BNL-NUREG-31667

INFORMAL REPORT
LIMITED DISTRIBUTION

ANALYSES OF SOILS FROM AN AREA ADJACENT TO THE LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITE AT SHEFFIELD, ILLINOIS

DRAFT REPORT

P. L. Piciulo, C. E. Shea, and R. E. Barletta

July 1982

NUCLEAR WASTE MANAGEMENT DIVISION
DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Materials Safety and Safeguards
Contract No. DE-AC02-76CH00016

BNL-NUREG-31667
INFORMAL REPORT
LIMITED DISTRIBUTION

ANALYSES OF SOIL FROM AN AREA ADJACENT TO THE LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITE AT SHEFFIELD, ILLINOIS

DRAFT REPORT

P. L. Piciulo, C. E. Shea, and R. E. Barletta

Manuscript Completed: July 1982

Donald G. Schweitzer, Head
Nuclear Waste Management Division
Department of Nuclear Energy
Brookhaven National Laboratory
Associated Universities, Inc.
Upton, New York 11973

NOTICE: This document contains preliminary information and was prepared primarily for interim use. Since it may be subject to revision or correction and does not represent a final report, it should not be cited as reference without the expressed consent of the author(s).

Prepared for the U.S. Nuclear Regulatory Commission
Office of Nuclear Materials Safety and Safeguards
Contract No. DE-AC02-76CH00016
FIN No. A-3159

ABSTRACT

Soil samples and field resistivity data were collected from an area adjacent to the Sheffield site. Specimens of Peoria Loess, Roxana Silt, Radnor Till, sand from the Toulon member, Hulick Till, and shale from the Pennsylvanian system were collected and analyzed. Resisitivities of the soils are all greater than 2500 ohm-cm, indicating an environment which can be moderately corrosive to steel. Measurements of soil pH range from 6.2 to 8.6. Determination of the total acidity of the soils indicates an alkaline environment. The moisture content of the soils are representative of a wet site. The ion content of the soils show high levels of calcium consistent with the calcareous nature of the soils. Both the extractable and exchangeable concentrations of calcium, magnesium, potassium, and sodium in the soils are reported. The content of the following soluble anions is also given: carbonate, bicarbonate, sulfate, sulfide, and chloride.

CONTENTS

CONTENTS, Continued

FIGURES

TABLES

ACKNOWLEDGMENTS

The authors thank Drs. Richard E. Davis and Samuel V. Panno for their helpful discussions during the course of this work. Personnel of the U.S. Geological Survey, especially Mr. Robert Striegel and Mr. Richard Healy, are acknowledged for their assistance with the sampling and the identification of the soil lithology. Ms. Elinor Norton is acknowledged for providing X-ray fluorescence data of soil samples.

Gratitude is extended to Ms. Nancy Yerry and Ms. Kathy Becker for their patient assistance in the preparation of this manuscript.

1. INTRODUCTION

The low-level radioactive waste disposal facility near Sheffield, IL, is presently maintained by U.S. Ecology, Inc. Nearly 3 million cubic feet of waste were buried in 21 trenches during the period from August 1967 to April 1978 while the site was operated by the Nuclear Engineering Company.(1) Burial operations were suspended in 1978 due to the lack of suitable licensed burial space.

The purpose of this report is to quantitatively describe a number of physical and chemical properties of soils from the low-level radioactive waste disposal site at Sheffield. The parameters discussed are necessary to evaluate the corrosivity of the burial environment on waste containers such as a 55-gal carbon steel drum. Understanding the corrosivity of the soils will help in predicting the time dependent failure of the waste container and the subsequent release of the radionuclides to the environment. Terms defining radionuclide release from waste packages are necessary input to mathematical models designed to describe the mobility of these nuclides at a disposal site. Refinement of the release term may improve the ability of a model to predict radionuclide migration. Knowledge of radionuclide migration is needed to evaluate the Sheffield site for closure and to evaluate the suitability of locations considered for future sites.

Materials commonly used for the containment and the solidification of radioactive waste are subject to degradation by underground corrosion. The underground corrosion of metals has been studied extensively by the National Bureau of Standards(2) and is generally site specific. Metals typically corrode by an electrochemical process although some chemical species are aggressive toward certain materials. Chloride ion, for example, causes pitting corrosion on stainless steel. Sulfate ions attack cement, which is a widely used solidification agent for radioactive waste. Data necessary to estimate the corrosivity of soils specific to the shallow land burial site at Sheffield have been obtained and are presented in this report. Similar data on soils from the low level radioactive waste disposal facilities at Barnwell, SC, and Hanford, WA, have been reported.(3) A comparison of results of the Sheffield soil with those of soils from Barnwell and Hanford will be presented.

2. METHODS OF SOIL COLLECTION AND ANALYSIS

2.1 Soil Collection

A map of the low-level radioactive waste disposal site, referred to as the Sheffield site, is shown in Figure 2.1. The Sheffield disposal facility is positioned on an area of 20 acres of rolling terrain about 3 miles southwest of Sheffield, IL, in Bureau County. A description of the geology and hydrology of the Sheffield site is being developed by the U.S. Geological Survey(1) (USGS). Briefly, the site is composed of unconsolidated Wisconsinan and Illinoian glacial sediments atop Pennyslvanian bedrock. The glacial history and the continuity of the sedimentary deposits at the site are interpreted by USGS from samples taken from boreholes and a 290-foot-long tunnel extending north-south beneath four trenches in the southeast quarter of the site.

Figure 2.2. shows the geologic section, labeled J-J', of the Sheffield site(1) describing the stratigraphic locations of the various sedimentary deposits. This is not a representation of the entire site but is applicable to the boring location for the collection of samples for this work. Samples were collected by coring in a location approximately 25 feet west of USGS boring 503 along a line between borings 503 and 504. The sampling location is outside the waste site boundary about 100 feet from boring 504 which is at the east end of trench 2. The geologic classification and lithologic description of the cores taken from boreholes 503 and 504 are given in Appendix A.

Sample identification numbers for Sheffield soils are listed in Table 2.1 together with sampling depth and soil type. These sample identifiers are used throughout this report. Deviations from this list are explained where necessary.

Thirteen Shelby tube samples (about 30 in. in length) were taken from the surface to a depth of 397 in., which marks the approximate beginning of the sand lens (Toulon Member). The formations sampled to this point were: Peoria Loess, Roxana Silt, and Glasford Formation. The Radnor Till member and the Toulon member are of the later formation. Sampling proceeded from the 397 in. depth using a split barrel sampler. Three samples were collected in the sand lens between the 397-in. and 547.5-in. depths. Two samples were collected in the Hulick Till member (547.5 in. to about 581 in.). One sample of weathered shale extending into the Pennsylvanian system was collected. The final sample depth was 605 in.

The Shelby tubes were labelled and the ends capped, taped and sealed with wax in the field to prevent loss of moisture. Soil collected using the split barrel sampler was placed in a plastic bag to maintain field moist conditions. A sample identification tag was placed inside the bag. The bag was folded and secured with rubber bands. This was then placed inside a second plastic bag, secured with rubber bands and labeled.

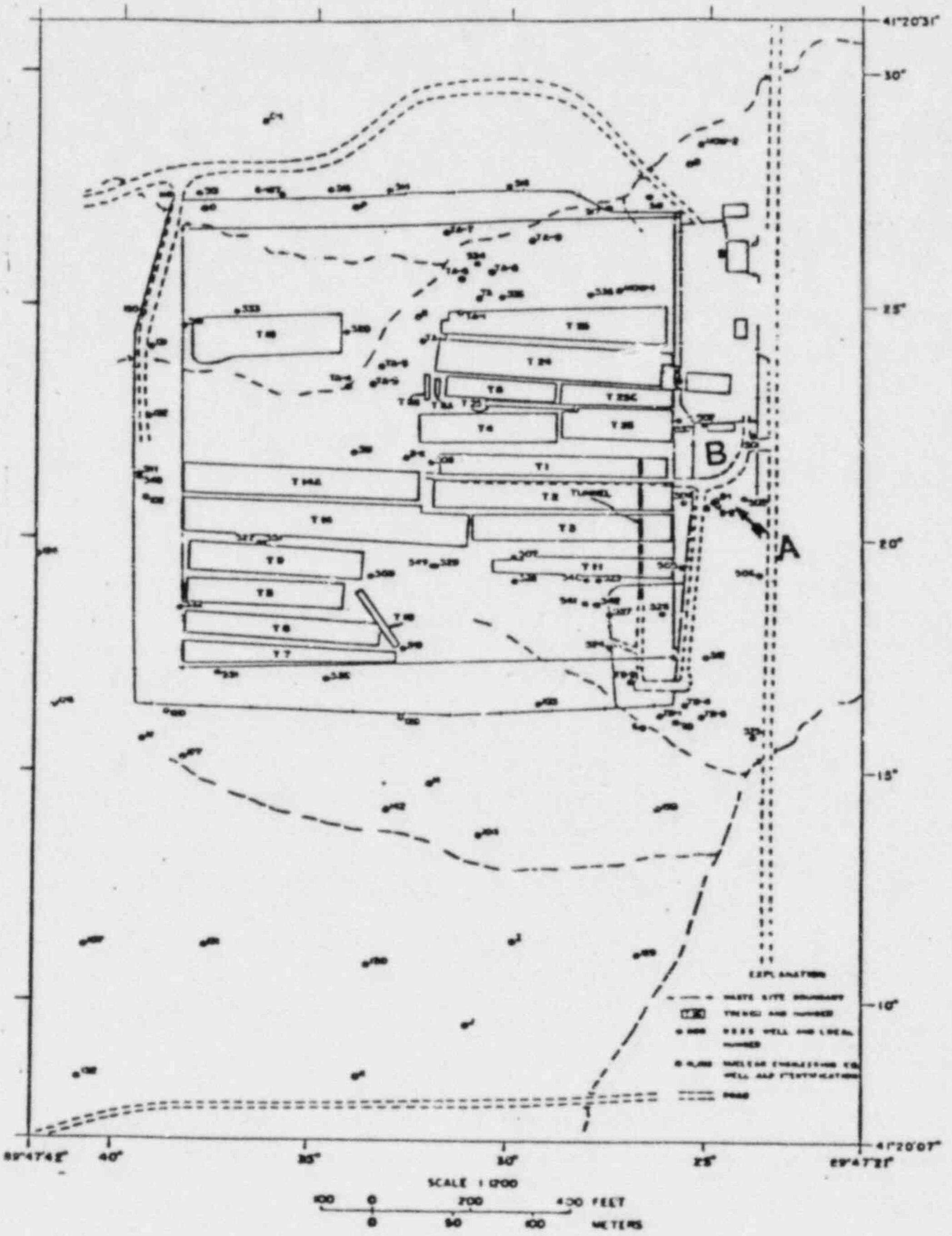

Figure 2.1 Map of the low-level waste disposal facility at Sheffield, IL, operated by U. S. Ecology.(1) The location of the BNL borehole is marked by the letter A. The location of the area where the earth resistivity was measured is marked by the letter B.

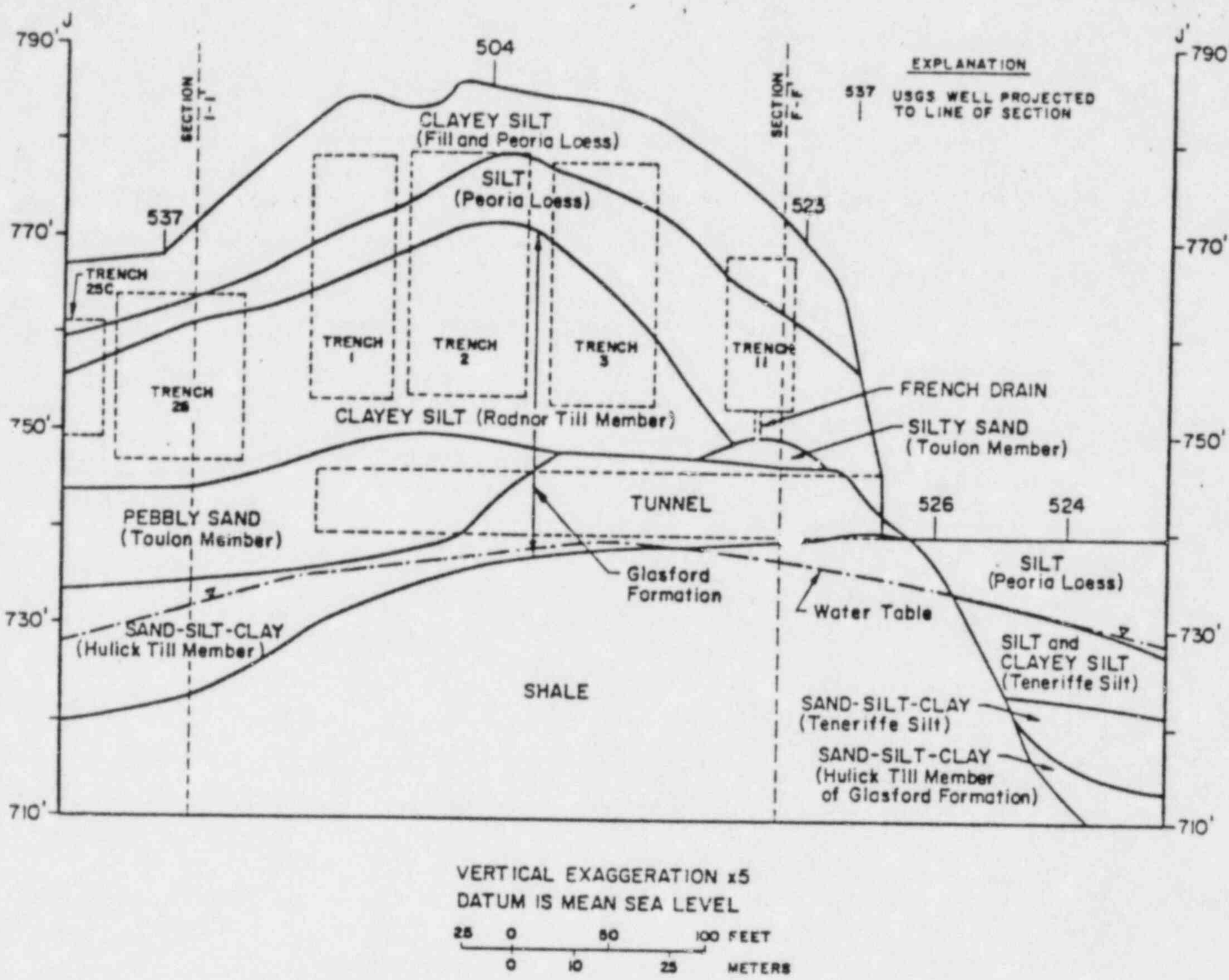

Figure 2.2 Geologic section J-J' of Sheffield site.(1)

Table 2.1

Sample Identification for Sheffield Soils

Sample ID	Depth (Inches)	Soil Type
S-1	0 - 34	Peoria Loess
S-2	34- 66	Peoria Loess
S-3	70- 96	Peoria Loess
S-4	96-122	Peoria Loess
S-5	122-144	Peoria Loess
	144-155	Roxana Silt
S-6	155-187	Roxana Silt
S-7	187-218	Roxana Silt
S-8	218-224	Roxana Silt
	224-250	Radnor Till
S-9	250-282	Radnor Till
S-10	289-323	Radnor Till
S-11	323-355	Radnor Till
S-12	355-386	Radnor Till
S-13	386-397	Radnor Till
S-14	397-414	Toulon (Sand)
S-15	460-484	Toulon (Sand only 6" recovery)
S-16	484-511	Toulon (Sand)
S-17A	524-547	Toulon (Sand)
S-17B	547-551	Hulick Till
S-18A	551-564	Hulick Till
S-18B	564-578	Hulick Till
S-19A	578	Hulick Till/Pennsylvanian Shale
S-19B		Pennsylvanian Shale
S-19C	to 605	Pennsylvanian Shale

On returning to BNL, the soil was removed from the Shelby tubes either by splitting open the tube or extruding the core. Specimens from 9 of the 13 Shelby tubes were selected for chemical analysis. Sample selection focused on using tubes containing one type of soil (e.g., S-3, Peoria Loess) and, eliminating tubes which contained distinct interfaces between soils (e.g., S-5 Peoria Loess, Roxana Silt). Soil from tube S-1 was not analyzed to avoid top soil and the vegetation present. Sample S-12 was not used since four other Radnor Till samples were selected for analysis. Two of the sand samples (S-14 and S-16) collected using the split barrel sampler were homogenized prior to the soil resistivity measurement and then divided into two samples for the remainder of the tests. This was necessary because neither sample S-14 or S-16 contained enough sand for the resistivity test. Sample S-15 was used for pH testing only and not for chemical analysis. Sample S-17 was not analyzed since it contained the interface between the Toulon and the Hulick Till members. Samples S-18A and S-18B were combined into one sample representative of Hulick Till. Similarly samples S-19B and S-19C were combined and analyzed as a specimen of Pennsylvanian Shale.

2.2 Resistivity Measurements

Resistivities were measured in the field and on laboratory samples. Field measurements, using the four electrode Wenner method, are termed, "earth resistivities." Laboratory measurements, using a Miller soil box, are called, "soil resistivities."

2.2.1 Field Resistivities

The location of the resistivity measurements at Sheffield is indicated by the letter B in Figure 2.1. The center point for the measurement was approximately 62 ft east of the fence at the waste site boundary and about 62 ft south of the USGS field trailer. This trailer is east of trench 26.

Earth resistivity measurements were made with a R-50 Stratameter D.C. electrical earth resistivity system (Soil Test, Inc.) according to the Wenner four electrode method described in ANSI/ASTM G57-78.(4) The procedure requires four metal electrodes be placed in the earth. Placement is along a straight line with equal separations (L) between the electrodes. A potential is applied to the outer electrodes causing a current (i) to flow through the earth. The voltage drop (E) is then measured across the inner electrodes. The resistivity (R) is calculated using the following formula:

$$R = 2\pi L \frac{E}{i} \tag{2.1}$$

Measurements are repeated at various electrode separations along a straight line in one direction. Then the series of measurements is repeated along a line perpendicular to the first.

The maximum electrode separation used for the field resistivity measurements was restricted to 40 ft because of limitations on available area. The measurements were made along lines in the north-south and east-west directions with a common center point. The electrodes were placed in the ground approximately 7 in.

2.2.2 Soil Resistivities

Soil resistivity was measured in the laboratory according to ANSI/ASTM G57-78(4) using a Miller soil box (M. C. Miller Company) connected to the resistivity meter used for the field measurements. A Beckman Digital Voltmeter was substituted for the voltmeter in the R-50 stratameter to measure the voltage drop across the inner electrodes of the soil box. Field moist soil, removed from the plastic bags or the Shelby tubes, was packed into the Miller soil box and the resistivity was measured. The same soil samples were then saturated with water, allowed to stand for about five days, and the resistivity of this paste was measured in the same manner. Soil resistivities in units of ohm-cm were calculated using the following equation:

$$R = \frac{E}{i} \frac{A}{L} \qquad (2.2)$$

where E equals the voltage drop across the potential pins of the soil box, and is the current flow through the soil. The quantity (A/L) is the ratio of the area of the soil box cross section to the spacing of the inner electrodes. For the soil box used, this ratio is equal to 1 cm.

The values reported were not corrected for temperature effects although the temperature at the time of the measurement was noted; this is discussed in Section 3.

2.3 Soil Moisture Content

The moisture content of the soil was determined according to the ANSI/ASTM D2216-71(5) method. Samples were dried in glass crucibles in an oven to constant mass. Results are calculated as the percent of moisture to dry weight of soil. The moisture content was measured on triplicate samples, with the average and standard deviation reported. Soil was taken from the center of the cores on opening the Shelby tube samples at BNL. For samples stored in plastic bags, soil was removed for moisture content analysis within four days of sample collection.

2.4 Soil pH Measurements

2.4.1 Measurements in Soil

The pH of the soil was measured using an Orion 220 pH temperature meter as prescribed by the standard test method, ANSI/ASTM G51-77.(6) Measurements were made in the soil stored in bags upon returning to BNL approximately 6 days after sample collection. The pH of the core soil was measured after splitting open the Shelby tubes.

The pH of the sand (Toulon Member) was measured in the field immediately after opening the split barrel sampler used for collection. On returning to BNL, the pH of the samples was again measured thereby providing some information on the effect of air and/or moisture loss on soil pH.

2.4.2 pH in 0.01 M $CaCl_2$

Peech(7) describes a method for determining the hydrogen ion activity of soils by measuring the pH of a mixture of air-dried soil and 0.01 M $CaCl_2$. The procedure requires mixing 10 g of air-dried soil and 20 mL of 0.01 M $CaCl_2$, after approximately 18 hours the pH of the liquid phase was measured. The pH of the stock 0.01 M $CaCl_2$ solution measured 6.6.

2.5 Chemical Analysis

Methods used for the chemical analysis of soil are described in a number of volumes.(7-10) The procedures selected for this work are outlined in this section. The reliability of the methods used was tested by Piciulo et al.(3)

The quantities of soluble ions in a soil are determined using a two step process: (1) a water extract of the soil is prepared and (2) a quantitative analysis of this extract is performed for each ion.

The water extracts of the soils were prepared by making a saturated paste of soil and water. This method is commonly used(7-10) and was preferred to a method using a fixed soil to water ratio (e.g., 1 part soil to 5 parts water) because the soluble ion content of a saturation extract is claimed to be representative of a natural soil solution.(7) It should be remembered, however, that the amount of that chemical species determined by the saturation extract method may be only a part of the total amount available for corrosive attack.

2.5.1 Drying of Soil

Soil samples for laboratory analysis were air-dried according to the method described by Dewis and Freitas.(8) The samples were spread on Plexiglass or aluminum trays and allowed to dry in a hood at ambient temperature and humidity until they were free flowing (2 to 5 days). Dried and crushed samples were stored in plastic bags prior to analysis.

2.5.2 Aqueous Soil Extract

The saturation extract of each soil used for the determination of water soluble constituents was prepared by mixing a portion of air-dried soil with enough deionized water to make a saturated paste. The quantities of soil and water used to make the aqueous extracts are listed in Table 2.2. After allowing each mixture to equilibrate overnight, (approx. 18 h), it was vacuum filtered through Whatman 541 filter paper. The extract was then filtered through Fisher 9-790-4A filter paper for further clarification. Several drops of 0.1% sodium hexametaphosphate were added to an aliquot of each sample immediately after filtering as specified by Bower and Wilcox (7) to prevent the precipitation of $CaCO_3$ from the extract on standing. This aliquot was used for the anion analyses (excluding sulfide). Approximately 20 mL of the extract was acidified with HNO_3 such that the resulting solution was 0.5 N in the acid. This solution was used for the atomic absorption analysis of cations. Acidification served to keep trace concentrations of metal ions in solution.

Variations in the water-soil mixtures used for the analysis of soluble ions will affect the final value of the amount of a species present per 100 g of dry soil. Sampling errors, those caused by variations in the soil samples collected, will also affect the accuracy of the results. Since it is not possible to estimate the extent of these errors, more than one sample was analyzed, where possible. The range of values observed provide a measure of the cumulative effect of both of these factors.

Table 2.2

Quantities of Soil and Water Used for the Aqueous Extractions of Sheffield Soils

Sample ID	g-Dry Soil	g-Water	Ratio Water/Soil
S-2	478	157	.33
S-3	537	155	.29
S-4	778	161	.26
S-6	540	157	.29
S-7	556	156	.28
S-9	593	199	.34
S-10	627	189	.30
S-11	633	274	.43
S-13	582	135	.23
S-14(16)A[a]	581	127	.22
S-14(16)B[a]	630	125	.20
S-18	565	251	.44
S-19	681	186	.27

[a] Samples S-14 and S-16 were homogenized and then divided into two equal samples.

2.5.3 Bicarbonate and Carbonate

The method used for the determination of bicarbonate and carbonate(7) requires a single potentiometric titation with 0.01 N H_2SO_4. A 15-mL aliquot of saturation extract was titrated to pH 8.2 to determine carbonate, and pH 4.5 to determine bicarbonate. There was no detectable carbonate in any of the soils tested. The detection limit and associated precision for bicarbonate measurement was 0.07 ± 0.01 meq/L.

2.5.4 Calcium, Magnesium, Potassium and Sodium

The saturated soil extracts and the ammonium acetate solutions containing exchangeable cations (see Section 2.5.8) were analyzed for calcium, magnesium, potassium and sodium on an Instrumentation Laboratories 951 atomic absorption (AA) flame spectrophotometer using the instrument specifications outlined for each element. An air-acetylene flame was used in all cases. To minimize ionization interferences in the AA analysis various recommended additives were used in samples and standards. Approximately 1 mg/mL potassium (as KCl) was added to the samples for calcium and sodium analysis. Samples analyzed for calcium and magnesium contained 0.1% lanthanum oxide and 1 mg/mL sodium (as NaCl) was added prior to potassium analysis. The detection limit and associated precision in units of meq/L are as follows: Ca, $5.00 \pm 0.06 \times 10^{-3}$; Mg, $0.31 \pm 0.01 \times 10^{-3}$; K, $7.8 \pm 0.3 \times 10^{-3}$; Na, $2.3 \pm 0.07 \times$

2.5.5 Chloride and Sulfate

The chloride and sulfate content of the saturation extract were determined by the Analytical Chemistry Services Group at Brookhaven National Laboratory. Chloride was analyzed colorimetrically using a Technican Autoanalyzer; the minimum detectable limit is 0.5 ± 0.04 µg/mL. Sulfate was analyzed using a Dionex Ion Chromatograph; the detection limit is 0.300 ± 0.005 µg/mL.

2.5.6 Sulfide Analysis

The quantity of sulfide present in the soil was estimated by extracting sulfide ions into an anti-oxidant buffer and determining the concentration by the method of standard additions using a solid state sulfide electrode (Graphic Controls Model PHI 92100) in conjunction with a double junction reference electrode (Graphic Controls Model PHE 54473). The relative electrode potential was measured as millivolts with a Lazar Model DPH digital pH meter.

Soil samples as collected were analyzed for sulfide rather than air-dried samples in an attempt to avoid the oxidation of any sulfide present on drying the soil in air. The details of the analytical procedure are described in Reference 3.

The measuring range of the sulfide electrode employed extends into the parts per billion (ppb) range. It was estimated by Piciulo et al.(3) that the detection limit for this method was approximately 20 ppb of sulfide. Test samples containing 50 ppb sulfide were analysed using the described method and the results indicate that the accuracy of the method is within 20% at this concentration. The reported results in mg-eq $S^{=}$/100g of dry soil are believed reliable within these limits. The moisture content of the soil was used to determine the dry weight of soil.

2.5.7 Total Acidity

The total acidity, also referred to as exchange acidity, was estimated in the soil sample using a modified titration method.(11) In each of two 100 mL test tubes 5 g of air-dried soil was mixed with 25 mL of 1 N NaCl solution. One mL of 0.2 N Na_2CO_3 was pipetted into one tube and 2 mL into the second. The tubes were shaken and allowed to stand for about 24 h when the pH of the solutions was measured. If the pH of the more alkaline solution was less than 8 an additional 1 mL of the sodium carbonate solution was added to each tube and the solutions allowed to equilibrate. This process was repeated until the pH of the more alkaline solution was above 8 and showed no further change with time. The pH of the two solutions was then plotted vs milliequivalents of added carbonate. The amount of alkali needed to bring the pH to exactly 8 was then determined by interpolation or extrapolation from this graph and is reported as mg-eq/100 g of dry soil. Denison and Ewing(11) indicate that this method is only accurate to 1 mg-eq/100 g soil. However, they add that this approximation is sufficient since variations due to soil sampling are greater than this amount.

2.5.8 Exchangeable Cations

The exchangeable bases in a soil are principally calcium, magnesium, potassium and sodium. These ions which are held within the mineral species of the soil and in organic compounds, can be reversibly exchanged with other positiviely charged ions in a soil solution. Ammonium ion (as ammonium acetate) was the exchanging species used in the procedure described by Piciulo et al.(3)

The total calcium content of four soil samples was estimated using X-ray fluorescence spectroscopy. The analyses were performed by the analytical chemistry group in the Department of Chemistry at BNL. Silica brick and USGS W1, containing 2.30% and 11.0% calcium oxide, were used as standards for the calcium determinations.

3. RESULTS AND DISCUSSION

3.1 Resistivity

An electrical resistivity survey of an area of earth can identify variations in subsurface materials. The depth to and thickness of sand, gravel, metal deposits and steeply-dipping contacts between different earth materials can be detected. Earth resistivities often supplement drilling programs or seismic surveys.

Resistivity is dependent on the flow of current through the material and thus reflects the amount of soluble ions in the soil and the moisture content. Figure 3.1 shows the influence of moisture content on soil resistivity. Since soil resistivity approaches a constant value with increasing water content, it is preferable to compare soil resistivities of saturated soils. Soil temperature also affects the apparent resistivity as indicated in Figure 3.2. Thus reported resistivities are often corrected to 15.5°C (60°F). Although this correction cannot be done for field measurements, it is conveniently done on laboratory samples. The following relation is suggested by the ASTM procedure(4) to correct resistivities between 0°C and 25°C.

$$R_{15.5} = \frac{R_t\ (24.5 + t)}{40} \qquad (3.1)$$

$R_{15.5}$ is the corrected resistivity using R_t the observed resistance at temperature t, in degrees Celsius. All laboratory measurements were performed with soil at 24°C, the temperature corrected resistivities are given in Section 3.1.2.

Resistivity is an often used criterion for estimating the corrosivity of soil.(2,12-16) It has been found that as soil resistivity decreases the corrosivity increases, provided other soil charateristics are similar. Table 3.1 lists data showing the influence of resistivity on the corrosion of steel pipelines. In Table 3.2, a classification of soil corrosivities vs resistivity is shown. This system is also based on the corrosion of steel pipe.

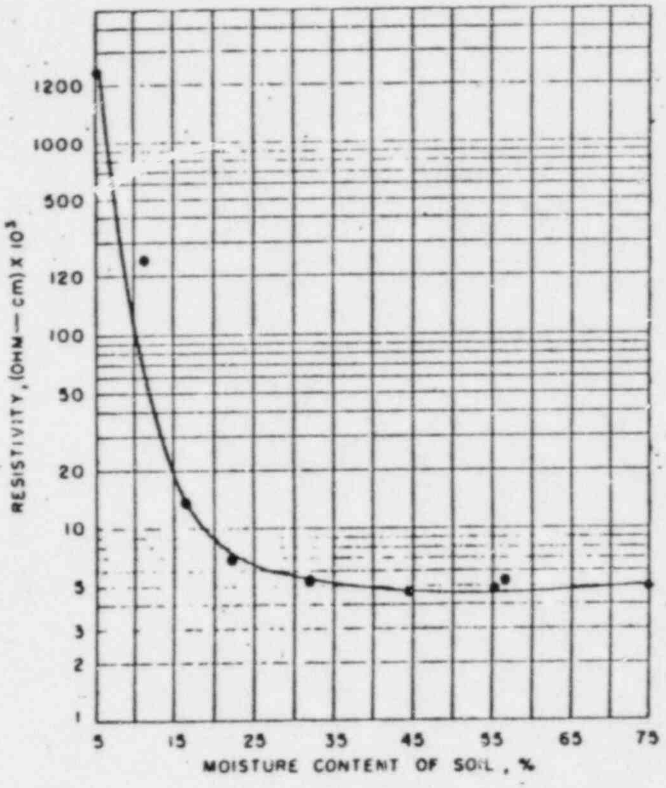

Figure 3.1 Effect of moisture content on resistivity of a clay soil.(2)

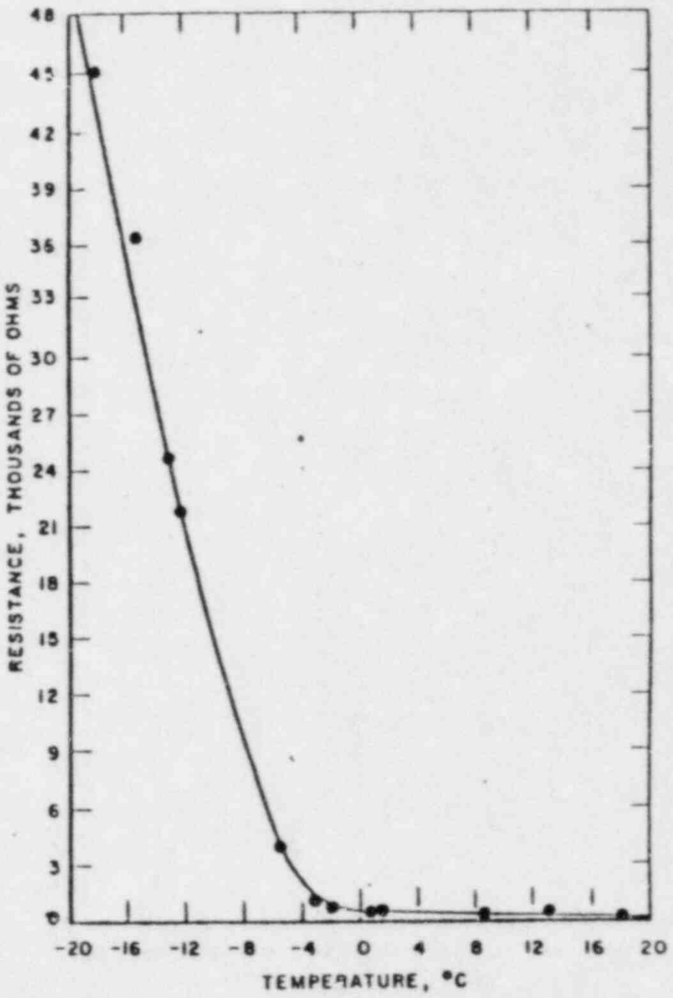

Figure 3.2 Effect of temperature on earth resistance.(2)

Table 3.1

Corrosion of Pipelines as Affected by
Soil Acidity and Resistivity(2,11)

Influence of Acidity - Soil Resistivity 4,000 to 5,000 ohm-cm

Soil Type	Total Acidity (mg-eq)[a]	Portion of Pipeline Requiring Repairs (%)
Wauseon fine sandy loam	7.5	6.3
Caneadea silt loam	12.2	13.3
Miami silt loam	16.8	22.8
Mahoning silt loam	18.1	20.9
Trumball clay loam	21.1	20.0
Crosby silt loam	22.0	30.8

Influence of Resistivity - Total Acidity 15 to 18 mg-eq[a]

Soil Type	Resistivity (ohm-cm)	Portion of Pipeline Requiring Repairs (%)
Lordstown fine sandy loam	11,450	3.3
Wooster loam	8,002	6.0
Volusia silt loam	5,473	13.6
Mahoning silt loam	4,903	20.9
Miami silt loam	3,982	22.8
Nappanee clay loam	1,009	57.0

[a] Milligram - equivalents of hydrogen ion per 100 g of soil.

Table 3.2

Soil Resistivity Classification in
Reference to the Corrosion of Steel Pipe(15)

Resistivity Range (ohm-cm)	Corrosivity
0 to 1000	Very severe
1001 to 2000	Severe
2001 to 5000	Moderate
5001 to 10,000	Mild
Greater than 10,000	Very mild

3.1.1 Earth Resistivities

The four electrode Wenner configuration is commonly used to measure earth resistivities.(4) Current flowing into the earth from the exciter (outer) electrodes develops hemispherical equipotential surfaces, if the material has uniform resistivity. The volume of earth through which the current passes is proportional to the distance between the electrodes. The potential measured across the inner electrodes is related to the resistivity of the material as described in Section 2.2.1.

The apparent resistivity measured using the four electrode method describes a weighted average of all the resistivities in the volume of material through which the current passes.(17) Since material near the surface is weighted more heavily than the deeper material, the electrode separation does not simply give a resistivity measurement at a corresponding depth. As the electrode separation is increased, there is an effect on the resistivity due to the deeper material. On changing from one electrode separation to a larger one, the change in the resistivity can be attributed to the materials at depth. The range of electrode separations over which a particular subsurface layer influences the apparent resistivity is related to the thickness of the zone. The material lying between the inner electrodes will influence the resistivity reading more than material between the outer electrodes. A rule of thumb claims that the material, at a depth less than one half of the electrode separation, has the greatest influence on the reading.(17) Material to the sides of the line of the electrodes also influences the apparent resistivity measured. Topographic features such as hills and cliffs, or more specifically for this work, a trench, either parallel to the line of the electrodes or perpendicular to either end of the electrode line can cause a redistribution of current density and effect the apparent resistivity reading. The presence of a near vertical contact plane of two materials having dissimilar resistivities can also influence the measurements. Readings made along perpendicular lines as prescribed by the Wenner method help one to recognize such variations.

Although temperature affects resistivity, the variation of soil temperature with depth is not expected to be large. The soil moisture content (which also influences resistivity) probably has seasonal variations due to climate thus affecting the resistivity measured in this manner. Thus, repeated measurements are necessary if variations in this parameter are of interest. However, laboratory measurements of resistivity of a saturated soil are often considered as limiting values. Such measurements were made and are discussed in Section 3.1.2.

The location where the earth resistivities were measured at Sheffield is marked by the letter B on the map of the burial site in Figure 2.1. Earth resistivities, measured along lines extending in the north-south and the east-west directions are plotted vs electrode separation in Figure 3.3. The data collected and the resulting resistivities are listed in Appendix B. The earth resistivity measurements range from approximately 3,000 ohm-cm to 6,000 ohm-cm. These values can be used to assess the soil as moderately corrosive to steel according to the classification given in Table 3.2.

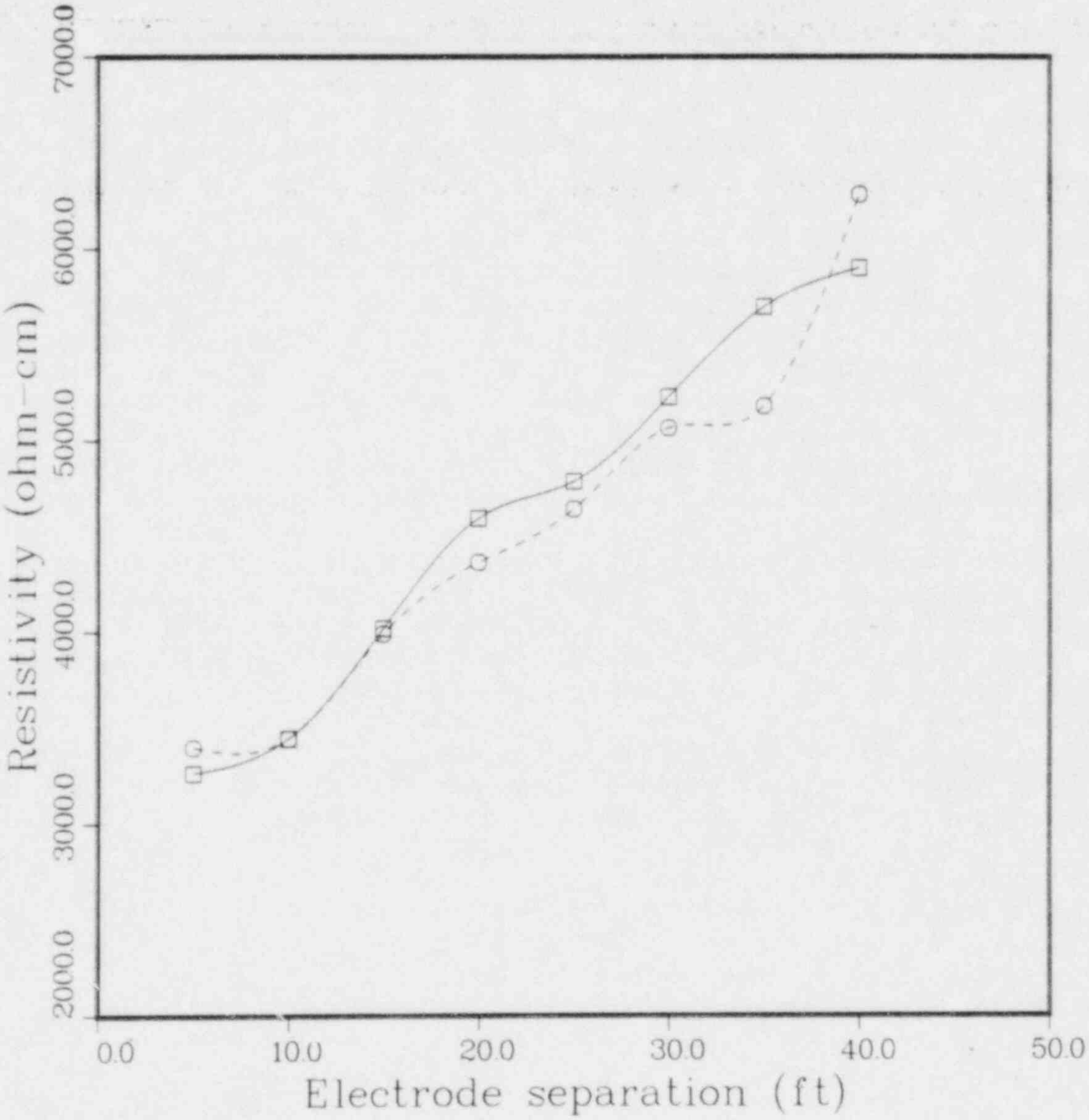

Figure 3.3 Earth resistivity measured on an area adjacent to shallow land burial site at Sheffield, IL.

The curves in Figure 3.3 show an increase in apparent resistivity with increasing electrode separation indicating the presence of higher resistivity material at depth. The differences between the curves are not believed significant. A discussion of soil resistivites in Section 3.1.2 shows that, of the six soil types tested, the sand recovered from Toulon member has a soil resistivity that is a factor of ten larger than that measured in other soils.

The resistivity data were also analyzed according to the Moore Cumulative Method which is described as a manipulative method with no theoretical considerations.(17) Resistivity readings taken at equally spaced electrode intervals are recommended. Since readings were taken in two directions and the values are similar, the average apparent resistivity is used for this treatment. The cumulative resistivity is defined as the sum of the apparent resistivity at each electrode separation and the resistivities of all preceeding electrode spacings. Figure 3.4 is a plot of cumulative resistivities vs electrode separation. Straight lines are drawn through the points such that the lines best fit the points. Selection of points for the lines is generally biased by some other knowledge of the geology of the area such as a borehole description. The electrode separations at which the lines intersect are considered to be equal to the depth to geologic boundaries. It is evident that several lines can be drawn through the points. If a larger data set were available, there may be more points to define a given line or it would be possible to draw more lines giving a more complex analysis. The intention of this analysis is to show that a description of the subsurface strata can be made from earth resistivity data along with core sampling data.

Four lines were drawn through the points in Figure 3.4 and they intersect at the following electrode spacings marked with arrows in the figure: 13 ft, 25 ft, and 35 ft. It is expected that an interface of two soil types exists at those depths. The core sampling data summarized in Table 3.3, and the geologic cross sections shown in Figure 2.2, help explain the Moore plot analysis. The cores listed in Table 3.3 were chosen because they surround the area on which the earth resistivity was measured. The area, east of the site boundary, lies between boring 504 and 537. The stratigraphy beneath this area is likely to resemble that shown between trench 1 and trench 26 in Figure 2.2

The depth of the first geologic boundary abstracted from the Moore plot is about 13 ft from the surface and may correspond with the depth to the bottom of the Peoria Loess formation. The listings in Table 3.3. show that the depth to this interface ranges from 10 ft to 18 ft.

The interface at a depth of 25 ft is likely to be at the bottom of the Radnor Till member. The lithology described in Table 3.3 shows that the depth to the Radnor Till member ranges from 21 ft to 39 ft and increases in depth from north (cores 501 and 502) to south (cores 503 and 504 and the BNL core). It was observed during the visit to Sheffield that the ground in this area has a rise on going from north to south. Additionally, the location of the resistivity measurement is south of boreholes 501 and 502, thus, it is likely that the Radnor Till in this area extends somewhat deeper than 21 ft.

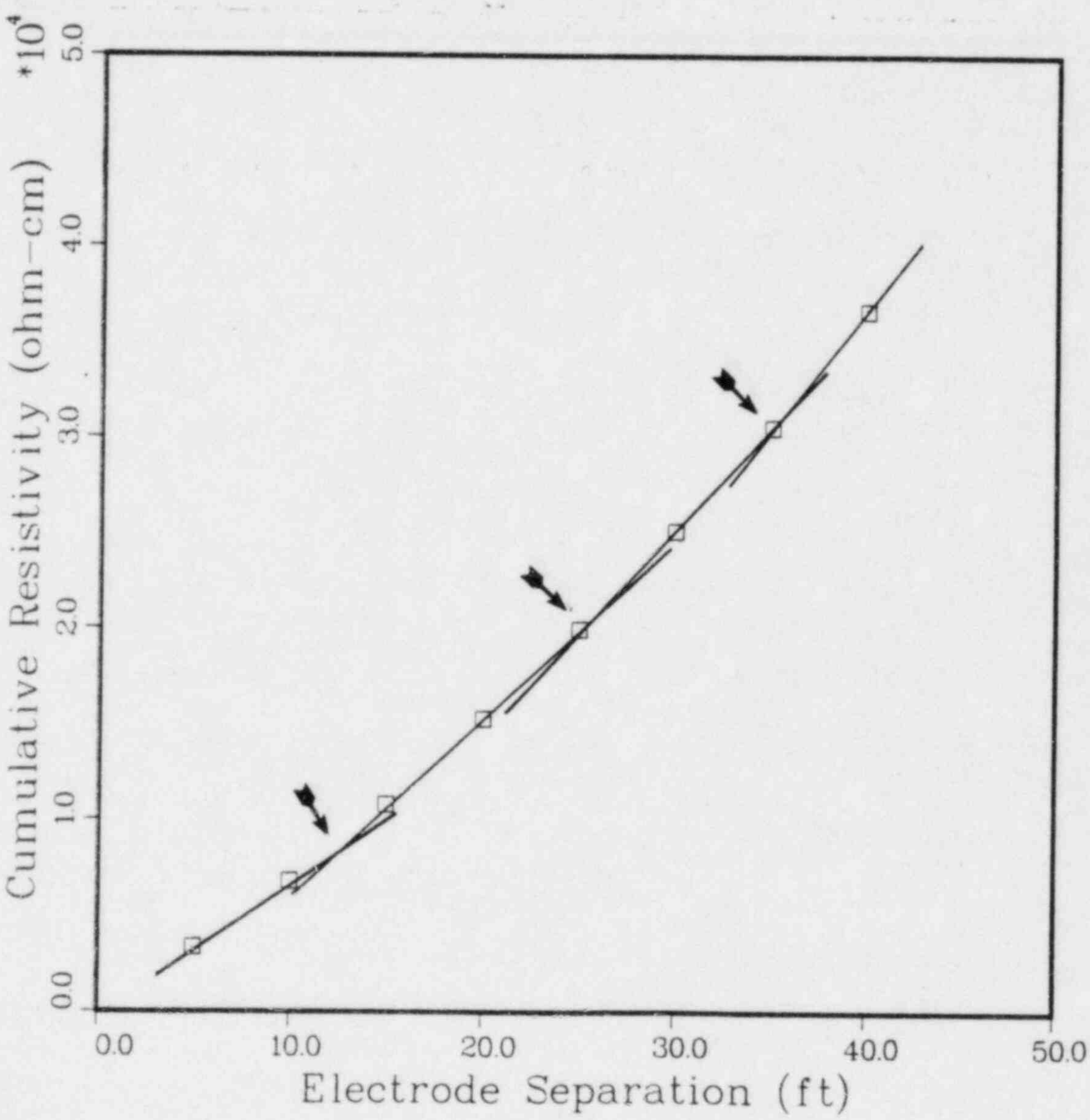

Figure 3.4 Moore cumulative plot of Sheffield resistivity data.

Table 3.3

Depth From Surface to Bottom of Soil Layers in Four USGS Cores and the BNL Core at Sheffield[a]

Soil Type	USGS Core No. 501	502	503	504	BNL Core
Fill	3	1	---	2	---
Peoria Loess	18	15	10	11	12
Roxana Silt	---	---	18	13	19
Teneriffe Silt	---	---	---	19	---
Radnor Till	21	21	31	39	33
Toulon	35	38	49	46	46
Hullick Till	44	42	50	48	48

[a] Depth rounded to nearest foot.

The third intersection observed on the Moore plot is at 35 ft and may correspond to the depth to the bottom of the sand layer. Table 3.3 shows that the depth to the bottom of the Toulon member ranges from 35 ft to 49 ft and an analysis similar to that given for the interface at 25 ft (the bottom of the Radnor Till) is applicable here.

The brief analysis described above indicates that earth resistivity data can supplement core sampling data to describe the subsurface soil boundaries in an area. Utilizing a resistivity analysis in an area where a new trench is to be excavated can help determine the soil stratigraphy in that area. A site with a complex geology like Sheffield may have trenches constructed in very different soil types. It can be seen in Figure 2.2 that Trench 1 extends between fill and Peoria Loess into Radnor Till. By comparison, Trench 2 is in fill and Peoria Loess. If the soil removed from a trench is used as backfill for that trench, then the soil surrounding the waste packages in the two trenches is different, and the corrosivity of these soils may or may not be similar. For future disposal sites having a complex geology, an analysis of earth resistivity data may detect soil strata and help assess a location for trench construction.

The analysis discussed above is not the only method used to interpret resistivity data.(17) Different methods are suitable to different geologic environments. A recent report(18) on the electrical resistivity survey of an area east of the Sheffield site focused on the extent of the sand of the Toulon member in that area. The thickness of the sand layer is estimated to range from 0 to 40 ft at depths of 0 to 23 ft. The description, by Foster and Erickson,(1) of soil from USGS Well 501, served as the geologic control for interpretation of the resistivity data. The utility of earth resistivity data for the analysis of burial sites warrants further examination.

3.1.2 Soil Resistivities

Soil resistivities measured using the Miller soil box are listed in Table 3.4. The precision of the resistivity value is given in parenthesis. Resistivities were measured on field moist soil samples (see Table 3.5 for moisture content) and on water saturated samples. The moisture content of the water saturated soils are also given in the Table. The resistivity value measured in saturated soil provides a limiting value for the soil resistivity and a means of comparing the resistivity of one soil to another. Soil resistivities measured on saturated soils are most often used to estimate soil corrosivity. The values measured in this work are consistent with the ranges of resistivity of different soils from this area described by Larson.(18)

Table 3.4

Soil Resistivities of Sheffield Samples[a]

		Water Saturated Soil	
Sample ID	Resistivity[b,c] (ohm-cm)	Resistivity[b] (ohm-cm)	Percent Moisture
S-4	9.3(0.2) E+3	6.5(0.1) E+3	29
S-7	6.3(0.1) E+3	5.7(0.9) E+3	29
S-10	3.4 E+3	4.0(0.6) E+3	35
S-14(16)[d]	6.2(0.8) E+4	1.3(0.2) E+4	22
S-18B	5.2(0.1) E+3	5.0(0.1) E+3	24
S-19C	3.2(0.1) E+3	2.5 E+3	27

[a] Resistivities were measured at 24°C and values listed in this table are corrected for temperature according to Equation 3.1.

[b] Number in parenthesis is the precision of the resistivity, a value is not given if less than 2%.

[c] The moisture content of the soil used in these measurements is given in Table 3.5.

[d] Samples S-14 and S-16 were homogenized prior to the resisitivity measurement.

It is immediately evident that the sand material (Sample S-14(16)) has the highest soil resistivity. Samples S-4, S-7, and S-10 indicate a decrease in resistivity with increasing sample depth; 9 ft, 17 ft, and 25 ft are the respective depths. The earth resistivities (Section 3.1.1) showed the opposite trend, and this was attributed to the influence of the high resistivity sand layer on the earth resistivity measurements.

Measurements made with water saturated soil indicate a decrease in soil resistivity from that measured using field moist soil in all but one case. Sample S-10 showed an increase in resistivity between the field moist soil and the saturated soil. The precision of the measurement indicates that the increase is not statistically significant. In fact, only the Peoria Loess (S-4) and the Toulon (S-14(16)) showed significant changes in resistivity with changes in moisture content. Based on the soil resistivities measured on the saturated soils, the corrosivity of the soils fall into three categories according to the classification given in Table 3.2.

• Moderately corrosive to steel:	Radnor Till, Hulick Till, and Pennsylvanian Shale
• Mildly corrosive to steel:	Peoria Loess and Roxana Silt
• Very mildly corrosive to steel:	Toulon member.

There are large variations in trench sizes at Sheffield, ranging in length from 35 to 580 ft, in width from 8 to 70 ft and in depth from 8 to 26 ft.(1) A trench may be constructed in one soil type (i.e., Peoria Loess) or several. Thus, the corrosivity of the burial environment is likely to vary from trench to trench. A trench constructed in Peoria Loess and Roxana Silt, with this material used as backfill, may be a somewhat less corrosive environment than a trench extending into Radnor Till. This assessment is based only on soil resistivity and does not reflect variations in soil aeration, moisture content and pH, all of which influence the corosivity of the burial environment.

3.2 Moisture Content

The percent moisture content of the soils collected from Sheffield range from 5 to 25 and are listed in Table 3.5. The moisture content of the Toulon member (S-14 and S-16) is significantly lower than that of the other soils. The value of 4.8 for the moisture content of Radnor Till S-13 is much lower than found for other samples of this soil. Sample S-13 may be a non-representative sample of Radnor Till from the Shelby tube containing the Radnor Till-Toulon member interface. If one considers that the trenches extend to a maximum depth of 26 ft, then soils above the sand are of greater importance to corrosion assessment and the range of moisture content is 14 to 25 percent.

Table 3.5

Moisture Content of
Sheffield Soil Samples

Sample ID	Percent Moisture Content[a]
S-2	14. (1)
S-3	15.6(0.6)
S-4	15.4(0.5)
S-6	22.4(0.5)
S-7	18.3(0.4)
S-9	18.6(0.2)
S-10	20.6(0.9)
S-11	25.2(0.8)
S-13	4.8(0.1)
S-14	5 (2)
S-16	5.8(0.9)
S-18A	12.1(0.4)
S-18B	11.2(0.6)
S-19B	11.8(0.1)
S-19C	10.9(0.1)

[a] Values in parenthesis are standard deviations of repeated measurements on specimens from a given sample.

3.3 Soil Acidity

3.3.1 pH of Soil

The pH of the soil samples, measured in the laboratory, is listed in Table 3.6. The pH values indicate soil ranging from slightly acidic (pH = 6.2, Sample S-18, Hulick Till) to slightly alkaline (pH = 7.8, Sample S-4, Peoria Loess). It is noteworthy that the samples showing the lowest soil pH values, S-13 and S-18, are measured in soil near the interfaces above and below the Toulon member. Additionally, these samples show the largest increase in pH on comparing values measured in the "field moist" sample with that measured in the saturated paste.

Table 3.6

Acidity of Sheffield Soils

	pH				
Sample ID	Soil	Soil: 0.01 M $CaCl_2$	Saturated Paste	Extract	Total Acidity[a]
S-2	7.4	7.48	7.7	7.66	5
S-3	7.5	7.54	7.8	7.84	7
S-4	7.8	7.60	7.8	7.72	(1)
S-6	7.2	7.55	7.7	7.71	(2)
S-7	7.1	7.49	7.6	7.72	ND
S-9	7.3	7.19	7.6	7.51	(2)
S-10	7.3	6.89	7.7	7.98	(3)
S-11	7.2	7.32	7.6	7.89	(3)
S-13	6.8	7.16	8.1	7.91	ND
S-14	7.5	----	---	----	----
S-16	7.6	----	---	----	----
S-14(16)A[b]	----	7.47	8.4	7.93	ND
S-14(16)B[b]	----	----	8.4	7.88	----
S-18	6.2	7.61	8.0	5.83	(2)
S-19	7.4	7.51	7.9	8.20	(2)

[a] Units are mg-eq per 100 g dry soil. ND indicates non-detectable. Values in parenthesis were determined by extrapolation, see text (Section 3.3.3) for explanation.

[b] Samples S-14 and S-16 were homogenized and then divided into two parts prior to analysis.

In the field, the pH was measured of the sand recovered from the Toulon member (Samples S-15 and S-16). This material was collected using a split barrel sampler and the pH was measured immediately after opening the barrel. Table 3.7 lists pH values recorded in the field and in the laboratory. Clearly the sand is alkaline and the pH of the soil decreases by about one pH unit on exposure to air. Sample S-15 was kept in a closed plastic bag and the pH measured 48 days later shows only a slight increase. It is not clear whether this increase is significant or an artifact of method for measuring pH of soil. However, the conclusion that the pH of the soil decreases on being removed from the ground and exposed to air remains unchanged.

Although the observation of the pH change in the Toulon member cannot be extended to the other soil types without actual data, it does indicate that the pH of the other soils measured in the laboratory sometime after collection must be considered with care.

Table 3.7

pH Measured in Samples From Toulon Member

Sample ID	pH	
	Field	Laboratory
S-15	8.6, 8.5	7.3 (7 days after collection) 7.7 (48 days after collection)
S-16	8.6, 8.5	7.6 (7 days after collection)

Also listed in Table 3.6 is the pH measured in the saturated paste used for the extraction of soluble ions. The average pH of the saturated paste is higher than the average pH of the "field moist" soil for each of the 6 soil types. Samples S-13 and S-18 show the largest increase in pH, 1.3 and 1.8, respectively. As stated before, these samples are immediately above and below the Toulon member. The sand from the Toulon member shows an increase of $\sim$0.9 pH units on comparing the field moist with the saturated soils, and the pH of the saturated sand is comparable to the pH of the sand measured in the field. The other soils show pH changes of 0.5 pH units or less under the same conditions of testing. This suggests that the acid properties of the sand in the Toulon member are significantly different from those of the other soils.

When evaluating the corrosivity of a burial environment the influence of the trench contents on the soil chemisty should also be considered. Reported pH measurements(25) of water samples collected from trenches and wells on the Sheffield site help to illustrate this influence. The pH of water from well 525 was reported to be 7.5. This pH is consistent with the pH values presently measured in soils and soil extracts. Water samples collected from the drains of trenches 14 and 18A had pH values of 5.0 and 6.8, respectively. The pH of the water from trench 14 clearly suggest an influence of the trench contents on the chemistry of the trench environment.

3.3.2 Hydrogen Ion Activity

Field pH measurements are generally used to relate soil pH to corrosion, however, uncertainties in making this measurement led to the use of other methods to characterize the soil acidity. Seasonal variations can result in the lowest soil pH values during a hot, dry season and highest values during cool and rainy season. Measurements of pH in water and salt solutions is helpful to provide an estimate of the pH that might be encountered in the soil. The use of 0.01 M $CaCl_2$ solution for measuring pH has several advantages. The soil electrolyte concentration will be insignificant as compared to the concentration of the $CaCl_2$ solution and pH of the soil mixture is independent over a wide range of dilutions. pH measurements in a suspension of one part soil with two parts of 0.01 M $CaCl_2$ solution should, therefore, provide a more accurate H^+ ion activity of the soil than measurements made on a soil suspension in pure water. The pH of the soil suspension in the salt solution should also be independent of the time of year (climatic conditions) when the soil was collected. The pH measured in 0.01 M $CaCl_2$ has been observed to be about 0.5 pH units lower than the pH measured in water, using one part soil to two parts liquid.(7) Table 3.6 lists the pH measured in a 1:2 mix of soil: 0.01 M $CaCl_2$, and the pH of the water extract of the soils use for the analysis of soluble ions.

Measurements using the Sheffield soils show that the pH of the 0.01 M $CaCl_2$ solution soil mixture is lower than the pH measured in the saturated paste and the extract of that paste. The pH of the soil-salt solution is comparable to the pH of the soil in all cases except sample S-18. The pH of the Hulick Till, (sample S-18) and the aqueous extract of that soil are comparable but considerably lower than the pH of the saturate paste and the salt-soil mixture. The low pH reported for the extract solution of S-18 is possibly in error, since for the other soils the pH of the extrtact is similar to that measured in the saturated paste. The pH of the soil S-18, may be low because the Hulick Till is a hard material making it difficult to get a good soil-electrode contact (i.e., the pH electrode) necessary for the measurement.

In general, the pH of the saturated pastes and the extracts are somewhat higher than the pH of the "field moist" soil and the soil-salt mixture. These differences suggest an effect of ionic strength (or dilution) on pH measurements of the Sheffield soils.

3.3.3 Total Acidity

The total acidity of soil was found to correlate with the corrosion of steel pipelines in soil(2,11,12,16) as shown in Table 3.1. Since the acidic component in soils may be only slightly dissociated, the soil pH may not provide an adequate indication of the acid capacity of the material. Although pH is a measure of hydrogen ion concentration and total acidity indicates the amount of ionizable hydrogen, one cannot assume that different soils having the same pH will necessarily have the similar total acidities.

The acidities of the Sheffield soils are listed in Table 3.6. Values given in parenthesis should be considered carefully. The method employed for the determination of total acidity requires two solutions (see Section 2.5.7) each having different pH values. At the intended end point the pH values of the two soutions should bracket pH = 8. Then by interpolation the amount of base needed to reach pH = 8 can be determined. This assumes that the titration curve of the soil has a well defined inflection point. Figure 3.6 shows the titration curves for a number of soils and indicates that the major assumption of the procedure used in this work is valid. However, several of the samples analyzed produced two solutions each having pH > 8. For these cases, the exchange acidity listed was determined by extrapolation and the values are given in parenthesis. Since there is no information about the shape of the titration curves for the Sheffield soils presently analyzed, it is not known what uncertainty exists in these values. This can be illustrated by examining the behavior of soil 7 in Figure 3.5. Extrapolating a straight line to pH = 8 through the first two data points above pH = 8 for soil 7 in Figure 3.5 would clearly give an erroneous acidity.

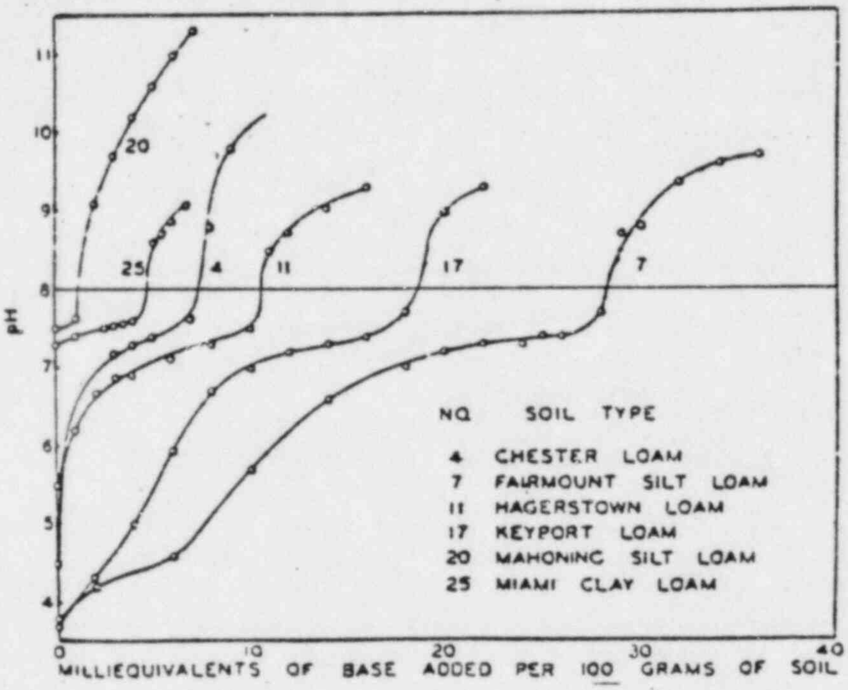

Figure 3.5 Titration curves of soils.(12)

The total acidity of a number of soils, indicated by ND in Table 3.6 could not be determined with this method. In these cases, the pH of the two solutions were greater than 8 and when extrapolation to pH = 8 was attempted, a negative value of exchange acidity was found. It is possible that the exchange acidity is very near zero. Hydrolysis of soil constitutents can contribute to the difficulty in the determination.

The total acidities of the Sheffield soils indicate an alkaline medium. Two of the three Peoria Loess samples are the only soils to show measurable exchange capacity. Since one of these soils reacted differently from the others, there is some uncertainty in interpreting the results. The analysis of samples from only one borehole can give non-representative results for the soils in question. On the other hand, the observation of measurable acidity in soils at the top of the borehole changing to alkaline soils with depth may be a real representation of the soil acidities.

3.4 Soluble Ions

Corrosion is influenced by the soluble salt content of a soil but no generic correlation is available for comparing soil corrosivity with chemical composition. Large variations in soluble salt content often exist between sampling points and there are inconsistencies in the rates of corrosion at locations where the chemical compositions of the soils are similar. However, the chemical composition of soil together with the physical parameters of the soil previously discussed can be used to estimate a soil's corrosivity. The quantity and type of soluble ions together with the moisture content of the soil determine the ability of the soil to conduct current and thus define the resistivity of the medium. Generally, corrosive soils contain large amounts of soluble salts resulting in low resistivity values. Mildly corrosive soils have such low concentrations of soluble salts that the concentrations are often not determined for soils with resistivities greater than 3000 ohm-cm.(2)

Intuitively one might expect that the amount of soluble cations will equal the amount of soluble anions. This is not the case for the soils analyzed in this work, which often show a higher cation content than anion content. However, the lack of agreement is in part attributed to analyzing the soil for a limited number of anions, excluding species such as phosphate and nitrate. It is also possible that the colloidal nature of a soil may result in a positively charged counter ion associated with a negatively charged colloid species, thus yielding a larger number of cations in solution than anions.

Some chemical components in soils are specifically aggressive to certain materials. Pitting failures in stainless steel are caused by chloride ions.(19,20) Sulfate ions are aggressive toward concrete.(16,21) Sulfide ions, which attack copper,(22) can also provide an indication of the presence of microorganisms.(2) Conversely, soluble salts in soils can provide protection against corrosion by the deposition of low solubility corrosion product on a metal surface.

The values for the soluble ion content of the soils reported in this section reflect the precision (i.e., two significant figures) of the analytical technique. However, variations among replicate analyses of a given soil type illustrate the uncertainty in measuring the ion content of that soil.

The results of the analysis of the Sheffield soil samples for soluble ion content are listed in Table 3.8.

No carbonate was detected in any of the soils analyzed. Bicarbonate was present in all samples ranging from 3.1 E-2 to 9.0 E-2 mg-eq per 100 g of soil. Sample S-18 showed a bicarbonate content considerably lower, 4.9 E-3 mg-eq per 100 g of soil, however, the extract used for this analysis had an unexplained low pH (see Table 3.6) and this may account for the observations. The results show a slight decrease in bicarbonate content with increasing depth to about 45 ft where the sand lens is encountered. The Pennsylvanian Shale showed the largest bicarbonate content of all the soils tested. The presence of bicarbonate is consistent with the calcareous nature of the soils.

Table 3.8

Soluble Ions in Sheffield Soil (mg-eq per 100 g of Dry Soil)[a]

Sample ID	Ca^{2+}	Mg^{2+}	K^+	Na^+	HCO_3^-	SO_4^{2-}	S^{2-}	Cl^-
S-2	6.3 E-2	2.9 E-2	1.9 E-3	7.7 E-3	5.9 E-2	1.4 E-2	ND	5.9 E-3
S-3	5.3 E-2	2.7 E-2	1.2 E-3	1.2 E-2	4.4 E-2	1.5 E-2	ND	3.8 E-3
S-4	6.4 E-2	3.5 E-2	3.6 E-3	6.9 E-3	5.3 E-2	1.4 E-2	ND	7.7 E-3
S-6	2.8 E-2	2.2 E-2	1.7 E-3	1.2 E-2	3.5 E-2	8.3 E-3	ND	9.1 E-3
S-7	4.3 E-2	3.0 E-2	6.7 E-4	9.8 E-3	4.0 E-2	2.1 E-2	ND	4.1 E-3
S-9	3.2 E-2	2.0 E-2	2.2 E-3	6.6 E-3	3.1 E-2	1.8 E-2	ND	3.6 E-3
S-10	4.0 E-2	2.9 E-2	3.4 E-3	8.4 E-3	4.0 E-2	2.2 E-2	ND	5.2 E-3
S-11	5.7 E-2	5.2 E-2	4.5 E-3	2.3 E-2	5.3 E-2	3.7 E-2	ND	7.0 E-3
S-13	3.1 E-2	2.3 E-2	8.0 E-4	4.7 E-3	3.6 E-2	9.8 E-3	ND	4.1 E-3
S-14(16)A[b]	4.5 E-2	3.2 E-2	1.4 E-3	1.1 E-2	3.5 E-2	2.4 E-2	ND	1.2 E-2
S-14(16)B[b]	3.5 E-2	2.5 E-2	9.6 E-4	8.2 E-3	3.2 E-2	1.6 E-2	NA	9.0 E-3
S-18	1.0 E-1	6.8 E-2	3.6 E-3	1.6 E-2	4.9 E-3	5.6 E-2	ND	1.4 E-2
S-19	2.6 E-1	1.4 E-1	6.6 E-3	1.7 E-2	9.0 E-2	2.8 E-1	1.4 E-3	1.2 E-4

---

[a] ND means not detectable. See Section 2. NA means not analyzed.

[b] Samples S-14 and S-16 were homogenized and then divided into two parts prior to analysis.

The sulfate content of the Sheffield soil shows a slight increase with increasing sample depth from the surface. The Pennsylvanian Shale has the largest sulfate content, several times that found in the other samples, indicative of a gypsiferous shale. The concentration of soluble sulfate ion present in the soils is expected to result in a negligible degree of attack on concrete.(16,21)

The chloride content measured in samples S-2 through S-13, which include Peroia Loess, Roxana Silt, and Rodnor Till, averages $6 \pm 2 \times 10^{-3}$ mg-eq per 100 g of soil. A slight increase in the concentration of chloride ion is seen in the sand from the Toulon member and the Hulick Till. The Pennsylvanian Shale shows the lowest chloride concentration. The aggressiveness of the chloride ion detected in these soils toward materials such as stainless steel cannot be simply evaluated. Pitting corrosion resulting from chloride in soils is, however, discussed elsewhere.(19)

Only in the sample of Pennsylvanian Shale (S-19) was sulfide ion detectable. Sulfide is generally present in small quantities and in strongly reducing soils. The redox potential of the soils tested is not available but alkaline soils as observed here are necessary for the presence of HS^- or S^{2-} ions. A strongly reducing environment and an oxygen deficient soil are factors favorable to the existenced of anaerobic bacteria which can convert soluble sulfates to sulfides. Oxidation on removing the soil from the earth and during storage prior to the analysis may have caused a decrease in the detectable sulfide ion. The oxidation of sulfide to sulfate may contribute to the large sulfate content found in sample S-19. The detection of sulfide suggests the presence of anaerobic bacteria.

3.5 Exchangeable Cations

The exchangeable cations in soils can influence the physical and chemical properties of soils.(10) Cations bound to soil minerals and to organic species can be reversibly replaced by the cations of salt solutions and acids. Although this is of limited importance regarding the corrosivity of a soil, it is significant when considering the ability of a soil to retain radionculides. It should be recognized, however, that the values of the cation exchange capacity of a soil can vary widely as a result of the procedure employed for the determination. The results of the analyses for exchangeable calcium, magnesium, potassium, and sodium are listed in Table 3.9.

As in the case of measuring the soluble ion content of the soils, the values in Table 3.9 reflect the precision (i.e., two significant figures) of the analytical technique used to determine the concentration of exchangeable cations in a given soil sample. Variations in the measured quantity of exchangeable cations from one sample to another of a given soil are greater than the precision of the analytical technique employed.

At the time of the preparation of this manuscript, the analysis of the exchangeable ions was not completed because of the unexpected high levels of calcium in several samples. The results available are given with an indication that the concentration of the species is greater than the value listed. X-ray fluorescence spectroscopy was used to estimate the total calcium content of 4 soil samples. The approximate upper bounds for exchangeable calcium in Peoria Loess, Radnor Till, Hulick Till and Pennsylvanian Shale are given in Table 3.9. The values are based on the total calcium determinations.

Table 3.9

Exchangeable Cations in Sheffield Soils
(mg-eq per 100 g of Soil)[a]

Sample ID	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}
S-2	>202 (360)[b]	>66	1.4 E-1	2.4 E-1
S-3	>181	>77	6.3 E-2	1.4 E-1
S-4	>183	>77	7.3 E-2	1.5 E-1
S-6	18	4.3	7.0 E-2	1.7 E-2
S-7	16	2.9	7.8 E-1	1.7 E-2
S-9	12	6.5	1.3 E-1	2.0 E-1
S-10	>62	>30	2.3 E-2	5.4 E-2
S-11	>67 (180)[b]	>32	1.8 E-1	2.9 E-1
S-13	58	19	6.1 E-2	2.5 E-1
S-14(16)A[c]	69	28	2.9 E-2	1.5 E-1
S-14(16)B[c]	48	9.4	2.8 E-2	2.3 E-1
S-18	>106 (270)[b]	>35	>1.6 E-1	>2.1 E-1
S-19	>84 (300)[b]	>22	5.1 E-2	>3.1 E-1

[a] See Section 2 for detection limits of each analysis.

[b] Numbers given in parentheses are the estimated upper bound values for total calcium as determined by X-ray fluorescence.

[c] Samples S-14 and S-16 were homogenized and then divided into two parts prior to analysis.

The same exchangeable cations mentioned above are the principle exchangable bases found in soils. The total of the exchangeable base plus the exchange acidity can provide an estimate of the cation exchange capacity of the soil.(7) Values of cation exchange capacity determined in this manner are probably low estimates since quantities of manganese, iron, ammonium, and other cations held in exchangeable form are neglected. A comparison of the exchange acidities (Section 3.3.3) to the amount of exchangeable cations in the Sheffield soils clearly indicates that the exchangeable bases dominate the cation exchange capacity. Additionally, calcium and magnesium are the major exchangeable ions found in these soils. This is to be expected since the soils from this area are highly calcereous.(23)

3.6 Comparison With Other Disposal Sites

The results of the analyses of soil samples from the low-level waste disposal sites at Barnwell, SC and Hanford, WA, have recently been reported.(3) These analyses include measurements of soil resistivity, soluble ion content, moisture content, and soil acidity. As reported in the present work, these parameters have also been quantified for soil samples from the Sheffield site. Comparison of these results can provide some indication of the relative corosivity of the soils at the three sites.

With the exception of the Toulon member, resistivities of the Sheffield soils are generally lower than those of the soils from Barnwell and Hanford. The sand from Sheffield, however, has a resistivity similar to that observed for the soils from the other sites. The lower resistivity of the Sheffield soils can be attributed to the soluble ion content which is distinctly higher than that found in the soils from either of the other sites. Based on the observed soil resistivities alone, the soils from Sheffield are expected to be more corrosive toward steel containers than soils from either Barnwell or Hanford. However, it should be recalled that based upon resistivity alone, the Sheffield soils are expected to be no worse than mildly corrosive to steel.

The moisture content of Sheffield soils is similar to that found in Barnwell which is consistent with the location of the sites in wet regions of the United States. Hanford, located in an arid region, had soils with moisture contents considerably lower than those of the soils from the other sites. Most of the corrosion of metals underground is the result of an electrochemical reaction.(2) Such a process requires an electrolyte to conduct current. Since soil moisture provides this electrolyte, wet sites are likely to be more corrosive to metals than sites located in arid regions.

The acid properties of the soils from the three sites vary. pH measurements indicate that Barnwell soils are generally acidic (pH ~5), Hanford soils showed neutral pH and the Sheffield soils are neutral to alkaline (pH to 8.6). The Sheffield soils showed a change in soil pH on contact with air. This property was not analyzed in the Barnwell and Hanford soils. In contrast to the soil pH measurements, determinations of soil total acidity showed that soils from each site are alkaline. Only a small amount of exchange acidity was detected in clay samples from Barnwell and loess from Sheffield.

Taken as a whole, measurements of soil pH and total acidity suggest that Sheffield soils are more alkaline than those from Hanford and Barnwell. There is a tendency for corrosion to be greater in soils having high total acidity or that are highly alkaline in nature.(16) Similarly, least corrosive soils have pH's ranging from 4.5 to 7.6, whereas the pH of most corrosive soils is between 4.2 and 9.4.(16) Based on this analysis, the Sheffield soils are likely to be more corrosive than soils from Barnwell and Hanford.

It appears from a comparison of the results of soil analyses of Hanford, Barnwell, and Sheffield, that the Sheffield site has the most corrosive soil of the three. However, none of the sites were believed to have soils which are severly corrosive to steel.

4. CONCLUSIONS

Data presented in this report can serve as a basis for the evaluation of the corrosivity of the soils at the Sheffield burial site. A number of reports are available which discuss the corrosion of metals and other materials in soil.(2,11,13-16,19,21,24)

Based on the data discussed in this report, the following is concluded:

- There is some variation in the resistivities of the different soils from this area. These resistivities can serve as a basis to evaluate the corrosivity of the soils. Radnor Till, Hulick Till, and Pennsylvanian Shale are classified as moderately corrosive to steel. Peoria Loess and Roxana Silt are expected to be somewhat less corrosive to steel than those listed above. Sand from the Toulon member is expected to be very midly corrosive to steel.

- Based on pH measurements and the total acidities of the soils, the environment is likely to range from slightly acid (pH = 6.2) to alkaline (pH = 8.6).

- The sulfate content of the soils is expected to result in a negligible degree of attack on concrete.

- The variation observed in the soil resistivities and the pH of the different soils together with the fact that the trenches at Sheffield are cut into different soil strata suggests that the corrosivity of all the trenches may not be the same.

- The corrosivity of a burial environment can depend not only on the soil chemistry, but also on the contents of the trench. Measurements of the pH of water samples from two trenches and one well at Sheffield, show significant differences. Waters from trenches 14 and 18A and well 525 had the following pH values: 5.0, 6.8, and 7.5, respectively.(25) The pH of water from well 525 is consistent with pH values reported here for soils and soil extracts. However, the pH measured of water from trench 14 clearly indicates the influence of the trench contents on the chemistry of the trench environment.

- Based on the comparison of the results of the analyses of soils from the Sheffield site with similar results for soils from the low-level radioactive waste disposal sites at Barnwell, SC and Hanford, WA, it is concluded that the Sheffield soils are relatively more corrosive to steel than soils from either of the other sites.

5. REFERENCES

1. J. B. Foster and J. R. Erickson, "Preliminary Report on the Hydrogeology of a Low-Level Radioactive Waste Disposal Site Near Sheffield, IL, U.S. Geological Survey, Open-File Report-79-1545, January 1980.

2. M. Romanoff, "Underground Corrosion," <u>NBS Circular</u> 579, PB-168 350, April 1957.

3. P. L. Piciulo, C. E. Shea, and R. E. Barletta, "Analyses of Soils at Low Level Radioactive Waste Disposal Sites," Draft Report, BNL-NUREG-31388, May 1982.

4. "Field Measurement of Soil Resistivity Using the Wenner Four Electrode Method," ANSI/ASTM G57-78. Available From American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, Copyrighted.

5. "Laboratory Determination of Water (Moisture) Content of Soil, Rock and Soil-Aggregate Mixtures," ASTM D2216-80. Available From American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, Copyrighted.

6. "pH of Soil For Use in Corrosion Testing," ANSI/ASTM G51-77. Available From American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103, Copyrighted.

7. C. A. Black, Editor, <u>Methods of Soil Analysis, Parts 1 and 2</u>, Number 9 in the Agronomy, American Society of Agronomy, Inc., Wisconsin, 1965.

8. J. Dewis and F. Freitas, "Physical and Chemical Methods of Soil and Water Analyses," <u>Soil Bulletin 10</u>, Food and Agriculture Organization of the United Nations, p. 19-21, 1970.

9. "Soil Survey Laboratory Methods and Procedures for Collecting Soil Samples," <u>Soil Survey Investigations Report No. 1</u>, U.S. Department of Agriculture, Revised April 1972.

10. "Diagnosis and Improvement of Saline and Alkali Soils," U.S. Salinity Laboratory Staff, <u>Agriculture Handbook No. 60</u>, U.S. Department of Agriculture, Reprinted August 1969.

11. I. A. Denison and S. P. Ewing, "Corrosiveness of Certain Ohio Soils," <u>Soil Science</u> 40, 287-299 (1935).

12. I. A. Denison, "Methods for Determining the Total Acidity of Soils," <u>Bureau of Standards Journal of Research</u> 10, 413-426 (1933).

13. E. Escalante, "Soils and Underground Corrosion" 17th Annual Liberty Bell Corrosion Course 1, NBS-561-362, 1979.

14. R. F. Stratfull, "A New Test for Estimating Soil Corrosivity Based on Investigation of Metal Highway Culverts," *Corrosion* 17, 493-496 (1961).

15. J. D. Palmer, "Soil Resistivity - Measurement and Analysis," *Materials Performance*, p. 41-46, January 1974.

16. M. J. Schieff, "What Is Corrosive Soil?" pp. 15/1-15/8 in *Proceedings of Western States Corrosion Seminar*, California State Polytechnical University, Pomona, CA, May 3-5, 1978.

17. *Earth Resistivity Manual*, Soiltest, Inc., Evanston, IL, 1979.

18. T. H. Larson, Illinois State Geological Survey, "A Surficial Electrical Resistivity Survey East of the Sheffield Low-Level Radioactive Waste Disposal Site, Bureau County, IL," ISGS Contract/Grant Report 1981-6, December 1981.

19. W. F. Gerhold, E. Escalante, and B. T. Sanderson, "The Corrosion Behavior of Selected Stainless Steels in Soil Environments," NBSIR 81-2228 (NBS), PB81-178154.

20. J. F. Bosich, *Corrosion Prevention for Practicing Engineers*, Barnes and Noble, Inc., New York, 1970.

21. G. L. Kalousek, L. C. Porter, and E. M. Harboe, "Past, Present, and Potential Developments of Sulfate-Resisting Concretes," *Journal of Testing and Evaluation* 4, 347 (1976).

22. T. M. Ahn and P. Sco, "Container Assessment - Corrosion Study of HLW Container Materials, Quarterly Progress Report July-September 1981," BNL-NUREG-51449, January 1982.

23. *Glossary of Geology*, R. L. Bates and J. A. Jackson, Editors, American Geological Institute, Falls Church, VA, 1980.

24. K. P. Fischer, "The Corrosion of Iron in Soils: The Effect of the Mineral and Chemical Constituents," p. 475-486 in *Scandinavian Corrosion Congress, 7th Proceedings*, Trondheim, Norway, May 26-28, 1978.

25. A. J. Weiss and P. Colombo, "Evaluation of Isotope Migration-Land Burial, Status Report Through September 30, 1979," NUREG/CR-1289, BNL-NUREG-51143, March 1980.

APPENDIX A

Geologic classification and lithologic description of cores from Sheffield low-level radioactive waste disposal site.(1)

Table A.1

Core 503

System	Series	Stage	Formation	Member	Depth (inches)	Thickness (inches)	Lithology
Quaternary	Pleistocene	Wisconsinan	Peoria Loess		36	36	A zone, clayey silt, dark-brown, leached, granular, abundant silans and organics; B zone, silty clay grading into clayey silt, yellowish-brown, leached, blocky, silans few, argillans abundant, some organics; (Modern Soil).
					124	88	Silt, brownish-yellow to olive-yellow, calcareous, weak blocky to weak platy, silans common upper part, few towards base, iron stains few.
			Roxana Silt		137	13	Clayey silt, brown, slightly calcareous, massive to weak platy, small white silt spots common.
					180	43	Silt, brown, leached, some secondary carbonates, weak platy, very friable, small white silt spots abundant.
					201	21	Clayey silt, brown, leached, some secondary carbonates, granular, friable.
					210	9	Sand-silt-clay, brown, leached, some secondary carbonates, blocky to granular.
		Illinoian	Glasford Formation	Radnor Till Member	244	34	Sand-silt-clay to clayey sand, pebbly, strong-brown to yellowish-red, leached, some secondary carbonates, massive to blocky, iron stains abundant, manganese stains few, argillans common to few; (Sangamon Soil).
					372	128	Sand-silt-clay to clayey silt, pebbly, brownish-yellow to light-olive-brown, leached upper 4 feet, calcareous towards base, massive, iron and manganese stains common, argillans common upper 4 feet, 1 inch silt layer.

Table A.1 (Continued)

Core 503–Continued

System	Series	Stage	Formation	Member	Depth (inches)	Thickness (inches)	Lithology
Quaternary	Pleistocene	Illinoian	Glasford Formation	Toulon Member	588	216	Sand (fn-cse), well-sorted, tan to light-brown, calcareous, majority of sand medium-grained, few pebbles.
				Hulick Till Member	594	6	Sand-silt-clay, pebbly, brownish-yellow, calcareous upper part, leached towards base, massive, iron stains few.
			?		600	6	Clayey silt, grayish-brown, leached, massive, iron stains few, abundant shale fragments, some coal; (Talus Breccia).

Table A.2

Core 504

System	Series	Stage	Formation	Member	Depth (inches)	Thickness (inches)	Lithology
Quaternary	Holocene		Fill		24	24	Clayey silt to silt, light-yellowish-brown to yellow, calcareous, weak blocky, mixture of till and silt.
	Pleistocene	Wisconsinan	Peoria Loess		76	52	Clayey silt, yellowish-brown, leached, A zone missing, B zones, blocky to massive, argillans common; (Modern Soil).
					128	52	Silt, light-yellowish-brown to olive-yellow, calcareous, massive to weak platy.
			Roxana Silt		158	30	Silt, light-yellowish-brown to yellowish-brown, calcareous, massive to platy, iron stains few.
		Illinoian	Teneriffe Silt		228	70	Silt to clayey silt, brown to dark-yellowish-brown, leached, some secondary carbonates, platy to weak blocky, argillans and manganese concretions few; (Sangamon Soil).
			Glasford Formation	Radnor Till Member	300	72	Clayey silt, pebbly, dark-yellowish-brown, leached, massive, argillans common, iron stains and concretions common; (Sangamon Soil).
					462	162	Clayey silt, pebbly, light-yellowish-brown, leached upper 30 inches, calcareous lower part, massive, iron stains common upper 5 feet, few sand lenses and pieces of coal.
				Toulon Member	552	90	Pebbly sand (fn-csc), well to moderately well-sorted, calcareous, few silty zones.
				Hulick Till Member	575	23	Sand-silt-clay, pebbly, yellowish-brown, calcareous, massive.
Pennsylvanian	Desmoinesian				587	12	Silty clay, dark-gray, slightly calcareous; (Weathered Shale).

APPENDIX B

EARTH RESISTIVITY DATA FOR SHEFFIELD

Table B.1

Earth Resistivity Data Measured in the East West Direction

SPACING (FEET)	VOLTAGE (MVOLTS)	CURRENT (MAMPS)	RESISTIVITY (OHM-CM)
5.0	341.00	100.00	3265.
10.0	180.00	100.00	3447.
15.0	140.00	100.00	4022.
20.0	120.00	100.00	4596.
25.0	100.00	100.00	4788.
30.0	91.00	100.00	5228.
35.0	85.00	100.00	5697.
40.0	77.00	100.00	5899.

Table B.2

Earth Resistivity Data Measured in the North South Direction

SPACING (FEET)	VOLTAGE (MVOLTS)	CURRENT (MAMPS)	RESISTIVITY (OHM-CM)
5.0	355.00	100.00	3399.
10.0	180.00	100.00	3447.
15.0	139.00	100.00	3993.
20.0	114.00	100.00	4366.
25.0	97.00	100.00	4644.
30.0	97.00	110.00	5066.
35.0	85.00	110.00	5180.
40.0	82.00	100.00	6282.

PDR

INTERIM REPORT

NRC Research and/or Technical Assistance Report

Accession No. -

Contract Program or Project Title: Study of Fuel Cycle Wastes

Subject of this Document: Analyses of Soils From an Area Adjacent to the Low-Level Radioactive Waste Disposal Site at Sheffield, Illinios

Type of Document: Informal Report

Author(s): P. L. Piciulo, C. E. Shea, and R. E. Barletta

Date of Document: July 1982

Responsible NRC Individual and NRC Office or Division:
Mr. Leroy Person
U. S. Nuclear Regulatory Commission
Mail Stop 905-SS
Washington, D.C. 20555

This document was prepared primarily for preliminary or internal use. It has not received full review and approval. Since there may be substantive changes, this document should not be considered final.

Brookhaven National Laboratory
Upton, New York 11973
Associated Universities, Inc.
for the
U.S. Department of Energy

Prepared for
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
Under Interagency Agreement DE-AC02-76CH00016
FIN A-3159