METAL AND INORGANIC WASTE RECLAIMING ENCYCLOPEDIA

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FOREWORD

This book describes 328 recent processes for reclaiming metal and inorganic wastes, and is arranged in encyclopedic form, alphabetically by the product recovered.

The recovery and recycling of these industrial wastes is assuming ever-increasing importance due to the need for ore and mineral conservation, and the requirements of pollution regulations. The technology of each specific recovery and recycling process is outlined, as well as background as to the origin of the waste material, some of the problems posed by the specific waste, and possible alternative processes for reclaiming, recovery, and recycling.

There is also an index listing the sources of waste feed materials, and each entry lists the product that may be reclaimed from the waste source.

Contents and Subject Index

Introduction

The recovery and recycling of industrial wastes are assuming ever-increasing importance in the 1980s due to a combination of the following factors.

(1) Increasing world scarcity of economically viable deposits of some ores.

(2) Increasing national and international efforts to conserve and control mineral prices along the lines of OPEC and petroleum.

(3) Increasing pressure in a somewhat unfriendly world for major nations in particular to be reasonably self-dependent as regards supplies of strategic commodities.

(4) Increased emphasis on pollution control and toxic materials control making dumping of waste slags and the like much less desirable.

(5) Rapidly increasing energy prices which accentuate in many cases the virtues of using recycled rather than virgin raw materials.

Due to the amount of material available, it was necessary to divide the material in order to make a volume of reasonable size and hence this book has a companion volume entitled *Organic and Polymer Waste Reclaiming Encyclopedia* (1).

These volumes will focus only on the technology available for the recycling of industrial wastes. Process economics will not be considered because of the following:

(a) Rapidly fluctuating prices of some ores and commodities.

(b) Rapidly increasing energy costs which make economics meaningless unless carefully dated and/or adjusted.

(c) Rapid monetary inflation in most countries which again makes costs very difficult to state accurately in terms of today's situation, or worse, of future projections.

In each case, an attempt will be made, not only to outline the technology of a specific recovery and recycling process, but to give some background as to:

- The origin of the waste material;
- Some of the problems posed by the waste; and
- Some possible alternative processes for recovery and recycling.

Emphasis is placed in this volume and in the companion volume on the recycling of industrial wastes, often within the factory fence, rather than on postconsumer wastes such as waste newspapers, discarded beverage bottles and the like. However, it will be appreciated that there is no clear line of demarcation between these areas. Thus, some industrial wastes may quickly end up as municipal wastes and must of necessity be recycled from that point.

U.S. Import reliance of selected minerals and metals are shown in Figure 1. These data emphasize the need for the U.S. to develop effective techniques for the recovery and recycling of many materials.

This volume is arranged like any dictionary or encyclopedia in alphabetical manner. Every effort is made to cross-index entries within this volume and frequent cross-references are also made to the companion volume, *Organic and Polymer Waste Reclaiming Encyclopedia* (1).

As the reader will observe, an index to the sources of waste feed for the various recycling processes is provided at the end of this volume. Together with the alphabetical arrangement by recovered material, this index of waste sources should make access to useful information both rapid and easy.

The majority of references in this volume are to U.S. Patents. A secondary source is the published work of the U.S. Bureau of Mines. A bibliography at the end of this volume lists the general publications cited in the text.

This volume, together with its companion volume, *Organic and Polymer Waste Reclaiming Encyclopedia*, represents an updating of an earlier work by the publisher of this volume entitled *Resource Recovery and Recycling Handbook of Industrial Wastes* (3) published in 1975.

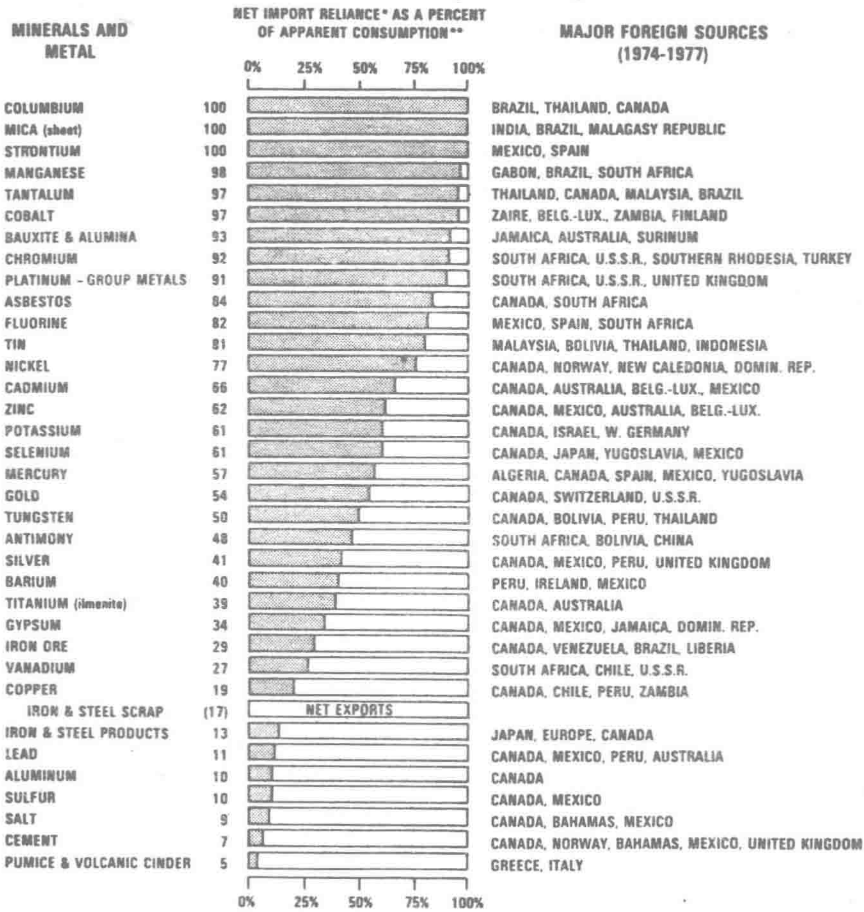
The reader's attention is also called to a number of other published works including a summary volume by Barton (4), monthly materials surveys by the U.S. Bureau of Mines (2), a volume of forecasts for resource recovery to the year 1990, made in 1975 (5), a discussion of energy use patterns for metal recycling (6), an Office of Technology Assessment review of technical options for the conservation of metals (7) and a series of bibliographies on solid waste reclamation and recycling prepared by the National Technical Information Service covering the period 1964 to July 1979 (8)-(13) and dealing with:

Packaging and Containers (8)
Plastics (9)
Metals (10)

Glass (11)
Paper (12)
Tires (13)

Detailed discussions of various metal scrap recycling processes and their environmental impacts have been reviewed by Nack et al (15).

Figure 1: U.S. Net Import Reliance of Selected Minerals and Metals as a Percent of Consumption in 1978



*Net Import Reliance = Imports - Exports + Adjustments for Government and Industry Stock Changes

**Apparent consumption = U.S. Primary + Secondary Production + Net Import Reliance

Source: Bureau of Mines, U.S. Department of the Interior (Import-Export Data from Bureau of the Census) Reference (2).

A

ABRASIVE MATERIAL FROM SCARFER SPITTINGS

Scarfer spittings are a steel mill waste material produced by scarfing steel ingots, blooms, slabs, billets and bars prior to or during processing to remove surface defects. Scarfing consists of rapidly removing the surface of steel by the use of a fuel containing oxygen applied to the surface by means of a torch or torches. The oxygen oxidizes a portion of the steel thereby generating heat and increasing the temperature to cause the steel to become molten. The partially oxidized generally globular product is referred to as scarfer spittings.

The scarfer spittings are cooled and flushed from the surface of the steel by high pressure water and are collected in a water bath. The scarfer spittings range in size from less than a No. 100 sieve size, that is, less than 0.149 mm to larger than 50.8 mm in diameter. The spittings are comprised of an outer shell of iron oxides surrounding an inner metallic core which has a chemical composition similar to that of the scarfed steel.

Scarfer spittings have no specific use. In recent years efforts have been directed to recycling the spittings in the steel mill to recover the iron which they contain. A portion of the spittings are mixed with mill scale, steel borings and the like and are used as part of the charge to a sinter strand to recover the iron. However, only the larger sized particles or spittings can be so used. Hence, most of the spittings must be removed from the mill and stored. In recent years, increased emphasis on the surface cleanliness of steel has resulted in an increase in the use of automatic scarfing machines to scarf the steel surfaces. As a result, the volume of scarfer spittings produced in a steel mill has increased, thereby increasing the time required to transport the spittings and the amount of storage space required for the spittings.

A process developed by *H.W. Hitzrot, Jr.; U.S. Patent 4,190,422; February 26, 1980; assigned to Bethlehem Steel Corporation* has as its object the use of scarfer spittings comprised of inner metallic cores and outer brittle shells of iron oxides for use in machine or manual blast cleaning equipment to blast clean metallic and nonmetallic surfaces. This process yields a product having a hardness of about R_c 20 to 35 and a lathlike martensitic matrix which can be used as a size-graded metallic abrasive having good toughness, extended service life and improved cleaning efficiency when compared with commercially available size-graded steel shot and grit abrasives.

The waste material is screened to simultaneously separate it from all the foreign matter collected therewith and also to separate it into a fraction containing particles larger than about 6.35 mm and a fraction containing particles smaller than about 6.35 mm. The fraction containing the larger particles is recycled in the steel mill. The fraction containing the smaller particles is charged into a grinding mill containing appropriate grinding media. The smaller fraction remains in the mill for a time so that the outer shells are broken into small pieces substantially all of which are removed from the surfaces of the inner cores. The pieces of the shells and the metallic cores are separated from each other by screening. The metallic cores are graded into a plurality of sizes by screening. The pieces of shells are recycled in the plant.

The metallic cores have a microstructure of untempered lathlike martensite substantially free from intergranular and intragranular cracking, a hardness of about R_c 20 to 35, and a grain size of between about 3 and 4 and are characterized by having good impact toughness and extended service life.

ABRASIVE MATERIAL FROM SPENT CATALYST

The last few decades have seen a steep rise in the use of heterogenous catalytic reactions. The ever increasing use of crude oil and its distillation products, which must be desulfurized to protect the environment, has led to a considerable increase in the use of catalysts useful in such reactions. In one widely used catalytic desulfurization process, the hydrocarbon starting materials are contacted with an MoCo catalyst on an alumina (Al_2O_3) carrier and the developing hydrogen sulfide is removed. In some instances, MoNi- and WNi-type catalysts or other metallic catalyst combinations are used.

During the catalytic reaction, the catalyst absorbs or adsorbs various chemical elements or compounds from the reactants and eventually becomes inactive. While the catalyst may be regenerated, it will eventually be spent and must be replaced. It is of considerable economic importance to utilize at least portions of such spent catalytic materials.

Various processes have been proposed for working up hydrodesulfurization catalytic materials of the indicated types. One process involves roasting the catalytic material with sodium chloride (NaCl) after calcining and then extracting vanadium, molybdenum, alumina, nickel and/or cobalt, the ammonium salts of molybdenum and vanadium as well as aluminum hydroxide ($Al(OH)_3$) being obtained after several process steps. Cobalt and nickel remaining in the extraction residue must be extracted in a further step if they are to be recovered.

Other processes work with soda (sodium carbonate) instead of sodium chloride. All the known processes are chemically complex and technically expensive, thus making them commercially unattractive. Furthermore, it is quite difficult to separate molybdenum from vanadium and cobalt from nickel.

It is the primary object of the following process to provide for preparing an abrasive material from spent catalytic materials of the indicated type, the alumina carrier component of the starting material providing the abrasive material and the metallic catalyst component providing valuable alloys which may be used directly or after refining in the steel and alloying industry, or which may be readily separated chemically into their chemical elements after having been stripped of the carrier.

This process has been described in some detail by *H. Zeiringer; U.S. Patent 4,142,871; March 6, 1979; assigned to Treibacher Chemische Werke AG, Austria.*

It is one in which an abrasive material is prepared from a starting material comprised of a spent metallic catalyst on an alumina carrier by melting the starting material with a reducing agent to obtain a melt consisting of a melt component including the alumina on an alloy residue, cooling the melt at a speed correlated with a desired crystallite size of the abrasive material to be obtained, and mechanically separating the melt component from the alloy residue before or after solidification, the melt component constituting the abrasive material.

The size of the corundum crystallites obtained in the process may be influenced within wide limits by the rate of cooling of the melt, the crystallite size of the abrasive determining its usefulness for various fields of utilization. Considerable differences in the crystallite sizes and the corresponding utility of the abrasive can be obtained by solidifying the melt very slowly in a block, on the one hand, and rapidly cooling by casting it over steel balls, on the other hand. The resultant sizes of the corundum crystallites may accordingly vary, depending on the method of cooling, from 1 mm to 0.001 mm.

The solid alumina product of the process is an excellent abrasive after comminution and classification into various grain sizes, with or without heat treatment. Depending on the type and amount of additives as well as the crystallite size, these abrasives may be used for polishing steel, precision polishing under very light pressures or polishing wood.

The catalyst component accumulating as an alloy at the bottom of the melting furnace vessel is either cast or tapped with the alumina melt component, or it is permitted to solidify therewith in a block. Depending on the type of catalyst, the alloy is comprised primarily of MoCo, WNi, MoCoVNi and various impurities, such as sulfur, carbon, silicon, iron, titanium or chromium. After the alloy has been mechanically separated from the abrasive component, it may be used directly in the steel or alloying industry. If impurities, such as silicon, sulfur or carbon, are present in undesirable amounts, the alloy may be refined in any conventional manner.

ALUMINA FROM ALUMINUM REDUCTION PLANT WASTES

In the production of metallic aluminum by electrolysis of reduction grade Al_2O_3, the electrolysis is generally carried out in reduction cells or pot lines which are lined with a carbonaceous material. During the life of the cells, this carbon lining is gradually destroyed by penetration of bath materials into the lining, for example, metallic aluminum, cryolite and alumina. Also, due to the high temperatures employed in the electrolytic reduction process, gradual aging of the carbonaceous lining takes place.

The combined result of penetration and aging can reach a stage where the further operation of the cell or cells reaches an economically prohibitive point and replacement of the carbonaceous lining becomes a must. The unusable or spent pot lining is then removed and in most instances stockpiled. In large aluminum reduction facilities, this lining replacement is a continuous process and, consequently, the quantity of spent lining stockpiled increases from day to day.