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Subquality Natural Gas Sweetening and Dehydration Potential of the Physical Solvent N-Formyl-Morpholine

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Introduction

Needs of the Gas Industry

Almost all gas produced in the United States requires processing before it is placed in the transmission system. For approximately 50% of the gas, this is just dehydration. The remainder, however, requires processing that is more complex and costly. A report to the Gas Research Institute[1] states that about 30% of the proven gas reserves contained sufficient nitrogen, carbon dioxide or hydrogen sulfide to be classified as a subquality. Figure 1 shows the distribution of non-associated gas with 2% or more CO_2 from that report. Figure 2 gives the distribution of non-associated gas with 4 ppm or more H_2S. Furthermore, these estimates may be low because many chemically-subquality wells are shut in after gas analysis, and the analysis is never reported. Since the major costs of exploration and drilling have already been paid, these wells could be put into service if more economic gas processing methods were developed. Table 1 summarizes the 1988 assessment of the lower-48 non-associated gas reserves.[1]

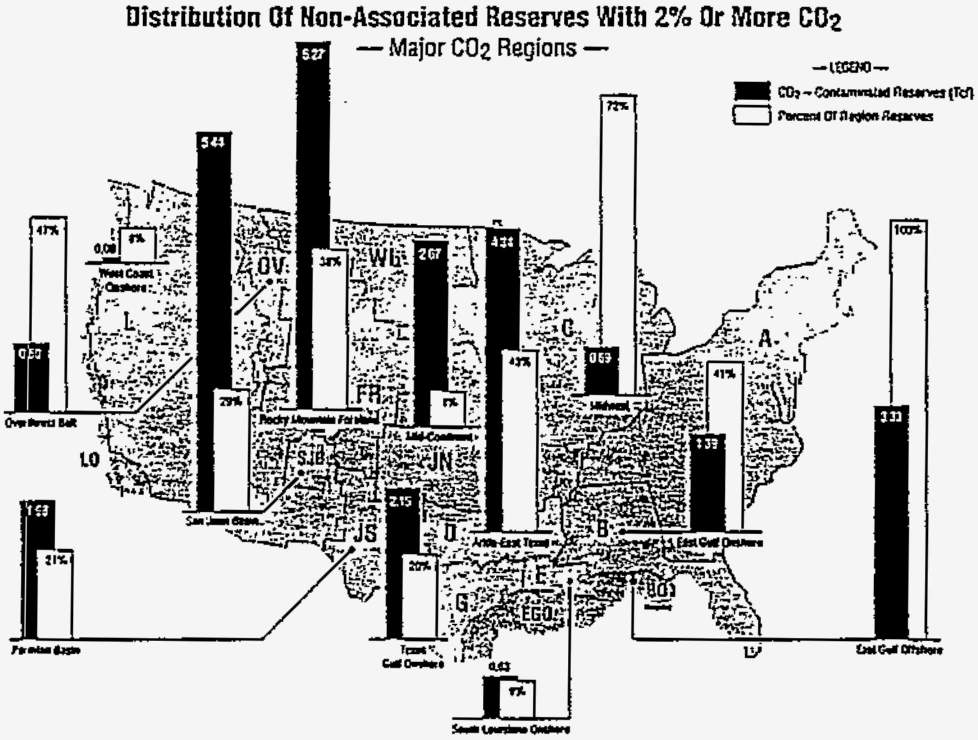


Figure 1. DISTRIBUTION OF NON-ASSOCIATED GAS WITH 2% OR MORE CO_2.

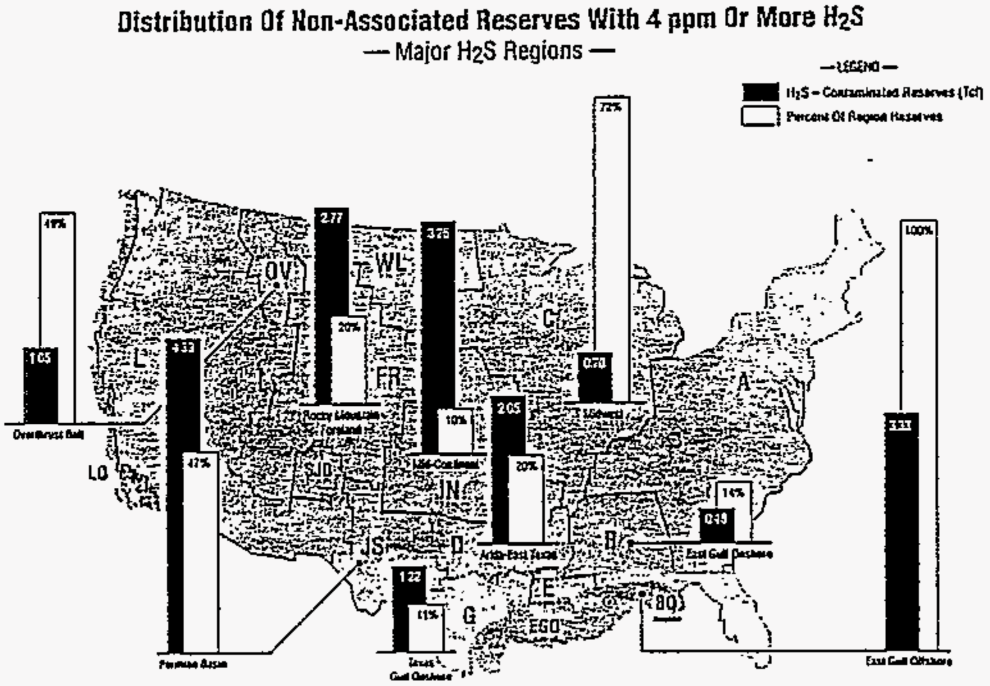


Figure 2. NON-ASSOCIATED GAS WITH 4 ppm OR MORE H_2S.

Table 1. SUMMARY OF THE 1988 ASSESSMENT OF THE LOWER-48 NON-ASSOCIATED GAS RESERVES.

Category	TCF
1988 Proven Raw Reserves	144.0
1988 Raw Production	14.7
Undiscovered/Undeveloped Gas	599.4
Discovered Non-Producing Low Quality Gas	135.0+

Another survey conducted by Tannehill and Gibbs[2] indicated that, the estimated cost of the new facilities is about $1.7 billion to meet the projected natural gas requirements over next ten years. Table 2 summarizes the estimates of the number of existing gas facilities and future facilities which are likely to be required for dehydration, gas treating and sulfur recovery processes.

TABLE 2. EXISTING AND PROJECTED GAS CONDITIONING FACILITIES

Category	Existing	1991	1992	1993	1994	1995	1996-2000	Total New
Dehydration	1271	80	93	92	94	107	516	982
Gas Treating	694	17	16	18	18	16	90	175
Sulfur Recovery	57	17	16	17	22	23	119	214

Research Objective and Program Approach

The Institute of Gas Technology (IGT) is developing gas processing technology that will reduce gas processing costs for current production and allow subquality gas to be economically produced that would have been otherwise, not produced. The experimental program being discussed in this paper has been in progress since 1990. It has primarily focused on the evaluation of N-Formyl Morpholine (NFM), shown in Figure 3, as a physical solvent for the cost-effective upgrading of subquality natural gas to pipeline quality. The selection of NFM for this program was based on previous work conducted by IGT in the selective removal of hydrogen sulfide, and carbon dioxide from coal gasifier effluents[3]. That work showed that the use of NFM resulted in a significant cost advantage over 107 other solvents for that application.

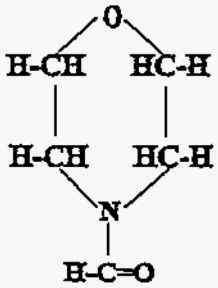


Figure 3. N-Formyl Morpholine ($C_5H_9O_2N$)

Figure 4 displays the project approach of this research program. Available literature data was collected and then supplemented by an experimental program that included vapor-liquid equilibrium, absorption rate, solvent stability, corrosion, and mass transfer data. This information was then used to calculate physical parameters that are integrated into a computer model to predict the behavior of this solvent system. From the computer models, designs of gas processing plants and economic estimations were conducted.

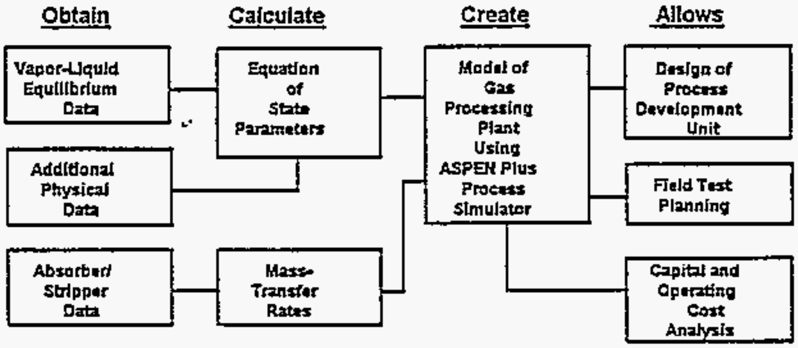


Figure 4. PROJECT APPROACH.

Laboratory Studies

Vapor-Liquid Equilibrium (VLE)

Figure 5 shows the VLE apparatus developed at IGT, which is capable of handling all sulfur species and operating from 25 to 3,000 psia and at temperatures from 60° to 300°F. This apparatus consists of a 1 liter vessel in which vapor and liquid phases are continuously circulated. On line phase sampling is conducted at system pressure and temperature. Small sample volumes (1 micro-liter samples for liquid and 1 milli-liter for gases) are withdrawn to ensure minimal disturbance of the system composition.

Over 1000 data points have been collected for mixtures of NFM and water over the following ranges of conditions:

Temperature, °F:	60-300
Pressure, Psia:	25-1,150
Gas Compositions:	
Single Component	CO_2, H_2S, COS, C_3H_8, and C_4H_{10}
Mixtures	CH_4, CO_2, H_2S, C_2H_6, C_3H_8, C_4H_{10}, C_4H_{12}, and C_6H_{14}

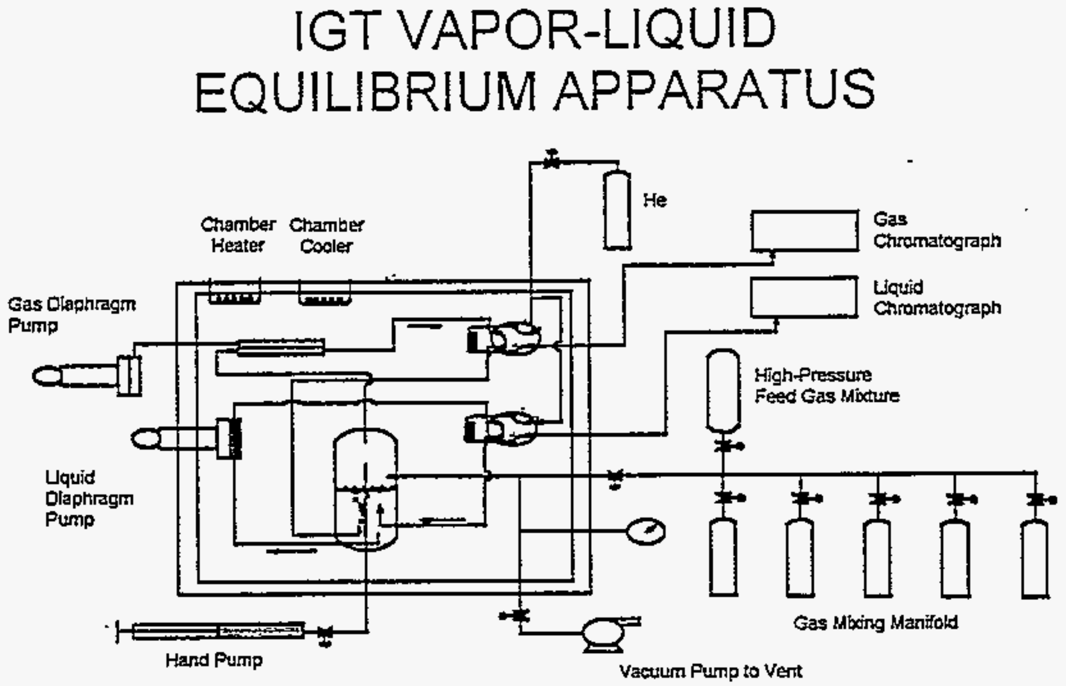


Figure 5. IGT Vapor Liquid Equilibrium Apparatus.

The data collected indicates the following solubility ranking by K-values (mole fraction of component "A" in the gas phase divided by the mole fraction of that component in the liquid phase at equilibrium) at 6891 kPa (1000 psia), 289 to 322K (60° to 120° F), and for the compositions tested:

$$CH_4 < C_2H_6 < C_3H_8 < n\text{-}C_4H_{10} < i\text{-}CH_{10} < CO_2 < C_5H_{12} < H_2S < C_6H_{14}$$

This ranking indicates a potential for using NFM in selective processes. For example, in relative terms the solubility of H_2S is roughly three times greater than CO_2 at the conditions tested.

Auto-refrigeration

Auto-refrigeration is the drop in system temperature associated with a pressure drop across a flash valve. This phenomena is being studied as a function of differential pressure, solvent concentration, and dissolved gas composition. A flash valve separates the absorption section from the regeneration section in a typical acid gas treating plant. The pressure drop across this valve can be quite large (several hundred psi) depending on the required absorption pressure and the pressure letdown required for regeneration. The major concern with NFM solvent systems is the possibility that the temperature drop across the flash valve might cause the solution to freeze. For the range of NFM solution concentration being considered for an industrial application, the melting point varies from 70.5°F for pure NFM to 51°F for NFM solution with 5 weight % water.

The exact freezing point of a non-pure solvent system that would be found in a gas processing application is difficult to quantify for several reasons. The most relevant is that it would be a function of composition including impurities. For the purposes of our industrial applications, rather than theoretical data, it was felt that melting points were more relevant. First the melting points have proven to be considerably more reproducible as a reference point. More importantly, for the NFM solvent system, a process designed to operate above its melting point will have a substantial margin of safety built in since we have found its melting point to be 10 to 15°F higher than the freezing points over the compositions of interest. Another factor to consider which substantially reduces the concern over the "Worst Case" of a freeze up is that the NFM solution contracts rather than expands, thereby eliminating the worry of vessels rupturing.

IGT is experimentally obtaining the heat release due to the throttling process. This information will be used to verify our thermodynamic models relative to regeneration duties, and more accurately predict how much, if any, heat is required to keep NFM solvent from freezing.

An apparatus to measure temperature changes/heat fluxes caused by degassing a rich solvent at pressures from 1000 psia to atmospheric pressure was designed, constructed, and calibrated. Figure 6 is a flow diagram of IGT's Auto-Refrigeration Unit (ARU) and shows how it interfaces with IGT's Vapor/Liquid Equilibrium (VLE) apparatus.

The ARU is positioned lower than the VLE cell, accordingly, when there is liquid in the VLE cell, the ARU is fully charged with solvent. Gas and liquid are continuously circulated throughout the system until equilibrium is achieved. Next, the ARU is isolated from the VLE cell. The pressure in the ARU is then slowly released. The volume of gas released is recorded, as well as temperature changes throughout the apparatus, until atmospheric pressure is achieved. With the mass of all ARU components and the mass, composition of the liquid and the gas, the cooling effect of the gas desorption can be calculated.

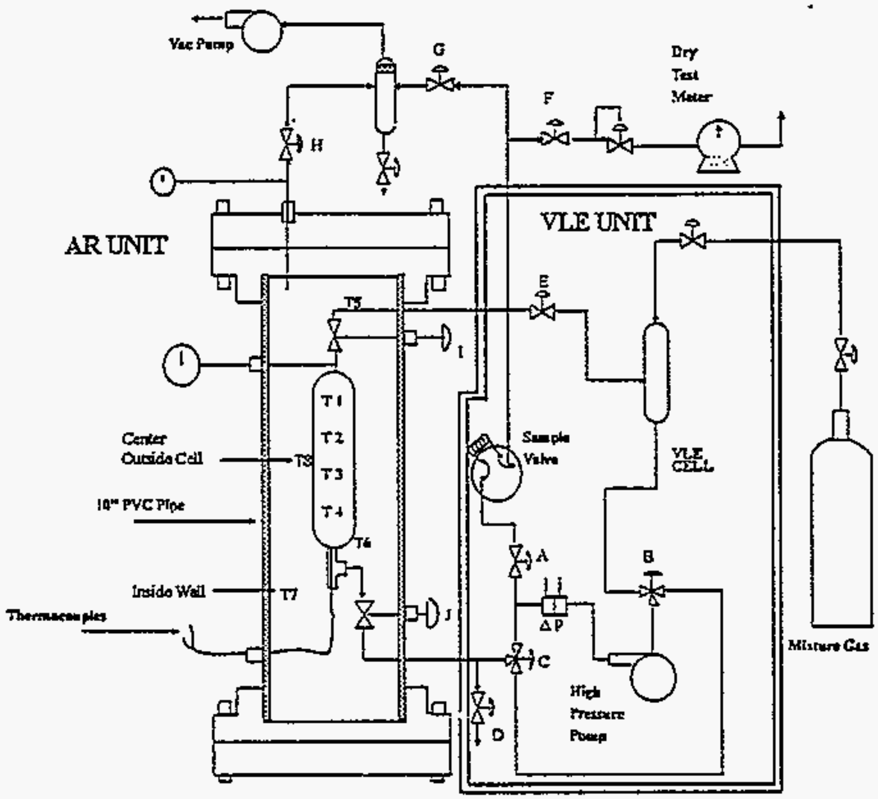


Figure 6. AUTO-REFRIGERATION SCHEMATIC DIAGRAM

Experiments using 100% NFM with 100% CO_2 gas are summarized in Table 3. Thus far it appears that not only does NFM absorb CO_2 more freely than water, but it appears to release CO_2 more easily with less heat loss than water. The heat release for CO_2/water solutions ranged from approximately 170 to 180 Btu/lb of CO_2 released while the heat released for CO_2/NFM solutions ranged from approximately 146 to 152 Btu/lb of CO_2 released. The results are encouraging, due to the fact that CO_2 desorption from NFM requires significantly less energy than that required for chemical solvents.

Table 3. NFM RUNS WITH 100% CO_2.

Starting Temperature, °F	Starting Pressure, psi	Btu/lb of CO_2 Released
89	500	146.3
74	265	152.6
74	700	151.9

Molecular Stability

The stability of a solvent has direct impact on its usefulness to the industry. If the solvent decomposes rapidly, or forms caustic compounds, or increases potential exposure to hazardous materials a process may not be feasible even if it has attractive absorption characteristics. Therefore, the thermal and chemical stability tests of the NFM solvent were conducted to investigate the potential effects of gas mixtures on solvent stability in gas sweetening applications. IGT conducted a total of four degradation tests.

Test # 1

Gas Composition	10 mole %	COS	
	10 mole %	CS_2 (added to liquid)	
	10 mole %	CH_3SH	
	70 mole %	Normal Gas Mixture Ratio	
		59.00%	CH_4
		23.00%	CO_2
		7.00%	C_2H_6
		6.00%	H_2S
		2.50%	C_3H_8
		1.25%	iC_4
		1.25%	nC_4
		100.00%	
Liquid Composition	95 wt.%	NFM	
	5 wt.%	H_2O	
Temperature	275°F		
Pressure	System initially charged with gas mixture to a pressure of 30 psia and then heated to 275°F.		

Sampling	Gas and liquid samples were taken twice a day during the first week, once a week thereafter, unless no changes were observed, thus the sampling rate was dropped to once in two weeks.
Run Duration	3 months.

The results from Test 1 indicated minimal degradation of NFM with exposure to large quantities of gases such as COS (Carbonyl Sulfide), CS_2 (Carbon Disulfide), H_2S (Hydrogen Sulfide). NFM degradation to morpholine that occurred was steady and minimal during the entire duration with a final count of 3600 ppm, i.e., 0.36% of NFM degraded to morpholine over a three month period at the above conditions.

Test 2 was conducted at the same conditions as Test 1 except that 100% air was used at 60 psia in place of the "Normal Gas Mixture." This test was run for about three weeks, during which time, the pressure in the cell steadily rose to 100 psia. Gas samples taken at that time indicated that the oxygen in the air reacted with the formyl group of the NFM resulting in hydrogen and carbon dioxide as the product gases. Oxygen degradation of NFM at high temperature was expected and does not differ appreciably from what occurs to commercial solvents at these conditions. Analysis of liquid samples shows that about 0.45% of the NFM reacted to form morpholine and its derivatives. A balance of components in the vessel indicate that all the oxygen in the system reacted with NFM on a 1:2 mole basis (O_2 to NFM) to form morpholine, CO_2 and hydrogen.

Test 3 was conducted at the same conditions as Test 2 except the temperature was lowered to 160 °F. Gas samples indicated that the oxygen in the air again reacted with NFM producing CO_2. However, no change in pressure was observed. The liquid analysis indicated that NFM degradation to morpholine was steady and very minimal during the entire duration of Test 3 with a final count of 370 ppm, i.e., 0.037% of NFM charged, degraded to morpholine over a period of four weeks.

Test 4 was initiated as continuation of Test 3. At the end of Test 3 the temperature was increased from 160°F to 212°F for the system (gas composition of O_2 & Argon 0.83%, Nitrogen 90.9% and CO_2 8.31% on mole basis). Again, no change in pressure was observed during the entire two weeks of this experiment. Liquid samples again indicated that NFM degradation was minimal with a final count of 300 ppm to morpholine for this test. A total of 0.067% NFM charged degraded to morpholine over a six week period during the entire duration of Test 3 and Test 4.

Based on the results of the stability experiments conducted, we do not anticipate any changes in plant operation and materials of construction requirements, due to the chemical and thermal characteristics of the NFM solvent system compared to standard commercial practice for gas sweetening processes.

Dehydration Potential of NFM

NFM's affinity for water implies that it may have an added benefit of being able to dehydrate saturated natural gas streams. This could allow for a cost effective means of conducting dehydration and acid gas removal in one process. Therefore, a series of experiments were conducted in IGT's VLE apparatus using NFM/H_2O with 100% methane to determine the equilibrium absorption potential of NFM.

Analysis of the results thus far indicate that the NFM solvent contains dehydration capacity when there is less than 1 weight %H_2O in the solvent. Under these conditions, it is theoretically possible to meet pipeline specification (moisture content of pipeline gas is about 7 lb/MM SCF) considering 20°F approach in the contactor. Additional equilibrium NFM/H_2O dehydration runs are planned to collect data over the temperature range of 70 to 120 °F.

As a test of our experimental procedure Triethylene Glycol (TEG), a commercial dehydration solvent, was also tested in IGT's VLE apparatus. As shown in Table 4, there is good agreement between the experimental results obtained with published data for TEG.[4]

Table 4. COMPARISON OF EXPERIMENTAL TEG RESULTS WITH PUBLISHED DATA.

Solvent Composition		Temp.°F	Pressure, psia	Dew Point, °F (Experimental)	Dew Point, °F (Published Data)
% TEG	% H_2O				
99.13	0.87	75.56	600	-6.5	
99.00	1.00	78.08	-	-	-9.5

Figure 7 shows that NFM has to be purer (i.e. have a lower percentage of water in the liquid phase) to achieve the same dew point as TEG. This implies that NFM may not be a cost effective substitute for TEG in a dehydration process. However, there is a real potential for cost effectively conducting the dehydration during acid gas removal with the NFM systems, since the solvent circulation rates are typically much higher for gas sweetening than gas dehydration systems.

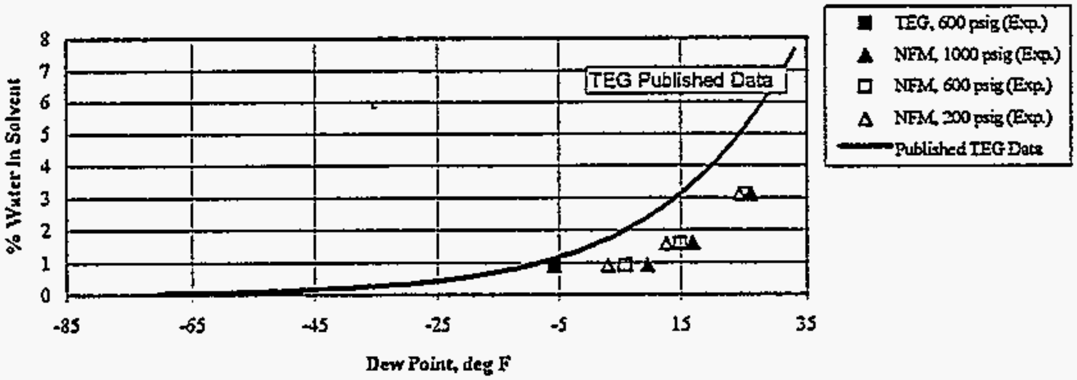


Figure 7. DEHYDRATION CAPACITY OF NFM COMPARED TO TEG

Computer Modeling

Background of Computer Model

ASPEN™ Plus process simulation software package was used to regress VLE and other data to obtain the appropriate equation of state coefficients. Peng-Robinson, Redlich-Kwong-Soave, Redlich-Kwong-ASPEN™ and Redlich-Kwong-UNIFAC thermodynamic models were investigated. The model which was able to give the best fit to the data over the relevant range was Peng-Robinson which modified with binary interaction coefficients. These coefficients were fitted from the data collected using the maximum likelihood principle to formulate the objective function, and then minimizing that function by the algorithms of Deming and Britt and Lueke[5].

Computer Modeling of a Gas Processing Plant

In order to estimate the performance of NFM as a solvent system, a model of a gas processing plant was created using ASPEN™ Plus Process simulation package. Figure 8 shows the design of a selective gas processing plant in which H_2S is removed in the first loop and CO_2 is removed in a second loop. In this process H_2S concentrated in one stream which is sent for further processing while a relatively clean CO_2 stream is generated in the second loop.

SELECTIVE ACID-GAS REMOVAL PROCESS

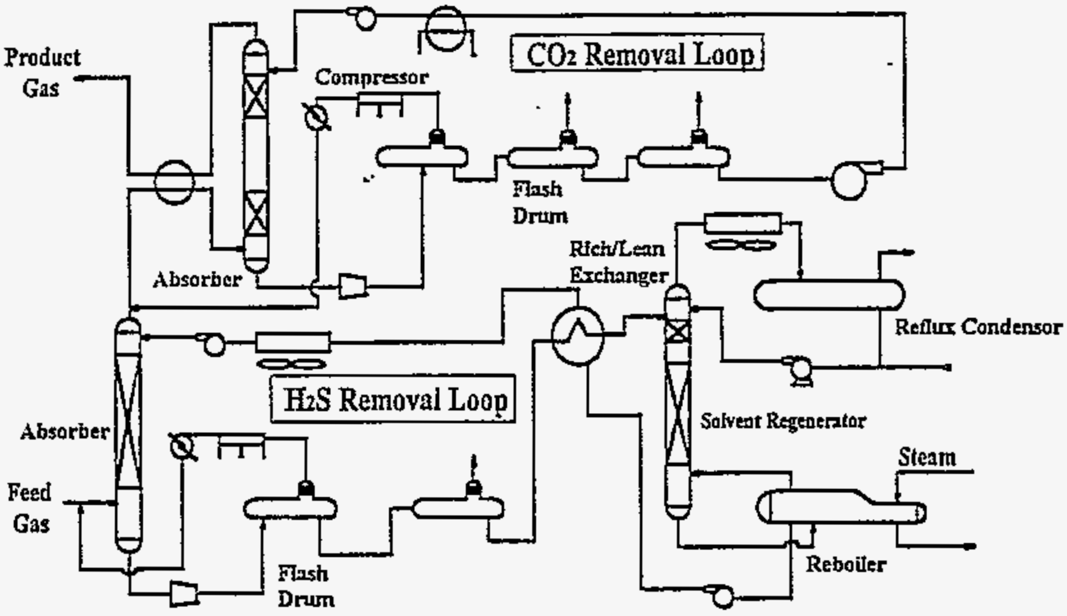


Figure 8. FLOW DIAGRAM OF SELECTIVE GAS PROCESSING PLANT

Table 5. GAS SPECIFICATIONS FOR COMPUTER MODELING

	Case A, Feed	Case B, Feed	Product Gas Specifications
Temperature, F	100	100	
Pressure, psia	1015	1015	
Flow, million SCFD	75	75	
Dry Basis Composition, mole %			
CH_4	91.0	59.0	
C_2H_6	0.0	4.0	
CO_2	6.3	35.0	< 2.0
H_2S	2.7	2.0	< 0.0004

Using the above design, simulations were performed for both a relatively low, and a high acid gas content feed composition. Table 5 shows the feed and product specifications while Table 6 summarizes the results of these cases.

Table 6. RESULTS OF SELECTIVE GAS PROCESSING SIMULATIONS

	Case A Product Gas	Case B Product Gas
Solvent	NFM	NFM
Solvent Circulation Rate, gal/hr	1936	2646
Temperature, F	38	35
Pressure, psia	1010	1010
Flow, million SCFD	69	46
Gas Composition, dry mole %		
CH_4	98.50	92.74
C_2H_6	0.0	5.7
CO_2	1.5	1.5
H_2S	0.00001	0.00001

<u>Comparison between NFM and a commercial physical solvent system</u>

As a reality check, a solvent manufacturer conducted simulations of the same Case A and B conditions using their proprietary models for a commercial physical solvent. Table 7 shows a comparison between NFM and the commercial solvent where the requirements of the commercial physical solvent is referenced as 100%. According to the models, there would be substantial savings in plant operating costs (40 to 50%), as well as in capital costs (15 to 30%). Since the commercial and NFM process are very similar and there are substantial savings in operating costs, there may be a significant cost incentive to substitute for the commercial physical solvent with NFM in existing systems.

Table 7. COMPARISON BETWEEN A COMMERCIAL SOLVENT AND NFM.

Solvent	Commercial Solvent Case A and B	IGT's NFM Case A	IGT's NFM Case B
Circulation Rate	100%	94%	75%
Total Power Required	100%	70%	37%
Total Refrigeration Duty	100%	58%	55%
Total Heat Duty	100%	68%	57%
Total Construction Costs	100%	85%	70%
Total Operating Costs	100%	60%	47%

Taking our analysis one step further, a confidence interval analysis was performed. In this study the three main interaction coefficients that derived from our data was varied by plus and minus three standard deviations. This means that we can be 95% confident that the "true value" of the binary interaction coefficient lies in this range.

Figure 9 shows the effects on the solvent circulation rate by varying the binary interaction coefficients one-at-a-time by plus and minus, three standard deviations around a base case. Case A was chosen as the base case for this study, since of the two conditions, this case showed the least advantage for NFM over the commercial physical solvent. As shown in this figure changing the interaction coefficients between H_2S-NFM and CH_4-NFM over the 95% confidence interval has little effect on total solvent circulation. However, varying the CO_2-NFM coefficient over the same confidence range does have a considerable impact on the solvent flow rates. In fact, over a large portion of the range, the NFM flow rate is estimated to exceed that of the commercial physical solvent, i.e., circulation rate greater than 100% of the commercial physical solvents.

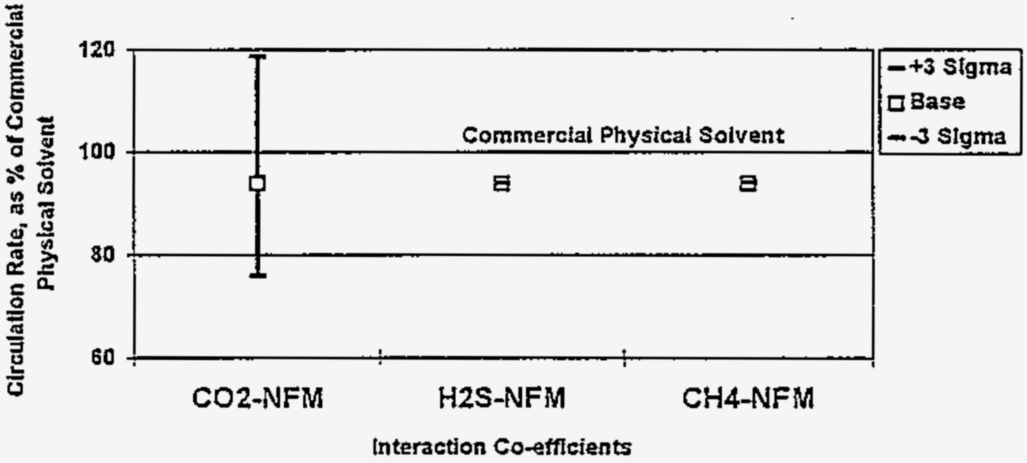


Figure 9. PARAMETRIC ANALYSIS OF INTERACTION COEFFICIENTS ON ESTIMATED SOLVENT CIRCULATION RATE.

Figure 10 shows the effect that these interaction coefficients have on operating costs for the same conditions (base, plus and minus three standard deviations).

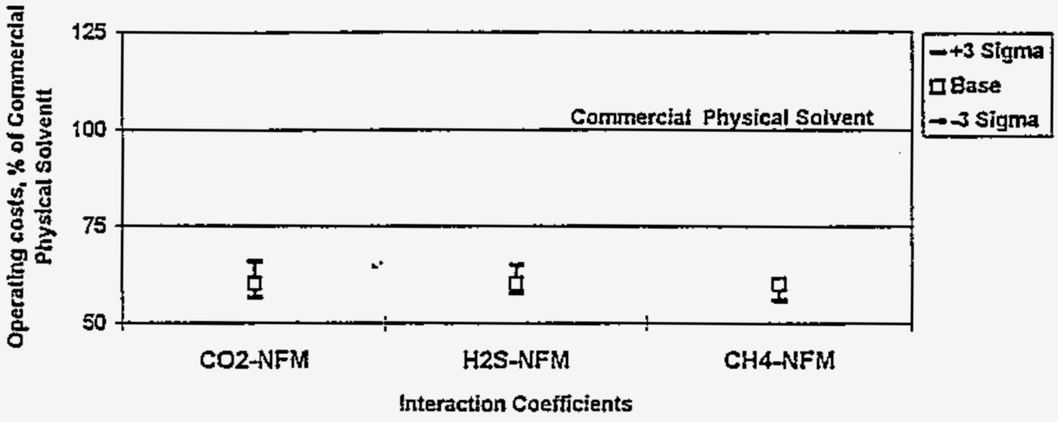


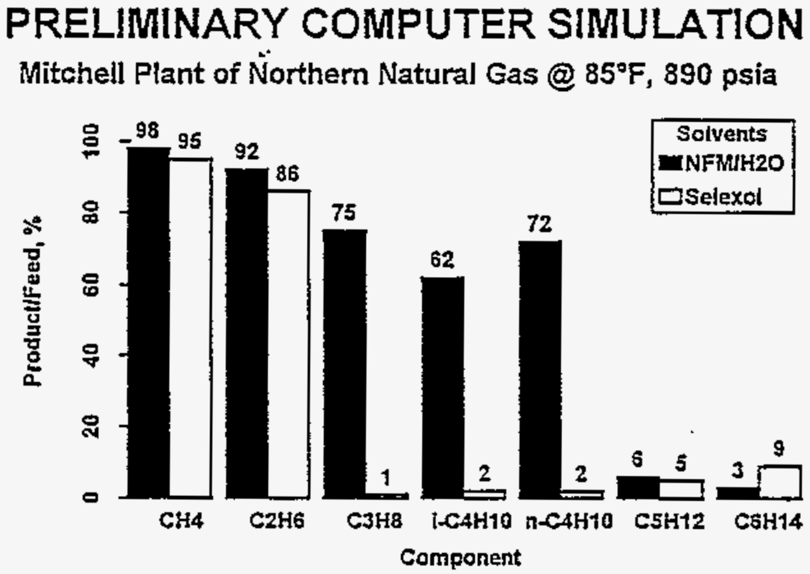
Figure 10. PARAMETRIC ANALYSIS OF INTERACTION COEFFICIENTS ON ESTIMATED SOLVENT OPERATING COSTS.

These results imply that although the circulation rate may significantly exceed that of the commercial solvent (by almost 20% in the case of the CO_2-NFM interaction coefficient variation), the operating costs were still significantly lower than those of the commercial physical solvent, i.e., in excess of 30%. As far as capital costs are concerned, the capital costs remained less than those for the commercial solvent by 10 to 15% over the 95% confidence interval.

In summary, the statistical analysis of the data obtained imply a 95% confidence that the NFM solvent system will significantly out perform the commercial physical solvent in both new and retrofitted applications for gas sweetening processes. Because of this high confidence level, sponsors of this research have authorized the construction of a pilot plant for the field testing phase of the NFM commercialization program.

Fate of C1-C6 hydrocarbons: a comparison with Selexol™ solvent system

Some details of a gas sweetening process using the physical solvent Selexol™ were published in 1978[6]. Although Selexol™ flow rates were not given in the article but product gas compositions were, and although there was not enough detail to duplicate the exact plant operation, we conducted a simulation of the process using ASPEN™ Plus with our NFM data. Figure 11 shows that as far as C1, C5 and higher hydrocarbons are concerned, there is little difference between Selexol™ and NFM. However, substantially more of C3 and C4 stay with the natural gas streams for the NFM process. This implies less off gases and subsequent processing, as well as more sales gas with a higher heating value for the NFM process compared to the Selexol™ process.



Selexol Information from "Selexol unit saves energy," Hydrocarbon Processing, April 1978.

Figure 11. COMPARISON OF THE FATE OF C1-C6 HYDROCARBONS FOR SELEXOL™ AND NFM.

Field studies

Type of sites

In conjunction with a program to evaluate structured packing contactors for gas sweetening applications, IGT is initiating a series of three tests to evaluate NFM under field conditions. IGT is planning on conducting tests at three different sites to determine NFM's performance in processing subquality natural gas streams with low (2 to 5%), medium (5 to 15%), and high (15% plus) total acid gas concentrations. IGT is looking for sites whose host would be receptive to letting IGT setting up a ten gpm test skid on a slip stream. IGT is currently discussing such a testing with the three potential gas sweetening locations shown in Figure 12.

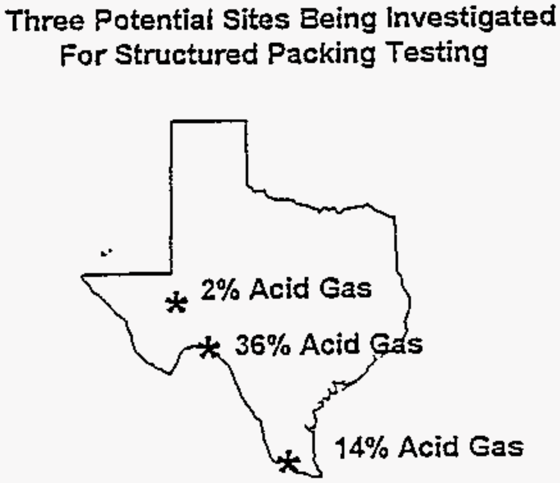


Figure 12. POTENTIAL FIELD SITES FOR TESTING NFM SOLVENT SYSTEM.

Skid Design

Table 8 gives a summary of the design specifications for the skid unit being built. Figure 13 shows the proposed skid flow diagram. This experimental skid has been designed to test both chemical and physical solvents, and can use structured packing as well as traditional gas-liquid contactors in a bulk acid gas removal process.

Table 8. SPECIFICATIONS FOR FIELD TEST SKID

Feed Gas Flow Rate, million SCFD	0.25 - 1.25
Acid Gas Content of Feed, mole %	2.0 - 40
Solvent Circulation Rate, gpm	3 - 15
Contactor Operating Pressure, psi	300 - 1200

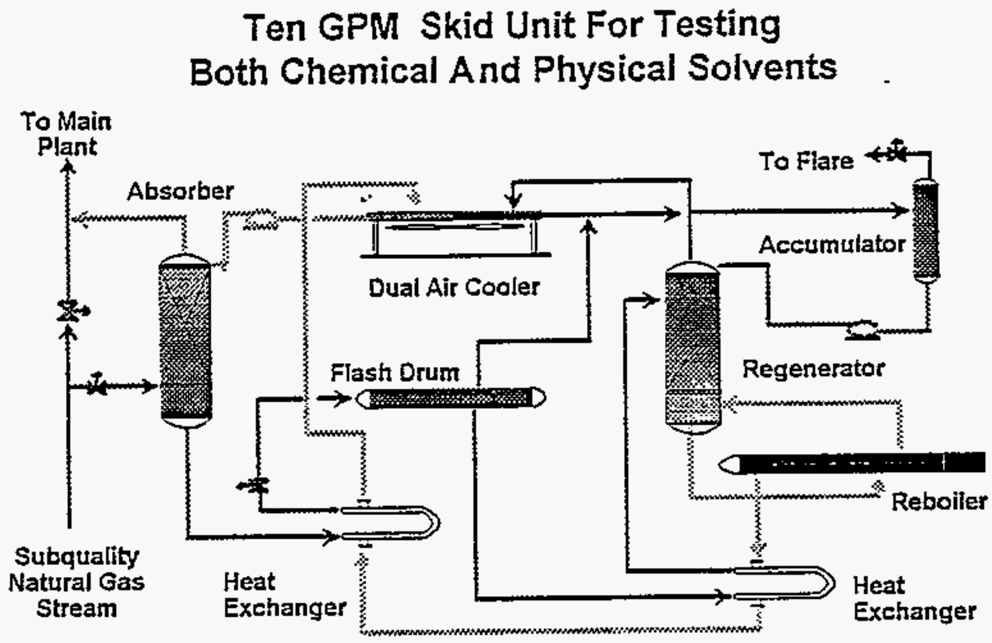


Figure 13. FLOW DIAGRAM FOR FIELD SKID.

Conclusions

The natural gas industry expends substantial resources to remove impurities from subquality natural gas, so that it can be marketed or used directly. The NFM technology being developed here, according to experimental data and computer simulations of gas processing plants indicate substantial savings in capital costs and operating costs. Comparison of computer simulations with published data for a gas processing plant indicate that 1.04 times more CH_4, 76 times more C_3H_8 and 32 times more C_4H_{10} remain in the marketable gas when NFM used in place of Selexol™. This characteristic of NFM increases quantity and heating value of sales gas and reduces the solvent regeneration costs.

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