REDOX TRANSFORMATIONS AND SULFUR SPECIATION IN FLUE GAS DESULFURIZATION SLUDGE

by

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As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Sajid Ali Barlas entitled Redox Transformations and Sulfur Speciation in Flue Gas Desulfurization Sludge and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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TABLE OF CONTENTS

Page

LIST OF ILLUSTRATIONS .................................................. 8
LIST OF TABLES .............................................................. 12
ABSTRACT ................................................................. 13

1. INTRODUCTION ......................................................... 14
   Background .......................................................... 14
   Introduction ......................................................... 15
   Goals and Objectives of Study ...................................... 18
   Practical Significance of Research ................................. 19

2. THEORY AND BACKGROUND ........................................ 20
   SECTION 1
   OXIDATION REDUCTION ................................................ 20
   Theory of Redox Reactions ......................................... 20
   LITERATURE REVIEW ................................................ 23
   Oxidation Reduction Reactions ..................................... 23
   Redox Measurements .................................................. 28
   Sulfate Reduction .................................................... 34
   Sulfide Oxidation ..................................................... 42

   SECTION 2
   ISOTOPE ANALYSIS .................................................... 45
   Stable Isotopes of Carbon and Sulfur ............................... 45
# TABLE OF CONTENTS -Continued

<table>
<thead>
<tr>
<th>3. EXPERIMENTAL MATERIALS AND METHODS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SECTION 1</td>
<td></td>
</tr>
<tr>
<td>OXIDATION REDUCTION</td>
<td>51</td>
</tr>
<tr>
<td>Site Description</td>
<td>51</td>
</tr>
<tr>
<td>Sampling Strategy</td>
<td>54</td>
</tr>
<tr>
<td>Physico-Chemical Analysis</td>
<td>54</td>
</tr>
<tr>
<td>Experiments under Anaerobic Conditions</td>
<td>54</td>
</tr>
<tr>
<td>Oxidation Experiments</td>
<td>58</td>
</tr>
<tr>
<td>Redox Electrode Calibration</td>
<td>59</td>
</tr>
<tr>
<td>Sulfide Electrode Calibration</td>
<td>60</td>
</tr>
</tbody>
</table>

| SECTION 2                           |      |
| ISOTOPE ANALYSIS                   | 61   |
| Sulfate Isotope                    | 62   |
| Sulfide Isotope                    | 63   |
| Carbon Isotope                     | 63   |

| 4. RESULTS AND DISCUSSION           | 65   |
| SECTION 1                           |      |
| OXIDATION REDUCTION                | 65   |
| Oxidation of Reduced FGD Sludge    | 65   |
| pH Changes during Oxidation        | 92   |
| Reduction of FGD Sludge            | 95   |
| Effect of Reduction on Se and B Solubility | 110 |
| Selenium Adsorption                | 116  |
TABLE OF CONTENTS - Continued

SECTION 2
INTERPRETATION OF ISIYTOPIC DATA ........................................... 120
   Likely Sources, Processes and their Isotopic Effects .................. 120
   Sulfur Isotopes ................................................................. 126
   Evidence of Bacterial Reduction ......................................... 127
   Carbon Isotopes ................................................................. 128
   Calculations ................................................................. 129

5. SUMMARY AND RECOMMENDATIONS .................................... 131
   Suggestions for Future Work ............................................. 132

6. APPENDIX ................................................................. 133
   Calculations of Isotopic Analysis ...................................... 133

7. REFERENCES ............................................................... 136
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Section of the FGD sludge profile showing highly reduced conditions</td>
<td>52</td>
</tr>
<tr>
<td>3.2</td>
<td>Section of the FGD sludge profile showing alternate reduced and oxidized layers</td>
<td>53</td>
</tr>
<tr>
<td>4.1</td>
<td>Changes in redox potential (Eh) during oxidation of reduced FGD sludge, under evaporating moisture condition.</td>
<td>67</td>
</tr>
<tr>
<td>4.2</td>
<td>Changes in redox potential of FGD sludge during first fast phase of chemical oxidation under evaporating moisture condition.</td>
<td>69</td>
</tr>
<tr>
<td>4.3</td>
<td>Changes in redox potential during second slow step of biological oxidation of FGD sludge under evaporating moisture content</td>
<td>70</td>
</tr>
<tr>
<td>4.4</td>
<td>Changes in redox potential during oxidation of reduced FGD sludge under evaporating moisture condition (non linear best fit)</td>
<td>71</td>
</tr>
<tr>
<td>4.5</td>
<td>Changes in sulfide (total) and soluble sulfate concentration during the oxidation of reduced FGD sludge under evaporating moisture condition</td>
<td>74</td>
</tr>
<tr>
<td>4.6</td>
<td>Change in soluble sulfate content of reduced FGD sludge during its exposure to the atmosphere</td>
<td>75</td>
</tr>
<tr>
<td>4.7</td>
<td>Changes in total sulfide content of reduced FGD sludge, during oxidation under evaporating moisture condition.</td>
<td>76</td>
</tr>
<tr>
<td>4.8</td>
<td>Effect of moisture content on the oxidation of sulfide present in reduced FGD sludge</td>
<td>79</td>
</tr>
<tr>
<td>4.9</td>
<td>Changes in total sulfide content of reduced FGD sludge, during oxidation under evaporating moisture condition.</td>
<td>80</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS - Continued

Figure 4.10  Changes in total sulfide content, during oxidation of reduced FGD sludge under constant moisture condition ............... 81

Figure 4.11  Changes in Eh of reduced FGD sludge as a function of moisture content ................................. 83

Figure 4.12  Effect of moisture content on oxidation of reduced FGD sludge .................................................. 84

Figure 4.13  Changes in Eh of reduced FGD sludge, when exposed to the atmosphere under constant moisture condition. 86

Figure 4.14  Changes in redox potential during oxidation of reduced FGD sludge under evaporating moisture condition (non-linear best fit). 87

Figure 4.15  Comparison of effect of mixing treatments (6 vs 12 hour) on change in redox potential of reduced FGD sludge during oxidation ............................................. 89

Figure 4.16  Effect of every six hour mixing on the oxidation of reduced FGD sludge when exposed to the atmosphere. ................................................................. 90

Figure 4.17  Effect of every twelve hour on the oxidation of reduced FGD sludge when exposed to the atmosphere ................................................................. 91

Figure 4.18  Changes in pH and Eh of FGD sludge during oxidation under evaporating moisture conditions. 94

Figure 4.19  Changes in Eh and pH of FGD sludge when incubated without addition of organic carbon with DI water ............................. 97
LIST OF ILLUSTRATIONS - *Continued*

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.20</td>
<td>Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on the Eh of FGD sludge during incubation</td>
<td>99</td>
</tr>
<tr>
<td>4.21</td>
<td>Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on the pH of FGD sludge during incubation</td>
<td>100</td>
</tr>
<tr>
<td>4.22</td>
<td>Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on the $pH+pe$ parameter of FGD sludge during incubation</td>
<td>101</td>
</tr>
<tr>
<td>4.23</td>
<td>Changes in Eh of FGD sludge when incubated without addition of organic carbon</td>
<td>102</td>
</tr>
<tr>
<td>4.24</td>
<td>Changes in Eh of reduced FGD sludge when incubated with 100 ppm of organic carbon</td>
<td>103</td>
</tr>
<tr>
<td>4.25</td>
<td>Changes in Eh of reduced FGD sludge when incubated with 1000 ppm of organic carbon</td>
<td>104</td>
</tr>
<tr>
<td>4.26</td>
<td>Changes in soluble sulfate and total sulfide concentration, during the reduction of FGD sludge as a function of redox potential</td>
<td>108</td>
</tr>
<tr>
<td>4.27</td>
<td>Phase diagram ($pH$ and Eh) of sulfur compounds in equilibrium with aqueous phase at 25°C and 101 kPa</td>
<td>109</td>
</tr>
<tr>
<td>4.28</td>
<td>Effect of incubation temperature (4±1°C vs 25±1°C) on redox potential of FGD sludge</td>
<td>111</td>
</tr>
<tr>
<td>4.29</td>
<td>Changes in soluble organic carbon with depth of FGD sludge profile during winter</td>
<td>112</td>
</tr>
<tr>
<td>4.30</td>
<td>Changes in selenium solubility during reduction of FGD sludge as a function of redox potential</td>
<td>114</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS - Continued

Page

Figure 4.31  Changes in boron solubility during reduction of FGD sludge as a function of redox potential .......................... 115

Figure 4.32  Selenium adsorption on FGD sludge ............................................. 118

Figure 4.33  Results of the isotopic analysis of the FGD sludge profile. .................................................. 121

Figure 4.34  Chemical processes relevant to sulfur and carbon isotopic fractionation and summary of their effects on isotopic ratio ................................. 122
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3.1</td>
<td>Summary of the physico-chemical analysis of sludge</td>
<td>55</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Parameters of best fit equation and rates of oxidation of FGD sludge</td>
<td>68</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Parameters of best fit equation and rates of change in the concentration of soluble sulfate and total sulfide during oxidation of FGD sludge</td>
<td>77</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Parameters of best fit equation and rates of oxidation of sulfide as effected by moisture content</td>
<td>82</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Parameters of best fit equation and rates of oxidation of FGD sludge as effected by moisture content</td>
<td>85</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Parameters of best fit equation and rates of oxidation of FGD sludge as effected by mixing treatments</td>
<td>92</td>
</tr>
<tr>
<td>Table 4.6</td>
<td>Parameters of best fit equation and rates of reduction of FGD sludge as effected addition of OC</td>
<td>106</td>
</tr>
<tr>
<td>Table 4.7</td>
<td>Results of chemical analysis of profile of the FGD sludge used for stable isotope analysis</td>
<td>124</td>
</tr>
</tbody>
</table>
ABSTRACT

Changes in redox potential (Eh), major sulfur species and the solubility of selenium and boron in reduced flue gas desulfurization (FGD) sludge, when exposed to atmosphere were studied in laboratory experiments. Also the effect of organic carbon and temperature on reduction of FGD sludge and changes in concentration of major S species was studied. Stable isotopic ratios of sulfur and carbon compounds were used to investigate the possible pathways of S transformation in FGD sludge disposal site. Oxidation of reduced sludge appears to be a two step process, a fast step of chemical oxidation followed by a slow step of biological oxidation and is significantly affected by moisture content and mixing of the sludge. With the addition of organic carbon Eh of the FGD sludge dropped exponentially and reduction of sulfate initiated at Eh of about -75 mV and was maximum in the range of -265 to -320 mV. Temperature of the profile and organic carbon appear to be the key factors affecting the rate and extent of reduction in flooded FGD sludge. Selenium solubility decreased four times as Eh dropped from 215 mV to -350 mV while boron solubility was unchanged in this range of Eh. Stable isotopic ratio of sulfate and sulfide are typical of bacterial reduction and suggest that only aqueous sulfate was being reduced. The low $\delta^{34}S$ values of CaSO$_4$ from the upper layers of profile indicate the production and upward movement of hydrogen sulfide gas in the FGD sludge.
CHAPTER 1

INTRODUCTION

Background

Food, air and water are the basic requirements of every living being. With the rapid increase in world population and industrialization, use of chemicals has increased considerably in the last few decades. Most of these chemicals are ultimately disposed in the environment (soil, air and water) directly or indirectly. The presence of these chemicals in the environment in higher concentrations, than normally found in undisturbed ecosystems, is believed to be responsible for many diseases in humans, animals and plants as well. Atmospheric pollution is considered a global problem, as air pollution can not be confined to a particular area or region. Emissions from burning of fossil fuels (coal and petroleum) and dust from wind erosion are among the major causes of air pollution. Industrial emissions are of more concern because of volume and nature of gases being released into atmosphere. Coal, the second most important source of energy after petroleum, contains sulfur which is released as sulfur dioxide upon burning of coal. Industrial sulfur emissions are among the most important causes of acid rain, which not only causes physical damage to the structures and vegetation but also changes the mobility and thus toxicity of heavy metals present in the soil, by changing the chemical properties of soils.
**Introduction**

Coal is the second most important source of energy in the world and is expected to surpass petroleum in the next 20 years. In the US coal is the most important electrical power generation fuel source producing nearly 56 percent of the nation's electrical energy (US Bureau of Census., 1990). 800 million tons of coal are consumed annually by electrical utilities (Wolk, 1990; and EPRI, 1989). As energy needs continue to grow, the emphasis on coal combustion will only increase. All coal contains reduced organic or inorganic S compounds. Combustion of coal transforms large quantities of reduced S to sulfur dioxide gas. Atmospheric releases of sulfur dioxide gas has been linked to acid rain which contributes to the acidification of poorly buffered lakes and possible forest decline (Gaffney et al., 1987). Recognition of the set of environmental problems caused by emissions of sulfur dioxide to the atmosphere (acid rains and poor air quality) has initiated international efforts to reduce these emissions (Kristensen et al., 1991). A consequence of these efforts is an increased establishment of facilities for flue gas desulfurization. Scrubbers are used to remove sulfur dioxide gas from the stack of emission gases. For each ton of coal that is burned in the generation of electricity between two and three hundred pounds of solid waste (fly ash and flue gas desulfurization sludge) are created. Over 80 million tons of solid combustion waste are generated annually in the united states (Ohio Coal Development Office., 1987; and EPRI., 1989), and levels are expected to increase to over 150 million tons by 1995 (Santhanam, 1985). These levels are expected to increase even more due to increased dependence on coal and stricter air pollution regulations,
forcing many uncontrolled sources to install particulate capture and sulfur emission control systems (David et al., 1992).

Although these wastes pass current Resource Recovery and Conservation Act (RCRA) standards as defined by the Toxicity Characteristic Leaching Procedure (TCLP) test, studies has shown that significant leaching of metals may occur, although below TCLP standards (Chu et al., 1978; Dressen et al., 1977 and Van der Sloot et al., 1985). The other environmental concerns include the emission of hydrogen sulfide gas and wind erosion from the area surrounding the evaporation ponds could deteriorate the air quality. While some of these material are used as soil amendment for acid soils or in wall board and other products, much of it is disposed of in slurry disposal ponds or landfills which are eventually buried or left to revegetate. Revegetation of FGD sludge is necessary to prevent erosion, reduce hydrogen sulfide emissions, avoid potential contamination of ground and surface waters, improve physical appearance, and allow the land to be returned to economic uses or wildlife habitat (Terman, 1978).

However the revegetation of these sites is difficult because of potential toxicity of redox active species under anaerobic conditions. Anaerobic conditions are evident from the rotten egg odor and blackish grey color of the reduced sludge, caused by periodic dry-down and re-flooding events of these sites. This is associated with excessive discharge from scrubbers as well as seasonal rainfall that brings runoff water in to the δ of the evaporation pond from a watershed area of 3 km². Reduction of sludge is the single most important chemical change brought about by flooding and it results directly from the
exclusion of oxygen and its consumption by microorganisms in the utilization of organic matter. Persistent anaerobic conditions can lead to the formation of compounds such as methane, hydrogen sulfide and or various organic acids. These compounds are toxic to plants and soil microorganism. Anaerobic conditions can also greatly change the solubility and mobility of heavy metals and nutrient elements present in the FGD sludge. Therefore, predicting the behavior of FGD sludge towards plant growth will require an understanding of the influence of period saturation and drying on the redox status and accompanied changes in the biogeochemistry of sulfur in the FGD sludge.

Oxidation and reduction (redox) potential, a measure of the oxidizing power of a system, plays an important role in determining the behavior of many elements in the environment. Redox reactions mediate the behavior of many chemical constituents in soils, sludge, and water as well as of the most aquatic systems in the environment. Indeed the energy to support non photosynthetic forms of life is largely derived from redox reactions (Bricker, 1982). Sillen (1967) referred to the redox potential as a master variable in the chemistry of the earth, oceans and atmosphere. The reactivities and mobilities of important elements in biological systems (Fe, S, N and C) as well as a number of other metallic elements depend strongly on redox conditions. Sulfur, an essential element for plant growth and a major constituent of FGD sludge, is redox active. It undergoes reduction in the absence of oxygen when adequate electron donors are present and its reduced products (sulfides and sulfites) are more phytotoxic than sulfate. Sulfide in soil causes several problems for root function and plant growth such as inhibition of nutrient uptake by roots.
(Joshi et al., 1980). Also sulfur and trace metals become unavailable for plant growth because they are immobilized by the precipitation of metal sulfides (Patrick and Mahaptra, 1968).

Keeping in view the important role of redox potential in the biogeochemistry of redox active elements (S and Se), it was imperative to study the effect of periodic flooding and subsequent drying on the redox potential and accompanied changes in major sulfur species in FGD sludge for successful revegetation of the disposal site.

**Goals and Objectives**

This study had two major goals. The first concern was to develop a quantitative understanding of redox kinetics during wetting and drying of FGD sludge. The second aspect of this study was to investigate the geochemistry of redox active species particularly S in the FGD sludge disposal site.

The following research objectives were pursued to meet the study goals

1) Determine the rate of change of redox potential during oxidation of reduced sludge and reduction of oxidized FGD sludge;

2) Determine the concentration of Se, B and major S species during oxidation and reduction of FGD sludge
Practical Significance of Research

Although the amount of FGD sludge produced annually will only increase, and with the imposition of governmental regulations in this area, environmentally acceptable uses and or disposal of these materials must be found, but there is a dearth of scientific literature on the geochemistry of FGD disposal ponds (Ainsworth et al., 1995). Therefore, an understanding of redox transformations and how it affects the geochemistry of S and trace metals in FGD sludge would enable us

- to develop strategies to successfully establish vegetation on this disposal site
- to evaluate the environmental protection offered by various disposal options for FGD sludge.
CHAPTER 2

THEORY AND BACKGROUND

This chapter treats the theory and background for studying redox kinetics and sulfur speciation in natural waters and soils, as almost no literature regarding these transformations in FGD sludge is available. The first section covers topics such as redox reactions, their significance and measurements, reduction of sulfate and oxidation of sulfide. The second section of the chapter briefly reviews the principles involved in using stable isotopes for explaining biogeochemical transformations that occur in reduced environments of lakes and estuarine waters and its application to FGD sludge systems.

Section 1

Oxidation Reduction

Theory of Redox Reactions

A chemical reaction in which an element undergoes a loss or gain of orbital electrons is referred to as oxidation or reduction and may be represented by the expression:

\[
\text{reduced species} \rightarrow \text{oxidized species} + n_e^\circ
\]

where \( n_e \) is the number of electrons involved per atom. The standard oxidation potential, \( E^\circ \), for a half cell reaction of this type is the potential that would occur if the two species are both present at unit activity at 25°C and one atmosphere pressure. When the activities of participating species differ from unity, the potential observed at equilibrium is termed
the redox potential (oxidation reduction potential). The redox potential (Eh) is related to the standard potential and the activities of participating substances by the Nernst equation:

$$Eh = E^o + \frac{RT}{nF} * \ln \frac{\text{oxidized state}}{\text{reduced state}}$$

where $E^o$ is the standard potential of the reaction, $R$ is the universal gas constant, $T$ is the absolute temperature in degrees Kelvin, $F$ is the Faraday constant, $n$ is the number of electrons involved in a half-cell reaction and $\ln$ (oxidized state/reduced state) is the natural logarithm of the ratio of the products of the activities of the oxidized species to that of the reduced species (Warren, 1976).

Energy for non photosynthetic forms of life is derived from the oxidation reduction reactions and thermodynamically speaking the driving force for the redox reactions is the tendency of the natural systems to attain equilibrium. During anaerobic respiration inorganic compounds are used as electron receptors (they are reduced) to release the energy from organic matter through oxidation. Upon the exhaustion of available oxygen, anaerobic bacteria utilize in a step wise manner, and in accordance with thermodynamic predictions, nitrate, manganese, ferric iron, followed by sulfate and then carbon dioxide.

The oxidation state of a medium can also be expressed quantitatively, as we express acidity(pH), by the negative logarithm of free electron activity, the pe value

$$pe = - \log(e')$$

For practical purposes the pe can be calculated from redox potential using the equation

$$pe = \frac{Eh(mV)}{59.2} \quad \text{(Lindsay, 1979).}$$
The large values of pe favor the existence of proton poor species (oxidized species) whereas small values of pe favor the electron rich (reduced) species. As the soil becomes saturated and oxygen supply drastically reduced, the pe of the soil solution drops below +11.0, enough electrons become available to reduce O$_2$(g) to H$_2$O(l). Below pe 5.0 oxygen is not stable in neutral soils, above pe 5.0 it is consumed in the respiration processes of aerobic microorganisms. As the pe decreases below 8.0, electrons become available to reduce nitrate(NO$_3$). This reduction is catalyzed by nitrate respiration (nitrate serves as a biochemical electron acceptor like O$_2$) involving bacteria that ultimately excrete NO$_2$, N$_2$, N$_2$O or NH$_4$. As the pe drops to the range of 7 to 5, electrons become plentiful enough to support the reduction of Fe and Mn in solid phases. Iron reduction does not occur until O$_2$ and NO$_3$ are depleted, but Mn reduction can be initiated in the presence of nitrate. As the pe value decreases below 2.0, a soil becomes anoxic and when pe drops below zero, electrons are available for sulfate reduction catalyzed by a variety of anaerobic bacteria. The chemical reaction sequence for the reduction of O, N, Mn, Fe and S induced by changes in pe is also a microbial sequence for the biological catalysis that mediate the reactions. Aerobic microorganisms that utilize O$_2$ to oxidize organic matter do not function below pe 5.0. Denitrifying bacteria thrive in the pe range between +10.0 and 0, for the most part. Sulfate reducing bacteria do not grow at pe values above +2.0(Sposito, 1989).

Poise is a useful concept in understanding potential measurements and the behavior of mixed systems. The poise of a redox system is its resistance to change in potential upon
the addition of small amounts of oxidant or reductant. Poise increases with the total
concentration of oxidants plus reductants, and for a fixed total concentration it is maximum
when the ratio of oxidant to reductant is equal to 1. The poor poise of natural aerated
systems is due to the absence of a reversible system in sufficiently high concentration

Literature Review

Oxidation Reduction Reactions

Several investigators have examined the effects of saturated conditions of soil on
the geochemical state in soils. Ponnamperuma (1965) observed that reduction of soil is the
single most important chemical change brought about by flooding and that it results directly
from the exclusion of oxygen and its consumption by microorganisms in the utilization of
organic matter. This depletion of oxygen and the establishment of anaerobic conditions can
occur with in 24 to 48 h (Takai et al., 1965, and Yamane and Sato, 1968).

When a soil or sludge is submerged, gas exchange between soil and air is drastically
curtailed. Oxygen and other atmospheric gases can enter the soil only by molecular
diffusion in the interstitial water. This process is 10,000 times slower than diffusion in gas
filled pores (Lemon and Kristensen, 1960 and Greenwood, 1961). Thus the oxygen
diffusion rate suddenly decreases when a soil reaches saturation by water. With in a few
hours of soil submergence microorganisms use up the oxygen present in water or trapped
in soil and render a submerged soil practically devoid of molecular oxygen. Evans and
Scott (1955) noted that the concentration of oxygen in the water used for saturating a soil
decreased to one-hundredth of its initial value in 75 minutes. Takai et al. (1956) found no oxygen in three soils one day after submergence. Turner and Patrick (1968) could not detect any oxygen in four soil suspensions within 36 hours of withdrawal of the oxygen supply. Also the low oxidation potentials reported by many workers for lakes, muds (Zobell, 1946), for saturated and submerged soils (Ponnamparuma, 1972) are further proof of absence of molecular oxygen in waterlogged soils and sediments.

Redox potential, a master variable in the chemistry of the earth, oceans and atmosphere (Sillen, 1967) provides the energy needed to support non photosynthetic forms of life (Bricker, 1982). Redox reactions mediate the behavior of many chemical constituents in soils, sludge, and water as well as most aquatic systems in the environment. The redox potential (Eh), have been measured in various natural systems including soil, biological, limnological, geochemical and marine systems because electrons are essential reactants in inorganic, organic and biochemical systems (Bohn, 1970). The oxidation reduction status of soils and sediments has been shown to influence strongly the mobility and plant availability of trace and toxic metals as well as the persistence and/or degradation of synthetic organic compounds such as pesticides and industrial organics. Knowledge of how redox conditions affect the environmental chemistry of contaminants will enable better predictions of fate and potential hazards of toxic materials in soils, sediments and water and should be useful in evaluating the environmental protection offered by various disposal options for contaminated soils and sediments (Gambrell and Patrick, 1988).
Bohn (1970) pointed out that the redox potential of most natural systems is a measure of all of the nonequilibrium mixed redox couples in contact with an electrode, and is quantitatively unrelated to the Nernstian distribution of single ion oxidation states. Platinum is the most widely used electrode because it is responsive to changes of redox conditions in natural systems. In oxidized systems, the low concentration of redox couples reduce the stability, reproducibility and general usefulness of redox potential measurements. In reduced systems, the higher concentrations of redox couples increase the stability and utility of redox potentials. The redox potential is most definitive in oxygen poor environments and therefore complements rather than supplements oxygen electrode and oxygen diffusion rate measurements.

Lindberg and Runnels (1984) analyzed the equilibrium state applied to Eh measurements. Computer modeling of 611 high quality analyses of normal ground waters from diverse geographic areas revealed that aqueous oxidation reduction reactions are generally not at equilibrium. Multiple redox couples present in individual samples yield computed Nernstian Eh values spanning as much as 1000 mV. The computed Eh values do not agree with each other nor do they agree with the single master value measured in the field with a platinum electrode. Because of internal disequilibrium, the use of any measured value as input to equilibrium hydrogeochemical computer models will generally yield misleading results for normal ground waters.

Grundt (1994) considered redox potential to be an intensity factor reported as the measured potential versus the standard hydrogen electrode (Eh). Many redox reactions in
natural systems are kinetically slow, are subject to microbial catalysis (for growth, respiration, fermentation etc) and to the influence of solid present, and are not in equilibrium with each other. As a result many natural systems are poorly characterized by intensity factors. If a potential measurement is to represent the thermodynamically defined intensity within a system that system must conform to the following three conditions:

- the system must be at homogenous chemical equilibrium
- the system must be at heterogenous chemical equilibrium with any solids present
- electrochemical equilibrium must exist between the electrode and the solution

Natural systems are generally in a dynamic rather than an equilibrium condition, and the concept of a single redox system characteristic of a static system can not be maintained. In the most favorable case measurement of Eh can be related to a particular redox system or systems in partial equilibrium. The redox system must be electrochemically reversible at the surface of the platinum electrode at a rate that is rapid compared with the electron drain or supply by way of the measuring electrode. In natural waters only the Fe$^{++}$/Fe$^{+++}$ and the $\text{H}_2\text{S}/\text{S}_n^2-$ systems corresponds to these limitations. The electrochemical reactions of hydrogen sulfide and polysulfide are known to be rapid at the surface of the platinum electrode. Hence the potentials obtained in the presence of these species should be explainable in terms of equilibrium of redox couple $\text{H}_2\text{S}/\text{S}_n^2-$; eventually these potentials might be utilized to infer redox processes involving the sulfur species.
Reducing environments are frequently characterized by the presence of hydrogen sulfide (even in very low concentrations). In these environments several factors such as slow diffusion of oxygen, the presence of organic matter or Fe(III) minerals, may result in the incomplete oxidation of $\text{H}_2\text{S}$, which yields polysulfide ($\text{S}_n^{2-}$) ions and thiosulfate ($\text{S}_2\text{O}_3^{2-}$). In sulfurous waters where hydrogen sulfide is the only reduced sulfur species present in significant concentrations, the redox potential of the environment is difficult to assess. Metastable sulfur species such as polysulfide and thiosulfates are stabilized in the reducing environments and they play an important role in redox processes (Boulegue and Michard, 1979).

Ponnampерума (1972) noted that although the platinum electrodes give precise and accurate potentials in buffer solutions and in solutions of reduced soils, they do not register steady state or reproducible potentials in poorly buffered media like aerated soils and natural waters. Morris and Stumm (1967) and Stumm and Morgan (1970) have attributed these defects due to absence of electroactive systems in sufficient high concentrations in aerobic media and to the presence of mixed systems that are not in equilibrium among themselves. Although soil or mud potentials have no precise thermodynamic significance they are semi-quantitative measures of soil reduction and lake sediments, and provide measurements of relative redox changes over varying conditions and time.
Redox Measurements

Redox potential, the oxygen diffusion rate (ODR) and oxygen electrode potentials are the only single measurement of the oxidation reduction status of natural systems. The oxygen electrode is suitable only in relatively aerobic systems. ODR measurements are difficult (Rickman et al., 1968) particularly at redox potentials less than 200 mV. This leaves redox potential measurements the only parameter that can be applied relatively easily to measure the oxidation reduction status of the natural systems. The redox characteristics of natural systems are typically defined in terms of the redox potential as measured at an inert electrode, usually platinum. But a number of other electrodes have also been used for this purpose that includes tungsten, titanium, graphite, and gold.

Shaik et al. (1985) evaluated the effectiveness of wax impregnated graphite electrodes (WIGE) and platinum wire electrodes (PWE's) in determination of two oxygen indicators, oxygen diffusion rate (ODR) and redox potentials (Eh) in aqueous solutions, soil suspensions and moist soils. The response of both electrodes to increasing concentrations of dissolved oxygen was linear. In soils the current-plateau region of both electrodes was a function of the soil moisture content. For redox measurements the WIGE gave excellent agreement but the PWE showed significant variation with the Nernst equation. They concluded that WIGE are less susceptible to poisoning by oxides, are more stable in the soil than PWE and have greater sensing area. On the other hand, Bohn (1968) reported that gold and graphite electrodes were unsuitable for redox measurements in soils.
and that the EMF of platinum electrodes though a mixed potential resultant of many redox couples, is a rough measure of the intensity of oxidation reduction conditions in the soils.

Rickman et al. (1968) reported that platinum electrodes are poisoned in aqueous and soils environments due to formation of oxide and sulfide coatings thereby causing inaccurate measurements of the redox potential. Baily (1971) found that bright platinum electrodes were poisoned under reducing conditions (-300 mV) and did not respond when the soil was oxidized. This poisoning may have resulted from $\text{H}_2\text{S}$ production under extreme reducing conditions (<=-200 mV) and may not occur under moderate reducing conditions.

Mansfeldts (1993) investigated the possible mechanical breakdown and electrode contamination effects on redox electrodes permanently installed in a soil characterized by changing redox conditions (-170 mV to 700 mV; pH 7.2) for a period of 20 months. The results showed that although the potentials for the electrodes used in soil were generally somewhat lower (11 to 33 mV) compared to the potentials of non installed electrodes, there were no visible coating on the surface which would restrict the qualitative interpretation of measured redox potentials. He suggested that redox potential of saturated or frequently saturated soils may be measured by permanent installation of the electrode. Also, Whisler et al (1974) found that with an Eh of -200 mV or greater electrodes functioned for as long as six months without losing their sensitivity.

The fact that platinum electrode potentials from natural aquatic systems do not correspond to the prevailing oxygen concentration has repeatedly been used as an argument
against the application of redox measurements in natural systems (Harrison, 1973; and Whitefield, 1984). The reason for this electrode performance is low electron exchange density of oxygen at the platinum surface (Bockris and Huq, 1970). Only in pure water and an extremely long response time, a linear relationship between the platinum electrode potential and concentration of dissolved oxygen is measurable (Schulldiner et al., 1966). Measured potentials in natural systems do not correspond well to the thermodynamically defined electron activity because of widespread disequilibrium, both homogenous and heterogenous (Lindberg and Runnells, 1984). Another reason for disagreement between calculated values of redox potential for a given system and that observed is due to the fact that aqueous electrons are in essence non-existent, therefore redox electrodes do not directly respond to the activity of aqueous electrons but rather to electron transfer from redox active solutes. Disequilibrium between these solutes prevents the attainment of a unique pe (Hostettler, 1984).

The factors affecting oxidation reduction processes in an Oxisol with a seasonal water table were studied by Couto et al. (1985) and reported that reduction does not occur in the lower part of the soil profile (below 40 cm) even when a high water table is present, primarily due to the lack of an energy source for microbial activity. It was suggested that organic matter present in the lower part of the soil profile is too stable and/or too low in available nutrients for reduction process to take place during the water logging period.

Norrstrom (1994) measured in situ redox potential of four groundwater discharge areas with a size of 3-4 m². Readings were taken in the upper 30 cm of the soil at two
depths. A method study showed that a longer equilibrium time than is usually reported. The main finding of the study was the large spatial variation within soils in the discharge zone; regions as small as 10 cm in diameter could have redox potentials covering several hundred mV. Differences in the distribution of the redox potential with depth may be explained by the structure of peat affecting flow patterns and the residence time of water. Branes and Back (1964) studied the geochemistry of iron rich ground waters of southern Maryland and concluded that the data obtained can be interpreted in terms of equilibrium between the ground waters and ferric minerals intermediate in properties between freely precipitated ferric hydroxide and hematite.

Bohn (1970) explained the possible reasons for the better performance of redox electrodes in reducing conditions than in oxidizing conditions. He suggested that in aerated soils the oxidized ions are present only at low concentration—the transition metal ions are less soluble than in their reduced states, soluble organic compounds are too rapidly oxidized to accumulate, and oxygen exchange currents at the electrode are low. The solution is poorly poised; the emf drifts and shows poor reproducibility. While in flooded soils, the greater concentrations of redox active ions and organic molecules and the high exchange currents of hydrogen bring about greater poise, emf stability and reproducibility, and more useful application of the results.

Eckert (1993) investigated the pe-pH-pH$_2$S relationship in lake Kinneret, Israel using a chemostat. The platinum electrode responded instantaneously to the addition of hydrogen sulfide. The result was the pe-pH-pH$_2$S (pH 7.00):
\[ \text{pe} = -4.5 + 0.59 \times \text{pH}_2\text{S} \]

The obtained regression line runs closely to the thermodynamic function with slightly more positive slope. They also reported that none of the other system components (SO\textsubscript{2-3}, SO\textsubscript{2-4}, NO\textsubscript{-3}, NO\textsuperscript{-2}, S\textsubscript{2}O\textsubscript{3}, NH\textsuperscript{+4}) that were added to the chemostat yielded a detectable change in the measured pe values. This can be explained by a higher standard exchange current density \((i_0)\) of H\textsubscript{2}S. Literature values for \((i_0)\) of various redox systems vary from 40 A.cm\textsuperscript{-2} for the Br\textsubscript{2}/Br\textsuperscript{-} system to 10\textsuperscript{-9} A.cm\textsuperscript{-2} for the O\textsubscript{2}/O\textsuperscript{-} system. In another experiment the change in redox parameter pe due to reduction of sulfate was investigated and it was reported that the change in values of pe measured in the chemostat with sulfur reducing bacteria closely followed the theoretical pe curve. During the first 50 h the pe decreased from 2.5 to -1.3. A one time injection of lactose (1 ml) caused a further pe drop to -2.5 due to release of H\textsubscript{2}S.

Dushing et al. (1992) studied the effect of the redox potential on leaching from stabilized/solidified fly ash and FGD sludge waste and showed that the redox potential has a significant effect on leaching of metals for individual species. Chromium leaching increased significantly under highly oxidizing conditions. Arsenic, vanadium, and iron leaching all increased under reducing conditions. He suggested that additional laboratory work is needed to develop methods and testing procedures to better investigate redox controlled leaching, and field investigations are needed to better define what actual state the wastes are in over time.

Whisler et al. (1974) studied redox potentials in soil columns intermittently flooded
with sewage water and observed that when soluble carbon was added to the sewage waters
the redox potential dropped to more negative values (-220 mV) than when ordinary sewage
water (200 mV) was used, indicating that the oxidation states of other redox active elements
besides nitrogen were changing.

Effect of oxidation reduction on the mechanism of B horizon (Spodic horizon)
formation in podzols was studied by Mckenzie et al. (1960). They observed that redox
potentials varied with degree of saturation, temperature and depth of soils horizon. They
also speculated that redox potential variations not associated with differences in soil
moisture were caused by variations in temperature and indirectly by the activities of soil
microorganisms.

Meek and Grass (1975) studied the redox potential in irrigated desert soils as
indicators of aeration status and concluded that factors important in controlling Eh were
temperature, flooding time, soil water content and energy source. A 5°C increase in
temperature at the 15 cm depth resulted in a 50 mV decrease in redox potential. The length
of saturation time correlated directly with decrease in Eh. The amount of energy available
to microorganisms has a major effect on how low the Eh decreased in flooded soil.

To summarize the literature reviewed above we can say that a great deal of
controversy exists in literature regarding the way redox potentials are measured and
interpreted. Several researchers have tried to establish a quantitative relationship between
the measured redox potential in soils and water and the calculated values, by means of the
Nernst equation. In many studies there was no quantitative relationship (Bohn, 1968, 1970,
and Lindberg and Runnells, 1964) while others were more successful (Barnes and Back, 1964; Ponnamperuma et al., 1967; Nordstrom et al., 1979, and Boulegue and Michard, 1979). This contradiction may result from some of the conditions which have to be fulfilled to obtain reliable measurements (Stumm, 1967; Stumm and Morgan, 1981). For example a redox couple must be present in great enough concentration to express their potential at the electrodes, otherwise the readings are mixed potentials of all redox couples present. This mixed potentials are a result of the fact that many redox reactions in natural systems are very slow in reaching equilibrium and different reactions proceed independently of each other. Different types of contaminants may also influence the measured value (e.g. oxides in aerated environments and sulfides in reducing environments (Whitefield, 1984).

**Sulfate Reduction**

The oxidation status of the medium greatly effects the biogeochemical processes taking place in that medium. During anaerobic respiration inorganic compounds are used as electron receptors (they are reduced) to release the energy from organic matter through oxidation. Upon the exhaustion of available oxygen, anaerobic bacteria utilize in a step wise manner, and in accordance with thermodynamic predictions, nitrate, manganese, ferric iron, followed by sulfate and then carbon dioxide.

The major features of sulfur biogeochemistry affecting its availability to plants and microorganisms, movement and toxicity are associated with changes in its oxidation state
and the resulting differences in chemical properties of these various chemical forms. In well aerated soil environment sulfur is present predominantly as sulfate, transformation of sulfur to sulfite and sulfate occur when there is no more oxygen present in the system and sulfate is used as an electron acceptor. The end product of sulfate reduction is the sulfide ion. The reduction of sulfate ion in the soil has a very favorable formation constant (Log $K^o = 20.74$) but requires redox conditions ($pH + pe > 4$) seldom encountered in surface soils (Lindsay, 1979). Sulfate reduction in a soil of pH 5 would occur only if the pe would drop below -1 which is equivalent to soil redox potential of -60 mV. Sulfate reduction is a microbially mediated biological process but it is controlled largely by physicochemical conditions and appears to be favored in neutral pH and is much likely to occur in acid soils ($pH < 5$) (Alexander, 1977).

Bacterial sulfate reduction is an important pathway for organic carbon mineralization, in this process organic compounds are mineralized and dissolved sulfate is reduced simultaneously by heterotrophic microorganisms. The rate of sulfate reduction in marine environment is primarily dependent on the amount and reactivity of decomposable organic carbon (Goldhaber and Kaplan, 1975, Lyons and Gaudette, 1979, Westrich and Berner, 1984).

The basic process involved in the oxidation of organic carbon by sulfate to form CO$_2$ and sulfides is shown below

$$\text{organic carbon} + \text{sulfate} \xrightarrow{\text{bacteria}} \text{CO}_2 + \text{sulfides}$$
This reaction is accomplished by anaerobic bacteria which are ubiquously distributed in all anaerobic environments from water logged soils to the anaerobic zones of lakes to deep sea sediments. Given a system devoid of oxygen these sulfate reducing bacteria can maintain growth and respiration under extreme environmental conditions of temperature, salinity and pressure (Postgate, 1984). In the environments where sulfate concentrations are high the process of reduction dictates the nature and rate of organic carbon remineralization (Ramm et al., 1992).

Charoenchamratcheep et al. (1987) studied the reduction and oxidation of acid sulfate soils of Thailand and reported that increasing the Eh decreased the concentration of reduced S and increased the concentration of soluble salts. In the Maha Phot soil the Eh increased from -150 to -30 and remained close to this value until all reduced sulfides in solution had oxidized. The sulfate concentration increased from 6 to 106 mg S kg$^{-1}$ soil while the pH decreased from 4.9 to 3.7 during this period.

Reduction of sulfate to sulfide in waterlogged soils depends upon soil redox potential and pH. Conell and Patrick, Jr (1969) reported that little or no sulfide accumulated with a redox potential above -150 mV or with a pH outside the range 6.5 to 8.5. This restriction of sulfate reduction to the pH range 6.5 to 8.5 does not necessarily mean that soils with normal pH values outside this range do not support sulfate reducers. After water logging, the pH of both acid and alkaline soils tends to shift towards the neutral point as a result of chemical reactions involving iron and manganese, that bring most waterlogged soils, regardless of original pH, into the pH range of sulfate reduction.
Connell and Patrick, Jr (1969) studied sulfate reduction to sulfide in waterlogged soils supplied with an energy source from which oxygen was excluded. Sulfide was detected in about two days after the soil was waterlogged and oxygen removed. The same 2-day lag period between the addition of sulfate and the appearance of sulfide occurred when the soil was allowed to become highly reduced before the addition of sulfate. Accumulation of sulfide was considerably slow in the subsoil horizons, requiring as long as 5 to 6 days for sulfide to appear. They also reported that the amount of sulfide precipitated from added H₂S in two soils was approximately equivalent to the amounts of ferrous iron released in the soil by waterlogging. They also found that nitrate was effective in inhibiting sulfate reduction. Where nitrate and sulfate were added to a waterlogged soil, no sulfide appeared until all of the nitrate had been reduced.

Goldhaber and Kaplan (1975) studied the sulfate reduction in recent marine sediments and concluded that besides temperature and pressure, which are cosmopolitan parameters influencing most biological processes, the rate of sulfate reduction is dependent upon (1) total organic carbon preserved in sediments; (2) state of complexing of the organic matter and its availability for biogenic degradation; (3) the environment of deposition and (4) the rate of sediment accumulation.

The effect of various chemical oxidants on inhibition of sulfide in a previously reduced soil was studied by Engler and Patrrick, Jr. (1973). Oxygen, KNO₃, MnO₂, ferric-triphosphate and FePO₄.₂H₂O were added both prior to flooding and after the soil reduction reached a maximum, at rates equivalent to 1000 ppm. The results indicated that
the more soluble oxidants had the greatest effect in maintaining more positive redox potentials and in delaying sulfate reduction to sulfide. The soluble oxidants KNO\textsubscript{3} and ferricitriphosphate delayed sulfide production by 17 and 9 days. The less soluble compounds MnO\textsubscript{2} and FePO\textsubscript{4}. 2 H\textsubscript{2}O were less effective in delaying sulfide production but persisted longer in preventing maximum sulfate buildup. Adding the oxidants after maximum sulfide accumulation showed the most pronounced effect on sulfide oxidation from KNO\textsubscript{3} and least effect from MnO\textsubscript{2}. Oxygen at the rate of 500 ppm was also a very effective oxidant. Sulfate reduction to sulfide and sulfide oxidation were apparently controlled by, or at best related to the redox potential since sulfate reduction and sulfide oxidation both appeared to commence at potentials in the vicinity of -100 mV.

Crozier et al. (1995) investigated production of methane and reduced sulfur gases \{H\textsubscript{2}S, CH\textsubscript{3}SH, (CH\textsubscript{3})\textsubscript{2}S, COS and CS\textsubscript{2}\} by both freshly collected and air dried, rewet soils from four wetlands in the Mississippi Alluvial plain. Peak production rates of both methane and H\textsubscript{2}S occurred in fresh soils than in dried soils in almost all cases. Presumably this lag time associated with drying was caused by an increase in potentially reducible manganese and iron. Nevertheless drying increased labile C levels. Production of methane was positively correlated with organic matter and labile C whereas production of S gas was positively correlated with initial SO\textsubscript{4} concentration. Dried soils produced similar total amounts of methane, less H\textsubscript{2}S and more of the other reduced gases than did fresh soils. No (CH\textsubscript{3})\textsubscript{2}S, COS or CS\textsubscript{2} was detected from fresh soil incubations. Also as a soil dries and inorganic species are oxidized concentrations of thermodynamically favored electron
acceptor species should increase. During the drying process some recalcitrant C is converted to labile forms (Sorensen, 1974). Thus the total amount of C available for conversion to CH$_4$ following rewetting may be as great as or greater than that produced by soils that have not experienced a drying period (Reddy and Patrick, 1975). Since lignin is relatively resistant to anaerobic decomposition (Tenny and Waksman, 1930, and Hackett et al., 1977) drying may facilitate lignin breakdown. In these soils with relatively high organic matter large amounts of lignin may have been present.

In two of the three studies by Van Dam (1987) where littoral sediments were exposed to the atmosphere during dry summer water sulfate concentration increased and pH decreased due to oxidation of reduced sulfur. In subsequent years however sulfate reduction resulted in an increased pH and alkalinity of pool water.

The role of sulfate reduction in alkalinity generation is well documented (Cook et al., 1986, and Giblin et al., 1990). For every equivalent of sulfur reduced an equivalent of alkalinity is generated:

$$2 \text{ CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow 2 \text{HCO}_3^- + \text{H}_2\text{S}$$

Oenema (1990) while studying the sulfate reduction in fine grained sediments in eastern Scheldt, Southwest Netherlands reported that reduction rates in summer varied between 14-68 mmol sulfate m$^{-2}$day$^{-1}$. The results also indicated that acid volatile sulfide was the major in situ reduced sulfur compound in the sediments. The sulfate reduction rate was calculated as the proportion of the added $^{35}$SO$_4$ recovered as reduced inorganic sulfur times the initial
dissolved sulfate pool size times a factor of 1.06 to account for discrimination against the heavier $^{35}$S isotope by sulfate reducing bacteria.

Pan (1985) studied the role of green manure in reduction of sulfate. He reported that in a red soil containing very little organic matter the sulfide content was very low even after it was submerged at a high temperature. The sulfide content increased several fold after the addition of green manure. Green manure also increased the concentration of $\text{H}_2\text{S}$ in red soil under submerged conditions.

Nageswarw et al. (1984) studied the transformation of added sulfate in relation to changes in Eh, pH, iron and manganese in flooded soils. The results suggested that transformation of added water soluble sulfate in soil was mainly governed by changes in Eh and partly by pH, iron and manganese. The extractable sulfate decreased moderately up to ten days and rapidly thereafter. The reduction of sulfate was hastened at a redox potential below -160 mV and or in the pH range of 6.4 to 7.7. They also noted that for laterite soils (low in organic matter and iron) although there was favorable pH range it took about 30 days of flooding to get 70% of the added sulfate reduced while in soils high in organic matter and iron it took about 20 days to get 70% of added sulfate reduced. The manganese (extractable in ammonium acetate) in all soils increased progressively and attained a peak value in about 20-30 days of submergence beyond which it decreased in some soils while remain constant in others.

Howarth and Teal (1979) studied the effect of temperature on sulfate reduction in a New England salt marsh and his results suggested that the rate of sulfate reduction when
plotted against temperature was not linear, with autumn rates higher and spring rates lower than would be expected. The high autumn rate could be caused by the pulse of readily available substrate as the grass plants mature and die.

Boulegue et al. (1982) investigated the sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware. He concluded that H₂S-H₂O and H₂S-S₈-H₂O systems are representative of the sulfur chemistry of most aqueous phases in reducing environments. Reduction of sulfate and oxidation of sulfide by oxygen are processes that are more likely to affect the sulfur chemistry in reducing environments. The reduction of sulfate is a bacterially catalyzed reaction yielding hydrogen sulfide. The redox conditions imposed on the environment are dependent on the couple HS/SO₄. This has been shown by Thorstenson (1970) who established that the ratio of the concentrations of the dissolved species (CH₄/CO₂, NH₃/N₂) were dependent on the redox processes of the sulfate reduction, and in agreement with the HS/SO₄⁻⁻ couple. He also observed that polysulfides, elemental sulfur and thiosulfate are the main intermediate products of oxidation of H₂S-H₂O system while complete oxidation yields sulfate ions.

**Sulfide Oxidation**

Reduced sulfur species may be removed from a reducing environment by chemical precipitation with transition or heavy metal ions, volatilization of the H₂S species in the aeration process of biologic oxidation and chemical oxidation by molecular oxygen present in the air or other oxidants. Hydrogen sulfide is a weak diprotic acid and therefore can
exist in three chemical forms in solution, \( \text{H}_2\text{S(aq)} \), \( \text{HS}^- \) and \( \text{S}^2^- \). The solution pH determines the distribution of these reduced species and is the predominant solution variable. In the pH range of natural waters the bisulfide ion \( \text{S}^2^- \) is the primary species while the hydrogen sulfide molecule \( [\text{H}_2\text{S(aq)}] \) becomes the predominant reduced sulfur species below pH 7 (O'Brien and Birkner, 1977).

Oxidation reaction of sulfide could proceed along two pathways

- oxidation of soluble sulfide
- oxidation of metal sulfide present as solid phase

The major end product of biological oxidation of sulfides are thiosulfate and sulfate (Goldhaber and Kaplan, 1974).

Connell and Patrick, Jr. (1969) reported that the oxidation of sulfide in the soil by oxygen was especially rapid, with one-half of the sulfide undergoing oxidation in 15 minutes with all being oxidized after 8 hours. They speculated that disappearance of sulfide was likely due to the chemical oxidation of sulfide to elemental sulfur, since the microbial conversion to sulfate would require a much longer time.

Janzen and Bettany (1987) measured the rate of sulfur oxidation in soils. They concluded that sulfur oxidation is exclusively a surficial reaction, only those atoms on the exterior of the sulfur particle being exposed to chemical or biological activity. Consequently the amount of sulfate produced per unit of time is a function of the total surface area of the sulfur present, not of its mass. This has been established in several investigations demonstrating a linear relationship between the amount of sulfate produced
and the total surface area of applied sulfur, irrespective of the amount of the applied sulfur (Fox et al., 1964; Janzen et al., 1982, and Laishley et al., 1983). The rate of oxidation expressed as function of initial surface area will still depend upon time, because surface area, like mass diminishes as oxidation proceeds, and the rate of decline will vary with the rate of oxidation.

Christian et al. (1992) investigated the ratio of biological and chemical oxidation during the aerobic elimination of sulfide by colorless sulfur bacteria. They reported that increasing substrate concentration results in an over proportional increase of chemical compared to biological oxidation. At a very low sulfide content chemical reaction is negligible whereas biological activity is already present at very low sulfide concentration. Within the range of 0.005 to 3.0 mM, chemical oxidation rose steadily from 0 to 18% of the total conversion: 3.0 mM exhibited the point of maximum biological activity and a further increase of sulfide content showed toxic effects. Also chemical sulfide oxidation rate rose with increasing pH and gave a narrow optimum at pH 7.0 and then increased by a local minimum at pH 8.0 and then increased again to about a 100 fold value compared with pH 1.0. Biological activity showed a similar distinct optimum at pH 7.0, where as it declined quickly with decreasing pH to 15% of the maximum value. They also reported a positive correlation between temperature and both chemical and biological oxidation rate. The chemical oxidation rate at 10°C turned to be approximately 0.45 micro mol.l⁻¹.h⁻¹ and showed a three fold increase at 20°C. This rate did not change significantly in the range between 20 and 30°C, and increased to 2.55 micro mol.l⁻¹.h⁻¹ at 40°C. Also Millero et al.
(1987) observed a tenfold increase in chemical oxidation rate following a rise in temperature from 0 to 30°C and from 30 to 65°C.

O'Brien and Birkner (1977) studied the kinetics of oxygenation of reduced sulfur species in aqueous solution. They reported that the \( S_{2}^{2-} \)(total)/\( O_{2} \) ratio affects the distribution of reaction products in the following ways: 1) a higher ratio along with total reduced sulfur concentration greater than \( 10^{-3} \) M, leads to formation of sulfur. 2) a low ratio favors the production of sulfite, thiosulfate and sulfate. The distribution of these products, however, is not affected by solution pH over the range 7.5 to 11. 3) At low pH(< 6.0) in dilute solutions the favored reaction product is presumably sulfate. Above pH 7.0 and for \( S_{2}^{2-} \) concentration below \( 10^{-3} \) sulfite, thiosulfate and sulfate are significant products.
Section 2

Isotope Analysis

Stable Isotopes of Sulfur and Carbon

Sulfur and carbon isotopes have been extensively used to trace the origin, transformation and movement of sulfur and carbon compounds in the atmosphere, rivers, lake waters and ground waters. S in FGD sludge is derived from the coal. During its movement from stack gases through scrubbers, pipes in to the evaporation pond it is exposed to various biogeochemical processes which are controlled mainly by redox status and biological activities. The $\delta^{34}$S and $^{32}$S ratio in sulfate and sulfide, $\delta^{13}$C and $^{14}$C in carbon is largely altered by the biogeochemical processes in the sludge. This ratio is the basis for study of processes influencing sulfur and carbon biogeochemistry in FGD sludge.

The stable isotope method, used in many geochemical and biological studies is based on the small difference in physicochemical behavior between isotopes of H, C, O and S. Carbon has two stable isotopes of which $^{12}$C is the more abundant (98.9%); $^{13}$C makes up about 1.1% (Mordeckai and Amiel, 1980), whereas sulfur has four stable isotopes ($^{32}$S, $^{33}$S, $^{34}$S, and $^{36}$S) whose percentages are approximately 95.0, 0.75, 4.20 and 0.017 respectively (MacNamara and Thode, 1950). The variation in the isotopic composition of C and S in natural material results from both equilibrium and kinetic fractionation. Two principal factors influencing the final isotopic composition of sulfate dissolved in precipitation are the isotopic composition of the sulfur source and the chemical transformation such as oxidation-reduction and the environments in which it occur
(aqueous, atmospheric). For example homogenous oxidation of $\text{SO}_2$ or $\text{HSO}_3^-$ in the atmosphere (which predominates in warmer months) is characterized by a kinetic isotope effect in both aqueous and gaseous phases resulting in sulfate with $\delta^{34}\text{S}$ isotopically lighter than the precursor $\text{SO}_2$. Heterogenous oxidation (which predominates in cooler months) involves both equilibrium and kinetic isotope effect. The resultant sulfate has $\delta^{34}\text{S}$ heavier than original $\text{SO}_2$ (Wadleigh et al., 1994).

Sulfate reduction in the sulfur cycle may be assimilatory or dissimilatory. During assimilatory reduction such as occurs in the plant metabolism of sulfate, the sulfur is reduced from a valence of +6 to a valence of -2 in the synthesized products (amino acids and proteins). On the other hand dissimilatory reduction of sulfate with the release of hydrogen sulfide often occurs in the bacterial reduction of sulfate. The turnover rates of sulfur in these latter dissimilatory processes exceeds those during assimilatory reduction by several orders of magnitudes. Accordingly the decisive biological control of the sulfur cycle is exercised by the sulfur reducing bacteria. It is during this dissimilatory reduction of sulfate to $\text{H}_2\text{S}$ that relatively large isotope effects occur. The bacterial reduction which takes place under anaerobic conditions in the presence of organic matter is therefore a major factor in the geochemical cycle of sulfur and accounts for the large fluxes of sulfur depleted in $^{34}\text{S}$ in to the lithosphere from hydrosphere (Thodes et al., 1951, and Kaplan and Rittenberg, 1964). In general sulfates tends to be enriched and sedimentary sulfides depleted in $^{34}\text{S}$, as one might expect from thermodynamic considerations. However there is no evidence of isotopic exchange between sulfate and sulfide below temperatures of
100°C. It is now well established that these deviations of $\delta^{34}$S from zero are due largely to the fractionation of sulfur isotopes in biologically mitigated reactions at low temperatures. The biological cycle of S is in part characterized by the activity of sulfur oxidizing bacteria and reducing bacteria which together account for the bulk of contemporary turn over rates in the biosphere (Alexander, 1971, Bass-Becking, 1925). Where as photosynthetic/ photolithotrophic sulfur bacteria oxidize reduced sulfur, *Desulfovibrio desulfuricans* or sulphate respires reduce sulfate to sulfide in anaerobic ecosystems in the presence of organic matter.

Theoretically speaking exchange reactions between sulfur compounds predicts enrichment of $^{34}$S in more oxidized species, the largest fractionation factor occurring in the exchange between H$_2$S and SO$_4^-$ exchange reaction, the two extreme oxidation states. The $^{34}/^{32}$S ratio provide a useful tracer for the origin of sulfate in the natural systems (Wadleigh et al., 1994). In nature there is no doubt that sulfate reducing bacteria are producing isotopically light sulfides and these depletions often exceed those found in laboratory experiments. During the respiratory oxidation of sulfate by thiobacillus, Kaplan and Rittenberg (1964) found that $\delta^{34}$S values -10 to -18 for sulfate for sulfate with respect starting sulfide, whereas dissimilatory sulfate reduction by *Desulfovibrio* in laboratory experiments have generated hydrogen sulfide ranging in $\delta^{34}$S from +3 to -46 as compared to original sulfate. Quantitatively the degree of fractionation in an inverse function of the reduction rate per unit cell.
Krouse and Thabatabai (1986) explained the observed significant variations in the $\delta^{34}S$ values of ground water. They argued that when the water table is high sulfate reduction occurs and the reduced product becomes immobilized. The unreacted sulfate becomes enriched in $^{34}S$ because $^{32}SO_4$ is preferentially reduced. The water table lowers retaining the $^{34}S$ enriched sulfate. However, the sulfide in upper horizons is then exposed to more aerobic conditions and oxidizes to sulfate, which is characterized by the $^{34}S$ depletion of the reactant sulfide. Repeated raising and lowering of the water table further enriches the deeper water and depletes the shallow water in $^{34}S$.

Brian (1986) used stable isotopic analyses of sediment cores to evaluate dissimilatory sulfate reduction in lake sediments of the Adirondack Mountains, New York. Increased sulfate reduction should lead to lower $\delta^{35}S$ values in the sediments for two reasons. Dissimilatory sulfate reduction occurs with a normal isotope effect such that product sulfides are depleted in $^{34}S$ relative to $^{32}S$ and have low $\delta^{34}S$ values (Chambers and Trudinger, 1979). Increase production and retention of sulfides in sediments will result in lower $\delta^{34}S$ values. Secondly isotopic fractionation may increase as sulfate levels increase. The isotopic composition of sulfides is approximately equal to that of sulfate when sulfate is present at the 10-15 microM concentrations characteristic of many undisturbed lakes but becomes increasingly depleted in $^{32}S$ as sulfate concentrations increase (Matrosov et al., 1975; Migdosov et al., 1974 and Migdosov et al., 1983). The magnitude of this $^{34}S$ depletion is variable but typically ranges between 10 and 70 $\%_o$ (Chambers and Trudinger, 1979). The increased environmental sulfate levels led to increased sulfate reduction in
lakes. The combined effects of increased sulfide addition and increased isotopic fractionation should result in $^{34}$S depletion in lake sediments. These depletions may function as indicators of sulfate loading and sulfate reduction activities.

In summary, stable isotopes of both sulfur and carbon have been extensively used in identifying and determining the source, transformations and movements of sulfur and carbon compounds in natural systems. These measurements are now finding increased application in environmental studies (tracing sulfur emitted from power plants and sulfide oxidation) as well. Isotopic fractionation takes place both during the oxidation of reduced sulfur compounds and reduction of oxidized sulfur species, but it is more profound during reduction. Many studies (McCready and Krouse, 1982, and Taylor et al., 1984) have shown that S isotope fractionation during pyrite oxidation is very minor. However some workers (Perason and Rightmire, 1980) suggested that during the sulfide oxidation significant fractionation takes place. Also the magnitude and extent of isotopic fractionation is highly variable and it depends upon the process involved in these transformation, and prevailing conditions under which these transformations takes place.
CHAPTER 3
EXPERIMENTAL MATERIALS AND METHODS

The purpose of this chapter is to describe the material used in this study as well as the methods adopted to accomplish the study goal. There are two sections of this chapter. The first section covers the major components of redox potential measurements, both under aerobic and anaerobic conditions as well as the methods used to determine sulfur species, various cation and anions and the changes in the solubility of selenium (Se) and boron (B). It also includes a brief account of the physical description of the study site, FGD sludge's physico-chemical properties, sampling time and procedure adopted to collect representative reduced FGD sludge samples and how to minimize the oxidation of reduced sludge during sampling, transportation and storage. At the end is brief description of calibration of redox and sulfide electrodes. The second section is related to isotopic analysis of sludge samples for carbon and sulfur isotopes. It includes a sampling strategy (time and location), collection, preservation, preparation of the samples for isotopic analysis.

Section 1
Oxidation Reduction

Although the production of FGD sludge has increased considerably in the past few decades only a few studies have looked at the use and management of the FGD sludge for better utilization or disposal of this material. A study was designed to investigate the
changes in oxidation reduction status of the FGD sludge disposal field. Three different sets of experiments were conducted in this study.

Site Description

The FGD sludge samples from a coal fired FGD sludge disposal site associated with Coronado electric power generating plant situated at St. Johns AZ were used in this study. The evaporation pond was formed by a cross-valley dam in a natural waterway. The average surface area of the pond including the δ is about 200 acres and the average volume of the pond is about 2200 acre feet. The pond is at an elevation of 5800 ft above sea level. The watershed drained by the dam is 1970 acres. The annual precipitation is about 10.5 inches. Generally, there is no vegetation on the pond δ howeversome salt ceders can be seen scattered in the δ during the spring. Also there is a marked difference in the redox boundary of the δ, during summer months all the profile except the upper few centimeters (<10 cm)is in highly reduced conditions (Eh < 380 mV), as evident from rotten egg odor and blackish grey color of the entire profile (Figure 3.1). During the winter months the redox boundary is lower in the profile (>50 cm), and also the intensity of reduction is not as high as in summer (very little smell of hydrogen sulfide and irregular reduced layers (Figure 3.2).
Figure 3.1 Section of the FGD sludge profile showing entirely reduced profile
Figure 3.2  Section of the FGD sludge profile showing alternate reduced and oxidized layers
**Sampling Strategy**

One of the foci during this study is to investigate the factors that are responsible for more reduced conditions in summer and less in winter. Here, it was imperative to think about an appropriate sampling time which may provide us information about factors that are responsible for this varying degree of reduction. For this purpose the sampling was done both during summer and winter and samples were analyzed for various parameters of interest.

**Physico-chemical Analysis**

Physico-chemical properties serve to help characterize a given site. Before using a site for research purpose it seems imperative to do its important physico-chemical analysis. Important physical parameters that have been determined using sludge samples are particle size analysis and sand fractionation. In the case of chemical analysis, pH, salinity status of sludge in terms of EC, and all major cation and anions, using 1:1 soil extract for soluble and solid samples for total concentrations. Results of Physico-chemical analysis have been presented in Table 3.1.

**Experiments under Anaerobic Conditions**

Although the production of FGD sludge has increased considerably in the past few decades only a few studies have looked at the potential use and/or management of the sludge disposal areas for the better disposal or utilization of this material. A study was
Table 3.1  Summary of physico-chemical properties of FGD sludge

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Number of samples</th>
<th>Minimum Value</th>
<th>Maximum Value</th>
<th>Average Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td>32.4</td>
</tr>
<tr>
<td>Silt</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td>62.6</td>
</tr>
<tr>
<td>Clay</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>pH (oxidized)</td>
<td>1:1</td>
<td>18</td>
<td>7.12</td>
<td>8.49</td>
<td>7.82</td>
</tr>
<tr>
<td>pH (reduced)</td>
<td>1:1</td>
<td>3</td>
<td>8.36</td>
<td>9.15</td>
<td>8.85</td>
</tr>
<tr>
<td>E.C.</td>
<td>dS/m</td>
<td>15</td>
<td>5.0</td>
<td>24.1</td>
<td>10.86</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg/l</td>
<td>5</td>
<td>36.3</td>
<td>382</td>
<td>124</td>
</tr>
<tr>
<td>Total C</td>
<td>%</td>
<td>5</td>
<td>2.15</td>
<td>6.5</td>
<td>3.26</td>
</tr>
<tr>
<td>Total OC</td>
<td>%</td>
<td>5</td>
<td>0.11</td>
<td>2.76</td>
<td>0.70</td>
</tr>
<tr>
<td>Total nitrate</td>
<td>%</td>
<td>15</td>
<td>0.01</td>
<td>0.07</td>
<td>0.02</td>
</tr>
<tr>
<td>Total sulfur</td>
<td>%</td>
<td>15</td>
<td>7.2</td>
<td>15.8</td>
<td>12.21</td>
</tr>
<tr>
<td>Soluble sulfate</td>
<td>ug/g</td>
<td>15</td>
<td>1920</td>
<td>6700</td>
<td>3923</td>
</tr>
<tr>
<td>Soluble chloride</td>
<td>ug/g</td>
<td>15</td>
<td>611</td>
<td>5660</td>
<td>2210</td>
</tr>
<tr>
<td>Soluble calcium</td>
<td>ug/g</td>
<td>15</td>
<td>480</td>
<td>1360</td>
<td>671</td>
</tr>
<tr>
<td>Total boron</td>
<td>ug/g</td>
<td>5</td>
<td>8.59</td>
<td>79.6</td>
<td>40.75</td>
</tr>
<tr>
<td>Total selenium</td>
<td>ug/g</td>
<td>15</td>
<td>0.72</td>
<td>8.12</td>
<td>3.86</td>
</tr>
<tr>
<td>Total potassium</td>
<td>ug/g</td>
<td>15</td>
<td>297</td>
<td>1520</td>
<td>765</td>
</tr>
<tr>
<td>Total magnesium</td>
<td>ug/g</td>
<td>15</td>
<td>1530</td>
<td>6880</td>
<td>3984</td>
</tr>
<tr>
<td>Moisture</td>
<td>%</td>
<td>5</td>
<td>25</td>
<td>100.1</td>
<td>50.19</td>
</tr>
</tbody>
</table>
designed to investigate the changes in oxidation reduction status of the FGD sludge in order to obtain a better understanding of the behavior of this material when subjected to periodic cycles of wetting and drying. Three experiments were performed in this study. The focus of the first experiment was to study the effect of flooding and drying on the redox potential of FGD sludge. Batch experiments were performed at room temperature (25±1°C) as well as 4±1°C using polypropylene centrifuge tubes. Polypropylene centrifuge tubes containing 5 g of sludge and 25 ml of deionized (DI) water (containing various concentrations of organic carbon) were stored under an argon atmosphere in an anaerobic chamber (PLAS LABS™ XPL-855-AC).

In a preliminary experiment to determine the effectiveness of nitrogen to remove air from the chamber, AAC was purged three times with nitrogen gas and reduced sludge was left in the chamber, 12 hours later the redox potential had decreased from -390 mV to -364 mV indicating that some air was still present in the AAC. But when the same experiment was repeated after purging the AAC three times with argon gas, the drop in the redox potential was only 8 mV in 12 hours indicating that argon was more effective in removing air from the chamber probably because of its higher purity and or density. The redox potential was only 8 mV in 12 hours indicating that argon was more effective in removing air from the chamber probably because of its higher purity and or density.

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The second experiment concentrates on the effect of available organic carbon on the reduction of FGD sludge. A series of batch experiments using three different rates of available carbon (25, 100 and 1000 ppm soluble organic carbon from sucrose) were performed under anaerobic conditions. To test the assumption that variations in redox boundary during summer and winter were caused by variable sulfate reduction rates as
affected by changes in temperature, another set of batch experiments was performed using two different temperatures (25±1°C and 4±1°C).

The purpose of the set of oxidation experiments was to study how redox potential changes as reduced FGD sludge is exposed to the atmosphere and what changes take place in the concentration of redox active species (S and Se). For this purpose the reduced sludge was exposed to the atmosphere by placing it in a container having an area of one cubic foot (12 in x 8 in x 1.5 in). A sub sample of 20 g was taken and mixed with varying amount of deaerated DI water depending upon the water content of the sample (to get a 1:1 ratio of mixture of FGD sludge and water). The combination redox electrode was placed in the mixture and Eh of the sample was recorded after a stable reading was obtained usually 10 minutes after the insertion of the electrode. Sulfide concentration in the oxidizing FGD sludge was determined potentiometrically using a sub sample of 50 g as described in section 3.1.6 of this chapter.

**Oxidation Experiments**

How fast redox potential would change, when reduced FGD sludge being exposed to atmosphere is mixed during its exposure, was the question addressed in another set of oxidation experiment. FGD sludge exposed to atmosphere was thoroughly mixed at regular intervals of time (6 and 12 hrs) changes in redox potential and pH were measured as described for the first set of oxidation experiments.
Moisture content of the FGD sludge plays an important role in redox reactions by limiting the diffusion of oxygen into the system. The purpose of third set of oxidation experiments was to determine how redox potential will change when sludge is exposed to atmosphere but moisture content is held almost constant (as is the case in the field) or when it is allowed to evaporate as would be the case when sludge is drained artificially by some sort of drainage system. In order to maintain moisture content during oxidation the water equal to amount of weight loss was added to the oxidizing sludge every hour while in the other treatment no water was added as sludge was being oxidized. Redox potential and pH were measured at regular intervals using sub samples taken from oxidizing FGD sludge.

**Redox Electrode Calibration**

As there is no direct calibration for redox electrode, the reliability of the electrode was checked by the following two ways. By comparing the electrode potential of a solution containing 0.1 M potassium ferrocyanide and 0.05 M potassium ferricyanide to that of a solution containing 0.36 M potassium fluoride in addition to 0.1 M potassium ferrocyanide and 0.05 M potassium ferricyanide (Orion, 1983).

The other test for the proper functioning of the electrode was to measure the redox potential of Zobell's solution (1.408 g potassium ferrocyanide K₄Fe(CN)₆·3 H₂O and 1.0975 g potassium ferricyanide K₃Fe(CN)₆ and 7.4555 g potassium chloride, KCl) which
is suppose to be 229 mV when measured, at 25°C, against Ag/AgCl reference electrode filled with saturated KCl (Standard Methods # 2580 A, 1992).

**Sulfide Electrode Calibration**

Sulfide is the dominant sulfur species in reduced environments. Potentiometric method using a silver/sulfide electrode coupled with a double junction reference electrode was employed for sulfide determination in sludge samples. As sulfide is prone to oxidation it was imperative to use an antioxidant to minimize the rate of oxidation during the calibration of sulfide electrode and measurement of sulfide concentration in the sample. The commercially available sulfide anti oxidant buffer (SAOB II™) was used for this purpose. The steps involved in calibration are as follow. Preparation of sulfide saturated stock solution by adding approximately 100 g of reagent grade sodium sulfide (Na₂S·9H₂O) in 100 ml of deaerated water. 10 ml of this saturated solution was added in to a 1L volumetric flask containing 500 ml of SAOB II and diluted to 1L with deaerated distilled water. The concentration of sulfide in this solution was determined by titrating 10 ml of this solution with 0.1 M lead perchlorate using the electrode pair as end point indicator. The sulfide concentration was calculated using the following equation

\[ C = 3206(V_t/V_s) \]

where

\[ C = \text{concentration as p.m. sulfide} \]
\[ V_t = \text{volume of titrant at end point} \]
V = volume of standard (10 ml)

Three standards containing 10, 100, and 1000 ppm sulfide were prepared using the stock solution, to cover the expected sample range, 25 ml of each SAOB II and deaerate DI water were added to each standard and electrode potential was measured. Three points were used to plot the calibration curve and in the same way sludge samples were prepared and sulfide concentration in the unknown sample was determined from calibration curve.

As the sulfide electrode is only capable of determining sulfide content in aqueous solutions it was necessary to bring all the sulfide present in the sample into aqueous solution. This was done by distilling the sample with HCl in a heating flask. 100 g of sample was added into flask and 50% concentrated HCl was added gradually with constantly stirring the flask using a magnetic stirrer and the H$_2$S liberated was collected in a beaker containing 500 ml of SAOB II solution.

The lower detection limit for the sulfide electrode, as given by manufacturers was $10^{-7} \text{M}$ (0.003 ppm) but in this study reproducible results were obtained only when sulfide concentration were higher than 1 ppm. Also since the pH of the samples after adding SAOB II was 13 or above it is assumed that all HS$^-$ and H$_2$S are completely converted to S$^2$-

**Section 2**

**Isotope Analysis**

Exchange and fractionation of atoms among various compounds of a redox active element, is likely to occur when such element undergoes geochemical transformations.
Isotopic analysis of sulfur and carbon compounds present in FGD sludge was performed in order to help explain some of the processes hypothesized to happen in sludge when it undergoes cycles of wetting and drying.

Stable isotope analyses are reported as δ values, which indicate how the abundance ratio of two isotopes in a sample differs in parts per thousand (per mil, ‰) from an internationally accepted standard.

\[
\delta^{34}\text{S} = \left[\frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}}\right] \times 10^3
\]

The standard for reporting δ^{34}\text{S} values in trolite (FeS) from the Canon Diablo meteorite whereas δ^{13}\text{C} with respect to PDB, the international carbon isotope standard. Positive and negative δ^{34}\text{S} values mean that the sample is enriched and depleted in δ^{34}\text{S} respectively in comparison to the standard.

**Sulfate Isotopes**

Sulfate was extracted from aqueous solution as follows: the solution was filtered, acidified with dilute HCl, and sulfate was precipitate as BaSO₄. The precipitate was washed and dried. In the case of sulfate from CaSO₄, the sludge was rinsed three times with de-ionized water, and sulfate was dissolved by boiling the sludge in dilute HCl. In reduced sludge, aqueous sulfate was leached out and precipitated under N₂ atmosphere. SO₂ was prepared from BaSO₄ according to the method of Coleman and Moore (1978).
Sulfide Isotope

Sulfide is the dominant sulfur species found in sludge under reduced conditions. For isotopic analysis of solid sulfide content of sludge, about 200 g of reduced sludge was distilled with HCl in a heating flask under a continuous stream of nitrogen, the resultant CO₂ and H₂S were dissolved in concentrated NaOH solution. The pH of the solution was adjusted to 5 in order to remove the carbonates. Lead nitrate solution was then added to precipitate sulfide as lead sulfide. This lead sulfide was then dried and ground. The finally ground sulfide sample was burned with copper oxide and silica at 950°C and SO₂ produced was separated from water and carbon dioxide, using vacuum lines.

For the determination of stable isotopes of aqueous sulfides, 100 g or larger of the sample of reduced sludge was mixed with 100 ml of deaerated deionized water (1:1) and was allowed to sit in anaerobic chamber (AAC) under argon atmosphere for two hours and the extract was filtered using Whatman #40, filter paper inside the AAC. The pH of the extract was adjusted to 5 by addition of dilute acid, in order to remove any dissolved carbonates. Lead nitrate solution was then added to precipitate sulfide as lead sulfide. The precipitate was invariably impure, but concentrated enough in PbS for preparation of SO₂ by the method of Robinson and Kusakabe (1975). This technique would combine sulfide from both minerals and fluids.

Carbon Isotope

For isotopic analysis of carbonate content of FGD sludge, sludge was first rinsed in de-ionized water, and dried. 30 mg of dried FGD sludge sample was placed in a two
portion flask, in the other arm of flask, 20 ml of 100% concentrated phosphoric acid (H$_3$PO$_4$) was added. Flask was attached to vacuum lines for 24 hours to remove all the air. Then phosphoric acid was mixed with sample and after the completion of reaction, the resultant CO$_2$ was separated from water (McCrea, 1951). Yields of CO$_2$ were determined by manometry.

The mass spectrometer VG-Micromass 602 with twin Faraday bucket collectors coupled to a ratio recording output stage for the determination of precise isotope ratio (the enrichment of a gas of unknown isotopic composition being related directly to that of a known standard) was used for isotopic analysis of sulfur dioxide and carbon dioxide gases obtained from samples. The analytical precisions ($2\sigma$) are: $\delta^{34}$S -- 0.24‰, $\delta^{13}$C -- 0.32‰.
CHAPTER 4
RESULTS AND DISCUSSION

This chapter presents the experimental results of the proposed study and explains the possible reasons for these results. There are two sections in this chapter. The first section deals with redox transformations and S speciation while the second section describes the results of stable isotope analysis.

Section 1
Oxidation Reduction

Oxidation of Reduced FGD Sludge

This section presents the data and discusses the changes in the redox potential of the reduced FGD sludge and the accompanying changes in the concentration of major sulfur species, when exposed to the atmosphere, and the effect of water content and mixing on the redox potential of the reduced sludge. \( E_h \) was used as an indicator of the oxidation status of the sludge. A highly reduced condition (\( E_h < -380 \text{ mV} \)) of the FGD sludge indicates that there is no dissolved molecular oxygen present in the system and all the redox active elements including sulfur, manganese, nitrogen, and selenium are present in their reduced forms. Since S is the only dominant redox active element in the sludge, therefore it was assumed that sulfide (\( H_2S(aq), HS^-, \text{ and } S^{2-} \)) is the dominant S species in reduced sludge at this redox potential.
Ponnampuruma (1973) reported that at the pH values of most anaerobic soils and sediments the bulk of the \( \text{H}_2\text{S} \) in the interstitial waters is present as undissociated \( \text{H}_2\text{S} \) and \( \text{HS}^- \), but the concentration of \( \text{S}_2^- \) is high enough to precipitate \( \text{FeS} \). Therefore one may expect that in a FGD sludge disposal site, redox potential will depend upon the relative concentration of hydrogen sulfide and poly sulfides (formed during incomplete oxidation of hydrogen sulfide or by the reaction of hydrogen sulfide with elemental sulfur), and since the redox couple \( \text{HS}^-/\text{Sn}_2^- \) is electroactive, changes in the concentration of \( \text{HS}^- \) or \( \text{Sn}_2^- \) will be reflected by the potential measured in \( \text{H}_2\text{S}-\text{S}_8-\text{H}_2\text{O} \) system (Boulegue et al., 1982).

When reduced sludge was exposed to atmosphere the concentration of sulfide and polysulfide species present in reduced sludge decreased by chemical and or biological oxidation, and the Eh of the system increased as shown in Figure 4.1. The initial Eh (- 383 mV) of the reduced sludge increased linearly during first 20 h of exposure to the atmosphere until it reached about 50 mV, at this point further increase in Eh became less rapid and it began to level off. But a careful observation of the Eh vs time curve will reveal the fact that from about 122 mV to 215 mV, there is a constant although slow increase in Eh over time. The redox potential reached a maximum steady state value near 215 mV. The experiment was repeated three times under the same set of conditions and close agreements were observed in all the three replicates. Figure 4.1 represents the average of three experiments. Rate of increase in Eh of FGD sludge, when exposed to atmosphere, was calculated by two different equations. In first case the data was divided in to two steps (fast initial step followed by slow step) and linear equation \( y = a + bx \) was
Figure 4.1 Changes in redox potential (Eh) during oxidation of FGD sludge under evaporating moisture condition
applied to both data sets as shown in Figure 4.2 and 4.3. Various parameters of equation are given in Table 4.1. During the first phase of fast chemical oxidation Eh increased at a rate of 23 mV/hr. A, while rate of increase was only 1.2 mV/hr.A, for the second slow step of biological oxidation. Therefore first step appears to be approximately 23 times faster than second and the possible explanation for this could be that the oxygen required by sulfide oxidizing bacteria is not available when sludge is saturated with water but once the moisture content decreases these aerobic bacteria become active and oxidize the remaining sulfide. In second case a non linear equation \( y = (a+cx)/(1+bx) \) was fitted to the data as shown in Figure 4.4. The increase in Eh was very rapid at a rate of 42.5 mV/h.A and gradually declined to 11.3 mV/h.A after 20 hours and dropped to 0.83 mV/hr.A, after 100 hours of exposure.

Table 4.1 \hspace{1cm} Best fit equations and rate of increase of Eh of FGD sludge when exposed to atmosphere

<table>
<thead>
<tr>
<th>Function</th>
<th>Coefficients</th>
<th>( r^2 )</th>
<th>rate of increase in Eh (mV/h.A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y = a + bx ) (step 1 of oxidation)</td>
<td>- 393.06</td>
<td>23.41</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y = a + bx ) (step 2 of oxidation)</td>
<td>70.54</td>
<td>1.08</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y = (a+cx)/(1+bx) ) non linear best fit</td>
<td>- 402.16</td>
<td>0.071</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.69</td>
<td>42.5</td>
</tr>
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<td></td>
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<td></td>
<td>11.31</td>
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<td></td>
<td></td>
<td></td>
<td>0.83</td>
</tr>
</tbody>
</table>
Figure 4.2 Changes in redox potential of FGD sludge during the first phase of fast chemical oxidation under evaporating moisture condition
Figure 4.3 Changes in redox potential during second phase of slow biological oxidation of the FGD sludge under evaporating moisture content
Figure 4.4  Changes in redox potential during oxidation of reduced FGD sludge, under evaporating moisture condition (non linear best fit)

\[ y = \frac{(a + cx)}{(1 + bx)} \]

Observed — Fitted
Based on the sludge composition (predominantly calcium sulfate) we can assume that sulfide and polysulfides are the main species being oxidized. In the beginning of the oxidation process, due to saturation oxygen supply was very limited, and sulfide oxidizing aerobic bacteria were not active therefore it represented chemical oxidation and with the passage of time water present in the sludge begin to evaporate and oxygen diffusion increased bacteria became active and thus in phase II microbiological oxidation was the dominant process with seemingly little chemical oxidation. The end products of this reaction are likely to be sulfite, thiosulfate and sulfate as the low ratio of reduced sulfur to oxygen favor this speciation (O'Brian and Birkner, 1977). Also since the oxidation of sulfur is exclusively a surficial reaction (Jazen and Bettany, 1987), its rate will decrease as the oxidation reaction proceeds and surface area diminishes. Therefore oxidation will not depend upon the mass of sulfide but rather on the total area being exposed to the atmosphere.

This conclusion about the initial fast chemical oxidation reaction followed by a slow microbially mediated oxidation reaction is supported by the earlier work of Conell and Patrick Jr. (1969). They observed, while studying sulfate reduction in waterlogged soils supplied with an energy source, that oxidation of sulfide in the soil by oxygen was rapid with one half of the sulfate being oxidized in 15 minutes and all sulfide oxidized after eight hours. They speculated that disappearance of sulfide was likely due to chemical oxidation of sulfide to elemental sulfur, since the microbial conversion to sulfate would require a much longer time. The work of Christian et al. (1992) also supports the two step oxidation
reaction of sulfide oxidation. They reported that increasing substrate concentration results in an over proportional increase of chemical oxidation compared to biological oxidation. At very low sulfide content chemical reactions are negligible whereas biological activity is already present at these very low sulfide concentrations.

Reddy et al. (1980) proposed a similar two step oxidation reaction based on oxygen consumption for oxidation of Fe$^{2+}$. They found that Fe$^{2+}$ was the dominant reductant in the fast oxidation reaction and speculated that O$_2$ consumption in phase I may be due to the water soluble Fe$^{2+}$ whereas part of the O$_2$ consumption in phase II was probably due to exchangeable Fe$^{2+}$. They also suggested that in phase I, O$_2$ consumption represented strictly chemical oxidation of Fe$^{2+}$, and phase II represented both chemical and microbiological oxidation.

The change in the concentration of major sulfur species (sulfate and sulfide) during the oxidation of FGD sludge is shown in Figure 4.5 while the best fit equations used to compute the rate of oxidation of both sulfate and sulfide are presented in Figure 4.6-7 and computed rates of oxidation in Table 4.2. Total sulfide (metal sulfide + free sulfide) concentration decreased sharply and about 80% of the total sulfide oxidized within 20 h of exposure to atmosphere. Fifty six hours after exposure to the atmosphere, the total sulfide concentration declined below the detection limit (1 ppm.). The time it took for oxidation of 80% of the sulfide is longer than that reported by Conell and Patrick, Jr. (1969), who reported that the oxidation of sulfide in the soil by oxygen was especially rapid, with one-half of the sulfide being oxidized in 15 minutes and all oxidized after 8 hours. The longer
Figure 4.5 Changes in sulfide (total) and soluble sulfate concentration during the oxidation of reduced FGD sludge under evaporating moisture condition.
Figure 4.6 Changes in soluble sulfate content of reduced FGD sludge during its exposure to atmosphere

\[ \ln y = \frac{a + cx}{1 + bx} \]

- Observed — Fitted
Figure 4.7  Changes in total sulfide content of the reduced FGD sludge during oxidation under evaporating moisture condition.

\[ \ln y = a + bx \]
Table 4.2  Best fit equations and various parameters for data showing rates of change in concentration of sulfate and sulfide during oxidation of FGD sludge

<table>
<thead>
<tr>
<th>Function</th>
<th>Coefficients</th>
<th>r²</th>
<th>rate of change in concentration(ppm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>$\ln y = a + bx$ (sulfide)</td>
<td>6.655</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>$\ln y = (a + cx)/(1+bx)$ (sulfate)</td>
<td>8.674</td>
<td>0.153</td>
<td>1.374</td>
</tr>
</tbody>
</table>

time in this experiment is probably owing to the fact that all sulfide present in the FGD sludge was not exposed to atmosphere at the same time and oxidized portion of the FGD sludge formed a coating around the remaining reduced FGD sludge and thus restricted its exposure to atmosphere. Also diffusion of air and thus oxygen was very slow in the beginning, due to higher moisture content of the sludge. Concurrent with the disappearance of sulfide was the increase in the concentration of dissolved sulfate. Oxidation of FGD sludge is different from sulfide oxidation in sediments, lakes or acid sulfate soils because of iron content. When iron is present only in the system pyrite is formed ($K = 10^{18.1}$) and less sulfur is present as soluble sulfate. In the case of FGD sludge, iron is present in trace amounts and pyrite formation is not significant. As a result soluble sulfate concentration
increased with the oxidation of the sludge (Figure 4.5). However, the continued increase in the concentration of soluble sulfate even after the disappearance of sulfide indicates the presence of other reduced S species such as thiosulfate and sulfite, which were not measured in this study. These intermediate products also oxidize when sufficient oxygen is present in the system, usually after the oxidation of sulfide. The change in the sulfide content of reduced FGD sludge as affected by moisture content during its oxidation was also studied and result is shown in Figure 4.8. The method of best fit was adopted to compute the rate of sulfide oxidation under different moisture contents. The best fit equations (Figure 4.9-10), the various parameters of the equations and the computed rates of sulfide oxidation at different time are presented in Table 4.3.

The initial rate of decrease in total sulfide content was similar for both cases but when moisture started evaporating, the rate of oxidation two hours after exposure, was 48.6 ppm/h of sulfide under evaporating moisture as compared to 21.4 ppm/h where moisture was kept constant. Similar trend was seen after 9 h, when it was 25.3 ppm/h as compared to 14.3 ppm/h. After 20 h, sulfide oxidation rate was 15.8 ppm/h in case of evaporating moisture as compared to 9.6 ppm in constant moisture treatment. To summarize the effect of moisture on sulfide oxidation, we can say, based on experimental results, that it took only 20 hours for 80% of the sulfide present in FGD sludge to oxidize under evaporating moisture conditions where as 67 h were needed for the same under constant moisture condition. We can conclude that oxidation of total sulfide is 3.3 times
Figure 4.8  Effect of moisture content on the oxidation of sulfide present in reduced FGD sludge
Figure 4.9 Changes in total sulfide content of the reduced FGD sludge during oxidation under evaporating moisture condition

\[ \ln y = a + bx \]
Figure 4.10  Changes in total sulfide content during oxidation of reduced FGD sludge under constant moisture condition
Table 4.3  Best fit equations and various parameters for data showing effect of moisture on rate of sulfide oxidation:

<table>
<thead>
<tr>
<th>Function</th>
<th>Coefficients</th>
<th>$r^2$</th>
<th>rate of sulfide oxidation (ppm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>ln $y = a + bx$</td>
<td>6.60</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>evaporating moisture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$y = a + bx^{0.5}$</td>
<td>779.8</td>
<td>76.31</td>
<td>-</td>
</tr>
<tr>
<td>constant moisture</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

faster when FGD sludge is either drained or moisture is allowed to evaporate than under saturated sludge.

Moisture content of the FGD sludge greatly influences the process of oxidation by retarding the diffusion of oxygen gas. The second experiment dealt with the question of how moisture content will affect the rate of oxidation. Figure 4.11 shows the change in redox potential of reduced FGD sludge as a function of moisture content when it is exposed to the atmosphere and moisture content is allowed to evaporate. Whereas Figure 4.12 shows the change in redox potential of reduced FGD sludge upon exposure to atmosphere with and without maintaining the initial moisture content of the FGD sludge. The reduced sludge was almost 100% saturated with water (% moisture w/w, 98%). In
$y = \frac{a + cx}{1 + bx + dx^2}$

Figure 4.11  Changes in Eh of reduced FGD sludge as a function of moisture content
Figure 4.12  Effect of moisture content on oxidation of reduced FGD sludge
order to quantify the effect of moisture content on rate of oxidation of FGD sludge, best fit method was employed (Figure 4.13-14) to compute the rate of change of Eh over time. The equation $y = \frac{a + cx}{1 + bx}$ was fitted to both data sets and different parameters are shown in Table 4.4.

<table>
<thead>
<tr>
<th>Table 4.4</th>
<th>Best fit equation, various parameters and rates of FGD sludge oxidation as affected by two different moisture contents:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>Coefficients</td>
</tr>
<tr>
<td>$y = \frac{a + cx}{1 + bx}$ evaporating moisture</td>
<td>-402.1 0.071 19.69</td>
</tr>
<tr>
<td>$y = \frac{a + cx}{1 + bx}$ constant moisture</td>
<td>-433.0 0.018 5.550</td>
</tr>
</tbody>
</table>

At the start of the experiment rate of oxidation is same for both treatments since initial conditions are same but after two h of exposure Eh under evaporating condition was increasing at a rate of 42.5 mV/h.A as compared to 13.5 mV/h.A under saturating conditions. The same trend was seen through out the experiment. But the difference in rate of oxidation decreased as the rate of oxidation decreased in both treatments over time. The Eh of the sludge become positive in 17 h under evaporating conditions where as it took 77
Figure 4.13  Changes in Eh of reduced FGD sludge when exposed to the atmosphere under constant moisture condition

\[ y = \frac{a + cx}{1 + bx} \]

- Observed — Fitted
Figure 4.14  Changes in redox potential during oxidation of reduced FGD sludge, under evaporating moisture condition (non linear best fit)

\[ y = \frac{a + cx}{1 + bx} \]
h to attain positive Eh when initial moisture content was kept constant. The rate of oxidation under evaporating moisture condition was three times faster than under constant moisture condition during the first few hours of exposure. But as a result of the diffusion of oxygen in to the water, after 20 h of exposure the oxidation under evaporating condition was only 1.5 times faster than oxidation under constant moisture. The two factors appear to be responsible for this significant difference in the rate of oxidation; 1) limited supply of oxygen under saturated condition and 2) more favorable conditions for sulfide oxidizing bacteria, which are aerobes in nature, under evaporating moisture during exposure to the atmosphere.

Another question of practical significance is how redox potential will change under field conditions, when reduced sludge is mixed during its exposure to the atmosphere and moisture content is kept constant. This question was the focus of a third oxidation experiment. The changes in Eh of reduced FGD as affected by two mixing treatments are shown in Figure 4.15 and best fit equations (Figure 4.16-17). The computed rates of oxidation are given in Table 4.5.

The initial rate of 6-h mixing (52.5 mV/h.A) was similar to that of 12 h mixing (56.2 mV/h.A) since both treatments were mixed at the start of the experiment. But after 26 h the rate was 38.5 mV/h.unit area in 6-h mixing as compared to 21 mV/h.A in 12-h mixing. Based on experimental data we can see that it took 37 h with 12-h mixing to have an Eh of 9.5 mV while it took less than 14 h to attain an Eh of 35.6 mv with 6-h mixing, Two points are evident from these results; 1) the rate of oxidation increased significantly
Figure 4.15 Comparison of effect of mixing treatments (6 vs 12 hour) on change in redox potential of reduced FGD sludge during oxidation.
Figure 4.16  Effect of every six hour mixing on the oxidation of reduced FGD sludge when exposed to atmosphere
Figure 4.17 Effect of every twelve hour mixing on the oxidation of reduced FDG sludge when exposed to atmosphere
because of mixing, as expected and 2) each time the reduced sludge was mixed, a sharp increase in the Eh was noticed. This can be explained by more evaporation of water because of mixing and also every time sludge is mixed a portion of reduced sludge is being exposed to air which enhances the process of oxidation of sulfide.

Table 4.5  Best fit equation, various parameters and rates of FGD sludge oxidation as affected by two mixing treatments:

<table>
<thead>
<tr>
<th>Function</th>
<th>Coefficients</th>
<th>r²</th>
<th>rate of sludge oxidation (mV/h.A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>y = a + bx + cx² + dx³</td>
<td></td>
<td>27.5</td>
<td>-0.41</td>
</tr>
<tr>
<td>6-h mixing</td>
<td>334</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>y = a + bx + cx² + d/x</td>
<td></td>
<td>7.44</td>
<td>0.03</td>
</tr>
<tr>
<td>12-h mixing</td>
<td>227</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

**pH Changes during Oxidation**

Almost all important reduction reactions that occur in nature involve the consumption of H⁺ ions resulting in a decrease in acidity or an increase in net OH⁻ ion concentration while oxidation can result in the production of free electron and thus
increased acidity. Also because of the complementary nature of pH and pe an Eh measurement can not be used to predict the presence of a particular redox couple unless pH is known (Stumm and Morgan, 1981).

The pH of reduced and oxidized FGD sludge along with other important physico-chemical properties of FGD sludge is given in Table 3.1. The reduced FGD sludge has a higher average pH (8.85) than that of oxidized sludge (7.82). The probable reason could be the reduction of sulfate and production of hydrogen sulfide and or sodium carbonate, which would lower the pH of the medium. Also we know that in waterlogged soils, sediments and lakes the pH is controlled by the redox and carbonate system (Ponnamperuma, 1971). The same can be applied to this system as calcium carbonate and calcium sulfate are the dominant constituent of FGD sludge. The change in pH of the oxidizing FGD sludge was measured each time a redox potential measurement was made. Changes in pH of the reduced FGD sludge as it oxidizes are shown in Figure 4.18. The unusual trend seen in this Figure 4.18 can be explained by considering that during the initial fast chemical oxidation of reduced sludge, the production of sulfuric acid and other sulfur compounds exceeds the acid neutralizing capacity of the sludge, therefore excess $\text{H}_2\text{SO}_4$ causes acidification and we observe a sudden drop in pH. But when carbonate and bicarbonate systems neutralize the excess $\text{H}_2\text{SO}_4$, after some lag time, the pH of the system again increases and becomes stable around 8.5. The calcium sulfate formed during the neutralization of sulfuric acid forms a coating around the calcite molecule and retards the
Figure 4.18  Changes in pH and Eh of FGD sludge during oxidation under evaporating moisture conditions
movement of sulfuric acid to calcite, because diffusion through solids is far more slower than diffusion through liquids. But when enough time is allowed the process of neutralization is completed and once again the carbonate system takes up the control of pH in the sludge.

**Sulfate Reduction**

The most important part of this study was to address the question of FGD sludge reduction, when subjected to saturation, during different time of the year and for varying duration of time. The reduction of FGD sludge is important as it would greatly affect the growth and establishment of vegetation at the disposal site, which is the main purpose of this project. Since sulfate is the only redox active species, present in large amount in the sludge, we can assume that reduction of FGD sludge is brought about by the reduction of sulfate present in sludge. The reduction of the sulfate ion in the soil environment has a favorable formation constant ($\log k = 20.74$ but requires redox conditions $\text{pH} + \text{pe}>4$, which is seldom encountered in surface soils (Lindsay, 1979). Although sulfate reduction is a microbially mediated biological process but it is controlled largely by physicochemical conditions and appears to be favored at neutral pH and is not likely to occur in acid soils ($\text{pH} < 5$) (Alexander, 1977).

Prior to the reduction experiment, solid and liquid waste coming from scrubbers was analyzed to determine whether sulfide, if any, is being added in to the pond from the scrubbers or all the sulfide present in sludge, is being produced in place, by the reduction
of sulfate. The sulfide content of incoming scrubber waste (solid + liquid) was below detection limit, whereas reduced sludge had 150 to 880 ppm sulfide per g of sludge, depending upon the time of the sampling (winter or summer). The first batch experiment was conducted to study the reduction of sulfate when FGD sludge is subjected to anaerobic conditions because of runoff waters after the event of rainfall. Deionized water without added carbon was used and the experiment was conducted at room temperature, the result of this experiment is shown in Figure 4.19. No significant reduction in the redox potential was observed during first many days of incubation. After 7 days redox potential decreased very slowly but it remained above 170 mV and thus no sulfate could be reduced despite incubation under saturated conditions for three months. However this preliminary experiment, led us to believe that there are not enough nutrients present in the FGD sludge to support the reduction of sulfate without some inputs from the outside sources. As this disposal site receives the runoff waters, in case of storm, from about a three square mile area surrounding it, the possible source of carbon could be the organic matter from plant residues, dissolved or suspended in water. But since summer months are very hot in this area the organic matter is likely to contain a recalcitrant fraction of humic and fulvic acids, so carbon from this organic matter is not readily available for microbial use. Since bacterial sulfate reduction is an important pathway for organic carbon mineralization, in this process organic compounds are mineralized and dissolved sulfate is reduced simultaneously by heterotrophic microorganisms. Also the rate of sulfate reduction is primarily dependent on the amount and reactivity of decomposable organic carbon
Figure 4.19 Changes in Eh and pH of FGD sludge when incubated with DI water without addition of organic carbon.
The second batch experiment was conducted to determine the effect of available carbon on the reduction of FGD sludge (primarily of sulfate). Three different concentrations of soluble organic carbon (0, 100 and 1000 ppm) from sucrose, were used in this reduction experiment and change in Eh and pH of the suspension were measured over time. The results are presented in Figure 4.20-22. Eh of the FGD sludge incubated without adding any organic carbon never dropped below 175 mV, as shown in Figure 4.19, however the small decrease from 235 mV to 175 mV was caused by the presence of small amounts of organic carbon in the sludge itself, whereas pH remained almost constant at 8.4. In case of 100 ppm organic carbon Eh dropped to about -150 mV after 200 hours of incubation, as shown in Figure 4.20 while pH decreased to 7.5. This treatment suggests that although sulfate is present in large quantities, but once the supply of available organic carbon is exhausted, reduction of sulfate would not proceed further, despite all other factors being favorable. The changes in Eh and pH of FGD sludge when incubated with 1000 ppm organic carbon are also shown in Figure 4.20. In this case, we can see that after the lag of only few hours, the reduction of the FGD sludge started and the reduction rate was almost three times faster than that of treatment with 100 ppm organic carbon. In order to compute the rate of reduction as effected by organic carbon best fit equations (Figure 4.23-25) were used and the computed rates are shown in Table 4.7. The rate of reduction after six hour for 100 ppm treatment was 3.77 mV/h.A where as for 1000 ppm it was 9.12 mV/h.A, which is almost 2.7 times faster than 100 ppm OC treatment. After 32 hours the difference
Figure 4.20 Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on the Eh of FGD sludge during incubation.
Figure 4.21  Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on pH of the FGD sludge during incubation
Figure 4.22  Comparison of the effect of different concentrations (0, 100, and 1000 ppm) of OC on the pe+pH parameter of FGD sludge during incubation
Figure 4.23 Changes in Eh of FGD sludge when incubated in DI water without addition of organic carbon.

\[ y = a + bx + cx^2 \]
Figure 4.24 Changes in Eh of FGD sludge when incubated with 100 ppm organic carbon
$y = A + b \exp(-x/c)$

Figure 4.25 Changes in Eh of FGD sludge when incubated with 1000 ppm organic carbon
between the rate for reduction of 100 ppm OC to 1000 ppm OC 3.42 mV/h.A., (6.5 mV/h.A as compared to 3.08 mV/h.A). To compare the three treatments (Figure 4.20) we can say that Eh dropped below -300 mV in less than 100 hours in case of 1000 ppm OC while Eh never dropped below -150 mV when 100 ppm of OC was added to the sludge and it remained above 170 mV when no OC was added.

The comparison of the changes in pH of three treatments is given in Figure 4.21. It shows that pH in case of 1000 ppm OC dropped from 8.6 to 6.4 and then increased to 7.85 and remained constant at this level. While pH decreased from 8.8 to 7.6 in case of 100 ppm OC and it did not change appreciably when no OC was added. We can conclude from this experiment that although sulfate reduction is a thermodynamically favorable reaction (log K of 20.74), but it may or may not be favored kinetically, as it is mediated microbially and if organic carbon is not added in the FGD sludge, sulfate will not be reduced. This was shown in first two treatments (0, and 100 ppm), where carbon was a limiting factor and therefore no and little reduction took place but when sufficient carbon was available redox potential dropped to the extent where methanogens start reducing carbon dioxide. Also the reduction of FGD sludge when OC is not a limiting factor, proceeds exponentially as shown in the best fit equations used to calculate the rate of reduction (Table 4.6).

These results concur with that reported by Jakobsen et al. (1981) for the reduction of soil suspension when incubated under anaerobic conditions. According to their results when no nitrate was present, Eh decreased to about -250 mV within about 50 h in Crowley
Table 4.6  Best fit equations, their parameters and computed rates of FGD sludge reduction as affected by concentration of organic carbon:

<table>
<thead>
<tr>
<th>Function</th>
<th>Coefficients</th>
<th>$r^2$</th>
<th>rate of sludge reduction (mV/h.A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y = a + bx + cx^2$ No OC added</td>
<td>a 57268, b -57.17, c 0.029</td>
<td>0.988</td>
<td>0.51 0.65 0.11</td>
</tr>
<tr>
<td>$y = a + b \exp(-x/c)$ 100 ppm OC</td>
<td>a -163.07, b 441.96, c 108.19</td>
<td>0.988</td>
<td>3.77 3.08 1.63</td>
</tr>
<tr>
<td>$y = a + b \exp(-x/c)$ 1000 ppm OC</td>
<td>a -361.9, b 628.04, c 70.97</td>
<td>0.971</td>
<td>9.12 6.5 2.37</td>
</tr>
</tbody>
</table>

and Mhoon soil suspensions and to -200 mV in Barataria Bay sediments. With nitrate present, the redox potential remained at a high level until all nitrate was reduced, after which it decreased to the values given above. The reduction of FGD sludge in experiments of this study was slower than that reported by other workers (McGeehan and Naylor, 1994) using soil subjected to flooding. According to the results of McGeehan and Naylor (1994) the $p_e+pH$ parameter declined rapidly during the first 2 d of flooding and reached a plateau near 2, whereas in case of FGD sludge, although the initial decrease was rapid, but it took 7 d for redox parameter ($p_e+pH$) to reach a plateau near 4 (Figure 4.22). The reason for the rapid decrease in redox potential of soil is perhaps due to the higher concentration of available carbon (1 g D-glucose kg$^{-1}$ soil) used by McGeehan and Naylor
(1994), and presence of sulfate reducing bacteria in higher number, since soils generally contain more organic matter, which encourages microbial activity.

The change in total sulfide and soluble sulfate content of the FGD sludge as it undergoes reduction are given in Figure 4.26. We can see that sulfide started to appear only when Eh dropped below -75 mV which is somewhat higher than usual reported in literature for sulfate reduction. But it is obvious from the figure that as Eh decreases below -150 mV a sharp increase in sulfide content of the sludge was probably due to highly favorable redox conditions for sulfate reducing bacteria. The phase diagram of sulfur compounds in equilibrium with the aqueous phase at 25°C and 101 kPa (Jakobson et al., 1981) is shown in Figure 4.27. The redox potentials and pH values over which sulfate reduction took place were close to those that can be predicted from the phase diagram for S/H₂O system. The presence of experimental data in the range that can be predicted from phase diagram indicates that even though a mixed potential was measured, the sulfate sulfide system was sufficiently dominant to prevail, as it was expected for this particular system.

The observed difference in reduction intensity (highly reduced conditions in the summer and relatively less reduction in the winter, was thought to be due to the effect of temperature on the activity of sulfate reducing bacteria. The temperature during the summer months at the disposal site can be as high as 120°F while it drops below zero during the winter months. Although temperature of the profile is less affected by the temperature fluctuations than the temperature of the surrounding air, the change in soil
Figure 4.26 Changes in soluble sulfate and total sulfide concentrations during the reduction of the FGD sludge as a function of redox potential.
Figure 4.27  Phase diagram (pH and Eh) of sulfur compounds in equilibrium with aqueous phase at 25°C and 101 kPa (After Jakobson et al., 1981)
temperature is sufficient to greatly affect the microbial activities. Cho and Ponnamperuma (1971) concluded, while studying the influence of soil temperature on the chemical kinetics of flooded soils and the growth of rice, that the rate of sulfate reduction in an anaerobic environment is temperature dependent. The third reduction experiment was designed to determine the redox potential changes as a function of temperature. The sludge containing 1000 ppm inorganic carbon was incubated at two different temperatures (25±1°C and 4±1°C). The results are given in Figure 4.28. The Eh of the FGD sludge incubated at room temperature decreased to -300 mV in three days and reached a plateau near -380 mV in less than ten days whereas almost no change in the redox potential took place in the sludge incubated at 4±1°C after 40 days. This clearly indicates that when all other factors are conducive for sulfate reduction, temperature of the medium controls the sulfate reduction in FGD sludge. We can also see from Figure 4.29 that during the winter various layers in the profile contain sufficient carbon suggesting that carbon was not a limiting factor for moderate reduction intensity and/or in some cases for little reduction of the FGD sludge (calcium sulfate). Temperature not only slows down the microbial activities but it also retards the rate of chemical reactions. Thus we can assume that temperature is the main factor responsible for varying the degree of sulfate reduction during the summer and the winter months.

**Effect of Reduction on Se and B Solubility**

Boron an essential plant nutrient, is present in sludge in considerable amounts.
Figure 4.28 Effect of incubation temperature (4±1°C vs 25±1°C) on redox potential of the FGD sludge.
Figure 4.29  Changes in total soluble organic carbon with depth of FGD sludge profile during winter
Although it is not redox active its availability to plants in highly pH dependent. At pH values below 6.0 it is present as boric acid B(OH)$_3$ and above pH 7.0 it is present as borate ion (B(OH)$_4$). Boron has the narrowest availability to toxicity ratio among all the essential nutrient elements. Selenium, although not present in high concentration in FGD sludge, was studied because of its redox active nature and because microbial processes play an important role in immobilization of Se through the maintenance of reducing conditions (Alemi et al., 1988 b). Its solubility increases as reduced sediments or soils are oxidized and thus increases its mobility. The result of Se and B solubility as measured during reduction of FGD sludge are shown in Figure 4.30 and 4.31.

The Se concentration in solution decreased significantly during the reduction of FGD sludge as shown in Figure 4.30. This decrease in Se solubility is probably due to transformation of selenate to selenite which is less soluble and mobile than selenate. The same mechanism was proposed by White et al. (1991), while studying the transport of selenium in ground water at the Kesterson Reservoir, California. They reported that Se transport was strongly retarded because of chemical reduction and precipitation mediated by microbial activity. Normally slow inorganic reduction rates were accelerated by microbial activity which utilized oxidized chemical species including selenate as electron donors during the oxidation of organic matter.

Boron solubility as measured by changes in B concentration in solution during the reduction of FGD sludge, was not affected by change in redox potential of the sludge. Minor changes in B concentration, seen during this experiment could be due to a change
Figure 4.30 Changes in selenium solubility during reduction of FGD sludge as a function of redox potential
Figure 4.31 Changes in boron solubility during reduction of FGD sludge as a function of redox potential.
Minor changes in B concentration, seen during this experiment could be due to a change in pH or even experimental errors.

**Selenium Adsorption**

The importance of Se both as an essential and hazardous element has prompted many investigations of its chemistry in soils and waters (Adriano, 1986). The presence of Se as selenite or selenate in soil seriously affects the growth of plants, as $\text{SeO}_4^{2-}$ (selenate) is more toxic than selenite at the same concentration level (Singh and Singh, 1979). Therefore it is necessary to understand the processes that control the mobility and transport of toxic elements. The behavior of selenium is influenced by the redox and pH of the system, by processes such as precipitation, formation of organic or inorganic complexes, biological interaction and adsorption. Se can exist in four oxidation states; selenide ($\text{Se}^2$), elemental selenium ($\text{Se}^0$), selenite ($\text{SeO}_3^{2-}$) and selenate ($\text{SeO}_4^{2-}$). Thermodynamic calculations indicate that selenide and elemental Se should be found in reducing, selenite in mildly reducing and selenate in oxidizing environments. Adsorption experiments have pointed out that the amount of selenite adsorbed depends on the presence of other anions. If strongly binding anions such as phosphate or certain organic acids are present in high enough concentrations relative to the concentration of selenite, then competition would cause selenite to be in a dissolved phase rather than a particulate phase environments (Balistrieri and Chao, 1987). Calcareous soils also retain selenite, but not selenate. Selenite leaching is increased by addition of sulfate($\text{SO}_4^{2-}$). When the concentration of
sulfate is sufficiently high it can compete with selenite ions for surface sites (Brown and Carte, 1969). Studies investigating the pH dependence of selenite adsorption on five alluvial soils suspended in a NaCl background solution showed that selenite adsorption was a function of pH. However no pH effect on selenite adsorption was observed when sulfate was present in the suspension (Neal et al., 1987). Singh et al. (1981) reported that adsorption of both selenite and selenate was influenced positively by organic carbon, clay content, CaCO$_3$, and CEC, and was negatively influenced by high salt content, alkalinity and pH.

Hayes et al. (1987), used an extended X-ray adsorption fine structure technique to study the direct evidence for the mechanism of selenate and selenite adsorption on colloidal surfaces. Measurements showed that selenate forms a weakly bonded, outer-sphere surface complex and that selenite forms a strongly bonded, inner-sphere complex. Neal et al. (1987), reported that addition of 100 mol CaCl$_3$ m$^{-3}$ resulted in an increase in selenite adsorption for pH > 5. They speculated that this increase may have occurred because of precipitation or because of increase in surface charge caused by Ca adsorption.

The adsorption of Se as SeO$_4^{2-}$ by FGD sludge is shown in Figure 4.32. Although Se adsorption by sludge increased with increasing concentration of Se in equilibrium solution in the range of 0.5 to 600 ppm, however this increase was not very consistent and adsorption behavior observed in two replications can not be explained by either of the generally used adsorption models (Langmuir or Freundlich adsorption isotherm). Possible reasons for this irregularity can be due to the presence of few adsorption sites as FGD
Figure 4.32  Selenium adsorption on the FGD sludge
sludge has only 5% clay size particle in it, presence of strongly binding anions like phosphate and sulfate in high concentration as it competes with selenite for adsorption sites (Neal et al., 1987). Although selenate and selenite adsorption is negatively influenced by alkalinity and pH, in this particular material these effects are minimal due to presence of a well buffered pH system that depends upon carbonates and bicarbonates. The above mentioned observations about Se adsorption behavior have environmental implications for revegetation practices involving the use of fertilizers containing phosphate, oxidation of reduced system, application of organic materials, and alkaline pH, all these practices may tend to increase the mobility of Se in the FGD sludge and thus its transport to ground water in the long run.
Section 2

Interpretation of Isotopic Data

In order to help explain some of the basic processes going on in the FGD sludge at disposal site (bacterial sulfate reduction, formation and upward movement of hydrogen sulfide gas), different layers of a whole profile of FGD sludge during the winter and a composite sample from fully reduced profile during the summer was isotopically analyzed for variation in stable isotope ratios of both sulfur and carbon. The winter profile of FGD sludge when reduction intensity is variable from layer to layer is shown in Figure 3.2. Some important chemical properties of profile are given in Table 4.7, while results of isotopic analysis are presented in Figure 4.33.

Likely Sources, Processes and their Isotopic Effects

The chemical processes that are relevant to S and C isotopic fractionation are shown in Figure 4.34, along with a summary of their isotopic effects. The principal processes leading to fractionation are:

a. The bacterial reduction of sulfate (Ohmoto and Rye, 1979) requires a supply of both sulfate and organic matter, and an anoxic environment. Reaction products are H$_2$S and CO$_2$. The H$_2$S commonly shows a broad range of values of $\delta^{34}$S, including values 25-35%$_{\infty}$ less than those of the sulfate. However, if the bacteria significantly deplete the sulfate supply (i.e. if the rate of sulfate supply is less than the rate of bacterial consumption) Rayleigh fractionation occurs, and progressively larger values of $\delta^{34}$S are generated in the
Figure 4.33 Results of the isotopic analysis of the FGD sludge profile.
Oxidation and gypsum precipitation have no isotopic effect, so that $\delta^{34}S$ of bulk gypsum decreases as a result of addition of $H_2S$. Isotopic exchange between calcite and aqueous bicarbonate results in decrease in $\delta^{13}C$ of calcite. No C-isotope effect from calcite-gypsum reaction.

Bacterial $H_2S$ is isotopically light with respect to sulfate source. Degree of fractionation depends on sulfate supply. Isotope content of $CO_2$ reflects organic source, with negative $\delta^{13}C$.

Figure 4.34  Chemical processes relevant to sulfur and carbon isotopic fractionation and summary of their effects on isotopic ratio
H₂S. If the system becomes closed to both sulfate and H₂S, complete reduction of sulfate may ensue, resulting in the generation of H₂S with a δ⁴S value the same as that of the original sulfate. Significant sulfate reduction at low temperatures can only occur by bacterial means, not by inorganic means, and no reduction is possible without a supply of organic matter. If the supply of organic matter limits bacterial reduction, Rayleigh fractionation is unlikely to develop.

b. Photosynthesis in plants fixes carbon with δ¹³C values commonly between -10 and -25‰, with C3 and C4 mechanisms having distinctive sub-ranges. The source of organic matter in the sludge ponds is not known, but is likely to be dissolved or suspended organic compounds in run-off from surrounding slopes. The dissolved organics would represent decomposition products of local plant material, and would have negative δ¹³C values, most likely <10‰.

c. Equilibria between solids and solutions. S-isotopes fractionate slightly between sulfate minerals and aqueous sulfate. Thode and Monster (1965) measured a fractionation of 1.6‰ between anhydrite (CaSO₄) and aqueous sulfate at 25°C. Calcite may exchange C-isotopes with dissolved species, particularly where the dissolved CO₂-calcite reaction leads to an appreciable solubility as calcium bicarbonate. The calcite-bicarbonate fractionation at 25°C is about 2.5‰ (Ohmoto and Rye, 1979). Bicarbonate is the principal species of dissolved inorganic carbon in the pH range 8-9.
Table 4.7 Some chemical properties of FGD sludge profile used for isotopic analysis

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>pH 1:1</th>
<th>Sulfate Sol. (ppm)</th>
<th>TC ppm</th>
<th>TIC ppm</th>
<th>TOC ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0</td>
<td>7.17</td>
<td>3860</td>
<td>69.34</td>
<td>47.24</td>
<td>22.1</td>
</tr>
<tr>
<td>0-5</td>
<td>8.26</td>
<td>11400</td>
<td>74.88</td>
<td>33.53</td>
<td>41.35</td>
</tr>
<tr>
<td>6-15</td>
<td>9.45</td>
<td>5700</td>
<td>17.4</td>
<td>11.07</td>
<td>6.33</td>
</tr>
<tr>
<td>16-30</td>
<td>8.4</td>
<td>4520</td>
<td>12.94</td>
<td>6.3</td>
<td>6.64</td>
</tr>
<tr>
<td>31-35</td>
<td>8.59</td>
<td>4350</td>
<td>15.68</td>
<td>5.98</td>
<td>9.7</td>
</tr>
<tr>
<td>36-45</td>
<td>8.41</td>
<td>2780</td>
<td>14.31</td>
<td>6.95</td>
<td>7.36</td>
</tr>
<tr>
<td>46-50</td>
<td>8.38</td>
<td>2830</td>
<td>24.11</td>
<td>7.59</td>
<td>16.52</td>
</tr>
<tr>
<td>51-65</td>
<td>8.17</td>
<td>2040</td>
<td>24.47</td>
<td>7.91</td>
<td>16.56</td>
</tr>
<tr>
<td>66-75</td>
<td>8.12</td>
<td>1980</td>
<td>10.92</td>
<td>5.0</td>
<td>5.92</td>
</tr>
</tbody>
</table>

d. Reactions such as the oxidation of $H_2S$ to sulfate will have no isotopic fractionation effect if all of the reactant is consumed.

Limitations and boundary conditions on chemical processes in the sludge include:

a. The supply of organic matter, potentially limiting sulfate reduction.

b. The isotopic composition of sulfur in the coal -- is it homogeneous? We do not know if any fractionation of S-isotopes occurs in the scrubbers, but the consistency of $\delta^{34}S$
values of CaSO$_4$ in the scrubber slurry and in the reduced layers of the pond (Figure 4.32) suggests homogeneity within a range of 1°/∞. It is assumed that there is no other significant sulfur source in the sludge pond.

c. The CaCO$_3$/CaSO$_4$ ratio of the scrubber slurry. There was no CaCO$_3$ in the slurry sample taken direct from the scrubber on 1/9/95. The content of CaCO$_3$ varies greatly from layer to layer in the sludge pond, suggesting broad variability of slurry composition. This will be discussed further in light of the isotope data. The sludge solids will be assumed to consist of gypsum and calcite only.

d. The C-isotope composition of the limestone -- is there more than one source? Processes of quarrying and grinding presumably smooth out the small-scale inhomogeneities characteristic of limestone.

e. The redox boundary of the profile sampled appeared to have retreated to depth as a result of low winter temperatures. Remnants of the reduced sludge suggest that the summer redox boundary was at about 10 cm, and the winter boundary at about 60 cm. Between these levels, the sludge was saturated with water and the intensity of oxidation was different in different layers, suggesting that advection of oxygen may be controlled by permeability differences between layers.

f. The solutes in the pore water. The water is sulfate-dominated, and in equilibrium with gypsum. Therefore the concentration of Ca in solution must be low, so that addition of CO$_2$ or carbonate would not result in the formation of new calcite.
Sulfur Isotopes

a. Input. The scrubber slurry on 1/9/95 contained CaSO$_4$ with $\delta^{34}S = 8.3\%_o$, and aqueous sulfate with $\delta^{34}S = 6.7\%_o$. The difference, 1.6 $\%_o$, corresponds with equilibrium fractionation.

b. In reduced sludge layers, $\delta^{34}S$ of CaSO$_4$ ranges between 7.6 and 8.6 $\%_o$, which may be taken as the same as $\delta^{34}S$ of the input CaSO$_4$. Layer no. 7 is an exception, but this layer appeared to be on the verge of becoming oxidized. Layer 5, a grey layer between oxidized layers, is considered to be a reduced layer on the verge of oxidation.

c. In oxidized sludge and layer 7, lower values of $\delta^{34}S$ (5.8 to 6.4 $\%_o$) were found. In aqueous sulfate from the upper layers (sample 2) and the evaporite crust (no.3), even lower values of $\delta^{34}S$ (2.9 to 4.0 $\%_o$) were found. The difference -- $\delta^{34}S$ of CaSO$_4$ greater than $\delta^{34}S$ of aqueous sulfate -- corresponds in sense to equilibrium fractionation, although the difference is larger than the 25°C fractionation. Temperatures in upper layers of the pond had been lower than 25°C for several weeks before sampling, which might explain a larger fractionation if isotopic equilibrium was maintained.

d. The value of $\delta^{34}S$ of sulfate from one reduced sample (no. 12) was 4.9 $\%_o$.

e. The $\delta^{34}S$ values of sulfide in reduced sludge range widely, from -19.0 to +3.9 $\%_o$. The -19 value corresponds to a sludge sample taken in summer. The other values are for samples taken on 1/9/95. The higher values approach those of solid CaSO$_4$ in the same samples.
Evidence of Bacterial Reduction

The $\delta^{34}S$ range of sulfide is typical of bacterial reduction. The higher values indicate a limitation of sulfate supply. This, in turn suggests that only aqueous sulfate is metabolized by the bacteria; the supply of sulfate as gypsum is abundant and undepleted (see % CaCO$_3$ data, Figure 4.2.2).

The low $\delta^{34}S$ values of CaSO$_4$ from the upper layers of the sludge require addition of isotopically light sulfate from an external source. It is not possible to make a batch of sulfate isotopically lighter by chemical means, e.g. partial reduction, because at equilibrium, sulfide is always lighter than sulfate. The likely source of light sulfur is H$_2$S from the reduced layers. The H$_2$S will migrate up the profile as gas if there is insufficient Fe or other metal to precipitate it at its source, and become oxidized to H$_2$SO$_4$ when it encounters an O$_2$-rich environment. The H$_2$SO$_4$ will be neutralized by calcite, resulting in the formation of gypsum. Thus the presence of low-$\delta^{34}S$ sulfate in both minerals and water of the oxidized layers is evidence of a source of light sulfate.

Bacterial reduction of sulfate ought to result in the generation of high-$\delta^{34}S$ aqueous sulfate in the reduced part of the profile. The one measurement does not show such an effect. The reason for this may be contamination, which is almost impossible to avoid during sampling. Exposure of the sample to O$_2$ will result in the oxidation of some sulfide to sulfate, causing a decrease in $\delta^{34}S$ of the bulk aqueous sulfate through mixing (but having no isotopic effect on the remaining sulfide).
Carbon Isotopes

a. δ^{13}C and % CaCO_{3} do not correlate, therefore the % CaCO_{3} is probably controlled by the input composition of the slurry from the scrubber. (An alternative would be to change the % CaCO_{3} in the oxidized layers by: 1. precipitating CaCO_{3} from a solution containing Ca^{2+} by adding CO_{2} from the reduced layers, or 2. dissolving CaCO_{3} away as a result of oxidizing H_{2}S. No.1 is not feasible because of lack of Ca^{2+} in solution. No. 2 will be tested in a calculation below.

b. Variations in δ^{13}C do not correlate with the oxidation state. The higher bracket of δ^{13}C values (3.2 to 3.7 ‰) may represent the δ^{13}C of the raw limestone added to the scrubber. There is no obvious mechanism for increasing δ^{13}C of the solid CaCO_{3} in the sludge. Partial reduction by bacteria will not take effect until all sulfide has been consumed, and even if it did occur, would not change δ^{13}C of remaining solid. Addition of isotopically heavy δ^{13}C requires a source of high-δ^{13}C carbon other than the limestone, and a mechanism for precipitating CaCO_{3}. Neither is available. Isotopic exchange between aqueous HCO_{3} resulting from bacterial reduction and solid CaCO_{3} can change δ^{13}C of the CaCO_{3}, but is likely to cause a decrease (see calculations). Therefore the maximum δ^{13}C of CaCO_{3} in the profile is interpreted as indicating δ^{13}C of the limestone.

c. Lower values of δ^{13}C (-1.7 to +2.0 ‰) could be generated by equilibrating CaCO_{3} and aqueous bicarbonate. A sample calculation is given below. This isotopic exchange is independent of the oxidation state, so it could occur anywhere in the profile,
provided conditions permit the accumulation of aqueous bicarbonate. Perhaps lack of water circulation for a time may be involved.

Calculations

The principle of the calculations is the conservation of isotopes. A reaction may re-distribute isotopes 1 and 2, but the amount of isotope 1 in reactants must be the same as the amount in products, and likewise for isotope 2. This is expressed in the following approximation, which is good for situations in which one isotope is much less abundant than the other

\[ n_1 \delta_1 + n_2 \delta_2 = n_3 \delta_3 + n_4 \delta_4 \]

where reactants 1 & 2 combine to form products 3 & 4, \( n \) = number of moles, and \( \delta \) is a parameter such as \( \delta^{34}\text{S} \).

Other symbols: \( x \) = mole fraction

initial state superscript \( ^0 \)

final state superscript \( ^1 \)

calcite subscript \( _c \)

gypsum subscript \( _g \)

a. Quantity of \( \text{H}_2\text{S} \) added to oxidized layers 4 and 6. The calculation gives the amounts of \( \text{H}_2\text{S} \) necessary to change \( \delta^{34}\text{S} \) of gypsum in each layer from an initial value of 8.0\%/o, to a final value as measured. Changes in the mole fraction of gypsum are taken into account, assuming that the sludge contains only gypsum and calcite. We do not know how
long it took to add the H$_2$S; in the oxidized layers, which become oxidized each winter, then apparently become reduced each summer, the effect on $\delta^{34}$S of the gypsum could be cumulative. An estimate of the sedimentation rate may help.

b. Change in % CaCO$_3$ resulting from addition of H$_2$S to the oxidized layer.

c. Change in $\delta^{13}$C of calcite of layer 6 as a result of adding bacterial CO$_2$, and converting some calcite to aqueous bicarbonate. The species have initial $\delta^{13}$C values fixed by parent materials, and adjust to isotopic equilibrium.

The detailed calculations are presented in Appendix 1.
CHAPTER 5

SUMMARY AND RECOMMENDATIONS

The production of flue gas desulfurization (FGD) sludge has increased significantly in the last few decades. Establishing vegetation is the most viable option to cover the FGD sludge disposal sites, in order to reduce the associated environmental concerns. Periodic flooding of these sites due to excessive discharge from FGD scrubbers or runoff water from surrounding watersheds, results in anaerobic conditions as evident from the rotten egg odor and presence of blackish grey layers of reduced FGD sludge. Generally reduced chemical species are more phytotoxic and adversely affect plant growth. An understanding of the geochemistry of a FGD disposal pond as affected by periodic flooding and subsequent drying was developed.

Changes in oxidation status of FGD sludge when subjected to flooding and subsequent drying and the associated changes in concentration of major sulfur species, together with the factors affecting these transformation were studied using batch experiments. The results of this study can be summarized as:

- Oxidation of reduced FGD sludge appears to be a two step process involving fast chemical oxidation followed by slow microbially mediated oxidation.
- Rate of oxidation of reduced FGD sludge depends upon moisture content and area of sludge being exposed to atmosphere.
• The low TOC content of FGD sludge and pond water suggest that runoff water from the watershed is the only likely source of substantial amount of organic carbon for very intense reduction in summer months.

• High summer temperature at the site, coupled with available organic carbon can reduce FGD sludge in a few days.

• Winter temperatures prevailing at the site are low enough to retard the reduction of FGD sludge, even when supply of available organic carbon is not limited.

• Shift in the redox boundary is caused by temperature fluctuations, as it slows down the microbial activities and mineralization of organic matter.

• Boron solubility is independent of redox status of FGD sludge.

• Oxidation of FGD sludge increases the solubility and thus mobility of selenium.

5.1 Suggestions for future work

There are a number of areas for research related to the topic of redox transformations. These include: the evaluation of effect of variable redox conditions on leaching of heavy metals from agricultural fields where compost sludge is applied as an amendment; the evaluation of the effect of different types of organic matter on rate of sulfate reduction in the FGD sludge disposal site; and finally to compare the results of the redox transformation of this laboratory by in situ studies by installing the redox electrodes in the study area and comparing the field data with the results obtained in this study.
APPENDIX
CALCULATIONS OF ISOTOPIC ANALYSIS

a) Amount of $\text{H}_2\text{S}$ added to oxidized layers in order to change $\delta^{34}\text{S}(\text{CaSO}_4)$,

Case 1  layer 6

Final state: $\delta^{34}\text{S} = 6.4\%$, %$\text{CaCO}_3 = 1.7$, %$\text{CaSO}_4.2\text{H}_2\text{O} = 83$

Original state: $\delta^{34}\text{S} = 8.0\%$, $x'_g = \frac{174}{83} = 0.73$; $x'_c = 0.27$

change to final state

by addition of $h$ moles of $\text{H}_2\text{S}$. For each mole of $\text{H}_2\text{S}$ added, 1 mole $\text{CaCO}_3$ is converted to $\text{CaSO}_4$ (assuming all sulfate from $\text{H}_2\text{S}$ is fixed as gypsum).

Take 1 mol of sludge in final state

$n^f_g = 0.73$, $n^f_c = 0.27$

This corresponds to the following amount of sludge in original state

$n^0_g = 0.73 - h$

isotopic balance equation:

<table>
<thead>
<tr>
<th>final</th>
<th>original</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n^f_g \times \delta^f_g = n^0_g \times \delta^0_g + h(\delta_{\text{H}_2\text{S}})$</td>
<td></td>
</tr>
<tr>
<td>$0.73(6.4)$</td>
<td>$(0.73-h) \times (8.0) + (h \times \delta)$</td>
</tr>
</tbody>
</table>

or

$4.67 = 5.84 - 8h + (h \times \delta)$

$h = -1.17/(\delta - 8)$

likely values of $\delta$: 0, -10, -20

Corresponding $h$ 0.15, 0.07, 0.04

Case 2: layer 4

Final state: $\delta^{34}\text{S} = 5.8\%$, %$\text{CaCO}_3 = 45.7$, %$\text{CaSO}_4.2\text{H}_2\text{O} = 54$
initial state: \[ x^i_g \frac{54.3}{174} = 0.41 \quad ; \quad x^i_c = 0.59 \]

\[ \delta^{14}S = 8.0^\circ_\text{oo}, \]

change to final state by addition of \( h \) moles of H\(_2\)S

Take 1 mole of sludge in final state
\[ n_g^f = 0.41, \quad n_c^f = 0.59 \]

corresponding amount of sludge in initial state
\[ n_g^i = 0.41 - h, \quad n_c^i = 0.59 + h \]

isotopic balance equation:

\[
\begin{align*}
\text{final} &\quad \text{original} \\
 n_g^f \times \delta_g^f &\quad = n_g^i \times \delta_g^i + h(\delta_{\text{H}_2\text{S}}) \\
0.41(5.8) &\quad = (0.41-h) \times (8.0) + (h \times \delta_{\text{H}_2\text{S}}) \\
\text{or} \quad h &\quad = \frac{-0.90}{\delta-8} \\
\text{likely values of } \delta: \quad &\quad 0, \quad -10, \quad -20 \\
\text{corresponding } h &\quad 0.11, \quad 0.05, \quad 0.03 \\
\end{align*}
\]

b) Changes in \% CaCO\(_3\) due to addition of H\(_2\)S. CaCO\(_3\) + H\(_2\)SO\(_4\) = CaSO\(_4\) + CO\(_2\) + H\(_2\)O

add 1 mole of H\(_2\)S - H\(_2\)SO\(_4\) - remove 1 mole CaCO\(_3\).

\[ x_c^f = 0.59 = n_c^f \quad \text{for 1 mole sludge, final state} \]

therefore
\[ x_c^i = x_c^f + h = 0.59 + 0.11 = 0.70 \quad \text{for largest addition of H}_2\text{S, as calculated above.} \]

let initial \%CaCO\(_3\) = \( C \)

\[ 0.70 = \frac{c}{100} \frac{c}{100 - c} \]

solving for \( C \), \( C = 57.3 \)
that is addition of 0.11 \( H_2S \) moles results in change of \( \%CaCO_3 \) from 57.3 to 54.3, a much smaller change than differences between layers. Therefore differences between layers are unlikely to results from dissolution of \( CaCO_3 \) as a result of oxidation of \( H_2S \).

C)
Carbon isotope balance:
For each mole of sulfate reduced to \( H_2S \), 2 moles of \( CO_2 \) produced.
For each mole of \( H_2S \) oxidized to \( H_2SO_4 \), 1 mole of \( CO_2 \) produced by reaction with calcite
Assuming \( h \) moles of \( H_2S \) are produced, and added to layer 6 (case 1, above)
initial state \( n_c^0 = 0.27 + h, \ \delta^{13}C = +3 \%/00 \)
plus 2 \( h \) moles of \( CO_2/HCO_3 \) \( \delta^{13}C = -15 \%/00 \) (for instance)
final state
\[
n_c^1 = 0.27, \ \delta^{13}C = \delta \text{ plus } 2h \text{ moles of } HCO_3 \text{ from bacteria}, \quad \delta^{13}C = \delta -2.5
\]
plus \( h \) moles \( HCO_3 \) from calcite, \( \delta^{13}C = \delta -2.5 \)
Balance
\[
2h(-15)_{HCO_3} + (0.27 + h)_{\text{calcite}}(3) = 3h(\delta -2.5) + 0.27 \delta_{\text{calcite}}
\]
solving the equation gives \( h = 0.15; \ \delta = -2.9 \%/00 \)
\[
h = 0.01 \quad \delta = -2.0 \%/00
\]
Therefore large additions of \( CO_2 \) (corresponding to \( H_2S \) production) lead to \( \delta^{13}C \) values in calcite that are 1) lower than original \( \delta^{13}C \); 2) about the same as observed in layer 6. This suggests \( H_2S/CO_2 \) production can account for \( \delta^{13}C \) range of calcite for bacterial sulfate reduction.
REFERENCES


Wolk, R. 1990. The future of coal based generation. EPRI J. 15:1
