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FATE AND CONSEQUENCES TO THE ENVIRONMENT OF REAGENTS ASSOCIATED WITH ROCK PHOSPHATE PROCESSING

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FATE AND CONSEQUENCES TO THE ENVIRONMENT OF REAGENTS ASSOCIATED WITH ROCK PHOSPHATE PROCESSING

FINAL REPORT

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Prepared for

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DISCLAIMER

PERSPECTIVE

Major reagents associated with phosphate beneficiation include the following: fatty acid (used as a phosphate collector in the rougher flotation step), amine (as a sand collector in the cleaner flotation step), fuel oil (as an extender), sodium silicate (as a sand depressant), soda ash or ammonia (as a pH modifier), and sulfuric acid (for washing away the collector on the rougher concentrate). Typical plant consumption of the various reagents is shown below:

Reagent	Usage, Lb/Ton Concentrate
Fatty acid	4 - 6
Fuel oil	4 - 10
Amine	1.5 - 2
Soda ash	4 - 6
Sulfuric acid	6 - 8
Sodium silicate	1 - 1.5

Florida phosphate operations produce roughly 20 million tons of concentrate each year. Therefore, all of the reagents listed above are used in millions of pounds annually. These reagents are generally considered harmless to the environment for three reasons: (1) many of the organic chemicals are biodegradable, (2) some portion of the reagents remain on the rock surface and ultimately end up in the solid fertilizer products, and (3) the acids and bases neutralize each other in the process of water recycling.

However, there has never been a published, definitive study with reliable information that could support the above assumptions. Concerns have been expressed about the possible effect of the reagent, particularly fuel oil on the quality of ground waters. This project addresses an overdue environmental issue, and the information presented in this report should be beneficial both to the general public and the phosphate industry.

Patrick Zhang
Research Director, Beneficiation & Mining

ABSTRACT

This study was designed to determine the fate and environmental consequences of reagents used for beneficiating Florida phosphate minerals. The project consists of five major components: 1) establishing an in-plant reagent balance by surveying and sampling and analysis of all plant streams; 2) investigating the leaching process and degradation pattern of the reagents by laboratory bench scale testing; 3) identifying the environmental fate of the reagents using sophisticated sample extraction and separation techniques and advanced assaying instruments; 4) determining the impact of reagents on ground water by soil boring and analyses, and well installation and monitoring; and 5) determining biodegradation rates for fatty acid, amine and fuel oil. Extensive data generated from this study indicate that the chemicals used in phosphate beneficiation pose little environmental problem.

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EXECUTIVE SUMMARY

The potential for environmental pollution to occur associated with flotation reagents used in the phosphate industry has been of concern for at least a decade. Furthermore, no detailed studies have previously been undertaken which define the residual impact flotation reagents may have on the subsurface environment In 1994, a research effort was initiated by the BCI Engineers and Scientists, Inc., under the direct supervision of the Florida Institute of Phosphate Research, to address this concern with respect to the fate and consequences of flotation reagents (fatty acids, fuel oils and amines) to the environment. The primary objectives of the research project were:

- To identify an appropriate methodology for the specific identification of flotation reagents: fatty acid, fuel oil, and amine,
- To determine the biodegradation rates of flotation reagents,
- To determine the soil attenuation of flotation reagents, and
- To trace the pathway(s) of flotation reagents to the environment

In order to accomplish the study objectives, the project was separated into two phases during a two-year period. Phase I included development of Standard Operating Procedures and a flotation reagents Method Detection Limit (MDL) analysis, laboratory investigations of the biodegradation and soil attenuation of the reagents, and laboratory and field flotation studies. Phase II included a field investigation of the ground water in clay settling areas and sand tailings areas, as well as in undisturbed areas both upgradient and downgradient of the mine study sites.

The Phase I of this study established a Standard Operating Procedure (SOP) and Method Detection Limit (MDL) for the specific identification and quantification of the reagents used in the phosphate industry. As indicated by the results of Performance Evaluation samples, all associated analytical data were acceptable in terms of both precision and accuracy. It is therefore concluded that the main objective of Quality Control, namely to produce verified data of known quality suitable for use in support of this project's primary goal of assessing the fate of selected flotation reagents was met.

Results of 28 day laboratory biodegradation testing showed that all reagents undergo degradation, but the level of biodegradation is variable. Fatty acid and amines are more readily biodegradable than the fuel oil. The biodegradation trend for the amines showed a maximum of approximately 53 percent, followed by fatty acid at 35 percent. The fuel oil showed the least biodegradation, as indicated, approaching slightly above 10 percent. The biodegradation of the control, which contained only glucose, was between 80 and 90 percent.

The soils attenuation study showed that sandy overburden has the ability to attenuate or reduce fatty acids and fuel oil quantities. Although no amines were detected in the original General Mill Tailings (GMT) water, it is presumed that negatively charged tailings sand, which is the dominant material transported in the GMT, would attenuate the cationic amines. Thus, there was no detection of amines in the GMT water.

To identify the distribution of reagents in the various “streams” within the beneficiation process and environment, both laboratory and field mass balances were attempted. The laboratory lab flotation did not provide a satisfactory mass balance, accounting for only 31 percent of the fatty acid recovery, 113 percent for the fuel oil, and 425 percent for the amines. Further assessment to evaluate the low recovery of the fatty acid and a high recovery for the amines did not improve the mass-balance results. However, a subsequent field flotation mass balance was achieved utilizing IMC-Agrico’s mass-balance program. The sample analysis and mass balance program indicated most of the reagents to be distributed in the clay settling and sand tailings (GMT) areas. This information further assisted with the assessment and observations made in the second phase of the research which investigated the presence or absence of the reagents in the ground water.

In Phase II, which was the field investigation of ground water, neither fatty acids nor amines were detected in the surficial aquifers underlying clay settling and sand tailings disposal areas. This finding is not surprising as both these reagents were shown to be biodegradable and also attenuated by sandy overburden. In contrast, fuel oils were detected in the surficial aquifer at all sand tailings disposal areas. Also, the fuel oil concentration decreased as the age of the sand tailing area increased. None of the nineteen intermediate aquifer wells sampled for this project indicated any fatty acid or amines and only one well located at an active sand tailings disposal area, indicated trace amounts of fuel oil.

The vertical migration of fuel oil constituents into the Intermediate aquifer appears to be mainly related to the degree of confinement between the surficial and intermediate aquifers. At the North Florida Phosphate District, despite detection of a trace amount of fuel oil in the intermediate aquifer there is a significant decrease in fuel oil concentrations compared to the overlying surficial aquifer.

This research effort has established a SOP and MDL for the specific identification and quantification of fatty acids, fuel oils and amines used in the flotation process in the phosphate industry. Furthermore, it has been shown that the biodegradation of these reagents vary, with amines being the most biodegraded followed closely by fatty acids and then the fuel oils. In addition, attenuation of fatty acids and fuel oils by the sandy overburden was observed. However, due to a lack of amines detection in the GMT water, it is presumed that the negatively charged sand tailings which dominate the GMT would attenuate the cationic amines. Although a laboratory mass balance of reagents was not attained, a field flotation mass balance was achieved utilizing IMC-Agrico’s mass-balance model. Both sample analysis and mass-balance model indicated most of the reagents to be distributed in the clay settling and sand tailings (GMT) areas. Finally, this study showed no detection of fatty acids or amines in the surficial or intermediate aquifers. In contrast, fuel oils were not only detected in the surficial aquifers at all sand tailings areas, but the fuel oil concentration decreased with the age of the sand tailings area. Fuel oil was also detected in trace amounts in one Intermediate aquifer well located in an active sand tailings area in North Florida, but appears to be related to the degree of confinement between the surficial and intermediate aquifers. There are no established concentration limits for fuel oils in ground water, but if the concentration limit of 5.0 mg/L in water, established for contaminated sites used for the Underground Storage Tanks program is used, the detected value of 0.6 mg/L is well below this limit. Thus there should be no concern in the environment from the use of flotation reagents in the beneficiation process of the phosphate industry in Florida.

The data generated during this project and related observations provide inadequate information on the extent or spatial distribution of the any fuel oil in the ground water systems at the specific location at each test site. Any conclusions with respect to the extent of fuel oil migration is beyond the scope of this project. Therefore, Phase III of this project is recommended which would address potential off site horizontal migration of fuel oils from sand tailings areas.

INTRODUCTION

Since phosphate was discovered in Florida in 1888, over one billion tons of phosphate has been mined. Of this tonnage, approximately 90 percent or 900 million tons were produced in what is called the “land-pebble district” of Polk and Hillsborough Counties, making this relatively small area the most productive in the world. In 1989, Florida production accounted for 40 million tons or approximately 80 percent of United States production and 30 percent of world production (Irwin 1991). It is evident from these statistics that the Florida phosphate mining industry has and continues to have a significant economic impact coupled with the potential for environmental impact as well.

MINING OPERATIONS

The phosphate deposits of central Florida are of marine origin. These marine phosphorites were formed in ancient seas and subsequently covered with layers of sand and clay ranging from 10 to 100 feet thick. In order to mine phosphate, the first step involves removal of the soils overlying the phosphate ore body using electrically powered draglines. The mining term, overburden, is used to describe this upper soil strata, which consists primarily of sand and clays. As the overburden is removed, it is stacked in piles within adjacent mine cuts. These piles, or spoil banks, are left in place for later use as fill material during land reclamation.

After the overburden has been removed, the dragline excavates the phosphate bearing ore, called “matrix”. Matrix thickness ranges from one to fifty feet and average twelve feet. The matrix is a relatively stiff mixture composed of three primary constituents: phosphate, sand, and clay. The phosphate occurs as either “pebbles” or finer particles. Typical matrix consists of approximately one-third phosphate, one-third sand, and one-third clay or clay sized particles (-150 mesh material). As it is excavated, the matrix is dumped alongside the mine cut into an earthen sump or “pit”. Here it is slurried with high-pressure water to form a pumpable mixture. This slurry is suctioned using a dredge type centrifugal pump and conveyed via pipes to a beneficiation plant.

MINERAL PROCESSING

At the beneficiation plant the matrix is physically and chemically treated to separate the phosphate rock, sand and clay fractions. Mineral processing, or beneficiation, includes washing, screening, sizing, and flotation. The product fractions, pebble and fine size phosphates (concentrate) are stockpiled for eventual transport to a chemical plant to be made into fertilizer, or they are sold directly as final products for other uses. The sand, (also called sand tailing) is returned to the mine cuts from which the matrix was removed, and the clays are pumped to containment areas for settling and dewatering. The water used to pump the waste clay and sand fractions is decanted and recycled back to the mine for reuse.

At the beneficiation plant, slurried matrix is disaggregated, washed and screened to recover pebble (+1mm) which is stockpiled for sale or later use in fertilizer production. The remaining fraction is cycloned to remove clay (-0.1mm) from flotation plant feed (-1mm +0.1mm). The pebble is stockpiled for sale or later use in fertilizer production. The coarse and fine fractions recovered by cycloning contain 70-80 percent sand, which is separated from fine phosphate materials using flotation.

Flotation is a process technique for upgrading ores by using air, water and flotation reagents in a flotation vessel. This process involves modifying and taking advantage of the differences in surface chemistry of the materials to be separated. A flotation cell contains a motor driven impeller with an airshaft and diffuser. Air is introduced through the center airshaft and exits into the slurry at the diffuser, which creates fine air bubbles and helps to distribute the ore particles.

Effective recovery or material separation requires that the processed particles adhere to the air bubbles and float to the top of the flotation vessel (Irwin, 1991). However, most minerals are naturally hydrophilic and will not freely adhere to the air bubbles; therefore, a collector chemical or flotation reagent must be used to make the mineral surface hydrophobic. Flotation reagents are heteropolar organic compounds that contain a hydrophilic (water-loving) polar head and a hydrophobic (water-hating) tail consisting of a long chain hydrocarbon. The hydrophilic region can be either positively or negatively charged. The hydrophilic pole of a collector reagent is adsorbed on the mineral surface by chemical bonding or electrostatic interaction. The hydrophobic pole of the collector attaches to air bubbles. Using these characteristics, flotation separation is readily obtained. With phosphate ore, either sand or phosphate can be floated depending upon the type of flotation reagent employed in the process.

The surface of quartz sand is negatively charged above pH 2. Phosphatic minerals do not become negatively charged until the pH is above 6 or 7. Consequently, at a neutral pH, a cationic flotation agent will selectively adsorb on quartz sand allowing it to be separated from phosphate minerals. The commonly utilized cationic flotation reagents are long chain amine salts. If phosphate minerals are to be floated, an anionic fatty acid is used as a collector because their carboxylate groups bond readily with calcium in apatite (phosphatic) minerals. Since anionic collectors do not adsorb on the negatively charged sand particles, only the phosphate minerals are floated. In practice, in order to upgrade or beneficiate phosphate ores economically, the phosphate mineral component is floated first for maximum recovery and then the sand is floated to further optimize grade and mineral recovery.

To float the phosphate first, a mixture of fatty acids and fuel oil is used as a collector. The commonly used fatty acids are a by-product blend of crude tall oils and low-grade fatty acids obtained from the paper industry. These include a mixture of:

oleic acid	$CH_3(CH_2)_7CH{=}{=}{=}CH(CH_2)_7COOH$
linoleic acid	$CH_3(CH_2)_4CH{=}{=}{=}CHCH_2CH{=}{=}{=}CH(CH_2)_7COOH$
linolenic acid	$CH_3CH_2CH{=}{=}{=}CHCH_2CH{=}{=}{=}CHCH_2CH{=}{=}{=}CH(CH_2)_7COOH$
abietic acid (rosin)	$C_{20}H_{30}O_2$

Because neutral molecules enhance collector efficiency they also reduce the quantities required to obtain satisfactory recoveries. Either No. 5 fuel oil or reclaimed oil is used in combination with fatty acid at a ratio of approximately 1:1 to make a fluid blend and control foaming during flotation. The phosphate industry uses approximately 120 million pounds of fatty acid and double that quantity of fuel oil per year in support of flotation processing.

The formation of a satisfactory bond between fatty acid and the phosphate minerals requires agitation for one to two minutes at a pH of 8.5 to 9. Sodium hydroxide (soda ash is used more often) or ammonia is used to effect the required pH adjustment. Conditioned ore is introduced into an aerated flotation-cell where the phosphate particles float away from a relatively clean sand tailing fraction. The sand residuals are either pumped to storage piles or to existing mine cuts for use as fill for land reclamation purposes.

The collected, partially upgraded, phosphate ore from this separation is called rougher concentrate, and usually still contains 10-20 percent sand. Further upgrading and sand removal requires a second flotation that is accomplished by floating the sand using a cationic collector. Before this can be done, the residual fatty acid and fuel oil on the rougher concentrate must be removed using a sulfuric acid wash at a pH of 3 to 4 in an agitation tank. The acid washed rougher concentrate is rinsed, dewatered and introduced into a conditioning box where a cationic collector is added.

No. 2 fuel oil is often added as an extender at this point in the process. From 0.1 to 1.0 pounds of cationic collector is required per ton of rougher concentrate depending on the mineralogical properties of the original ore. The phosphate industries use approximately 18 million pounds per year of cationic collectors.

The cationic collectors used to float sand belong to a family of amines. The cationic and hydrophilic region of these amines is a protonated NH^+ group. Their hydrophobic regions are made up of (16-18) carbon chains. The fatty acids are reacted with ammonia, heated to produce amides, dehydrated to form nitriles and finally hydrogenated to create long chain primary amines. Secondary amines are produced by reacting the fatty acids with short chain ethylamines such as diethylenetriamine to produce condensate amines.

These condensate amines are actually fatty amido-amines. These synthesized products work well in flotation because they have polar heads and two long chain hydrophobic hydrocarbon tails. Diethylenetriamine fatty amido-amine condensate has long been in standard use by the industry. However, for cost related reasons, other by-product amines from the petroleum industry are often substituted for the diethylenetriamine.

To enhance performance and in order to disperse these long chain amines, acetic acid is added to form amine salt. These neutralized salts are usually solids at ambient temperatures. For this reason they are blended with frothers to make them fluid and more easily dispersible in water. This approach is cost effective and often produces better performance. These blends are called flotation amines in the industry.

Frothers are surfactant agents that aid in controlling froth during flotation. They help to create and stabilize fine air bubbles. Common frothers include alcohols, glycols or terpenes. By-product terpenes are obtained from the paper industry. The alcohols and glycols are purchased from commercial chemical supplies.

In some cases fine particles of phosphate will float with the sand, resulting in poor separation. In such cases a phosphate depressant such as a modified starch may be used. Starch acts by coating phosphate particles, which allows for better separation. The resulting sand and phosphate concentrate fractions are both neutralized and washed. All recovered sand is utilized in land reclamation.

PURPOSE OF STUDY

The Florida phosphate industry spends about $50,000,000 per year to purchase a range of beneficiation reagents such as fatty acids, fuel oils and amines to recover fine phosphates or concentrate from mined matrix. It is speculated that the ultimate fate of up to 30 percent of these beneficiation reagents is unaccounted for and may be released to the environment. It is currently assumed that the unaccounted reagent quantities are disposed of along with waste clay and sand from the mineral processing or beneficiation plant or are adherent on final product materials. Of the 40 million metric tons of phosphate rock produced in Florida annually, approximately 24 million metric tons are in the form of concentrate. To produce a ton of concentrate the industry uses about 4.7 pounds of fatty acid, 12 pounds of fuel oil, 4.3 pounds of soda ash and 1.8 pounds of amines.

Residual reagents originating from these beneficiation facilities may impact the surrounding subsurface environment if they seep into the ground water systems. The fate of any chemical free in natural environments depends on such factors as the structure, water solubility, sorptive tendencies, dissociation constants, volatility and more. Other factors that affect the fate of a chemical in the environment include its susceptibility to chemical transformation processes such as hydrolysis, photolysis, oxidation or reduction and biodegradation (Brink 1981). The degree of impact to the subsurface environment and ground water systems depends on the type of contaminant, toxicity, seepage potential, hydraulic conductivity of the soils, direction and rate of migration of the contaminant, site hydrogeology, soil/contaminant interaction and general geology of the area.

The overall goal of this study was to provide useful information to the phosphate industry and evidence that would ease concern with respect to suspected environmental pollution potentially associated with the flotation reagents used in the industry. If reagent residuals are found to be adversely affecting the environment, appropriate remedial measures may need to be developed.

With the above in mind, the primary objectives of this research project were:

- To identify an appropriate methodology for the specific identification of flotation reagents: fatty acid, fuel oil, and amine,
- To determine the biodegradation rates of flotation reagents,
- To determine the soil attenuation of flotation reagents, and
- To trace the pathway(s) of flotation reagents to the environment

In order to accomplish the study objectives, the project was separated into two phases over a two-year period. Phase I included development of Standard Operating Procedures and a flotation reagents Method Detection Limit (MDL) analysis, laboratory investigations of the biodegradation and soil attenuation of the reagents, and laboratory and field flotation studies. Phase II included a field investigation of the ground water in clay settling areas and sand tailings areas, as well as in undisturbed areas both upgradient and downgradient of the mine study sites.

Several studies (Bromwell & Carrier 1987; PEI 1986; and Garlanger et al. 1983) have been conducted to assess water quality at mining and phosphate fertilizer plants. These studies have addressed and evaluated the impact of inorganic constituents and signature ions in the subsurface environment. However, very little information is known about the ultimate fate of the organic compounds used in support of phosphate rock beneficiation. Earlier studies (Garlanger et al. 1983 and 1984) assumed that these reagents are either biodegradable or are decomposed by sulfuric acid added during processing. However, no detailed studies have been undertaken which define the residual impact flotation reagents may have on the subsurface environment (Zhang 1993). Consequently, there are lingering associated environmental concerns for the industry, which are frequently raised in the context of new permitting projects.

Therefore, this reagent study was commissioned to identify and quantify the amounts of flotation reagents (fatty acid, fuel oil, and amines) used in a phosphate beneficiation facility and to assess their fate and potential consequences in the environment.

IDENTIFICATION AND QUANTIFICATION OF FLOTATION REAGENTS

OBJECTIVES

In order to determine the fate of reagents (fatty acid, fuel oil, and amines) in the environment with confidence, it was necessary to first identify appropriate methodologies for the specific identification of flotation reagents and to establish the analytical Method Detection Limits (MDL) for both precision and accuracy. A MDL is defined as the minimum concentration of a chemical that can be measured within a 99 percent confidence interval for an analyte concentration greater than zero and is determined from the analysis of a sample in a given matrix containing the analyte.

This section describes the approach used to develop the specific analytical Standard Operating Procedure (SOP), which details the complete and specific analytical method for each of the three reagents in both soil and water matrices.

MATERIALS AND METHODS

As an initial step, BCI requested that FIPR staff prepare several Blind Performance Evaluation (PE) samples. These samples were spiked with known amounts of fatty acids, fuel oils (also referred to as total extractable hydrocarbons) and amines. Samples were spiked with either single reagents or reagent mixes; and, the concentrations were not provided to the testing laboratory. American Technical and Analytical Services, Inc. (ATAS) was retained to complete all required flotation reagent analyses.

RESULTS AND DISCUSSION

For each of the reagents, a discussion section is provided for each of the following:

- Method selection, development and optimization
- Interpretation of PE sample results
- Quality control samples
- Accuracy and precision

A case narrative and resulting data for the PE samples are presented in Appendix A (unpublished; copy available for inspection in FIPR Library). Standard Operating Procedures specific to each of the reagents included in this study were developed using this approach. A full discussion of each protocol is provided in Appendix B.

Amines Method Selection, Development and Optimization

ATAS extracted the samples using the continuous liquid-liquid extraction method and analyzed by the Gas Chromatography/Mass Spectrometry procedure (GC/MS, method reference USEPA 8270 for semi-volatile organic compounds). The list of analytes identified contains several low molecular weight amines.

Prior to continuous liquid-liquid extraction, ATAS extracted the samples using a manual separatory funnel. The continuous liquid-liquid method is the extraction method required by the United States Environmental Protection Agency (USEPA) for Superfund Site analyses. This extraction presents minimal matrix problems and generally produces higher analytical precision; overall it gives a high extraction efficiency. When compared to the recoveries obtained from separatory funnel extraction, the continuous liquid-liquid extraction proved to produce better recoveries. Hence, all analyses employed use the 18-hour continuous extraction method.

ATAS conducted a literature search and review and studied research papers on amines to choose an appropriate analytical procedure. Based on this search, ATAS chose a GC/MS protocol for the analysis of amines using “on column” injection. ATAS obtained a pure Amine Standard and analyzed an Octadecyl Amine Standard by GC/MS. ATAS also analyzed BCI supplied material. Their analyses did not reveal a C18 type amine compound but showed more than a dozen peaks. For this reason ATAS chose to utilize the ten most abundant component peaks to calculate the final concentrations of the BCI amine material. These results are identified as total fatty amines in the data summaries. It is important to note that the BCI supplied amine material bore no similarity to the octadecyl amine standard.

Amines Performance Evaluation Sample Results

BCI Sample #	ATAS Reported Concentrations mg/L	BCI Spiked Concentrations mg/L	% Recovery
970507-2	2.41	3.55	68
970507-4	21.4	26.5	80
970508-7	2.38	3.3	72

The PE samples did not contain any of the component peak #9 material present in the originally supplied BCI amine used in GC/MS calibration.

A method blank and two Laboratory Control Samples (LCS) were analyzed with the above set of PE samples. The blank showed no detection (ND) and the LCS recoveries were calculated at 56 percent and 64 percent respectively.

Amines Quality Control Samples

The Quality Control Samples are analyzed in conformance with the criteria established for each method.

Quality Control Evaluation Criteria

Method Blank: A blank sample, an aliquot of either deionized water or sand, was analyzed for each analyte of interest. A “ND” (not detected) confirms the absence of contamination.

Laboratory Control Sample (LCS): A blank sample spiked with a known quantity of the analyte of interest was analyzed with each batch of field samples. The results of recovery were used to evaluate the accuracy of the measurement process.

Laboratory Control Sample Duplicate: A duplicate LCS recovery establishes the relative percent difference (RPD) between two Laboratory Control Samples. This RPD is used to compare the two values and is reported as an absolute number. The RPD serves to measure the precision.

Matrix Spike (MS): An aliquot of a field sample was spiked with a known amount of the analyte of interest and analyzed like the remaining field samples in order to identify the possible interferences in that matrix.

Matrix Spike Duplicate (MSD): A second aliquot of sample was spiked and analyzed to measure the precision of the method in presence of possible interferences.

Surrogate Interpretation

Surrogates are compounds that are similar to the analytes of interest which are added to each sample, before extraction. The sample is then processed as required in the method. The surrogate recovery results are used as an internal Quality Assurance/Quality Control (QA/QC) to evaluate the total bias of the extraction and analytical procedure.

Fatty Amines surrogate: The laboratory used the following six surrogate compounds:

Surrogates	Control Range %
Nitrobenzene	35-114
Terphenyl d14	33-141
2-Fluorophenol	21-100
2-Fluorobiphenyl	43-116
Phenol d5	10-94
2, 4, 6 Tribromophenol	10-23

Control limits are the range estimated by the USEPA.

The same set of six surrogate compounds used in EPA SW846 Method 8270 were used to spike project samples. Surrogate recoveries were tracked as suggested in the EPA QC acceptance criteria. Under these procedures, test data are deemed acceptable if one acid and one base/neutral (B/N) surrogate fall outside the specified ranges as long as no surrogate recovery is below 10 percent. If the above criterion is not met, the laboratory must re-extract the tested sample and re-analyze. In all cases, the study surrogate results were well within the acceptable QC ranges.

Amines Accuracy and Precision

Accuracy is the degree of agreement between a given result and the true or expected value of the measured analyte. LCS and spike analyses are typical QC approaches used to gain understanding of accuracy.

It is important to note that analyses of organics in water and soil samples performed by GC or GC/MS are typically accurate to 80 percent ± 40 percent. For this reason LCS and LCSD recoveries of 56 percent and 64 percent for total amines obtained by ATAS during this study are well within the acceptable range.

Precision is the degree of mutual agreement characteristic of independent measurements as the result of repeated application of the same analytical procedure. It defines the closeness of results to one another. Precision is determined by calculating the RPD of two duplicate samples.

The results of the two LCS recoveries performed by ATAS show a RPD of 15 percent. For organic analytical data, RPDs of ± 30 percent are not uncommon and are deemed acceptable.

Fatty Acids Method Selection, Development and Optimization

Fatty Acids were analyzed by ATAS with gas chromatography using a flame ionization detector (GC/FID). The samples were extracted by the Association of Official Analytical Chemists (AOAC) method using boron trifluoride as the derivatization agent.

ATAS developed this procedure after several trials. The procedure is based on the AOAC procedure in which the sample is extracted in methylene chloride and then esterified using BF_3 and hexane.

Fatty Acids Performance Evaluation Sample Results

BCI Sample #	ATAS Reported Concentrations Mg/L	BCI Spiked Concentrations Mg/L	% Recovery
970508-2	3.12	6.8	46
970508-3	10.4	12.7	82
970508-9	8.77	16.5	53

Fatty Acids Quality Control Samples

A method blank and two LCSs were also analyzed with the above set of PE samples. The blank showed no detection (ND) and the LCS and LCSD recoveries were 94 percent and 59 percent, respectively.

Although the data was acceptable based on typical organic analyses by GC, the large RPD (45%) between the two LCSs was a concern. For this reason ATAS analyzed four additional LCSs which are presented below. The extraction procedure was modified by adjusting the hexane volume.

Sample ID	Concentration mg/L	Spike Level mg/L	% Recovery
Blank	<1	NA	NA
LCS1	3.99	5.0	80
LCS2	5.90	5.00	118
LCS3	4.64	5.00	93
LCS4	4.12	5.00	82

Fatty Acids Accuracy and Precision

The results obtained from analysis of the four additional LCSs showed acceptable recovery levels in all cases. Although the RPD between LCS 1 and 2 was high, the new data exhibited acceptable levels of accuracy and precision overall.

Fuel Oil Method Selection, Development and Optimization

ATAS performed this analysis by Gas Chromatography (GC/FID, modified 8015). This analysis is based on a solvent extraction gas chromatography procedure. The method was based on USEPA method 8000, modified 8015, Iowa State method OA2, and Florida FL-PRO. This procedure is typically used for analyses of total extractable Petroleum Hydrocarbons. The compound P-Terphenyl d14 was used as a surrogate and the BCI supplied fuel material was used to prepare the LCS and Matrix Spikes.

ATAS has a successful track record of analyzing hundreds of samples using this method under Underground Storage Tank (UST) regulations. The P-Terphenyl recoveries were tracked against previous ATAS water samples using this surrogate. Because no previous recovery data were available for the BCI material, the Kerosene recovery range was used for these LCS and LCSD samples. However, after analyzing numerous project ground water and QC samples, enough data points were accumulated to establish a specific control range. Subsequent analyses were tracked using ATAS's newly established control range.

In regard to the interfering peaks seen in the PE sample spiked with fuels, amines, and fatty acids, the laboratory reported all of the hydrocarbon peaks and eliminated all interfering peaks associated with amines and fatty acids. (Reference: FL-PRO). Also, ATAS modified its extraction procedure to eliminate the acidification step to minimize interference owing to the presence of fatty acids and amine hydrocarbons.

Fuel Oil Performance Evaluation Sample Results

BCI Sample #	ATAS Reported Concentrations mg/L	BCI Spiked Concentrations mg/L	% Recovery
970507-5	2.12	2.9	73
970507-6	8.52	11.4	75
970508-6	2.72	1.1	247

Fuel Oil Quality Control Samples

Sample 970508-6 was spiked with all three of the evaluated reagent components, fatty amines, fatty acids, and fuels. It is apparent from the above results that the hydrocarbons from the fatty acids and amines were extracted during testing, along with the fuels, causing interference and elevated recovery. Based on several states' UST programs, it was decided that all hydrocarbon peaks should be considered, however, fuel oil standards should be used to eliminate other interfering peaks from fatty acids and amines, when calculating fuels in the subsequent project samples. According to FL-PRO (Florida Department of Environmental Protection) for water samples, LCS recoveries between 55 percent and 118 percent are acceptable. LCS recoveries were also within acceptable ranges.

Fuel Oil Accuracy and Precision

A method blank and two LCS were analyzed simultaneously with the above set of PE samples. The blank showed no detection (ND) and the LCS results showed 92 percent and 94 percent recoveries.

CONCLUSIONS

As is evident from the results of the Performance Evaluation, all study associated analytical data are acceptable in terms of both precision and accuracy. In addition, the LCSs analyzed with each batch of samples exhibit acceptable recovery levels.

Overall and in all cases, ATAS's results showed good precision based on the RPDs obtained from both duplicate LCS and Duplicate Matrix Spike samples. No method blanks exhibited detectable levels of the analytes of interest. Based on the review of the procedures, interviews with key laboratory personnel, data review, QC results, checks for data precision and accuracy, all data were deemed to be of acceptable quality.

Our overall conclusion was that ATAS had met the main objective of developing appropriate SOPs and MDLs for the specific identification of flotation reagents and Quality Control, namely to produce verified data of known quality suitable for use in support of the project's primary goal of assessing the fate of selected flotation reagents.

BIODEGRADATION

OBJECTIVES

The fate of phosphate beneficiation reagents in the natural environment depends on many factors such as chemical structure, water solubility, sorptive tendencies, dissociation constant, volatility of the chemical, hydrolysis, photolysis, oxidation, reduction, and biodegradation. Additionally, other factors also affect the susceptibility of the chemicals in a particular environment: temperature, rainfall, wind, topography, soils, hydrology and the aerobic character of the location. In nature, most of the above factors occur and interact simultaneously in the same location. Therefore it is difficult to differentiate which factors or combination are controlling in terms of the rate at which degradation proceeds if it occurs at all. Different environments vary in the effectiveness in these regards. Nevertheless, it is evident that biodegradation is the predominant degradation mechanism in soils and water, and that microorganisms account for an overwhelming share of all biodegradations.

The degradation of organic compounds may be rapid or slow depending on local environmental conditions. Glucose is readily metabolized in an oxygen-rich environment containing a healthy microbial population. The rate at which biodegradation occurs is also related to chemical structure. Complex molecules are metabolized more slowly than simple compounds. The foundation of domestic wastewater treatment is based on the ability of microorganisms to degrade or metabolize organic compounds.

Several basic types of biodegradation experiments have been performed on a variety of different organic compounds and are reported in the literature. Water samples from lakes, streams, rivers, and other water bodies can have organic compounds added to them in batch experiments. In these experiments the disappearance of the tested chemical is measured. An alternative approach is to add organic chemicals to a water/soil sample selected to simulate in situ conditions. Activated sludge from a waste water treatment plant or other microbial supply source can be used as a seed material to promote the degradation of specific organic compounds. Radiolabeled isotopes of carbon, specifically ^{14}C can be used to investigate biodegradation by measuring $^{14}CO_2$ respiration. Oxygen consumption and carbon dioxide evolution can also be measured to characterize biodegradation.

For the purpose of this project a specific test procedure (Birch and Fletcher 1991) was utilized to assess the biodegradability of beneficiation reagents under aerobic conditions. This method is comparable to other techniques and is appropriate to biodegradation testing of insoluble and volatile compounds.

MATERIALS AND METHODS

The following materials were tested for biodegradation:

Glucose	Fuel Oil
Amine	Fatty Acid/Fuel Oil
Fatty Acid	Fatty Acid/Fuel Oil with double the amount of phosphate nutrient

Biological degradation is broadly acknowledged as the primary mechanism via which organic chemicals are removed from the environment. In the natural world biodegradation proceeds in steps or stages and most often involves the action of a series of microbes all adapted to metabolize different chemical substrates. Primary biodegradation is the process step during which a complex chemical compound is biologically altered to change its original chemical character. A chemical can undergo primary biodegradation, but be quantitatively converted to an intermediate chemical compound that is resistant to further reduction. Ultimate or complete biodegradation is the point in this process at which a chemical has been fully degraded to form simple and commonly recycled compounds i.e. carbon dioxide, water, nitrate, ammonia, inorganic salts, etc. The methods most widely used to analyze ultimate biodegradation employ quantitative measurement of oxygen uptake, dissolved organic carbon removal, and carbon dioxide gas production. Specifically this procedure involves seeding or inoculating a medium containing the material to be tested with suitable microbial mix in the presence of excess oxygen and monitoring the rate of biodegradation using appropriate analytical tracking procedures.

The method (Birch and Fletcher 1991) involved placing a known quantity of the material to be tested in sealed vessels containing a mineral salt medium and a microbial inoculum. This mix was incubated for 28 days. A full description of this analytical procedure is provided in Appendix C. The upper one third of the vessel was not filled to allow sufficient headspace required for complete oxidation of all test chemical carbon to carbon dioxide. Factors known to influence biodegradation rates in laboratory tests include temperature, nutrient amounts, the type and source of microbes, among many others. Standard testing employs incubation at a temperature of 37^{o} C. The nutrient mix was maintained in accordance with the analytical procedure. The microbe (*Pseudomonas aeruginosa*) utilized for the testing purposes of this project was obtained in pure culture from the American Type Culture Collection. Carbon dioxide was continuously produced during biodegradation testing and was present within the test vessel in both the liquid and gaseous phases. At selected time intervals during the 28-day incubation period sample volumes are collected from the test vessels and analyzed for carbon dioxide in both the liquid and gaseous phases. Control vessel testing was employed as well. Control set up and handling was the same as for specific testing except for the absence of reagent materials. Our recent testing included the simultaneous conduct of a glucose test material analysis performed along with the phosphate flotation reagents. The purpose of this testing was to compare the biodegradation of the flotation reagents to a known compound.

RESULTS AND DISCUSSION

Biodegradation results are summarized in Figures 1 through 7. These percent biodegradation versus time plots are provided for each tested chemical. The results of the biodegradation testing showed all reagents undergo degradation, but the level of biodegradation is variable.

The percent biodegradation of the control, which contained only glucose, was between approximately 80 and 90 percent after approximately 20 days. It was interesting to note that the Solid Glucose was degraded to a greater extent than the Glucose solution, contrary to what was expected. The biodegradation trend for the amines showed a maximum of 53 percent, followed by fatty acid at 35 percent degradation after 20 days. The fuel oil showed the least biodegradation, as previously indicated, approaching slightly above 10 percent. A combination of the fatty acid and fuel oil showed a maximum biodegradation averaging 45 percent, which was between that of the fatty acid and amine individually. Addition of soluble phosphorus as nutrient showed a degradation of slightly over 40 percent. This observation was again, contrary to an expected higher degradation over that of the reagent mixture alone.

The analytical procedure of Birch and Fletcher (1991) is similar to the Sturm CO_2 Production Test, but simpler. The vessels used to incubate the reagents and microbes via the former method are small enough so many more replicates can be analyzed. The respective test and control vials are sealed while incubating to prevent volatile materials from being released during degradation. Biodegradation of organic compounds is a complex process moderated by numerous variables. For this reason it is difficult to reasonably extrapolate laboratory test results to the natural or mine environment.

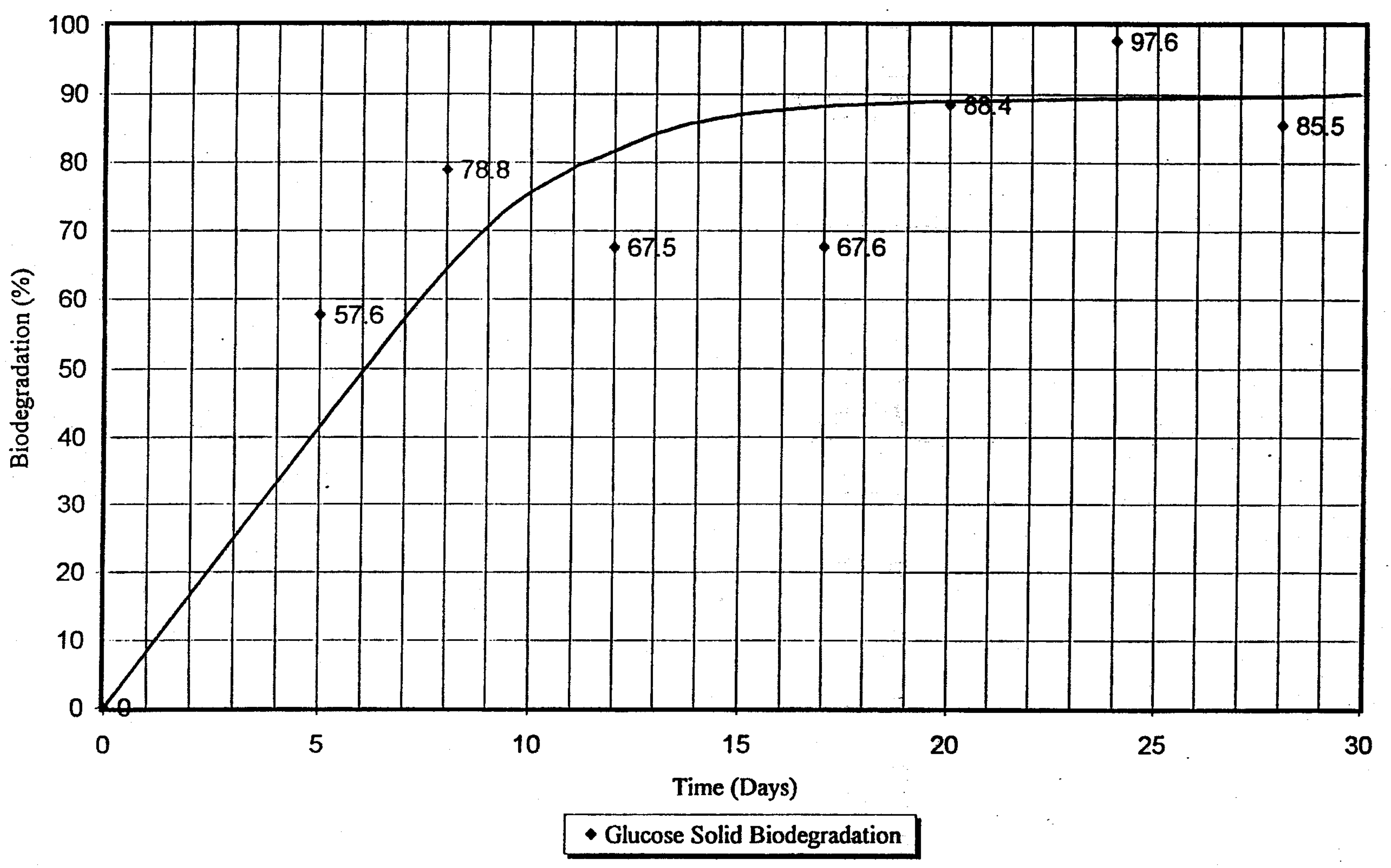

Figure 1. Glucose Solid Biodegradation.

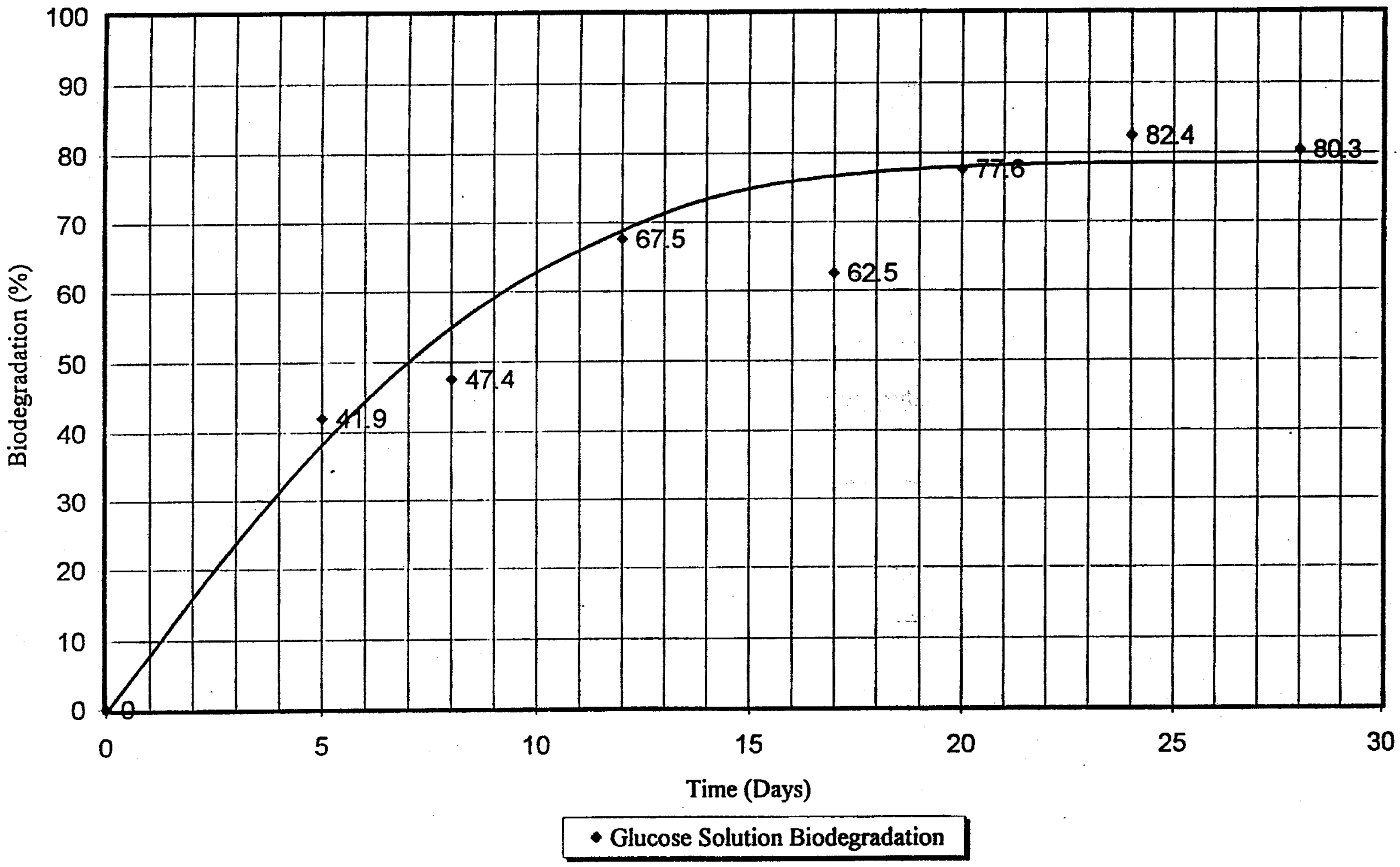

Figure 2. Glucose Solution Biodegradation.

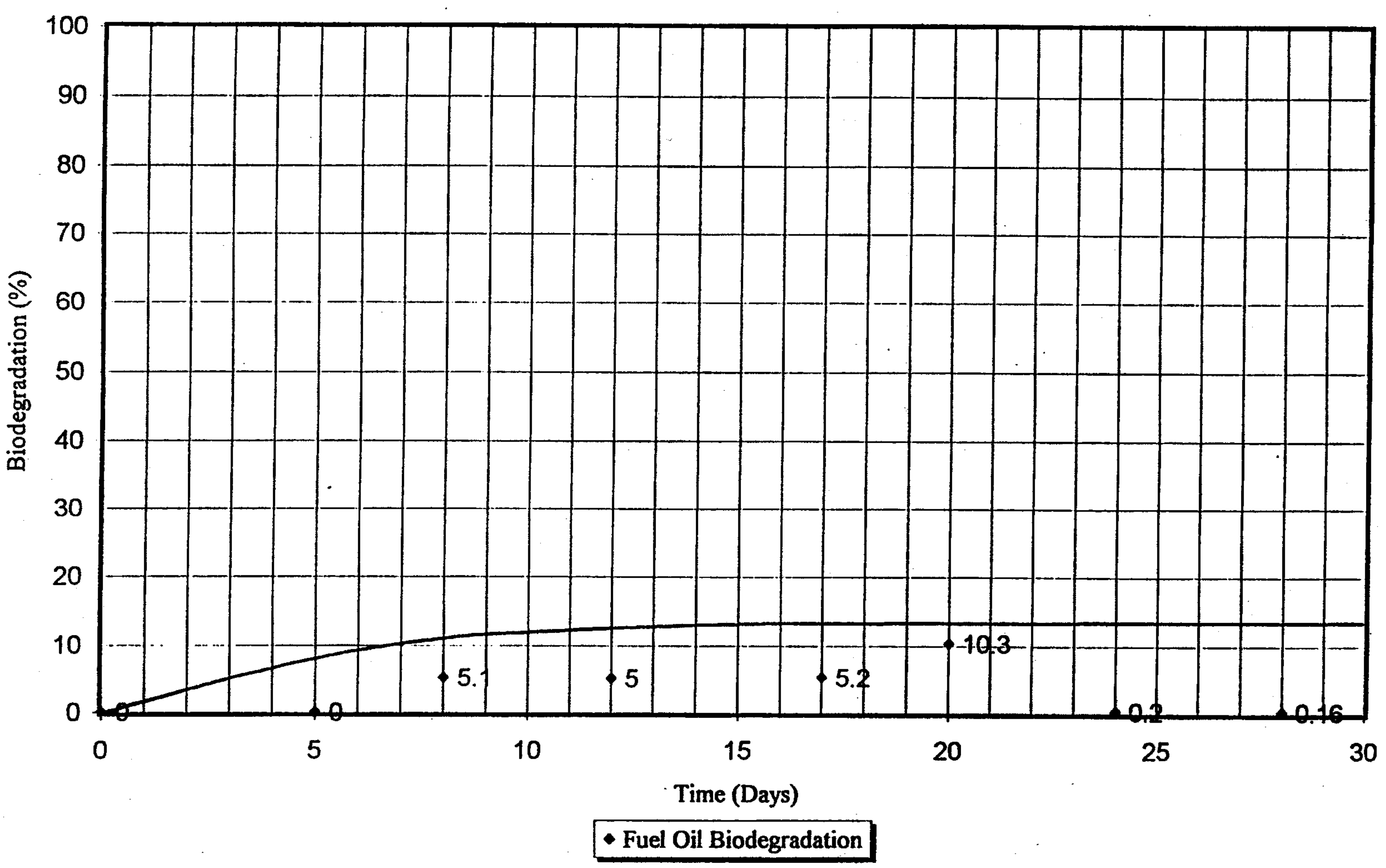

Figure 3. Fuel Oil Biodegradation.

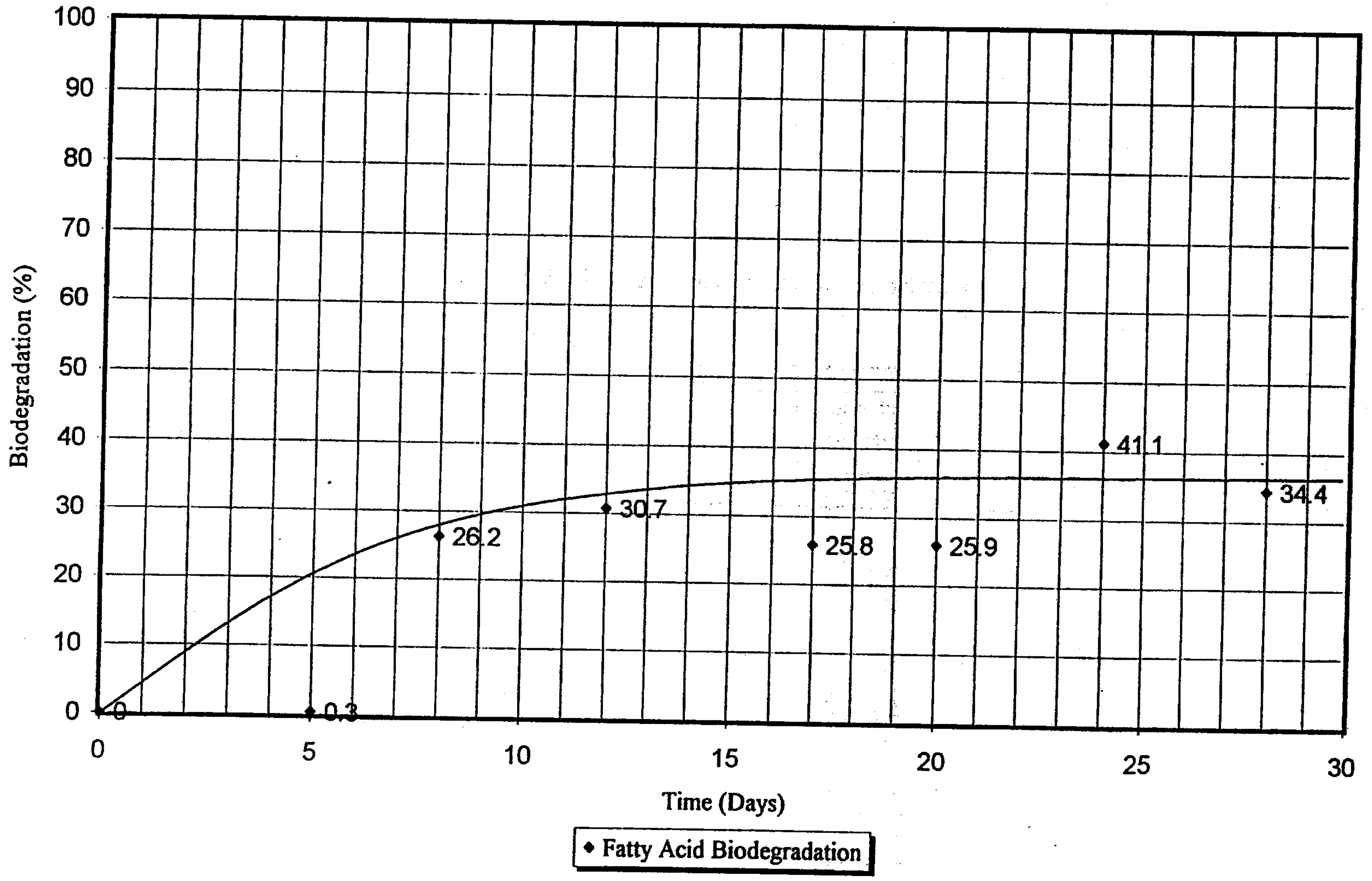

Figure 4. Fatty Acid Biodegradation.

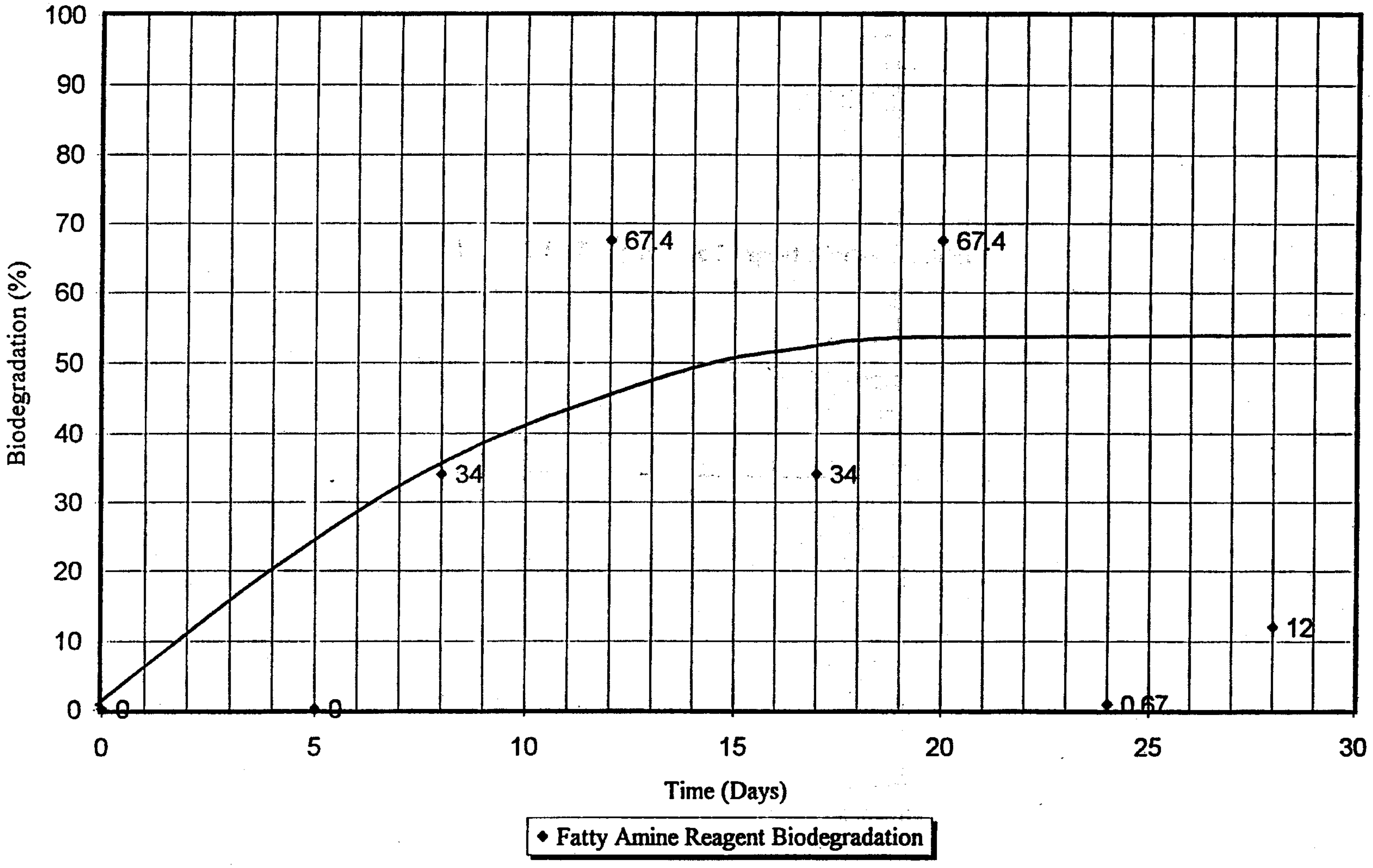

Figure 5. Fatty Amine Reagent Biodegradation.

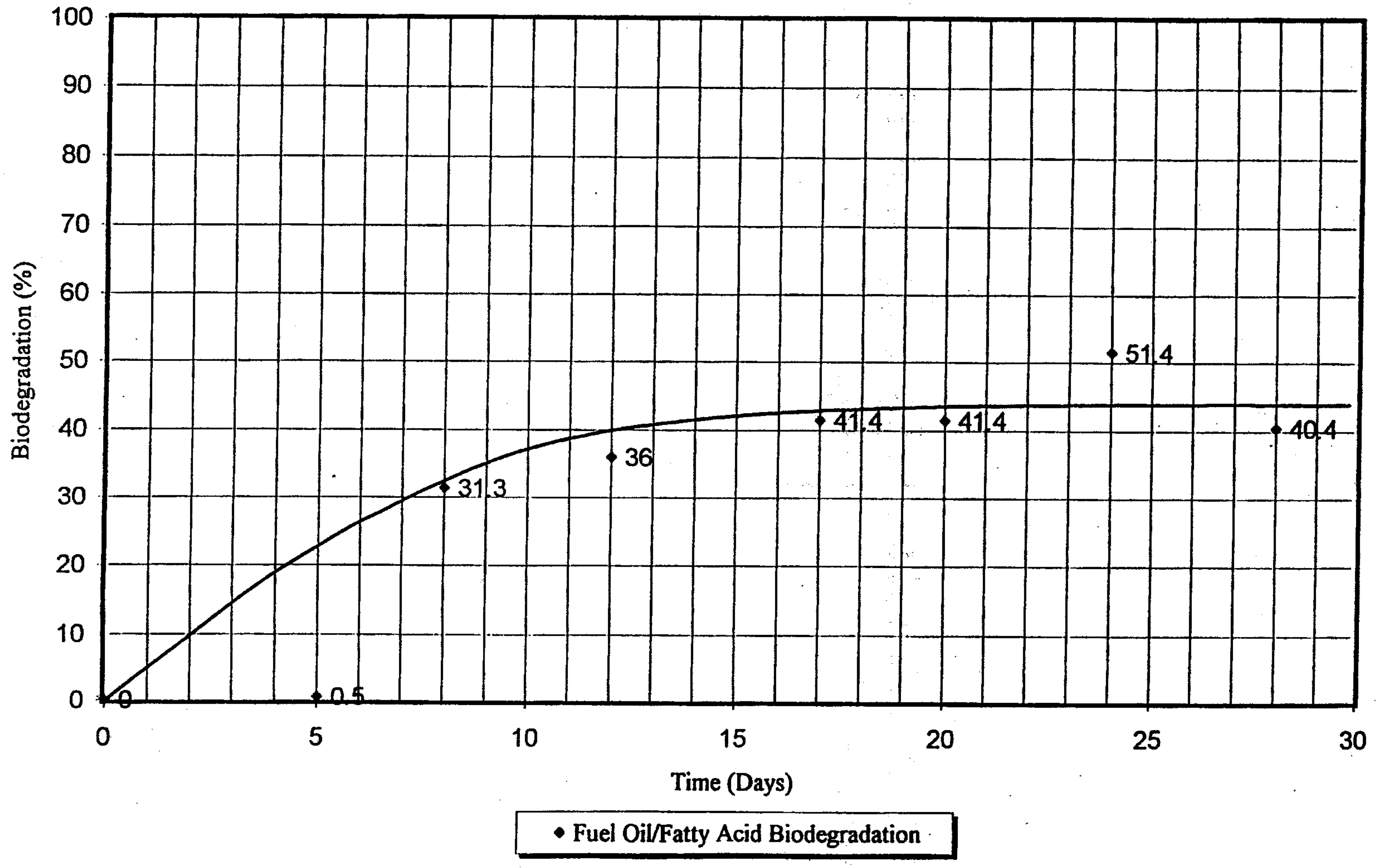

Figure 6. Fuel Oil/Fatty Acid Biodegradation.

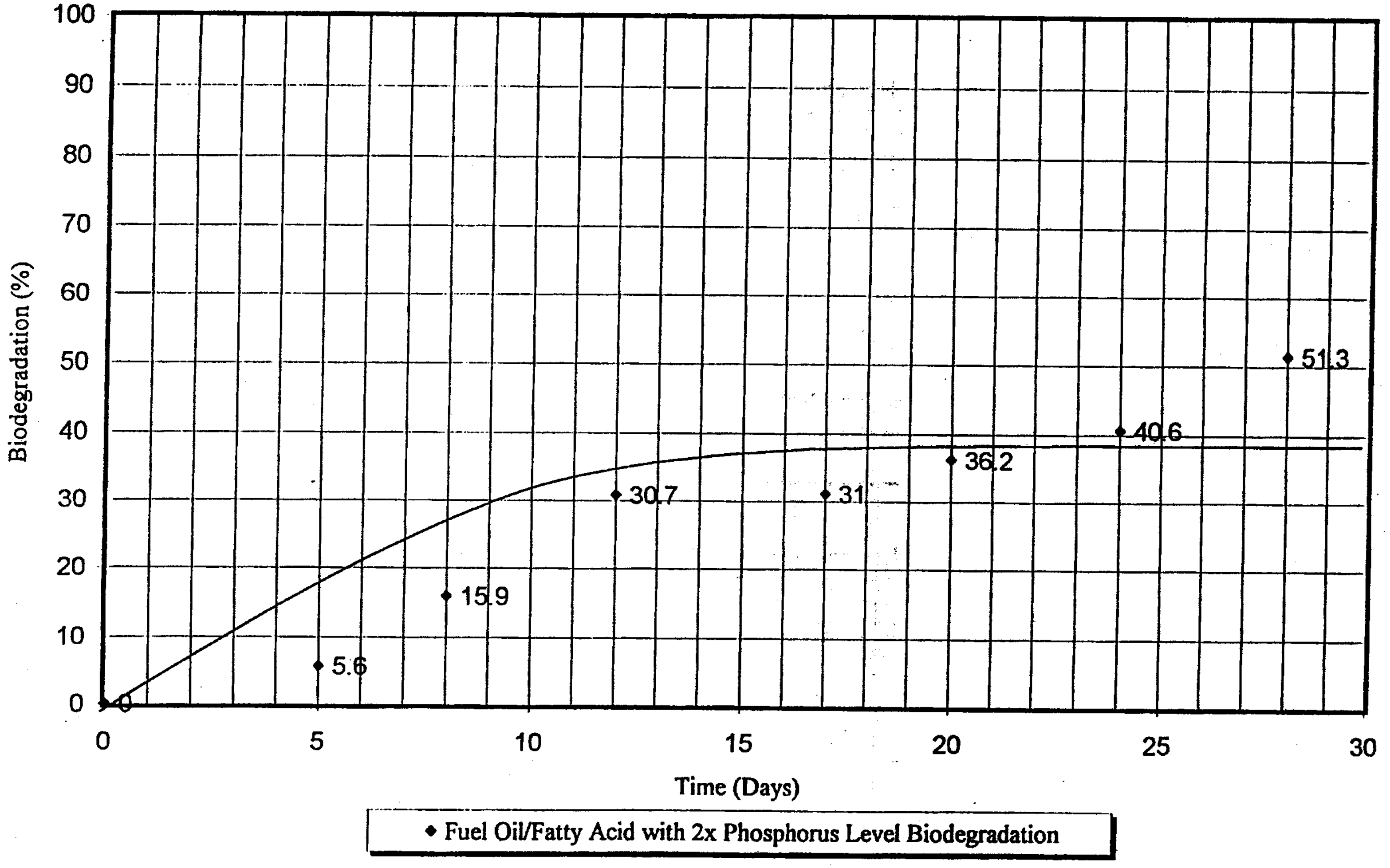

Figure 7. Fuel Oil/Fatty Acid with 2x Phosphorus Level Biodegradation.

CONCLUSIONS

Based on the results of our testing we conclude that fatty acid and amines are readily biodegradable. Fuel oil is resistant to biodegradation as compared to reagent fatty acids and amines. The degree of this difference would require additional testing to quantify.

SOIL ATTENUATION

OBJECTIVES

The movement of organic chemicals in the environment is significantly influenced by their sorption potential in a given environment. Characterization of the chemical and physical properties of the sorbate (organic chemical), the sorbent (soil/geological media) and the solvent (water) are important keys to the understanding and quantification of the sorptive behavior of an organic sorbate on a given sorbent. The chemical structure of the sorbate and sorbent are important because they dictate the mechanism of attenuation. However, it is beyond the scope of this project to identify the actual mechanisms of attenuation of the flotation reagents on the solid phases.

The aim of this study was to ascertain the fate of flotation reagents in the environment, specifically their retention, or their lack thereof, after being transported with the associated General Mill Tailings (GMT) water, more commonly referred to as Sand Tailings water, to its disposal areas (mine cuts). For purposes of this study the difference between the added reagent quantity and that found in the liquid phase was considered to be sorbed on the soil materials (sand) present in the evaluated process stream. This approach allowed the determination of the extent of partitioning of the reagents between the liquid and solid phases as a function of time.

MATERIALS AND METHODS

Mine-Cut Soil Material

Soil material was collected from active mining areas in the central Florida mining district. Two types of soil materials were collected. The first material was a sandy overburden material, which was collected from spoils adjacent to a mine cut. The second material was clay collected from the base of a mine cut. These soil materials were provided by IMC-Agrico from an active mining site at Four Corners Mine.

Flotation Reagent Sources

General Mills Tailings water was collected in five-gallon buckets directly from discharge pipes at the IMC-Agrico Four Corners beneficiation plant. Relatively clear water was decanted from each bucket and mixed to create a composite water sample for use in the study.

Lysimeter Preparation

Each lysimeter was constructed using a PVC tube as shown in Figure 8. The inside of the lysimeter was coated with teflon film. The study was conducted at BCI's laboratory facility in Lakeland, Florida.

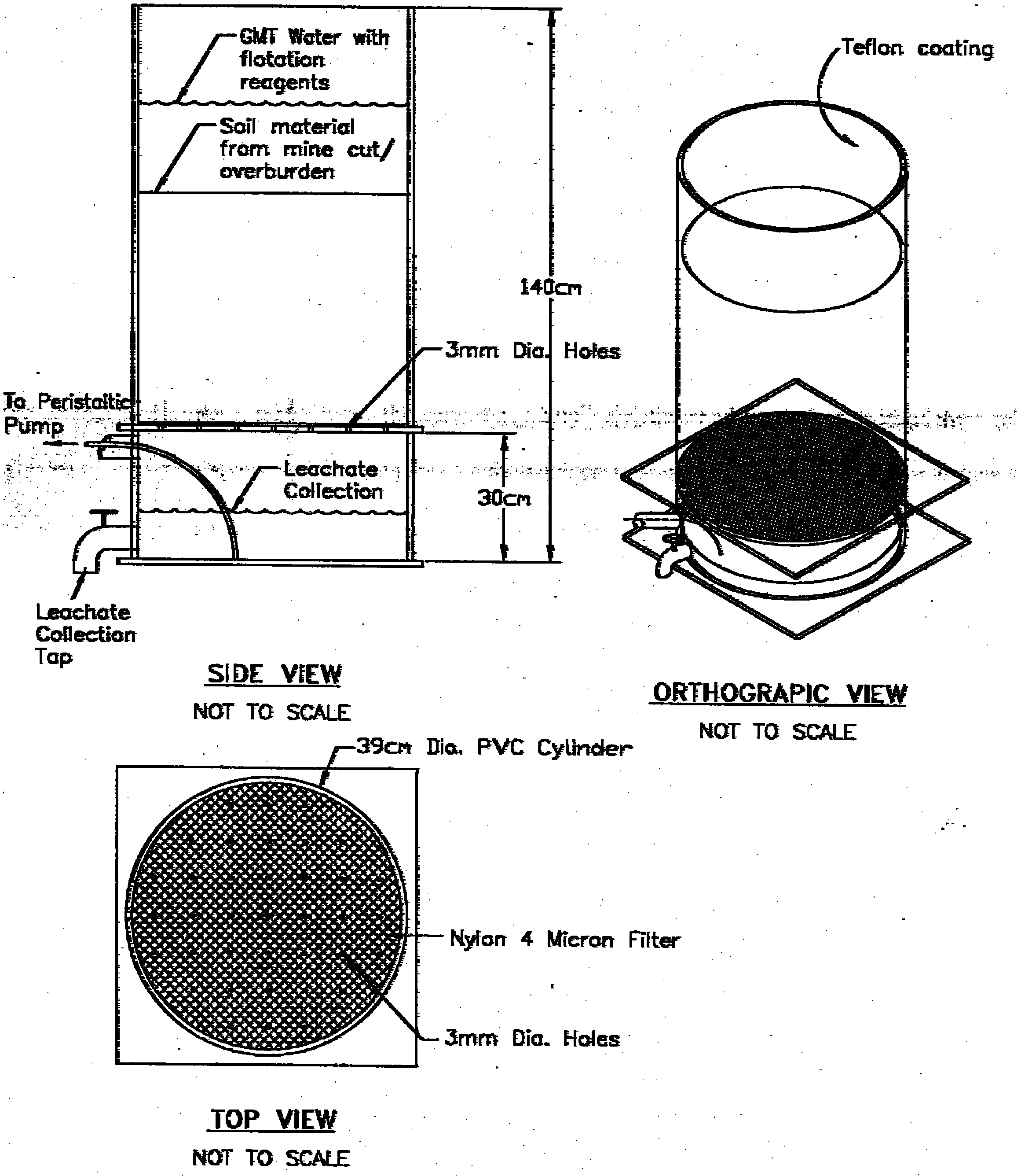

Figure 8. Lysimeter System For Extracting Leachate From Soil Material.

A series of lysimeters was set up containing the previously mentioned soil materials. The respective soil materials were compacted in separate lysimeters to approximate field conditions based on historical data for in situ density of these materials. The clay was compacted in two inch layers to a height of 10.8 inches, which is approximately 1.0 cubic foot. The moist unit weight or bulk density was determined to be 109.9 lbs per cubic foot (pcf) at 45 percent moisture. This equates to a dry unit weight of 75.8 pcf.

Similarly, the sand was compacted at three to four inch layers to a height of 32 inches, which is approximately equivalent to 3.0 cubic feet. At 21 percent moisture, the moist unit weight was determined to be 114.2 pcf. The dry unit weight was 94.4 pcf. During compaction of the sandy sample, several liters of water drained from the sample into the collection chamber of the lysimeter. The moisture content was determined to be approximately 7 percent of the original sample weight, changing the final unit weight to 106.7 pcf. The sandy overburden material was sent for the identification and quantification of reagents prior to lysimeter set up.

Three lysimeters containing clay were set up for leachate collection at three prescribed intervals; 1, 15, and 30 days. Similarly, three lysimeters containing sandy overburden were also set up for leachate collection after 24 hours and 19 days. The first two lysimeters containing overburden were leached with a composite of all flotation process water that was generated in a laboratory flotation by the FIPR technicians at their laboratory in Bartow, Florida. A four liter aliquot of this process water was added to each lysimeter. The leached water was sent for reagent analysis to ATAS. The 19 day leachate was recirculated three times through the same overburden column prior to its collection at 19 days.

The third overburden lysimeter was leached with GMT water composite collected from the pump discharge at the IMC-Agrico Four Corners Mine. The water accumulated in the collection chamber of this lysimeter during sand compaction was suctioned into appropriate containers using a peristaltic pump and sent to ATAS for reagent analysis. The tubing of the peristaltic pump was flushed using distilled water and was also collected for analysis.

A 10 liter aliquot of the composite water was added to collect a sufficient leachate volume after 24 hours (Day 1). On subsequent days, every 24 hours, five liter aliquots were added to insure ample leachate volume were generated for analyses. The water was added carefully to the surface of the sand to minimize the disturbance at the surface. This process was continued for 10 days, every 24 hours, until all the composite GMT water volume was used. The tubing used to collect leachate samples was flushed using distilled water at the beginning of each leachate sample collection. These pre-flush water samples were not analyzed except for the flush water prior to the first leachate collection, as described previously. A sample of the composite GMT water was analyzed to determine the input (original) concentrations of each of the studied flotation reagents.

It was anticipated due to the reported permeability of clay, ranging from 1×10^{-6} to 10^{-9} cm/sec, that it might be difficult to collect a sufficient quantity of leachate water from clays for analysis in the time frame of the project. Furthermore, it was assumed that if the GMT disposal liquid remained in the lysimeter for a significant time period, other processes such as biodegradation might affect the results and lead to erroneous conclusions. Because the tested sandy materials are known to have permeabilities ranging from 1 to 0.001 cm/sec, sufficient leachate was expected to support 24-hour sample collection without any difficulty.

RESULTS AND DISCUSSION

As anticipated, the clay containing lysimeter did not produce any leachate in 30 days despite absence of freestanding liquid at its surface. Clays are well known to have a high water-holding capacity and low transmissivity. After a review of these data with the FIPR Technical Advisory Committee, it was decided that no further testing would be performed using the clay soil fraction.

In contrast, the sandy overburden generated sufficient leachate for reagent analyses. As expected, the composite process water from the laboratory flotation contained all three reagents. The concentration of fatty acid was 10.9 mg/L, fuel was 18.6 mg/L, and amine was 1.6 mg/L. The 24 hour leachate analysis showed none of the reagents to be present. Similarly, for the 19 day leachate, none of the reagents were detected. Based on the anticipated dilution due to existing natural water in the lysimeter (approximately 10 liters), it was calculated that the concentrations of the reagents would be diluted to 3.1 mg/L fatty acid, 5.1 mg/L fuel oil, and 0.5 mg/L amine. The MDL for each reagent was well below these diluted concentration levels to enable their detection, if present. The lack of reagent detection in either of the leachate samples suggest that the sandy overburden has capacity to attenuate these reagents.

The sandy overburden as well as the drainage water collected during compaction in the lysimeter showed no detectable concentration of any of the reagents. Similarly, the first peristaltic pump and tubing flush water was analyzed for amine only, and as expected, none was detected. As indicated earlier, in the beneficiation flow process the amine is added in the final step to further optimize phosphate grade and mineral recovery. Thus, it was assumed the GMT water was mostly amine tail water. After further query, the GMT water was determined to be a combination of mostly rougher tail and amine tail water. This sample of composite GMT water contained 1.3 mg/L fatty acid, 3.38 mg/L of fuel oil, and no amine.

The results from analysis of the 10 leachate samples are shown in Table 1. The lab data and QA/QC results for the reagents analysis of the original sandy overburden, drainage water (due to compaction), composite GMT water and the subsequent leachate samples are provided in Appendix D.

Table 1. Reagent Concentrations in Leachates.

Leachate Number (Days)	Fatty Acid Concentration (mg/L)	Fuel Oil Concentration (mg/L)	Amine Concentration (mg/L)	Fatty Acid Soil Attenuation %
1	6.1	0.474	ND	NA
2	ND	ND	ND	100
3	ND	ND	ND	100
4	0.48	ND	ND	63
5	0.642	ND	ND	51
6	0.809	ND	ND	37
7	0.705	ND	ND	46
8	0.94	ND	ND	28
9	ND	ND	ND	NA
10	1.05	ND	ND	20

ND = Not Detected
NA = Not Analyzed

The amine test results are consistent in that none was detected in the composite GMT water or in the collected leachates. This finding is not surprising since the surface of sand is negatively charged and therefore, the cationic amine would bind to the sand surface. The GMT sands appear to provide ample sorption sites for the amines, thus there is no amine detection in the GMT water.

The first overburden leachate sample contained 0.474 mg/L of fuel oil. As indicated, the composite GMT water sample contained 3.38 mg/L. However, none of the subsequent leachates contained a detectable concentration of fuel oil. No conclusive statements can be made regarding fuel oil observations in the first leachate sample. In addition, the first leachate showed a relatively high concentration of fatty acids whereas leachate nine contained no fatty acid. These findings can not be verified due to the lack of ample leachate samples for reanalysis, but are very unlikely results and therefore, were regarded as outlier data points.

Ignoring leaches one and nine, the remaining data show an expected trend of increasing fatty acid concentrations in the leachate over time (Figure 9). The leachate concentration should be low or non-detectable initially since most of the fatty acids, if not all, are expected to be adsorbed on the soil. This is noted because the sand was determined to contain <0.5 percent organic matter and although none of the other overburden constituents were determined, only a small fraction is expected in this dominantly sandy material. Nonetheless, these soil constituents appear to have sufficient adsorption capacity to attenuate the trace fuel oil and initially, the fatty acid.

In reality, the mass balance (reagent volume versus soil volume) is heavily weighted in favor of the sandy material. For this reason a low organic assay is consistent with a conclusion that the available adsorption opportunities far exceed that needed to tie up all the fatty acid residuals. More sandy material arrives (more adsorption surfaces) with each volume of GMT water. For these reasons no lack of adsorptive opportunities exists and this may explain why no fatty acid or amines are free in the surrounding aquifer systems.

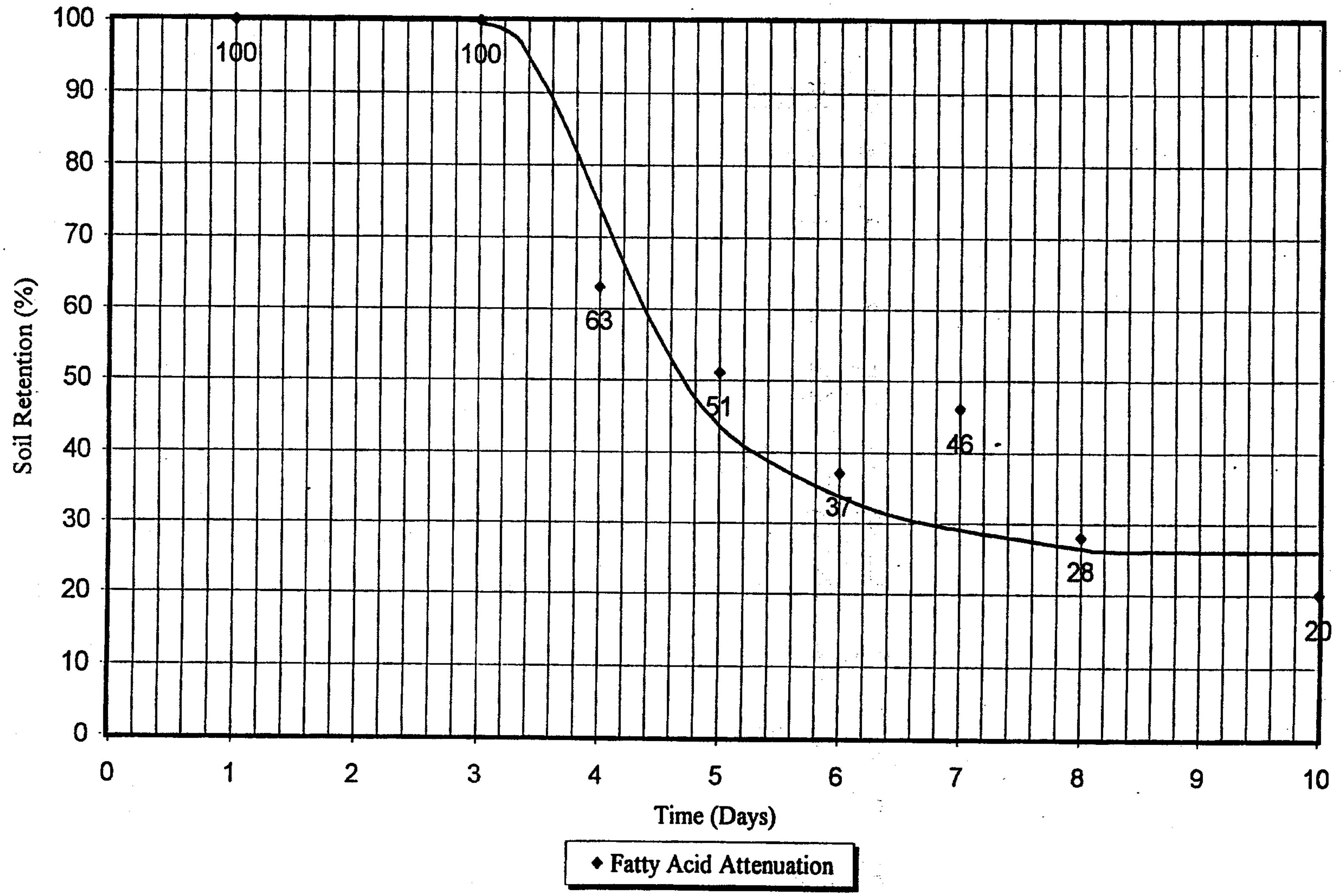

Figure 9. Fuel Oil/Fatty Acid Attenuation in Sandy Overburden.

LABORATORY FLOTATION MASS BALANCE

OBJECTIVES

A laboratory flotation was conducted by BCI and FIPR staff at the FIPR lab in Bartow, Florida. The objective of this laboratory test was to establish a mass-balance of reagents within the flotation process and generate a better understanding on the distribution of reagent in the various associated process fractions.

MATERIALS AND METHODS

This section describes the procedure used to perform the lab flotation and the various samples collected for testing. Figure 10 provides a schematic of the actual procedure used during this testing including the various collection points used during the final flotation test-run to obtain samples for qualitative and quantitative assay of the reagents present in each process stream.

All apparatus was scrubbed and washed with tap water prior to the flotation run. All testing reagents and the coarse rougher feed were obtained from the IMC-Agrico Four Corners facility to maintain consistency between the field mass-balance study discussed in the next section and the laboratory testing described below.

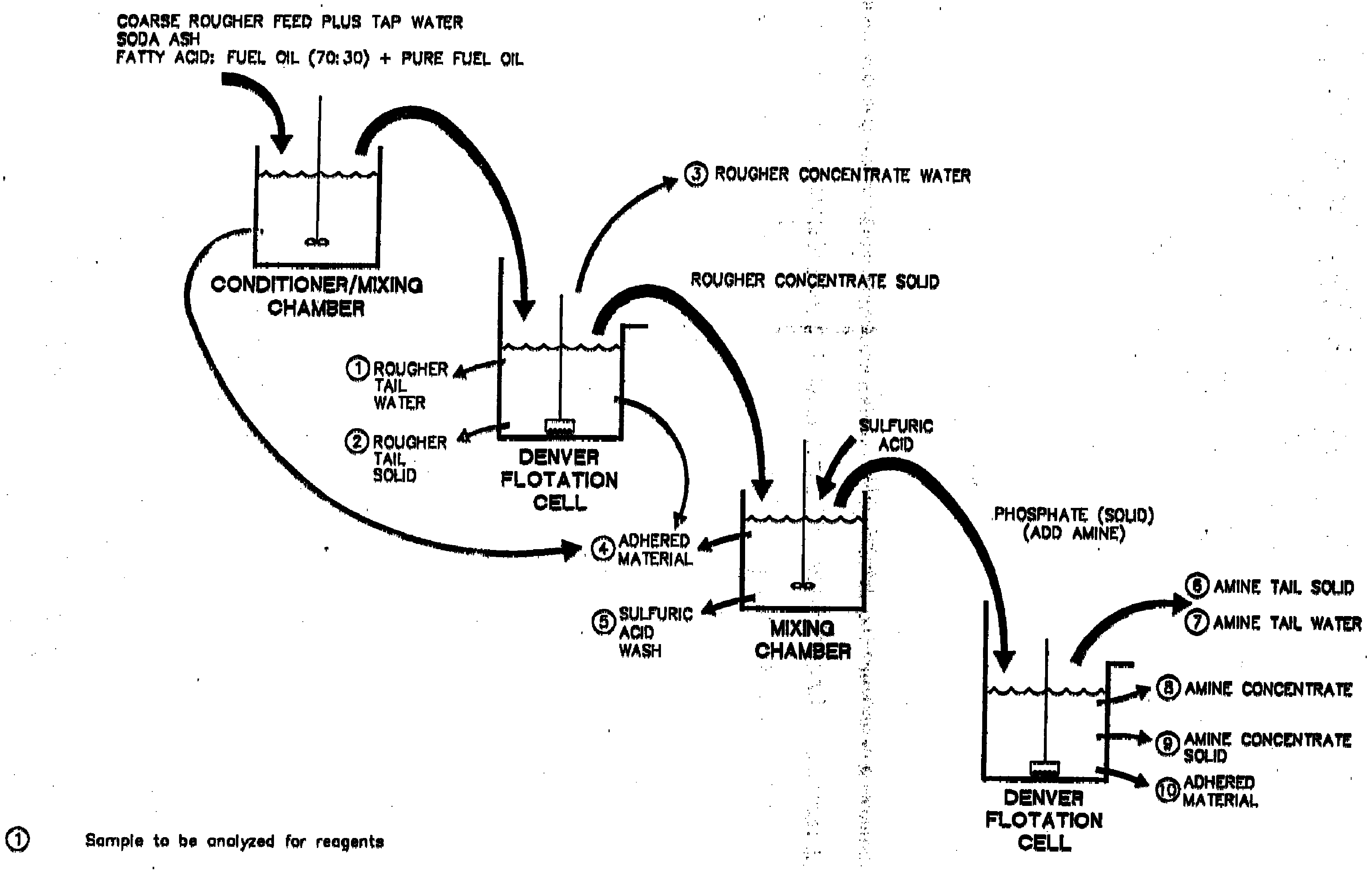

Figure 10. Lab Flotation Flow Diagram.

Standard Crago Flotation process used by the industry was followed. Due to the substantial quantity of liquid samples needed to identify and quantify the reagents, and because of the limitations of the equipment available to produce the required liquid volumes, six flotation tests using 500 grams of feed on a dry basis were individually floated. A 70:30 mixture of fatty acid:fuel oil and a five percent amine solution from the IMC-Agrico Four Corners plant were used in the flotation. It should be noted here, the 70:30 mixture of fatty acid: fuel oil and five percent amine solution are as indicated later in this section, very different in concentration. These mentioned concentrations were only a general concentration level indicated by the beneficiation process personnel at IMC-Agrico Four Corners Plant and will be used in the text for consistency. Extra fuel oil was used to create a mixture of close to 60:40 fatty acid:fuel oil to make the fluid blend and to control foaming during the flotation process.

A moist rougher feed was added to a conditioning cell along with tap water to create a slurry of 70 percent solids. Soda ash was also added and the contents were thoroughly mixed using an electric stirrer at a speed of approximately 374 rpm. The pH of the conditioned slurry was between 9.0 and 9.2. The 70:30 mixture of fatty acid:fuel oil was added at 0.322g per run. In addition, 0.038g of pure fuel oil was added for a contact period of 90 seconds. Both the 70:30 mixture and the pure fuel oil were added as drops and their weight determined by the average weight per drop. After final conditioning the slurry was transferred to a stainless steel Denver flotation cell and floated at 1200 rpm until the recoverable phosphate rich material (rougher concentrate) was collected. The experience of FIPR staff was relied on as the decision basis for terminating the individual flotation runs.

The excess water was decanted from the rougher concentrate. The remaining sand and associated water in the flotation cell, the rougher tail fraction, was collected separately for later analysis of its solid and liquid phases. Once this step was complete, the conditioning chamber, stirrer and flotation cell units were wiped using kemwipes and lab water. These fractions were also retained for later analysis.

The rougher concentrate was acidified using 10 percent sulfuric acid solution at a pH of about 3.2 and subsequently washed with tap water until its nominal pH was neutral. The acid wash liquid was decanted and retained for analysis as well.

The rougher concentrate generated using the above described procedures was then transferred back into a clean Denver flotation cell. Successive aliquots (7.6g, 5.5g and 6.5g) of five percent of amine were added up to a total of 19.6g. Again, the amine was added as drops and their weight determined as indicated. The reason for adding the three aliquots of amine is that the first two aliquots did not result in acceptable sand removal. The floated sand, also known as amine tails, along with its associated water were also collected for analysis.

The resulting concentrated phosphate solids, or amine concentrate, and its associated water component were collected for analysis as well. Finally, the flotation cell units and all containers were wiped using kemwipes and tap water and composited for later analysis. Figure 11 shows the lab flotation block diagram and indicates the points in processing at which solid and water samples were collected.

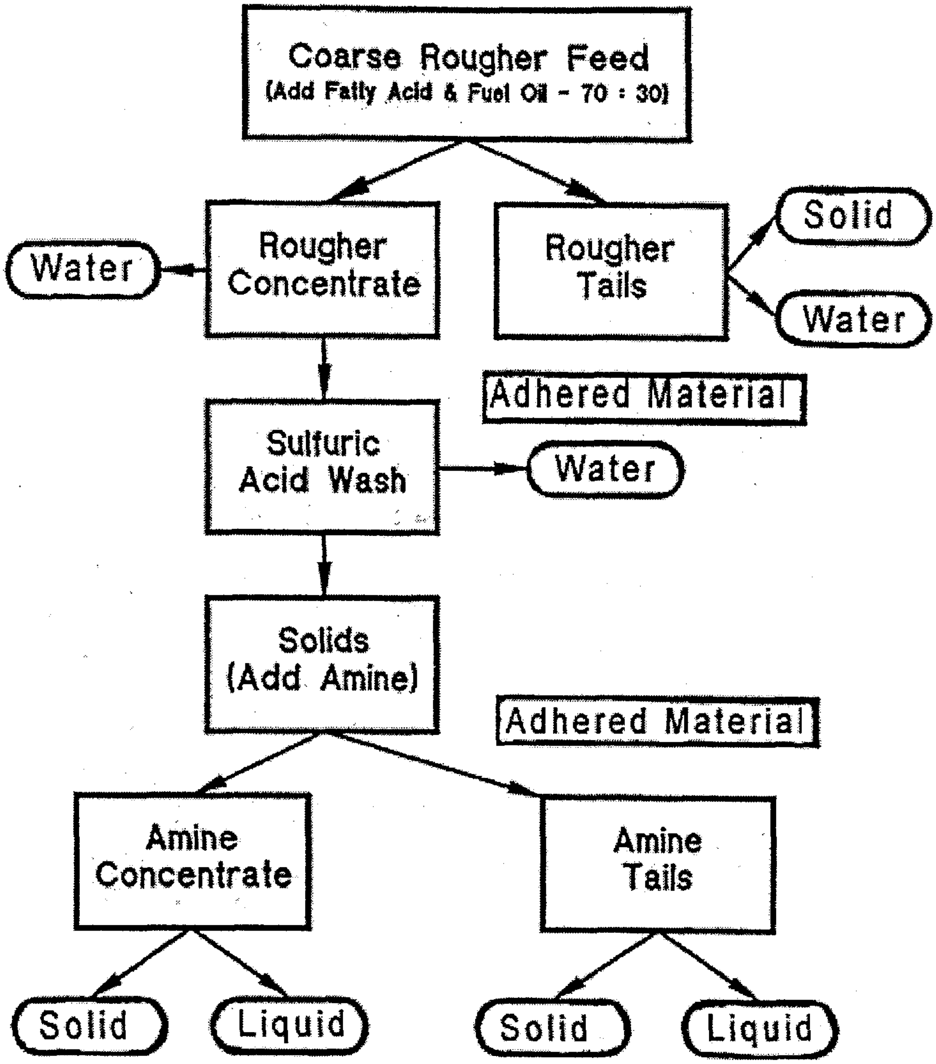

Figure 11. Lab Flotation Block Diagram.

All liquid samples obtained from each of the six flotation runs were weighed prior to decanting into separate five-gallon PVC buckets. The buckets were then weighed to independently verify the weight of individual collected samples.

The following samples were collected and sent to ATAS for analytical quantification of flotation reagents:

1. Coarse rougher feed (solid)
2. Rougher concentrate (liquid)
3. Rougher tails (solid and liquid)
4. Adhered material (kemwipes/water composite)
5. Acid wash (liquid)
6. Amine concentrate (solid and liquid)
7. Amine tails (solid and liquid)
8. Adhered material (kemwipes/water composite)

RESULTS AND DISCUSSION

The quantity of both solid and liquid samples collected during laboratory flotation testing is included in Appendix E. The analytical results from ATAS are provided in Appendix F. A summary of the analytical data and their correction is shown in Table 2.

Table 2. Lab Flotation Reagents Analytical and Corrected Data.

Sample	Fatty Acid		Fuel Oil		Amine	
	Analytical Results mg/L or mg/kg	Corrected Mass mg	Analytical Results mg/L or mg/kg	Corrected Mass mg	Analytical Results mg/L or mg/kg	Corrected Mass mg
Coarse Rougher Feed	2.93	2.93	ND	NC	ND	NC
Rougher Concentrate Water	ND	NC	12.1	12.1	1.10	4.53
Rougher Tails Solid	16.5	34.7	23.5	49.4	2.70	5.68
Rougher Tails Water	ND	NC	8.84	12.7	0.34	4.88
Sulfuric Acid Wash	28.5	24.4	102	87.2	4.30	36.8
Adhered Material 1	6.51	6.51	12.1	12.1	1.0	1.0
Amine Concentrate Solid	5.33	4.74	20.6	18.3	3.00	2.67
Amine Concentrate Water	ND	NC	3.69	2.97	0.360	2.89
Amine Tails Solid	19.3	12.6	249	162	8.20	5.35
Amine Tails Water	ND	NC	5.10	13.9	0.570	1.33
Adhered Material 2	ND	NC	1.49	1.49	ND	NC

ND = Not Detected
NC=Not Corrected

Based on ATAS's initial analytical results, the recoveries of the three assessed reagents were as follows:

- Fatty acid recovery = 22%
- Fuel oil recovery = 165%
- Amine recovery = 11%

It was evident that these recoveries were unacceptable and further investigation was needed. It was known that the concentration of the five percent amine solution provided by IMC-Agrico was only estimated. For this reason, an amine sample of the reagent material used in the lab flotation test was sent to ATAS for analysis. In addition, the fatty acid:fuel oil (70:30) mixture was also sent for analysis.

Upon analysis, the five percent amine solution was revealed to contain only 780 mg/L amine or 0.078% (Appendix F). This value was substantially lower than expected. Similarly, the fatty acid:fuel oil (70:30) mixture contained 876,000 mg fatty acid/Kg and 838,000 mg fuel oil/L, a ratio closer to 50:50. These concentration differences are attributed to variances in reagent preparation. Recalculated recoveries adjusted for the above discrepancies were as follows:

- Fatty acid recovery = 31%
- Fuel oil recovery = 113%
- Amine recovery = 425%

As would be expected, the recoveries of both the fatty acid and fuel oil improved, but that of fatty acid was still low. On the other hand, the amine recovery increased, but was unacceptable.

It is well known that for economic reasons the phosphate industry does not normally use pure product reagent materials. Instead they utilize mixtures of various commercially available complex compounds of variable chemical character. Furthermore, the selected reagents are frequently changed based on current availability and fluctuating cost. Based on this additional information, we requested ATAS to reanalyze the original fatty acid:fuel oil mixture and the five percent amine solution as "standards" to compare the rest of the lab flotation samples against. This approach would allow for a direct comparison of all fatty acid and amine concentrations in the various process streams with the respective standards. In other words, the peaks identified in the calibration on the standards would be used for calculating the concentration of fatty acids and amines in all process samples produced in the laboratory flotation. This effort, however, did not significantly improve the mass-balance.

A couple of unexpected observations, however, were made regarding the distribution of the flotation reagents in the various process streams. Fatty acids were detected in the coarse rougher feed. As indicated earlier, it was determined that some of the water from the flotation process is actually recirculated and appears to be the likely reason for the presence of fatty acid in the feed material. Amine were detected in all the rougher concentrate and rougher tail samples including the acid wash sample which contained a significant quantity. The cause of the amine detection is unknown, since amines are only added after acid washing in the second flotation to further upgrade the rougher concentrate. Despite rinsing with acid (acid wash), which appeared to remove a large portion of the fatty acid and fuel oil, there was still a considerable concentration of both reagents in the solid portion of the amine concentrate and amine tail samples.

FIELD FLOTATION MASS BALANCE

OBJECTIVES

The goal of this portion of the project was to accurately characterize the ultimate distribution and redistribution of flotation reagents utilized at IMC-Agrico Four Corners Beneficiation Plant. Float plant specific objectives relevant to this determination were:

- Identification of appropriate sampling locations for the specific flotation reagents.
- Accurate measurement of the concentration of flotation reagents at selected locations within the plant to support a mass balance determination based on IMC-Agrico's mass balance formula.

MATERIALS AND METHODS

Sampling locations were selected to measure flotation reagent concentrations within an existing flotation plant (Figure 12). The primary sample point selection criteria were the points in the plant where reagents would enter and exit the process. IMC-Agrico staff were relied on for insight in these regards. Following collection, the plant samples were immediately transported to the analytical laboratory (ATAS) for analysis. The results generated during this test were utilized to calculate a mass balance based on IMC-Agrico's formula and computer program.

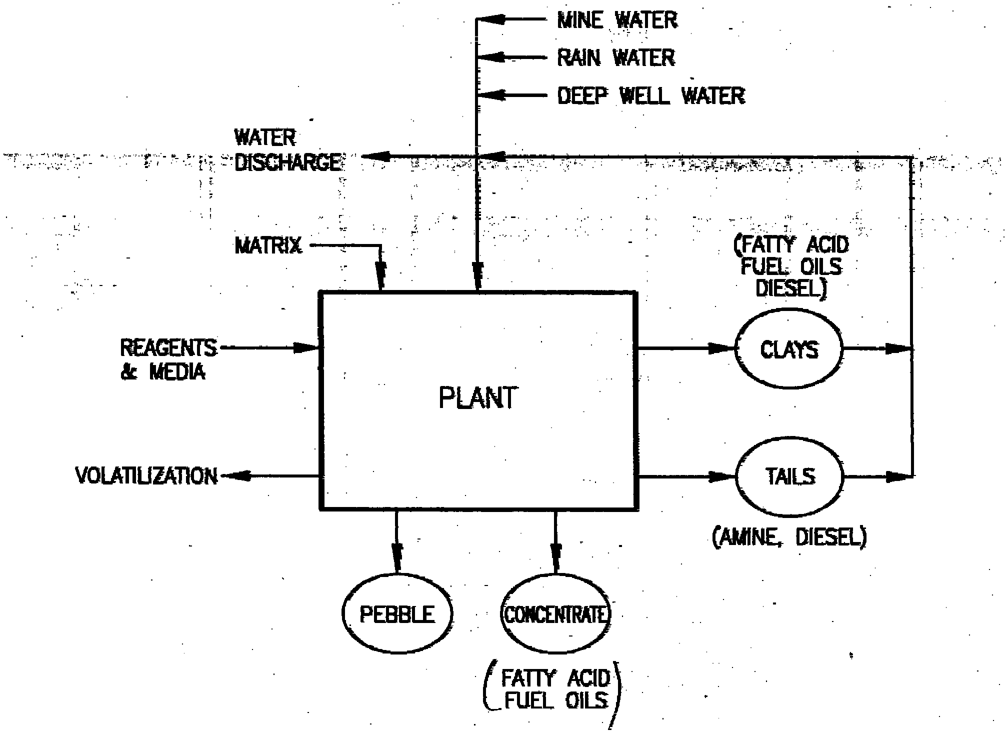

Figure 12. General Plant Reagent Block Flow Diagram.

Field Sampling

A thorough understanding of the operation of each flotation plant is critical to the selection of appropriate sampling locations because flotation plant designs vary from one company to another. Also, as is the case at most facilities, many modifications of original designs have been implemented throughout the years. The basic operation involves processing the feed in a “rougher” float to upgrade the phosphate content and then cleaning it in an “amine” float to meet final product requirements. There are variations from the above procedures including pre-flotation sizing, bulk unsized feed flotation, scalping, and spirals. The pre-flotation sizing is for size segregated float feeds. Scalping is from the “almost pebble” fraction which bypasses flotation and is a non-salable product for internal company use due to its low grade. The flotation circuit specific to IMC-Agrico Four Corners mine is shown in Figure 13.

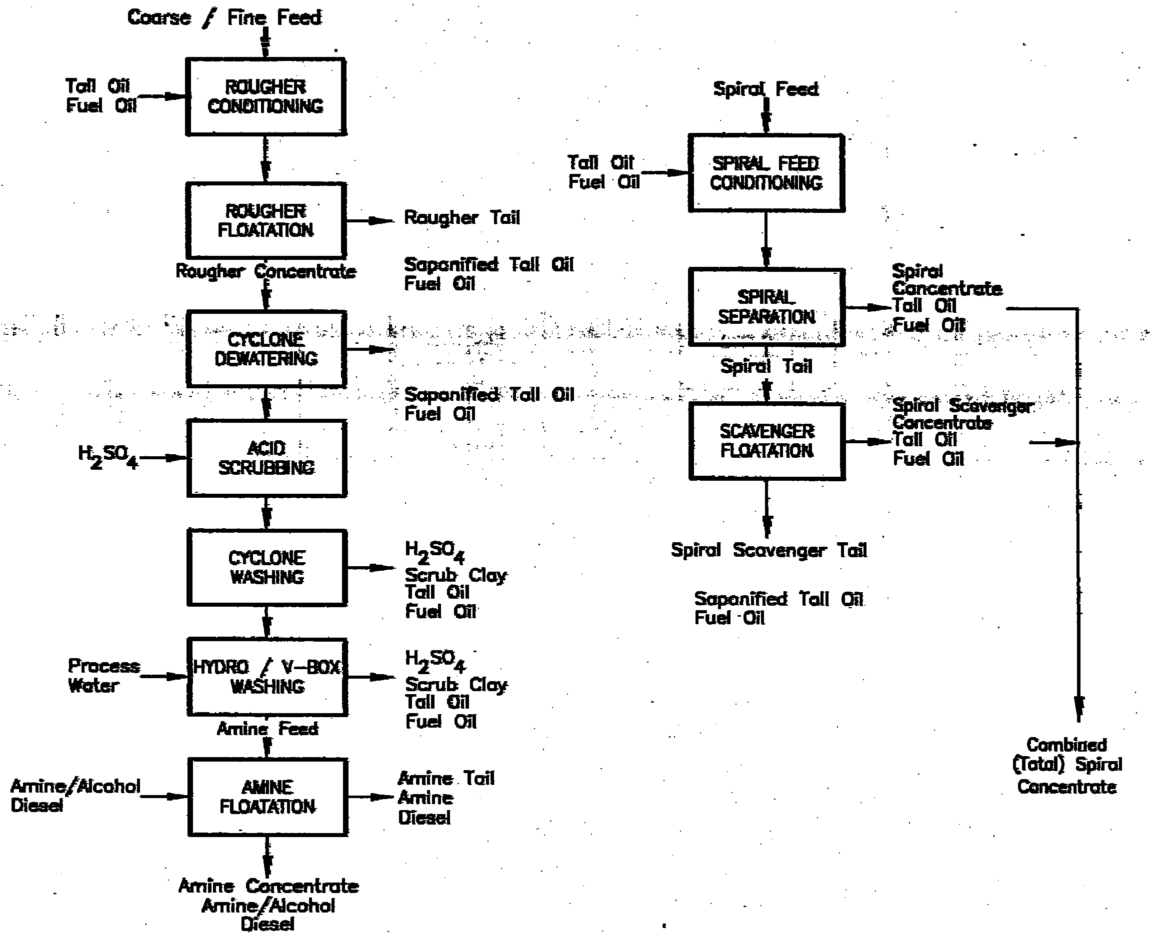

Figure 13. Four Corners Flotation Circuit Flow Diagrams.

Sampling for the reagents included 12 locations:

1. North Primary Clays
2. South Primary Clays
3. Secondary Clays
4. Launder Overflow (MCK Falls)
5. Acid Wash Water
6. Amine Concentrate
7. Spiral Concentrate
8. Scalp/IP
9. General Mill Tailings (GMT)
10. Pebble
11. Matrix Flow From Mine
12. Plant Return Water

GENERAL INFORMATION AND PROCESS DISCUSSION

An initial approach for the determination of a field mass balance utilized a general non-specific analytical procedure (Total Organic Carbon, TOC). Due to the non-specificity and other interfering background carbon sources, specific reagent analytical procedures were necessary.

Conventional froth spirals, belts, and column flotation machines are all variations on the same process but differ in mechanical application. The general process involves an organic acid or fatty acid, which becomes saponified by the addition of ammonia or caustic and then reacts with the phosphate/silica feed. The RCOO ion will form a bond with the open calcium sites on the surface of the phosphate mineral, but does not react with the silica surface. The ionic head attached to the surface of the phosphate with the long chain hydrocarbon extending out from the surface creates what is called a hydrophobic surface. This non-polar hydrocarbon repels water molecules. This reagentized surface is further treated by application of fuel oil to extend the hydrocarbon tails. The oils also serve as a froth reduction agent. This reagentized slurry is then diluted and put into agitated cells where air bubbles are introduced. The hydrophobic phosphate particles are attracted to air, agitated, and after attachment to the bubbles, rise to the top of the float cell. The froth of phosphate is removed by rotating paddles.

The rougher flotation process is not completely effective. If good recovery is required, fair quantity of silica that reports to the froth product (rougher concentrate) need to be separated. In order to produce a salable product a second flotation process is conducted to remove the residual silica. In this float a different reagent is introduced, an amine based compound, and silica is floated away from the phosphate. Before this process can be accomplished, the feed is prepared from amine flotation by passing through an acid scrubber to remove the fatty acid coatings on the phosphate. Additionally, a counter-current rinse is used to separate the non reagentized rougher concentrate solids from the oily water. The concentrate from the amine flotation process is the final salable product.

RESULTS AND DISCUSSION

Table 3 shows the raw analytical values at the time of sample collection. The quality control information on the analytical procedures can be reviewed in Appendix G.

Table 3. Raw Analytical Concentrations of Reagents in Various Streams.

No.	Stream	Fuel Oil Concentration	Amine Concentration	Fatty Acid Concentration
1	N Primary Clays	40.40	< 17.0	12.9
2	S Primary Clays	54.80	< 17.0	29.6
3	Secondary Clays	3.51	< 0.50	< 1.92
4	Launder Overflow	2.75	0.31	< 1.32
5	Acid Wash Water	1.60	0.22	< 1.25
6	Amine Concentrate	< 3.00	2.2	20.5
7	Spiral Concentrate	210	19	327
8	Scalp/IP	< 3.00	< 17.0	< 1.0
9	GMT (Avg. North/South)	27.6	0.62	7.61
10	Pebble	< 3.00	< 17.0	< 1.0
11	Matrix Flow From Mine	1.26	< 0.50	< 2.86
12	Plant Return Water	0.622	< 0.50	< 1.11

Concentrations are in mg/L or mg/kg depending on the matrix part only

Tables 4-6 are the results from the IMC-Agrico mass balance program. The first column is the sampling location. There are the 12 previously referenced locations and the three reagents. Column two is the original analytical results obtained from ATAS analytical laboratories. The mass balance program does not allow for "less than values" to be inputted, therefore, the detection limit value was imputed for calculation extrapolation. Column three is the adjusted value up or down depending on the fit into the program. The reagent being balanced is inputted as 100 percent as parts per million. The last column is the percent recovery of the reagent at the specific sampling point. The values are greater than 100 percent because some of the reagents are recirculated in the plant return water and the matrix from the mine.

Table 4. Amine Mass Balance Data.

No.	Stream	Original Concentration	Adjusted Concentration	Percent Recovery
1	N Primary Clays	0.50	0.90	33.75
2	S Primary Clays	0.50	0.91	35.54
3	Secondary Clays	0.50	0.83	26.35
4	Launder Overflow	0.31	0.40	8.89
5	Acid Wash Water	0.22	0.25	4.23
6	Amine Concentrate	2.20	2.40	2.32
7	Spiral Concentrate	19.00	27.09	14.32
8	Scalp/IP	1.00	1.01	0.27
9	GMT	0.60	0.85	13.93
10	Pebble	1.00	1.06	1.38
11	Matrix Flow From Mine	0.50	0.13	4.54
12	Plant Return Water	0.50	0.28	36.44
13	Fatty Acid Reagent	0.00	0.00	0.00
14	Fuel Oil Reagent	0.00	0.00	0.00
15	Amine Reagent	1000000.00	999999.94	100.00

Concentrations are in mg/L or mg/kg depending on the matrix part only.

Evaluation of the amine mass balance indicate a large percentage in the clays. Clays are a large volume of the material in the beneficiation process and the reagents then to adhere to the clays. The analysis for which the mass balance was calculated indicated that the amine concentrate sample has a lower percentage of amine than the spiral concentrate. These values appeared to be reversed. Additional samples were collected and analyzed and the results were comparable to the original concentrations. A possible explanation for this apparent discrepancy may be the location of the spiral concentrate tank. A portion of the amine tail launders is located directly over the total spiral concentrate tank. In addition, the majority of any spillage from the amine tank launder could last for a long time because the entire feed bin would be affected. The lower than expected amine concentration from the amine concentrate product might explain as follows. The amine concentrate from the amine cells has a high percent solids (50-60%). Additional make-up water is added to the sump to reduce the percent solids to 30 percent for pumping purposes. The amine concentrate solids should not have much amine attachment and the additional make-up water is relatively amine-free. The primary amount of amine in the water originally in the float cells goes with the amine tails. The GMT samples have a substantial value for amines. The amine tails are combined into the GMT explaining for the high value in the tailings sample.

Table 5. Fuel Oil Mass Balance Data.

No.	Stream	Original Concentration	Adjusted Concentration	Percent Recovery
1	N Primary Clays	40.40	22.72	38.95
2	S Primary Clays	54.80	21.09	37.48
3	Secondary Clays	3.51	3.40	4.89
4	Launder Overflow	2.75	2.70	2.74
5	Acid Wash Water	1.60	1.59	1.20
6	Amine Concentrate	3.00	3.00	0.13
7	Spiral Concentrate	210.00	203.28	4.90
8	Scalp/IP	3.00	3.00	0.04
9	GMT	23.00	20.50	15.32
10	Pebble	3.00	3.00	0.18
11	Matrix Flow From Mine	1.26	1.28	2.03
12	Plant Return Water	0.62	0.63	3.81
13	Fatty Acid Reagent	0.00	0.00	0.00
14	Fuel Oil Reagent	1000000.00	1000000.00	100.00
15	Amine Reagent	0.00	0.00	0.00

Concentrations are in mg/L or mg/kg depending on the matrix part only

Evaluation of the fuel oil mass balance indicated again in a large percentage in the clays. Clays have a large capacity to absorb reagents because of the large surface area and the mass balance verifies this fact. The spiral concentrates is the material going to the acid plant for further processing and not being disposed into the environment directly. It was expected that there should be more fuel oil in the acid wash sample. This expectation is from a process point of view. The acidified rougher concentrates, directly from the acid scrubbers, is first pumped to the cyclones located above the acid wash boxes. These cyclones produce an overflow of approximately 65 percent solids and an overflow that goes directly to the secondary slimes launder. The purpose of cyclones is to remove as much of the lower pH water and oil and fatty acid scum as possible so that the minimum of process water is required in the wash boxes to bring the pH of the slurry back to neutral. As a result, the majority of acid and dissolved oil and fatty acid is directed to the secondary slimes. The overflow from the acid wash boxes is discharged from the plant directly as acid wash water and this is the sampling location for the sample designed "acid wash water".

Table 6. Fatty Acid Mass Balance Data.

No.	Stream	Original Concentration	Adjusted Concentration	Percent Recovery
1	N Primary Clays	12.90	14.60	24.68
2	S Primary Clays	29.60	38.85	68.08
3	Secondary Clays	1.92	1.95	2.77
4	Launder Overflow	1.32	1.33	1.33
5	Acid Wash Water	1.25	1.26	0.94
6	Amine Concentrate	20.50	20.61	0.90
7	Spiral Concentrate	327.00	342.32	8.14
8	Scalp/IP	1.00	1.00	0.01
9	GMT	5.00	5.11	3.77
10	Pebble	1.00	1.00	0.06
11	Matrix Flow From Mine	2.86	2.78	4.37
12	Plant Return Water	1.11	1.07	6.31
13	Fatty Acid Reagent	1000000.00	1000000.00	100.00
14	Fuel Oil Reagent	0.00	0.00	0.00
15	Amine Reagent	0.00	0.00	0.00

Concentrations are in mg/L or mg/kg depending on the matrix part only

Evaluation of the fatty acid mass balance is very similar to the fuel oil. A large percentage was found in the clays. Additionally, higher concentrations were expected in the acid wash sample. The above description explaining the sampling location may indicate the reason for the perceived lower values of fatty acid reagent in the "acid wash water" sample.

Table 7. Estimated Reagent Distribution.

Location	Fatty Acids	Fuel Oil	Amines
Clay	65-85%	65-75%	60-80%
Sand tailings	5-10%	10-20%	15-20%
Product	10-15%	5-10%	15-20%

Table 7 is an estimation of reagent distribution based on the results of the field mass balance. The majority of reagents are distributed to the clays. A smaller percentage are distributed to the product and the sand tailings area.

ENVIRONMENTAL EVALUATION

OBJECTIVES

The goal of this portion of the project was to evaluate the potential for shallow ground water system impacts based on the release of flotation reagents. For this reason, a limited ground water assessment that focused on identifying reagent constituents in the surficial and intermediate aquifers was performed at mining operations in North and Central Florida. The following primary tasks were included in this assessment:

- Standard penetration test (SPT) and rotary wash borings were completed to characterize local hydrogeologic conditions at the assessed operations.
- Monitoring wells were installed in areas having appreciable flotation reagent release potential, including clay settling impoundments and sand tailings disposal sites. Both shallow and deep monitor wells were installed to allow for sampling of the surficial and intermediate aquifers, respectively.
- Ground water samples were collected and analyzed for the presence of residual flotation reagents.

Monitoring wells were installed at three phosphate mine sites in the North Florida and Central Florida Phosphate Districts. Individual borehole and monitoring well locations were specified for purposes of 1) determining unaffected or background water quality in the surficial and intermediate aquifers; 2) providing the ground water samples required to analyze for the presence of reagent contamination; and 3) providing the hydrogeologic data necessary to assess the horizontal and vertical migration potential of reagent constituents in the tested locations.

MATERIALS AND METHODS – NORTH FLORIDA PHOSPHATE DISTRICT

SPT Borings

Seven standard penetration test (SPT) borings were made at selected locations at the PCS Phosphate Swift Creek Mine near White Springs, Florida for purposes of characterizing the subsurface geology and to assist in the selection of suitable surficial and intermediate aquifer ground water monitoring wells locations (Figure 14).

The SPT borings were completed in general accordance with ASTM Standard D-1586. Soil samples were collected from the borings using a 1.4 inch I.D. split spoon sampler driven with a 140-pound slide hammer falling a distance of 30 inches. Each boring was sampled continuously over the first 10 feet and at five foot intervals thereafter. Borings B-2 through B-8 were completed to depths ranging from 41 to 81 feet. All the borings were logged in the field by a BCI geologist. Soil samples were classified according to the United Soil Classification System. Core logs for the North Florida Phosphate District borings are provided in Appendix H.

Monitor Wells

Seven separate surficial and intermediate aquifer monitoring wells were installed in pairs in order to obtain ground water samples for reagent analysis. One shallow well and one intermediate aquifer well was installed in the vicinity of each soil boring location. Monitoring well locations at the Swift Creek Mine are shown in Figure 14.

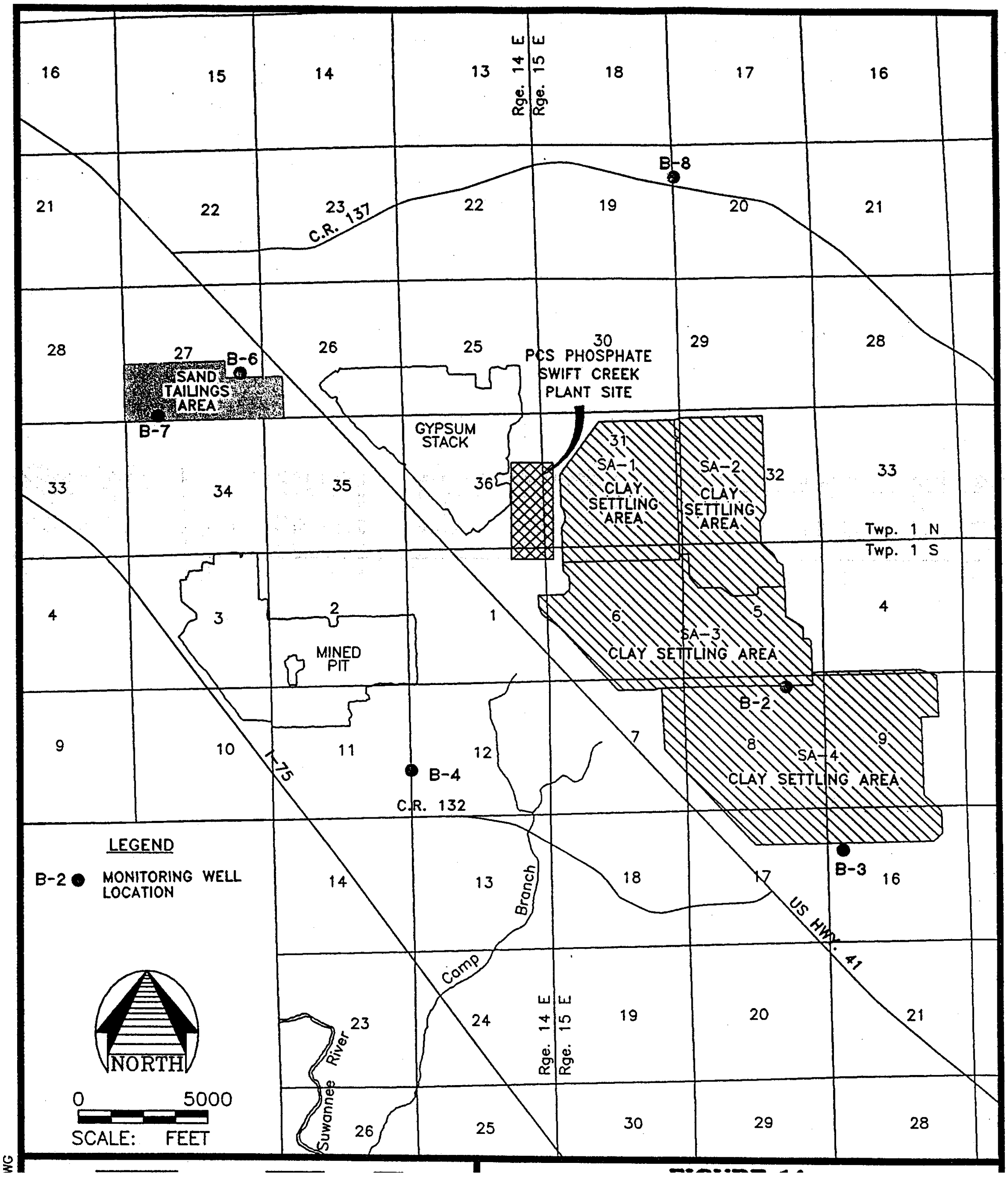

Figure 14. Site Location Map PCS Phosphate Monitoring Wells, Hamilton County, Florida.

CENTRAL FLORIDA PHOSPHATE DISTRICT

SPT Borings

Thirteen SPT borings were completed at various locations in southern Polk, eastern Hillsborough, and northern Manatee counties at the Cargill Ft. Meade Mine and the IMC-Agrico Four Corners Mine. In most cases these borings were sampled continuously over the first 10 feet and the five-foot intervals thereafter until hard, consolidated materials were encountered. At that point, wash cuttings were collected at five to 10 foot intervals to the bottom of the borehole. Boring logs for the Central Florida Phosphate District locations are included in Appendices I and J.

Monitor Wells

Surficial and intermediate aquifer monitoring wells were installed in pairs at each of the SPT boring locations shown in Figures 15 and 16. The intermediate aquifer wells at the IMCA-7I and IMCA-10I locations are an exception. They were installed adjacent to existing surficial aquifer monitoring wells.

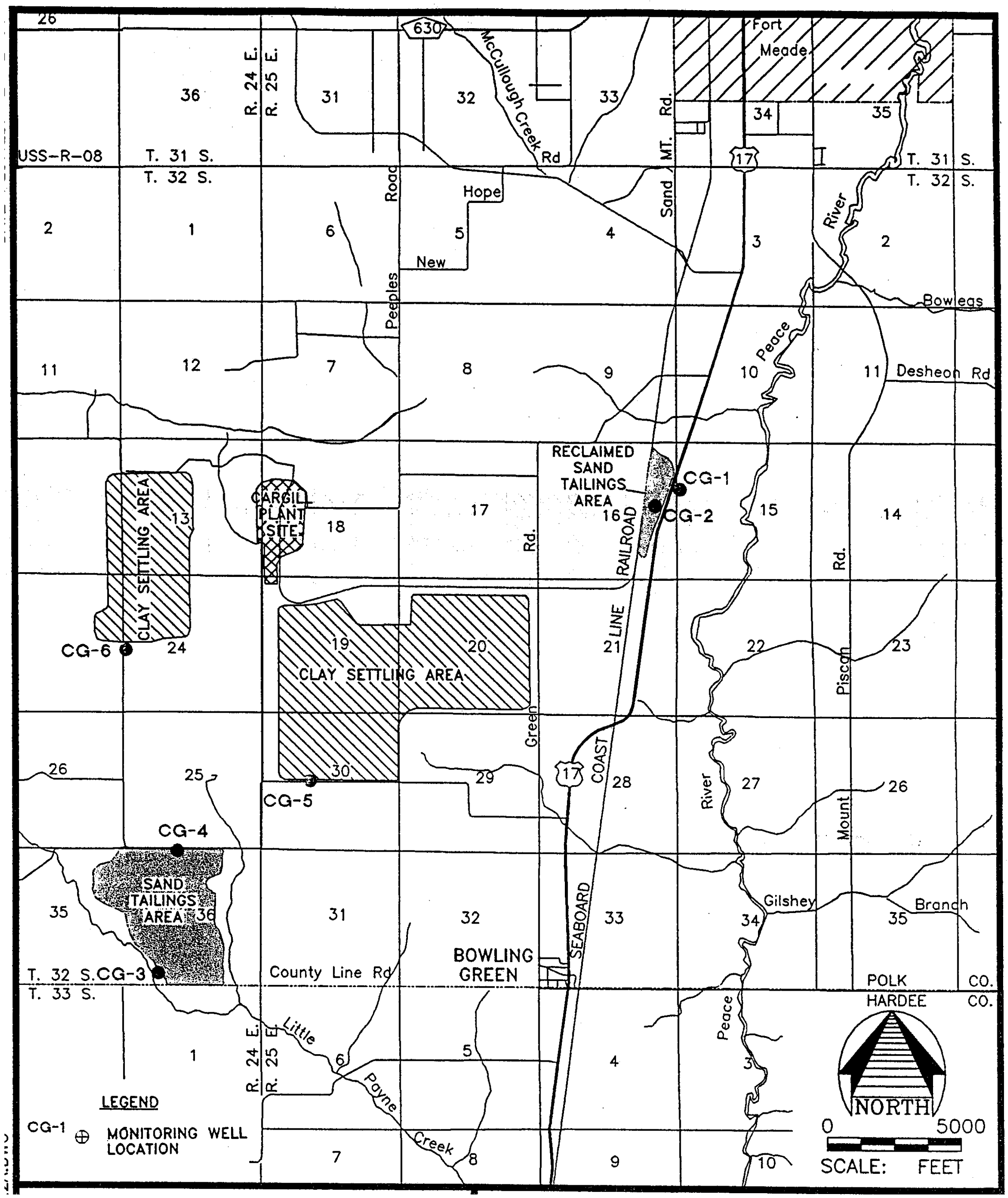

Figure 15. Site Location Map Cargill Monitoring Wells, Polk County, Florida.

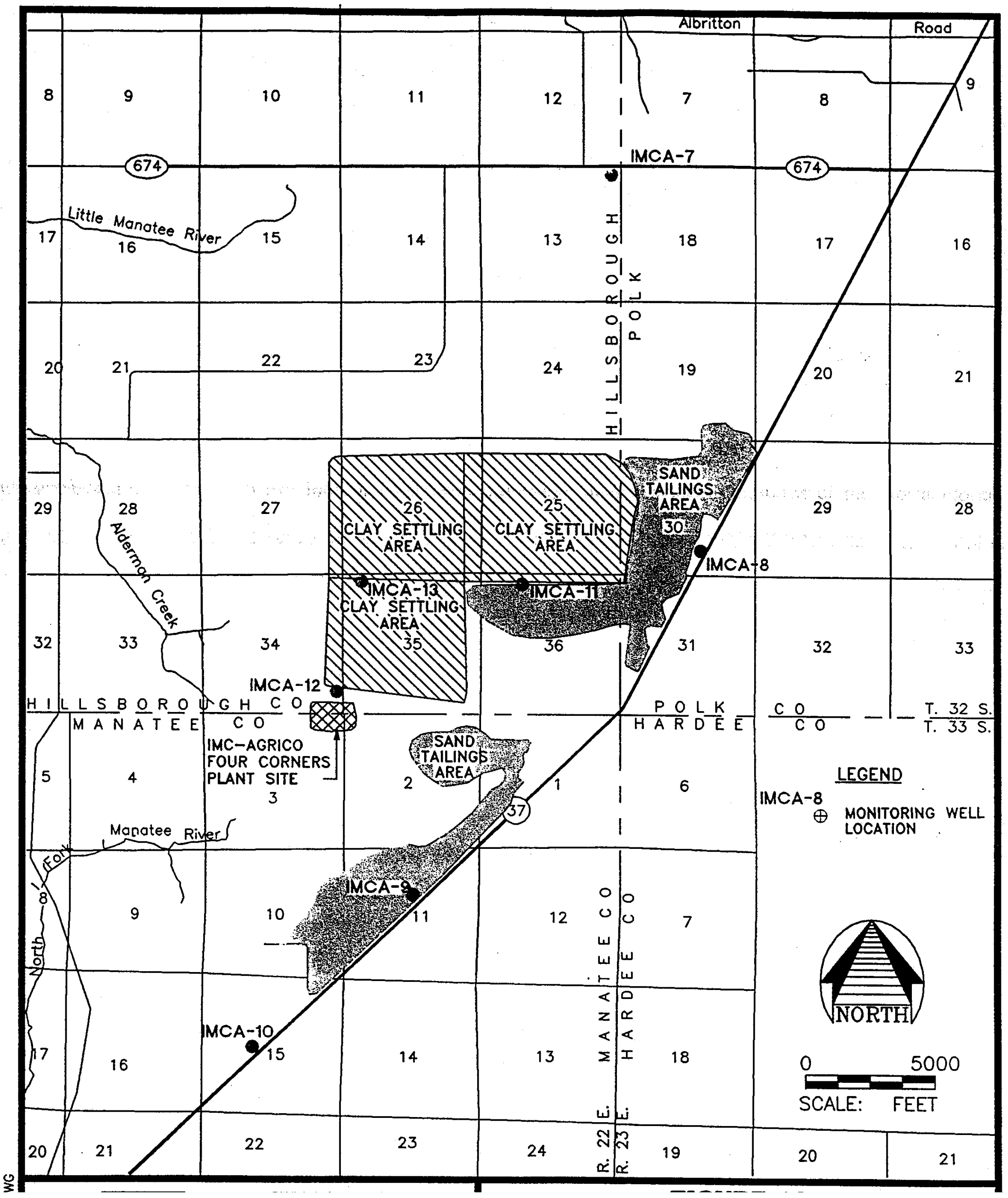

Figure 16. Site Location Map IMC-Agrico Monitoring Wells, Hillsborough, Manatee, And Polk Counties.

HYDROGEOLOGIC SETTING

North Florida Phosphate District

The North Florida Phosphate District is underlain by several hundred feet of marine sands, clays, limestones and dolomites ranging from early Tertiary Oligocene to recent in age (Ceryak et al., 1983). The oldest rocks penetrated by water wells are assigned to the mid-Eocene (42-29 million years) Avon Park Formation. The significant geologic and hydrogeologic units of the North Florida Phosphate District monitoring locations are summarized in Table 8. Descriptions of each unit based on Ceryak et al. (1983), Rupert (1989), and Scott (1988, 1992) are summarized below.

Table 8. North Florida Phosphate District Regional Geologic and Hydrogeologic Units.

System	Series	Stratigraphic Unit	Lithology	Hydrogeologic Unit
Quaternary	Holocene	Undifferentiated classic & alluvial deposits	Fine to medium grained sand, clayey sand,	Surficial Aquifer System
	Pleistocene			
	Miocene	Hawthorn Group		Intermediate Aquifer System
		1) Statenville Formation	Interbedded phosphatic sands, clays, and dolostones	
Tertiary		2) Coosawhatchee Formation	Interbedded sands, clays, and fossiliferous dolostones	
		3) Marks Head Formation	Variable interbedded sands, clays and dolostones	
		4) Penny Farms Formation	Interbedded carbonate sands and clays	
	Oligocene	Suwannee Limestone	Marine Limestone, cream to white, soft, porous, hard & silicified in upper portions.	Upper Florida Aquifer System
	Eocene	Ocala Limestone	Marine limestone, fossiliferous, white to tan, soft & chalky, hard and dolomitic in lower portions	
		Avon Park Formation	Marine limestone, fossiliferous, gray to brown, dolomitic, carbonaceous	

Avon Park Formation

The Middle Eocene Avon Park Formation is composed of porous dolomite interbedded with dolomitic limestones. The Avon Park and Ocala Limestone formations are the geologic units of the Florida aquifer in the North Florida Phosphate District. The Avon Park formation occurs at depths ranging from 400 to 450 feet in this area.

Ocala Limestone

The Upper Eocene Ocala Limestone was assigned Group status in earlier literature and was subdivided into three formations. In ascending order of depth, they are the Inglis, Williston and the Crystal River formations. All three units are fossiliferous and are differentiated by content and abundance. In recent literature the Ocala Limestone has been assigned formation status. The Ocala Limestone is a primary host for the Florida Aquifer in the northern area of the state. Many drinking water wells in the North Florida Phosphate District access water from the upper region of the Ocala Limestone formation.

Suwannee Limestone

The Suwannee Limestone overlies Ocala Limestone in most of the North Florida Phosphate District and typically consists of fossiliferous, calcareous marine limestone. The Suwannee ranges from 10 to 150 feet thick. The formation pinches out in Columbia and Baker counties to the east.

Hawthorn Group

The Hawthorn Group is a series of Lower and Middle Miocene phosphatic clays, sands, limestones and dolomites unconformably overlying Suwannee Limestone. Four formations of the Hawthorn Group are recognized in the North Florida Phosphate District. They are, in ascending order of depth, the Penny Farms Formation, the Marks Head Formation, the Coosawhatchee Formation and the Statenville Formation. The thickness of the Hawthorn Group in the district varies locally between 50 and 150 feet. Clay units in the Hawthorn Group comprise a confining unit overlying the Florida aquifer. The carbonate units within the Hawthorn, where present, serve locally as an intermediate aquifer system. The Statenville Formation is a phosphate bearing formation and is extensively mined in the district.

Pleistocene and Holocene Sediments

Undivided Pleistocene and Holocene sediments, consisting of quartz sands and clayey sands overlie the Hawthorn Group. These units represent relict Pleistocene marine sands and Holocene aeolian and alluvial deposits. Undifferentiated deposits in the North

Florida Phosphate District are generally less then 50 feet thick and comprise the surficial aquifer in the area.

Central Florida Phosphate District

The geology of the Central Florida Phosphate District consists of a thick sequence of carbonate rocks of Eocene to Oligocene age overlain by classic deposits. The significant geologic and hydrogeologic units of the Central Florida Phosphate District are summarized in Table 9. Descriptions of each unit, taken from Scott (1988 and 1992), are presented below.

Avon Park Formation

The Middle Eocene Avon Park Formation is composed of porous dolomite with interbedded dolomitic limestone and comprises a portion of the Florida aquifer in the region.

Ocala Limestone

The Late Eocene, Ocala Limestone crops out in extreme northwestern Polk County (near the border with Pasco, Lake, and Sumter counties) and is present in the subsurface throughout the remaining portions of the district. There are two subdivisions of the formation; a lower unit of granular limestone overlain by an upper unit of variably carbonate muddy to granular limestone. Both units are fossiliferous. In the Central Florida Phosphate District, the Ocala Limestone is up to 200 feet thick.

Suwannee Limestone

The Oligocene Suwannee Limestone is a sandy, fossiliferous limestone unconformably overlying the Ocala Limestone. The unit is locally dolomitized and silicified. Within the district, the Suwannee Limestone ranges from 75 to 200 feet thick.

Hawthorn Group

The Hawthorn Group is a complex series of phosphate bearing, carbonate and siliciclastic sediments of Miocene age. Hawthorn sediments are present throughout the district. The Hawthorn Group has been subdivided (in ascending order) into the Arcadia and Peace River formations.

Arcadia Formation

The Arcadia Formation is divided into two lower members, the Nocatee and the Tampa, overlain by an upper undivided section. The Tampa member is a slightly phosphatic to non-phosphatic, sandy limestone. A blue-green, clay unit is typically present at the base of the Tampa member. The Nocatee member is a mixture of carbonate-cemented quartz sands, phosphorite, and minor clay. The upper portion of the Arcadia Formation consists of sandy, clayey, phosphatic dolomites and limestones interbedded with sand and calcareous clay units. In the Central Florida Phosphate District, the Arcadia Formation ranges from 30 feet to over 250 feet in thickness.

Peace River Formation

The Peace River Formation is divided into a lower section and the upper Bone Valley Member. The formation is present in all areas of the district and is generally less than 50 feet thick. The economic phosphate deposits in the Central Florida Phosphate District are included in the Peace River formation. The lower section of the Peace River consists of clayey, dolomitic, variably phosphatic quartz sands, to sandy, phosphatic, dolomitic clays. The Bone Valley Member consists of a mixture of sand to gravel sized phosphate grains mixed with variable amounts of quartz sand and clay. The unit hosts the bulk of mineable phosphate deposits in the district and reaches a maximum thickness of 50 feet.

Undivided Surficial Sediments

The Hawthorn Group is unconformably overlain by undivided marine terrace sands, clayey sands and clays which range from Pliocene to Pleistocene in age (5.3 million to 10,000 years). Thickness of these sediments range from 10 feet to as much as 120 feet in upland ridge areas.

Table 9. Central Florida Phosphate District Regional Geologic and Hydrogeologic Units.

<table>
<tr><th>System</th><th>Series</th><th>Stratigraphic unit</th><th>General lithology</th><th>Hydrogeologic unit</th></tr>
<tr><td>Quaternary</td><td>Holocene and Pleistocene</td><td>Surficial sand, terrace sand</td><td>Predominantly fine sand; interbedded clay</td><td>Surficial Aquifer system</td></tr>
<tr><td></td><td>Pliocene</td><td>Surficial sand, terrace sand</td><td>Fine sand and interbedded clay</td><td rowspan="2">Confining Unit</td></tr>
<tr><td rowspan="6">Tertiary</td><td rowspan="4">Miocene</td><td rowspan="2">Hawthorn Group
1) Peace River Formation
Bone Valley Member</td><td rowspan="2">Sand, clay and phosphate</td></tr>
<tr><td rowspan="2">Intermediate Aquifer System</td></tr>
<tr><td rowspan="2">2) Arcadia Formation
Tampa Member</td><td rowspan="2">Clay and sandy limestone</td></tr>
<tr><td>Lower Confining Unit</td></tr>
<tr><td>Oligocene</td><td>Suwannee Limestone</td><td>Limestone, sandy limestone, fossiliferous</td><td rowspan="2">Upper Florida Aquifer</td></tr>
<tr><td>Eocene</td><td>Ocala Limestone</td><td>Limestone, chalky, foraminiferal, dolomitic</td></tr>
</table>

REGIONAL HYDROGEOLOGY - NORTH FLORIDA PHOSPHATE DISTRICT

Surficial Aquifer

The surficial aquifer in the North Florida Phosphate District is generally hosted within the undifferentiated Pleistocene and Holocene sands. The surficial aquifer is unconfined and receives recharge primarily from the infiltration of rainfall and to a lesser extent by upward seepage from the underlying intermediate aquifer (Ceryak et al., 1983).

Intermediate Aquifer

The intermediate aquifer in the North Florida Phosphate district underlies the surficial aquifer and is largely contained within permeable sand and carbonate units of the Hawthorn Group. When clayey confining units are absent in the Upper Hawthorn, the intermediate aquifer may be recharged by downward seepage from the overlying surficial aquifer. Similarly, if clay beds or dolomitic limestone beds are absent in the Lower Hawthorn, the intermediate aquifer may be in hydraulic contact with the underlying Floridian aquifer (Rupert, 1989). The thickness of the intermediate aquifer generally corresponds to the thickness of the Hawthorn Group sediments, ranging from 50 to 150 feet in the North Florida Phosphate District.

Florida Aquifer

The Florida aquifer system is comprised of several hundred feet of Eocene through Miocene age limestones including the Avon Park Formation the Ocala Limestone and the Suwannee Limestone. The top of the Florida aquifer in the district generally occurs at depths ranging from 100 to 250 feet.

REGIONAL HYDROGEOLOGY-CENTRAL FLORIDA PHOSPHATE DISTRICT

Surficial Aquifer

The surficial aquifer in the Central Florida Phosphate District consists of undivided classic deposits of Holocene and Pleistocene age. These surficial deposits generally consist of fine to medium grained sands that become increasingly clayey and phosphatic with depth. The surficial aquifer is unconfined and generally ranges from approximately 25 to 50 feet thick over most of the Central Florida Phosphate District (Scott, 1988).

Intermediate Aquifer

The intermediate aquifer consists of Miocene age deposits of the Hawthorn Group and is generally confined by impermeable clayey deposits. The upper confining units consist of the calcareous clays and phosphatic units of the Bone Valley Member of the Peace River Formation. The intermediate aquifer consists of permeable water-bearing limestone and dolomite units within the Arcadia Formation (Scott 1988) and ranges in thickness from 125 and 425 feet Figure 17 shows the potentiometric surface of the intermediate aquifer (September 1994) in the study area (from WRI 84-4018) along with the locations of the monitoring well sites.

Upper Florida Aquifer

Within the Upper Floridian aquifer there is a vertically continuous series of carbonate rocks ranging in thickness from 1,000 to 1,200 feet in the Central Florida Phosphate District. The carbonate units of the Florida include the Suwannee Limestone and the Ocala Limestone, and the Avon Park Formation of Oligocene and Eocene age (Scott, 1988). Clay units at the base of the Hawthorn Group form a confining unit at the top of the aquifer. The upper Florida is the primary source of water for all municipal, industrial and agricultural production wells in the area.

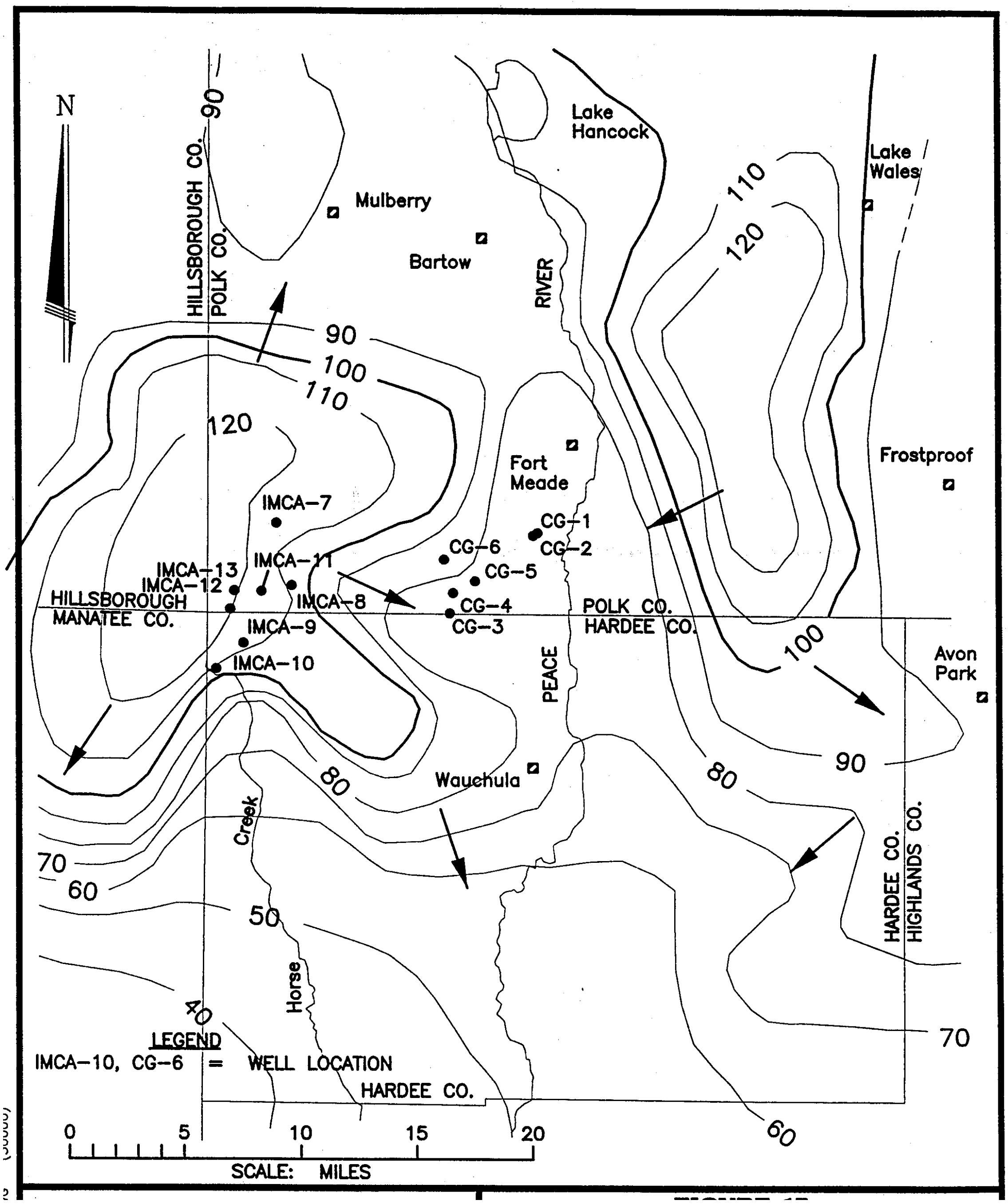

Figure 17. Potentiometric Surface of the Intermediate Aquifer, Central Florida Phosphate District.

MONITORING WELL METHODS

Installation

Standard four and one-quarter inch hollow-stem auger methods were utilized to install the shallow, surficial aquifer wells at both the PCS Phosphate sites in the North Florida Phosphate District and at the Cargill and IMC-Agrico sites in the Central Florida Phosphate District. Six of the intermediate aquifer wells at the PCS Phosphate site were also installed using hollow-stem auger methods. The remainder of the intermediate aquifer wells were installed utilizing mud rotary methods with a nominal borehole diameter of six inches. Construction diagrams for all monitoring wells are included in Appendices K to M.

Each well consists of a minimum of a 10-foot section of threaded, factory decontaminated, two-inch diameter, 0.010-inch PVC slotted screen, followed by solid casing extending to approximately three feet above grade. The screened portion of each well was sandpacked with a clean 20/30 grade silica sand to a minimum level of one foot above the top of the screen, followed by a minimum one foot bentonite or fine sand seal and cement grout to the surface. After allowing the cement grout to set for a minimum of 24 hours, each well was developed for a minimum of 30 minutes using either a rig mounted centrifugal pump (surficial wells at PCS Phosphate), a B-K hand pump (intermediate wells at PCS Phosphate), or a stainless steel Grundfos submersible pump. Each well was completed with an above ground protective casing and fitted with a locking cap. All equipment and material utilized for the soil borings and installation of monitor wells was thoroughly decontaminated using a high-pressure steam cleaner capable of producing water at a temperature in excess of 200°F.

North Florida Phosphate District

Monitoring well locations at the PCS Phosphate Swift Creek Mine site are shown in Figure 14. Monitoring wells MW-B4S, MW-B4I, MW-B8S, MW-B8I were installed as background wells in order to assess ground water quality in areas undisturbed by mining. Monitoring wells MW-B2S, MW-B2I, MW-B3S and MW-B3I were installed in and downgradient of active clay settling areas SA-3 and SA-4. Monitoring wells MW-B6S, MW-B6I, MW-B7S and MW-B7I (new) were installed in active sand tailings areas northwest of the PCS Phosphate Swift Creek Plant site. Boring logs for wells completed in the North Florida Phosphate District are included in Appendix H. Well construction details are included in Appendix K. Monitoring well installation data are provided below in Table 10.

Table 10. Monitor Well Installation Data - North Florida Phosphate District.

Location/Well ID	Well Type	Monitoring Point	Sec., Twp., Rng.	Depth	Screened Interval	Date Completed
Site 2 – PCS: MW-B2S MW-B2I	Surficial Intermediate	Clay settling area	NE¼ Sec. 8; T1S, R15E	24 ft. 79 ft.	14 - 24 ft. 59 - 79 ft.	11/28/95 11/28/95
Site 3 – PCS: MW-B3S MW-B3I	Surficial Intermediate	Clay settling area	NW¼ Sec. 16; T1S, R15E	19 ft. 54 ft.	9 - 19 ft. 44 - 54 ft.	11/28/95 11/28/95
Site 4 – PCS: MW-B4S MW-B4I	Surficial Intermediate	Background	SE¼ Sec. 11; T1S, R14E	19 ft. 49 ft.	9 - 19 ft. 39 - 49 ft.	11/30/95 11/30/95
Site 6 – PCS: MW-B6S MW-B6I	Surficial Intermediate	Sand tailings area	SE¼ Sec. 27; T1N, R14E	19 ft. 49 ft.	9 - 19 ft. 39 - 49 ft.	12/01/95 12/01/95
Site 7 – PCS: MW-B7S MW-B7I(new)	Surficial Intermediate	Sand tailings area	SW¼ Sec 27; T1N, R14E	19 ft. 60 ft.	9 - 19 ft. 45 - 60 ft.	2/13/96 8/23/96
Site 8 – PCS: MW-B8S MW-B8I	Surficial Intermediate	Background	NE¼ Sec. 19; T1N, R15E	25 ft. 76.5 ft.	15 - 25 ft. 56.5 - 76.5 ft.	12/18/96 12/17/96

In general, the surficial aquifer wells were installed in the near surface clayey sand and sand units. The intermediate aquifer wells were completed within the sandy clays, clays and dolomitic limestones of the Hawthorn Group. The surficial wells ranged in depth from 19 to 25 feet and the intermediate wells ranged in depth from 39 to 79 feet. Diagrams showing the generalized stratigraphy and hydrogeology for each monitoring well location are included in Appendix N.

Central Florida Phosphate District

The locations of monitoring wells installed at the Cargill Fort Meade and IMC-Agrico Four Corners Mine sites are shown in Figures 15 and 16. Monitor wells CG-1S, CG-1I, CG-3S, CG-3I, IMCA-7I and IMCA-10I were installed as background wells in order to assess ground water quality in undisturbed areas. Monitoring wells CG-5S, CG-5I, CG-6S, CG-6I, IMCA-11S, IMCA-11I, IMCA-12S, IMCA-12I, IMCA-13S and IMCA-13I were installed downgradient of active and formerly active clay settling areas. Monitoring wells CG-2S, CG-2I, CG-4S, CG-4I, IMCA-8S, IMCA-8I, IMCA-9S and IMCA-9I were installed downgradient of recently utilized sand tailings areas. Monitoring wells CG-2S, CG-4S, CG-8S, CG-9S, IMCA-11S, IMCA-13S were installed in former sand tailings disposal areas. Boring logs for the Central Florida Phosphate District monitoring wells are included in Appendices I and J. Well construction details are included in Appendices L and M. Monitoring well installation data are summarized below in Table 11.

Table 11. Monitor Well Installation Data - Central Florida Phosphate District.

Location/Well ID	Well Type	Monitoring Point	Sec., Twp., Rng.	Depth	Screened Interval	Date Completed
Site 1 – Cargill: CG-1S CG-1I	Surficial Intermediate	Background: Up-gradient	SW cnr Sec. 10; T32S, R25E	23 ft. 85 ft.	3 - 23 ft. 55 - 85 ft.	11/15/96 11/18/96
Site 2- Cargill: CG-2S CG-2I	Surficial Intermediate	Sand tailings Area	E½ Sec 16; T32S, R25E	17 ft. 70 ft.	2 - 17 ft. 50 - 70 ft.	11/20/96 11/20/96
Site 3- Cargill: CG-3S CG-3I	Surficial Intermediate	Background: Down-gradient	SW¼ Sec. 36; T32S, R24E	18 ft. 95 ft.	3 - 18 ft. 70 - 95 ft.	11/21/96 11/22/96
Site 4- Cargill: CG-4S CG-4I	Surficial Intermediate	Sand tailings Area	N½ Sec. 36; T32S, R24E	30 ft. 105 ft.	5 - 30 ft. 80 - 105 ft.	11/25/96 11/26/96
Site 5- Cargill: CG-5S CG-5I	Surficial Intermediate	Clay settling area	Sec. 30; T32S, R25E	25 ft. 105 ft.	5 - 25 ft 80 - 105 ft.	11/26/96 12/02/96
Site 6- Cargill: CG-6S CG-6I	Surficial Intermediate	Clay settling area	W½ Sec. 24; T32S, R24E	20 ft. 100 ft.	5 - 20 ft. 75 - 100 ft.	12/03/96 12/03/96
Site 7- IMCA: IMCA-7I	Intermediate	Background	NE¼ Sec. 13; T32S, R22E	100 ft.	75 - 100 ft.	12/05/96
Site 8- IMCA: IMCA-8 IMCA-8I	Surficial Intermediate	Sand tailings Area	SE¼ Sec. 30; T32S, R23E	20 ft. 110 ft.	5 - 20 ft. 85 - 110 ft.	12/12/96 12/12/96
Site 9- IMCA: IMCA-9S IMCA-9I	Surficial Intermediate	Sand tailings Area	N½ Sec. 11; T33S, R22E	25 ft. 110 ft.	5 - 25 ft. 85 - 110 ft.	12/10/96 12/10/96
Site 10- IMCA: IMCA-10I	Intermediate	Background	W½ Sec. 15; T33S, R22E	110 ft.	85 - 110 ft.	12/09/96
Site 11- IMCA: IMCA-11S IMCA-11I	Surficial Intermediate	Clay settling area	NW¼ Sec. 36; T32S, R22E	17 ft. 105 ft.	2 - 17 ft. 80 - 105 ft.	12/16/96 12/13/96
Site 12- IMCA: IMCA-12S IMCA-12I	Surficial Intermediate	Clay settling area	SE¼ Sec. 34; T32S, R22E	18 ft. 100 ft.	3 - 18 ft. 75 - 100 ft.	12/19/96 12/20/96
Site 13- IMCA: IMCA-13S IMCA-13I	Surficial Intermediate	Clay settling area	NW¼ Sec 35; T32S, R22E	17 ft. 120 ft.	2 - 17 ft. 95 - 120 ft.	12/16/96 12/18/96

In general, the surficial wells were installed in the undivided surficial sand and clayey sands. The intermediate aquifer wells were installed within the clayey, dolomitic limestones of the Hawthorn Group. The surficial wells ranged in depth from 17 to 30 feet and the intermediate wells from 70 to 120 feet. Diagrams showing the generalized stratigraphy and hydrogeology for each monitoring well location are included in Appendices O and P.

GROUND WATER SAMPLING METHODS

Ground water samples were collected from all monitoring wells in June 1997. Additional samples were collected during the period August through November 1997 from wells CG-2S, CG-2I, IMC-11S, IMC-11I, MW-B7S, MW-B7I(N). These wells were re-sampled for fuel oil analysis based on the results of initial testing.

All monitoring wells were sampled using a decontaminated, stainless steel submersible pump, in accordance with procedures specified in BCI's Comprehensive Quality Assurance Plan (CompQAP Plan #930109G).

RESULTS AND DISCUSSION

The initial sampling of the ground water monitoring wells was conducted during June 1997. The resulting data are summarized in Tables 12, 13 and 14 with the complete analytical results presented in Appendix Q. For this initial sampling event, no detectable concentrations of fatty acids or amines were present in any of the ground water samples. However, fuel oil was detected in samples from three surficial aquifer wells located at PCS Phosphates, Cargill, and the IMC-Agrico mine sites. In addition, fuel oil was also detected in one of the intermediate aquifer wells at the PCS Phosphates' site.

Table 12. Concentration of Reagents Detected in the IMC-Agrico Monitoring Well Data.

Monitor Well Number	Fatty Acid mg/L	Fuel Oil Mg/L	Amine Mg/L
IMC-7S	ND	ND	ND
IMC-7I	ND	ND	ND
IMC-8S	ND	ND	ND
IMC-8I	ND	ND	ND
IMC-9S	ND	ND	ND
IMC-9I	ND	ND	ND
IMC-9ID	ND	ND	ND
IMC10S	ND	ND	ND
IMC-10I	ND	ND	ND
IMC-11S	ND	0.835	ND
IMC-11I	ND	ND	ND
IMC-11ID	ND	0.448	ND
IMC-12S	ND	ND	ND
IMC-12I	ND	ND	ND
IMC-12ID	ND	ND	ND
IMC-13S	ND	ND	ND
IMC-13I	ND	ND	ND

ND = Not Detected
I = Intermediate Well
D = Duplicate Sample

Table 13. Concentration of Reagents Detected in the Cargill Monitoring Well Data.

Monitor Well Number	Fatty Acid mg/L	Fuel Oil mg/L	Amine Mg/L
CG-1S	ND	ND	ND
CG-1I	ND	ND	ND
CG-2S	ND	2.47	ND
CG-2I	ND	ND	ND
CG-3S	ND	ND	ND
CG-3I	ND	ND	ND
CG-3ID	ND	ND	ND
CG-4S	ND	ND	ND
CG-4I	ND	ND	ND
CG-5S	ND	ND	ND
CG-5I	ND	ND	ND
CG-5ID	ND	ND	ND
CG-5B	ND	ND	ND
CG-6S	ND	ND	ND
CG-6I	ND	ND	ND

ND = Not Detected
S = Surficial Well
I = Intermediate Well
D = Duplicate Sample

Table 14. Concentration of Reagents Detected in the PCS Phosphates Monitoring Well Data.

Monitor Well Number	Fatty Acid mg/L	Fuel Oil mg/L	Amine mg/L
MW-B2S	ND	ND	ND
MW-B2I	ND	ND	ND
MW-B2ID	ND	ND	ND
MW-B3S	ND	ND	ND
MW-B3I	ND	ND	ND
MW-B45	ND	ND	ND
MW-B4I	ND	ND	ND
MW-B6S	ND	ND	ND
MW-B6I	ND	ND	ND
MW-B7S	ND	6.31	ND
MW-B7I	ND	1.52	ND
MW-B7SD	ND	5.75	ND
MW-B8S	ND	ND	ND
MW-B8I	ND	ND	ND

ND = Not Detected
S = Surficial Well
I = Intermediate Well
D = Duplicate Sample

The three surficial aquifer wells with detectable fuel oil were installed in active and inactive sand tailings areas. Similarly, the single intermediate aquifer monitor well that showed a trace amount of fuel oil (PCS Phosphate mine site), was installed in an active sand tailings area.

In order to verify these results, confirmatory sampling and testing of water from the surficial monitoring wells which indicated detectable fuel oil was conducted from August through October 1997. After further evaluation of the core logs from the vicinity of the sand tailings associated intermediate monitoring well at PCS Phosphate, it was decided that a new well would be installed to assure that entry into the intermediate aquifer zone had been achieved. The new intermediate well (monitoring well B-7I) was installed in August 1997 and resampled for fuel oil analysis in August and November 1997. The resulting analytical data are included in Appendix Q and summarized in Table 15. Comparable levels of fuel oil were reported for the surficial aquifer monitor wells and the single intermediate aquifer well at the PCS Phosphate site for both resampling events. Furthermore, for both the initial and resampling events duplicate ground water sampled were collected. These data further substantiate the presence of fuel oil constituents in these monitor wells.

Table 15. Fuel Oil Concentration in Monitor Well Water at Each Mining Site.

Well Number	Fuel Oil Concentration (mg/L)		
	June 1997	August – October 1997	November 1997
IMC-Agrico			
IMC-11S	0.8	8.5	--
IMC-11SD	0.5	--	--
Cargill			
CG-2S	2.5	0.6	--
CG-2SD	NS	0.6	--
PCS Phosphates			
MW-B7S	6.3	1.7	--
MW-B7SD	5.8	1.6	--
MW-B7I	1.5	1.4	0.6
MW-B7ID	NS	--	--

-- = Not Sampled
S = Surficial
I = Intermediate
D = Duplicate sample

Two important observations can be made with respect to the detection of fuel oil in ground water at the sand tailings areas. First, data show a general decrease in ground water fuel oil concentrations with increasing age of each respective sand tailings area. The highest concentration of fuel oil was detected at the PCS Phosphate site, where the monitor well was installed in an active sand tailings disposal area. Chronologically, the Cargill sand tailings monitoring area has been inactive for approximately five to seven years and showed a lower fuel oil concentration. The IMC-Agrico sand tailings area site is approximately ten years old and exhibited the lowest concentration of fuel oil in ground water.

Secondly, as shown by the local presence of fuel oil in the intermediate aquifer at the PCS Phosphates site, the vertical migration of fuel oil constituents appears to be controlled by the local hydrogeologic setting, specifically the presence (or absence) of a clay confining unit between the surficial and intermediate aquifer. As previously described, the intermediate aquifer in the North Florida Phosphate District underlies the surficial aquifer and is largely contained within permeable sand and carbonate units of the Hawthorn Group. When the clayey confining units are absent from the Upper Hawthorn, the intermediate aquifer is directly recharged by downward seepage from the overlying surficial aquifer. As shown by the boring logs, this confining unit appears to be irregular in the Northern Florida Phosphate District (Appendix G). This interrupted nature of the confining unit results in variably facilitated recharge to the intermediate aquifer from downward seepage from the surficial aquifer. This recharge effect is substantiated by the similar water level elevations in the surficial and intermediate wells observed at many of the well sites at PCS Phosphates.

In the Central Florida Phosphate District, the intermediate aquifer is confined by thick clay units in the upper Hawthorn Group. As a result, minimal recharge to the intermediate aquifer occurs, substantially reducing the potential for vertical migration of fuel oil constituents.

CONCLUSIONS

The absence of both fatty acids and amines in ground water samples from all of the surficial and intermediate aquifers confirms that these two flotation reagents do not migrate into the ground water system from the sand tailings disposal areas. On the other hand, the potential for migration of residual fuel oil appears to be a component of local geological character. Despite its clear presence, the data generated during this study indicate that fuel oil degradation occurs over time as attested to by the concentration differences found in ground water from the sampled mine sites.

The vertical migration of fuel oil constituents appears to be mainly related to the degree of confinement and rate of recharge between the surficial and intermediate aquifers. At the North Florida Phosphate District, despite detection of fuel oil in the intermediate aquifer, there is a significant decrease in fuel oil concentrations compared to the overlying surficial aquifer. Given that the vertical migration of ground water is relatively slow, this suggests that similar degradation effects are occurring to reduce the concentration of fuel oil constituents.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The research effort conducted for this project has addressed its primary objectives, which were to identify an appropriate methodology for the specific identification of flotation reagents; fatty acid, fuel oil, and amine, to determine the biodegradation and soil attenuation of flotation reagents, and to trace the pathway(s) of flotation reagents to the environment. Furthermore, data is presented that would provide useful information to the phosphate industry with respect to suspected environmental pollution potentially associated with the flotation reagents used by the phosphate industry.

This study clearly established a Standard Operating Procedure and Method Detection Limit for the specific identification and quantification of the reagents used in the phosphate industry. As indicated by the results of the Performance Evaluation samples, all associated analytical data were acceptable in terms of both precision and accuracy. Good precision was shown based on the RPDs obtained from both duplicate LCS and Duplicate Matrix Spike samples. In addition, the Laboratory Control Samples analyzed with each batch of samples exhibited acceptable recovery levels. None of the method blanks exhibited detectable levels of the analytes of interest. It is concluded that the main objective of Quality Control, namely to produce verified data of known quality suitable for use in support of this project’s primary goal of assessing the fate of selected flotation reagents was met.

The results of the biodegradation testing showed that all reagents undergo degradation, but the level of biodegradation is variable. The fatty acid and amines are more readily biodegradable than the fuel oil. The biodegradation trend for the amines showed a maximum of approximately 53 percent, followed by fatty acid at 35 percent. The fuel oil showed the least biodegradation, as indicated, approaching slightly above 10 percent. The biodegradation of the control, which contained only glucose, was between approximately 80 and 90 percent.

The soils attenuation study showed the sandy overburden to have ability to attenuate fatty acids and fuel oil. Although no amine was detected in the original GMT water, it is presumed, as indicated previously, the negatively-charged sand surfaces would attenuate the cationic amines. Thus, there was no detection of amines in the GMT water. The mass balance (reagent volume versus soil volume) is heavily weighted in favor of the sand. For this reason a low organic assay is consistent with a conclusion that the available adsorption opportunities far exceed that needed to tie-up all the fatty acid residuals. More sand arrives (more adsorption surfaces) with each volume of GMT water. For these reasons no lack of adsorptive opportunities ever exists and this may explain why no fatty acid is free in the surrounding aquifer systems.

To identify the distributions of reagents in the various streams within the beneficiation process and into the environment both laboratory and an actual field mass balances were attempted. The laboratory lab flotation did not provide a satisfactory mass balance, accounting for only 31 percent of the fatty acid recovery, 113 percent for the fuel oil, and 425 percent for the amines. Further assessment to evaluate the low recovery of the fatty acid and a high recovery for the amines did not reveal any justifiable results. Use of the reagents in the laboratory flotation as “standards” for comparing all process stream samples, did not produce any significant improvement in recoveries. However, the field flotation mass balance was achieved utilizing the IMC-Agrico’s mass-balance program. The sample analysis and mass balance model indicated most of the reagents to be distributed in the clay settling and sand tailings (GMT) areas. This information further assisted with the assessment and observations made in the second phase of this research which investigated the presence or absence of the reagents in the subsurface water.

In Phase II, which was the field investigation of ground water, neither fatty acids nor amines were detected in the surficial aquifers underneath the clay settling and sand tailings disposal areas. This finding is not surprising as both these reagents were shown to be fairly biodegradable and also attenuated by the sandy overburden. Fuel oils, however, were detected in the surficial aquifer at all sand tailings disposal areas, but the concentration decreased as the age of the sand tailing area increased. None of the 19 intermediate wells sampled for this project indicated any fatty acid or amines and only one well located at an active sand tailings disposal area indicated trace amounts of fuel oil. The vertical migration of fuel oil constituents appears to be mainly related to the degree of confinement and rate of recharge between the surficial and intermediate aquifers. At the North Florida Phosphate District, despite detection of a trace amount of fuel oil in the intermediate aquifer there is a significant decrease in fuel oil concentrations compared to the overlying surficial aquifer. Given that the vertical migration of ground water is relatively slow, this suggests that similar degradation effects are occurring to reduce the concentration of fuel oil.

RECOMMENDATIONS

The data generated during this project and related observations provide inadequate information at least, on the extent or spatial distribution of the any fuel oil in the ground water systems at each test site. Any conclusions with respect to the extent of fuel oil migration is beyond the scope of this project.

Therefore, a Phase III of this project is recommended which would address the potential off site horizontal migration of fuel oils from sand tailings areas.

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