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## Management of Arsenical Wood Preserving Residuals by Recovery and Immobilization

**Ronald J. Turner**  
U.S. Environmental Protection Agency  
Cincinnati, Ohio

**Mary Beth Foerst**  
IT Corporation  
Cincinnati, Ohio



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**INTRODUCTION**

Pentavalent arsenical compounds of varying formulations have been used as wood preservatives in substantial quantities for over 50 years. Currently, there are five arsenical wood preservative formulations listed in the American Wood Preservers Association Standards: Type A, B, and C chromated copper arsenate (CCA), ammoniacal copper arsenate, and ammoniacal copper zinc arsenate. Type C CCA wood preservative contains 34 percent arsenic, 18.5 percent copper, and 47.5 percent chromium. Type C is the predominant arsenical, water soluble, wood preservative formulation used in the U.S. for applications such as decks, docks, foundation and marine piling, fences, and utility poles. (1)

The EPA is evaluating performance of alternative technologies, including processes utilizing immobilization and metal recovery/reuse, for treatment of CCA wood preserving wastes. The arsenic residual wastes are classified under the Resource Conservation and Recovery Act (RCRA) as F035. The category includes wastewater, process residuals, drippage, and spent formulations generated at plants that use inorganic preservatives containing arsenic or chromium. The disposal of waste CCA treated wood is not specified in the F035 classification.

**CHARACTERISTICS OF ACTIVE CCA FACILITIES**

The distribution of preservative use by the wood preserving industry in 1989 is summarized in Table 1. Seventy seven percent of these plants use inorganic arsenical wood preservatives.

The CCA is shipped to the treatment facility as a 50 percent concentrate. The concentrate is diluted with water to a 1-2 percent CCA working solution. The preservative is applied by pressure processes. The two methods used commercially are full cell and modified full cell. The treatment cycle consists of 1) applying an initial vacuum to remove air entrained in the wood; 2) flooding the treatment vessel with preservative; 3) pressurization to about 150 psig; 4) draining the excess preservative; 5) depressurizing and applying a vacuum to remove free liquid from the wood; 6) returning the free liquid to the work tank; 7) and opening the treatment vessel and removing the wood. The complete cycle takes about one hour. The treated lumber sits on a drip pad for about 24 hours before transfer to storage.

Wood preservation facilities using inorganic compounds typically have no net generation of wastewater. The rain runoff from storage and liquids from the sump under the treatment vessel are filtered and recycled to the work tank. The screenings and other potentially hazardous solid process wastes are drummed for offsite disposal. This is F035 as defined in 55FR 504501, 12/6/90. The quantity of waste generated annually range from a few drums at newer facilities to a dozen or more drums from older facilities, due to housekeeping practices and other production factors. The facilities are required to manage their process residuals by contracting with commercial waste removal and

RCRA-permitted/disposal companies. Some facilities rely on the suppliers of the preservatives for waste consolidation and shipment.

Three CCA wood treatment facilities were visited by EPA for sampling and analysis. The metals data are summarized in Table 2. The highest arsenic concentration in the samples from residues destined for offsite disposal was 15 percent. The highest chromium concentration was 9 percent. Copper was also present in concentrations up to 10 percent. Other toxic metals in the screened solid samples in low or moderate concentrations included lead (80 to 190 mg/kg), mercury (1 to 3 mg/kg), and cadmium (0 to 200 mg/kg). Additional elements were present at concentrations considered typical for these waste streams.

#### IMMOBILIZATION

The treatment process of immobilization, also known as solidification/stabilization (s/s), chemical fixation or encapsulation, is commonly applied when the contaminants consist of "heavy" metals such as cadmium, trivalent chromium, and lead at low to moderate concentrations. Additives or binders are mixed with the waste to immobilize and reduce the solubility of the inorganic hazardous constituents. Binding agents typically used are Portland cement, cement and flyash, lime and flyash, and dust from cement and lime kilns.

If the form of arsenic in the waste is arsenite or arsenate (oxyanions), the usual metal hydroxide formation mechanism does not apply and the stabilization of arsenic with conventional binders can be unsatisfactory and result in incomplete immobilization.(1) The arsenic in the screened solids were not speciated. However, the arsenate in the CCA is reduced to arsenite in the wood preserving process.

#### Purpose and Scope

The objectives of the immobilization studies were to determine if this technique can be applied to inorganic wood preserving wastes and to characterize the effect of immobilization on the waste. Two immobilization tests were conducted with F035 obtained in cooperation with a commercial treatment, storage and disposal facility (TSD). One series of tests was conducted at a research facility, and employed conventional binders such as cement and flyash; the other represented the process in service at the TSD for wastes containing chromium or other heavy metals: a waste shredder, conveyor belt, blender, pugmill, and a final ribbon blender. Portland cement was the binder used by the TSD for the F035. The unconfined compressive strength test was used by the research facility to measure the physical strength and the Toxicity Characteristic Leaching Procedure (TCLP) was used as an indication of the chemical leachability of the contaminants from the immobilized waste. The TSD's RCRA permit requires chromium reduction from hexavalent to trivalent and a TCLP less than 5.0 mg/L prior to final disposal in a landfill cell.

#### TSD Procedures

The TSD received 43 drums of F035 waste which were consolidated from six different CCA wood treating facilities. The drums were emptied into a 20 cubic foot steel rolloff container and mixed with a backhoe for 30 minutes. About 6 cubic feet of the mixture was transferred to an 8 foot diameter trough for additional mixing prior to collecting the F035 samples for analytical characterization and laboratory tests. The rolloff container with the remaining material was then moved to the stabilization facility for processing. Portland cement was added at 20 percent by weight in the pugmill. Ferrous sulfate was added to the first blender at a predetermined rate (not known to the EPA) based on the mass feed rate of the waste. Grab samples were obtained from the front, middle, and rear of an open, plastic lined 20 cubic foot container on the back of the truck which received the stabilized mix. The volumetric increase due to treatment was estimated at between 30 and 40 percent.

#### TSD Results

The TCLP results are summarized in Table 3. The total arsenic concentration of the F035 before stabilization was about 3 percent. The TCLP of this material was 39 mg/L. After stabilization, the TCLP value was 0.12 mg/L versus the maximum permitted concentration of 5.0 mg/L. The total chromium concentration was over 1 percent in the F035, with a TCLP of 9.2; after stabilization, the TCLP was 0.75mg/L. The leachability of copper, lead and antimony were also lowered by stabilization.(2)

#### Waterways Experiment Station Procedures

Several buckets of the untreated F035 were transported to the Waterways Experiment Station (WES), U.S. Army Corps of Engineers, Vicksburg, MS for immobilization tests with three binder systems: cement, kiln dust, and lime/fly ash. Preparation of the test specimens included an initial screening to determine the appropriate water/binder/waste ratios for evaluation. Determination of the optimal ratio was based on the results of the Cone Index Test performed on the initial screening samples after they had cured for 48 hours. The screening tests involved mixing binder, water, and waste in a Hobart K4555 mixer at three water-to-waste weight ratios: 0.0, 0.05, and 0.10. A total of three binder/waste ratios for the cement and kiln dust binders and four binder/waste ratios for the lime/fly ash binder were evaluated. Final binder/waste ratios were 0.10, 0.15, and 0.20 for cement, 0.1, 0.2, and 0.3 for kiln dust, and 0.1/0.1, 0.1/0.2, 0.2/0.1, and 0.2/0.2 for lime/fly ash. No additional water was required.

#### WES Results

The TCLP results for arsenic and chromium are shown in Table 4. All samples were cured for 28 days. These data show that treatment with cement, kiln dust, or lime/fly ash did not effectively immobilize the arsenic or chromium to the 5.0 mg/L target values.(3)

**RECOVERY**

The extraction of the copper, chromium, and arsenic from the F035 residue or "soil" may be preferable to direct immobilization and land disposal if the metals can be recovered for reuse. The amount of material requiring land disposal would also be diminished. A total of 30 bench-scale extraction tests were conducted at EPA's Test and Evaluation Facility (T&E) in Cincinnati, Ohio, with the untreated F035 from the TSD. The T&E treatability tests use 1M solutions of sulfuric acid, hydrochloric acid, sodium hydroxide, and ammonium hydroxide. The metals data from the inhouse leaching study are shown in Table 5. The results indicate that the arsenic in the extracted residues (unstabilized) from these tests would not pass the TCLP test. Only the 3 hour extraction with heated sulfuric acid gave a residue that passed the TCLP test.

Lewis Environmental Services Inc., conducted separate bench-scale extraction tests with F035 from an undisclosed source under a Small Business Pollution Prevention Grant funded by EPA. This process used strong sulfuric acid in a counter current leaching step to recover the metals for reuse in the wood preserving process. A water wash was treated separately with activated carbon for additional metals recovery. The treated "soil" passed the TCLP for arsenic (Table 6). Pilot-scale tests of the system are scheduled at one of the CCA supplier's facility. (1)

**CONCLUSIONS**

The arsenic and chromium TCLP results were more favorable from the TSD cement and ferrous sulfate immobilization process than any of the three binder systems tested at the Waterways Experiment Station. The mechanism for this decreased mobility or the long term stability of the material is not known. Although it appears technically feasible to recover the metal values from F035 residues, there is presently little interest from metal recycling facilities to accept wastes with large amounts of arsenic. The CCA wood preserving chemical suppliers and wood preservers are encouraged to continue their efforts towards reuse. Arsenic fixation processes may be applicable (e.g. Cashman Process, developed to treat arsenic-containing base metal sulfide concentrates by hydrometallurgical processes), but additional studies may be required. The recycle of waste CCA treated wood into useful, environmentally safe products is another area for future research.

**DISCLAIMER**

Although the research described in this paper was funded wholly or in part by the United States Environmental Protection Agency, it has not been subject to the Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. This paper is not intended to determine whether immobilization treatment of F035 is a viable alternative.

**REFERENCES**

- (1) Workshop on Removal, Treatment, and Disposal, Arsenic and Mercury, EPA/600/R-92/105, August 17-20, 1992 Alexandria, VA.
- (2) Waste Characterization and Treatability Report for Inorganic Wood Preserving Waste: F035, September 30, 1992 (Internal EPA Report)
- (3) F035 Stabilization/Solidification Study, Waterways Experiment Station, November 2, 1992 (Internal EPA report)

TABLE 1  
DISTRIBUTION OF PRESERVATIVE USE FOR 1989

<u>Plants Treating With</u>	<u>No. of Plants</u>
CREOSOTE	43
CREOSOTE/PENTACHLOROPHENOL	9
CREOSOTE/INORGANICS	21
PENTACHLOROPHENOL/INORGANICS	15
PENTACHLOROPHENOL	19
INORGANICS	420
CREOSOTE/PENTACHLOROPHENOL/INORGANICS	<u>17</u>
TOTAL	544 <sup>1</sup>

<sup>1</sup> Pressure Treaters Only. Non Pressure Plants (9) Not Included

Source: Micklewright (1990)

TABLE 2. METALS DATA FROM F035 SAMPLING AT THREE  
CCA WOOD TREATING FACILITIES\*

ANALYTE	AQUEOUS			SOLIDS	
	PROCESS RECYCLE STREAM (mg/L)	TREATMENT RE- TORT SUMP (mg/L)	FREE DRIPPAGE (mg/L)	SCREENED SOLIDS (mg/kg dry weight)	RESIDUAL SOLIDS TCLP EXTRACT (mg/L)
ANTIMONY	12-70	0.1-3	5-45	50-1,500	0.1-1
ARSENIC	3,000-4,000	10-900	700-2,400	8,000-150,000	2-250
BARIUM	0.2-3	0.02-0.6	0.7-2	40-450	0.07-0.25
BERYLLIUM	<0.05	<0.05	<0.05	0.2-1	<0.005
CADMIUM	2-7	0.01-0.9	0.5-1.5	0-200	0-0.08
CHROMIUM	3,000-6,000	10-900	800-2,300	5,000-90,000	0-14
COPPER	1,800-2,100	3-280	300-900	3,000-104,000	19-205
LEAD	0.2-2.4	0.01-0.05	0.1-0.2	80-190	<0.002
MERCURY	0.03-0.3	0-0.003	0.005-0.06	1-3	<0.0002
NICKEL	0.1-0.7	0.01-0.2	0.1-0.3	0-250	0.03-0.6
SELENIUM	2.5	0-0.5	0-0.5	0-65	<0.25
SILVER	0-0.25	0-0.05	0-0.05	2.6-6.5	<0.025
THALLIUM	0-1.7	0-1.7	0-1.7	100-250	<0.85
ZINC	3-19	0.1-3.5	4-7	140-650	0.07-2.4

\* The three facilities visited were 30+, 10+, and <2 years old. One grab sample from each of the aqueous process recycle streams, the treatment cylinder sumps, and the post-treatment free drippage; grab samples of the residual solids from the filter screens.

TABLE 3. METALS DATA FROM F035 STABILIZATION/SOLIDIFICATION TREATABILITY STUDY CONDUCTED AT A TREATMENT, STORAGE, AND DISPOSAL (TSD) FACILITY†

ANALYTE	SOLIDS	AQUEOUS (TCLP EXTRACT OR SOLID)		
	BEFORE TREATMENT (mg/kg or ppm)	BEFORE TREATMENT (mg/L or ppm)	AFTER TREATMENT (mg/L or ppm)	REGULATORY MAX. LEVEL* (mg/L or ppm)
ANTIMONY	540	1.0	<0.6	NR
ARSENIC	30,500	39	0.12	5.0
BARIUM	93	<2.0	<2.0	100.0
BERYLLIUM	<1.0	<0.05	<0.05	NR
CADMIUM	<1.0	<0.05	<0.05	1.0
CHROMIUM	12,500	9.2	0.74	5.0
COPPER	8,300	10.4	0.33	NR
LEAD	73	<0.03	<0.03	5.0
MERCURY	10.8	<0.001	<0.001	0.2
NICKEL	25	<0.4	<0.4	NR
SELENIUM	<1.0	<0.05	<0.05	1.0
SILVER	<2.0	<0.1	<0.1	5.0
THALLIUM	NA	NA	NA	NR
ZINC	44	<0.2	<0.2	NR

\* Maximum concentrations or levels of regulated metal contaminants in the TCLP extract shown here for comparison are as per Federal Register/Vol. 55, No. 61/Thursday, March 29, 1990/page 11862.

† Each 500 gm sample was a composite of several grab samples (total of three for the laboratory).

NA - Not analyzed

NR - Not regulated as a TCLP contaminant

**TABLE 4. METALS DATA FROM F035 STABILIZATION/SOLIDIFICATION  
TREATABILITY STUDY AT WATERWAYS EXPERIMENT STATION\***

ANALYTE	BEFORE TREATMENT (ppm)	AFTER TREATMENT TCLP		
		CEMENT (mg/L)	KILN DUST (mg/L)	LIME/FLY ASH (mg/L)
ARSENIC	77,000	9	32	28
CHROMIUM	20,000	16	20	15

\* One sample from each type of binder for TCLP, performed in triplicate.

TABLE 5.

TCLP METALS DATA BASED ON F035 BENCH-SCALE LEACHING EXPERIMENTS CONDUCTED AT  
U.S. EPA'S TEST AND EVALUATION (T&E) FACILITY  
[AQUEOUS (TCLP SOLID EXTRACT)]

ANALYTE	TCLP BEFORE TREATMENT (mg/L)	TCLP AFTER TREATMENT (mg/L)*					REGULATORY MAX. TCLP LEVEL (mg/L)
		LEACHING AGENT†					
		H <sub>2</sub> SO <sub>4</sub> ††	HCl	H <sub>2</sub> O	NaOH	NH <sub>4</sub> OH	
ARSENIC	22.0	17.8	20.3	17.0	26.0	22.0	5.0
BARIUM	0.5	0.7	1.2	0.6	0.8	0.8	100.0
CADMIUM	0.03	0.25	0.06	0.05	0.08	0.07	1.0
CHROMIUM	0.12	0.02	0.05	0.002	0.02	0.005	5.0
COPPER	10.1	6.8	9.3	4.9	2.8	2.2	NR
LEAD	ND	ND	ND	ND	0.02	0.01	5.0
MERCURY	0.002	0.001	ND	ND	ND	0.005	0.2
SILVER	ND	0.003	0.01	ND	ND	0.01	5.0
SELENIUM	0.01	0.07	0.08	0.06	0.03	0.03	1.0

\* Average value of all laboratory results obtained in the F035 leaching experiments; a total of 30 leaching experiments.

† Experiments were performed with 1 M solutions at the following pH levels: pH 2 and 4 for sulfuric acid and hydrochloric acid; pH 7 for water; and pH 10 and 12 for sodium hydroxide and ammonium hydroxide.

†† One experiment performed with sulfuric acid at pH 2 and a leaching period of 180 minutes passed the TCLP standard for metals.

ND = Not detectable at or above method detection limit.

NR = Not regulated as a TCLP contaminant.

TABLE 6  
TCLP TEST RESULTS OF LEWIS ENVIRONMENTAL  
ACID LEACHED SOIL\*

		REGULATORY LEVELS
ARSENIC	0.71 MG/L	5.0 MG/L
CHROMIUM	0.22 MG/L	5.0 MG/L

\* NUMBER OF SAMPLES NOT PROVIDED BY VENDOR

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16. ABSTRACT  Chromated copper arsenate (CCA) is the predominant wood preservative used in the U.S. (67% by volume of wood treated). The residuals from pressure treatment of lumber consist of washdown waters, dripage, treating cylinder sediment, spent formulations and filter screenings. Analyses of these materials indicate arsenic, copper, and chromium concentrations of 1-3 percent each. The solid residues are currently land disposed in RCRA permitted facilities after stabilization and meeting a leachate standard of 5.0 mg/L for arsenic and chromium characterisitic wastes. Bench-scale research studies were conducted by the EPA and the private sector to investigate the extractability of the arsenic and metals for reuse by the wood preserving facilities and to determine whether the solid residues are rendered nonhazardous by extraction. Stabilization techniques were also evaluated for immobilization of the arsenic and other metals. The feasibility for recovery of CCA from treatment residues has been demonstrated. Conventional stabilization did not effectively immobilize the arsenic or chromium.		
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