

## **GEOCHEMICAL CONDITIONS IN BURIED TRANSURANIC WASTE MONITORED USING IN SITU DEGRADATION OF CHLORINATED SOLVENTS**

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### **ABSTRACT**

In the late 1960s, drums containing sludge generated during the machining of plutonium metal were buried at the Idaho National Engineering Environmental Laboratory radioactive waste Subsurface Disposal Area. The sludge consists of carbon tetrachloride mixed with lubricating oil, contaminated with plutonium, and solidified with calcium silicate. The release and migration of transuranic elements from these drums is of concern, but predicting their long-term mobility requires information on the biogeochemical conditions in the waste. Vapor samples have been collected from soil gas above the waste disposal pits, in the vadose zone beneath the waste, and from vapor ports installed into waste. Gas samples consistently show very high concentrations of carbon tetrachloride and chloroform, although chloroform is not known to have been disposed in the Subsurface Disposal Area. Chloroform is a degradation product of carbon tetrachloride, and is readily formed under anaerobic conditions. Other known degradation products, such as methyl chloride are detected in the pits at low concentrations. A few gas samples collected from burial pits have been analyzed for oxygen, methane, and hydrogen. Oxygen is lower than atmospheric concentrations, hydrogen has been found in relatively high concentrations, and traces of methane are also detected. The relative abundance of halogenated aliphatic compounds, degradation products, and other gases, provides a method of evaluating the redox potential of the buried waste. The mobility of transuranic elements is sensitive to redox conditions and the gas-phase chemistry can provide data to assess the mobility of the transuranic elements. Plutonium occurs in the +III, +IV, +V, or +VI valence state in the environment depending on the pH and redox potential. Under methanogenic conditions, the redox potential is sufficiently low that plutonium in the drums may be converted from the tetravalent form ( $\text{Pu}^{4+}$ ) to the trivalent form ( $\text{Pu}^{3+}$ ), which is more soluble, and thus more mobile. Analysis of gas phase chemistry can provide insights into the biogeochemical processes and geochemical environment in the buried waste, which can be used to evaluate the long-term fate of transuranic elements.

### **INTRODUCTION**

At the radioactive waste Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL), the mobility of buried transuranic (TRU) waste is a primary concern in the evaluation of risk and remedial alternatives. The mobility of TRU elements, most notably plutonium and neptunium, is significantly altered by the valence state of the actinide, and will depend on the redox environment of the buried waste. Oxidation-reduction reactions involve the transfer of electrons between reactants and many of the reaction products are gaseous -  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ . Chlorinated aliphatic compounds are also involved in redox transformation either biotically or abiotically in a reducing environment. The gas-phase composition will depend on the metabolic pathways and on the terminal electron-accepting processes. This paper presents preliminary data from an investigation into the composition of the gas phase in TRU waste pits at the INEEL with the objective to identify the biogeochemical transformations occurring. From this information, we will be able to quantify the oxidation potential in the buried waste, from which the mobility of TRU elements can be calculated using thermodynamic models. We will have an estimate of the rates at which transformation reactions are occurring, from which the long-term biogeochemistry of the waste can be predicted. This knowledge will be used to develop better conceptual and quantitative models of the short- and long-term changes that will

occur in the waste. The results will support technically defensible remedial action decisions involving excavation or *in situ* stabilization of TRU waste.

## Background

The chemical composition of gas emanating from a subsurface waste site is controlled by a number of factors, but the most important of these is the action of microbiological organisms. Microbes are recognized as playing a significant role in subsurface geochemical cycles [1] and are important for biogeochemical cycling of actinides [2, 3, 4]. Other sources of gas include corrosion of metal drums and metallic actinides, radiolysis of water and organic compounds, and volatilization of co-disposed organic compounds. Of these processes, only radiolysis is unique to radioactive waste. All of the other processes are common to other landfill-type waste disposal operations. Different metabolic pathways used by microorganisms to obtain energy for life can result in a gas phase with a different chemical composition. The following section briefly discusses the processes that take place in buried TRU waste and the impact these processes will have on the chemical composition of the gas phase.

## Microbiological Processes

There are two basic energy-yielding metabolic strategies available to microorganisms, fermentation and respiration [1]. In fermentation, electrons are retained within an organic molecule or molecular hydrogen. In respiration, electrons are transferred to an external acceptor, such as  $O_2$ ,  $NO_3^-$ ,  $Fe(III)$ ,  $SO_4^{2-}$  or  $CO_2$ . Respiration is more efficient than fermentation. The amount of energy available from a terminal electron-accepting process is a function of the free energy of the reaction and the relative concentrations of the reactants and the products [1]. Energy availability from a particular process will change over time depending on changes in environmental concentrations of reactant and product species [5, 6]. The metabolic pathways available to microbes are shown schematically in Fig. 1. Under aerobic conditions, oxygen is the preferred electron acceptor. Microbes oxidize organic compounds (complex and simple) directly to  $CO_2$  and  $H_2O$  by respiration.

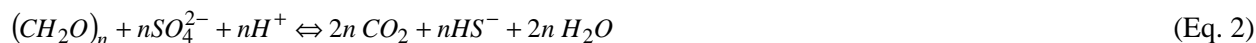


Direct oxidation of buried organic matter by molecular oxygen is not common in municipal landfills where organic loading is very high. In the buried TRU, with much lower organic carbon loading, this may be a viable process. In this case, there would be an approximate balance between oxygen consumption and  $CO_2$  production, with some loss for biomass production [4].

Under reducing conditions, microbes use a number of different metabolic pathways to extract energy from electron donors. Facultative anaerobes break down complex organic molecules (like cellulose and sugars) to simpler organic acids and alcohols. This process generates  $CO_2$  and  $H_2$  as byproducts. Once complex organic molecules are broken into more easily degraded organic compounds, anaerobic respiration can occur. Because there is little or no oxygen available, other terminal electron acceptors such as nitrate, ferric iron, and sulfate must be used. Electron acceptors are used in a distinct order, with acceptors that provide more energy being used first. Nitrate is the preferred electron acceptor once oxygen is depleted. Anaerobic respiration using nitrogen species as the electron acceptor can produce several possible gas byproducts, depending on the microbe present. Nitrogen species, such as  $NO_3^-$  and  $NO_2^-$ , are used as electron acceptors leading to gas-phase products such as  $NO$ ,  $N_2O$ , and  $N_2$ .

Anaerobic respiration can also proceed using metals as electron acceptors once the nitrate is gone. Manganese and iron are common elements in soil that occur in oxidized form and can be used as electron acceptors. Actinide elements can also serve as electron acceptors, if they are in the oxidized valence state

in the waste [4, 7]. Use of these metals for respiration does not produce unique gas-phase byproducts, and so if iron is the dominant electron acceptor, we may not see a unique gas-phase signature. Ferrous iron is much more soluble than ferric iron, and as respiration proceeds, ferrous iron will accumulate in solution. This decreases the energy available from the electron transfer reaction, and eventually, microbes will switch to an electron acceptor that provides more energy, such as sulfate. Sulfate is reduced to sulfide, and provides a partial pressure of H<sub>2</sub>S gas in the vapor phase.



When the other electron acceptors have been reduced to concentrations where microbes can no longer extract energy, anaerobic bacteria can produce CH<sub>4</sub> by using CO<sub>2</sub> as the electron acceptor and H<sub>2</sub> as the electron donor (*i.e.* CO<sub>2</sub> reduction).



The other methanogenic pathway is fermentation of organic compounds such as acetate or methanol. Bacteria ferment acetate into CH<sub>4</sub> and CO<sub>2</sub>.



Microbes can degrade hydrocarbons under reducing conditions [8, 9, 10], so it is likely that microbes are using the n-alkane hydrocarbons (C<sub>n</sub>H<sub>2n+2</sub> n > 20) in the lubricating oils disposed with some of the TRU waste sludge as an energy source.

In summary, carbon dioxide will be produced under both aerobic and anaerobic conditions in the waste. Hydrogen will be produced by fermenting bacteria breaking down primary organic compounds. Anaerobic respiration can produce NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, or H<sub>2</sub>S, depending on the primary electron acceptor. Methane will only be produced under the most reducing conditions where methanogenesis is occurring.

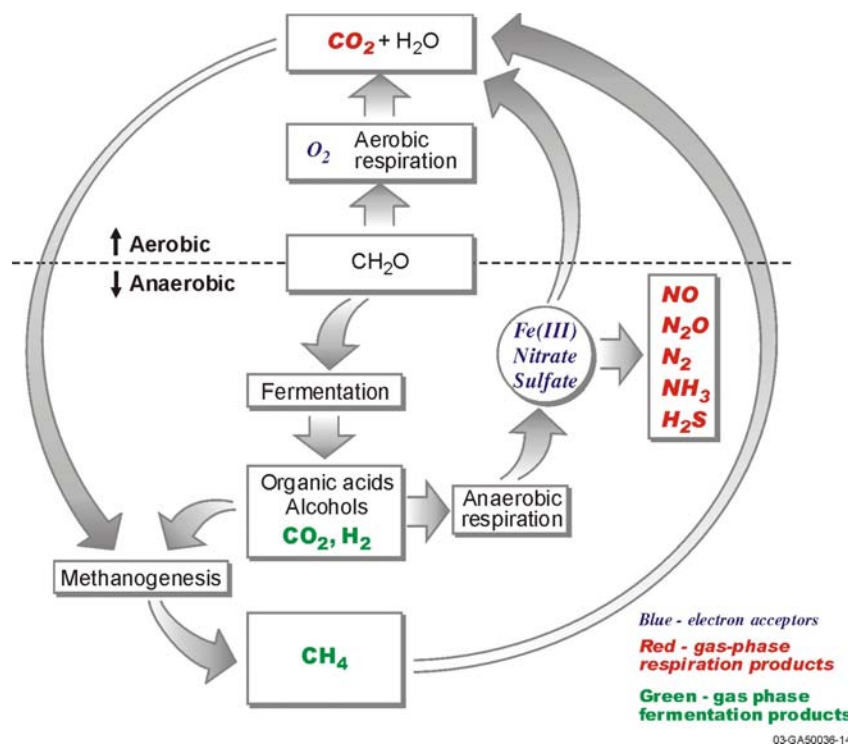
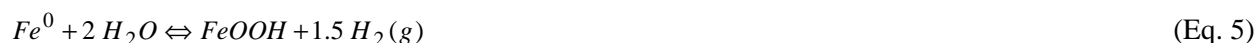


Fig. 1 Schematic diagram of microbiological processes that can generate gases in buried waste.

### Abiotic Processes

Abiotic sources of  $H_2$  include the corrosion of metal drums and metallic actinides and radiolysis of water and organic matter. The hydrolysis of carbon steel drums would generate iron oxide (goethite) and  $H_2$ .



In a study of gas generation in TRU drums, Hollis et al. [11] found that drums containing waste metals had more  $H_2$  gas generation than drums without metal. They concluded that corrosion of metals was the most important process for  $H_2$  generation in TRU waste drums. Other important  $H_2$  generating processes were radiolysis of organic matter by alpha radiation and fermentation of cellulose waste.

### Degradation of Chlorinated Aliphatic Compounds

Chlorinated aliphatic hydrocarbons, such as carbon tetrachloride, tetrachloroethylene, and trichloroethylene, are a significant component of TRU waste sludge buried at the SDA [12], and are a component of TRU waste at other radioactive waste disposal sites [13]. Because degradation of these hydrocarbons is dependent upon the redox conditions in the waste, information about them can also contribute to an understanding of the biogeochemical conditions in the waste [14, 15]. For example, chlorinated aliphatic compounds can have chlorine atoms replaced by hydrogen (reductive dechlorination) in anoxic environments [16, 17]. This can happen through abiotic and biotic pathways. Abiotic dechlorination of carbon tetrachloride is facilitated by reduced iron and sulfur species [18, 19]. Biotic pathways include dehalorespiration, where microbes obtain energy from degradation of chlorinated compounds, and cometabolism, where chlorinated compounds are degraded as a side effect of other microbial activity [15, 20, 21]. We are, therefore, interested in what information can be gained from the volatile organic compounds concerning the redox potential. In carbon tetrachloride, the carbon atom is in

the +IV valence state relative to the more electronegative chlorine. The half-cell reduction potential for carbon tetrachloride to chloroform is on the order of 0.68 V [16], placing carbon tetrachloride above nitrate in terms of reduction potential. If redox conditions in the waste are poised at a potential as high as this, then it is unlikely that methanogenesis would be occurring, because methanogenesis commonly requires potentials as low as -0.2 V. Degradation of chlorinated solvents, therefore, must also be considered when evaluating the redox potential of the buried waste.

## EFFECTS OF BIOGEOCHEMICAL ENVIRONMENT ON TRANSURANIC WASTE MOBILITY

Significant work has been done on identifying the terminal electron-accepting process (TEAP) in aquifers and saturated sediments from measurement of dissolved species [1, 5, 6]. A significant indicator of the TEAP is the  $H_2$  gas concentration [22]. Other metabolic products of the terminal-electron accepting process, such as  $N_2O$  and  $H_2S$ , are gas-phase products. Given the cost and hazards associated with sampling buried TRU waste, indirect means of assessing the TEAP in the waste would provide a method to determine microbial metabolic processes. There is a progression of terminal electron accepting species that has been identified in aquifers and aquatic sediments and is shown schematically in Fig. 2. In buried waste, a simple progression may not exist, because different electron acceptors may be in use at different locations (microenvironments) at the same time. Hydrogen gas concentration is a good indicator of the TEAP in a groundwater or aquatic sediment. When  $H_2$  gas measurements can be co-located with measurements of metabolic byproducts, quantitative estimates of the energy available to microbes can be made [5, 6].

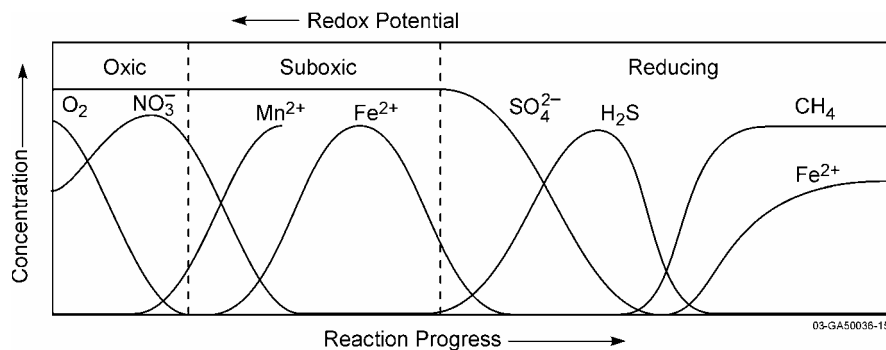


Fig. 2 Conceptual changes in concentrations of redox parameters with time in the buried waste as microbes consume more energetic electron acceptors [17].

Actinide elements exist in the environment in one or more valence states [23, 24]. Neptunium can be present in the +IV and +V valence states, and plutonium can be present in +III, +IV, +V, and +VI valence states. Terminal electron accepting processes used by microbes will poise the redox potential of the waste at or near a particular Eh while the microbes are using that redox couple. The impact this will have on the solubility of actinides can be evaluated by superimposing the redox couple potentials on a solubility diagram of the actinide elements.

Neptunium will be present in solution primarily in the +V valence state in oxic environments, but is readily reduced to the +IV valence state in suboxic or reduced environments [23, 25]. Neptunium (V) forms weak carbonate complexes in oxic ground water (Fig. 3) and solubility is limited by a sodium-neptunium(V)-carbonate mineral [25, 26]. The solubility of neptunium gradually decreases with decreasing Eh as more of the neptunium is reduced to the +IV valence state. The low solubility of the neptunium(IV) oxide ( $NpO_2$ ) helps to stabilize the tetravalent form of neptunium [4]. The minimum neptunium solubility is reached below an Eh of 0 Volts.

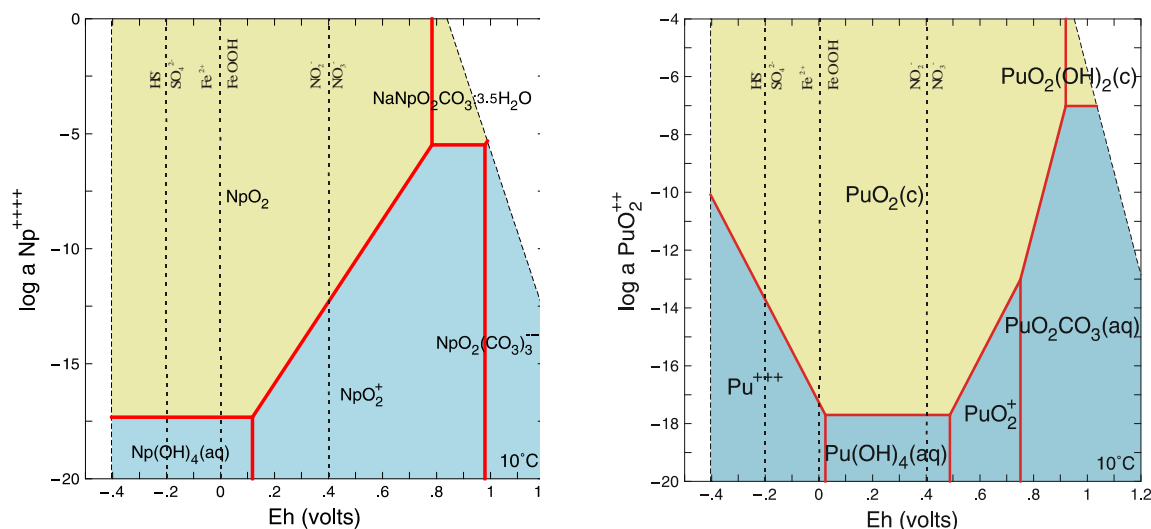


Fig. 3 Solubility of neptunium (left) and plutonium (right) as a function Eh at pH 7 in solution with 0.01 molal  $\text{HCO}_3^-$ , and 0.1 molal  $\text{Na}^{+2}$ .

Plutonium occurs in multiple valence states under the range of possible environmental pH and Eh conditions [4, 23, 24]. Plutonium phases precipitated from aqueous solutions do not yield good x-ray diffraction patterns, so precipitated solids are only characterized as Pu(IV) hydrous oxides or polymers [25, 26]. As shown in Fig. 3, formation of carbonate complexes appreciably stabilizes Pu(VI) in solution in oxic environments, but under most conditions, the Pu(IV) solid phases control plutonium concentrations [27]. Under methanogenic conditions, Pu(IV) can be reduced to Pu(III), which is more soluble than the tetravalent form of plutonium. There is some circumstantial evidence that iron-reducing bacteria can reductively solubilize  $\text{PuO}_2$  to Pu(III) [2]. Minimum solubility for plutonium occurs between Eh of 0 and .45 Volts. At Eh values below 0 Volts, Pu(III) can be formed, which will increase plutonium solubility under methanogenic conditions.

From knowledge of the active terminal electron-accepting process, the Eh at which the waste is poised can be determined. Redox couples that could exist in buried TRU waste are superimposed on Fig. 3, with the Eh value where the terminal electron-accepting process will poise the waste shown as a dotted line. The intersection of the dotted line with the solubility of the actinide reflects the relative mobility of the actinide at that redox potential. From these considerations, an Eh in the waste that was poised by the ferric - ferrous iron redox potential would create the minimum solubility for neptunium and plutonium. Under conditions more reducing, for example at the sulfate - sulfide boundary, or under methanogenic conditions, plutonium could be reduced to the Pu(III) valence state, and increase in solubility. Combining knowledge of the thermodynamic properties of the actinide elements with understanding of the biogeochemical environment, we can assess current mobility in the buried waste. By adding information on the rates of transformation and the masses of substances available, we can predict future biogeochemical environments, which forms the basis of predicting future mobility.

## STUDY LOCATION AND CHARACTERISTICS

We are testing our hypothesis in TRU waste disposal pits at the INEEL in southeastern Idaho. Significant site and waste characterization has been completed, which we can draw upon in our investigation [12]. An extensive network of gas sampling probes has been installed in the vadose zone around the buried TRU waste, and two disposal pits have been instrumented with gas sampling probes pushed directly into the

buried waste. This existing infrastructure provides an opportunity to rapidly obtain field data from which to develop models of *in situ* biogeochemical conditions and waste processes.

The SDA at the INEEL was established in 1952, covered 5.2 ha, and was used for shallow land disposal of solid radioactive waste [12]. In 1958 the landfill was expanded to 35.6 ha. Transuranic and mixed wastes, mostly from the U.S. Department of Energy Rocky Flats Plant in Colorado, were disposed here through 1970. Mixed waste containing hazardous chemical and radioactive contaminants was accepted through 1984. Since 1985, disposals in the SDA have been limited to low-level radioactive waste. Waste is buried in pits, trenches, and soil vault rows. From 1952 to 1963, waste streams were not segregated, and TRU waste was co-disposed with low-level radioactive waste. Waste packaged in drums or wooden crates was stacked horizontally in pits and trenches. Starting in 1963 (and continuing through 1969), drums of TRU waste from the Rocky Flats Plant were dumped into pits rather than stacked. Disposal of waste characterized as TRU waste was discontinued in 1970.

### **Transuranic Waste Inventory and Composition**

As a starting point for predicting future changes in buried TRU waste, we have to have some knowledge of the composition of TRU waste. Transuranic waste is in the form of contaminated materials and process waste sludges. Contaminated materials can be combustible (*e.g.* wood, plastic, anti-contamination clothing, kimwipes, rags, cardboard, laundry lint) or noncombustible (*e.g.* hand tools, power tools, pipe, lead bricks, glove boxes, cement, air filters). Process waste sludges for the principal TRU waste streams buried at the INEEL fall into two classes: inorganic precipitates and solidified organic liquids [28]. Waste streams 741 and 742 consist of a wet, inorganic sludge produced from treating aqueous process waste streams, such as ion-exchange column effluent, distillates, and caustic scrub solutions, generated by plutonium recovery operations. The sludge was produced by precipitating plutonium and americium out of aqueous solutions by addition of base and flocculation. The sludges contain hydrated oxides of iron, magnesium, aluminum, silica, plutonium and americium. Organic wastes such as degreasing agents, lathe coolant (a mixture of lubricating oil and carbon tetrachloride), and hydraulic oils were generated primarily by plutonium fabrication operations. Organic liquids were passed through a 5  $\mu\text{m}$  filter to recover plutonium before disposal. Investigation into the form of plutonium in the organic waste stream [29] showed that plutonium was present both in particulate (0.8  $\mu\text{m}$  to 5  $\mu\text{m}$ ) and dissolved (<0.01  $\mu\text{m}$ ) forms with very little of the plutonium falling between 0.01 and 0.8  $\mu\text{m}$ . The particulate plutonium was determined to be plutonium dioxide ( $\text{PuO}_2$ ) by x-ray diffraction. The filtered liquids were mixed with calcium silicate to form a paste or "grease-like" material and given waste code designation 743.

Waste sludge was placed inside one or two polyethylene bags, and then sealed inside a standard 55-gal drum. Portland cement or oil dry was added to the drum to absorb free liquids. Contaminated materials were packaged in plastic bags, metal paint cans, cardboard cartons, or polyethylene bottles. These packages were then placed in polyethylene bags and sealed in 55-gal drums or sometimes in plywood boxes [28].

Much of the combustible TRU waste will be susceptible to biodegradation in the disposal pits. Contaminated material such as wood, paper, paper products, kimwipes, rags, cloth coveralls, and cardboard can be biodegraded. The 743 sludge contains lubricating oils that provide a biodegradable carbon source. Some of the waste packaging, including plywood and cardboard boxes, will also be susceptible to biodegradation. Transuranic waste is not associated with the very high amounts of biodegradable organic matter from household waste commonly found in sanitary waste landfills, but organic carbon sources are expected in the buried TRU waste.

Based on waste disposal records and process knowledge for waste generation activities, estimates of the inventory of TRU radionuclides and associated hazardous constituents have been developed for the INEEL SDA [12, 30]. The actinide inventory is on the order of 280,000 Ci. The largest source of TRU activity is currently from Am-241, which will decay to Np-237. An estimated 1,100 metric tons of solvents contaminated with TRU elements were co-disposed with the TRU waste. Carbon tetrachloride is the principal volatile organic contaminant making up about 75% of the total. Other significant solvents are 1,1,1-trichloroethane, tetrachloroethylene, and trichloroethylene. Based on review of records and waste generation processes at the Rocky Flats Plant, essentially no chloroform was disposed at the SDA [30].

### **Observation and Sampling Probes in the Waste**

Characterization of buried waste is a difficult task. In 1999, the INEEL installed a series of probes directly into waste pits to obtain more information about the composition and activity. A direct-push sonic system was used so that no cuttings or contamination were brought to the surface. Two kinds of probes were installed:

- Type A probes are hollow stainless-steel casing with the bottom sealed to permit borehole logging in the waste zone,
- Type B probes contain various types of instruments to collect samples or to obtain measurements on waste characteristics. Type B probes include tensiometers to measure water tension, suction lysimeters to collect water samples, and vapor ports to collect gas samples. Another Type B probe is the visual probe. Visual probes consist of transparent polycarbonate tubes, which permit visual inspection of the overburden, waste zone, and underburden using a miniature video camera.

Vapor monitoring ports are being sampled in two areas of the SDA. The organic sludge focus area is an area in one of the waste disposal pits where a large number of drums of 743 sludge generated from processing of plutonium at Rocky Flats Plant is buried. The depleted uranium focus area contains depleted uranium that was roasted, or oxidized, to stabilize the otherwise pyrophoric material. There are a total of nine vapor probes installed in these two areas at depths between 1.5 m and 6.2 m below ground surface. Vapor ports are monitored periodically for volatile organic compounds. Emphasis is placed on three compounds that risk assessment models [31] show could pose an unacceptable risk: carbon tetrachloride, methylene chloride, and tetrachloroethylene. Samples are also collected for a more complete suite of volatile organic compounds, which includes degradation products of the more prevalent volatile organic compounds. In addition, samples are periodically collected for redox-indicator gas analysis including O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>.

Hydrogen may be produced by microbial and abiotic processes that take place under strongly reduced conditions, while methane is produced only by biotic pathways. The prevalence of hydrogen over methane



(Table I) and the relatively low levels of carbon dioxide, suggest that abiotic processes, such as drum corrosion, have more effect on the gas-phase chemistry in the pit than biotic processes such as fermentation. Oxygen and hydrogen can coexist metastably if there is not a catalyst to initiate a reaction. The presence of these two gases in the pit likely results from atmospheric gases diffusing down through the cap and mixing with waste-degradation products diffusing out of the drums. This leads us to believe that there are microenvironments in the buried waste where more reduced conditions exist. Hydrogen and CH<sub>4</sub> produced in these microenvironments diffuses out into the void space between waste containers.

Table I Results of recent gas-phase redox gas analyses of samples collected from vapor ports installed in transuranic waste pits at the SDA

Date Sampled	Probe	Port Depth (m)	Oxygen (ppmv)	CO <sub>2</sub> (ppmv)	Methane (ppmv)	Hydrogen (ppmv)
6/10/2002	743-08-VP1	6.2	55,300	3,200	630	12,200
11/20/2002	743-08-VP2	4.1	19,000	2,000	310	–
2/18/2003	743-08-VP2	4.1	53,000	7,000	320	8,810
5/21/2003	743-08-VP1	6.2	58,000	10,000	–	–
8/6/2003	743-08-VP1	6.2	53,000	10,000	260	8,310
6/10/2002	DU-10-VP2	3.0	162,000	2,700	30	80
5/21/2003	DU-10-VP2	3.0	115,000	2,100	–	–
8/6/2003	DU-10-VP2	3.0	140,000	3,000	< 70 U	< 180 U
	Air		210,000	400	< 1	< 1

flags: U – nondetect

Chlorinated solvents from the 743 sludge are very apparent in gas samples from shallow probes installed in the cap over the waste, from Type B probes installed in the waste, and from vapor ports installed in the deep vadose zone beneath the pits. Results of gas analyses on samples collected from Type B probes installed into disposal pits (Table II), show that chloromethanes with 1, 2, 3, and 4 chlorine atoms are present. Chloroform was not a component of the 743 sludge waste stream, and there are no known chloroform disposals of any significance in the SDA. Likewise, chloromethane is not a known component of buried TRU waste. Small quantities of methylene chloride were shipped to the INEEL from Rocky Flats. We hypothesize that the chloroform, most of the methylene chloride, and chloromethane are being generated *in situ* by reductive dechlorination of the carbon tetrachloride. Whether this is taking place biotically or abiotically is not known. Both processes have been commonly discussed in the literature [15, 32, 33, 34, 35, 36].

Table II Results of Recent Gas-Phase Chlorinated Methane Analyses of Samples Collected From Vapor Ports Installed in Transuranic Waste Pits at The SDA

Date Sampled	Probe	Port Depth (m)	Carbon tetra-chloride (ppmv)	Chloro-form (ppmv)	Methylene chloride (ppmv)	Chloro-methane (ppmv)
11/20/2002	743-08-VP2	4.1	42,000	19,000	550	1,500
2/18/2003	743-08-VP2	4.1	47,000	11,000	500	680
5/21/2003	743-08-VP1	6.2	29,000	12,000	730	1,400
8/6/2003	743-08-VP1	6.2	26,000	9,800	710	950
5/21/2003	DU-10-VP2	3.0	2,400	540	27	, 670 U
8/6/2003	DU-10-VP2	3.0	2,800	650	< 65 U	< 90 U

flags: U – nondetect

Table III Selected Chemical Properties of the Chloromethanes. Relative Reaction Rates from [16].

Chemical	Carbon tetrachloride	Chloroform	Methylene chloride	Chloromethane
Formula	CCl <sub>4</sub>	CCl <sub>3</sub> H	CCl <sub>2</sub> H <sub>2</sub>	CClH <sub>3</sub>
Valence of C	+4	+2	0	-2
Relative reduction rate	High	Low	Very Low	Very Low
Relative oxidation rate	Very Low	Low	High	High

Carbon tetrachloride contains carbon in a very oxidized valence state (Table III), and is readily reduced to chloroform under reducing conditions. Chloroform is much less readily reduced, and so concentrations of chloroform reduction products (methylene chloride and chloromethane) would be expected to be much lower than the concentration of chloroform. Because carbon tetrachloride is an oxidized compound, it will be relatively stable once it diffuses out of the drums in the oxidized vadose zone around the pits. Chloroform is not readily oxidized, and so is also relatively stable in the vadose zone. Both methylene chloride and chloromethane are easily oxidized. It is likely that when the gases diffuse out of the pits and into the surrounding sediments microbes oxidize or cometabolize the more reduced chloromethanes so they will not be present in the environment. A sampling program is planned for vapor ports in and around buried TRU waste this fiscal year to test this hypothesis.

#### **SOURCE TERM EVOLUTION MODELING**

Application of multiple process models to interpret gas data obtained from a waste site will allow us to quantify the biogeochemical processes occurring in buried TRU waste. Once the biogeochemical processes are quantified, we can predict how the waste environment will evolve over time, and how that changing environment will affect the mobility of TRU waste material. These predictions are a critical step in identifying source term evolution in performance assessment studies. Such predictions require, of course, that we make a number of assumptions about the specific physical and chemical conditions of the waste. By considering a number of simplifying assumptions about boundary conditions of the subsurface environment, and several alternative initial conditions, we can use mathematical models of gas generation processes to simulate how the depletion of organic matter, corrosion of sealed TRU waste drums, and other waste alterations will occur in the environment identified through our analysis of gas composition.

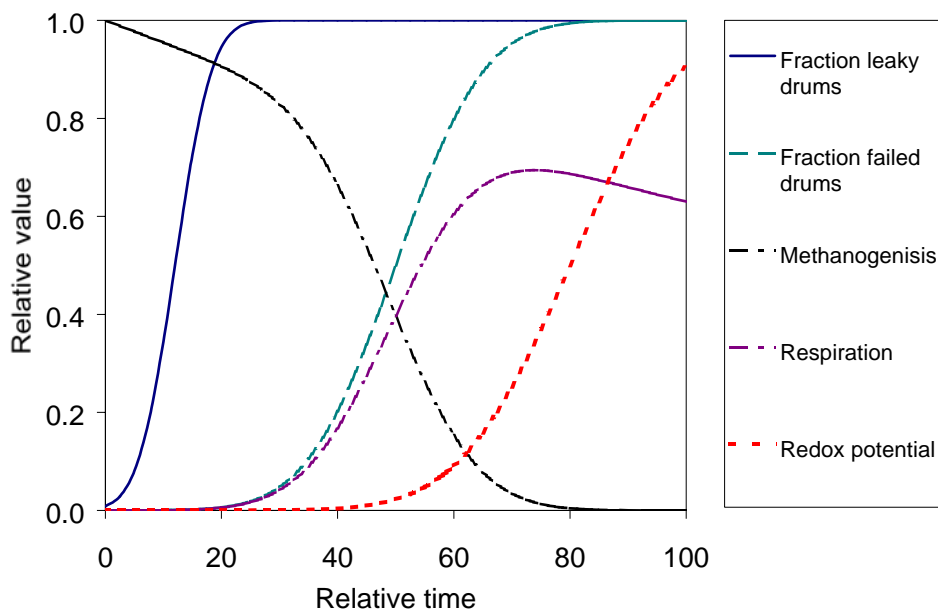


Fig. 4 Conceptual model of the changes in importance of methanogenesis and respiration in TRU waste as waste drums fail, allowing electron receptors to reach the waste.

At this time, our models are only conceptual, and we have not begun developing process-based mathematical models. As an example of the type of long-term predictions possible, we show in Fig. 4 a conceptual model of the effects of waste transformation in a buried TRU waste site. Soon after burial, drums begin to leak, allowing gases generated in the waste drums to escape. During the early stages of their decay, the drums are intact enough that diffusion of oxygen into the drums is severely limited and liquids, potentially carrying other electron acceptors, cannot enter. In the anaerobic conditions that prevail at that stage, fermentation of the organic material in the drums, followed by methanogenesis takes place. Methane and  $H_2$  escape from the drums into the void space between the drums. Over time, the drums continue to corrode, and eventually lose completely their ability to limit gas and liquid exchange with the surrounding medium. Once this occurs, infiltration can carry electron acceptors to the waste (dissolved sulfate, nitrate) and oxygen diffuses more rapidly into the waste. Methanogenesis is then replaced by respiration (anaerobic and aerobic) and the oxidation / reduction potential in the waste, previously held at very low potentials because of methanogenesis, begins to rise. As the organic matter in the waste is depleted, the redox potential rises until fully oxic levels are reached. The changes in redox conditions in the waste can be directly related to TRU waste mobility in flow and transport studies for performance assessment. The objective of our modeling effort, however, is not to conduct transport modeling but rather to (1) predict the evolution of the waste over time and (2) provide estimates of how the evolving biogeochemical environment will likely affect TRU waste mobility. In this illustration, for example, mathematical models of the processes affecting gas generation, combined with waste inventory and geochemical data, would provide a means of determining the time scale over which the illustrated processes would occur.

## SUMMARY

Characterization of buried TRU waste to support remedial action decisions represents a significant challenge to the Department of Energy. Monitoring and sampling approaches that can provide information on the mobility and long-term stability of buried waste that do not require penetration into the

waste will be more cost effective and much safer than drilling and sampling. Gas-phase chemistry in and around the waste is related to the biotic and abiotic processes taking place inside the waste. From the chemical composition of the gases, we can infer the processes taking place. From an understanding of the geochemical environment under which those processes take place, we can infer the geochemical conditions in the waste. This understanding of conditions within the waste and changes in those conditions over time will permit a better understanding of the long-term stability of buried TRU waste.

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