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Use of Sorbent Materials for Treating Hazardous Waste

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LIST OF ACRONYMS

AFB	Air Force Base
ARDEC	(Army) Armament Research and Development Environmental Center
CTC	Concurrent Technologies Corporation
DLA	Defense Logistics Agency
DoD	Department of Defense
DRMS	Defense Reutilization and Marketing Service
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
IEC	Industrial Ecology Center
LDR	Land Disposal Restrictions
NADEP-JAX	Jacksonville Naval Aviation Depot
NCDEE	National Defense Center for Environmental Excellence
PFT	Paint Filter Test
SS	Stainless Steel
TCLP	Toxicity Characteristic Leaching Procedure

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- Naval Aviation Depot, Jacksonville, FL
- Tobyhanna Army Depot, PA
- Tinker Air Force Base, OK

Technical material contained in this report has been approved for public release.

1.0 EXECUTIVE SUMMARY

The Department of Defense (DoD) spends millions of dollars each year to dispose of hazardous liquid wastes from military facilities.

The Defense Logistics Agency (DLA) alone spent \$23 million during fiscal year 1994 to dispose of 64 million pounds of liquid hazardous materials. This cost figure encouraged the DLA to find a better and cheaper disposal solution. Recognizing that industry uses sorbent materials to absorb chemical and oil spills in industry, the DLA thought these materials could also be used to treat liquid hazardous wastes. Therefore, through an Environmental Security Technology Certification Program (ESTCP) funding, DLA tasked the National Defense Center for Environmental Excellence (NDCEE) under an existing contract managed by the Army Armament Research and Development Energy Center (ARDEC) Industrial Ecology Center (IEC) to evaluate sorbents for this purpose. The NDCEE is operated by Concurrent Technologies Corporation (CTC), a non-profit organization headquartered in Johnstown, Pennsylvania.

Hazardous waste disposal is expensive. If liquid hazardous wastes could be effectively treated by sorbents, cheaper sanitary landfill facilities could be used. This project sought to identify, demonstrate and validate a simple, efficient and cost-effective technology based on sorbents. Three representative DoD wastes were chosen for investigation: paint wastes, degreasing solvents, and acidic electroplating waste.

Following preliminary screening, six classes of non-biodegradable sorbents were tested: non-biodegradable peat, non-encapsulating polymeric, encapsulating polymeric, zeolitic, clay, and cellulosic. Bench-scale investigations on surrogate wastes showed: (1) waste acids containing heavy metals (nickel, cadmium, chromium, lead and zinc) up to 100 ppm could be rendered non-hazardous using treated clay sorbents; (2) no sorbent acceptably treated ignitable paint-related waste; and (3) no sorbent acceptably treated chlorinated solvent degreasing waste.

Although these tests showed that sorbents are not a universal cost-effective solution, the most successful sorbent/waste combination, a treated attapulgite clay, was subsequently used in on-site demonstrations during August and September 1997 for stabilization of the acidic metal-finishing waste generated by three DoD facilities. These facilities were the Naval Aviation Depot, Jacksonville, Florida, Tobyhanna Army Depot, Pennsylvania, and Tinker Air Force Base (AFB), Oklahoma. The treated attapulgite clay successfully solidified and stabilized acidic waste containing up to 100 ppm heavy metals.

A cost analysis of this application to heavy-metal-contaminated spent electroplating bath contents showed that the savings realized by using the treated attapulgite clay mixture depend on the cost of conventional off-site hazardous waste disposal, which varies from site to site. Cost savings might only be marginal. Clay treatment costs were estimated at \$0.78 per pound of waste acid treated compared to the conventional hazardous waste disposal cost of \$0.45 to \$1.25 per pound.

As a general solution, sorbents are not recommended for treating hazardous waste streams generated by the DoD, although they have considerable value for spill control purposes. At heavy metal concentrations above 100 ppm, an appropriate use of the treated attapulgite clay may be in spill neutralization and containment through solidification, but the sorbed material would have to be

managed as hazardous waste unless further treatment could be applied to reduce the toxicity hazard of the heavy metals. However, use of sorbent clays may be an attractive waste management option for very small volume generators of acidic heavy-metal contaminated streams. Another possible niche is waste battery acid, due to favorable performance with lead contaminants.

2.0 TECHNOLOGY DESCRIPTION

2.1 DEVELOPMENT HISTORY

Sorbent materials are used to absorb chemical and oil spills in industry today. Therefore, sorbents were considered candidates for a cost-effective treatment for hazardous liquid wastes. The overall project to find a viable sorbent technology comprised four phases:

Phase I - sorbent materials were selected for bench-scale evaluations, a regulatory assessment was undertaken, and DLA's liquid hazardous wastes were categorized.

Phase II - six sorbents were evaluated at bench-scale on three waste streams.

Phase III - a preliminary economic analysis was performed by comparing the best sorbent material tested to current practices of waste treatment.

Phase IV - on-site demonstrations were performed at three Department of Defense (DoD) facilities using the most promising waste/sorbent combination.

In Phase I, sorbent technology was assessed through literature searches, vendor information, regulatory review, and previous test applications (ref. 1). As a result, six classes of non-biodegradable sorbents were recommended for testing: non-biodegradable peat, non-encapsulating polymeric, encapsulating polymeric, zeolitic, clay, and cellulosic. The selection was limited to those sorbents listed or certified as non-biodegradable, thus suitable for landfill disposal, and in a class well established in the marketplace. The majority of DoD-generated liquid wastes that have high disposal costs were categorized into three groups: paint related waste, degreasing solvent waste, and aqueous heavy-metal containing waste. This gave a bench-scale matrix with 18 (6 x 3) combinations. Candidate waste streams selected in Phase I of this project represent more than 90% of the liquid hazardous wastes disposed by the Defense Reutilization and Marketing Service (DRMS).

In Phase II, the sorbents were evaluated on a bench-scale (ref. 1). Of the 18 combinations of sorbent/hazardous waste, only one—attapulgite clay treated with additives—for treatment of aqueous heavy metal waste passed all three tests required before being permitted for landfill disposal. The Phase III preliminary economic analysis (ref. 2) showed that while the commercial vendor-supplied product (Spill-X-A, Ansul Products) was too expensive, formulating the product from its chemical components would allow cost-effective treatment. Other clay mixtures (vermiculite and bentonite) with additives did not satisfy either treatability or economic requirements.

The Environmental Security Technology Certification Program (ESTCP) funded on-site demonstrations performed at Jacksonville Naval Aviation Depot (NADEP-JAX), Tobyhanna Army Depot, and Tinker Air Force Base (AFB). These demonstrations constituted Phase IV of the project. A Task Plan, including test plan, safety plan, and QA/QC plan was written (ref. 3).

2.2 PROCESS DESCRIPTION

Sorbent materials are defined as solid materials that take up and hold liquids by means of absorption, adsorption, or both. Clay type materials are used extensively as sorbent materials since they are able to absorb and bind organic liquids within their bulk lattice. Also, their ability to bind inorganic compounds via their ion exchange capacity makes these materials very effective in spill clean-up and, therefore, likely candidates for a cost-effective treatment of DoD hazardous liquid wastes.

A surrogate, acidic, heavy-metal containing waste was formulated for bench-scale testing. This surrogate contained approximately 100 ppm Cd, with approximately 500 ppm each of Cr, Pb, Ni, and Zn, in a 10% (by volume) HNO₃ solution.

In order to reduce the cost of sorbent to an acceptable level, the on-site demonstrations were conducted with a treated attapulgite clay mixture sorbent formulated (with the concurrence of the vendor) from the component raw materials found in the successful commercial sorbent (Spill-X-A, Ansul Inc., Marinette, Wisconsin). The formulation was approximately 86.25% attapulgite clay (Mg-Al-silicate), 8% magnesium oxide, 5% sodium carbonate, and 0.75% dispersant (Petro AGS). It could be formulated at an approximate cost of \$0.20/lb compared to \$0.70/lb purchase price of vendor-supplied material. The sorbent was used in a 2:1 ratio (by weight) with liquid waste streams (i.e. 0-5:1 liquid waste: sorbent).

2.3 TECHNICAL ADVANTAGES

The major advantages are the avoidance of hazardous waste disposal costs, transportation off-site, possible need to transfer to drums, and preparation of associated mandated manifest documentation. It is also an easy-to-operate, low technology process, which does not increase concerns for operator safety/hazard over conventional practices.

2.4 TECHNICAL DISADVANTAGES

An additional process step (mixing of waste with the sorbent) is involved, which necessitates investment in mixing equipment, and additional materials handling. Also, it is a method for stabilization, not destruction, of wastes. It does not have universal application to a given category of hazardous wastes, only to specific waste/sorbent combinations.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

This project's objectives were to identify, demonstrate and validate a simple, efficient and cost-effective technology using sorbents to treat DoD-generated hazardous wastes.

Data were generated to support the following criteria for waste/sorbent combinations:

- Suitability for immobilizing free liquids
- Suitability for eliminating characteristically hazardous properties or constituents
- Waste/sorbent material compatibility
- Waste volume increase/decrease
- Treatment economics

To be permitted for land disposal, sorbed wastes would have to meet three requirements:

1. Pass the EPA's Paint Filter Test (PFT) (ref. 4).
2. Meet the Land Disposal Regulations (LDR) for the chemical constituents.
3. Eliminate the ignitability or corrosivity of the waste, if applicable.

The PFT determines the presence of free liquids in the sorbent/waste mixture. The PFT test calls for a specific mass of sample to be placed in a funnel lined with a paint filter. The sample is left standing for 5 minutes. Any free liquid visible below the funnel indicates sample failure. If moisture in the sorbed mixture does not drain from the filter within a predetermined time then the mixture passes the PFT.

The Land Disposal Restrictions requires that the waste does not leach a hazardous constituent as measured by the Toxicity Characteristic Leaching Procedures (TCLP). The focus of the TCLP testing for this work was cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn). To pass the TCLP, the leachate must contain less than 5 mg/l for Cr, Pb, Ni, 6.3 mg/l for Zn, and 1 mg/l for Cd.

The sorbent/waste mixture cannot be land disposed if it poses a characteristic hazard (ignitability, corrosivity, reactivity or toxicity). The characteristic hazard of interest in this application is corrosivity. If the pH of the sorbent/waste mixture is above 2.0 standard pH units, and below 12.5 standard pH units, then the mixture is not characteristically corrosive.

The LDR regulations for the metals of concern are 1.0 mg/l Cd, 5.0 mg/l Cr, 5.0 mg/l Pb, 5.0 mg/l Ni, and 5.3 mg/l Zn.

Details of the required performance standards for ignitability and corrosivity may be found in ref. 5 and ref. 6 respectively.

Three major factors were investigated to establish the effectiveness of each sorbent:

1. The compatibility of each sorbent with each waste stream.
2. The ability of the sorbed material to pass the EPA's Paint Filter Test (PFT).

3. The ability of the sorbents to retain, or bind, the constituents that are listed in the LDR Phase II standards for that specific waste.

A Task Plan (Test Plan, Safety Plan, and QA/QC Plans) was written for the on-site demonstrations (ref. 3).

In addition to these factors, other testing was performed to determine the efficiency of each sorbent, namely:

1. The L-Test (Sorbency Testing) (ref. 7) was used to determine the maximum amount of waste that each sorbent was capable of sorbing. The L-Test puts a specific mass of sorbent (contained within a nylon mesh container) into the waste, and subjects it to standard immersion and drainage times. To be conservative, half of the L-Test value was chosen as the waste:sorbent application ratio to allow for variations in mixing and to ensure no free liquids would result. A minimum mixing ratio was also set at 0.5:1 waste:sorbent to put an upper limit on the volume increase of the treated waste, and to ensure that adequate mixing would be possible.
2. Volume, mass and temperature changes were used to determine how the volume and mass of the waste were affected by the addition of sorbents.

3.2 PHYSICAL SETUP AND OPERATION

Three DoD-relevant waste streams were selected for Phase I bench-scale testing: (1) paint-related wastes; (2) aqueous, heavy metals waste; and (3) degreasing solvent waste.

Paint-related wastes contained methyl ethyl ketone, toluene, and xylene. This stream was chosen to determine (1) if sorbents could reduce or eliminate waste ignitability, and (2) if sorbents could retain or bind the hazardous organic solvent components to meet the LDR Phase II standards.

The aqueous, heavy metals waste was a surrogate consisting of five metals: 104 mg/l cadmium (Cd), 498 mg/l chromium (Cr), 538 mg/l lead (Pb), 512 mg/l nickel (Ni), and 511 mg/l zinc (Zn) in a 10% by volume nitric acid (HNO₃) solution. This waste was chosen to determine (1) if the sorbent can neutralize an acidic liquid, and (2) to determine if the sorbent can retain or bind the metals in order to meet the LDR Phase II standards.

The LDR regulations for the metals of concern are 1.0 mg/l Cd, 5.0 mg/l Cr, 5.0 mg/l Pb, 5.0 mg/l Ni, and 5.3 mg/l Zn.

The degreasing solvent waste was chosen to determine if sorbents can retain or bind the organic solvents responsible for making the waste hazardous. This wasted stream was not flammable and contained no heavy metals. It consisted of trichloroethylene, trichloroethane, tetrachloroethylene, and motor oil. The solvents represent the majority of the degreasing solvents used in DoD and industrial operations.

Testing both during Phase II and during the Phase IV on-site demonstrations was conducted using laboratory glassware and hand-held stirrers. All selected sorbents were tested following procedures

contained in the EPA's LDR requirements. Waste-to-sorbent mixing ratio was fixed by the L-Test results and was not varied.

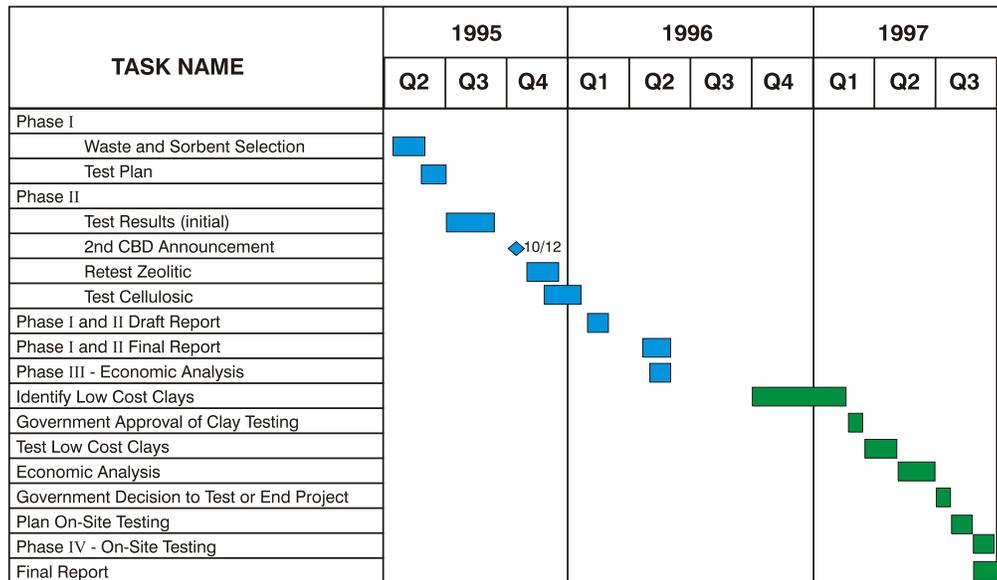
For a real-world application, the sorbents would need to be added to a waste stream in a process vessel for mixing (except to clean up spills).

The work was conducted by one person wearing a protective laboratory coat, eye glasses and gloves.

To validate the bench-scale results, Phase IV on-site testing was conducted at three DoD facilities: Jacksonville Naval Air Depot (NADEP-JAX), Florida (18 Aug 1997); Tobyhanna Army Depot, Pennsylvania (4 Sept 1997); and Tinker Air Force Base, Oklahoma (9 Sept 1997). The DoD facilities each supplied approximately 1 liter of D002, F006 and F019 wastes.

Work performed at each DoD site consisted of:

- Mix sorbent and acid.
- Measure temperature and volume changes.
- Measure liquid and paste pH.
- Test for free liquids in mixture (PFT).
- Return sample for TCLP.



3.3 MEASUREMENT OF PERFORMANCE/MONITORING PROCEDURES

The aqueous heavy metal baseline testing quantified the concentration of the metals through Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), and pH level was determined through Electrometric Measurement.

The provisions for sampling plan, data quality and QA/QC may be found in the Task Plan (ref. 3).

3.4 ANALYTICAL PROCEDURES

Details of the analytical methods used (e.g. TCLP) may be found in ref. 8, ref. 9, and ref. 10.

The QA objective for Task Phase IV was to use standard accepted protocols to generate the sorbent performance data. The aqueous heavy metal sample was obtained from a source using the methods described in EPA SW-846. For example, solutions from a process bath were drawn from the top of the bath using a triple-water-rinsed bailer and placed into the appropriate container. For sampling from smaller openings (e.g., drums with bung holes) either a clean glass tube or clean (triple rinsed) colliwasa was used. Samples were split for “as-is” analyses, and for “sorbed” analyses. All samples were labeled and logged into a tracking log book. The sampler completed a chain of custody log indicating the sample identification, quantity of sample, time and date, and sampler signature.

Sorbent waste stream combinations were tested to determine if the sorbents immobilize the free liquid waste and if the sorbents stabilize the hazardous constituent. Approximately 500 ml of aqueous heavy metal solution were evaluated with the clay sorbent. The laboratory tests were conducted according to U.S. EPA and ASTM protocols. Copies of the test methods were provided in the QA/QC Plan for Phase II (ref. 3). These methods were used as the basis for meeting the comparability QA objective.

Once the wastes were treated with the appropriate sorbent, all mixtures received a PFT to determine the presence of free liquids. If the mixture failed the PFT, indicating free liquids, no further tests were conducted.

Sorbed samples and “as-is” liquid samples were packaged, labeled, and shipped to CTC for TCLP metals analysis to determine if these treated samples meet LDR for their heavy metals constituents.

3.5 DEMONSTRATION SITE/FACILITY BACKGROUND AND CHARACTERISTICS

To validate the bench-scale results, on-site testing was conducted at three DOD facilities. Jacksonville Naval Air Depot, Florida; Tobyhanna Army Depot, Pennsylvania; and Tinker Air Force Base, Oklahoma. These facilities were chosen based on their annual amount of generated waste and desire to reduce their disposal costs.

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

Results of bench-scale testing may be found in Tables 1-3.

Table 1. Immobilization of Free Liquids (Paint Filter Test Results).

Sorbent Category	Waste Stream		
	Paint Related	Aqueous Heavy Metals	Degreasing Solvents
Peat (non-biodegradable)	Pass	Pass	Pass
Polymeric (non-encapsulating)	Fail	Pass	Fail
Polymeric (encapsulating)	Fail	Pass	Pass
Zeolitic	Pass	Pass	Pass
Clay	Pass	Pass	Pass
Cellulosic	Pass	Pass	Pass

Table 2. Stabilization of Hazardous Constituents to Meet LDRs.

Sorbent Category	Waste Stream		
	Paint Related	Aqueous Heavy Metals	Degreasing Solvents
Peat (non-biodegradable)	Fail	Pass (Pb only)	Fail
Polymeric (non-encapsulating)	NT	Fail	NT
Polymeric (encapsulating)	NT	Pass (Cd, Cr, Pb only)	Fail
Zeolitic	Fail	Pass (Pb only)	Fail
Clay	Fail	Pass (Cd, Cr, Pb, Ni, Zn)	Fail
Cellulosic	Fail	Fail	Fail

NT = Not tested due to previous test failure.

Table 3. Elimination of Flammability and Corrosivity.

Waste Stream and Test		
Sorbent Category	Paint-Related, Ignitability	Aqueous Heavy Metals, Corrosivity
Peat (non-biodegradable)	Fail	Fail
Polymeric (non-encapsulating)	NT	Fail
Polymeric (encapsulating)	NT	Fail
Zeolitic	Fail	Pass
Clay	Fail	Pass
Cellulosic	Fail	Fail

NT = Not tested due to previous test failure.

On-Site Demonstrations

It can be seen in the on-site demonstration results that all waste stream/sorbent combinations passed the PFT at the 0-5:1 mixing ratio (by weight) of liquid waste to sorbent. Results of on-site testing may be found in Tables 4-6. More details are available in the final Phase IV technical report (ref. 11).

In general, for each waste stream tested, there was heat generation and evolution of gases (presumably CO₂) during processing. The sorbed materials exhibited temperature rises ranging from 35°C (HCl) to 53°C (H₂SO₄). The final sorbed material showed an increase in waste volume, which ranged from 240% to 290%, and a slight (3%) decrease in mass.

Site 1: NADEP-JAX

Table 4 indicates that at NADEP-JAX, the treated sorbed waste passed all test criteria for the spent Activator for Steel (HCl) and for the spent Activator for Nickel (H₂SO₄). It failed the TCLP test for nickel (5 mg/l) for the Plasma Strip (HNO₃) waste. However, in this case, the initial nickel concentration was relatively high (1,030 mg/l), and although the after treatment TCLP failed the LDR limits, 98% removal was achieved. Thus, successful treatment with a starting concentration similar to the other heavy metal constituents would likely have resulted in a successful outcome.

Site 2: Tobyhanna Army Depot

According to Table 5, at Tobyhanna, the treated sorbed waste failed the TCLP criteria for cadmium (1 mg/l), nickel (5 mg/l) and zinc (5.3 mg/l) for the spent Magnesium Bright Dip (H₂SO₄), although the starting concentrations were high (2,700 - 10,500 mg/l). The treated sorbed waste also failed the TCLP criteria for cadmium (1 mg/l) and zinc (5.3 mg/l) for the Cad Stripper (HCl) waste. Again, the starting concentrations were very high (5,000 - 13,100 mg/l).

Site 3: Tinker AFB

Table 6 shows that at Tinker AFB, the treated sorbed waste just failed the TCLP criterion for cadmium (1 mg/l), while passing for the other four metals, on the Chromium Stripping (HCl) waste. The sorbed waste failed the TCLP criterion for nickel (5 mg/l) for both the spent "Tank 600" and "Tank 604" Stripping (HNO₃) wastes.

Table 4. Jacksonville Naval Air Depot Demonstration Results.

Material	Acidity Untreated pH	Metals, Untreated, ppm	Acidity After Treatment	Metals, After Treatment TCLP, ppm	TCLP Metals LDR Limits ppm	Overall Test Results
Plasma Strip, Nitric Acid	44.5 wt. % pH < 0	Cd 18.2 Cr 24.9 Pb 0 Ni 1030 Zn 28.5	Pass pH = 8.12	Cd 0.14 Cr <0.02 Pb 0 Ni 12.7 Zn 0.10	1 5 5 5 5.3	Pass Pass Pass Fail Pass
Activator for Steel, Hydrochloric Acid	18.5 wt. % pH < 0	Cd 63.3 Cr 174 Pb 0 Ni 5.4 Zn 23.1	Pass pH = 8.64	Cd 0.61 Cr 0.03 Pb 0 Ni <0.04 Zn 0.08	1 5 5 5 5.3	Pass Pass Pass Pass Pass
Activator for Nickel, Sulfuric Acid	55.2 wt. % pH < 0	Cd 0 Cr 26.7 Pb 0 Ni 23.6 Zn 2.3	Pass pH = 7.69	Cd 0 Cr <0.02 Pb 0 Ni 0.28 Zn 0.06	1 5 5 5 5.3	Pass Pass Pass Pass Pass

Note: LDR limits are pH 2-12.5

Table 5. Tobyhanna Army Depot Site Demonstration Results.

Material	Acidity/pH	Metals, Initial (mg/l)	Immobilize Liquid	Paste pH	Metals, TCLP (mg/l)	Pass/Fail
Mg Bright Dip (H ₂ SO ₄)	44.8 wt. % pH = 1.22	Cd . . . 10,500 Cr 57.9 Pb 64.2 Ni 2,830 Zn 2,710	Pass (Yes)	Pass pH = 8.35	Cd 123 Cr . . . <0.02 Pb . . . <0.06 Ni . . . 38.7 Zn . . . 29.3	Fail
Cad Stripper (HCl)	23.4 wt. % pH < 0	Cd 5,020 Cr 47.1 Pb 14.8 Ni 20.6 Zn . . . 13,100	Pass (Yes)	Pass pH = 7.83	Cd 72.5 Cr . . . <0.02 Pb . . . <0.06 Ni . . . <0.06 Zn 166	Fail

Table 6. Tinker AFB Site Demonstration Results.

Material	Acidity/pH	Metals, Initial (mg/l)	Immobilize Liquid	Paste pH	Metals, TCLP (mg/l)	Pass/ Fail
Chromium Stripping (HCl)	19.3 wt. % pH <0.03	Cd 162 Cr 1,430 Pb 39.9 Ni 33.8 Zn 19.4	Pass (Yes)	Pass pH = 9.03	Cd 1.8 Cr 0.46 Pb ... <0.06 Ni 0.35 Zn ... <0.02	Fail
"Tank 600" Stripping (HNO ₃)	32.6 wt. % pH < 0	Cd 15.7 Cr 55.9 Pb 21.1 Ni ... 24,000 Zn 265	Pass (Yes)	Pass pH = 8.81	Cd 0.14 Cr ... <0.02 Pb ... <0.06 Ni ... 305.4 Zn 1.5	Fail
"Tank 604" Stripping (HNO ₃)	41.6 wt. % pH <0	Cd 7.7 Cr 24.3 Pb 14.2 Ni 7,280 Zn 56.5	Pass (Yes)	Pass pH = 8.52	Cd ... <0.02 Cr ... <0.02 Pb ... <0.06 Ni ... 100.6 Zn 0.44	Fail

4.2 DATA ASSESSMENT

Discussion of chain-of-custody, accuracy, precision, and comparability may be found in the Phase I and Phase II final report (ref. 1).

Bench Testing

Three sets of screening tests were performed on all 18 combinations of sorbents and waste streams. Results are shown in Tables 1 through 3.

Table 1 shows that all sorbents but the polymers were effective at immobilization of free liquids. Table 2 shows that all sorbents failed to reduce the hazardous constituents for paint related wastes and for degreasing solvents. The clay sorbent was the only sorbent that effectively treated the aqueous, heavy metal waste. The peat, polymers, and zeolitic sorbents gave positive results for stabilizing some of the five contained metals.

Table 3 shows that all of the sorbents failed the ignitability test for paint-related wastes. Although no free liquid existed, the sorbent material was still ignitable. Only the clay and zeolitic sorbent passed the corrosivity test for the aqueous heavy metal wastes. In accordance with regulations, the pH must be adjusted to between 2 and 12.5.

Of the 18 combinations of sorbent/hazardous waste, only treated clay, when applied to aqueous, heavy metal wastes, passed all three tests for all chemical constituents.

Field Testing (Phase IV)

The sorbent clay successfully treated two of the eight industrial acid waste products against which it was tested. One was a hydrochloric acid activator bath used for steel parts at Jacksonville Naval Air Depot. The bath contained 18% hydrochloric acid and 63 parts per million (ppm) of cadmium, 174 ppm of chromium, 5.4 ppm of nickel, and 23.1 ppm of zinc. After treatment with the clay sorbent, the pH was 8.6 and all metals passed the TCLP tests. The other successful test was on a 55% sulfuric acid bath used for nickel parts which contained 26.7 ppm of chromium, 23.6 ppm of nickel, and 2.3 ppm of zinc. After treatment with the clay sorbent, the pH was 7.7 and all metals passed TCLP tests. These data are shown in Table 4.

Tests performed at Tobyhanna Army Depot and at Tinker Air Force Base failed due to high metal content as measured by TCLP tests.

The successful sorbent neutralized AND solidified the liquid heavy-metal contaminated waste stream if < 100 ppm contaminants.

General Conclusions

As a result of bench testing and on-site demonstrations, the following conclusions were reached:

- Clays with additives can sufficiently treat waste acids containing up to 100 ppm of heavy metals to render them non-hazardous; thereby, making them suitable for landfill disposal.
- Six classes of sorbents tested did not treat strong acidic wastes with concentrations greater than 1,000 ppm of heavy metals.
- Six classes of sorbents tested did not treat ignitable wastes (e.g., paint-related wastes) nor did they treat chlorinated solvent wastes.
- Two out of six sorbents tested (treated attapulgite clay and zeolitic) were good for heavy metals. None were good for paint wastes or for chlorinated degreasing solvents.

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5.0 COST ASSESSMENT

Cost Basis

Disposal of contents of one metal finishing bath of spent acid (stripping, cleaning, pickling, activation, etc.) per year.

Approximate volume = 4,000 gals. (typical for large DoD shop)

Approximate weight = 40,000 lbs.

(Density of acid is 10lb/gall [i.e. S.G. = 1.2])

2 parts sorbent/additive mixture added to 1 part acid.

30 batches per year.

2 hours labor required for each batch.

Equipment Requirements

A mixing vessel would be required to mix sorbent with waste acid. This would be stainless steel (SS), jacketed for cooling, fitted with an blade-type impeller, and with bottom discharge. Treated sorbed waste would drop on to an auger feeder to lift it into a dumpster for bulk disposal as non-hazardous solid waste.

It is assumed that an existing holding tank may be used to store accumulated spent acids, prior to treatment or sorbent processing.

Raw Materials

The formulated clay sorbent with additives product is an attapulgite clay with sodium carbonate and magnesium oxide additives to neutralize acid components of the waste. It also contains dispersants to enhance the flow of the sorbent and increase its contact with the waste. This clay mixture revealed the clay could be produced for approximately \$0.20 per pound.

A cost assessment of sorbent treatment compared with the existing hazardous waste disposal practice is presented in Table 7. Cases 1-3 represent the possible site-to-site variation in hazardous waste disposal costs. Using a mixture of two parts of clay to one part of acid waste results in a waste treatment cost of about \$0.76 per pound. Consequently, treatment with the clay mixture sorbent may be less expensive than the current estimated disposal costs of \$0.45 to \$1.25 per pound, depending on site-to-site variations.

Table 7. Annual Waste Disposal Cost Comparison.

Cost Category	Annual Cost (\$)			
	Existing Procedure Case 1: \$0.40/lb. Hazwaste Disposal	Existing Procedure Case 2: \$0.60/lb. Hazwaste Disposal	Existing Procedure Case 3: \$1.20/lb. Hazwaste Disposal	Innovative Clay Sorbent Treatment and Disposal
Capital Costs				
Mixer Vessel (500 gal., SS, jacketed, 1.5 hp blade impeller)	\$0 ²	\$0 ²	\$0 ²	\$3,000
Auger (1 hp)	\$0	\$0	\$0	\$1,000
Operating Costs				
Equipment Amortization (10%)	\$0	\$0	\$0	\$400
Equipment Maintenance (5%)	\$0	\$0	\$0	\$200
Sorbent Purchase ¹	\$0	\$0	\$0	\$16,000
Labor (additional 60 hrs/yr @ \$25/hr for innovative clay sorbent treatment)	\$1,000	\$1,000	\$1,000	\$2,500
Electricity, cooling water (1,000 Kwh)	\$0	\$0	\$0	\$100
Drums (80 acid @ \$10 for acid) ³	\$800	\$800	\$800	\$0
Other Disposables (rags, etc.)	\$50	\$50	\$50	\$100
Transportation ⁴	\$0	\$0	\$0	\$0
Manifesting (4 hrs/yr @ \$25/hr)	\$100	\$100	\$100	\$0
Hazardous Waste Disposal	\$16,000	\$24,000	\$48,000	\$0
Solid Waste Disposal (\$0.10/lb)	\$0	\$0	\$0	\$12,000 ³
Safety Training (4 hrs/yr @ \$25/hr)	\$100	\$100	\$100	\$100
Total Operating Cost (\$)	\$18,050	\$26,050	\$50,050	\$30,800
TOTAL ANNUAL COST (\$)	\$18,050	\$26,050	\$50,050	\$31,400
Cost Per lb Acid (\$)	\$0.45	\$0.66	\$1.25	\$0.78

Notes:

1. Assume synthetic attapulgite clay plus MgO/Na₂CO₃ additive mixture is formulated offsite and may be purchased for \$0.20/lb delivered.
2. No need for mixing vessel; assume existing holding tank would be used.
3. Sorbed waste disposed in bulk in dumpster
4. Included in waste disposal charge.

6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

The cost assessment was an extrapolation from laboratory-scale testing, and is accurate to +/- 30% at best. For applicable wastes, savings up to \$0.30 per lb of waste can result.

Depending on the site-specific cost of off-site hazardous waste disposal, the use of the sorbent technology may provide attractive cost savings. However, the cost savings to be realized may only be marginal considering the uncertainty in the cost assumptions made, and the susceptibility to change in material costs, labor rates, and waste disposal charges.

6.2 PERFORMANCE OBSERVATIONS

Performance using real-world waste streams was not as good as with the surrogate waste tested at bench scale because of the higher metal and acid concentrations. The applicability of the treated attapulgite clay sorbent as a treatment for DoD acidic hazardous waste streams is limited to waste streams containing heavy metals up to 100 ppm.

The treated attapulgite clay was not able to stabilize high concentrations (> 100 ppm) of heavy metals in aqueous electroplating wastes. At heavy metal concentrations above 100 ppm, an appropriate use of the treated attapulgite clay may be in spill neutralization and containment through solidification, but the sorbed material would have to be managed as hazardous waste unless further treatment could be applied to reduce the toxicity hazard of the heavy metals.

All performance testing was conducted at laboratory bench scale. The reproducibility of the results using full-scale process equipment has yet to be determined. Scale-up issues concerning mixing and heat transfer might arise.

6.3 OTHER SIGNIFICANT OBSERVATIONS

The results demonstrate that sorbent treatment is viable for a narrow range of wastes. Within this range, this method of treatment provides a one-step approach to neutralizing strong acids and to stabilizing heavy metal contamination such as lead, cadmium, chromium, nickel, and zinc.

However, use of sorbent clays to completely eliminate hazardous waste generation may be an attractive option for very small volume generators of acidic heavy-metal contaminated streams.

Another possible niche application is treatment of lead-containing battery acid waste.

6.4 REGULATORY AND OTHER ISSUES

In order to be permitted for land disposal, sorbed wastes have to meet these three regulatory requirements:

- Pass the Paint Filter Test (PFT).
- Land Disposal Restrictions (LDRs) for the chemical constituents.

- Eliminate the flammability or corrosivity of the waste, if applicable.

There was no regulator involvement with this development of sorbent technology.

6.5 END-USER/OEM ISSUES

The DoD has approximately 50 electroplating shops that generate waste liquids and sludges containing strong acids and heavy metals. For some of these wastes, the clay sorbent treatment process is a lower-cost, one-step alternative to the current off-site disposal option. Strong acids can be neutralized and heavy metal contaminants such as lead, cadmium, chromium, nickel and zinc can be stabilized (when present below 100 ppm).

As an aid to technology transfer, the Defense Logistics Agency recently published an article in Metal Finishing journal (ref. 12).

Industrial applications most likely to benefit from use of sorbent clay are electroplating, activation, anodizing, desmutting, etching, passivation, chemical milling, bright dipping, pickling, and chemical cleaning. Vendor claims of the ability of sorbents to treat hazardous waste should be considered with caution.

6.6 LESSONS LEARNED

The technical results of this investigation did not validate all the hazardous waste treatment claims of many sorbent vendors. One manufacturer protested the Phase I results, which indicated that its product did not pass any of the required tests. However, retesting did not change the initial results of this product's inability to treat hazardous waste.

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APPENDIX A

Points of Contact

Mr. Ronald Patun
Concurrent Technology Corporation
100 CTC Drive
Johnstown, PA 15904-1935
Telephone: (814) 269-2719
Fax: (814) 269-2798
E-mail: patun@ctc.com

Mr. Mike Downs
Jacksonville Naval Air Depot
Telephone: (904) 542-2200

Mr. Tom Wildoner
Tobyhanna Army Depot
Telephone: (717) 895-6498

Mr. Michael Sullivan
Environmental and Safety Office
Defense Logistics Agency
Fort Belvoir, VA 22060
Telephone: (703) 767-6236
E-mail: michael-sullivan@hq.dla.mil

Mr. Mike Patry
Tinker Air Force Base
Telephone: (405) 736-5185

Mr. Garry O. Kosteck
Industrial Ecology Center, Building 172
AMSTA-AR-WET; B 172
US Army, Armament Research Development
& Engineering Center
Picatinny Arsenal, NJ 07806-5000
Telephone: (973) 724-6755
E-mail: gkosteck@pica.army.mil

Mr. Tom Lawson
Ansul, Inc.
1 Stanton Street
Marinette, WI 54143
Telephone: (715) 735-7411



ESTCP Program Office

**901 North Stuart Street
Suite 303
Arlington, Virginia 22203**

**(703) 696-2117 (Phone)
(703) 696-2114 (Fax)**

**e-mail: estcp@estcp.org
www.estcp.org**