Characterization and Application of Colloidal Gas Aphrons for Groundwater Remediation.

Pradeep Gopal Chaphalkar
Louisiana State University and Agricultural & Mechanical College
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Characterization and application of colloidal gas aphrons for groundwater remediation

Chaphalkar, Pradeep Gopal, Ph.D.
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CHARACTERIZATION AND APPLICATION OF COLLOIDAL GAS APHRONS FOR GROUNDWATER REMEDIATION

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural And Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Civil Engineering

by

Pradeep Gopal Chaphalkar
B.E., University of Bombay, India, 1980
M.E., University of Bombay, India, 1986
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ABSTRACT

This study examines the basic properties of colloidal gas aphrons (CGAs) that are relevant to their applications in soil and groundwater decontamination. Results of experiments on the applicability of CGAs in the removal of organics from aqueous solutions and in the subsurface environment are presented.

CGAs are dispersed microbubbles in an aqueous surfactant solution. When introduced into an aqueous system, CGAs undergo variation in sizes and numbers with time due to coalescence and/or creaming. To address the dynamic changes in the size, a particle size analyzer was utilized to characterize the suspension. An increase in the concentration of surfactant was found to increase air entrapment and the stability of the CGA suspension but reduced mean diameter of the dispersion. The study also revealed that CGA characteristics were influenced by the ionic nature of the surfactant.

CGAs were utilized in a flotation process to remove pentachlorophenol (PCP) from an aqueous solution. The removal of PCP by CGAs generated from a cationic surfactant was found to be higher than that generated from anionic surfactant. However, the removal of PCP was found to be influenced more by air entrapment and the diameter of the suspension, than the charges on the encapsulating film. When compared with conventional flotation techniques used by other researchers, CGA flotation was found to be superior.

1-D solute transport and mixing were studied with CGA suspension and aqueous solution in packed sand columns. The breakthrough curves for both the
solutions showed early breakthrough and tailing. Mobile-immobile model (MIM) was able to describe the solute transport in columns by both aqueous solutions and CGAs. For aqueous solutions the dispersivity was found to increase with the length of the column due to "scale effect." However, in case of CGA suspension the dispersivity was seen to reduce with the column length.

Gamma ray densitometry was utilized to determine the mobility of the CGAs in soil columns. The gas saturation profile was found to be influenced by the concentration of the surfactants and the properties of the porous media.
CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Presently cleanup of the subsurface environment poses a major challenge to the scientific community. Historically, landfills have been the most common method for disposing of hazardous waste materials, but many of the sites that were once used for landfills or surface impoundments for hazardous wastes have now become Superfund Sites. In 1988 there were nearly 30,000 sites in the United States identified as potential hazardous sites, of which nearly 1,200 sites were on the National Priority (Superfund) List (USEPA, 1988). The Comprehensive Environmental Response, Compensation and Liabilities Act (CERCLA), known also as the Superfund Act of 1980, along with the Resource Conservation and Recovery Act (RCRA) have made landfill disposal very costly (Kostecki and Calabrese, 1989). The cost of incinerating contaminated soils from hazardous waste sites is estimated to be in the range of $600 to $1,000 per cubic yard and the cost of disposal at an approved hazardous waste disposal site is approximately $300 per cubic yard (Clarke, 1990). Inexpensive remediation procedures are needed to reduce the costs to the society, which will mitigate the effects of hazardous substances released into the subsurface environment. In recent years, innovative technologies such as soil washing, in-situ soil flushing, and bioremediation are gaining popularity, and it is apparent that these improved technologies can generate significant savings in the form of money and time.
Furthermore, in-situ cleanup methods are necessary for the contaminated sites that are inaccessible or too large to excavate and treat.

In-situ soil washing is the process of mobilization of contaminants that are subsequently removed from the soil using a recovery well for further treatment. Washing of contaminated soils has inherent advantages because it converts solid wastes into liquid wastes that are manageable with relative ease. Secondly, reduction in the volume of the waste is possible by concentration of pollutant from liquid wastes. Approximately 68% of Superfund Records of Decision (RODs) select groundwater pump and treat as a remedy to achieve aquifer restoration. However, recent research suggests that these systems may require protracted periods of time to make significant reductions in the quantity of contaminants associated with both the liquid and solid phases that constitute the subsurface matrix (Travis and Doty, 1990). Extended periods for remediation are highly undesirable as the operation and maintenance costs associated with the remediation are usually large. Also, many of the organic liquids that are common ground water pollutants cannot be efficiently extracted by pump and treat methods due to their low solubilities in water and high interfacial tension with water (Taber, 1990). At sites involving NAPLs or zones of low permeability, the restoration process can be particularly complicated. Even highly soluble contaminants may become trapped in the finer pore structure because of the preferential flow in high permeability zones.

In-situ soil washing can be considerably enhanced by using a variety of surfactants as reported by several researchers (Ellis et al., 1985; Ang and Abdul,
1991; Francisco, 1992; Liu, 1993). Part of the EPA's SITE (Superfund Innovative Technology Evaluation) remediation research has been directed at in-situ flushing of contaminated soil with the aid of aqueous surfactant solutions. Solubilization of the contaminants by the surfactants partitions more to the mobile phase. Flushing the contaminated soil or aquifer with surfactant solution therefore yields better removal efficiencies. Although researchers have conducted a number of promising laboratory studies, none of the field tests have been highly successful (Nash, 1987; Fountain et al., 1991; Abdul et al., 1992, West and Harwell, 1992). One of the main reasons of the failure of soil washing by surfactant is that it does not overcome the problem of preferential flow, making the process less efficient (Palmer and Fish, 1992).

One promising technique that overcomes the problem of preferential flow is the application of microbubbles or colloidal gas aphrons (CGA) to soil. Application of the CGAs to the soil blocks the high permeability layers or streaks and at the same time is able to solubilize the contaminants. The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (Sebba, 1971). CGAs consist of approximately 66% by volume gas and therefore form a low density liquid. These microbubbles do not coalesce easily and are remarkably different from conventional soap bubbles in their stability and flow through properties (Sebba, 1982). Two important considerations in the application of CGAs are i) their small size, resulting in a large surface area to volume ratio, and ii) the existence of a double film of surfactant encapsulating the gas that retards the coalescence of the bubbles.
CGAs have been shown to be useful in a variety of environmental applications. Our studies have shown that the CGA flotation process is more effective than conventional sparged air or solvent sublation in separation of the organics from aqueous waste streams (Chaphalkar et al., 1993). Based on the results reported in the literature and ongoing research on the application of CGAs to mobilize organics from soil columns (Roy et al., 1992b; Roy et al., 1993), it appears that this technology may be very effective in decontamination of soils. CGAs are also able to mobilize colloids from the soil matrix since air-water interface in motion is very effective in transporting colloids in a porous media (Wan and Wilson, 1992). Implications of facilitated colloidal particle transport are manifold. Bacteria is one of the colloids of concern in remediation; they can get preferentially attached to the air-water interface and therefore can be transported to the site of contamination. Jackson and Roy (1993), found that CGAs were able to transport the bacteria through a column much better than water or surfactant solution. CGAs can not only enhance transportation of microorganisms, but additionally can increase the available oxygen in the soil to facilitate biodegradation of organics.

1.2 DISSERTATION OBJECTIVE AND APPROACH

For the effective application of CGAs to decontaminate the subsurface environment, a better understanding of CGA properties and flow characteristics is essential. This research was therefore undertaken to examine the generation and properties CGAs. The study also included application of CGAs in aqueous streams.
and its flow through properties in soils. In particular, the objectives of this investigation were to:

- Examine the variables for generating CGAs of consistent properties.
- Characterize CGAs in terms of size distribution and stability
- Study variables affecting the characteristics of CGAs
- Compare effectiveness of CGAs for the separation of organics from aqueous solutions
- Examine and model the solute transport by CGAs
- Develop a setup to study flow of CGAs in porous media
- Study factors affecting the efficiency of CGAs in soil washing

This dissertation consists of four manuscripts, each focusing on a specific part of this research, which was directed toward developing a technology for the generation and application of CGAs. In chapter one a general introduction and objectives of this dissertation are provided. Chapter two reviews the literature on the generation, characterization, and application of CGAs. Chapter three, which is published in Separation Science and Technology, discusses the generation and characterization of CGAs. In this chapter, factors affecting the size distribution and stability of CGAs are discussed. For this study, CGAs were generated using cationic, anionic and nonionic surfactants at different concentrations, and the effect of these factors on the characteristics of the suspension was examined. The application of CGAs in the removal of pentachlorophenol (PCP) from the aqueous phase is presented in chapter four. This manuscript has been accepted for publication in Separation Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Science and Technology. For this study, microgas dispersions were generated using cationic, anionic and nonionic surfactants and were used in an adsorptive bubble flotation process in a semi-batch mode, to remove PCP from the aqueous phase. The removal efficiencies of PCP were determined at three different pH values. The results from this study were compared with the removal efficiencies using conventional flotation techniques used by other researchers. Chapter five has been submitted to Journal of Environmental Systems. This study was conducted to analyze the solute transport in columns with CGA suspensions and compare that with the aqueous solution. Experiments were conducted on packed sand columns with three different lengths and attempts were made to model the flow. Chapter six describes the development of a setup to study the transport of CGAs in the porous media. A setup has been developed that utilizes gamma ray densitometry for an on-line determination of the moisture contents of porous media. This chapter discusses the advancement of the CGA front in soil columns, as affected by the soil composition, surfactant concentration and length of the media. Finally, conclusions of this dissertation are incorporated in the chapter seven and the recommendations for the future study are listed in chapter eight.
CHAPTER 2

LITERATURE REVIEW

This literature review will focus on i) colloidal gas aphrons: properties and application, ii) flotation technique, iii) solute transport in porous media, and iv) transport of CGAs in porous media.

2.1 COLLOIDAL GAS APHRONS

The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (Sebba, 1971). Initially, CGA dispersions were generated by using a venturi flume (Sebba, 1971). Later, another efficient method was developed to produce CGAs in large quantities (Sebba, 1985). The most striking feature of a CGA suspension is its stability. CGAs are stable enough to be pumped from the point of generation to the point of application.

The fundamental properties of CGAs were studied and discussed by Sebba (1982). He hypothesized that the encapsulating soap film has an inner as well as an outer surface and that these surfaces have surfactant monolayers adsorbed on them (Fig. 2.1). The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, thereby increasing its stability. "Stability" of microbubble dispersion can be defined as the length in time over which the number of bubbles and their size distribution remains constant. CGA dispersions, if left undisturbed, will eventually cream and be converted to ordinary foam, leaving a clear aqueous layer below.
Figure 2.1 Structure of an air bubble, a soap bubble and a CGA

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2.1.1 Size Distribution and Stability of CGAs

Various techniques have been applied to determine the diameter of a microbubble in solution. Amiri and Woodburn (1990) carried out an analysis of the rate of rise of CGA bubbles in a measuring cylinder and showed that it is equivalent to that of hindered rising of a 35 μm spherical bubble with a 0.75 μm outer shell. Photographic techniques have also been used for the determination of bubble sizes (Cheng and Lemlich, 1983; De Vries, 1972). In these techniques, the bubbles were observed in the plane of contact between them and the glass wall. Longe (1989) studied bubble size distributions in CGA suspensions and factors affecting their distribution. He examined bubbles in a specially designed cell under a microscope. However, his observations did not incorporate changes in size distribution patterns with time. When introduced into an aqueous system, CGAs in the dispersion undergo variation in both size and number density with time because of coalescence and/or creaming. These dynamic changes have not been addressed in the literature.

Earlier the stability of CGAs in studies was measured by rapidly transferring about 200 mL of CGA suspension into a 250 mL cylinder. The volume of liquid drained was measured with respect to time and interpreted in terms of life or stability of CGAs (Longe, 1989). These observations, however, did not take into account the stability of a CGA dispersion when mixed in an aqueous system. In practice, CGAs have to be pumped into a solution for the purpose of separation or flotation, but a study of their stability under field conditions has not been carried out.
2.1.2 Application of CGAs

CGAs have been shown to be useful in a variety of environmental applications. CGAs have also been used in the microflotation of colloids and in the removal of heavy metal ions from wastewater using precipitate flotation (Gregory et al., 1980; Cirrilo et al., 1982; Sebba and Barnett, 1981). Roy et al. used CGAs to separate dyes from water by flotation (1992) and the results indicate that CGAs can be effectively applied in the separation of synthetic dyes from wastewater and in treating contaminated sites. The ability of CGAs to adhere and be retained as small bubbles in various saturated and subsurface matrices has been demonstrated by Michelsen et al. (1984). They observed 60% degradation of phenol after a combination of CGAs and pseudomonas putida was injected into a contaminated sand matrix.

Very little information is available in the literature regarding the use of CGAs for soil flushing (Roy et al., 1993; Longe 1989). Roy et al. (1992b) studied the performance of CGAs and surfactants in flushing 2,4-dichlorophenoxy acetic acid (2,4-D) from soil. They observed that there is no significant difference in the performance of the two processes of soil flushing for a highly soluble compound like 2,4-D, and suggested that CGAs will be more effective for hydrophobic compounds rather than hydrophilic compounds. CGA suspensions were also used to wash automatic transmission fluid (ATF) from fine silty loam (Roy et al., 1993). CGA suspensions were found to be more effective than conventional surfactant solutions and water. In six pore volumes, CGA suspensions removed 50%, conventional surfactant solutions 42%, and water flood removed only 20% of ATF. Longe (1989) conducted
a study to determine the performance of CGAs for soil flushing of hydrophobic compounds. He observed removals of up to 88% for some organics, which was in contrast to only 10% removal of the same organics using a surfactant.

2.2 FOAM FLOATATION

There are number of techniques that utilize the surface-active nature of the compounds at air-water interface to bring about their removal from the aqueous phase. In his book, Lemlich (1972) provided an introduction to the principles and applications of foam floatations. A book by Wilson and Clark (1985) provides modelling approach and reviews processes. A collection of symposium papers covering most aspects was edited by Somasundaran and Grieves (1977).

In the case of separation with CGAs, the mechanism of flotation is somewhat different. The process may involve either solubilization of the solute within the film surrounding a CGA, or adsorption on the film surface, or a combination of both. The adsorption and/or solubilization by a CGA occurs because of the unique structure of CGA described above.

CGAs have also been used to float suspended particulates and bubble entrained flocs. This dispersion has been effectively used to remove phosphate slime, coal ash, and clay fines from solutions (Sebba and Yoon, 1982; Sebba and Barnett, 1981). Honeycutt et al. (1983) utilized CGAs to successfully harvest unicellular algae. Lohse (1988), demonstrated the effectiveness of CGAs in removing algae from fresh water using countercurrent flotation chamber. In another study, fine oil droplets few
microns in diameter were removed successfully from aqueous streams (Michelsen et al., 1986)

2.3 SOLUTE TRANSPORT IN POROUS MEDIA

One dimensional transport of a nonreactive solute in saturated porous media is generally described with the convective dispersive equation (CDE)

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \]  

(1)

where \( C \) denotes solute concentration (M L\(^{-3}\)), \( t \) time (T), \( x \) distance (L), \( D \) the dispersion coefficient (L\(^2\) T\(^{-1}\)) and \( v \) the pore water velocity (L T\(^{-1}\)). Dispersion coefficient \( D \) is sometimes described as a linear function of pore water velocity i.e.

\[ D = \lambda v \]  

(2)

where \( \lambda \), also known as dispersivity (L), is a constant.

One of the limitations of this model stems from the fact that, in practice, flow and mixing of solute in the transport process is dominated by larger pores resulting in stagnant water bodies in the matrix. Experimental evidence of these effects has been documented in a review article by Wierenga (1982). Also, CDE fails to take into account the apparent large variation in the microscopic pore-water velocities especially that occur at high flowrates. To address these problems, resulting from apparent heterogeneities, Coats and Smith (1964) proposed a model by adding a capacitance term to the convective dispersive equation as,
\[ \beta \frac{\partial C_m}{\partial t} + (1 - \beta) \frac{\partial C_{im}}{\partial t} = D_m \frac{\partial^2 C_m}{\partial x^2} - v \frac{\partial C_m}{\partial x} \]  (3)

where \( C_{im} \) is the solute concentration in the stagnant zone, \( D_m \) is dispersion coefficient of the flowing fraction and \( \beta \) is the flowing fraction. Subscripts "m" and "im" denote the mobile and immobile phases of water contents in porous media respectively. The mass transfer between the flowing and stationary phase is proposed to be a first order reaction,

\[ (1 - \beta) \frac{\partial C_{im}}{\partial t} = \alpha (C - C_{im}) \]  (4)

where \( \alpha \) is the rate constant \((T^{-1})\). The flowing fraction \( (\beta) \) is expressed as,

\[ \beta = \frac{\theta_m}{\theta} \]  (5)

where \( \theta \) is volumetric water content \((L^3L^{-3})\) that comprises mobile and immobile water phase. The dispersion coefficient \( D \) for the overall mobile-immobile region can be defined in terms of the dispersion coefficient of the flowing fraction,

\[ D = D_m \beta \]  (6)
This modified approach assumes that the liquid phase in the porous media remains partitioned in mobile and immobile regions. Convective-dispersive transport is restricted to the mobile water phase while transfer of solutes from the immobile phase is assumed to be diffusion limited. Substitution of equations (5) and (6) into equations (3) and (4) yielded the following equations:

\[
\theta_m \frac{\partial C_m}{\partial t} + \theta_{lm} \frac{\partial C_{lm}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \tag{7}
\]

\[
\theta_{lm} \frac{\partial C_{lm}}{\partial t} = \alpha (C_m - C_{lm}) \tag{8}
\]

where \( q \) is the liquid flux (LT\(^{-1})). Analytical solutions for equations (6) and (7) have been discussed for variety of initial and boundary conditions by De Smidt and Wierenga (1979). In case of unsaturated flow, early breakthrough and tailing of the chemicals that are not adsorbed or excluded by the media have been shown to be caused by the immobile fraction water in the unsaturated soils (van Genutchen and Wierenga, 1977; Rao, 1980). The MIM model therefore has not only been used to describe solute transport through saturated porous media, but several researchers have used the model to describe breakthrough curves from unsaturated media as well (De Smidt and Wierenga, 1984).

CDE assumes that the effective dispersivity remains constant for any length of the column for a constant velocity, but in practice it is found to increase with the distance from the source. This phenomenon is called "scale effect," and is well
reported in the literature (Gelhar et al., 1985; Sudicky and Cherry, 1979 and Dagan, 1984). It occurs due to local variation in the water velocity along the direction of motion, causing the solute to spread differently in longitudinal direction. Since the local variation in the velocity increases with the distance, the dispersion would increase until the velocity differences normal to the direction of the flow are smoothed by transverse mixing (Khan and Jury, 1990).

2.4 TRANSPORT OF CGAs IN SOILS

Understanding of the flow CGAs through porous media is important in its application in the subsurface environment for hazardous waste remediation. There is however, a paucity of information available in the literature. Fugate (1985) studied the flow of CGAs through a 2-D flume and noted that CGA tended to accumulate near the point of injection, forming a stationary front. However, in another study carried out by Longe (1989), two separate fronts of gas and liquid were observed. Gas front followed the liquid front owing to its lower permeability. Solute transport by CGA suspension, however, was not considered in these studies.

Although CGA is a homogeneous fluid at the time of pumping, within the porous media separation of air and solution phase may occur and the resulting fluid will behave like a two-phase fluid. It is possible that the mechanism by which CGAs are transported within porous media may be similar to that of a foam.

2.4.1 Foam Flow in Porous Media

Use of foam for recovery of oil recovery was first proposed by Bond and Holbrook (1958), since then gas flooding has become one of the fastest growing
enhanced oil recovery (EOR) techniques. Essentially, the ability of foam to preferentially block the larger pores is utilized in this process to reduce the fingering problem. Several researchers have proposed different mechanisms to explain foam flow in a porous media. It seems that the foam propagation depends on several factors like surfactant type and concentration, physical and chemical characteristics of the porous media, nature and concentration of the contaminant, and hydraulic conditions, among others. Most of these theories are able to explain individual observations, but generalization is not possible. Transport of foam in the porous media, therefore, can only be modeled approximately.

Foam in a porous media is in form of gas phase dispersed in an interconnected wetting surfactant solution that is composed of liquid bridges and lamellae. Surfactant solution occupies the smallest pores and transports separately from the foam phase. The amount of surfactant solution conducted by flowing lamellae and liquid bridges is very small compared to that conducted by the completely liquid filled pore channels (Bond and Bernard, 1966; Holm, 1968). Bubbles do not maintain their identity during the transport through a porous media, rather, they are shaped according to the nature of porous media. Foam texture, which is nothing but the size distribution and the number of bubbles, arises from complex mechanisms that cause bursting or regeneration of the bubble. The kinetics of foam generation and collapse not only depends on surfactant type, composition and concentration but also on the gas and liquid flow rates within the media (Ransohoff and Radke, 1988; Friedmann and Jenson, 1986; Jamenez and Radke, 1989). The effective surfactant concentration will
vary within the soil matrix because of its interactions with the soil particles. Harwell (1992), has reviewed the number of types of surfactant behavior that can reduce the effective surfactant concentration: precipitation, liquid crystal formation, formations of coacervate phase, partitioning into trapped residual phase, or adsorption onto the solid surfaces. Additionally, the interactions of contaminants with the surfactant solution depend on the temperature, electrolyte concentration, and the concentration of the contaminant.

Finally, Mahmood and Brigham (1987) have compiled speculations of several researchers about possible mechanisms of foam flow in a porous media.

1. **Bubble Flow**: Foam flows as a homogeneous fluid with gas uniformly dispersed in the surfactant solution. The implicit assumption in this theory is that the size of bubbles is small compared to the pore or capillary constrictions so that the bubbles do not need to distort when passing through.

2. **Intermittent Flow**: Foam flows in such a way that liquid is transported by a continuous network of liquid membranes, while gas flows as a discontinuous phase through breaking and reforming the bubbles.

3. **Trapped Gas Flow**: Some gas in the foam is trapped in the porous media while the remainder flows as a free phase and the fraction of flowing gas is generally small compared to trapped gas fraction.

4. **Membrane Flow**: Foam is generated as lamellae at specific locations in the porous media. The propagation of the foam therefore is conditional to the geometry of the pores.
5. **Tubular-Channel Flow**: Foam flows through channels consisting of tubular bubbles moving along and extending over several pore spaces. These tubes cause trapping of gas or liquid by making them discontinuous. The volume trapped depends upon the operating conditions and pore geometries.

6. **Segregated Flow**: Foam flows only through gas channels carrying a small amount of surfactant with it. The majority of the liquid flows through separate channels, the number and distribution of which depends upon its saturation.
CHAPTER 3

A STUDY OF THE SIZE DISTRIBUTION AND STABILITY OF COLLOIDAL GAS APHRONS USING PARTICLE SIZE ANALYZER*

Application of colloidal gas aphrons (CGA) in decontaminating soils and aqueous solutions is one of the emerging innovative technologies. Lab studies on in-situ flushing using CGAs has been demonstrated to be one of the promising technologies for remediation of hazardous waste sites. However, the properties and characteristics of the CGAs are not known fully. This research addresses the size distribution and stability of CGAs as studied by using a particle size analyzer. Cationic, anionic and nonionic surfactants were used to generate the CGAs. Size distribution spectrum and volume fraction of microbubbles in sample solutions were studied as functions of time. The effects of surfactant concentrations used to produce CGAs and the presence of an electrolyte, such as sodium chloride, on the characteristics of the suspension were also studied. CGA size was found to have a wide range of values. MD of the suspension was found to be characteristic of the surfactant. The presence of an electrolyte was found to affect only the characteristics of CGAs produced from the ionic surfactants, whereas no effect was observed on CGAs generated from a nonionic surfactant.

* This Chapter reprinted from Separation Science and Technology, Vol 28(6), pp 1287-1302, 1993, by courtesy of Marcel Dekker. Inc.
3.1 INTRODUCTION

The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (1971). Initially, Sebba generated CGA dispersions by using a venturi flume (1971). Later, he developed another efficient method to produce CGAs in large quantities (1985). The most striking feature of a CGA suspension is its stability. CGAs are stable enough to be pumped from the point of generation to the point of application.

CGAs have been shown to be useful in a variety of environmental applications. They are more effective than conventional sparged air in the separation of organics from aqueous waste streams (Caballero et al., 1989). CGAs have also been used in the microflotation of colloids and in the removal of heavy metal ions from wastewater using precipitate flotation (Gregory et al., 1980; Cirillo et al., 1980, and Sebba and Barnett, 1981). The ability of CGAs to adhere and be retained as small bubbles in various saturated and subsurface matrices has been demonstrated by Michelsen et al. (1984). They observed 60% degradation of phenol after a combination of CGAs and pseudomonas putida was injected into a contaminated sand matrix.

The fundamental properties of CGAs were studied and discussed by Sebba (1982). He hypothesized that the encapsulating soap film has an inner as well as an outer surface and that these surfaces have surfactant monolayers adsorbed on them (Fig.3.1). The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, thereby increasing its stability. "Stability" of a microbubble dispersion can be defined as the length in time...
Figure: 3.1 Structure of an air bubble, a soap bubble and a CGA
over which the number of bubbles and their size distribution remain constant. CGA dispersions, if left undisturbed, will eventually cream and be converted to ordinary foam, leaving a clear aqueous layer below. In studies thus far, the stability of CGAs was measured by rapidly transferring about 200 mL of CGA suspension into a 250 mL cylinder. The volume of liquid drained was measured with respect to time and interpreted in terms of life or stability of CGAs (Longe, 1989). These observations, however, did not take into account the stability of a CGA dispersion when mixed in an aqueous system. In practice, CGAs have to be pumped into a solution for the purpose of separation or flotation, and therefore a study of their stability is important under conditions when CGAs are pumped and mixed with an aqueous stream.

Various techniques have been applied to determine the diameter of a microbubble in solution. Amiri and Woodburn (1990) carried out an analysis of the rate of rise of CGA bubbles in a measuring cylinder and showed that it is equivalent to that of hindered rising of a 35 μm spherical bubble with a 0.75 μm outer shell. Photographic techniques have also been used for the determination of bubble sizes (Cheng and Lemlich, 1983; De Vries, 1972). In these techniques the bubbles were observed in the plane of contact between them and the glass wall. Longe (1989) studied bubble size distributions in CGA suspensions and factors affecting their distribution. He examined bubbles in a specially designed cell under a microscope. However, his observations did not incorporate changes in size distribution patterns with time. When introduced into an aqueous system, CGAs in the dispersion undergo
variation in both size and number density with time because of coalescence and/or creaming. So far, these dynamic changes have not been addressed in the literature.

The shortcomings of the above methods can be overcome by using a particle size analyzer to examine the size and stability of CGAs. Particle size analyzers, when equipped with a flow-through cell, allow us to add CGA samples in a mixing chamber. The mixed solution is then circulated continuously through a "viewing" cell where a laser beam is utilized to monitor the bubbles in the system. The analyzer allows us to collect data periodically, enabling the determination of size distribution as a function of time. The samples can thus be mixed with water, and the dynamic nature of the bubble size distribution can be determined in an aqueous environment to simulate the use of CGAs in flotation columns.

This study presents the results of size distribution and stability analysis of CGAs generated from cationic, anionic, and nonionic surfactants in concentrations above, below, and near their critical micellar concentration (CMC) values. The effect of the ionic strength of the solution on the characteristics of CGA was also studied.

3.2 EXPERIMENTAL

3.2.1 Surfactants

CGAs were generated using Tergitol 15-S-12 (Union Carbide), sodium dodecylbenzene sulfonate (Sigma), and hexadecyltrimethylammonium bromide (Eastman Kodak). Tergitol is a nonionic surfactant that has an average chain length of 15 carbon atoms with a CMC value of 0.15 mM (MW =738). Sodium dodecylbenzene sulfonate (DDBS) is a salt of dodecylbenzene sulfonic acid with a
chain of 12 carbon atoms. It is an anionic surfactant with a CMC value of 1.5 mM (MW =348.5). Hexadecyltrimethylammonium bromide (HTAB) is a cationic surfactant with a chain of 16 carbon atoms and has a CMC value of 0.9 mM (MW =364.6).

3.2.2 Production of CGAs

Based on methods suggested by Sebba (1985), a unit was fabricated in our laboratory for the production of CGAs. A 0.5 hp motor was fitted on top of a 3 L cylindrical container (Fig. 3.2). A flat disk, 50 mm in diameter, was mounted at the end of a shaft. The level of the surfactant solution was initially adjusted to be approximately 15 mm above the disk, which can rotate up to 8000 rpm. Two flat baffles were fixed to the lid of the container. The disk when rotated at very high speeds, creates strong waves on the liquid surface. The waves strike the baffles, and upon re-entering the solution they entrain air in the form of a microbubble dispersion or colloidal gas aphrons (CGA).

3.2.3 Size Distribution of CGAs

Size distribution of CGAs was determined using a particle size analyzer (Microtrac 7995-10, Leeds and Northrup). The analyzer can "sense" objects such as droplets, soil particles and bubbles. It utilizes a low angle, forward scattering laser beam projected through a viewing cell through which the sample is circulated. The amount and direction of light scattered by the particles is processed by an optical filter and directed to a photodetector. Electrical signals proportional to the transmitted light are processed by a microcomputer to form a multichannel histogram of particle size.
Figure 3.2 Schematic drawing of CGA generator
distribution in terms of the volume of particles in each of the channels. The output also provides volume mean diameter and standard deviation, percentile range of the diameter and mean area of the particles. The analyzer covers a particle size range from 1.6 to 300 μm. A CGA suspension (50 mL) was added to the mixing chamber which held approximately 275 mL. The solution from the mixing chamber was circulated by a centrifugal pump through the viewing cell. The particle size analyzer was set to analyze the sample repetitively every 2 minutes.

3.3 RESULTS AND DISCUSSION

3.3.1 Structure of a CGA

Figure 1 illustrates the differences in the structures of an air bubble, a soap bubble, and a gas aphron. An air bubble in pure water can be treated as a cavity enclosed by water. When surfactant molecules are present in water, any cavity introduced in water creates a water-gas interface where surfactants are adsorbed. In the case of colloidal gas aphrons, the encapsulating soap film has an inner as well as an outer surface, and both these surfaces have surfactant monolayers adsorbed on them. These layers can be treated as expanded monolayers and consist largely of water, which has properties different from the bulk water because of enhanced hydrogen bonding. The sandwiched layer can therefore be treated as a different phase from the bulk water since surfactant molecules at this surface have hydrophilic ends pointing inward and hydrophobic ends pointing outward. Further, there is an interface between that phase and the water with the hydrophobic ends facing the soapy shell.
The encapsulation of a colloidal gas aphron in a double layer of surfactant molecules retards its coalescence because when two aphrons collide, the momentum may not be enough to break the barrier of the six intervening surfactant stabilized interfaces before the bubbles can coalesce.

3.3.2 Parameters of Particle Size Analysis.

The volume of sample material in the circulating system that is used for an analysis is referred to as the "sample loading." The analyzer responds to this loading and reports its measurement as a dimensionless number, $V_s$. A typical plot of $V_s$ versus mass/volume of particles or bubbles in the system is linear up to a certain value of mass in the sampling system, which depends on sample characteristics. Further addition of sample to the circulating system beyond this value, gives rise to a multiple scattering-attenuation effect, reducing the slope of the plot which then becomes nonlinear. In this study the addition of 50 mL of CGA suspension into the circulating system was found to fall within the optimum range of loading that was comparable in all cases of CGA used. The lower limit of sample loading is determined by the system noise and particle or bubble density needed to give statistically valid data. The least measurable $V_s$ value that was reproducible was found to be approximately 0.002.

The quantity $V_s$ was therefore used as a surrogate parameter, equivalent to the sample load in the circulating system, to determine the "stability" of the CGA suspension. In this study, "stability" of CGAs was determined as the time span for which $V_s$ of the suspension remained measurable.
The parameter "mean diameter" (MD), which is calculated from the mean volume of the suspension, was used as a single parameter to identify the average size distribution of suspension. This was necessary because the size distribution of CGA at any given time varies over a wide range and it would be very difficult to extract useful information from the data collected. Figure 3.3 shows size distribution curves for DDBS near its CMC value at 2 minute intervals. It was also observed that the MD for the same surfactant remained more or less stable (Fig. 3.4), which further strengthens our argument that it can be used as a single parameter in characterizing the size distribution of a CGA suspension.

3.3.3 Microbubble Size Distribution

In an earlier work, Sebba (1982) had reported that the aphrons seem to be largely composed of bubbles between 10 and 30 μm in diameter. However Longe (1989) found recently that the majority of bubbles diameter range approximately between 10 and 130 μm, with a mean value for all test conditions between 51 and 61 μm (Table 3.1). These studies were conducted at static conditions under a microscope where the CGAs were drawn into a viewing cell.

The results of the present study, along with the results of Longe (1989), are presented in Table 1 for comparison. It was found that in our system, wherein a CGA suspension was pumped into a mixing chamber and circulated through a viewing cell, the range of microbubble size distribution was much wider than previously reported. A majority of the bubbles were found to have diameters between 30 and 300 μm, rarely falling below 30 μm. The mean diameter was found to be
Figure: 3.4 Changes in CGA characteristics due to different surfactants (Concentration near CMC)
TABLE 3.1
Comparison of CGA size distributions

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>SIZE DISTRIBUTION (Longe, 1989)</th>
<th>PARTICLE SIZE ANALYZER RESULTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min - Mean - Max</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>DDBS 200 mg/l</td>
<td>13 - 61 - 129</td>
<td>29</td>
</tr>
<tr>
<td>DDBS 500 mg/l</td>
<td>14 - 61 - 120</td>
<td>25</td>
</tr>
<tr>
<td>DDBS 500 mg/l + NaCl 200 mg/l</td>
<td>12 - 57 - 107</td>
<td>24</td>
</tr>
<tr>
<td>DDBS 750 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>DDBS 1000 mg/l</td>
<td>15 - 53 - 104</td>
<td>22</td>
</tr>
<tr>
<td>TERGITOL 50 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>TERGITOL 100 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>TERGI 100 mg/l + NaCl 200 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>TERGITOL 500 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>TERGITOL 1000 mg/l</td>
<td>14 - 51 - 98</td>
<td>21</td>
</tr>
<tr>
<td>HTAB 200 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>HTAB 328 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>HTAB 328 mg/l + NaCl 200 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>HTAB 500 mg/l</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Note: (1) All sizes are in microns.
      (2) The percentile distribution reported is at t = 2 min.
characteristic of the surfactant, as the following discussion will demonstrate. The
standard deviation of bubble diameter varied between 50 and 77 μm for ionic
surfactants and between 29 and 35 μm for the nonionic surfactant. When introduced
into an aqueous system, CGAs in the dispersion undergo variation in size and number
with time because of coalescence and/or creaming, and these effects are reflected in
our study, which shows larger bubble sizes with a wider distribution than reported
earlier. It should be noted that particle size analysis is a direct measurement of the
bubble sizes at that particular time, and therefore it is a reliable measure of the size
ranges.

3.3.4 Effects of Surfactant Type

Figures 3.4 shows the V_τ and mean diameter of CGA suspension plotted versus
time for all three surfactants at their CMC values. It reveals that the variation in the
range of mean diameter of the CGAs was specific to the surfactant. Mean diameter
of CGAs generated with sodium dodecylbenzene sulfonate (DDBS) ranged between
118 and 138 μm, while for hexadecyltrimethylammonium bromide (HTAB) the range
was between 104 and 117 μm. For Tergitol, the mean diameter ranged from 46 to
66 μm.

It was noted that V_τ, the surrogate parameter for the volume occupied by the
bubbles in the circulating system, and its decay with time also remained specific to
the surfactant. At time t = 2 minutes, CGAs generated with Tergitol had the largest
V_τ value while HTAB and DDBS had V_τ values that were comparable. Interestingly,
the "stability," defined as the time span for which V_τ of the suspension remained
measurable, was found to be unaffected by the initial value of $V$, and remained nearly similar. In short, it appeared that CGAs generated from all three surfactants had comparatively similar degrees of stability but Tergitol CGAs had a larger air content than the other two surfactants at $t = 2$ minutes. Since there are no net charges on CGA generated from nonionic surfactants, collective surface repulsive forces on the bubble are probably smaller, which may allow bubbles to get closer, thus increasing the entrapped air volume. The data reflect that the bubbles generated from a nonionic surfactant will be compressed, and consequently they will be of smaller diameter compared to bubbles generated from ionic surfactants.

3.3.5 Effects of Surfactant Concentration

The concentration of surfactant in solutions used to generate CGAs was thought to be likely to influence the characteristics of microbubble dispersions. To study this effect, CGAs were generated using three types of surfactants at concentrations below, near and above CMC levels. The results are presented in Figs. 3.5-3.7. In general, it was found that an increase in the concentration of the surfactant increased $V$, and increased the stability of the suspension. The increase in $V$, was found to be specific to each surfactant. However, an increase in initial $V$ did not increase the stability of CGA proportionately. Since decay of the bubbles in the circulating system was approximately exponential, the bubbles remained in suspension only a few minutes longer.

Longe (1989) reported that increasing the concentration of DDBS beyond CMC only slightly influenced CGA characteristics. However, in this study, increasing the
Figure: 3.5 Effects of surfactant concentration on the characteristics of CGA (Surfactant Tergitol)
Figure 3.6 Effects of surfactant concentration on the characteristics of CGA (Surfactant DDBS)
Figure: 3.7 Effects of surfactant concentration on the characteristics of CGA (Surfactant HTAB)
concentration of DDBS from 500 mg/L to 750 mg/L was found to increase $V_*$ almost threefold. Interestingly, in the case of HTAB the increase in concentration beyond CMC did not influence $V_*$ (Figure 3.7). Similar results were seen in the case of Tergitol (Fig. 3.6) where an increase in $V_*$ was found to be only marginal for an increase in concentration from 100 to 500 mg/L; furthermore, the initial $V_*$ was found to be nearly equal for concentrations 500 and 1000 mg/L. In practice, the parameter $V_*$ can therefore be utilized to determine the optimum concentration of surfactants that would yield maximum air entrapment for the application of CGAs.

The increase in concentration, however, tended to reduce the mean diameter of the suspension of all three surfactants (Figs. 3.5-3.7). This observation follows the logic that an increase in the numbers of surfactant molecules beyond a certain value tends to crowd them on the microbubble surfaces, thereby reducing the interfacial tension between the bubble and the bulk water. Reduction in the interfacial tension would therefore reduce the bubble size.

3.3.6 Effects of Ionic Concentration

Figure 3.8 shows the effect of the addition of 200 mg/L NaCl on CGAs generated from ionic surfactants with concentrations near their CMC. For ionic surfactants (DDBS and HTAB), the presence of salt increased their $V_*$ in the system and reduced the mean diameter of the suspension. These results are a direct consequence of the ionic nature of the encapsulating film. The presence of ions in a CGA solution generated from an ionic surfactant would compress the film surrounding the bubble, shrinking its diameter. The increase in $V_*$ can also be attributed to this...
Figure: 3.8  Effects of NaCl on the characteristics of CGA (Surfactant DDBS and HTAB)
factor (Fig. 3.8). In contrast, the properties of CGA made from the nonionic surfactant (Tergitol) were not affected by the ionic strength of the solution (Fig. 3.9).

3.4 CONCLUSIONS

The usefulness of a particle size analyzer is demonstrated in analyzing the size distribution and stability of CGA. Microscopic analysis of the suspension, as carried out by earlier researchers, assessed the properties of CGAs at the time of generation, but particle size analysis carried out in a continuous flow cell gives a clue about the stability and size distribution under realistic conditions in real time. When introduced into an aqueous system, CGAs in a dispersion undergo variation in sizes and numbers with time due to coalescence and/or creaming. These dynamic changes can be addressed by using particle size analysis such as the one utilized in this study.

The parameters mean diameter (MD) and $V_s$, which is equivalent to the bubble volume fraction in the circulating system, were used to characterize CGAs produced under different conditions. The results were considerably different from those reported earlier. CGA size was found to have a wide range of values. MD of the suspension was found to be characteristic of the surfactant. In general, it was found that an increase in the concentration of surfactant increased both $V_s$ and the stability of the suspension but reduced the mean diameter of CGAs. The increase in $V_s$ was also found to be specific to the surfactant. The effect ions in the solution used for the generation of CGAs revealed the ionic nature of the encapsulating film around the bubbles. The presence of an electrolyte was found to affect only the characteristics
Figure: 3.9  Effects of NaCl on the characteristics of CGA (Surfactant Tergitol)

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of CGAs produced from the ionic surfactants, whereas no effect was observed on CGAs generated from a nonionic surfactant.
CHAPTER 4

FLOTATION USING MICROGAS DISPERSIONS FOR THE REMOVAL OF
PENTACHLOROPHENOL FROM AQUEOUS SOLUTIONS

Microgas dispersions called colloidal gas aphrons (CGAs) were generated using cationic, anionic and nonionic surfactants and were used in an adsorptive bubble flotation process in a semi-batch mode, to remove pentachlorophenol (PCP) from the aqueous phase. The aqueous solution was maintained at pH values using buffers. CGAs generated with Tergitol, which is a nonionic surfactant, was found to be the most efficient in the removal of PCP and the efficiency remained nearly independent of pH. The charges on the encapsulating film of CGAs may explain the higher percentage of adsorption of PCP on the CGAs generated using hexadecyltrimethylammonium bromide (HTAB) as compared to CGAs generated using sodium dodecylbenzene sulfonate (DDBS). For all the surfactants, an increase in concentration improved the removal efficiency. These results were compared with the removal efficiencies using conventional flotation techniques used by other researchers. Solvent sublation appears to be effective in the removal of PCP but even in the presence of a surfactant it required 300\% more air volume per volume of liquid when compared with CGA flotation.

* This manuscript has been accepted for publication in Separation Science and Technology and is here reproduced courtesy of Marcel Dekker Inc.
4.1 INTRODUCTION

Pentachlorophenol (PCP) is a priority pollutant that has been used extensively in agricultural and industrial applications. PCP contamination of water and sediments is well documented in the literature. In a study conducted in Michigan, 156 of the 223 industrial and municipal sewage sludges were found to have PCP concentrations ranging from 0.2 to 8490 mg/kg (Jacobs et al., 1987). A USEPA report (1980) indicates that acute and chronic toxicity to freshwater aquatic life due to PCP occurs at concentrations as low as 55 and 3.2 µg/L, respectively. For saltwater aquatic life, the corresponding values are 53 and 34 µg/L. The recommended level in drinking water is 1.01 mg/L, but the undesirable taste and odor threshold in water is 30 µg/L.

In this study the effectiveness of a modified flotation method that uses microbubble dispersions to remove PCP from an aqueous stream was studied and compared with conventional floatation process. Diffused aeration has long been utilized to remove volatile and surface active organics from wastewaters. However, for surface inactive compounds called "colligends," a surface active material or surfactant needs to be added to the solution to form a complex with the compound, making it hydrophobic, so that it gets adsorbed at the air bubble surface in a flotation process. This process is called foam flotation (Clarck and Wilson, 1983). The adsorbed compound at the interface then rises to the surface with the bubble and is concentrated at the surface in the foam formed atop the aqueous phase, from where it can be skimmed off. This method is especially effective for the separation of materials at low concentrations.
The microgas dispersion utilized in this study is called colloidal gas aphrons (CGAs). This name was proposed by Sebba (1971). These bubbles display different properties than the conventional gas cavities in aqueous solutions (air bubbles) because of the nature of its encapsulating film. The most striking feature of a CGA suspension is its small bubble size, which yields a very large specific surface area per unit volume. CGA suspension entraps around 66% air by volume but is stable enough to be pumped from the point of generation to the point of application. CGAs therefore have been shown to be useful in a variety of environmental applications. They have been used in the microflotation of colloids and in the removal of heavy metal ions from wastewater using precipitate flotation (Gregory et al., 1980; Cirillo et al., 1982, and Sebba and Barnett, 1981). Roy et al. (1992) recently demonstrated an application of CGA flotation in separating synthetic dyes from an industrial waste.

In this study CGAs were generated using cationic, anionic and nonionic surfactants in concentrations below and at their critical micellar concentration (CMC) values. CGAs thus generated were used in an adsorptive bubble flotation process to remove PCP from a buffer solution at three different values of pH. These results were compared with the removal efficiencies using conventional flotation techniques.

4.2 EXPERIMENTAL

4.2.1 Chemicals

A pH 10.1 buffer was prepared by addition of 11 ml of 1 N NaOH to 0.025 M NaHCO₃ and a pH 3.0 buffer was prepared by adding 4 ml of 1 N H₂SO₄ to 0.005 M NaH₂PO₄ solution. pH 7.4 solution was prepared from a 10% stock solution of
0.087 M KH$_2$PO$_4$ and 0.304 M Na$_2$HPO$_4$. PCP stock solution was prepared by dissolving 0.8 gm in 100 ml methanol. To achieve 8 mg/L concentration of PCP in the aqueous solutions, 1 ml of stock was diluted to a liter.

CGAs were generated using Tergitol 15-S-12 (Union Carbide), sodium dodecylbenzene sulfonate (Sigma), and hexadecyltrimethylammonium bromide (Eastman Kodak). Tergitol is a nonionic surfactant that has an average chain length of 15 carbon atoms with a CMC value of 0.15 mM (MW =738). Sodium dodecylbenzene sulfonate (DDBS) is a salt of dodecylbenzene sulfonic acid with a chain of 12 carbon atoms. It is an anionic surfactant with a CMC value of 1.5 mM (MW =348.5). Hexadecyltrimethylammonium bromide (HTAB) is a cationic surfactant with a chain of 16 carbon atoms and has a CMC value of 0.9 mM (MW =364.6).

### 4.2.2 Production of CGAs

Based on methods suggested by Sebba (1985), a unit was fabricated in our laboratory for the production of CGAs. Briefly, it consisted of 0.5 HP motor fitted on top of a cylindrical container that held approximately 3 liters of liquid. A flat disc, 50 mm in diameter, is mounted at the end of a shaft. The level of the surfactant solution is initially adjusted approximately to be 15 mm above the disc, which can rotate up to 8000 rpm. Two flat baffles are fixed to the lid of the container. The disc when rotated at very high speeds creates strong waves on the liquid surface which strike the baffles and upon re-entering the solution, entrain air in a form of microbubble dispersion or colloidal gas aphrons (CGA). Size distribution of CGAs
was determined using a particle size analyzer (Microtrac 7995-10, Leeds and Northrup). A detailed description of the CGA apparatus and size distribution can be found in our previous work (Chaphalkar et al., 1993).

4.2.3 Experimental Setup

A glass column, 100 cm in height and an internal diameter of 8 cm was used for the flotation experiments. The height of liquid in the column was maintained at 60 cm, which gave a total liquid volume of 2.8 liters. Two stopcocks were positioned at 15 and 45 cm from the bottom to allow samples to be collected from different heights. A pulse of 50 ml of CGA suspension was pumped from the bottom of the column with a Masterflex positive displacement pump (Cole Parmer Inc.) at a constant flow rate of 35 ml/min. This was followed by a period of 10 minutes during which no CGAs were introduced thus allowing the bubbles to rise to the top. Samples were collected from the bottom and top sections but since the difference in the concentrations was found to be insignificant, only the concentrations of the samples collected from the top port are reported.

4.2.4 Analysis

Analysis of pentachlorophenol was performed using a Hewlett Packard 1050 liquid chromatograph equipped with a multiple wavelength detector. Reverse phase Envirosepp-PP, (125 X 3.2 mm) column by Phenomenex was used for chromatography. Wavelength for detection was set at 213 nm with a 6 nm bandwidth and the reference wavelength was set at 400 nm with an 80 nm bandwidth. Mobile
phase flow was set at 0.5 ml/min and consisted of 90% methanol and 10% solution of 0.025 M NaH₂PO₄, which was adjusted to pH 3 by addition of 1 N H₂SO₄.

4.3 RESULTS AND DISCUSSION

4.3.1 Structure of a CGA

The fundamental properties of CGAs were studied and discussed by Sebba (1982). An air bubble in pure water can be treated as a cavity enclosed by water. When surfactant molecules are present in water, any cavity introduced in water creates a water-gas interface where surfactants are adsorbed. In the case of colloidal gas aphrons, Sebba hypothesized that the encapsulating soap film has an inner as well as an outer surface and that these surfaces have surfactant monolayers adsorbed on them. In a separation processes that utilizes CGAs, solubilization of the organics occurs in these layers. The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, increasing its stability. "Stability" of microbubble dispersion can be defined as the length in time over which the number of bubbles and their size distribution remains constant. CGA dispersions, if left undisturbed will eventually cream and be converted to ordinary foam, leaving a clear aqueous layer below.

4.3.2 Results of Particle Size Analysis of CGAs

The detailed results of particle size analysis can be found in our previous publication (Chaphalkar et al., 1993). In most cases, CGAs were found to have diameters between 30 µm and 300 µm, rarely falling below 30 µm. The mean diameter (MD) which is calculated from mean volume of the suspension was found
to be characteristic of the surfactant and found to be affected slightly by its concentration. The volume of sample material in the system is reported by the instrument as a dimensionless parameter "$V_v$." The quantity $V_v$ was therefore used as a surrogate parameter to represent the ability of the CGA suspension to entrap air over time and its stability in the system. The data is presented in Table 4.1, which lists MD, standard deviation and initial $V_v$ of a CGA suspension. From Table 4.1 it is apparent that CGAs generated from nonionic Tergitol had a larger air content than those generated from ionic DDBS or HTAB.

The data also indicate that the variation in the range of mean diameter of the CGAs and its initial air entrapment in the dispersion was specific to the surfactant. Concentration of surfactant in the solutions used to generate CGAs was found to influence the characteristics of microbubble dispersions. In general the increase in concentration of ionic surfactants was found to reduce the mean diameter and increase $V_v$ of suspension for all three surfactants (Chaphalkar et al., 1993).

4.3.3 Ion Flotation

Addition of surfactant to water beyond a certain value changes the physical characteristics of the solution. The concentration at which these changes occur is called the critical micellar concentration (CMC). Physically, aggregation of long chain surfactants into large units, called micelles, begins to occur at that concentration and they behave as colloids (Adamson, 1982). The colloids thus formed are capable of solubilizing otherwise insoluble organic molecules from the suspension by incorporating them into the micellar structure. At surfactant concentrations below the
TABLE 4.1

Initial size characterization of CGAs produced with different surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (mg/L)</th>
<th>V&lt;sub&gt;i&lt;/sub&gt;</th>
<th>Particle Size Analyzer Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>MD (μ)</td>
</tr>
<tr>
<td>Tergitol</td>
<td>50</td>
<td>0.022</td>
<td>63.0</td>
</tr>
<tr>
<td>Tergitol</td>
<td>100</td>
<td>0.1163</td>
<td>68.6</td>
</tr>
<tr>
<td>HTAB</td>
<td>200</td>
<td>0.0102</td>
<td>148.1</td>
</tr>
<tr>
<td>HTAB</td>
<td>328</td>
<td>0.0183</td>
<td>105.9</td>
</tr>
<tr>
<td>DDBS</td>
<td>200</td>
<td>0.0072</td>
<td>131.9</td>
</tr>
<tr>
<td>DDBS</td>
<td>500</td>
<td>0.0134</td>
<td>119.2</td>
</tr>
</tbody>
</table>

MD = Mean Diameter  
V<sub>i</sub> = Initial Volume of CGAs in the System
CMC, data available in the literature shows essentially no enhancement in organic solute solubilization for relatively soluble organics. However, in the case of water-insoluble organic solutes, significant increase in its solubility has been reported even in the presence of surfactant concentrations below its CMC (Kile and Chiou, 1989). The relationship of moles of solubilizate with moles of surfactant is linear over a wide range of concentration above the CMC. Although micelles may solubilize organics, unlike monomers they have no tendency to adsorb at the air-water interface. In an ion flotation process, gas cavities are introduced in an aqueous solution that contains a dissolved surface active agent. These molecules are adsorbed at the gas-water interface with their hydrophilic end oriented toward water, which enables them to form an ion pair with oppositely charged species in the solution. This attraction can be purely columbic or a chemical bond may form between the two. The solute-laden bubble is then buoyed to the surface where it will concentrate the ions in the froth. However, once the surfactant concentration reaches CMC levels, separation efficiency reduces dramatically because micelles have no tendency to adsorb at the air-water interface and therefore do not float with the bubble. Efficiency of removal drops because micelles solubilize the organics and retain them in the aqueous solution. In an ion flotation process therefore, it is important that the surfactant should be at a concentration below CMC.

In the case of separation with CGAs the mechanism of flotation is somewhat different. The process may involve, either solubilization of the solute within the film surrounding a CGA or adsorption on the film surface, or a combination of both. The
adsorption and/or solubilization by a CGA occurs because of the unique structure of CGA as described above. Figure 4.1 illustrates the solubilization process schematically in the presence of micelles and CGAs. When the concentration of surfactant in the aqueous solution is below its CMC, solute molecules will be distributed between CGAs and the monomers. At concentrations above CMC, surfactant molecules will form micelles but because the CGAs are in high concentration, the solute will distribute mostly between CGAs and monomers. Theoretically it is therefore possible to achieve separation by using CGA dispersions even at CMC concentrations and above.

4.3.4 Effects of Surfactant Type on the Removal of PCP

Pentachlorophenol is a weak hydrophobic acid with a pKₐ of 5.25. At pH < 2.7, only about 0.1% of PCP remains in ionic form, while at pH > 10 nearly all of it will be in the dissociated form. Its sodium salt is highly water soluble, but in its pure form its solubility depends on pH and is reported to be 14 mg/L under acidic conditions. The initial concentration of PCP in these experiments was 8 mg/L that ensured that all of the PCP was in the dissolved form.

The charge on the encapsulating film was thought to affect the removal efficiencies of PCP from the solution. To study this effect, CGAs generated from the three types of surfactants were used in the separation process. Figure 4.2 shows at pH 10.1, the percentage removal using CGAs produced at the CMC concentrations. The reason for the higher removal by Tergitol may be its small bubble diameter in the suspension and higher air entrapment (Table 4.1) even when it is mixed in a solution.
Figure 4.1 Schematic of the solubilization process in the presence of CGAs and micelles
Figure: 4.2 Removal of PCP by different surfactants under alkaline conditions.
Smaller bubble size would not only yield higher surface area but the bubbles would also tend to rise slowly to the surface thereby increasing the contact time. Higher surface area, coupled with greater contact time would result in better removal rates of PCP. The large difference in the removal efficiencies between HTAB and DDBS however cannot be attributed solely to the above factors. The difference in their mean diameter and $V_*$ is not large enough to justify the disparities in the removal efficiencies. The charges on the encapsulating film can explain the higher percentage of adsorption of PCP on the CGAs generated by the HTAB as compared to CGAs generated using DDBS. At pH 10.1 most of the PCP will be present in the ionic form and ion pairing with HTAB molecules in the CGA film will improve its efficiency of the removal. Repulsive forces between DDBS and the phenolate ion would hinder the adsorption process, yielding poor recovery.

### 4.3.5 Effect of pH on the Removal of PCP

Aqueous solutions were maintained at pH 3.0, 7.4 and 10.1 by using buffers to study the effect of ionization of PCP on the removal efficiencies. Figure 4.3 shows the effect of pH on the removal of PCP from aqueous solution under these conditions. It can be seen that the effect is more pronounced for ionic surfactants. In the case of Tergitol, which is a nonionic surfactant, the removal is nearly independent of pH. In the case of anionic DDBS, the removal percentage improved from 15.1% to 35.6%, when pH changed from 10.1 to 3.0. The net negative surface charges on CGAs generated with the anionic surfactant may reduce the formation of phenolate-surfactant complexes thus producing negligible removal under basic conditions when
Figure 4.3 Comparison of surfactants in the removal of PCP at their CMC concentration
only phenolate ions exist in the aqueous solution. However, the hydrophobic nature of PCP under acidic conditions will enable adsorption of PCP on the CGA film, yielding higher removal. This conjecture appears to be supported by the removal efficiencies of CGAs generated from the cationic surfactant HTAB. The removal at pH 10.1 is 80.8% while at pH 3.0 it drops to 68.1%.

Figure 4.4 compares the removal of PCP by CGAs generated from all three surfactants at pH 3.0 at their CMC concentration. Although under acidic conditions, virtually all the PCP is in the undissociated form, the removal efficiency using Tergitol is higher, again because of the smaller size and far higher air entrapment for CGAs produced using Tergitol as compared to ionic surfactants. However, the difference in the efficiencies of HTAB and DDBS can not be ascribed to these factors. As Table 4.1 shows, initial MD and V, values are nearly comparable for both the surfactants. It can be attributed only to the differences in their ionic nature. It is most likely that, because of its positive charges HTAB forms complexes with PCP and is able to remove it more efficiently.

4.3.6 Effect of Concentration of Surfactant on the Removal of PCP

The removal efficiencies for all the three surfactants at various concentrations are shown in Figures 4.5 through 4.7. As expected, for all the surfactants, increase in their concentration improved the removal efficiency. The removal of PCP from the solution decreased with each pulse of CGA, except in the case of Tergitol at the CMC concentration.
Figure: 4.4 Effects of surfactant type on the removal of PCP under acidic conditions.
Figure: 4.5 Removal of PCP by HTAB
Figure 4.6  Removal of PCP with DDBS
Figure: 4.7 Removal of PCP by Tergitol
For HTAB (Figure 4.5), the removal increased about 10% with an increase in its concentration from 200 mg/L to 328 mg/L (CMC) at all pH values. As mentioned above, for both the concentrations of HTAB, removal is higher under alkaline conditions. Figure 4.6 shows the removal of PCP by CGAs produced with DDBS at different concentrations. It was observed that at 200 mg/L of DDBS, the removal was negligible at all pH values. Apparently at concentrations below its CMC, the CGAs generated from this anionic surfactant failed to adsorb PCP even at pH 3.0, when PCP in the solution exists in its hydrophobic undissociated form. However, at the CMC concentration the removal was a modest 34.6% and seemed to increase with each pulse, so it is conceivable that the removal can increase further with additional pulses of CGAs. Similar results were obtained for CGAs generated with Tergitol (Figure 4.7). The removal in the first pulse remained the same, for both concentrations of Tergitol. However, at the CMC the incremental removal by the second pulse is better than the first one. The incremental removal is seen to reduce again in the third and fourth pulses.

The increase in removal at the micellar concentrations of the surfactants above their CMC indicates that the adsorption of PCP must be occurring on the film of CGA, in the aqueous phase, much more than being solubilized in a micelle. Since micelles do not float, the removal in an ion flotation process is reported to drop precipitously when the solution reaches micellar concentration. In the case using CGAs that does not seem to be the case because PCP concentration in the encapsulating film may be far in excess of that within the micelle (Fig 4.1).
4.3.7 Comparison of CGA Suspension for Flotation with Conventional Techniques

There are other conventional flotation techniques that utilize the surface active nature of compounds to separate them at the air-bubble interface from aqueous phase. The simplest form of this technique is air stripping. In this technique a porous stone or a glass frit is used to introduce air bubbles at the bottom of a column. The hydrophobic organics adsorb on the rising bubbles, effecting their removal. This method is extremely inefficient in practice for non-volatile organics because of the lack of adsorptive capacity of the bubbles and the redistribution of solute, back into the aqueous phase at the surface when the bubble bursts. Solvent sublation, which was first introduced by Sebba (1962) is another technique that overcomes this drawback. In this technique a layer of organic solvent is maintained atop the aqueous phase to prevent the redistribution. In the case of CGA flotation, the chances of redistribution of solute back to the aqueous phase are reduced since, the gas dispersion after rising to the surface forms an ordinary foam and the solute remains adsorbed in that matrix.

Table 4.2 presents the data for the comparison of flotation by CGA and conventional techniques carried out by Valsaraj and Thibodeux (1991). The initial concentration of PCP in the aqueous phase was nearly the same in both the cases. To compare the efficiency of removal under different conditions, the ratio of volume of air injected to the volume of aqueous solution in the column \( \frac{V_{a}}{V_{l}} \) was used. Since both the experiments were carried out in a semi-batch mode but for different liquid volumes, this ratio would give us an absolute volume of air per liquid volume required.
### TABLE 4.2
Comparison of batch flotation of PCP by different techniques

<table>
<thead>
<tr>
<th>Method of Flotation</th>
<th>Efficiency E</th>
<th>$V_L$ (ml)</th>
<th>$V_o/V_L$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Stripping*</td>
<td>0.05</td>
<td>1450</td>
<td>19.1</td>
<td>3.0</td>
</tr>
<tr>
<td>Solvent Sublation^b</td>
<td>0.80</td>
<td>1450</td>
<td>17.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Solvent Sublation^c</td>
<td>0.98</td>
<td>800</td>
<td>0.45</td>
<td>3.0</td>
</tr>
<tr>
<td>Solvent Sublation with HTAB^d</td>
<td>0.98</td>
<td>800</td>
<td>0.15</td>
<td>8.9</td>
</tr>
<tr>
<td>CGA (HTAB)^e</td>
<td>0.68</td>
<td>2800</td>
<td>0.05</td>
<td>3.0</td>
</tr>
<tr>
<td>CGA (HTAB)^e</td>
<td>0.85</td>
<td>2800</td>
<td>0.05</td>
<td>10.1</td>
</tr>
<tr>
<td>CGA (Tergitol)^f</td>
<td>0.81</td>
<td>2800</td>
<td>0.05</td>
<td>3.0</td>
</tr>
<tr>
<td>CGA (Tergitol)^f</td>
<td>0.92</td>
<td>2800</td>
<td>0.05</td>
<td>10.1</td>
</tr>
</tbody>
</table>

$V_L$ = Total Volume of aqueous phase in the column (ml).
$V_o$ = Total Volume of air injected into the column to achieve the indicated removal Efficiency, E (ml).
$Q_a$ = Air flow rate, ml/s.

**Note:** Other Conditions of the experiments are as follows

a) $Q_a = 1.1$ ml/s; No solvent on top; No surfactant added.
b) $Q_a = 3.0$ ml/s; Solvent, mineral oil (15 ml); No surfactant added.
c) $Q_a = 3.0$ ml/s; Solvent, decyl alcohol (30 ml); No surfactant added.
d) $Q_a = 3.0$ ml/s; Solvent, decyl alcohol (15 ml); HTAB $5 \times 10^{-5}$ M
e) CGA flow rate = 0.583 ml/s, HTAB $2.1 \times 10^{-5}$ M
f) CGA flow rate = 0.583 ml/s, Tergitol $3.5 \times 10^{-6}$ M
for a given degree of removal of PCP. The volume of air, $V_o$ in the case of CGA was calculated from the observation, that nearly 66% of CGA suspension volume is comprised of air.

The removal efficiency of conventional air stripping was far less than solvent sublation. Extrapolating the results we should expect that the ratio $V_o/V_L$, for 95% removal of PCP by air stripping will be far too large. In the case of solvent sublation, a layer of mineral oil on top of the aqueous phase improves the efficiency as well as reduces the $V_o/V_L$ ratio but a layer of decyl alcohol does even better. For CGA flotation the ratio $V_o/V_L$ is very small. Without the presence of a surfactant in solvent sublation there is a difference of an order of magnitude in air volume per volume of liquid when compared to CGA flotation. When solvent sublation was carried out in the presence of HTAB under basic conditions (pH = 8.9), it required 300% more air volume per volume of liquid and more than twice the amount of surfactant when compared with CGA flotation under similar conditions (pH = 10.1). CGA flotation is more effective because of its small bubble size and its ability to solubilize as well as adsorb the solute. It is therefore conceivable that CGA flotation can be equally effective as solvent sublation and still remain economical because it uses far lower volume of air per liquid volume in flotation.

4.4 CONCLUSIONS

Microgas dispersions were generated using cationic, anionic and nonionic surfactants and were used in an adsorptive bubble flotation process to remove PCP from an aqueous phase. The aqueous solution was maintained at three different values
of pH by buffering the solutions. The charge on the encapsulating film was found to affect the removal efficiencies of PCP from the solution. CGA generated with Tergitol, which is a nonionic surfactant, was found to be most efficient in the removal of solute and the efficiency remained nearly independent of pH. In the case of anionic DDBS, the removal percentage improved from 15 % to 35 %, when pH changed from 10.1 to 3.0. Apparently at concentrations below its CMC, the CGAs generated from this anionic surfactant failed to adsorb PCP even at pH 3.0, when PCP in the solution exists in its hydrophobic undissociated form. The reason for the higher removal by Tergitol may be its small bubble diameter in the suspension and higher air entrapment even when it is mixed in a solution. The large difference in the removal efficiencies between HTAB and DDBS however can be attributed solely to the charges on the encapsulating film. The ionic nature of adsorption of PCP is revealed even in its undissociated form because CGAs generated from HTAB were more efficient in the alkaline range than in acidic range. Increase in concentration of the surfactants improved the removal efficiency. The increase in removal at the micellar concentrations of the surfactants above their CMC indicates that in the aqueous phase the adsorption of PCP must be occurring on the film of CGA, much more than being solubilized in micelle.

These results were compared with the removal efficiencies using conventional flotation techniques used by other researchers. The removal efficiency of air stripping was found to be far less than solvent sublation and that of CGA flotation. Solvent sublation appears to be most effective in the removal of PCP but even in the presence
of HTAB it required 300% more air volume per volume of liquid when compared with CGA flotation.
CHAPTER 5

SOLUTE TRANSPORT IN PACKED SAND COLUMNS BY COLLOIDAL GAS AERHONS: EXPERIMENTAL EVIDENCE AND MODELING APPROACH

5.1 INTRODUCTION

Accidental spills, improper disposal practices, and leakage from underground storage tanks result in contamination of the subsurface environment. Because of the expenses involved in subsurface remediation by conventional methods, like incineration and landfill disposal, in-situ procedures such as "pump and treat" technology have been adopted for many sites. Approximately 68% of Superfund Records Decisions (RODs) selected groundwater "pump and treat" as a means to achieve aquifer restoration in 1990 (Travis and Doty). Depending upon the nature of contamination and geologic conditions, this treatment can take several years. Even highly soluble contaminants get trapped in the finer pore structure and are difficult to remove due to the preferential flow in high permeability zones. In-situ remediation can be considerably enhanced by using a variety of surfactants (Liu and Roy, 1993; Ellis et al., 1985; Ang and Abdul, 1991). Flushing the contaminated soil or aquifer with surfactant solution yields better removal efficiencies because of the increased solubilization of contaminants partitions more to the mobile phase. However, even this modification in the "pump and treat" technology does not overcome the problem of preferential flow, making the process less efficient.
One of the promising techniques that overcomes the problem of preferential flow is the application of microbubbles or colloidal gas aphrons (CGA) to soil. Application of the CGAs to the soil blocks the high permeability layers or streaks and solubilizes the contaminants. The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (1971). CGAs consist of approximately 66% gas by volume and therefore form a low density liquid. These microbubbles do not coalesce easily and differ remarkably from conventional soap bubbles (Fig. 5.1) in their stability and flow through properties (Sebba, 1982). The most striking feature of a CGA suspension is its stability which allows them to be pumped from the point of generation to the application site. CGAs have been shown to be useful in a variety of environmental applications. Our studies have shown the enhanced effectiveness of CGA flotation process over conventional sparged air or solvent sublation in separation of the organics from aqueous waste streams (Chaphalkar et al., 1993). Based on the results reported in the literature and our ongoing research on the application of CGAs to mobilize organics from soil columns (Roy et al., 1992; Roy et al., 1993), it appears that this technology may be very effective in decontamination of soils. CGAs have also been found to enhance transportation of microorganisms and can increase the available oxygen in the soil so as to enhance biodegradation of organics in the soil (Jackson and Roy, 1993). The potential usefulness of CGA technology for in-situ remediation of hazardous waste sites suggests that additional information should be obtained on the transport of CGA in soil matrix. Study of solute transport in porous media is essential to our understanding and application of various subsurface
Figure: 5.1 Structure of an air bubble, a soap bubble and a CGA
remediation technologies. In view of this, the current study was undertaken (i) to investigate mixing of solutes in packed soil columns when CGA suspensions are injected, (ii) to study the possible mechanism of solute transport in columns using CGAs as a flushing solution, and (iii) to study suitability of mobile immobile model (MIM) to describe the flow of CGAs in porous media.

5.2 THEORY

Due to hydrodynamic dispersion, contaminants migrating through subsurface spread in longitudinal and transverse directions of flow. The longitudinal dispersion occurs primarily due to velocity variations at the pore levels, which in turn occur due to differing pore sizes. Transverse spreading results from the molecular diffusion that occurs due to concentration gradients. Advection, mechanical dispersion, and molecular diffusion are the most important phenomena that affect the concentration distribution of a solute as it moves through a porous medium. Other factors such as adsorption, precipitation, degradation, and anion exclusion may influence the transport process of solute in the soil, however, they were considered negligible in this study.

One dimensional transport of a nonreactive solute in saturated porous media is generally described with the convective dispersive equation (CDE)

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}
\]  

(1)
where \( C \) denotes solute concentration (\( M \cdot L^{-3} \)), \( t \) time (\( T \)), \( x \) distance (\( L \)), \( D \) the dispersion coefficient (\( L^2 \cdot T^{-1} \)), and \( v \) the pore water velocity (\( L \cdot T^{-1} \)). Dispersion coefficient \( D \) is sometimes described as a linear function of pore water velocity i.e.

\[
D = \lambda v
\]

(2)

where \( \lambda \), also known as dispersivity (\( L \)) is a constant.

One of the limitations of this model stems from the fact that in practice larger pores dominate the flow and mixing of solute in the transport process, resulting in stagnant water bodies in the matrix. The stagnation of water usually results from dead end pore spaces, intra-aggregate water, and thin films that surround the particles within the porous media. Also, CDE fails to take into account the apparent large variation in the microscopic pore-water velocities that occur especially at high flowrates. To address these problems resulting from apparent heterogeneities, Coats and Smith (1964) added a capacitance term to the convective dispersive equation. The equation therefore is given,

\[
\beta \frac{\partial C_m}{\partial t} + (1 - \beta) \frac{\partial C_{im}}{\partial t} = D \frac{\partial^2 C_m}{\partial x^2} - v \frac{\partial C_m}{\partial x}
\]

(3)

where \( C_{im} \) represents the solute concentration in the stagnant zone, \( D_m \) the dispersion coefficient of the flowing fraction, and \( \beta \) the flowing fraction. Subscripts "m" and "im" denote the mobile and immobile phases of water contents in porous media.
respectively. The mass transfer between the flowing and stationary phase is proposed to be a first order reaction,

\[(1 - \beta) \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (4)\]

where \( \alpha \) represents the rate constant \((T^{-1})\). The flowing fraction \((\beta)\) is expressed as

\[\beta = \frac{\theta_m}{\theta} \quad (5)\]

where \( \theta \) denotes the volumetric water content \((L^3L^{-3})\) that comprises of mobile and immobile water phase. The dispersion coefficient \( D \) for the overall mobile immobile region can be defined in terms of the dispersion coefficient of the flowing fraction:

\[D = D_m \beta \quad (6)\]

This modified approach assumes that the liquid phase in the porous media remains partitioned in mobile and immobile regions. Convective-dispersive transport is restricted to mobile water phase while transfer of solutes from the immobile phase is assumed to be diffusion limited. Substituting equations (5) and (6) in equations (3) and (4) the following equations are obtained:

\[\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \quad (7)\]
where q represents the liquid flux \((LT^{-1})\). Analytical solutions for equations (6) and (7) have been discussed for variety of initial and boundary conditions by De Smedt and Wierenga (1979). Parker and van Genuchten (1984) have provided an analytical solution to the mobile immobile model (MIM) for the following initial and boundary conditions (Solution is provided in Appendix A):

\[-D \frac{\partial C}{\partial x} + \nu C = \nu C_0(t) \quad x = 0, \quad t > 0 \quad (9a)\]

\[-\frac{\partial C}{\partial x} = 0 \quad x \to \infty, \quad t > 0 \quad (9b)\]

\[C = C_i(x) \quad x > 0, \quad t = 0 \quad (9c)\]

where the subscripts 0 and i denote the inlet and initial concentration respectively.

The boundary condition (9a) arises from an assumption that at the injection plane, a boundary layer of infinitesimal thickness develops over which the system parameters change from those of a perfectly mixed inlet reservoir to those of the bulk porous media (Parker and van Genuchten, 1984). Furthermore, for the ion that is not native to soils, the initial concentration \(C_i(x)\) within the soil profile is assumed to be zero.
For the present study a pulse of solute with concentration $C_p$, was introduced for a time $t_p$. The inlet boundary condition (9a) was therefore modified as

$$-\frac{D}{v} \frac{\partial C(t)}{\partial x} + C(t) = C_p \quad x = 0, \quad 0 < t < t_p \quad (10a)$$

$$-\frac{D}{v} \frac{\partial C(t)}{\partial x} + C(t) = 0 \quad x = 0, \quad t_p < t < \infty \quad (10b)$$

where $C_p$ and $t_p$ denote the concentration and the duration of the pulse respectively.

In case of unsaturated flow, early breakthrough and tailing of the chemicals not adsorbed or excluded by the media, have been shown to be caused by the immobile fraction of water in the unsaturated soils (van Genuchten and Wierenga, 1977; Rao et al., 1980). MIM model therefore has not only been used to describe solute transport through saturated porous media, but several researchers have used the model to describe breakthrough curves from unsaturated media as well (De Smedt and Wierenga, 1984).

5.2.1 Transport of CGAs through Porous Media

CGAs differ in their structure from ordinary soap bubbles since their encapsulating film has an inner as well as an outer surface and these surfaces have surfactant monolayers adsorbed on them (Fig. 5.1). The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, thereby increasing its stability. "Stability" of microbubble dispersion can be defined as the length of time during which the number of bubbles...
and their size distribution remains constant. CGA dispersions, if left undisturbed, will eventually cream and convert to ordinary foam, leaving a clear aqueous layer below.

In a soil washing/flushing operation the contaminant is initially removed by displacing the trapped globules and later it is transported in its solubilized form. Preliminary work with CGAs in our laboratory has indicated that solubilization is the dominant mechanism of contaminant removal (Roy et al., 1993). CGAs offer a way of lowering the interfacial tension between organics and water while at the same time providing the viscous forces needed for an efficient areal sweep.

The concept behind using CGA lies in the fact that the gas phase will block the larger pores with lamella. As a result, the suspension is forced through smaller pores where the contaminant is trapped at residual saturation. This flushing medium would prove helpful in heterogeneous medium where high permeability regions will remain plugged, thereby forcing the CGAs to flow through the low permeability contaminated regions. Although the CGA suspension is a homogeneous fluid at the time of pumping, within the porous media separation of the air and solution phase may occur thus resulting in two-phase flow system. The mechanism by which CGAs are transported within porous media may be similar to that of foam. Fugate (1984) studied the flow of CGAs through a flume and noted that they tended to accumulate near the point of injection, forming a stationary front. However, in another study carried out by Longe (1989), two separate fronts of gas and liquid were observed. The gas front followed the liquid front owing to its lower permeability. Solute transport by CGA suspension, however, was not considered in these two studies.
Opinions differ among researchers about the mechanism by which the foam or its components move through porous media. Mahmood and Brigham (1987) have summarized possible mechanisms for flow of foam in a porous media as follows:

1. **Bubble Flow**: Homogeneous flow of gas and the surfactant solution

2. **Intermittent Flow**: Foam flows in such a way that liquid is transported by a continuous network of liquid membranes, while gas flows as a discontinuous phase through breaking and reforming the bubbles.

3. **Trapped Gas Flow**: Some gas in the foam is trapped in the porous media while the remainder flows as a free phase. The flowing fraction of the gas is generally small compared to the fraction of trapped gas.

4. **Membrane Flow**: Foam is generated as lamella at specific locations in the porous media.

It should be noted that in most of these studies, the porous media was first saturated using surfactant solution with concentrations ranging from 1% to 5%, and air was then injected into the porous media. Since CGAs are generated with much lower surfactant concentrations and pumped as a homogeneous liquid, their behavior in the porous media may not be identical to that of the foam. Also, because of the intricate nature of CGAs and the complex nature of the porous media, probably no single model can completely describe the transport of CGA in the soils. In practice it is more likely that in the porous media more than one mechanism is at work that varies spatially as well as temporally. Our visual observations during column flushing experiments with CGAs have further indicated this.
5.3 MATERIALS AND METHODS

5.3.1 Production and Characterization of CGAs

Based on methods suggested by Sebba (1985), a unit was fabricated in our laboratory for the production of CGAs. It consisted of a motor fitted on top of a 3 liter cylindrical container. A flat disk, 50 mm in diameter, was mounted at the end of the shaft that was rotated at 8000 rpm. The level of the surfactant solution is initially adjusted to be approximately 15 mm above the disk. Strong waves are created on the liquid surface when the disk is rotated at very high speeds. The waves strike the baffles that are fixed to the lid of the container. On reentering the solution, the waves entrain air in the form of microbubble dispersion or colloidal gas aphrons. Size distribution of CGAs was determined using a particle size analyzer (Microtrac 7995-10, Leeds and Northrup). A detailed description of the CGA apparatus and size distribution analysis can be found in our previous work (Chaphalkar et al., 1993).

In this study CGAs were generated using a nonionic surfactant Tergitol 15-S-12 (MW =738) at its critical micellar concentration (CMC) 0.15 mM. Samples of the surfactant were obtained from Union Carbide Inc. Tergitol was selected because, being nonionic it is less likely to be adsorbed on the negatively charged sand. Furthermore, CGAs generated with Tergitol were observed to be smaller and remained in suspension for longer time than both cationic and anionic surfactants (Chaphalkar et al., 1993). Most of the microbubbles had diameters between 30 and 200 μm. The mean diameter of the microbubbles was found to vary between 65 and 80 μm and the standard deviation of bubble diameter varied between 29 and 35 μm.
5.3.2 Experimental Procedure

The sand used in this study was tested to be free from organic and inorganic impurities. Sieve analysis of the sand revealed a $d_{50}$ of 0.85 mm and $d_{90}/d_{10}$ ratio of 2.86. Glass columns (6.3 cm ID) with lengths of 2.5, 11.5 and 30 cm were packed by adding sand in 90 gm portions and were compacted to achieve an approximate bulk density of 1.66 gm/cc. Stainless steel screens were placed on top and bottom of the packed sand. The experimental setup is shown in Figure 5.2. Two sets of experiments were carried out using Cl$^-$ as a nonreactive tracer. The effluent was collected using fraction collector. In the first set of experiments, breakthrough curves were obtained with aqueous solution pumped with a Masterflex positive displacement pump (Cole Parmer Inc.) at a constant flow rate between 8.5 and 9.0 ml/min. For these experiments, the column was initially saturated with 0.05 M KNO$_3$ solution, and a pulse equivalent to one pore volume of 0.1 M NaCl was pumped in at the same rate. The column was then flushed with 0.05 M KNO$_3$ solution to obtain the Cl$^-$ breakthrough curves.

For the second set of experimental runs, the column was initially saturated with 0.05 M KNO$_3$, and a pulse of CGAs generated with 0.1 M NaCl and 0.15 mM Tergitol was pumped into the column. Gas comprises approximately 66% of CGA suspension by volume. Since the time of CGA tracer pulse equaled the aqueous pulse time, the actual volume of tracer pumped with CGA was less than one pore volume. The volumetric measurements of the effluent began as soon as the first bubble appeared at the effluent end. The column was then flushed with CGAs generated with
Figure: 5.2  Schematic experimental setup
0.05 M KNO₃ and 0.15 mM Tergitol to obtain the breakthrough curves. After each CGA run the contents of the column were removed and its moisture contents were determined using gravimetric analysis.

5.4 RESULTS AND DISCUSSION

The experimental results on Cl⁻ breakthrough using water and CGA suspension for three different column lengths are shown in Figures 5.3 and 5.4 respectively. Experimental observations appear to skewed, showing both early arrival and slow approach to the final concentration. Because of the inability of the CDE model to fit the data, an attempt was made to fit the Cl⁻ breakthrough generated by water and CGA suspension using MIM.

The program CXTFIT developed by Parker and van Genuchten (1984) allows one to fit the analytical solution of equations (7) and (8) for the dimensionless concentrations \( \frac{C_i}{C_p} \) as a function of number of pore volumes, \( T \):

\[
T = \frac{v \cdot \frac{t}{L}}{L}
\]

where \( v \) represents the pore water velocity, \( L \) the length of the column, and \( t \) the time at the measurement. The curve fitting method minimizes the sums of squares of the residuals between the observed and the calculated concentrations. In this study, the observed data was fitted for parameters \( D_m \), number of pore volumes in the tracer pulse \( T_p \), \( \beta \), and \( \omega \). The dimensionless parameter \( \omega \) is used to calculate the reaction rate constant (\( \alpha \)) and is defined as:
Figure: 5.3  Solute transport by CGA suspension

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Figure: 5.4 Solute transport by aqueous solution

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\[ \omega = \alpha \frac{L}{q} \]  

(12)

The predictions by MIM are shown by the solid lines in Figures 5.3 and 5.4. Close agreement between the experimental data and the predictions for different column lengths validates the applicability of MIM for predicting the solute mixing process in soil matrix using both water and CGA suspension.

Figure 5.3 shows the breakthrough curves of solute with CGAs for different column lengths. Although the shape of the breakthrough curves by the CGAs resembles the tracer displacement with aqueous solution (Fig. 5.4), there seems to be a difference in the tailing portion of the curve. In the case of CGA runs, the tailing becomes more pronounced as the column length increases, indicating that the reaction between mobile and immobile fraction becomes a dominant feature of the flow in the longer column. The opposite occurs for the aqueous breakthrough where tailing diminishes with an increase in the column length (Fig. 5.4).

CDE assumes that the effective dispersivity remains constant for any length of the column for a constant velocity, but in practice it increases with the distance from the source. This phenomenon called "scale effect" is well reported in the literature (Gelhar et al., 1985; Sudicky and Cherry, 1979 and Dagan, 1984). It occurs due to local variation in the water velocity along the direction of motion, causing the solute to spread differently in the longitudinal direction. Since the local variation in the velocity increases with the distance, the dispersion would increase.
until the velocity differences normal to the direction of the flow are smoothed by transverse mixing (Khan and Jury, 1990). Figure 5.5 shows the plot of fitted dispersivity versus column length for aqueous solutions and CGAs. For aqueous solutions, the dispersivity increases with the length of the column. These results are consistent with the hypothesis that dispersivity will approach a constant value if the residence time in the column is sufficient to smooth out solute variations by lateral mixing. For CGA runs, dispersivity decreased with an increase in length of the column between 2.5 cm and 30 cm (Fig. 5.5). Although CGA suspension is homogeneous at the time of pumping, it should be noted that separation of air and aqueous phase occurs within the porous media. This situation is analogous to that of a stagnant CGA solution in a column where the bubbles cream to the top and coalesce. Because of the smaller flow through periods, the flow remains more or less homogeneous in the smaller columns. Therefore, separation of air and liquid phases may not be significant in the short columns. The extended residence time in the longer columns, however, will cause separation of phases. Our visual observations confirmed the evidence of phase separation in the longer columns. The effluent from the longer columns appeared in the form of a train of large bubbles separated by the liquid phase. In the case of long columns, flow of the liquid phase occurred only through the narrow channels because the phase separation blocked the high permeability pores by the lamellae. The reduced dispersivity indicates that flow through long columns would resemble plug flow conditions.
Figure: 5.5 Variation of dispersivity with length of column
The pore velocity of CGA suspension was determined by dividing the liquid flux with the volumetric moisture contents of the column at the end of the run. For CGA suspension, the pumping rate was maintained the same as that of the aqueous solution. Liquid flow, however, remained restricted to narrow channels, which resulted in reduction of liquid flux with increasing length of the column. Figure 5.6 shows the decrease in pore water velocity with increasing column lengths. The time for the solute pulse of CGAs was kept the same as that of the aqueous solution. However, since entrapped air constitutes nearly 60-70% of CGA suspension, the tracer volume pumped for the CGA runs was less than that for the aqueous solution. In CGA runs, the fitted value $T_p$ decreased with increasing length of the column because of the reduction in liquid flux (Table 5.1).

The best estimates of the parameters fitted to the curve for CGAs and the aqueous solution are given in Table 5.1. It can be seen that the fitted parameters $\alpha$ and $\beta$ do not show a definite trend. Khan and Jury (1990) found similar results when they applied the mobile-immobile model to a nonreactive tracer by aqueous solutions in columns. The mobile water fraction ($\beta$) reduced from 0.99 to 0.7 for the aqueous solution. In case of aqueous solution, the rate constant $\alpha$ for the reaction between mobile and immobile phases of aqueous solution, varied between 0.01 and 0.12. Cool et al. (1987) report that such a variation in the apparent rate constant $\alpha$ indicates that either the reactions did not follow first order chemical kinetics or that the reaction was not diffusional controlled.
TABLE 5.1

Fitted parameters to solute transport by aqueous solution and CGA suspension

<table>
<thead>
<tr>
<th>Length (cm)</th>
<th>( v ) (cm/Hr)</th>
<th>( D_m ) (cm(^2)/Hr)</th>
<th>( D ) (cm(^2)/Hr)</th>
<th>( \lambda_m ) (cm)</th>
<th>( \lambda ) (cm)</th>
<th>( \alpha ) (Hr)</th>
<th>( \beta )</th>
<th>( T_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>43.3</td>
<td>8.98</td>
<td>8.89</td>
<td>0.21</td>
<td>0.21</td>
<td>0.07</td>
<td>0.99</td>
<td>1.13</td>
</tr>
<tr>
<td>11.5</td>
<td>44.3</td>
<td>18.89</td>
<td>13.03</td>
<td>0.43</td>
<td>0.29</td>
<td>0.12</td>
<td>0.69</td>
<td>1.04</td>
</tr>
<tr>
<td>30.0</td>
<td>45.7</td>
<td>28.45</td>
<td>23.90</td>
<td>0.62</td>
<td>0.52</td>
<td>0.01</td>
<td>0.84</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Solute Transport by CGA Suspension

<table>
<thead>
<tr>
<th>Length (cm)</th>
<th>( v ) (cm/Hr)</th>
<th>( D_m ) (cm(^2)/Hr)</th>
<th>( D ) (cm(^2)/Hr)</th>
<th>( \lambda_m ) (cm)</th>
<th>( \lambda ) (cm)</th>
<th>( \alpha ) (Hr)</th>
<th>( \beta )</th>
<th>( T_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>39.2</td>
<td>9.36</td>
<td>7.21</td>
<td>0.24</td>
<td>0.18</td>
<td>0.23</td>
<td>0.77</td>
<td>0.70</td>
</tr>
<tr>
<td>11.5</td>
<td>32.8</td>
<td>4.84</td>
<td>4.07</td>
<td>0.15</td>
<td>0.12</td>
<td>0.24</td>
<td>0.84</td>
<td>0.73</td>
</tr>
<tr>
<td>30.0</td>
<td>26.3</td>
<td>0.83</td>
<td>0.71</td>
<td>0.03</td>
<td>0.03</td>
<td>0.12</td>
<td>0.86</td>
<td>0.29</td>
</tr>
</tbody>
</table>

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Figure: 5.6 Variation of pore water velocity with column length
For CGA suspension, the $\alpha$ values were higher than for aqueous solution. This could be a result of the complex hydrodynamics of the CGA flow in porous media. When a CGA pulse with Cl$^-$ ions is applied to the column, it may leave behind lamella with high concentration of the solute in the pores. The subsequent CGA suspension would come in contact with these films at random. This type of mixing precludes the gradient induced elution encountered in aqueous solution. In case of CGAs, the mobile fraction $\beta$ varied within small range for all column lengths. The moisture contents of the columns at the end the CGA runs were also found to be very similar irrespective of the column length. This significant observation suggests that although the flow was blocked in the large channels, the flowing fraction did not change, and equilibrium was established between the flowing and stationary portions of the porous media.

5.5 CONCLUSIONS

Solute transport in coarse sands by aqueous solution is better described by the mobile-immobile model (MIM) than the conventional CDE because the latter fails to predict the early breakthrough and tailing of the breakthrough curve. Furthermore, predictions using MIM model fit the experimental data very well. For experimental runs using aqueous solutions, the dispersivity increased with an increase in the length of the column, whereas the opposite was true for the runs using CGA solutions. The plot of dispersivity versus column length for aqueous solution indicated that dispersivity will attain a constant value when using a column long enough to smooth out the variation in the interstitial velocities. The MIM model also predicted the
breakthrough curves of the solute with CGAs. However, the dispersivity for CGA suspension decreased with the column length, indicating that flow through long columns would resemble plug flow conditions.
CHAPTER 6

INVESTIGATION OF FLOW OF COLLOIDAL GAS AFRONS
IN THE POROUS MEDIA

6.1 INTRODUCTION

During the recent years in-situ remediation procedures of the contaminated soils have gained importance because of the expenses involved in conventional disposal methods like incineration and landfill. The cost of incinerating contaminated soils from hazardous waste sites is estimated to be in the range of $600 to $1,000 per cubic yard and the cost of disposal at an approved hazardous waste disposal site is approximately $300 per cubic yard (Clarke, 1990). Alternative methods such as pump and treat technology have been adopted for many sites. Approximately 68% of Superfund Records Decisions (RODs) selected groundwater pump and treat as a remedy to achieve aquifer restoration (Travis and Doty, 1990). Depending on the nature of contamination and geologic conditions, this treatment may take several years. At sites involving NAPLs or zones of low permeability, restoration process can be particularly complicated. Many of the organic liquids that are common ground water pollutants cannot be efficiently extracted by pump and treat methods due to their low solubilities in water and high interfacial tension with water (Taber, 1990). Even highly soluble contaminants get trapped in the finer pore structure that are difficult to remove because of the preferential flow in high permeability zones. In-situ soil washing can be considerably enhanced by using a variety of surfactants as reported by several researchers (Ellis et al., 1985; Ang and Abdul, 1991; Oma et al., 1991;
Flushing the contaminated soil or aquifer with surfactant solution yields better removal efficiencies because the increased solubilization partitions more contaminants to the mobile phase. Although researchers have conducted a number of promising laboratory studies, none of the field tests have been highly successful (Nash, 1987; Fountain et al., 1991; Abdul et al., 1992, West and Harwell, 1992). One of the main reasons of the failure of soil washing by surfactant is that it does not overcome the problem of preferential flow, making the process less efficient (Palmer and Fish, 1992).

One promising technique that overcomes the problem of preferential flow is the application of microbubbles or colloidal gas aphrons (CGA) to soil. Application of the CGAs to the soil, blocks the high permeability layers or streaks and at the same time is able to solubilize the contaminants. The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (Sebba, 1971). CGAs consist of approximately 66% by volume gas and therefore form a low density liquid. These microbubbles do not coalesce easily and are remarkably different from conventional soap bubbles (Fig. 6.1) in their stability, flow through properties (Sebba, 1982). The most striking feature of a CGA suspension is its stability. CGAs are stable enough to be pumped from the point of generation to the application site. Due to their properties, CGAs have been shown to be useful in a variety of environmental applications. Our studies have shown that the CGA flotation process is more effective than conventional sparged air or solvent sublation in separation of the organics from aqueous waste streams (Chaphalkar et al., 1993). Based on the results reported in the
Figure: 6.1 Structure of an air bubble, a soap bubble and a CGA
literature and our ongoing research on the application of CGAs to mobilize organics from soil columns (Roy et al. 1992b; Roy et al., 1993), it appears that this technology may be very effective in decontamination of soils.

CGAs are also able to mobilize colloids from the soil matrix. Wan and Wilson (1992) studied the transport of colloids in the porous media due gas-aqueous interface and found that the interface in motion effectively stripped particles from solid surface and carried them along. Since flow of CGAs in soil is in the form of free flowing lamellae, they are able to sweep the colloids from the soils. Implications of facilitated colloidal particle transport are manifold. Bacteria are one of the colloids of concern in remediation; they can get preferentially attached to the air-water interface and therefore can be transported to the site of contamination. Findings of Jackson and Roy (1993), suggest that CGAs were able to transport the bacteria through a column much better than water or surfactant solution. CGAs cannot only enhance transportation of microorganisms but additionally, can increase the available oxygen in the soil to facilitate biodegradation of organics in the soil. Organic contaminants in a soil matrix are adsorbed mainly on the organic and clay particles. With the help of CGAs they may be flushed out to remediate the soils. According to Vidyasagar (1993), who studied removal of naphthalene from soil columns by CGAs, the efficiency of removal of naphthalene could be roughly correlated with turbidity of the effluent.

The potential usefulness of CGA technology for in-situ remediation of hazardous waste sites suggests that additional information should be obtained on the
transport of CGA in soil matrix. This study was designed to investigate the transport of CGAs in soil columns. Effects of soil composition, surfactant concentration and rate of injection on the transport of CGAs were also studied.

6.2 BACKGROUND

6.2.1 Transport of CGAs through Porous Media

In a soil washing/flushing operation the contaminant may be removed by initially by displacing the trapped globules of the contaminant and later by contaminant solubilization. Some of the preliminary work with CGA in our laboratory has however indicated that solubilization is the dominant mechanism of contaminant removal (Roy et al., 1993). CGAs differ in their structure from ordinary soap bubbles because the encapsulating film has an inner as well as an outer surface and these surfaces have surfactant monolayers adsorbed on them (Fig. 6.1). The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, thereby increasing its stability. "Stability" of microbubble dispersion can be defined as the length in time over which the number of bubbles and their size distribution remain constant. CGA dispersions, if left undisturbed, will eventually cream and be converted to ordinary foam, leaving a clear aqueous layer below.

The idea behind using CGA is that the gas phase will block the larger pores so that surfactant solution is channeled though smaller pores where the contaminant is trapped at residual saturation. This will also help in heterogeneous medium where high permeability region will be plugged, forcing the CGAs to flow through the low
permeability contaminated region. Fugate (1984) studied flow of CGA through a flume and noted that CGA tended to accumulate near the point of injection, forming a stationary front. However, in another study carried out by Longe (1989), two separate fronts of gas and liquid were observed. Gas front followed the liquid front owing to its lower permeability. These different behaviors of CGAs in a porous media may have been caused because of the differences in the dimensions of the flume and imposed pressure gradients. Although CGA is a homogeneous fluid at the time of pumping, within the porous media separation of air and solution phase may occur and the resulting fluid will behave like a two-phase fluid. It is possible that the mechanism by which CGAs are transported within porous media may be similar to that of a foam.

6.2.2 Foam Transport in Soils

Use of foam for recovery of oil recovery was first proposed by Bond and Holbrook (1958), since then gas flooding has become one of the fastest growing enhanced oil recovery (EOR) techniques. Essentially the ability of foam to preferentially block the larger pores is utilized in this process to reduce the fingering problem. Several researchers have proposed different mechanisms to explain foam flow in a porous media. Raza (1970) found that propagation of foam is significantly different from that of a high viscosity Newtonian fluid and the relative permeability-saturation relationship is not applicable in case of foam flow because of the associative nature of fluids that comprise foam. Most of these theories are able to explain individual observations, but generalization is not possible. Especially because, the
foam propagation depends on several factors like surfactant type and concentration, physical and chemical characteristics of the porous media, nature and concentration of the contaminant, hydraulic conditions among others. It is no wonder that observations made by independent studies may seem contradictory. Transport of foam in the porous media, therefore, can be modeled only with certain approximation.

Foam in a porous media is in form of gas phase dispersed in an interconnected wetting surfactant solution that is composed of liquid bridges and lamellae. Surfactant solution occupies the smallest pores and gets transported separately from the foam phase. The amount of surfactant solution conducted by flowing lamellae and liquid bridges is very small compared to that conducted by pore channels filled completely with liquid (Bond and Bernard, 1966; Holm, 1968). Bubbles do not maintain their identity during the transport through a porous media, rather they are shaped according to the nature of porous media. Foam texture, which is nothing but the size distribution and the number of bubbles, arises from some complex mechanisms that causes its bursting or regeneration. The kinetics of foam generation and collapse not only depends on surfactant type, composition, and concentration but also on the gas and liquid flow rates within the media (Ransohoff and Radke, 1988; Friedmann and Jenson, 1986; Jamenez and Radke, 1989).

The effective surfactant concentration will vary within the soil matrix because of its interactions with the soil particles. Harwell (1992), has reviewed the number of types of surfactant behavior that can reduce the effective surfactant concentration: precipitation, liquid crystal formation, formation of coacervate phase, partitioning into
trapped residual phase, or adsorption onto the solid surfaces. Additionally the
interactions of contaminants with the surfactant solution depend on the temperature,
electrolyte concentration, and the concentration of the contaminant.

Mahmood and Brigham (1987) have summarized possible mechanisms for flow
of foam in a porous media.

1. Bubble Flow: Homogeneous flow of gas and the surfactant solution

2. Intermittent Flow: Foam flows in such a way that liquid is transported by a
   continuous network of liquid membranes, while gas flows as a discontinuous
   phase through breaking and reforming the bubbles.

3. Trapped Gas Flow: Some gas in the foam is trapped in the porous media,
   while reminder flows as a free phase. The fraction of the flowing gas
   however, is generally small when compared to trapped gas fraction.

4. Membrane Flow: Foam is generated as lamellae at specific locations in the
   porous media. The propagation of the foam therefore is conditional to the
   geometry of the pores.

It should be noted that, in most of these studies that involved foam transport,
porous media was saturated with surfactant solutions, with the concentrations between
1 and 5% into which air was injected at high pressure. Since CGAs can be generated
with much lower surfactant concentrations and pumped as a homogeneous liquid, its
behavior in the porous media may not be identical to that of foam. Furthermore,
because of the intricate nature of CGAs and the complex nature of the porous media
it is unlikely that any single model can completely describe the transport of CGA in
the soils. In practice it is more likely that, in the porous media more than one mechanism is at work that varies spatially as well as temporally. Our visual observations during column flushing experiments with CGAs have also indicated as such.

6.3 MATERIALS AND METHODS

6.3.1 Production and Characterization of CGAs

Based on methods suggested by Sebba (1985), a unit was fabricated in our laboratory for the production of CGAs. Briefly it consisted of a motor fitted on top of a 3 liters cylindrical container. A flat disk, 50 mm in diameter, was mounted at the end of the shaft that was rotated at 8000 rpm. The level of the surfactant solution is initially adjusted to be approximately 15 mm above the disk. Strong waves are created on the liquid surface when the disk is rotated at very high speeds. The waves strike the baffles, which are fixed to the lid of the container, and while reentering the solution the waves entrain air in the form of microbubble dispersion or colloidal gas aphrons. Size distribution of CGAs was determined using a particle size analyzer Microtrac 7995-10 (Leeds and Northrup, St. Petersburg, FL). A detailed description of the CGA apparatus and size distribution analysis can be found in our previous work (Chaphalkar et al., 1993).

In this study CGAs were generated using a nonionic surfactant Tergitol 15-S-12 (MW =738) at its critical micellar concentration (CMC) 0.15 mM. Samples of the surfactant were obtained from Union Carbide Inc. Tergitol was selected because, being nonionic it is less likely to be adsorbed on the negatively charged sand.
Furthermore, CGAs generated with Tergitol were observed to be smaller and remained in suspension for longer time than both cationic and anionic surfactants (Chaphalkar et al., 1993). Most of the microbubbles had diameters between 30 and 200 μm. The mean diameter of the microbubbles was found to vary between 65 and 80 μm and the standard deviation of bubble diameter varied between 29 and 35 μm.

6.3.2 Experimental Procedure

Two types of soils were used in this study. First one was coarse sand whose sieve analysis of the sand revealed that d_60 was 0.85 mm and the ratio d_60/d_10 was 2.86. Second type of soil was air dried and ground till it passed through sieve with 2 mm openings. Texture analysis was conducted using hydrometer, which indicated that the soil consisted of 7% clay, 10% silt and 83% fine sand. Glass columns (5.9 cm ID) with lengths of 10 and 30 cm were packed by adding soils in 100 gm portions and were compacted, to achieve an approximate bulk density of 1.76 gm/cc for the sand and 1.53 gm/cc for the soil. Stainless steel screens were placed on top and bottom of the packed columns.

Initially columns were saturated with degassed deionized water with constant head and then water was pumped rapidly for 30 min to drive out entrapped air. Experiments were conducted at two flow rates of 4.5 ml/min and 9.5 ml/min using metering pumps (Fluid Metering Inc., New York). CGAs were pumped and the liquid effluent was collected. Moisture contents of the column were determined after each pore volume using gamma ray densitometry technique described in the following section. When the gas saturation profile of the column was found to be stable, CGA
pumping was stopped and the column was flushed with one pore volume of water to observe the resaturation of the media.

6.3.3 Gamma Ray Densitometry

In order to visualize flow of CGA within a column, a single source gamma ray densitometry system was utilized. Gamma rays are attenuated during their passage through any matter depending on its density. This attenuation can be calibrated to assess the liquid contents of the soil. The technique of monoenergetic gamma beams to assess soil bulk density was first suggested by Van Bavel et al. (1956). Since then, this technique has found wide applications in the in-situ measurement of bulk density and volumetric solution contents of the soil.

A schematic drawing of the complete gamma ray densitometry system is shown in Figure 6.2. The system consists of a 30 mC $^{137}$Cs source, placed in a lead shield. The source is collimated to a 2 mm beam by a 10 cm long lead block. Tungsten shutter plug is mounted on the source that can be operated by a remote control device (Canberra Nuclear, Phoenix, AZ) for safe operation. The detector assembly placed on the opposite side of the column, consisted of a thallium activated NaI crystal in series with a photomultiplier base Model # 276 (EG&G Ortec, Oak Ridge, TN). The detector assembly is enclosed in a lead box with 1.5 cm thick walls. Detector is collimated to a 4 mm hole in 5 cm thick lead block to receive the radiation. The photomultiplier tube is connected to 92X Spectrum Master multichannel buffer (EG&G Ortec, Oak Ridge, TN) that serves as an amplifier and high voltage power supply. The whole assembly of source and detector is mounted on a platform, which
Figure: 6.2  Schematic assembly of gamma ray setup
can be raised or lowered with respect to the column by gears and motor drive. Intensity of gamma ray was measured as the area under the curve of 662-KeV peak. The data acquisition is performed by a PC compatible software Mastro (EG&G Ortec, Oak Ridge, TN).

Water content measurements are based on the assumption that monoenergetic gamma rays are attenuated exponentially as given by the expression,

\[ I = I_0 \exp[-\mu \rho x] \quad (1) \]

where \( I \) is measured beam intensity through material, \( I_0 \) is the incident beam intensity, \( \mu \) is the mass absorption coefficient, \( \rho \) is density of the absorbing material, and \( x \) is path length through that material. In case of monoenergetic gamma rays, the attenuation is exponentially additive. Therefore when mass absorption coefficients of each component in a column, that consists of glass, soil, and water are known, the gamma ray attenuation of the individual component can be determined simultaneously.

The attenuation equation for a moist soil after neglecting air, is

\[ \frac{I_m}{I_o} = \exp[-S(\mu_s \rho_s + \mu_w \theta) - 2S_c \mu_c \rho_c] \quad (2) \]

where \( \frac{I_m}{I_o} \) is the ratio of the transmitted to incident radiation flux for moist soil, \( \mu_c \), \( \mu_s \), and \( \mu_w \) are the mass attenuation coefficients for the column material, soil and water respectively, \( \theta \) is mass of water per unit bulk volume of soil, \( \rho_c \) is the density of the
container, \( S_c \) is the thickness of its wall, \( \rho_s \) is the bulk density of the soil and \( S \) is the thickness of soil. The corresponding equation for a dry soil is

\[
I_d/I_o = \exp(-S\mu_g\rho_s - 2S_c\mu_c\rho_c)
\]

Division of the equation 1 and 2 yields the equation for moisture contents of the soil

\[
\theta = \frac{\ln(I_m/I_d)}{-\mu_w S}
\]

The greatest source of error in the measurement of liquid content of soil is the measurement of gamma ray intensity itself. Since the standard deviation of the number of radioactive decay events counted is equal to the square root of that number, the longer counting periods yield more accurate measurements. In a system like ours where the liquid saturation varied with time, it was necessary to balance between the precision of saturation measurement and poor resolution, by adjusting time of measurement. Gardner (1986) has provided following simplified expression for the standard deviation in the saturation measurements (Details in Appendix B);

\[
\sigma_\theta = 1/[\mu_w S(I_m'/t)^{1/2}]
\]

where \( I_m' \) are the number of counts for a moist soil per time and \( t \) is the time for which the measurement was taken. In this study, the acquisition time for sand was fixed at one minute and for soil it was fixed at three minutes. The 95% confidence
interval for this study was calculated to be $\pm 3.5\%$ for the sand, and $\pm 1.7\%$ for the soil.

6.4 RESULTS AND DISCUSSION

Pumping of CGAs into the columns resulted in the reduction in liquid saturation of the porous media. Gamma ray densitometry was used to determine the liquid saturation at various levels of the column. Localized variations in the density of the column that developed during packing, were also reflected in the initial moisture contents of the column. To accommodate these variations, the moisture contents of column at every level were expressed in "saturation units," which were calculated as the percentage of the original liquid saturation. The initial saturation units at all levels of the column were therefore treated as equal to one hundred. The liquid saturation profiles measured at various times was then plotted as saturation units against the column levels, which were measured from the bottom to top. To measure the moisture contents of the column at different experimental conditions, column was scanned by gamma rays from bottom upwards after every pore volume of liquid was collected. In this study, only the liquid phase of CGAs was monitored and the results are expressed as a function of pore volumes of the effluent.

6.4.1 Sand Column Experiments

CGAs were generated using Tergitol concentrations at 1 and 10 times the CMC level. Figure 6.3 shows the liquid saturation profiles at different times for 10 cm sand column when CGAs generated with Tergitol at 1 CMC, were injected in it. Our observations indicate that movement of gas phase in the porous media is very erratic.
Figure: 6.3 Saturation profile in 10 cm sand column
spatially as well as temporally. The saturation profiles reveal the complex behavior of CGAs in a porous media. Persoff et al. (1991) observed similar phenomenon, when they studied the foam flow in sandstone cores. The curves (Fig. 6.3) show that when CGAs are injected into the column the reduction of saturation is not uniform; it varies from its lowest near the inlet to its highest at the outlet. Similar observation was reported by Fugate (1985) in his 2-D studies. Figure 6.4 shows similar profiles under identical conditions for 30 cm sand column. In both cases, after pumping CGAs for 5 pore volumes, when the saturation profile was seen to be stable, the inflow was switched to water. For both column lengths, even after flushing the column with one pore volume of water, the saturation levels were sustained below the profile obtained after pumping one pore volume of CGAs.

To determine the effect of the direction of injection on the movement of CGAs, investigations were conducted in the 30 cm sand columns. The results (Figure 6.5) show that the change in the direction of the flow did not alter the liquid saturation profile markedly. The pressure drop across the column for this experiment was lower than 2 psi. However, the difference in the pressure gradient due to position of the injection was probably insignificant when compared to the pressure drop across the column. During the transport of CGA suspension through a porous media, air and liquid phases may get separated, but the movement of gas phase will be slowed due to entrapment within the matrix. The CGA transport through sand was therefore seen to be dependent primarily on the pressure gradient.
Figure: 6.4 Saturation profile in 30 cm sand column
Figure: 6.5  Effect of direction of flow on the saturation profile of 30 cm and column
Studies were also conducted to determine the effects of rate of injection on the liquid saturation profile. In these experiments, CGAs were injected in 30 cm sand columns at the rate of 4.5 ml/min, and the saturation profiles were then compared with those obtained by injection rate of 9.5 ml/min. As the figure 6.6 shows, that the saturation profile at the end of the run, for both injection rates remained nearly the same. Because of the presence of the surfactants in CGAs and the associative nature of its components, the CGAs movement in a porous media is governed strictly by the mobility of the bubbles. Apparently in this range of injection rates, the CGA mobility is not affected.

6.4.2 Effects of Surfactant Concentration

Figure 6.7 shows the effect of surfactant concentration on the saturation profile in 30 cm sand column. For CGAs generated by Tergitol at 10 CMC, the saturation units ranged from 6%, at the inlet end to 23.1% at the outlet end after pumping two pore volumes. In these runs the injection was stopped after second pore volume because the saturation profile had reached apparent equilibrium. In comparison, when five pore volumes of CGAs, generated at 1 CMC were injected, the saturation units ranged from 67.8%, at the inlet end, to 44.2%, at the outlet end. Similar results were obtained for 10 cm soil columns (Fig. 6.8). After injection of five pore volumes of CGAs generated with Tergitol at 1 CMC, the liquid saturation at the inlet remained at 66.2% as compared to 22.3% for CGAs generated with Tergitol at 10 CMC. Several other studies involving foam flow, have identified surfactant concentration as a controlling factor (Nahid, 1971; Bernard, 1965). In theory, when a film surface
Figure 6.6  Effect of flow rate on the saturation profile of 30 cm sand column
Figure: 6.7 Effect of concentration of surfactant on the saturation profile of 30 cm sand column
Figure: 6.8 Effect of concentration of surfactant on the saturation profile of 10 cm soil column
expands due to pressure, the concentration of the surfactant molecules on the film reduces. This reduction of surfactant molecules on the film, causes immediate replenishment from the bulk solution. At high concentration of the surfactants, this movement is faster and naturally the film exhibits better elasticity. In our earlier studies, increase in the surfactant concentration was found to increase the stability and air entrapment of the CGA suspension and at the same time decrease its mean diameter (Chaphalkar et al., 1993). It is therefore possible, that due to increased stability of the film and higher air entrapment, the bubbles may migrate farther at the higher concentration of the surfactant.

As mentioned above, after CGA injections, the influent was switched to deionized water to examine the possible resaturation of the media. Figures 6.9 and 6.10, show the effect of pumping water into 10 cm and 30 cm sand columns respectively, after they were saturated with gas. Similar experiments were performed using soil columns and these results are presented in Figures 6.11 and 6.12. These results indicate that the large pores blocked by the lamellae are not accessible to the flow of water in a porous media. Similar observations have been reported by Bernard et al. (1965) which demonstrate that foam resists the erosive action of injected water in a porous media.

6.4.3 Effects of Type of Soil

Particle size of the media affected the movement of the CGAs significantly. The inlet pressure for the 30 cm soil column was in the range of 14 psi and that for the 10 cm soil column was in the range of 6 psi after pumping six pore volumes of
Figure: 6.9  Effect of water flushing on the saturation profile in 10 cm sand column
Figure: 6.10 Effect of water flushing on the saturation profile in 30 cm sand column
Figure: 6.11 Saturation profile in 10 cm soil column
FLOW DIRECTION

FLOW RATE 9.5 ml/min

CONC 10 CMC

PV 1 — PV 3 — PV 5

Figure: 6.12 Saturation profile in 30 cm soil column
CGAs. However, in the 30 cm sand column the inlet pressure was below 2 psi. Figure 6.11 presents the saturation profiles for 10 cm soil column for CGAs generated at 10 CMC Tergitol and in Figure 6.12 the saturation profiles for 30 cm soil column are shown for the same concentration. In both these figures the proximity of the curves for different pore volumes indicates that the increase in the gas saturations after first pore volume was minimal. When compared with the saturation profiles for sand for CGAs generated with Tergitol at 1 CMC (Fig. 6.3 and 6.4), this difference is noticeable. However, in sand columns for CGAs generated with Tergitol at 10 CMC, the profile was nearly constant after first pore volume. These results signify that in a porous media, the degree of gas saturation will depend on particle size as well as concentration of the surfactant.

When CGAs are injected into the column the pressure gradient within soil may not be linear. The gas phase, predominant near the inlet would offer higher resistance to the flow than the free flowing liquid. At the corresponding levels in the column, the saturation levels in 30 cm columns were lower than that for 10 cm column (Fig. 6.11, 6.12). This phenomenon is especially noticeable when comparing saturation profiles at equilibrium for 10 cm and 30 cm soil columns.

Another noticeable observation was that the breakthrough time of the CGA’s gas phase was very short (approximately two to three minutes) for all the soil column experiments, while in sand columns the breakthrough occurred after pumping nearly half a pore volume of CGAs.Apparently, due to the high resistance in the soil columns, the separated gas phase immediately escaped through the large carrying
channels. In the sand columns the separation of air and gas phases may not be a significant factor near the inlet end of the column and even after the occurrence of separation of phases, low resistance of the sand columns would lead to a late gas breakthrough.

6.4.4 Colloid Transport by CGAs

In these experiments, fine colloidal particles were seen to wash off with the effluent when CGAs were pumped into the column. However when water was pumped, the amount of fines in the effluent was negligible. Similar phenomenon was also observed by other researchers in our laboratory (Darjee, 1993; Vidyasagar, 1993). Wan and Wilson (1992) observed that gas water interface adsorbed negatively charged polystyrene latex and clay particles over a wide range of ionic strengths. Once the particles were adsorbed onto the interface it was found to be difficult to detach them by shear stress. The gas water interface effectively stripped particles from the solid surfaces and carried them along. Since clay particles and air water interface are both negatively charged (Usui and Dasaki, 1981; Yoon and Yordan, 1986), the attraction could not be explained by extended DLVO theory. Wan and Wilson (1992) speculated that either the existing expressions of structural forces in DLVO theory are incomplete or that the particles remain trapped at the interface due to the capillary forces when they penetrate the energy barrier of the interface due to their kinetic energy. However the mechanism of overcoming the energy barrier of the gas-water interface by the clay particle is still not understood.
Due to transport of colloids, the pore structure in the soil column was seen to change while CGAs were pumped. Initially worm holes of approximately 1 mm in diameter and 5 to 10 mm long could be seen on the surface of the columns through which small bubbles were seen to pass. Over the time of pumping these holes would get bigger and signs of erosion were clearly visible. However, in every experiment when the influent was switched from CGAs to water, these cavities were seen to fill up with turbid water and collapse. The pressure immediately rose at least threefold when compared with CGAs. Pressure data shown in Figure 6.13 was typical.

The mobilization of the colloids was able to alter the pore structure in soil column. These holes were expanding due to the steady removal of the fine particles from the matrix. However, cavities thus created did not close, because the slow moving lamellae did not dislodge the larger particles. However when pumping was switched from CGAs to water, the abrasive action of the flow dislocated the large particles surrounding the cavities and clogged up the passages created by CGAs. This phenomenon was not observed when CGAs were pumped in sand columns because the quantity of fine particles in the matrix was very small and therefore their removal did not affect the pore structure.
Figure: 6.13 Changes in inlet pressure in 30 cm soil column
CHAPTER 7
CONCLUSIONS

A considerable amount of research has shown that soil washing with CGAs is a successful alternative to improve the pump and treat technology. However, a review of soil washing by CGAs indicates a lack of understanding and predictability of the process. Few studies have addressed the transport of organics with CGAs in the soil but little or no information is available on the interactions that occur within soil matrix and how they affect the various process. Laboratory studies presented here are based on only three surfactants. The first study examines the size distribution and stability of CGAs by using a particle size analyzer. Cationic, anionic and nonionic surfactants were used to generate the CGAs. Changes in the size distribution and stability of microbubbles were studied as functions of time. The effects of surfactant concentrations used to produce CGAs and the presence of an electrolyte, such as sodium chloride, on the characteristics of the suspension were also studied. The following are the specific conclusions that can be drawn about this microbubble suspension:

- The usefulness of a particle size analyzer is demonstrated in analyzing the size distribution and stability of CGA.
- When introduced into an aqueous system, CGAs undergo variations in size and numbers with time due to coalescence and/or creaming. These dynamic changes can be addressed only by using particle size analysis such as the one utilized in this study.
• The parameters mean diameter (MD) and $V_s$, which is equivalent to the bubble volume fraction in the circulating system, can be used to characterize CGAs produced under different conditions.

• Increase in the concentration of surfactant increased both $V_s$ and the stability of the suspension, but reduced the mean diameter of CGAs. The increase in $V_s$ was also found to be specific to the surfactant.

• CGA's diameters ranged between 10 and 300 $\mu$m but MD of the suspension was found to be characteristic of the surfactant.

• The presence of an electrolyte was found to affect only the characteristics of CGAs produced from the ionic surfactants, whereas no effect was observed on CGAs generated from a nonionic surfactant.

• The effect of NaCl in the solution used for the generation of CGAs revealed the ionic nature of the encapsulating film around the bubbles.

Since the stability and size distribution of the CGA suspension was specific to the type of surfactant, study was undertaken to ascertain whether it would reflect in their ability to adsorb organics from aqueous solutions. For these studies CGAs were generated using the same three surfactants used in the earlier work and were used in an adsorptive bubble flotation process to remove Pentachlorophenol (PCP) from an aqueous phase. PCP is a weak hydrophobic acid with a $pK_a$ of 5.25. At pH < 2.7, only about 0.1% of PCP remains in ionic form, while at pH > 10 nearly all of it will be in the dissociated form. Its sodium salt is highly water soluble, but in its pure form its solubility is reported to be 14 mg/L. The aqueous solution was therefore
maintained at three pH values using buffers to study the effect of ionic charge on the flotation process. Finally the removal efficiencies by CGAs were compared with conventional flotation techniques used by other researchers. The following are the specific conclusions that can be drawn about flotation by CGAs:

• The charge on the encapsulating film was found to affect the removal efficiencies of PCP from the solution.

• CGA generated with Tergitol, which is a nonionic surfactant, was found to be most efficient in the removal of the solute and the efficiency remained nearly independent of pH. The reason for the higher removal by Tergitol may be its small bubble diameter in the suspension and higher air entrapment when compared with other surfactants.

• For a cationic surfactant, (HTAB), the removal at pH 10.1 was 81% which decreased to 68.1 at pH 3.0. The charges on the encapsulating film of CGAs may explain the higher percentage of adsorption of PCP on the CGAs generated using HTAB as compared to CGAs generated using anionic DDBS.

• In the case of CGAs generated with anionic DDBS at CMC, the removal percentage improved from 15% to 35%, when pH changed from 10.1 to 3.0. However, at concentrations below its CMC, the CGAs failed to adsorb PCP even at pH 3.0, when PCP in the solution exists in its hydrophobic undissociated form.
• Increase in concentration of the surfactants improved the removal efficiency, for all the surfactants.

• In comparison with solvent sublation and that of CGA flotation, the removal efficiency of air stripping was negligible. Solvent sublation appears to be most effective in the removal of PCP but even in the presence of HTAB it required 300% more air volume per volume of liquid when compared with CGA flotation.

Behavior of CGAs in the soils is still largely speculative. This study was conducted to analyze the solute transport in columns with CGA suspensions and compare that with the aqueous solution. CGAs were generated with Tergitol because, being nonionic, it is less likely to be adsorbed on the negatively charged sand. Furthermore, CGAs generated with Tergitol were observed to be smaller and more stable when compared with other surfactants. Attempts were made to model the transport of Cl\(^-\) with CGAs. The transport was studied in three column lengths. The following are the specific conclusions that can be drawn about solute transport by CGAs in sand:

• Solute transport in the coarse sands by the aqueous solution is better described by the mobile-immobile model (MIM) than the conventional CDE because the latter fails to predict the early breakthrough and tailing of the breakthrough curve.

• Predictions using MIM model were found to fit the experimental data very well for aqueous solutions as well as CGA suspension.
• The dispersivity was found to increase with an increase in the length of the column for experimental runs using aqueous solution due to "scale effect".

• The plot of dispersivity versus column length for aqueous solution indicated that it will attain a constant value only when the column is long enough to smooth out the variation in the interstitial velocities.

• Dispersivity for CGA suspension was however seen to reduce with the column length indicating that the flow was channeled through narrow channels that reduced the interstitial velocity variation.

The means to study the movement of CGAs within a soil matrix are not well developed. The flow of CGAs in the porous media causes reduction in its liquid saturation. Gamma ray densitometry provides a tool that can be utilized to determine moisture contents in a porous media. On-line monitoring of the moisture contents in the porous media provided information that led to better understanding of the behavior of CGAs in soil. In this study, two types of soils were used to pack 10 cm and 30 cm glass columns. CGAs generated with Tergitol at different concentrations were injected at two rates to determine the factors affecting the process. The following are the specific conclusions that can be drawn about the movement of CGAs in soils:

• Gamma ray densitometry is a very useful tool to monitor the liquid saturation profile of the porous media when studying CGA movement in soils.
• Concentration of the surfactant affects the liquid saturation profile in the porous media.
• The pore structure affected the rate of movement of the gas front. In sand, gas saturation reached over 90% when CGAs generated with Tergitol concentrations at 10 CMC were pumped. The maximum gas saturation was only 66% when Tergitol concentration was at CMC.
• The rate and the direction of pumping had little or no effect on CGA movement in the soil columns.
• When CGAs are injected into a column the pressure gradient in the column may not be linear. In 30 cm columns the migration of CGA front was faster and gas saturations were higher when compared with 10 cm column under similar conditions.
CHAPTER 8
RECOMMENDATIONS

Based on the findings of the study it seems appropriate to undertake further research in the following areas:

• Mean diameter of a CGA was found to be specific to the type of the surfactant. Further research is necessary to understand and model this behavior. This study may be expanded to include the effect of chain length and the nature of the hydrophobic group on a surfactant, since it may affect the thickness and the stability of the encapsulating film of a CGA.

• Effect of only one electrolyte on the characteristics of CGA has been reported here. The effects of presence of other salts such as the ones used as inorganic nutrients in biodegradation on the properties of CGAs should be undertaken.

• In this study flotation experiments were carried out in semi-batch mode. This work can be extended to continuous mode operation under different configurations of the flow.

• Type of porous media affects the transport of CGAs in soil. Solute transport by CGAs may be studied for different composition of soils. Surfactant breakthrough studies can also be included in this work, since the liquid phase may flow separately than the gas phase.
• Pressure drop across the length of a column during the transport of CGAs may not be linear, due to the presence of gas front. Future research should be carried out in the columns that are fitted with pressure transducers along the length to monitor the pressure data. Study of pressure drop may give better picture about the dynamic alteration in the porous media when CGAs are pumped.

• Another possible area of investigation is the transport of colloids in porous media by CGAs under different ionic conditions.

• Expanding the current state of knowledge about application of CGAs to 2-dimensional and possibly 3-dimensional study.
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APPENDIX A

ANALYTICAL SOLUTION FOR THE MOBILE-IMMOBILE MODEL

The governing equations for the two-region (mobile immobile) model are,

\[ \theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x} \]  

\[ \theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \]

where \( C_m \) and \( C_{im} \) are the resident concentrations of the mobile and immobile liquid phases, respectively; \( \theta_m \) and \( \theta_{im} \) are the mobile and immobile volumetric water contents such that, \( \theta = \theta_m + \theta_{im} \); \( D_m \) is the dispersion coefficient for the mobile region, and \( \alpha \) is a first-order rate constant that governs the rate of solute exchange between the mobile and immobile regions.

The following dimensionless variables are introduced:

\[ T = \frac{vt}{L} \]  

\[ z = \frac{x}{L} \]  

\[ \beta = \frac{\theta_m}{\theta} \]
where, \( L \) is an arbitrary positive distance from the origin, \( v_m = q/\theta_m \) and \( D \) is defined for the two-region model as \( D = D_m \theta_m/\theta \). Substituting these variables into (1) and (2) yields equation as given below,

\[
\beta \frac{\partial C_1}{\partial T} + (1 - \beta) \frac{\partial C_2}{\partial T} = \frac{1}{P} \frac{\partial^2 C_1}{\partial z^2} - \frac{\partial C_1}{\partial z} \tag{9}
\]

\[
(1 - \beta) \frac{\partial C_2}{\partial T} = \omega (C_1 - C_2). \tag{10}
\]
For the modified initial and boundary conditions of this study,

\[- \frac{D}{v} \frac{\partial C(t)}{\partial x} + C(t) = C_p \quad x = 0, \quad 0 < t < t_p\]

\[- \frac{D}{v} \frac{\partial C(t)}{\partial x} + C(t) = 0 \quad x = 0, \quad t_p < t < \infty\]

\[\frac{\partial C}{\partial x} = 0 \quad x \to \infty, \quad t > 0\]

\[C = C_i(x) \quad x > 0, \quad t = 0\]

where the subscripts 0 and i denote the inlet and initial concentration respectively and where \(C_p\) and \(t_p\) denote the concentration and the duration of the pulse respectively.

The solution for the concentration \(C\) in terms of the reduced variables, is

\[C(z, T) = \begin{cases} 
C_i + (C_o - C_i) A(z, T) & 0 < T < T_o \\
C_i + (C_o - C_i) A(z, T) - C_o\alpha A(z, T - T_o) & T > T_o
\end{cases}\]

where,

\[A(z, T) = \int_0^T \int_{a,b} f(z, \tau) J(a, b) \, d\tau\]

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The function $g(z, \tau)$ is defined as,

$$
g(z, \tau) = \left( \frac{P}{\pi \beta \tau} \right)^{\frac{1}{2}} \exp \left[ - \frac{P \beta z - \tau}{4 \beta \tau} \right] - \frac{P}{2 \beta} \exp(Pz) \text{erfc}\left(\frac{P}{4 \beta \tau} \right) (\beta z + \tau)
$$

The function $J(a,b)$ is often referred to as Goldstein's $J$-function;

$$
J(a,b) = 1 - e^{-b} \int_{0}^{a} e^{-\lambda} I_{0} \left[ \frac{2}{\sqrt{b \lambda}} \right] d\lambda
$$

$I_{0}$ in this function represents a zero-order Bessel function and

$$
a = \frac{\omega \tau}{\beta}
$$

and

$$
b = \frac{\omega (T - \tau)}{(1 - \beta)}
$$
APPENDIX B

ERROR ANALYSIS OF GAMMA RAY INTENSITY

Since the variance in gamma-ray emission is the gamma-ray count itself, count intensity, $I$, must be replaced by the number of counts, $It$, where $t$ is the counting time, thus

$$\theta = -\ln \left( \frac{I_n t}{I_d t} \right) / (\mu_w S)$$  \hspace{1cm} (1)

and the variance, with reasonable assumptions, becomes

$$\sigma^2_\theta = \sigma^2_{\ln(I_n t/I_d t)} / (\mu_w S^2)$$  \hspace{1cm} (2)

so that the standard deviation is

$$\sigma_\theta = \sigma_{\ln(I_n t/I_d t)} / (\mu_w S)$$  \hspace{1cm} (3)

To reduce the error, the counting time for $I_d t$, which is measured infrequently and usually under conditions where time is not pressing, is increased by a factor of 3 or 4 over that of $I_n t$. However, the computation requires that $t$ be the same for both $I_n t$ and $I_d t$. Hence the longer count $I_d t'$ is reduced to comparable size through division by $n$, where $n = t'/t$. Thus $I_d t'/n$ is the time-equivalent count to $I_d t$ and may replace it in equations (2) and (3).
The standard deviation of $\ln(I_m t/I_d t'/n)$ is,

$$
\sigma_{ln}(I_m t/I_d t'/n) = \frac{I_d t'/n}{I_m t} \sigma(I_m t/I_d t'/n) \tag{4}
$$

$$
= \frac{I_d t'/n}{I_m t} \frac{1}{I_d t'/n} \left[ \sigma_{I_d t'}^2 + \frac{(I_m t)^2}{(I_d t'/n)^2} \sigma_{I_d t'}^2 \right]^{1/2} \tag{5}
$$

using Eq. 4 with

$$
\sigma_{I_d t'} = (I_m t)^{1/2} \tag{6}
$$

and

$$
\sigma_{I_d t'/n} = (I_d t')^{1/2}/n \tag{7}
$$

Eq. 3 becomes

$$
\sigma_0 = 1/[\mu_\psi S(I_m t)^{1/2}] \left[ 1 + I_m t/(I_d t') \right]^{1/2} \tag{8}
$$

$$
= 1/[\mu_\psi S(I_m t)^{1/2}] \left[ 1 + I_m t/(n I_d t) \right]^{1/2} \tag{9}
$$
when \( n \) is 3 or 4, the second term under the radical may be neglected with only small effect on \( \sigma_\theta \) (ca 10%), so that Eq. 5 becomes

\[
\sigma_\theta = \frac{1}{[\mu_w S (I_m t)^{1/2}]}
\]  

(10)
APPENDIX C

LETTER OF PERMISSION

phone 504/388-8548
fax 504/388-5990

Pradeep Chaphalkar
Dept. of Civil Engr.
3513 CEBA
Louisiana State Univ.
Baton Rouge, LA 70803

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VITA

Pradeep Gopal Chaphalkar was born on May 10, 1957 in Pune, India. He joined Sardar Patel College of Engineering in Bombay University and graduated in 1980 with a Bachelor of Engineering in Civil Engineering. After working for nearly one year on construction sites, he returned to studies and joined Victoria Jubilee Technical Institute in Bombay for Masters degree in Civil Engineering. While completing his Masters, he taught various civil engineering courses as a full time lecturer at the same institute for more than four years. He obtained Masters with Environmental Engineering as Major in 1986. He worked as an environmental engineering consultant before he came to USA. He joined LSU in Fall 1987 and since 1988 he started working toward his Ph. D. under the direction of Dr. Dipak Roy.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: PRADEEP COPAL CHAPHALKAR

Major Field: CIVIL ENGINEERING

Title of Dissertation: CHARACTERIZATION AND APPLICATION OF COLLOIDAL GAS APHRONS FOR GROUNDWATER REMEDIATION

Approved:

[Signatures of Major Professor and Chairman, Dean of the Graduate School]

EXAMINING COMMITTEE:

[Signatures of Committee Members]

Date of Examination:

NOVEMBER 12, 1993