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ANALYSES OF SOILS AT COMMERCIAL RADIOACTIVE WASTE DISPOSAL SITES*

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ABSTRACT

Brookhaven National Laboratory, in order to provide technical assistance to the NRC, has measured a number of physical and chemical characteristics of soils from three commercial low-level radioactive waste disposal sites. Samples were collected from an area adjacent to the disposal site at Sheffield, IL, and from two operating sites: one at Barnwell, SC, and the other near Richland, WA. The soil samples, which were analyzed from each site, were believed to include soil which was representative of that in contact with buried waste forms.

Results of field measurements of earth resistivity and of soil pH will be presented. Additionally, the results of laboratory measurements of resistivity, moisture content, pH, exchange acidity and the soluble ion content of the soils will be discussed. The soluble ion content of the soils was determined by analysis of aqueous extracts of saturated soil pastes. The concentrations of the following ions were determined: Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, HCO_3^{-}, $CO_3^{=}$, $SO_4^{=}$, Cl^{-}, $S^{=}$.

INTRODUCTION

To provide information which will aid in assessing the effect of a burial environment on the performance of a waste form or a high integrity container, BNL has made field measurements at and collected and analyzed soil samples from two operating commerical low-level radioactive waste disposal sites: one operated by Chem-Nuclear Systems, Inc., is located at Barnwell, SC, the other operated by U.S. Ecology is on the Hanford reservation near Richland, WA. Samples were collected from an area adjacent to a third disposal site at Sheffield, IL. A full report of this work is given elsewhere.(1,2)

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Materials commonly used for the containment and the solidification of radioactive waste are subject to degradation by underground corrosion. To estimate the period of containment of radioactive waste buried in a steel drum or a metallic high integrity container, one must consider the soil chemistry of the trench material. The underground corrosion of metals has been extensively studied by the National Bureau of Standards(3) and is generally site specific. Metals typically corrode by an electrochemical process. For non-metallic containers and stablized waste, the agressiveness of various chemical constituents in the soil toward the materials must be considered in determining waste form or container stability. Cement, for example, cement, a common solidification medium is subject to degradation due to high concentration of sulfate in soils.(4)

SOIL SAMPLE COLLECTION

Data necessary to estimate the corrosivity of soils from several shallow land burial sites have been collected and are presented here. In this regard, it was intended that the samples collected and analyzed be representative of the soil material that will contact the buried waste forms.

Soils at the Barnwell site consist of sandy clay beneath a layer of silty sand. On excavating a trench, the silty sand is first stripped from the area and piled for later use as backfill material. The rest of the soil taken from a trench is sandy clay, making up the trench wall. The characterisitics of the silty sand, which is used as trench backfill material, were determined.

The soils at the Hanford site consist of sands, silts, and gravels. Sampling was done in Trench 8, which was open at that time. There appeared to be four different soil types along the trench wall. The soil removed during trench construction is piled adjacent to the trench and later used as backfill. The pile of backfill material was sampled in a number of locations. As for Barnwell, it is the results of the analyses of this soil which will be presented.

The Sheffield site is composed of unconsolidated Wisconsinian and Illinoian glacial sediments atop Pennsylvanian bedrock. The glacial history and the continuity of the sedimentary deposites at the site were interpreted by the US Geological Survey.(5) The sampling location was outside the site boundary about 100 feet from USGS boring 504 which is at the east end of Trench 2. Thirteen Shelby tube samples (3 in. diam. and 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 containing the Radnor Till member and the Toulon member. Sampling proceeded from the 397-in. depth using a split barrel sampler. Three samples were collected in the sand lens. Two samples were collected in the Hulick Till member and one sample of weathered shale extending into the Pennsylvanian system was collected. The final sample depth was 605 in.

METHODS

Earth resistivity measurements were made according to the Wenner four electrode method described in ANSI/ASTM G57-78. The procedure requires four metal electrodes be placed in the earth 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:

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

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.

Soil resistivity was measured in the laboratory according to ANSI/ASTM G57-78 using a Miller soil box (M. C. Miller Company) connected to the resistivity meter used for the field measurements. A water-saturated soil paste was packed into the Miller soil box; the current and the voltage were recorded. Soil resistivities in units of ohm-cm were calculated using the following equation:

$$R = \frac{E}{i} \cdot \frac{A}{L}$$

where E equals the voltage drop across the potential pins of the soil box, and i equals 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 resistivities are corrected to 15.5°C using the following equation:

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

where R_t is the observed resistivity at temperature t in degrees Celsius.

Several methods were employed to assess the soil acidity. First, the pH of the soil was measured near a sampling location as prescribed by the standard test method, ANSI/ASTM G51-77. Second, a procedure described by Peech(6) was used for determining the hydrogen ion activity of the soils. The method requires mixing 10 g of air-dry soil and 20 mL of 0.01 M $CaCl_2$.

Approximately 18 hours was allowed for equilibration before the pH of the liquid phase was measured. Finally, the pH of the aqueous extract used for the analysis of soluble chemical constituents in the soils was measured.

The exchange acidity of a soil sample was estimated using a previously described modified titration method.(7) This method has an accuracy of approximately 1 meq/100 g soil, however, this approximation is sufficient since variations due to soil sampling are greater than this amount.

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 air-dry soil and water.

Each saturated paste was vacuum filtered through Whatman 541 filter paper after equilibrating for 2 hours. The extract was then filtered through Fisher 9-790-4A filter paper for further clarification. Bower and Wilcox(6) specify the addition of several drops of 0.1% sodium hexametaphosphate to an aliquot of each sample immediately after filtering 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 were acidified with 0.5 N HNO_3. This extract was used for the atomic absorption analysis of cations. Acidification served to keep trace concentrations of metal ions in solution.

Bicarbonate was determined by a potentiometric titation of the soil extract with 0.01 N H_2SO_4 as specified by Bower and Wilcox(6) to a pH = 4.5 endpoint.

The extracts were analysed 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.

The chloride ion and the sulfate ion contents of the soil extract were determined by the Analytical Chemistry Services Group at Brookhaven National Laboratory. Chloride was analyzed colorimetrically using a Technicon Autoanalyzer and sulfate was analyzed using a Dionex Ion Chromatograph.

The quantity of sulfide present in the soil was estimated by extracting sulfide ions into an anti-oxidant buffer. The sulfide concentration was determined by standard additions using a solid state sulfide ion selective electrode.

RESULTS AND DISCUSSION

Figure 1 is a plot of the apparent earth resistivity over an area of the shallow land burial site of Barnwell, SC. The data were measured in an area west of Trench 37, which was being built up with the sandy clay removed from previously excavated trenches. The silty sand layer present over the site was first stripped away. A trench will be constructed in this area after allowing the earth to settle for a number of years. These results indicate no dramatic changes in resisitivity with depth in the area studied.

The apparent resistivities, ranging from 1.5 to 1.0 x 10^5 ohm-cm, decrease as the electrode separation increases. This indicates the presence of a material at depth having a lower resistivity than surface soil. This may be due to an increase in moisture content with increasing depth. Resistivity decreases with increasing water content.(2) However, variations in resistivity may also be the result of soil buildup operations in the area of the measurements.

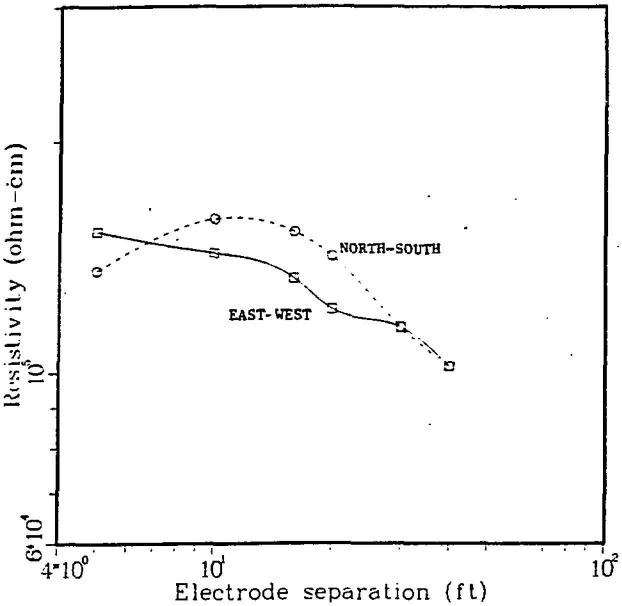

Figure 1. Earth resistivity measured on shallow land burial site at Barnwell, SC.

Earth resistivity data from Hanford shown in Figure 2 were measured over an undistributed area between Trench 6 and Trench 8. The electrode separation in the north-south direction was limited to 60 ft because of the locations of the trenches.

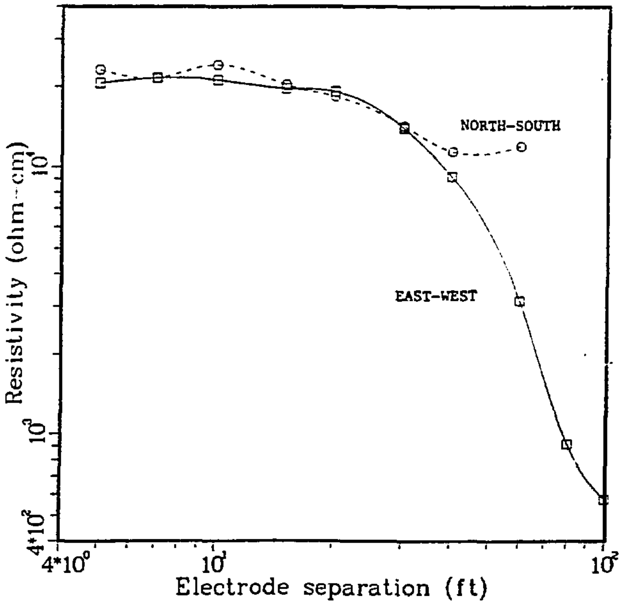

Figure 2. Earth resistivity measured on an undisturbed area of the shallow land burial site at Hanford, WA.

The apparent earth resistivities of Hanford soils decrease with increasing electrode separation. Moisture content of the soil cannot explain this since it was found to decrease with depth(1) and a decrease in moisture would result in an increase in resistivity. Conditions such as compactness and ion content are likely to account for the observed resistivities.

Figure 3 shows the resistivity recorded over a capped trench (Trench 6) at Hanford. This data is dramatically different from that measured in the undisturbed area. The resistivities measured to an electrode separation of approximately 20 ft, are only slightly lower over Trench 6 than the corresponding resistivities measured in the undisturbed area. It is likely that measurements made to an electrode separation of about 20 ft reflect chiefly the resistivity of the trench cap, whereas, measurements beyond the 20-ft electrode separation are influenced by the trench contents.

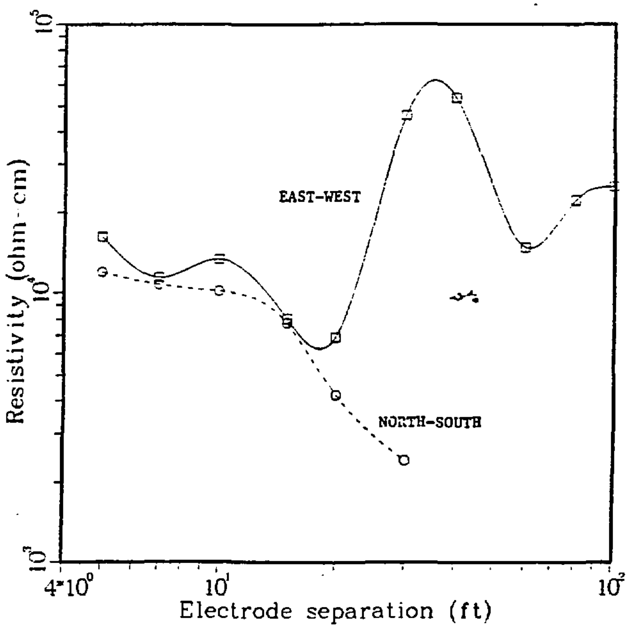

Figure 3. Earth resistivity measured over Trench 6 at the shallow land burial site at Hanford, WA.

Earth resistivity data measured at Sheffield are shown in Figure 4. The apparent resistivity increases with increasing electrode separation indicating the presence of higher resistivity material at depth. The differences between the two curves are not believed significant. The increasing resistivity is attributed to the influence of sand in the Toulon member which has a soil resistivity that is a factor of ten larger than that measured in other soils (see below).

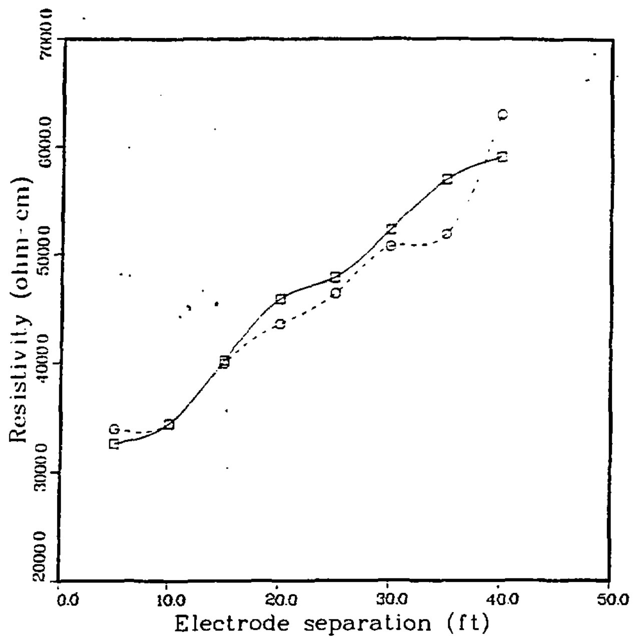

Figure 4. Earth resistivity measured on an area adjacent to shallow land burial site at Sheffield, IL.

Soil resistivities measured on saturated soils are most often used to estimate soil corrosivity.(2) The average values measured on water-saturated samples of backfill material from Barnwell and Hanford are given in Table 1. In both cases, the resistivity data indicate soils which are very mildly corrosive to steel. This conclusion is based on a resistivity classification with reference to the corrosion of steel pipes.(7) The laboratory measurements of saturated soil resistivity are comparable to the earth resistivity at small (5-ft) electrode spacings. The large resistivities of these soils are indicative of a small soluble ion content, and therefore, the resulting decrease in resistivity with increasing water content is small.

Soil resistivities of water-saturated samples from Sheffield average 4.7×10^3 ohm-cm excluding the resistivity of sand from the Toulon member which measured 1.3×10^4 ohm-cm. Based on the resistivities measured on the saturated soils, the corrosivity of the soils ranges from moderately corrosive to steel to very mildly corrosive to steel.(7) This variation in corrosivity together with large variations in trench depth at Sheffield (i.e., trenches enter into differing soil types) is likely to result in burial envrionments which differ from trench to trench. For example, a trench constructed in Peoria Loess and Roxanna Silt, with this material used as backfill, may be 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 may influence the corrosivity of the burial environment.

Table 1. AVERAGE VALUES OF SOME SOIL PROPERTIES

	Resistivity (ohm-cm)	pH[a] Soil	Extract	in $CaCl_2$	Total Acidity[b]
Barnwell	1.2×10^5	5.0(0.2)	4.9(0.9)	4.0(0.1)	<2
Hanford	1.8×10^4	5.5(0.6)	7.4(0.1)	7.5(0.1)	<2
Sheffield	4.7×10^3[c]	7.2(0.4)	7.7(0.6)	7.4(0.2)	<7

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[a] Numbers in parenthesis are standard deviations.
[b] Units = meq per 100 g of soil.
[c] Average of resisitivities of soils sampled excluding sand from Toulon member which had a resistivity of 1.3×10^4 ohm-cm.

Actual field measurements of pH in Barnwell and Sheffield soils are not available. The pH value listed in Table 1 are the averages of those measured in the soil immediately after opening the sample bags in the laboratory. The measured pHs indicate that Barnwell soils are acidic and that Sheffield soils are neutral.

Field measurements of the pH of Hanford soils are unreliable since low moisture content and high resistivity make the measurement of soil pH difficult. The acidic pH listed in Table 1 for the Hanford backfill soil was not believed to be a realistic measure of the soil acidity since soils from that region of the U.S. are generally alkaline.

Although soil pH is generally used to assess soil corrosion, the uncertainties encountered in the direct measurement of soil pH led to the use of alternate methods to characterize the soil acidity. Measurements of pH in the $CaCl_2$ solution soil mixtures and in the aqueous extracts of the soils are summarized in Table 1 with standard deviations given in parentheses. The pH of the aqueous extract of the Barnwell soil is comparable to that observed in the soil, whereas, the pH in the $CaCl_2$ solution is somewhat lower. In any event, the backfill material at the Barnwell site is an acidic medium. Hanford data show a different behavior. Measurements of pH in the aqueous extract are the same as found in the $CaCl_2$ solution and 2 pH units higher than that measured in the soil. These measurements suggest that the Hanford backfill soil is neutral. Measurements of pH of the Sheffield soils extracts and of the soils in $CaCl_2$ solution indicate neutral soils as found by direct pH measurements.

The exchange acidities of soils from the three sites are also listed in Table 1. In backfill soils from Barnwell and Hanford, the exchange acidity is small or an alkaline reaction was observed when the measurement was attempted. When testing the soils from Sheffield, all but two samples of Peoria Loess had very small exchange acidities. The two samples of Peoria Loess had acidities measuring 5 and 7 meq/100 g of dry soil. Exchange acidity is reported(3,7,8) to correlate with the corrosion of steel pipelines in soil. The values observed here are consistent with those measured for the least-corrosive soils.

The average concentrations of some soluble ions in backfill soils from Barnwell and Hanford are listed in Table 2. Also listed are the ranges of concentrations of the various ions measured in the Sheffield soils. The range of values are given since several soil types were tested and different combinations of soils could have been used as backfill material to a trench. It is immediately evident that the ion content of Sheffield soils is larger than that of either Barnwell or Hanford soils. This is consistent with the large differences in soil resistivities measured for the sites. Although corrosion is influenced by the soluble salt content of the soil, no generic correlation is available for comparing soil corrosivity with chemical composition. However, some chemical components in soils are specifically aggressive toward certain materials. Cement, a common solidification medium is subject to degradation due to high concentrations of sulfate in soils. Similarly, chloride ions in soil can cause pitting failures in stainless steel,(9,10) which is a candidate material for high-integrity containers. The sulfate content of the soils from the three sites is expected to result in a negligible degree of attack on cement.(4) The concentrations of chloride ion found in these soils are considerably smaller than in soils studied by Gerhold et al.(9) which showed only superficial corrosion of AISI 300 series stainless steels.

Table 2. AVERAGE CONCENTRATION OF SOLUBLE IONS (x 10^3)[a]

	Ca^{++}	Mg^{++}	K^+	Na^+	HCO_3^-	$SO_4^=$	$S^=$	Cl^-
Barnwell	3	b	3	6	2	5	0.3	1
Hanford	40	7	4	70	40	6	0.3	2
Sheffield	28-260	20-140	1-7	5-23	5-90	8-280	~1	<1-14

[a] Units = meq per 100 g of soil. Ion concentrations were measured in extract from saturated soil paste.

[b] Not detected.

CONCLUSIONS

Data presented here can serve as a basis to evaluate the corrosivity of a burial environment toward waste forms and waste containers. Based on the soil resistivities, the Barnwell and Hanford soils are expected to be mildly corrosive to steel. The acidity of the soils from the two sites also indicate soils which are mildly aggressive to steel. Comparable data for the Sheffield soils suggest that they are relatively more corrosive to steel than soils from either of the other sites.

It is noteworthy, however, that the corrosivity of a burial environment toward a waste form or high integrity container can depend not only on the soil chemistry, but also on the contents of the trench. For example, field measurements of the pH of water samples from trenches at Maxey Flats, Kentucky, are reported to range from 2.2 to 12 4.(11) Additionally, 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.(11) 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 an influence of the trench contents on the chemistry of the trench environment. Changes in trench chemistry may also be inferred from resistivity measurements made over a capped trench, such as that from the trench at Hanford. Therefore, to estimate the period to failure of a waste container or a waste form as a result of underground corrosion, time-dependent changes in the trench environment should be considered in addition to the soil chemistry.

ACKNOWLEDGEMENTS

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