INTRODUCTION

The study of oxidation-reduction processes in soils began in the 1900's (Gillespie, 1920) and has since been applied to biological, limnological, and geochemical systems (Bass Becking, 1960). Early petroleum related studies concerned the redox characteristics of sediments, the preservation of organic material, and the ultimate generation of petroleum (Zobell, 1946, Krumbein and Garrels, 1952). Ground water investigations showed that water with hydrocarbon gases are distinguished by low redox potentials (Germanov etal., 1059). Other subsurface studies proposed the use of a redox logging tool (Pirson, 1968). Early near surface oil exploration studies started with the Hilbig Oil Field (Baijal, 1962, Pirson, 1968) and have led to the development of electrode arrays for the in-situ analysis of near surface redox potentials (Thompkins, 1993).

The pH and Eh probability plots are a compilation of 1034 soil samples collected in 18 survey areas. Twelve of the surveys are over productive oil and gas fields while 6 are from barren areas. The productive areas exhibit a larger slope then the barren areas for Eh while the inverse is true for pH. A generalized interpretation of the data suggests that productive areas have a greater number of low Eh values relative to barren areas and a higher number of lower pH values relative to barren areas. This tends to corroberate the existence of the "geochemical chimney" effect often reported over oilfields. The Eh-pH diagrams show the location of these readings in Eh-pH space. The data fall within the bounds of mineral systems that are often referenced in the literature regarding surface geochemical techniques and measurements.

MICROSEEPAGE RELATED REDOX MODELS

Two models have been proposed which would explain the presence of redox phenomena in near surface soils over oil fields. The first model promotes the mineralogical oxidation of the vertically seeping hydrocarbons are the primary cause of redox lows detected in the near surface (Pirson, 1976). Early theories suggest that natural zeolites in the reservoir seal initiate the cracking of large aliphatic hydrocarbons in smaller molecules which results in a net negative charge within the area of hydrocarbon microseepage. The adjacent oxidizing areas establish a path of electrical flow from the electron generating oil reservoir (Pirson, 1976, Thompkins, 1993). The current theory relies on hydrocarbon, rock, and water interactions that produce

organic acids and acid anions (OAA's). For instance, iron oxides react with hydrocarbons to produce pyrite, oxygenated organic compounds, and CO_2.

The second model states that the redox anomalies associated with oil fields are related to microbial oxidation of the vertically seeping hydrocarbons, and not to the hydrocarbons themselves (Price, 1986). Low molecular weight hydrocarbons, which are most often associated with near surface direct hydrocarbon techniques, have a very low reactivity caused by their saturated bonding. These bonds can only be broken under strenuously reactive conditions (Garland, 1975, Price, 1986). By oxidizing the hydrocarbons, the microbes mediate changes in available reactive chemical species that can take up liberated electrons, thereby changing the mineralogy above hydrocarbon deposits.

THE CHEMICAL RELATIONSHIP OF PH AND EH

Oxidation and reduction can be viewed in terms of an exchange in electrons. Due to the migration of electrons between oxidants, or electron acceptors, and reductants, which lose electrons, a potential difference is set up within the redox system that can be measured using an inert platinum electrode. The range of redox potentials of natural environments is limited in aqueous systems by the oxidation of water to molecular oxygen (E_0 = 1230 mV) and the reduction of hydrogen ion to molecular hydrogen (E_0 =0.00 mV) (Mason, 1949, Bass Becking, 1960, Bohn, 1971). Three types of oxidative processes can occur; 1) the addition of oxygen to an oxidizable substance, 2) removal of hydrogen from a substance, and 3) the removal or loss of electrons from a substance.

Oxygen plays an important role in whether a system is oxidizing or reducing. Sediments with very reactive organic matter have an initial rapid microbial oxygen consumption rate, while sediments with more refractory organic material have a much lower oxygen consumption rate though the general trends are similar (Yu, 1985). In the reduction process of soils, oxygen consumption is a result of 1) microbial respiration where it is used as an electron acceptor, 2) chemical oxidation of reduced Fe and Mn, and 3) the biological oxidation of NH_4^+, carbon, and sulfides (ZoBell, 1946, Bohn, 1971, Reddy, 1980, and Brannon, 1983) .

 Organic matter is the principal source of electrons in the soil and can produce reducing substances during its decomposition (Yu, 1985, Sposito,

1989). The higher the organic matter content the higher the amount of reducing substances.   Expressed qualitatively, the higher the amount of reducing substances, the lower the redox potential. Quantitatively, the relationship between the logarithm of the amount of reducing substances and the Eh has a correlation coefficient of -0.905 (Yu, 1985).   Though the correlation is fair, the relationship of reducing substances to organic matter is not completely linear, which is due to differences in composition. It has also been shown that Eh is dependent on the type of organic matter being oxidized and is not related to the oxidizing potential of any specific microbial population (Brannon, 1983, Yu, 1985). During redox reactions in soils the organic part of the reducing substance is the most active and the determinative component, and the production of inorganic reducing substances, such as ferrous iron, is only the result of further interactions between organic reducing substances and other electron acceptors in the soil (Yu, 1985).

In aqueous solutions, hydrogen ion concentrations are measured in terms of pH using a scale of 0 to 14. The formation of reduced species almost always results in proton consumption, which decreases soil acidity, while oxidation can create free protons which increase soil acidity (Yu, 1985, Sposito, 1989). In most redox reactions the participation of H^+ ions affects the pH having a direct affect on the quantity of various reducing substances in the soil. Upon amending a soil with organic matter, a sharp decrease in pH occurs, exerting a pronounced influence on the Eh.   As an example, when holding Fe^{2+} activity and Eh constant, the calculated Eh would be lowered 177 mV for a every unit decrease in pH, while at constant pH, an order of magnitude change in Fe^{2+} activity can only cause a 59 mV change in calculated Eh (Brannon, 1983).   This pH decrease is closely related to small changes in pCO_2 (Krumbein and Garrels, 1953, Ponnamperuma et al, 1966, Brannon, 1983) and the formation of organic acids (Brannon, 1983).

The oxidation-reduction in a natural system is the result of the opposing rates of electron donation and acceptance of a redox couple at equilibrium. Due to the enormous variation in redox couple distribution true equilibrium cannot be achieved, and the redox measurements are probably "mixed potentials" (Bohn, 1971). The lack of effective coupling and the slowness of redox reactions means that catalysis is required if equilibrium is to occur. In soil solutions, the catalysis of redox reactions is mediated by microbial organisms (Bohn, 1971, Stumm and Morgan, 1981, Sposito, 1989), though

the soil organisms only affect the rate of a reaction and will have little effect if the reaction is not favored (Sposito, 1989).

RELATIONSHIP OF BACTERIA TO THE DOMINANT REDUCING PARAMETERS

Early investigations of redox processes in soils revealed the importance of bacteria and a supply of organic material. The figure of bacteria vs. Eh shows the effect of bacteria, that are suspended in different organic media, on Eh. The Bacillus coli, was suspended in a 0.9 percent sodium chloride solution with the addition of a little "broth". Measurements were taken with a bare platinum electrode. Bacillus mycoides was grown on agar and suspended in broth and measures with an amalgam electrode. The unknown soil aerobe was grown on agar and suspended in a mixture of equal parts of 0.1 M Na_2HPO_4 and 0.1 M NaH_2PO_4 (Gillespie, 1920). Differences in Eh intensity are related to either the type of electrode employed in the measurement or the type of organic media used. The comparison of water logged soils shows an initial rapid decrease in Eh which begins to level out after four to six days. This trend has been documented by many researchers. In each case the oxygen and pH decreases, causing a non-equilibrium redox condition in the soil solution which results in a Eh decrease. Over longer periods of time as the system attempts to approach equilibrium the pH and Eh will approach one another.

Reddy (1971) proposed a two phase reduction of iron and manganese related to oxygen consumption. Phase I represents the chemical oxygen demand while Phase II represents the microbial respiration. The authors state that because the oxygen consumption rate constant did not correlate with total or extractable carbon, which determines the microbial respiration, that Phase II of the reaction may not be totally a microbial process. Upon running their model, and replacing NH_4 -N (r^2 =0.82) with total extractable carbon, the model performed equally as well (r^2 =0.82). This is consistent with the findings of Brannon et. al. (1983) who found that the sediment oxygen consumption rate was highly correlated with dissolved organic carbon concentration (r^2 =0.86). This would indicate that the Phase II reactions are primarily dependent on the presence of carbon or nitrogen. Other investigators (Ponnamperuma et. al., 1966, Brannon et. al., 1983, Yu, 1985) found that iron accounts for a major part of the active reducing substances in the latter stages of soil redox reactions. Based on long exposure time (Ponnamperuma et. al., 1966), ferroan carbonates are favored within the

reducing zone with the concentration of Ca^{2+} being the limiting factor (Surdam et. al., 1993). Manganese activity was minor in all reported studies.

The graphs comparing carbon, iron, and pH are derived from three separate data sets. In each case as carbon content increases as the pH decreases. This was previously stated to be related to changes in pCO_2. Two data sets show rapid increases in iron with rapid increases in carbon content. This increase seems to occur when iron is greater than 1.5 % which is the amount of Fe_2O_3 that is soluble and can be moved by reducing agents under laboratory conditions (Surdam et. al., 1993). In two of the studies (Ponnamperuma et al, 1966, Brannon et. al., 1983) the greatest change in pH occurred in those samples with the highest iron content.

In rocks containing approximately 1 to 2 % iron in the presence of hydrocarbons the redox reactions resulted in CO_2 production 2 to 20 times greater then in simple oil - water mixtures. The CO_2 increase is related to the formation of organic acids and acid ions the have the potential to significantly affect the pH, oxidation potential, and pCO_2 of the system, which in turn affects the systems capacity to dissolve or precipitate carbonate mineral species in the reservoir as well as rocks within the hydrocarbon seepage area.

RELATIONSHIP OF MINEROLOGY TO THE DOMINANT REDUCING PARAMETERS

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TURKEY CREEK OIL SEEP
The Turkey Creek oil seep is a well documented area of alteration related to leaking hydrocarbons. The area is located approximately 12 miles west of Denver, Colorado, USA. Oil production was established 2500 feet to the west of the area in 1955 from a depth of 8980 feet. For a detailed description please see Reid, 1992.

Soil samples were taken coincident with a traverse used for an Induced Polarization study (Reid et. al., 1992). The samples were analyzed for Eh, pH, bacteria count, and hydrocarbon content. The lowest Eh values are found in the area of the oil seep, as well as moderate to high bacteria counts, and high hydrocarbons. The data tends to support the second redox model.

ALFALFA COUNTY, OKLAHOMA
A field in the SE/4 of Section 24, T 25 N-R 12 W in Alfalfa County, Oklahoma was sampled and analyzed for hydrocarbon content, pH, Eh, and bacteria. The traverse of Eh and microbial data are inversely related. The Eh decreases and the bacteria increases when associated with hydrocarbon production.

CONCLUSIONS
From the data presented in the literature the common parameters that control soil Eh are 1) pH, which in turn is sensitve to variations in pCO_2, 2) the presence of labile organic matter, 3) the presence of a non-specific microbial population, and 4) the presence of Fe, Mn, and other electron acceptors.

The soil sample survey in the Turkey Creek oil seep area shows an Eh anomaly coincident with high pH values, high bacteria counts, and high hydrocarbon concentrations, with Eh minima at the oil seep. The maximum Induced Polarization survey values are also located at the oil seep indicating the presence of the redox zone.

The Alfalfa County survey again showed Eh anomalies coincident with high pH values, high bacteria counts, though the high hydrocarbon values are located nearer the production and are not necessarily associated with the Eh, pH, and bacteria anomalies.