

# **METAL AND INORGANIC WASTE RECLAIMING ENCYCLOPEDIA**

by

**Marshall Sittig**

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**NOYES DATA CORPORATION**

**Park Ridge, New Jersey, U.S.A.**

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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 .....	1
Abrasive Material from Scarfer Spittings .....	5
Abrasive Material from Spent Catalyst .....	6
Alumina from Aluminum Reduction Plant Wastes .....	7
Alumina from Red Mud from Bayer Process .....	10
Aluminum from Acetylene Scrubbing Solutions .....	12
Aluminum from Aluminum-Glass Cloth Residues .....	13
Aluminum from Electrical Conductor Scrap .....	16
Aluminum from Fly Ash .....	16
Aluminum from Furnace Skim or Dross .....	20
Aluminum from Municipal Waste .....	27
Aluminum from Nonferrous Sludges .....	28
Aluminum from Scrap Aluminum .....	28
Aluminum from Solid Propellant Waste .....	45
Aluminum Fluoride from Aluminum Reduction Plant Wastes .....	46
Aluminum Foil from Paper/Foil Laminates .....	48
Ammonia from Ammonia-Soda Plant Effluents .....	49
Ammonia from Ammonoxidation Process Wastes .....	51
Ammonia from Textile Treating Effluents .....	52
Ammonia from Urea Plant Wastewater .....	58
Ammonia-Base Pulping Liquor from Spent Pulping Liquor .....	61
Ammonium Nitrate from Nuclear Fuel Processing Waste .....	65
Ammonium Perchlorate from Solid Propellant Waste .....	66
Ammonium Sulfate from Acrylonitrile Process Effluents .....	67
Ammonium Sulfate from Caprolactam Manufacture .....	67
Ammonium Sulfate from Storage Battery Plate Wash Water .....	68
Antimony from Polyester Still Bottoms .....	72
Antimony from Scrap Antimony .....	74
Antimony Pentachloride from Spent Catalysts .....	74
Arsenic from Copper Smelter Flue Dusts .....	75
Asbestos from Waste Asbestos Slurries .....	76

Barite from Drilling Muds .....	78
Beryllium from Scrap Beryllium .....	78
Beryllium from Stainless Steel Pickle Liquors .....	78
Bismuth from Debismuthizing Dross .....	78
Bleach-Fix Solutions from Spent Photographic Solutions .....	81
Bleach Liquor from Spent Bleachery Effluent .....	84
Boric Acid from Cyclohexane Oxidation Wastes .....	85
Building Bricks from Red Mud from Bayer Process .....	87
Cadmium from Battery Scrap .....	89
Cadmium from Zinc Refinery Flue Dusts .....	93
Calcium Fluoride from Phosphate Pond Waters .....	95
Calcium Fluoride from $UO_2$ Process Wastewaters .....	100
Cast Iron from Scrap Automobiles .....	100
Caustic from Caustic Sludges .....	100
Cement from Cement Kiln Dust .....	101
Cement from Ready Mix Concrete Residues .....	102
Chlorided Alumina Catalyst from Spent Catalyst .....	105
Chlorine from Aluminum Chloride Electrolysis .....	106
Chlorine from Ilmenite Chlorinator Dust .....	108
Chlorine from Wastewaters .....	108
Chromic Acid from Spent Etching Solutions .....	109
Chromic Acid from Waste Chromic Acid Solutions .....	111
Chromium from Chromic Anhydride Production .....	112
Chromium from Cooling Tower Blowdown Water .....	113
Chromium from Electroplating Rinse Waters .....	114
Chromium from Nonferrous Sludges .....	120
Chromium from Scrap Chromium .....	121
Chromium from Tannery Wastes .....	121
Chromoxyfluoride Catalysts from Spent Catalysts .....	126
Cobalt from Scrap Cobalt .....	127
Cobalt from Sintered Metal Carbides .....	127
Cobalt from Spent Catalysts .....	127
Colored Glass from Mixed Glass Waste .....	130
Columbium from Scrap Columbium .....	131
Columbium from Spent Catalysts .....	131
Copper from Acetylene Scrubbing Solutions .....	131
Copper from Brass Mill Dusts .....	131
Copper from Copper Refinery Anode Slimes .....	133
Copper from Electrical Scrap .....	142
Copper from Mixed Scrap .....	146
Copper from Nonferrous Sludges .....	151
Copper from Scrap Automobiles .....	151
Copper from Smelter Flue Dust .....	152
Copper from Smelter Slags .....	154
Copper from Spent Catalysts .....	157
Copper from Spent Etching Solutions .....	159
Copper Catalyst from Adipic Acid Manufacture Wastes .....	162
Cryolite from Pot Line Recovered Particulates .....	162
Dicalcium Phosphate from Phosphate Pond Waters .....	166
Dinitrogen Monoxide from Adipic Acid Process Off-Gases .....	166

Ferric Chloride from Spent Pickle Liquor .....	167
Ferroalloys from Plating Sludges .....	169
Ferronickel from Spent Catalysts .....	174
Ferrous Metals from Municipal Waste .....	174
Ferrous Sulfate from Spent Pickle Liquor .....	179
Ferrovanadium from Pig Iron .....	179
Fertilizer from Flue Gas Scrubber Sludge .....	180
Fertilizer from Municipal Wastes .....	182
Fertilizer from Spent Sulfuric Acid .....	187
Flocculating Agent from Red Mud from Bayer Process .....	189
Fluorosulfuric Acid from Spent Catalysts .....	190
Fluosilicic Acid from Phosphoric Acid Manufacture .....	194
Foundry Sand from Used Foundry Sand .....	197
Gadolinium from Bubble Memory Unit Scrap .....	211
Gallium from Alumina Plant Liquors .....	212
Gallium from Bubble Memory Unit Scrap .....	214
Gallium from Phosphorus Furnace Flue Dust .....	214
Germanium from Zinc Smelter Flue Dusts .....	221
Glass from Glass Container Waste .....	222
Glass from Laminated Glass Scrap .....	229
Glass from Municipal Waste .....	231
Glass from Scrap Automobiles .....	241
Glass from Television Picture Tubes .....	241
Glass Fibers from Glass Fiber Scrap .....	242
Gold from Mine Waste Dumps .....	244
Gold from Plating Waste Solutions .....	246
Gold from Scrap Gold .....	247
Gold from Silver Refinery Muds .....	247
Gold from Wastewaters .....	247
Hydrofluoric Acid from Spent Pickle Liquors .....	253
Hydrogen Chloride from Chlorination of Organics .....	253
Hydrogen Chloride from Dilute HCl Solutions .....	258
Hydrogen Chloride from Incineration Gases .....	259
Hydrogen Chloride from Oxychlorination Process Exit Gases .....	263
Hydrogen Chloride from Spent Pickle Liquor .....	267
Hydrogen Fluoride from Alkylation Process .....	268
Hydrogen Fluoride from Furnace Pot Linings .....	276
Iodine from Acetoxylation Process Wastes .....	281
Iodine from Dehydrogenation Process Wastes .....	282
Iridium from Spent Catalysts .....	284
Iron from Oxygen Converter Slags .....	290
Iron from Red Mud from Bayer Process .....	291
Iron from Rolling Mill Scale .....	292
Iron from Scrap Iron .....	292
Iron from Scrap Tires .....	292
Iron from Spent Pickle Liquor .....	294
Iron from Steel Mill Furnace Dusts .....	297
Iron Oxide from Ilmenite Chlorinator Dust .....	312
Iron Oxide from Rolling Mill Sludge .....	315
Iron Powder from Machining Scrap .....	318

Lead from Gun Club Soils. . . . .	323
Lead from Lead Refinery Dross . . . . .	325
Lead from Lead Scrap. . . . .	326
Lead from Solder Skimmings . . . . .	327
Lead from Storage Battery Scrap . . . . .	329
Lead from TEL Manufacturing Wastes . . . . .	347
Lead from Zinc Refinery Flue Dusts. . . . .	348
Lead Carbonate from Storage Battery Manufacture . . . . .	349
Lead Oxide from Flue Dusts. . . . .	349
Lime from Sewage Sludge Incineration Residues. . . . .	351
Magnesia from Scrap Furnace Lining Brick . . . . .	355
Magnesium from Cell Sludges . . . . .	356
Magnesium from Scrap Magnesium . . . . .	356
Magnesium from Tracer Ammunition . . . . .	360
Mercury from Brine in Chlor-Alkali Plants . . . . .	362
Mercury from Caustic/Chlorine Process Sludges . . . . .	365
Mercury from Scrap Mercury . . . . .	370
Mercury from Spent Catalysts. . . . .	370
Metals from Mixed Metal Slimes . . . . .	374
Metals from Oily Scrap Metals. . . . .	377
Metals from Plastic/Metal Composite Parts . . . . .	378
Molybdenum from Copper Sulfide Ores . . . . .	379
Molybdenum from Scrap Molybdenum. . . . .	381
Molybdenum from Smelter Flue Dust. . . . .	381
Molybdenum from Spent Catalysts . . . . .	381
Molybdenum from Tungsten Lamp Manufacture . . . . .	384
Nickel from Battery Scrap. . . . .	386
Nickel from Bright Nickel Plating Baths . . . . .	386
Nickel from Nonferrous Sludges . . . . .	390
Nickel from Plating Rinse Waters . . . . .	391
Nickel from Scrap Nickel . . . . .	394
Nickel from Spent Catalysts . . . . .	395
Nickel from Superalloy Scrap . . . . .	400
Nitric Acid from Used Acrylic Fiber Spinning Solutions. . . . .	403
Nitrogen Tetroxide from Cellulose Spin Bath . . . . .	403
Nonferrous Metals from Municipal Waste . . . . .	404
Nonferrous Metals from Scrap Automobiles . . . . .	404
Olive Processing Liquor from Olive Processing Wastes. . . . .	408
Palladium from Plating Waste Solutions . . . . .	409
Palladium from Spent Catalysts. . . . .	409
Paving Material from Fly Ash and Water Treatment Sludge. . . . .	410
Platinum from Plating Waste Solutions . . . . .	411
Platinum from Platinum Metals Refinery Effluent . . . . .	411
Platinum from Spent Catalysts . . . . .	411
Platinum Metals from Precious Metals Scrap . . . . .	413
Plutonium Oxide from Nuclear Fuel Process Scrap . . . . .	414
Porous Ceramics from Fly Dusts . . . . .	414
Portland Cement from Coal Ash Slag . . . . .	415
Portland Cement from Oxygen Converter Slags. . . . .	418



Pozzolan from Fly Ash .....	418
Rhenium from Molybdenum Sulfide Roaster Gases .....	423
Rhenium from Wastewaters .....	424
Rhodium from Plating Waste Solutions .....	425
Rhodium from Spent Catalysts .....	425
Ruthenium from Spent Catalysts and/or Scrap Electrodes .....	429
Salt Cake from Aluminum Refining .....	431
Scandium from Uranium Process Sludges .....	434
Selenium from Copper Refinery Anode Slimes .....	435
Selenium from Urethane Reaction Products .....	440
Selenium from Xerographic Equipment Discards .....	442
Silver from Copper Refinery Anode Slimes .....	447
Silver from Electroplating Wastes .....	449
Silver from Mine Waste Dumps .....	450
Silver from Scrap Photographic Film .....	450
Silver from Scrap Silver .....	459
Silver from Silver-Brazed Stainless Steel Scrap .....	459
Silver from Spent Photoprocessing Solutions .....	461
Silver from Wastewaters .....	470
Sodium Ferrocyanide from Halogen Tin Electroplating Sludges .....	470
Sodium Hydroxide from Spent Pulping Liquor .....	470
Sodium Nitrate from Heat Treating Operations .....	476
Sodium Nitrite from Absorber Liquor .....	481
Sodium Sulfite from Spent Pulping Liquor .....	481
Sodium Sulfite from TNT Process Wastes .....	489
Sodium Thiocyanate from Used Acrylic Fiber Spinning Solutions .....	490
Soil Modifiers from Titanium Dioxide Process Waste .....	491
Stainless Steel from Stainless Steel Scrap .....	492
Steel from Machining Scrap .....	492
Steel from Scrap Automobiles .....	492
Steel from Scrap Steel .....	497
Steel from Whole Scrap Tires .....	502
Strontium Nitrate from Tracer Ammunition .....	502
Sulfate Cooking Liquor from Spent Pulping Liquor .....	502
Sulfur from Hydrocracking Process Effluents .....	506
Sulfur Dioxide from Spent Sulfuric Acid .....	506
Sulfuric Acid from Spent Pickle Liquor .....	509
Sulfuric Acid from Spent Sulfuric Acid .....	516
Sulfuric Acid from Titanium Dioxide Process Waste .....	519
Tantalum from Spent Catalysts .....	522
Tellurium from Copper Refinery Anode Slimes .....	522
Thallium from Zinc Smelter Flue Dusts .....	523
Tin from Dross from Hot Dip Coating .....	524
Tin from Halogen Tin Electroplating Wastes .....	524
Tin from Scrap Tin .....	528
Tin from Slags .....	529
Tin/Aluminum Alloy from Multilayer Bearings .....	529
Titanium from Scrap Titanium .....	529
Trisodium Phosphate from Aluminum Bright Dipping Effluent .....	530
Tungsten from Sintered Metal Carbides .....	534

Tungsten from Spent Catalysts .....	535
Tungsten from Tungsten Scrap .....	537
Tungsten Carbide from Scrap Mining Bits .....	538
Uranium from $UO_2$ Process Wastewaters .....	539
Uranium Oxide from Nuclear Fuel Process Scrap .....	542
Vanadia-Titania Catalyst from Spent Denitration Catalyst .....	545
Vanadium from Spent Catalysts .....	546
Vanadium Catalyst from Adipic Acid Process Wastes .....	549
Water Treating Agent from Spent Cracking Catalyst .....	553
Wool Scouring Liquor from Spent Scouring Liquor .....	553
Yttrium Oxysulfide from Color TV Tube Manufacture .....	555
Zinc from Brass Mill Dusts .....	559
Zinc from Brass Skimmings .....	559
Zinc from Electroplating Wastes .....	563
Zinc from Galvanizing Wastes .....	566
Zinc from Nonferrous Sludges .....	567
Zinc from Scrap Automobiles .....	567
Zinc from Steel Mill Furnace Dusts .....	567
Zinc from Zinc Scrap .....	572
Zinc Chloride from Spent Catalysts .....	573
Zinc Chloride from Used Acrylic Fiber Spinning Solutions .....	576
Zirconium from Spent Pickle Liquor .....	576
Organic and Polymer Waste Reclaiming .....	579
Sources of Waste Feed Materials .....	584
References .....	590

## 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.

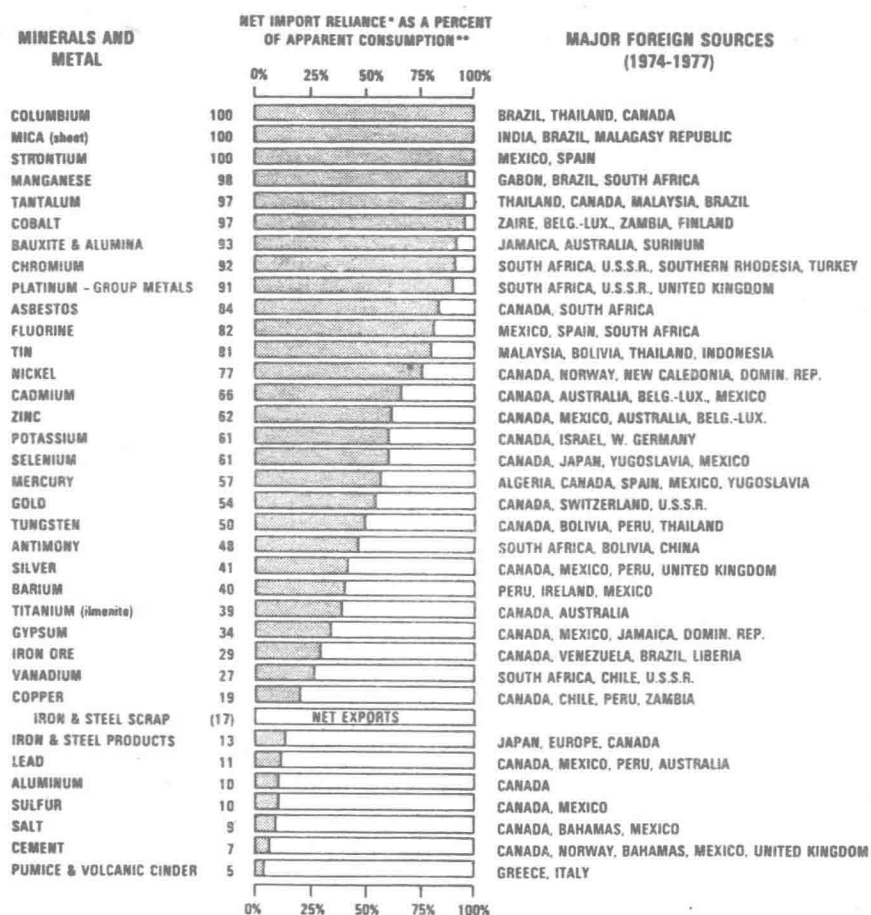
The reader's attention is also called to a number of other published works including a summary volume by Barton (4), monthly materials surveys by the U.S. Bureau of Mines (2), a volume of forecasts for resource recovery to the year 1990, made in 1975 (5), a discussion of energy use patterns for metal 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  $\text{Al}_2\text{O}_3$ , 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.