Br ₂	0.54	0.892	9.063			1.48	c
75	15 wt% Ca Br ₂	0.85	0.976	9.452	69.8	0.0792		
76	20 wt% Ca Br ₂	1.13	0.844	9.452			9.98	c
77	30 wt% Ca Br ₂	1.79	0.805	9.932	72.9	0.0492	23.24	c
78	5 wt% Zn Br ₂	0.36	0.854	8.704	72.0	0.2738		
79	10 wt% Zn Br ₂	0.75	0.919	9.063	73.6	0.1356	0.84	c
80	15 wt% Zn Br ₂	1.18	0.830	12.084	72.3	0.1148		
81	20 wt% Zn Br ₂	1.64	0.875	9.452	73.6	0.0905	7.00	c
82	30 wt% Zn Br ₂	2.71	0.844	9.932	73.2	0.0866	14.20	c
83	5 wt% MeOH	1.54	0.917	8.251				
84	10 wt% MeOH	3.05	0.896	8.146				
85	15 wt% MeOH	4.54	0.887	8.094				
86	40 wt% MeOH	11.68	0.833	7.808			37.00	
87	50 wt% MeOH	14.53	0.827	7.768				
88	5 wt% Ethylene Glycol	0.81	0.904	8.388				
89	10 wt% Ethylene Glycol	1.63	0.877	8.444				
90	15 wt% Ethylene Glycol	2.46	0.853	8.500				
91	20 wt% Ethylene Glycol	3.3	0.844	8.556				
92	30 wt% Ethylene Glycol	5.01	0.833	8.651				
93	5 wt% Glycerol	n.a.	0.962					
94	10 wt% Glycerol	1.11		8.543			7.00	a

Table 1 (continued)

No.	Solution	molarity	Water Activity	Density at 60°F [ppg]	Temp [°F]	Resistivity [ohm-m]	ΔT [°F]	Ref.
95	12.5 wt% Glycerol	n.a.					5.50	a
96	20 wt% Glycerol	2.26		8.697			11.00	a
96	20 wt% Glycerol	2.26					9.50	a
97	30 wt% Glycerol	3.5	0.942	8.959			16.72	a
97	30 wt% Glycerol	3.5	0.942	8.959			14.80	a
98	40 wt% Glycerol	n.a.	0.826					
99	5 wt% AquaCol-S	0.084	0.920	8.397				
100	10 wt% AquaCol-S	0.17	0.938	8.512			2.10	d
100	10 wt% AquaCol-S	0.169	0.917	8.453			2.10	d
101	15 wt% AquaCol-S	0.26	0.872	8.527				

^(*) density at 77°F, measured in JIP phase 1

molarity = mol / liter solution

n.h. = No hydrate formation in test

n.a. = Not available

The sources of the measured temperature suppressions (ref.: Table 1, column 9) are :

- a : Yousif & Young, 1987⁴
- b : Phase 1 (this project)¹
- c : Phase 2 (this project)
- d : Ebeltoft, Yousif and Soergaard, 1997¹⁴

Table 2
Measured Gas Hydrate Equilibrium Temperature and Pressure

Solution	Run ID	Temperature [°F]	Pressure [psia]
10 wt% Calcium Bromide	CBRR1P5500	81.50	5600
	CBRR2P4000	78.50	3800
	CBRR3P3000	75.00	2800
	CBRR4P1500	69.00	1330
20 wt% Calcium Bromide	CABR1P5500	73.00	5080
	CABR2P4000	70.50	3820
	CABR3P3000	67.50	2840
	CABR4P1500	62.20	1363
30 wt% Calcium Bromide	CARR1P5500	58.00	4850
	CARR2P4000	56.20	3785
	CARR3P3000	53.10	2855
	CARR4P1500	49.70	1525
10 wt% Sodium Formate	NAFR1P5500	75.60	5130
	NAFR2P4000	73.00	3680
	NAFR3P3000	71.00	2800
	NAFR4P1500	66.00	1280
20 wt% Sodium Formate	NFAR1P5500	65.80	5000
	NFAR2P4000	64.50	3825
	NFAR3P3000	62.20	2980
	NFAR4P1500	57.20	1480
30% Sodium Formate	NFMR1P5500	50.00	4545
	NFMR2P4000	47.40	3595
	NFMR3P3000	44.80	2660
	NFMR4P1500	40.95	1264
10 wt% Zinc Bromide	ZBRR1P5500	81.95	5230
	ZBRR2P4000	79.20	3972
	ZBRR3P3000	76.40	3010
	ZBRR4P1500	71.30	1503
20 wt% Zinc Bromide	ZNBR1P5500	75.85	5085
	ZNBR2P4000	73.40	3955
	ZNBR3P3000	70.60	2985
	ZNBR4P1500	65.30	1430
30 wt% Zinc Bromide	ZNRR1P5500	67.45	4820
	ZNRR2P4000	66.00	3817
	ZNRR3P3000	63.10	2825
	ZNRR4P1500	59.10	1465
15 wt% Potassium Formate	KFMR1P5500	74.00	5065
	KFMR2P4000	71.50	3890
	KFMR3P3000	68.50	2980
	KFMR4P1500	64.30	1480
30 wt% Potassium Formate	KFAR1P5500	57.10	4596
	KFAR2P4000	55.80	3870
	KFAR3P3000	53.10	2812
	KFAR4P1500	48.90	1532
50 wt% Potassium Formate	KFAR1P5500	No Hydrate Formation	

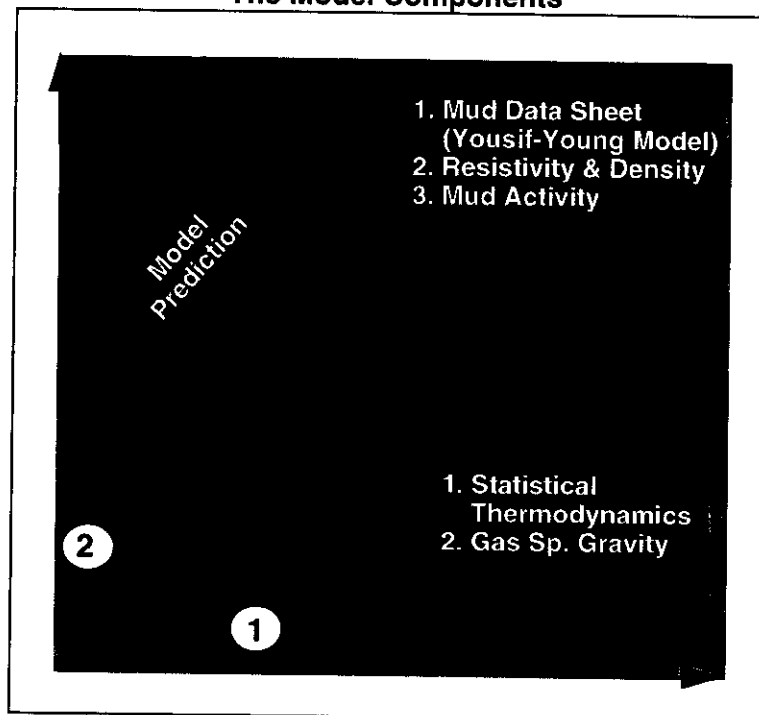
4. Features of the hydrate prediction model, WHyP

WHyP is the state-of-the-art hydrate prediction model specifically tailored for use by drilling personnel. To use the model, only minimal prior knowledge of the phase behavior of natural gas hydrates is required. **WHyP** is Windows 95® compatible and is linked to an Excel interface for user friendly data input/output. The model is designed to be simple and easy to run while at the same time, maintaining high flexibility to accept a wide range of input data. The model can be run in a **prediction mode** or a **design mode**.

The **design mode** is a unique feature added to allow an interactive execution of the program. The **design mode** helps the user to interactively vary the amount and type of inhibitor to keep the mud system outside the hydrate region for a given BOP pressure and temperature. The user must select one inhibitor, and input the temperature and pressure conditions. If the selected inhibitor is not adequate to inhibit hydrates at the specified mudline pressure and temperature, the program will request that you abort.

The following section describes the models used in WHyP. For a closer study of these, the references at the end of this report should be helpful. Figure 1 shows the models used by WHyP. The methods to determine the pure water line (line 1) are described in section 4.2, and section 4.3 treats the models for determining the temperature suppression, ΔT .

Figure 1
The Model Components



By determining the phase line 1 and the ΔT , phase line 2 which represents the hydrate equilibrium conditions of an inhibited mud can be determined as illustrated in Figure 1.

4.1 WHyP input and output

The computer program requires the characterization of both the hydrocarbon phase (the gas kick fluid) and the aqueous phase (drilling fluid). **WHyP** can be used for prediction of hydrate equilibrium at pressures up to 10,000 psi (70.0 MPa). It allows for a maximum temperature suppression of 55.8 °F (31.0 °K). These limitations were set by the experimental data available during development of the model. Anytime the concentration of the selected inhibitor(s) exceeds the saturation limit or the model accuracy in predicting the hydrate temperature suppression, ΔT , the program will abort.

The **WHyP** program allows for input data in either SI or field units. The output will be in the chosen unit system. The user interface is built up through a series of screens, starting by identifying the hydrate forming natural gas (section 4.2). Next the user identifies the drilling fluid in use (section 4.3), or asks the program to design a sufficiently inhibited mud (in the design mode). Finally the thermal conditions are specified. **WHyP** will let you calculate either hydrate temperature at set pressure or hydrate pressure at set temperature. The program can also calculate the entire hydrate equilibrium line (up to 10,000 psi (70.0 MPa)), and plots up to 5 hydrate lines on the output sheet for visual comparison.

4.2 Prediction of the Hydrate Phase Line - identifying the gas kick fluid

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

4.2.1 Statistical thermodynamic method

The statistical thermodynamic theory of van der Waals and Platteeuw² represents the backbone for the **WHyP** model. This part of the model provides the main predictive tool for the hydrate phase equilibrium of pure water/natural gas systems (shown as line 1 in Figure 1).

WHyP accepts the following species in the gas kick fluid :

Table 3
Accepted Gas Components

Methane	C1	Heptane	n-C7	Hexadecane	n-C16
Ethane	C2	Octane	n-C8	Heptadecane	n-C17
Propane	C3	Nonane	n-C9	Octadecane	n-C18
Isobutane	i-C4	Decane	n-C10	Nonadecane	n-C19
Normal Butane	n-C4	Undecane	n-C11	Eicosane	n-C20
Isopentane	i-C5	Dodecane	n-C12	Carbon dioxide	CO2
Normal pentane	n-C5	Tridecane	n-C13	Nitrogen	N2
Cyclopentane	c-C5	Tetradecane	n-C14	Hydrogen sulfide	H2S
Hexane	n-C6	Pentadecane	n-C15		

WHyP assumes that there is sufficient water present to form hydrates. The solubility of hydrocarbons in water is negligible. It calculates equilibrium of structure I and II hydrates, and allows for a 2 phase flash to account for gas and condensate.

In the following is a brief introduction to the statistical thermodynamic approach to hydrate equilibrium calculations. A more detailed description can be found in the literature². 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.

A multiple component and multiple phase system is at thermodynamic equilibrium when the chemical potential, μ of each component is the same in all phases

Van der Waals and Platteeuw calculated the chemical potential of water in the hydrate state from a fictitious state of empty lattice (MT) added the effect of the guest molecules (K) stabilizing the cavities (i)

$$\mu^H = \mu^{MT} + RT \sum_i v_i \ln \left(1 - \sum_K y_{Ki} \right)$$

Langmuir adsorption theory gives the probability (Y_{Ki}) of a cavity (i) being occupied by a hydrate forming molecule (K). C_{Ki} is the Langmuir adsorption constant at the specified temperature

$$y_{Ki} = \frac{c_{Ki} f_K}{1 + \sum_{j=1} c_{ji} f_j}$$

A general expression for the chemical potential of water in the co-existing phase is made by relating it to some reference state (0) :

$$\mu^w = \mu_w^0 + RT \ln \left(\frac{f^w}{f_w^0} \right)$$

Combined to the final equation of energy equilibrium of water in existing phases. Δ represents the difference between the fictitious empty lattice condition and the co-existing water phase (liquid or ice) at reference condition.

$$\frac{\Delta\mu_0}{RT_0} - \int_{T_0}^T \frac{(\Delta H_0 + \Delta C_p (T - T_0))}{RT^2} dT + \int_0^P \frac{\Delta V}{RT} dP = \ln(a_w) - \sum_i v_i \ln \left(1 - \sum_K y_{Ki} \right)$$

The water activity is the term in the energy balance that reflects the effect of hydrate inhibitors.

$$\ln\left(\frac{f_w}{f_w^0}\right) = \ln a_w$$

WHyP uses the Suave-Redlich-Kwong equation of state to calculate the fluid phase fugacities of all components in all phases present.

4.2.2 Gas specific gravity method

In the absence of a reliable composition of the gas kick fluid, the statistical model of van der Waals and Platteeuw² cannot be used. To overcome this difficulty (unknown gas composition), a specific gravity correlation³ is included in the program to determine the pure water line (line 1 in Figure 1).

This empirical correlation uses only the specific gravity, γ of the kick fluid to predict the hydrate equilibrium temperature at a given pressure. The method is less accurate than the thermodynamic approach of van der Waals and Platteeuw. It is only to be used as a first estimate of the hydrate equilibrium temperature when gas composition data are not available. The specific gravity correlation introduced in **WHyP** is an improvement over the previous method³. Included in the new specific gravity correlation are the hydrate equilibrium data measured since the publication of the original method in 1944. The equation developed and included in this computer code is:

$$T, ^\circ F = -15.428 + 24.422 \ln(\gamma_s) + 12.604 \ln(P, psia)$$

4.3 Prediction of the Hydrate Temperature Suppression, ΔT - identifying the drilling fluid

When the drilling fluid contains hydrate inhibitors, such as salts and glycols, other tools are required to determine the suppressing effect, or ΔT of these inhibitors.

With **WHyP** the user can chose to input the weight fraction of each inhibitor present in the drilling fluid or the mud filtrate resistivity and density. A direct input of the measured or calculated solution activity can also be selected by the user.

The advantage of the activity and the resistivity methods is that the hydrate temperature suppression, ΔT , can be determined for a drilling fluid of unknown composition.

4.3.1 Mud Activity Method

This method uses measured activity of the drilling fluid to predict the hydrate temperature suppression, ΔT . This is the most accurate of the methods, provided that the activity measurements are good. The water activity is a direct measure for inhibitor concentration according to classical thermodynamics.

For the gas hydrate base line (line 1 in figure 1), the water activity is very close to unity. This changes as impurities enter the water rich phase, and in an inhibited system, the term mostly effected by the impurities is the water activity. The classical approach to determining gas hydrate equilibrium is by assuming that the water activity is the only parameter (in the energy balance) that effects the equilibrium temperature (or pressure) through the inhibition.

4.3.2 Drilling Fluid Composition Method

This method determines the hydrate temperature suppression, ΔT , from the weight percentage of each inhibitor in the solid free mud formulation⁴. The method can be used for mixed inhibitors when the composition of the drilling fluid is known. The **WHyP** model allows for use of the following inhibitors:

**Table 4
Accepted Inhibitor Components**

Inhibitor	Concentration limit (wt %)	Inhibitor	Concentration limit (wt %)
NaCl	26.4	Methanol	40.0
KCl	25.5	Ethylene Glycol	40.0
CaCl ₂	30.0	Propylene Glycol	40.0
NaBr	47.5	Glycerol	40.0
CaBr ₂	32.0	Polyalkylene Glycol	40.0
ZnBr ₂	32.0	NaCOOH	42.0
		KCOOH	50.0

A correlation for mixed inhibitors was developed by Yousif and Young⁴, and further improved in phase 1 of this project¹. This model uses the assumption that inhibitors will shift the hydrate equilibrium temperature regardless of the pressure. An empirical expression was developed, giving the hydrate temperature suppression, ΔT as a polynomial of the inhibitor concentration, x_{in} :

$$\Delta T = 84.998x_{in} + 1821x_{in}^2 - 3522x_{in}^3$$

The inhibitor mole fraction, x_{in} is calculated by Hammerschmidt's equation for inhibitor concentration, modified for mixed solutions:

$$x_{in} = \frac{\sum \left(((n-1)\alpha + 1) \frac{wt\%_s}{M_{w_s}} \right) + \frac{wt\%_g}{M_{w_g}}}{\sum \left(\frac{wt\%_s}{M_{w_s}} \right) + \frac{wt\%_g}{M_{w_g}} + \frac{wt\%_w}{M_{w_w}} - \beta_{mix}}$$

where α is the mixture's degree of ionization, and β is a correction factor accounting for the synergetic effects between salt and glycol in mixed inhibitors. This factor was fitted to experimental data from a range of mixed solutions. When the mud consists of either salts or glycol (not mixed), this factor equals zero and the inhibitor fraction converges to Hammerschmidt's original equation. A closer description of this expression is given in appendix A.

4.3.3 Resistivity and Density Method

This method, which was developed as part of phase 1 of the Novel Hydrate Prediction Methods Joint Industry Project¹, determines the hydrate temperature suppression, ΔT , using the resistivity and density of the mud filtrate. The resistivity and density used as input for this method must be measured at the same temperature. This method is not valid for use when bromide or formate salts are present.

The composition of mixed solutions of chloride salts (NaCl, KCl, CaCl₂) and glycol can be calculated as functions of the resistivity and density

$$R_{mix}, \rho_{mix} \leftrightarrow w_s, w_g$$

After calculating the inhibitor fraction of the mixed solution, the model proceeds with the method in section 4.3.2.

5. Results - the model calculations compared to experimental data

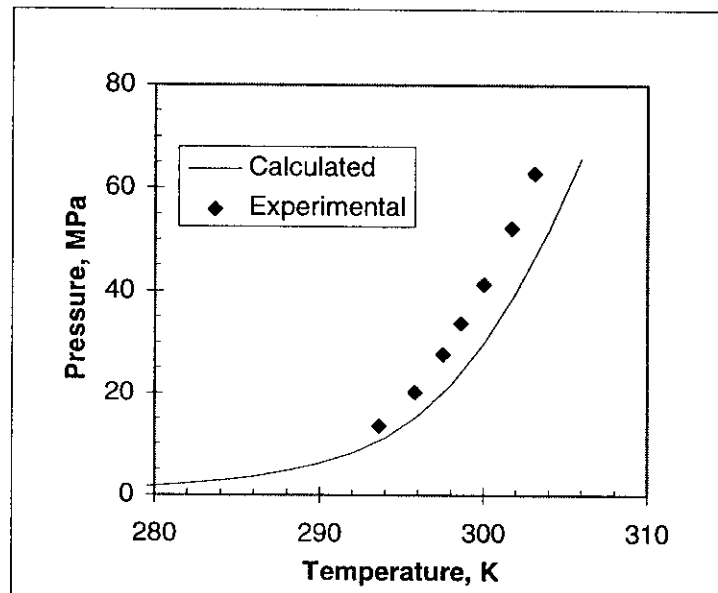
5.1 Prediction of the hydrate phase line of a gas mixture with no inhibitor in the drilling fluid

In the following section, measured gas hydrate equilibrium of selected gas mixtures from published literature are plotted with the equilibrium calculated using WHyP.

5.1.1

Gas composition: 90.6 wt% C1, 6.6 wt% C2, 1.8 wt% C3, 0.5 wt% iC4, 0.5 wt% nC4
no inhibitor in the drilling fluid
(McLeod, H.O., Campbell, J.M. (1961)⁵)

Figure 2
Hydrate Phase Equilibrium



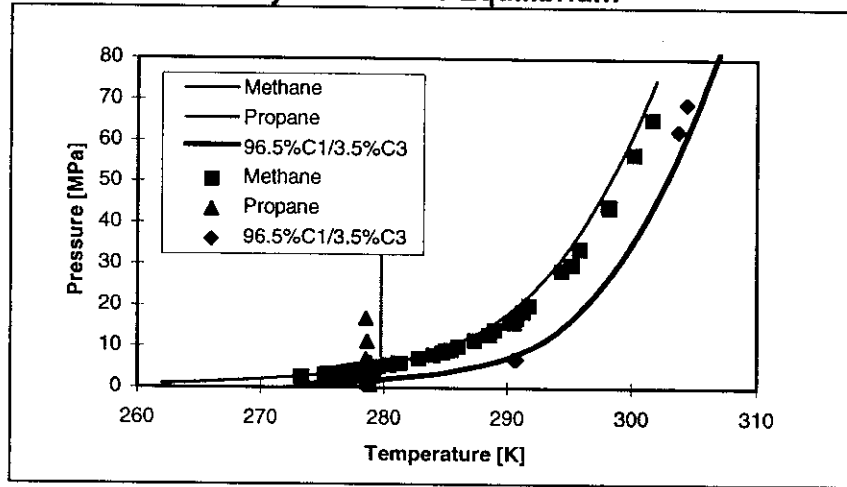
5.1.2

Gas composition: 96.5 wt% C1, 3.5 wt% C3. Shown with 100 wt% C1^{7,8,9,10} and 100 wt% C3^{9,11}

no inhibitor in the drilling fluid

(McLeod, H.O., Campbell, J.M. (1961)⁵)

Figure 3
Hydrate Phase Equilibrium



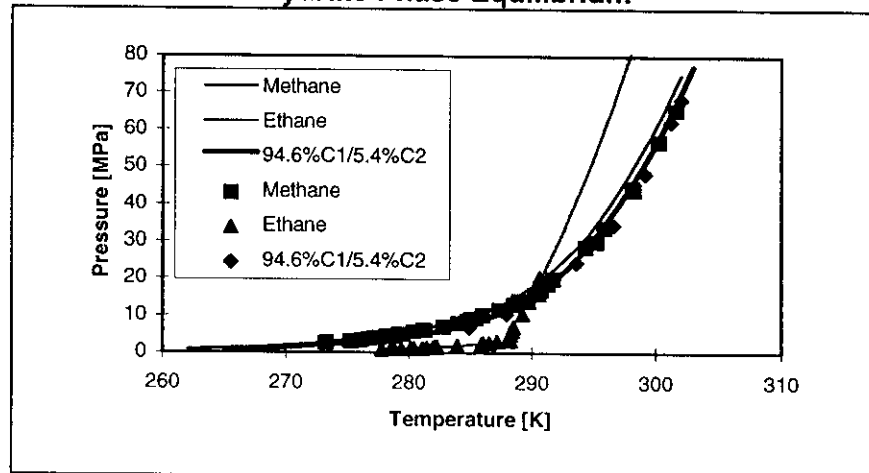
5.1.3

Gas composition: 94.6 wt% C1, 5.4 wt% C2. Shown with 100 wt% C1^{7,8,9,10} and 100 wt% C2^{12,13,14}

no inhibitor in the drilling fluid

(McLeod, H.O., Campbell, J.M. (1961)⁵)

Figure 4
Hydrate Phase Equilibrium



5.2 Prediction of the hydrate phase line of a gas mixture with bromides and formates in the drilling fluid

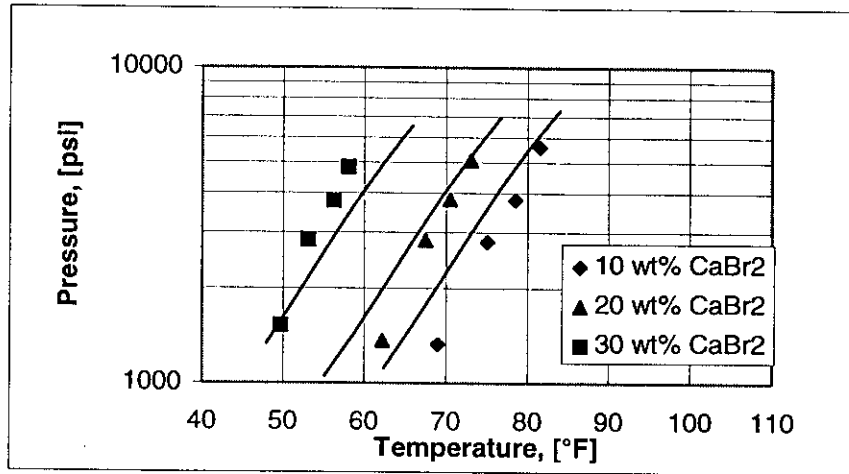
In this section the experimental data in table 2 are compared to the model predictions.

5.2.1

Gas composition: Green Canyon

Drilling fluid containing 10, 20 and 30 weight% CaBr₂

Figure 5
Hydrate Phase Equilibrium

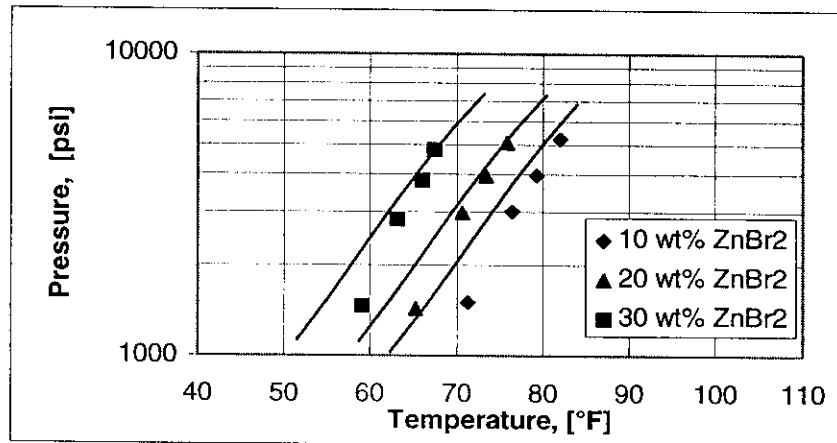


5.2.2

Gas composition: Green Canyon

Drilling fluid containing 10, 20 and 30 weight% ZnBr₂

Figure 6
Hydrate Phase Equilibrium

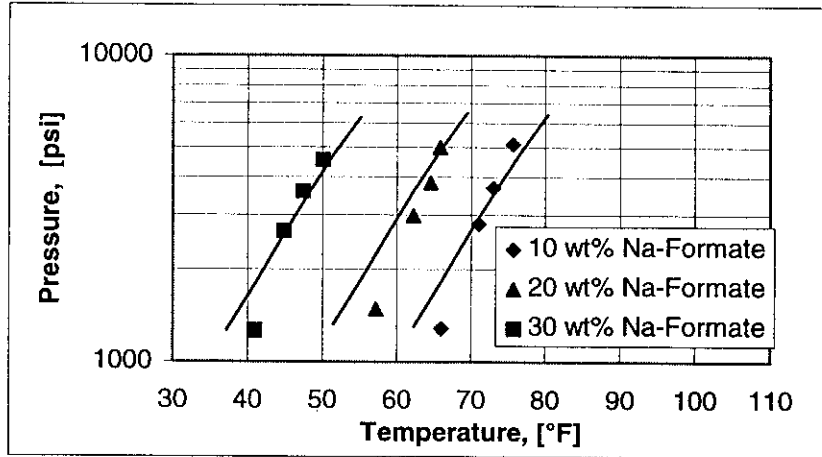


5.2.3

Gas composition: Green Canyon

Drilling fluid containing 10, 20 and 30 weight% Sodium formate

Figure 7
Hydrate Phase Equilibrium

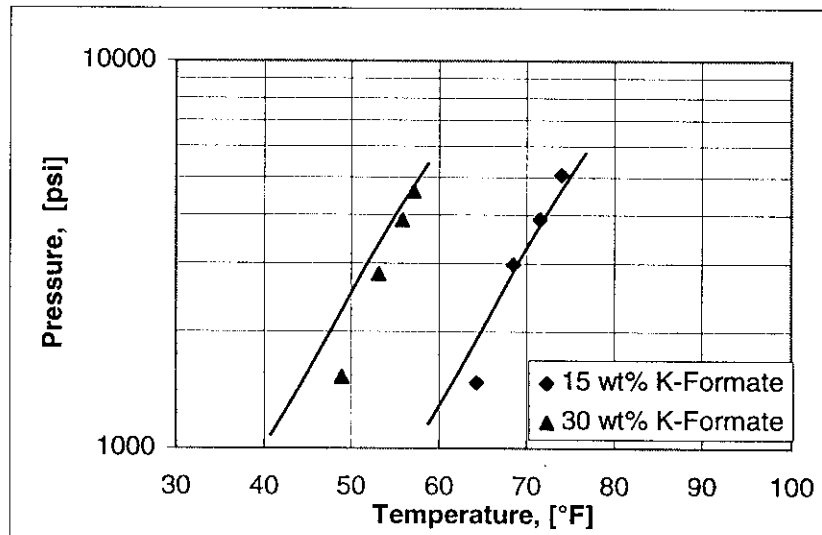


5.2.4

Gas composition: Green Canyon

Drilling fluid containing 15 and 30 weight% Potassium formate

Figure 8
Hydrate Phase Equilibrium



5.3 Prediction of the hydrate temperature suppression, ΔT using the measured water activity

When measured activity is used to identify the drilling fluid, the deviations between measured and calculated temperature suppression, ΔT , is mainly due to measurement error. The method is consistent with classical thermodynamic theories.

The Mean square error (M.S.E.) is defined :

$$M.S.E. = \sqrt{\frac{\sum_{j=1}^n \epsilon_j^2}{n}}$$

Where ϵ is the individual test's deviation between calculated and measured temperature suppression, and n is the number of samples tested.

Table 5 shows the WHyP predictions of hydrate temperature suppression from measured activity. The data are scattered, and for the 51 samples in Table 5, the mean square error is 8.46°F. To evaluate this deviation, the measured activity of some chloride solutions were compared to tabulated activities, showing a scatter in the activity measurements of up to 0.08 (mean square error of .047). Figure 9 shows a comparison between measured hydrate temperature suppression and suppression calculated by WHyP, using measured and tabulated activity. The MSE is 6.99°F for the calculations with measured activity and 2.17°F for temperature suppression calculated with tabulated activity. Based on these results we conclude that the uncertainty in activity measurements causes most of the error when the method is used. This method should be applied with care, and not at all if there is uncertainty about the accuracy of the measured activity data.

Figure 9
Test of Accuracy in Activity Measurements

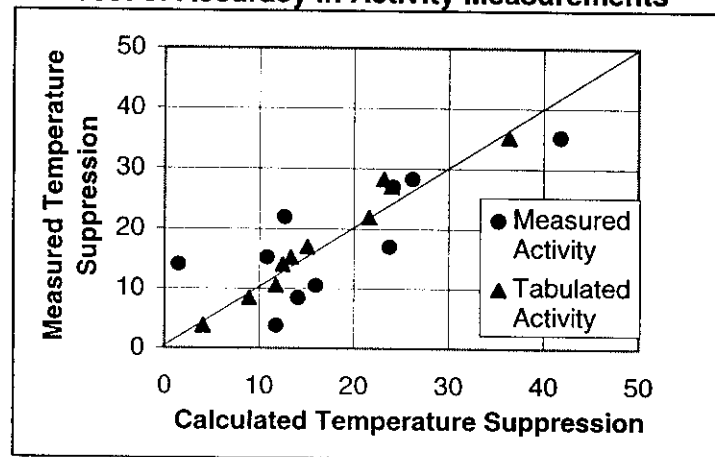


Table 5
Temperature Suppression Calculated from Measured Activity

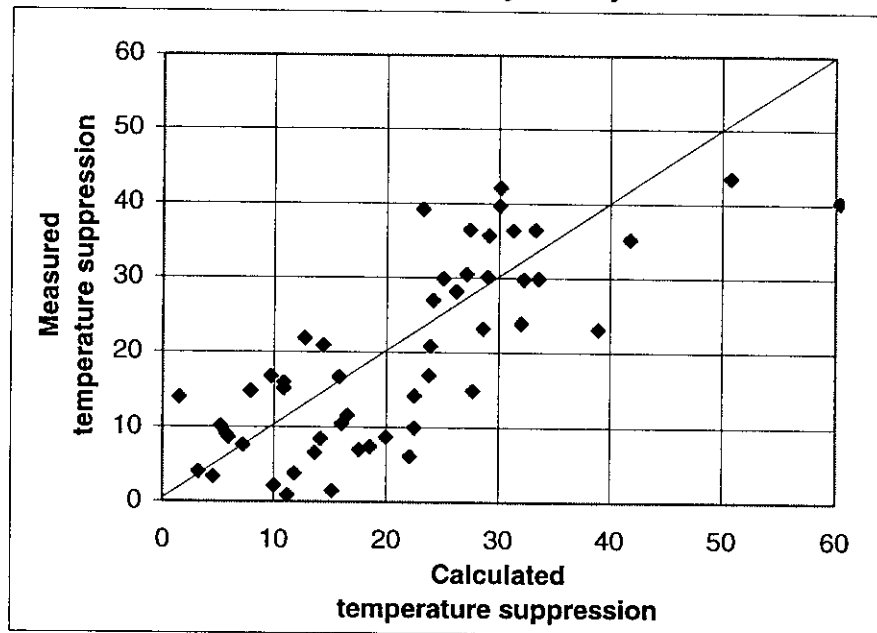
Item	Sample	measured		calculated	
		Water Activity	ΔT (°F)	ΔT^* (°F)	ϵ [°F]
1	5 wt% NaCl + 5 wt% MeOH	0.9568	8.60	5.86	-2.74
2	10 wt% NaCl + 10 wt% MeOH	0.8972	21.00	14.36	-6.64
4	5 wt% NaCl + 5 wt% Ethylene Glycol	0.9020	6.60	13.65	7.05
5	10 wt% NaCl + 10 wt% Ethylene Glycol	0.9294	16.80	9.70	-7.10
6	20 wt% NaCl + 10 wt% Ethylene Glycol	0.7962	39.70	30.05	-9.65
12	20 wt% NaCl + 10 wt% Glycerol	0.8022	35.70	29.06	-6.64
13	20 wt% NaCl + 20 wt% Glycerol	0.7957	42.10	30.13	-11.97
15	23.4 wt% NaCl + 10 wt% Glycerol	0.6315	40.30	60.41	20.11
16	22.1 wt% NaCl + 15 wt% Glycerol	0.6798	43.50	50.74	7.24
18	3 wt% NaCl + 5 wt% KCl + 5 wt% Glycerol	0.9472	7.60	7.20	-0.40
19	5 wt% NaCl + 5 wt% KCl + 15 wt% Glycerol	0.9213	15.90	10.86	-5.04
20	10 wt% NaCl + 10 wt% KCl + 10 wt% Glycerol	0.7443	23.20	38.88	15.68
21	5 wt% KCl + 5 wt% Glycerol	0.9665	3.35	4.53	1.18
23	10 wt% KCl + 10 wt% Glycerol	0.9585	9.10	5.63	-3.47
24	5 wt% CaCl ₂ + 5 wt% Glycerol	0.9762	4.00	3.20	-0.80
26	10 wt% CaCl ₂ + 10 wt% Glycerol	0.9617	10.10	5.18	-4.92
27	20 wt% NaCl + 20 wt% GEO MEG	0.8126	36.50	27.37	-9.13
29	20 wt% NaCl + 10 wt% AquaCol-S	0.7771	36.50	33.23	-3.27
30	10 wt% KCl + 10 wt% AquaCol-S	0.8826	11.60	16.52	4.92
31	10 wt% NaCl + 10 wt% KCl + 10 wt% AquaCol-S	0.8144	30.50	27.08	-3.42
32	20 wt% Na-Formate + 10 wt% AquaCol-S	0.8026	30.20	29.00	-1.20
33	20 wt% NaCl + 10 wt% HF100N	0.7889	36.40	31.25	-5.15
34	15 wt% KCl + 30wt% HF100N	0.8271	29.90	25.05	-4.85
35	30 wt% CaCl ₂ + 70 SynTec	0.7998	n.h.	29.46	n.a.
36	5 wt% NaCl	0.9149	3.75	11.80	8.05
37	10 wt% NaCl	0.8988	8.42	14.14	5.72
38	12.5 wt% NaCl	0.8859	10.50	16.03	5.53
39	20 wt% NaCl	0.8199	28.23	26.20	-2.03
40	20.44 wt% NaCl	0.8328	27.00	24.15	-2.85
41	26 wt% NaCl	0.7281	35.20	41.76	6.56
42	10 wt% NaCl + 10 wt% KCl	0.8344	20.90	23.90	3.00
45	20 wt% KCl	0.8353	17.00	23.76	6.76
48	14.42 wt% CaCl ₂	0.9889	14.00	1.49	-12.51
49	15 wt% CaCl ₂	0.9213	15.20	10.86	-4.34
50	19.22 wt% CaCl ₂	0.9084	21.90	12.72	-9.18
53	10 wt% Na-Formate	0.8462	6.17	22.06	15.89
57	20 wt% Na-Formate	0.8107	14.93	27.68	12.75
58	30 wt% Na-Formate	0.7753	29.93	33.53	3.60
59	40 wt% Na-Formate	0.8386	39.20	23.24	-15.96
62	15 wt% K-Formate	0.8599	8.73	19.95	11.22
66	30 wt% K-Formate	0.7844	23.95	32.00	8.05
68	50 wt% K-Formate	0.6697	n.h.	52.70	n.a.
69	21 wt% Ca-Nitrate	0.8690	7.40	18.56	11.16

Table 5 (continued)

Item	Sample	Water Activity	ΔT (°F)	ΔT^* (°F)	ϵ [°F]
71	20 wt% NaBr	0.8875	16.72	15.79	-0.93
72	30 wt% NaBr	0.7829	29.80	32.25	2.45
74	10 wt% CaBr ₂	0.8917	1.48	15.17	13.69
76	20 wt% CaBr ₂	0.8435	9.98	22.48	12.50
77	30 wt% CaBr ₂	0.8053	23.24	28.56	5.32
79	10 wt% ZnBr ₂	0.9190	0.84	11.19	10.35
81	20 wt% ZnBr ₂	0.8754	7.00	17.59	10.59
82	30 wt% ZnBr ₂	0.8435	14.20	22.47	8.27
97	30 wt% Glycerol (16.7)	0.9423	14.80	7.88	-6.92
100	10 wt% AquaCol-S	0.9276	2.10	9.96	7.86
				MSE :	8.46

n.h. = No hydrate formation
n.a. = Not available

Figure 10
Measured and Model Predicted Hydrate Temperature suppression, ΔT
using Mud Activity in WHyP



5.4 Prediction of the hydrate temperature suppression, ΔT using the inhibitor concentration (wt%)

This model can be applied with high accuracy to a wide range of inhibitor concentrations. The 67 samples in table 6 give a mean square error of 1.75°F.

Some caution should be used when applying the model to mud with high concentration of salts (close to saturation), as other components in the mud might effect the solubility limits.

Table 6
Hydrate temperature suppression calculated from mud composition

Item	Sample	meas. Calculated		
		ΔT (°F)	ΔT^* (°F)	ϵ [°F]
1	5 wt% NaCl + 5 wt% MeOH	8.60	7.70	-0.90
2	10 wt% NaCl + 10 wt% MeOH	21.00	19.35	-1.65
4	5 wt% NaCl + 5 wt% Ethylene Glycol	6.60	6.54	-0.06
5	10 wt% NaCl + 10 wt% Ethylene Glycol	16.80	17.97	1.17
6	20 wt% NaCl + 10 wt% Ethylene Glycol	39.70	39.16	-0.54
7	10 wt% NaCl + 10 wt% Propylene Glycol	18.04	16.15	-1.89
8	5 wt% NaCl + 5 wt% Glycerol	5.12	5.54	0.42
9	10 wt% NaCl + 10 wt% Glycerol	12.68	14.79	2.11
10	10 wt% NaCl + 20 wt% Glycerol	19.50	20.55	1.05
11	10 wt% NaCl + 30 wt% Glycerol	26.61	26.86	0.25
12	20 wt% NaCl + 10 wt% Glycerol	35.70	33.93	-1.77
13	20 wt% NaCl + 20 wt% Glycerol	42.10	44.19	2.09
14	20 wt% NaCl + 20 wt% Glycerol	46.91	44.19	-2.72
15	23.4 wt% NaCl + 10 wt% Glycerol	40.30	41.54	1.24
16	22.1 wt% NaCl + 15 wt% Glycerol	43.50	44.18	0.68
17	20.8 wt% NaCl + 20 wt% Glycerol	45.90	46.44	0.54
18	3 wt% NaCl + 5 wt% KCl + 5 wt% Glycerol	7.60	7.36	-0.24
19	5 wt% NaCl + 5 wt% KCl + 15 wt% Glycerol	15.90	14.60	-1.30
20	10 wt% NaCl + 10 wt% KCl + 10 wt% Glycerol	23.20	28.36	5.16
21	5 wt% KCl + 5 wt% Glycerol	3.35	5.54	2.19
22	5 wt% KCl + 10 wt% Glycerol	5.66	5.77	0.11
23	10 wt% KCl + 10 wt% Glycerol	9.10	9.91	0.81
24	5 wt% CaCl ₂ + 5 wt% Glycerol	4.00	4.66	0.66
25	5 wt% CaCl ₂ + 20 wt% Glycerol	8.23	8.73	0.50
26	10 wt% CaCl ₂ + 10 wt% Glycerol	10.10	11.73	1.63
28	5.3 wt% NaCl + 12.8 wt% AquaCol-S	7.40	8.80	1.40
29	20 wt% NaCl + 10 wt% AquaCol-S	36.50	33.08	-3.42
30	10 wt% KCl + 10 wt% AquaCol-S	11.60	9.54	-2.06
31	10 wt% NaCl + 10 wt% KCl + 10 wt% AquaCol-S	30.50	27.48	-3.02
32	20 wt% Na-Formate + 10 wt% AquaCol-S	30.20	30.90	0.70
36	5 wt% NaCl	3.75	3.60	-0.15
37	10 wt% NaCl	8.42	9.24	0.82
38	12.5 wt% NaCl	10.50	12.67	2.17
39	20 wt% NaCl	28.23	24.68	-3.55
40	20.44 wt% NaCl	27.00	25.45	-1.55
41	26 wt% NaCl	35.20	35.55	0.35
42	10 wt% NaCl + 10 wt% KCl	20.90	19.61	-1.29
43	5 wt% KCl	1.62	2.38	0.76
44	10 wt% KCl	6.92	5.87	-1.05
45	20 wt% KCl	17.00	14.85	-2.15
46	5 wt% CaCl ₂	2.34	2.96	0.62
47	5 wt% CaCl ₂	2.34	2.96	0.62
48	14.42 wt% CaCl ₂	14.00	14.12	0.12
49	15 wt% CaCl ₂	15.20	15.21	0.01

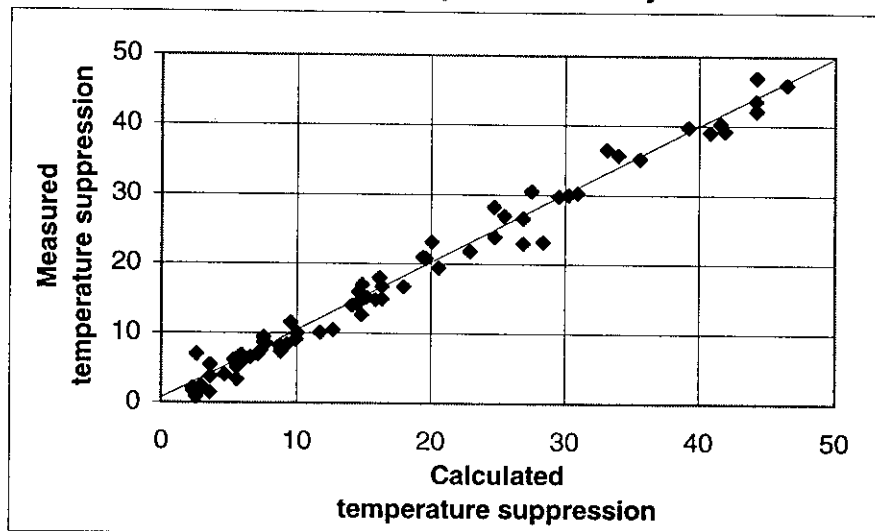
Table 6 (continued)

	Sample	ΔT (°F)	ΔT^* (°F)	ϵ [°F]
50	19.22 wt% CaCl ₂	21.90	22.89	0.99
51	21 wt% CaCl ₂	23.00	26.87	3.87
52	26 wt% CaCl ₂	39.00	40.81	1.81
53	10 wt% Na-Formate	6.17	5.36	-0.81
57	20 wt% Na-Formate	14.93	16.32	1.39
58	30 wt% Na-Formate	29.93	30.23	0.30
59	40 wt% Na-Formate	39.20	41.87	2.67
62	15 wt% K-Formate	8.73	7.57	-1.16
66	30 wt% K-Formate	23.95	24.76	0.81
68	50 wt% K-Formate	n.h.	52.32	n.a.
71	20 wt% NaBr	16.72	16.34	-0.38
72	30 wt% NaBr	29.80	29.52	-0.28
74	10 wt% CaBr ₂	1.48	3.55	2.07
76	20 wt% CaBr ₂	9.98	10.04	0.06
77	30 wt% CaBr ₂	23.24	20.05	-3.19
79	10 wt% ZnBr ₂	0.84	2.55	1.71
81	20 wt% ZnBr ₂	7.00	7.14	0.14
82	30 wt% ZnBr ₂	14.20	14.46	0.26
94	10 wt% Glycerol	7.00	2.60	-4.40
95	12.5 wt% Glycerol	5.50	3.59	-1.91
96	20 wt% Glycerol (11.0)	9.50	7.56	-1.94
97	30 wt% Glycerol (16.7)	14.80	15.84	1.04
100	10 wt% AquaCol-S	2.10	2.34	0.24
			MSE :	1.75

n.h. = No hydrate formation

n.a. = Not available

Figure 11
Measured and Model Predicted Hydrate Temperature Suppression, ΔT
using Mud Composition in WHyP



5.5 Prediction of the hydrate temperature suppression, ΔT using the measured mud filtrate resistivity and density

This model was developed based on the observation of a correlation between the resistivity of ionic aqueous solutions and their effect on gas hydrate temperature suppression. This correlation was developed in phase 1 of this project, and a detailed description is given in the report from phase 1¹.

The 37 samples in table 7 give a mean square error of 3.34°F.

Table 7
Hydrate temperature suppression calculated from mud filtrate resistivity and density

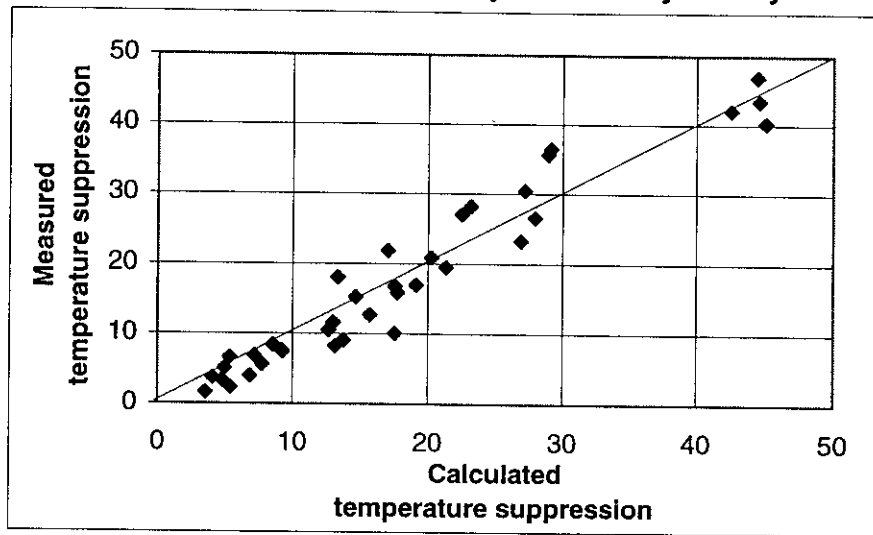
Item	Sample	measured				calculated	
		Temp [°F]	Resistivity [ohm-m] ^(*)	Density [ppg]	ΔT [°F]	ΔT* [°F]	ε [°F]
4	5 wt% NaCl + 5 wt% Ethylene Glycol	60.0	0.1417	8.698	6.60	5.33	-1.27
5	10 wt% NaCl + 10 wt% Ethylene Glycol	60.0	0.1203	9.052	16.80	17.52	0.72
7	10 wt% NaCl + 10 wt% Propylene Glycol ^(*)	77.0	0.1005	8.983	18.04	13.32	-4.72
8	5 wt% NaCl + 5 wt% Glycerol	60.0	0.1390	8.702	5.12	4.94	-0.18
9	10 wt% NaCl + 10 wt% Glycerol ^(*)	77.0	0.1083	9.138	12.68	15.67	2.99
10	10 wt% NaCl + 20 wt% Glycerol ^(*)	77.0	0.1209	9.355	19.50	21.32	1.82
11	10 wt% NaCl + 30 wt% Glycerol ^(*)	77.0	0.1559	9.592	26.61	27.95	1.34
12	20 wt% NaCl + 10 wt% Glycerol	60.0	0.0524	9.774	35.70	28.92	-6.78
13	20 wt% NaCl + 20 wt% Glycerol	60.0	0.0709	10.072	42.10	42.54	0.44
14	20 wt% NaCl + 20 wt% Glycerol	60.0	0.0927	10.072	46.91	44.47	-2.44
15	23.4 wt% NaCl + 10 wt% Glycerol	60.0	0.0799	10.112	40.30	45.09	4.79
16	22.1 wt% NaCl + 15 wt% Glycerol	60.0	0.0685	10.144	43.50	44.60	1.10
18	3 wt% NaCl + 5 wt% KCl + 5 wt% Glycerol	60.0	0.1354	8.901	7.60	9.21	1.61
19	5 wt% NaCl + 5 wt% KCl + 15 wt% Glycerol	60.0	0.1386	9.251	15.90	17.74	1.84
20	10 wt% NaCl + 10 wt% KCl + 10 wt% Glycerol	60.0	0.0525	9.708	23.20	26.91	3.71
21	5 wt% KCl + 5 wt% Glycerol	60.0	0.1174	8.721	3.35	4.79	1.44
22	5 wt% KCl + 10 wt% Glycerol ^(*)	77.0	0.1505	8.795	5.66	7.77	2.11
23	10 wt% KCl + 10 wt% Glycerol	60.0	0.1223	9.095	9.10	13.75	4.65
24	5 wt% CaCl ₂ + 5 wt% Glycerol	60.0	0.1586	8.787	4.00	6.84	2.84
25	5 wt% CaCl ₂ + 20 wt% Glycerol ^(*)	77.0	0.2151	9.035	8.23	13.16	4.93
26	10 wt% CaCl ₂ + 10 wt% Glycerol	60.0	0.1386	9.243	10.10	17.53	7.43
28	5.3 wt% NaCl + 12.8 wt% AquaCol-S ^(*)	77.0	0.1932	8.805	7.40	9.28	1.88
29	20 wt% NaCl + 10 wt% AquaCol-S	60.0	0.0883	9.680	36.50	29.11	-7.39
30	10 wt% KCl + 10 wt% AquaCol-S	60.0	0.0825	9.096	11.60	13.00	1.40
31	10 wt% NaCl + 10 wt% KCl + 10 wt% AquaCol-S	60.0	0.0556	9.680	30.50	27.18	-3.32
36	5 wt% NaCl ^(*)	77.0	0.1283	8.617	3.75	4.08	0.33
37	10 wt% NaCl ^(*)	77.0	0.0649	8.918	8.42	8.57	0.15
38	12.5 wt% NaCl	60.0	0.0734	9.105	10.50	12.67	2.17
39	20 wt% NaCl	60.0	0.0530	9.584	28.23	23.18	-5.05
40	20.44 wt% NaCl	60.0	0.0512	9.585	27.00	22.51	-4.49
42	10 wt% NaCl + 10 wt% KCl	60.0	0.0512	9.513	20.90	20.24	-0.66
43	5 wt% KCl ^(*)	77.0	0.1316	8.588	1.62	3.55	1.93
44	10 wt% KCl ^(*)	77.0	0.0672	8.862	6.92	7.20	0.28
45	20 wt% KCl ^(*)	68.0	0.0472	9.453	17.00	19.11	2.11
47	5 wt% CaCl ₂ ^(*)	77.0	0.1449	8.680	2.34	5.41	3.07
49	15 wt% CaCl ₂ ^(*)	68.0	0.0689	9.150	15.20	14.67	-0.53
50	19.22 wt% CaCl ₂ ^(*)	68.0	0.0509	9.345	21.90	17.02	-4.88
						MSE :	3.34

(*1) Density at 77°F measured in phase 1¹

(*2) Density at 68°F, tabulated, CRC, 48th edition

(*3) Measured resistivity (table 1) converted by temperature dependency to fit measured density.

Figure 12
Measured and Model Predicted Hydrate Temperature Suppression, ΔT
using Mud Filtrate Resistivity and Density in WHyP



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APPENDIX A

The data used by WHyP for calculation of temperature suppression from mud composition

The inhibitor components specific properties were collected from the literature when available, some slightly modified for better representation of hydrate temperature suppression. The method of calculating gas hydrate temperature suppression from inhibitor concentration uses the ionized fraction of salt rather than the total fraction.

The general expression for inhibitor fraction is :

$$x_{in} = \frac{\sum \left(((n-1)\alpha + 1) \frac{wt\%_s}{M_{w_s}} \right) + \frac{wt\%_g}{M_{w_g}}}{\sum \left(\frac{wt\%_s}{M_{w_s}} \right) + \frac{wt\%_g}{M_{w_g}} + \frac{wt\%_w}{M_{w_w}} - \beta_{mix}}$$

Where wt%_s, wt%_g and wt%_w are salt, glycol and water weight percent (g / 100g) respectively. M_s, M_g and M_w are salt, glycol and water molecular weight. β is the interaction coefficient between salt and glycol.

The interaction coefficient, β is calculated by :

$$\beta_{mix} = \hat{b}_1 * wt\%_w * wt\%_g * M_{w_s} * \sqrt{wt\%_s * wt\%_g} * \left(1 - \hat{b}_2 * \sqrt{\frac{wt\%_s}{M_{w_s} * M_{w_g}}} \right)$$

When either fraction of salt or glycol goes to zero, β disappears and the inhibitor fraction is reduced to Hammerschmidt's original equation. The empirical constants b₁ and b₂ fitted from experimental data.

The degree of ionization (α) for salt in water is available in the literature. Table A.1 contains the polynomial fit for degree of ionization used by WHyP.

Table A.1
The Salt Properties in WHyP

	Mw (g/mole)	Degree of ionization, α (c = wt% / Mw)	Concentration limit	
			(wt%)	(c)
NaCl	58.440	0.1 *(4.0033554 + (65.9587579 + (21.604556 + (3.383139 + 0.1959452 *ln(c)) *ln(c)) *ln(c)) *ln(c))	26.4	0.452
KCl	74.555	0.730430 - (3.09047 - (16.01070 - 47.1227 *c) *c) *c	25.5	0.320
CaCl2	110.986	0.754608 - (2.40036 + (4.74824 + 2.06364 *c) *c) *c	30.0	0.270
NaBr	102.894	1.379254 - (4.93934 - (19.86963 - 38.9332 *c) *c) *c	47.5	0.462
CaBr2	199.888	0.938196 - (1.594105 - 0.890007 *c) *c	32.0	0.160
ZnBr2	261.238	0.938196 - (1.594105 - 0.890007 *c) *c	32.0	0.122
NaCOOH	68.008	0.237573 + (0.317955 - 2.37197 *c *c) *c	42.0	0.618
KCOOH	84.120	0.237573 + (0.317955 - 2.37197 *c *c) *c	50.0	0.594

Modifications :

Calcium chloride (CaCl₂) degree of ionization :

The tabulated degree of ionization was found to respond better over the entire concentration range, when the inhibitor fraction was given the form :

$$x_{in} = \frac{\left((2 + \sqrt{wt\% / 10})\alpha + 1 \right) \frac{wt\%_s}{M_{w_s}} + \frac{wt\%_g}{M_{w_g}}}{\frac{wt\%_s}{M_{w_s}} + \frac{wt\%_g}{M_{w_g}} + \frac{wt\%_w}{M_{w_w}} - \beta_{mix}}$$

Bromide and Formate degree of ionization :

The degree of ionization was not found tabulated for CaBr₂, ZnBr₂, NaCOOH and KCOOH. Instead a fictive value was fitted from the experimental data of gas hydrate temperature suppression.

**Table A.2
The Glycol Properties in WHyP**

	Mw (g/mole)	Concentration limit	
		(wt%)	(c)
Methanol	32.042	40.0	0.579 ⁽¹⁾
Ethylene Glycol	62.029	40.0	0.645
Propylene Glycol	76.090	40.0	0.526
Glycerol	92.095	40.0	0.434
Polyalkylene Glycol	100 ⁽¹⁾	40.0	0.400 ⁽¹⁾

(1) Using modified molecular weight

Modifications :

Methanol (MeOH) molecular weight :

The model predicts too high inhibiting effect of methanol when using the true molecular weight (Mw = 32.042 g/mole). A better response is observed when the molecular weight is corrected by :

$$M_{w_{MeOH}}^* = M_{w_{MeOH}} \sqrt{\frac{\ln(wt\%)}{0.7923}}$$

Polyalkylene Glycol molecular weight :

The model predicts too low inhibiting effect of polyalkylene glycol when using the true molecular weight (Mw = 600 g/mole). A better response is observed when a fictitious molecular weight of 100 g/mole is used.