NUREG/CR-5464
RW, CY, CO, CJ, CC

NUREG/CR--5464
TI92 002690

Anion Retention in Soil: Possible Application to Reduce Migration of Buried Technetium and Iodine

A Review

Manuscript Completed: September 1991
Date Published: October 1991

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Prepared for
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NRC FIN 8958

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ABSTRACT

Anion exchange characteristics of soils are of interest in view of an increased concern about anion (such radionuclides as I^-, IO_3^-, and TcO_4^-) in soil leading to contamination of ground water. By simple electrostatic interaction, soils with high anion exchange capacity (AEC) greatly reduce the migration of anions through soil. The amorphous clays allophane and imogolite, derived from volcanic parent material, are found to be among the most important soil components capable of developing appreciable amounts of positive charge for anion exchange even at about neutral pH. The magnitude of the surface charge of these amphoteric materials depends on the ratio of SiO_2/Al_2O_3, soil pH and concentration of electrolyte. Decreases in the SiO_2/Al_2O_3 ratio and soil pH result in an increase in soil AEC. Allophane and imogolite rich soils have an AEC ranging from 1 to 18 meq/100g at pH about 6. The presence of other types of silicate minerals, organic and inorganic ligands tends to lower AEC of the soils. Highly weathered soils dominated by Fe and Al oxides and kaolinite may develop a significant amount of AEC as soil pH falls. On a wide range of those soils, AEC ranges from 0 to 2 meq/100g at about pH 6.

The retention of radionuclides, iodine (I) and technetium (Tc), by soils is associated with both soil organic matter, and Fe and Al oxides, whereas sorption on layer silicate minerals is negligible. Anaerobic conditions greatly increase Tc retention by soils, which is related to the lower solubility of Tc (IV) and its complexation with organic matter fractions. Fe and Al oxides become more important in the retention of anionic iodide (I^-), iodate (IO_3^-) and pertechnetate (TcO_4^-) as pH falls, since more positive charge is developed on the oxide surfaces. Soil allophane and imogolite develop more positive charge than Fe and Al oxides at given pH conditions, and are thus expected to retain more I and Tc although few studies have been conducted on the sorption of I and Tc by soil allophane and imogolite. It is calculated that a surface plough soil (2 million pounds soil per acre) with 5 meq/100g AEC, as is commonly found in andisols, shall retain approximately 5900 kg I and 4500 kg Tc, respectively, by the anion exchange mechanism.

Further studies on the potential use of andisol as a barrier to retard the migration of I and Tc through the soil are recommended. It is conceivable that an anion exchanger such as an andisol could be used to modify the near field environment of a radioactive waste disposal facility. The anion exchange material would retard migration of anions away from the disposal site and thus prevent contamination of ground water. This whole disposal system would then offer similar migration resistance to anions as is normally afforded to cations by usual and normal soils.

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FOREWORD

On May 23, 1991, the U. S. Nuclear Regulatory Commission (NRC) held a meeting at Rockville, MD. The meeting was an informal one-day brainstorming session on the identification of new or innovative means for inhibiting radionuclide releases migration from Low Level Radioactive Waste (LLW) disposal facilities.

Participants included NRC staff and research investigators from Brookhaven National Laboratory, Idaho National Engineering Laboratory, National Institute of Standards and Technology, Pacific Northwest Laboratory, Sandia National Laboratory, and University of California, Berkeley, who have dealt with various elements of radioactive waste disposal and performance assessment.

The question before the group was "how could LLW disposal be done better?" The meeting was opened by Mel Silberberg, Chief, Waste Management Branch, Research, USNRC. Various new and innovative ideas were put forth at the meeting. Dr. Robert K. Schulz of the University of California discussed possible use of a natural anion exchanger, andisol, for trench liners to retard migration of anionic radioisotopes such as iodine and technetium. As a result of the meeting the NRC invited the University of California to review the subject of anion exchange in soils, with special attention to andisols. This report is that review.

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ACKNOWLEDGEMENTS

Funding for this project was provided by the Waste Management Branch, Division of Regulatory Applications, Office of Nuclear Regulatory Research. Dr. Edward O'Donnell is the Project Manager, Mr. Mel Silberberg is Chief of the Waste Management Branch, and Dr. Bill M. Morris is Director of the Division of Regulatory Applications.

INTRODUCTION

Anion exchange reactions are common, particularly in soils with variable charges. It is of interest in view of an increased concern about anion (such as radionuclides TcO_4^-, I^- and IO_3^-) contamination in soils and ground waters. The use of soil minerals for waste anion removal from phosphogypsum leachate has been tested by Murray et al. (1985). However, the effectiveness of minerals to remove anions depends on a number of parameters: the charge characteristics of the minerals, the chemical properties of the anions and their reaction mechanisms with the minerals. Two types of reactions between anions and soil minerals are recognized: specific adsorption and non-specific adsorption. Specific adsorption refers to incorporation of the anions as a ligand in the coordination shell of an adsorbent while non-specific adsorption refers to adsorption of anions by simple coulombic interaction with positive charges. This report summarizes our present knowledge of the surface charge characteristics and anion exchange properties of a number of soils and minerals, and factors influencing their charge characteristics. Emphasis is given to the non-specific anion exchange of soils, and particular attention is given to the retention of two radionuclides, I and Tc, in soils.

ANION EXCHANGE ON ALLOPHANIC SOILS

Allophane and Imogolite in Soil

Soils containing allophane and imogolite develop from most volcanic parent materials, especially those rich in mafic materials, and from sedimentary and metamorphic rocks whose component particles derived from volcanic rock. These soils rarely, if ever, form from granitic parent, materials or from those largely lacking in Al and Fe (e.g. quartzites, limestones). Thus, the established geographic distribution of allophane, imogolite and allophanic constituents has been connected with the areas of recent volcanic activity throughout the Pacific ring of volcanism, West Indies, Africa, Italy, Australia, Hawaii, and the Pacific west of the United States (Wada, 1977; Simonson and Rieger, 1967; Lai and Swindale, 1969; Baham and Simonson, 1985; Hunter and Busacca, 1987; Southard and Southard, 1989).

Allophane is a non-crystalline aluminosilicate mineral with a very short range crystal structure relative to that of layer silicates and Al and Fe hydroxides. It consists of discrete hollow spherules, or polyhedra, 3.5 - 5.0 nm in diameter with SiO_2/Al_2O_3 ratios between 1 and 2 (Wada, 1980). Imogolite has a one dimensional tubular structure, about 2 to 5 nm in diameter and several µm in length, caused by curling of a gibbsite sheet on replacement of an hydroxyl layer by orthosilicate anions. The overall composition can be represented by the idealized formula $SiO_2Al_2O_3\ 2.5H_2O$ (Wada, 1977). A summary of elemental analysis of less than 0.2 µm fractions separated from weathered volcanic ash and pumices (Wada and Yoshinaga, 1969) showed that the SiO_2/Al_2O_3 ratio of the clays in which allophane predominated was in a range from 1.3 to 2.0, while that of clays in which imogolite predominated was in a narrow range from 1.05 to 1.15.

Anion Exchange Characteristics

In contrast to soils with a clay mineralogy dominated by crystalline layer silicates, which have very little positive charge or very low anion exchange capacity (AEC), soils containing the amorphous clay allophane and imogolite have a noticeable amount of AEC, especially in acidic pH ranges. However, the sign and magnitude of surface charge of these amphoteric materials are dependent on a number of factors: the silica content of the hydrous aluminosilicate phase, pH, and concentration of electrolyte (Gonzales-Batista et al., 1982; Clark and McBride, 1984). Because the sign and magnitude of the surface charge of the these soils are so dependent on solution parameters, it is meaningless to quote the surface charge characteristics of such constant potential colloids unless the precise experimental conditions and techniques for their determination are also given.

Effect of SiO_2/Al_2O_3 Ratio

The influences of SiO_2/Al_2O_3 ratio on the surface charge characteristics of six allophanic soil clays originating from climatosequence of andisols were studied by Gonzales-Batista et al. (1982). They observed that a decrease in the silica content is related to an increase in pH_0 and point of zero net charge (PZNC) (Fig. 1), where pH_0 is the pH for which the net charge resulting from the adsorption of H^+ and OH^- ions is zero; and PZNC is the pH for which the net surface charge is zero, or at the PZNC, the cation exchange capacity (CEC) is equal to the anion exchange capacity (AEC). Such a relationship is also summarized in Table 1 for both synthetic and natural allophanic clays (Perrott, 1977; Gonzales-Batista et al., 1982; Theng, et al., 1982; Clark and McBride, 1984). The changes of PZNC and AEC at pH 6 were plotted in Fig. 2a and Fig. 2b, respectively. Despite the polyminerlalic nature and different origins of these samples, their zero charge parameter (PZNC, Fig. 2a) shows a similarity to that of pure synthetic gels, i.e. an increase in the silica content is related to a decrease in PZNC. However, as can be noticed from Fig. 2a and 2b, at a given SiO_2/Al_2O_3 ratio, the PZNC and AEC values of natural soil clays are mostly lower than the synthetic allophane and imogolite. This can be understood because of the presence of other types of minerals, and the presence of organic and inorganic ligands, such humic acid and phosphate, which can be specifically adsorbed on the surface. Figs. 2a and 2b also indicate that, in general, these soils have SiO_2/Al_2O_3 ratios between 1 and 2, PZNC between 4 and 7, and AEC between 1 and 18 meq/100g.

Three clays richest in silica (Chio, Aguamansa-I, and Synthetic allophane-8, Table 1) are not only characterized by the lowest PZNC but also by a permanent negative charge, since the cation exchange capacities (CEC) of the three clays are 28, 26, and 32 meq/100g, respectively (not shown in Table 1). Similarly, Wielemaker (1984) found that an increase in the ratio of SiO_2 to Al_2O_3 or SiO_2 to Fe_2O_3 depressed the pH_0 to levels as low as that of amorphous Si. Henmi and Wada (1976) also noticed that the silica rich allophanes show a tendency to have more tetrahedral Al than allophanes rich in aluminum.

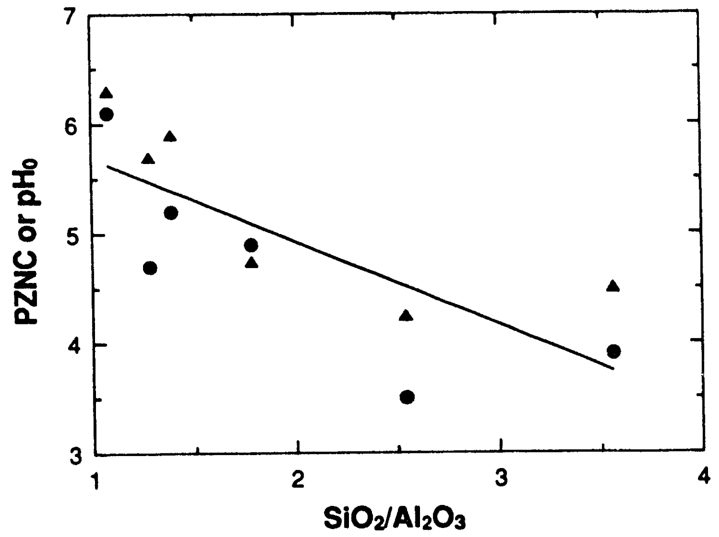

Fig. 1. Relationships between SiO_2/Al_2O_3 ratios and PZNC (○) or pH$_0$ (△) for several selected andisols (after Gonzales-Batista et al., 1982).

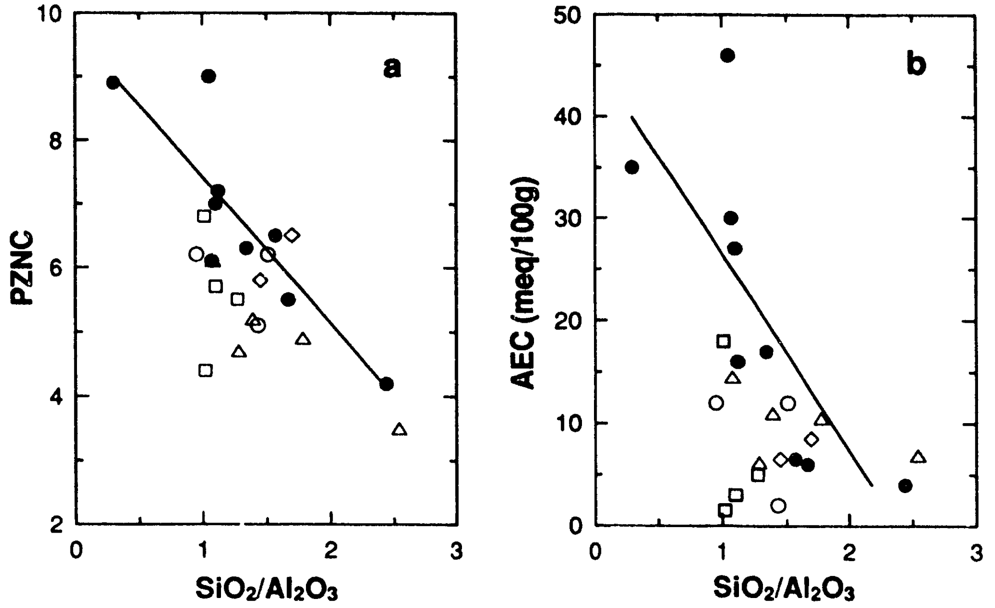

Fig. 2. Relationships of SiO_2/Al_2O_3 ratios with (a) PZNC and (b) AEC at pH 6 for soils containing mainly allophane and imogolite (open symbols) and for synthetic allophane and imogolite (solid circle and the regression line). Different open symbols, ○, □, △ and ◇ represent data obtained from Clark and McBride, 1984, Theng, et al., 1982, Gonzales-Batista et al., 1982, and Perrott, 1977, respectively.

Table 1. Relationships of SiO_4/Al_2O_3 molar ratio with PZNC and AEC (meq/100g) at pH 6 for soils containing mainly allophane and imogolite, and for synthetic allophane and imogolite.

Sample	SiO_4/Al_2O_3	PZNC	AEC pH 6	Origin	Reference
		Soils Containing Allophane and Imogolite			
Egmont soil	0.95	6.2	12	New Zealand	Clark and McBride, 1984
Imogolite	1.01	6.8	18	Japan	Theng et al., 1982
Andesitic Tephra	1.02	4.4	1.5	New Zealand	Theng et al., 1982
Las Aves	1.08	6.1	14.5	Spain	Gonzales-Batista et al., 1982
Silica Springs	1.10	5.7	3	New Zealand	Theng et al., 1982
Rhyolitic Tephra	1.27	5.5	5	New Zealand	Theng et al., 1982
Akaka	1.28	4.7	6.2	Hawaii, USA	Gonzales-Batista et al., 1982
Dos Cupressos	1.39	5.2	11	Spain	Gonzales-Batista et al., 1982
KnP soil	1.43	5.1	2	New Zealand	Clark and McBride, 1984
Te Akatea	1.45	5.8	6.5	New Zealand	Perrott, 1977
Te Akatea	1.51	6.2	12	New Zealand	Clark and McBride, 1984
Waihi	1.70	6.5	8.5	New Zealand	Perrott, 1977
Aguamansa-II	1.78	4.9	10.5	Spain	Gonzales-Batista et al., 1982
Aguamansa-I	2.54	3.5	6.9	Spain	Gonzales-Batista et al., 1982
Chio	3.56	3.9	3	Spain	Gonzales-Batista et al., 1982
		Synthetic Allophane and Imogolite			
Allophane-4	0.30	8.9	35		Perrott, 1977
Imogolite	1.05	9.0	46		Clark and McBride, 1984
Imogolite	1.07	6.1	30		Clark and McBride, 1984
Allophane-1	1.10	7.0	27		Clark and McBride, 1984
Allophane-5	1.12	7.2	16		Perrott, 1977
Allophane-2	1.34	6.3	17		Clark and McBride, 1984
Allophane-6	1.57	6.5	6.5		Perrott, 1977
Allophane-3	1.67	5.5	6		Clark and McBride, 1984
Allophane-7	2.44	4.2	4		Perrott, 1977
Allophane-8	4.90	--	-1.5		Perrott, 1977

Although Table 1 and Fig. 2 show that positive charge (PZNC and AEC) increased generally with increasing alumina content at a given pH, the synthetic imogolite($SiO_2/Al_2O_3 \approx 1$) showed anomalously high values of PZNC and AEC than the allophanes. This result may illustrate the inherent differences in charge and surface properties of allophane and imogolite despite the common structural unit which the two minerals incorporate. Theng et al. (1982) observed that substantial positive charge of an imogolite soil clay remained at neutral-alkaline pH range, while allophane has essentially zero positive charge in this pH range. Imogolite was found to have an AEC about 40 meq/100g at pH 4 and about 20 meq/100g at pH 6, whereas three allophane rich soil samples have AECs varied from 10 to 25 meq/100g at pH 4, and from 0 to 5 meq/100g at pH 6. They suggested that high positive charge of imogolite clays at about neutral-alkaline pH may be related to the possible development of permanent positive charge.

Mineralogical and chemical analyses of Ando soils have indicated that their major ion-exchange materials also differ from horizon to horizon (Wada, 1977). Humus complexed with Al and Fe dominated in A1 horizon soils, whereas allophane, imogolite and allophane-like constituents occur in B horizon soils. Wada and Okamura (1980) studied the charge characteristics of four Ando A1 soils, and found that no positive charge appeared in these soils at pH values 5 to 8.54 except for one containing allophane and imogolite. However, Espinoza et al. (1975) found that two Andepts (surface soils, 0-20 cm) maintained about 1 meq/100g AEC between pH 5 and 6. Inignez and Val (1982) reported that PZC of an andisol increased with depth (0-100 cm) and ranged from 4.07 to 5.55.

Effect of pH and ionic strength

The influences of pH and salt concentration on charge characteristics of allophanic soils can be shown in a number of studies (Espinoza et al., 1975; Gonzales-Batista et al., 1982; Theng et al., 1982; Okamura and Wada, 1983; Clark and McBride, 1984; Pardo and Guadalix, 1988). Espinoza et al. (1975) reported that the retention of NO_3^- was influenced by both pH and ionic strength. The lower the pH, and the higher the ionic strength, the higher amounts of NO_3^- was retained. Perrott (1977) studied a range of synthetic amorphous aluminosilicates, hydrous alumina, hydrous silica and two soil clays on their retention of Na^+ and Cl^-. In the pH range investigated (3-9), only negative charges could be detected in the hydrous silica and the most siliceous aluminosilicate ($SiO_2/Al_2O_3 = 4.9$). On the other hand, only positive charges were detected in the hydrous alumina, whereas both positive and negative charges were detected in the more aluminous aluminosilicates and the soil allophanes. Two different mechanisms were suggested: for hydrous silica, the pH dependent negative charge arises from ionization of the weakly acidic surface silanol groups ($Si\text{-}OH = Si\text{-}O^- + H^+$), whereas for the hydrous alumina this charge arises from the protonation of the hydrous oxide surface on the acid side of the PZC ($Al\text{-}OH + H^+ = Al\text{-}OH_2^+$). No negative charge would be expected when the pH of the suspension is less than the zero point of charge, which is about 9.

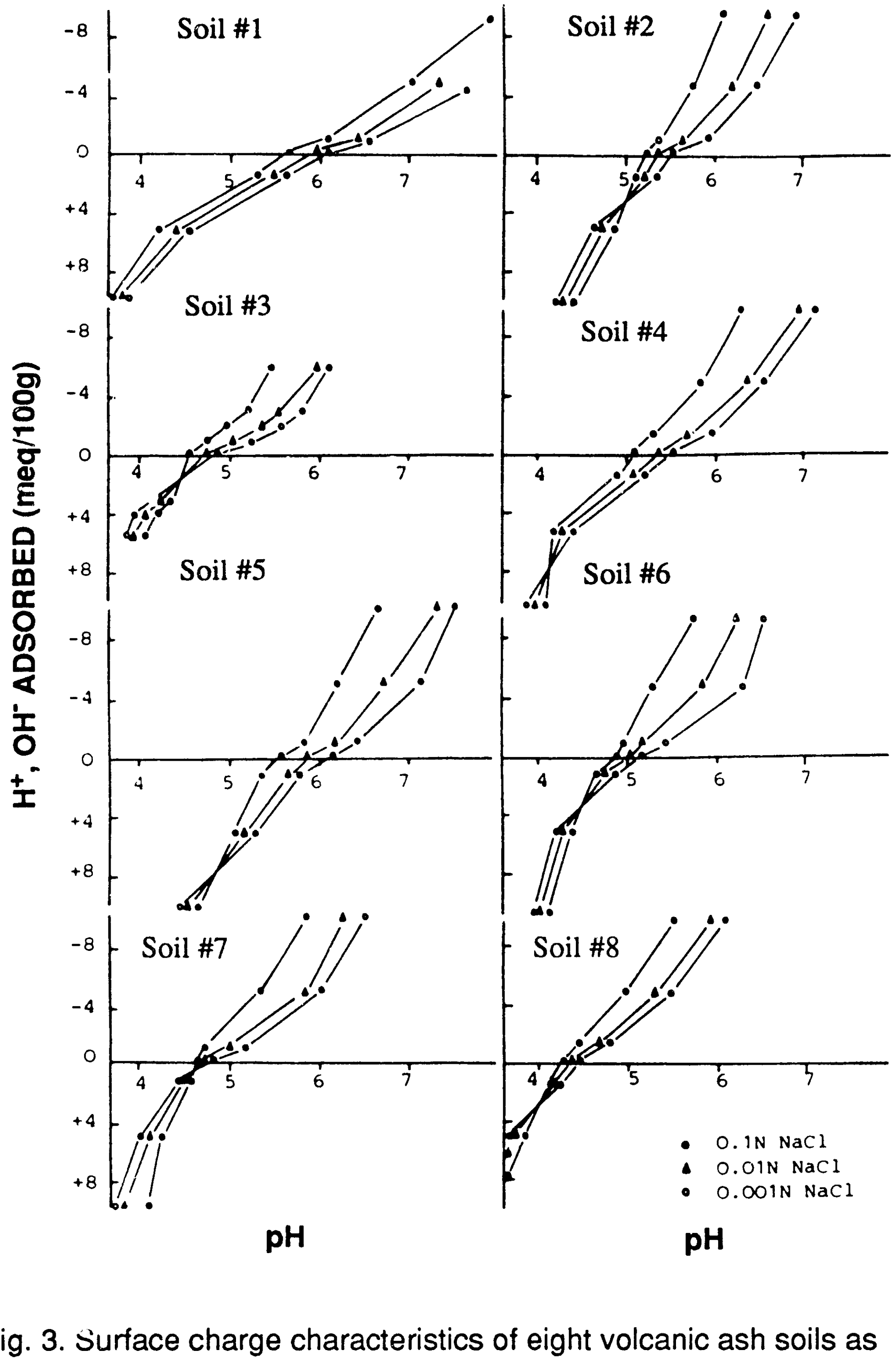

Fig. 3. Surface charge characteristics of eight volcanic ash soils as influenced by pH and NaCl concentration (after Pardo and Guadalix, 1988).

Pardo and Guadalix (1988) investigated the surface charge characteristics of eight volcanic-ash-soils from Spain and found that the magnitude and sign of the charge were influenced by the pH as well as the concentration of NaCl (Fig. 3). On the alkaline as well as on the acid side of the PZC, an increase of the concentration of the electrolyte caused an increase of OH^- and H^+ adsorption, or, which was the same, a negative or positive net charge increased. In all the soils, the variation of the charge as a function of the pH was more or less similar, with the exception of soil #1 which showed the lower effect of pH on the net surface charge, because this soil contained dominantly well-crystallized minerals, such as illite. Similarly, Theng et al. (1982) observed that the charge characteristics of a soil containing halloysites showed little variation with pH.

Okamura and Wada (1983) reported the changes of AEC and CEC with pH and NH_4Cl concentration of five Dystrandept B horizon soils, two weathered pumices and two Red-Yellow soils containing components with variable charge (Fig. 4). Similarly, they found that an increase of the concentration of NH_4Cl caused an increase of AEC and CEC, while a decrease of pH caused an increase of AEC but a decrease of CEC. No measurable amount of AEC was found for weathered pumice M-7-7 and soil W-116 between pH 5 and 8 because these two soils contain large quantities of halloysite and montmorillonite. Two empirical equations were developed that relate the AEC and CEC with the pH (4 to 8) and NH_4Cl concentration (0.005 to 0.1M) of the solution, and can be represented by the following regression equations:

$$\log \mathrm{AEC} = a\,\mathrm{pH} + b \log \mathrm{C} + c \qquad \text{and}$$

$$\log \mathrm{CEC} = a'\,\mathrm{pH} + b' \log \mathrm{C} + c'$$

where *a, b,* and *c,* and *a'*, *b'* and *c'* are constants for each soil sample, which correlate with the kind of ion-exchange materials present. The curves (solid lines in Fig. 4) represent the AEC values calculated using these two equations. It appears, therefore, that these two equations are generally good to describe adsorption equilibria in which Cl^- and OH^-, and NH_4^+ and H^+ compete for anion and cation exchange sites, respectively. They may be potentially useful to characterize and predict the retention of anion and cation by the soil.

Effect of Drying and Temperature

The drying of soils derived from volcanic ash and some highly weathered soils can cause irreversible changes in their chemical and physical properties (Schalscha et al., 1965; Phillips et al., 1986). One effect of drying such soils is the changes of their AEC and CEC. Unfortunately, the data concerning such an effect in soil are both fragmentary and conflicting. Balasubramanian and Kanehiro (1978) reported a decrease in CEC of soils upon drying, and attributed this effect to an increased aggregation of the hydrated amorphous Fe and Al oxides, with a concomitant loss of reactive surface area. However, an increase in the CEC values of soils containing allophane and/or imogolite upon drying or heating was observed by Harada and Wada

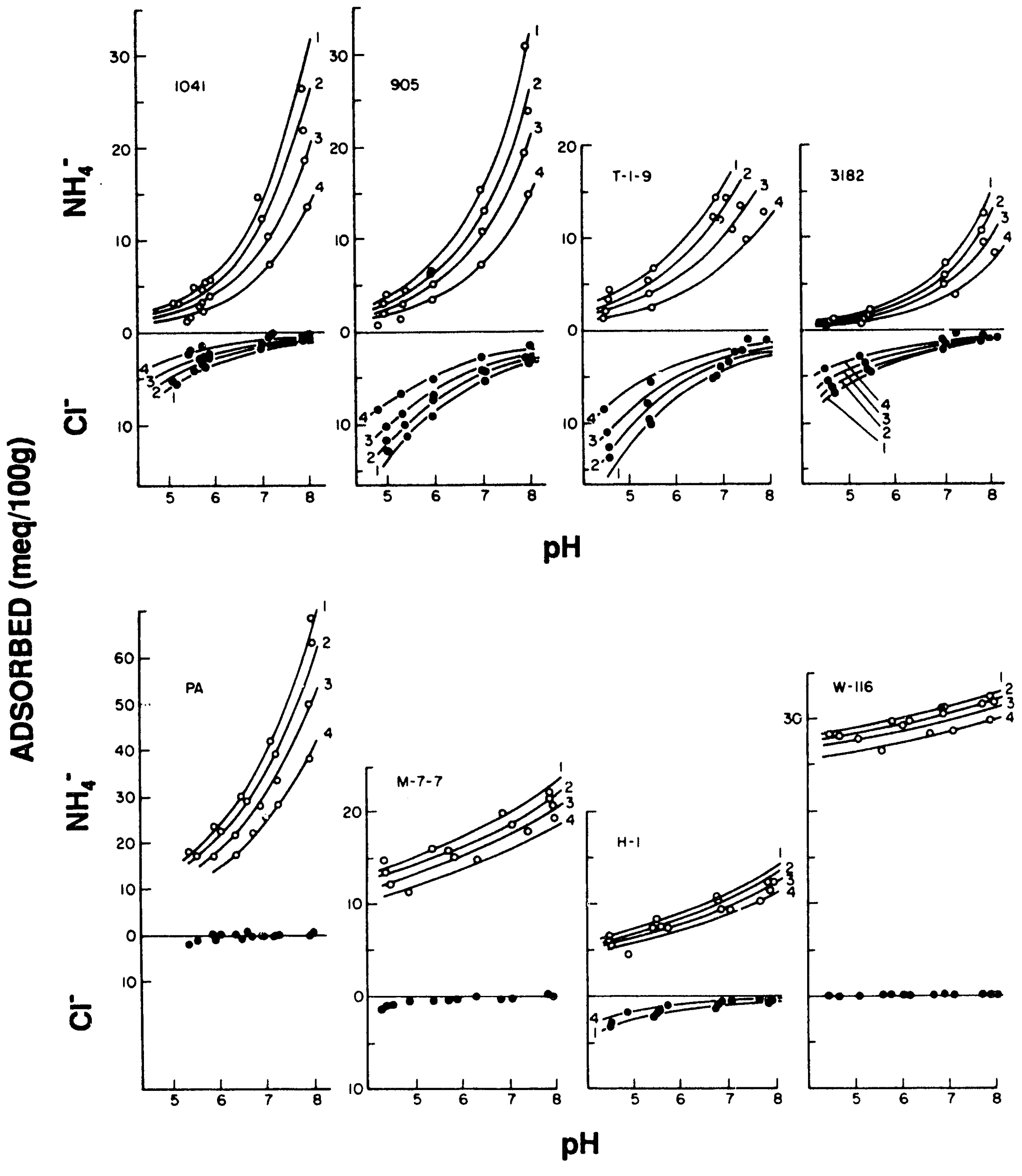

Fig. 4. Surface charge characteristics of Andept B horizon soils (T-1-9, 3182, 1041, and 905), weathered pumices (PA and M-7-7), and Red-Yellow soil B (H-1 and W-116) at different pH values and from NH_4Cl concentrations: 1=0.1M, 2=0.05M, 3=0.02M, and 4=0.005M (after Okamura and Wada, 1983).

(1974). They indicated that the negative charge could develop on dehydration, possibly including changes in the coordination of some surface Al atoms. There are also observations which suggest an increase of the net negative charge upon drying or heating of the sample. Sadzawka et al. (1972) observed that the pH of Andepts suspended in salt solutions was lowered by about 0.5 pH unit or more when the soils were dried at 110 °C. On the other hand, the AEC values (Harada and Wada, 1974) of soils and clays containing allophane and/or imogolite decreased upon heating at 105-110 °C. Wada (1977) reported that a slight decrease in the AEC values of imogolite and allophane when the temperature of the solution was raised. However, Phillips et al. (1986) found that oven-drying soil increased AEC of three New Zealand soils from A and B horizons (ranged from 30 to 50%).

ANION EXCHANGE ON NON-ALLOPHANIC SOILS

The colloid fraction of soils (clay and humified organic matter) carries a net negative charge and, in general, this tends to repel anions. Nevertheless, sorption of anions by soils does occur, particularly under acid conditions, some of the sorption being nonspecific and some specific to particular anions. Nonspecific sorption occurs at the localized positive charges that occur (1) on free hydrous oxides of iron and aluminum, and (2) at the edges of aluminosilicate clay mineral lattices where the oxygen atoms are not fully coordinated by aluminum or silicon atoms. These positive charges, which increase with decreasing pH, attract anions electrostatically, and the anions are readily exchangeable with those in the soil solution.

Several authors (Hendershot and Lavkulich, 1983; Sakurai et al., 1989; 1990) have related the soil charge characteristics with the mineralogical composition, organic matter content and percentage of amorphous oxides of the soils, pointing out that the point of zero charge (PZC) reflects the overall mineralogical composition and the organic matter content of the soils. In general, it seems clear that the percentage of Fe and Al oxides as well as short range order clay minerals tend to raise the PZC values towards the higher pH values, while the presence of organic matter tend to shift the PZC towards lower pH values. In another words, an appreciable amount of AEC may occur only on those soils containing high amounts of Al and Fe oxides or hydroxides but low amounts of soil organic substances.

Soil Minerals with Variable Charge

Table 2 lists the PZCs of several minerals which contribute to soil variable charge. Al and Fe hydrous oxide surfaces can generate a significant number of positive charges as the pH falls. Goethite (α-FeOOH), for example, is positively charged below a pH of 8-8.5 (the exact value depends on the preparation method of the oxide). For gibbsite [γ-Al(OH)$_3$] it is close to 9. The maximum charge which a hydrous oxide can accept depends upon the oxide and can be determined by both experiment (Atkinson et al., 1967) or by calculation from lattice parameters. Parfitt (1978) indicated that by consideration of the 100 and 010 faces of goethite separately, it can be calculated that there is a maximum of one positive charge per 0.37 nm^2 and one negative charge per 0.70 nm^2, and that this agrees with Atkinson's work. Similar calculations may be done with other oxides.

Table 2. Points of zero charge for several soil minerals.

Mineral	PZC	Reference
Goethite (α-FeOOH)	8 - 8.5	Mott, 1981
Hematite (α-Fe_2O_3)	8.4	White and Zelazny, 1986
Gibbsite [γ-$Al(OH)_3$]	9.0	Mott, 1981
Corundum (α-Al_2O_3)	9.1	Sposito, 1984
Hydroxyapatite [$Ca_5(PO_4)_3OH$]	8.5	Bell et al., 1972
Kaolinite [$Si_4Al_4O_{10}(OH_8)$]	4.7	Sposito, 1984
Calcite ($CaCO_3$)	10	Sposito, 1984
Quartz (α-SiO_2)	2.0	Sposito, 1984
Organic Matter	2.0	Bell et al., 1972

The PZC of Si-OH (silanol) surfaces, on the other hand, is at pH of about 2 (Mott, 1981). Therefore, adsorption of anions is not usually expected on these minerals unless pH is less than 2. There are few ionizable groups there, and as matter of the fact, these minerals carry a substantial amount of permanent negative charge so that PZC can not be actually measured without dissolving the mineral. Kaolinite carries no permanent negative charge, and therefore exhibits a relatively high PZC (4.7, Table 2). Studies (Mott, 1981) have shown that kaolinite can sorb anions onto their positive sites, and indeed demonstrate their hydrous oxide-like behavior. Illite of various kinds also appear to have some anion sorption capacity. This can doubtless be attributed to their character as hydrous minerals, and in the soil environment, to contamination by Fe and Al coatings. Of other clay mineral types, smectites have been shown to have an almost negligible capacity for anions, and indeed negative adsorption has been observed. Although the true micas have not been systematically investigated so far, there is evidence that these minerals only sorb anions if their surface are contaminated with aluminum or iron hydroxide species.

Effect of Fe and Al Coatings

In soils, mineral grains are usually coated to a greater or lesser extent by the products of pedogenesis. Often these coatings consist of amorphous materials released from primary minerals by weathering or those translocated and deposited. In the presence of these coatings, the surface charge depends not only the charge of the mineral grains themselves but also on the charge developed by the amorphous coating materials. Sakurai et al. (1989; 1990) found that crystalline Fe oxides coexisting with kaolinite were the dominant components of the variable charge in the strongly weathered soils, and amorphous alumino-silicates (allophane and allophane-like materials) were the dominant components of the variable charge in the volcanic ash soils. Table 3 lists the changes of PZC of kaolinite, montmorillonite, two strongly weathered soils (one oxisol and one ultisol) after coating with different amounts of Fe and Al hydroxides (Sakurai et al., 1990). The results clearly showed that PZC of the soils and clays increased with increasing addition of Al and Fe hydroxides.

Table 3 also shows that Fe coating is more effective in increasing PZC of kaolinite than Al coating, whereas in all cases Al is more effective in increasing PZC of montmorillonite and the two soils. Oades (1984) indicated that Al hydroxide was much more efficient in blocking negative charges than Fe hydroxides, and the effect of the blocking was due not only to the higher charge of the Al hydroxides but also to their shape. Spherical Fe hydroxides may increase the amount of positive charge in the clay- or soil-hydroxide system, but their effect on the blocking of the negative charged sites may be limited (Sakurai et al., 1990). Planar Al hydroxides, however, may cover a large area and also occupy inter-lamellar spaces, as indicated by the XRD analysis, and, thus, neutralize and block a large number of negatively charged sites.

Table 3. PZC values of the samples treated with various amounts of Al and Fe (Sakurai et al., 1990).

Sample	Uncoated	Al-Coating			Fe-Coating		
		2%	6%	10%	2%	6%	10%
Kaolinite	3.88	4.33	5.38	5.53	4.74	6.10	6.30
Montmorillonite	3.04	3.95	4.07	4.38	-	-	3.32
Oxisol	2.80	4.63	6.78	6.78	4.04	4.69	5.63
Ultisol	2.44	4.47	5.23	5.02	2.91	4.30	5.08

AEC of Highly Weathered Soils

The existence of considerable amount of positive charge or AEC in highly weathered tropical soils is well-known (van Raij and Peech, 1972; Grove et al., 1982; Gillman, 1985; Paven et al., 1985). For example, Paven et al. (1985) reported that AEC of seven acid soils from southern Brazil, dominated with kaolinite, was ranged from 3.2 to 4.4 meq/100g at pH 2.0, and ranged from 0.5 to 2 meq/100g at pH 6, while that at pH 7 - 7.5, was too small to measure. Grove et al. (1982) studied the charge characteristics of 20 acid soils (including 14 ultisols and 2 oxisols), and found that AECs of soils (determined by 0.2 M NH4Cl at pH 5.5) ranged from 0 to 0.8 meq/100g and were positively correlated with extractable Al contents in soils (Fig. 5).

Several investigators suggested the existence of positive permanent charge in oxisols (Fitzpatrick et al., 1978; Tessens and Zauyah, 1982). They found that this positive permanent charge in oxisols was related to isomorphic substitution of Ti(IV) for

Fe (III) in iron oxides. Table 4 lists the positive permanent charge determined by Cl$^-$ adsorption at pH above 7.

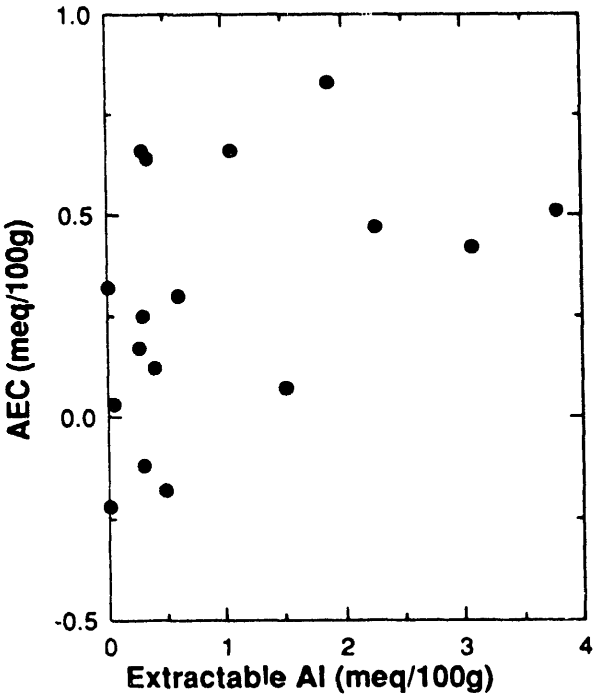

Fig. 5. AEC of soil clays as influenced by extractable Al content (after Grove et al., 1982).

Table 4. Positive permanent charge (meq/100g) determined by Cl$^-$ adsorption at pH above 7 (Tessens and Zauyah, 1982).

Soil Name	pH	Pos. Charge	Soil Name	pH	Pos. Charge
Harimau	7.73	0.20	Jeranggau	7.10	0.99
Munchong	7.01	0.58	Kuantan	7.50	1.44
Prang (1)	7.02	0.45	Segamat	8.80	1.42
Prang (2)	7.08	1.15	S. Mas	7.28	1.27
Beserah	9.43	0.06			

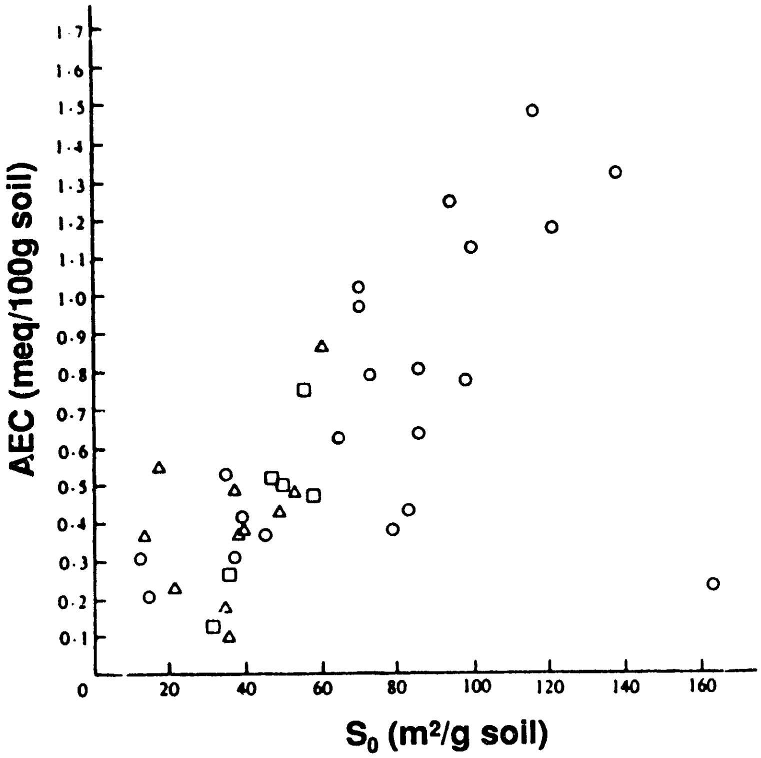

Fig. 6. The relationships between AEC and specific surface areas (S_0) of soil clays. Δ, O, and □ represent Kaolin soils, hematite/goethite soils, and mica soils, respectively (after Skjemstord and Koppi, 1983).

The AEC of kaolinitic soils at field pH was reported by Skjemstord and Koppi (1983). They found that AEC of 37 soils at field pH varied from 0.09 to 1.97 meq/100g with a mean of 0.61 meq/100g. Interestingly, they found that AEC of soils was related to the specific surface (S_0) of the soils (Fig. 6), which accounted for about 70% of the variance. However, it can be seen from Fig. 6 that high AEC of soils is associated with the presence of hematite/goethite, or high surface area was due to the contribution of iron minerals.

Wong et al. (1990) recently studied the delay in the leaching of NO_3^- in soils (oxisols, Alfisols, Ultisols and Inceptisols) from South America, Africa and South East

Asia, and found that the delay was in a good correlationship with AEC of soils (0 to 1.7 meq/100g). The higher the AEC is, the more delay in the leaching of NO_3^-. Apparently, the presence of positive charge in these soils played a significant role in holding NO_3^-. Similar observations were made by several workers (Elliott and Sparks, 1981; Meisingger et al., 1982; Wang and Yu, 1989; Toner et al., 1989). Studies on soils from the Middle Atlantic region also revealed that AEC increased with depth, paralleling accumulation of clay and Al and Fe oxides (Toner et al., 1989). Furthermore, the AEC values were found to increase with decreasing pH, indicating pH-dependent variable charge was operative.

AEC of Other Soil Types

Misra et al. (1989) studied charge characteristics of 11 soil samples from Inceptisols, Alfisols and Entisols, and found that the pH_0 of Alfisols and Entisols varied between 3.05 and 3.85, and that of the Inceptisols between 2.2 and 2.25. All soils had a very low AEC, ranged from 0.05 - 0.94 meq/100g at pH_0. No AEC should, therefore, be expected at field pH values of these types of soils. Duquette and Hendershot (1987) measured AEC of 12 soil samples from various parts of Quebec, Canada, and found that AEC values of these soils were all less than 1 meq/100g between pH 3 and 8.

The AEC and CEC of a number of soils formed on basaltic, granitic and metamorphic parent materials in the high rainfall area of tropical north Queensland were investigated by Gillman and Sumper (1986). The dependence of AEC on pH was found to vary with the clay mineralogical composition and organic matter content. The basaltic soils have greater amounts of AEC, reflecting the influence of iron and aluminum oxides, which are positively charged below their points of zero charge. AEC at pH 6 (on basaltic soils) ranged from 0.1 - 0.7 meq/100g, whereas on granitic and metamorphic soils AEC was very low and ranged from 0 - 0.2 meq/100g. They also observed that the basaltic soils were distinct from the granitic and metamorphic soils by the variation in pH_0 with depth. Clearly, the high oxide content of the basaltic soils causes high pH_0 values at depth, an effect which is attenuated in the surface layers by the presence of organic matter.

Soil organic matter is the only major soil component other than silicate clays with a low PZC (about 2, Table 2). Gillman (1985) studied the influence of organic matter and phosphate content on the PZC of variable charge components in oxidic soils, and found that soils with low organic matter content and low extractable phosphate have high pH_0 values. Regression analysis showed that pH_0 was reduced by about one pH unit for each 1% increase in organic carbon or for each 100 mg/g increase in extractable P. Stepwise linear regression showed that soil organic matter accounted for 42% of the variation in pH_0, but this was significantly ($P<0.05$) increased to 68% when acid extractable phosphorus was included, and finally to 78% following inclusion of free iron, the later also being a significant increase. Similarly, Cavallaro and McBride (1984) found that oxide removal increased the CEC and virtually eliminated the AEC at pH 3 and 5.5, while shifting the positive zeta potential (PZC) of the B-horizon clay toward negative values. On oxidation, however, increased the AEC at pH 3 and markedly shifted the PZCs of both A and B-horizon clays toward more positive values (Table 5). This was attributed by these authors to the removal of adsorbed organics from oxide surfaces.

Table 5. AEC of soil clays (Fragiochrept, NY) with different treatments (Cavallaro and McBride, 1984).

	pH 3		pH 5	
Treatment	A horizon	B horizon	A horizon	B horizon
Untreated	1.4	2.1	0.9	0.1
Oxalated	0.6	0.2	0.0	0.0
CBD	0.1	0.0	0.0	0.0
NaOCl	13	10	0.9	0.3

ANION COMPETITION

Competition between anions for sorption by soil occurs whenever mixed anions or a mixture of pollutants is added to soil. Yet it has been little studied and is poorly understood (Barrow, 1989). In a field soil, the most abundant anions naturally present are probably the organic anions, hydroxyl, bicarbonate, nitrate, silicate, sulfate, and phosphate (Mott, 1981). Some competitions are well known: for example, silicate has been used to enhance the availability of phosphate (Roy et al., 1971). Different values of the AEC can be obtained depending on the anion species used for the experiment. In general, the AEC values increased in the order: $NO_3 < Cl < CH_3COO << SO_4$. The much higher value for sulfate ion is interpreted in terms of specific adsorption.

A model was developed for the competition of anions in soil by Barrow (1983, 1989). The model considers that the competition comprises both ordinary competition between ions for adsorption sites and the electrostatic interactions which occur because reaction with one anion makes the surface more negative and, therefore, less favorable for reaction with a second anion. It has been claimed that the model describe well for competition among molybdate, phosphate and arsenate (Barrow, 1983; 1989). However, it should be indicated that these anions can undergo specific interactions with soil surfaces, while few studies, if any, examined the competition between those non-specific adsorbed anions, such as Cl^- and NO_3^-.

RETENTION OF ^{129}I AND ^{99}Tc IN SOILS

Iodine

Soil Chemistry of Iodine

Radioactive isotopes of iodine are produced during the processing of products of nuclear fission, which may be discharged to the sea or the atmosphere (Whitehead, 1984). Appreciable amounts of ^{129}I have been found in soils of the U.S.A., Europe and Japan (Muramatsu et al., 1990). ^{129}I has a long radiological half life (1.59x10^{7} years, Ticknor and Cho, 1990) and tends to be persistent in the soil environment (Boone et., 1985; Kocher, 1991). Kocher (1991) predicted that the mean residence time of ^{129}I in the first 1 m of surface soil was about 4000 years. It appears, therefore, that understanding the behavior and retention of iodine in soil is important.

The chemistry of iodine is relatively complex. Iodine can exist in a number of valence states, it is chemically reactive, and forms various inorganic and organic compounds. Of the simple inorganic forms of iodine that may exist in the soil solution, iodide (as I^- or I_3^-) is likely to dominate in the soils of humid temperate areas, although iodate (IO_3^-) may be the major inorganic form in alkaline soils in arid areas. (Whitehead, 1984). This view is supported by the Eh-pH diagram for iodine indicating the stability of the various species in aqueous solution (Fig. 7). Muramatsu et al. (1990) have demonstrated that iodide (I^-) and iodate (IO_3^-) are the ones most commonly detected in the rain water collected after the Chernobyl accident.

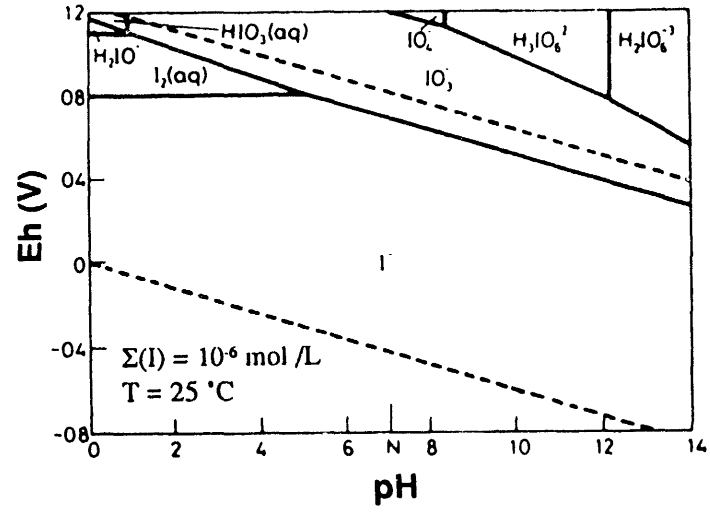

Fig. 7. Eh and pH diagram for iodine/water system (after Ticknor and Cho, 1990).

The natural iodine content of a soil reflects, in part, the inputs that have occurred over the course of its development and, in part, the soil's ability to retain iodine against leaching and volatilization. Inputs occur predominantly through transfers from the atmosphere. In general, relatively little iodine is released by the weathering of rocks, and the influence of soil parent material on iodine content is likely to be exerted mainly through its influence on the retention of iodine from the atmosphere (Whitehead, 1984). Reviews suggest that for surface soils on a worldwide basis the average content is about 5 mg/kg. However, iodine contents greater than 20 mg/kg have also been reported for forest and upland soils in two regions of Japan, which probably related to high Fe and Al contents in soils (Yuita, et al. 1982a,b).

Retention of Iodine in Soil

Studies of the sorption of iodide (I^-) and iodate (IO_3^-) by soils, and by materials representing soil components, indicate that these ions undergo specific sorption or retention both by hydrous oxides and by organic mater. Whitehead (1973), for example, reported that sorption of iodine by soil was associated with both soil organic matter and iron and aluminum oxides, with the oxides being increasingly important under more acidic conditions. The maximum amounts sorbed by two surface soils (0-10 cm) at pH 6.6 to 6.8 were 25 and 6 mg/kg soil, respectively. At this pH, the amounts of iodide sorbed were found to be closely related to the contents of organic matter but not to iron or aluminum oxides or clay. Whereas at pH $<$ 5, the removal of iron and aluminum oxides resulted in a marked reduction in iodide sorption. Whitehead (1974) further observed that freshly precipitated ferric and aluminum oxides sorbed substantial amounts of iodide from solutions of pH < 5.5 but the amount decreased to zero as the pH approached 7. However, Muramatsu et al. (1990) reported that only ferric oxide sorbed substantial amounts of I^- and IO_3^-, while sorptions of I^- and IO_3^- by Al oxide were very low (Fig. 8), which probably related to aging of Al oxide.

The degree of correlation between the contents of iodine and other soil components provides some indication of the components that are responsible for I retention. Results obtained with 18 soil profiles in the United Kingdom indicated that hydrous aluminum and iron oxides (oxalate-soluble Al and Fe) were important components, with aluminum oxide usually being the more important (Whitehead, 1978). The content of organic matter was also positively correlated with iodine content in these soils and, while involved in retention over a wide range of pH, organic matter appeared to be more important than the aluminum and iron oxides in calcareous soils.

Ticknor and Cho (1990) recently studied the interaction of iodide and iodate with a number of minerals, calcite, chlorite, epidote, goethite, gypsum, hematite, kaolinite, bentonite, muscovite, and quartz, at pH range of 7.5 - 8.0. No detectable iodide sorption was noted from any of the solution on any of these minerals (probably high pH used, very little amount of positive charge on the mineral surfaces). Iodate, however, was removed from solution by several minerals. Only the bentonite clay, calcite, gypsum and muscovite showed little or no sorption of iodate. Chlorite and hematite showed the most sorption of iodate under the wildest range of experimental conditions.

It was suggested that replacement of hydroxyl groups at exposed edge sites or H_2O ligands on hydrous oxide surface is the mechanism accounting for high iodate sorption on chlorite and hematite.

The sorption of iodine from water onto kaolinite, bentonite, quartz sand, Fe_2O_3, Al_2O_3 and humic acid were also examined by Muramatsu et al. (1990). They found that neither I^- nor IO_3^- were sorbed by quartz sand (Fig. 8). The sorption by kaolinite and bentonite were very low after shaking several days. The low sorption capacity of I^- and IO_3^- by clay minerals could be explained by the fact that they carried negative charges which would tend to repel anions. However, the sorption of I^- and IO_3^- on humic acid (Fig. 8) was substantially higher than that on clay minerals, indicating that soil organic matter plays an important role in iodine retention in soils.

Drying and heating the soil prior to its equilibration with water were found to markedly reduce I^- and IO_3^- adsorption (Whitehead, 1973; Muramatsu et al., 1990). Fig. 9 indicates that more than 95% of the I^- was adsorbed on the wet soil within 1 hour of shaking, whereas adsorption of I^- by the heated soils was very low during the first

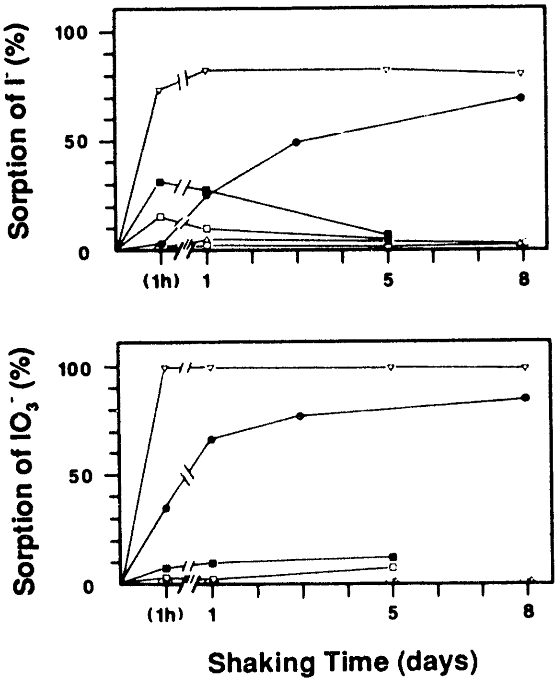

Fig. 8. Sorption of I^- and IO_3^- by kaolinite (□), bentonite (■), Fe_2O_3 (▽), Al_2O_3 (△), quartz (○) and humic acid (●) (after Muramatsu et al., 1990).

stage of shaking. On increasing the shaking time, the adsorption of I^- by the samples that were air dried or heated at 100 °C increased to about 98% after 12 days, but the adsorbability of the soil heated at 200 °C did not increase. The adsorption of IO_3^- by wet, air and heated (100 and 200 °C) soil samples were similar to that of I-. These findings indicate that I^- and IO_3^- are retained by the soil fraction which could be decomposed by heating at 100 - 200 °C. The possible candidates for such fractions in soil are though to be, among others, organic matter and/or microorganisms.

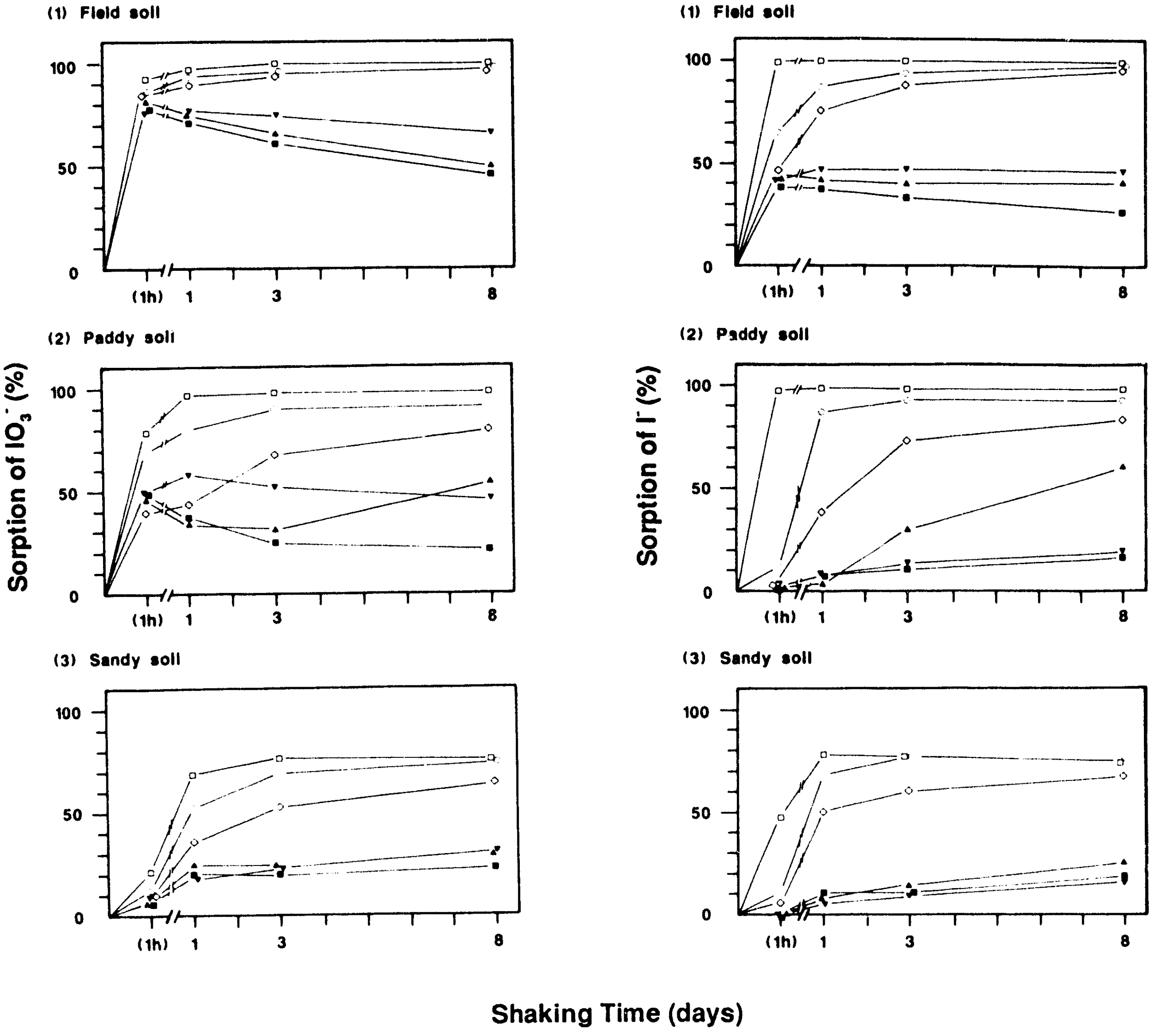

Fig. 9. Effect of heating soil on the sorption of I^- and IO_3^- by soils at different temperatures: untreated (□), air-dried (o), heated at 100 °C (◊), 150 °C (▲), 200 °C (□) and 300 °C (▼). (after Muramatsu et al., 1990).

Merzweiler et al. (1987) investigated the iodine contents of 220 soil samples and found that the average concentration of iodine was 3.13 mg/kg, and soil organic matter was the primary adsorbent of soil iodine. Bors and Martens (1989) found that sorption of ^{125}I increased with increasing organic C content of different horizons of a Chernozem and a Podsol. Sterilization decreased sorption, indicating the participation of soil microflora in the sorption process. By autoclaving the soil, Raja and Babcock (1961) also reported that the I^- sorption by soil was greatly reduced, suggesting the importance of microorganisms in the iodine fixation. Similarly, Bunzl and Schimmack (1989) demonstrated that gamma-irradiation (microorganisms do not usually survive a radiation of 25kGy) caused a considerable decrease in the sorption capacities of radioactive I^- and some other nuclides by soil.

Technetium

Soil Chemistry of Technetium

All isotopes of Technetium (Tc) are radioactive, the longest lived isotope (^{97}Tc) has a half life of 2.6×10^6 years, whereas ^{99}Tc has a half life of 2.1×10^5 years. ^{99}Tc is a fission product that is formed from ^{99}Mo after the natural fission of ^{238}U and in nuclear reactors by the bombardment of ^{235}U with thermal neutrons (Coughtrey et al., 1983). Soil environments receive Tc mainly from atmosphere fallout derived from the above processes. The most stable and characteristic oxidation state of Tc in slightly acid, neutral or basic aqueous solution in equilibrium with the atmosphere is the pertechnetate ion (TcO_4^-) in which Tc is in its heptavalent state (Coughtrey et al., 1983). This is also shown by the Eh-pH diagram of Tc (Hanke et al., 1986). Various Tc(V), Tc(IV) or Tc(III) species may be formed under reduced conditions (Pilkington, 1990). However, the most stable of these oxidation states is generally Tc(IV), although the nature of the species is uncertain, the most common suggestions being TcO_2 (Bondietti and Francis, 1979). The reduced Tc species are rapidly oxidized to Tc-VII by atmospheric oxygen, and therefore, Coughtrey et al. (1983) suggested that Tc-VII is the form which is most likely to occur in fallout that enter surface soils.

The pertechnetate ion is easily soluble. For example, the solubility of sodium pertechnetate is 11 mol/L. However, in alkaline solution and at low redox potential, the Tc(IV) species produced by the reduction of Tc(VII) are much less soluble, in the order of 10^{-7} - 10^{-8} mol/L over a range from pH 4 to 10 (Pilkington, 1990). In the presence of air, Hanke et al. (1986) found that the solubility of TcO_2 depends on the mass of TcO_2 and that it increases linearly with time. The solubility of technetium in contact with hydrated technetium dioxide was investigated by Pilkington (1990). He found that pH had little effect on the measured solubility of Tc over the range of 1 - 12.5. However, the presence of organic degradation products increased the measured solubility of Tc by about a factor of 10, indicating the complexation between the organic decomposition products and the technetium. Wildung et al. (1986) suggested that low molecular weight organic ligands may serve to increase the solubility of reduced forms of Tc, whereas complexation with the higher molecular weight organic ligands, particularly insoluble organic ligands, may lead to insolubilization.

Retention of Technetium in Soil

A number of studies have shown that retention of Tc by soils is related to the physico-chemical properties of soils (Gast et al., 1978; Balogh and Grigal, 1980; Wildung et al., 1986; Schulte and Scoppa, 1987; Bunzl and Schimmack, 1990). Firstly, the retention of Tc in soils is determined by the oxidation states of soils, due to the vast difference in the solubility between TcO_4^- and TcO_2. Secondly, in general, soils containing low amounts of clay, organic carbon and Al/Fe oxides show very little adsorption, whereas those containing relatively high amounts of clay, organic carbon and Al/Fe oxides can sorb substantial higher amounts of Tc.

Routson et al . (1977) studied the sorption of Tc (TcO_4^-) on two soils of extreme weathering intensities and found that Tc was very poorly sorbed by the soils. Sisson et al. (1979) observed that a sandy loam soil was unable to sorb Tc from acidic ground water. Bowen (1966) reported that, in aerobic conditions, 90% of added Tc was readily extractable from soils and assumed to remain in solution either as the free ion or weakly adsorbed to ion-exchange sites. Less than 10% of the added Tc can be expected to be fixed by soil colloids. Similarly, Wildung et al. (1977) reported that 78 to 88% of the TcO_4^- which was added to soil could be extracted easily thirty days after application. In contrast to that under aerobic conditions, Cataldo et al. (1978) reported that sorption of Tc by soils could exceed 97% in two to five weeks under anaerobic conditions. Similarly, Bowen (1966) indicated that in very acid or anaerobic soils only 30% of the added Tc can be expected to remain free or weakly bound while over 60% can be bound rapidly to soil minerals or organic complexes.

Wildung et al. (1986) investigated Tc sorption on 30 soils representing 9 of the 10 soil orders of the United States. Based on Tc sorption characteristics, they classified the soils into two groups, the forest-marshland soils and the grassland-shrub soils, which were distinguished by markedly different ($p<0.05$) physico-chemical properties, with the forest-marshland soils exhibiting higher organic carbon and amorphous Fe, Al contents and lower pH values than the grassland-shrub soils. Soils developed primarily under grassland shrub vegetation and arid to semi-arid conditions sorbed less than 5.7% Tc (initially as TcO_4^-) from solution after 48 h equilibration. In contrast, soils developed in forests and marshlands under humid and subhumid conditions exhibited up to 30% Tc sorption over the same period. When soil properties were compared to Tc sorption in all soils at the 48 h equilibration time, sorption was highly correlated ($p<0.01$) to organic C, total N, extractable Fe and Al, several clay and silt fractions and pH (Table 6). The latter was inversely correlated to Tc sorption, substantiating the importance of pH-dependent sorption sites, which would tend to increase in positive charge with decreased pH on both the organic and oxidic mineral fractions. The highest correlation coefficients occurred with organic C, total N, extractable Fe and Al and the coarse clay fraction. After 1050 h of equilibration, the same properties were highly correlated ($p<0.01$) with Tc sorption, but the organic C and

N components increased in importance (higher r values, Table 6) whereas the amorphous Fe and Al fraction decreased in importance (lower r values). The results were further verified by the multiple regression analysis, indicating the major influence on Tc sorption by amorphous Al and Fe oxides at earlier times and organic C at later times during the equilibration period. Similarly, Schulte and Scoppa (1987) showed that the sorption of Tc on surface soils with a broad range of physico-chemical properties varied from < 1% to 31% of the initially added Tc, while 80% of the variability was attributed to differences in concentrations of organic C, Fe and Al oxides, and clays in the soils. The roles of organic fractions and amorphous Fe oxides on Tc sorption were also shown by Landa et al. (1977) with the method of selective dissolution (Fig. 10). Hydrogen peroxide treatment essentially stopped sorption of Tc, whereas the dithionite treatment reduced Tc sorption.

Table 6. Significant correlation coefficients ($p < 0.01$) relating properties of soils investigated to Tc sorption for equilibration times of 48 h (r_{48}) and 1050 h (r_{1050}) (Wildung et al., 1986).

Soil Property	r_{48}	r_{1050}
Organic carbon	0.67	0.85
Total nitrogen	0.71	0.87
Ammonium oxalate iron	0.74	0.62
Ammonium oxalate aluminum	0.72	0.51
Fine clay	0.58	0.71
Coarse clay	0.71	0.61
Medium silt	0.58	0.49
pH	-0.56	-0.62

Sheppard et al. (1990) recently studied the sorption of Tc under both aerobic and anaerobic conditions by 34 soils, 27 of which were organic soils. They reported that the key variables affecting Tc retention were redox or aeration status of the soil and organic matter content. Under aerobic conditions, Tc was not significantly retained by the seven mineral soils, and was only slightly retained by the organic soils. However, under anaerobic conditions, Tc was retained about 2 orders of magnitude higher than that under aerobic conditions. The retention on the 7 mineral soils tended to increase as clay content and organic matter content increased, whereas on those organic soils, it increased with pH and with the degree of humification. Wolfrum and Bunzl (1986) reported that sorption of Tc (expressed as distribution coefficient, Kd*) by humic substances increased when the concentration of electrolyte ($CaCl_2$) or the

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* $$Kd = \frac{\text{Amount of Tc sorbed per gram of solid}}{\text{Amount of Tc per cm}^3\text{ of solution}}$$

amount of dissolved oxygen was decreased (Table 7). Two mechanisms of Tc sorption were suggested by these authors: (1) reduction to less soluble species and (2) complexation with organic matter fractions. Evidences of the complexation between soil humic acid (HA) and Tc were presented by van Loon et al. (1986). They indicated that such complexes could be readily synthesized, either directly by chemical reduction in the presence of HA or indirectly by microbial action.

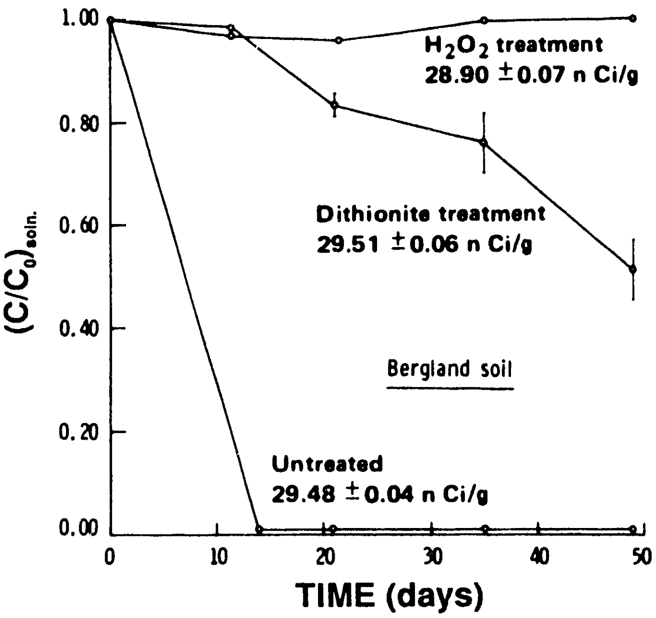

Fig. 10. Effect of pretreatment of soil with hydrogen peroxide and sodium dithionite on sorption of Tc by Bergland soil from aqueous solution at 25 °C (after Landa et al., 1977).

Table 7. Distribution coefficients (Kd, cm^3/g) for the sorption of Tc by peat as a function of the concentration of the supporting electrolyte $CaCl_2$ and the dissolved oxygen (Wolfrum and Bunzl, 1986).

O_2 dissolved, mg/L	0.05M $CaCl_2$	0.005M $CaCl_2$
0.5	17.7	41.0
4.6	10.9	21.0
8.4	5.8	9.7

A particular interesting finding is that reduced Tc species (precipitates or HA-Tc complexes) are not resolubilized by complexing agents such as EDTA and DTPA, which are known to form stable Tc complexes (Stalmans et al., 1986). This would indicate that EDTA and DTPA complexes cannot match the stability of the Tc humate complexes. At present, there appear to be no suitable methods that enable quantitative distinction to be made between these various possible insoluble forms. It appears, however, that HA plays a significant role in that it may lock reduced Tc into relatively stable complexes. Stalmans et al. (1986) indicated that when hydroxyl groups are adjacent to carboxylic groups, conditions are quite favorable for the formation of stable Tc complexes. Similarly, Schulte and Scoppa (1987) showed that reduced Tc has a strong tendency to coordinate with ligands containing highly polar groups and positively charged ligands. The remobilization of Tc would require the oxidation of lower valent to pertechnetate. It is not surprising, therefore, that Landa et al. (1977) observed that sorption of Tc was not significantly influenced by the presence of large amounts of Cl^- and PO_4^{3-}. Whereas, the lack of sorption exhibited by the low organic matter soils, the reduction in sorption following H_2O_2 digestion of the soil, and the high recoveries of sorbed Tc on extraction with NaOH again suggest a role for the living and/or nonliving organic fractions of the soil.

The influences of microflora on Tc retention in soils are through establishing the proper redox conditions, conducive to the reduction of Tc (Stalmans et al., 1986), and through directly uptaking Tc from soil. Even under aerobic conditions, Landa et al. (1977) and Wildung et al. (1986) pointed out that Tc retention in soil could not totally preclude chemical reduction at micro-sites on particle surfaces, especially for soils containing relatively high amounts of organic matter. Henrot (1989) recently studied the influences of soil bacteria on the bioaccumulation and solubility of Tc. He found that aerobic bacteria had no apparent effect on TcO_4^-, and they did not accumulate Tc nor modify its chemical form. However, anaerobic bacteria exhibited high bioaccumulation and reduced TcO_4^-, enabling its association with organics of the growth medium. Up to 70% of the total Tc in the growth medium was bioaccumulated and/or precipitated in the presence of sulfate reducing bacteria. The remaining Tc in soluble form was found to be entirely associated with organics. Similar observations were made by Lembrechts and Desmet (1989). Tc accumulation by plants has also been reported since TcO_4^- ion in soil has the potential for competing with nutrient ions for membrane carrier sites (Cataldo et al., 1978, 1989; Dehut et al., 1989; Vandecasteele et al., 1989).

CONCLUDING REMARKS

Soils containing the amorphous clays allophane and imogolite may develop a noticeable amount of positive charge for anion exchange. However, the magnitude of surface charge of these amphoteric materials is dependent on a number of factors: the SiO_2/Al_2O_3 ratio, pH and concentration of electrolyte. In general, a lower SiO_2/Al_2O_3 ratio and pH, and a higher electrolyte concentration result in a higher anion exchange capacity (AEC). Soils dominated with allophane and imogolite have an AEC ranging from 1 to 18 meq/100g at pH about 6 (Fig. 2). However, this value is relatively low compared with that of synthetic allophane and imogolite, presumably due to the complexation of soil allophane and imogolite with soil organic and inorganic ligands, as well as the dilution by other types of silicate minerals. Imogolite develops more positive charge than allophane at a given pH. The possible development of permanent positive charge on imogolite has been suggested (Theng et al., 1982).

Soil minerals, other than allophane and imogolite, capable of developing a substantial amount of positive charge include: goethite, hematite, gibbsite, corundum and hydroxyapatite. These minerals have a points of zero charge (PZC) ranging from 8 to 9.1, and therefore become positively charged unless pH exceeds the PZC. The PZCs of silanol (Si-OH) surfaces of most layer silicate minerals and organic matter are very low (about 2). Their presence in soil may, therefore, largely eliminate AEC of soils. Similarly, specifically adsorbed anions, such as phosphate, sulfate, and organic acids also decrease PZC of soils, and render soils to be more negatively charged. Coatings of Al and Fe oxides on silicate minerals or the presence of these oxides in highly weathered soils can develop a significant amount of AEC as soil pH falls, although the magnitude of AEC of the soils may not be as high as that on soils dominated with allophanic materials. On a wide range of acid soils, oxisols and ultisols, AEC ranges from 0 to 2 meq/100g at pH about 6. Several investigators have suggested the existence of permanent positive charge in oxisols.

The retention of radionuclides ^{129}I and ^{99}Tc anions in soil involves both specific and non-specific sorption, and is further complicated by soil redox reactions. In the literature reviewed, sorption of I and Tc by soils is found to be associated with both soil organic matter and Fe and Al oxides, whereas sorption on layer silicate minerals is negligible. Anaerobic conditions greatly increase Tc retention by soils, which is related to the lower solubility of Tc (IV) and its complexation with organic matter fractions. Fe and Al oxides become more important in the retention of anionic iodide (I^-), iodate (IO_3^-) and pertechnetate (TcO_4^-) as pH falls, since more positive charge is developed on the oxide surfaces. Soil allophane and imogolite develop more positive charge than Fe and Al oxides at given pH conditions, and are thus expected to retain more I and Tc although few studies have been conducted on the sorption of I and Tc by soil allophane and imogolite. It is recommended that further studies on the potential use of andisol as a barrier to retard the migration of I and Tc through the soil shall be carried out.

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(2-84)
NRCM 1102,
3201, 3202

U.S. NUCLEAR REGULATORY COMMISSION

BIBLIOGRAPHIC DATA SHEET

SEE INSTRUCTIONS ON THE REVERSE

1. REPORT NUMBER (Assigned by TIDC, add Vol No., if any)
NUREG/CR-5464

2. TITLE AND SUBTITLE
Anion Retention in Soil: Possible Application to Reduce Migration of Buried Technetium and Iodine
A Review

3. LEAVE BLANK

4. DATE REPORT COMPLETED

MONTH	YEAR
September	1991

5. AUTHOR(S)
B. Gu, R.K. Schulz

6. DATE REPORT ISSUED

MONTH	YEAR
October	1991

7. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Department of Soil Science
University of California
Berkeley, CA 94720

8. PROJECT/TASK/WORK UNIT NUMBER

9. FIN OR GRANT NUMBER
B8958

10. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code)
Division of Regulatory Applications
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555

11a. TYPE OF REPORT
Technical

b. PERIOD COVERED (Inclusive dates)

12. SUPPLEMENTARY NOTES

13. ABSTRACT (200 words or less)

This report summarizes a literature review of our present knowledge of the anion exchange properties of a number of soils and minerals, which may potentially be used as anion exchangers to retard migration of such anions as iodide (I^-), iodate (IO_3^-) and pertechnetate (TcO_4^-) away from the disposal site and thus prevent contamination of ground water. The amorphous clays allophane and imogolite, derived from volcanic parent material, are found to be among the most important soil components capable of developing appreciable amounts of positive charge for anion exchange even at about neutral pH. The magnitude of the surface charge of these amphoteric materials depends on the ratio of SiO_2/Al_2O_3, soil pH and concentration of electrolyte. Decreases in the SiO_2/Al_2O_3 ratio and soil pH result in an increase in soil AEC. Allophane and imogolite rich soils have an AEC ranging from 1 to 18 meq/100g at pH about 6. Highly weathered soils dominated by Fe and Al oxides and kaolinite may develop a significant amount of AEC as soil pH falls. On a wide range of those soils, AEC ranges from 0 to 2 meq/100g at about pH 6.

The retention of radionuclides, iodine (I) and technetium (Tc), by soils is associated with both soil organic matter, and Fe and Al oxides, whereas sorption on layer silicate minerals is negligible. Fe and Al oxides become more important in the retention of anionic I^-, IO_3^- and TcO_4^- as pH falls, since more positive charge is developed on the oxide surfaces. Although few studies, if any, have been conducted on I and Tc sorption by soil allophane and imogolite, it is estimated that a surface plough soil (2 million pounds soil per acre) with 5 meq/100g AEC, as is commonly found in andisols, shall retain approximately 5900 kg I and 4500 kg Tc, respectively, by the anion exchange mechanism. It is conceivable that an anion exchanger such as an andisol could be used to modify the near field environment of a radioactive waste disposal facility. This whole disposal system would then offer similar migration resistance to anions as is normally afforded to cations by usual and normal soils. Future studies on this subject are recommended.

14. DOCUMENT ANALYSIS – a. KEYWORDS/DESCRIPTORS

Anion exchange
Allophane
Imogolite
Hazardous waste disposal
Radionuclide migration
Toxic waste disposal
LLW disposal
Iodine
Technetium

b. IDENTIFIERS/OPEN-ENDED TERMS

15. AVAILABILITY STATEMENT
Unlimited

16. SECURITY CLASSIFICATION
(This page)
Unclassified
(This report)
Unclassified

17. NUMBER OF PAGES

18. PRICE

END

DATE FILMED

12 1 20 1 91