AN OVERVIEW OF THE BUREAU OF MINES' RECYCLING RESEARCH

Robert S. Kaplan

U.S. Bureau of Mines
2401 E Street, NW
Washington, D.C. 20241

Summary

To meet its twin objectives of encouraging recycling and alleviating waste disposal problems associated with mineral and metallurgical processing, the Bureau of Mines conducts a varied and extensive research program. This program is conducted about 85 percent in-house and 15 percent in universities, colleges, and technical schools. Industrial input concerning program content is sought through contacts with trade associations, such as the National Association of Recycling Industries and the Institute of Scrap Iron and Steel, as well as with individual companies. Other sources of input include academia and other governmental organizations. The Bureau's program includes basic, long-range research to advance technology in recycling. Broad based input to this program results in real world needs being addressed.

Introduction

Currently there are two objectives for the Bureau's recycling research:

- Encourage greater conservation of strategic and critical metals, as well as other mineral-based materials of importance to the U.S. enconomy, by providing new and/or improved recycling technology.

- Devise safe, cost effective methods to alleviate disposal problems associated with the processing of ores and waste materials resulting from the converting of mineral based materials into useable products.

The program is divided into four program elements:

- Recovery of Co, Ni, and Cr from scrap and wastes

- Recycling Al, Cu, Pb, and Zn

- Recycling other metals and nonmetals

- Making processing wastes environmentally acceptable

Most of the recycling research is conducted at six Bureau of Mines research centers located in Avondale, MD (a Washington, DC suburb); Tuscaloosa, AL; Rolla, MO; Salt Lake City, UT; Reno, NV; and Albany, OR. A small portion of the work is performed by contractors. In addition, the Bureau supports a Generic Mineral Technology Center on Mineral Industry Waste Treatment and Recovery. Examples of projects in each of the four program elements and under the Generic Mineral Technology Center will be discussed later; but first a little history.

Authority for the Bureau's recycling research stems from the Bureau's Organic Act of 1910, as amended in 1913. This act stressed the conservation of metals and minerals; recycling being a very effective form of conservation. Additional authority is imparted by the Mining and Minerals Policy Act of 1970, which states in part "...it is the continuing policy of the Federal Government... to foster and encourage... the use and recycling of scrap..."

The first Bureau Report of Investigations dealing with recycling was published in 1920. From a review of the reports published from 1920 until the late 1940's it appears that recovery of valuable metals, particularly gold and silver, from tailings received the major emphasis in a limited program. However, some effort was expended on resource recovery from metallurgical wastes, e.g., slags and drosses, and on the utilization of mineral wastes to make new products.

Beginning in the late 1940's, it appears that the recycling program began to grow and to produce significant accomplishments. In the late 1950's at the request of the General Services Administration (GSA), the Bureau developed a vacuum distillation and selective condensation process

that permitted the recovery of cadminum and magnesium from surplus World War II bomb casings. This allowed the GSA to dispose of 8,826,000 casings while returning 800,600 kg of cadmiun metal, with a value of $3.6 million, to the economy[1]. In the late 1960's, a breakthrough resulted in technology for recovering cobalt and tungsten carbide from scrap cemented carbide tool bits. This patented technology involves heating the scrap in molten zinc to dissolve the cobalt, distillation of the zinc, and grinding of the remaining carbide and cobalt, which is friable, to reuseable powder[2].

The Solid Waste Act of 1965 provided strong impetus to the Bureau's recycling research program. The appropriations resulting from this act allowed a substantial contract research program to develop. Many of these contracts dealt with new uses for wastes, e.g., bricks made from mineral processing tailings. In addition, two major projects and many smaller projects were begun at Bureau research centers. The two major projects focused on the recovery of metals and other materials from municipal solid waste (MSW) and junked cars.

The project on MSW produced technology for recovering useable ferrous and nonferrous metal, and glass fractions from both incinerated and unburned refuse[3,4]. In addition, the unburned MSW yielded an organic fraction that could be further processed to recover materials such as plastics or to produce a fuel useable in boilers. Tests conducted by the Bureau in cooperation with industry showed that the glass fraction recovered from incinerated MSW could be used to produce amber beer bottles, that the ferrous fraction from incinerated and unburned MSW could be used to make steel without further treatment (some products had compositions similar to COR-TEN type steels), and that the ferrous fraction from unburned MSW could be detinned and baled to yield a premium ferrous scrap[5,6]. Aluminum, in the form of used beverage cans, could be recovered from unburned MSW. As a result of these studies, plants for the separation of unburned MSW into useable fractions were built by private companies in Baltimore County, MD and Monroe County, NY.

Initially the research on junk cars was aimed at determining the amounts of the various materials contained therein and at solving an air pollution faced by processors producing bales of ferrous scrap from incinerated junk cars. The amounts of the various materials were determined by hand dismantling 15 cars varying in age and manufacturer[7]. Additional work continued through the early 1980's when four Japanese cars were hand dismantled[8]. The air pollution-related research demonstrated that incinerators for burning the organics out of junk cars prior to their being baled could be designed with an afterburner so as not to emit particulates[9]. As automobile shredders for producing high quality shredded ferrous scrap became more prevalent in the late 1960's, the Bureau shifted its emphasis to recovering nonferrous metals from cars.

Following shredding, magnets are used to separate the ferrous product from the nonferrous metals and nonmetallics (nonmagnetic shredder reject). Until the mid 1970's, nonmagnetic shredder rejects were discarded. However, in the late 1960's, the Bureau of Mines initiated research aimed at recovering a nonferrous metals concentrate from the nonmagentic shredder rejects. Two techniques were investigated: air classification and water elutriation [10,11]. Depending on conditions, air classification yielded products containing from 74 to 89 percent metal. Metal recoveries ranged

from 96 to 61 percent. Water elutriation yielded products containing 96.9 to 99.5 percent metal; recoveries ranged from 94.2 to 83.2 percent. Various techniques are available for separating the nonferrous metals into aluminum, zinc, copper, and stainless steel fractions. These include use of heavy media and sweating.

One of the smaller projects (resulting from the Solid Waste Act of 1965), processing of scrap tungsten carbide tool bits, already has been mentioned. Two others are worth noting; both also involve the recovery of strategic and critical metals from metallurgical wastes.

Solutions containing hexavalent chromium and sulfuric acid are used as etchants in a variety of metal finishing operations. As the solutions are used, hexavalent chromium is reduced to trivalent chromium resulting in reduced etching rates. When the etching rate becomes unacceptably slow, the solutions are discarded. Therefore, the Bureau developed a process whereby treatment of these waste solutions in a three compartment diaphragm cell results in oxidation of the trivalent chromium in the anode chamber and transfer of the metals dissolved during etching to the catholyte[12]. For example, when waste brass etchants are treated in this manner, all of the trivalent chromium is oxidized and more than 40 percent of the copper and zinc are removed. Spotts has developed a complete economic evaluation of this process[13]. At least five companies are using this patented technology.

The other project involves recovery of chromium and nickel present in the particulate wastes generated during the manufacture of stainless and speciality steel. These wastes include bag-house dusts, mill scale, and grinding swarf. Research has shown that at least 90 percent of the iron, chromium, nickel, and molybdenum contained in these wastes can be recovered economically by blending them with coke breeze reductant (in the proportions in which the wastes are generated), pelletizing them, and charging them back into the production electric arc furnace in amounts not to exceed 20 percent of the regular scrap charge[14]. The technology has been demonstrated successfully, in melts up to 20 tons, at a stainless steel plant.

Current Program

Recovery of Co, Ni, and Cr Materials From Scrap and Wastes

This coordinated research effort features a number of approaches to the problem of processing superalloy scrap. Three of the most interesting approaches will be discussed in some detail. They involve identification, electrolytic refining, and formation of intermetallic compounds.

Accurate identification allows sorting of uncontaminated superalloy scrap by type so that it can be remelted directly. Currently, identification requires highly skilled sorters who take into account the source of the alloy and its function (such as a turbine blade). However, as these alloys have become more complex it has become increasingly difficult for humans to sort them using these methods. In recognition of the problem, and at the urging of the scrap industry, the Bureau of Mines has undertaken research to instrument the sorting process.

One technique being investigated is instrumented spark testing. Although sparks from most superalloys can not be differentiated by the human eye, it was thought that the sparks from each alloy would produce a unique spectrum. Using a laboratory spectrophotometer, the variation in intensity with the wavelength of the light generated by the spark can be determined[15]. The data is fed to a small computer where the spectrum of the unknown alloy is compared to spectra of known alloys stored in the computer's memory. A direct readout identifying the unknown alloy results. However, even highly accurate identification techniques will not promote recycling in situations where two alloys are physically attached to one another and cannot be separated.

When superalloy scrap is not suitable for remelting because it is contaminated, its constitutent metals must be recovered as pure elements or compounds. A major impediment to this recovery stems from the resistance of various alloys to acid attack. Thus, it may take hours or days to dissolve massive pieces of scrap (such as turbine blades). Two procedures to overcome this impediment are being investigated by the Bureau of Mines.

One procedure involves pyrometallurgical and electrolytic refining of the scrap to produce a cobalt-nickel master alloy. A pure cobalt-nickel master alloy was chosen for two reasons. First almost all superalloys contain cobalt and nickel. Thus, the pure master alloy should find wide application.

Second, the similar thermodynamic properties of cobalt and nickel make them very hard to separate. The scrap is melted and many of the other elements, e.g., chromium, are oxidized into a slag. The remaining metal is then cast into an anode for electrorefining. The impurities in the anode form a sludge while the cobalt and nickel deposit as the aforementioned master alloy. Reduction of the slag results in recovery of the metals, such as chromium, that were removed from the molten scrap by oxidation.

The second procedure consists of melting the superalloy scrap with aluminum or zinc to obtain a material that can be dissolved rapidly[16]. Melting the scrap with aluminum at about 800° C in the proportion 70:30 results in a brittle intermetallic compound. Alternatively, the scrap can be dissolved in zinc at about 800° C in the proportion 30:70 and the zinc then vaporized from the solution to leave a brittle residue. Both the intermetallic compound and the residue are highly reactive, more than 90 percent of the material dissolving in 6N HCl at 95° C in 1 hour. Current research is focused on the problem of recovering the dissolved metals from chloride solutions. An electrochemical method is being sought.

Recycling Al, Cu, Pb, and Zn

Two projects have been selected that could illustrate the breadth and diversity of approach of this part of the program. The first deals with the recovery of aluminum from drosses, the second, with utilization of zinc recovered from zinc bearing wastes.

When the oxides that form on the surface of aluminum being held molten in reverberatory furnaces are skimmed off, the resulting dross contains prills of aluminum. Commercial recovery of this aluminum is accomplished by smelting the solid dross in the presence of an equal amount of salt flux consisting of equal parts of KCl and NaCl plus 5 percent cryolite. Sometimes the dross, which may contain 20 to 80 percent Al, is ground and screened, causing the aluminum to concentrate in the +20 mesh fraction. The salt causes environmental problems in terms of potentially hazardous emissions produced during furnacing operations and the leachability of the salt slag waste. Through analysis of data on the vapor pressure over salt solutions (both literature values and data from our research) as well as of phase relationship data for these solutions generated within our laboratories, we have concluded that although small amounts of fluoride make the salt fluxing more effective, the fluoride can be added as NaF instead of as cryolyte. This change in practice shows high promise for eliminating the emission problems. Leaching from the salt slag waste discarded after removal from the smelting furnace can be minimized or eliminated by minimizing or eliminating the use of salt. To accomplish this, ultrasonic energy is being investigated by Bureau of Mines researchers as a possible way of breaking the oxide coating surrounding the aluminum droplets in the dross, thereby encouraging coalescence of the droplets.

Zinc can be recovered from wastes either pyrometallurgically (by fuming) or hydrometallurgcially. Pyrometallurgical recovery, though practiced extensively on wastes rich in zinc, is expensive and can cause environmental problems. Hydrometallurigcal technology for obtaining zinc bearing solutions of sufficient purity and concentration for electrowinning has been elusive. Many impurities have a negative effect on current efficiency and/or promote the formation of dendrites, which leads to the formation of bridges between electrodes and consequent short circuiting. Using the solution for electrogalvanizing steel circumvents many of these problems. Because the layer of zinc on the steel is very thin, dendrites never have a chance to form and cause shorts. Therefore, it is possible to operate at much higher current density, i.e., much higher deposition rates. In fact, under these conditions,some of the impurities promote fine grained deposits.

Recycling Other Metals and Nonmetals

Iron and steel scrap is one of the most important scrap materials, in terms of both tonnage and volume. Any technology that will make steelmaking with scrap more efficient will encourage the use of scrap. The Bureau of Mines has determined that shredded scrap, and other relatively finely divided iron and steel material, can be continuously charged to electric arc furnaces while simultaneously being preheated by the furnace offgas. Both continuous charging and preheating decrease the quantity of energy required to make steel and thus increase furnace productivity. Continuous charging eliminates the need to remove the top of the furnace three to four times during a heat to add solids (backcharging) as the metal in the furnace melts. Elimination of back charging eliminates the tremendous loss of time and heat (radiated from the hot metal to the cold surroundings as well as shell heat losses while the furnace is standing idle). Preheating with the offgas not only conserves energy, it also speeds up melting thereby increasing production rate and decreasing the shell heat losses per ton of steel made.

Phosphogypsum, a $CaSO_4$ byproduct from the production of phosphoric acid used to make fertilizer, constitutes a severe waste problem. Some 330 million tons are being stored in huge stacks in Florida. However, it also is a potential sulfur resource. Therefore, the Bureau of Mines, in cooperation with the Florida Institute for Phosphate Research and the producers of phosphate chemicals, is investigating a process for converting $CaSO_4$ to CaS and decomposing the CaS to sulfur. Preliminary research has shown that conversion in excess of 90 percent can be obtained with an iron oxide catalyst at temperatures 200° to 250° C lower than if catalysts are not used. Future efforts will concentrate on optimizing this conversion and on decomposing the CaS to sulfur.

Making Processing Wastes Environmentally Acceptable

Almost all processing of minerals and metals produce wastes, and many of these wastes may cause environmental problems. Two wastes currently being studied are mineral-processing slimes and arsenic bearing fumes. Mineral-processing wastes frequently occur in the form of slimes that require years to settle naturally; thus, they are impounded in large ponds. Arsenic, on the other hand, is usually present in wastes in a form that can be leached. If leaching occurs, the arsenic is then able to enter surface water, ground water, or aquifers where it can present a serious health hazard.

The Bureau first attacked the problem of dewatering phosphate slimes. Flocculating the slimes with polyethlyene oxide, a long-chain polymer, and pumping the slimes to an inclined static screen and then to a rotating trommel screen liberates the water. The dewatered solids have a solids content of about 20 percent; a level that could require 10 years to achieve by natural settling[17]. This technology was found to be applicable to other slimes containing clay solids[18,19]. We now have turned our attention to red muds, a waste produced when alumina is leached from bauxite with NaOH. These red muds are produced at a rate of about 5 million tons per year. Furthermore, they entrain significant amounts of NaOH as they settle. Adapting the technology for dewatering phosphate slimes to the dewatering of red muds has required the following changes: (1) replacing the polyethylene oxide with a polyacrylamide flocculant, (2) redesigning the mixer for combining the flocculant and the red mud, and (3) eliminating the static screen.

Bureau research has shown that arsenic bearing wastes can be reacted with $TiCl_4$ to produce TiO_2 and gaseous $AsCl_3$. Reaction of the $AsCl_3$ with hydrogen yields metallic arsenic and HCl. The reactions can take place concurrently with the $TiCl_4$ and hydrogen brought in contact with the waste simultaneoulsy, or the reactions may take place consecutively.

Generic Center Research

One final aspect of the Bureau's recycling research program should be mentioned: the Generic Mineral Technology Center on "Mineral Industry Waste Treatment and Recovery." This is one of five generic centers and has been funded at about $750,000 per year through the Office of Mineral Institutes since the inception of the program in 1982. Originally, the center was based at the University of Nevada-Reno with satellite activities at the Montana College of Mineral Science and Technology, the New Mexico Institute

of Mining and Technology, the University of Idaho, and the Iowa State University. In FY 1985 participation in the Generic Technology Centers was opened up to all 31 schools in the Mineral Institute Program. As a result, the South Dakota School of Mines and Technology was added to the generic technology center on mineral industry wastes.

The generic technology center program on mineral industry wastes is somewhat broader than the in-house research program. For example, in addition to such classic study subjects as the recovery of arsenic from wastes, schools in this program also are addressing the problems of water flow and acid generation in hard rock mines, and water flow in tailings.

References

1. H. S. Caldwell, Jr. and M. J. Spendlove, "Recovery of Magnesium and Cadmium From Incendiary Alloys by Vacuum Distillation," RI 5476, Bureau of Mines, 1959, 17 pp.

2. P. G. Barnard, A. G. Starliper, and H. Kenworthy, "Reclamation of Refractory Carbides From Carbide Materials," U.S. Patent 3,595,484, 1971.

3. J. J. Henn, "Updated Cost Evaluation of a Metal and Mineral Recovery Process for Treating Municipal Incinerator Residues," IC 8691, Bureau of Mines, 1975, 44 pp.

4. R. S DeCesare, F. J. Palumbo, and P. M. Sullivan, "Pilot-Scale Studies on the Composition and Characteristics of Urban Refuse," RI 8429, Bureau of Mines, 1980, 32 pp.

5. H. V. Makar, R. S. Kaplan, and L. Janowski, "Evaluation of Steel Made With Ferrous Fractions From Urban Refuse," RI 8307, Bureau of Mines, 1975, 26 pp.

6. W. L. Hunter, "Steel From Urban Waste," RI 8147, Bureau of Mines, 1976, 16 pp.

7. K. C. Dean and J. W. Sterner, "Dismantling a Typical Junk Automobile To Produce Quality Scrap," RI 7350, Bureau of Mines, 1969, 17 pp.

8. J. W. Sterner, D. L. Steele, and M. B. Shirts, "Hand Dismantling and Shredding of Japanese Automobiles to Determine Materials Contents and Metal Recoveries," RI 8855, Bureau of Mine, 1984, 25 pp.

9. C. J. Chindgren, K. C. Dean, and J. W. Sterner, "Construction and Testing of a Junk Auto Incinerator," TPR 21, Bureau of Mines, 1970, 8 pp.

10. L. J. Froisland, K. C. Dean, L. Peterson, and E. G. Valdez, "Recovering Metal From Nonmagnetic Auto-Shredder Reject," RI 8049, Bureau of Mines, 1975, 18 pp.

11. D. K. Steele and J. W. Sterner, "A Water Elutriator System for Recovering Nonmagnetic Metals From Automobile Shredder Rejects," RI 8771, Bureau of Mines, 1983, 22 pp.

12. D. M. Soboroff, J. D. Troyer, and A. A. Cochran, "Regeneration and Recycling of Waste Chromic Acid-Sulfuric Acid Etchants," RI 8377, Bureau of Mines, 1979, 13 pp.

13. D. A. Spotts, "Economic Evaluation of a Method To Regenerate Waste Chromic Acid-Sulfuric Acid Etchants," IC 8931, Bureau of Mines, 1983, 7 pp.

14. P. G. Barnard, W. M. Dressel, and M. M. Fine, "Arc Furance Recycling of Chromium-Nickel From Stainless Steel Wastes," RI 8218, Bureau of Mines, 1977, 10 pp.

15. W. D. Riley, B. W. Dunning, Jr., and D. M. Soboroff, "Spectral Characteristics of Grinding Sparks Used for Identification of Scrap Metal," RI 8932, Bureau of Mines, 1985, 13 pp.

16. G. B. Atkinson, "Increasing the Leaching Rate of Bulk Superalloy Scrap by Melting With Aluminum," RI 8833, Bureau of Mines, 1983, 11 pp.

17. B. J. Scheiner, A. G. Smelley, and D. R. Brooks, "Large-Scale Dewatering of Phosphatic Clay Waste From Central Florida," RI 8611, Bureau of Mines, 1982, 11 pp.

18. A. G. Smelley, B. J. Scheiner, M. M. Ragin, and J. R. Zatko, "Debrining of Potash Clay Waste Slurries," RI 8741, Bureau of Mines, 1983, 11 pp.

19. P. M. Brown and B. J. Schiener, "Dewatering of Coal-Clay Waste Slurries From Preparation Plants," RI 8824, Bureau of Mines, 1983, 8 pp.

RECYCLE AND SECONDARY RECOVERY OF METALS

Proceedings of the International Symposium on Recycle and Secondary Recovery of Metals and the Fall Extractive and Process Metallurgy meeting sponsored by the Physical Chemistry Committee of The Metallurgical Society of AIME held in Fort Lauderdale, Florida, December 1-4, 1985.

Edited by

Patrick R. Taylor
Department of Metallurgical and Mining Engineering
University of Idaho
Moscow, Idaho

Hong Y. Sohn
Department of Metallurgy and Metallurgical Engineering
University of Utah
Salt Lake City, Utah

Noel Jarrett
Alcoa Technical Center
Alcoa Center, Pennsylvania

A Publication of The Metallurgical Society, Inc.

Library of Congress Cataloging-in-Publication Data

International Symposium on Recycle and Secondary Recovery of Metals (1985 : Fort Lauderdale, Fla.)
Recycle and secondary recovery of metals.

Includes bibliographies and index.
1. Metallurgy--Congresses. **2.** Slag--Congresses. **3.** Scrap metals--Recycling--Congresses. **I.** Taylor, Patrick R. **II.** Sohn, Hong Yong. **III.** Jarrett, Noel. **IV.** Metallurgical Society of AIME. Physical Chemistry of Extractive Metallurgy Committee. **V.** Extractive and Process Metallurgy Meeting of the Metallurgical Society of AIME (1985 : Fort Lauderdale, Fla.) **VI.** Title.
TN605.I544 1985 669'.042 85-21792
ISBN 0-87339-007-5

A Publication of The Metallurgical Society, Inc.
420 Commonwealth Drive
Warrendale, Pennsylvania 15086
(412) 776-9000

Printed in the United States of America.
Library of Congress Catalogue Number 85-21792
ISBN NUMBER 0-87339-007-5