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Use of Cryogens To Reclaim Nonferrous Scrap Metals

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by

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ABSTRACT

Three cryogenic systems that utilized liquid nitrogen, dry ice, and methanol with dry ice were investigated in conjunction with crushing and classifying techniques. The systems were used to aid in separating and reclaiming the metallic components contained in insulated wires, shredded automobile nonferrous metal concentrates, small motors, generators, and rubber tires.

Wire strands, 2 to 6 inches long and insulated with polyvinyl chloride and neoprene, were chilled at -60° and -195° C, then roll-crushed and processed by water elutriation; this procedure resulted in two products--a sink fraction that was 99 percent metallic and a float fraction that was 99 percent nonmetallic.

Excellent separation of zinc die-casting alloys from copper and aluminum contained in shredded automobile nonferrous metal concentrates was attained by chilling at -72° C for 1 minute, crushing in a grateless hammer mill, and screening. From the screened products, 97.2 and 100 percent of the copper and aluminum, respectively, were recovered in the plus 1-inch fraction, and 100 percent of the zinc was recovered in the minus 1-inch fraction of over 97 percent zinc die-cast purity.

Laboratory experimental results comparing direct and indirect chilling indicated that a sufficiently low temperature could be attained by indirect chilling to permit use of a liquid CO_2 -dry ice system on insulated wires and mixed nonferrous metallic concentrates.

INTRODUCTION

Scrap such as insulated copper wire, small motors, automobile tires, and nonferrous concentrates from automobile shredders contains materials that become brittle at low temperatures and other materials that remain malleable. Crushing of the chilled materials to shatter the embrittled portion followed

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by magnetic separation, screening, and/or gravity separation was studied for recovering the individual components. Temperatures studied ranged from -30° to -195° C and were varied to suit the type of material being tested. Cryogenics (chilling materials) tested included (1) dry ice with methanol for temperatures as low as -80° C and (2) liquid nitrogen to attain temperatures as low as -195° C.

Cryogenic techniques for aiding in the shredding of automobiles are presently under investigation in Liege, Belgium, by Robert George & Co.⁴ In this process, bundled automobile scrap is directly chilled by liquid nitrogen and fed to a shredder. The shredded material is magnetically separated into ferrous and nonferrous fractions. The embrittlement of the ferrous components by chilling and consequent ease of crushing supposedly offsets the cost of the procedure. In other work, a patent has been issued to J. B. Schorsch of the Union Corp., Verona, Pa.⁵ The procedure encompasses feeding insulated wire staples into a low-temperature refrigerating tank, pulverizing the embrittled insulation in crushing rolls, and screening the wire from the crushed insulation.

The research reported here was designed to extend the cryogenic embrittling technique to other types of materials to improve the economics of conventional processing. Embrittling temperatures for various materials were determined, and a system was developed for chilling materials by indirect cooling rather than by dipping the materials directly into the refrigerant. A comparison of residence times for direct versus indirect chilling is presented.

MATERIALS TESTED

Primary attention in this investigation was given to materials with appreciable metallic content such as insulated copper wires, small motors, generators, and nonferrous metal concentrates recovered from automobile shredding operations, or materials that are expensive to crush, such as automobile tires.

In the past, small motors and generators generally have been hand-dismantled, partially dismantled and leached, or directly charged into copper converters. Tires have either been shredded to separate the rubber from the beading, burned in an incinerator, or discarded in a landfill. Copper wire formerly was insulated with rubber, fabric, and paper, and was incinerated to remove the insulation. Today, copper wire insulation is principally plastic, and burning that results in the emission of noxious vapors such as chlorine is prohibited unless a scrubber is used on the incinerator to remove the noxious substance.

The small motors, generators, tires, and insulated wire used for laboratory testing were obtained from local scrap yards. The generators were removed from junked automobiles, and the small motors were removed from

⁴ Iron & Steel. Cryogenic Scrap Processing. V. 44, No. 5, October 1971, pp. 346-348.

⁵ Schorsch, J. B. (assigned to Union Corp.). Method and Apparatus for Stripping the Insulation From Metallic Wire. U.S. Pat. 3,527,414, Sept. 8, 1970.

household appliances and automobiles. The tires were stripped from cars received for processing. The insulated copper wire treated was a typical scrap mixture of single strands and small cables. The individual wires were insulated primarily with polyethylene, polyvinyl chloride (PVC), or neoprene, although some of the wires tested were covered with silicone, Teflon,⁶ cotton, paper, or glass. In the main, the reclaimed wires were essentially pure copper, but several wires were plated with either silver or aluminum. The average weight of the wire and insulation, in percent, was 75 and 25, respectively.

The nonferrous metal concentrates were obtained by processing nonmagnetic rejects from automobile shredder operations. First, the rejects were treated by air classification to remove the light material. The heavy product from this operation (about 70 percent metallics) was then treated by water classification to remove most of the remaining nonmetals. The heavy product from the water classification was 98 percent metal. After removing the iron fraction by magnetic separation, screening on 3-inch and 1-inch screens to obtain the minus 3-inch plus 1-inch fraction, and handpicking the pieces of glass from this fraction, a 100-percent-pure nonferrous metal concentrate was obtained. Recovery of nonferrous metals in this concentrate was approximately 95.5 percent.

EQUIPMENT USED

Chilling Chamber

Cryogenics used in this investigation were liquid nitrogen, dry ice, and dry ice and methanol. For preliminary testing, a 5-gallon aluminum container, insulated with a 4-inch-thick inner layer of styrofoam and a 3-inch-thick outer layer of fiber glass, was used as the holding vessel (fig. 1). The

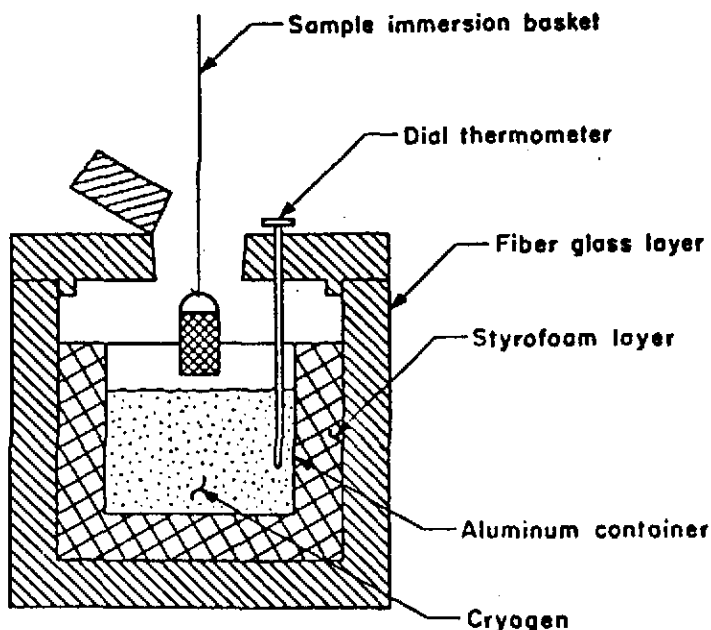


FIGURE 1. - Chilling Chamber.

materials to be chilled were placed in a copper wire basket or suspended on a piece of wire, immersed directly into the cryogen, and immediately fed to the crushing apparatus.

Crushing Apparatus

Crushing equipment used in the tests consisted of a ball mill, hammer mill, impact crusher, jaw crusher, and a set of rolls. The rolls worked most effectively with the wires, whereas the hammer mill handled the chunks of tires and shredded automobile concentrates

⁶Reference to specific products is for identification only and does not imply endorsement by the Bureau of Mines.

better than any other crushing device used. The fragmented materials were screened or water classified to produce marketable products.

Water Elutriation and Screening

Water elutriation was the most effective method investigated for upgrading insulated wire. A schematic diagram of the elutriator used is shown in figure 2. The feed capacity of the elutriator was not established; however, it did handle without any mechanical difficulties 6-inch-long strands of wire. Size fractionation by screening appeared to be the most effective means for selectively recovering the die-cast fragments in the shredded automobile reject material.

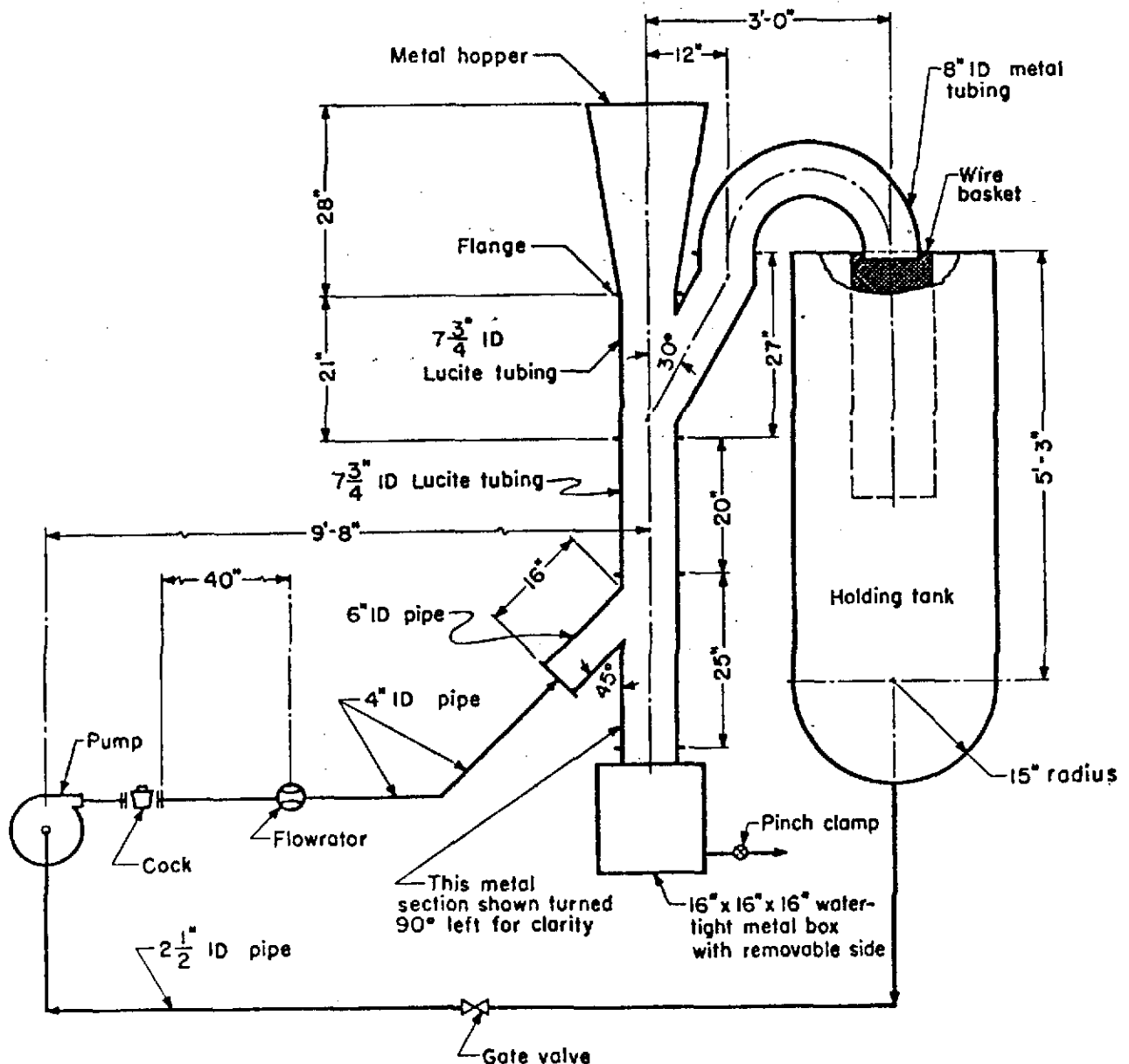


FIGURE 2. - Water Elutriating Column for Processing Crushed Insulated Wires.

IMMERSION CHILLING EXPERIMENTAL RESULTS

The temperatures at which various types of scrap materials become embrittled and the length of time required to induce embrittlement were first determined. Methanol with dry ice added in varying concentrations was used on materials that became brittle above -80°C , and liquid nitrogen was used on materials that became brittle between -80°C and -195°C . In later experiments, 1/2-pound samples of specific materials were processed to estimate the amount of cryogen required to treat a ton of each.

Chilling Procedures

Individual samples of each of the materials tested were suspended on a piece of copper wire, immersed in the cryogen for periods ranging from 5 seconds to 10 minutes, and crushed. For the dry ice-methanol system, the temperature of the methanol was readily adjusted by varying the amount of dry ice used. Starting at -10°C , the temperature was decreased by increments of 10° until the minimum temperature of -80°C was attained. For each temperature, samples of the materials were immersed in the cryogen for a specific period of time, and immediately crushed with a hammer on an anvil. A Chromel-Alumel thermocouple in a copper well was used to monitor the temperature. Temperatures remained constant for long periods of time when chilling small samples. When used with liquid nitrogen, the thermocouple and the sample were simultaneously immersed in the liquid nitrogen and removed as soon as the desired temperature was indicated. Time required to attain the specific temperature was recorded. Results of these tests are presented in table 1.

Treatment of Insulated Wires

Several pounds of assorted 1-, 2-, and 6-inch strands of wire insulated by PVC and neoprene were processed at -60°C in methanol with dry ice and at -195°C in liquid nitrogen. The samples were placed in a 1/2-pound-capacity wire basket, dipped in the cryogen, and immediately dropped into a set of rolls. The crushed insulation was then separated from the wire by water elutriation. Weight of the cryogen used to process 1/2 pound of wire was recorded. Results of these tests were extrapolated to 1-ton samples to give the approximate cryogen requirements shown in table 2. Photographs of feed material, intermediate products, and final products are shown in figure 3.

Passing chilled wires through rolls was the most effective way of fragmenting the insulation. In some instances, the pressure from the rolls caused the fractured neoprene insulation to adhere to the wires, but the agitation in the water elutriator separated the attached insulation to produce a clean product.

TABLE 1. - Embrittling points of materials

Samples	Embrittling temperature, ° C	Minimum immersion time	Remarks
DRY ICE REFRIGERANT PLUS METHANOL			
PVC-insulated single-strand and multistrand wire.	-40	5 sec	Brittle.
Neoprene- and fabric-insulated wire.	-40	5 sec	Do.
PVC-, fabric-, and paper-insulated wire.	-60	5 sec	Do.
PVC outer insulation with polyethylene inner insulation.	-60	5 sec	PVC insulation brittle but polyethylene not brittle.
Small pieces of rubber from auto scrap.	-70	5 sec	Brittle.
Chunks of rubber tires, beaded and beadless.	-80	5 sec	Brittle (marginal).
Die-casting alloys.....	-30	5 sec	Do.
LIQUID NITROGEN REFRIGERANT			
Pieces of steel from auto body.	-130	2.8 min	Brittle.
Small electrical motor and armature.	-130	2.8 min	Housing brittle.
Copper.....	-	-	Not brittle at -195° C.
Generator.....	-130	2.8 min	Housing brittle.
Generator armature.....	-130	2.8 min	Brittle, but very hard to crush.
Aluminum.....	-	-	Not brittle at -195° C.
Chunk of rubber tire.....	-100	1.5 min	Brittle.
Small motor armature.....	-130	2.8 min	Do.
Teflon.....	-	-	Not brittle at -195° C.

TABLE 2. - Cryogen requirements for insulated wire

System	Temperature, ° C	Immersion time	Reagents used, lb/ton wire		
			Methanol	Dry ice	Liquid N ₂
Methanol with dry ice (850 lb dry ice per ton methanol).	-60	2 min	360	260	-
Liquid N ₂	-195	45 sec	-	-	1,576

Separation of wire from insulation by water classification produced a cleaner product than that from screening or air classification. Water classification of crushed wire at a water circulation rate of 120 gallons per minute produced a sink fraction, which collected in an enclosed chamber at the bottom of the column, and an overflow fraction. Results of two water classification tests are presented in table 3; test 1 uses a methanol with dry-ice-treated product, and test 2 uses a liquid-nitrogen-treated product.