CO_2: PROPERTIES AND HANDLING WITH SAFETY CONSIDERATIONS

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ABSTRACT

The increasing use of CO_2 in varied oilfield applications generates the need for a thorough knowledge of CO_2 properties. These properties are responsible for the way CO_2 must be handled in order to use it safely and effectively. The chemical and physical properties will be discussed for CO_2 alone and in combination with other liquids and the mixtures subsequent affects on equipment. These characteristics and effects can cause numerous safety problems. Safety procedures to be discussed include logistics, maintaining breathable air quality, and several aspects of metal integrity.

INTRODUCTION

Carbon dioxide was recognized as a molecular entity distinct from other gasses by Van Helmont in the early 1600s. Its use in the oil field is only 30-35 years old. Understanding the physical and chemical properties of carbon dioxide is winning fully half the battle of using it sucessfully. Many of its most useful oilfield applications and its major safety considerations stem from its physical properties, while longer range problems and equipment precautions are based on its chemical properties.

PHYSICAL PROPERTIES

Carbon dioxide by definition is the molecular structure of one carbon atom bonded by two double bonds to two oxygen atoms. It is normally written as a chemical formula of the form CO_2. Depending on the temperature and pressure to which it is subjected, it may exist as a gas, a solid or a liquid. Each of these states has a set of physical properties which must be considered.

At normal temperature and atmospheric pressure CO_2 is a gas. It is odorless and colorless, not flammable, with a density 1.5 times that of air. It will not support combustion, nor sustain life. As a gas, CO_2 is readily expandable and is soluble in various liquids. Expansion of the CO_2 is governed by the two rules applicable to most gasses. If you raise the temperature, it expands reducing the density of the gas. In the treating fluid pumped into a well or injected by itself as a liquid under certain pressure, CO_2 becomes at some point a gas. When the well is opened to flow the well back, the gas expands as the pressure is reduced and lightens the hydrostatic pressure of well bore fluids, allowing the well to flow. Please note the gas lift characteristics of the CO_2 is caused by the portion of the gas which is not soluble.

CO_2 solubility is very dependent on pressure and to a certain extent on the fluids present. Its solubility in 40 oil is about 4 times greater than it is in water. Solubility in brines is less than that of water being limited by the brines salinity. CO_2 solubility increases with pressure. At higher pressure all the CO_2 may be soluble in the liquid, which means higher and higher concentrations of the gas must be pumped to receive any gas lift benefits. See figure 1. Conversely, more CO_2 solubility is exactly what is desired in EOR projects. Higher treatment pressure forces more CO_2 into solution in heavy crudes and promotes greater viscosity reductions.

CO_2 may exist simultaneously as a liquid, a solid and a gas at its triple point, -69 F and 60.43 psig. See figure 2. At temperature and pressure below the triple point CO_2 may be either a solid or a gas depending upon exact conditions. Dry ice at a temperature of -109 F and atmospheric pressure will sublime to the gas state without going through the liquid state. If the dry ice sublimes at less than atmospheric pressure, or from the partial pressure effect (a moving atmosphere) a lowering of temperature will occur.

Liquid CO_2 can exist only within the limited range shown in figure 2, of high pressures and low temperature. The specific gravity of liquid CO_2 is 1.02, a fact that has led to the unfortunate idea that in frac treatment designs it can be considered just like water. Even in pure liquid CO_2 stimulation jobs such assumptions can lead to systematic errors whose magnitude increase rapidly with job size. If maintained at appropriate low temperatures and pressures during the job, they define the pressure gradient of liquid CO_2 as .468. Friction pressures were determined from experimental data and shows similar traits to H_2O, in small tubing but some what lower pressures in larger pipe. The more important question then becomes: Where does the liquid reach critical temperature? After that point neither the hydrostatic gradient nor the friction pressure data can be used. Also, the low compressibility of the liquid disappears as it has now become a gas. In carbonated fluids, this assumption of water characteristics is more inaccurate. Again, we have a two phase system with changing temperatures and pressures both of which affect the solubility of the CO_2 in the treating fluid. All of these factors of course affect the hydrostatic of the fluids.

At temperatures above the triple point and below 87.8 °F, CO_2 liquid and gas may exist in equilibrium in a closed container. Within the temperature range between triple point and 87.8 °F, the pressure exerted by the liquid gas equilibrium depends entirely on the temperature. Above the critical temperature, CO_2 cannot exist as a liquid, so all CO_2 in the container would be gas. As the temperature above critical point rises with the CO_2 in any closed container, large increases in pressure are produced. More detailed information about the states of CO_2 and its equilibrium phases is given in figure 3.

CHEMICAL PROPERTIES

The chemical properties of CO_2 are the characteristic ways in which it undergoes a chemical reaction. CO_2 gas is usually defined as inert since it does not easily react with other gasses in the atmosphere. However, it does react a good deal in solution, with plants and other living tissues, metals (in solid form) and at elevated temperatures with many other molecules in all forms. In looking at chemical reactions, two concepts are important to us, kinetics and equilibrium. The first envolves the rate of reaction which is influenced by 4 general factors: 1) the nature of the reactants, 2) the effective concentration, 3) the temperature, 4) the presence of catalysts. The product of a chemical reaction will often react to produce the starting materials. For example under identical conditions the following two reactions occur:

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$
$$2NH_3 \longleftarrow N_2 + 3\ H_2$$

Ultimately the time comes when the rate of reaction of the top equation equals the rate of reaction of the bottom. At this point there is no net observable change, and we call this equilibrium. Please note, both reactions are still going on and any change of circumstance to the reaction will cause it to change.

The most important reaction of CO_2 for our purposes is that which occurs when CO_2 is mixed with water: $H_2O + CO_2 = H_2CO_3$ which is carbonic acid. In water the H_2CO_3 dissociates to form ions H_3O^+ and HCO_3^-. These ions finally come to form an equillibrium with the undissociated form. The number of H_3O^+ ions present determine the pH of any acid. Carbonic acid has a pH of three, which means it is a weak acid when compared with an acid like HCl. As can be seen from figure 4, as CO_2 is added to water the pH drops swiftly and levels off just above 3. At this point the dissociation rate of the H_2CO_3 is the controlling factor of the two reactions. Before the 30 SCF/BBL point, the reaction was controlled by the availability of the CO_2 molecule for reaction.

Because carbonic acid is weak acid and reacts slowly with metals at normal surface temperatures, some people have been lulled into thinking the corrosion it causes is minimal, and that it really doesn't require inhibition. This statement could be true under the following conditions: with the reaction equations at equillibrium, in a static cell, with the same fluid contacting the same metal surface, at a low temperature for a short time. However, none of these conditions exist when either treating with, or producing CO_2 or carbonated liquids. Mitigating the corrosive effects of this weak acid are the major concern of most engineers associated with stimulation and completion practices employing CO_2 and especially any flooding project. CO_2 corrosion is also of major concern in pipelines, gathering systems and several varities of surface equipment.

EQUIPMENT CONSIDERATIONS

Equipment considerations fall in two distinct categories: those concerned with handling liquid and/or gaseous CO_2 alone, and those which handle carbonated fluids. Obviously what you need in any given piece of equipment depends on what you expect it to do and how long you need it to last. CO_2 is not a cryogenic material but if you expect to store or pump liquid CO_2, your equipment better be able to handle low temperature and high pressure. All service companies who pump carbonated treating fluids either use the suppliers special trailer or their own to transport CO_2. Figure 5 shows a cross section of a CO_2 trailer. Basically it consists of a welded pressure vessel covered by an insulated outer shell. Pressures inside the trailers are kept between 140 and 300 psi. If the pressure should drop below 80 psi, dry ice would form. Normally the bottom of the pressure tank is liquid CO_2 with a vapour layer above it. The amount of vapour is determined by the temperature. The pressure present in the transport will drop as the contents are removed which will cause a lowering of the temperature. Extremely low temperatures in the transport may cause metal embrittlement.

Some service companies pump CO_2 only through pumpers equipped with special manifolds. Others claim to use conventional triplex plunger fluid ends. In either case two rules are invariably followed. All foreign material is removed and no water is left in the pumps. Some service companies fill their pumps with methanol to insure that no water is left behind. The second rule is that fluid ends must be sufficiently cooled to relieve stress contractions before pumping liquid CO_2 to high pressures.

For those whose only dealings with CO_2 will be when a service company treats a well, there are certain characteristics to be considered in choosing and protecting the well's production equipment. While certain companies and wervice companies have pumped pure liquid CO_2, I do not recommend this process be used except through well heads specifically designed for CO_2 injection. Regular well heads of carbon steel under go embrittlement and severe stress due to contraction from the cold. This can be dangerous both at the time of treatment and/or later if the stressed metal is weakened. In pumping any carbonated fluid, the following should be considered as part of the treatment design. The hydrostatic of the fluid may fluctuate from the planned hydrostatic as it may be uncertain as to where the liquid CO_2 will gassify totally. When it does there will be a lightening of the hydrostatic which will produce an increased surface treating pressure. Tubing and casing should be chosen accordingly. When treating through tubing and a packer, the packer type should be chosed carefully. Also for warm (200 BHST) or deep (8000') wells, computer simulations should be run to see if cooling will unseat packer or pull tubing into. If severe cooling of treating fluid does not cause tubular or packer problems, it could still cause problems with oil recovery due to parafins or other solids dropping out of the chilled oil. The time to find out is before the treatment is pumped. Along the same line of thought the oil needs to be checked for its reaction with CO_2 as crudes have been known to form a stable foam with CO_2 which can make an effective plug.

As with any energized fluid, flowback of carbonated fluids needs to be handled carefully. Minimum requirements for a safe effective flowback is a steel flowline which is anchored every 15 to 20 feet with crossed stakes driven into the ground. The line itself should have as few bends as possible and should be made up so that rotations tighten connections. Flowback should be controlled with a choke, a positive one if any abrasives might be returned. Flowback rates should be carefully considered. They should be calculated to keep turbulence present and to keep gas slippage to a minimum. Rates should be low enough to make full use of reservoir energy but not so low as to cause gas slippage or kill the well. Rates too high will cause excessive drawdown on the formation and lower bottom hole flowing pressure. The result of the latter can be in complete return of the treating fluid.

For those who are, or will be associated with any aspect of CO_2 flooding, the prime equipment consideration has to be how to make the system last. The corrosive nature of the carbonic acid entrained in both injected fluids and those produced makes this difficult. Answers to the problem are as numerous as the papers published on flooding the last two years. The two most common practices appear to be the use of tube and shell heat exchangers and the insertion of stainless or other corrosion resistant alloys at critical points. Most of the publications noted that confining the corrosive returns to the tube section of heat exchangers allows one to construct the more expensive shell of carbon steel. Those majors who tried ordinary heater treaters replaced them quickly with the tube and shell models. Tubes are recommended to be made from 3162 stainless.

In the Paradis CO_2 flood project, many steps were taken to tailor the solutions to corrosion problems to the exact needs of each system. For example, the gathering system for their CO_2 was 20 and 24 inch pipe overhead in the plant that produced it as a by-product. Stainless was too expensive for use here. To protect the pipe from corrosion, they had it sand blasted, coated with zinc primer and two coats of epoxy material. Welds were sanded and hand brushed with multiple coats of coal tar epoxy. They used an existing carbon steel pipeline to transport the dried, low pressure CO_2 gas to their injection facilities. Corrosion here was minimal and controlled by injection of corrosion inhibitor at the rate of three quarts per day. They use at the point of highest corrosion, the inlet heat exchangers of the gathering system, a stainless steel tube bundle inside a shell coated in the same manner as the gathering system.

SAFETY PRECAUTIONS

Once a treatment or flood has been designed and the proper equipment obtained the process of ensuring that personnel and equipment function safely depends on protecting them from four problems, cold, projectiles, line ruptures and asphyxiation. Obviously in flood situations exposure of personnel is more limited, but the same types of accidents could occur.

In large stimulation treatments such as energized fracturing jobs or CO_2 foam fracs, these hazards effect more people directly. The first consideration is the cold. The temperature of dry ice is -109° F. The temperature of pipe containing dry ice is the same. Direct contact with the skin at these temperatures will cause freezing of the tissues or frost bite. Contact with the liquid can cause an effect similar to a burn or frost bite depending on the temperature. Exposure to the very cold vapours of subliming dry ice can also cause frost bite. Should such a problem occur, wash the skin with unheated water and apply cold compresses. For serious burns or damage to the eyes, contact a doctor, immediately.

Equipment must also be protected when exposed to severe cold. As we pointed out earlier, stress factors for metals are increased with low temperatures. Therefore, pumping units, threads, rubber seats and tubular goods must be carefully inspected before CO_2 is pumped. Any equipment in contact with the liquid CO_2 which have moving parts must be very clean and completely dry prior to the introduction of CO_2. One drop of water can freeze to a hardness to halt moving parts at these temperatures. For this same reason, never add cylinder CO_2 to liquid CO_2 systems. The complete system, pumps and lines must be cooled down before high pressure pumping begins. Proper cooling occurs by bleeding CO_2 through the lines up to the wellhead until they become frosted over.

Gaseous CO_2 is heavier than air and will displace it settling to low places. CO_2 is the regulator of the breathing function of our bodies. Although it is considered non poisonous, prolonged exposure to concentrations of CO_2 as low as 3.5% may adversely affect breathing. If one remains in such an atmosphere long enough unconsciousness and death may result. Since the gas is odorless and colorless, its presence is not readily detectable. Shortness of breath would be the first warning sign. At any sign of shortness of breath or lightheadedness, or hyper-ventilation, leave the area immediately. Dizziness and other symptoms may not be noticed in time before an individual becomes unconscious. The most hazardous areas are those which are low and enclosed, so stay out of areas where CO_2 is stored and dry ice is present. Proper care must be taken when entering a cellar or any low spot that is not well ventilated. A second person should be present watching from a safe distance and be able to affect rescue. If self contained breathing apparatus is not available, a rope should be tied about the body of the person entering the suspected area. Then in the event of trouble, the second person can drag him out of the affected area. Never enter an empty CO_2 storage tank without a self contained breathing apparatus. (note a chemical gas mask is no help). In areas where a high volume leak of CO_2 could occur, as in massive or foam fracs, injection systems, pipelines and compressor stations, it is recommended that all personnel in the area have access to self contained breathers and that lifelines be installed to guide them off location or out of the danger area.

Should an accident occur, immediately remove the victim from the affected area and give him oxygen if available. If breathing has stopped give artificial resuscitation and get the person to medical aide.

Projectiles on location are usually dry ice, foreign matter in the lines or pieces of equipment or line that has ruptured. Dry ice will form anywhere in a line that the pressure drops below 80 psi. Projectile incidents occur when dry ice plugs are formed in hose or lines as they are disconnected after a treatment. The line is full of dry ice. As it warms it sublimes, but pressures at the ends of the line are atmospheric so ice seals them off. The sumblimation continues at the center and builds pressure until there is an explosive discharge of the solid plug. If the plug cannot be discharged, the line will rupture, which is a more dangerous situation. This is the situation which is more likely to occur if there is a plug formed in the closed line and no way to bleed the line. An ice plug may be detected by checking pressures. If everything appears to have been lbed off and pressure readings at two points differ, an ice plug is probably present.

Please also note that dry ice is not the only ice that can form making an efficiently plugged line. Water freezes at 32° F, and acid and brines at lower temperatures. On carbonated jobs, the liquid CO_2 enters the mainline from -22° F upward. This temperature difference can present a real problem if proper care is not taken. If the mainline fluid is not moving when the liquid CO_2 enters it then it will form solid ice. If the liquid CO_2 is not moving, or is at a lower pressure than the mainline, then fluid will freeze off between the mainline and the check valve on the CO_2 line.

Line ruptures with their attendant shrapnel, jets of pressured liquids and sometimes missile like behaviour are the most serious threat on any energized treatment. CO_2 should be treated in this respect with the same care given nitrogen. Liquid or solid CO_2 vapourizing into gas in a contained space develops the same high pressures as does nitrogen. We know that shut downs occur and dry ice will form, but the lines and equipment can be rigged to prevent excessive pressure build up in the lines. Very strict operational procedures include the following: Never shut in a line filled with liquid CO_2 at both ends without either venting it immediately and/or monitering the pressure in that line. Between any two block valves in any CO_2 lines, there must be a bleed valve and a pressure relief valve placed at the lowest point. When venting any CO_2 line, it must be vented from the lowest point. As the pressure is released, gas will form at the higher parts of the system and expand. As you continue to remove liquid, the gas continues to expand in the pipe forcing more liquid outside, where its vapourization into gas and the subsequent cooling does not freeze the liquid in the pipe. This method minimizes the formation of dry ice. Please note, it does not prevent its formation. Lines that have been vented should be knocked loose and dry ice removed. (After knocking lines loose, they can be left lying on the ground for 15-20 minutes before inspection or racking up.) Once transport valves have been opened they should not be closed until transport is finished. Liquid CO_2 should not be pumped into the well until it has been mixed with treating fluids.

Further safety precautions are taken concerning the piping and connections. The use of special CO_2 steel hoses and 4" aluminum piping is preferred. The integral joints are made up with special lubricants and in the case of the aluminum pipe, bars are used for tightening not hammers. Suction lines are as short as possible and must either be on the ground or adequately supported. The lengths of all treating lines are kept to a minimum to reduce heat absorption by the system. The number of low points is also minimized.

As personnel safety is the most important aspect, all personnel are kept away from lines filled with CO_2 as much as possible. Remote controll vents are used. Protective clothing is required when a manual vent must be operated. CO_2 lines are not tested with CO_2, water or acid.

If an emergency has occured, such as parted treating line, the immediate action is to cease pumping, and if possible close the wellhead valves, the frac tank valves and the CO_2 transport valves. With these valves closed you gain a minimum of control and time with which to handle the situation. Steps have to follow in this order for maximum safety benefits. Shut down the pumps. Evacuate all personnel to a safe location up wind. When or if safe to do so, return to well and close master valve, open CO_2 vent valves and then close CO_2 transport valves. Note: Before approaching CO_2 lines, check remote panel guages. Be sure lines are not yet over pressured prior to operating vents. If lines are over pressured, open only remote controlled vents until excess pressure is relieved. Do not close off transport valves until suction system vents are open. When attempting to evacuate or treat injured personnel, remember you have ten to fifteen minutes before CO_2 trapped in the lines develops enough pressure to cause another dangerous rupture. Use your brain - don't become another casualty.

In non-emergency shut downs, such as ballout, of short duration in cold weather only, the pumps and booster pumps are shut down. The CO_2 transport valves are left open as the transports act as a vapour space reservoir for short times. If the pressure which must be monitored continuously starts to rise, or the duration of the shut down lengthens, then the lines must be vented and the CO_2 transport valves closed after the vents are opened. Before pumping is resumed, lines should be inspected for dry ice and start up procedures followed.

Shut down at the end of treatment can be made safer if these guidelines are followed. It is recommended that the CO_2 pumper shut down before fluid pumpers so that the main treating line will not contain CO_2. Pumper and booster pump should be slowed to idle and the ground vent valve opened. The valve between the CO_2 line and the main line is then closed. The CO_2 liquid valves are closed on the transports. If possible, purge the lines with vapour from the transports, keeping all personnel clear of the area. When pumper is venting only gas, open all vents in the suction and discharge lines and leave open. Kill all engines after well head has been shut in and pressure bled from the treating lines, open the valve between main and CO_2 lines. Wait at least 10 to 15 minutes before rigging down any discharge and suction lines. Be sure all pressure has been relieved from all sections of the lines and all valves are open.

Previously we discussed how to handle the CO_2 while the job had been stopped because of a ballout (or screen out) situation. Now, what do you need to consider about safely conducting a short term or intermittant flowback? From a strictly safety point of view we would not like to have much flow from the formation into the wellbore and certainly would prefer not to see formation fluids and gases at the surface. Flows must be limited to as small a volume as possible. Ball Sealers used with carbonated fluids should be heavier than the gasified fluid so they can fall to the bottom of the well. We do not want them at the surface. Bleed back should take place only long enough to unseat the balls and should be stopped long enough to allow all the balls to fall to bottom. During this procedure, everyone should be upwind, out of the way except those actively needed to open valves and monitor pressure and the person controlling the flowback. The service company will usually supply both of these persons.

Now, we come to flowing back the well after the service company has left location. We already discussed the need for a secured steel flow line. Keep flexible parts of the line and bends to a minimum. All bends must be anchored at the bend. Use a positive choke. The first turn downstream from the choke should be a "T" with a solid bullplug. Connect flowline to well head so that any rotation will tighten screwed connections. Use a double valve system. The valve closest to the well is #1. The second valve is the flow control valve or #2. The master or #1 valve should always be either fully open or fully closed. It is opened first and closed last. (Valves should not be overhead high from the ground or rig floor.)

With the equipment and flowline set up properly, take care of yourself. Don't get any part of your body in front of the bleed off. Get any extra personnel away from the flowline before opening the well. Don't expose yourself to the area where the CO_2 is being vented. Don't try to do all this alone. Have someone a safe distance back watching you and the well for unusual circumstances. (They may need to rescue you if the worst happens.) Please start with a small choke 1/2" maximum until you see how the well behaves. Increase choke size in small steps. Stay back from the well head and flowline whenever possible. Large gas flows, gassified liquid, or intermittent slug flows of liquids and gas can cause excessive line vibrations and stress the metals of the flowline.

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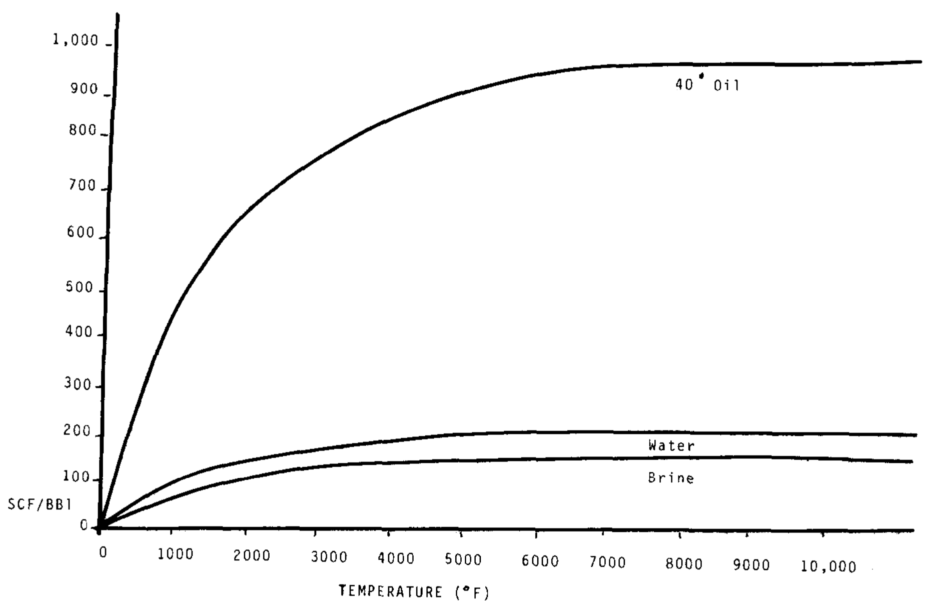

Figure 1 - Solubility of carbon dioxide

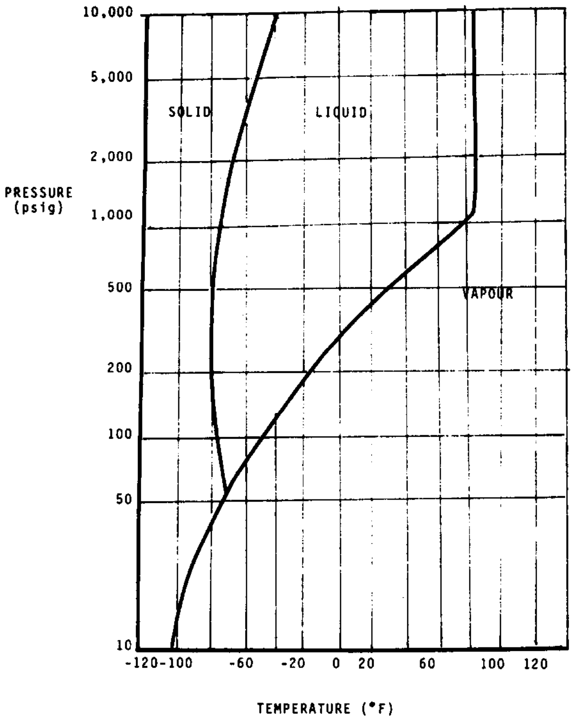

Figure 2

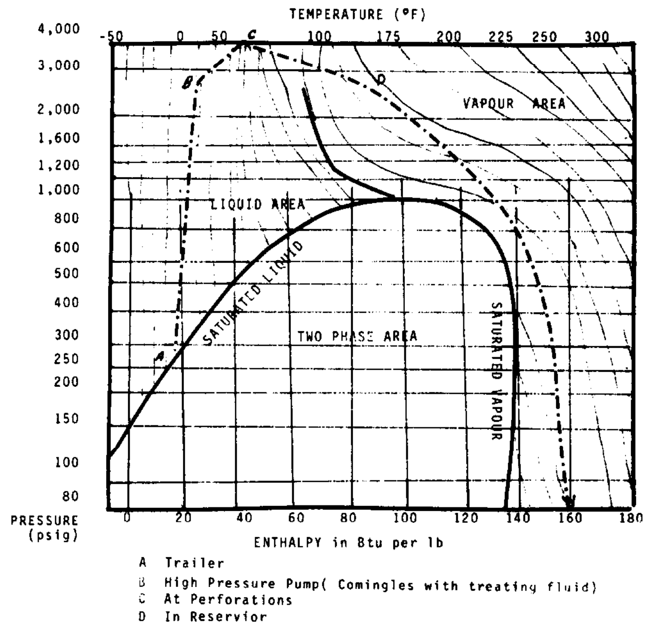

Figure 3

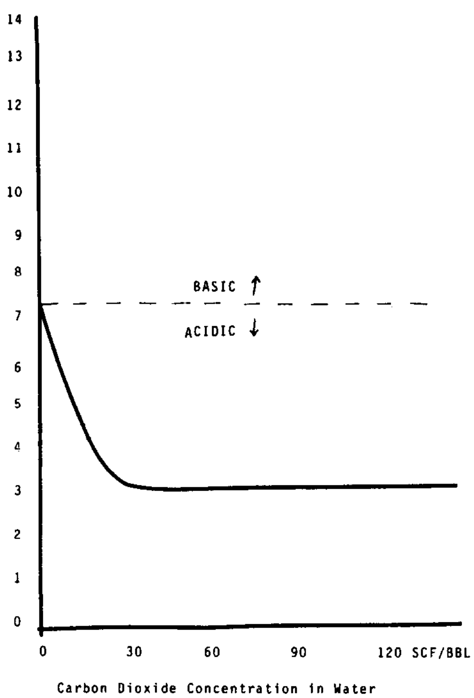

Figure 4 - pH level vs carbon dioxide concentration

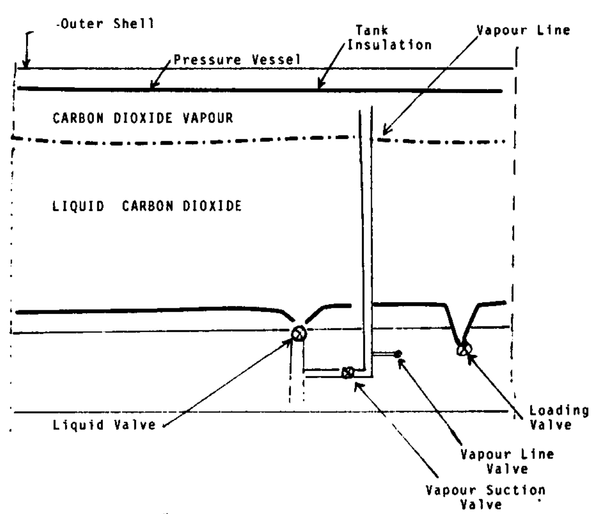

Figure 5 - Cross section CO_2 trailer