COLLOIDAL GAS APHRONS: GENERATION, FLOW CHARACTERIZATION AND
APPLICATION IN SOIL AND GROUNDWATER DECONTAMINATION

by

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(ABSTRACT)

This study examines the fundamental properties of Colloidal Gas Aphrons, CGA, relevant to its application in soil and groundwater decontamination. It also presents the results of laboratory experiments on the applicability of CGA in treating soils contaminated with organic chemicals.

CGA is a collection of spherical, 10 to 100 micron-sized gas bubbles dispersed in an aqueous surfactant solution with a volumetric gas fraction (quality) of at most 0.74. It is characterized by its quality, bubble size, stability and apparent viscosity. The stability can be described by the half life, the time needed for 50% of its liquid phase to separate by gravitational drainage.

CGA is a non-Newtonian fluid. The apparent viscosity is higher than that of its liquid or gas phase and increases with increase in quality. At quality above 0.6, CGA is a pseudoplastic fluid and can be modelled by the power law. In this quality range, apparent viscosity decreases with increase in shear rate. Measured apparent viscosity can be as high as 25 centipoise at low shear rates for a CGA quality of 0.72. But at low quality, CGA is best described by the Bingham fluid model.

CGA flow through porous media follows the discontinuous fluid flow model with the liquid phase advancing faster than the gas phase. The presence of CGA bubbles causes considerable reduction of effective mobility compared to water flow. The bubbles act to reduce the effective flow area by first blocking the wider pores and re-directing flow to narrower pores. The tenacity of the bubbles in the presence of adequate surfactant molecules account for its flow characteristics in porous media.
CGA is more effective in flushing hydrophobic organics from saturated sand-packed columns compared with surfactant flushing. CGA provides the surface active agent needed to lower the interfacial tension of the non-wetting phase and at the same time creates enough viscous force to mobilize any trapped fluid. Its ability to preferentially block large pores in a heterogeneous media and direct fluid flow to smaller pores also contributes to the demonstrated effectiveness as a soil flushing agent.
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CHAPTER 1
INTRODUCTION

Large quantities of soil contaminated with toxic chemicals can be found in most parts of the world particularly in industrialized countries. These contaminants are often released from abandoned waste sites, accidental spills and industrial effluents. In many cases, groundwater contamination also exists. The response to this problem in the United States was the enactment of the Comprehensive Environmental Response, Compensation, and Liability Acts (CERCLA or Superfund) of 1980. The act authorized the Environmental Protection Agency (EPA) to ameliorate damage from past disposal practices by identifying and cleaning-up abandoned hazardous waste disposal sites.

Cleanup remedies of hazardous waste sites can generally be classified into two categories: containment measures and permanent treatment techniques. Containment measures are designed to restrict the movement of the contaminants and reduce exposure to humans and the environment. Permanent treatment technologies are designed to permanently change, destroy or reduce the toxicity, mobility or volume of the hazardous material.
In the past soil treatment relied more on containment measures. The hot spots were excavated and landfilled in permitted disposal facilities while the less contaminated soils were capped. For the treatment of contaminated groundwater, above-ground techniques have often been used. This involves containing the contaminated water, pumping from the ground, treatment on site and re-injection into the ground or return to a public works facility or a surface water body.

A number of limitations with these cleanup methods exist that make cleanup goals difficult to realize. There have been instances where permitted landfills have latter required cleanup. Capping would also need continual maintenance to prevent failure. Above-ground techniques for groundwater decontamination rely on the contaminant's removal from the ground along with groundwater. However, this is not often the case. Most aquifers are found in complex geological settings. As a result, not all the contaminated water can be pumped to the surface for treatment even with the installation of containment barriers. Furthermore, contaminants that are hydrophobic in nature preferentially adhere to the soil and are not readily pumped out with the water.

A recognition of the limitations of these treatment technologies prompted the Unites States Congress to enact the 1986 amendments to the Superfund Act to create a comprehensive program of research, development, demonstration and training to promote the development of alternative and innovative treatment technologies (U.S. Congress, 1986; U.S. EPA, 1986). The program is aimed at providing the treatment technologies necessary to implement new cleanup standards that require a greater reliance on permanent remedies at Superfund sites. Within the framework of this initiative, the use of Colloidal Gas Aphrons, CGA, to facilitate soil and groundwater decontamination is addressed in this study.

CGA is a collection of spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution. The volumetric gas content is no more than 74 percent and the size of its bubbles are generally less than 100 microns in diameter (typically 10-90 microns). CGA is a class of Kugelschaum type foams (wet foams) that is uniquely characterized by the colloidal size of its
bubbles. As such it was first called microfoam (Sebba, 1971) and later renamed Colloidal Gas Aphrons (Sebba and Barnett, 1981).

There are a number of potential applications of CGA in treating polluted soil and water. These can be grouped into three major categories: flotation, in-situ biodegradation and soil washing. CGA can be used to float suspended particulates, bubble entrained flocs, ions, and hydrophobic compounds from solution. It can also be used as a source of oxygen and nutrients for enhancement of in-situ biodegradation in saturated soil systems. The increased stability of CGA over gas sparging, the small and controllable size of bubbles, the large surface area and the wide range of choices of bubbles' interfacial properties through the choice of appropriate surfactant (anionic, cationic, nonionic or mixed surfactants), widens the scope of technological application.

Crucial to effective application of CGA in soil and groundwater decontamination measures such as biodegradation and soil flushing is a better understanding of CGA's properties and flow characteristics. This study was therefore undertaken to examine the properties of CGA salient to it's injection, retention and movement in the subsurface environment. In particular, the objectives of this investigation were to:

- Examine the design variables for generating CGA of consistent properties using the Spinning Disc method
- Examine the possible mechanisms of CGA formation by the Spinning Disc method
- Characterize CGA in terms of size distribution and stability of it's bubbles
- Investigate the rheological properties of CGA pertinent to its flow through porous media
- Study, both visually and quantitatively, the flow characteristics of CGA through saturated porous media
- Investigate the potential of CGA as a flow smoothing agent
- Demonstrate the practicability of using CGA as a soil washing agent.

INTRODUCTION
The report is divided into 9 chapters. Chapter 1, the introductory chapter, presents the rationale behind the study. In Chapter 2 a review of current clean-up techniques and potential applications of CGA technology is presented. Chapter 3 addresses the generation of CGA by the Spinning Disc method. It includes the design considerations and a discussion of possible formation mechanisms. The size characterization of CGA bubbles and CGA stability are discussed in Chapters 4 and 5 respectively. Studies on the rheological properties of CGA are presented in Chapter 6. The results of experiments using a modified Brookfield viscometer and a capillary viscometer are discussed. In Chapter 7, studies on CGA flow through porous media are reported. Possible CGA flow mechanisms are discussed as well as qualitative and quantitative results of CGA flow through sand packed slabs and columns. The relevance of these results in terms of using CGA as a flow smoothing agent is also discussed. The use of CGA as a soil washing agent is examined in Chapter 8. The results of flushing sand contaminated with different hydrophobic organics are presented. The performance of CGA flushing is also compared with surfactant flushing. Lastly, the major conclusions and recommendations are presented in Chapter 9.
CHAPTER 2

BACKGROUND

The contamination of the subsurface environment by toxic chemicals released from abandoned waste sites, accidental spills and industrial effluents and the continuing threat of releases is of growing concern worldwide. There are over 17-million waste disposal facilities in the United States alone releasing more than 6.5-billion cubic meters of contaminant laden liquids into the ground each year (U.S. Environmental Protection Agency, 1977). These toxic materials eventually find their way to aquifers.

As at June 1988, there were 29,463 sites in the United States identified as potential hazardous waste sites. Of these, 1,177 are on the National Priority List as the worst hazardous waste sites (Inside EPA’s Superfund Report, 1988). Sites such as the Love Canal in New York (a 16 acre landfill located just south-east of Niagara falls where 43 million pounds of industrial chemicals were dumped between 1947 and 1952) (Silker and Mercer, 1982) and the Stringfellow in California (a 22-acre hazardous waste site east of Los Angeles that received 34-million gallons of liquid wastes including spent acids, heavy metals and pesticides between 1922 and 1956) (Ember, 1985) were once in the center of the hazardous waste debate. The presence of these toxic materials in the environ-
ment has been cited as the cause of many illnesses including cancer, respiratory problems, blood disease and birth defects.

In response to the problem of contamination from abandoned hazardous waste disposal sites, the United States Congress enacted in 1980 the Comprehensive Environmental Response, Compensation, and Liability Acts (CERCLA or Superfund). The act authorized the Environmental Protection Agency (EPA) to ameliorate damage from past disposal practices by identifying and cleaning-up abandoned hazardous waste disposal sites. Cleanup remedies of hazardous waste sites are often site specific because of the differences in terms of size, proximity to people, geology and wastes involved. These can generally be classified into two categories: containment measures and permanent treatment techniques. Containment measures are designed to seal the waste, restrict the movement of the contaminants and prevent further groundwater contamination, and reduce exposure to humans and the environment. Permanent treatment technologies are designed to permanently change, destroy or reduce the toxicity, mobility or volume of the hazardous material through chemical, physical, biological or thermal processes (U.S. EPA, 1985, 1981; Englund and Mafica, 1987).

2.1 **SOIL TREATMENT**

Until recently, contaminated soils were often treated by containment techniques. The hot spots were excavated and landfilled in permitted disposal facilities while the less contaminated ones were simply capped. Following the Superfund Amendments and Reauthorization Act of 1986, more permanent techniques are now being used to treat contaminated soils. These permanent treatment techniques have been grouped into three classes: thermal treatment technologies, physical/chemical treatment technologies and biological treatment technologies (USEPA, 1988). Thermal treatment
technologies involve the use of high temperatures to destroy or detoxify hazardous wastes. They include fluidized bed incineration, rotary kiln incineration, infrared thermal incineration, wet air oxidation, pyrolytic incineration and vitrification. Thermal treatment is very suitable for treating soils contaminated by organic compounds. The organic waste is essentially destroyed completely. Under proper operating conditions removal efficiency often exceed 99.99 percent. However, the technique is not useful for soils with heavy metals as the primary contaminant. The metals cannot be broken down to non-hazardous substances by any treatment method. Metals that may vaporize during incineration are often difficult to remove using conventional air pollution control equipment. Also, an element such as trivalent chromium can be oxidized to a more toxic valence state, hexavalent chromium in combustion systems with oxidizing atmospheres. Additionally, elevated levels of halogenated organic compounds may produce corrosive acid gases capable of attacking refractory material or impacting air emission systems.

Under physical/chemical treatment technologies, physical processes separate the waste by physical means. It produces residuals that require additional treatment or disposal in an environmentally safe manner. Chemical processes alter the chemical structure of the wastes to less hazardous constituents. The physical/chemical treatment processes include chemical extraction, soil washing, in-situ soil flushing, low temperature thermal stripping, in-situ vacuum and steam extraction, stabilization/solidification, chemical reduction-oxidation and in-situ vitrification.

There are four biological treatment techniques applicable to soils and sludges. These are composting, slurry-phase treatment, solid-phase treatment and in-situ biodegradation (USEPA 1985). (In-situ biodegradation is discussed separately.) Essentially they all involve bio-oxidation of organic matter by micro-organisms. In composting, a small percentage of biodegradable waste is stored with highly biodegradable and structurally firm material in the presence of an appropriate microbial population. Adequate aeration, optimum temperature, moisture and nutrient contents, are also necessary. Slurry-phase bioremediation involves first creating an aqueous slurry of the waste and intimately mixing with microorganisms in a mobile reactor. Appropriate environmental conditions for optimal microbial degradation of target contaminants are maintained through addi-
tion of nutrients and pH control. Solid-phase treatment uses conventional soil management practices to enhance the microbial degradation of contaminants in an above grade system. It can be designed to contain and treat soil leachate and volatile organic compounds.

### 2.2 GROUNDWATER TREATMENT

Groundwater is inevitably a primary target of hazardous chemicals in the environment. As a result, current efforts for hazardous waste remediation often involve some type of groundwater treatment. The treatment technology can either be above-ground or in-situ. Above-ground treatment techniques involve containing the contaminated water, pumping from the ground, treatment on site and re-injection into the ground or return to a public works facility or a surface water body. The selection of appropriate treatment technologies is based on types and concentration of contaminants, cleanup goals and knowledge of performance characteristics from prior similar cleanup experiences. Groundwater pumping and treating was selected 50 percent of the time during the first 5 years of the Superfund program (U.S. General Accounting Office, 1986).

The choice of appropriate above-ground treatment techniques depends largely on whether the contaminants are classified as organic or inorganic compounds. Organic contaminants are typically removed using air stripping and/or activated carbon adsorption. The main treatment technologies evaluated for removal of inorganic contaminants are chemical addition (including chemical precipitation), removal of suspended solids, reverse osmosis, ion exchange and electrodialysis (Nyer, 1985). Of these, chemical precipitation is the most commonly selected method for removal of inorganic contaminants from aqueous wastes at hazardous waste sites (Higgins and Romanow, 1987).
2.2.1 Air Stripping

For groundwater contaminated by volatile organic compounds, air stripping is the most popular above-ground treatment technology of which four basic configurations exist. These are diffused aeration, countercurrent packed towers, cross-flow towers and coke tray aerators (Kavanaugh and Trussell, 1980). Countercurrent packed tower air stripping appears to be the most cost effective above-ground technique for groundwater cleanup (Ball et al., 1984; Ruggiero, 1984; Goers and Hubbs, 1981).

The theory of countercurrent packed tower air stripping is well developed in the literature (Byers, 1987; Roberts et al., 1985; Perry et al., 1984; Kavanaugh et al., 1980, Treybal, 1980; Sherwood et al., 1975; Eckert, 1975). Air and contaminated water flow countercurrently to one another in the packed column. Water flows downwards over the packing as a film while the air flows upwards as a continuous phase. Solute transfer is effected through the gas-liquid interphase. The driving force here is the difference between the actual liquid phase solute concentration and the corresponding value for gas-liquid equilibrium. For sparingly soluble compounds including most volatile compounds of interest, the equilibrium partitioning behavior can be represented adequately by Henry's law for ideal dilute solutions.

Packed tower air stripping efficiency is influenced by the type of organic contaminant, air-to-water ratio, temperature of feed, type of packing and geometry of the tower. The overall resistance to interphase mass transfer is the sum of both the gas-phase and liquid-phase resistances (Onda et al., 1968). If the solute is volatile enough, the gas-phase resistance can be neglected. As the volatility of the solute decreases however, gas phase resistance becomes increasingly significant and must be taken into consideration (Roberts et al., 1985; Ball et al., 1984; Kavanaugh et al., 1980; Mackay and Wolkoff, 1973). The height of packing required to achieve a desired separation is governed by a number of variables such as the desired level of removal, the volatility of the solute, the air-to-
liquid flow ratio, the liquid flow rate and the physico-chemical conditions that may influence the mass transfer rate.

The choice of packing material is essential in the performance of a countercurrent packed column stripper. A good packing material would be one that provides a large interfacial area with minimum pressure drop. In practice, only a fraction of the packing’s surface is wetted sufficiently for mass transfer. This inefficient use of packing media is one of the major drawbacks of the packed tower stripping process. Also huge amount of air is needed to achieve intimate air-water contact with the attendant high energy and investment costs. When concentrations of compounds in the exiting air are well below acceptable air emission limitations, effluent air is released to the atmosphere. Otherwise, effluent air has to be passed through activated carbon adsorbers to concentrate the pollutants for possible recovery, thermal destruction or land disposal.

2.2.2 Activated Carbon Adsorption

Traditionally, municipal water treatment facilities use activated carbon adsorption systems as the primary means of removing organic contaminants from groundwater (Guswa et al., 1984). Activated carbon process is effective for removal of a broad range of contaminants over a variety of treatment conditions and concentrations typical of groundwater contamination. Adsorption occurs when the organic molecule contacts and adheres to the activated carbon’s surface through physical and/or chemical forces. Solubility is the key parameter in determining how well an organic compound will adsorb. That is the forces that attract the organic molecule to the carbon surface must be sufficiently strong enough to counter the forces that keep it in solution. Thus the lower the solubility, the better the adsorption efficiency.
The adsorption efficiency of activated carbon is affected by a number of factors including nature of the organic compound, the effective surface area of the carbon, pH, temperature, and interference from other solutes in solution. The primary design criteria are surface loading rate and empty bed contact time. Under normal operating conditions, contaminated water is treated at a surface loading rate of between 2 and 7 gallons per minute per square foot and an empty bed contact time of between 10 and 60 minutes (Higgins and Romanow, 1987). Other important design criteria include bed volume (a function of contact time and design flow rate) and vessel configuration (series or parallel flow). Series flow is usually used for pollutants that are difficult to remove and hence require maximum contact time, while parallel flow is used when large flow variations are expected or when large through-put with a shorter contact time is desired.

One unique advantage of carbon adsorption is the ability to concentrate organic materials in dilute solutions several thousand-fold. When the contaminants are physically adsorbed, recovery/recycle and activated carbon regeneration are possible. But for chemi-sorbed compounds, the spent activated carbon has to be disposed off in landfills or destroyed by incineration. Other drawbacks of the activated carbon process include inability to handle non-polar organics and many inorganics, and operational limitations associated with periodic shut-down and regeneration and/or disposal. The process often involves large capital and operating costs and as such are not always cost-effective (Stallings et al., 1985).

2.3 IN-SITU BIODEGRADATION

In-situ biodegradation of soils and aquifer contaminated by hazardous chemicals involves contacting microorganisms with the hazardous materials in-place and providing the necessary environment for growth to metabolize the toxic components to non-toxic or less-toxic species. It involves con-
tacting microorganisms with the contaminant in an environment conducive for growth to metabolize the toxic components to non-toxic or less toxic species. The microorganisms can be native microbes whose activity is stimulated by the addition of nutrients not present in sufficient quantities or microbes that have been acclimated to growth on the contaminants and are fed into the soil.

The biodegradability of synthetic organic compounds is determined by a number of interactive environmental and chemical factors. Major environmental factors include type of microorganisms, temperature, pH, and nutrient and oxygen availability. The chemical factors are the chemical properties of the hazardous compound (chemical structure, concentration and formulation), and the chemical properties of the soil (content of organic matter, clay, other interacting compounds and water saturation, and pH). An a priori assessment of the potential for biological activity involves the characterization of each of these factors as it exists in the subsurface.

The rate of metabolic activity of microorganisms increases with temperature until an upper limit is reached where thermal denaturing and destruction of the enzymes set in. Except for certain thermophilic organisms that have been found to thrive at temperatures between 55-60 degrees, most microbes have their optimal growth between 20 and 40 degrees (Morrill et al., 1982). Biological activity occurs under both reducing and oxidizing conditions and at extreme levels of pH in various geologic environments, from pH < 2 to pH = 12 (Kretschek and Krupta, 1984). However, the type of subsurface microorganism present and their effects on subsurface chemistry are greatly dependent upon the pH of the system.

Various groups of microorganisms manifest different nutrient requirements. The availability of suitable nutrients and energy sources thus, in part, determine the types of organisms that exist in a given environment. The presence of hazardous pollutants that are organic in nature can act as additional nutrient sources. Microorganism's sensitivity to oxygen depends on whether they are aerobic (oxygen dependent) or anaerobic (does not require oxygen for growth). Most halogenated compounds, including many pesticides and one- and two-carbon aliphatic compounds require
anaerobic microbes for maximum degradation (Kobayashi and Rittmann, 1982). But others such as benzene and phenol are best degraded under aerobic conditions (Kretschek and Krupta, 1984).

Both the chemical properties of the hazardous waste and that of the soil affect, interactively, the degree to which hazardous materials are susceptible to microbial attack. The degradation of compounds like benzoic acids, phenyl-acetic acids and carbofuran is catalyzed by clay with the rate of degradation increasing with increasing clay content. The biodegradation of others such as simazine, atrazine and trichlorobenzyl chloride is however inhibited by high clay content (Morrill et al., 1982).

In general, whether biodegradation is enhanced, inhibited or unaffected is dependent upon the nature of the interacting compounds as well as the chemical and biological characteristics of the surrounding medium. Due to the diversity of organic compounds that are classified as hazardous, proper chemical evaluation of the wastes and site-specific environmental conditions are necessary.

2.4 APPLICATION OF CGA TECHNOLOGY

CGA is a collection of spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution. The volumetric gas content is not more than 74-percent and the size of the bubbles are less than 100-microns (typically 10-100 microns). CGA is a class of Kugelschaum foams (wet foams). As such it was first called microfoam (Sebba, 1971) but latter renamed colloidal gas aphrons (Sebba and Barnett, 1981).

There are a number of potential applications of CGA in treating polluted soil and water. These can be grouped into three major categories: flotation, in-situ biodegradation and soil flushing. The increased stability of CGA over gas sparging, the small and controllable size of the bubbles, the
large surface area and the wide range of choices of bubbles' interfacial properties through the choice of appropriate surfactant (anionic, cationic, nonionic or mixed surfactants), widens the scope of technological application.

CGA can be used to float suspended particulates, bubble entrained flocs, ions and hydrophobic compounds from solution. In this wise, CGA has been used to effectively remove phosphate slimes, copper ions, coal ash and clay fines from solution (Rodate, 1988; Sebba, 1987, 1985b; Sebba and Yoon, 1982b; Sebba and Barnett, 1981; Auten and Sebba, 1984). Honeycutt et al. (1983) has used CGA to successfully harvest unicellular algae. Recently, Lohse (1988) demonstrated the effectiveness of CGA in removing algae from fresh water using a countercurrent flotation chamber. Micron-sized oil droplets have also been removed from aqueous streams using CGA (Michelsen et al., 1986a,b). The flotation of fish wastes from aqua-culture systems which are hydrophilic in nature has also been documented (Barnett and Liu, 1980).

The ability of CGA to float various biological and particulate materials is due to the fact that CGA flotation occurs by more than one mechanism. Thus in the flotation of charged particles with charged CGA, there is a coulombic type of attraction between the particles and the bubbles' interface which is oppositely charged. Particles can also be held by the elasticity existing at the bubbles' interface as shown in the flotation of graphite and micron-sized coal particles. Yet another mechanism explains the flotation of particles that are too big to be levitated by the much smaller bubbles. These particles are buoyed to the surface by a combined action of two or more CGA bubbles (Sebba, 1982).

Using CGA to deliver oxygen for biodegradation enhancement has been ascertained in saturated soil systems (Smith, 1988; Michelsen et al., 1988a,c; 1985; 1984a,b,c; Fugate, 1984;) and in bench scale bioreactors (Kaster, 1988). Michelsen et al. (1984) have demonstrated the use of CGA to introduce oxygen to enhance the biodegradability of phenol suspended in a saturated impoundment sediment. CGA containing pseudomonas putida and nutrients were introduced through a 1-ml pipette injector into an 8-cm diameter center section of the sediment. The CGA was made using
0.3-g/l sodium-dodecyl-benzene-sulphonate solution to produce a 50-percent air dispersion. A 3 to 4 fold effectiveness was realized compared to direct air sparging.

The use of CGA as a potential oxygen source for in-situ biodegradation of flowing groundwater has been studied in a vertical slice test cell 7-ft x 7-ft x 5-in (Michelsen et al., 1988a). CGA proved to be a feasible means for delivery and retention of supplemental oxygen in the saturated subsurface of sand as well as a simulated alluvial fan material. In similar bench scale studies, CGA sparged into various unconsolidated saturated soil matrices, were picked up and retained for prolonged periods of time (Michelsen et al., 1984a). During these tests, 70 to 82% of the air incorporated into CGA made with Tergitol 15-S-12 (a nonionic surfactant) were initially retained. Thirty days later, 70 to 80% of these bubbles still remained in the saturated sand matrix as dispersed air or coalesced bubbles.

2.5 SUMMARY

There is need for the development of alternative and innovative technologies for the cleanup of contaminated soils and groundwater according to the Superfund Amendments and Reauthorization Act of 1986. Most current cleanup techniques either do not provide permanent long-term remedies or have somewhat limited scopes of application.

Technologies available for treating contaminated soil, as alternatives to land disposal include thermal, physical/chemical and biological treatment technologies. In the case of groundwater treatment, air stripping and activated carbon adsorption are the most popular. In-situ biodegradation is also beginning to emerge as a viable alternative for treating soils and groundwater contaminated with organic compounds.
Within the framework of the initiative to use permanent treatment technologies at Superfund sites, CGA technology offers a number of potential applications in treating contaminated soil and water. These include flotation, in-situ biodegradation and soil washing. CGA has been used to float suspended particles, bubble entrained flocs, and suspended particles under laboratory conditions. The use of CGA to deliver oxygen and nutrients for enhancement of biodegradation in saturated soil systems is also promising.
3.1 DEFINITION

Colloidal Gas Aphrons, CGA, can be defined as a collection of spherical, micron-sized gas bubbles dispersed in an aqueous surfactant solution with a volumetric gas fraction (quality) of at most 0.74 and 95 percent of its bubbles not exceeding 100 microns in diameter.

Stated simply, CGA is a sub-set of Kugelschaum type foams that is uniquely characterized by the colloidal size of its bubbles. It does not include the much drier Polyederschaum type foams which have been the subject of study by many investigators. A CGA quality of 0.74 corresponds to the highest possible packing density of uniformly-sized spheres. Bubbles less than 100 microns in diameter are spherical.

CGA can be viewed too as an immiscible two phase system with the discontinuous phase being a compressible gas and the continuous phase an incompressible liquid. It is also a multicomponent
system with at least one component in the gas phase and at least two components (water and a
surface active agent) in the liquid phase.

This class of wet foams was first called microfoam (Sebba, 1971) and later renamed Colloidal Gas
Aphrons (Sebba and Bernett, 1981).

3.2 **CGA GENERATION BY THE SPINNING DISC**

**METHOD**

Most techniques used in foam generation can be adapted to produce CGA. A review of such
methods has been carried out recently (Suggs, 1987).

Here at VPI&SU, the generation techniques that have been used include:

- Venturi Throat Generator (Sebba, 1971)
- High Speed Commercial Blender (Michelsen et al., 1984b)
- Spinning Disc Generator (Sebba, 1985a)
- Packed Bed Generator (Suggs, 1987)
- Spinning Cylinder Generator (Michelsen, 1988b)

In this work, CGA is produced using the spinning disc generator. First developed by Sebba
(1985a), the spinning disc CGA generator is a mechanical gas-liquid contactor. It relies on the
development of surface waves (or an auxiliary system) to introduce gas to the liquid phase. The
gas is subsequently broken into small bubbles and entrained.
3.2.1 Design Considerations

Like most mechanical gas-liquid contactors, three components are crucial to the design of the spinning disc generator:

- a shearing device
- a holding vessel
- baffles

The spinning disc generator utilizes a flat metal disc, a form of disc-type radial-flow impeller, as the shearing device.

There are two basic types of impellers commonly used in mechanical type agitators. These are the axial-flow impellers and the radial-flow impellers. In gas-liquid systems, radial-flow impellers are more effective than axial-flow impellers and thus preferred despite the fact that a higher power level is usually required for the same level of operation. The upward flow of buoyant gas bubbles destroys, often completely, the flow pattern of axial-flow impellers (Oldshue, 1983). In the case of CGA generation, the effectiveness of the disc-type radial flow impeller is aided by the presence of a surface active agent. This lowers the gas-liquid interfacial tension and hence keeps power consumption low.

The size of the spinning disc is important in relation to fluid flow velocity and fluid shear rate. The flow velocity determines the development of surface waves at the gas-liquid interface while the average shear rate and maximum shear rate are important in determining the ultimate size of the bubbles.

Studies with impellers have shown that at constant power, a large impeller produces high flow and low shear rates while a small impeller produces low flow and high shear rates (Oldshue, 1983). As will be discussed later, both factors are important in CGA formation by the spinning disc method.
The flow velocity affects the surface waves that are responsible for air induction while fluid shear rate accounts for bubble breakup. In systems where an optimum flow-to-fluid shear ratio exists, a vessel diameter-to-impeller diameter of about 3 has been found to be most effective (Oldshue, 1983). Here, a comparative ratio of 2.5 is used.

The location of the disc relative to the vessel bottom, liquid free surface and position of the baffles have effect on power consumption. Usually, there is a reduction in power consumption as the disc moves closer to the tank bottom due to the throttling of suction for the bottom half of the impeller. Similarly, less power is drawn as coverage is reduced. For open impellers, the uniform operating condition for power consumption is for the distance between the impeller and vessel bottom to be equal to impeller diameter while the distance to the liquid surface is at least three impeller diameters (Oldshue, 1983).

In the case of the spinning disc generator, the liquid free surface changes with time as CGA is formed. The ultimate height depends on the desired gas fraction in the product. Hence from practical considerations, the disc is lowered into the liquid phase just enough to initiate CGA formation.

Though CGA can be produced in the spinning disc generator without baffles, a high percentage of the bubbles may be bigger than 100 microns due to excessive vortexing and a high swirl component. The presence of baffles help to:

- direct fluid flow from the disc, producing the required vertical currents
- ensure that the entire fluid passes through the disc zone where maximum shearing effect exists
- enhance bubble breakage through impingement action
- change the flow pattern from rotary to mixing
- prevent excessive swirling and vortexing
- assure stable and consistent power utilization.
Excessive baffling can occur when the baffles are too close to the vessel walls. Excessive baffling is counter-productive as it tends to:

- inhibit air induction by damping surface waves
- cause localized mixing, creating non-homogeneity of product
- increase power consumption

Figure 1 shows the fluid flow patterns with no baffles, adequate baffling and excessive baffling.

During generation some of the mechanical energy is converted to heat resulting in a gradual rise in temperature of CGA. Since the product quality is temperature dependent, a cooling facility is essential. This can be incorporated within the vessel or inside the vessel or baffles' walls when space is crucial. It can also be positioned external to the vessel to avoid obstructing the hydrodynamic flow inside the vessel. This last option is adopted here.

### 3.2.2 Equipment Description

The equipment set-up for generating CGA is shown in Figure 2. It consists of a stainless steel disc 6.20-cm (2.44-in) in diameter and 0.16-cm (0.06-in) thick mounted horizontally on the lower end of a vertical shaft. The shaft is connected to a 1/12 horse power electric motor equipped with a variable speed controller. The shaft is held in a bearing housing which is clamped to a rigid framework to minimize vibration induced creep. Two rigid baffles made of plexiglas are attached to a baffle support such that they lie in the same vertical plane and equidistant from the shaft. The baffles 3.81-cm (1.5-in) wide and 20.3-cm (8.0-in) long are made of 0.64-cm (0.25-in) thick plexiglas. They are shaped at the lower end to encompass the spinning disc. They are positioned 1.9-cm (3/4-in) from the vessel walls and 2.5-cm (1-in) from the bottom.
Figure 1. Fluid Flow Patterns for Different Baffling Situations
LEGEND:

1. Ice Bath  
2. Cooling Coil  
3. Feed Tank  
4. Screw Jack  
5. Metering Pump  
6. Flow Control Valve  
7. Spinning Disc  
8. Baffle  
9. Generating Vessel  
10. Baffle Support  
11. Dust Cover  
12. Support Bearings  
13. Vertical Shaft  
14. Variable Speed Motor  
15. CGA Outlet

Figure 2: Spinning Disc CGA Generator Assembly
A cylindrical vessel 23-cm (9.0-in) long, 15-cm (6-in) in diameter and 0.64-cm (0.25-in) thick serves as the generation vessel. The vessel is made from transparent plexiglas for easy visualization. Four ports are located on the vessel as shown in Figure 3. The ports allow for input of surfactant solution, withdrawal of CGA and circulation of CGA through a cooling coil. The CGA outlet port is located just above the spinning disc in the vicinity of highest shear stress. A screw jack is placed below the vessel so that it can be raised or lowered as necessary. There is also a plexiglas lid attached to the support bearing to help keep away dust and foreign objects.

Cooling of CGA is achieved with the aid of a cooling coil made from a spiral copper tubing, 0.64-cm (0.25-in) inner diameter that is immersed in an ice bath. Flow of fluids in and out of the generating vessel are controlled using peristaltic metering pumps.

### 3.2.3 Materials

Apart from water, the only material needed to generate CGA is a surfactant. Surfactant molecules accumulate at the bubble interface to form an elasticized monolayer film of the expanded type that helps to increase the stability of the bubble. The amount of surfactant needed is very small. For ionic surfactants, this is usually in the vicinity of the critical micelle concentration (cmc) or higher. When concentrations much lower than the cmc are used, the bubbles tend to be bigger and less stable. The mechanistic role of surfactants in CGA formation is discussed in details latter.

The following three surfactants were used in this study. Their properties are given in Table 1.

- Sodium dodecylbenzene sulfonate (Sulfonate AA-10, anionic), a mixture of sodium alkylbenzene sulfonate with average chain length of 12 carbon atoms.
Figure 3: Design Specifications for Spinning Disc CGA Generator
• Alkyloxypolyethylenoxyethanol (T-15S12, non-ionic), an ethoxylate of secondary alcohol having an average chain length of 15 carbon atoms. The average mole of ethylene oxide in each molecule is 12.
• Cetyl pyridinum chloride (cationic).

### 3.2.4 Operation

Both batch and continuous operation are possible with the spinning disc generator.

In the batch mode, a known volume of surfactant solution, usually 1 liter, is put in the vessel. The screw jack is raised until the spinning disc is 2.5-cm (1-in) below the liquid surface. CGA production starts almost immediately the motor is turned on provided the rotational speed is high enough to create the flow velocity needed for air induction through surface waves and sufficient shear rate for bubble breakup. Agitation speed is related to the initial volume of fluid, desired CGA quality, vessel geometry, and baffle dimensions.

As the volume of CGA grows in the vessel, the ratio of the liquid surface above the spinning disc to the diameter of the disc increases. The vortexing action diminishes simultaneously until at some point near complete damping occurs. At this time, the surface waves are not strong enough to induce additional air into the system.

If the level of the disc is raised further, air induction and hence product quality increase is possible. However, the location of the disc relative to the bottom of the vessel also increases leading to poor fluid mixing in this region. On the other hand, if the distance is too high, the liquid phase begins
Table 1. Properties of Surfactants Used in This Study.

**Sodium Dodecylbenzene Sulfonate (NaDBS)**

- Chemical Family: Anionic Surfactant, non-biodegradable
- Chemical Structure: A mixture of sodium alkylbenzene sulfonate with an average chain length of 12 carbon atoms
- Chemical Formula: \(CH_2(CH_2)_{10}CH_2C_6H_4SO_3Na\)
- Average molecular weight = 348
- Active ingredients = 98%
- CMC in distilled and de-ionized water = 1.0x10^{-3} kmol/m^3
- CMC in 0.1 kmol/m^3 NaCl = 1.0x10^{-4} kmol/m^3
- Surface tension at CMC in aqueous solution = 32 dynes/cm
- Surface tension at CMC in 0.1 kmol/m^3 NaCl = 30 dynes/cm
- Manufacturer: Tennessee Chemical Company
  3475 Lenox Road, N.E., Atlanta, Georgia 30326
- Trade Name: Sulfonate AA-10

**Alkylpolyethyleneoxyethanol (T-15S12)**

- Chemical Family: Non-ionic Surfactant, biodegradable
- Chemical Structure: An ethoxylate of secondary alcohol having an average chain length of 15 carbon atoms and an average of 12 moles of ethylene oxide in each molecule
- Chemical Formula: \(C_{21-25}H_{35-29}O(CH_2CH_2O)_{12}CH_2CH_2OH\)
- Average molecular weight = 728
- Active ingredients = 100%
- Surface tension in 0.1 wt. % aqueous solution = 32 dynes/cm
- Manufacturer: Union Carbide Corporation, Ethyl Oxide Division
  Old Ridgebury Road, Danbury, Connecticut 06817
- Trade Name: Tergitol 15-S-12

**Cetyl pyridinium chloride (CPC)**

- Chemical Family: Cationic Surfactant
- Chemical Formula: \(C_{15}H_{31}ClN.H_2O\)
- Average molecular weight = 358
- Active ingredients = 99%
- Manufacturer: Pfaltz and Bauer Inc., Connecticut.
to separate and collect at the bottom and a higher agitation speed would be needed to remedy the situation.

Once CGA is formed, the stirrer speed can be cut back considerably and still maintain the integrity for some hours. The agitation creates a random motion that ensures each bubble is essentially surrounded by the continuous aqueous phase at all times. As long as this is the case and in the presence of sufficient surfactant molecules stabilizing the bubble interface, bubble coalescence does not occur. But too low an agitation rate results in poor mixing and bubble degradation. The critical agitation speed needed to maintain the integrity of CGA varies with quality and fluid level in the vessel. Starting with 1-liter of surfactant solution, an agitation speed of 5,400-rpm normally produces a 64% CGA quality at 28°C with the given set-up.

CGA produced this way can be used slowly over a period of time without any significant deterioration. As the level of CGA in the vessel drops, the disc is lowered or the agitation speed reduced or both to prevent any development of large surface waves capable of inducing air into the system.

Some of the mechanical energy of agitation is turned into heat which over time causes significant temperature rise of CGA. In order to maintain a constant temperature, CGA is circulated through a spiral copper tube immersed in an ice bath. The circulation rate is adjusted to maintain an isothermal condition at the desired fluid temperature. If left uncontrolled, the temperature rise over a 1 hour period can be as much as 20°C as shown in Figure 4.

To operate in the continuous mode, CGA is first produced in the batch mode as described above. Then using a metering pump, surfactant solution is fed into the vessel at a rate equivalent to the output rate of the liquid component of CGA. Under this condition, a new equilibrium is established. If the output rate of CGA is low, less than 1% of the fluid in the vessel leaving per minute, the residence time is often sufficient to maintain the product quality. As CGA output rate increases, the quality drops and a higher agitation rate would be needed to restore the original quality.
SURFACTANT = 0.5 g/1 NaDBS
STIRRING SPEED = 5400 rpm
ROOM TEMP. = 23°C

Figure 4: Typical Temperature Profile During CGA Generation Without External Cooling
A situation may also be reached where the fluid residence time in the vessel is too short leading to wide distribution in bubble size.

### 3.3 MECHANISM OF CGA FORMATION

The first step in the formation of CGA is the comminution of the gas and liquid phases. Except when an auxiliary source of air is employed, the gas phase is introduced by the vortexing surface waves. This means that a turbulent situation is necessary for CGA to be formed. Once in the liquid phase, the bubbles breakup into smaller ones through a series of interdependent processes that often results in a dispersion of bubbles 10 to 100 µm in size.

#### 3.3.1 Hydrodynamic Forces

That some degree of turbulence is needed to form CGA suggests hydrodynamic (inertial) forces to be a significant factor that leads to initial bubble breakup. The inertial force of a bubble resulting from shear and turbulent forces is counteracted by the bubble's surface force. The ratio of these two forces is known as the Weber number.

\[
We = \frac{\text{inertial forces}}{\text{surface-tension forces}} = \frac{\rho D V^2}{\gamma} \tag{3-1}
\]

where \( \rho \) = density of the gas

\( D \) = bubble diameter

\( V \) = bubble velocity

\( \gamma \) = surface tension
When the Weber number exceeds a critical value, the bubble becomes unstable and breakup may occur. If the turbulent shear field is uniform and processes such as coalescence and inter-bubble diffusion do not occur, bubble size distribution will approach an equilibrium when all the bubbles large enough for the Weber number to exceed the critical ratio have split. According to Hinze (1955), for dispersion processes in turbulent flow, the critical Weber number that determines the maximum drop size is about 1. Evidently, the difference in phase density, the presence of a surface active agent and the occurrence of other processes such as inter-bubble diffusion would significantly affect the critical Weber number.

During the breakup process, the externally applied hydrodynamic pressure is opposed by the internal pressure of the bubble. The origin of this internal pressure can best be understood by considering what happens on a molecular scale at a gas-liquid interface. The attraction between molecules in the liquid state is far greater than that between the molecules in the gaseous state. This results in a net force pulling the surface molecules away from the gas phase. In order to bring molecules to the interface from the liquid and expand it, work has to be done against the free surface energy.

For a spherical bubble of radius $r$, the total surface free energy would be $4\pi r^2 \gamma$. Increasing the radius by $dr$ would create a change in surface free energy by $8\pi r dr \gamma$. At equilibrium, this will have to be balanced by the work against the pressure drop across the interface, $\Delta P$.

That is

$$4\pi r^2 dr \Delta P = 8\pi r dr \gamma \quad (3-2)$$

And

$$\Delta P = \frac{2\gamma}{r} \quad (3-3)$$
\( \Delta P \) is the difference between the internal pressure of the bubble and ambient pressure of the continuous fluid.

Equation (3-3) is often referred to as the Laplace equation (Adamson, 1982). The equation implies that a lower \( \gamma \) and a higher \( r \) will enhance bubble breakup. Indeed the surface tension of pure water is so high (73 dynes/cm\(^2\)) that bubble breakup is tedious without a surface active agent. Secondly, the bubbles will rupture easily on contact due to the absence of an interfacial film. Hence a surface active agent is always needed. The surfactant molecules are adsorbed at the interface displacing water molecules. This results in a lower surface tension thus facilitating bubble breakup. At the same time an interfacial film is created which helps to stabilize the bubble.

The adsorption of surfactant molecules at the gas-liquid interface is often correlated by the Gibbs adsorption equation.

\[
d_y = \sum_{i=1}^{n} \Gamma_i d\mu_i \tag{3-4}
\]

where \( d_y = \) change in surface tension of the solvent
\( \Gamma_i = \) surface excess concentration of component \( i \)
\( d\mu_i = \) change in chemical potential of component \( i \)

Generally, for dilute aqueous surfactant solutions in the absence of other electrolytes, the Gibbs equation is used in the form (Rosen, 1978)

\[
d_y = -2.303 \# RT \Gamma_2 d(\log C_2) \tag{3-5}
\]

where \( \# \) is the number of particles per surfactant molecule whose surface concentration changes when the surfactant concentration in the bulk, \( C_2 \), changes.
The adsorption of surfactant molecules at the interface leads to the development of an interfacial tension gradient which exerts a tangential stress along the surface of the bubbles. This in turn impedes the tangential motion of the interface and hence causes a considerable resistance to film drainage.

The lowering of surface tension of the air-water interface by most ionic surfactants is often a function of surfactant concentration up to a point where micelles begin to form in the bulk liquid. This concentration at which the monomeric form in which the surfactant exists in very dilute solution aggregates to form a cluster (micelle) is termed the critical micelle concentration (CMC). Above the CMC, the concentration of surfactant molecules at the interface does not change. Excess surfactant molecules therefore go into the bulk liquid. Thus when new interfaces are created surfactant molecules are drawn from the bulk liquid rather quickly to stabilize them.

3.3.2 Interbubble Gas Diffusion

During formation, an array of bubbles are found initially in CGA ranging from sub-micron bubbles to those greater than 100 \( \mu m \) in size. With time, the big bubbles become smaller while those smaller than 25 \( \mu m \) tend to disappear (Sebba, 1982a).

The tendency for small bubbles to disappear in CGA is a consequence of the greater internal gas pressure. The pressure difference across a curved interface is given by the Laplace and Young equation (Adamson, 1982)

\[
\Delta P = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

where \( r_1 \) and \( r_2 \) = principal radii of curvature
\( \gamma = \) interfacial tension
For spherical bubbles, this reduces to the classical Laplace equation

\[ \Delta P = 2\frac{\gamma}{r} \]  

(3 - 7)

According to equation (3-7), the internal pressure of a bubble exceeds the average hydrodynamic pressure in the surrounding liquid phase. This excess pressure is directly proportional to the surface tension, \( \gamma \) and inversely proportional to the bubble radius, \( r \). Hence the higher the surface tension the higher the internal pressure. That is the presence of a surfactant which acts to lower the surface tension will inhibit interbubble gas diffusion. For a given fluid of known \( \gamma \), the tendency for interbubble gas diffusion to occur increases with decreasing bubble radius. Thus for two bubbles of different radius, there exists a driving force for mass transfer in the direction of the larger bubble through the liquid layer separating the two bubbles.

\[ \Delta P_{12} = \Delta P_1 - \Delta P_2 = 2\gamma \left( \frac{1}{R_1} - \frac{1}{R_2} \right) \]  

(3 - 8)

where \( R_1 \) and \( R_2 \) are the radii of the small and big bubbles respectively.

As gas diffuses out of the small bubble, it gets smaller in size and internal gas pressure rises further promoting gas flux. Simultaneously the internal area across which the gas molecules are transferred is reduced, slowing down the diffusion rate.

Interbubble gas diffusion rate can be estimated from Fick's law

\[ \frac{dn}{dt} = -ADS \frac{\Delta P}{\Delta x} \]  

(3 - 9)

where \( A \) = area of the diffusion interface (\( cm^2 \))
\( D \) = diffusion coefficient (\( cm^2/sec \))
\( S \) = solubility (\( molecules/ml-atm \))
\( \Delta P \) = pressure drop across interface (\( atm \))
\( \Delta x \) = thickness of the diffusion barrier (\( cm \))
If we represent $J = DS/\delta x$, then

$$\frac{dn}{dt} = J A \Delta P$$ (3 - 10)

In equation (3-10), $J$ is a measure of the resistance to mass transfer which takes into account the distance between the 2 bubbles, packing structure of surfactant molecules at the interface, chemical structure (hydrophobic and hydrophilic groups) of the surfactants, contact time, presence of other materials at the interface, and viscosity of the continuous phase.

### 3.3.3 Interbubble Collision

The turbulent condition that exists during CGA generation suggests that the bubbles would collide with each other rather frequently. When this occurs, three things can possibly happen to the bubbles:

- They are not affected significantly.
- They breakup into smaller bubbles.
- They coalesce into bigger ones.

All of these three processes appear take place over different ranges of bubble diameter.

According to Sebba (1982a), interbubble collision has not been observed to result in coalescence of CGA bubbles 25 to 50 $\mu$m in size. Instead, the bubbles show momentary bulging on contact and then drift apart. In this case the interfacial film resistance is strong enough to prevent coalescence.
For bubbles greater than 150 µm, bubble fission or coalescence is a possibility as has been observed in microbubbles colliding in solutions containing high concentrations of surfactants (Hills, 1974).

In Hills' experiment, dust-free air was injected into a 25-g/l NaDBS surfactant solution (marketed as Shell Teepol) through a fine hypodermic needle. The collision and subsequent stages of disintegration were observed visually and by high-speed photography. The terminal rate of rise of the bubbles was used to estimate bubble diameters using Stokes law. Microbubbles of 150 - 250 µm diameter were found to disintegrate into smaller bubbles of diameter 35 - 45 µm. The progeny diameters were independent of the size of the progenitors. However, bubbles with diameter greater than 350 µm exhibited random coalescence. The probability of coalescence fell rapidly as the bubble size was reduced, and no case was observed in 250 collisions for diameters below 300 µm.

Though the surfactant concentration needed to generate CGA by the spinning disc technique is much less than that used in Hills' study, the remarkable similarity is that the size of the progeny bubbles are in the same range as CGA bubbles.

A model developed by Yount (1983) also predicts the existence of a threshold diameter for bubble coalescence within a liquid in the neighborhood of 380 µm. The predicted value is rather insensitive to the model assumptions and agrees reasonably well with experiment.

The effect of interbubble collision on CGA formation can therefore be seen as occurring according to the three proposed mechanisms depending on the size of the bubble in question. For bubbles greater than 350 µm, bubble coalescence is dominant, those in the size range 150 - 250 µm undergo bubble fission while those less than 100 µm are not affected by interbubble collision.
3.4 **SUMMARY**

In this chapter, the factors affecting the generation of CGA by Spinning Disc method and the mechanisms of formation have been discussed.

In the generation of CGA by the Spinning Disc method, the three most important design components are the spinning disc, the baffles and the holding vessel. The size and relative position of these components are crucial to the generation of CGA of consistent properties. Both batch and continuous CGA generation are possible with this method. In either case, only low production rates can be sustained without loss of integrity.

The presence of a surface active agent is crucial to the formation of CGA. The amount of surfactant present does influence the ease of formation and subsequent stability of CGA. For ionic surfactants, concentrations just above the CMC are most appropriate. The rise in CGA temperature during generation by the Spinning Disc method can be substantial. As a result, a cooling device is necessary. It's design should have minimum impact on the hydrodynamic flow within the vessel. High temperature, usually above 60°C can impede CGA generation as a result of bubble instability.

Hydrodynamic forces play a major role in CGA formation. The externally acting hydrodynamic force has to be greater than that due to the interfacial tension for bubble break-up to occur. The ultimate size of the bubbles are influenced by interbubble diffusion with the smaller bubbles, usually below 25 µm, loosing their gas content to the bigger ones. The effect of interbubble collision on CGA formation depends on the size of the bubbles. Bubbles less than 100 µm are generally not affected by interbubble collision. Those in the 150-250 µm size range undergo bubble fission while bubble coalescence occurs primarily with those greater than 350 µm.
CHAPTER 4

CGA BUBBLE SIZE DISTRIBUTION

One of the most important parameters for characterizing CGA is the size distribution of its bubbles. The stability and rheological properties of CGA are influenced, not only by the average size of the bubbles, but also by the size distribution. The diameter of CGA bubbles lie in the 10 to 100 micron range. In this size range, CGA bubbles can be assumed to be perfectly spherical, a shape they adopt rather spontaneously as a consequence of the positive surface tension existing at the gas-liquid interface.

Microscope-assisted photographic techniques are the most common methods for bubble size determination (Cheng and Lemlich, 1983; De Vries, 1972; Chang et al., 1956). Time is crucial in these techniques because under static conditions, the size and morphology of the bubbles change due to coalescence, creaming and diffusion problems. To minimize these problems, the technique of freezing and cutting through to measure the size distribution of bubbles in a plane cross-section has been suggested (Chang et al., 1956). Another approach is to quickly observe the bubbles in the plane of contact between the foam and a flat glass wall and neglecting the slight degree of distortion of the bubbles by the glass wall (De Vries, 1972). It is also possible to focus on a plane in the upper layers of a strongly illuminated foam (De Vries, 1972).
Selecki and Wasiak (1984) have suggested a continuous and direct capillary method for bubble size determination of static foams. In the method, foam is continuously sucked into a glass capillary of exactly known diameter. Inside the capillary, bubbles take the form of gas cylinders separated by liquid films. The capillary is projected on a screen where phototransistors connected with an electronic device are placed to measure the length of the gas cylinders and hence their equivalent diameters. This technique was found to work for bubbles 400 to 3500 microns in diameter.

The application of the continuous and direct method of Selecki and Wasiak would most likely be hindered by the in-availability of precision capillary tubes that can project 10-100 microns bubbles into cylindrical shapes. Size determination of CGA bubbles appears to be limited therefore, to the photomicrographic method. This is the method used in this study.

4.1 EXPERIMENTAL

4.1.1 Equipment and Procedure

The set-up for the determination of CGA bubble size consists of a CGA generator assembly and a microscope/camera assembly. The CGA generator assembly is as described in Figure 2. CGA was generated using the batch mode at a speed of 5400-rpm for 10-minutes. The temperature was maintained at 28°C. The quality of CGA was about 64%.

The microscope set-up consists of a Nikon Biological Microscope (OPTIPHOT) mounted on a mobile cart for versatility. A video camera connected to a black and white monitor (17-in diagonal screen) is mounted on the microscope. Pictures relayed to the monitor by the video camera are taken using a 35-mm camera (Minolta X-700) mounted on a tripod stand. This arrangement was
used instead of directly mounting the 35-mm camera on the microscope because of better illumination and ease of operation. Figure 5 shows the microscope assembly.

A viewing cell was fabricated to fit into the microscope and allow for a continuous flow of CGA. This way, changes in bubble size as a result of coalescence, creaming or diffusion can be minimized. The viewing cell is shown in Figure 6. It is a modified version of that used by Suggs (1988).

The cell was made from a Lexan block 2.5-in long, 1.25-in wide and 0.75-in high. The viewing chamber was a 0.25-in hole recessed 3/32-in at the center of the block. The viewing chamber was covered with a square glass plate 1-in by 1-in by 1/16-in thick. The glass plate was held in place by a top cover made from 1/4-in thick lexan which has been recessed on one side to accommodate the glass plate. A silicone form-a-gasket glue was applied between the glass plate and the top cover as a seal. The cover was then bolted to the main body carefully. The illumination of the chamber was achieved through a 1/2-in hole at the bottom of the block. The hole was recessed until the thickness of the space between it and the chamber was only 3/32-in.

Delivery and discharge entrances to the viewing chamber were 1/4-in holes aligned at 45 degrees. This angle entrance approach was designed to help clean the chamber of bubbles that tend to adhere to the glass surface through the impingement action of the incoming CGA. The inlet and outlet ends of the cell were fitted with 1/4-in male swagelok. CGA flow into the cell was achieved and controlled with a Masterflex metering pump equipped with a flow control and a switch.

CGA at 28°C was allowed to flow through the viewing cell at a rate just high enough to keep the viewing chamber free of hanging bubbles (about 200 ml/min). Once a good steady flow of CGA was achieved, the pump was stopped and the picture taken within 3 seconds using a 5X metallurgical objective.
Figure 5: Microscope Assembly for CGA Bubble Size Determination
Figure 6: CGA Viewing Cell

GASKET

COVER

BODY

INPUT

FOR MICROSCOPE'S EYE-PIECE

GLASS PLATE

FLOW PATH

OUTPUT

FOR LIGHT FROM MICROSCOPE
Photomicrographs of CGA were analyzed using a computer assisted Kontron Image Analyzer (a service provided by Mining Engineering Department). The image analysis program involves the following step:

- Input of image information from an external device (television camera), digitization and storage
- Gray image processing for improved contrast
- Feature extraction using global or local contrast
- Feature analysis using suitable parameters (size, shape, density etc.)
- Data output and storage, statistical data processing

A total of 20 pictures were analyzed. Each picture contained between 100 and 200 bubbles. The pictures represent CGA generated with three different surfactants, four different surfactant concentrations and the effect of an electrolyte. Some of the photomicrographs are shown in Figures 7 to 10. The computer provided statistical information on the number of bubbles, the maximum and minimum bubble diameter, average bubble size and the standard deviation from the mean. A histogram of length (bubble diameter) for every 2-micron change in length was also plotted.

4.1.2 Results and Discussion

Figures 11 to 17 give the histogram of bubble diameter for the different test conditions. Three pictures of CGA were examined for each case (representing more than 300 bubbles) except in one case where 2 pictures were examined.

In general, no bubble smaller than 10-microns or greater than 150-microns in diameter was observed. The number of bubbles also appear to be uniformly distributed over the entire range of bubble sizes. Most of the bubbles lied in the 15-microns to 100-microns size range. The mean bubble size for all the cases examined varied between 52-microns and 61.3-microns.
SURFACTANT = 5.0-g/l Sodium dodecylbenzene sulfonate
CGA QUALITY = 64%

SURFACTANT = 1.0-g/l Sodium dodecylbenzene sulfonate
CGA QUALITY = 64%

Figure 7: Photomicrographs of CGA - I
SURFACTANT = 0.5-g/l Sodium dodecylbenzene sulfonate
CGA QUALITY = 64%

SURFACTANT = 0.2-g/l Sodium dodecylbenzene sulfonate
CGA QUALITY = 64%

Figure 8: Photomicrographs of CGA - II
SURFACTANT = 1.0-g/l Alkyloxy polyethylenoxyethanol
CGA QUALITY = 64%

Figure 9: Photomicrographs of CGA - III

SURFACTANT = 1.0-g/l Cetyl pyridinium chloride
CGA QUALITY = 64%
SURFACTANT = 0.5-g/l Sodium dodecylbenzene sulfonate
+ 0.2-g/l Sodium chloride

CGA QUALITY = 64%

Figure 10: Photomicrographs of CGA - IV
Figure 11. Histogram of CGA Bubbles made with 5.0-g/l NaDBS
Figure 12. Histogram of CGA Bubbles made with 1.0-g/l NaDBS
Figure 13. Histogram of CGA Bubbles made with 0.5-g/l NaDBS
Figure 14. Histogram of CGA Bubbles made with 0.2-g/l NaDBS
Figure 15. Histogram of CGA Bubbles made with 0.5-g/l NaDBS & 0.2-g/l NaCl
Figure 16. Histogram of CGA Bubbles made with 1.0-g/l T-15S12
Figure 17. Histogram of CGA Bubbles made with 1.0-g/l CPC
4.1.2.1 Effect of Surfactant Concentration

CGA made with four different concentrations of NaDBS were compared. The concentrations used were 5.0-g/l, 1.0-g/l, 0.5-g/l and 0.2-g/l. Table 2 summarizes the effect of surfactant concentration on bubble size distribution. The table shows that changing the concentration of NaDBS from 5.0-g/l to 0.2-g/l slightly influenced the minimum bubble size which dropped by 17% from 15.7-microns to 13.1-microns. On the contrary the maximum bubble diameter increased by 43% from 90-microns to 128.6-microns. The mean bubble size also showed an increase from 52-microns to 60.6-microns, a change of nearly 17%.

The change in mean and maximum bubble size did not start to be significant until the concentration of the surfactant dropped below 0.5-g/l. This is consistent with the behavior of surfactants like NaDBS that show increase in surface tension with decrease in concentration below the CMC. The CMC of NaDBS is 0.35-g/l when no electrolyte is present. Below this concentration, CGA bubbles become increasingly unstable promoting the formation of bigger bubbles. Non-availability of surfactant molecules to stabilize the enormous interfacial area of the microbubbles become a limiting factor and the interfacial tension may no longer be at its minimum.

Another interesting observation was that as the surfactant concentration decreased, the size of the smallest bubbles decreased while the maximum bubble size increased. As the size of the bubbles increase the internal pressure decreases according to Laplace equation. The pressure difference between the small and the big bubbles also increase. This promotes interbubble diffusion particularly between the very small and the very big bubbles. The result is the widening of the gap between the two ends of the bubble size range as observed.
### TABLE 2

**CGA Bubble Size Characterization: Effect of Surfactant Concentration**

**Test Conditions**

Surfactant = NaDBs  
CGA- Quality = 64%  
- Generation Speed = 5400 rpm  
- Generation Time = 10 min.  
- Temperature = 28 °C

<table>
<thead>
<tr>
<th>CONC.</th>
<th># OF BUBBLES</th>
<th>BUBBLE SIZE (µm)</th>
<th>% OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/l</td>
<td></td>
<td>MIN</td>
<td>MAX</td>
</tr>
<tr>
<td>5.0</td>
<td>470</td>
<td>15.7</td>
<td>90.0</td>
</tr>
<tr>
<td>1.0</td>
<td>443</td>
<td>14.8</td>
<td>103.7</td>
</tr>
<tr>
<td>0.5</td>
<td>360</td>
<td>13.6</td>
<td>119.6</td>
</tr>
<tr>
<td>0.2</td>
<td>301</td>
<td>13.1</td>
<td>128.6</td>
</tr>
</tbody>
</table>
TABLE 3

CGA Bubble Size Characterization:
Effect of Surfactant Type

Test Conditions

Surfactant Con. = 1.0 g/l
CGA- Quality = 64%
- Generation Speed = 5400 rpm
- Generation Time = 10 min.
- Temperature = 28 °C

<table>
<thead>
<tr>
<th>SURFACANT TYPE</th>
<th># OF BUBBLES</th>
<th>BUBBLE SIZE (µm)</th>
<th>% OF BUBBLES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MIN</td>
<td>MAX</td>
</tr>
<tr>
<td>NaDBS</td>
<td>443</td>
<td>14.8</td>
<td>103.7</td>
</tr>
<tr>
<td>CPC</td>
<td>445</td>
<td>14.4</td>
<td>99.8</td>
</tr>
<tr>
<td>T-15-S-12</td>
<td>504</td>
<td>13.6</td>
<td>98.2</td>
</tr>
</tbody>
</table>
# TABLE 4

CGA Bubble Size Characterization: Effect of Electrolyte

**Test Conditions**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CGA- Quality</th>
<th>Generation Speed</th>
<th>Generation Time</th>
<th>Temperature</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5-g/l NaDBS</td>
<td>64%</td>
<td>5400 rpm</td>
<td>10 min.</td>
<td>28 °C</td>
<td>NaCl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ELECTROLYTE CONC., g/l</th>
<th># OF BUBBLES</th>
<th>BUBBLE SIZE (µm)</th>
<th>% OF BUBBLES</th>
<th>&lt; 100 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIN</td>
<td>MAX</td>
<td>MEAN</td>
<td>SD</td>
</tr>
<tr>
<td>0.0</td>
<td>13.6</td>
<td>119.6</td>
<td>61.3</td>
<td>25.0</td>
</tr>
<tr>
<td>0.2</td>
<td>11.8</td>
<td>106.9</td>
<td>57.4</td>
<td>24.1</td>
</tr>
</tbody>
</table>

**CGA Bubble Size Distribution**
4.1.2.2 Effect of Surfactant Type

Table 3 summarizes the effect of different types of surfactant on the size distribution of CGA bubbles. The three surfactants used are Sodium dodecylbenzene sulphonate (NaDBS, an anionic surfactant), Cetyl pyridinium chloride (CPC, a cationic surfactant), and Alkyloxypolyethyleneoxyethanol (T-15S12, a non-ionic surfactant). The properties of these surfactants are given in Table 1. A concentration of 1.0-g/l was used.

The smallest bubbles were given by T-15S12 with a mean of 50.5-microns. The minimum bubble size was 13.6-microns and the maximum 98.2-microns. NaDBS was next in the list with a mean bubble size of 53.2-microns. However about 1% of its bubbles were greater than 100-microns. The size of the bubbles ranged from 14.8-microns to 103.7-microns. The mean bubble size of CPC was 53.3-microns, about that of NaDBS. But unlike NaDBS, no bubble exceeded the 100-microns size mark. Its bubbles ranged from 14.4-microns to 99.8-microns in size.

According to the definition of CGA (chapter 3), all the three surfactants made CGA of excellent quality at the concentration of 1.0-g/l. The relatively smaller sizes of bubbles made with T-15S12 can be attributed to its non-ionic nature. Unlike the other two surfactants, there is no net charge on the interface of bubbles made with T-15S12. As a result, the attractive force between the bubbles and hence the coalescence tendency are minimized.

4.1.2.3 Effect of Electrolyte

CGA made with 0.5-g/l NaDBS solution containing 0.2-g/l sodium chloride (NaCl) was compared with that without any salt. As shown in Table 4, the presence of NaCl lowered both the minimum and the maximum bubble size. The minimum bubble size decreased from 13.6-microns to
11.8-microns while the maximum bubble size decreased from 120-microns to 107-microns. The mean bubble size also decreased correspondingly from 61.3-microns to 57.4-microns.

The presence of an electrolyte increases the effective concentration of an ionic surfactant. The electrolyte ionizes in solution and one of the ions is adsorbed at the interface of the bubble along with the surfactant. The ion that is adsorbed at the bubble's interface is determined by the hydration energy with preference for those with higher hydration energy. In this case, it is the $Cl^-$ ion. The $Cl^-$ ions creep between the dodecybenzene sulphonate group at the bubble's interface to further lower the interfacial tension. Since the interfacial force acting outwards from the bubble has been lowered, the bubble shrinks to return to equilibrium according to Laplace equation.

4.2 SUMMARY

Microscope-assisted photographic technique is suitable for determining the size and size distribution of CGA bubbles. The technique utilizes a carefully designed viewing cell under a microscope and a video camera to project the bubbles to a screen. The screen image is then captured on a negative, developed, printed and subsequently analyzed using an image analyzer.

CGA generated with the Spinning Disc method has a bubble size range between 15 and 100 microns. The mean bubble size varied between 52 and 61-microns for all the test conditions examined. For ionic surfactants like NaDBS, concentrations above the CMC produce bubbles that are smaller and less dispersed in size than with surfactant concentrations below the CMC. At low concentrations, the surfactant molecules are no longer sufficient to stabilize the increasing interfacial area as the bubbles become smaller.
All three surfactants examined produced CGA of excellent quality at concentrations above 0.1 percent by weight. The non-ionic surfactant used (T-15S12) gave the smallest bubble sizes at this concentration. At low surfactant concentrations, the presence of an electrolyte such as sodium chloride helped to decrease the size of CGA bubbles by increasing the effective concentration of the surfactant. This suggests that electrolytes that can also act as nutrient supplements in in-situ biodegradation could be added safely during CGA generation. Such an electrolyte would reduce the cost of surfactant and create smaller and possibly more stable CGA bubbles. It would also provide nutrition for the microorganisms while the bubbles supply oxygen.
STABILITY OF CGA

The stability of CGA, as defined here is its ability to resist change in bubble size, liquid content or degree of dispersion. That is a stable CGA is that whose bubbles maintain an average size and are uniformly distributed through the continuous liquid phase. This definition is different from the literature definition of foam stability. In the case of foam, stability is related to the intrinsic nature of the films to resist rupture.

The constitution of CGA, however, mitigates against this stability concept. CGA is a gas-liquid mixture with the gas bubbles much smaller, than conventional (dry) foam bubbles. The liquid content is higher too. The difference between the properties of these two phases act in a way to promote instability. As a result CGA cannot retain its integrity without some external hydrodynamic force. In this sense, CGA cannot be regarded as a stable system.
5.1 PROCESSES CONTROLLING CGA STABILITY

5.1.1 GRAVITATIONAL DRAINAGE AND CREAMING

As a result of density difference, there is a tendency for the liquid and gas phases to want to separate. Continuous agitation is therefore necessary to preserve the integrity of CGA. If agitation is stopped or if the hydrodynamic force acting on CGA bubbles is less than the buoyancy force, the bubbles rise to the top. Simultaneously, there is a hydrodynamic outflow of liquid from around the bubbles. Thus the bubbles cream upwards as the liquid drains downwards.

As CGA bubbles rise they expand. When the gas to liquid ratio exceeds 0.74, the bubbles begin to arrange themselves in a polyhedral manner separated by thin liquid films (lamellae). Further drainage of the liquid in the lamellae and plateau borders continues under the influence of capillary pressure and plateau border suction. When the liquid film becomes sufficiently small (less than 0.1 \( \mu m \)) the effects of the London - van der Waals forces and the repulsive force of any electrostatic double layer also become important. Eventually, the films rupture and the bubbles coalesce.

Studies on foam drainage reported in literature have essentially concentrated on capillary drainage and the intrinsic resistance of the lamellae to rupture (Malhotra and Wasan, 1987; Huang et al., 1986; Narsimhan and Ruckenstein, 1986(a,b); Nishioka, 1986, Djabbarah and Wasan, (1985); Hahn et al., 1985; Ross, 1985, Lin and Slattery, 1982). In the case of CGA, the liquid film between the bubbles is sufficiently large that the only phenomenon of interest is gravity drainage and bubble creaming.

In the study of gas-liquid systems, the presence of surface active agents have been found to significantly affect the rise velocity of non-interacting bubbles (Furler and Ross, 1986; Kelkar et al., 1983; Levan and Newman, 1976; Griffith, 1962, Levich, 1962). According to Levich (1962), the adsorbed
solute is not uniformly distributed on the surface of an ascending bubble. At the downstream part of the bubble, the surface concentration exceeds the equilibrium value, while that on the upstream part is less than equilibrium. This surface concentration dis-equilibrium results from the viscous drag of the medium acting on the interface. This leads to the development of a surface tension gradient that causes tangential stress along the bubbles interface, lowering the surface tension where the adsorbate concentration is greater.

Consequently, the interfacial liquid flows from the downstream part, where the surface tension is lower, to the upstream part of the bubble. Since this flow opposes that induced by the shear stress in the outer fluid of the interface, the net flow of the interface is restrained. The result is an increase in bubble rigidity and a lowering of both the internal gas circulation within the bubble and the bubble rise velocity.

If the surface tension gradient is sufficiently large, complete rigidity of the interface and inhibition of circulation of bubbles' internal gas results. Under this condition, the gas bubble behaves like a solid sphere of the same density and the terminal rise velocity can be described by Stoke's law.

The limit of validity of Stoke's law (Re < 1) is also the criteria for a rigid interface on a rising bubble (Furler and Ross, 1986). CGA bubbles are very small and as such fall into this category of behaving like non-deformable spheres. Thus under steady state conditions, gravitational drainage force can be equated to the opposing hydrodynamic force for CGA bubbles of radius $r$ dispersed in a liquid of viscosity $\mu$ according to Stoke's law.

\[
\frac{4}{3} \pi r^3 \Delta \rho g = 6\pi \mu r U \tag{5.1}
\]

And

\[
U = \frac{2gr^2 \Delta \rho}{9\mu} \tag{5.2}
\]
where $\Delta \rho$ is the density difference between the two phases, $g$ is acceleration due to gravity, and $U$ is the bubble rise velocity.

The above equation holds only for uniform, non-interacting non-deformable spheres. Given the polydisperse nature of CGA bubbles, a modification is necessary.

If we consider $n_i$ bubbles with an effective mass of $\frac{4}{3} \pi r_i^3 \Delta \rho$, the center of mass will have a velocity of

$$U = \frac{1}{V} \sum_i \frac{4}{3} \pi r_i^3 n_i U_i$$

(5.3)

$$V = \text{total volume of dispersed phase}$$

Therefore

$$U = \frac{8 \pi g \Delta \rho}{27 \mu V} \sum_i n_i r_i^5$$

(5.4)

Thus if the time needed to drain half of the liquid phase of CGA in a given column of height $h$ is defined as the half life, then from equation (4.4) the half life of CGA can be written as

$$t_{1/2} = \frac{h}{2} \frac{27 \mu V}{8 \pi g \Delta \rho} \frac{1}{\sum_i n_i r_i^5}$$

(5.5)

That is the half life of CGA is inversely proportional to the fifth power of the bubble radius.
5.1.2 BUBBLE COALESCENCE

From thermodynamic considerations, CGA is an unstable system. The large interfacial area of the bubbles also carry with it considerable amount of energy. In order to minimize the surface free energy of the system, processes that encourage bubble coalescence are thermodynamically favored.

For a homogeneous system, the Helmholtz free energy equation in the differential form is (Smith and van Ness, 1975)

\[ dE = -SdT - PdV + \sum (\mu_i d\eta_i) \]  

(5.6)

where \( E \) = Helmholtz free energy

\( S \) = Entropy

\( T \) = Temperature

\( P \) = Pressure

\( V \) = Volume

\( \mu_i \) = chemical potential of component \( i \)

\( \eta_i \) = number of moles of component \( i \)

The Helmholtz equation can be modified for CGA to include the interfacial energy of the bubbles.

\[ dE = -SdT - PdV + \sigma dA + \sum (\mu_i d\eta_i) \]  

(5.7)

where \( \sigma \) = surface tension of the fluid

\( A \) = interfacial area

In the absence of chemical reactions, equation (5.7) can be written for a closed isothermal system as

STABILITY OF CGA
\[ dE = -PdV + \sigma dA \] (5.8)

The necessary condition for thermodynamic equilibrium of an isothermal closed system under constant pressure is

\[ (dE)_v, T \leq 0 \] (5.9)

That is, at constant volume and temperature, a process would be irreversible if it proceeds in such a manner as to cause a decrease in the Helmholtz free energy. According to equation (5.8) however, for Helmholtz free energy to decrease, the gas phase volume has to increase and/or the interfacial area reduced. This can only be brought about through bubble coalescence which means a favorable reversibility of the process. The expansion of the gas phase also means increased gas buoyancy and eventual phase separation.

In the case of CGA, the drive towards phase separation is opposed by the applied shear force while bubble coalescence is inhibited by the presence of the interfacial film of adsorbed surfactant molecules. The difference between the concentration of the surfactant adsorbed at the interface and the aqueous solution produces an elasticity often referred to as Gibbs-Marangoni elasticity which helps to stabilize the film. The Gibbs-Marangoni can be explained as follows.

When the thin film at a bubble's interface is stretched, the surface area increases. This causes a momentary decrease in the number of surfactant molecules per unit area of the surface and a corresponding increase in surface tension. This temporary phenomenon is called the Marangoni effect. Thereafter, surfactant molecules diffuse to the surface of the newly stretched film until an equilibrium is established between the amount of surfactant molecules at the interface and that in the bulk of the fluid. At this final equilibrium position, there are, nevertheless, fewer surfactant molecules per unit area of the surface and hence higher surface tension than the starting value. According to the Gibbs effect, this stretched film will try to contract like an elastic skin to regain its original structure.

STABILITY OF CGA
The combined action of the Gibbs and Marangoni effects is to stabilize CGA bubbles against infinitesimal fluctuations at the surface. Thus any perturbation that tends to increase the bubble’s interfacial area is met by an increase in surface tension that acts to oppose the change. Indeed, if the Gibbs-Marangoni elasticity is absent, as in the case of pure liquids, CGA cannot be made. As long as the bubbles are completely surrounded by the liquid phase, therefore, and in the presence of sufficient surfactant molecules in solution, they resist coalescence.

5.1.3 EFFECT OF TEMPERATURE

The stability of CGA is temperature dependent. At temperatures below 40°C the stability of CGA is good provided some agitation is maintained. Above this temperature, CGA instability increases rather sharply and above 65°C the system breaks down.

The dependence of CGA stability on temperature can best be examined from the development of an equation of state assuming that the gas phase obeys ideal gas law.

\[ P_V T = nRT \]  

(5.10)

where \( P_T \) = total pressure acting on the bubble

\[ = P + \Delta P \]

\( P = \) external pressure
\( \Delta P = \) Laplace (interfacial) pressure

\( V = \) volume of bubble
\( n = \) number of molecules per bubble

\( T = \) temperature

Equation (4.10) can be combined with the Laplace equation \( \Delta P = 2\gamma/r \) to give
\[ PV + \frac{2y}{r} \left( \frac{4}{3} \pi r^3 \right) = nRT \]

That is

\[ PV + \frac{2}{3} \gamma A = nRT \]  \hspace{1cm} (5.11)

Equation (5.11) was first developed by Ross (1969) for foams by considering foam collapse as a sequence of processes occurring between successive quasi-equilibrium states. It has been proved to hold for single spheres and assemblages of spheres, whether uniform or non-uniform in size (Morrison and Ross, 1983). The equation suggests a dependence of bubble size on temperature under the same hydrodynamic conditions.

5.2 EXPERIMENTAL

5.2.1 Equipment and Procedure

CGA was generated using NaDBS with and without an electrolyte added (sodium chloride, NaCl). Starting with 1-liter of surfactant solution, CGA was generated as described previously using the batch method (see Figure 2). Each batch was generated for 10-minutes at a speed of 5400-rpm. The temperature of CGA was maintained at 28°C.

The stability of CGA was measured by transferring about 200-ml rapidly into a 250-ml graduated cylinder (Figure 18). The volume of the liquid drained was then read as a function of time. The total volume of liquid was determined from the weight and density. CGA stability was measured
in terms of half life, the time needed for 50% of the liquid content to drain to the bottom. Different surfactant concentrations were used ranging from 10.0-g/l to 0.02-g/l. The effect of electrolyte concentration was also examined.

5.2.2 Results and Discussion

The results of CGA drainage time as a function of liquid drained are tabulated in Appendix A. The effects of surfactant and electrolyte concentrations on the half life of CGA are presented in Figures 19 and 20.

The liquid drainage of CGA creates a situation whereby the top part is dry relative to the bottom. Also bubble fractionation appears to occur with the bubbles at the CGA/liquid interface containing very small bubbles and increasing in size towards the top. Thus in keeping with the definition of CGA as a gas in liquid dispersion having at most 0.74 gas fraction, only the early stages of the drainage process best represent the stability criterion. Consequently, we define the stability of CGA in terms of the half life, the time needed for 50% of the liquid content to drain to the bottom.

Suggs (1987) had used a comparative definition for CGA stability. A 250-ml graduated cylinder was filled with CGA to the 250-ml mark and the liquid drained recorded as a function of time. The height after 1 minute drainage time was called the “H’ factor”. This he found to be a fast screening procedure. He also defined a normalized H factor as the ratio of H’ to the final liquid height after all bubbles have coalesced.

The definition of CGA stability in terms of half life used in this work ensures that liquid drainage would principally be by gravity action and that the contribution of inter and intra- bubble forces would be insignificant. From the practical side, the half life concept of CGA stability also helps to
Figure 18: CGA Stability Measurement
eliminate any slight variation in CGA quality or sample size as each stability test is normalized with respect to these variables.

The effect of surfactant concentration on the stability of CGA (defined in terms of half life) is shown in Figure 19. The figure also shows the effect of adding 0.1-g/l NaCl. When no electrolyte was present, CGA stability improved up to a surfactant concentration of 5.0-g/l. At a higher concentration of 10.0-g/l however, CGA stability showed a decline. The change in the stability of CGA was most significant at low concentrations. At very low concentrations, below 0.2-g/l, CGA, if formed, is highly unstable. The bubbles separate and coalesce almost as readily as they are formed. As mentioned earlier, NaDBS has a CMC of 0.35-g/l in distilled and deionized water. Thus as surfactant concentration drops below this value, there would be insufficient surfactant molecules at the bubbles' interface to lower the Gibbs-Marangoni elasticity that would otherwise have stabilized the film.

Adding 0.1-g/l of NaCl was found to increase the stability of CGA according to Figure 19. The most significant increase was observed at low surfactant concentrations. More particularly, very low concentrations of NaDBS that would not normally form CGA do so with the addition of NaCl. The presence of an electrolyte lowers the CMC of ionic surfactants. In the case of NaDBS, the CMC has been found to drop by an order of magnitude from 0.35-g/l in the absence of NaCl to about 0.035-g/l when 5.8-g/l NaCl is added. When this occurs, smaller and more stable bubbles can be formed at the same surfactant concentration. The results presented in chapter 4 indeed confirm that the addition of NaCl does result in the formation of smaller bubbles.

As shown in Figure 20, CGA made with 0.1-g/l NaDBS became increasingly stable as the added amount of NaCl increased up to 1.0-g/l. But at higher concentrations, the stability began to decrease. This phenomenon is similar to that observed with increasing surfactant concentration. At concentrations much higher than the CMC, the interfacial tension of ionic surfactants often tend to increase slightly. In this concentration range, the Gibbs-Marangoni elastic behavior of the
Figure 19: Effect of Surfactant Concentration on Stability of CGA

- SURFACANT = NaDBS
- CGA QUALITY = 0.64
- TEMPERATURE = 28°C

□ = No NaCl
△ = 0.1 g/l NaCl
Figure 20: Effect of Sodium Chloride Concentration on CGA Stability

SURFACTANT = 0.1 g/l NaDBS
CGA QUALITY = 0.64
TEMPERATURE = 28°C

□ = No NaCl
interface is impaired by the number of surfactant and/or electrolyte molecules present and intermolecular forces are no longer insignificant.

Given the low cost of NaCl compared to NaDBS, the addition of an electrolyte such as NaCl in CGA production can be very beneficial cost-wise. However, the ultimate application of CGA would have to be considered as well. Whereas the half life of NaDBS-based CGA could be prolonged by the addition of NaCl, in a soil environment it's retention has been found to be less (Foss, 1989). Evidently, the ionic constitution of the application medium and the desired result would determine if the presence of an electrolyte would be beneficial.

When CGA is intended for use to enhance in-situ biodegradation in the subsurface environment that is contaminated with biodegradable organics, salts such as dipotassium hydrogen phosphate, potassium nitrate and ammonium phosphate can be incorporated. In addition to CGA bubbles providing oxygen for aerobic microbes, these salts would provide nutrients to supplement the growth of microorganisms. These microorganisms often metabolize the toxic compounds to non-toxic or less toxic species. Thus, an increase in microbial population would also mean an increase in the rate of biodegradation.

5.3 SUMMARY

CGA is not a stable system. It has no intrinsic resistance to change in bubble size or degree of dispersion. Continuous agitation is required to preserve it's integrity. The hydrodynamic force acting on the bubbles has to be at least equal to the buoyancy force to prevent the separation of the gas and liquid phases. CGA's stability is temperature dependent. It's stability decreases with increase in temperature. At high temperatures (above 65°C), complete breakdown occurs.
The stability of CGA is best described by the half life, the time needed for 50% of its liquid phase to separate by gravitational drainage. The stability of CGA, as defined by the half life, is enhanced by increase in surfactant concentration particularly at low concentrations. CGA made with NaDBS was highly unstable at concentrations below the CMC (0.35-g/l).

CGA's stability can be enhanced at low surfactant concentrations by the addition of an electrolyte. The electrolyte increases the effective concentration of the surfactant and lowers the CMC of ionic surfactants. The result is the formation of smaller bubbles (chapter 4) and increase in surfactant concentration density at the bubbles interface, factors that improve the stability of CGA. For applications of CGA in in-situ biodegradation, electrolytes such as potassium phosphate, potassium nitrate, and ammonium phosphate can be used. Apart from improving the stability of CGA, these salts would also increase the rate of biodegradation by providing the often needed nutrients to facilitate microbial growth.
CHAPTER 6

RHEOLOGICAL PROPERTIES OF CGA

CGA is a compressible non-Newtonian fluid with a defined shear stress versus shear rate relationship (shear diagram) whose potential applications are influenced by its peculiar rheological properties.

Foam is generally referred to in literature as a pseudoplastic fluid with bulk viscosities markedly greater than the sum of the separate viscosities of its constituents. For dry foam, the apparent viscosity increases with increasing quality at any given shear rate but decreases as shear rate increases (Patton et al., 1983; Raza and Marsden, 1967; Marsden and Khan, 1966; Fried, 1961). When foam quality falls below 0.54, apparent viscosity becomes independent of shear rate (Mitchell, 1969; Minssieux, 1974). This suggests that the apparent viscosity of CGA would exhibit two regions, one of shear rate dependence and another that is independent of shear rate.

Except for Minssieux (1974) who reported the use of Fann and Epprecht coaxial cylinder viscometer, foam viscosity is commonly measured using the concept of fluid flow through a smooth capillary tube (Harris and Reidenbach, 1987; Hirasaki and Lawson, 1985; Patton et al., 1983; Fried, 1961). This technique is more suitable for CGA than the former which may be more prone to
bubble coalescence and liquid drainage. In general the flow problems must be solved so that the basic shear diagram is independent of the instrument.

In this investigation, two methods were used to study the rheological behavior of CGA.

• a modified Brookfield Digital viscometer
• a capillary viscometer

6.1 Modified Brookfield Digital Viscometer

6.1.1 Equipment and Procedure

A Brookfield laboratory viscometer was used to measure the viscosity of CGA (Figure 21). The viscometer operates by rotating a sensing element (a spindle) in a fluid and measuring the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the spindle through a beryllium copper spring. The degree to which the spring is wound, detected by a rotational transducer, is proportional to the viscosity of the fluid. For a given spring deflection, the actual viscosity is inversely proportional to the spindle speed and shear stress is related to the spindle’s size and shape. Continuous readouts of percent full scale, viscosity and shear stress are provided by means of the integral three-digit LED display.

The Brookfield viscometer was designed to handle single phase liquids. In order to use it for CGA, a two phase mixture, some modification was necessary. The adapter tube assembly was redesigned to incorporate an inlet port and an outlet port for CGA as shown in Figure 22. The modification was necessary to minimize the coalescence and phase separation of CGA. Without the modifica-
Figure 21: Brookfield Digital Viscometer
tion wide fluctuations in readings would result. The viscosity of CGA would increase with time as the bubbles cream to the top.

CGA was generated in the batch mode as discussed in Chapter 3. The variables examined were surfactant type, surfactant concentration and CGA quality. The properties of the surfactants used are given in Figure 1. CGA temperature in the generating vessel was 28°C. CGA quality was varied between 0.4 and 0.7 either by diluting with surfactant solution after formation for low quality or by using auxiliary air supply for high quality.

For a given test run, CGA of desired properties was generated and allowed to flow continuously through the adapter tube. The flow rate used was 60 ml/min. This was set after some trial tests were carried out. Trial tests were also used to set the viscometer speed at 6-rpm. This was the speed that maintained the scale readings within 10 to 90 percent of the full scale. Only one type of spindle was available. This limited the viscosity range that could be investigated. After all setting was completed, the viscosity of distilled and deionized water was measured and found to be 1.04-cp at 23°C.

6.1.2 Results and Discussion

The results are presented in Figures 23, 24 and 25. During measurement, the readings fluctuated widely. It was also observed that the bubbles going into the adapter tube were much larger than those coming out. This was an indication that significant coalescence was occurring.

The results show that the apparent viscosity of CGA is always higher than that of water. The lowest recorded value of 11-cp was for CGA of .43 quality made with 0.5-g/l T-15S12. Distilled and deionized water gave a viscosity reading of 1.04-cp.
Figure 22: Brookfield Viscometer Modified Adapter Tube
CGA quality showed the most significant effect on the apparent viscosity of CGA (Figure 23). For CGA quality less than 0.60, apparent viscosity increased rather slightly with increase in CGA quality. Above a 0.60 quality however, apparent viscosity of CGA rose sharply as the quality increased. Neither surfactant concentration nor surfactant type showed any significant influence on the apparent viscosity of CGA (Figures 24 and 25 respectively).

That the apparent viscosity of CGA is quality dependent, particularly at quality above 0.60 is logical. As CGA quality increases, the distance between the bubbles decreases. This leads to a corresponding increase in the cohesive force between them. Thus when a shear force is applied, as it is the case during viscosity measurement, there is an increase in the viscous resistance of the fluid. Additional viscous resistance is also created by the interfacial film of the bubbles. Higher quality means more bubbles per unit surface area of the rotating sensing element and hence higher viscous resistance, that is higher apparent viscosity. Neither a change in the type of surfactant molecules nor in surfactant concentration (except at very high concentrations) can viscous resistance offered by CGA of specified property. Consequently, these two variables do not influence CGA’s apparent viscosity.

The apparent viscosity of CGA is unaffected by surfactant concentration as long as the stability of CGA is maintained. When surfactant concentration is too low, below the CMC for ionic surfactants, the bubbles coalesce rather easily during flow causing a lowering of apparent viscosity. Also at high surfactant concentrations, 10-g/l and above, the apparent viscosity may begin to show an increase because of the large number of surfactant molecules present in the continuous phase.
SURFACTANT = T-15S12
CONC. = 0.5 g/l
CGA FLOW RATE = 1.0 cm$^3$/s
CGA TEMP. = 28°C

Figure 23: Effect of Quality on Apparent Viscosity of CGA
SURFACTANT CONC = 0.5 g/l
CGA QUALITY = 0.60
CGA FEED RATE = 1.0 cm³/s
CGA TEMP. = 28°C

Figure 24: Effect of Surfactant Type on Apparent Viscosity of CGA
Figure 25: Effect of Surfactant Concentration on Apparent Viscosity of CGA
6.2 Capillary Viscometric Technique

6.2.1 Theory

For steady pipe flow described in cylindrical coordinates \((r, \theta, z)\), the shear stress, \(\tau_{rz}\) shear rate, relationship derived from the basic shear diagram is

\[
\tau_{rz} = -\mu_a \left( \frac{dU_z}{dr} \right) \quad (5.1)
\]

where \(\mu_a\) = apparent fluid viscosity

\(U_z\) = fluid velocity

From the equation of motion (Bird et al., 1960) or from a simple force balance, the expression for the shear stress is obtained as

\[
\tau_{rz} = -\frac{r}{2} \frac{dp}{dz}
\]

At \(r = R\) (wall), \(\tau_{rz} = \tau_w\), and \(U_z = 0\)

Therefore,

\[
\tau_w = \frac{R}{2} \frac{dp}{dz} \quad (5.2)
\]

And

\[
\tau_{rz} = -\frac{r}{R} \tau_w \quad (5.3)
\]
The expression for the velocity is

$$ U_z = \int_r^R \left( -\frac{dU_z}{dr} \right) dr $$  \hspace{1cm} (5.4)

And the volume flow rate is given by

$$ Q = \int_0^R U_z 2\pi r dr $$  \hspace{1cm} (5.5)

Eliminating $r$ from equations (5.4) and (5.5) using equation (5.3)

$$ U_z = \frac{R}{\tau_w} \int_{\tau_{rz}}^{\tau_w} \left( -\frac{dU_z}{dr} \right) d\tau_{rz} $$  \hspace{1cm} (5.6)

And

$$ Q = 2\pi \left( \frac{R}{\tau_w} \right)^2 \int_0^{\tau_{rz}} U_z \tau_{rz} d\tau_{rz} $$  \hspace{1cm} (5.7)

Combining equations (5.6) and (5.7)

$$ \frac{4Q}{\pi R^3} = \frac{8}{\tau_w^3} \int_0^{\tau_{rz}} \left[ \int_{\tau_{rz}}^{\tau_w} \left( -\frac{dU_z}{dr} \right) d\tau_{rz} \right] d\tau_{rz} $$  \hspace{1cm} (5.8)

Integrating by parts (Oldroyd, 1956)

$$ \frac{4Q}{\pi R^3} = 4 \int_0^{\tau_{rz}} \left( -\frac{dU_z}{dr} \right) d\tau_{rz} $$  \hspace{1cm} (5.9)

Equation (5.9) is the general equation that relates the flow to the velocity gradient in the system.

RHEOLOGICAL PROPERTIES OF CGA
For a Newtonian fluid

\[ \tau_{rz} = - \mu \frac{dU_z}{dr} \]  

(5.10)

In this case, equation (5.6) is reduced to the classical Hagen-Poiseuille equation.

\[ U_z = -\frac{R^2}{4\mu} \frac{dp}{dz} \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \]  

(5.11)

And equation (5.9) becomes

\[ \tau_w = \mu \frac{4Q}{\pi R^3} = \mu \frac{R}{2\mu} \frac{dp}{dz} \]  

(5.12)

If following equation (5.12), a capillary shear diagram is defined as a plot of \( \frac{4Q}{\pi R^3} \) versus \( \tau_w \) for Newtonian fluids; by analogy a definition for non-Newtonian fluids can similarly be defined as

\[ \tau_w = \mu_{ap} \frac{4Q}{\pi R^3} \int_0^{\tau_w} \left( -\frac{dU_z}{dr} \right) d\tau_{rz} \]  

(5.13)

where \( \mu_{ap} = \) pipe apparent viscosity

The relationship between the pipe apparent viscosity and apparent viscosity is

\[ \tau_w = -\mu_{ap} \left( \frac{dU_z}{dr} \right)_w = \mu_{ap} \left( \frac{4Q}{\pi R^3} \right) \]  

(5.14)

The term \( \frac{4Q}{\pi R^3} \) is sometimes referred to as the pseudo-shear rate (Brodkey, 1963).
6.2.1.1 The Power Law

The power law or the Ostwald and de Waele law, a two component empirical model, is the simplest and more commonly used empirical correlation for describing the flow of pseudoplastic fluids (Patton, 1983; Ikoku, 1979; Mungan, 1971, 1972; Savin, 1969; Gogarthy, 1967; Dambon, 1967).

The definition of the power law from a basic shear diagram is

\[ \tau_{rz} = -K \left| \frac{dU_z}{dr} \right|^{n-1} \left( \frac{dU_z}{dr} \right) \]  

(5.15)

where \( n \) and \( k \) are constant.

Similarly, the power law based on the capillary diagram is

\[ \tau_w = K' \left( \frac{4Q}{\pi R^3} \right)^{n'} \]  

(5.16)

Here, \( n' \) is not necessarily constant.

An alternative way of writing equation (16) is (Metzger and Reed, 1955)

\[ n' = \frac{\frac{d[\ln \tau_w]}{d[\ln \left( \frac{4Q}{\pi R^3} \right)]}} \]  

(5.17)

Equation (5.9) can also be differentiated to give

\[ \frac{d[\tau'_w(4Q/\pi R^3)]}{d\tau_w} = 4\tau'_w \left( -\frac{dU_z}{dr} \right)_w \]  

(5.18)

Further differentiation and manipulation of equation (5.18) gives
\begin{equation}
\left( - \frac{dU_z}{dr} \right)_w = \frac{3}{4} \left( \frac{4Q}{\pi R^3} \right) + \frac{1}{4} \left( \frac{4Q}{\pi R^3} \right) \frac{d[ \ln(4Q/\pi R^3) ]}{d[ \ln \tau_w ]}
\end{equation}

Substituting equation (5.17) into (5.19)

\begin{equation}
\left( - \frac{dU_z}{dr} \right)_w = 3n' + \left( \frac{4Q}{\pi R^3} \right)
\end{equation}

At \( n' = 1 \), equation (5.20) reduces to Newton's law with \( K' = \mu \)

Equation (5.20) is useful in obtaining basic shear diagram from capillary data. The value of \( n' \) is obtained from a log-log plot of \( \tau_w \) versus \( 4Q/\pi R^3 \) at a given value of shear rate. This value of \( n' \) is used in equation (5.20) together with \( 4Q/\pi R^3 \) to obtain \( - dU_z/dr \). Equation (5.14) is then used to compute \( \mu_a \) and \( \mu_{ap} \) accordingly.

### 6.2.1.2 Bingham Model

The Bingham model is often written for a steady state condition as

\begin{align*}
\tau_{rz} &= - \mu' \frac{dU_z}{dr} \pm \tau_0 \quad \text{if } |\tau_{rz}| > \tau_0 \\
\frac{dU_z}{dr} &= 0 \quad \text{if } |\tau_w| < \tau_0
\end{align*}

According to the model, a material flows somewhat like a Newtonian fluid when the shear stress is greater than the yield stress \( \tau_0 \) but remains rigid when it is less than \( \tau_0 \).

Integration of the above equation is done in two parts from 0 to \( \tau_0 \) and from \( \tau_0 \) to \( \tau_w \). In terms of the pipe apparent viscosity, the result is (Brodkey, 1963)
\[ \frac{1}{\mu_{ap}} = \frac{1}{\mu'} \left[ 1 - \frac{4}{3} \frac{\tau_0}{\tau_w} + \frac{1}{3} \left( \frac{\tau_0}{\tau_w} \right)^4 \right] \quad \tau_{rz} > \tau_0 \]  

(5.22a)

And

\[ \frac{1}{\mu_{ap}} = \text{Infinite} \quad \tau_{rz} \leq \tau_0 \]  

(5.22b)

Equation (5.22) can be rearranged to fit the capillary shear diagram as

\[ \frac{4Q}{\pi R^3} = \frac{\tau_w}{\mu'} \left[ 1 - \frac{4}{3} \frac{\tau_0}{\tau_w} + \frac{1}{3} \left( \frac{\tau_0}{\tau_w} \right)^4 \right] \]  

(5.23)

\( \tau_0 \) is obtained from the intercept of a plot of \( \tau_w \) versus \( \frac{4Q}{\pi R^3} \) and \( \mu' \) computed from equation (5.23).

6.2.2 Experimental

6.2.2.1 Equipment and Procedure

The setup for studying the rheological behavior of CGA using the capillary viscometric technique is shown in Figure 26.

CGA was generated batchwise using the spinning disc generator as discussed in chapter 3. The surfactant used was NaDBS. Except where surfactant concentration was a variable, a 0.5g/l solution was used. CGA temperature was maintained at 28°C. CGA quality was varied from 0.3 to 0.72 by diluting with surfactant solution for low quality or by using auxiliary air supply for high quality. Quality measurements were carried out as described in chapter 3.
Figure 26. Schematic Diagram for Capillary Viscometry Measurement
The viscometer tube was made of precision bore glass capillary, 0.16-cm inside diameter, .27-cm thick walls and 29-cm long. Pressure drop across the tube was measured using a U-tube manometer A damper, a 0.6-cm inside diameter by 2 feet long horizontal tube, was positioned between the manometer and the capillary tube to help prevent the flow of CGA in the direction of the manometer. The damper was also connected to an air source at the manometer end. At the start of each measurement, air was let into the system momentarily through a toggle valve such that the pressure in the damper was higher than that across the capillary tube. Excess air in the damper gradually bled through the capillary until a steady state was achieved when the pressure drop across the capillary just equaled the manometer reading. At this time the reading of the manometer was taken as being the pressure drop across the capillary tube.

6.2.2.2 Sources of Error

There are undesirable sources of error associated with the capillary viscometric method. These include end effects, geometry, wall effects and flow instability. Capillary end effects do create additional pressure drop resulting in over-estimation of shear stress. Usually, these pressure losses involve frictional losses and kinetic energy corrections associated with the change in velocity and the development of the velocity profile. No adequate expression exists for correlating foam flow because of the complexity of the problem. A good design of the capillary tube that minimizes end effects is therefore essential in the use of the capillary viscometer.

Capillary tube geometry, both length and diameter, also influence the shear diagram and subsequently the apparent viscosity of foam (Patton et. al, 1983; Metzger and Brodkey, 1963). Study with 0.97 quality foam (Patton et. al, 1983) has shown that apparent viscosity increases with increasing capillary diameter but decreases with increasing length. As the diameter of the capillary decreases, the effect of length becomes less pronounced.
Slip at the capillary wall and the thixotropic nature of CGA may also contribute to the complications in the measurement of shear stress. For a given shear rate, increase in length or decrease in diameter will increase the residence time of a fluid element leading to an increase in breakdown and a lowering of shear stress. When slip is present, an increase in diameter will cause an increase in shear stress; but no effect of changing capillary length on the shear stress in the presence of slip as long as steady state conditions exist (Brodkey, 1963).

The compressibility of CGA should not create any significant error provided the pressure drop is relatively low. Also, no significant viscous heating effect due to flow is expected. However, a rise in fluid or ambient temperature would cause a decrease in apparent viscosity (Harris and Reidenbach, 1987).

### 6.2.2.3 Results and Discussion

Capillary data of pressure drop versus flow rate at different CGA quality is presented in Appendix B. Sample calculations are also presented in Appendix B.

The plot of shear stress (equation 5.2) versus pseudo-shear rate \( \frac{4Q}{\pi R^3} \), is shown in Figure 27 for CGA quality varying from 0.30 to 0.72. The figure shows two regions. The first occurs at CGA quality below 0.60. In this region, there is a linear relationship between the shear stress and the shear rate with a defined yield stress, \( \tau_0 \). This pattern is characteristic of Bingham plastic fluids. On the same plot, water (a newtonian fluid) exhibits a zero yield stress. As CGA quality increases above a 0.60 quality, the shear diagram becomes increasingly non-linear and more pseudoplastic in nature. The shear stress versus shear rate diagram is also shown on a log-log plot in Figure 28. The figure shows a switch from an upward looking concave curve to a linear one at a CGA quality of about 0.60 as well.
Assuming the Power Law holds for CGA flow, equation 5.20 has been used to obtain the basic shear rate, \((-dU/dr)_w\). The value of \(n'\) in the correction factor, \(\frac{3n' + 1}{4n'}\), is obtained from the slope of a log-log plot of \(\tau_w\) versus \(4Q/\pi R^3\) at a given value of shear rate (equation 5.16). Figure 29 gives the capillary shear stress versus shear rate relationship according to this model. The figure shows a linear correlation for data obtained with CGA quality above 0.60 as predicted by the power law model. As CGA quality decreases below 0.60, the shear stress versus shear rate relationship gradually becomes non-linear showing that the power law is not adequate in the low quality range.

The pipe apparent viscosity of CGA using the unadjusted pseudo-shear rate values are presented in Table 5. Table 6 gives the apparent viscosity values calculated using the power law model. Sample calculations are shown in Appendix B. The tables show that the pipe apparent viscosity of CGA is higher than the corresponding apparent viscosity predicted by the power law by a factor ranging from 1.07 to 1.52. Both viscosity values show the same trend of increase in apparent viscosity with increase in CGA quality and decrease in shear rate. The values for the apparent viscosity as a function of shear rate and CGA quality plotted in Figures 30 and 31. According to these figures, the change in apparent viscosity with increase in shear rate in very small at low CGA quality. But as CGA quality increases, apparent viscosity changes more rapidly with change in shear rate. For a pseudoplastic fluid, the apparent viscosity decreases with increase in shear rate.

The Bingham plastic model has also been used to calculate the apparent viscosity of low quality CGA. The results are shown in table 7 as well. The values of apparent viscosity predicted by this model are less than those predicted by the power law and are roughly independent of shear rate. A Bingham fluid has a constant apparent viscosity above a given shear stress, like a Newtonian fluid.

As discussed earlier, it is rather conclusive from literature that in those situations where foam has fluid-like properties, it behaves as a non-Newtonian fluid. Because most studies have been limited to very high quality foam, it is often described as a pseudoplastic fluid. This is also the case with

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CGA when the quality is above 0.60. CGA with a quality lower than 0.60, however, fits the Bingham plastic fluid model much better as demonstrated in this studies.

That low quality behaves like a Bingham fluid is expected. The colloidal size of CGA bubbles make the viscous effect created by their interfacial film less pronounced at low CGA quality. Thus as the bubbles flow bubble deformation and shear-induced coalescence would be significantly reduced if present. Indeed, CGA would tend to flow as a particulate system with the bubbles behaving more like rigid particles.

6.3 SUMMARY

In this chapter, the rheological properties of CGA have been examined using both the modified Brookfield viscometer and the capillary viscometer. The results show that the apparent viscosity of CGA is higher than that of the continuous phase. Measured viscosities at high CGA quality can be as much as 10 orders of magnitude higher than that of the liquid phase and $10^4$ times higher than the gas phase viscosity. The presence of micron-sized bubbles have a significant effect on the flow characteristics of CGA.

CGA quality has the most significant effect on apparent viscosity, increasing with increasing quality. At low CGA quality, the apparent viscosity of CGA is only slightly higher than that of the continuous phase. As CGA quality is increased, the corresponding increase in apparent viscosity is exponential. For the same CGA quality, apparent viscosity is independent of surfactant concentration above the CMC for ionic surfactants.
The shear stress versus shear rate relationship at low CGA quality, below 0.60, is a linear one and apparent viscosity appears to be invariant to shear rate. Thus in the low quality domain, CGA can be said to behave like a Bingham plastic fluid. As CGA quality is increased, it gradually becomes more pseudoplastic in nature and conforms better to the power law. The pseudoplastic nature of high quality CGA is well demonstrated at CGA quality above 0.60. Above this quality range, apparent viscosity changes significantly with shear rate. At relatively low shear rate and CGA quality of about 0.70, the apparent viscosity of CGA can be as high as 24-cp.

That CGA has a low apparent viscosity is advantageous in field applications because the pressure force needed to move it through the soil would be correspondingly low. Also, the non-dependence of apparent viscosity on shear rate at low CGA quality suggests that variable flow rates can be used in the field without lowering the the scouring ability of CGA.
Figure 27: Plot of Shear Stress versus Pseudo-Shear Rate for CGA
SURFACTANT = 0.5 g/l NaDBS
CGA TEMP. = 28°C

Figure 28: Log-Log Plot of Shear Stress versus Pseudo-Shear Rate
Figure 29: Log-Log Plot of Shear Diagram for CGA (Power Law)

RHEOLOGICAL PROPERTIES OF CGA
<table>
<thead>
<tr>
<th>$4Q/\pi R^3$ s$^{-1}$</th>
<th>CGA QUALITY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>.30</td>
</tr>
<tr>
<td>414.4</td>
<td>5.16</td>
</tr>
<tr>
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<td>( \frac{4Q}{\pi R^3} ) s(^{-1} )</td>
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TABLE 6
APARENT VISCOSITY OF CGA USING THE POWER LAW, \( \mu_a \) (cp)
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<td>1.97</td>
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**TABLE 7**

**APPARENT VISCOITY OF CGA USING THE BINGHAM LAW, $\mu'$ (cp)**
Figure 30: Effect of Shear Rate on Apparent Viscosity of CGA

SURFACTANT = 0.5 g/l NaDBS
CGA TEMP. = 28°C
Figure 31: Effect of Quality on Apparent Viscosity of CGA
Understanding the flow of CGA through porous media at macro- and micro-pore levels is important in its application in the subsurface environment for hazardous waste remediation. In this chapter, models that may describe the flow of CGA through porous media are discussed. Since CGA can be regarded as a class of wet foam or a gas/liquid mixture, information available in literature on these systems are reviewed. Results of CGA flow through visual laboratory models and through sand-packed columns are presented. The results are discussed in terms of CGA's effectiveness as a flow smoothing agent in porous media of non-uniform pore structure.
7.1 MODELS FOR CGA FLOW THROUGH POROUS MEDIA

Opinions differ among researchers as to the mechanism by which foam like mixtures and their components are propagated through the network of pores in a porous media. Some of these differing views can be broadly classified into the following:

- Pore channel model
- Homogeneous fluid flow model
- Discontinuous fluid flow model
- Bubble train/pop and burst model
- Immobile gas saturation model

7.1.1 Pore Channel Model

Immiscible two phase flow in porous media are generally considered to exhibit pore channel flow (Dullien, 1976; Collins, 1976; Bear, 1972). Here the two fluids are assumed to flow through separate and different pore channels. Neither fluid influences the flow behavior of the other and Darcy's law can be applied to each phase separately. Fluid permeability would therefore be a function of saturation only and Darcy's equation can be written for each phase as

\[ v_1 = -(k_{e1} \mu_1)(\Delta P_1 - \rho_1 g) \]  

(7 - 1a)

\[ v_2 = -(k_{e2} \mu_2)(\Delta P_2 - \rho_2 g) \]  

(7 - 1b)
where \( \mathbf{v} \) = seepage velocity vector
\( k_e \) = effective permeability
\( \mu \) = viscosity
\( P \) = pressure
\( \rho \) = density of the fluid
\( \mathbf{g} \) = gravity vector

The extension of Darcy’s law to multiphase fluid flow is often credited to Muskat and co-workers (1937). The validity of the law for multiphase flow holds only if the effective permeabilities are independent of pressure gradient for a given saturation.

For flow of gas/liquid mixtures through porous media with no surface active agent present, Darcy’s law has been shown to hold appreciably well (Dullien, 1976; Scheidegger, 1964; Leverett and Lewis, 1941). In the case of foam however, the situation is different. Raza (1970), Marsden and Khan (1966), and Bernard and Holm (1964) have shown independently that the permeability of foam is not a single function of saturation because of the associative nature of it’s components.

The presence of a surface active agent in CGA leads to the formation of a highly resilient film between the gas and liquid components. Individual bubbles are separated from one another by the liquid films. The stability of the films are governed by the dynamic surface tension and viscoelasticity of the surface. Interfacial properties are therefore more likely to govern CGA mobility. As such, the pore channel flow cannot adequately describe CGA propagation in porous media.
7.1.2 Homogeneous Fluid Flow Model

The homogeneous fluid flow model (or the plug flow model) considers foam like mixtures to flow as a homogeneous fluid with the gas and the liquid phases moving at the same rate. Fried (1961) first proposed this mechanism based on his observation that when externally generated foam is allowed to flow into a porous media, foam also flows out. Subsequently, other researchers such as Aizad and Okandan (1976), Albrecht and Marsden (1970), David and Marsden (1969), Raza and Marsden (1967), and Marsden and Khan (1966) have supported this proposition. The model regards foam as a continuum with high apparent viscosity. The plug-type flow behavior is responsible for permeability reduction according to these investigators.

Experimental evidence accumulated over the years show that the homogeneous fluid flow model cannot adequately describe foam propagation in porous media. Using a transparent porous media, Holm (1968) observed that foam films are pushed by the internal gas phase until some limiting point. Thereafter, the film breaks and the gas escapes only to get trapped behind the next liquid film or liquid plug near a pore throat.

The work of Minssieux (1974) shown in Figure 32 reveals that liquid saturation along a porous media under foam flow is very uniform except for inlet-end effect. Since pressure in the column decreases along the flow path, gas expansion should result in increasing gas saturation if foam were moving as a continuum. This is contrary to Minssieux's observation again showing a flaw in the mechanism.

The homogeneous fluid flow mechanism can only be considered

- for a very porous medium where the size of the injected CGA bubbles are much smaller than the mean pore diameter of the medium
Figure 32: Saturation Profile of Porous Medium During Steady-State Foam Flow Experiments (Minssieux, 1974)
• the flow rate is high enough to prevent bubble creaming and eventual coalescence within the medium
• foam quality is at most 0.74
• surfactant concentration is high enough (at least above the cmc) such that the bubbles remain relatively stable
• materials that easily destabilize foam bubbles such as organic contaminants are absent in the medium

These conditions are too idealistic and do not often exist. The homogeneous fluid flow mechanism can therefore be ruled out for most practical applications.

7.1.3 Discontinuous Fluid Flow Model

The discontinuous fluid flow model, also referred to as the Film Breaking-Reforming Model, was first proposed by Holm (1968). According to the model, foam continually separates into gas and liquid and reforms foam in the porous medium. The gas phase moves discretely through the medium by rupturing and reforming films along the flow path while the liquid moves as a free phase via the film network.

The discontinuous fluid flow mechanism fits the observation of Minssieux (1974) of uniform liquid saturation along a porous medium (Figure 32). It also suggests that the mobility of both phases would be different. This would allow for the preferential entrapment of the gas phase over the liquid phase resulting in increased gas saturation during unsteady state foam flow as has been observed by Mast (1972), Nahid (1971), and Kolb (1964).

As reported later in this chapter, the mobility of the gas and liquid phases of CGA are indeed different with the liquid phase advancing faster than the gas phase. However, the breaking and re-
forming of gas bubbles during flow is unlikely. This is because when compared with conventional foams, CGA have much smaller bubbles and higher liquid content. As a result the bubbles are more resilient.

7.1.4 Bubble Train/Pop and Burst Model

Sharma et al. (1984) have explained foam flow in porous media in terms of bubble stability. For highly stable foam (usually in the presence of high surfactant concentration), foam flow follows the bubble-train mechanism where the bubbles pass through the pore constrictions one at a time. The shape and size remains approximately the same before and after the pore-neck but may undergo temporary deformation at the pore-neck (Figure 33). For situations when the bubble stability is low (low surfactant concentration), the pop and burst mechanism has been suggested. Here the bubbles bust into smaller ones as they pop through the pore necks of the porous medium. The bubbles may then coalesce into bigger ones before entering the next pore channel (Figure 33).

The bubble train mechanism tends to be in line with the homogeneous fluid flow mechanism, while the pop and burst mechanism is of the discontinuous fluid flow type. These two mechanisms are more likely to hold in steady state CGA flow than under unsteady state flow conditions provided the applied inlet pressure is higher than the blocking pressure of the medium. Other factors that would influence the efficacy of the model include those already discussed under the homogeneous fluid flow and the discontinuous fluid flow mechanisms.
Figure 33: The Bubble Train/Burst and Pop Model (Sharma et al., 1984)
7.1.5 Immobile Gas Saturation Model

Some researchers have observed that when foam flows through a porous medium, a portion of the gas phase is trapped within the medium as an immobile phase (Mast, 1972; Nahid, 1971; Kolb, 1964). The trapped gas blocks some of the flow channels and increases the gas saturation of the medium above that corresponding to the quality of incoming foam. Blockage of flow channels causes increased resistance to flow through the medium. If the pumping pressure is not sufficiently high, flow will cease. To maintain flow, a pressure higher than the blocking pressure will be necessary.

Both pumping pressure and surfactant concentration have been identified as factors controlling trapped gas saturation (Nahid, 1971; Bernard, 1965). Increase in either pumping pressure or surfactant concentration will often result in increased gas saturation. Other variables such as gas to liquid ratio and average pore diameter of the medium would also have effect. As will be shown in the experimental section of this chapter, substantial gas hold-up does occur in a porous medium during CGA flow. Gas saturation was always higher than CGA quality and was particularly influenced by the surfactant concentration and pore structure of the medium.

7.1.6 Remarks

The complex structure of pores inside a porous media and the intricate nature of CGA suggests that no single model can accommodate all the factors associable with CGA propagation in porous media. In fact two or more of these flow mechanisms may occur side by side in a porous media as has been observed by Owete and Brigham (1981). These investigators have studied, under laboratory conditions, pore level behavior of foam in heterogeneous and homogeneous porous micro-models previously filled with surfactant solution into which air was injected.
They observed that in the heterogeneous micromodel, air and liquid propagation were by a combination of channel flow (with liquid confined to small pores) and the discontinuous fluid flow model. The break and reform process was due to snap-off actions at pore constrictions. In the homogeneous micromodel, the wetting phase formed a continuous liquid network around the matrix. The air phase was found to propagate as tubular bubbles moving and extending over several pores.

While the design of the study by Owete and Brigham is somewhat different from that carried out in this study (i.e. Owete and Brigham introduced the gas and liquid phases into the porous matrix separately whereas comminution between both phases was achieved in CGA before injection in this study) their observation that propagation could be by more than one mechanism is in agreement with that observed during CGA flow. As discussed later in this chapter, both the discontinuous model and the gas saturation model appear to fit CGA flow through porous media.

7.2 **CGA FLOW VISUALIZATION STUDIES**

Visual laboratory models offer a valuable tool in the study of multiphase flow through porous media at micro- and macro-pore levels. At the micro-pore level, Owete and Brigham (1981) used an etched silicon wafer anodically bonded to a glass plate, simulating a monolayer of porous matrix, to visually observe the flow characteristics of foam under varying air injection rates, pore dimensions and surfactant concentration. Campbell and Orr (1985) have also reported pore-level visual observation of high-pressure carbon dioxide floods in two-dimensional pore networks etched in glass plates.
The effects of interfacial tension on fluid displacement behavior through flow visualization cells formed by thin layers of sintered glass beads have been studied by Horrof and Morrow (1988). Peterson et al. (1984) used a slab of consolidated plastic particles to visualize surfactant flood of an oil-saturated porous medium. Sarma (1986) has also reported the use of a rectangular plexiglas model packed with glass beads to obtain qualitative and quantitative descriptions of viscous fingering in fluid-fluid displacements in a porous medium. Studies using similar visualization cells have been reported by Williams and Dawe (1987), Egbogah and Dawe (1980), Wardlaw and Cassan (1978), and by Kyle and Perrine (1965).

In this study, a flow visualization cell was used to study the penetration and dispersion of CGA through well characterized soil/groundwater systems. The frontal advancement of the gas and liquid phases of CGA and pressure drop across the cell were monitored as a function of CGA properties and flow variables. The results are discussed both qualitatively and quantitatively. The qualitative analysis helps to gain a visual insight of the flow mechanism while quantitative analysis is aimed at finding out the effect of different parametric variables.

7.2.1 EXPERIMENTAL

7.2.1.1 Equipment and Procedure

Essentially there are three parts to the flow visualization study - the CGA generation system, the visualization cell and an effluent recovery system.

CGA Generation: CGA generation assembly ia as described previously in chapter 3. Three surfactants were used - Sodium dodecylbenzene sulfonate (NADBS), Alkyloxypolyethylenoxyethanol (T-15S12) and Cetyl pyridinium chloride (CPC). Their properties
are given in Table 1. The temperature of CGA was maintained at 28°C while surfactant concentration, CGA quality and flow rate were varied as necessary. A dye, 0.025-g/l bromophenol blue, was added to the surfactant solution to improve the visual and photographic observations of the flow of CGA and its components.

**Visualization Cell:** The visualization cell is shown in details in Figure 34. It is a transparent rectangular model made from two plexiglas plates. The plates were machined at both ends to create recessed rectangular grooves across the width which served as inlet and outlet regions. A 1/4-in thick spacer was placed between the two plates to separate them. Thus a porous media region 25.4-cm x 38.1-cm x .803-cm was created with a 25.4-cm x 1.91-cm x 2.54-cm outlet groove. The inlet groove acted as a distributor allowing CGA to be distributed evenly across the width of the cell. The outlet groove eliminated the directional flow which would have resulted from all the fluid converging towards a single point. The cell was sealed with silicone-rubber glue and 62 socket cap screws. Two holes fitted with 1/4-in male type swageloks were drilled at each end. These were used as inlet port, outlet port and pressure taps.

**Materials:** Three different testing sands were used in the study. Their properties as well as those of the test models are given in Table 8. Particle density was determined by measuring the volume of liquid displaced by 200-g of sand in a 250-ml graduated cylinder that contained 130-ml of water.

**7.2.1.2 Procedure**

The set-up for the flow visualization studies is shown in Figure 35. The rectangular cell was packed with appropriate test sand using a 1/2-in feed port at the corner of the outlet end. A flush type screw cap was used to seal the feed port after loading the cell. At the recovery end, the gas liquid effluent flowed into a separator. The gas phase was then passed into a graduated cylinder inverted
Figure 34: CGA Flow Visualization Cell
Figure 35: Set-Up for CGA Flow Visualization Studies
TABLE 8
Properties of Packed Visualization Cell

CELL SPECIFICATIONS

Width = 10.0 in (25.4 cm)
Spacing = 3/6 in (0.80 cm)
Length of Packed Region = 15 in (38.1 cm)
Length of Inlet Region = 1/2 in (1.27 cm)
Length of Outlet Region = 1 in 2.54 cm)
Volume of Packed Region = 47.4 in$^3$ (776 cm$^3$)
Packing Material = Ottawa Testing Sand

PACKING SPECIFICATIONS

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<th>II</th>
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<td>Void Fraction</td>
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<tr>
<td>Absolute Permeability (darcy)</td>
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<td>88</td>
<td>42</td>
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in a trough of water. The volume of the liquid effluent was also measured. A masterflex peristaltic pump equipped with digital display and flow control was used to inject and control all fluids.

With the cell mounted in the upright position, air was displaced from the cell with carbon dioxide for about 1-hour at a flow rate of 5 to 8 standard liters per minute. The cell was then flooded slowly with a known volume of distilled and de-ionized water to determine the pore volume and the porosity. After determining the pore volume, it was flushed with at least 6 pore volumes of distilled and deionized water to remove any dissolved carbon dioxide. To determine the permeability of the packed cell, water was passed through at different low flow rates. The pressure drop across the cell was measured at steady state and the permeability determined from Darcy’s equation.

\[
k = \frac{QL}{A\Delta H} \left( \frac{\mu}{\rho g} \right) \tag{7-2}
\]

where 
- \(k\) = intrinsic permeability, \(s\)
- \(Q\) = volumetric flow rate, \(cm^3/s\)
- \(L\) = flow length, \(cm\)
- \(A\) = cross sectional area
- \(\Delta H\) = pressure drop, \(cm\) of water
- \(\mu\) = viscosity, \(g/cm\cdot s\)
- \(\rho\) = density of the fluid, \(g/cm^3\)
- \(g\) = acceleration due to gravity, \(cm/s^2\)

\(k\) is converted from seconds to darcy by dividing by \(0.987 \times 10^{-4}\)

CGA was pumped into the cell at a given flow rate between 0.1 and 0.8 \(cm^3/sec\). Three cell positions were examined:

- upright position with CGA injected from the bottom
- sideways with CGA injected from one side
The variables studied were surfactant type, soil type, and CGA input rate. The frontal advancement of CGA, and its liquid and gas components were monitored as a function of time using a 35mm Minolta camera (model X700). The pressure differential across the cell was also monitored using test pressure gauges.

7.2.1.3 Results and Discussion

Qualitative Analysis: Photographs of the cell taken during the test runs were analyzed to determine the frontal movement of CGA and its components through the unconsolidated porous matrix. A set of such photographs is presented in Figure 36. The use of a blue dye in the liquid phase of CGA helped to improve the photographic contrast.

On entering the cell, CGA first dispersed across the width of the cell filling the entrance zone. This was generally the case irrespective of the mounting position. As CGA moved along the length of the cell, the liquid phase and the gas phase developed different fronts with the liquid phase advancing faster than the gas bubbles. The gas bubbles were retarded by the medium. Thus after some time, two rather uniform advancing fronts could be noticed, one for the liquid phase and another showing the front of the gas bubbles with the liquid phase of incoming CGA passing by. Formation of fingers was not visible at the CGA-gas interface and only slightly visible at the CGA-liquid interface. Fingering is known to decrease when the mobility of the displacing fluid is reduced.

The inherent fluid in the cell was displaced by the advancing CGA-liquid phase. Thus at CGA-liquid break-through, all the liquid in the porous matrix of the cell had been displaced. No CGA-gas break-through occurred ahead of CGA-liquid break-through. There was usually a mixing
zone between the liquid originally present in the cell and the CGA-liquid and between the CGA-gas and CGA-liquid zones. The size of these zones varied depending on the permeability of the medium, increasing with decreasing permeability. Figure 37 is a schematic representation of the different fronts at CGA-liquid break-through.

The retardation of CGA bubbles resulted in a gradual pressure increase as the flow progressed. Thus the distance between the CGA-liquid phase and CGA-gas phase increased with time until CGA-liquid break-through. As a result of the liquid component of incoming CGA which had to move through the retarded gas bubbles, some of the liquid phase was always present in the region. Results discussed latter (Figure 46) show that the mobility rate of the liquid phase could be as much as twice that of the gas phase.

Quantitative Analysis: Here, a quantitative analysis of the effects of flow rate, volume of CGA injected, surfactant type, soil particle size and cell orientation are presented. These variables are discussed in terms of pressure drop across the cell and the position of the CGA-gas and CGA-liquid fronts. The volume of CGA injected is dimensionalized in terms of the pore volume of the packed cell. The pore volume is the volume of void in the cell that can be occupied by the liquid or gas phase.

Effect of Flow rate: The movement of CGA through the sand packed cell as characterized by CGA flow rate is presented in Figures 38 to 41. Both NaDBS and T-15S12 showed similar pressure drop/flow rate characteristics. At a constant flow rate, the pressure drop initially rises rapidly and then tails off as CGA penetrates the cell (Figures 38 and 39). The tail-off of the pressure drop corresponds to the break-through of the CGA-gas phase which usually occurred after 3 or more pore volumes of CGA had been injected.
Figure 36: Pictures of Frontal Advancement of CGA with Time
Figure 37: Schematic Representation of Frontal Advancement of CGA
At very low CGA flow rate, the rise in pressure drop was less rapid. But at higher flow rate, no significant difference was observed in the pressure drop/CGA volume gradient. The same is true of the frontal movement of CGA-gas front as a function of CGA flow rate (Figures 40 and 41). Since CGA of constant quality (gas fraction) was used in these tests, the relationship between the pressure drop and total gas injected into the cell or between the CGA-gas front and the total gas phase injected would be as given by these figures.

When CGA flows through a porous medium that is not initially saturated with a surfactant solution, as in this case, the bubbles in the advancing front would coalesce more readily. The surfactant molecules at the bubbles interface that help to stabilize them would easily be stripped off through mixing action with the inherent fluid and by adsorption by the packing medium. As a result, less surfactant molecules would be available to stabilize the bubbles. If, therefore, the movement of the bubbles through the medium is relatively slow the problem of bubble coalescence would be increased significantly. The situation could in fact approach that of a stagnant CGA column where the bubbles would cream to the top and begin to coalesce. In this case the creaming and coalescence action would occur within the pores. Furthermore, since CGA bubbles move slower than the liquid phase, bubble coalescence at low flow rate would be further enhanced. In other words, the argument advanced in chapter 5 that some hydrodynamic force is always needed to stabilize CGA would still apply in this case.

Observations of the size of CGA bubbles during flow through packed columns discussed later do reveal that the sizes of CGA bubbles coming out a packed medium are often larger than those of inlet ones and when the flow rate is too low, no bubbles are seen at the outlet, only the gas releases as in gas sparging. Another observation that supports this is the fact that once CGA flow stops, the very small CGA bubbles within the medium soon disappears, leaving dry pores that are now filled by the gas phase of the CGA bubbles. That is a situation of no flow would result in CGA bubble coalescence. Since the high pressure drop observed during CGA flow is attributed to the bubbles, any move towards loss of bubble integrity would also result in a slower pressure development. Thus to minimize this problem, the flow rate of CGA has to be high enough such that the
effective hydrodynamic force mitigates against any perturbation at the interface that can promote coalescence.

The results shown in Figures 40 and 41 demonstrate, except at very low CGA flow rate, a linear relationship between the movement of the CGA-gas front and the volume of CGA injected. Since the quality of CGA was kept constant, the movement of the CGA-gas front can be said to be linearly dependent on the amount of gas phase present. That is there is a gas saturation level within the cell that has to be reached before CGA bubbles can advance forward. The magnitude of this gas phase saturation and the effect of other process variables will be examined further in the next section.

That large pressure drops are required to move CGA through soil is evident from Figures 38 and 39. This may pose practical limitations in terms of field applications. On the other hand, it is very beneficial for mobility control in the subsurface environment. Large pressure drops imply more efficient areal sweep and selective plugging or diversion of flow from high-permeability to low-permeability regions.

**Effect of Surfactant Type:** Figures 42 through 46 show the effect of using different surfactant types on CGA flow through the visualization cell. Of the three surfactants used, T-1 SS 12 showed the most rapid rise in pressure drop and earliest CGA-gas break-through as CGA was injected. This was followed by NaDBS which was just slightly higher than CPC (Figure 42). In terms of the maximum pressure drop, however, the reverse was true with CPC having the highest pressure drop at break-through (16-psi) followed by NaDBS (15-psi) and T-15S12 the lowest (14-psi) (Figure 43 at CGA-gas front = 1).

The difference in performance between these three surfactants becomes more evident when we compare the CGA-frontal movement as a function of volume of CGA injected (Figure 44). The
fastest moving front was T-15S12 bubbles and the slowest CPC bubbles. The performance of NaDBS was mid-way requiring about 3 pore volumes of CGA at CGA-gas phase break-through. There is no significant difference in the CGA-liquid front between the surfactants as shown in Figure 45. The break-through of the CGA-liquid phase occurred at about 1.5 pore volume. The plot of the CGA-gas front versus the CGA-liquid front (Figure 46), shows that the mobility rate of the CGA-liquid phase is roughly twice that of the CGA-gas phase for all three surfactants. The CGA bubbles are held longer because of the resistance to flow encountered as they move through the pores and constrictions in the medium. This will be discussed further in the next section.

Two possible factors that could account for the observed differences in the movement of CGA with these three surfactants are differences in bubble size and the bond strength between the bubble and the sand’s surface. As reported in chapter 4 under bubble size measurement, the mean bubble diameter of CGA generated with CPC, NaDBS and T-15S12 were found to be 53.5µm, 53.2µm and 50.5µm respectively. The smaller CGA bubbles generated with T-15S12 would display a higher mobility rate through the medium. A more probable explanation is the net charge of the surfactant when in solution. Because T-15S12 is a nonionic surfactant, the bubbles would experience less adsorption to the negatively charged sand packing. In addition to enhancing the mobility, coalescence would be reduced. As a result there would be a faster pressure build-up as observed. But the lower force of adsorption coupled with smaller bubbles would result in early break-through of the CGA-gas phase, a lower holding volume of the gas phase and consequently a lower pressure drop at CGA-gas phase break-through.

On the other hand, CPC which is a cationic surfactant would produce bubbles that would adhere stronger to the negatively charged packing medium. This in conjunction with their relatively larger bubbles would move less rapidly through the packed medium and lead to a higher pressure drop at break-through. The slow pressure build-up could be caused by increased coalescence at initial bubble contact with the sand’s surface. NaDBS has the same negative charge as the packing and its performance would fall in between these two cases as observed.
Effect of Cell Orientation: Figure 47 shows the results of pressure drop as a function of CGA volume injected with the cell mounted in the vertical, horizontal and flat positions. Initially, there was no significant difference in the performance of the three positions. Towards the middle of the cell, the vertical position showed a higher pressure drop than the other two positions. In the second half of the cell, however, both vertical and horizontal positions showed a gradual decline in pressure drop build-up. The pressure drop history of the flat position was more consistent and eventually gave the highest pressure drop at CGA-gas break-through. The decline in pressure gradient for the vertical and horizontal positions is a consequence of gravity effect on the bubbles which would tend to induce an upward movement, expand and/or coalesce the bubbles with a corresponding pressure loss.

For the CGA frontal movement, Figure 48, the result is similar. No significant difference occurred between the three positions through the first half of the cell again showing that gravity effect did not influence the mobility of CGA in this region. But in the second half of the cell, the vertical position did show a more rapid movement of the CGA-gas front. In this region, the gravity segregative effect was giving the bubbles some mobility enhancement. The bubbles would then expand and/or coalesce into bigger ones leading to a lowering of pressure gradient as discussed earlier. Thus to eliminate the influence of gravity on the performance characteristics, most of the tests were carried out with the cell in the flat position.

Effect of Particle Size: In Figures 49 through 52, the results of the effect of varying the particle size of the packing media on the flow characteristics of CGA are presented. The specifications for the three different packings are given in Table 8. As shown in Figure 49, the pressure gradient is strongly dependent on the size of the packing material, increasing with decreasing particle size. As expected, the position of the frontal advancement of the CGA-gas component changed with the smallest size packing requiring the most CGA injection before break-through (Figure 50).
The ease with which CGA moves through a porous media would depend, not only on the permeability of the medium, but also on the sizes of the pores and throats, the presence of dead end pores and the heterogeneity of the system. The lower the permeability the less the resistance to fluid flow. Large pore and throat dimensions would lower the pressure drop as a result of decreased resistance to flow; but dead end pores would increase it. Also, the more heterogeneous the medium the higher the tendency to produce increased instability at the CGA-gas front as the bubbles are propagated through pores and throats of different dimensions. This would increase bubble coalescence, increase the mobility of the gas phase and subsequently lower the pressure gradient.

Of interest in field applications is the change in pressure drop with CGA flow compared to water flow. This is presented in Figure 51. It turns out that when the pressure drop for CGA flow through the same medium, is thus normalized, CGA proves to be more effective in blocking the more permeable medium media than a less permeable one. This permeability correction potential of CGA is the more evident when one considers the relationship between the mobility of the liquid phase of CGA relative to the gas phase (Figure 52).

The unique ability of CGA to preferentially block high permeable porous media over less permeable ones is important in achieving a more uniform fluid flow and fluid saturation in porous media. This is investigated further in the next section.
Figure 38: Pressure Drop versus Volume of CGA at Different Flow Rates

SURFACTANT = 0.5 g/l NaDBS
PACKING = 20–30 mesh
POSITION = FLAT

FLOW RATE (cm³/s)

△ = 0.33
+ = 0.75
O = 1.17
* = 1.58
□ = 2.00
Figure 39: Pressure Drop versus Volume of CGA at Different Flow Rates
Figure 40: Relative Position of CGA-Gas Front versus CGA Volume
Figure 41: Relative Position of CGA Front versus Volume OF CGA
FLOW RATE = 0.75 cm³/s
PACKING = 20-30 mesh
POSITION = FLAT

Figure 42: Pressure Drop versus CGA Volume for Different Surfactants
PACKING = 20-30 mesh
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm³/s
POSITION = FLAT

Figure 43: Pressure Drop versus Frontal Movement of CGA-Gas for Different Surfactants
SURFACANT

\[ \triangle = T-15S12 \]

\[ + = \text{NaDBS} \]

\[ \square = \text{CPC} \]

PACKING = 20–30 mesh
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm\(^3\)/s
POSITION = FLAT

Figure 44: Relative Position of CGA–Gas Front versus CGA Volume:
Effect of Surfactant Type

CGA FLOW THROUGH POROUS MEDIA 137.
PACKING = 20–30 mesh
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm$^3$/s
POSITION = FLAT

Figure 45: Relative Position of CGA–Liquid Front versus CGA Volume
PACKING = 20-30 mesh
FLOW RATE = 0.75 cm³/s
POSITION = FLAT

SURFACTANT
(Conc = 0.5 g/l)

△ = T-15S12
+ = NaDBS
□ = CPC

Figure 46: Relative Position of CGA-Gas Front versus CGA-Liquid Front
SURFACTANT = T-15S12
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm$^3$/s
PACKING = 20–30 mesh

Figure 47: Pressure Drop versus CGA Volume Injected for Different Cell Positions
Figure 48: Relative Position of CGA Front versus CGA Volume Injected: Effect of Position
Figure 49: Pressure Drop versus CGA Volume Injected: Effect of Size of Packing

SURFACTANT = T-15S12
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm$^3$/s
POSITION = FLAT

PACKING DIAM.
Δ = 0.718 mm
+ = 0.343 mm
□ = 0.254 mm

CGA FLOW THROUGH POROUS MEDIA
Figure 50: Relative Position of CGA-Gas Front versus CGA Volume: Effect of Particle Size

CGA FLOW THROUGH POROUS MEDIA
Figure 51: Pressure Drop versus CGA Volume Injected:
Effect of Packing Size

PACKING DIAM.

\[ \triangle = 0.718 \text{ mm} \]
\[ + = 0.343 \text{ mm} \]
\[ \square = 0.254 \text{ mm} \]
SURFACTANT = T-15S12
CONC. = 0.5 g/l
FLOW RATE = 0.75 cm$^3$/s
POSITION = FLAT

PACKING DIAM.
$\triangle$ = 0.718 mm
$+$ = 0.343 mm
$\square$ = 0.254 mm

Figure 52: CGA-Gas Front versus CGA-Liquid Front for Different Packings
7.3 FLOW SMOOTHING IN POROUS MEDIA USING CGA

In this section, the use of CGA as a flow smoothing agent in porous media of non-uniform pore structure is examined. Results of CGA flow through porous media reported earlier in section 7.2 showed that, compared to water, the relative pressure drop increases as the permeability of the medium increases. Thus when CGA was flowed through sand slabs of different particle sizes, the pressure drop decreased as the particle size increased, but the pressure drop relative to water flow increased dramatically. This observation suggests that CGA will move preferentially in the direction of lower flow resistance (wider pores), and that the degree of permeability reduction is higher in such systems. Once the larger pores are blocked, fluid flow is diverted into smaller ones. The result is the smoothing out of the flowing fluid through the entire cross section of the porous medium.

Selective plugging or diversion of flow from high to low permeability regions of heterogeneous porous media poses tremendous advantage in the application of CGA including it's use to displace hydrophobic contaminants from soil (see chapter 8).

The concept of using CGA to preferentially block large pores in porous media is similar to the idea of using foam as a blocking agent. The use of foam as a blocking agent in porous media was first suggested by Bond and Holbrook (1968). Since then, several investigators have studied the idea under both laboratory and field conditions. (Holm and Garrison, 1988; Phillip, 1987; Heller et al., 1985; Owete and Brigham, 1981; Bernard et al., 1980, 1965 Albrecht and Marsden, 1970; Holm, 1970; and Raza, 1970; Bernard and Holm, 1964).

Albrecht and Marsden (1970) observed that after steady foam flow has been established at a certain injection pressure and the injection pressure is decreased, foam flow will cease at some pressure.
The pressure when foam flow stops is called the blocking pressure. According to these researchers, the blocking pressure will increase if the injection pressure or the surfactant concentration increases. Raising the injection pressure would force more bubbles into smaller and dead-end pores while an increase in surfactant concentration would improve the stability of the bubbles. As a result resistance to flow would be increased.

The blocking of porous media by foam has been studied in the laboratory in terms of permeability lowering to gas flow (Bernard and Holm, 1964), and aqueous flow (Bernard et al., 1965). In both studies, foam was found to significantly decrease the permeability of consolidated and unconsolidated porous media. According to Bernard and Holm (1964), foam succeeded in lowering the permeability of loose sand better than tightly packed sand. Reduced permeability to gas as a result of foam injection ranged from factors of $3 \times 10^{-5}$ to $6 \times 10^{-3}$. Permeability lowering of porous media to water by foam was found to be related to the trapped gas saturation (Bernard et al., 1965). The relative ease with which foam is able to move into larger pores would increase gas saturation and lower permeability in such media. As the concentration of surfactant increased, so was the trapped gas saturation with a corresponding decrease in permeability. Increase in surfactant concentration would increase gas phase saturation through increase in bubble stability.

In the steam-foam drive process, a technique commonly used in tertiary oil recovery, foam is used to lower gas relative permeability thereby enhancing steam drives. Such a reduction in steam mobility by foam has been found to be up to 40-fold under laboratory conditions (Dilgren et al., 1982). Several field enhanced oil recovery tests have also shown that foam enhances the steam drive process through the selective plugging of large pores (Falls et al., 1988; Plog and Duerksen, 1985; Brigham, 1984; Eson, 1983; and Greaser, 1980).

These findings point to the fact that foam preferentially blocks large pores that often account for early break-through of injection fluids which would normally result in poor areal sweep efficiency. Once the large pores are blocked, injection fluid can be directed into the smaller, less permeable pores that are often of interest in most field applications.
In order to quantify the flow smoothing characteristics of CGA in terms of variables that can be measured under laboratory conditions, a series of steady state CGA flow through unconsolidated porous media was performed. The pressure drop of these experiments was measured for given flow conditions and the results analyzed in terms of gas phase saturation, mobility and blocking tendency of CGA.

Under uniform flow conditions, the average mobility of CGA can be defined as the ratio of superficial flow velocity to the pressure gradient.

\[ \lambda_{av} = \frac{Q/A}{\Delta P/L} \]  

(7 - 3)

where \( \lambda_{av} \) = average CGA mobility in \( cm^2/(atm.s) \) or darcy/cp  
\( Q \) = total volumetric flow rate of CGA at atmospheric conditions  
\( \Delta P \) = pressure drop across the porous medium  
\( A \) = cross-sectional area of the sample  
\( L \) = length of the sample

Mobility, as defined above, is inversely proportional to the pressure drop across the medium. For flow of homogeneous or non-associated fluids, mobility reduces to the permeability of the porous medium, in darcy, divided by the fluid viscosity, in centipoise. Since for non-interacting, Newtonian fluids, the calculated permeability is independent of both the sample dimensions, the flow rate and fluid viscosity, the mobility of such fluids would also be independent of sample dimensions and flow rate. In the case of CGA flow, only sample dimensions can be assumed not to influence mobility. Thus experimental determination of CGA mobility had to be under constant flow rate and pressure drop. Because of the compressible nature of CGA due to the presence of a gas phase, the volumetric flow rate is defined at pump inlet (atmospheric) conditions.

It is also possible to define the relative mobility of CGA, the mobility of CGA relative to the mobility of a single phase such as water.
\[ \lambda_{rel} = \frac{\lambda}{\lambda_o} \quad (7-4) \]

where \( \lambda_{rel} = \) relative mobility
\( \lambda = \) CGA mobility
\( \lambda_o = \) mobility of a water

For a given porous media of defined geometry, the relative mobility would be the ratio of the pressure drop for single phase flow \( \Delta P_o \), to that of CGA flow.

\[ \lambda_{rel} = \frac{\Delta P_o}{\Delta P} \quad (7-5) \]

7.3.1 EXPERIMENTAL

7.3.1.1 Equipment and Materials

The set-up for this study is presented in Figure 53. The CGA generation assembly is as described in chapter 3. All three surfactants given in Table 1 were used (NaDBS, T-15S12 and CPC). The temperature of CGA was kept at 28°C while surfactant concentration and CGA quality were varied as desired.

The porous medium was a Corning pyrex glass column, 3.81-cm inside diameter, 0.44-cm thick walls and either 30.8-cm or 15.4-cm long. The shorter length was used for low permeability packing to keep the maximum pressure drop below the column’s design limit. The column was packed with either sand or glass beads of desired size distribution. Two aluminum blocks, 0.64-cm thick, machined out to create a recessed circular groove for fluid entry and exit from the column were fitted at the ends. A stainless steel screen covering each groove was secured between the block and
a gasket that creates a good seal with the glass column. A sectional drawing of the column and its fittings is given in Figure 54.

Ottawa testing sands (20-30 mesh and 50-70 mesh) and glass beads of different particle sizes were used as packings (Table 9). These are good standard materials that allow for easy reproduceability and more accurate determination of the effects of experimental variables. The packed column was prepared by closing one end and gradually pouring a pre-determined weight of packing material into it. A fixed weight of material was used for each test in order to maintain a constant porosity. The optimum weight of packing material needed to give the closest packing was determined through a series of trial packings. The column was kept vibrating as sand was poured in slowly. Once the packing was completed, the aluminum end-plate was tightened. Care was taken not to allow sand particles to be trapped between the column and the gasket at the end of the end-plate. To ensure tight packing, air was allowed to flow through the column at pressures up to 25 psi during which particle movement along the column wall was carefully observed. Any particle movement was taken as a sign of loose packing so that the column had to be dismantled and repacked. The process was repeated until a satisfactory packing was obtained.

7.3.1.2 Procedure

The packed column was flushed vertically with carbon dioxide for at least 30 minutes to displace interstitial air. Carbon dioxide being heavier than air would readily displace it. Deionized and distilled water was then pumped into the carbon dioxide filled packed column using a metering pump to determine the pore volume. The high solubility of carbon dioxide in water also helps to eliminate trapped gas bubbles in the porous medium. The absolute permeability of the packed column was determined by pumping water through at different low flow rates using the Darcy equation. Darcy's law holds very well at Reynolds number less than about 1. The low pressure drop was measured using a piezometer.
Figure 53: Set-up for Column Flow Studies

1. Surfactant Solution  6. CGA Generator
2. Metering Pump      7. Packed Column
5. Pressure Regulator 10. Effluent Collector
Figure 54: Sectional Drawing of Column and Fittings
TABLE 9

Column and Packing Specifications For Flow Studies

COLUMN SPECIFICATIONS

Length = 30.8 cm
Diameter = 3.81 cm
Total Volume = 351 cm$^3$
Diameter/Length Ratio = 1/8
Inlet Diameter = \( \frac{5}{16} \)
Column Diameter
Packing Material = Ottawa Testing Sand

PACKING SPECIFICATIONS

<table>
<thead>
<tr>
<th></th>
<th>Column A</th>
<th>Column B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve Size (mesh)</td>
<td>20-30</td>
<td>50-70</td>
</tr>
<tr>
<td>Mean Particle Size (mm)</td>
<td>0.718</td>
<td>0.254</td>
</tr>
<tr>
<td>Weight of Packing (g)</td>
<td>600</td>
<td>566</td>
</tr>
<tr>
<td>Volume of Packing (cm$^3$)</td>
<td>228</td>
<td>215</td>
</tr>
<tr>
<td>Void Fraction</td>
<td>0.350</td>
<td>0.387</td>
</tr>
<tr>
<td>Absolute Permeability (darcy)</td>
<td>293</td>
<td>37</td>
</tr>
</tbody>
</table>
For each flow experiment, the column was positioned horizontally on a wooden support. CGA of desired properties was generated as described previously and pumped into the column until the pressure difference remained constant. This required at least 4 pore volumes of CGA. Pressure drop across the column was measured by means of an Omega Model DP-50 differential pressure transducer and recorded. The pressure drop was converted into an electrical signal using a demodulator. The electrical signal is then sent to a chart recorder for continuous recording of the pressure drop. Calibration of the transducer was done in-situ with a high precision test pressure gauge. The gas saturation was determined gravimetrically by weighing the column before and after each experiment. At this time the pressure had dropped rapidly. Water was then pumped through at the same flow rate as CGA. The pressure rose again and became steady at water break-through. This steady pressure was recorded as a measure of the blocking tendency of CGA.

7.3.1.3 Results and Discussion

The variables examined were surfactant concentration, surfactant type, CGA quality, CGA injection rate and grain size of the packing material. Ottawa testing sand was used for most of the tests except where the effect of particle size was examined. In such tests, glass beads were used because they offer different particle sizes having better size homogeneity. Since the primary constituent of both materials is silica, no significant difference in performance is expected as a result of chemical composition. The results are discussed in terms of gas saturation after CGA flow, pressure drop at steady CGA flow, CGA mobility at steady state, and the blocking tendency of CGA in a porous media.

Effect of Surfactant Concentration: Figure 55 shows the effect of surfactant concentration on the pressure drop across a sand-packed column when a steady CGA flow is maintained. The surfactant
used was NaDBS. The concentration was varied between 0.5-g/l and 10.0-g/l. Bubble instability did not allow for successful testing at lower concentrations. For the two types of sand tested, no significant effect of surfactant concentration was found on the pressure drop in this concentration range. Since the surfactant concentrations were above the CMC, bubble stability would be approximately constant. Hence the pore structure of the medium would primarily determine the steady state pressure drop as shown in Figure 55.

When the gas saturation level in the sand-packed column was determined, surfactant concentration did show some effect (Figure 56). The gas saturation increased as the surfactant concentration was increased. In studies involving foam flow, surfactant concentration was also identified as a factor controlling trapped gas saturation (Nahid, 1971; Bernard, 1965). In these studies, increase in surfactant concentration resulted in increased gas saturation.

Gas saturation is defined as a percentage of the pore space that is occupied by the gas phase after a steady CGA flow. This would be at least be equal to CGA quality. Because of the gas phase retardation during flow, the gas saturation exceeded the quality of CGA. In general, CGA was very effective in maintaining a high residual gas saturation, above 90 percent. The values of gas saturation reported in literature for foam is usually around 80 percent or less (Bernard and Holm, 1964, Bernard et al., 1965, Minssieux, 1974). The gas distribution is also expected to be almost uniformly distributed along the length of the column according to Minssieux (1974).

**Effect of CGA Quality:** The relationship between pressure drop and CGA quality is a linear one according to Figure 57. The pressure drop across the sand-packed column rose from 11 to 17.3 psi as quality was increased from 0.3 to 0.7. In the same manner, CGA mobility decreases from 1.4 to 0.9 cm$^2$/atms.s as CGA quality rises over the same range (Figure 58). These observations are consistent with the fact that more bubbles have to be forced through the porous medium as CGA quality rises.
Increasing CGA quality showed a very modest increase in gas saturation according to Figure 59. Whereas CGA quality changed from 0.3 to 0.7, the corresponding change in gas saturation was only from 94.6 to 96.4, about 2 percent. The significant amount of gas phase passing through the column as CGA quality is increased did not result in a corresponding increase in gas saturation suggesting that the ultimate gas saturation is largely determined by the pore structure. That is the bubbles are slowed down and advance forward only when the desired saturation level dictated by the pore structure of the medium is reached. Once CGA break-through has occurred and steady CGA flow is achieved, the number of bubbles entering or leaving the medium would affect the overall pressure drop and CGA mobility more significantly than the gas saturation.

**Effect of Injection Rate:** The relationship between the volumetric rate of injection of CGA and pressure drop is given in Figure 60. The Figure shows that by changing the injection rate of CGA from 0.2 to 0.8 cm$^3$/s, no significant change in the total pressure drop across the column occurred. This agrees with previous results. As shown in Figure 38, except at low flow rates, the pressure drop/CGA volume curves are the same for different flow rates. Also, there is no apparent change in gas saturation in the column over the same injection rate according to Figure 61.

For incompressible viscous fluid flow through a porous media, the pressure drop is a function of fluid flow rate according to Darcy's equation (Equation 7.1). Darcy's law can also be applied to multiphase fluid flow when no surface active agent present (Dullien, 1976; Scheidegger, 1964) provided the effective permeabilities of the phases are independent of the pressure gradient for a given saturation. But because of the presence of a surfactant in CGA and the associative nature of CGA's components, the situation is different. The surfactant in CGA creates a highly resilient film between the gas and the liquid components. CGA flow is therefore governed strictly by the mobility of these bubbles. Thus, while flow rate might have some contribution to CGA mobility, the structure of the pores, as discussed later, appears to be far more important in determining CGA mobility. Since gas saturation remained approximately constant over this flow range, the blockage of the medium
to flow is the same and as a result the pressure drop did not change. This explains why the pore channel model, an extension of the Darcy equation, cannot adequately describe CGA flow in porous media.

Effect of Surfactant Type: The effect of surfactant type on pressure drop and gas saturation are shown in Figures 62 and 63 respectively. The pressure drop for CPC is found to be significantly higher by about 25% than for NaDBS and T-15S12 both of which peaked at about 16-psi. Gas saturation did not show any significant difference for the three surfactants. The much higher pressure drop observed with CPC can be attributed to its cationic properties. The positive charge on the molecules would result in a stronger bond with the negatively charged sand particles. While this did not influence the saturation level, it did reduce the mobility of the bubbles considerably giving rise to the high pressure drop. T-15S12 is a neutral surfactant and NaDBS has the same negative charge as the sand packing. Thus in field application, the choice of a surfactant would depend, in part on the residual charge in the porous medium and whether a high or low pressure drop is desirable.

Effect of Particle Size: The effects of particle size on CGA flow through a porous medium are shown in Figures 64 through 68. For these experiments, glass beads were used. It is much easier to obtain homogeneous particle sizes over a wider range than with sand. Since CGA flow is a surface phenomenon, no change in performance is expected except for those attributable to improved sphericity, surface smoothness and size uniformity of the particles. CGA quality was maintained at 0.64 using a 1.0-g/l NaDBS solution. A constant injection rate of 0.40 cm$^3$/s was also used.

Particle size has a very significant influence on the pressure drop across a porous medium during CGA flow according to Figures 64 to 66. The values of the steady state pressure drop ranged from
about 1-psi for a 3.0-mm packing material to nearly 100-psi for a 0.23-mm packing. The break-through time of the CGA gas phase corresponds with the flattening of the pressure drop profile and increased as the particle size of the packing decreased. An inverse proportionality was found between the pressure drop and particle size according to Figure 65. On a log-log scale, the plot gave a straight line with a slope of -1.97 (Figure 66).

\[ \Delta P = 2.86 \, dp^{-1.97} \]  

That is the steady state pressure drop is inversely proportional to the square of the particle diameter.

The resistance to flow of CGA through a porous medium is affected by the properties of the pore system, the sizes of the pores and pore necks as well as the pore-to-pore neck ratio. As the absolute value of the pores and pore necks decrease, the flow resistance would increase for a give pore-to-pore neck ratio. Also a decrease in this ratio would mean a decrease in pressure drop. Dietz et al. (1985) have suggested estimating pore diameter from a simple permeability formula

\[ k = 6 \, d_{pore}^2 \]  

where \( k \) is the permeability in millidarcies and \( dp \) is the pore diameter in microns. The formula is based on the graph by Krombein and Monk (Bear, 1972). Using this equation, estimated values of pore sizes are presented in the table below.

<table>
<thead>
<tr>
<th>Packing Diameter (mm)</th>
<th>Permeability (darcy)</th>
<th>Pore Diameter (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>43</td>
<td>85</td>
</tr>
<tr>
<td>0.46</td>
<td>157</td>
<td>162</td>
</tr>
<tr>
<td>0.70</td>
<td>305</td>
<td>225</td>
</tr>
<tr>
<td>1.5</td>
<td>1570</td>
<td>510</td>
</tr>
<tr>
<td>3.0</td>
<td>5480</td>
<td>956</td>
</tr>
</tbody>
</table>
The table shows an increase in pore diameter as the grain size increases. A lesser degree of variation in pore neck size is expected. Thus as the size of the packing increased, there was a corresponding increase in the size of the pores, resulting in the observed decrease in pressure drop.

Particle size of the packing medium had the most significant effect on gas saturation, decreasing with increasing particle size according to Figure 56. Except for very fine particles, the gas saturation versus particle size relationship appears to be a linear one. As the pores become wider, the ability of the medium to retain CGA bubbles decreases. Notwithstanding, the gas saturation level is still higher than that of the influent CGA.

The mobility of CGA as a function of different sizes of packing is presented in Figure 68. The figure shows CGA mobility increasing exponentially with particle size again. On a log-log plot (Figure 69), the relationship is a straight line with a positive slope of 1.95. That is

\[
y = 0.83 dp^{1.95}
\]

Again this shows that the wider the pores of a porous medium, the easier it is for CGA to move through. The higher mobility of CGA in more permeable formations means that CGA would preferentially move in these systems. Thus if the flow of CGA is stopped, CGA would exert a blocking effect in these pores. If a single phase fluid is now allowed to flow through the formation, it would be directed into the narrower pores. This way a more effective areal sweep of the formation would be possible.

**Blocking Potential of CGA:** The blocking potential of CGA was characterized using the mobility of water through a porous matrix that has been subjected to CGA flow relative to the mobility of water through the same porous media filled with water. This definition of relative mobility is a
Figure 55: Effect of Surfactant Concentration on Pressure Drop across a Sand-Packed Column Flooded with CGA
SURFACTANT = NaDBS
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm³/s

Figure 56: Effect of Surfactant Concentration on Gas Saturation of a Sand-Packed Column Flooded with CGA
SAND SIZE = 20–30 mesh (841–595 μm)
SURFACTANT = 1.0 g/l NaDBS
INJECTION RATE = 0.40 cm³/s

Figure 57: Effect of Quality on Pressure Drop Across a Sand–Packed Column Flooded with CGA
Figure 58: Effect of Quality on CGA Mobility through a Sand-Packed Column.

SAND SIZE = 20–30 mesh
SURFACTANT = 1.0 g/l NaDBS
INJECTION RATE = 0.40 cm³/s
Figure 59: Effect of Quality on Gas Saturation of a Sand-Packed Column Flooded with CGA

SAND SIZE = 20–30 mesh (841–595 um)
SURFACTANT = 1.0 g/l NaDBS
INJECTION RATE = 0.40 cm³/s
SAND SIZE = 20–30 mesh (841–595 um)
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.84

Figure 60: Effect of Injection Rate on Pressure Drop across a Sand-Packed Column Flooded with CGA
SAND SIZE = 20–30 mesh (841–595 um)
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64

Figure 61: Effect of Injection Rate on Gas Saturation of a Sand–Packed Column Flooded with CGA
SAND SIZE = 20–30 mesh (841–595 um)
SURFACANT CONC = 1.0 g/l
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm³/s

Figure 62: Effect of Surfactant Type on Pressure Drop across a Sand–Packed Column Flooded with CGA
SAND SIZE = 20–30 mesh (841–595 μm)
SURFACTANT CONC = 1.0 g/l
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm$^3$/s

Figure 63: Effect of Surfactant Type on Gas Saturation of a Sand–Packed Column Flooded with CGA
Figure 64: Pressure Drop across a Glass Beads-Packed Column Flooded with CGA as a Function of CGA Volume Injected
Figure 65: Effect of Particle Size on Pressure Drop across a Glass Beads-Packed Column Flooded with CGA
Figure 66: Log–log Plot of Pressure Drop versus Particle Size for CGA Flow through a Glass Beads–Packed Column

PACKING = GLASS BEADS
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm³/s
Figure 67. Effect of Particle Size on Gas Saturation of a Glass Beads—Packed Column Flooded with CGA

PACKING = GLASS BEADS
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.84
INJECTION RATE = 0.40 cm³/s
Figure 68: Mobility of CGA versus Particle Size for CGA Flow through a Glass Beads–Packed Column

PACKING = GLASS BEADS
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm³/s
PACKING = GLASS BEADS
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm /s

Figure 69: Log-Log Plot of CGA Mobility versus Particle Size for CGA Flow through a Glass Beads—Packed Column
measure of the resistance to fluid flow through the medium as a result of the presence of CGA in the pores. The relative mobility should be less than 1 for CGA to have any blocking effect. The smaller the relative mobility the more effective the blocking action.

The relative mobility as a function of experimental variables are shown in Figures 70 to 73. In general, the mobility of water through CGA filled pores is about 100 times lower than those without CGA. The relative mobility is not constant with particle size according to Figure 70. It first decreases with particle size up to a size of about 1.0-mm and then starts increasing. According to equation 7-1, the pore diameter of a 1.0-mm packed column is about 330-\(\mu\)m. As discussed in chapter 3, bubbles become unstable when their size exceed 350-\(\mu\)m. Since the size of the bubbles would eventually correspond to size of the medium’s pores after CGA flow has stopped, such an increase in relative mobility in this range is not unexpected.

Relative mobility did not show any significant change with CGA quality over the range of CGA quality studied (Figure 71). This seems to agree with Figure 59 which shows the effect of CGA quality on gas saturation. All the gas saturation values obtained were above 94% and always higher than the quality of CGA. Since increasing CGA quality did not increase gas saturation, the blocking potential of CGA bubbles is not expected to change either. Thus from a practical point of view, the lowest possible CGA quality could be most desirable because of lower pressure drop (Figure 57).

Surfactant concentration has a significant impact on the relative mobility (Figure 72) but CGA injection rate does not (Figure 73) over the flow range examined. Relative mobility decreased with surfactant concentration up till a concentration of 5.0-g/l and started to increase beyond that. In the low concentration range, increase in surfactant concentration would mean higher stability of the bubbles without an appreciable change in the rheology of the continuous phase. In this range, the interfacial tension would either decreases or remains constant. The overall effect therefore would be for relative mobility to decrease. But at high surfactant loading, an increase in interfacial tension is often the case corresponding to an increase in relative mobility.
The change in relative mobility as surfactant concentration increased is the same as that observed on the effect of surfactant concentration on gas saturation (Figure 56). Thus it can be inferred that increase in surfactant concentration causes an increase in gas saturation which in turn acts to block the pores of the porous medium and reduce area available for flow. Similar results have also been reported by Bernard et al. (1965). They found that permeability lowering of porous media to water by foam was related to the trapped gas saturation. The relative ease with which foam is able to move into larger pores would increase gas saturation and lower permeability in such media.

These results support the fact that in an heterogeneous porous media, CGA would flow preferentially into large pores, block these pores and redirect the flow of any displacement fluid into the less accessible pores. Such a flow smoothing phenomenon has tremendous advantage in the use of CGA to displace contaminants from soil. In the next chapter, the effectiveness of CGA in flushing out hydrophobic organics from the soil is presented.

7.4 SUMMARY

The structure of pores inside a porous medium is very complex. The shape of the pores is irregular and complicated. They may be inter-connected, isolated or dead-end pores. Flow through such a network would be equally complicated. The intricate nature of CGA, a two phase, multicomponent, compressible, non-Newtonian fluid poses additional problems to it's propagation through porous media. Also, influential variables such as CGA quality, surfactant concentration, surfactant concentration and nature of the fluid in the porous medium could further complicate the flow.

CGA flow through porous media differs from the flow of a simple gas/liquid mixture without a surface active agent. The presence of a surfactant in CGA leads to the formation of a highly resil-
Figure 70: Effect of Particle Size on Mobility Reduction of Water through a Glass Beads-Packed Column after Flow of CGA

PACKING = GLASS BEADS
SURFACANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64
INJECTION RATE = 0.40 cm³/s
Figure 71: Effect of Quality on Mobility Reduction of Water through a Sand-Packed Column after Flooding with CGA

SAND SIZE = 20–30 mesh
SURFACTANT = 1.0 g/l NaDBS
INJECTION RATE = 0.40 cm³/s
Figure 72. Effect of Surfactant Concentration on Mobility Reduction of Water through a Sand-Packed Column after Flooding with CGA
SAND SIZE = 20–30 mesh
SURFACTANT = 1.0 g/l NaDBS
CGA QUALITY = 0.64

Figure 73: Effect of Injection Rate on Mobility Reduction of Water through a Sand–Packed Column after Flooding with CGA
ient film between the gas and liquid components. Individual bubbles are separated from one another by the liquid films. The stability of the films are governed by the dynamic surface tension and visco-elasticity of the surface. Interfacial properties are therefore more likely to govern CGA mobility.

During CGA flow, the gas and liquid phases propagate through porous media at different rates with the liquid phase advancing faster than the gas phase. This suggests that the discontinuous fluid flow model is more applicable to CGA flow. The model supports the idea that the mobility of both phases would be different. It agrees with the observation of Minssieux (1974) of uniform liquid saturation along a porous medium during foam flow. It also allows for the observed preferential entrapment of the gas phase over the liquid phase resulting in increased gas saturation.

The retardation of CGA bubbles during flow often results in a high pressure drop. While this may pose practical limitations in the field, it is very beneficial for mobility control in the subsurface environment. Large pressure drops imply more efficient areal sweep and selective plugging or diversion of flow from high-permeability to low-permeability regions. The relative ease with which CGA moves through a porous medium is influenced the most by the pore structure of the medium. The wider the pores, the less the resistance to CGA flow. Large pore and throat dimensions would lower the pressure drop as a result of decreased resistance to flow; but dead end pores would increase it. Another significant factor is the type of surfactant. CGA made with surfactants that have an opposite charge to that on the surface of the porous medium would be retarded creating a higher pressure drop and lower mobility rate.

After CGA flow, the residual gas content of a porous media was always higher than that of the CGA. Increase in surfactant concentration increased gas phase saturation through increase in bubble stability. Also as the packing size of the medium decreased, gas saturation increased with a corresponding increase in permeability. In general, CGA was very effective in maintaining a high residual gas saturation, above that reported in literature foam flow probably due to the colloidal size of CGA bubbles that allowed it to penetrate the small pores. In terms of flow mechanism, the
observed high gas saturation which was always higher than that of the influent CGA suggests that
the immobile gas saturation model can also be used to explain CGA flow through porous media.

CGA proved to be very effective in reducing the permeability of a porous medium to water flow. The CGA bubbles blocked some of the pores and reduced the effective flow area. CGA was more effective in blocking a more permeable medium than a less permeable one. The higher mobility of CGA in more permeable formations means that CGA would preferentially move in these systems. Thus if the flow of CGA is stopped, CGA would exert a blocking effect in these pores. If a single phase fluid is now allowed to flow through the formation, it would be directed into the narrower pores. This unique ability of CGA to preferentially block high permeable porous media over less permeable ones is important in achieving a more uniform fluid flow and more effective areal sweep in porous media. Such a flow smoothing phenomenon makes the use of CGA for soil flushing very attractive.
In response to the problem of contamination of the environment (land, water and air) by hazardous and toxic chemicals and the continuing threat of releases, the United States Congress enacted in 1980 the Comprehensive Environmental Response, Compensation, and Liability Acts (CERCLA or Superfund). The act authorized the Environmental Protection Agency (EPA), among other things, to develop countermeasures to mitigate the effects of hazardous substances that are released into the environment. One of such possible countermeasures, the use of CGA for treatment of saturated and subsurface soils contaminated with hydrophobic chemicals, is proposed here.

Hydrophobic organic compounds are those that are relatively non-polar, insoluble in water (water solubility of $< 100\text{mg/l}$), and have large octanol-water partition coefficient ($> 100$). Many of such compounds contaminate the environment. According to a recent study of soils and groundwater near 225 hazardous waste sites conducted for EPA (Ellis et al., 1985), 17 percent were found to be contaminated with hydrophobic organics such as polychlorinated biphenyls (PCBs), chlorinated hydrocarbon pesticides, polynuclear aromatics, oil and grease.
Hydrophobic compounds are of concern because of their potential toxic effects. They are usually adsorbed strongly to the soil (Coates and Elzerman, 1986; Miller and Weber, 1986; Karickhoff, 1984; Griffin and Chou, 1980). Also, they are generally recalcitrant to biodegradation (Gibson, 1984; Wilson et al., 1983; Kobayashi and Rittmann, 1982). These lead to increased accumulation in sediments and organisms. Their presence in the environment has been cited as the cause of many illnesses including cancer, respiratory problems, birth defects and blood disease.

The popular technique of water injection/recovery in which groundwater is drawn from the soil, treated above ground to remove the contaminant and then returned to the soil through injection wells or to nearby streams cannot be applied effectively on hydrophobic compounds because of the strong forces that act to keep the organics in the soil. Water alone cannot flush them out. Techniques that will first weaken the binding forces before displacement are therefore desirable.

Attempts have been made to overcome the soil/organic bond by using surfactant solutions. Texas Research Institute (1979) completed several laboratory column and two-dimensional modeling studies on the use of surfactants to enhance gasoline recovery from sand. Up to 40 percent of the residual gasoline after initial flooding was removed from the sand using a surfactant combination of commercial non-ionic Hyonic PE-90 and anionic Richonate-YLA. They also completed a study on surfactant-enhanced gasoline recovery in a large-scale model aquifer (Texas Research Institute, 1982). Three surfactant application procedures were tested: a single application that percolated through the sand bed, multiple applications by percolation and daily application into the water table. The percentages of gasoline removed were 6, 76 and 83 respectively.

Ellis et al., (1985) have demonstrated the use of aqueous nonionic surfactants for cleaning soil spiked with PCBs, petroleum hydrocarbons, and chlorophenol under laboratory conditions. Using a shaker table and soil column tests, up to 92 percent of PCBs were removed with a surfactant solution containing 0.75 percent each of Adsee 799 (Witco Chemical) and Hyonic NP-90 (Diamond Shamrock). A solution containing 2 percent each of these surfactants also removed 93 percent of
the petroleum hydrocarbons. Because of the high surfactant concentration, the formation of an emulsion is likely making phase separation rather difficult.

Unlike laboratory observations, in-situ soil washing under field conditions is not expected to be that successful largely because of poor areal sweep efficiency. The surfactant solution would channel through the path of least resistance that most probably contained the least contaminant. This indeed has been found to be the case at the fire training area of Volk Air National Guard Base, Wisconsin (Nash, 1987). Contaminated soil from this site was recompacted into glass columns creating a simulated in-situ environment and washed with a mixture of Adsee 799 and Hyonic NP-90 in the laboratory. The result was very encouraging. However, when this was tried in the field, the technique did not work. There was no significant difference between soil that had been washed and soil that had not been washed.

Several techniques have been used in the petroleum industry to improve the sweep efficiency and displacement efficiency of oil in tertiary oil recovery (enhanced oil recovery). The residual oil trapped in the pore structure of oil reservoirs after oil production under natural reservoir pressure (primary recovery) and water flooding (secondary recovery) are no longer economical is the target of tertiary oil recovery techniques. The primary objective of these techniques is to mobilize the residual oil trapped in the form of ganglia by either lowering interfacial tension or by increasing the viscous forces of the displacing fluid.

The case of soils contaminated by hydrophobic chemicals is similar to a reservoir with trapped oil. The use of CGA offers a way of lowering the interfacial tension between the organic and reservoir fluid while at the same time providing the viscous forces needed for efficient areal sweep.
8.1 FORCES ACTING ON HYDROPHOBIC COMPOUNDS IN POROUS MEDIA

Under dynamic conditions, there are two principal and opposing forces acting on a hydrophobic fluid in a porous media

- capillary forces
- viscous forces

The capillary forces are the resistance forces that help to entrap the non-wetting phase. They exist as a result of the difference between the non-wetting phase and the wetting phase of two immiscible fluids in porous media. The viscous forces of the displacing fluid act as the driving force to mobilize the non-wetting phase.

Mobilization of a trapped hydrophobic compound will occur only when the viscous forces of the displacing fluid exceeds the capillary forces. The ratio of the viscous forces to capillary forces is called the capillary number.

The various dimensionless forms of the capillary number proposed by different investigators have been summarized by Tabor (1981) and by Larson and co-workers (1981). Irrespective of the correlating group, it is generally agreed that the level of residual non-wetting phase in a porous media decreases with increase in capillary number. Figure 74 shows a typical correlation reported by Foster (1973).

There are two possible ways of increasing the capillary number according to it's definition

- increase viscous forces
- decrease interfacial tension
Figure 74: Dependence of Residual Oil on Capillary Number (Foster, 1973)
Viscous forces can be increased by increasing the effective viscosity of the displacing fluid. As presented in chapter 4, the apparent viscosity of CGA is much higher than that of water or a surfactant solution. Consequently, one can achieve some degree of increase in viscous forces through the viscous action of CGA bubbles as they move through the media.

The surfactant laden aqueous phase of CGA helps to lower the interfacial tension. With the use of an appropriate surfactant, the interfacial tension can be lowered from about 20 or 30 dynes/cm to $10^{-3}$ or $10^{-4}$ dynes/cm at the oil/surfactant solution interface (Ling et al., 1987).

Ultra-low interfacial tension plays an important role in the displacement of non-wetting fluids from porous media. A very low interfacial tension increases the mobility of the non-wetting phase and minimizes re-entrapment in the porous media. The lowering of interfacial tension is very much dependent on the charge density at the interface. The minimum in interfacial tension has been found to occur when the equilibrated aqueous phase concentration was at CMC; when the concentration of the surfactant monomer in the aqueous phase is maximum (Sharma and Shah, 1985).

A high surface charge density implies a high electrical repulsion between the non-wetting phase and the medium. This produces a low viscosity between the non-wetting/wetting and soil/fluid interfaces. A low interfacial viscosity is important in the coalescence of the non-wetting phase. The coalesced phase forms a bank that is subsequently displaced out of the porous media.
8.2 EXPERIMENTAL

8.2.1 Equipment and Materials

The main apparatus used to carry out the CGA displacement studies is outlined in Figure 75. It consists of a CGA generation system, a sand packed column and an effluent recovery system.

CGA was generated using the spinning disc technique as described in chapter 3. The surfactant used was NaDBS (see Table 1 for surfactant properties). CGA temperature was maintained at 28°C for all tests while surfactant concentration, CGA quality and flow rate were varied as necessary.

The sand-packed column consisted of Corning pyrex glass column 30.8 cm long, 3.81 cm inside diameter and 0.44 cm thick walls. End fittings were made from 1/4 in aluminum blocks. The sectional drawing of the column and its fittings is shown in Figure 54. Two types of testing sand were used for this work; 20-30 mesh (841-595 µm) and 50-70 mesh (297-210 µm). The sand is clean Ottawa testing sand. It is essentially silica with a negative surface charge. Details of the column and packings are given in Table 7. 25 ml graduated tubes were used to collect the liquid effluents. A concentrated solution of aluminum sulfate was used as a de-emulsifier.

Five different organic chemicals were used - Hexane, Decane, Tetradecane, Hexadecane and Hexachloro-1-3-butadiene. Their physical properties are given in Table 7. The lighter hydrocarbons (Hexane to Tetradecane) represent possible pollutants at an Air Force Base. Hexadecane, a diesel oil surrogate, was used for the parameter studies. Hexachloro-1-3-butadiene is a priority pollutant according to EPA listing (Federal Register, July 9, 1987).
Figure 75: Set-up for CGA Flushing Studies
8.2.2 Procedure

The sand packed column was prepared by closing one end and gradually pouring into it a prede-
termined weight of sand. A constant sand weight was used for each test in order to maintain a
constant porosity. The optimum weight of sand needed to give the closest packing was determined
through a series of trial packings. The column was kept vibrating as sand was poured in slowly.

Once the packing was completed, the aluminum end-plate was tightened. Care was taken not to
allow sand particles to be trapped between the column and the gasket at the end of the end-plate.

To ensure tight packing, air was allowed to flow through the column at pressures up to 25 -psi
during which particle movement along the column wall was carefully observed. Any particle
movement was taken as a sign of loose packing so that the column had to be dismantled and re-
packed. The process was repeated until a satisfactory packing was obtained.

The packed column was flushed vertically with carbon dioxide for at least 30 minutes to displace
interstitial air. Carbon dioxide would readily displace air since it is heavier. Deionized and distilled
water was then pumped in using a metering pump to determine the pore volume. The high solu-

bility of carbon dioxide in water helped to eliminate trapped gas bubbles in the porous medium.

The absolute permeability of the packed column was determined by pumping water through it at
different low flow rates using the Darcy equation. Darcy's law holds very well at Reynolds number
less than about 1. Pressure drop was measured using precision pressure gauges.

For a given test run, the saturated sand-packed column was flooded with a hydrophobic chemical
to the lowest possible water content at a feed rate of 10 ml/min. The volume of the organic content
was determined from the amount pumped in and the volume of water displaced. Both agreed
within less than 1 percent for all tests further indicating that no gas phase was present at this time.

Subsequently, the column was flooded with at least 1 pore volume of water at the rate of 2 ml/min.
Less than 0.7 pore volume was needed to achieve water breakthrough. The amount of organic
displaced was measured and hence the residual organic in the column (ROIP) was determined.
CGA of desired quality was generated as described previously and pumped into the column. At least 6 pore volume of CGA was injected for each test. The effluent was collected in 25-ml graduated test tubes and the organic recovery determined. In some instances an oil emulsion was formed particularly when high surfactant concentrations were used. A drop or two of concentrated aluminum sulfate solution was used as de-emulsifier.

The variables examined were surfactant concentration, CGA quality, CGA feed rate, type of contaminant and soil type. The surfactant concentration was varied between 10.0 g/l and 0.5 g/l. CGA quality ranged from 0.7 to 0.4; while CGA feed rate was between 0.1 cm³/sec and 0.8 cm³/sec. The soil types and organic types are as listed in Table 10.

8.2.3 Results and Discussion

Figures 76 through 78 show the typical removal curves - percentage of residual organic (organic left after water flooding) that was removed versus pore volume of CGA injected. The result of using surfactant solution alone is shown in Figure 79. The first set of CGA bubbles that entered the column readily coalesced on contact with the oil phase. The duration of this phase decreased with increase in surfactant concentration, CGA quality and CGA flow rate. As the rate of bubble coalescence decreased, CGA formed a displacement front that moved across the column rather uniformly, sweeping the organic phase along. The frontal advance was accompanied by a rise in pressure drop similar to that reported in chapter 7.

In general, very little oil was removed with the first one to two pore volumes of CGA. As the CGA front approached the end of the column, organic recovery jumped up sharply and soon leveled off. Usually, between 3 and 6 pore volumes of CGA was needed to reach the condition where organic removal rate became very small. This also corresponded to the break-through of the CGA-gas
TABLE 10

Column Specifications and Organic Materials for Flushing Tests

COLUMN SPECIFICATIONS

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>30.8 cm</td>
</tr>
<tr>
<td>Diameter</td>
<td>3.81 cm</td>
</tr>
<tr>
<td>Total Volume</td>
<td>351 cm³</td>
</tr>
<tr>
<td>Diameter/Length Ratio</td>
<td>1/8</td>
</tr>
<tr>
<td>Inlet Diameter</td>
<td>5</td>
</tr>
<tr>
<td>Column Diameter</td>
<td>16</td>
</tr>
<tr>
<td>Packing Material</td>
<td>Ottawa Testing Sand (20-30 mesh)</td>
</tr>
</tbody>
</table>

ORGANIC COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>86.2</td>
<td>0.6603</td>
</tr>
<tr>
<td>Decane</td>
<td>142</td>
<td>0.7300</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>226.5</td>
<td>0.7733</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>198.4</td>
<td>0.7628</td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td>260.8</td>
<td>1.554</td>
</tr>
</tbody>
</table>
Such a high volume of CGA was needed because of the problem of bubble coalescence. In some of the tests, up to 80 percent of the residual organic content (organic left in the column after flooding with water) was removed by flushing with CGA.

During the experiment, it was observed that after injecting 6 pore volumes of CGA, further removal of organic was negligible in most cases. Thus the removal efficiency after injecting 6 pore volumes of CGA was calculated for each set of experiment to determine the effect of experimental variables. In all, 23 tests were performed including two where surfactant solution was used instead of CGA as in surfactant flushing (tests # 12 and 13). The results are summarized in Table 11 and are discussed in terms of the effects of surfactant concentration, CGA quality, CGA feed rate and organic type. They are also compared with surfactant flushing.

### 8.2.3.1 Effect of Surfactant Concentration

Surfactant concentration has a significant effect on the organic removal efficiency from soil with CGA as shown in Figure 80. Using NaDBS, it was found that at concentrations less or equal to 1.0-g/l, the removal efficiency was about 5 percent. But when the surfactant concentration was raised to 2.5-g/l, the removal efficiency rose to 66 percent. Further increase in surfactant concentration to 5.0-g/l and 10.0-g/l resulted in 76 and 80 percent removal efficiency, a slight improvement over the 2.5-g/l concentration.

The poor removal efficiency at low surfactant concentrations can be attributed to the poor stability of CGA bubbles at these concentrations in the presence of organic molecules. Thus if one considers the situation on a molar basis, CGA made with a 0.5-g/l surfactant solution would require 5 times the volume of CGA to stabilize the CGA front compared to CGA made with a 2.5-g/l solution. Once the CGA front is stabilized, additional surfactant is not of much advantage. Surfactant concentrations often used in surfactant flushing studies reported in the literature are much higher, about
15- to 40-g/l (Nash, 1987; Ellis et al., 1985; Texas Research Institute, 1979, 1982). As will be discussed later, CGA flushing does achieve much higher removal efficiency than surfactant flushing at comparatively lower surfactant concentration because of the higher sweep efficiency.

8.2.3.2 Effect of CGA Quality

Three tests were performed to examine the effect of CGA quality. As shown in Figure 81, increasing CGA quality from 0.5 to 0.6 increased removal efficiency from 43 to 50 percent compared to an 80 percent removal efficiency for a CGA quality of 0.70. This trend corresponds to that observed for the effect of quality on the rheological properties of CGA (chapter 6). CGA behaves as a Bingham plastic fluid at quality below 0.6 and as a pseudoplastic fluid above this quality range. This results is a jump in CGA apparent viscosity at high quality. As CGA becomes more viscous, the capillary number decreases. As a result the removal efficiency increases.

That CGA is more effective in soil flushing at higher CGA quality is consistent with earlier observations of decrease in CGA mobility as CGA quality increases (Figure 58), and increase in gas saturation with increase in CGA quality (Figure 59). The less mobile the CGA bubbles and the more the number of bubbles, the better the viscous action.

8.2.3.3 Effect of Feed Rate

Using a 20-30 mesh sand and hexadecane, organic removal was found to be linearly related to the feed rate of CGA (Figure 82). At 0.10 cm$^3$/s removal efficiency was found to be 8.5 percent compared to 88 percent removal efficiency at 0.60 cm$^3$/s. With a 50-70 mesh sand a similar linear performance was observed except that removal efficiency soon leveled off at 0.40 cm$^3$/s with an efficiency of about 65 percent (Figure 83). The leveling off of removal efficiency for the less per-
meable medium was due to the problem of maintaining the high flow rate at high pressure drop. The flow rate gradually reduced as the pressure drop rose above the pumps design limit of about 35-psi.

CGA bubbles need a minimum hydrodynamic force to prevent them from coalescence. As a result, at very low flow rate, bubble coalescence would be high, particularly in the presence of an organic phase. This would lead to low capillary number and therefore poor removal efficiency. Also the relatively high pressure force needed to move CGA into low permeability media would make the clean-up of such systems costly.

8.2.3.4 Effect of Organic Type

The results shown in Figure 84 demonstrate that CGA is effective in flushing a variety of organic contaminants from soil. No particular correlation can be observed on the effect of organic properties on removal efficiency. In general the optimum amount of CGA needed to achieve a desired clean-up level would be influenced, among other factors, by the extent to which the contaminant destabilizes the CGA bubbles and prevents the development of the displacement front.

8.2.3.5 Comparison with Surfactant Flushing

Figure 79 compares the removal efficiency of CGA to flushing with surfactant solution. CGA flushing is 3 to 7 times more effective in removing residual organic content than surfactant flushing alone. Unlike with CGA, removal only occurred with the first 2 pore volumes injected during surfactant flushing.
In surfactant flushing, capillary number is increased only by decreasing interfacial tension and not by increasing the viscous forces of the displacing fluid. The surfactant solution cannot exert sufficient driving force on the oil phase. Once break-through occurs therefore, the surfactant solution would channel through, following the path of least resistance. CGA flushing achieves both. It lowers the interfacial tension through the action of its surfactant molecules. In addition, capillary number is further increased through increase in effective viscosity of the displacing fluid. As a result, a higher displacement efficiency is possible.

To achieve a high removal efficiency with surfactant flushing, a much higher surfactant concentration is required. According to studies at the Texas Research Institute (1979, 1982) and by Elis and co-workers (1985), up to 40-g/l surfactant solution may be required. Because of such high levels of surfactant, emulsions are often formed in surfactant washing making organic recovery more difficult.

Another advantage of CGA flushing over surfactant flushing is the ability of CGA bubbles to preferentially block large pores in a porous medium and direct fluid flow in the direction of smaller pores. This was discussed in the previous chapter in terms of relative mobility. The advantage of this is that residual organics trapped in such micro-pores can be mobilized better.

8.3 SUMMARY

In this chapter, the use of CGA as a soil flushing agent has been discussed. CGA is very effective in flushing a variety of hydrophobic organics from soil. The technique provides the surface active agent needed to lower the interfacial tension of the non-wetting phase while at the same time cre-
### Table 11. Summary of Hydrophobic Organic Displacement Studies

<table>
<thead>
<tr>
<th>Test #</th>
<th>Soil Type</th>
<th>Organic</th>
<th>ROIP % PV</th>
<th>Surfactant Conc. g/l</th>
<th>CGA Quality</th>
<th>CGA Feed Rate cm³/s</th>
<th>Removal % ROIP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B</td>
<td>Hexadecane</td>
<td>20.1</td>
<td>10.0</td>
<td>0.5</td>
<td>0.40</td>
<td>43.2</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td></td>
<td>23.5</td>
<td>10.0</td>
<td>0.6</td>
<td>0.40</td>
<td>50.3</td>
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<tr>
<td>3</td>
<td>B</td>
<td></td>
<td>30.9</td>
<td>10.0</td>
<td>0.7</td>
<td>0.40</td>
<td>79.5</td>
</tr>
<tr>
<td>4</td>
<td>B</td>
<td></td>
<td>30.9</td>
<td>5.0</td>
<td>0.7</td>
<td>0.40</td>
<td>75.5</td>
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<tr>
<td>5</td>
<td>B</td>
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<td>30.1</td>
<td>2.5</td>
<td>0.7</td>
<td>0.40</td>
<td>66.1</td>
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<tr>
<td>6</td>
<td>B</td>
<td></td>
<td>27.6</td>
<td>1.0</td>
<td>0.7</td>
<td>0.40</td>
<td>5.9</td>
</tr>
<tr>
<td>7</td>
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<td>23.6</td>
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<tr>
<td>8</td>
<td>B</td>
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<td>33.1</td>
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<tr>
<td>9</td>
<td>B</td>
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<td>B</td>
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<td>31.6</td>
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<td>18.8</td>
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<td>0.7</td>
<td>0.40</td>
<td>10.2</td>
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**Legend**

Soil Type A = 20-30 mesh Ottawa testing sand  
Soil Type B = 50-70 mesh Ottawa testing sand  
ROIP = Residual Oil in Place  
= Oil left after water flooding  
PV = Pore Volume = 136.3 cm³
ating enough viscous force and areal sweep to mobilize the trapped hydrophobic compound. CGA is also able to preferentially block the large pores and direct fluid into the smaller pores that often trap most of the residual organics.

CGA’s effectiveness as a flushing agent depends on the formation of a stable CGA front that is capable of mobilizing the trapped hydrophobic compound. This is favored by relatively high surfactant concentrations (above the CMC for ionic surfactants), high CGA flow rate and high CGA quality. At low surfactant concentrations, low CGA flow rate or low quality, CGA bubbles are easily coalesced by the organic phase and removal efficiency is poor.

CGA flushing can be 3 to 6 times more effective than surfactant flushing at the same surfactant concentration and flow rate. And unlike the latter, emulsification does not often occur with CGA flushing. Hence phase separation and product recovery is more feasible. In field applications, the problem of channeling and poor areal sweep often encountered with surfactant flushing is not expected with CGA flushing. But the problem of very high pressure force required to force CGA into soils with low permeability could limit its application in such media.
Figure 76: Hexachloro-1-3-butadiene Removal versus Volume of CGA Injected
Figure 77: Hexane Removal versus Volume of CGA Injected
SAND SIZE = 20–30 mesh
ORGANIC = Hexadecane
SURFACTANT = 10.0 g/l NaDBS
CGA QUALITY = 0.70
INJECTION RATE = 0.40 cm$^3$/s
MAXIMUM = 65 psi

Figure 78: Hexadecane Removal versus Volume of CGA Injected
SAND SIZE = 20–30 mesh
ORGANIC = Hexadecane
SURFACTANT = 2.5 g/l NaDBS
INJECTION RATE = 0.40 cm³/s
MAXIMUM = 0.0 psi

Figure 79: Hexadecane Removal versus Volume of Surfactant Solution Injected
Figure 80: Organic Removal as a Function of Surfactant Concentration
Figure 81: Organic Removal Efficiency as a Function of CGA Quality

- SAND SIZE = 50-70 mesh (297-210 um)
- ORGANIC = Hexadecane
- SURFACTANT = 10.0 g/l NaDBS
- CGA INJECTED = 8 pore volume
- INJECTION RATE = 0.40 cm³/s
SAND SIZE = 20–30 mesh (841–595 um)
ORGANIC = Hexadecane
SURFACTANT = 2.5 g/l NaDBS
CGA QUALITY = 0.70
CGA INJECTED = 6 pore volume

Figure 82: Organic Removal Efficiency as a Function of CGA Flowrate
Figure 83: Organic Removal Efficiency as a Function of CGA Flowrate

SAND SIZE = 50–70 mesh (297–210 um)
ORGANIC = Hexadecane
SURFACTANT = 2.5 g/l NaDBS
CGA QUALITY = 0.70
CGA INJECTED = 6 pore volume
SAND SIZE = 20–30 mesh (841–595 um)
SURFACANT = 2.5 g/l NaDBS
CGA QUALITY = 0.70
CGA INJECTED = 8 pore volume
INJECTION RATE = 0.40 cm³/s

Figure 84: Removal Efficiency for Different Organics

SOIL FLUSHING USING CGA
9.1 CONCLUSIONS

The major conclusions from this research are as follows:

- In the generation of CGA by the Spinning Disc method, the three most important design components are the spinning disc, the baffles and the holding vessel. The size and relative position of these components are crucial to the generation of CGA of consistent properties. While batch and continuous CGA generation are possible with the Spinning Disc method, only low production rates can be sustained without loss of integrity.

- The presence of a surface active agent is crucial to the formation of CGA. The amount of surfactant present does influence the ease of formation and subsequent stability of CGA. For ionic surfactants such as sodium dodecylbenzene sulfonate, concentrations above the CMC produce bubbles that are smaller and more uniform than with surfactant concentrations below...
the CMC. At low concentrations, the surfactant molecules are no longer sufficient to stabilize the increasing interfacial area as the bubbles become smaller.

- Hydrodynamic forces play a major role in CGA formation. The externally acting hydrodynamic force has to be greater than that due to the interfacial tension for bubble break-up to occur. The ultimate size of the bubbles are influenced by interbubble diffusion with the smaller bubbles, usually below 25 $\mu$m, losing their gas content to the bigger ones. The effect of interbubble collision on CGA formation depends on the size of the bubbles. Bubbles less than 100 $\mu$m are generally not affected by interbubble collision. Those in the 150-250 $\mu$m size range undergo bubble fission while bubble coalescence occurs primarily with those greater than 350 $\mu$m.

- CGA bubble size and size distribution analysis is possible with a microscope-assisted photographic technique and a carefully designed viewing cell. For CGA generated by the Spinning Disc method, the bubbles' range from 15 to 100 microns in size.

- At low surfactant concentrations, the presence of an electrolyte such as sodium chloride helped to decrease the size of CGA bubbles by increasing the effective concentration of the surfactant.

- The stability of CGA can be described by the half life, the time needed for 50% of it's liquid phase to separate by gravitational drainage.

- CGA is not a stable system. It has no intrinsic resistance to change in bubble size or degree of dispersion. Continuous agitation is required to preserve it's integrity. The hydrodynamic force acting on the bubbles has to be at least equal to the buoyancy force to prevent the separation of the gas and liquid phases. CGA's stability is temperature dependent. It's stability decreases with increase in temperature. At high temperatures (above 65°C), complete breakdown occurs. The rise in CGA temperature during generation by the Spinning Disc method can be substantial particularly in warm weather. This can also reduce the stability of CGA if a cooling device is not incorporated.

- CGA's stability can be enhanced at low surfactant concentrations by the addition of an electrolyte. The electrolyte increases the effective concentration of the surfactant and lowers the CMC of ionic surfactants. The result is the formation of smaller bubbles and increase in

CONCLUSIONS AND RECOMMENDATIONS
surfactant concentration density at the bubbles interface, factors that improve the stability of CGA.

- For applications of CGA in in-situ biodegradation, electrolytes such as potassium phosphate, potassium nitrate, and ammonium phosphate can be used. Apart from improving the stability of CGA, these salts would also increase the rate of biodegradation by providing the often needed nutrients to facilitate microbial growth. Their use could also result in substantial cost reduction by lowering surfactant consumption.

- The apparent viscosity of CGA is higher than that of the continuous phase. Measured viscosities at high CGA quality can be as much as 10 orders of magnitude higher than that of the liquid phase and $10^4$ times higher than the gas phase viscosity. The presence of micron-sized bubbles have a significant effect on the flow characteristics of CGA.

- CGA quality has the most significant effect on apparent viscosity, increasing with increasing quality. At low CGA quality, the apparent viscosity of CGA is only slightly higher than that of the continuous phase. As CGA quality is increased, the corresponding increase in apparent viscosity is exponential. For the same CGA quality, apparent viscosity is independent of surfactant concentration above the CMC for ionic surfactants.

- The shear stress versus shear rate relationship at low CGA quality, below 0.60, is a linear one and apparent viscosity appears to be invariant to shear rate. Thus in the low quality domain, CGA can be said to behave like a Bingham plastic fluid. As CGA quality is increased, it gradually becomes more pseudoplastic in nature and conforms better to the power law. The pseudoplastic nature of high quality CGA is well demonstrated at CGA quality greater than 0.60. Above this quality range, apparent viscosity changes significantly with shear rate. That CGA has a low apparent viscosity is advantageous in field applications because the pressure force needed to move it through the soil would be correspondingly low. Also, the non-dependence of apparent viscosity on shear rate at low CGA quality suggests that variable flow rates can be used in the field without lowering the scouring ability of CGA.

- CGA flow through porous media differs from the flow of a simple gas/liquid mixture without a surface active agent. The presence of a surfactant in CGA leads to the formation of a highly

CONCLUSIONS AND RECOMMENDATIONS
resilient film between the gas and liquid components. Individual bubbles are separated from one another by the liquid films. The stability of the films are governed by the dynamic surface tension and visco-elasticity of the surface.

- During CGA flow, the gas and liquid phases propagate through porous media at different rates with the liquid phase advancing faster than the gas phase. This suggests that the discontinuous fluid flow model is more applicable to CGA flow. The model supports the idea that the mobility of both phases would be different. It allows for the observed preferential entrapment of the gas phase over the liquid phase resulting in increased gas saturation.

- The retardation of CGA bubbles during flow often results in a high pressure drop. While this may pose practical limitations in the field, it is very beneficial for mobility control in the subsurface environment. Large pressure drops imply more efficient areal sweep and selective plugging or diversion of flow from high-permeability to low-permeability regions.

- The relative ease with which CGA moves through a porous medium is influenced the most by the pore structure of the medium. The wider the pores, the less the resistance to CGA flow. Large pore and throat dimensions would lower the pressure drop as a result of decreased resistance to flow; but dead end pores would increase it. Another significant factor is the type of surfactant. CGA made with surfactants that have an opposite charge to that on the surface of the porous medium would be retarded creating a higher pressure drop and lower mobility rate.

- The residual gas content of a porous media is higher than that of the influent CGA and above that reported in literature for foam flow. The colloidal size of CGA bubbles allows for better penetration of small pores. Increase in surfactant concentration increases gas phase saturation through increase in bubble stability. Also as the packing size of the medium decreases, gas saturation increases with a corresponding increase in permeability. The observed high gas saturation which was always higher than that of the influent CGA suggests that the immobile gas saturation model can also be used to explain CGA flow through porous media.

- CGA has proved to be very effective in reducing the permeability of a porous medium to water flow. CGA bubbles act to reduce the effective flow area by blocking the more permeable
pores. Because CGA has a higher mobility in more permeable formations it would preferentially move in these systems. Thus if the flow of CGA is stopped, CGA would exert a blocking effect in these pores. If a single phase fluid is now allowed to flow through the formation, it would be directed into the narrower pores.

- CGA is very effective in flushing a variety of hydrophobic organics from soil. The technique provides the surface active agent needed to lower the interfacial tension of the non-wetting phase while at the same time creating enough viscous force and areal sweep to mobilize the trapped hydrophobic compound. The ability of CGA to preferentially block large pores and direct fluid into smaller pores that often trap most of the residual organics contributes to its effectiveness.

- CGA flushing is more effective than surfactant flushing at the same surfactant concentration and flow rate. And unlike the latter, emulsification does not often occur with CGA flushing. Hence phase separation and product recovery is more feasible. In field applications, the problem of channelling and poor areal sweep often encountered with surfactant flushing is not expected with CGA flushing. But the problem of very high pressure force required to force CGA into soils with low permeability could limit its application in such media.

9.2 RECOMMENDATIONS

- The technique used in this study for generating CGA is not suitable for many field applications because of the low production rate. Other techniques that are more suitable for large scale production should be pursued. Current efforts are in this direction in the development of the Spinning Cylinder generator. The findings reported in this study with respect to the variables critical to mechanical generation of CGA and formation mechanisms would be helpful in design considerations.
• The definition of CGA stability using the half life concept should be adopted. This definition of stability corrects for variations in sample size and initial timing error. It also allows for a more accurate representation of the stability of low quality CGA.

• Only the effect of one electrolyte (sodium chloride) on the stability and bubble size of CGA has been reported in this work. The effects other salts that are particularly useful as nutrients in biodegradation have on CGA properties (bubble size, stability, apparent viscosity) should be studied.

• The studies on CGA rheology could be expanded to include the effect of capillary length and diameter (or capillary length to diameter ratio). These factors affect the measured apparent viscosity. The data can be compared with Bagley's method for correlating capillary viscometer data using tubes of different lengths and diameters (Bagley, 1957).

• Another possible area for future investigation is a pilot scale 2-dimensional and possibly 3-dimensional soil flushing test using CGA. This would shed more light on the limitations in field applications particularly with respect to pressure drop. The effect of organic content and clay content of the soil could be examined as well. The ultimate would be to have some field testing done to access the technology particularly in comparison with surfactant flushing. Candidate sites would be where surfactant flushing has been proved not to be very effective.

• High pressure drops have been observed in this study during CGA movement through low permeability soil systems. This could be a major limiting factor in current efforts to examine enhancement of in-situ biodegradation in subsurface environments. Application of CGA in such environments that are not highly porous or that contain significant amount of fine matter could be through a trench approach. Thus in-situ biodegradation of contaminated groundwater can be enhanced by digging a trench to intercept groundwater flow. The trench would be packed with a material that is porous enough to minimize pressure drop during CGA injection and at the same time demonstrate good CGA retention properties. Once this interceptor trench is saturated with CGA, oxygen and nutrients would be gradually released to contaminated groundwater as it flows across.
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Appendix A

CGA STABILITY MEASUREMENT DATA
**TABLE A.1**

**EFFECT OF SURFACTANT (NaDES) CONCENTRATION**

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<th>DRAINED LIQUID ml</th>
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<th>5.0 g/l</th>
<th>2.0 g/l</th>
<th>1.0 g/l</th>
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**CGA**

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**Quality**

| .641 | .641 | .639 | .636 | .633 | .638 | .641 | .640 |

**Half Life,s**

| 496 | 480 | 464 | 394 | 306 | 224 | 116 | 6 |

* Did not form CGA

CGA STABILITY MEASUREMENT DATA

225


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<tr>
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<td></td>
<td>1012</td>
<td>820</td>
<td>612</td>
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<table>
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<tr>
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<th>206</th>
<th>204</th>
<th>208</th>
<th>206</th>
<th>208</th>
<th>210</th>
</tr>
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<tbody>
<tr>
<td>Liquid Vol. (ml)</td>
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<td>74.8</td>
<td>76.4</td>
<td>72.2</td>
<td>75.0</td>
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<td>Quality</td>
<td>.637</td>
<td>.635</td>
<td>.637</td>
<td>.625</td>
<td>.653</td>
<td>.646</td>
<td>.633</td>
<td>.514</td>
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<td>Half Life (s)</td>
<td>484</td>
<td>470</td>
<td>419</td>
<td>334</td>
<td>276</td>
<td>208</td>
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CGA Stability Measurement Data
TABLE A.3
CGA STABILITY: EFFECT OF SODIUM CHLORIDE CONCENTRATION
(SURFACTANT = 0.1-g/l NaDES)

<table>
<thead>
<tr>
<th>DRAINED LIQUID ml</th>
<th>10.0 g/l</th>
<th>5.0 g/l</th>
<th>1.0 g/l</th>
<th>0.5 g/l</th>
<th>0.2 g/l</th>
<th>0.1 g/l</th>
<th>0.05 g/l</th>
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<tbody>
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<td>22</td>
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<td>27</td>
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<td>142</td>
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<td>255</td>
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<td></td>
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</tbody>
</table>

CGA VOL. ml 208 206 204 204 206 206 208
LIQUID VOL. ml 76 75.1 74.5 75.4 74.0 75.0 79.0
QUALITY .635 .635 .635 .630 .640 .646 .620
HALF LIFE s 220 229 226 220 216 208 183

CGA STABILITY MEASUREMENT DATA 227
Appendix B

CGA VISCOMETRY MEASUREMENT DATA AND SAMPLE CALCULATIONS
<table>
<thead>
<tr>
<th>RATE ml/min</th>
<th>PRESSURE DROP (cm Hexachloro-1-3-butadiene) FOR DIFFERENT CGA QUALITY</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>27.6 34.0 49.9 72.8</td>
<td>11.6</td>
</tr>
<tr>
<td>40</td>
<td>24.8 30.2 43.8 64.0 89.3</td>
<td>10.0</td>
</tr>
<tr>
<td>50</td>
<td>21.8 26.0 38.3 55.5 77.7</td>
<td>8.5</td>
</tr>
<tr>
<td>45</td>
<td>18.8 22.4 32.5 46.8 65.2 91.0 110.0</td>
<td>7.0</td>
</tr>
<tr>
<td>35</td>
<td>15.8 18.7 26.9 38.8 52.5 77.5 94.8</td>
<td>5.4</td>
</tr>
<tr>
<td>30</td>
<td>12.7 14.8 20.8 29.4 41.0 65.8 73.6</td>
<td>3.9</td>
</tr>
<tr>
<td>25</td>
<td>9.5 10.8 13.6 18.9 27.4 42.0 49.0</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>8.2 9.2 10.7 12.7 16.2 25.0 28.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Surfactant = NaDBS; Concentration = 0.5-g/l; Temperature = 28°C

Manometer Fluid = Hexachloro-1-3-butadiene; Density = 1.665-g/l
TABLE B.2
SAMPLE CALCULATION FOR APPARENT VISCOSITY BY THE POWER LAW

CGA QUALITY = 0.72

<table>
<thead>
<tr>
<th>$4Q/\pi R^3$ s$^{-1}$</th>
<th>$\tau_w$ (pa)</th>
<th>n$'$</th>
<th>$3n'+1$</th>
<th>$4n'$</th>
<th>$\left(\frac{dU_z}{dr}\right) w$ s$^{-1}$</th>
<th>$\mu_a$ (cp)</th>
<th>$\mu_a$ (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>414.4</td>
<td>11.0</td>
<td>.720</td>
<td>1.08</td>
<td>1.08</td>
<td>454.7</td>
<td>26.6</td>
<td>24.3</td>
</tr>
<tr>
<td>621.6</td>
<td>14.4</td>
<td>.663</td>
<td>1.13</td>
<td>1.13</td>
<td>700.6</td>
<td>23.2</td>
<td>20.6</td>
</tr>
<tr>
<td>828.8</td>
<td>16.6</td>
<td>.590</td>
<td>1.17</td>
<td>1.17</td>
<td>972.8</td>
<td>20.0</td>
<td>17.0</td>
</tr>
<tr>
<td>1036</td>
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<td>.540</td>
<td>1.21</td>
<td>1.21</td>
<td>1257</td>
<td>18.4</td>
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</tr>
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<td>1243</td>
<td>21.4</td>
<td>.502</td>
<td>1.25</td>
<td>1.25</td>
<td>1551</td>
<td>17.2</td>
<td>13.8</td>
</tr>
<tr>
<td>1450</td>
<td>23.3</td>
<td>.483</td>
<td>1.27</td>
<td>1.27</td>
<td>1838</td>
<td>16.1</td>
<td>12.7</td>
</tr>
<tr>
<td>1658</td>
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<td>.483</td>
<td>1.27</td>
<td>1.27</td>
<td>2102</td>
<td>14.9</td>
<td>11.8</td>
</tr>
</tbody>
</table>

$*\tau_w = 0.22521 \times \mu_{\text{manometer fluid}}$
STEPS FOR CALCULATION OF APPARENT VISCOITY BY THE POWER LAW

Step 1. The Pseudo-Shear Rate is calculated from the volumetric flow rate and the capillary dimensions (Column 1)

Step 2. The shear stress is calculated from the measured pressure drop in dynes/cm² (Column 2)

Step 3. The shear stress is plotted against the pseudo-shear rate on a log-log scale. The slope n' is evaluated at different pseudo-shear rates (column 3)

Step 4. The correction factor \((3n' + 1)/4n'\) is computed (Column 4)

Step 5. The shear rate is calculated by multiplying the pseudo-shear rate with the correction factor (Column 5)

Step 6. The pipe apparent viscosity, \(\mu_{ap}\) is calculated from columns 1 and 2 (Column 6)

Step 7. The apparent viscosity, \(\mu_a\) is calculated from columns 4 and 2 (Column 7)
TABLE B.3
SAMPLE CALCULATION FOR APPARENT VISCOSITY BY THE BINGHAM FLUID LAW

OGA QUALITY = 0.30

<table>
<thead>
<tr>
<th>$\frac{4Q}{\pi R^2} \text{ s}^{-1}$</th>
<th>$\tau_w^\star$ (pa)</th>
<th>$\tau_0$</th>
<th>Corr. ** Factor</th>
<th>$\mu_{\text{ef}}$ (cp)</th>
<th>$\mu'$ (cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>414.4</td>
<td>2.14</td>
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<td>.245</td>
<td>5.16</td>
<td>1.27</td>
</tr>
<tr>
<td>828.8</td>
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<td>1.28</td>
<td>.416</td>
<td>3.45</td>
<td>1.44</td>
</tr>
<tr>
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<td>1.28</td>
<td>.526</td>
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</tr>
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<td>1658</td>
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<td>.654</td>
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<td>1.55</td>
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<tr>
<td>2486</td>
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<td>1.28</td>
<td>.696</td>
<td>2.25</td>
<td>1.56</td>
</tr>
</tbody>
</table>

$\star \tau_w = 0.22521 \times P_{\text{manometer fluid}}$

** Correlation Factor = $\left[1 - \frac{4}{3} \frac{\tau_0}{\tau_w} + \frac{1}{3} \left(\frac{\tau_0}{\tau_w}\right)^4\right]$. 

CGA VISCOMETRY MEASUREMENT DATA AND SAMPLE CALCULATIONS . 232
Step 1. The Pseudo-Shear Rate is calculated from the volumetric flow rate and the capillary dimensions (Column 1).

Step 2. The shear stress is calculated from the measured pressure drop in dynes/cm² (Column 2).

Step 3. The shear stress is plotted against the pseudo-shear rate on a log-log scale. The value of $\alpha$ is evaluated at the y-intercept (Column 3).

Step 4. The correction factor* is computed (Column 4).

Step 5. The pipe apparent viscosity, $\mu_{ap}$, is calculated from columns 1 and 2 (Column 6).

Step 6. The apparent viscosity, $\mu'$, is calculated from columns 1, 2, and 4 (Column 6).

* Correction Factor = \[1 - \frac{4}{3} \frac{\tau_0}{\tau_w} + \frac{1}{3} \left( \frac{\tau_0}{\tau_w} \right)^4\]
Appendix C

SAMPLE DATA ON CGA FLOW VISUALIZATION STUDIES
TEST # 1

Packing = Ottawa Testing Sand, 20-30 mesh
Cell Position = Vertical
Flow Length = 15 in
Voidage = 0.38
CGA: Surfactant = T-15S12
Quality = 0.64
Flow Rate = 20 ml/min
Temperature = 28 °C

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>PORE VOLUME INJECTED</th>
<th>PRESSURE DROP (psi)</th>
<th>CGA FRONT (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.4</td>
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</tr>
<tr>
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<td>0.142</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
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<td>0.851</td>
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<td>5.6</td>
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<td>15.0</td>
</tr>
</tbody>
</table>
**TEST # 6**

Packing = Ottawa Testing Sand, 20-30\(^{\circ}\)mesh  
Cell Position = Flat  
Flow Length = 15 in  
Voidage = 0.38  
CGA: Surfactant = T-15S12  
Quality = 0.64  
Flow Rate = 45 ml/min  
Temperature = 28 °C

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>PORE VOLUME INJECTED</th>
<th>PRESSURE DROP (psi)</th>
<th>CGA FRONT (in)</th>
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<tbody>
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</tr>
<tr>
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<td>3.19</td>
<td>14.2</td>
<td>15.0</td>
</tr>
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</table>
### TEST # 7

Packing = Ottawa Testing Sand, 20-30 mesh  
Cell Position = Flat  
Flow Length = 15 in  
Voidage = 0.38  
CGA: Surfactant = T-15S12  
Quality = 0.64  
Flow Rate = 70 ml/min  
Temperature = 28 °C

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>PORE VOLUME INJECTED</th>
<th>PRESSURE DROP (psi)</th>
<th>CGA FRONT (in)</th>
</tr>
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<tbody>
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</tr>
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<td>3.1</td>
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<tr>
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<td>0.579</td>
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<td>7.1</td>
</tr>
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<td>1.24</td>
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<td>8.2</td>
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<td>9.0</td>
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<td>9.8</td>
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Packing = Ottawa Testing Sand, 20-30 mesh
Cell Position = Flat
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    Voidage = 0.38
CGA: Surfactant = T-15S12
    Quality = 0.64
    Flow Rate = 95 ml/min
    Temperature = 28 °C

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Packing = Ottawa Testing Sand, 20-30 mesh  
Cell Position = Flat  
Flow Length = 15 in  
Voidage = 0.38  
CGA: Surfactant = T-15S12  
Quality = 0.64  
Flow Rate = 120 ml/min  
Temperature = 28°C

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SAMPLE DATA ON CGA FLOW VISUALIZATION STUDIES
TEST # A-2

Packing = Ottawa Testing Sand, 20-30 mesh
Cell Position = Flat
Flow Length = 15 in
Voidage = 0.38
CGA: Surfactant = NaDBS
Quality = 0.62
Flow Rate = 45 ml/min
Temperature = 28 °C

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SAMPLE DATA ON CGA FLOW VISUALIZATION STUDIES 240
TEST # B-3

Packing = Ottawa Testing Sand, 20-30 mesh
Cell Position = Flat
Flow Length = 15 in
Voidage = 0.38
CGA: Surfactant = CPC
Quality = 0.62
Flow Rate = 45 ml/min
Temperature = 28 °C

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Packing = Ottawa Testing Sand, 20-30 mesh  
Cell Position = Sideways  
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Voidage = 0.38  
CGA:  
Surfactant = T-15S12  
Quality = 0.63  
Flow Rate = 45 ml/min  
Temperature = 28 °C

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Packing = Ottawa Testing Sand, 20-30 mesh  
Cell Position = Vertical  
Flow Length = 15 in  
Voidage = 0.38  
CGA: Surfactant = T-15S12  
Quality = 0.63  
Flow Rate = 45 ml/min  
Temperature = 28 °C

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TEST # D-1

Packing = Ottawa Testing Sand, 50-70 mesh  
Cell Position = Vertical  
Flow Length = 15 in  
Voidage = 0.37  
CGA: Surfactant = T-15S12  
Quality = 0.61  
Flow Rate = 45 ml/min  
Temperature = 28 ° C

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SAMPLE DATA ON CGA FLOW VISUALIZATION STUDIES 244
DATA ONE;
  INPUT Q P1 P2 P3 P4 P5 P6 P7 P8;
  Y = 41.4466 * Q;
  A = .22521;
  T1 = AMP1;
  T2 = AMP2;
  T3 = AMP3;
  T4 = AMP4;
  T5 = AMP5;
  T6 = AMP6;
  T7 = AMP7;
  T8 = AMP8;

LOG_Y = LOG10(Y);
LOG_T1 = LOG10(T1);
LOG_T2 = LOG10(T2);
LOG_T3 = LOG10(T3);
LOG_T4 = LOG10(T4);
LOG_T5 = LOG10(T5);
LOG_T6 = LOG10(T6);
LOG_T7 = LOG10(T7);
LOG_T8 = LOG10(T8);

CARDS;
70  27.6  34.0  49.9  72.8  .  .  .  . . 11.6
65  24.8  30.2  43.8  64.0  89.3  .  .  .  . 10.0
55  21.8  26.0  38.3  55.5  77.7  .  .  .  .  8.5
45  18.8  22.4  32.5  46.8  65.2  91.0 110  .  .  7.0
35  15.8  18.7  26.9  38.8  52.5  77.5 94.8  .  .  5.4
25  12.7  14.8  20.8  29.4  41.0  64.8 73.6  .  .  3.9
20  9.5  10.8  13.6  18.9  27.4  42.0 69.0  .  .  2.3
15  8.2  9.2  10.7  12.7  16.2  25.0 28.0  .  .  1.5

DATA MYNOTES;
LENGTH COLOR FUNCTION STYLE $ 8 POSITION $ 1 TEXT $ 20 ;
XSYS='2'; YSYS='2'; SIZE=1;
INPUT FUNCTION 'X' 'Y' POSITION STYLE COLOR TEXT &;
PROC GPLOT DATA=ONE;
AXIS1 LOGBASE=10
LABEL=(F=XSWISS H=1.3 C=BLUE 'SHEAR RATE, s')
VALUE=(F=SIMPLEXU H=1.2 C=RED)
COLOR=RED LENGTH=5.2 IN OFFSET=(0,0);
AXIS2 LOGBASE=10
LABEL=(A=90 H=1.3 F=XSWISS C=BLUE 'SHEAR STRESS, pa')
VALUE=(F=SIMPLEXU H=1.2 C=RED)
COLOR=RED LENGTH=5.2 IN OFFSET=(0,0);
PLOT T1*Y T2*Y T3*Y T4*Y T5*Y T6*Y T7*Y / OVERLAY FRAME
ANNOTATE=MYNOTES VAXIS=AXIS2 HAXIS=AXIS1;
SYMBOL1 V=SQUARE C=RED H=1.1;
SYMBOL2 V=SQUARE C=RED H=1.1;
SYMBOL3 V=SQUARE C=RED H=1.1;
SYMBOL4 V=SQUARE C=RED H=1.1;
SYMBOL5 V=SQUARE C=RED H=1.1;
SYMBOL6 V=SQUARE C=RED H=1.1;
SYMBOL7 V=SQUARE C=RED H=1.1;
SYMBOL8 V=PLUS C=RED H=1.1;
FOOTNOTE1 C=RED F=SIMPLEX H=1.1
'SFigure 28: Log-Log Plot of Shear Stress versus Pseudo-Shear Rate';
DATA ONE;
INPUT V1 P1 V2 P2 V3 P3 V4 P4 VS PS;
CARDS;
0.0 0.3 0.0 0.2 0.0 0.3 0.0 0.3 0.0 0.3
0.284 0.9 0.319 2.3 0.414 2.5 0.337 1.8 0.426 2.3
0.426 2.3 0.678 4.2 0.579 4.2 0.505 3.2 0.638 3.8
0.567 3.3 0.638 5.6 0.745 5.3 0.674 4.2 0.851 5.0
0.709 4.3 0.798 6.7 0.910 6.5 0.842 5.6 1.06 6.0
0.851 5.0 0.957 7.6 1.08 7.2 1.01 6.0 1.28 7.0
1.06 5.8 0.125 8.5 1.04 8.2 1.18 6.9 1.49 7.9
1.12 6.8 0.128 9.1 1.41 9.0 1.35 7.7 1.70 8.7
1.17 7.7 0.144 10.0 1.57 9.6 1.52 8.5 1.91 9.4
2.13 8.2 0.160 10.7 1.86 10.7 1.68 8.8 2.13 10.2
2.48 8.8 0.176 11.4 2.07 12.1 1.85 9.4 2.54 11.0
2.84 9.3 0.191 12.0 2.23 12.6 2.02 9.9 2.59 11.5
3.19 9.8 0.207 12.6 2.40 13.2 2.19 10.4 2.77 12.0
3.55 10.3 0.223 13.0 2.57 13.6 2.36 11.0 2.98 12.1
0.239 13.4 0.273 14.0 2.53 11.4 3.19 12.1
0.255 13.7 0.290 14.2 2.70 11.9 .
0.271 14.0 0.306 14.2 2.86 12.2 .
0.287 14.2 0.323 14.2 3.03 12.3 .
0.303 14.2 . . 3.20 12.4 .
0.319 14.2 . . 3.37 12.5 .
2.8 3.5 2.8 2.8 2.8 2.2 2.8 1.6 2.8 1.0

DATA MYNOTES;
LENGTH COLOR FUNCTION STYLE $ 8 POSITION $ 1 TEXT $ 20 ;
XSYS='2'; YSYS='2'; SIZE=1;
INPUT FUNCTION X Y POSITION STYLE COLOR TEXT &;
CARDS;
LABEL .25 19.0 6 TRIPLEX BLUE SURFACTANT
LABEL 1.1 19.0 6 TRIPLEX BLUE = 0.5 g/l Ti5S12
LABEL .25 18.3 6 TRIPLEX BLUE PACKING
LABEL 1.1 18.3 6 TRIPLEX BLUE = 20-30 mesh
LABEL .25 17.7 6 TRIPLEX BLUE POSITION
LABEL 1.1 17.7 6 TRIPLEX BLUE = FLAT
LABEL 3.0 5.0 6 TRIPLEX BLUE FLOW RATE
LABEL 3.1 4.5 6 TRIPLEX BLUE = (cm/s)
LABEL 3.0 3.5 6 TRIPLEX BLUE = 0.33
LABEL 3.0 2.8 6 TRIPLEX BLUE = 0.75
LABEL 3.0 2.2 6 TRIPLEX BLUE = 1.17
LABEL 3.0 1.6 6 TRIPLEX BLUE = 1.58
LABEL 3.0 1.0 6 TRIPLEX BLUE = 2.00
PROC GPLOT DATA=ONE;
AXIS1 ORDER=(0.0 1.0 2.0 3.0 4.0)
LABEL=(F=XSWISS H=1.3 C=BLUE 'CGA VOLUME INJECTED, pv')
VALUE=(F=SIMPLEX H=1.2 C=RED)
COLOR=RED OFFSET=(0,0) LENGTH=5.2 IN
MINOR=(N=1);

AXIS2 ORDER=(0.0 5.0 10.0 15.0 20.0)
LABEL=(A=90 H=1.3 F=XSWISS C=BLUE 'PRESSURE DROP, psi')
VALUE=(F=SIMPLEX H=1.2 C=RED)
COLOR=RED OFFSET=(0,0)
MINOR=(N=1);

PLOT P1*V1 P2*V2 P3*V3 P4*V4 P5*V5 / OVERLAY FRAME
ANNOTATE=MYNOTES VAXIS=AXIS2 HAXIS=AXIS1;
SYMBOL1 V=TRIANGLE C=RED H=1.2;
SYMBOL2 V=PLUS C=RED H=1.2;
SYMBOL3 V=O C=RED H=1.2;
SYMBOL4 V= C=RED H=1.2;
SYMBOL5 V=SQUARE C=RED H=1.2;

FOOTNOTE1 C=RED F=SIMPLEX H=1.1
'Figure 39: Pressure Drop versus Volume of CGA at Different Flow Rates';
//A020TIMO JOB 46668, LONGE, TIME=1, REGION=1536K
/*PRIORITY STANDARD
/*ROUTE PRINT VTVM1.TIMO
/*JOBPARM LINES=1, ACCTPG
//STEP1 EXEC SAS
//SYSIN DD *
OPTIONS DEVICE=VER80 NOTEXT82;
OPTIONS LS=72;
TITLE1 H=2 'SPACE';
TITLE2 H=2 'SPACE';
TITLE3 H=3 'SPACE';
DATA ONE;
INPUT V1 X1 V2 X2 V3 X3 V4 X4 V5 X5;
CARDS;
0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
.142 .00 .160 .01 .165 .02 .168 .05 .142 .02
.284 .01 .319 .08 .331 .11 .337 .13 .284 .11
.426 .03 .478 .16 .496 .20 .505 .21 .567 .26
.567 .06 .638 .25 .745 .31 .674 .29 .780 .36
.709 .07 .798 .31 .869 .35 .842 .35 .922 .41
.851 .09 .957 .37 .993 .41 1.01 .41 1.06 .46
1.14 .15 1.12 .43 1.16 .47 1.18 .47 1.21 .52
1.42 .21 1.28 .49 1.32 .47 1.35 .53 1.35 .55
1.84 .33 1.44 .54 1.49 .57 1.52 .63 1.49 .61
2.84 .53 1.60 .58 1.65 .63 1.68 .68 1.63 .64
.176 .63 1.90 .68 1.85 .74 1.77 .68
.91 .68 1.99 .72 2.02 .78 1.91 .71
2.07 .73 2.15 .77 2.19 .82 2.06 .75
2.23 .78 2.32 .81 2.36 .87 2.27 .81
2.47 .84 2.48 .86 2.53 .91 2.48 .86
2.71 .97 2.73 .93 2.70 .95 2.62 .90
.97 .98 .98 .98 .94 .77 .94
.29 .98 .29 .98 .94 .29 .97
2.8 .22 2.8 .18 2.8 .14 2.8 .10 2.8 .06

DATA MYNOTES;
LENGTH COLOR FUNCTION STYLE $ 8 POSITION $ 1 TEXT $ 20;
XSYS='2'; YSYS='2'; SIZE=1;
INPUT FUNCTION X Y POSITION STYLE COLOR TEXT &;
CARDS;
LABEL .25 .95 6 TRIPLEX BLUE SURFACTANT
LABEL 1.1 .95 6 TRIPLEX BLUE = 0.5 g/l NaDBS
LABEL .25 .91 6 TRIPLEX BLUE PACKING
LABEL 1.1 .91 6 TRIPLEX BLUE = 20-30 mesh
LABEL .25 .87 6 TRIPLEX BLUE POSITION
LABEL 1.1 .87 6 TRIPLEX BLUE = FLAT
LABEL 3.0 .50 6 TRIPLEX BLUE FLOW RATE (cm /s)
LABEL 3.1 .27 6 TRIPLEX BLUE = 0.33
LABEL 3.0 .22 6 TRIPLEX BLUE = 0.75
LABEL 3.0 .18 6 TRIPLEX BLUE = 1.17
LABEL 3.0 .14 6 TRIPLEX BLUE = 1.58
LABEL 3.0 .06 6 TRIPLEX BLUE = 2.00

-PROC GPHLOT DATA=ONE;
Figure 40: Relative Position of CGA-Gas Front versus CGA Volume.

AXIS1 ORDER=(0.0 1.0 2.0 3.0 4.0)
LABEL=(F=XSWISS H=1.3 C=BLUE 'CGA VOLUME INJECTED, pv')
VALUE=(F=SIMPLEXU H=1.2 C=RED)
COLOR=RED OFFSET=(0,0) LENGTH=5.2 IN
MINOR=(N=1);

AXIS2 ORDER=(0.0 0.2 0.4 0.6 0.8 1.0)
LABEL=(A=90 H=1.3 F=XSWISS C=BLUE 'CGA-GAS FRONT')
VALUE=(F=SIMPLEXU H=1.2 C=RED)
COLOR=RED OFFSET=(0,0)
MINOR=(N=1);

PLOT X1*V1 X2*V2 X3*V3 X4*V4 X5*V5 / OVERLAY FRAME
ANNO TATE=MYNOTES VAXIS=AXIS2 HAXIS=AXIS1;
SYMBOL1 V=TRIANGLE C=RED H=1.2;
SYMBOL2 V=PLUS C=RED H=1.2;
SYMBOL3 V=O C=RED H=1.2;
SYMBOL4 V= C=RED H=1.2;
SYMBOL5 V=SQUARE C=RED H=1.2;

FOOTNOTE1 C=RED F=SIMPLEX H=1.1
'Figure 40: Relative Position of CGA-Gas Front versus CGA Volume.';
DATA ONE;
  INPUT V1 P1 V2 P2 V3 P3;
CARDS;
   0.0  .0  .16  .0  .31  .9  .47  1.12  1.28  1.44  1.60  1.76  1.91  2.07  2.23  2.39  2.55  2.87  3.19  3.8  2.6;
   3.6  2.9  7.3  10.0 11.4 12.0 12.6 13.4 14.2 15.1 15.7 15.3 15.9 16.5 17.1 17.7 18.3 19.0 19.6 20.3 21.0;
   21.7 22.4 23.1 23.8 24.5 25.2 25.9 26.6 27.3 28.0 28.7 29.4 30.1 30.8 31.5 32.2 32.9 33.6 34.3 35.0;
   35.7 36.4 37.1 37.8 38.5 39.2 39.9 40.6 41.3 42.0 42.7 43.4 44.1 44.8 45.5 46.2 46.9 47.6 48.3 49.0;

DATA MYNOTES;
  LABEL FUNCTION X Y POSITION STYLE COLOR TEXT$ 8 POSITION$ 1 TEXT$ 20 ;
  XSYS='2'; YSYS='2'; SIZE=1;
  INPUT FUNCTION X Y POSITION STYLE COLOR TEXT &;
CARDS;
  LABEL 1.95 9.0 6 TRIPLEX BLUE SURFACTANT
  LABEL 2.8 9.0 6 TRIPLEX BLUE = T-15S12
  LABEL 1.95 8.2 6 TRIPLEX BLUE CONC.
  LABEL 2.8 8.2 6 TRIPLEX BLUE = 0.5 g/l
  LABEL 1.95 7.4 6 TRIPLEX BLUE FLOW RATE
  LABEL 2.8 7.4 6 TRIPLEX BLUE = 0.75 cm /s
  LABEL 1.95 6.6 6 TRIPLEX BLUE POSITION
  LABEL 2.8 6.6 6 TRIPLEX BLUE = FLAT
  LABEL 2.8 4.8 6 TRIPLEX BLUE PACKING DIAM.
  LABEL 2.8 3.8 6 TRIPLEX BLUE = 0.718 mm
  LABEL 2.8 3.0 6 TRIPLEX BLUE = 0.343 mm
  LABEL 2.8 2.2 6 TRIPLEX BLUE = 0.254 mm
PROC GPLOT DATA=ONE;
AXIS1 ORDER=(0.0 1.0 2.0 3.0 4.0)
  LABEL=(F=XT2 SWISS H=1.3 C=BLUE 'CGA VOLUME INJECTED, pv')
  VALUE=(F=SIMPLEX H=1.2 C=RED)
  COLOR=RED OFFSET=(0,0) LENGTH=5.2 IN
  MINOR=(N=1);
AXIS2 ORDER=(0.0 5.0 10.0 15.0 20.0 25.0)
  LABEL=(A=90 H=1.3 F=XT2 SWISS C=BLUE 'PRESSURE DROP, psi')
  VALUE=(F=SIMPLEX H=1.2 C=RED)
  COLOR=RED OFFSET=(0,0)
  MINOR=(N=1);
PLOT P1*V1 P2*V2 P3*V3 / OVERLAY FRAME ANNOTATE=MYNOTES
  VAXIS=AXIS2 HAXIS=AXIS1;
SYMBOL1 V=TRIANGLE C=RED H=1.2;
SYMBOL2 V=PLUS C=RED H=1.2;
SYMBOL3 V=SQUARE C=RED H=1.2;
FOOTNOTE1 C=RED F=SIMPLEX H=1.1
  'Figure 49: Pressure Drop versus CGA Volume Injected: ';
FOOTNOTE2 C=RED F=SIMPLEX H=1.1
  'Effect of Size of Packing';
/\
//
DATA ONE;
  INPUT Q CV;
  CGA=6XQ/336;
CARDS;
  24  3.42
  48  5.26
  72  7.37
  96  8.95
 120 27.4
 144 45.5
 168 68.2
 192 73.4
 216 75.5
 240 77.1
 264 78.4
 288 78.9
 312 78.9
 336 78.9
 360 78.9;
DATA MYNOTES;
  LENGTH COLOR FUNCTION STYLE$ 8 POSITION$ 1 XSYS='2';
   YSYS='2'; SIZE=1;
  INPUT FUNCTION X Y POSITION STYLE CARDS;
LABEL 0.2 96.0 6 TRIPLEX BLUE SAND SIZE
LABEL 1.4 96.0 6 TRIPLEX BLUE = 20-30 mesh
LABEL 0.2 92.0 6 TRIPLEX BLUE ORGANIC
LABEL 1.4 92.0 6 TRIPLEX BLUE = Hexane
LABEL 0.2 88.0 6 TRIPLEX BLUE SURFACTANT
LABEL 1.4 88.0 6 TRIPLEX BLUE = 2.5 g/l NaDBS
LABEL 0.2 84.0 6 TRIPLEX BLUE CGA QUALITY
LABEL 1.4 84.0 6 TRIPLEX BLUE = 0.70
LABEL 0.2 80.0 6 TRIPLEX BLUE INJECTION RATE
LABEL 1.4 80.0 6 TRIPLEX BLUE = 0.40 cm /s
LABEL 0.2 76.0 6 TRIPLEX BLUE MAXIMUM
LABEL 1.4 76.0 6 TRIPLEX BLUE = 11.5 psi
PROC GPLOT DATA=ONE;
AXIS1
  LABEL=(F=XSWISS H=1.3 C=BLUE 'CGA VOLUME INJECTED, pv')
FOOTNOTE1 C=RED F=SIMPLEX H=1.1
'Figure 77: Hexane Removal versus Volume of CGA Injected';
/* Figure 77: Hexane Removal versus Volume of CGA Injected */
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