

Changes to  
FINAL REPORT

Reclamation of Brine Contaminated Soil:  
Clearview Demonstration Project

SUBMITTED TO:

Oklahoma Conservation Commission

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# **1. INTRODUCTION**

## **1.1 Background**

One of the largest breakthroughs for industrial society has been the discovery and subsequent use of the earth's natural resources (i.e., coal, oil, gas, etc.). All aspects of utilizing these natural resources have possible negative environmental implications. Stringent regulations have been enacted within the last 25 years placing due emphasis on the measurement and minimization of the negative consequences associated with resource utilization. Two problems that could impact water quality are addressed in this study are: (1) reclamation of soils that are damaged due to improper handling of brine during oil exploration; and (2) utilization of the ever increasing amount of solid waste produced by the combustion of coal.

Oilfield activities have caused concern due to the production of brine during drilling operations. Typically, this waste by-product is disposed of by deep well injection. Brine is one of the most recognized sources of non-point source pollution in the state of Oklahoma. Improper handling, transport, and disposal of this by-product pose threats to the nearby surface and ground water resources, as well as arable soils with which it may come in contact. The two primary effects of brine on soil and soil fertility are: (1) the degradation of the physical structure of the soil; and (2) the alteration of the normal osmotic gradient existing between plant roots and the soil. Common amendments used for the reclamation of brine contaminated soils include a calcium source, fertilizer, and an organic source (Burley, 1988).

Another problem facing our society today is the ash produced as a result of coal combustion. The combustion of coal is one of the principal methods used to generate electricity; however, it generates in excess of 100 nearly 50 million tons of waste ash each year in the United States (American Coal Ash Association, 1998 Davidson, 1993). Approximately 290% of this waste ash is used commercially while the remaining 7180% must be disposed of, typically in landfills or disposal ponds (Burnet, 1987). New regulations devised to protect surface and ground water require more carefully designed disposal methods which consequently increase the cost of disposal. Due to the problems associated with disposal, efforts are being made to utilize ash, thereby reducing the quantity that must be disposed in landfills. For these reasons, alternative uses for ash require investigation. Currently, the primary uses for waste ash are construction related.

To conform to EPA emission regulations, coal-fired power plants have employed effective methods to remove SO<sub>2</sub> from exhaust gases. One method is through fluidized bed combustion (FBC). In this procedure, a finely ground sorbent (typically limestone) is introduced during the coal combustion phase and the exhaust gas/coal/lime mix is passed through a cyclone. The large char is recycled to increase combustion efficiency (JAPCA, 1987). The addition of limestone produces an ash residue that is primarily composed of calcium constituents and various metal oxides. Therefore, the FBC process results in an ash residue that contains alkaline oxides (specifically CaO) and trace elements which may be useful for reclamation of brine disturbed soils (Stout, et. al., 1988).

## **1.2 Project Area Description**

In Oklahoma, there are a number of brine damaged areas located in wetlands or along riparian corridors. The site selected for this study is consists of 60 acres located along Clearview Creek near the town of Clearview in Okfuskee County (Figure 1.1). The site consists of 60 acres located along Clearview Creek in Sections 19

**Figure 1.1 Clearview Demonstration Study Site Location**

and 30 of T11N, R11E. The site has been severely impacted from a leaking oilfield disposal pit which discharged its contents across a large segment of Clearview Creek and the surrounding riparian

corridor. Previous analyses showed high levels of salt, chromium, and lead at the site, and that these constituents were traveling down Clearview Creek and into Alabama Creek. Alabama Creek was identified in Oklahoma's Section 319 Assessment report as being impaired due to salt and sediment contributions from salt damaged areas.

### **1.3 Goals and Objectives of this Study**

The three goals of the project and their respective measures are listed below:

- Goal 1: Reduction of NPS pollutant discharge from site.  
Measure: 70% reduction in concentration of pollutants leaving site.
- Goal 2: Stabilization and re-vegetation of site.  
Measure: Photographic and standard ecological measures of vegetation pattern and coverage.
- Goal 3: Transfer of information gathered during this project to other sites with a goal of five site remediation projects per year.  
Measure: Number of projects initiated and completed each year.

The specific objectives of this study were to obtain a basic understanding of the physical and chemical properties of brine contaminated soil, to determine the impacts of the brine contaminated area on adjacent water bodies, to determine the advantages of using FBA as a supplemental alternative soil amendment for these types of soils, and to use this information on a specific brine contaminated site to improve both soil quality and productivity.

It was hypothesized that FBA could be used as a supplemental source of calcium for amending brine disturbed soils. It was also hypothesized that the FBA would not only provide some of the calcium necessary for the physical integrity of the soil; but would also provide micro nutrients needed for propagation of vegetation. The FBA amendment could be used in conjunction with a source of organic waste, in the form of turkey litter, which would provide the essential macro nutrients (i.e., nitrogen, phosphorus, and potassium). In addition, gypsum will be employed as the primary supplementary source of calcium.

An important factor to consider when utilizing FBA as a soil amendment is the pH of the ash being added to the soil. FBA is highly alkaline and can markedly increase the pH of the soil. Because plants thrive within a relatively neutral pH range, it may be necessary to add an amendment that will help maintain the pH of the soil within an acceptable range. The most common agricultural amendment for decreasing soil pH is elemental sulfur.

### **1.4 Partnerships and Implementation Scope of Study**

#### **1.4.1 Participants**

The Clearview Brine Reclamation Demonstration Project was a cooperative effort of the University of Oklahoma, the Water Quality Division of the Oklahoma Conservation Commission, the Okfuskee County Conservation District, and the Natural Resource Conservation Service (NRCS). Crucial to the success of the project was the participation and cooperation of the citizens in and around Clearview. Other agencies involved with the initial project include the Office of the Secretary of the Environment, the Oklahoma Corporation Commission, and the U.S. Environmental Protection Agency. The Okmulgee County Conservation District and the Oklahoma Department of

Environmental Quality implemented additional remediation activities at the Clearview site after completion of all monitoring activities associated with this project.

Initial field sampling, laboratory testing, and soil amendment design studies were completed by Ms. Terri Pyle at the University of Oklahoma. Portions of her research thesis have been extracted to develop Chapter 3 of this document.

#### **1.4.2 Pre-Implementation Studies**

In order to achieve the stated objectives, several work tasks were completed. Prior to implementation of the remediation plan, a thorough site investigation was necessary to obtain background information and determine the extent of damage that had taken place at the Clearview site. Soil samples were collected and analyzed to determine the integrity of the soil, both chemically and physically. A water quality monitoring program was established to determine how the site had impacted water quality in adjacent water bodies. Finally, laboratory experiments were performed to determine optimum application rates for the proposed soil amendments. Laboratory bench-scale experiments were conducted to formulate the most suitable combination of amendments to improve soil quality and productivity of the brine impacted land. A leach study was performed to determine the concentrations of various metals which could leach from the amended soil.

Personnel from NRCS conducted a land survey of the Clearview site and developed design drawings for re-grading and contouring activities (see Appendix A). They also conducted a site inspection prior to implementation of the remediation technology and provided job oversight during implementation.

#### **1.4.3 Implementation Activities**

Implementation of the remediation technology commenced with extensive dirt work (i.e., re-grading and contouring) to prepare the site soils. Soil amendments were then incorporated at the specified application rates. The site was sprigged with Bermuda grass and covered with a hay mulch. The restored lands were not irrigated and no further chemicals were added.

#### **1.4.4 Post-Implementation Activities**

Post implementation activities consisted of monitoring and site maintenance monitoring. Monitoring activities consisted of periodically collecting and analyzing water samples from the surface water sampling sites, and a limited number of soil samples. The site was visually inspected on a routine basis (i.e., during monthly sampling episodes). Acute maintenance problems were noted and rectified in a timely manner. Approximately one year after implementation of the remediation technology, anchored hay bales were installed to arrest erosion from isolated areas in which vegetation had not been re-established. Re-seeding of these areas was then attempted. Approximately four years after implementation of the original remediation technology, the localized areas of denuded soil were treated with sewage sludge and gypsum and re-seeded. The final re-seeding activities occurred after completion of the monitoring activities associated with this project. consisted of periodically collecting and analyzing water samples from the surface water sampling sites, and a limited number of soil samples.

#### **1.5 Work Plan Task Completeness**

The Work Plan for this project identified nine different work tasks. The specific tasks and

their dates of completion are outlined below.

1. Quarterly reports detailing project activities - one month after the end of each quarter.
2. Annual report - included with annual report of all 319 activities. (July 1 of each year)
3. Contact with all affected landowners. (January 2, 1994)
4. Completion of site recovery strategy, along with submittal and subsequent approval by the USEPA prior to implementation. (April 1, 1994)
5. Completion of landowner agreements. (May 1, 1994)
6. Implementation of site recovery through erosion control, re-establishment of riparian areas, and wetland development. (Completed by September 1, 1995)
7. Submittal of a Quality Assurance Project Plan 60 days prior to the initiation of monitoring. (August 1, 1994)
8. Initiation of water quality monitoring program. (October 1, 1995)
9. Publication of a brochure detailing project activities and successes. This would include photographic documentation of before/after conditions as well as implementation activities. Brochure will be submitted to EPA prior to publication for review and approval. (August 1, 1999)

## **2. LITERATURE REVIEW**

### **2.1 Properties of Natural Soils**

Soils are classified as either organic or inorganic (mineral) in nature. Organic soils are very productive and can contain as much as 20% organic matter by weight. Inorganic, or mineral, soils are much lower in organic matter, containing roughly 1 to 6% by weight (Brady, 1990). These mineral soils occupy much of the total land.

Mineral soils consist of four major components; inorganic or mineral material, organic matter, soil air, and soil water. The inorganic portion of the soil is comprised of primary and secondary minerals which vary drastically in physical and chemical composition. Primary minerals are those that have persisted with very little change in composition since they were extruded from molten lava (Brady, 1990). These include quartz, mica, and feldspars and are most commonly found in the sand and silt fractions. Secondary minerals are those that have undergone weathering and are altered forms of iron oxides and silicate clays. These minerals are primarily found in the clay and, to a lesser degree, the silt fractions.

Clays consist of very small particles ( $< 0.002\text{mm}$ ) which have a large surface area per unit weight. These finer particles dictate much of the chemical, physical, and biological processes which occur in soils. Clay particles have charges, or exchange sites, on their surfaces which attract ions and water. The attraction and repulsion of particles toward each other are governed by the presence and intensity of the surface charge.

In most clays, a negative charge predominates; therefore, cations are attracted to the negatively charged surface. This attraction gives rise to a micelle, creating an ionic double layer. The inner layer consists of the negatively charged colloid and the associated strongly held cations. The outer layer is made up of the bulk solution containing loosely held cations attracted to the negative surface as well as water molecules. The cations adsorbed onto the particle surface are subject to exchange with other cations present in the soil solution.

The cation exchange capacity (CEC) of a soil is determined by summing the exchangeable cations that the soil can adsorb and is expressed in terms of centimoles of positive charge per kilogram of soil (Brady, 1990). The CEC of a given soil depends on the colloids present in the soil (e.g., a clay soil will have a higher CEC than a sandy soil due to the surface charge present in clays). The pH of a soil can also influence the CEC.

The percentage cation saturation is defined as the fraction of the CEC satisfied by a given cation. The percentage cation saturation of essential elements such as calcium and potassium governs the uptake of these elements by plants (Brady, 1990). Another factor which influences the uptake of essential elements is the other ions adsorbed on the colloid surface. According to Bohn, et. al., (1979), the strength of cation adsorption onto the surface of the colloid is dependent on the charge associated with the cation being adsorbed (e.g.,  $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+$ ).

Physical properties, such as plasticity, cohesion, dispersion, and flocculation, greatly influence the geotechnical uses of soils. Plasticity is the pliability or capability of a soil to be molded. Soils consisting of  $> 15\%$  clay exhibit plasticity (Brady, 1990). The liquid limit of a soil is the moisture content at which the soil is no longer plastic but becomes fluid-like. Soils with large ranges between the plastic and liquid limits are hard to deal with in the field. The cohesiveness of a soil indicates the tendency for clay particles in the soil to stick together (Brady, 1990). Cohesion is predominantly due to hydrogen bonding associated with clay surfaces. The dispersion of a soil is due to the repulsion of the negatively charged surfaces. Flocculation is the opposite of dispersion

and is very beneficial to agricultural soils because it leads to formation of stable aggregates.

### 2.1.1 Salt-Impacted Soils

Saline soils comprise nearly one-third of soils located in arid and semi-arid regions in the United States (Brady, 1990). The basic source of these salts is the weathering of primary minerals exposed on the earth's crust. Additional sources include fossil salts, atmospheric salts, local salt accumulations, and anthropogenic activities. During the process of chemical weathering, salt constituents are gradually released and made soluble. Saline soils often occur in areas that receive salts from other locations, with water being the dominant carrier. In humid regions, these soluble salts are easily flushed into nearby streams and transported to the oceans. In arid regions, however, leaching and transport of soluble salts is limited due to insufficient rainfall and higher evaporation rates. A build-up of soluble salts frequently occurs in soils with low permeability, in depressional areas that collect drainage water, or in areas subject to seepage or occasional flooding (Schaller and Sutton, 1978).

Soluble salts that accumulate in soils consist primarily of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  as cations and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  as anions. Other less dominant ions found are:  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{NO}_3^-$ . Salt-affected soils are classified by their content of soluble salts and the exchangeable sodium percentage (ESP) or, more recently, the sodium adsorption ratio (SAR) (Page, et. al., 1982). Soluble salts are estimated by measuring the electrical conductivity (EC) of the soil solution from a saturated soil paste. This has proven to be a valid estimation of soluble salts present since salts are composed of ions which conduct electricity. Brady (1990) defines ESP as the extent to which the adsorption complex of a soil is occupied by sodium. ESP is calculated using the following equation:

$$\text{ESP} = \frac{\text{exchangeable sodium (cmol/kg of soil)}}{\text{cation exchange capacity (cmol/kg of soil)}} * 100 \quad (1)$$

A more simplistic determination which gives information on the comparative concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in the soil solution is referred to as the sodium adsorption ratio (SAR). The SAR is defined as follows:

$$\text{SAR} = \frac{[\text{Na}^+]}{\{ \frac{1}{2}([\text{Ca}^{2+}] + [\text{Mg}^{2+}]) \}^{1/2}} \quad (2)$$

where  $[\text{Na}^+]$ ,  $[\text{Ca}^{2+}]$ , and  $[\text{Mg}^{2+}]$  are expressed in terms of millimoles per liter. The SAR of a soil takes into account that the adverse effect of sodium is controlled by the presence of calcium and magnesium ions.

As shown in Table 2.1, saline soils generally have a pH less than 8.5 because the salts present consist mostly of neutral salts, like chlorides and sulfates of Ca, Mg, and Na. However, sodium seldom comprises more than half of the soluble cations present in the soil which has an

**Table 2.1 Classification of Salt-Affected Soils Based on pH, EC, and SAR**

	<b>pH</b>	<b>Electrical Conductivity (EC) mmohs/cm</b>	<b>Sodium Adsorption Ratio (SAR)</b>
Saline	< 8.5	> 4	< 13 - 15
Sodic	> 8.5	< 4	> 13 - 15
Saline-Sodic	< 8.5	> 4	> 13 - 15
Normal	6.5 - 7.2	< 4	< 13 - 15



SAR value of less than 15. When adequate drainage is available, the excessive soluble salts can be removed from the root zone. Saline soils are often flocculated, so their permeability to water is similar and sometimes exceeds that of similar non-saline soils (Schaller and Sutton, 1978). These soils can be recognized by the white crust of salt which forms on the surface of the soil. Saline-sodic soils have a high concentration of both soluble salts and adsorbed sodium which can be detrimental to plants. Leaching of these soils in the absence of Ca, may actually lead to the formation of a sodic soil.

Sodic soils contain sufficient sodium to interfere with the growth of most crop plants. The pH of these soils is greater than 8.5 due to the high concentrations of alkali salts. The dominant cation is sodium, which is toxic to plants. As the ESP of soils increase, the soil becomes dispersed, is less permeable to water, and exhibits poor structural stability (Schaller and Sutton, 1978). At high ESP values, most of the clay and humus particles in the soil become unattached or dispersed. When this takes place, the soil will appear discolored as the humus is carried upward by capillary water and deposited on the surface as evaporation occurs. Hence, these soils are often termed black alkali soils. These are the soils which were investigated in this study.

## **2.1.2 Brine Contaminated Soils**

### **2.1.2.1 Background**

The objective of the Federal Water Pollution Control Act (FWPCA), amended as the Clean Water Act in 1987, is to “restore and maintain the chemical, physical, and biological integrity of the Nation’s water” (Environmental Statutes, 1993). This includes the protection of both surface and ground water. Recently, protection of our Nation’s waters has become a significant concern due to problems arising from non-point source pollution. The purpose of Section 319 of the FWPCA is to specifically manage pollution resulting from non-point sources. Salt-damaged soils resulting from oilfield activities are one of the most common sources of non-point source pollution in the state of Oklahoma.

Oil is found in deep horizons rich in mineral salts. The water existing in these formations is highly concentrated with dissolved salts. Cates (1993) provides a general classification of waters based on TDS as shown in Table 2.2. Typical components which can be found in brines include  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . Typical concentrations of the major and minor constituents found in brine is shown in Table 2.3. The most abundant ions present in brine are  $\text{Na}^+$  (>23,000 mg/L) and  $\text{Cl}^-$  (>35,500 mg/L).

Contamination of surface and ground water by brine is a major environmental concern facing the oil industry today. Brine is encountered in the subsurface, usually below fresh ground water, and is inadvertently produced when drilling for crude oil. It has little economic value and must be separated from the oil. Brine is typically disposed of by deep-well injection, however, potential threats to the environment result from improper handling, transport, and disposal practices.

### **2.1.2.2 Impacts of Brine Contamination on the Environment**

Brine releases disturb both the physical structure of the soil and alters the normal osmotic gradient existing between the soil and the plant roots (Burley, 1988). Soil structure is sensitive

**Table 2.2 Classification of Waster Based on TDS (mg/L) (Cates, 1993)**

<b>Classification</b>	<b>TDS, mg/L</b>
Fresh	0 - 1,000
Slightly Saline	1,000 - 3,000
Moderately Saline	3,000 - 10,000
Very Saline	10,000 - 35,000
Brine	> 35,000

**Table 2.3 Typical Concentrations (mg/L) of Ionic Constituents Present in Brine (Cates, 1993)**

<b>Descriptive Term</b>	<b>Constituent</b>	<b>Concentration (mg/L)</b>
Dominant	Na <sup>+</sup>	> 23,000
	Cl <sup>-</sup>	> 35,500
Major	Ca <sup>2+</sup>	> 4,000
	Mg <sup>2+</sup>	> 2,400
Minor	K <sup>+</sup>	> 40

to brine because the clay particles in the soil act as a sodium-sensitive ion exchange medium. Divalent calcium and magnesium ions bind negatively charged clay particles into aggregates. During a brine spill, these divalent cations are replaced by monovalent sodium which cannot preserve this aggregated state. The soil swells and disperses quite easily, resulting in excessive erosion. The reduction of pore space makes leaching of excess sodium difficult because the collapsed clay structure becomes impervious to water. Poor drainage results when the downward movement of water is impeded due to the low soil permeability. Salts migrate with the soil water and accumulate on the soil surface due to capillarity followed by evaporation. As salts accumulate, the osmotic gradient which exists between the soil and plant roots reverses, decreasing the availability of nutrients and water to plants (Pessarakli, 1991). Vegetation may deteriorate due to dehydration and nutrient deficiencies. The loss of vegetation makes the soil highly susceptible to erosion. The large quantity of soil particles carried by erosion, as well as the excess soluble salts leaching from a brine contaminated area, have detrimental effects on adjacent water bodies

### **2.1.3 Common Reclamation Strategies for Salt-Impacted Soils**

The most common methods used in the reclamation of salt-impacted soils include: (1) employment of an effective drainage system; (2) addition of appropriate soil amendments; and (3) planting salt-tolerant crops.

Soil drainage refers to both the speed and the efficiency with which water is removed from the ground surface. This can be achieved by either runoff or percolation through the soil to underground spaces (Pessarakli, 1991). Thus, when applying a drainage system, both the topography and the internal soil drainage are important factors to consider. Because most salts which interfere with plant growth are quite soluble, they can be leached and removed provided that there is proper drainage when water percolates through the soil.

Soil amendments recommended for rehabilitating salt-impacted soils generally consist of a calcium source, organic matter, and, if necessary, a pH adjuster. Calcium is required to displace sodium from the root zone. A traditional source of calcium is gypsum ( $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ ) because it is inexpensive and readily available. The amount of gypsum required will vary widely, depending upon the percentage of exchangeable sodium and the soil texture. It has a relatively low solubility; therefore, penetration to the root zone is relatively slow. The soil and added amendments should be well mixed by discing or tilling to promote chemical reactions between the added calcium source and the soil surface exchange sites. Additional mineral fertilizers may be required to provide essential nutrients for vegetation.

In addition to gypsum, an organic fertilizer may be needed. The essential plant nutrients (nitrogen, phosphorus, and potassium) may be provided by the addition of an organic waste material. The addition of an organic waste material serves as food for microorganisms and provides protection against surface moisture evaporation. Organic residue remaining in the soil after microbial digestion becomes soil organic matter which is immobile, and therefore does not cause a pollution problem (Rechcigl, 1995). Because water is known to bind to organic matter, this waste material can increase the water available to plants. Organic matter may influence the following physical properties of the soil; bulk density, aggregation and aggregate stability, soil water retention and porosity, hydraulic conductivity, and soil strength (Rechcigl, 1995). It also improves soil infiltration, tilth characteristics, as well as the cation exchange capacity.

Elemental sulfur is the most common amendment used to adjust the pH of alkaline soils.

However, sulfur must first be oxidized to sulfate. According to Rechcigl (1995), several diverse autotrophic bacteria of the *Thiobacillus* genus are the primary oxidizers of S in soil. The reaction is as follows:



The quantity of sulfur required to lower the soil pH into an acceptable range will depend on the initial pH of the soil, the desired pH of the soil, and the acid-buffering capacity of the soil.

The ability of plants to grow in salty soils depends on the properties of the plant, salt, and soil. Factors pertaining to the plant include its physiological makeup, its stage of growth, and its rooting habits (Brady, 1990). Typical salt tolerant plants include barley, Bermuda grass, fescue, salt grass, and wheat (Pessarakli, 1991). Other factors to consider include the salts which are present, their concentrations, and their distribution within the soil. Establishment of vegetation on damaged lands is imperative in order to prevent further degradation.

## **2.2 Fluidized Bed Ash (FBA)**

### **2.2.1 Background -- Coal Combustion for Energy Production**

One of the principal uses of coal in the United States is for generation of electricity. When coal is burned in the presence of an adequate amount of oxygen, carbon dioxide is produced, and as a result of this reaction, energy is generated. There are two problems associated with the combustion of coal which must be considered; (a) the huge amount of ash produced as a result of the combustion process, and (b) the possibility of emitting  $\text{SO}_x$  and other contaminants into the atmosphere.

In conventional boilers, combustion of coal produces three different kinds of coal combustion byproducts (CCB's) ash; fly ash, bottom ash, and boiler slag. Bottom ash and boiler slag are removed from the bottom of the coal-fired boiler, while fly ash exits with exhaust gases and must be removed by some type of particulate collection device (Burnet, 1987). Often, fabric bag filters or electrostatic precipitators are used to remove particulates.

The production of ash as a by-product has become an increasing environmental concern due to the problems associated with its collection and disposal. Utilities worldwide are currently producing more than 300 million tons of coal ash each year (Burnet, 1987). The United States alone is producing in excess of 100 nearly 50 million tons of fly ash annually ((American Coal Ash Association, 1998 Davidson, et. al., 1993). Disposal of coal combustion solid waste is not a small problem. Even if these wastes were environmentally benign, the quantities produced annually demand attention (Davidson, et. al., 1993). Presently, landfilling is the most common method of ash disposal. However, passage of the Federal Water Pollution Control Act (FWPCA) of 1972 and the Resource Conservation Recovery Act (RCRA) of 1976, have placed additional requirements on the disposal of coal ash due to the chemical and physical properties of the various ashes (Church, et. al., 1980). While there is no single answer for effective management of these wastes, finding alternative uses for these products is becoming increasingly attractive as an alternative to disposal. Clearly, it would be desirable to increase the utilization of fly ash and thereby decrease the amount to be disposed of.

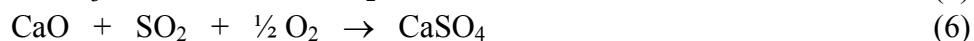
The second problem associated with coal combustion is the possibility of emitting pollutants such as  $\text{SO}_x$  and particulates into the atmosphere. Unfortunately, all fossil fuels, including natural

gas, coal, gasoline, and oil, are known to contain undesirable inorganic impurities which are converted to oxides that are considered additional air pollutants. At this time it is still not economically feasible to remove impurities prior to the combustion process; therefore, they must be dealt with during the combustion or post-combustion processes. To conform with EPA standards, all large coal-fired power plants constructed after September 1978 are required to employ effective desulfurization systems for removing pollutants from the exhaust gases (Smith and Harris, 1987). In most cases, fabric bag filters or electrostatic precipitators are installed in addition to flue-gas desulfurizers to eliminate the emission of particulates and sulfur oxides into the atmosphere.

### 2.2.2 The FBC Process

An alternative method for minimizing adverse air quality impacts is the atmospheric fluidized bed combustion (FBC) process. Fluidized bed technology was developed in Germany in the 1920's and has just recently been considered an emerging energy conversion process which allows high efficiency of energy conversion and minimization of adverse air quality impacts. The major advantage of FBC is that coal with a high sulfur content can be burned without the use of flue-gas desulfurization equipment, while still maintaining air quality standards (Grimshaw, et. al., 1985). The FBC process reduces a significant amount of environmental degradation associated with conventional energy production from coal; however, it also produces a significant amount of waste ash which must be disposed.

In the FBC process, crushed coal is burned, at a controlled velocity and an optimum temperature, in a turbulent bed of finely ground sorbent (typically ground limestone). These solids are held in suspension by an upward flow of air, thus exhibiting characteristics of a liquid (Stout, et. al., 1988). During combustion, any sulfur present in the parent coal is oxidized to sulfur oxides ( $\text{SO}_x$ ). When the limestone is exposed to heat during the combustion process, calcination takes place to form calcium oxide ( $\text{CaO}$ ). It is this calcium oxide which reacts with the sulfur oxides to produce  $\text{CaSO}_4$ . The reactions are as follows:



The sorbent requires in excess of the stoichiometric dosage to ensure a complete reaction with any combustion gas which may be present. Therefore, the fluidized bed ash produced is a granular material consisting of  $\text{CaSO}_4$ , unreacted  $\text{CaO}$ , coal ash, and small quantities of other mineral oxides due to their presence in the parent coal (Adriano, et. al., 1980).

### 2.2.3 Properties of FBA

The physical and chemical characteristics must be considered prior to using the ash for disposal. Fly ash is defined as the portion of ash produced during coal combustion that has a sufficiently small particle size allowing it to be carried away from the boiler in the flue-gas stream (El-Mogazi, et. al., 1988). It is composed mainly of silicaglasses and minerals enriched with trace metals (Kirby and Rimstidt, 1994). The properties of ash are dependent on the composition of the parent coal, conditions during combustion, efficiency of emission control devices, storage and handling of by-products, and climate.

Fluidized bed ash (FBA) consists of many small, irregularly-shaped particles ranging in size from 25 to 2000 micrometers in diameter, with specific gravities ranging from 2.65 to 3.05 g/cm<sup>3</sup> (Kilgour, 1992). Generally, the size of the particles depends on the sorbent material used, the fuel type, the temperature at which the coal is burned, and fluctuations in the operating conditions (Berry and Anthony, 1987).

The inorganic constituents of ash are typically those present in rocks and soils, primarily Si, Al, Fe, and Ca. FBA contains a significant amount of Ca due to the addition of limestone during the combustion process. Because coal is known to contain every naturally occurring element, small quantities of each of these may also be present in the ash material.

Most major elements tend to be present in relatively stable particle cores rather than on the surface of the particle where most chemical and physical reactions take place. It is thought that this is because these elements are not volatilized during combustion, but instead form a melt and remain in this condensed form (El-Mogazi, et. al., 1988). It is also hypothesized that other metals, such as Cd, Ni, Se, Cr, Ni, Zn, and Pb, become volatilized during combustion, then condense onto the surfaces of the ash particles as the flue-gas cools. These trace elements become concentrated on smaller particles due to their larger surface areas (El-Mogazi, et. al., 1988). This information becomes important when trying to determine which trace elements are more likely to become mobile. Other factors which influence the solubility characteristics of various species present in ash are the type of extractant, the ash-to-solution ratio, the number of extractions, and the length of the extraction time (El-Mogazi, et. al., 1988).

#### **2.2.4 Disposal versus Use**

Over 70 percent as stated earlier, of the 1050 million tons of ash produced in the U.S. annually, 80% is disposed of as a solid waste. Currently, landfilling is the major means of disposal. However, even this practice is becoming more difficult due to the scarcity of available land, the high costs of the disposal operations, and the possibility of contaminating surface and ground waters (Sheih, 1990). While landfilling remains the least expensive disposal option, new regulations designed to protect surface and ground waters are calling for careful and, consequently, more costly solid waste disposal methods.

The most significant piece of legislation impacting the disposal of coal residue is the Resource Conservation and Recovery Act (RCRA) of 1976. This and the subsequent enactment of the Clean Water Act (CWA) in 1977 imposed serious constraints on ponding ash which was the primary means of disposal at the time (Burnet, 1987). The United States Environmental Protection Agency established drinking water standards which aid in the classification of hazardous solid waste based on concentrations of components found in their leachates. Currently, fly coal ash residues have been exempted from being classified as a hazardous waste; FBA is still being studied pending further study. These decisions were based on a study performed on coal residue using two leaching tests; (1) the EPA Toxicity (TCLP) test, and (2) the ASTM Standard Method B 3987-81 (Burnet, 1987). Results of these tests revealed very low levels of elements present in the leachates. In fact, most were well below drinking water standards. This is expected to lead to a permanent nonhazardous classification of coal ash (Burnet, 1987).

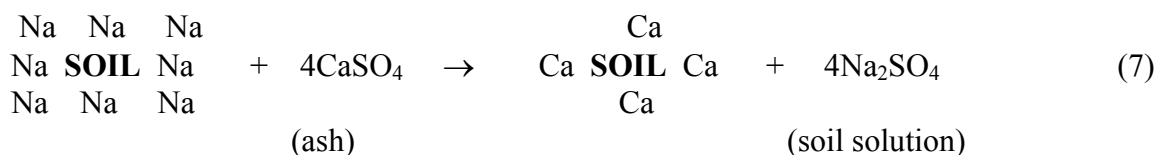
The ever-increasing amount of ash waste that must be disposed of each year is creating a tremendous dilemma. Only about 320% of fly ash waste is being used each year; thus fly ash is the largest fraction of coal residue and is the least utilized. Perhaps the main reason for not utilizing

more of the coal ash waste is the presence of more abundant and inexpensive raw materials. Minimization and utilization are two viable approaches to solving the problems associated with any waste. The most common uses for coal fly ash are as a construction material. These uses include: manufacture of concrete, fill for various construction sites, production of lightweight aggregates, and road base stabilization (Smith and Harris, 1987). Other less extensive uses of coal fly ash include sanitary landfill covers and liners, strip mine reclamation and soil conditioning.

### 2.3 FBA as an Amendment for Brine Disturbed Soils

Brine contaminated soils are very susceptible to erosion. The two main reasons for this are (1) replacement of divalent cations by sodium which creates a dispersive soil, and (2) loss of vegetation due to osmotic effects that impact water and nutrient uptake. The reclamation of brine contaminated soils requires the following: (a) the establishment of an effective drainage system, (b) the replacement of exchangeable sodium by divalent cations (namely, calcium), (c) the addition of organic matter to improve soil structure and aggregation, (d) a soil pH adjuster, and (e) establishment of vegetation to prevent further degradation.

Because of the FBC process, FBA contains a significant amount of calcium as well as other mineral oxides. As seen in Table 2.4, the main constituents of FBA are  $\text{CaSO}_4$ ,  $\text{CaO}$ , and  $\text{CaSO}_3$ . The abundance of calcium in FBA makes it useful for the replacement of monovalent sodium. The Ca provided from the FBA reacts with the sodic soils as follows:



It should be noted that  $\text{CaSO}_4$  is much more soluble than  $\text{CaO}$  and  $\text{CaSO}_3$  which must be further oxidized to  $\text{CaSO}_4$ .

While FBA is not a practical source of essential plant nutrients (nitrogen, phosphorus, and potassium), it can serve as a supplementary supply of micro nutrients in the form of trace elements to the soil. Important micro nutrients typically found in FBA include iron, manganese, boron, copper, and zinc (Stout, et. al., 1988). All of these elements are required by plants in small amounts. Analyses have shown that FBA contains most of the essential nutrients required for plant growth; however, if they are excessive or disproportionate in the soil, they can become toxic to plants or animals (Stout, et. al., 1988). Stout, et. al., (1988) further states that no phytotoxic effects of micro nutrients have been observed when FBA was used as a lime source. Adriano, et. al., (1980) stated that both field and greenhouse studies indicated that CCBs fly ash might benefit plant growth and could improve agronomic properties of the soil. In most cases, the ash is added to the soil at a rate of less than 5-10% by weight. Addition of FBA has also been shown to increase the water holding capacity of the soil. Rechcigl (1995) suggests that this increase could be partly due to the particle size, as well as the porosity of the FBA particles. Although the addition of FBA may change the water-holding capacity, it may not appreciably change the amount of water available to plants (El-Mogazi, et. al., 1988). Other factors affected by the addition of FBA include pH, soluble salt content, soil texture, bulk density, moisture content, and exchangeable capacity (Wyrley-Birch, et. al., 1987).

**Table 2.4 Mineralogical Analysis of a Typical Fluidized Bed Combustion Waste (Rechcigl, 1995)**

<b>Constituent</b>	<b>FBC (% by weight)</b>
CaSO <sub>4</sub>	52.00
CaSO <sub>3</sub> · ½H <sub>2</sub> O	0.60
CaO	33.00
MgO	0.80
NaCl	0.30
P <sub>2</sub> O <sub>5</sub>	0.02
Fe <sub>2</sub> O <sub>3</sub>	4.50
SiO <sub>2</sub> + insolubles	7.00



### 2.3.1 Environmental Considerations

Important considerations to take into account when selecting an appropriate application rate of FBA include its effect on pH, soil microbial activity, heavy metal loadings, pollution of surface and ground waters, and possible cementing or impedance of water flow due to the pozzolanic properties of the ash (Wyrley-Birch, et. al., 1987). Typically, the application rates are so low that the possibility of cementing is negligible.

The first concern when using FBA as a soil amendment is the effect it has on soil pH. FBA contains many alkaline oxides, particularly CaO, which makes it a good substitute for agricultural limestone. The total lime content, expressed as the neutralizing potential of the material compared to an equal amount of ground limestone ( $\text{CaCO}_3$ ), ranges from 31 to 100%, averaging 60% (Rechcigl, 1995).

When CaO comes in contact with water,  $\text{Ca(OH)}_2$  is produced as shown below:



This reaction causes highly alkaline conditions and may result in pH's as high as 12 to 12.5. Depending on the initial pH of the soil, a pH adjuster will probably be necessary to lower the pH to an acceptable value. Plants require a relatively neutral pH (6.5 to 7.2) so it is imperative that the pH be monitored closely. If the pH is elevated above this acceptable range, elemental sulfur may be used to counteract this effect. Elemental sulfur can be oxidized by microbial activity to yield acidic conditions as described in a previous section.

According to Rechcigl (1995), the addition of ash may also interfere with microbially mediated processes of organic matter decomposition and the cycling of nutrients such as C, N, S, and P in the biosphere. This inhibition has been primarily attributed to the effects the FBA has on pH and electrical conductivity in the soil. Other investigations have suggested that the decrease in soil microbial activity could be due to the toxic concentrations of Cd, Cr, and Zn (Rechcigl, 1995). However, the addition of an organic amendment with low C:N ratio will increase the organic matter content and CEC and result in greater microbial activity (Rechcigl, 1995). It should be noted that effects on microbial activity are negligible at low application rates ( $< 10$  to 12%).

Another concern when using FBA as a soil amendment is the possibility of polluting nearby surface and ground waters with heavy metal impurities which may be present in the coal prior to combustion. Several studies have reaffirmed that FBA is not a toxic substance based on the USEPA TCLP test. In Table 2.5, the leaching potential of FBA is compared with the National Primary Drinking Water Standards (NPDWS) and the Oklahoma Water Quality Standards (OWQS) for acute and chronic toxicity in Table 2.5. All toxic metals are below the NPDWS and OWQS standards except Cr, which is nearly twice the standard. However, it has been shown that if FBA is applied to soil at moderate rates ( $< 2$  to 5%), the potential contamination of ground water by toxic metals is not a concern (Rechcigl, 1995).

Ground and surface water pollution is not the only concern heavy metals pose on the environment. Other concerns include crop effects, risk to livestock, and potential food chain bioaccumulation. Consequences from excessive levels of metals in soil depend on numerous complex reactions between the trace ions and components of soil, i.e., solid, liquid, and gaseous phases (Rechcigl, 1995). Acceptable concentrations of trace metals in surface soils will vary depending on the local condition of the soil and the land use. Currently, most research involving

**Table 2.5 Leaching Potentials (mg/L) of Fluidized Bed Ash for Toxic Metals in Relation to the National Drinking Water Standards (NPDWS) (Rechcigl, 1995)**

Toxic Metal	FBA	NPDWS	OWQS	
			Acute	Chronic
As	< 0.04	0.05	0.36	0.19
Ba	< 1.00	1.00	NA	NA
Cd	< 0.01	0.01	formula*	formula
Cr	0.09	0.05	NA	0.05
Pb	< 0.04	0.05	formula	formula
Hg	0.0005	0.002	0.0024	0.0013
Se	0.001	0.01	0.02	0.005
Ag	< 0.04	0.05	NA	NA

\* Standards for cadmium and lead are calculated using stream hardness concentrations.

heavy metals loadings has been in relation to the application of sewage sludge on agricultural land. Stout, et. al., (1988) indicate that FBA has very low levels of heavy metals compared to sewage sludge. Stout, et. al., (1988) also suggest that the oxide form of heavy metals in FBA renders them much less available to plants than the organic forms present in sewage sludge. Table 2.6 shows acceptable ranges of nutrients and heavy metals in soils, as well as ranges present in a typical sample of FBA. It is important to note that the levels of heavy metals in FBA are within ranges normally found in soils. Still, it is important that these heavy metals loadings not exceed loadings recommended for sewage sludge as shown in Table 2.7 (Stout, et. al., 1988).

**Table 2.6 Average Concentrations ( $\mu\text{g/g}$  of dry material) and Typical Ranges for Some Components Found in Fluidized Bed Ash and Soils (Stout, et al., 1988)**

		FBA	SOILS		
(Micrograms per gram of dry material)					
Group	Component	Average	Range	Average	Usual Range
Essential plant nutrients	Ca	380,000	240,000 - 460,000		
	Mg	7,100	5,000 - 12,000		100 - 1,500
	K	2,500	500 - 8,000		
	P	430	380 - 500		400 - 3,000
	Fe	11,000	800 - 16,000	----	14,000 - 40,000
	Mn	485	210 - 685	850	200 - 3,000
	Mo	0.19	0.12 - 0.28	2	0.2 - 5
	B	110	95 - 170	10	2 - 100
Heavy Metals	Cu	15	12 - 19	20	2 - 100
	Zn	55	29 - 105	50	10 - 300
	Ni	21	13 - 29	40	5 - 500
	Pb	3.2	1.5 - 7.5	10	2 - 200
	Cd	0.5	----	0.5	0.01 - 0.70
	Cr	15	9 - 23	200	5 - 1,000
Phytotoxics	Se	0.29	0.16 - 0.58	----	0.1 - 2
	Al	10,000	4,000 - 20,000	----	14,000 - 40,000

**Table 2.7 Maximum Cumulative Heavy Metal Loadings on Soil (pounds/Acre) Based on Textural Class of Soil (Stout, et al., 1988)**

<b>Heavy Metal</b>	<b>Loamy sand, sandy loam</b>	<b>Fine sandy loam, very fine sandy loam, loam, silt loam</b>	<b>Silt, clay loam, sandy clay loam, silty clay loam, sandy clay, silty clay, clay</b>
	<b>----- Pounds per Acre -----</b>		
Cd	2	3	4.5
Zn	50	150	300
Cu	25	75	150
Ni	10	30	60
Pb	100	300	600
Cr	100	300	600

### **3.0 METHODOLOGY (Pyle, 1996)**

#### **3.1 Site Characterization Studies**

An initial site assessment was necessary to provide background information and to determine the extent of damage caused by brine at the Clearview site. The site assessment included the following: development of a surface soil sampling plan, analysis of control and composite soils, and assessment of water quality of nearby creeks.

##### **3.1.1 Field Sampling and Analyses**

###### **3.1.1.1 Soil Samples**

The soil samples used in this study were collected at the Clearview site under the supervision of John Haberer, the Soil Scientist at the Okfuskee County Conservation District (OCCD).

###### **3.1.1.2 Water Samples**

Water samples were collected from bodies directly affected by the brine damaged land at the Clearview site. Sampling locations were chosen in collaboration with Dan Butler, Aquatic Biologist, with the Oklahoma Conservation Commission - Water Quality Division (OCC-WQD).

###### **3.1.1.3 Sampling Methodology**

Environmental sampling can be tedious because the materials being sampled are quite variable and complicated. It is imperative to develop precise sampling protocols to ensure valid and accurate data. Table 3.1 is an outline of a general sampling protocol for environmental applications (Keith, 1988).

###### **3.1.1.4 Soil Sampling Methodology**

Soil sampling locations were determined in collaboration with the area soil scientist at OCCD. Soils were collected for two purposes: (1) to provide a general profile of the affected area, and (2) to provide a representative composite sample to be used in the laboratory studies.

###### **3.1.1.5 Soil Profile**

The soil profile was examined to give a general idea of the extent of brine contamination in the affected area. The constituents of concern included pH, EC, total and extractable calcium and sodium, chloride, and sulfate. These parameters were chosen because of their importance in defining brine contaminated soils.

Soil samples were taken at 21 different locations as shown in Figure 3.1. Sampling sites 1 and 2 were chosen to obtain control or unaffected soil samples. These samples were used as a comparison to determine the extent of damage of the affected area. Sites 3 through 13 were chosen to determine spatial variability related to the movement of contaminants as they travel the Clearview Creek corridor. Sites 14 through 21 were chosen for comparison with existing data collected by OCCD in 1989.

At each site, samples were taken from two different depths; (1) 0 to 6 inches, and (2) 6 to 12 inches. Thus, a total of 42 soil samples were collected. Rocks and vegetation were

**Table 3.1 Outline of a Generalized Sampling Protocol (Keith, 1988)**

<b>Main Point (Program Purpose)</b>	<b>Subelements</b>
Analytes of interest	Primary and secondary chemical constituents and criteria for representativeness
Locations	Site, depth, and frequency
Sampling points	Design, construction, and performance evaluation
Sample collection	Mechanism, materials, and methodology
Sample handling	Preservation, filtration,, and field control samples
Field determinations	Unstable species and additional sampling variables
Sample storage and transport	Preservation of sample integrity

**Figure 3.1 Sampling Locations for Soils Collected at the Clearview Site for a Soil Profile**



cleared from the surface prior to sampling. Soil samples were collected using a hand auger, then transferred to plastic sample bags with an airtight seal. The samples were transported to the laboratory and immediately prepared for chemical analysis. The samples were allowed to air-dry, then pulverized using a porcelain mortar and pestle and passed through a No. 40 sieve. The sieved soil samples were placed back in plastic sample bags until analyzed.

#### **3.1.1.6 Composite Soil Sample**

A composite sample was collected for both physical and chemical analyses. The physical parameters of concern were moisture content, particle size, bulk density, plastic and liquid limits, and dispersivity. The chemical parameters analyzed were pH, electrical conductivity (EC), nutrients, cation-exchange-capacity (CEC), exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), selected metals, and selected anions. Analytical procedures utilized are outlined in Appendix BA.

Composite sub-samples were collected at four different locations within the affected area, as shown in Figure 3.2. The other four locations were chosen along the Clearview Creek corridor and composited to represent a worst-case scenario. The sample collected outside the area served as a control.

Soil samples were collected from a depth interval of 0 to 8 inches using a shovel. This depth interval was chosen because it represents the plow layer, which is the layer of concern when reclaiming agricultural land. The composite sub-samples were collected, transported, and prepared as described in the previous section. The composite sample was prepared with equal weights of the four individual sub-samples.

#### **3.1.1.7 Water Sampling Methodology**

The water monitoring program was designed to assess the impacts of the brine contaminated site on adjacent water bodies. As seen in Figure 3.3, Clearview Creek flows directly through the affected area and then into Alabama Creek. Existing data collected from these creeks has shown elevated concentrations of dissolved ions commonly present in brine; therefore, many of the water samples were analyzed for parameters traditionally associated with brine. Samples were also analyzed for basic water quality parameters.

The sampling locations were chosen to determine impacts on both Clearview Creek and Alabama Creek. The four locations are shown in Figure 3.3. Site 1, located on Clearview Creek immediately downstream from the affected area, was chosen to determine the quality of water exiting the Clearview site. Site 4, located downstream from the confluence of Clearview and Alabama creeks, was chosen to assess the impacts of Clearview Creek on Alabama Creek. Sites 2 and 3 were chosen to assess the water quality of Clearview Creek and Alabama Creek prior to influence from the Clearview site.

Grab samples were collected on a monthly basis at each sampling location. The samples were collected in 500 ml polyethylene bottles. The bottle lids were also polyethylene and had a polyethylene foam liner to prevent leakage. Both the bottles and caps were rinsed several times in the creek, slightly downstream, to prevent stirring up sediment at the actual sampling location. For collection, the bottles were submerged, filled until no head space was left, and then capped tightly.

**Figure 3.2 Sampling Locations of Soil Collected at the Clearview Site for Laboratory Studies**

**Figure 3.3 Water Sampling Locations at the Clearview Site**

Samples were also taken following high-flow events using a single-stage sampling device. The device consists of a sample container, an air exhaust, an intake, and a bottle seal. A diagram of these components is shown in Figure 3.4 (OCC-WQD, 1995). The samplers were constructed by

attaching a series of sampling components to a 2" x 8" wooden board. The components were attached so that the intakes were at one foot intervals from the creek bottom. The samplers were installed and maintained according to OCC-WQD guidelines (OCC-WQD, 1995). The samples were collected in half-gallon polyethylene bottles and were composited based on volume following OCC-WQD Standard Operating Procedure (SOP) No. 4 (OCC-WQD, 1995).

When the surface of the water rises to the level of the intake nozzle, water enters the sample bottle. As the creek rises, the water in the intake also rises. As shown in Figure 3.4 (OCC-WQD, 1995), when the elevation of the water level "W" reaches the crown of the intake "C", flow starts over the weir of the intake and siphons water into the sample bottle. The bottle continues to fill until the sample rises to the fill mark "F", and water is forced up to the air exhaust to the elevation of the creek "W". As the creek rises to the level of the exhaust port "D", air is trapped in the air exhaust. No flow can pass through altering the original sample as long as sufficient air remains in the tubes. The exact dimensions used for the single-stage samplers are shown in Figure 3.4 (OCC-WQD, 1995). These dimensions were specific for low-velocity sampling (i.e., velocities less than 4 fps).

### **3.1.2 Field Analyses**

Several basic water quality parameters were measured in the field at the time of sample collection. These parameters include; electrical conductivity (EC), temperature, pH,  $E_h$ , dissolved oxygen (DO) and alkalinity. All field measurements followed Standard Operating Procedures (SOP's) as outlined by the OCC-WQD. Field determinations were made at the same locations as the samples collected for laboratory analyses.

### **3.1.3 Laboratory Measurements**

For every sampling episode, three water samples were collected at each location. The samples were labeled as follows: (1) Parameters, (2) Nutrients, and (3) Metals. The parameters sample was collected for turbidity, total suspended solids (TSS) and total dissolved solids (TDS), and anions analyses. The nutrients sample was collected for ammonia, total Kjeldahl nitrogen (TKN), and total phosphorus (TP) analyses. This sample was preserved by the addition of 1 mL of concentrated sulfuric acid ( $H_2SO_4$ ). The metals sample was collected for selected total metals analyses and was preserved by the addition of 2 mL of concentrated heavy-metals-grade nitric acid ( $HNO_3$ ). All samples were placed on ice until they were transported to the laboratory. They were stored in a 4°C refrigerator until analysis. Table 3.2 is a list of preservation methods and holding times for all sample analyses used in this study (USEPA, 1983). Analytical procedures are outlined in Appendix BA.

## **3.2 Rehabilitation Design Studies**

### **3.2.1. Materials**

The soil amendments considered in this study included; (a) fluidized bed ash (FBA), (b)

**Figure 3.4 Diagram of Sample Components and Dimensions Used in the Single-Stage Sampler**  
**Table 3.2 Preservation and Holding Times Required for Water Analyses (USEPA, 1983)**

Measurement	Preservative	Holding Time
Turbidity	Cool, 4°C	48 Hours
TSS/TDS	Cool, 4°C	7 Days
Chloride	Cool, 4°C	28 Days
Nitrate	Cool, 4°C	48 Hours
Phosphate	Cool, 4°C	48 Hours
Sulfate	Cool, 4°C	28 Days
Ammonia	Cool, 4°C H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 Days
Total Kjeldahl Nitrogen	Cool, 4°C H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 Days
Total Phosphorus	Cool, 4°C H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 Days
Total Metals	Cool, 4°C HNO <sub>3</sub> to pH < 2	6 Months

gypsum, (c) sulfur dust, and (d) turkey litter. The FBA was provided by Brazil Creek Minerals Inc, located in Fort Smith, Arkansas. The gypsum and sulfur were purchased from a local nursery. The brand of gypsum used was Hoedown analytical grade 0-0-0, with 23.00% Ca and 16.50% S from  $\text{CaSO}_4$ . The brand of sulfur used was Hi-Yield wettable dusting sulfur with the active ingredients being 90.0% sulfur and 10.0% inert ingredients. The turkey litter was provided by Hollingsworth Litter Service located in Springdale, Arkansas. Analysis of the litter was provided with the sample. The analysis was done by the Cooperative Extension Service at the University of Arkansas, Department of Agriculture. The broiler litter contained 56 pounds/ton N, 48 pounds/ton  $\text{P}_2\text{O}_5$ , 36 pounds/ton  $\text{K}_2\text{O}$ , and had a moisture content of 30%.

### **3.2.2 Soil Amendment Application Rates**

This section describes the procedures used to determine the application rates of the four amendments (i.e., FBA, gypsum, turkey litter, and sulfur). Soil pH was the main criterion used to determine the optimum application rate in the batch studies. All batch studies were conducted on both the control and the composite soil samples.

#### **Gypsum**

The gypsum application rate was determined based on literature values and the rate suggested by the manufacturer.

#### **Turkey Litter**

The turkey litter application rate was based on literature values and suggestions from the Oklahoma Cooperative Extension Service.

#### **FBA**

Batch studies were conducted to determine the optimum application rate for FBA. The first batch study consisted of soil and FBA only. 100 grams of soil was used per sample. FBA was added at the following application rates; (a) 0.1%, (b) 0.5%, and (c) 1.0% by weight. The samples were mixed well and deionized water was added to make a saturated soil paste. The pH of the mixture was measured immediately and in 24 hours to determine the time-dependent effects FBA has on the soil pH. This study was performed in duplicate.

The second batch study consisted of soil, FBA, gypsum, and turkey litter. 300 grams of soil was used for this batch. This batch was similar to the first except gypsum and turkey litter were added to determine the pH effects they had on the system. Gypsum was added at an application rate of 9 tons/acre or 2.13 g/300 g of soil. Turkey litter was added at an application rate of 30 tons/acre or approximately 7.5 g/300 g of soil. FBA was varied at the following application rates; (a) 2 lbs/acre 0.1%, (b) 10 lbs/acre 0.5%, and (c) 20 lbs/acre 1.0% by weight. The samples were mixed and the pH was measured of the saturated soil paste. This study was performed in duplicate.

The third batch study was identical to the second, but sulfur dust was added to help lower the pH of the system. Gypsum and turkey litter were added at the same application rate as above. FBA was added at 2 and 10 lbs/acre 0.1% and 0.5%. The pH of the batches were measured over a 17 day period or until the pH was within an acceptable range for plant growth. This study was performed in duplicate.

Other information considered for determining the application rate of FBA included metals

analyses performed on the soil and FBA.

### **Sulfur**

A batch study was also conducted to determine the optimum application rate of sulfur dust. Gypsum and turkey litter were added at the same application rates discussed previously. FBA was added at an application rate of 20 lbs/acre 1% by weight. Sulfur dust was added at 1, 5, and 10 tons/acre. The pH values of the batches were measured until they reached a level acceptable for plant growth or 24 days, whichever came first.

#### **3.2.3 Leach Studies**

Leach studies were conducted to determine concentrations of soluble metals leachable from the amendments applied to the soil at the Clearview site. The samples were as follows: soil only; soil plus each individual amendment; soil plus FBA, sulfur, and turkey litter; soil plus gypsum, sulfur, and turkey litter; and soil plus all amendments. Various combinations of these amendments were added for comparative studies. The amendments were incorporated at the optimum application rates as determined from the batch studies. The studies included both control and composite soil samples, and each was performed in triplicate. The samples were shaken for 24 hours in polyethylene bottles at a 1:10 solid:liquid ratio using deionized water as the extract solution. Following each 24 hour cycle, the samples were centrifuged and filtered through a 0.45 micron cellulose membrane filter. A fresh extract solution was added for the next 24 hour shake cycle. This procedure was repeated a third time. The extracts were analyzed for the following chemical properties: pH, EC, selected soluble metals (Ca, Na, K, Mg, Cd, Pb, Cu, Cr, Fe, Se, and Zn), and selected soluble anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ ) according to the methods described previously.

### **3.3 Rehabilitation Plan Implementation**

Site rehabilitation activities included earthwork, adding soil amendments, and revegetation. The high walls created by years of erosion were reduced to < 6 degree slope. Culverts and drop structures were placed in the deep gullies, and diversion ditches were installed to retard incoming overland flow from surrounding fields. The existing channel of Clearview Creek was leveled off to provide a stream bed capable of transmitting a large volume of water over a wide area. Accumulated trash was buried on site, away from the drainage area. After the land had been brought to an acceptable shape, it was tilled and prepared to receive the soil amendments. The amendments were added in the following order: FBA, gypsum, sulfur dust, and turkey litter. Following each amendment, the land was disced to incorporate the amendment into the soil. Bermuda grass (*Cynodon dactylon*) was then sprigged on the reclaimed land. After sprigging, the land was covered with hay mulch to protect the loose soil and amendments from erosion. Prior to the second growing season, hay bales were anchored in isolated locations to reduce runoff and erosion in areas where vegetative cover had not been established.

#### **3.3.1 Materials**

The materials utilized during rehabilitation included the native soils, FBA, gypsum, sulfur dust, turkey litter, and Bermuda grass.

#### **3.3.2 Loading Rates**



During field implementation, the loading rates for all of the soil amendments were identical to those used in the laboratory studies described previously.

### **3.4. Post Implementation Monitoring Plan**

#### **3.4.1 Water Sampling**

The water quality-monitoring program was designed to determine the impacts of the brine-affected area on receiving water bodies. It is important to note that Clearview Creek is an intermittent stream. During prolonged periods without rain, the water table drops below the level of the Clearview Creek channel, leaving only isolated pools separated by the dry creek bed. Even though no measurable flow can be determined between the surface pools, subsurface flow can continue to transport contaminants down the creek channel. Even during dry periods, contaminants can migrate, eventually discharging into Alabama Creek. Therefore, the creeks were monitored on a monthly basis to account for seasonal fluctuations. During periods of low flow, the water sampling stations sometimes did not yield sufficient quantities of water to provide representative samples.

#### **3.4.2 Fluid Levels**

Fluid levels were measured daily at the four surface water sampling locations for a period of nine months; two months prior to remediation and seven months after remediation. Rating curves (i.e., stage versus discharge) for Alabama and Clearview Creeks have not been developed; hence, flow rates can not be calculated from the fluid level measurements.

## **4.0 RESULTS AND DISCUSSION**

### **4.1 Site Soils**

Results of soil sample chemistry taken at two different depths (i.e., 0 to 6 inches and 6 to 12 inches) are shown in Tables 4.1. and 4.2, respectively. Soluble salt concentrations are expected to accumulate in surface soils due to capillary movement of water followed by evaporation; however, no correlation could be made with the soil samples. It was also difficult to correlate the elevated concentrations and the movement of contaminants down the Clearview Creek corridor. Soils within the affected area were found to be surprisingly variable from one location to the next, making it difficult to develop isoconcentration contour maps.

Ratios of sample concentrations to the maximum concentration were calculated for selected data (e.g., EC, chloride, and soluble sodium of the soils sampled at 0 to 6 inches) and compared to their distance from a reference site, or site 17 (See Figure 3.1). The samples located down the length of the affected area were used for comparison (i.e., samples from sites 3,4,5,6,8,10,11,12,13, and 17). As observed in Figure 4.1, the contaminant concentrations for EC, chloride, and soluble sodium generally increase with distance from site 17. This can be explained due to their proximity to the Clearview Creek corridor. Those samples taken close to the drainage area are highly concentrated because the contaminants are transported down this drainage channel during rain events. The creek is seasonal and will run dry when there is little precipitation. As the water evaporates, the soluble salts are left behind to precipitate on the soil surface, resulting in high concentrations of salts.

### **4.1.2 Composite and Control Soil Samples**

#### **4.1.2.1 Physical Properties**

The physical soil properties of concern included; soil moisture content, bulk density, soil texture, liquid and plastic limits, and dispersivity. The results of these analyses are shown in Table 4.3 for both the composite and control soil samples.

Soil texture of the control and composite samples was determined using the hydrometer method. As shown in Table 4.4, the control sample was a sandy loam and the composite sample was a clay loam. The elevated clay content of the composite soil was assumed to be due to weathered parent material and deposited material which had accumulated over time due to the extensive erosion within the affected area. The pinhole test results for the control sample were inconclusive due to its low clay content.

Bulk densities were determined using two different methods; the excavation method and the clod method. These methods gave inconsistent results. The bulk density of the control sample, at a moisture content of 16.1%, was 1.77 and 1.31 g/cm<sup>3</sup>, as determined by the excavation and clod methods, respectively. The composite sample was determined to have a bulk density of 1.62 and 1.50 g/cm<sup>3</sup>, at a moisture content of 14.4%. The discrepancies of the data obtained by the two different methods could be due to experimental error. Specifically, in the excavation method it was imperative to find a level area since the volume of the excavation was measured by dispensing water from a graduated cylinder. Because of the excessive erosion at the Clearview site, it was difficult to find a level area at some sampling locations.

**Table 4.1 - Selected Chemical Analyses of a Surficial (0 to 6 inches) Soil Plan of the Affected Area at the Clearview Site**

Site	pH	EC (mS/cm)	Cl <sup>-</sup> (ppm)	SO <sub>4</sub> <sup>2-</sup> (ppm)	Soluble Ca <sup>2+</sup> (ppm)	Total Ca <sup>2+</sup> (ppm)	Soluble Na <sup>+</sup> (ppm)	Total Na <sup>+</sup> (ppm)
1	8.1	0.384	41	40	45	653	14	41
2	7.9	0.480	134	27	200	1,021	72	179
3	7.4	47.1	20,866	81	551	3,030	6,690	8,692
4	7.5	36.1	14,336	185	1,530	7,726	5,575	9,509
5	7.1	46.8	7,391	112	1,101	5,890	7,680	11,309
6	7.2	80.6	11,746	162	1,168	5,876	13,235	17,781
7	7.2	62.3	9,232	412	1,222	6,257	10,150	10,912
8	7.6	43.4	10,290	117	459	2,542	6,664	8,779
9	7.6	9.0	1,214	605	2,795	9,372	961	1,441
10	7.6	39.2	9,245	192	653	2,934	6,838	9,524
11	7.8	24.4	4,921	61	472	2,551	2,657	3,724
12	7.3	0.378	62	22	2,713	14,956	116	184
13	7.7	19.8	4,069	58	1,289	6,852	3,197	4,697
14	7.7	2.95	358	2,007	391	1,711	438	545
15	7.7	6.11	2,250	1,507	398	2,222	1,386	1,426
16	7.7	10.8	3,392	95	411	3,216	2,982	3,105
17	7.2	17.0	6,406	299	442	2,272	2,662	5,418
18	7.5	11.7	3,941	103	391	2,034	1,891	3,523
19	6.7	40.5	18,929	63	453	3,111	6,027	9,001
20	6.7	.981	3,028	56	764	4,973	13,647	22,996
21	7.4	21.9	8,399	80	716	4,721	3,575	5,788

**Table 4.2 - Selected Chemical Analyses of a Soil Plan (6 to 12 inches) of the Affected Area at the Clearview Site**

Site	pH	EC (mS/cm)	Cl <sup>-</sup> (ppm)	SO <sub>4</sub> <sup>2-</sup> (ppm)	Soluble Ca <sup>2+</sup> (ppm)	Total Ca <sup>2+</sup> (ppm)	Soluble Na <sup>+</sup> (ppm)	Total Na <sup>+</sup> (ppm)
1	7.7	.152	11	19	10	179	11	38
2	7.4	.559	131	29	69	736	110	180
3	7.6	27.1	10,675	46	1,238	4,049	3,880	6,408
4	7.6	25.9	5,324	96	2,003	6,715	4,157	7,422
5	7.0	42.0	4,297	58	1,824	5,567	5,349	6,710
6	7.7	45.2	10,002	155	1,664	5,113	7,597	9,447
7	7.0	17.1	3,517	124	1,982	6,441	2,197	2,690
8	7.6	14.4	2,522	81	399	2,132	2,134	3,321
9	7.5	17	2,417	2,020	4,226	15,255	2,417	4,121
10	7.8	5.81	844	124	1,621	2,771	1,312	1,907
11	7.3	27.7	6,192	46	367	1,931	4,327	7,652
12	8.0	1.04	40	29	1,998	3,429	164	316
13	7.4	18.5	3,692	64	2,001	5,852	2,757	4,697
14	7.5	6.79	221	6,265	256	1,334	1,662	2,071
15	7.5	6.92	1,670	1,924	1,184	2,186	1,584	2,059
16	6.8	31.2	13,581	172	786	1,978	4,660	6,023
17	7.3	19.4	8,166	346	840	1,799	2,919	5,351
18	7.3	18.1	7,287	82	2,129	3,035	6,027	7,953
19	7.3	29.7	14,066	42	1,116	2,899	5,291	6,574
20	7.6	8.56	3,199	39	712	4,115	1,628	1,992
21	7.3	26.3	11,348	61	801	4,671	4,295	7,475

**Figure 4.1: Ratio of Soil Concentrations to Maximum Concentrations versus Distance From Sample Site 17 (adapted from Pyle, 1996)**

**Table 4.3      Various Physical Properties of the Clearview Soil.**

	<b>Soil Sample</b>	
<b>Parameter</b>	<b>Control</b>	<b>Composite</b>
Soil Moisture Content (%)	16.1 ± 0.35	14.4 ± 1.5
Bulk Density - In Situ (g/cm <sup>3</sup> )	1.77	1.62
Bulk Density - Clod (g/cm <sup>3</sup> )	1.31 ± .01	1.50 ± .01
Particle Size Analysis - Hydrometer	Sandy loam	Clay loam
Liquid Limit (%)	21.8	25.1
Plastic Limit (%)	14.7	17.4
Plasticity	7.1	7.7
Dispersivity	Not dispersive	ND3 - Slightly dispersive

**Table 4.4      Textural Analysis of the Clearview Soil.**

	<b>Soil Sample</b>	
<b>Parameter</b>	<b>Control</b>	<b>Composite</b>
Clay (%)	14	36
Silt (%)	31	28
Sand (%)	55	36
Classification	Sandy loam	Clay loam

#### 4.1.2.2 Chemical Properties

The results of the soluble salts and nutrients analyses are shown in Table 4.5. As expected, concentrations of most constituents typically found in brine were substantially higher in the composite sample than in the control sample. The parameters most significantly influenced by the brine contamination included conductivity, sodium, and chloride concentration.

The negative and positive charges in the soil solution must be equal according to the condition of electroneutrality. The concentrations of soluble cations and soluble anions, in meq/L, were summed for both the control and composite soil samples. The cation-anion charge balance error (CBE) was calculated for each soil sample using the following equation (Cates, 1993):

$$\text{CBE} = \{(\Sigma \text{Cations} - \Sigma \text{Anions}) / (\Sigma \text{Cations} + \Sigma \text{Anions})\} \times 100. \quad (22)$$

The CBE calculated for the control sample was less than 0.1%; whereas, the CBE calculated for the composite sample was approximately 9%. This slight charge imbalance for the composite sample is probably due to incomplete analysis for all cationic species.

The higher pH value for the composite soil sample can be attributed to the elevated sodium concentrations. The sodium-soil complex (micelle) undergoes hydrolysis according to the following reaction (Brady, 1990):



In turn, the released sodium ions have adverse effects on plant metabolism and nutrient uptake.

Exchangeable cations, cation exchange capacities, exchangeable sodium percentages, and sodium absorption ratios of the soils are shown in Table 4.6. The data suggests that the composite sample is a saline-sodic soil based on the EC and ESP values.

The results of total metals analyses performed on the soils are compared with typical values in Table 4.7. Again, concentrations of alkali and alkaline earth metals are significantly higher in the composite soil due to the brine contamination. Lead and zinc concentrations in the composite soil are higher than average; however, all of the heavy metals concentrations are within the typical ranges outlined by Stout, et. al. (1988).

## 4.2 Results of FBA Analysis

A sample of the Brazil Creek Minerals FBA was analyzed to determine the lime content, pH, and heavy metals content of the ash. This data was used to determine an optimum application rate for the reclamation of the Clearview site. The results of these analyses are compared to typical ranges as shown in Table 4.8 (Stout, et. al., 1988). The pH of the FBA was 11.9, which was expected due to the large amounts of basic metal oxides present, typically CaO and MgO. It is these metal oxides that make this material suitable as an ideal substitute for agricultural limestone. The limemine content in FBA typically ranges from 31 to 100%, averaging 60%, and is expressed as the neutralizing potential of the material compared to an equal amount of ground CaCO<sub>3</sub> or agricultural limestone (Rechcigl, 1995). The FBA used in this study was determined to have a lime content of 55% CaCO<sub>3</sub> equivalency.

Most of the metals of concern in the FBA were determined to be within the typical FBA

**Table 4.5 Soluble Cations, Anions, and Nutrient Analysis of the Clearview Soil.**

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		Clearview Soil	
Category	Parameter	Control	Composite
Soluble Cations (ppm)	pH	6.6 ± 0.4	7.5 ± 0.9
	EC (mS/cm)	1.95 ± 0.2	57.6 ± 4.2
	Na <sup>+</sup>	11 ± 1	8,406 ± 607
	Ca <sup>2+</sup>	23 ± 3	1,923 ± 152
	K <sup>+</sup>	4.1 ± 0.3	8.4 ± 0.3
	Mg <sup>2+</sup>	12.6 ± 0.9	483 ± 29
Anions (ppm)	Cl <sup>-</sup>	34.2	15,529
	NO <sub>3</sub> <sup>-</sup>	0.42	48.2
	PO <sub>4</sub> <sup>3-</sup>	0.2	0
	SO <sub>4</sub> <sup>2-</sup>	25.6	107
Nutrients* (ppm)	N-NO <sub>3</sub>	0	65
	P	27	7
	K	199	355

\* Analyzed by the Oklahoma Cooperative Extension Service



**Table 4.6      Exchangeable Cations, CED, ESP, and SAR Analyses of the Clearview Soil.**

	<b>Soil Sample</b>	
<b>Parameter</b>	<b>Control</b>	<b>Composite</b>
Exchangeable Na <sup>+</sup> (meq/L)	2.6 ± 0.3	491 ± 9
Exchangeable Ca <sup>2+</sup> (meq/L)	15.6 ± 0.6	21.9 ± 0.8
Exchangeable K <sup>+</sup> (meq/L)	41.2 ± 0.2	100 ± 1
Exchangeable Mg <sup>2+</sup> (meq/L)	63.4 ± 2	19.3 ± 0.6
Cation Exchange Capacity (meq/100g soil)	79 ± 9	495 ± 57
Cation Exchange Capacity (meq/L)*	94.4 ± 6	582 ± 72
Exchangeable Sodium Percentage (%)	2.1 ± 0.3	75.1 ± 0.3
Sodium Adsorption Ratio	2.6	242

\*      Calculated by summation of exchangeable cations.

**Table 4.7      Metals Analysis of the Clearview Soil Compared with Typical Ranges for Soils (Stout, et. a., 1988).**

	<b>Clearview Soil</b>		<b>Typical Soil</b>	
<b>Parameter</b>	<b>Control</b>	<b>Composite</b>	<b>Average*</b>	<b>Range*</b>
Ca (ppm)	756 ± 54	3,209 ± 195		
Mg (ppm)	1,177 ± 47	3,882 ± 111		100 - 1,500
K (ppm)	2,056 ± 134	5,129 ± 114		
Na (ppm)	43.2 ± 1.0	9,725 ± 94		
Al (ppm)	9,078 ± 722	32,375 ± 1,647	—	14,000 - 40,000
B (ppm)	0.5	1.93	10	2 - 100
Cd (ppm)	0.017 ± 0.008	0.085 ± 0.020	0.5	0.01 - 0.70
Cr (ppm)	6.64 ± 2.32	44.5 ± 3.3	200	5 - 1,000
Cu (ppm)	2.17 ± 0.23	11.6 ± 0.5	20	2 - 100
Fe (ppm)	5,292 ± 220	26,434 ± 2,484	—	14,000 - 40,000
Mn (ppm)	87.1 ± 2.2	510 ± 68	850	200 - 3,000
Ni (ppm)	11.9 ± 1.3	28.3 ± 0.8	40	5 - 500
Pb (ppm)	3.03 ± 0.19	16.7 ± 1.4	10	2 - 200
Zn (ppm)	20.7 ± 2.0	88.0 ± 11.4	50	10 - 300

\* Information from Stout, et. al., 1988.

**Table 4.8 Comparison of Results of Total Metals Analysis of Brazil Creek Minerals FBA to Typical FBA Values (Stout, et. al., 1988).**

	<b>FBA</b>		
<b>Parameter</b>	<b>Brazil Creek</b>	<b>Average*</b>	<b>Range*</b>
pH	11.9 ± 0.1		
EC (mS/cm)	27.2 ± 0.9		
Lime Content (% CaCO <sub>3</sub> equiv.)	55 ± 3		
Ca (ppm)	272,620 ± 4,904	380,000	240,000 - 460,000
Mg (ppm)	13,085 ± 468	7,100	5,000 - 12,000
K (ppm)	3,373 ± 153	2,500	500 - 8,000
Na (ppm)	491 ± 9		
Al (ppm)	20,578 ± 863	10,000	4,000 - 20,000
B (ppm)	0.13	110	95 - 170
Cd (ppm)	0.17 ± 0.01	0.5	—
Cr (ppm)	44.2 ± 4.2	15	9 - 23
Cu (ppm)	19.1 ± 0.8	15	12 - 19
Fe (ppm)	55,423 ± 3,809	11,000	800 - 16,000
Mn (ppm)	580 ± 15	485	210 - 685
Ni (ppm)	39.1 ± 1.4	21	13 - 29
Pb (ppm)	24.3 ± 2.0	3.2	1.5 - 7.5
Zn (ppm)	62.7 ± 4.0	55	29 - 105

\* Information from Stout, et. al., 1988.

ranges presented in Table 4.8. However, chromium, nickel, and lead were slightly higher than expected; therefore, these metals were analyzed in all extracts obtained from the leach study.

### **4.3 Application Rates**

Recommended application rates for the composite soil sample were determined for each of the proposed amendments (i.e. gypsum, turkey litter, FBA, and sulfur) based on the results of series of batch studies and literature values.

#### **Gypsum**

The composite soil sample contained high concentrations of sodium, which had to be addressed for the reclamation strategy. The conventional reclamation practice for the removal of sodium from soil is by leaching. Gypsum is the most common soil amendment for removing sodium from soil particles via the cation exchange mechanism.

The amount of gypsum required is dependent on both the soil texture and the exchangeable sodium percentage. Based on the information in the Oklahoma State Extension Service Fact Sheet No. 2226, gypsum should be added to the Clearview soil at an application rate of 18 tons per acre. However, it should be added in two or more applications of no more than 10 tons (OSCEC < 1995). The application rate used in the laboratory portion of this study was 9 tons per acre as suggested by the manufacturer.

#### **Turkey Litter**

Organic matter was used as an amendment because of its influence on physical properties of the soil. The incorporation of 20 to 30 tons per acre of organic matter into the plow layer creates large pores or channels for water to enter the soil (OSCES, 1995). This promotes soil aggregation, improving soil infiltration and tilth characteristics of the soil.

Turkey litter was used as the source of organic matter because of its nutrient content and availability. The type of litter used was a broiler litter, which consisted of bedding (hay, wood shavings, etc.) and manure. At 30% moisture content, the broiler litter contained the following; 56 pounds N per ton, 48 pounds P<sub>2</sub>O<sub>5</sub> per ton, and 36 pounds K<sub>2</sub> per ton), as provided by the distributor. Because the Clearview soil was in such poor physical condition, turkey litter was added at an application rate of 2230 tons per acre as suggested by Ray Rydlin of the Oklahoma State Cooperative Extension Service.

#### **FBA**

Several batch studies were set up to determine the recommended application rate for FBA. Optimum rates were determined primarily by the effects FBA had on the soil pH.

For the first batch study, FBA was applied at varying application rates and no additional amendments were added. The increase in pH was directly related to the amount of FBA added (Figure 4.2). All batches resulted in pH values above the range of 6.5. to 7.2, which is optimum for plant growth. This was expected due to the alkaline nature of FBA.

The second batch study used soil with gypsum and turkey litter added at an application rates of 5 tons/acre. Results from the previous batches indicated that FBA added at an application rate of 1.0% by weight resulted in a pH greater than 10 for the composite soil; therefore, it was

**Figure 4.2 - Effects of FBA on Soil pH (adapted from Pyle, 1996)**

eliminated from this batch study. The pH was measured until it reached an appropriate value for plant growth (i.e., approximately 7). It is important to note the immediate effects the varying application rates have on the pH. As shown in Figure 4.3, the pH of the soil mixture with 0.1% FBA was approximately 7.6; remaining in an appropriate range for plant growth. However, the soil mixture containing 0.5% FBA had an initial pH greater than 8. The batches consisting of 0.1% FBA reached an acceptable pH level in approximately 8 days (Figure 4.4). After 17 days, the pH of the 0.5% FBA batch was still above 7.5. Based on the results of these batch studies, the suitable application rate for FBA was determined to be 0.1% by weight, or approximately 1 ton/acre.

The heavy metals loading was calculated by multiplying the concentration of each heavy metal determined, to obtain a total loading. Table 4.9 compares the FBA heavy metals loading to that recommended for sewage sludge (Stout, et. al., 1988).

### **Sulfur**

A batch study was used to determine the application rate of sulfur. The recommended application rates for gypsum, turkey litter, and FBA were added to soil. Sulfur dust was added at the following application rates: 1 ton/acre, 5 tons/acre, and 10 tons/acre. The pH of the batches that were measured until the pH reached 7.5 (Figure 4.5). All three-application rates required followed the same general trend, taking 24 days to reach this final pH. The reason for this delay was that 1% FBA was used instead of 0.1% FBA to demonstrate a worst-case scenario which might be encountered in the field application due to “hot spots”. Based on the results in Figure 4.5, a sulfur application rate of 1 ton/acre was deemed adequate to decrease the pH to an acceptable range.

#### **4.4 Leach Studies**

As shown in the batch studies, FBA has a considerable effect on soil pH. The FBA is primarily composed of hydrolyzable metal oxides, which react immediately upon wetting. The addition of sulfur has proven to be a successful pH adjustor; however, based on the batch studies the reaction is slow, taking approximately one week to counteract the pH increase. Therefore, of the data collected in the leach study, the results from the first extract are the most important.

Of equal significance is the possibility of heavy metals leaching from the amended site into adjacent water bodies. Alabama Creek is listed by the Oklahoma Water Resources Board as a warm water aquatic community (WWAC); therefore, the heavy metals concentrations must conform to certain criteria as outlined in the water quality standards (OWRB, 1995). The metals concentrations used in the calculation of total heavy metals loading (i.e. Cd, Cr, Cu, Ni, Pb, and Zn) were determined from the extract solutions and compared to these criteria (Table 4.10).

The criteria for the heavy metals of concern were dependent on total hardness. The total hardness was estimated from the calcium and magnesium concentration in the first extract of the composite soil with all amendments, and then used to calculate the acute and chronic water criteria for warm water aquatic communities (Table 4.10).

The pH of the first extract from the composite soil containing all amendments was determined to be 6.88, which was lower than expected. It was anticipated that FBA would have a more significant effect on pH, especially in the first extract.

All of the heavy metal concentrations analyzed were below the calculated acute values for WWAC, but Cd, Cr, Cu, and Pb did not conform to the chronic values calculated. However, it is

**Figure 4.3 - Effects of FBA on pH of Soil Amended with Gypsum and Turkey Litter (adapted from Pyle, 1996)**

**Figure 4.4 - Effects of FBA on pH of Soil Amended with Gypsum and Turkey Litter and Sulfur (adapted from Pyle, 1996)**



**Table 4.9      Comparison of Heavy Metals Loading with Maximum Loadings for Sewage Sludge (Stout, et. al., 1988).**

<b>Metal</b>	<b>Heavy Metal Loading in Soil (pounds/A)</b>	<b>Heavy Metal Loading in FBA (pounds/A)</b>	<b>Total Heavy Metal Loading (pounds/A)</b>	<b>Maximum Loadings for Sewage Sludge (pounds/A)*</b>
Cd	0.17	0.00034	0.17	4.5
Zn	179	0.125	179	300
Cu	23.6	0.038	23.64	150
Ni	65.8	0.078	57.75	60
Pb	34.0	0.048	34.05	600
Cr	90.7	0.088	90.79	600

\* Information from Stout, et. al., 1988.

\* (Stout, et. al., 1988)

**Figure 4.5 - Effects of Sulfur on pH of Soil Amended with FBA, Gypsum and Turkey Litter (adapted from Pyle, 1996)**

**Table 4.10      Comparison of Heavy Metal Concentrations Found in the First Extract of the Leach Study with Warm Water Aquatic Community (WWAC) Criteria as**

**Determined by the Oklahoma Water Resources Board (OWRB, 1995).**

<b>Parameter</b>	<b>Composite All Amendments</b>	<b>Acute Criteria (ppm)</b>	<b>Chronic Criteria (ppm)</b>
pH	6.88	NA	NA
Cd	<0.05	0.11	0.003
Cr	<0.5	—	0.05
Cu	0.07	0.07	0.04
Ni	<0.1	4.10	0.46
Pb	<0.1	0.4	0.02
Zn	0.06	0.34	0.31

important to note that these values are enforced for Alabama Creek and the extract values were calculated for the soil solution at the Clearview site. It is assumed that the concentrations of these metals would decrease by the time they migrated to Alabama Creek.

#### **4.5 Revegetation**

Re-establishment of vegetation at the study site can be evaluated by comparing aerial photographs before (Figure 4.6) and after (Figure 4.7) implementation of the remediation plan (note that both figures are to the same scale). The white areas in Figure 4.6 are indicative of zones of no vegetative cover and/or accelerated soil erosion due to the effects of oilfield brine. The white areas in Figure 4.6 were treated during implementation of the remediation plan. The white areas in Figure 4.7, which are significantly smaller than in Figure 4.6, indicate zones where the remediation activities were not able to re-establish vegetative cover. The denuded soil areas are outlined on each photograph. The difference in white area after and before treatment corresponds to land area successfully revegetated (reclaimed). Thus, this project was very successful at reclaiming denuded land; one of the stated goals of this project.

Qualitatively, the post-implementation photograph shows an obvious improvement in terms of vegetative cover. Comparing the two photographs, it can be conservatively estimated that at least 750 percent of the impacted soils were effectively re-vegetated.

A more quantitative estimate of the degree of revegetation was developed by actually measuring the outlined areas on both photographs and comparing the difference. The outlined areas were measured using a planimeter. The measurements showed that the denuded area depicted in Figure 4.6 is reduced by more than 75% as shown in Figure 4.7.

#### **4.6 Water Quality**

##### **4.6.1. Introduction**

One of the stated goals for this project was a reduction in the NPS pollutant discharge from the site. The proposed measure of attainment for that goal was a 70% reduction in the concentrations of pollutants leaving site. The specific pollutants identified in the Work Plan included chloride, sulfate, chromium, arsenic, lead, and barium.

The surface water monitoring plan was designed to assess changes in water quality both before and after implementation of the remediation plan. Monitoring stations 2T (upstream) and 1G (downstream) are situated to assess the impacts of the study area on the water quality in Clearview Creek. Monitoring stations 3U (upstream of the confluence) and 4R (downstream of the confluence) are situated to assess water quality impacts of Clearview Creek on Alabama Creek.

Considering the geographic locations of the monitoring stations relative to one another (Figure 4.8), a generic model for the water quality data can be formulated. Prior to implementation of the remediation plan, the impacted area would definitely be expected to contribute excessive loads of brine-related constituents (e.g., chloride, sodium, calcium, magnesium) to waters flowing down Clearview Creek. Constituent concentrations should be significantly higher at monitoring station 1G than at monitoring station 2T. Moreover, the concentrations of these brine-related constituents should decrease, due to dilution, as the water flows downstream toward the confluence with Alabama Creek. The upstream reaches of Alabama Creek are not affected by discharges of oilfield brine or runoff from brine-impacted areas; hence, the concentrations of brine-related

**Figure 4.6 Aerial Photograph of Clearview Site Prior to Remediation Activities**

**Figure 4.7 Aerial Photograph of Clearview Site After Remediation**

**Figure 4.8 - Schematic Diagram of Clearview Site Water Quality Model**

constituents at monitoring station 3U would be expected to be significantly lower than those at 1G. The concentrations at monitoring station 4R should also be lower than those at 1G due to dilution.

The conceptual water quality model described above would also apply immediately after implementation of the remediation plan. However, the concentrations of certain soluble salts (e.g., sodium) at monitoring station 1G should actually increase immediately after remediation. The concentrations at 1G would decrease over time as the excess salts in the soils of the study area are flushed out. Soluble constituents related to the specific soil amendments should also increase immediately after remediation, then decrease over time. Assuming the remediation plan to be effective, concentrations of the brine constituents at the downstream monitoring stations (1G and 4R) would be expected to eventually fall below their pre-remediation levels.

Remediation activities were initiated during June of 1995 and were completed in August of 1995. The pre-implementation monitoring period includes all samples taken before September of 1995. The post-implementation period includes all samples taken after August of 1995.

#### **4.6.2 Pre-Implementation Monitoring**

The data in Table 4.11 indicate a definite trend of increased electrical conductivity (EC) of water discharging from the Clearview site. According to the average values shown in Table 4.11, the EC at Site 1G was 40 times greater than the control site located upstream of the affected area (2T). The extreme increase is related to the high concentrations of soluble salts found in the soils of the study area. However, the impacted area had only a slight effect on the EC values of Alabama Creek. This could be due to dilution from seepage prior to the confluence of the two creeks, and due to the higher rate of flow of Alabama Creek relative to Clearview Creek.

Sodium and chloride analyses also indicate increases in concentrations between upstream and downstream locations on both Clearview and Alabama Creeks (Tables 4.12 and 4.13). Increases in sodium and chloride were more pronounced during extended periods with little to no precipitation. The sodium concentration at the downstream site (1G) was 100 times greater than that found at the upstream site (2T). Chloride exhibited a similar trend, with lower overall increases in concentrations during rainy seasons. As expected, these two parameters showed the greatest impact due to their abundance in brine.

Total suspended solids (TSS) concentrations were most pronounced for 1G (Table 4.14). These high TSS values indicate high sediment loadings during runoff events. During rainfall events, the saline-sodic soils in the affected area disperse quite readily, resulting in these high sediment loadings. The particles washed into Clearview Creek also contributed to the high TSS values found downstream in Alabama Creek.

#### **4.6.3. Post-Implementation Monitoring**

The water quality data for the four monitoring stations are plotted in Figures 4.9 through 4.16. The time varying concentrations are plotted for each of the NPS parameters, except lead and chromium which did not show concentrations above detection limits, plus four additional brine related constituents; calcium, magnesium, sodium, and potassium. The graphs for Clearview Creek show water quality data for monitoring stations 1G and 2T. The graphs for Alabama Creek show water quality data for monitoring stations 3U and 4R. The water quality data analytical results are included in



**Table 4.11 Conductivity Data for Water Samples Collected at Clearview and Alabama Creeks.**

	<b>Conductivity (mS/cm)</b>					
	<b>Clearview Creek</b>			<b>Alabama Creek</b>		
<b>Date</b>	<b>Upstream</b>	<b>Downstream</b>	<b>Ratio</b>	<b>Upstream</b>	<b>Downstream</b>	<b>Ratio</b>
95-01-20	0.088	0.644	7.3	0.254	0.261	1.0
95-01-27*	0.066	0.428	6.5	0.112	0.159	1.4
95-02-02	0.098	0.841	8.6	0.175	0.235	1.3
95-03-15*	0.075	0.417	5.6	0.119	0.171	1.4
95-03-22	0.134	0.807	6.0	0.223	0.298	1.3
95-04-28	0.123	0.652	5.3	0.133	0.162	1.2
95-05-01*	0.061	0.249	4.1	0.136	0.158	1.2
95-05-19	0.188	1.234	6.6	0.250	0.321	1.3
95-05-24*	0.071	0.410	5.8	0.120	0.142	1.2
95-06-16	0.168	0.87	5.2	0.198	0.245	1.2
95-07-18	0.336	no flow	–	0.621	0.659	1.1
95-08-14	0.168	no flow	–	0.515	0.865	1.7
95-09-17	no flow	2.33	–	0.561	2.13	3.8
95-10-05	0.133	2.66	20	0.407	0.830	2.0
96-01-25	0.185	8.67	47	0.398	0.430	1.1
96-02-22	0.206	no flow	–	0.463	0.627	1.4
96-03-30	0.110	1.83	17	0.332	0.460	1.4
96-04-13	0.167	5.88	35	0.432	0.470	1.1
Average	0.140	4.274	13	0.303	0.479	1.5
Std Dev	0.069	2.760	13	0.167	0.472	0.6

\* Indicates high-flow events.

**Table 4.12 Sodium Concentrations (ppm) Determined in Water Samples Collected at Clearview and Alabama Creeks.**

	<b>Sodium (ppm)</b>					
	<b>Clearview Creek</b>			<b>Alabama Creek</b>		
<b>Date</b>	<b>Upstream</b>	<b>Downstream</b>	<b>Ratio</b>	<b>Upstream</b>	<b>Downstream</b>	<b>Ratio</b>
95-01-20	5.8	76.7	13	19.6	26.9	1.4
95-03-15*	3.6	26.2	7	12.6	20.6	1.6
95-03-22	8.1	94.9	12	15.8	26.0	1.6
95-04-28	8.1	75.5	9	12.4	19.9	1.6
95-05-01*	1.8	35.8	20	9.5	13.4	1.4
95-05-19	1.9	158.4	83	18.5	22.5	1.2
95-05-24*	1.8	197.7	110	12.0	81.4	6.8
95-06-16	1.7	99.9	59	12.4	18.2	1.5
95-07-18	2.3	no flow	–	51.9	63.6	1.2
95-08-14	2.7	no flow	–	41.8	95.4	2.3
95-09-17	<D.L.	886.9	–	58.1	289.9	4.9
95-10-05	7.4	374.1	51	26.9	104.9	3.9
Average	3.8	203	41	24.3	65	2.5
Std Dev	2.8	260	37	16.9	77	1.8

\* Indicates high-flow events.

**Table 4.13 Chloride Concentrations (ppm) Determined in Water Samples Collected at Clearview and Alabama Creeks.**

	Chloride (ppm)					
	Clearview Creek			Alabama Creek		
Date	Upstream	Downstream	Ratio	Upstream	Downstream	Ratio
95-01-20	5.6	330.4	59	33.6	45.0	1.3
95-01-27*	3.2	170.8	53	16.6	29.8	1.8
95-02-02	6.1	223.4	37	13.1	34.4	2.6
95-03-15*	2.2	32.5	15	20.3	27.5	1.4
95-03-22	7.9	183.6	23	23.6	42.8	1.8
95-04-28	7.7	137.1	18	11.7	29.7	2.5
95-05-01*	3.4	69.4	20	10.2	19.3	1.9
95-05-19	11.5	295.7	26	25.4	40.7	1.6
95-05-24*	2.7	301.6	112	13.6	139.5	10
95-06-16	9.8	202.2	21	24.8	285.8	12
95-07-18	31.6	no flow	–	84.5	94.3	1.1
95-08-14	4.1	no flow	–	68.2	173.6	2.5
95-09-17	no flow	2,221.6	–	78.9	584.5	7.4
95-10-05	4.5	812.5	181	40.5	195.5	4.8
96-01-25	6.6	3,070.4	465	29.9	46.7	1.6
96-02-22	5.8	no flow	–	37.4	81.9	2.2
96-03-30	3.3	460.3	139	32.5	66.2	2.0
96-04-13	3.9	761.9	195	42.2	53.5	1.3
Average	7.05	618	97	33.7	111	3.3
Std Dev	6.82	868	123	22.4	138	

\* Indicates high-flow events.

**Table 4.14 Total Suspended Solids (ppm) in Water Samples Collected at Clearview and Alabama Creeks.**

	Total Suspended Solids (ppm)					
	Clearview Creek			Alabama Creek		
Date	Upstream	Downstream	Ratio	Upstream	Downstream	Ratio
95-03-15*	495	8,970	18	875	1,650	1.9
95-03-22	11	93	8.5	11	21	1.9
95-04-28	9	24	2.7	25	3	0.1
95-05-01*	22	22	1.0	38	33	0.9
95-05-19	5	8	1.6	13	3	0.2
95-05-24*	17	18,600	1,094	1,240	6,280	5.1
95-06-16	4	1	0.3	4	16	4.0
95-07-18	6	no flow	–	21	4	0.2
95-08-14	50	no flow	–	51	51	1.0
95-09-17	no flow	7	–	46	39	0.8
95-10-05	35	37	1.1	14	40	2.9
96-01-25	8.3	60	7.2	22	28.3	1.3
96-02-22	66.7	no flow	–	15	30	2.0
96-03-30	7.7	50	6.5	52	43	0.8
96-04-13	9.8	36	3.7	17	19	1.1
Average	53.5	2,325	104	163	551	1.6
Std Dev	128	5,733	328	369	1,639	1.4

\* Indicates high-flow events.

included in Appendix CB.

Impacts of the remediation plan on the water quality of either Clearview Creek or Alabama Creek are not readily discernible for the post-implementation monitoring data. Certain parameters do appear to show a slight increase in concentration immediately following implementation of the remediation plan; as expected since the amendments will leach certain constituents. However, the surge in concentration is relatively short-lived and the latter concentrations seem to remain elevated above the pre-implementation values. For most parameters the latter time data are near or below the water quality standards, as discussed below. The monitoring results for some of the other NPS parameters are contrary to the water quality model described above. Finally, some of the parameters exhibit anomalous behavior that could only be attributed to analytical variability. The results for each parameter are discussed individually below.

#### **4.6.3.1. NPS Parameters**

##### Lead and Chromium

All of the analytical results for lead and chromium were less than their detection limits. Although no comparative analysis can be developed, the data do indicate there is no discernible impact of the soil amendments used in the remediation plan on lead or chromium levels in surface waters flowing through the area of interest

##### Chloride

The post-implementation monitoring results for chloride are depicted in Figure 4.9. For Clearview Creek (Figure 4.9a), the concentration of chloride is much higher at the downstream location (1G) than the upstream location (2T). Moreover, the chloride concentration does increase immediately following implementation of the remediation plan; however, the surge in concentration is relatively short-lived and the latter concentrations seem to approach but remain elevated above the pre-implementation values. The chloride data for Alabama Creek (Figure 4.9b) show a similar pattern, although dampened in magnitude. It is important to note that the concentration of chloride in Alabama Creek only exceeds the water quality criteria for one sampling episode immediately following implementation of the remediation plan, as depicted on Figure 4.9b.

##### Sulfate

The post-implementation monitoring results for sulfate are depicted in Figure 4.10. For Clearview Creek (Figure 4.10a), the concentration of sulfate is higher at the downstream location (1G) than the upstream location (2T). There appears to be a slight increase in sulfate concentration immediately following implementation of the remediation plan, which could possibly be attributed to the sulfur dust used for remediation. However, data for some of the later sampling episodes show even higher sulfate concentrations, which is contrary to the water quality model proposed for the remediated site, i.e., decreasing concentrations over the long term. The elevated concentrations of sulfate during the later sampling episodes might be the result of slow release of sulfate from the sulfur dust used for remediation. Laboratory studies to evaluate leaching of sulfate from the amended soils over time were not conducted.

The increase in the post-implementation sulfate concentrations is more evident for Alabama Creek (4.10b); however, the concentrations contradict the water quality model proposed for the watershed. The sulfate concentrations in Alabama Creek upstream of the confluence (3U) are higher

than the concentrations downstream of the confluence (4R). The elevated sulfate concentrations could be due to activities upstream of the confluence. These results indicate that sulfate cannot be

**Figure 4.9a Chloride Concentrations in Clearview Creek**

**Figure 4.9b Chloride Concentrations in Alabama Creek**



**Figure 4.10a Sulfate Concentrations in Clearview Creek**

Figure 4.10b Sulfate Concentrations in Alabama Creek

Creek (4.10b); however, the concentrations contradict the water quality model proposed for the watershed. The sulfate concentrations in Alabama Creek upstream of the confluence (3U) are higher than the concentrations downstream of the confluence (4R). The elevated sulfate concentrations could be due to activities upstream of the confluence. These results indicate that sulfate cannot be used for assessing water quality impacts due to the remediation plan implemented at the study site. However, all sulfate concentrations are well below the water quality standards, rendering the results inconsequential for this particular site.

#### Arsenic

The post-implementation monitoring results for arsenic are depicted in Figure 4.11. The arsenic concentrations in Clearview Creek (Figure 4.11a) are highly variable. On at least two occasions, the upstream concentrations actually exceed the downstream concentrations. The arsenic concentrations in Alabama Creek (Figure 4.11b) exhibit similar behavior, with the upstream concentrations actually exceeding the downstream concentrations on more than one occasion. None of the sample results from Alabama Creek exceed the numerical criteria for acute toxicity (0.036 mg/l) or chronic toxicity (0.019 mg/l) for arsenic, rendering the concentration trends inconsequential.

#### Barium

The post-implementation monitoring results for barium are depicted in Figure 4.12. The limited number of barium samples from Clearview Creek (Figure 4.12a) show wide variability. There is no discernible increase in barium concentrations after implementation of the remediation plan. The barium concentrations in Alabama Creek (Figure 4.12b) also show wide variability. The upstream concentrations exceed the downstream concentrations on more than one occasion which is contrary to the water quality model proposed for the watershed, but may be due simply to normal analytical variability.

### **4.6.3.2. Brine Parameters**

#### Calcium

The post-implementation monitoring results for calcium are depicted in Figure 4.13. For Clearview Creek (Figure 4.13a), the concentration of calcium is much higher at the downstream location (1G) than the upstream location (2T). There also appears to be an increase in concentration immediately following implementation of the remediation plan; however, there are some inexplicable spikes in the downstream calcium concentration in the early part of 1996. In addition, the spikes in calcium concentration at the downstream location do not necessarily coincide with increased levels of calcium at the downstream monitoring station on Alabama Creek (Figure 4.13b). The calcium concentrations in Alabama Creek show an increase immediately after implementation of the remediation plan, followed by a general decreasing trend. This pattern would seem to indicate that the excess soluble salts were flushed from the impacted soils due to the remediation plan.

#### Magnesium

The post-implementation monitoring results for magnesium are depicted in Figure 4.14. The magnesium concentrations for both creeks appear relatively steady until the resumption of sampling in early 1996. It is important to note the dramatic increase in concentrations of magnesium starting in

1996. This is most probably attributable to analytical variability. All personnel involved with the project were replaced during the three month period (October 1995 to January 1996) between sampling events, which probably contributed to variations in analytical and reporting procedures. The dramatic increase in magnesium concentrations at all four sampling stations coincides with the

Figure 4.11a Arsenic Concentrations in Clearview Creek

**Figure 4.11b Arsenic Concentrations in Alabama Creek**

**Figure 4.12a Barium Concentrations in Clearview Creek**

**Figure 4.12b Barium Concentrations in Alabama Creek**



**Figure 4.13a Calcium Concentrations in Clearview Creek**

**Figure 4.13b Calcium Concentrations in Alabama Creek**

**Figure 4.14a Magnesium Concentrations in Clearview Creek**

**Figure 4.14b Magnesium Concentrations in Alabama Creek**

magnesium concentrations for both creeks appear relatively steady until the resumption of sampling in early 1996. It is important to note the dramatic increase in concentrations of magnesium starting in 1996. This is most probably attributable to analytical variability. All personnel involved with the project were replaced during the three month period (October 1995 to January 1996) between sampling events, which probably contributed to variations in analytical and reporting procedures. The dramatic increase in magnesium concentrations at all four sampling stations coincides with the change in project personnel. The underlying cause for the dramatic change in sample results (e.g., change in sampling procedures) is not known.

The elevated concentrations of magnesium might be the result of delayed flushing due to the soil amendments used for remediation. However, laboratory studies to evaluate leaching of magnesium from the amended soils over time were not conducted.

### Sodium

The post-implementation monitoring results for sodium are depicted in Figure 4.15. For Clearview Creek (Figure 4.15a), the concentration of sodium is much higher at the downstream location (1G) than the upstream location (2T). There is also a dramatic increase in sodium concentration immediately following implementation of the remediation plan. Similar patterns are exhibited for the monitoring data from Alabama Creek (Figure 4.15b). These trends seem to indicate that the soluble salts were flushed from the impacted soils due to implementation of the remediation plan.

### Potassium

The post-implementation monitoring results for potassium are depicted in Figure 4.16. The potassium concentrations for Clearview Creek (Figure 4.16a) appear to increase steadily after implementation of the remediation plan; however, the elevated concentrations through 1996 may be attributable to analytical variability as discussed above. The potassium concentrations for Alabama Creek (Figure 4.16b) appear to show a pattern of slight increase after the remediation plan was implemented; however, the extreme jump in concentrations in 1996 are inconsistent with the water quality model proposed for the watershed.

#### **4.6.4 Summary**

The water quality data presented above do not consistently shows no discernible impacts of the remediation plan. Although some parameters do appear to show slight increases in concentration immediately following implementation of the remediation plan, the increases are relatively short-lived and some of the latter concentrations seem to remain elevated above the pre-implementation values. However, the latter time data for most parameters are near or below the water quality standards developed for Alabama Creek, rendering any trends or changes in concentration inconsequential. The stated goal of a 70% reduction in NPS pollutants is really not applicable does not make sense given that the post-implementation concentrations are below water quality standards.

**Figure 4.15a Sodium Concentrations in Clearview Creek**

**Figure 4.15b Sodium Concentrations in Alabama Creek**

**Figure 4.16a Potassium Concentrations in Clearview Creek**



**Figure 4.16b Potassium Concentrations in Alabama Creek**

## **5.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS**

### **5.1 Summary**

This project involved laboratory and field investigations of an innovative technology for treating brine impacted soils and waters. Fly ash, a byproduct of coal combustion, is generally considered to be a waste material. However, this study proposed to demonstrate that the calcium contained in fly ash can be used as a soil amendment to better flush accumulated salts from brine-impacted soils.

In order to demonstrate the viability of the proposed technology, a field demonstration site was selected. The demonstration site had been heavily impacted by oilfield brine that had been released due to line leaks and spills. Surface soils were devoid of vegetation and were highly eroded. The accelerated erosion rates had resulted in a scarred landscape and increased accumulations of sediments in surface watercourses.

The physical features of the field demonstration site were characterized through surveillance and surveying activities. Subsequent soil sampling and analysis was used to characterize the spatial distribution of accumulated salts throughout the study area. A site sampling plan was implemented to retrieve soils for laboratory testing.

Laboratory batch and leaching studies were used to develop design parameters for the field demonstration study. Various combinations and loading rates for the soil amendments were tested using brine-impacted soils from the demonstration site.

Field scale application rates for the soil amendments were specified as a result of the laboratory studies. The innovative remediation technology was implemented by re-shaping the land features, incorporating the soil amendments at the specified application rates, and re-seeding the site using salt tolerant Bermuda grass. The performance of the technology was assessed by conducting monthly sampling episodes for one year after implementation. Surface water samples were retrieved and analyzed for chemical constituents of brine and the soil amendments. The concentrations of these constituents over time were studied to assess the long term and short term impacts of the remediation technology.

Best management practices (BMP's), including installation of hay bales for erosion control, spot re-seeding to establish vegetative cover, and a one-year livestock exclusion agreement, were conducted after implementation of the innovative remediation technology. Additional soil stabilization techniques were implemented at the site after at the conclusion of monitoring activities associated with this project.

### **5.2 Conclusions and Recommendations**

From the information presented previously above, a series of conclusions and recommendations can be developed.

#### **5.2.1 Participation and Cooperation**

A critical aspect of this project was the participation and cooperation of community leaders, local conservation service staff members, and political office-holders. These efforts were especially notable at the Clearview site due to the complexity of the land ownership patterns and the number of potentially affected parties. The local citizens even agreed to a one-year livestock exclusion from the site. Only a committed populace could have reached a consensus and allowed the study to proceed.

#### **5.2.2 Laboratory Studies**

Laboratory investigations, using site specific media, are essential for successful design and field implementation of this technology. The soil batch studies, used for testing various loading rates of each of the proposed soil amendments, were able to accurately reflect conditions that would result from field applications of the technology. Identification of the changes in soil pH, and measures to control those changes, were especially critical.

### 5.2.3 Remediation Goals

The goals developed for this study were not totally in concert with the technical objectives of the proposed remediation technology. Moreover, the blanketing statements contained in the goals and their associated measures of attainment were presumptuous given the untested status of the proposed remediation technology. The shortcomings of the project goals are discussed individually below.

Goal 1:           Reduction of NPS pollutant discharge from site.  
Measure: 70% reduction in concentration of pollutants leaving site.

This goal and proposed performance measure conflict with the technical objectives of the remediation technology. The remediation technology is actually designed to cause a dramatic, short-term increase in the concentrations of brine-related parameters, including chloride, leaving the site. The long term objective would be to reduce the concentrations of brine related parameters exiting the site. Hence, a time frame Time frames associated with the performance measure needs to be specified.

More importantly, most of the NPS pollutants delineated in the Work Plan are constituents associated with the various soil amendments proposed to be used at the study site. The concentrations of these parameters in nearby surface waters are expected to increase above background levels after implementation of the remediation technology. It is desirable to minimize the mass flux of these constituents from the site, but it is counterintuitive to expect neither a short term or long term decreases in their concentrations relative to the background (i.e., pre-implementation) concentrations should be expected.

An inherent goal for any remediation project is to achieve prescribed water quality standards. As evidenced by the post-implementation monitoring data, most of the concentrations in Alabama Creek are below the water quality standards. It is not cost-effective to propose ludicrous to propose reducing the concentrations of the constituents that do not pose a water quality problem.

Additional monitoring during an extended post-implementation period would no doubt have shown water quality improvements in Clearview Creek. Over the years, the remediated site would become more stabilized, as the purged contaminants are transported downstream, and the vegetative cover becomes firmly re-established. Experience with similar remediated sites has shown that surface water quality parameters tend to stabilize after 3 to 5 years.

A better and substitute measure of success for in-stream conditions might be attained from physical and biological assessments. Annual physical evaluations could measure changes and improvements in habitat. Over time, we would expect to see marked improvements in the fish and macro invertebrate community. These improvements could be documented with bio-assessment and/or bioassay studies. Sites such as this, that have high toxicity potentials, should be automatic candidates for bioassay work. All of these methods could be used to show improvements over a longer time frame or extended post implementation period.

At the close of this project, the Okfuskee and Okmulgee County Conservation Districts, the

Natural Resource Conservation Service, the Oklahoma Conservation Commission, and the University of Oklahoma are all still involved in addressing some of the problems at the site. All parties involved remain interested and determined to stabilize this project and show it a success.

Goal 2:           Stabilization and re-vegetation of site.  
                  Measure: Photographic and standard ecological measures of vegetation pattern and coverage.

Several different photographic measures can be used to document attainment of the stated goal. As discussed earlier (Section 4.5), comparing pre- and post-implementation aerial photographs shows that the denuded acreage at the site decreased by more than 75%. In addition, visual comparisons of pre- and post-implementation still photographs of the site show dramatic improvements in the vegetative cover. Copies of the pre- and post-implementation photographs are found in Appendix E.

A standard ecological measure of vegetation pattern and coverage could include pre- and post-implementation site assessments by qualified experts. Included below are the pre- and post-implementation assessments of the Clearview site.

#### **Pre Implementation Assessment - 1993**

Mark Maples

NRCS - District Conservationist

Okfuskee County Conservation District

Prior to the dirt work or any shaping activities at the Clearview Project, the site, approximately 68 acres, appeared to be a total waste land. Spills from the oil field operation and outdated methods of operation had salted the area, killing the vegetation and leaving bare soil. Without adequate ground cover the site was soon at the mercy of the elements, which quickly rendered it a severely eroded area.

Dispersed areas made up nearly 100 % of the site. Rills and gullies were so deep and plentiful that not even a four wheeler could traverse the area.

At the site the only remnants of vegetation were a few salt cedars (tamarak) that struggled to exist on top of some non dispersed mounds. Thick stands of little bluestem, India grass, and some switch grass thrived in areas adjacent to the site. Cedars, oaks, and other woody plants also surrounded the area, but nothing survived on the site.

#### **Post Implementation - March 2000**

Larry D. Farris

Retired NRCS Agronomist

Okfuskee County Conservation District

The Clearview site has been adequately reclaimed through shaping, soil amendments, and revegetating. The original planting done in 1996 provided Bermuda grass cover on the majority of the site. The west slope of the project from one end to the other is now covered with an excellent Bermuda grass and clover stand. The channel bottom is also well established in vegetation and is stable. There had been no vegetation established on some of the slopes along the side drains. In the fall of 1999 there was another attempt made to get a cover of "Jose" Tall Wheat and Bermuda grass on these areas. So far the results of that planting are only marginally successful. There remains areas that

are totally void of any vegetation. It appears that the buffering agents used may not have been evenly distributed. There is a solid cover of young plants in some areas followed by an abrupt change to bare ground.

The reason that bare ground continues to exist is that some of the area is still too high in sodium and chlorides to support vegetation. It is my opinion though that the project is adequately vegetated to maintain the resource base. Overall I would continue to view the site as being sensitive and fragile. I would not recommend that the area be opened up to any prolonged grazing in the near future.

The dramatic improvement in vegetative pattern and coverage is documented from the above site assessments. Combining these on-site assessments with the photographic evidence is clear indication that the project has attained the stated goal.

Goal 3: Transfer of information gathered during this project to other sites with a goal of five site remediation projects per year.  
Measure: Number of projects initiated and completed each year.

Although desirable, this goal is premature. I, i.e., it is not reasonable to expect the technology to be adapted prior to completion of technology transfer activities which would describe the technology. Technology transfer activities are typically completed near the end of the project. Moreover, data pertinent to these specified performance measures may not be attainable and certainly would not be generated until after completion of the project.

Certain aspects of the remediation technology developed for the Clearview Project have been implemented at oilfield and other remediation sites throughout the state of Oklahoma (see Table 5.1). The Okmulgee County Conservation District undertook the task of coordinating with various agencies in an effort to remediate severely impacted sites. The District Manager, David Ledford, spearheaded the effort by acquiring all materials and equipment, coordinating with landowners, developing the conservation plans, operating the equipment, and implementing all practices on the ground.

From Table 5.1 it is clear that information developed during the Clearview Project has been transferred to other sites. In fact, the stated goal of five sites per year has been met or exceeded in each of the last three years. It is envisioned that the technology developed for the Clearview Project will see expanded applications as information relative to the technology is distributed. A variety of related information transfer activities have been completed for this project. A brochure describing the innovative technology and the results of the study has been distributed to petroleum production companies, governmental agencies, and consulting firms. In addition, the project has been summarized in several conference presentations.

Table 5.1 Remediation Sites Utilizing Technology Developed from the Clearview Project

YEAR FINISHED	ACRES	SITE NAME	PROCESS
1997	3	McCart	Ripped, Gypsum, Bio-Solids, Seeded, Hay Mulched, & Fenced.
1997	1	Smith	Shaped, Ripped, Gypsum, Bio-Solids, Seeded, Wood Chips, & Fenced.

1997	0.5	Viersen	Ripped, Gypsum, Bio-Solids, Seeded, Hay Mulched, & Fenced.
1997	9	Price	Shaped, Gypsum, Bio-Solids, Seeded, Hay Mulched, & Fenced.
1997	4	Carpenter	Shaped, Gypsum, Bio-Solids, Seeded, & Hay Mulched.
1998	8	Roane	OERB-Pond, Shaped, Ripped, Gypsum. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1998	4	Watson 2	OERB-Shaped, Ripped, Gypsum, Fenced. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1998	4	Watson 3	OERB-Shaped, Ripped, Gypsum, Fenced. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1998	2	Lawson	OERB-Shaped, Ripped, Gypsum, Fenced. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1998	1	Miller	OERB-Shaped, Gypsum. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1999	4	Robison	Shaped, Ripped, Gypsum, Bio-Solids, Seeded, Hay Mulched, & Fenced.
1999	7	Mims	OERB-Shaped, Ripped, Gypsum, Fenced. OCCD-Bio-Solids, Sprigged, Hay Mulched.
1999	120	Enid	Poultry Litter, Fly Ash. ( <i>non oil field site</i> )
1999	3	Red Oak	Poultry Litter, Fly Ash. ( <i>non oil field site</i> )
1997 - '99	60 60 25 10 70 80 3	Eagle Pitcher Hamilton Bryan Stites Brannon Jacobs #2 Brannon Jacobs #4 Stuccobur	These mining ( <i>non oil field</i> ) sites were also addressed with much of the same technology.

### Remediation Technology

The proposed remediation technology focused only on liberating the accumulated salts from the impacted soils. Once mobilized, the salts need to be transported offsite or they will simply re-precipitate on soils in low lying areas. The effects of this phenomenon are readily observable at the Clearview site; areas where vegetative cover was not established are predominantly located in the low lying zones near the creek channel. Future studies that involve cChemical-based remediation technologies that are designed to flush contaminants should incorporate must include hydraulic measures (e.g., subsurface drains, sumps) to collect and remove the contaminants into the overall design.

### Monitoring

The pre- and post-implementation monitoring activities should focus on assessing mass fluxes, rather than simply on dissolved concentrations. As noted previously, the concentrations of most of the NPS pollutants and brine-related parameters are directly affected by weather conditions. Low-flow conditions in the surface watercourses, especially Clearview Creek, can produce elevated concentrations due to evaporation; high-flow conditions can produce low concentrations due to dilution. The concentrations of the target analytes should be accompanied by flow rates to assessing changes in mass flux. Water level measurements were recorded during this study, but stage versus discharge relationships have not been developed for either watercourse.

The pre- and post-implementation monitoring activities should also focus on subsurface media, most notably the shallow ground water. The effectiveness of the remediation technology is influenced largely by subsurface transport and fate processes. Moreover, concentrations in the surface waters can be influenced by numerous sources unrelated to the study site. Ground water monitoring wells and/or soil water lysimeters should be included in the monitoring network for assessing the effectiveness of the remediation technology. Budget constraints did not allow for an extensive ground water monitoring network to be included in this study.

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APPENDIX A  
NRCS DESIGN DRAWINGS

APPENDIX B

ANALYTICAL PROCEDURES

APPENDIX CB  
WATER QUALITY DATA

## APPENDIX DC

### BROCHURE AND DISTRIBUTION LIST

## APPENDIX ED

### PRE AND POST IMPLEMENTATION PHOTOGRAPHS