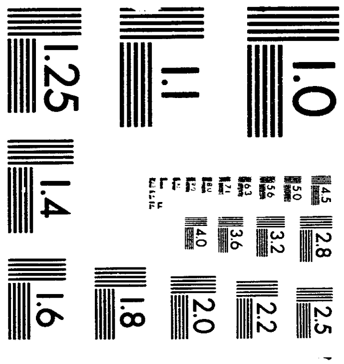

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Title: **CASE STUDIES OF CORROSION OF MIXED WASTE AND TRANSURANIC WASTE CONTAINERS**

Author(s): STANLEY T. KOSIEWICZ

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CASE STUDIES OF CORROSION OF MIXED WASTE AND TRANSURANIC WASTE DRUMS

STANLEY T. KOSIEWICZ
Los Alamos National Laboratory, PO Box 1663, MS K570
Los Alamos, New Mexico 87545

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ABSTRACT

This paper presents three case studies of corrosion of waste drums at the Los Alamos National Laboratory (LANL). Corrosion was not anticipated by the waste generators, but occurred because of subtle chemical or physical mechanisms. In one case, drums of a cemented transuranic (TRU) sludge experienced general and pitting corrosion. In the second instance, a chemical from a commercial paint stripper migrated from its primary containment drums to chemically attack overpack drums made of mild carbon steel. In the third case, drums of mixed low level waste (MLLW) soil corroded drum packaging even though the waste appeared to be dry when it was placed in the drums.

These case studies are jointly discussed as "lessons learned" to enhance awareness of subtle mechanisms that can contribute to the corrosion of radioactive waste drums during interim storage.

BACKGROUND

Mild steel drums are some of the most frequently used containers for the interim storage of mixed low level wastes (MLLW) and transuranic wastes (TRU). Department of Energy (DOE) facilities have hundreds of thousands of such drums in interim storage. Delays in both treatment and disposal options for these wastes increase not only their storage times, but also the potential for container degradation.

This paper presents information on three unusual cases of drum corrosion experienced at LANL during the past three years. None of these incidents caused release of any of the contained radionuclide components. The corroded drums were all placed in overpack containers as a precautionary measure pending treatment or final disposal.

CORROSION OF CEMENTED SLUDGE DRUMS

In the first case, pitting and general corrosion degraded 1-2 year-old, 55-gallon mild steel drums containing a cemented TRU sludge wasteform. Routine inspection of the exterior of the drums uncovered corrosion blisters and streaking of the drums' walls. Examination of the drum interiors showed fairly extensive corrosion of both the drum walls and the drum lids. Chemical analysis of corrosion products showed primarily iron with higher concentrations of manganese which could have originated from localized concentrations (nodules?) of it. Manganese is added to the steel as an alloying material to scavenge sulfur. The manganese nodules could then be the areas for corrosion initiation.

The waste generator did not anticipate this corrosion because the TRU sludge had its pH adjusted to 9 to 13 prior to its cementation. Then it was emplaced directly into the drums. Corrosion would be expected to occur at a more acidic pH (e.g. 5.5 to 6.5) in the anode region of the corrosion area. While no free liquids were found, a pH of 12 to 13 was measured by litmus paper on a moist section of a corrosion tubercle inside one of the drums. This apparently contradictory pH observation can be explained by corrosion theory. Figure 1a shows that the center of a tubercle can have a pH of 5 to 6.5 while Figure 1b shows the outer region can be basic as a result of displacement of corrosion products to the cathodic region of the corrosion cell.

The following hypothesis can explain the initiation of the pitting corrosion even though the cemented waste form was initially basic. Most of the pitting corrosion tubercles were observed to occur either at the interface of the cement monolith and the headspace gases inside the drum or at areas were the cement layer coating on the drum wall is very thin. At these regions, the pH of the cement could become more acidic through absorption of carbon dioxide from the headspace gases. The carbon dioxide could be continuously replenished as gases are "inhaled and exhaled" through the drum lid filters which are a recent requirement for TRU waste containers. The driving force for this breathing is diurnal temperature variation which can cause thermal expansion and contraction of contained gases with subsequent pressurization, then depressurization of drum headspaces. At LANL, daily waste storage temperatures may vary as much as 50°F during the summer months. This can produce pressure differentials large enough to force gas movements.

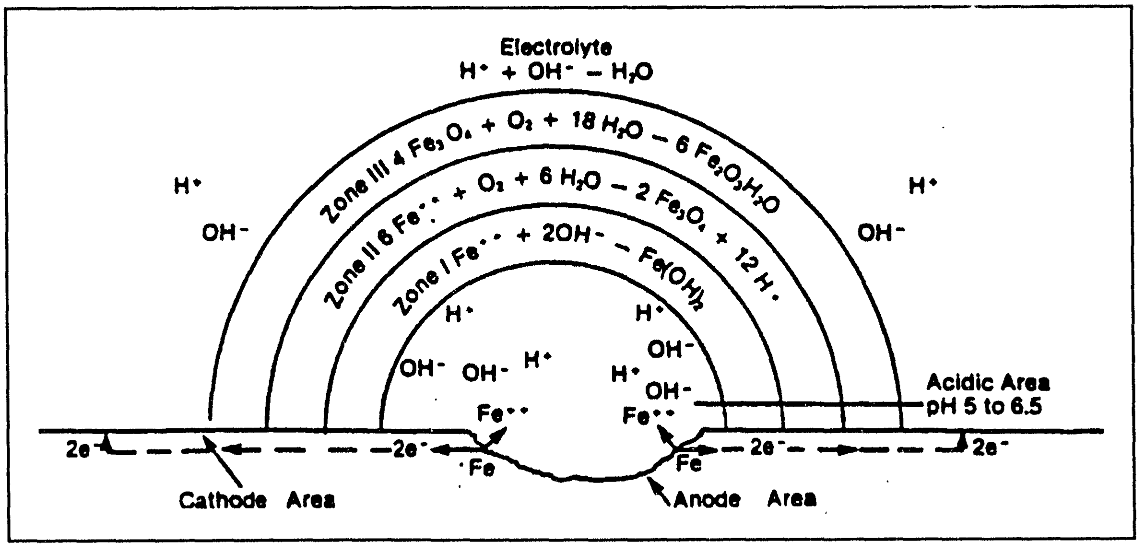

Fig. 1a. Anode reactions. (from Ref. 1)

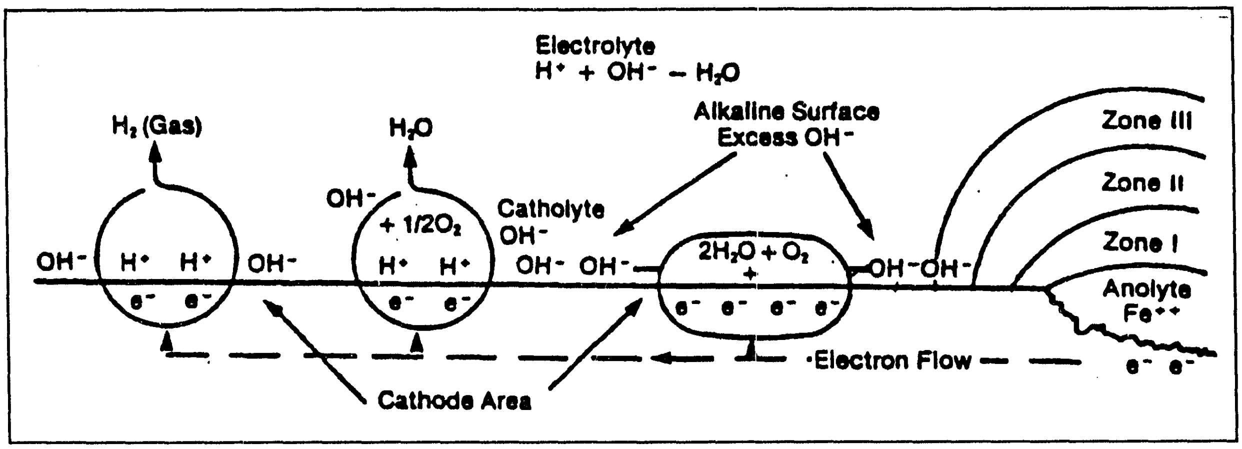

Fig. 1b. Cathode reactions. (from Ref. 1)

A publication by Hobbs[2] substantiates the proposed hypothesis. His paper reports on corrosion experiments which verify the decrease in pH (i.e. towards more acidic) of high level wastes contained in carbon steel tanks as air is purged through the tank. The purging is intended to remove radiolytically-generated hydrogen, but it also reduces hydroxide ion. The latter is decreased through reaction with carbonic acid to form carbonate and bicarbonate ions. The weakly dissociated carbonic acid is formed by the absorption of atmospheric carbon dioxide.

Additional support for the hypothesis was provided by examination of unvented cemented-sludge drums. Two drums which had been retrievably buried for ten years showed much less interior and exterior corrosion. These drums did not have filters in their lids, nor were they subject to wide temperature fluctuations because of the thermal mass of the overlying earthen cover. Both of these factors would prevent replenishment of carbon dioxide within the headspaces of the drums.

Future containers for this waste stream will consist of drums with a polyethylene liner that is bonded directly to the drum's interior wall via a rotational molding process. These drums are manufactured by ENPAC Corporation (Cleveland, OH).

CORROSION OF MIXED WASTE PAINT STRIPPER DRUMS

In a second case, a 55-gallon drum containing a 30-gallon drum with paint stripper-contaminated rags appeared to be pressurized because of its bulging lid. An assessment method was devised wherein an industrial hygienist determined that the drum was not pressurized. Then, the overpack drum was opened for examination of its contents.

Figure 2 shows the interior surface of the lid of the 55-gallon drum. It was covered by features which resembled stalactites. These were quite thin and hollow. They were attached to a coating on the drum lid that appeared to be glazed. Chemical analysis of the products on the drum lid and wall showed that they were primarily iron. No exterior rusting of the overpack drum was visible.

The following hypothesis can reasonably explain these observations. The primary components of the paint stripper, a commercial product called "Chemstrip," are methylene dichloride, methanol, and isopropanol. The boiling point of methylene dichloride is low, 105°F. Summer temperatures in the drum storage area are sometimes as high 120°F. Consequently, the methylene chloride could vaporize inside the 30-gallon drum and escape from it if the gasket on its lid were not tightly sealed[3]. Inside the 55-gallon drum, the organic vapors could condense on the drum lid

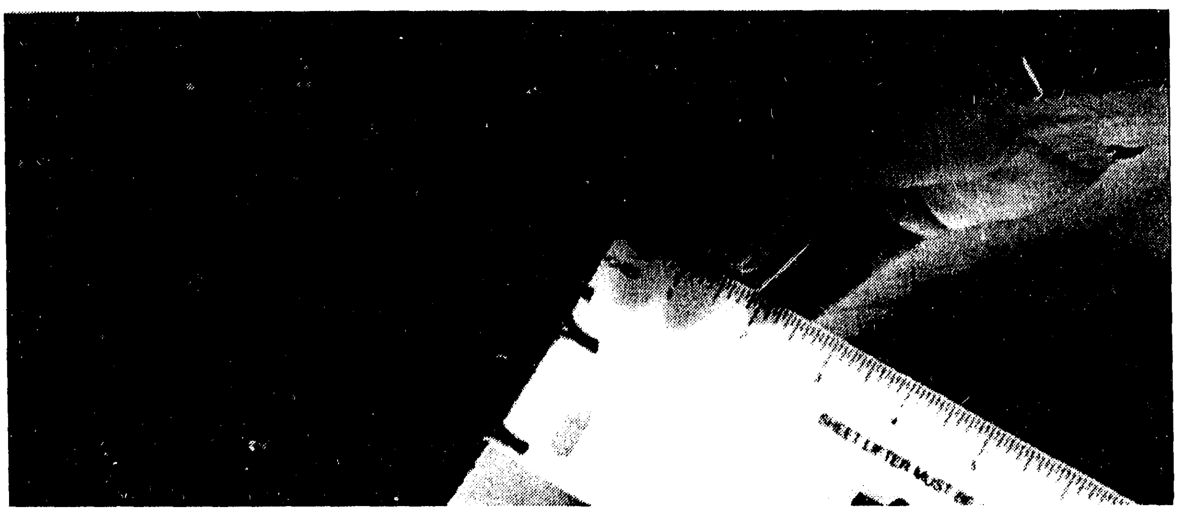

Fig. 2. Rust stalactites on lid of 55-gallon drum.

because of the cooler night temperatures. This cycle could be continuously repeated with the diurnal temperature variations causing the drums to behave like reflux condensers.

As vapors condensed to form a liquid on the lid, some corrosion could occur followed by subsequent dripping to produce the rust stalactites observed on the lid. Condensation on the drum walls would cause corrosion of them.

During the summer months, wall temperatures of black drums exposed directly to the sun can be as high as 160--180 °F[4]. If a drum of this waste were exposed to direct sunlight while temporarily stored on a loading dock, the potential could have existed for relatively high temperatures to cause the proposed mechanism to occur with high probability. For this waste stream, temperature control of the storage area may be an important consideration since the potential for mobility of the contained chemical is enhanced because of its low boiling point.

CORROSION OF MIXED LOW LEVEL WASTE SOIL DRUMS

In the third case study, blistering was observed on the exteriors of drums containing a mixed low level waste. The drums contained suspect-lead, suspect-radionuclide contaminated soil from a decommissioning and decontamination operation. The soil appeared to be dry when placed in the drums. Neither lead nor radionuclides were found in the blistering product, although some sulfate was. A drum manufacturer proposed that surface contamination prior to painting might be the initiator of the blisters.

Since sulfate was present, a hygroscopic salt potentially could have been trapped on the drum surface by the paint film. Diurnal temperature variations could pump water vapor through the film to the salt with subsequent condensation on the cooler metal surface (see Figure 3). Through repeated vaporization and condensation cycles, the paint film could peel away slightly from the steel to form a blister. This appeared to be an attractive hypothesis to explain the blistering phenomenon.

However, it was incorrect. As a prudent measure, some of these drums were opened to obtain visual confirmation that the blistering only affected the exterior of the drums. Some liquid dripped off the lids on opening. This was attributed to the indigenous water content of the local soils. This

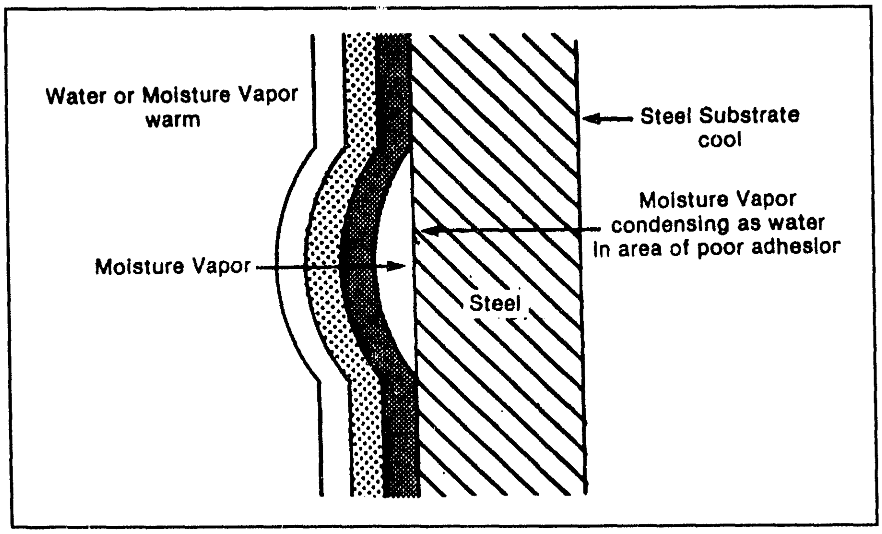

Fig. 3. The thermal gradient effect on a coating with poor adhesion. (from Ref. 1)

may range from 3 to 10% depending on the depth from which the soil was obtained. One of these waste drums could contain 500 pounds of soil, and consequently, as much as 50 pounds of water.

There was a very thick coating of corrosion product over the interior walls of the drums. At an area where there was a blister on the drum's exterior, there was a pitting corrosion tubercle on the interior. In some cases, the tubercles had breached the drum wall. Consequently, the exterior blisters were produced by the corrosion which was occurring inside the drum. While some microbiologically induced corrosion (MIC) cannot be discounted, the MIC contribution would be limited by the lack of suitable nutrients[5]. Farmer[6] suggested that dirt on metal surfaces can form crevices with the potential for subsequent crevice corrosion; such corrosion proceeds rapidly. Use of plastic liners inside the drums would be one way to eliminate corrosion of these waste containers.

CONCLUSIONS:

These three case studies illustrate some of the subtle physical or chemical mechanisms that can cause corrosion of waste drums. Protection of the interior of waste containers through liners or formed-in-place liners is desirable. Temperature control for waste storage areas may be desirable for certain waste forms to decrease the effects of diurnal temperature variations.

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