



Project Summary

Metal Recovery/Removal Using Non-Electrolytic Metal Recovery

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Radiator repair shops most commonly use hot caustic solutions to clean radiator sections before resoldering. These "boil-out" solutions become contaminated with dirt, rust, paint, and metals such as lead, copper, zinc, and tin. Metal levels as high as 18,000 ppm lead, 500 ppm copper, 1,000 ppm zinc, and 2,500 ppm tin have been reported. The project summarized here investigated onsite recovery of these metal values as an alternative to current disposal practices.

Cooling the used solutions allowed dissolved metals to settle along with other solids and allowed reuse of up to 80% of the solution. This settled material was effectively stripped of metal hydroxides by using sodium sulfide. The hydroxide precipitate was then treated with two leachants to remove copper and leave a lead-rich sludge suitable for recovery by smelting. Ammonium carbonate was an effective copper leachant; ammonium persulfate was ten times less effective than ammonium carbonate.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH to announce key findings of the research project that is fully documented in a separate report of

the same title (see Project Report ordering information at back).

Introduction

The "boil-out" tank using hot caustic solutions is one of the prime components of the repair line in radiator repair shops. In the United States and Canada over 8,000 facilities use boil-out tanks for radiator preparation. These radiators are almost entirely composites of copper, lead, zinc, and tin, and also alloys that can be dissolved to a considerable extent during the boil-out treatment. One study found that wastewater from these treatments commonly exceeded discharge standards and that bulk discharge of used solutions is commonly practiced (Figure 1).

Wastes generated from the radiator repair process include rinsewater from the rinse booth and sludge that settles to the bottom of the boil-out tank. Some rinses are configured so that they discharge directly to the sewer, whereas others rinse in a closed loop using water from a reservoir. Sludge generation with either mode of operation ranges from 30 to 300 gal per yr. In Minnesota (where shops in this study are located), disposal costs for this material range from \$175 to \$225 per 55-gal drum. Hazardous waste haulers consider the material to be primarily a strong caustic solution and



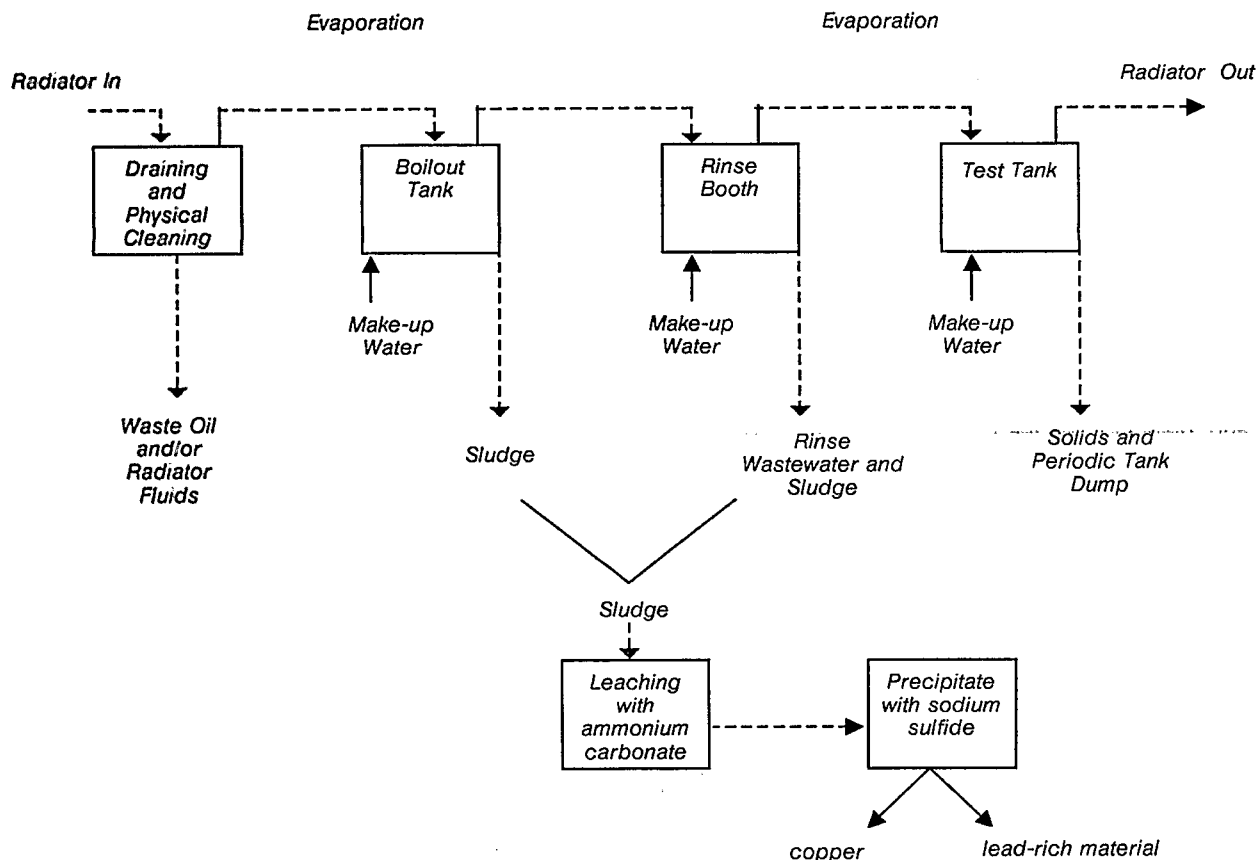


Figure 1. Flow Diagram of the Radiator Repair and Cleaning Process.

only secondarily to be a lead-bearing material.

Initial characterization of the study wastes and work reported elsewhere showed these kinds of wastes contain high levels of heavy metals, especially copper and lead. This information, plus the fact that many radiator repair shops are small (2 to 10 employees) and can ill-afford any additional costs, suggested the need for a procedure that might prepare the waste for recovery rather than for disposal. The copper and lead fractions are of particular interest, especially for recovery of lead by smelting. Since elevated levels of copper are a contaminant for secondary uses of lead, it was proposed to separate the two fractions onsite, leaving a supernatant suitable for discharge to a treatment system, a copper-rich solution, and a lead-rich solid that could be dewatered for further recovery.

Procedures

Leaching tests have been performed to both test the effectiveness of ammonium persulfate and ammonium carbonate as a copper leachant and sodium sulfide as a copper precipitant. These tests using the sludges described in Table 1 indicated that a significant amount of copper could be put into solution and the sodium sulfide would precipitate the ionic copper to leave a nearly copper-free filtrate.

Sludge B was drawn from a 23-gal ultrasonic cleaning unit. The caustic solution was prepared with the use of a proprietary compound containing sodium hydroxide. This sludge represented frequently changed solutions and therefore had lower concentrations of metals.

Sludge C was drawn from an identical ultrasonic cleaning unit, but in this case, the tank was emptied and the solids allowed to settle for 60 hr. This sludge represented solutions with higher

Table 1. Characterization of Sludges

| Metal | Sludge "B" | Sludge "C" | Sludge "D" |
|-------|------------|------------|------------|
| Pb | 8,730 ppm | 17,500 ppm | 4.8% |
| Zn | 462 ppm | 980 ppm | .6% |
| Sn | 2,010 ppm | 2,400 ppm | 6.1% |
| Cu | 350 ppm | 120 ppm | 5.2% |

concentrations of metals and also longer use.

Sludge D was drawn from the bottom of a conventional hot-caustic radiator boil-out tank. This equipment is prevalent throughout the industry and constitutes the standard practice. The sludge represented solutions with high

concentrations of earthy and sandy solids as well as metals.

Leaching and Precipitation

Cooled caustic liquids and sludges were treated with sodium sulfide in a 1 to 20 weight ratio, stirred thoroughly, and then allowed to settle. Precipitation of ionic metals was done with sodium sulfide. Ammonium persulfate and ammonium carbonate were used to separate the copper and lead fractions. The purpose was to put the copper into solution in its ionic form. This solution could then be decanted and the copper precipitated. Bench-scale leaching tests were performed in 1-L plastic jars, and a "U.S. Stoneware" jar mill provided agitation, mixing, and blending between the leachate solution and the sludge sample.

In the case of copper solutions "stripped" from sludges, copper was the major component of the precipitate. Precipitation of all ionic metals in the liquid portions of sludges B and C was tested. The objective was to determine the efficiency of sodium sulfide in yielding an easy-to-settle precipitate and a supernatant low in heavy metal concentrations.

Results and Discussion

Testing showed that a significant amount of copper could be leached into solution and that sodium sulfide would precipitate the ionic copper to leave a nearly copper-free filtrate. Ammonium carbonate was found to be the most efficient leachant for this leaching procedure. Eighty percent of the copper was extracted without neutralization or optimization of the leachant/copper ratio, an important factor for a process performed onsite by available labor. Ammonium persulfate attained a maximum copper concentration of only 1,280 ppm in the leachate, as opposed to 10,600 ppm using ammonium carbonate.

The precipitate produced by treatment with sodium sulfide proved difficult to filter, but settled readily. Metal concentrations were reduced by as much as 800:1. Only tin concentrations were not significantly reduced; however, this metal is not currently regulated as hazardous.

Conclusions and Recommendations

Tests showed that ammonium carbonate efficiently leached ionic copper into solution and that sodium sulfide precipitated the ionic copper to leave a nearly copper-free filtrate. The results of

this project indicate that copper can be effectively separated from radiator boil-out tank sludge by a single leaching with ammonium carbonate. Although some equipment and labor would be necessary, shops with large volumes of waste could justify this procedure to provide an acceptable feedstock for secondary lead refining. Smaller shops using ultrasonic boil-out tanks could precipitate all metals from their solution using sodium sulfide to either reduce waste volumes or provide a lead-rich material for secondary smelting, if copper concentrations are low enough.

Because ammonium carbonate leaching of boil-out solutions from standard equipment seems to involve more steps and procedures than would be cost-effective for a small radiator shop, further research is needed to develop this method as an intermediate step preformed by a collector/processor.

This study was conducted through the Minnesota Technical Assistance Program (MnTAP) and the Minnesota Waste Management Board. The full report was submitted in fulfillment of Cooperative Agreement CR 813437-01 under the partial sponsorship of the U.S. Environmental Protection Agency.

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James S. Bridges is the EPA Project Officer (see below).

The complete report, entitled "Metal Recovery/Removal Using Non-Electrolytic Metal Recovery," (Order No. PB90-250 150/AS; Cost: \$17.00, subject to change) will be available only from:

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