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ELECTROCHEMICAL DECONTAMINATION OF PAINTED AND HEAVILY CORRODED METALS.

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ABSTRACT

The radioactive metal wastes that are generated from nuclear fuel plants and radiochemical laboratories are mainly contaminated by the surface deposition of radioactive isotopes. There are presently several techniques used in removing surface contamination involving physical and chemical processes. However, there has been very little research done in the area of soiled, heavily oxidized, and painted metals. Researchers at Los Alamos National Laboratory have been developing electrochemical procedures for the decontamination of bare and painted metal objects. These methods have been found to be effective on highly corroded as well as relatively new metals. This study has been successful in decontaminating projectiles and shrapnel excavated during environmental restoration projects after 40+ years of exposure to the elements. Heavily corroded augers used in sampling activities throughout the area were also successfully decontaminated. This process has demonstrated it's effectiveness and offers several advantages over the present metal decontamination practices of media blasting and chemical solvents. These advantages include the addition of no toxic or hazardous chemicals, low operating temperature and pressure, and easily scaleable equipment. It is in our future plans to use this process in the decontamination of gloveboxes destined for disposal as TRU waste.

Introduction.

Radioactive metal wastes generated from nuclear fuel plants or radiochemical laboratories are mainly contaminated by the surface deposition of radioactive isotopes. In most cases, the radioactivity is located in a 10 μm thick surface layer\(^1\). Therefore any surface layer removing method should be useful as a decontamination technique.

Radioactive metal decontamination techniques can be divided into three groups: chemical, electrochemical, and physical. In chemical decontamination an acid and/or complexing agent\(^2\) (sometimes combined with an reducer\(^3\) or oxidant\(^4,5\)) is applied to dissolve a surface metal oxide layer or metal itself. In electrochemical decontamination a metal surface dissolution reaction is driven by an electric current flow. Physical decontamination methods include simple mechanical removing of contaminants as well as more advanced techniques such as plasma arc gouging.

Electrochemical decontamination is considered a very useful method because of a high waste volume reduction factor and easy application to metal wastes of various shapes. Many studies have been done in developing and optimizing various electrochemical decontamination processes\(^6,7\). However, there exist very little literature about decontamination of heavily corroded or painted metals. A treatability study consisting of two waste streams was implemented to research the viability of electrochemical decontamination of highly corroded metal. The first stream consisted of corroded metal projectiles and various pieces of shrapnel that were unearthed during environmental restoration (ER) activities at Los Alamos National Laboratory (LANL). The projectiles were used in tests which dated back to 1940's. These metal objects were contaminated with natural uranium. The second waste stream consisted of strontium-90 contaminated augers and drill heads. These augers and drill heads had been used to collect soil samples in an unrelated ER project. Corrosion was present on the augers and drill heads but was much less severe than the corrosion present on projectiles and shrapnel. It was our goal to...
process these metal pieces and remove radioactivity to background level. Upon doing this, the augers and drill heads can be reused in future ER projects and the projectiles and metal shrapnel can be sent to a smelter as recycled metal.

The decontamination of painted metals is a unique problem limited to few analytical laboratories dealing with radioactive samples. At LANL, the investigation into depainting and decontamination was fueled by gloveboxes and fume hoods that had been painted every year to immobilize traces of radioactive material. Over the years, several paint layers were accumulated, each one containing some radioactivity. Another use for this technology is the decontamination of lead safes used for storing radioactive samples. The interior and exterior of these safes has been painted to change removable contamination into fixed radioactive contamination.

Decontamination of painted metal consists of removing paint layers and, in some cases, a thin layer of metal. Like bare metal decontamination methods, decontamination of painted metal can be chemical, physical or electrochemical. Chemical paint removal methods consists of applying chemical agent causing chemical changes in paint structure like hydrolysis or oxidation of the paint. Ultra high pressure water, high pressure sand or CO₂ blasting and paint dissolution in solvent - paint stripper are the examples of physical painted metal decontamination. Electrochemical decontamination is the least known method. It consists of applying a DC current to cause paint stripping.

Although this technology can be applied to many types of painted metal, we investigated paint stripping on steel gloveboxes and lead safes.

Experimental details.

All decontamination experiments were conducted in a aqueous solution baths. In the electrochemical decontamination steps, Dimensionally Stable Anodes (DSA, a titanium grid covered with a rare earth oxides) and carbon steel cathodes were used. The solution composition varied depending on the object to be decontaminated. A Soersen DCR 20-115B2 rectifier was used as a DC power source.

Surface radioactivity was measured before and after each step of decontamination. The β + γ radioactivity was measured with Eberline SRM 100 monitor with 15.5 cm² of probe surface area. An Eberline TA55HF monitor was used to determine α radioactivity (with 72 cm² probe). Because decontamination to a background level was our goal, only the total radioactivity was measured without the distinction of removable and fixed contamination.

Thickness of dissolved metal layer was calculated on base of the charge passed through the solution. An uniform dissolution rate was supposed, independent of geometrical configuration.

Electrochemical decontamination of painted metal was conducted in 0.1 M Na₂SO₄ + 10⁻⁴ M NaOH solution. In this procedure, the objects to be depainted were made cathodic and DSA was used as the anode. If paint was well intact and provided no exposed metal surfaces for electrical contact, the object was scratched in 1.5x1.5 cm grid. This provided electrical contact with the power supply leads and exposed some metal surface for electrical contact with solution. Current varied form 15 to 400 mA/cm² (calculated from the whole, painted and exposed surface). Voltage depended on applied current and varied from 10 to 20 V. Solutions were not externally heated or cooled. However, the temperature would rise to 60 - 100°C due to ohmic heating. Current was applied for 3 to 30 min. and loose paint was removed with plastic scrub or paper towel.

A ASTM # f23359-95a method was used to determine initial and residual paint adhesion. Paint removal efficiency was calculated as a percent of surface from which paint was removed.

Results.

Projectiles.

A total of 38 projectiles were received. They varied in size from 2 to 4 inches (5 to 10 cm) in diameter, 1 to 30 inches (2.5 to 76 cm) in length, and 0.5 to 80 lb. (0.23 to 36 kg) in weight (total 1050 lb = 476 kg). All projectiles were covered with a thick layer of soil, dust, and rust. According to records, the projectiles were contaminated with uranium. Three projectiles were covered with a yellow cake of uranium oxides. The initial contamination level varied from just above background to 10⁵ cpm (counts per minute) β + γ and up to 5000 cpm α.

Due to soil and corrosion, there was no possibility to establish an electrical contact with projectile. Therefore an initial wash in 0.2 M citric acid solution was applied to remove the loose dirt, soil, and some corrosion products. After washing some radioactivity was removed (Fig. 1).
Electrolytic decontamination was used as the second and third steps. Initially, projectiles were made cathodic in 0.1 M H2SO4. DSA served as the anode. Current flow (up to 100 mA/cm²) causes a reduction of the surface layer iron oxides and hydrogen gas evolution. Reduction of the surface oxides lowers an adhesion of the thick rust layer to the projectile. At the same time, hydrogen bubbles strip pieces of rust off the projectile’s surface. During cathodic decontamination no metals were dissolved and the composition of electrolyte did not change. After filtering off soil and pieces of rust, the electrolyte was reused. After this step a majority of the corrosion products were removed easily from projectile’s surface.

Finally, projectiles were made anodic in the same solution. A stainless steel beaker served as both the electrolytic cell and cathode. The projectiles were connected to the positive pole of a rectifier. Current flow (about 10 mA/cm²) caused dissolution of the thin surface layer of the projectile. Depending on the contamination level various electrolysis times were used. The shortest time of electrolysis (2 hours) resulted in stripping of 25 μm thick layer from the surface. During the typical time of electrolysis (4 hours) 50 μm of metal was removed. In three cases electrical currents up to 40 mA/cm² were used and electrolyses were conducted for 48 hours. This allowed for 2400 μm (2.4 mm) of the projectile’s surface to be dissolved (supposing that the dissolved metal was iron).

Surface radioactivity was measured after each step of the decontamination. The results for 6 projectiles are presented in Fig 1.

Generally all projectiles could be divided into four groups: a) projectiles decontaminated with citric acid, b) projectiles which needed all three steps of decontamination, c) projectiles on which some additional radioactive sources were exposed after citric acid wash, d) projectiles with volume contamination.

The first three groups are represented in the graph below. The projectiles described as “with screw” and “#18” belong to group (a), “nail” and “middle” to belong to group (b), and “large” and “drill” - to group (c).

Only 3 projectiles belonged to group (d). All three projectiles were initially covered with a yellow cake and possessed an upper part that was badly damaged. Initial radioactivity readings showed up to 75,000 cpm β + γ and 5000 cpm α. Washing in citric acid removed the yellow cake from the top of the projectiles but it did not result in contamination decrease. Both, cathodic and anodic decontaminations failed to lower the radioactivity on these three projectiles. A 2.4 mm thick layer of the projectile’s surface was removed before further efforts were abandoned. It was concluded that these projectiles were volume rather than surface contaminated. Average projectile density, 15.7 g/cm³, and composition of electrolyte after anodic dissolution of projectile surface (28.6 g/L of U, 24.0 g/L of Fe) suggest that an uranium was a major component of these projectiles’ alloy.

All but three projectiles were decontaminated to meet free release criteria. One projectile marked “1945” (mark become visible after decontamination) is to be displayed in Los Alamos Science Museum.

The chemical composition of solutions from each step of decontamination was determined using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy). In each case RCRA (Resource Conservation and Recovery Act) elements were present but concentrations were below disposal limits (100 ppm for Ba, 5 ppm for As, Ag, Cr and Pb, 1ppm for Cd and Se, 0.2 ppm for Hg).

Shrapnels

Fifty shrapnel pieces of various sizes and compositions were received (56 lb., 25.4 kg total). The majority of them (45) were made of brass (83% Cu, 34 % Zn, 2.8% Pb), 3 were made of aluminum, 2 - steel. In Toxicity Characteristic Leaching Procedure (TCLP) test brass shrapnels leached 8.3 ppm of lead and were therefore considered a Mixed Low Level Waste. Both aluminum and steel shrapnel passed TCLP tests.

Treatment procedure involved overnight washing in 1 M acetic acid and anodic dissolution. Stainless steel beakers or aluminum foils were used as cathodes. Voltage was kept below 4 V, current depended on dimensions of a shrapnel. For the smaller pieces 0.1 A was used, for the larger ones the current was equal to 3 A. This translates to current density approximately 50 mA/cm². The time of electrolysis depended on contamination level. Less contaminated pieces were electrolyzed for 4 hours, more contaminated ones up to 20 hours. This is equal to a 260 to 1300 μm thick surface layer being stripped in order to achieve decontamination. One acetic acid solution was used for electrolysis of up to 10 shrapnel.
During the electrolysis some metal powder was deposited on cathode. This powder was removed and the electrolyte solution was filtered before reuse. The metal powder consisted of copper, lead and cadmium and it did not pass the TCLP test (8.3 ppm of Pb, 1.0 ppm of Cd in the TCLP test).

![Graph of results](image)

**Figure 1. Results of projectiles decontamination**

Five shrapnel pieces consisted of separable smaller parts. These pieces were disassembled and each part was monitored for contamination and treated separately. In two cases contamination was found on surfaces exposed after the disassembly. Small non-metallic parts from the disassembly were rinsed with diluted (0.2 M) nitric acid. Rinse solution contained no RCRA elements. This solution was disposed of to the Radioactive Wastewater Treatment Plant (RWTP) and the non-metallic parts to the laboratory radioactive trash boxes.

Six brass shrapnel were very badly damaged and contained deep cracks and holes. They required electrolysis for up to 20 hours. Even after this amount of time, some dark spots on shrapnel’s surface remained radioactive. Tests showed that these dark spots are insulators and during electrolysis only shrapnel’s bare metal was dissolved. These spots remained unchanged. Radioactivity was removed from these spots by rinsing them with 1 - 2 mL of 30% HNO₃.

Aluminum and steel shrapnel, as well as steel screws from shrapnel disassembly were first washed in 0.2 M HCl. After acid wash the radioactivity of aluminum pieces and screws was reduced to the background level. The ICP-AES analysis showed no presence of RCRA elements and the solution was disposed of to the RWTP. Two steel pieces were still radioactive (one up to 400 cpm β + γ, second up to 700 cpm β + γ; no α). They were electrolyzed in the same manner as the brass shrapnel.

Examples of treatment results are presented on the graphs below. All shrapnel shown on the graph were made of brass.

Each step of treatment removed some decontamination. Washing in acetic acid removed some loose dirt and part of the contamination. Anodic decontamination lowered the radioactivity to background level and brass shrapnel recovered their gold-like appearance. All shrapnel were decontaminated and meet the free release criteria.
Augers and drill heads.

A total of 3 drill heads and 20 augers were received and treated (~1900 lb. = 862 kg). These objects were contaminated with Sr90 and this contamination was fixed. Alpha contamination was found neither on augers nor on drill heads. The contamination with β + γ emitters was a spot-type and activity varied from 400 cpm to over 2000 cpm.

![Graph](image1)

**Figure 2.** Results of shrapnel decontamination.

The augers and drill heads were subjected to a two-step decontamination. The first step consisted of an overnight washing in 0.1 M H₂SO₄. The wash bath had a volume of 100 L. During the overnight washing a surface layer of the auger was dissolved and the acid concentration decreased below 10⁻² M. From acid concentration drop, auger's surface area (15200 cm²), and supposing uniform dissolution of auger we calculated that 50 μm thick layer was dissolved. In the morning the washed auger was removed and rinsed with tap water and a new auger was placed in the bath. Concentrated sulfuric acid was added to reach H₂SO₄ concentration 0.1 M and a new auger was left in the bath till the next day. No stirring was used. One volume of the bath was used to wash 5 augers. The solution from the bath was subjected to ICP-AES analysis and chromium concentration was found to be 500 ppm and iron concentration was found to be 30 g/L. This solution was neutralized to pH between 6 and 7 in order to precipitate chromium and iron hydroxides. After separation only 0.5 ppm of chromium was found in this solution. No other RCRA elements were present and the solution was disposed to the RWTP.

The cake was filtered under vacuum and dried. Solid hydroxides (a mixture of Fe(II), Fe(III) and Cr(III) hydroxides) passed the TCLP test and were disposed of as a low-level waste.

After the first step of decontamination the augers and drill heads remained radioactive and were submitted to a second step. This step consisted of electrolytic removal of a metal surface layer. An auger (or a drill head) served as an anode and a carbon steel grid was used as a cathode. 100 L of 0.1 M
H₃PO₄ was used as an electrolyte. The augers were electrolyzed for 16 hours with 30 A current (it allowed to dissolve 42 μm thick iron layer). The voltage did not exceed 4 V. After the electrolysis the augers were rinsed with tap water and allowed to dry. The radioactivity was then measured again. After the separation of a small amount of solid (iron phosphate), the electrolyte solution was analyzed by ICP-AES. No RCRA components were found and the solution was disposed to the drain.

All objects were decontaminated to the background level, free released and reused by the ER project. The decontamination procedure produced about 33 lb. (15 kg) of chromium and iron hydroxides, 0.44 lb. (0.20 kg) of iron phosphate and 4.41 lb. (2 kg) of soil collected from the bottom of the tank. All these solids passed TCLP test and were disposed of as a low level waste.

Painted metals.

Preliminary paint removal investigations were done with uncontaminated brass, aluminum, lead, and carbon and stainless steel objects. The study focused on effectiveness of paint stripping and radioactivity removal from objects. No records describing the paints that were encountered during the study were available. Paint was easily and completely removed from all but aluminum metal substrates. The depainted, bare metal surface were clean and bright. We have found no dependency of paint removal efficiency on initial paint adhesion. However, the paint possessing the greatest adhesion did offer the least amount of electrical contact.

Decontamination and depainting investigation involved only lead. These objects included painted lead safes that had been contaminated by various radioisotopes. In some cases the radioactive contamination was removed with the paint layers. However, some objects did require additional bare metal decontamination after the paint was removed. In all cases, radioactivity was brought to background levels. Results are presented on Fig. 3.

**Figure 3.** Results of decontamination by Electrochemical Depainting (EDP).

**Discussion and Conclusions.**

**Electrolytic decontamination of bare metals.**

Electrolytic decontamination allowed for the removal of radioactive components to a background level from all but three of the treated objects. These three objects were made of uranium alloy as discussed earlier.

In comparison with literature data (10 μm) a much thicker surface layer had to be removed: 25 to 50 μm for projectiles; 260 to 1300 μm for shrapnel, and 50 to 100 μm for augers. The shrapnel exhibited the widest range of surface dissolution. In some cases over a 1 mm thick surface layer was dissolved. This could be a result of ununiform current distribution during electrolytic decontamination. Radioactivity was removed relatively easily by dissolving a 10-50 μm thick layer from the flat surfaces of the brass.
shrapnel. This was confirmed by radioactivity measurements. After the first hour of electrolysis (what corresponds to 65 μm layer dissolved) a majority of the shrapnel's surface was free of contamination. The only radioactivity found resided within deep cracks and holes or within dark electrically insulated spots. The rate of metal dissolution inside these cracks and holes was much slower than dissolution from surfaces parallel to counter electrodes. This results in the thickness of metal dissolved inside cracks to be substantially lower than and average value calculated from electrical charge.

There is a second difference with literature data. The lowest values of dissolved metal thickness are 3-5 times higher than literature data. This can be explained by the way the objects geometrical surface was calculated. To determine surface area, the object was approximated by the closest geometrical body. The surface areas of the projectiles were calculated based on a cylinder, a rectangular prism was used for shrapnel, and a cylinder and a flat with a flat metal strip (blades) for augers. The exposed surface area of the objects were pitted by corrosion. Therefore, true surface area could be a several times larger than that of a smooth geometrical figure. Taking this into account, the differences between literature values (10 - 20 μm) and experimental values (25 -100 μm) become meaningless.

Electrolytic decontamination of painted metals.

There are two aspects of electrochemical paint decontamination: the mechanism of paint removal and applicability of the method on the large scale.

Three mechanisms could be responsible for electrochemical paint removal:

1. Reduction of the surface layer of metal oxides leading to substantial decrease of paint adhesion.
2. Mechanical removing of the paint by gaseous hydrogen forming between paint and a metal surface. This is accomplished by the electrolysis of water. At the cathode (the metal to be depainted) H\(^+\) cations and/or water is reduced and hydrogen gas is generated:
   \[ 2H^+ + 2e^- \rightarrow H_2 \text{ (gas)} \]
   \[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]
3. Paint hydrolysis on the border between paint and bare metal. Due to water reduction a pH on the surface of the metal can be locally very high. This is demonstrated in the above equation by the generation of OH\(^-\) on the cathode.

This study does not supplied any arguments to choose one of these three possibilities. In our opinion all three mechanisms work together.

Applicability of any method is governed by three factors: effectiveness (if it works), costs, and safety. Experiments showed the electrochemical depainting works very well for lead, brass and steel but did not supply enough data to fully predict costs of the operation. However, we have collected sufficient information to compare the safety of presented process with other available paint removal processes. The most probable application for large scale EDP would be processing the painted, heavily contaminated gloveboxes that exist within the LANL complex. Therefore, we can compare our techniques with those that have been proposed to depaint and decontaminate these gloveboxes.

Electrochemical decontamination of painted metals is a low temperature, ambient pressure method. In the best conditions paint removal rate was about 5000 cm\(^2\) per minute. This means that an average glovebox could be depainted in 3 to 5 hours. Mechanical means using paint strippers (chemical or solvent based) and abrasives have taken weeks of manual labor to accomplish the same square footage of cleaning. High pressure methods can achieve the same rate of paint removal but present many hazards when operating in the glovebox environment. Extremely intensive water (or CO\(_2\)) jets can easily cut through gloves, flesh, plastic or even glass. EDP leaves a bright shiny metal surface which is very desirable and will be a good indicator of decontamination for future use of the glovebox. EDP and ultra high pressure water decontamination are the only techniques leaving bright metal surface without additional polishing step.

REFERENCES.


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