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RECOVERY OF PRECIOUS METALS FROM MILITARY ELECTRONIC COMPONENTS

I.H.Gundiler
New Mexico Bureau of Mines & Mineral Resources, Socorro, NM 87801

J.D.Lutz and P.G.Neiswander
Sandia National Laboratories, Albuquerque, NM 87185-0730, USA

ABSTRACT: Sandia National Laboratories developed a process to identify and remove the hazardous sub-components from dismanled weapon components utilizing real-time radiography and abrasive water-jet cutting. The components were then crushed, granulated, screened, and separated into an aluminum and a precious-and-base-metals fraction using air-tables. Plastics were further cleaned for disposal as non-hazardous waste.

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1 INTRODUCTION

To comply with the recent arms reduction treaties, many nuclear weapon systems in the United States (US) arsenal will be retired and dismantled during the next decade. The weapon systems targeted include artillery rounds, aircraft-delivered bombs, and tactical and strategic missile warheads. The weapon hardware dates from the 1950's through the 1980's and encompasses a wide range of designs and materials. Although weapon dismantlement is not a new activity, the increased rate of weapon system retirements coupled with stricter disposal requirements has created a need for improved dismantlement and disposal processes (Cameron, 1993). These processes must minimize waste and maximize materials recovery and recycling.

Sandia National Laboratories (SNL) is the engineering laboratory responsible for the design of much of the electronic and electro-mechanical components in US nuclear weapons. SNL is currently involved in developing and demonstrating innovative technologies applicable for the dismantlement, recycle, treatment, and disposal of weapon components and related materials (Wheelis, 1993). In Figure 1, a B-61 multi-purpose nuclear bomb is shown, broken down into its various components. The large metal cylinder is the "physics package" containing radioactive materials and high energy explosives. The remaining components are primarily of SNL design.

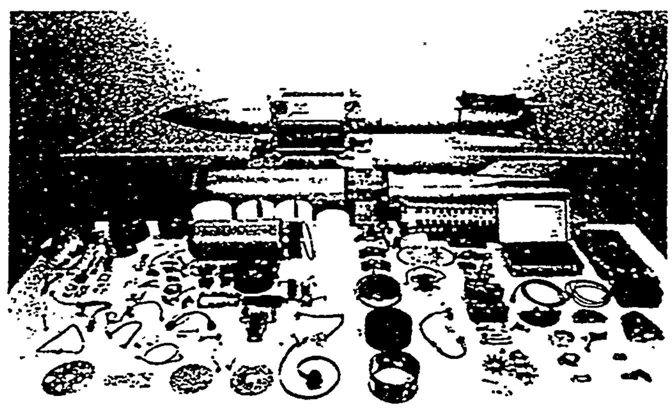

Figure 1. A B-61 nuclear bomb is broken down into four major sub-assemblies which are dismantled separately (front).

The electronic and electro-mechanical components traditionally designed by SNL often contain small quantities of hazardous, radioactive, reactive, and toxic materials located in internal subcomponents. These complex components (such as firesets, radars, and pre-flight controllers) are very compact and usually are potted with an epoxy material to make them more rugged. These attributes make it difficult to separate them into traditional material streams. In addition, these assemblies contain a variety of heavy metals and a significant amounts of precious metals. Estimates indicate that such hardware contains from $5,000 to $15,000 worth of gold, silver, palladium, and platinum per ton of material. In general, this nuclear weapon hardware represents a material stream totaling some 100 - 300 tons of material per year for the next 10 to 15 years. This stream is roughly 30% aluminum, 10% copper, 10% ferrous, 1% precious metals, 25% other metals and inorganics, and 25% organic materials. If separated properly, the majority of material can be recovered through recycling rather than disposed of as hazardous or non-hazardous waste.

The Sandia National Laboratories proposed and demonstrated an "end-to-end" process which included several major steps. These are: (1) hazard-separation, (2) demilitarization/ sanitization, (3) material separation, and (4) recycling and treatment. During hazard-separation, weapon components would have the smaller sub-components containing hazardous materials cut-out. These smaller sub-components would be separated and treated as hazardous waste. The remaining assembly (the bulk of the material) would be processed for metals recycling and precious metal recovery. During demilitarization and sanitization, all non-hazardous components would be crushed to remove any classification restrictions and to prevent further military use. This process would also act to liberate materials sufficiently to allow material separation as a precursor to recycling. The crushed material would then be processed for material separation.

1.1 Hazard separation processing

Hazard separation processing serves an important function, the separation of weapon components into readily disposable waste streams and non-hazardous, recyclable materials. The types of "hazards" requiring removal include: radioactive materials, small explosives, reactive metals and oil-filled components.

The Hazard Separation System (HSS) is based upon two primary components; the abrasive water-jet technology and real-time radiography. In the system, a Phillips 450 KeV x-ray system is used to produce real-time x-ray images on demand for the weapon components to be processed. The x-ray images are input to a computer workstation where they are used to develop or modify cutting tool paths for the water-jet cutting system. The computer workstation also provides database functions and a software interface through which the operator interacts with the entire HSS.

The water-jet system itself is a precision cutting system (Jet Edge, Inc., Minneapolis, MN). It produces a focused, high pressure stream of water which is mixed with an abrasive material, usually 60/80 mesh garnet, making a very effective cutting tool. The tool is mounted on a 3-axis, computer controlled gantry. A programmable controller converts the tool paths generated at the computer workstation into the necessary cutting program and drives the gantry. Multiple components can be processed from the same tool path. Effluents are recovered and filtered, with filtered water reused in the system. Solid materials are captured and analyzed for proper disposal.

The HSS was assembled at SNL (Figure 2) and it is currently operated as a research and development facility to support the transfer of the technology to main weapon disassembly facilities within the Department of Energy (DOE) and the Department of Defense (DoD). In Figure 3, water-jet was used to remove a thermal battery (foreground) from a pre-flight control unit. The thermal battery contains both explosive and reactive materials.

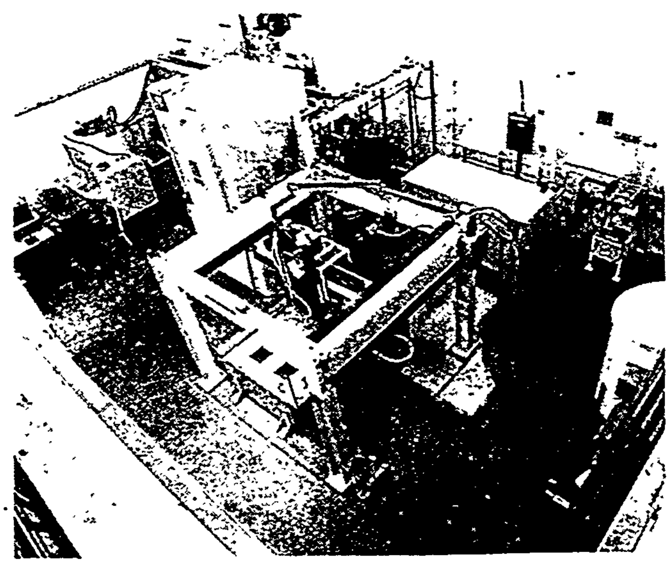

Figure 2. Hazard separation system at SNL. X-ray unit (upper left) and water-jet (center).

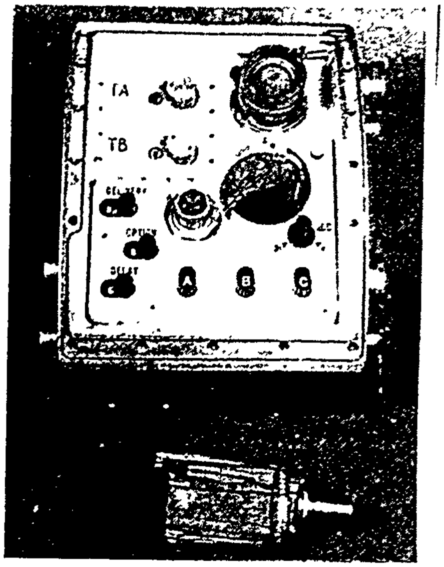

Figure 3. A thermal battery removed from a pre-flight control unit (foreground).

1.2 Demilitarization and Sanitization

Demilitarization and sanitization processing occurs after hazard separation. Demilitarization is the process of altering the wepon components to the extent that they may not be used for their intended purpose. Furthermore, many components (including most complex electronic and electro-mechanical devices) are classified. Sanitization refers to removal of all classified traits from these components before releasing them to industry for recycling and precious metal recovery. SNL has proposed size-reduction techniques as an efficient means for accomplishing both demilitarization and sanitization. In addition, such a process could be used to prepare the material for subsequent material separation processing and/or thermal treatment.

The size-reduction processes investigated for their applicability to material separation were: (1) cryo-fracture with hydraulic press, (2) shredding, (3) cryo-fracture with forging-hammer, and (4) impact hammer-milling. All processes were demonstrated using real weapon components and materials. Approximately two tons of material were rubblized during the demonstration period. The processes were compared for efficiency, size reduction capability, and material liberation capability.

2 GRANULATION AND METALS SEPARATION

Separation of aluminum, copper, and precious metals from plastics was investigated using hammermill-crushed material. Screen analysis of this material showed that 58% was retained on 7 mm(3 mesh) and 88% was retained on 2 mm(10 mesh) screens. Representative samples of these fractions were used in various separation tests. The New Mexico Bureau of Mines and Mineral Resources (NMBM&MR) assisted SNL in designing and conducting the particle size reduction, separation, and metals recovery and recycling tests.

2.1 Eddy-current separation

Eddy-current separators (ECS) are finding widespread applications in recycling and secondary recovery processes (Borsecnik, 1992). This technology has become affordable and economical to use in recent years with the advent of rare-earth magnets (Norrgran and Wernham, 1991).

ECS tests were conducted at Eriez Magnetics (Erie, PA) with +7 mm fraction of hammermill-crushed material (Figure 4).

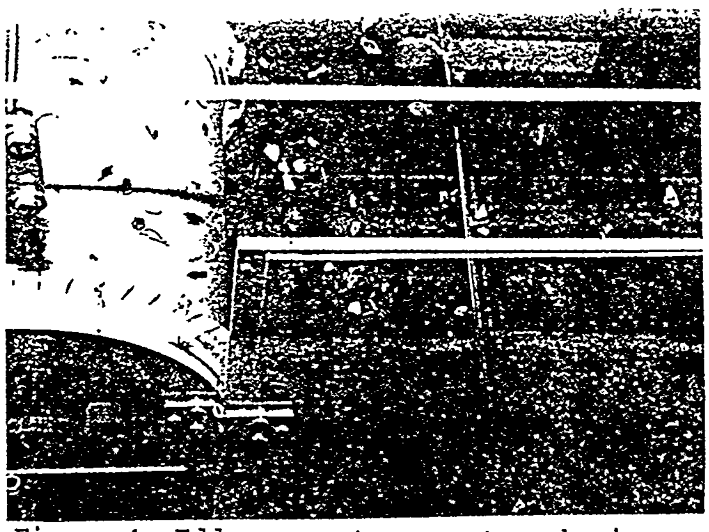

Figure 4. Eddy-current separator showing coarse aluminum particles in-flight.

This fraction yielded an aluminum concentrate which analyzed 92% aluminum, 5% copper and 2.5% zinc. It consisted of 22 wt% of the total crushed material. However, the gold loses to aluminum fraction were considerably high (up to 100 g/t) because of incomplete liberation. The finer size fractions did not yield acceptable separation efficiency.

2.2 Granulation and gravity separation

Gravity separation tests were conducted at Triple-S/Dynamics (TS/D) Dallas, TX, using air-tables. Air-tables were used extensively for mineral processing at the turn of the century. Presently, they are widely used in agricultural applications and in recycling industries, most notably in the separation of plastic insulation from chopped copper and aluminum cables.

Initial experiments with hammermill-crushed material did not yield satisfactory separation. Therefore, all three fractions were recombined and granulated using (TS/D) radial-knife type 150 hp granulator, equipped with punched-plate type discharge screens with 6.35 mm (1/4 inch) diameter holes. The granulated material was screened through 2 mm (10 mesh) and 1 mm (20 mesh) screens, and these fractions were tested on air-tables separately.

The best separation efficiency was obtained with the +2 mm fraction, which consisted of 77% of the granulated material. A heavy metals fraction rich in iron (39%), copper (30.5%), and precious metals, and a light metals fraction analyzing 93% aluminum and 4% copper were obtained (Figure 5). Approximately 90% of aluminum present in the crushed components was recovered in the aluminum concentrate.

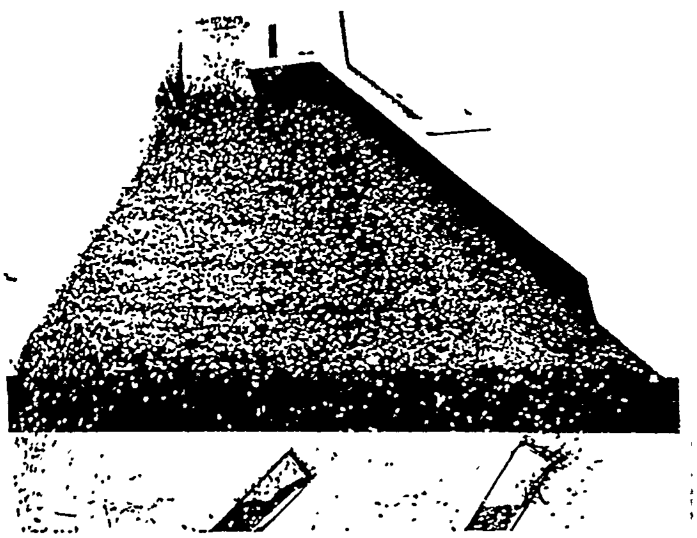

Figure 5. Air-table separation of plastics and aluminum from heavy metals (far right)

Finer size (-2 mm) material mostly consisted of the brittle phases (ceramics) and were poor in organic content. These fractions were also richer in precious metals than the +2 mm fraction. Separation efficiency was also low for small particles due to shape effects. Therefore, these fractions were combined with the heavy-metals concentrate of +2 mm air-table products for processing for copper and precious metals recovery.

3 DISPOSAL OF GRAVITY SEPARATION TAILINGS

The tailings fraction of the +2 mm air-table separation products consisted mostly of plastics and graphite (loss on ignition, LOI, 77%), ceramics, and less than 3% metals. Metallic inclusions were mostly aluminum flakes which were carried into the light fraction, and thin copper wires entrained with the plastics. This fraction accounted for about 23 wt% of the granulated material.

Preliminary tests using U.S. Environmental Protection Agency (EPA) Toxic Characteristics Leaching Procedure (TCLP) indicated that the coarse table tailings met the regulatory limits for all regulated metals (i.e. chromium, mercury, selenium, silver, and zinc) except lead and cadmium. Because disposal of this material to a hazardous-waste depository would be costly (due to its low bulk density and high volume), alternative methods of disposal and other means of rendering this material non-hazardous were investigated.

3.1 Electrostatic Separation

High-tension electrostatic separators (HTES) have recently found widespread application in separation of metallic contaminants from plastics, such as aluminum from recycled food and beverage containers. They are also used to recover metals and clean the plastics from wire-chopping operations.

Electrostatic separation tests were conducted at Carpco, Inc, (Jacksonville, FL). Approximately 7.5 wt.% of air-table tailings were recovered in the conductor fraction which consisted of mostly graphite, with minor amounts of aluminum and copper fragments. The concentrations of these metals in the non-conductor tailings were reduced to 20% of the original values. Lead and cadmium concentrations were also reduced to 442 and 51 mg/kg, respectively. Thus, the lead concentration in the non-conductor fraction was below the regulatory limit for lead (500 mg/kg) but cadmium was at the regulatory limit (50 mg/kg).

After HTES treatment, coarse non-conductor tailings can also be considered a fairly high quality fuel. The calorific value of the cleaned tailings was determined as 21 MJ/kg (9100 Btu/lb), which is comparable to sub-bituminous coals used in power plants in the southwestern United States. Possibilities to ship the tailings to coal-fired power plants, or waste-to-energy plants, were also explored.

3.2 Chemical Treatment

The TCLP tests also showed that lead and cadmium can be removed from the tailings by leaching with a dilute acid solution. Acid leaching, however, would require separation and disposal of lead and cadmium from the effluents. Another option to render the air-table tailings non-hazardous for disposal to a landfill is the fixation of lead and cadmium on solids as insoluble phosphates (Ruby, et al.,1994). One of the available technologies was originally developed to immobilize heavy metals in the ash residues from waste-to-energy power plants. This process is now licensed to other industries by Wheelabrator Environmental Systems, Inc. (Hampton, NH). Fixation tests conducted on gravity separation tailings, and TCLP tests before and after phosphate treatment, showed that the tailings would pass the test for both lead and cadmium, i.e., less than 5 ppm lead and 1 ppm cadmium in the leach solution.

4 RECOVERY OF PRECIOUS METALS

Smelting is the most widely used method for recovering precious metals (PM) from printed circuit boards and other electronic scrap (Hoffman, 1992). Recovery methods typically include the removal of organic material by thermal decomposition, dissolution of PM-bearing scrap in molten copper, oxidation of impurities to slag, and casting of ingots. Copper ingots are usually shipped to a copper refinery for PM recovery.

Smelting tests were conducted at two secondary smelters in Chicago (IL). Organics were charred and the roasted cinder was screened through 1mm (20 mesh) screens. The screen undersize was assayed with conventional fire assay techniques. The oversize material was melted in copper in a crucible furnace with flux additives. Slag and melt were then sampled and assayed separately. A sample of granulated material used for separation tests and a composite PM concentrate of separation products were also assayed similarly. The concentrate was produced by combining the (-2 mm) screen undersize with (+2 mm) heavy metals fraction of air-table products.

The assay results (Table 1) for rubblized (forge-hammer-crushed) and granulated materials reflect the variability of PM content between the lots of weapon component samples.

Table 1. Precious metal assays of SNL material and separation products.

Assay*	Rubblized	Granulated	Concentrate
Gold	11.67	9.95	21.3
Silver	49.46	59.77	123.5
Palladium	2.26	2.68	10.3
Platinum	ND	1.75	2.7
Copper	15.2%	NA	32.3%

*Troy ounces per short ton (oz/st)= 34.3 grams per metric tonne.
NA: Not-analyzed, ND: None detected.

These results also show that the concentrate is approximately twice as high in PM values. Thus, when (+2 mm) aluminum fraction (midds) and the air-table tailings (plastics) are separated, the material to be treated at a smelter would be reduced 50% by weight (67% by volume) and it would be twice as concentrated in precious metals.

5 OUTLINE OF THE SEPARATION PROCESS

Results of the separation tests described above indicated a number of benefits from reducing the amount of material to be treated at a smelter through removal of coarse aluminum and plastics. These benefits include recovery and recycling of aluminum, disposal of bulk of the plastics as non-hazardous waste, and reducing the transportation costs and smelting charges.

The mechanical separation process proposed involves granulating and screening the crushed material, and separating the screen oversize (+2 mm) using a dry (gravity) separation process into a heavy metals, a medium specific gravity (aluminum) fraction, and a light fraction of mostly plastics and ceramics. A conceptual flowsheet for the proposed separation process is given in Figure 6.

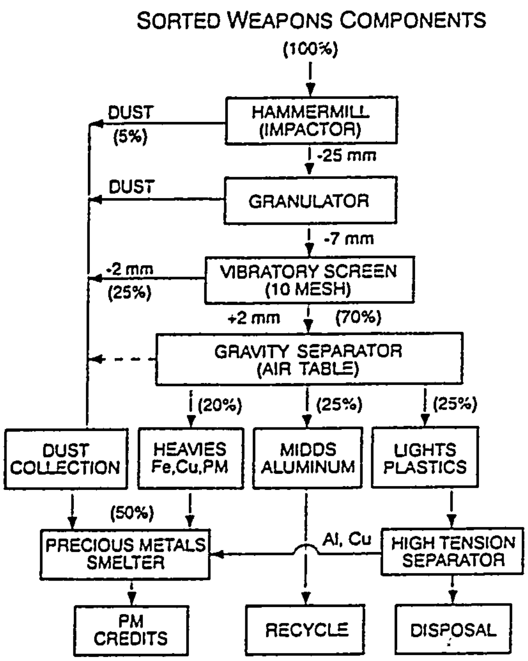

Figure 6. Flowsheet of the proposed separation and recycling process.

The recycle value of the recovered aluminum is minimal as compared to the value of precious metals. However, smelting costs will be reduced by 50% when coarse aluminum and plastics are separated from the material to be treated at the smelter. Furthermore, aluminum is a troublesome diluent for the PM smelters. Once it is removed from the smelter feed, a more favorable treatment rate can be negotiated (Garino, 1989). Savings in the treatment charges would pay for the separation equipment (excluding the crusher and dust collection system) in the first year, and annual operating expenses for subsequent years. In addition, recycling aluminum would save energy and demonstrate a commitment to recycling, consistent with SNL objectives.

6 TREATMENT OF HAZARDOUS SUBCOMPONENTS

SNL also investigated plasma arc technology for treatment and disposal of weapon component materials, including hazardous subcomponets, radioactive and energetic materials. Variations of this technology, which have in common the use of a high energy plasma torch to provide heat into a reactor, is currently being used in the treatment of various waste streams.

The plasma arc technology investigated by SNL, developed by Plasma Energy Applied Technology (PEAT) Inc., Huntsville, AL, differs from other plasma based thermal processes. It is not a combustion but a pyrolysis process in which oxidation of metals are minimized under reducing conditions. Organics are destroyed under hydrogen-rich environment and halogens are captured as hydrogen halides, minimizing the formation of halogenated organics. The inorganics are partitioned between the slag and the metal phases in which precious metals are also recovered.

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