

Microbial Redox Effects on the Attenuation of Fe and Zn in Landfill Leachate Plume

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Synopsis

Modified batch tests were conducted to evaluate the bacteria-induced redox and pH effects on the attenuation of iron and zinc in landfill site. Test results show that under aerobic, denitrification, and Fe(III) reduction conditions, zinc was soluble when $\text{pH} < 7$ but precipitated as hydroxides and carbonates when $\text{pH} > 7.2$. Under sulfate reduction conditions, zinc sulfides were formed. Iron was insoluble under aerobic, denitrification, and natural pH conditions. Elevated soluble iron was observed in Fe(III) reduction and sulfate reduction conditions. A combination of nearly neutral pH and extremely low Eh conditions tends to promote zinc insolubilization but iron solubilization in landfill sites.

Key words: landfill, leachate, redox potential, anaerobic respiration, contamination

1. Introduction

Solid waste is an increasing problem faced to all countries around the world. Up to now, it has been proved that landfilling is a cost-effective method to dispose of the solid wastes. Following its decomposition in a landfill site the organic fraction of the waste will begin to undergo degradation through chemical and microbiological action. Water present in waste, rainwater infiltration during and/or after the landfilling process and groundwater penetration can result in the generation of leachate. During decomposition process landfill gas, typically including carbon dioxide, methane and hydrogen sulfide, are also produced.

In order to prevent the ecological environments from being polluted, modern engineered landfills are designed based on two basic principles: containment and attenuation. Generally, bottom liner system and cover liner system are the most important containment barriers in solid waste disposal facilities,

which are successfully employed to isolate the landfilled waste, minimize the production of leachate and to cutoff the leakage of leachate. Properly designed landfill can cut down greatly the leakage of leachate, but can not to cut off absolutely the leachate, especially when some of the uncertainties are considered such as that in civil engineering design, landfill operation, and the occurrence of geological hazards nearby the landfill site. It is wise to believe that each engineered landfill is a closed system in a short term but an open one in its lifespan or in a geological term. Therefore, it is necessary to pay great attention to the natural attenuation processes even in modern engineered landfill sites.

Microbial metabolism is one of the most important events occurred in municipal solid waste (MSW) landfills during decomposition. Numerous studies have shown that microbial respiration couples the inorganic redox chemistry of soil or groundwater to the oxidation of organic carbon (e.g., Lovley and Phillips, 1988) and results in a sequence of redox

reactions. The redox conditions within landfills begin to be recognized as a significant environmental factor, taking in account to study their effects on the geotechnical properties of clay liners (Kamon et al., 2001). Also, the redox conditions within leachate plume constitute an important part of the chemical framework controlling the behavior of the contaminants in the plume. Redox reactions strongly affect the behavior of pollutants leached from the landfill (Lyngkilde and Christensen, 1992; Rugge et al., 1995). The objective of this study is to evaluate the redox effect on the solubility of zinc (Zn) and iron (Fe) in attempt to understand the possible attenuation mechanisms of heavy metals in landfill leachate plume.

2. Redox Reactions in Landfill Sites

Simply, a landfill life can be divided into aerobic and anaerobic stages according to the degradation of organic fraction within a landfill. Also, it can be divided into five stages in detail according to the composition change in landfill gas constitutes as shown in Fig.1: (1) aerobic, (2) anaerobic non-methanogenic, (3) anaerobic methanogenic unsteady, (4) anaerobic methanogenic steady, and (5) mature aerobic stages. The production of landfill gas, in particular the methane and carbon dioxides, indicates that anaerobic respiration prevails in landfills. Even within leachate plume, a sequence of redox zones were also monitored because the leachate from landfill is usually rich in dissolved organic carbon materials, which are used by bacteria as nutrients and energy source to drive redox reactions there (Lyngkilde and Christensen, 1992; Christensen et al., 1994; Bjerg et al., 1995).

The oxidative breakdown of external organic substrates occurs in a sequence of decreasing energy-yielding pathways as shown in Table 1: aerobic respiration, denitrification, manganese reduction, iron reduction, sulfate reduction, and fermentation (Robertson et al., 1996). From a biochemical point of view, the energy-yielding metabolic pathways consist of complex electron transfer chains (Madigan et al., 1997). From a geochemical point of view, the significant reaction in biological metabolism is a redox reaction, the final electron transfer from organic pollutants to an external electron acceptor (Lovley and Chapelle, 1995). It was found that strongly reduced redox conditions will develop close to the landfill and the plume will develop a redox gradient along as well as

transversal to the main groundwater flow direction. In the outskirts of the plume, the redox conditions will approach the redox conditions of the pristine aquifer (Lyngkilde et al., 1992; Christensen et al., 1994; Bjerg et al., 1995; Christensen et al., 2000).

The basic thermodynamic theory about the differences in energy yields of these reactions has been used to explain the distributions of active bacterial populations in subsurface environments, and to explain the spatial or temporal distribution of redox zones in which each pathway dominates (see Table 1). It has been proved that the overall distribution of redox zones in leachate plume agrees with this thermodynamic theory by the in-situ monitoring results from Ontario Landfill, Canada (Nicholson et al., 1983), Vejen Landfill, Denmark (Lyngkilde and Christensen, 1992), Grindsted Landfill, Denmark (Bjerg et al., 1995), and Norman Landfill, USA (Cozzarelli et al., 2000).

In consideration of field investigations along with the sequence of redox reactions, a conceptual redox zonation model downgradient from a landfill was constructed by Baedecker and Back (1979) to illustrate the temporal and spatial development of redox reactions (see Fig.2). In the first stage as the leachate seeps through the landfill into the highly oxygenated environment of either the unsaturated or saturated zones, the organic compounds decompose to form the most oxidized species that are stable at the highest redox values. During the later stages continuous degradation of organic compound causes greater reduction of redox levels to where NH_4^+ is the dominant N species; H_2S is the dominant S species at pH of less than about 7 and HS^- at slightly higher pH values. The reduction of SO_4^{2-} uses the last source of oxygen, other than organic matter itself, and organic compounds then degrade by processes of fermentation to form CO_2 , and NH_4 . Combined effects of the above reactions and groundwater flow results in the idealized zonation.

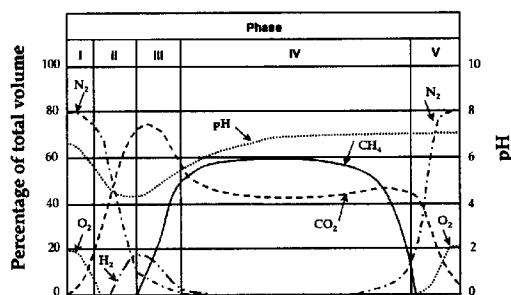


Fig.1 Landfill gas production with time (Adapted from Farquhar & Rovers, 1973; Sarsby, 2000)

Table 1 Sequence of progressive reduction of redox intensity by organic pollutants (Stumm and Morgan, 1996)

O ₂ consumption:	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \frac{1}{4}\text{O}_2 = \frac{1}{4}\text{CO}_2 + \frac{1}{4}\text{H}_2\text{O}$	(1)
Denitrification:	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \frac{1}{5}\text{NO}_3^- + \frac{1}{5}\text{H}^+ = \frac{1}{4}\text{CO}_2 + \frac{1}{10}\text{N}_2 + \frac{1}{2}\text{H}_2\text{O}$	(2)
Nitrate reduction:	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \frac{1}{8}\text{NO}_3^- + \frac{1}{4}\text{H}^+ = \frac{1}{4}\text{CO}_2 + \frac{1}{8}\text{NH}_4^+ + \frac{1}{8}\text{H}_2\text{O}$	(3)
Production of soluble Mn(II):	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \frac{1}{2}\text{MnO}_2(\text{s}) + \text{H}^+ = \frac{1}{4}\text{CO}_2 + \frac{1}{2}\text{Mn}^{2+} + \frac{1}{8}\text{H}_2\text{O}$	(4)
Fermentation:	$\frac{3}{4}\{\text{CH}_2\text{O}\} + \frac{1}{4}\text{H}_2\text{O} = \frac{1}{4}\text{CO}_2 + \frac{1}{2}\text{CH}_3\text{OH}$	(5)
Production of soluble Fe(II):	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \text{FeOOH}(\text{s}) + 2\text{H}^+ = \frac{1}{4}\text{CO}_2 + \frac{7}{4}\text{H}_2\text{O} + \text{Fe}^{2+}$	(6)
Sulfate reduction:	$\frac{1}{4}\{\text{CH}_2\text{O}\} + \frac{1}{8}\text{SO}_4^{2-} + \frac{1}{8}\text{H}^+ = \frac{1}{8}\text{HS}^- + \frac{1}{4}\text{CO}_2 + \frac{1}{4}\text{H}_2\text{O}$	(7)
Methane fermentation:	$\frac{1}{4}\{\text{CH}_2\text{O}\} = \frac{1}{8}\text{CH}_4 + \frac{1}{8}\text{CO}_2$	(8)

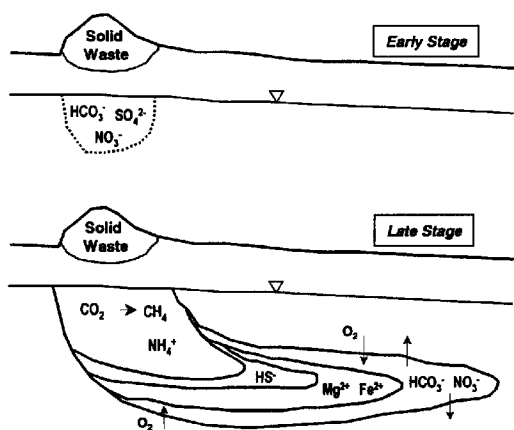


Fig.2 Conceptual redox zonation in landfill leachate plume (After Baedeker and Back, 1979)

The quantitative measure of electron availability in redox reactions is defined as redox potential, and denoted as *Eh*. A measurement of *Eh* indicates whether the redox couples are in an oxidized or reduced state. There are four general ranges of redox conditions encountered in soil at pH 7: above + 400 mV for oxidized soils, + 400 to + 100 mV for moderately reduced soils and - 100 to - 300 mV for highly reduced soils (Patrick and Mahapatra, 1968).

Oxidized conditions in soils are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks. Analysis on the redox conditions in paddy soils, swamp and marsh soils, and lake and marine sediments shows that reduced soils are characterized by (1) water saturation, (2) an absence of molecular

oxygen, (3) anaerobic microbial activity, and (4) bio-availability of organic compounds. In fact, reduced conditions in soils are brought about by the absence of oxygen. This is caused by the reason that oxygen is consumed at a greater rate than it can be transported into the soil system, such as the waterlogged soils or soils contaminated with oxygen consuming compounds. The consumption could either be chemical or biological. The biological consumption of oxygen is the results of microorganisms utilizing the organic compounds either originally contained in the soils or have entered the soil system as organic contaminants.

The redox effect on the fate and transport of pollutants in soil-water systems comes from two ways. First, redox reactions can affect the forms, mobility, and toxicity of multivalent metals by involving these metals directly in the redox reactions. And second, redox reactions can change the environmental conditions, such as *Eh* and pH, during redox processes so as to affect indirectly the behavior and toxicity of some other metals with mono-valence.

Redox reactions of soil oxidants are represented by the following half-cell reduction equation:



where *Ox* is the oxidized component or electron acceptor, *Red* is the reduced component or electron donor, *m* is the number of hydrogen ions involved in the reaction, and *n* is the number of electrons involved in the reaction.

The redox reaction can be defined quantitatively through the change in Gibbs free energy (ΔG)

$$\Delta G = \Delta G^0 + RT \ln \frac{\text{Red}}{(\text{Ox})(\text{H}^+)^m} \quad (2)$$

where ΔG^0 is the standard free energy change, R is the gas constant, and T is absolute temperature. The Nernst equation expresses the redox reaction in terms of electrochemical energy (millivolts) using the relationship $\Delta G = -nEF$

$$Eh = E^0 - \frac{RT}{nF} \ln \frac{(\text{Red})}{(\text{Ox})} - \frac{mRT}{nF} \ln \text{H}^+ \quad (3)$$

where Eh is the redox potential, E^0 is the standard half cell potential, F is the Faraday constant, n is the number of electrons exchanged in the half-cell reaction, m is the number of protons exchanged, and the activities of the various oxidized and reduced components are shown in parentheses. Substituting values of $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ for R , $9.65 \times 10^4 \text{ C mol}^{-1}$ for F , and 298 K for T and using the relationship $\ln(x) = 2.303 \log(x)$, Eq(3) simplifies to

$$Eh(\text{mV}) = E^0 + \frac{59}{n} \log \frac{(\text{Ox})}{(\text{Red})} - \frac{59}{n} \text{pH} \quad (4)$$

Inspection of Eqs. (3) and (4) reveals that redox potential (Eh) increases with increasing activity of the oxidized component, decreases with increasing activity of the reduced component, and increases with an increase in H^+ activity (or a decrease in pH).

3. Materials and Methods

Modified batch tests were conducted to evaluate the effects of both redox potential and pH on the solubility of metals (see Fig.3). A closed microcosm reactor was developed to cultivate the native bacteria in the soil used in attempt to control the redox potential of soil-water system by microbial activities (see Fig. 4). Nutrients were applied to the microcosm for bacteria growth, and the soil suspension was continuously stirred and bubbled with N_2 or O_2 gas, inducing an anaerobic or aerobic respiration in the soil-water system.

Marine clay sampled from Osaka Bay was used for the experiment as a clay liner material due to the consideration that marine clay is used as bottom

barrier in coastal landfill sites in Japan. The basic properties of Osaka marine clay are listed in Table 2. Iron and zinc were selected as target pollutants to investigate the Eh and pH effects on the mobility of heavy metals in landfill sites. Iron is an abundant component in the natural environments, and iron reduction has been termed as the most important chemical change that takes place in the development of anaerobic soils. Zinc is a heavy metal, which poses biological toxicity and is mostly encountered in the leachate from both hazardous and municipal solid waste landfill sites.

Wet Osaka marine clay, having 100 g of dry soil portion, was transformed to a plastic bottle. Distilled water was added to obtain a dry soil-to-water ratio of 1:10. To apply bacteria with carbon, nitrogen, and phosphorous with the nutrient ratios (C:N:P) of 120:10:1, 3000 ppm (final concentration) of sodium acetate, CH_3COONa , and 300 ppm of ammonium dihydrogenphosphate, $(\text{NH}_4)_2\text{HPO}_4$ were added. Ferric chloride (FeCl_3) and zinc chloride (ZnCl_2) were added to enhance the target pollutants of Fe and Zn.

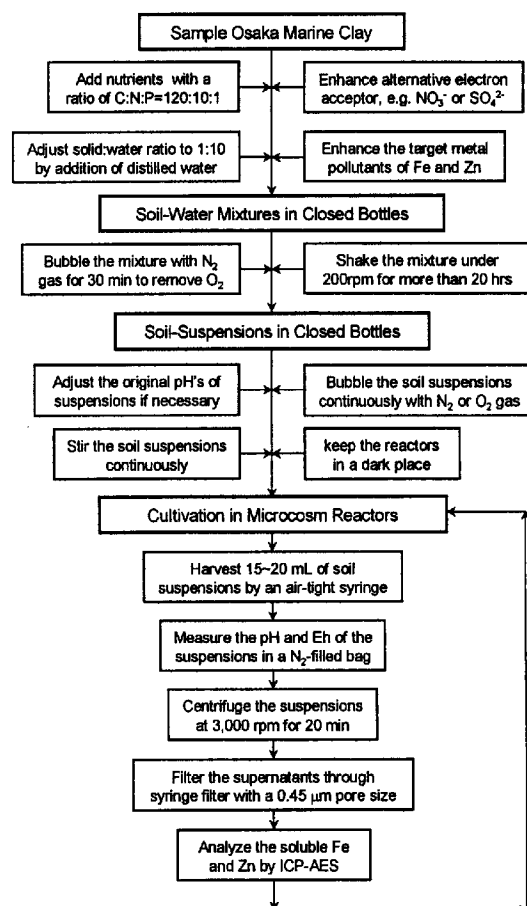


Fig.3 Flow chart for bacteria culture batch test

The soil-water mixture was bubbled with nitrogen gas for 30 minutes to remove the dissolved oxygen, and then shaken under 200 rpm for more than 20 hours to obtain a soil suspension with an equilibrium state between the solid and liquid phases.

The soil suspension was transported to a flat bottom flask of 1000 mL, the microcosm reactor, and a 5 cm magnetic stirring bar, coated with Teflon to prevent excess wears on the flask and the stirring bar, was inserted into the flask. The suspension was bubbled by N₂ or O₂ gas at a flow rate of 45 or 90 mL/min under a pressure of 0.1 MPa. An anaerobic condition was maintained in suspension continuously by stirring and nitrogen gas bubbling the soil suspension, while aerobic condition was maintained by oxygen gas bubbling. The escaping gas from an outlet of the reaction flask was submerged in water so as to maintain a slightly positive gas pressure inside the flask and to prevent atmospheric oxygen from diffusing into the microcosm (see Fig.4).

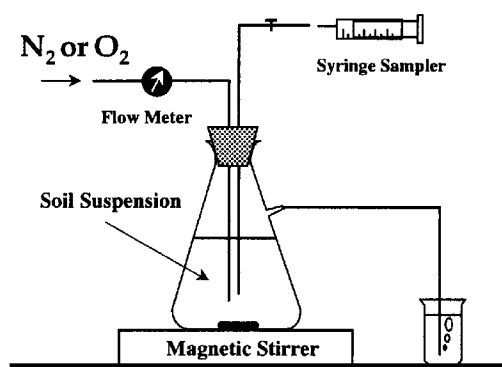


Fig.4 Setup of the modified bacteria culture batch test

Table 2 Basic properties of Osaka marine clay

Particle density (g/cm ³)	2.72
Natural water content (%)	100.4
Liquid Limit (%)	93.3
Plastic Limit (%)	26.6
Grain size distribution (%)	
Gravel (>2 mm)	0
Sand (2 mm~0.075 mm))	2.1
Silt (0.075-0.005 mm)	52.1
Clay (<0.005 mm)	45.8
pH measured in suspension	7.52
pH measured in pore water	7.39
Eh measured in suspension (mV)	-377
Eh measured in pore water (mV)	62.0
Total organic carbon (TOC) (%)	0.63

After certain incubation duration, 15-20 mL of suspension sample was taken out from another outlet tube by an airtight syringe sampler. The *Eh* and pH of the suspension were measured immediately in a glove bag filled with nitrogen gas. Then, the suspension was centrifuged at 3,000 rpm for 20 min and the supernatant was filtered through syringe filter with a 0.45 μ m pore size. Filtered solution was analyzed for cations by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Table 3 shows the test conditions used. All the tests can be classified as three categories: Aerobic tests, including reactors Nos.1, 2, 3, and 4 where oxygen gas was used to pass through the soil suspensions; anaerobic tests with nitrate as electron acceptor, such as reactors Nos.5, 6, and 7 where nitrogen gas was used to pass through the soil suspensions; anaerobic test with sulfate as electron acceptor, such as reactor No.8 where nitrogen gas was used to pass through the soil suspension.

4. Test Results and Analysis

4.1 Calibration of measure redox potential

The common method of measuring redox potential is to immerse a platinum (Pt) electrode along with a reference electrode into a solution; the electrodes are connected to a potentiometer that measures the potential difference between the two electrodes. The measured redox potentials do not necessarily correspond to the standard state redox potentials, the thermodynamic values. This is because there is an enormous difference between the thermodynamic concept of an electrochemical potential, and a measured electrochemical potential. The first is a theoretical construct, while the second results from a practical exercise in analytical chemistry.

Generally, the redox reactions in natural groundwater or soil systems are lack of internal equilibrium (Grundi, 1994). Still, soil is a complex system in which several redox couples coexist, the measured redox potential is a mixed potential that represents the overall potential of several redox couples reacting simultaneously. Some redox couples (such as CO₂-CH₄ and NO₃⁻-NO₂⁻) do not react in a reversible manner at the electrode surface and have a slow chemical kinetics of redox reactions. Actually, the only redox couple that may respond kinetically fast and have sufficient ion activity is the Fe³⁺/Fe²⁺ redox couple. Because of these reasons, redox potential measured in soil solution cannot be relied

on to reflect the thermodynamic reaction potentials (Stumm and Morgan, 1996; Christensen et al., 2000).

Redox potential measurements in many oxidized systems are poorly reproducible, because of the very low concentrations of soluble, chemically reactive species present. On the other hand, redox potential measurements are more satisfactory indicators of the intensity of reduction of anaerobic systems (Patrick et al., 1968; Stumm and Morgan, 1996).

Figure 5 compares the theoretical Eh of important redox couples (solid lines) with the electrode-measured Eh range over which these couples are found to be active in accepting electrons in soils (black boxes). Large discrepancies between theoretical and measured Eh are obvious in Fig.5 for the O_2 - H_2O , NO_3^- - N_2 , and Mn oxide- Mn^{2+} couple. The first two are explained by inert behavior of O_2 , NO_3^- and N_2 at the Pt electrode, the discrepancy for the Mn couple may have more to do with an inappropriate choice of Mn oxide (MnO_2) to represent soil Mn in the oxidized state and the exact nature of this Mn is not known (McBride, 1994).

In order to compare the redox potentials of several soil samples having different pH values, measured redox potentials are usually needed to be adjusted to pH=7. The calibration principle can be explained as followings.

Usually, accompanying with the transfer of electrons in redox reactions, protons also are transformed (see Table 1). Therefore, Eh is not independent to pH as shown in Eq.(4).

When pH equals pH_0 and 7, Eq.(4) will be

$$Eh_0(mV) = E^0 + \frac{59}{n} \log \frac{(Ox)}{(Red)} - 59 \frac{m}{n} pH_0 \quad (5)$$

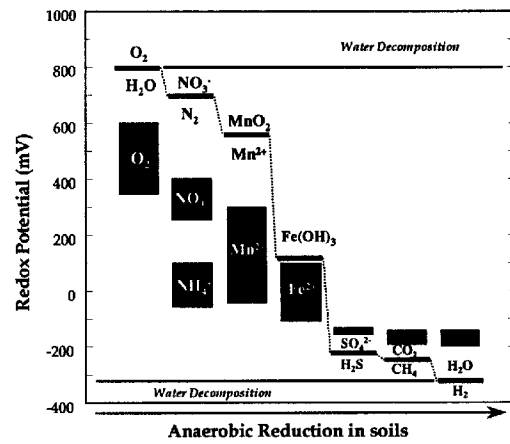


Fig.5 Theoretical and measured redox potential in soil solution at pH=7 (Adapted from McBride, 1994)

$$Eh_7(mV) = E^0 + \frac{59}{n} \log \frac{(Ox)}{(Red)} - 59 \frac{m}{n} 7 \quad (6)$$

Eq.(5) – Eq.(6) gives

$$Eh_7(mV) = Eh_0 + 59 \frac{m}{n} (pH_0 - 7) \quad (7)$$

If the ratio of protons to electrons (m/n) is unity, Eq.(7) changes as

$$Eh_7(mV) = Eh_0 + 59(pH_0 - 7) \quad (8)$$

It is clear from Eq(8) that there is a 59 mV change in Eh per pH unit in redox reactions. The relationship of 59 mV/pH has been used by many

Table 3 Conditions used in bacteria culture batch tests

Reactor	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
Solid/Water	1:10	1:10	1:10	1:10	1:10	1:10	1:10	1:10
CH ₃ COONa (ppm)	3000	3000	3000	---	3000	3000	3000	3000
NH ₄ H ₂ PO ₄ (ppm)	300	300	300	---	300	300	300	300
FeCl ₃ (ppm)	1000	1000	1000	1000	1000	1000	1000	1500
ZnCl ₂ (ppm)	1000	1000	1000	1000	1000	1000	1000	1500
NaNO ₃ (ppm)	1000	1000	1000	1000	1000	1000	1000	---
Na ₂ SO ₄ (ppm)	---	---	---	---	---	---	---	1000
pH Adjust	Yes	Yes	No	No	Yes	Yes	No	No
Bubble Gas	O ₂	O ₂	O ₂	O ₂	N ₂	N ₂	N ₂	N ₂
Gas Pressure (MPa)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Gas Flow (mL/min)	45	45	45	45	45	45	45	90
Incubation Time (Days)	77	77	77	77	77	77	77	110

researchers to adjust measured redox potentials at a given pH for comparison between different mediums (Aomine, 1961; Patrick and Turner, 1968; Bohn, 1969 and 1971; Ponnampetuma, 1972).

It has been found that in monoelemental chemical systems, the theoretically derived Eh/pH slope of -59 in the above equation, coincide closely with experimentally determined slopes (Collins et al. 1970; Hem, 1973). But in soil systems containing many redox couples, which range widely in concentration, there is little basis for expecting Eh/pH slopes to coincide with those determined theoretically or measured in simple aqueous systems. Bohn (1969) explained that different systems might yield dissimilar Eh/pH slopes because of the complexity of the reactions regulating changes in pH and Eh and the variability in these reactions from one natural system to the next. He pointed out that many silicates, carbonates, and soluble hydroxides, which buffer pH, are not sensitive to change in redox potentials.

An interaction do exists between pH and Eh in chemical reactions of natural systems, but in many cases it is difficult to ascertain what the relationship is. The Eh/pH slope in Eq.(8) is convenient and has been used with reasonable success in making comparison. It was found that the electrode-measured redox potential is a mixed redox potential, and is mainly a response to Fe^{3+}/Fe^{2+} couple that is reversible and reaches equilibrium quickly (Chapelle et. al., 1996; Stumm and Morgan, 1996; Chapelle, 2001). This seems explain why measured Eh/pH slope in natural soil-water systems coincide closely with the theoretically derived $Eh-pH$ slope in Eq.(8).

The redox potential observed in natural soil-water system are mixed potential, which is a response of several redox reactions occurring at same time. Generally, it is considered that under certain redox potential, only one important redox reaction dominates the system. The redox potential below which one oxidized component begins to be reduced is called the critical redox potential. Table 4 lists some of the critical redox potentials for several important redox reactions at $pH=7.0$. It is believed

that calibrating the measured redox potential to $pH=7.0$ by use of the equation (8), and then comparing it with the critical redox potentials listed in Table 4 is a easier way to reveal the dominant redox reactions occurred in each reactor.

4.2 Aerobic tests

Soil suspensions in the reactors Nos.1 to 4 were characterized by higher levels of redox potentials as shown in Table 5. This is because oxygen was used to bubble the soil suspensions. Iron is a redox sensitive element; its concentration can be controlled by both Eh and pH. In aerobic conditions, iron are usually existed as ferric iron, $Fe(III)$, which is soluble only in a strong acid condition such as in reactor No.1 where the initial pH was as low as 3.9. That was why low levels iron concentration even after 77 days oxidization was maintained in reactor No.1 (see Fig.6). But in aerobic and near neutral conditions, ferric iron is insoluble and this can be proved by the fact that the concentrations of soluble Fe in reactors Nos.2, 3, and 4 became zero after the bubbling of the suspensions by oxygen gas a few days later (see Figs.7, 8, and 9).

Figure10 shows the relationship between pH and concentration of soluble zinc, in which all the concentration-pH data from reactors Nos.1, 2, 3, and 4 were plotted together as shown in 'aerobic conditions'. From Fig.10 it is obviously that soluble zinc is strictly controlled by pH: zinc precipitated out from solution when pH was higher than 7.2, however became elevated when pH decreased lower than 7. Usually, it is considered that zinc is not affected by Eh directly because of its mono-valence. This is true under aerobic conditions from the test results as discussed above.

Analysis of $Eh-pH$ diagrams for reactors Nos.1, 2, 3, and 4 (only for reactor No.3 is shown in Fig.11) indicates that hydroxide and carbonate of zinc were the main forms of precipitation. This means that the formation of zinc hydroxides and carbonates are responsible for the attenuation of zinc under aerobic, neutral and weak alkaline conditions.

Table 4 Critical redox potential for stirred soil suspensions

Redox Reaction	$Eh7$ (mV)	References
$O_2 \rightarrow H_2O$	~ 330	Turner and Patrick (1968)
$NO_3^- \rightarrow N_2$	$220 \sim$	Bohn (1971)
$Mn^{4+} \rightarrow Mn^{2+}$	$200 \sim$	Turner and Patrick (1968)
$Fe^{3+} \rightarrow Fe^{2+}$	$120 \sim$	Patrick (1964), Bohn (1971)
$SO_4^{2-} \rightarrow S^{2-}$	$-150 \sim$	Connell and Patrick (1968)

Table 5 Changes in *Eh* and pH and predicted dominant redox reactions in each reactors

Reactor No.	pH			<i>Eh</i> (mV)			Mean <i>Eh</i> 7 (mV)	Soluble Fe (ppm)		Soluble Zn (ppm)		Dominant Redox Reactions
	Initial	Final	Mean	Initial	Final	Mean		Initial	Final	Initial	Final	
1	3.9	2.8	3.2	180	409	379	156	283.0	37.8	379.6	507.3	Denitrification
2	5.0	7.2	7.6	145	323	284	320	20.8	0.0	297.3	0.0	Denitrification
3	6.7	8.7	8.7	128	272	258	358	0.0	0.0	100.1	0.0	Oxygen Reduction
4	6.6	8.6	8.0	141	235	239	296	0.0	0.0	138.7	0.0	Denitrification
5	3.9	4.5	4.4	166	131	127	-24	243.9	297.6	381.1	375.0	Iron Reduction
6	5.1	5.5	5.4	115	93	84	-13	45.4	58.2	292.4	238.7	Iron Reduction
7	7.0	8.1	8.6	68	17	35	130	0.0	0.0	52.4	0.0	Denitrification
8	6.5	7.0	7.1	-55	-180	-158	-154	42.1	102.4	190.2	0.0	Sulfate Reduction

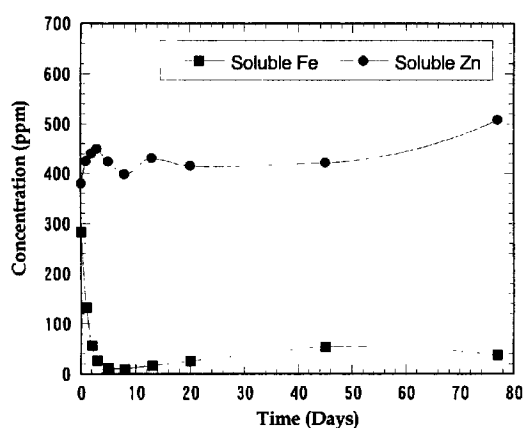


Fig.6 Changes in soluble Fe and Zn in reactor No.1

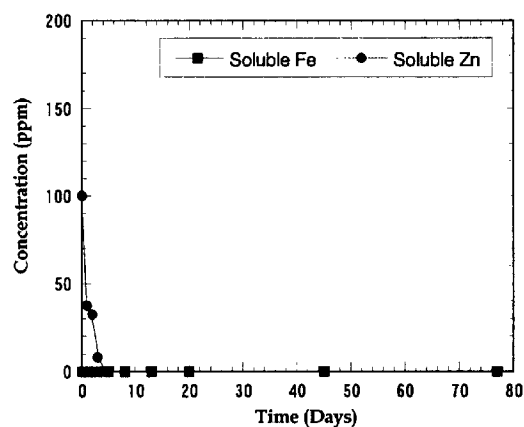


Fig.8 Changes in soluble Fe and Zn in reactor No.3

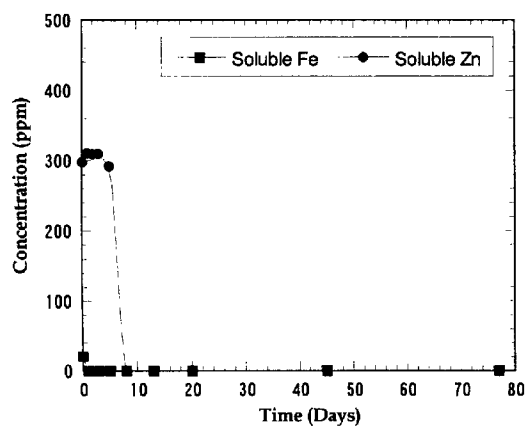


Fig.7 Changes in soluble Fe and Zn in reactor No.2

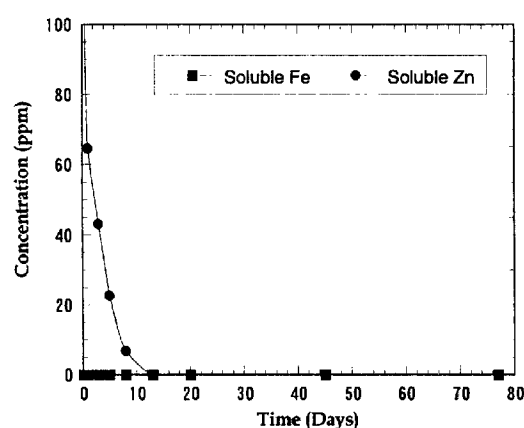


Fig.9 Changes in soluble Fe and Zn in reactor No.4

4.3 Anaerobic tests

The final *Eh* of soil suspensions in reactors Nos. 5, 6, and 7 distributed between 17~131 mV (see Table 5). In acid condition, soluble Fe in these anaerobic tests maintained higher levels than that in

aerobic conditions mentioned before (see Figs.12, 13, and 14). Also, the final soluble Fe was decreased with the increase in pH, e.g., 297.6 ppm at pH 4.5, 58.2 ppm at pH 5.4 and 0 ppm at pH 8.1 as shown in Table 5. Again, these results prove the fact

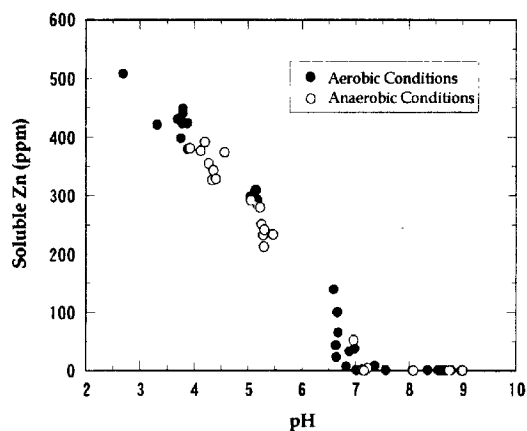


Fig.10 Relationship between soluble Zn and pH in reactors Nos.1, 2, 3, 4, 5, 6, and 7

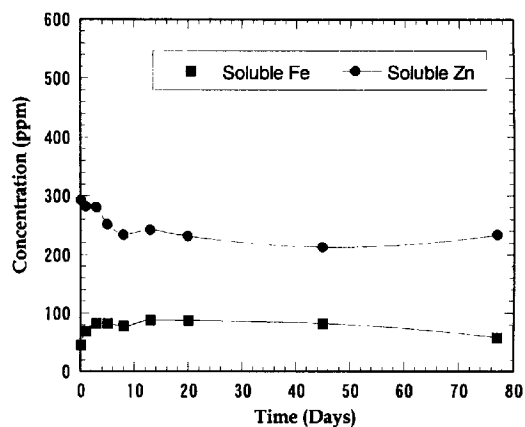


Fig.13 Changes in soluble Fe and Zn in reactor No.6

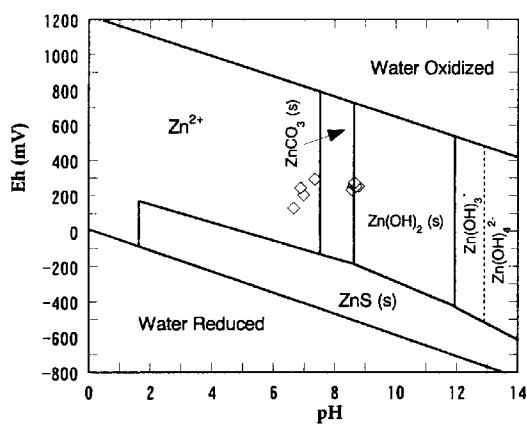


Fig.11 *Eh*-pH diagram for Zn system in reactor No.3 (*Eh*-pH diagram after Hem, 1972)

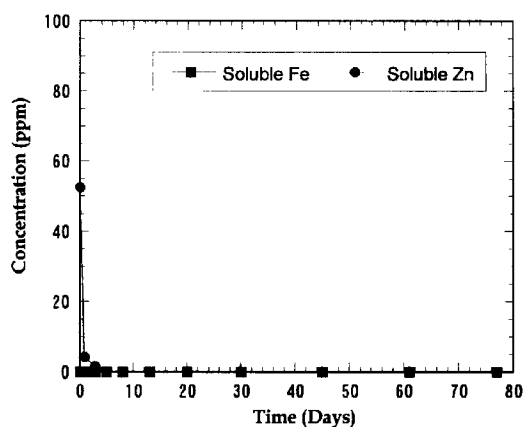


Fig.14 Changes in soluble Fe and Zn in reactor No.7

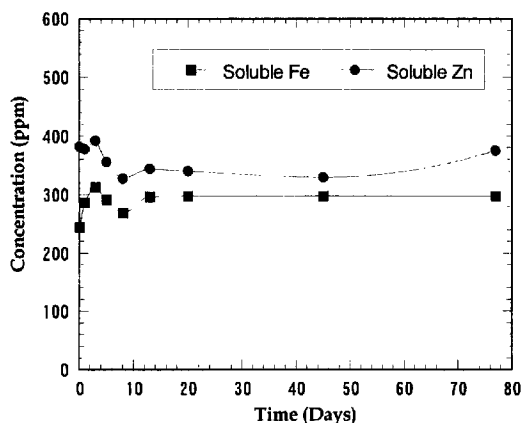


Fig.12 Changes in soluble Fe and Zn in reactor No.5

that Fe is controlled by both *Eh* and pH.

Analysis of *Eh*-pH diagrams for reactors Nos.5,

6, and 7 indicates that, in acid and moderate reduced conditions, soluble Fe was mainly controlled by the reduction of ferric iron to ferrous iron, while in neutral and weak alkaline conditions soluble Fe was mainly controlled by iron hydroxides.

The relationship between soluble Zn and pH under 'anaerobic conditions' as in reactors Nos.5, 6, and 7 is also shown in Fig.10, compared with the test results under 'aerobic conditions' as in reactors Nos.1, 2, 3, and 4. From Fig.10 it seems that the pH-dependent properties of soluble zinc in both aerobic and anaerobic conditions are the same. This means that pH is the only factor that controls the solubility of Zn even in moderate reduced conditions. Thus, it is reasonable to conclude that, in acid and moderate reduced conditions, zinc existed in soluble ionic form; but in neutral and weak alkaline conditions zinc precipitated out from solution as insoluble hydroxides and carbonates.

4.4 Strongly reduced test

Reactor No.8 is characterized by the strongly reduced conditions where redox potential was decreased from -55 to -180 mV within 111 days testing period (see Table 5). The changes in soluble Fe and Zn with test time are shown in Fig.15. Soluble Fe, at first, was increased from 42.1 to 156.5 ppm in 62 days, and then decreased to 102.4 ppm at the end of the test. Soluble Zn was decreased to zero after 30 days from the beginning of the test. Because of the reduction of ferric iron to ferrous iron, measured soluble Fe was increased before 62 days (see Fig.15). After redox potential was decreased to -150 mV, sulfate reduction occurred (Connel and Patrick, 1968). The reduced products of sulfate reacted with soluble Fe, and iron sulfide was formed. The formation of iron sulfide is considered to be mainly responsible for the decrease in soluble iron after its concentration peak at 62 days.

Figure 16 is the pH-Eh diagram for zinc system in reactor No.8. From Fig.16 it can be seen that the formation of zinc sulfide precipitation was responsible for the decrease of soluble zinc. This illustrates that under strongly reduced conditions, especially at sulfate reduction stage, the reduced products of sulfate reacted with soluble zinc and zinc sulfide precipitations were formed. This is considered to be another zinc attenuation mechanism different from that in reactor No.1 to No.7 where hydroxides and carbonates of zinc were formed.

4.5 Dominant redox reactions

Fluctuations in *Eh* and pH of soil suspensions became very little after 10 days for reactors Nos.1 to 7 and after 40 days for reactor No.8, indicating that reactions within soil-water systems tended to be dynamically stable. The statistical data of *Eh* and pH at these nearly stable stages are shown in Table 5 (called mean pH and mean *Eh*, respectively). Mean redox potentials were adjusted to pH = 7.0 according to Eq.(8), called mean *Eh*7 and also shown in Table 5. Comparing the mean *Eh*7 in Table 5 with the critical *Eh*7 in Table 4 enables a prediction of the dominant redox reactions occurred in each reactor (see Table 5).

It can be found from Table 5 that denitrification dominated reactors Nos.1, 2, and 4 even though the soil suspensions were bubbled with oxygen gas for almost 75 days. Some of the researchers believed that denitrification is strictly an anaerobic process. Nevertheless, other researchers found that denitrification can occur in the presence of oxygen

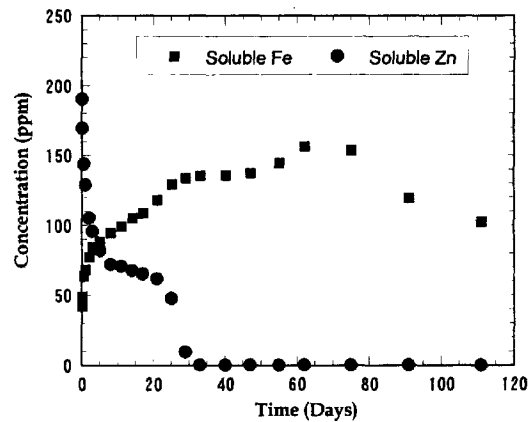


Fig.15 Changes in soluble Fe and Zn in reactor No.8

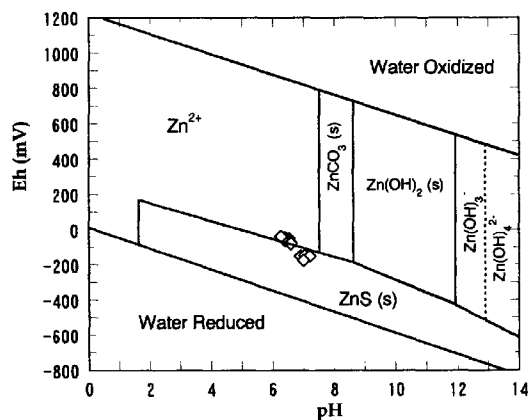


Fig. 16 *Eh* and pH diagram for Zn system in reactor No.8 (*Eh*-pH diagram after Hem, 1972)

despite oxygen's ability to inhibit denitrification (e.g., Wilson and Bouwer, 1997). The experimental results obtained from this research support the conclusion that denitrification occurs in both aerobic and weak anaerobic conditions.

Reactors Nos.5 and 6 were dominated by Fe(III) reduction reactions, while reactor No.7 arrived at the end of denitrification and soon began the reduction of Fe(III) if the redox potential *Eh*7 would decreased to 120 mV. Reactor No.8 was dominated by sulfate reduction reactions according to the results of Connell and Patrick (1968) listed in Table 4. Analyzing the dominant redox reactions is helpful to distinguish the relative importance of *Eh* and pH effects on soluble Fe and Zn.

Figure 17 shows the effects of both *Eh* and pH on solubility of iron. From Fig.17 and Table 5, it can be known that at oxygen reduction and denitrification stages, as that in reactors Nos.1, 2, 3, 4, and 7, iron existed mainly in oxidized, insoluble form, usually as

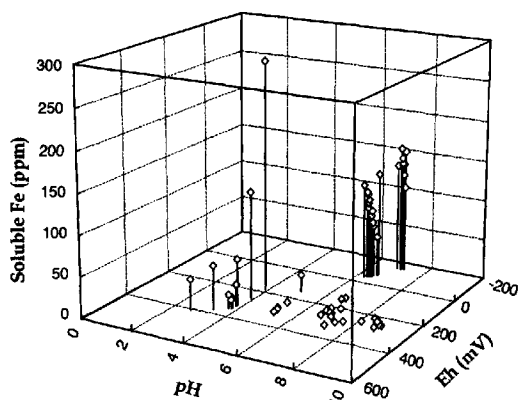


Fig.17 Effects of *Eh* and pH on solubility of Fe in all reactors

hydroxides. Only did when pH was very low as the case in reactor No.1, portion of ferric iron was dissolved. While at iron reduction stage as that in reactors Nos.5 and 6, elevated levels of soluble iron were measured, showing that the reduction of Fe(III) to Fe(II) plays an important role in iron solubility. In addition to *Eh* effect, pH also affected the concentration of soluble iron in Fe reduction stage. This can be seen from the fact that the final *Eh* of both reactors Nos.5 and 6 were almost the same (93 ~ 131 mV), while the soluble Fe was increased from 58.2 to 297.6 ppm with the decrease of pH from 5.5 to 4.5 (see Table 5).

At sulfate reduction stage, elevated soluble Fe was measured, which resulted from the reduction of Fe(III) to Fe(II). Behind the increased background, the formation of iron sulfide was considered to be responsible for the decrease in soluble Fe.

Although Zinc is not subjected directly to redox transformation due to its single valence state, its soluble levels are influenced by a number of processes that are regulated by redox potential. It was considered that under oxidizing condition, Zn is associated with Fe(III) and Mn(IV) oxides and soluble phases. Under reducing condition, Zn tends to be associated with insoluble sulfides, large molecular humic compounds and carbonates and thus decreases the mobility (Guo et al., 1997). This research indicates that, at oxidizing, denitrification, and iron reduction stages, soluble zinc seems to be controlled by pH only because the zinc concentration dependency with pH shows the same tendency even at different redox levels (see Fig.10). When redox potential was decreased so low that sulfate reduction happen, the formation of zinc sulfide precipitation

became another mechanism that controlling the attenuation of zinc.

It must be pointed out that the final pH values of all tests except reactor No.1 were increased to be larger than the initial ones as shown in Table 5. Exactly explanation about the process of pH change under various test conditions needs additional chemical and biological researches. However, it is clear that the increasing tendencies of pH were related to biological metabolism. Usually, aerobic respiration generates carbonic anaerobic conditions; the oxidation of organic carbon by anaerobic respiration pathways generates HCO_3^- , and hence increases the alkalinity (Christensen et al., 1994). Further, both iron reduction and sulfate reduction utilize protons and therefore contribute to the generation of alkalinity in the environment of organism. Recent observations have indicated that Fe(III)-reducing and sulfate-reducing bacteria may be the main route for alkalization if carbon substrates are in short supply. These observations, from another hand, indicate that redox reactions have an effect on the mobility of metals in soil water by changing indirectly the pH of the system.

5. Practical Implication

pH is one of the most important environmental factors of soil, affecting the solubility and biological availability of pollutants, and thus their toxicity and leaching potential. Metabolic reactions not only have a profound effect on subsurface redox conditions, but also influence soil water pH and alkalinity, which, in turn, affects other non-biological reactions such as sorption, solution and precipitation.

The concentration of metals in the soil solution is governed by a number of interrelated processes, including precipitation-dissolution reactions, adsorption-desorption reactions, reduction-oxidation reactions, and inorganic and organic complexations.

Zinc is a heavy metal, which poses biological toxicity and is mostly encountered in the leachate from both hazardous and municipal solid waste landfill sites. The natural attenuation behavior of it was usually evaluated without consideration of redox reactions catalyzed by bacteria. Test results of this research imply that zinc in landfill leachate might be attenuated effectively under aerobic and intermediate anaerobic conditions if pH is increased to neutral or weak alkaline conditions. Also zinc might be attenuated under strongly reduced conditions if decomposition of landfills comes to the sulfate

reduction stage. Actual observation is needed to prove the later mechanism.

As a redox-sensitive element, iron in soil and groundwater has been studied by many researchers. Up to now, elevated soluble iron concentrations have been monitored in many organic polluted sites (Lovley, 1991) and landfill sites (Lyngkilde and Christensen, 1992) due to the reduction of Fe(III) to Fe(II) catalyzed by microbiological activities. This phenomenon, in fact, has become an indicator revealing successfully the fact that soil-water system has been polluted by organic-rich contaminants.

The reactions most important in controlling pH of leachate are: (1) degradation of organic material producing CO_2 and smaller amounts of NH_3 , which form the HCO_3^- , H^+ and NH_4^+ ions; (2) reduction of CO_2 to CH_4 ; (3) reduction of SO_4^{2-} to H_2S and additional CO_2 ; (4) reduction of NO_3^- to N_2 or CH_4 and additional CO_2 ; (5) reduction of Fe^{3+} to Fe^{2+} ; (6) silicate hydrolysis of feldspar; and (7) H^+ exchange on clays. The first three are generally the most important reactions because of the high concentrations of these species (Baedecker and Back, 1979).

Typically pH values of landfills are generally in the range of 6.5-7. The pH in landfills is lower primarily because of generation of large amounts of CO_2 from waste materials, which forms carbonic acid as an intermediate product and dissociates to H^+ and HCO_3^- . On the other hand, in marine sediments, typically pH values are in the 7-8 ranges because the buffering by dissociation of calcareous material provides a major source of HCO_3^- that consumes H^+ to raise the pH. Compared with onland landfill sites, coastal landfill sites, where marine clay is employed as soil liner layer, provide a weak alkaline pH environment that tends to promote the attenuation of zinc in leachate.

It is difficult to predict how low the redox potential will be reached in each specific landfill site. However, in the case of coastal landfill sites as that in Osaka Bay, Japan the measured redox potential of marine clay was as low as -377 mV (seen Table 2), which do induce the sulfate reduction and promote the attenuation of zinc in leachate.

It must be stressed that the data produced in the laboratory microcosms should not be interpreted as the concentrations that will be present in pore waters in the field under similar physiochemical conditions. Metal solubilization in the microcosms may be promoted by continuous stirring. Also, in disposal environment, gradual leaching and removal of metals

may keep levels lower than found in the microcosms. The imposed chemical environments of the laboratory microcosms do reflect the relative changes in solubility of metals if the sediment chemical environment were changed in the field by leachate from landfills.

6. Conclusions

Based on the test results, the following conclusions can be made:

- (1) Microorganism plays an important role in redox potential and pH changes in soil-water system polluted by organic compounds from landfill leachate.
- (2) Under denitrification and Fe(III) reduction conditions, zinc is soluble and its solubility is controlled only by pH. When pH is increased higher than 7.2, zinc is precipitated as hydroxides and carbonates. Under sulfate reduction conditions, the formation of zinc sulfides becomes another attenuation mechanism of zinc.
- (3) Under aerobic and denitrification conditions, iron exists in oxidized status, which is insoluble in natural pH conditions in soil.
- (4) Under Fe(III) reduction conditions, iron exists in ferrous iron status, which is soluble and its solubility is increased with the decrease of pH. Under sulfate reduction conditions, formation of iron sulfides is responsible for a certain drop of high levels of soluble iron.
- (5) Low redox potential and alkaline conditions induced by anaerobic respiration in landfill sites tend to prompt the insolubilization of zinc but solubilization of iron, in particular in the case that natural marine clay is used to serve as a clay liner layer in offshore landfill sites.

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要 旨

廃棄物処分場の浸出水に含まれる金属イオンを対象として、微生物活動による還元反応および pH が粘土層による亜鉛および鉄の緩衝作用に与える影響を実験的に検討した。その結果、嫌気性／脱窒／鉄イオン還元条件下において、亜鉛は pH=7 以下の場合に溶解性を示し、pH=7.2 以上の場合には水酸化亜鉛および炭酸亜鉛の沈殿を形成した。また、硫酸還元状態下においては硫化亜鉛を形成した。一方、鉄については嫌気性／脱窒／自然条件の pH 下においては溶解性を示さず、鉄イオン還元／硫酸還元条件において溶解性が上昇する傾向が観察された。このことは、pH が中性域で酸化還元電位が非常に低い環境下にある廃棄物処分場においては、鉄は溶解するものの、有害重金属である亜鉛は水溶性を示さないと推測できる。

キーワード：廃棄物処分場、浸出水、酸化還元電位、嫌気性代謝、汚染