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Corrosion Inhibition by Control of Gas Composition During Mist Drilling

Thomas E. Hinkebein, Tracy L. Snyder

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CORROSION INHIBITION BY CONTROL OF
GAS COMPOSITION DURING MIST DRILLING

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ABSTRACT

Chemical compositional specifications have been generated for inert gases which reduce drill string corrosion when used in conjunction with mist drilling processes. These specifications are based on the assumption that the corrosion rate is dependent on the dissolved gaseous species concentrations. Data taken both from the literature and from a mist drilling field test with nitrogen in Valle Grande, NM, relate corrosion rates to fluid compositions. These solution compositions are then associated with gas phase compositions using equilibrium data available from the literature and material balances.

Two sources of gas were considered: cryogenically purified nitrogen from air and exhaust gas from a diesel engine, which contain (in addition to N_2 and O_2) CO_2 , NO_x , SO_2 , H_2O , and CO . A maximum concentration of 50 ppm O_2 in the gas phase is recommended to alleviate pitting corrosion. If diesel exhaust is used, CO_2 , NO_x , and SO_2 react with water to form acids. However, all CO_2 present in the exhaust gas will be allowed downhole where it is recommended that it be partially neutralized by a carbonate buffer. This buffer can be formed to maintain a pH between 7 and 8 at acceptable costs. Similarly, all NO_x and SO_2 may be left in the exhaust gas since the neutralization of these minor species is relatively inexpensive. CO is not a corrosive species and need not be removed. H_2O must be removed prior to compression of the exhaust gases so that acidic condensate does not damage the compressors. Moreover, a maximum of 50 ppm H_2O in the gas phase (dew point = $-44.3^\circ C$) is recommended.

These specifications are seen to be dependent on temperature, pressure, solution salt concentration and pH. Corrosion rates

increase rapidly with increasing temperature so that at 140°C, the corrosion rate is ten times that at 60°C. Thus, more oxygen may be tolerated at lower temperatures. As the pressure decreases to approximately the vapor pressure of water, water preferentially excludes oxygen and more oxygen may be tolerated in the wellbore. Increasing the concentration of salt in the water leads to higher corrosion rates while also excluding oxygen from solution. pH control between 9 and 12.5 represents the normal corrosion control measure when drilling with air-mist. When using inerted gases, reduced pH provides adequate protection and pH's as low as 7 appear to be acceptable with further experimentation providing verification.

The option of using an inert gas as a substitute for air is concluded to be a viable way of reducing drill string and casing corrosion.

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CORROSION INHIBITION BY CONTROL OF GAS COMPOSITION DURING MIST DRILLING

1. Introduction

At this time a need exists for the compositional specifications of inert gas drilling fluids so that an orderly development of processes to supply these gases may proceed. Two processes are considered in this report to yield a N_2 based low oxygen gas: Nitrogen may be obtained from cryogenically distilled air or from the exhaust gas of a diesel engine and catalytic converter combination. For both of these processes, an acceptable level of oxygen must be determined, while for the second process levels of CO_2 , NO_x , SO_2 , CO and H_2O must also be specified. In both of these cases, the compositional specifications will be made to reduce corrosion in the drill pipe, casing and other surface equipment.

The problem of drill string corrosion in geothermal environments has been particularly severe when air is used as the drilling fluid. Drilling with air has several benefits, including increased penetration rates, the alleviation of lost circulation control during drilling, and reduced formation and reservoir impairment. However, the presence of large amounts of oxygen in the air leads to significant corrosion rates in drill string and casing steel. When the corrosion rate exceeds 50 mpy, it is normally considered that corrosion costs are excessive. The reduction of these high corrosion rates by minimizing the amount of O_2 in the drilling fluid is investigated in this paper. In air drilling operations, this corrosion problem may be marginally controlled by the addition of polymerizing agents which act to coat the steel and the cuttings⁽¹⁾ by the addition of NH_3 , and by the addition of large amounts of $NaOH$. These polymerizing agents form both a chemical diffusion barrier which keeps oxygen from reaching the steel surface and an elastic coating which protects the steel from erosion. $NaOH$ additions act to suppress the cathode reaction in the corrosion cell, as is discussed below.

The typical corrosion process which is encountered when iron is in the presence of oxygen is described by the following equations and depicted in Figure 1:

CORROSION REACTION

Figure 1. Mechanism of Oxygen-based Corrosion

Metallic iron is oxidized to ferrous ion at the anode while oxygen is reduced to hydroxyl ion at the cathode (iron carbide). Electrons released at the anode migrate through the iron to the site of oxygen reduction. In solutions containing very few ionic species, the ferrous ion may migrate only a short distance because of its electrical charge. Consequently, the cathode and anode must be situated proximately so that a precipitate of $\text{Fe}(\text{OH})_2$ tends to cover the corrosion site and hence limit the magnitude of corrosion. In the presence of other anionic species, such as Cl^- , the Fe^{++} ion and the OH^- ion may migrate considerable distances away from the steel surface. In this case, the insoluble $\text{Fe}(\text{OH})_2$ precipitates in the bulk solution (rather than on the pipe surface) so that less protection is afforded to the steel. Corrosion control in the geothermal well is typically accomplished by trying to suppress the cathode reaction by increasing the concentration of OH^- in Eq.(2). In typical situations the pH is controlled between 9 and 12.5. Another way of accomplishing this same purpose would be to reduce the amount of oxygen which comes in contact with the steel.

Since air contains an abundance of oxygen, two techniques have been proposed to limit the oxygen in the gas stream used for drilling. Oxygen may be removed by a cryogenic distillation or by reacting oxygen with diesel fuel in a diesel engine and catalytic converter combination. In the first process, arbitrarily low levels of oxygen in the nitrogen stream may be obtained at the expense of greater energy requirements and larger size equipment. In the second case, air is mixed with diesel fuel and fed to a diesel engine operating at constant load on site. The exhaust from this engine is then mixed with a stoichiometric amount of fuel, then completely combusted in a catalytic converter to yield a gas with low levels of residual oxygen⁽³⁾. In both of these cases a rational basis is needed in order to specify the composition of the gas. Of primary importance here is the level of oxygen in the cryogenically purified gas and the diesel exhaust gas, and the levels of CO_2 , SO_2 , NO_x , H_2O and CO in the diesel exhaust gas. This report describes the specification of criteria for these gaseous components.

The methodology used here will be to determine the maximum amounts of species in the gas through their correlation to corrosion rate information. It is possible to obtain a very rough correlation between corrosion rates on carbon steel similar to drill string steel and the concentration of species dissolved in water which contacts the steel surface. This correlation will be based on data available in the literature, though its applicability to drill string steel may be limited. This data will be used, however, even though a strong need exists to obtain more appropriate data on the steel actually used in the well. The concentration of each component of the

gas actually dissolved in the water phase may then be related to the amount of each component in the gas phase through material balance and equilibrium calculations. These latter calculations are expected to be considerably more representative of the actual physical situation than the corrosion rate correlation. Hence, most of the uncertainty in the discussion which follows lies in the determination of corrosion rates as a function of solution composition.

2. Review of Corrosion Rate Data

A review of the literature of corrosion of mild steel in reduced oxygen aqueous environments can give some information about the dependence of corrosion rate as a function of oxygen content, pH, temperature, and NaCl concentration. This information shows that these parameters are coupled and influence the corrosion rate in complex and sometimes inconsistent ways. These inconsistencies may be attributed to the variations in the steel used for the individual corrosion tests. The variation in oxygen content in the steel can have a profound effect on corrosion rates that are observed. In order to use these data in subsequent analyses, a considerable amount of judgment has been used to develop a workable simplified model.

2.1. Oxygen Concentration and Temperature

The variation in corrosion rate as a function of both solution oxygen concentration and temperature is shown in Figure 2 for four different studies. In Figure 2, data obtained in the corrosion field test reported by Caskey⁽²⁾ shows much lower corrosion rates than those reported by DeBerry, Ellis and Thomas⁽⁴⁾ for corrosion in sea water at the same temperature. Similarly, the low temperature field test data exhibits lower corrosion rates than that reported by Uhlig^(5, p. 94). These low corrosion rates may be the result of two factors. First, the steels used for these different corrosion tests are different. Second, in the geothermal corrosion field test⁽²⁾ the solution chemistry was more protective of the steel; the pH was maintained at a level of 8 or greater and a small amount of corrosion inhibitor was added to the solution. Nonetheless, it is observed that the slope of the curves of corrosion rate vs. oxygen concentration approaches a straight line on the log-log plot with a unit slope. This indicates a linear dependence of corrosion rate on oxygen concentration with up to an order of magnitude variation in the corrosion rate at a given oxygen concentration.

Data of Heitz and Manner⁽⁶⁾ reveal a similar linear dependence of corrosion rate on oxygen concentration. These authors note additionally that corrosion which occurs at oxygen concentrations of less than 50 parts per billion (ppb) is uniform in nature whereas corrosion at higher oxygen

Figure 2. Variation in Corrosion Rate with Solution Oxygen Concentration. Data (▲) are those of Caskey⁽³⁾.

concentrations is characterized as a pitting type of corrosion. The pitting corrosion is far more serious and its avoidance is the basis for the oxygen acceptance criteria. It may also be noted that the onset of pitting corrosion at 50 ppb O_2 can be better characterized than the corrosion rate at higher oxygen concentrations.

The thermal dependence of corrosion rate may also be estimated from this data (shown in Figure 2). This data seems to suggest that corrosion rates increase with temperature. Data of Caskey⁽²⁾ show almost an order of magnitude increase in corrosion rate as the temperature is increased from 38°C to 121°C. On the other hand, Heitz and Manner show that the corrosion rate decreases as the temperature increases (as long as uniform corrosion at less than 50 ppb O_2 occurs). The observation of these latter investigations is likely the result of the formation of stable protective films which significantly retard uniform corrosion. At higher oxygen concentrations, pitting corrosion rates were observed to increase at higher temperatures.

One would normally expect a rate phenomena to be governed by an Arrhenius expression showing an exponential temperature dependence. Corrosion is more complicated since diffusional processes occur in series with the chemical reaction. A mathematical expression for this dependence⁽⁷⁾ is

$$r = \frac{Ak_m e^{-E/RT}}{k_m + Ae^{-E/RT}} C_{O_2} \quad (3)$$

where k_m is the diffusional resistance term and $Ae^{-E/RT}$ is the Arrhenius term with activation energy, E , and C_{O_2} is the solution concentration of oxygen. If we attempt to fit the data of Caskey⁽²⁾ to Eq(3), data at only two temperatures were reported so that just two of the constants in Eq(3) may be determined. For this reason an Arrhenius expression is used in place of Eq(3), and it is recognized that the constants must assume some average value. The expression which results from fitting Caskey's data is

$$r = 13.7 C_{O_2} \exp \left\{ \frac{-2440}{T+273} \right\} \quad (4)$$

where C_{O_2} is the concentration of O_2 in solution in ppb, T is the temperature in °C and r is the corrosion rate in mpy. For the purposes of this discussion, the exact form of the

corrosion rate expression as a function of temperature is less important than the maximum corrosion rate actually observed since this maximum information most directly affects the selection criteria. Hence, Eq(4) is considered sufficiently refined for this discussion in light of the wide variability in the observed corrosion rates.

2.2. pH

The effect of pH on the corrosion rate is reported in several studies and shown in Figure 3. In the low temperature data of Uhlig^(5,p.99), the corrosion rate shows little variation above a pH of 4. In more acidic solutions the corrosion rate increases rapidly as protective surface films of $\text{Fe}(\text{OH})_2$ dissolve. In a higher temperature study by Heitz and Manner⁽⁶⁾, significantly greater corrosion rates were obtained and the corrosion rate increased rapidly below a pH of 7. Heitz and Manner speculate that their high corrosion rates in this pH study may be the result of very short time duration tests where surface films are given inadequate time to form and hence protect the metal surface. In both studies, there appears to be a nearly exponential relationship between pH and corrosion rate.

2.3. NaCl Concentration

NaCl in solution acts to increase the corrosion rate by reducing the ability of $\text{Fe}(\text{OH})_2$ to form a cohesive surface film. When NaCl is present in solution, the anode and the cathode tend to be more widely separated. Fe^{++} released at the anode is more free to migrate larger distances before combining with OH^- released from the cathode. The $\text{Fe}(\text{OH})_2$ precipitate thus formed does not deposit in such a way as to cover the anode and thus corrosion proceeds at a rapid rate. For solutions containing reduced amounts of oxygen this increase in corrosion rate is approximately linear.^(5,p.113)

The combined effects of both pH and NaCl content may be added to the corrosion expression, Eq. (2), to yield

$$r = 13.7 C_{\text{O}_2} \exp\left\{\frac{-2440}{T+273}\right\} + \exp\{4(4-\text{pH})\} + 4.9 C_{\text{NaCl}}, \quad (5)$$

where C_{NaCl} is the concentration of NaCl expressed in weight percent. Although this corrosion rate expression is used in the subsequent analysis, the gaseous composition criteria presented herein may be easily modified as more consistent data are obtained.

Figure 3. Variation of Corrosion Rate with pH

3. Oxygen Level

Oxygen enters the wellbore by two paths when drilling with mist, as shown in Figure 4. Water is pumped from the mud pits and is combined with a gas stream before going down the center of the drill pipe. The water contains dissolved oxygen in an amount up to the equilibrium amount of oxygen in water at the temperature and salt concentration existing in the mud pits. Oxygen also enters the wellbore through the vapor phase. It is the composition of this gas phase that it is desired to set bounds on. Once both streams are inside the wellbore, it is assumed that oxygen rapidly partitions itself in an equilibrium manner between the vapor and liquid phases. For the reduced oxygen concentrations that will be considered here, more oxygen will enter with the water stream than with the gas stream. On the inside of the wellbore, oxygen will thus be transferred from the liquid to the vapor phase.

While inside the wellbore, water entering in the form of mist readily coats the drill pipe as depicted in Figure 5. Steel is a water wettable material with a surface energy far in excess of that of water, so that a thin film of water forms on the metal surface. This film of water is also assumed to be in chemical equilibrium so that the oxygen present in this film is primarily responsible for the oxygen-based corrosion at the metal surface. As was mentioned in Section 2.1, significant pitting corrosion is observed when the concentration of oxygen in the water phase exceeds 50 ppb. Although a more relaxed concentration specification may be adapted, it is felt that additional oxygen will enter the system through leaks and joint makeup procedures in addition to the formally analyzed routes of gas and water entry. Furthermore, long equilibration times will lead to larger solution oxygen concentrations. Hence, 50 ppb is chosen as the maximum tolerable solution concentration of oxygen at the bottom of the drill string where corrosion rates are highest. Calculations which relate the solution concentration of oxygen to inlet gas and water conditions are presented in Appendix A.

3.1 Temperatures and Pressures in the Wellbore

In order to perform the calculations relating solution oxygen concentration to gaseous compositions, it is necessary to estimate the temperatures and pressures which exist in the borehole during mist drilling. Data was taken from the corrosion field test reported by Caskey⁽²⁾ to determine this information. At the top of the drill string the temperature and pressure are known. 60°C was chosen as a representative inlet temperature and 250 psig is an average delivery pressure. The blowby line pressure was observed to average 22 psig and the exit mist temperature was 238°F when 1100 SCFM of N₂ gas was pumped through the wellbore.

Figure 4. Idealized Borehole Showing Entry Paths For Oxygen Into the Wellbore

OXYGEN CONCENTRATION

MATERIAL BALANCE
ALL OXYGEN DOWN HOLE IS
DISTRIBUTED BETWEEN
GAS AND WATER PHASES

EQUILIBRIUM (ASSUMED)

$$\text{HENRY'S LAW } H = \frac{P_{O_2}}{X_{O_2}}$$

FOR THIS ANALYSIS IT IS ASSUMED
THAT SUFFICIENT TIME HAS ELAPSED TO
ALLOW COMPLETE THERMODYNAMIC EQUILIBRIUM
BETWEEN GAS AND LIQUID PHASES.

Figure 5. Formation of Liquid Film Allows Partition of Oxygen Between Gas and Liquid Phase With Liquid Phase Controlling Corrosion

Downhole conditions may be inferred from this data. Inside of the drill string, the mist passes through the complete length of the drill pipe. If we assume incompressible flow, we find that at 1100 SCFM, the pressure increases from 250 psig at the top of the drill string to 265.5 psig at the bottom of the drill string. This increase in pressure represents the difference between the hydrostatic pressure gradient and the frictional flow losses over an assumed 4000 ft length of drill pipe. With such a small change in pressure, the incompressible flow assumption is valid. A similar estimate of annular pressure drop reveals that the bottom hole pressure in the annulus is approximately 40 psig. Hence, most of the pressure transition occurs through the drill bit. At 40 psig (52.2 psia), the ambient boiling point of water is 283.6°F (139.8°C). If the bottomhole temperature was to rise above approximately 140°C, then liquid water in the mist drilling fluid would evaporate and moderate the bottomhole temperature while drilling operations are in progress. If the hole is shut-in for a period of time, then higher pressures and consequently higher temperatures may be encountered. For the corrosion field test⁽²⁾, it was assumed that the fluid temperature at the bottom of the hole was 250°F (121°C), in agreement with the above analysis. For other conditions it is assumed that bottomhole temperatures may rise as high as 175°C which represents the worst condition from a corrosion point of view.

3.2 Calculational Results - Effect of Oxygen Levels on Corrosion Rates

The concentration of oxygen in water is linearly dependent on the gas phase composition of oxygen, but this linear relationship is dependent on temperature, pressure, salt concentration and the gas-to-liquid (G/L) ratio. For a specific case where the temperature is 175°C, the pressure is 250 psig, and the concentration of NaCl is 0.1%, the results of the calculations are presented in Figure 6. Here, the concentration of oxygen in the water increases as more water is added to the mixture entering the wellbore. The range of values for G/L varies from a low value of 3.3 (which corresponds to 1100 SCFM of gas and 330 gpm of water) to a G/L of 11 (which corresponds to 1100 SCFM of gas and 100 gpm of water). If the maximum concentration of oxygen allowed in the liquid phase is determined to be 50 ppb, then the incidence of pitting corrosion should be minimized as mentioned before (Section 2.1). To have this criterion satisfied at a G/L of 3.3 SCF/gal, the maximum allowable concentration of oxygen in the gas phase is 50 ppm. This concentration of oxygen becomes the design criteria for allowable oxygen in the inert gas.

If the amount of liquid in the drilling fluid mist is reduced, then greater amounts of oxygen in the gas stream may

Figure 6. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water for the Case Representative of the Inside of the Drill Pipe at the Bottom of the Wellbore

be tolerated while still maintaining 50 ppb of oxygen in the liquid phase. At 50 ppb oxygen, 175°C, 0.1% NaCl, and pH of 7 or more, Eq(5) may be used to provide a crude estimation of the corrosion rate for these conditions. This corrosion rate is 3.4 mpy and is much less than an industry standard acceptable corrosion rate of 50 mpy and hence the corrosion criterion used here should allow for a conservative design.

The effect of having increased amounts of NaCl is seen in Figure 7. As mentioned in Section 2.3, NaCl tends to increase the corrosion rate; however, at the same time, the amount of oxygen in the water phase is reduced as the concentration of NaCl increases as indicated by the lowering of the equilibrium lines in Figure 7. At a G/L of 3.3 SCF/gal and 3.5% NaCl, the concentration of oxygen in the gas phase may be increased from 50 ppm, observed in the previous case, to 90 ppm in order to yield the same liquid phase O₂ concentration of 50 ppb. However, at this higher salt concentration, the estimated corrosion rate climbs by an order of magnitude to 20.1 mpy. If the drilling fluid were to be a concentrated brine or if strong mixing with a brine formation fluid occurred, the corrosion rate would be even higher. For example, at a solution oxygen concentration of 50 ppb, 175°C, and 22% NaCl the anticipated corrosion rate would reach an unacceptable 110 mpy. Hence, the presence of salt is undesirable from a corrosion point of view, though if a given water salinity is available, higher oxygen concentrations in the inlet gas stream become allowable as the salinity increases.

The effect of a lower temperature corresponding to the approximate temperature which occurs inside the drill pipe at the top of the drill string is shown in Figure 8. For 250 psig, 60°C, and 0.1% NaCl, at the lowest gas to liquid ratio, 3.3 SCF/gal, the concentration of oxygen in the water may not be reduced below 61 ppb. Even at this relatively high oxygen concentration, however, the estimated corrosion rate using Eq(5) is 1.0 mpy. If we allow the concentration of oxygen in the gas phase to rise to 50 ppm, then the concentration of oxygen in the water rises to 82 ppb as shown in Figure 8 and the expected corrosion rate (Eq. 5) is 1.2 mpy. If this corrosion rate is compared to that at the higher temperature, the effect of temperature is to increase the corrosion rate by a factor of 3 from the top of the drill string to the bottom.

The effect of using more saline waters at the top of the drill string is shown in Figure 9. Once again, salt tends to drive oxygen out of the water phase, but this reduction in solution oxygen concentration does not result in a decreased corrosion rate. The chlorides present more than compensate for the reduced solution concentration of oxygen, resulting in an increase in corrosion rate.

Figure 7. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water at Conditions Representative of the Bottom of the Wellbore. The Effect of Higher Salt Concentrations is Shown

Figure 8. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water for the Case Representative of the Inside of the Drill Pipe at the Top of the Wellbore

Figure 9. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water For the Case Representative of the Inside of the Drill Pipe at the Top of the Wellbore: Effect of Increased Salt Concentration

Figure 10. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water at Conditions Representative of the Annulus at the Top of the Wellbore

Figure 11. Relationship Between Oxygen in the Gas Phase vs. Oxygen in the Water at Conditions Representative of the Annulus at the Bottom of the Wellbore

If the pressure is reduced, as would be the case in the annulus, the water approaches its boiling point and oxygen tends to be driven out of solution as shown in Figure 10 and 11. In both of these cases the concentration of oxygen in the water phase never gets above 3 ppb when the concentration of oxygen in the gas is 50 ppm. However, even at these low oxygen concentrations, the corrosion plus erosion phenomena in the annulus are dramatically affected by the oxygen levels. Erosion tends to remove surface films so that the corrosion mechanism can proceed at a more rapid rate. It has been observed that the external or annular corrosion rate is an order of magnitude greater than that predicted by Eq(5)⁽²⁾.

4. Acid Formers

Besides oxygen, other species are present in the gas stream which acidify the water and consequently increase the corrosion rate. As was discussed in Section 2.2, the corrosion rate appears to be fairly constant at pH values greater than 4 (at low temperature) or 7 (at high temperature). The three species NO_x , SO_2 , and CO_2 are capable of reducing the pH of the water system. NO_x and SO_2 are present in the exhaust gas of a diesel engine in relatively small amounts while CO_2 is the primary combustion product.

4.1 NO_x

In the presence of excess air, the combustion of diesel fuel is accompanied by the formation of several oxides of nitrogen. The appropriate reactions are given below.⁽⁸⁾

All three species will be present in diesel exhaust. Nitrous oxide is a relatively stable non-acid forming compound. Nitric oxide will react with excess oxygen to form nitrogen dioxide according to the reaction

This reaction is fairly rapid at atmospheric conditions and for the purposes of this calculation is assumed to occur completely. Nitrogen dioxide will then react with water to form nitric acid according to the reaction

Nitric acid is a strong acid (completely dissociated) and must be neutralized by the addition of NaOH to maintain the neutral pH necessary to minimize corrosion.

In order to determine the relative proportions of the oxides of nitrogen in diesel exhaust, a rough estimation procedure was employed which used only chemical equilibria evaluated at the combustion temperature as shown in Appendix B. From these calculations the combustion temperature was 1700°K and the exhaust gas contained 1000 ppm NO, 12 ppm NO₂ and 0.5 ppm N₂O. Hence, the majority of the NO_x was nitric oxide. A similar equilibrium calculation for Eq(9) revealed that at downhole conditions, the equilibrium molar ratio of NO₂/NO was 67.5. Therefore, the nitric oxide generated in the diesel exhaust should react to form NO₂. Reaction rates for these reactions were not considered since the total amount of NO_x in the gas stream is small and the resultant economic impact of this species is also small.

If it is assumed that nitric oxide is completely converted to nitric acid in solution, then it will be necessary to add NaOH to the solution to neutralize the HNO₃. In the case above, where 1000 ppm of NO in 1100 SCFM exhaust gas enters the wellbore, 170 lbs/day of NaOH must be added to solution to neutralize the acid formed. At a current price of \$.71/lb of NaOH, the cost of this chemical addition is \$120/day. If NO_x is reduced below 1000 ppm in the exhaust stream, then the anticipated caustic addition will be linearly reduced.

4.2. SO₂

SO₂ is present in the exhaust of a diesel engine as a result of the combustion of sulfur present in the fuel. For a normal diesel fuel which contains 0.22% S, the combustion of this fuel with a stoichiometric amount of air results in a gas which contains 315 ppm SO₂. When this specie combines with water, sulfurous acid (H₂SO₃) is formed. In the most conservative treatment of this specie, two hydrogen ions must be neutralized for each SO₂ molecule present in the diesel exhaust. Hence, 1100 SCFM of gas will require 45.9 lbs of NaOH/day at a cost of \$33/day in order to maintain a neutral pH in the downhole drilling fluid.

4.3. CO₂

Carbon dioxide reacts with water yielding carbonic acid, which then dissociates to form a hydrogen ion and a bicarbonate

ion (Eq. 11). The bicarbonate ion can further dissociate to form a carbonate ion and another hydrogen ion, though the equilibrium constant is four orders of magnitude less than that for the first reaction (Eq. 12). (Equilibrium constants for these reactions at 25°C and 60°C appear in Appendix C.)

The H_2CO_3 - HCO_3^- system can act as a buffer to maintain the pH. Upon introduction of OH^- (Eq. 13) or H^+ (Eq. 14), the following reactions occur, resulting in a buffering action:

If the concentrations of H_2CO_3 and HCO_3^- are equal (the optimum buffer), the corresponding pH is 6.4 at 25°C and is 6.2 at 60°C (see Appendix D).

4.3.1. Methods of Controlling CO_2

CO_2 control is necessary due to the high levels of CO_2 present in diesel exhaust. A typical exhaust gas analysis is given in Table I below for an air/fuel ratio of 17. The analysis given is on a water-free basis.

Table I Diesel Exhaust (Air/Fuel = 17) ⁽¹⁰⁾

<u>Component</u>	<u>Volume Percent</u>
CO_2	12.00
O_2	3.55
CO	0.48
H_2	0.25
N_2	83.51
H_2O	12.54

Several methods of carbon dioxide removal or control were considered in this study. Procedures investigated included:

1. molecular sieves
2. freezing (cryogenics)
3. liquid extraction using amines
4. buffering action

4.3.1.1. Molecular Sieves

Use of molecular sieves to "strain out" carbon dioxide seems at first a logical means of CO₂ removal. However, this method of CO₂ removal is most feasible when the feed stream has less than 1.5 mole percent CO₂⁽¹¹⁾ (diesel exhaust is 12%). In addition, the critical molecular diameters of carbon dioxide (and water) are only within 0.2 Å units of nitrogen (see Table II below). Any water present will be removed preferentially to CO₂. Therefore, molecular sieves are not considered a viable means of CO₂ removal.

Table II⁽¹²⁾

<u>Critical Diameter, Å</u>	
CO ₂	2.8
CO	2.8
N ₂	3.0
H ₂ O	3.2

4.3.1.2. Cryogenic Removal

The second alternative for carbon dioxide elimination is by cryogenic removal. The exhaust gas must first be dried, then compressed, cooled, and expanded. Solid or liquid CO₂ would be removed and the remaining gas would consist largely of nitrogen along with some oxygen, carbon monoxide, and hydrogen. This gas would then be compressed before entering the drill string.

There are several complications with this method. First, freezing carbon dioxide at atmospheric pressure (approximate pressure after expansion) requires a temperature of -109.3°F. To achieve such a low temperature requires cascade cycles which will significantly increase equipment cost. Most importantly, removal of solidified CO₂ from inside the process equipment presents a major obstacle, as CO₂ would tend to ice up on surfaces. Liquid CO₂ would be much easier to handle, but pressures of 77 psia or greater are necessary for CO₂ to

exist in the liquid state. The number of cascade cycles would increase because of limitations on expansion pressure. In addition, cryogenic removal of CO₂ does not become feasible until the inlet gas stream consists of 40-50% CO₂ or more.(13)

4.3.1.3. Liquid Extraction Using Amine

Use of aqueous amine solutions to remove CO₂ from a process stream has been practiced in the natural gas industry for a number of years. The most widely used amines are monoethanolamine (MEA) and diethanolamine (DEA). The reaction of 1 mole of CO₂ with 2 moles of MEA, for example, to form a carbamate salt, is

R = (C₂H₄OH) for MEA

This reaction is quite rapid at low CO₂/MEA loading and at moderate temperatures. At higher acid gas loadings and increased temperature, the CO₂ partial pressure driving force is lower and the reaction rate decreases when acid gas loadings are greater than stoichiometric (0.5). The CO₂ - H₂O equilibrium reactions forming bicarbonate and carbonate ions (see Equations 11 and 12) along with Equation 16 below must also be included:(14)

The reaction sequence is similar for DEA ((C₂H₄OH)₂NH), though stoichiometric CO₂/DEA loading is 1.0.

After the CO₂ is adsorbed by the MEA or DEA, it is driven off by applying heat to the acid-rich solution. The lean solution is then cooled and recycled back to the contactor.

The basic requirement for the amine system is that it can handle 1.6 million standard cubic feet per day (MMSCFD) inlet gas at a CO₂ concentration of 12% by volume (Appendix E). Use of a DEA system was recommended because a higher acid loading is possible, hence lower circulation rates are required. In addition, DEA is less susceptible to fouling and thermal degradation.(15) The outlet CO₂ concentration would be from 400 to 1000 ppm, given the inlet conditions(13, 16).

Due to the remoteness of most drilling sites, all electricity required must be generated on location. Electrical power requirements are quite small, as only a small amine unit of pumping capacity 30-35 gallons per minute is necessary. A diesel-powered electric generator to operate the pumps and cooling fans is assumed to be available. However, the diesel generator will consume only 13 or 14 percent of the total energy requirement for the process. More diesel fuel will be consumed in regeneration of the amine by heating. The burner may have to be slightly modified in design, as most are designed to burn natural gas or propane, or operate on process steam. A forced draft burner may be necessary to use diesel, but should not present large design problems.⁽¹⁶⁾

Site preparation for an amine unit is also necessary. A concrete pad must be poured in order to provide support for the skid-mounted unit, which includes a tower approximately thirty feet high. This cost would then be incurred after every new relocation of a drilling operation. In the following economic analysis, successive preparations of new sites were not included. This could substantially increase the costs, as average time spent in mist-drilling a well is about 2 weeks.

Equipment life is estimated to be 10 to 15 years. Using ordinary annuity over an equipment life of 10 years, total capital and operating costs ranged between \$520 and \$950 per day. (See Appendix F for an analysis of costs incurred given by three different sources.) Information obtained from two personal industrial contacts was used to calculate daily costs of \$520 and \$650. These may be much more realistic than the high of \$950 per day, which was based on information in a journal article.⁽¹⁴⁾ However, it is evident in all cases that the majority of the cost (2 to 3 times the equipment cost) is in energy, or operating costs. As aforementioned, costs will be significantly higher due to transportation costs and site preparation. Overall, these relocation costs will make the use of amine extraction of CO₂ less economically desirable.

4.3.1.4. Buffering Action

The fourth and one of the most feasible methods of CO₂ control is by utilizing the buffering action of the H₂CO₃ - HCO₃⁻ system. As the solubility of CO₂ in water at 60°C is limited (according to the value of the Henry's Law constant), only small amounts of carbonic acid will be formed by the reaction of dissolved CO₂ and water. The buffer is made by adding sodium hydroxide in amounts which will partially neutralize the acid present. The resultant bicarbonate ions (HCO₃⁻) and remaining unneutralized carbonic acid thus form the buffer system. In order for this method to be economically feasible, the pH should be 8 or less. This is less than an accepted

value of pH 10 (or more) currently practiced in most drilling operations. But according to Uhlig⁽⁵⁾, the corrosion rate is independent of pH in the ranges of 4 to 10, and is dependent only upon the rate of oxygen diffusion to the metal surface in this range.

Calculated daily sodium hydroxide costs incurred over a two week period for different pH's are given in Table III. Due to the logarithmic nature of pH, a drop of 1 pH unit results in an order of magnitude decrease in caustic required and can represent a substantial cost savings. Furthermore, if some of the CO₂ is removed using a catalytic converter on the diesel exhaust, caustic usage and costs will decrease in direct proportion to the CO₂ concentration.

A sample calculation from which Table III was derived appears in Appendix G. Conditions inside the drill pipe were assumed to be 250 psig at 60°C. Total solution volume (water) in the mud pits is approximately 1500 barrels. Costs are given on a per day basis, averaged over a drilling period of two weeks. If the pH used is between 7 and 8, costs are relatively low and corrosion should not be a significant problem.

Table III

Average Daily Sodium Hydroxide Cost for Buffer (dollars)

mol fraction CO ₂	pH						
	4	5	6	7	8	9	10
.12	-	2	22	217	2175	21,746	217,465
.10		2	18	181	1812	18,122	181,221
.05		1	9	91	906	9,061	90,610
.01		-	2	18	181	1,812	18,122
.005		-	1	9	91	906	9,061
.001			-	2	18	181	1,812

5. Water Specification

Although water itself is not a harmful component in the gas mixture, liquid water will combine with the acid formers

SO₂, NO, and CO₂ to yield a very acidic corrosive solution. Thus, it is necessary to remove enough water from the exhaust gas so that liquid water does not form within the gas compressors.

When the exhaust gas enters the gas compressors (after the removal or neutralization of the aggressive species), the total pressure in the compression chamber rises and the concentration of water vapor increases. If this concentration exceeds the concentration of a saturated vapor mixture, then droplets of water will form. These droplets will then very rapidly equilibrate with the acid formers. Since the vapor pressure of water decreases rapidly with temperature, minimum temperatures of metal surfaces inside the compressor must be considered. Water concentrations low enough so that condensation will not occur on those surfaces must then be specified. As a first approximation, there will be surfaces inside of the compressors which may get as cold as 32°F(17). At this temperature the vapor pressure of water is 0.0886 psia and a water system will exist entirely in the vapor phase as long as the partial pressure of water is less than the vapor pressure. If the internal pressure in the compressor is 1000 psia, then the maximum concentration of water is

$$Y_{H_2O} = \frac{0.0886 \text{ psia}}{1000 \text{ psia}} = 9 \times 10^{-5} \frac{\text{moles } H_2O}{\text{moles gas}}$$

where Y_{H_2O} is the mole fraction H₂O in the gas. Converting this to mass units, the maximum concentration of water in the gas phase is 57 ppm (dew point, -43.2°C).

The removal of water from a gas can be accomplished by many methods, all of which need not be reviewed here. The essential point is to show that feasible and economical processes do exist for the purpose of this process. As the exhaust gas comes from the diesel engine, it contains 12.5% H₂O. Most of this water may be removed by cooling the gas to ambient conditions. If the gas is cooled to 70°F, the residual water in the gas will be 2.5%. The removal of this residual water may be accomplished passing the gas through a CaSO₄ drying bed, where water is removed by the reactions

The partial pressure of water for the first equilibrium is 3.04×10^{-2} mm Hg (as calculated from Free Energy data in the Handbook of Chemistry and Physics⁽¹⁸⁾) so that at a total pressure of 1 atm, water in the gas will be reduced to 31 ppm. Thus, the gas will be drier than that required to prevent condensation inside of the compressor.

The economics of this process have not been analyzed in detail but rather examined to see that the process is not overly expensive. If it is proposed to remove water from the inlet gas, approximately 3.6 tons of CaSO_4 will be required to dry the gas pumped down the well during one day. Although this is a large amount of CaSO_4 , it may be regenerated either on site by heating above 163°C or by shipping it to a regeneration facility. If the regeneration is to be accomplished on site, a smaller amount of CaSO_4 could be regenerated at a more frequent interval. In either event, the heating requirement for a 2 week period would be 3.64×10^7 BTU or equivalently 270 gal of diesel fuel will supply this heat load. Hence, the fuel cost to regenerate the gas drying beds will be approximately \$340 over the two week time period or approximately \$24 per day.

6. Carbon Monoxide

Carbon monoxide is typically present in the exhaust gas of a diesel engine in amounts up to several percent. This specie is a reducing agent and its presence in the exhaust gas is beneficial in the respect that it will tend to scavenge oxygen from the downhole environment. Additionally, the carbon balance for the combustion of fuel requires that all carbon in the fuel end up as CO or CO_2 so that CO in the exhaust gas reduces the amount of CO_2 . In each of these cases, however, no credit is taken for CO in the exhaust gas because the kinetics of the oxygen scavenging reaction are likely too slow to be of significant benefit. The expected reduction in CO_2 partial pressure is too small to consider for the normal range of operation of a diesel engine. Hence, no limitation is imposed on CO levels in the exhaust gas.

7. Conclusions and Recommendations

1. Specifications have been generated for the composition of an inert gas to be used in mist drilling on the basis that the gas attains an equilibrium with the water and that corrosion takes place in this latter phase. If the gas is generated by cryogenically purifying air, then only a specification of 50 ppm maximum of O_2 in the gas is required. This specification will keep the oxygen concentration in the solution below 50 ppb where pitting corrosion is not expected to occur. If the gas is the purified exhaust gas from a diesel engine, then additional

specifications are required for CO₂, NO_x, SO₂, CO, and H₂O. These specifications are listed below:

<u>Gas Phase Component</u>	<u>Gas Phase Specification</u>
O ₂	50 ppm
NO _x	1000 ppm
SO ₂	None
CO ₂	None
CO	None
H ₂ O	50 ppm (Dew Point = -44.3°C)

2. A strong functional relationship exists between the concentration of oxygen in the gas and pH, salt concentration and temperature of the liquid coexisting with the gas.

a. Conventionally, the solution pH is maintained between 9.5 and 12 when the drilling fluid used is air. However, lower values of pH are allowable when an inert gas is substituted for air since reduction of oxygen concentration acts to suppress the corrosion cathode reaction instead of simple reliance on high pH to retard the reduction of O₂. It is recommended that laboratory experiments be conducted to investigate corrosion rates at lower pH's.

b. Corrosion rates increase exponentially as the temperature increases so that higher bottom hole temperatures would dictate the use of a reduced oxygen content in the gas stream. The 50 ppm level for maximum O₂ concentration in the gas corresponds to a bottom hole temperature of 175°C, the upper range of temperatures expected for the bottom of the borehole. The given specification will be conservative at lower temperatures.

c. Corrosion rates increase as the salt concentration increases. If the salt concentration in the drilling fluid is high, the solubility of oxygen in the liquid also decreases so that more oxygen may be tolerated in the gas phase. However, the decrease in oxygen solubility does not offset the increase in corrosion rate caused by the presence of Cl⁻.

3. The primary corrosive action of CO₂, NO_x and SO₂ are as acid formers which reduce the liquid pH and hence promote corrosion. These species must either be neutralized or removed to minimize their corrosive effect.

a. Only minor costs are incurred to neutralize acids formed from NO_x and SO_x in the exhaust gas emissions.

b. Formation of a $\text{H}_2\text{CO}_3\text{-HCO}_3^-$ buffer system can be economically advantageous to other physical methods of CO_2 removal, as the buffer will prevent further adsorption of CO_2 in the liquid phase and subsequent formation of carbonic acid.

c. Use of a portable, skid-mounted amine extraction unit may also prove to be economically feasible for CO_2 removal. Costs range between \$500 and \$950 per day over a period of 10 years (excluding successive site preparation costs).

4. Water removal is necessitated to prevent severe corrosion problems in the gas compressors. Condensation of water upon compression and subsequent absorption of CO_2 , NO_x and SO_2 would lead to the presence of a very corrosive solution in the compressors. Hence, the gas must be dried to 50 ppm of H_2O (Dew Point = -44.3°C) to minimize this problem.

5. The presence of CO in the gas is slightly beneficial and will be tolerated, within safety limits, at any level.

6. The costs associated with neutralizing the acid formers CO_2 , NO_x , and SO_2 are acceptable if the pH of the solution downhole may be controlled between 7 and 8. At higher pH values caustic costs become prohibitive, and alternative CO_2 removal schemes are more attractive.

Appendix A

Liquid Phase Oxygen Concentration - Computational Methods

The method of relating solution oxygen concentration to the incoming amounts of water and gas is presented below. First, consider the equilibrium between oxygen in the liquid phase and oxygen in the gaseous phase as described by Henry's Law.⁽¹⁹⁾ For pure water, Cramer⁽¹⁹⁾ gives an expression for the Henry's law constant of

$$\ln H = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \frac{a_3}{T^3} + \frac{a_4}{T^4} \quad (A1)$$

where T is the absolute temperature in °K and H is the Henry's law constant given in MPa for values of $a_0, \dots, a_4$ of

$$\begin{aligned} a_0 &= -35.4408 \\ a_1 &= 5.58970 \times 10^4 \\ a_2 &= -2.67211 \times 10^7 \\ a_3 &= 5.80947 \times 10^9 \\ a_4 &= -4.91667 \times 10^{11} \end{aligned} \quad (A2)$$

This expression fits Cramer's data with a standard deviation of 5.6%. The Henry's Law constant expresses the ratio between the partial pressure of oxygen in the gas phase to the mole fraction of oxygen in the liquid as

$$H = \frac{P_{O_2}}{X_{O_2}} \quad (A3)$$

Cramer also determined the modification to the Henry's Law constant for varying salt concentrations. In the presence of salt in solution, the solubility of oxygen decreases and the variation in the Henry's Law constant is given by

$$\log \frac{H}{H^0} = k_s m_s \quad (A4)$$

where H^0 and H are the Henry's Law constants for pure water and in the brine, respectively, m_s is the molality of the dissolved salt and k_s is the salting out coefficient, whose value is presented graphically in Cramer's paper. This data was fitted to within 1.5% with a quadratic polynomial as shown,

$$k_s = 3.546 \times 10^{-6} (t - 155)^2 + 0.0888 \quad (A5)$$

where t is the temperature in $^{\circ}\text{C}$.

At higher pressures which may be encountered in the well-bore a correction for pressure may also be required. The variation of the Henry's Law constant with pressure is given by⁽²⁰⁾

$$\left(\frac{\partial \ln H}{\partial p} \right)_T = \frac{\overline{v}_1^{\infty}}{RT} \quad (A6)$$

where p is the partial pressure of oxygen in the gas phase, in atmospheres, $\overline{v}_1^{\infty}$ is the partial molar volume of the solute, oxygen, at infinite dilution, R is the ideal gas constant, and T is the absolute temperature. Data obtained from the International Critical Tables⁽²¹⁾ was used to determine the best value of $\overline{v}_1^{\infty}$ at 25°C . Hence Eq(A6) becomes

$$\left(\frac{\partial \ln H}{\partial p} \right)_T = \frac{2.4028}{T} \text{ atm}^{-1} \text{ } ^{\circ}\text{K}. \quad (A7)$$

At higher temperatures, $\overline{v}_1^{\infty}$ was varied in exactly the same ratio that water expands.

Water density data taken from Reference (18) was fitted to a quadratic polynomial and Eq(A7) was modified to predict the pressure dependence of Henry's Law:

$$\ln \frac{H_p}{H_1} = \frac{2.4028(.8918 + 1.0651 \times 10^{-3} T - 2.382 \times 10^{-6} T^2)}{T} (p - 1) \quad (A8)$$

where H_1 is the Henry's Law constant at one atmosphere. By successive application of the salting out correction and the high pressure correction, the appropriate value of the Henry's Law constant may be obtained. The concentration ratio between the vapor phase oxygen and solution oxygen is then determined.

In the material balance calculation, all oxygen is allowed to partition itself between the vapor and liquid phases. This calculation is accomplished in an iterative fashion by assuming all oxygen to be initially present in the gaseous phase. The solution concentration of oxygen may then be calculated in equilibrium with this assumed initial gas composition. Based on the amount of oxygen removed from the gas phase, a new gaseous composition may be calculated. Subsequently, a new liquid phase composition is determined using Henry's Law. This calculation is repeated until the composition of the gas and liquid phase approach a constant value satisfying both equilibrium or Henry's Law and the material balance equations.

The total amount of oxygen entering the wellbore is determined as follows. Oxygen in the gas phase enters at a rate of

$$T_{O_2G} = G(.08081 \times 10^{-6}) \phi \quad (A9)$$

where T_{O_2G} is the mass flow rate of oxygen in lbs/min, G is the volumetric gas flow rate in SCFM and ϕ is the oxygen concentration in the gas phase in ppm.

Oxygen is dissolved in the liquid water phase as determined by the atmospheric equilibration and is quantitatively expressed by rearranging Eq(A3)

$$X_{O_2} = \frac{(0.21)(0.83 \text{ atm})}{H(60^\circ\text{C}, \% \text{NaCl}, 0.83 \text{ atm})} \quad (A10)$$

X_{O_2} is the solution oxygen mole fraction at a water temperature of 60°C , arbitrary salt concentration and under an oxygen partial pressure assumed present at 7000 ft elevation where the atmospheric air pressure is 0.83 atm. The mole fraction oxygen is converted to a mass fraction, C_{O_2} , as

$$C_{O_2} = \frac{X_{O_2}(32)}{X_{O_2}(32) + (1 - X_{O_2})18} ,$$

and the total oxygen mass flow rate in the water is given by

$$T_{O_2W} = L(8.2265) C_{O_2} , \quad (A11)$$

where T_{O_2W} has units of lbs/min of O_2 and L is the water flow rate in gal/min.

The sum of Eq(A9) and (A11) gives us the total oxygen flow rate into the wellbore,

$$T_{O_2} = T_{O_2G} + T_{O_2W} . \quad (A12)$$

As a first approximation the molar ratio of oxygen to inert species in the gas, assuming all oxygen is in the gaseous phase, is

$$R = \frac{\left(\frac{28}{32}\right)(T_{O_2})}{G(.08081) - T_{O_2G}} , \quad (A13)$$

and hence the mole fraction of oxygen in the gas phase is

$$Y_{O_2} = \left(\frac{R}{1+R}\right)(1 - Y_{H_2O}) \quad (A14)$$

where Y_{O_2} is the mole fraction of oxygen in the gas phase and Y_{H_2O} is the mole fraction of water in the gas phase. The mole fraction of water in the gas phase is determined by dividing the vapor pressure of water by the total pressure at the location of interest in the drill string. The vapor pressure of water was obtained by fitting data from the CRC Handbook(18) to the form

$$\ln P_{H_2O} = \frac{-A}{t+B} + C \quad (A15)$$

where t is the temperature in $^{\circ}C$ and A , B , and C are constants presented in Appendix G. Additionally, the vapor pressure of water is lowered by the presence of salt, $NaCl$, in the water phase. Data available from the International Critical Tables

(21, vol. 3, p. 370) was used to obtain a correlation between the mole fraction of water in the water solution and the vapor pressure lowering as would be expected from Raoult's Law. Hence,

$$C_1 = a + b X_{H_2O} + c X_{H_2O}^2 \quad (A16)$$

where X_{H_2O} is the mole fraction of water in the aqueous salt solution and a , b , and c are constants given in Appendix A. C_1 is then multiplied by P_{H_2O} given in Eq(A15) to obtain

$$P_{soln} = C_1 P_{H_2O} \quad (A17)$$

where P_{soln} is the vapor pressure of the water and salt solution. In this manner, Y_{H_2O} is determined.

The partial pressure of oxygen is determined next from

$$P_{O_2} = P_T Y_{O_2} \quad (A18)$$

where P_T is the total pressure at the point of interest.

Finally, the mole fraction of oxygen in the water phase is determined by solving Eq(A3). As an initial guess, it is assumed that all of the oxygen is in the gaseous phase. Next, the amount of oxygen in the liquid phase that would be in equilibrium with this gaseous phase is calculated. In the following step of the calculation, oxygen absorbed by the liquid phase must be subtracted from the gas phase. Thus, T_{O_2} must be replaced by $T_{O_2} - \epsilon$ in Eq(A13) where ϵ is the weight of oxygen (per minute) present in the liquid water phase. These calculations are repeated until ϵ converges to a value which satisfies both the material balance and equilibrium equations. At this point the calculation is terminated. The complete calculation scheme is presented as part of a computer program in Appendix H.

Appendix B

Chemical Equilibrium for NO_x

For the formation of N₂O, NO and NO₂ the free energies of these reactions are⁽¹⁸⁾

$$\Delta G_{\text{N}_2\text{O}} = 18650 - 1.57T \log T - 0.27 \times 10^{-3} T^2 + \frac{0.92 \times 10^5}{T} + 23.47T$$

$$\Delta G_{\text{NO}} = 21590 - 0.28T \log T + 0.45 \times 10^{-3} T^2 - \frac{0.03 \times 10^5}{T} - 2.2T$$

and

$$\Delta G_{\text{NO}_2} = 7730 + 0.53T \log T - 0.265 \times 10^{-3} T^2 + \frac{0.605 \times 10^5}{T} + 13.74T$$

These free energies are evaluated at 1700°K, at which temperature the concentration of NO in the exhaust gas will be 1000 ppm in agreement with observation⁽³⁾. At 1700°K,

$$\Delta G_{\text{N}_2\text{O}} = 49500 \text{ cal/mole}$$

$$\Delta G_{\text{NO}} = 17600 \text{ cal/mole}$$

$$\Delta G_{\text{NO}_2} = 33500 \text{ cal/mole}$$

Since $\Delta G = -RT \ln K$, where K is the equilibrium constant, then

$$K_{\text{N}_2\text{O}} = 5.1 \times 10^{-7}$$

$$K_{\text{NO}} = 5.8 \times 10^{-3}$$

$$K_{\text{NO}_2} = 5.5 \times 10^{-5}$$

where

$$K_{N_2O} = \frac{p_{N_2O}}{p_{N_2}^{1/2} p_{O_2}^{1/2}}$$

$$K_{NO} = \frac{p_{NO}}{p_{N_2}^{1/2} p_{O_2}^{1/2}}$$

$$K_{NO_2} = \frac{p_{NO_2}}{p_{N_2}^{1/2} p_{O_2}^{3/2}}$$

and p's are partial pressures of the components.

For $p_{N_2} = 16.17$ atm and $p_{O_2} = .6875$ (10, p. 9-146),

$p_{N_2O} = 6.8 \times 10^{-6}$, $p_{NO} = 1.9 \times 10^{-2}$ and $p_{NO_2} = 1.5 \times 10^{-4}$ atm.

Converting these partial pressures to mole fractions, we obtain

$$Y_{N_2O} = 3.6 \times 10^{-7}$$

$$Y_{NO} = 1.0 \times 10^{-3}$$

$$Y_{NO_2} = 7.8 \times 10^{-6},$$

or expressed on a weight basis,

$$m_{N_2O} = 0.5 \text{ ppm}$$

$$m_{NO} = 1000 \text{ ppm}$$

$$m_{NO_2} = 12 \text{ ppm}.$$

Appendix C

Equilibrium Constants of Carbon Dioxide Reactions

From the CRC Handbook of Chemistry and Physics(18), the free energies and enthalpies of formation of the components in the CO₂ equilibrium reactions are listed below (in Kcal/mol):

	ΔG_f°	ΔH_f
CO ₂ (aq)	- 92.31	- 98.69
HCO ₃ ⁻	-140.31	-165.18
CO ₃ ⁼	-126.22	-161.63
OH ⁻	- 37.595	- 54.957
H ₂ O(1)	- 56.69	- 68.32
H ⁺	0	0

Reaction I - First Dissociation of Carbonic Acid

by Hess' Law, $\Delta G^\circ = (0 + -140.31) - (-56.69 + -92.31) = 8.69$
Kcal/mol

and $\Delta H^\circ = (0 + -165.18) - (-68.32 + -98.69) = 1.83$ Kcal/mol

$$K_{298} = \left(- \frac{\Delta G_{298}}{RT} \right) = - \left(\frac{8690}{(1.987)(298)} \right) = 4.23 \times 10^{-7}$$

$$\ln \frac{K_2}{K_1} = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_2 = K_1 \exp \left[- \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

$$\text{at } 60^\circ\text{C}(333^\circ\text{K}), K = 4.23 \times 10^{-7} \exp \left[- \frac{1830}{1.987} \left(\frac{1}{333} - \frac{1}{298} \right) \right] = 5.853 \times 10^{-7}$$

Reaction II - Second Dissociation of Carbonic Acid

$$\Delta G^\circ = (0 + -126.22) - (-140.31) = 14.09 \text{ Kcal/mol}$$

$$\Delta H^\circ = (0 + -161.63) - (-165.18) = 3.55 \text{ Kcal/mol}$$

$$K_{298} = \exp \left(- \frac{14090}{(1.987)(298)} \right) = 4.63 \times 10^{-11}$$

$$\text{at } 60^\circ\text{C}(333^\circ\text{K}), K = 4.63 \times 10^{-11} \exp \left[- \frac{3550}{1.987} \left(\frac{1}{333} - \frac{1}{298} \right) \right] = 8.70 \times 10^{-11}$$

Appendix D

pH of $\text{H}_2\text{CO}_3\text{-HCO}_3^-$ Buffer System

First dissociation reaction of carbonic acid is

so

$$K = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

If $[\text{H}_2\text{CO}_3] = [\text{HCO}_3^-]$, which is the optimum buffer for addition of either an acid or base, then $[\text{H}^+] = K$ and $\text{pH} = -\log K$.

$$\text{At } 25^\circ\text{C}, \text{pH} = -\log(4.23 \times 10^{-7}) = 6.37.$$

$$\text{At } 60^\circ\text{C}, \text{pH} = -\log(5.853 \times 10^{-7}) = 6.23.$$

Appendix E

Inlet Gas Mass Flow Conditions

Given inlet conditions of 1100 SCFM diesel exhaust, 12.6% CO₂ by volume at 250 psig and 60°C (-140°F), by the Ideal Gas Law,

$$PM = \rho RT \text{ where } M = \text{average molecular weight}$$

$$\rho = \text{density.}$$

The average molecular weight is approximately

$$M = (.874)(28) + (.126)(44) = 30.016 \text{ lb/lb mol}$$

$$\text{so } \rho = \frac{PM}{RT} = \frac{1 \text{ atm} \left| \frac{30.016 \text{ lb}}{\text{lb mol}} \right| \frac{1 \text{ lb mol } ^\circ\text{R}}{.7302 \text{ atm ft}^3} \left| \frac{1}{492^\circ\text{R(Standard)}} \right| = \frac{.08355}{\text{lb/ft}^3}$$

Mass flow rates are

$$\frac{1100 \text{ SCF}}{\text{min}} \left| \frac{.08355 \text{ lb}}{\text{ft}^3} \right| = 91.9 \text{ lb/min gas}$$

$$\frac{1100 \text{ SCF}}{\text{min}} \left| \frac{60 \text{ min}}{\text{hr}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| = 1.584 \text{ MMSCFD.}$$

CO₂ to be removed is

$$\frac{1100 \text{ SCFM}}{359 \text{ SGF}} \left| \frac{1 \text{ lb mole}}{\text{mol gas}} \right| \left| \frac{.12 \text{ CO}_2}{\text{lb mol}} \right| \left| \frac{44 \text{ lb}}{\text{lb mol}} \right| = 16.2 \text{ lb/min CO}_2$$

$$= 11.65 \text{ tons/day CO}_2$$

Appendix F

Amine Unit Economics

A. Cost data from Ref. (14) are given below for a plant capacity of 1,000 standard short tons inlet gas per day, based on an equipment life of 10 years:

Annual Amortized Capital Expenditure	\$ 692,000
Total Annual Utility Cost	<u>\$3,199,000</u>
Net Annual Operating Cost	\$3,891,000

Capacity of the diesel exhaust inert drilling system is

$$\frac{1100 \text{ SCF}}{\text{min}} \times \frac{.08355 \text{ lb}}{\text{ft}^3} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{24 \text{ hr}}{\text{day}} \times \frac{\text{ton}}{2000 \text{ lb}} = 66.17 \text{ ton/day}$$

Using the sixth-tenths rule for equipment cost from Peters and Timmerhaus⁽²²⁾ and a linear estimate for operating costs,

Capital Expenditure	\$692,000	$\times \left(\frac{66.17}{1000} \right)^{0.6}$	$\times \frac{1}{365}$	= \$371.71
Operating Cost	\$3,199,000	$\times \left(\frac{66.17}{1000} \right)$	$\times \frac{1}{365}$	= <u>\$579.94</u>
Net				\$951.65

the net costs per day are \$951.65 per day.

B. By Reference (13) the system required for the given inlet conditions is a 25 gpm amine system with 3 pumps. The installed Gulf Coast price would be approximately \$250,000.

Equipment costs using the method of ordinary annuity over 10 years equipment life on \$250,000 at 15% interest is \$49,813.02 per year or \$136.47 per day.

Energy requirements necessary are 25 hp electric (total pump capacity and cooling fan) and 1.5 MM Btu/hr to operate the diesel-fired heater (for amine regeneration).

A method of computing the low heat value of diesel is given in the Standard Handbook for Mechanical Engineers. (10)

$$\begin{aligned}
 H &= 26-15d & H &= \text{weight percentage of hydrogen} \\
 &= 26-15(0.9) & d &= \text{specific gravity at } 60/60\text{F} \\
 & & & \text{(assumed value of 0.9)} \\
 &= 12.5
 \end{aligned}$$

The high heat value of diesel at constant volume in Btu/lb is given by

$$\begin{aligned}
 Q_v &= 22,320 - 3,780d^2 \\
 &= 19258.2 \text{ Btu/lb.}
 \end{aligned}$$

The low heat value of diesel at constant pressure in Btu/lb is given by

$$\begin{aligned}
 Q_p &= Q_v - 90.8H \\
 &= 19258.2 - 90.8(12.5) \\
 &= 18123.2 \text{ Btu/lb .}
 \end{aligned}$$

Diesel fuel requirements to operate the heater are then

$$\frac{1.5 \times 10^6 \text{ Btu}}{\text{hr}} \left| \frac{\text{lb}}{18123.2 \text{ Btu}} \right| \left| \frac{\text{gal fuel}}{(8.33)(0.9) \text{ lb}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| = 264.96 \text{ gal/day.}$$

Diesel fuel required to generate electricity to operate the fans and pumps is

$$\begin{aligned}
 &\frac{25 \text{ hp}}{\text{hp-hr}} \left| \frac{2545 \text{ Btu}}{\text{hp-hr}} \right| \left| \frac{1 \text{ lb}}{0.9 \text{ elec. eff.}} \right| \left| \frac{1 \text{ lb}}{0.3 \text{ diesel eff.}} \right| \left| \frac{1 \text{ lb}}{18123.2 \text{ Btu}} \right| \\
 &\left| \frac{\text{gal fuel}}{(8.33)(0.9) \text{ lb}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| = 41.62 \text{ gal/day.}
 \end{aligned}$$

Total fuel consumption and corresponding cost is

$$\Sigma \text{fuel} = 264.96 + 41.62 = 306.58 \text{ gal/day} \times \$1.25/\text{gal} = \$383.23/\text{day}$$

Net Daily Costs are: Capital Expenditure \$136.47

Operating Cost 383.23

Net \$519.70

C. By Reference (16), a 30 gpm DEA system (300 psig) system is required. Energy required is 20 hp for cooling and 1.8 MM Btu/hr for the heater.

Total costs would be about

Equipment Cost \$250,000

Installation 100,000

Total \$350,000

Using the method of Ordinary Annuity over 10 years on \$350,000 at 15% interest computes to \$69,738.22 per year or \$191.06 per day.

Horsepower to run the amine pumps (for an incompressible fluid, work = $v\Delta P$) is

$$\frac{30 \text{ gal}}{\text{min}} \left| \frac{300 \text{ lb}_f}{\text{in}^2} \right| \left| \frac{144 \text{ in}^2}{\text{ft}^2} \right| \left| \frac{\text{ft}^3}{7.48 \text{ gal}} \right| \left| \frac{\text{hp-min}}{33,000 \text{ ft lb}_f} \right| \left| \frac{.75 \text{ motor eff.}}{.8 \text{ pump eff.}} \right| = 8.8 \text{ hp.}$$

Total pump and fan work and corresponding fuel consumption is

$$\Sigma \text{hp} = (20 + 8.8) \text{ hp} \times \frac{2545 \text{ Btu}}{\text{hp-hr}} \left| \frac{.9 \text{ generator eff.}}{.3 \text{ engine eff.}} \right|$$

$$\frac{1 \text{ lb}}{18123.2 \text{ Btu}} \left| \frac{\text{gal fuel}}{(8.33)(0.9) \text{ lb}} \right| \left| \frac{24 \text{ hr}}{\text{day}} \right| = 48.28 \text{ gal/day.}$$

Diesel fuel required to operate the regenerator is

$$\frac{1.8 \times 10^6 \text{ Btu}}{18123.2 \text{ Btu}} \times \frac{1 \text{ lb}}{(8.33)(0.9) \text{ lb}} \times \frac{\text{gal fuel}}{\text{day}} \times 24 \text{ hr} = 317.95 \text{ gal/day.}$$

Total fuel consumption is

$$\Sigma \text{ diesel fuel} = 48.28 + 317.95 = 366.23 \text{ gal/day} \times \$1.25/\text{gal} \\ = \$457.79/\text{day.}$$

Overall daily costs are thus

Capital Expenditure	\$191.06
Operating	<u>457.79</u>
Net	\$648.85

Appendix G

Sodium Hydroxide Costs for a Buffer System - Sample Calculation

The assumed operating conditions are that 1100 SCFM diesel exhaust gas enter the drill pipe at 250 psig and 60°C, and the mud pits will hold 1500 barrels of solution.

The solubility of a gas in a liquid is given by Henry's Law, which is

$$H = \frac{P_i}{X_i}, \text{ where } H \text{ is the Henry's Law constant}$$

P_i is the partial pressure of a component in the gaseous phase

X_i is the mole fraction of the component in the liquid phase.

Also, the partial pressure of a component in the gas phase is its mole fraction times the total system pressure, or

$$P_i = Y_i P_T \text{ where } P_i \text{ is the partial pressure of a component in the gaseous phase}$$

Y_i is the mole fraction of the component in the gaseous phase

P_T is the total pressure of the system.

From the Chemical Engineers' Handbook⁽²³⁾ at 1 atmosphere pressure and 60°C, H for CO_2 in water is 3410 atm.

From Appendix C, it is known that for the reaction,

The total pressure, P_T , is given by

$$P_T = \frac{250 + 12.2}{14.7} = 17.387 \text{ atm,}$$

and therefore $P_{CO_2} = Y P_T = 17.387 Y$. Thus,

$$X = \frac{P}{H} = \frac{17.387Y}{3410} = 0.005231 Y.$$

$$\frac{0.005231 Y \text{ mol } CO_2}{\text{mol } H_2O + \text{mol } CO_2} \left| \frac{1 \text{ mol } H_2O}{18 \text{ g}} \right| \left| \frac{1 \text{ g}}{\text{cm}^3} \right| \left| \frac{1000 \text{ cm}^3}{1} \right| = 0.2906Y \frac{\text{mol } CO_2}{1} = [H_2CO_3]$$

$$5.853 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \text{ where } [H^+] = 10^{-pH}$$

$$\begin{aligned} \text{so } [HCO_3^-] &= 5.853 \times 10^{-7} \frac{[H_2CO_3]}{[H^+]} = \frac{(5.853 \times 10^{-7})(0.2906Y)}{10^{-pH}} \\ &= \frac{1.701 \times 10^{-7} Y}{10^{-pH}} \end{aligned}$$

For the first dissociation reaction only the amount of bicarbonate (HCO_3^-) is equivalent to the amount of NaOH required for neutralization. Hence,

$$\begin{aligned} &\frac{1.701 \times 10^{-7} Y \text{ mol NaOH}}{10^{-pH} 1} \left| \frac{1500 \text{ bbl}}{1} \right| \left| \frac{42 \text{ gal}}{\text{bbl}} \right| \left| \frac{3.785 \text{ l}}{\text{gal}} \right| \left| \frac{40 \text{ g}}{\text{mol}} \right| \left| \frac{1 \text{ lb}}{454 \text{ g}} \right| \left| \frac{\$0.71}{1 \text{ lb NaOH}} \right| \\ &= (\$) \frac{2.537 \times 10^{-3} Y}{10^{-pH}} \quad \text{(cost per 2 week period, the average time before replacing the mud system).} \end{aligned}$$

For normal diesel exhaust where $Y = 0.12$ and a pH of 8 is desired,

$$\begin{aligned} \text{cost} &= \frac{(2.537 \times 10^{-3})(0.12)}{10^{-8}} = \$30,444/2 \text{ weeks} \\ &\text{or } \underline{\underline{\$2175/\text{day}}} \end{aligned}$$

Appendix H

Computer Program for Calculating Solution Oxygen Concentrations

```
C      PROGRAM CORRODE CALCULATES THE CONCENTRATION OF OXYGEN PRESENT
C      IN THE LIQUID PHASE IN EQUILIBRIUM WITH OXYGEN IN THE GAS
C      PHASE AT SPECIFIED TEMPERATURE, PRESSURE, LIQUID FLOW RATE,
C      GAS FLOW RATE, AND SALT CONCENTRATION IN THE WATER PHASE.
C
C      PROGRAM CORRODE(INPUT,OUTPUT,TAPES = INPUT,TAPE6 = OUTPUT)
      REAL KS,MS,L
100  CONTINUE
C
C      READ IN DATA
C
      WRITE (6,*)"READ IN CONCENTRATION OF O2 IN GAS PHASE (PPM)"
      READ (5,*) PHI
      IF (PHI .EQ. 0.0) GO TO 200
      WRITE (6,*)"READ IN THE DRILLING FLUID TEMPERATURE(DEG. C)"
      READ (5,*) TC
      WRITE (6,*) "READ IN THE BOREHOLE PRESSURE(PSIG)"
      READ(5,*) P
      WRITE (6,*)"READ IN PERCENT CONCENTRATION OF NACL IN WATER"
      READ (5,*) C
      WRITE (6,*) "READ IN THE PH OF THE INPUT WATER"
      READ(5,*) PH
      WRITE (6,*)"READ IN THE WATER FLOW RATE IN GAL/MIN"
      READ(5,*) L
      WRITE(6,*)"READ IN THE GAS FLOW RATE IN SCFM"
      READ (5,*) G
      WRITE (6,*) PHI,TC,P,C,PH,L,G
C
C      CALCULATE THE HENRY'S LAW CONSTANT
C
      T = TC + 273.16
      EPS = 1.0E-14
      H = HS(60.,C) * HP(60.0,-2.5,233000.,C)
C
C      CALCULATION OF THE LIQUID PHASE OXYGEN CONCENTRATION
C
      X02 = (0.21 * 0.83 )/H
      C02 = (X02 * 32.)/(X02 * 32. + (1. - X02) * 18.)
      T02W = L * 8.2265 * C02
      T02G = G * .08081 * PHI/ 1.0E06
      T02 = T02W + T02G
      T020 = T02
      T02W0 = T02W
30  PHICORR = T02 * 1.0E06/( T02W + G * 0.08081)
      PH20 = PRESSUR (TC,C)
      YH20 = (PH20 * 14.7)/(P + 14.7)
      R = (.875 * T02)/(G* 0.08081 - T02G)
      Y02 = (R/(1. + R)) * (1. - YH20)
```

```

P02 = ((P + 14.7)/14.7) * Y02
H = HS(TC,C) * HP(TC,P,PHICORR,C)
X02 = P02/H
EPSOLD = EPS
EPS = (L * 8.2265/18.0) * X02/(1.0 - X02)
IF (ABS((EPS/EPSOLD) - 1.0) .LT. 1.0E-03) GO TO 50
T02 = T020 - EPS * 32.
T02W = T02W0 - EPS * 32.0
GO TO 38

```

C
C
C

CALCULATION OF THE ESTIMATED CORROSION RATE

```

50 PPB02 = X02 * 32. * 1.0E09/(X02 * 32.0 + (1.0 - X02) * 18.)
RATE = 13.7 * PPB02 * EXP(-2440./(TC + 273.16))
RATE = RATE * EXP(4. * (4.0 - PH)) + 4.88 * C
WRITE (6,*) "CORROSION RATE AT AN O2 CONCENTRATION OF",PPB02,"PPB"
WRITE (6,*) "TEMPERATURE OF ",TC,"DEG.C ", "PH OF ",PH, "AND"
WRITE (6,*) "NACL CONCENTRATION OF ",C," % ", "IS ",RATE,"MPY"
WRITE (6,300)
300 FORMAT (//)
GO TO 100
200 STOP
END

```

C
C
C
C
C

FUNCTION SUBPROGRAM PRESSUR CALCULATES THE VAPOR PRESSURE OF THE BRINE SOLUTION AT SPECIFIED TEMPERATURE AND SALT CONCENTRATION

```

FUNCTION PRESSUR(TC,C)
T = 1.8 * TC + 32.
Y = (-1457.985867 + 14.30383319 * T)/(T + 373.7972647)
PH20 = EXP(Y)/14.7
XNACL = (C/58.448)/((100. - C)/18. + C/58.448)
XH20 = 1.0 - XNACL
C1 = -8.006610687 + 16.3604092 * XH20 - 7.355634045*(XH20**2)
PRESSUR = C1 * PH20
RETURN
END

```

C
C
C

FUNCTION SUBPROGRAM HP MODIFIES THE HENRY'S LAW CONSTANT FOR
HIGHER PRESSURE

```

FUNCTION HP(TC,P,PHI,C)
EXTERNAL PRESSUR
VR = 2.4028 * (1.00208 - 2.355E-04* TC - 2.375E-06*(TC**2))/0.99707 *
P1= 1. + P/14.7
R = 0.875 * PHI/(1.0E06 - PHI)
PH20 = PRESSUR (TC,C)
YH20 = PH20/P1
Y02 = (R/(1.0 + R)) * (1.0 - YH20)
P02 = P1 * Y02
IF (P02 .LE. 1.0) GO TO 10
HP = EXP(VR * (P02 - 1.0) / (TC + 273.15))
GO TO 20
10 HP = 1.0
20 RETURN
END

```

C
C
C
C
C

FUNCTION SUBPROGRAM HS CALCULATES THE HENRY'S LAW CONSTANT
AT SPECIFIED TEMPERATURE AND SOLUTION SALT CONCENTRATION
THROUGH THE USE OF THE SALTING OUT COEFFICIENT

```

FUNCTION HS(TC,C)
REAL KS,MS
T = TC + 273.16
A0 = -35.4408
A1 = 5.58970E04
A2 = -2.67211E07
A3 = 5.80947E09
A4 = -4.91667E11
Y = A0 + A1/T + A2/(T**2) + A3/(T**3) + A4/(T**4)
HT = EXP(Y)
H = HT * 9.8692
KS = 3.5463059E-06*(TC + 155.1)**2 + 0.0888
MS = 17.109 * C/(100. - C)
HS = H * EXP(2.30259 * KS * MS)
RETURN
END

```

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