

# **Rare Earth Technology and Applications**

**CHEMICAL TECHNOLOGY REVIEW No. 154**

**ndc**

# **RARE EARTH TECHNOLOGY AND APPLICATIONS**

**Edited by F. Villani**

**NOYES DATA CORPORATION**

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

**1980**

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# **RARE EARTH TECHNOLOGY AND APPLICATIONS**

## FOREWORD

The detailed, descriptive information in this book is found in U.S. patents issued since January 1973 that deal with rare earth technology and applications.

This book is a data-based publication, providing information retrieved and made available from the U.S. patent literature. It thus serves a double purpose in that it supplies detailed technical information and can be used as a guide to the patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced commercially oriented review of rare earth technology and applications.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data are employed to bring these durably bound books to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The table of contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

## 15 Reasons Why the U.S. Patent Office Literature Is Important to You —

1. The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical commercial process information assembled here than is available from any other source.
2. The technical information obtained from the patent literature is extremely comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure."
3. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature.
4. An important feature of the patent literature is that it can serve to avoid duplication of research and development.
5. Patents, unlike periodical literature, are bound by definition to contain new information, data and ideas.
6. It can serve as a source of new ideas in a different but related field, and may be outside the patent protection offered the original invention.
7. Since claims are narrowly defined, much valuable information is included that may be outside the legal protection afforded by the claims.
8. Patents discuss the difficulties associated with previous research, development or production techniques, and offer a specific method of overcoming problems. This gives clues to current process information that has not been published in periodicals or books.
9. Can aid in process design by providing a selection of alternate techniques. A powerful research and engineering tool.
10. Obtain licenses — many U.S. chemical patents have not been developed commercially.
11. Patents provide an excellent starting point for the next investigator.
12. Frequently, innovations derived from research are first disclosed in the patent literature, prior to coverage in the periodical literature.
13. Patents offer a most valuable method of keeping abreast of latest technologies, serving an individual's own "current awareness" program.
14. Copies of U.S. patents are easily obtained from the U.S. Patent Office at 50¢ a copy.
15. It is a creative source of ideas for those with imagination.

# INORGANIC CHEMICAL INDUSTRY PROCESSES, TOXIC EFFLUENTS AND POLLUTION CONTROL 1978

by Marshall Sittig

*Chemical Technology Review No. 118*

*Pollution Technology Review No. 52*

While industrial inorganic chemistry may seem less glamorous than the complex chemistry of the life sciences, the progress in wonder drugs, miracle fibers and recombinant DNA is basically dependent on the uninterrupted flow of "heavy" chemicals, such as sulfuric acid, chlorine and sodium hydroxide.

The present book provides helpful directions for making these inorganic chemicals. The arrangement is encyclopedic starting with alumina and ending with various zinc compounds. The process details provide a wide choice of raw materials due to a changing economy and partial cutoff of the customary supplies, e.g., natural gas, which in inorganic processing is a most convenient source of hydrogen, carbon, carbon monoxide and carbon dioxide. Careful perusal of this book will reveal many alternate sources and energy-sparing processes.

Contaminated wastewater and air pollution problems are considerable, but new commercial processes are shown, as well as detailed technology from the U.S. patent literature. Because of the stable nature of this industry, established processes and obsolete equipment units remain sufficiently profitable to continue in use. Still, considerable progress in pollution control has been achieved during the past 5 or 6 years and is reflected in this book. The following chemicals have received detailed treatment:

Alumina	Cuprous Oxide	Potassium Nitrate
Aluminum Chloride	Ferric Chloride	Potassium Perchlorate
Aluminum Fluoride	Ferrous Sulfate	Potassium Permanganate
Aluminum Sulfate	Fluorine	Potassium Sulfate
Ammonia	Helium	Silver Nitrate
Ammonium Chloride	Hydrochloric Acid	Sodium Bicarbonate
Ammonium Diuranate	Hydrogen	Sodium Bisulfite
Ammonium Hydroxide	Hydrogen Fluoride	Sodium Borohydride
Ammonium Nitrate	Hydrogen Peroxide	Sodium Bromide
Ammonium Phosphate	Iodine	Sodium Carbonate
Ammonium Sulfate	Iron Blue Pigments	Sodium Chlorate
Antimony Oxide	Iron Oxide Pigments	Sodium Chloride
Arsenic Acid	Lead Carbonate	Sodium Chromate
Arsenic Oxides	Lead Nitrate	Sodium Cyanide
Barium Carbonate	Lead Oxides	Sodium Dichromate
Barium Sulfate	Lead Sulfate	Sodium Fluoride
Beryllium Hydroxide	Lithium Carbonate	Sodium Sulfide
Beryllium Oxide	Lithium Hydroxide	Sodium Hydrosulfite
Borax	Magnesium Chloride	Sodium Hydroxide
Boric Acid	Magnesium Sulfate	Sodium Metal
Boron Trichloride	Manganese Sulfate	Sodium Perchlorate
Bromine	Mercuric Chloride	Sodium Phosphates
Cadmium Pigments	Mercuric Oxide	Sodium Silicate
Cadmium Sulfide	Mercuric Sulfide	Sodium Silicofluoride
Calcium Arsenate	Mercurous Chloride	Sodium Sulfite
Calcium Carbide	Molybdate Chrome Pigments	Sodium Thiosulfate
Calcium Carbonate	Nickel Sulfate	Stannic Oxide
Calcium Chloride	Nitric Acid	Stannous Chloride
Calcium Hydroxide	Nitrogen & Oxygen	Strontium Carbonate
Calcium Oxide	Nitrous Oxide	Sulfur Chlorides
Calcium Phosphate	Phosphate Rock	Sulfuric Acid
Carbon Dioxide	Phosphoric Acid	Sulfuryl Chloride
Carbon Monoxide	Phosphorus	Superphosphoric Acid
Chlorine & Caustic	Phosphorus Oxychloride	Supported Catalysts
Chlorosulfonic Acid	Phosphorus Pentasulfide	Thallium Carbonate
Chrome Green Pigment	Phosphorus Pentoxide	Thionyl Chloride
Chrome Yellow Pigment	Phosphorus Trichloride	Titanium Dioxide
Chromic Acid	Potassium Chlorate	Ultramarine Pigments
Chromic Oxide Pigment	Potassium Chloride	Zinc Chloride
Cobalt Compounds	Potassium Dichromate	Zinc Oxide
Cobalt Oxide	Potassium Iodide	Zinc Sulfate
Copper Sulfate	Potassium Metal	Zinc Yellow Pigment



# CORROSION INHIBITORS 1979

## RECENT DEVELOPMENTS

by J.S. Robinson

*Chemical Technology Review No. 132*

There are both multipurpose and highly specialized corrosion inhibitors described in this new work. Corrosion is an ever-present problem in industry, but it is clear from the nearly 300 processes and techniques detailed here that research is making substantial strides in supplying products to overcome it. The book comprises chemicals, such as sequestering agents and oxygen scavengers; and physical barriers, such as coatings.

The author has arranged the processes according to their most significant end use, as shown below. The first chapter, for instance, covers substances used to overcome the problems encountered in water engineering. It encompasses both antisclalants and corrosion inhibitors, the latter often being required during scale removal operations.

It should be emphasized that some inhibitors serve in several capacities—the benzotriazole derivative found under lubricants may well be ideal for circulating water systems.

Chapter headings and **examples of some** important subtitles follow below. The number of processes per topic is shown in parentheses following chapter headings.

### 1. CIRCULATING WATER SYSTEMS (69)

#### Cooling Water

Phosphonomethylamino Carboxylates  
Phosphorus-Free Inhibitors  
Inhibitor of Low Pollution & Toxicity  
Inhibitor in Seawater Coolant  
Maleic-Furan Copolymers for Boilers  
Hydrazine Compound as Oxygen Scavenger  
Scale Removal and Acid Cleaning  
Inhibitor for Hydrofluoric Acid  
Heat Exchanger Agents  
Municipal Water Supplies  
Pyrophosphate-Zinc Combination  
Coated Chlorine Evaporator Chamber

### 2. OIL WELL AND REFINERY USE (39)

Alkynoxymethylamines in Drilling Fluids  
Amine Bisulfites in Water Flooding  
Alkylpyridines in Water Flooding  
Pipelines and Tanks  
Macrocyclic Tetramine Films  
Acid-Gas Treatment  
Cu-S-Monoethanolamine Formulation  
Antifoulant and Anticorrosive Processing  
Quaternary Ammonium Demulsifiers

### 3. CONSTRUCTION MATERIALS (34)

Corrosion-Resistant Concrete and Gypsum

Rust Treatment—Primers, Pigments, Resins  
Silicone-Acrylic-Polyurethane Coatings  
Topcoated Phosphated Bolts, Nuts,  
Washers  
Carboxymethylated Derusting Agents  
Circuit Breaker Phosphate-Chromate Coat  
Multilayered Wax Coating for Marine Use  
Inhibiting Shellfish and Algae Adhesion

### 4. FUELS AND LUBRICANTS (47)

C<sub>21</sub>-Dicarboxylic Acid Motor Fuel Formula  
Aminoalkylpropanediols in Motor Fuels  
Halogen Treatment of Motor Fuels  
Hydraulic Fluids  
Benzotriazole Metal-Working Fluid  
Residual Fuel—Mg-Si-Mn Combination  
Tetrahydrobenzimidazole Lubricant  
P<sub>2</sub>S<sub>5</sub> Adducts as Lubricating Oils  
Silicone-Perfluorocarbon Polymer Grease

### 5. INORGANIC TREATMENT OF METAL (50)

Phosphatizing with Alkylolamine Additive  
Quaternary Amino Polymer Pickling Bath  
Halogenated Alkynoxymethylamine Pickle  
Polymeric Electrodeposition  
Zn-Li Silicate-Latex Coating  
Zn-Al Hot Dip Coating  
Metal-Urea Chromating Composition  
Hydrophobic Silicon Oxide Layers  
Carbide-Reinforced Superalloys  
Vacuum-Tight Metal-to-Ceramic Seals

### 6. ORGANIC TREATMENT OF METAL (29)

Tannin-Phosphate-Ti-Fluoride Formula  
Alkanolamine Mist or Spray Inhibitor  
Dicyclohexylammonium Pelargonate  
Ascorbic Acid Compositions  
Corrosion-Inhibiting Rubber  
Radiation-Polymerized Coatings  
1,2-Fused-1,3-Dinitrogen Heterocyclics  
Sulfur Dioxide-Schiff Base Adducts

### 7. ADDITIONAL APPLICATIONS (29)

Detecting and Evaluating Corrosion  
Alkyltin Tarnish Protectives  
Inert Gas for Storage Protection  
3-Component Synergistic Hydrocarbons  
Reaction Vessels & Process Equipment—  
Chromium Dioxide Synthesis  
Acrylonitrile Plants  
Nuclear Reactors  
Coal- or Gas-Carrying Pipelines  
Noncorrosive Solid Detergent  
Inhibition of Toothpaste Tube Swelling  
Polyphosphonic Acid Sequestering Agent



# INCINERATION OF INDUSTRIAL HAZARDOUS WASTES AND SLUDGES 1979

by Marshall Sittig

*Pollution Technology Review No. 63*

This is another volume in our Pollution Technology Review series which is especially designed to provide help and advice for strict compliance with present and projected rules and regulations of the Resource Conservation and Recovery Act (RCRA) as interpreted by the EPA.

This book, dealing with incineration and related combustion processes, such as pyrolysis, can be of vital importance to the interests of the affected companies, who must see to it that incineration, combustion, and other burning operations are conducted with proper attention to complete destruction of the toxic materials, and efficient scrubbing of the effluent gases, followed by appropriate treatment of the scrubbing liquors. A condensed table of contents follows here:

- 1. TYPES OF WASTES WHICH CAN BE INCINERATED**  
Classes of Wastes  
Hazardous Wastes & Chemicals  
Mixed Sludge and Refuse
- 2. WASTE DISPOSAL ALTERNATIVES**  
Landfills  
Landspreading  
Composting  
Ocean Dumping  
Deep Well Disposal
- 3. REGULATORY REQUIREMENTS**  
EPA Air Pollution Regulations  
Hazardous Waste Incineration  
OSHA Worker Protection  
State Regulations  
The Resource Conservation and Recovery Act (RCRA)  
Regulations Under RCRA
- 4. FACTORS IN INCINERATOR SYSTEM SELECTION**  
Waste Toxicity  
Disposal Rate  
Corrosiveness  
Operating Temperature  
Material Selection  
Waste Heat Recovery
- 5. VARIABLES AFFECTING COMBUSTION**  
Combustibility  
Residence Time in the Combustion Zone
- 6. FEED PREPARATION FOR INCINERATION**  
Handling of Wastes in Drums  
Evaporative Concentration  
Admixture with Combustibles  
Co-Incineration of Sludge and Municipal Refuse  
Institutional Constraints  
Funding
- 7. INCINERATOR DESIGN EXAMPLES**  
New Sludge Incineration System  
Retrofit of an Existing Multiple-Hearth Sludge Incinerator
- 8. INCINERATOR TYPES**  
Afterburners  
Catalytic Incinerators  
B.F. Goodrich Commercial Scale Catoxid Process  
Cyclonic Furnaces  
Direct Flame Thermal Incinerators  
Electric Furnaces  
Flares  
Fluidized Bed Incinerators  
Liquid Waste Combustors  
G.E. Liquid Injection Incinerator  
Marquardt SUE Sudden Expansion Burner  
Preenco Liquid Injection Incinerator  
Molten Salt Incinerators  
Atomics International  
Molten Salt Reactor  
Multiple Chamber Incinerators  
Multiple Hearth Incinerators  
Eimco BSP Multiple Hearth Furnace  
Open Pit Burning  
Pebble Bed Incinerators  
Rotary Kiln Incinerators  
Chem-Trol Process  
Hyon Waste Management Services Inc.  
Rotary Kiln  
Pollution Controls Inc. Rotary Kiln  
Rollins Rotary Kiln
- 9. WET AIR OXIDATION UNITS**  
Resource Recovery Inc.  
Zimpro, Inc.

# LANDFILL DISPOSAL OF HAZARDOUS WASTES AND SLUDGES 1979

by Marshall Sittig

*Pollution Technology Review No. 62*

The Resource Conservation and Recovery Act (RCRA), passed 1976, created a Federal and State regulatory authority over both solid and hazardous wastes. The projected regulations will become fully effective by June 30, 1980. These will have profound effects on industrial waste disposal practices, particularly those for hazardous wastes.

The Department of Transportation has currently compiled a list of about 300 poisons, pesticides and priority pollutants considered to be hazardous waste materials.

In this book, the landfill technology and the directions for the disposal of unwanted hazardous and toxic substances are based on reports and guidelines mostly issued by the EPA. A condensed table of contents follows here.

## **1. WASTE SOURCES**

Hazardous Wastes  
Treatment Plant Sludges

## **2. WASTE DISPOSAL ALTERNATIVES**

The Conventional Sanitary Landfill  
Landspreading  
Composting  
Incineration  
Ocean Dumping  
Deep Well Disposal

## **3. REGULATORY REQUIREMENTS**

Federal Regulations  
State Regulations  
Local Regulations & Permits

## **4. WASTE PREPARATION**

Hazardous Wastes  
Treatment Plant Sludges

## **5. PUBLIC RELATIONS AND PUBLIC PARTICIPATION**

Objectives  
Advantages & Disadvantages

## **6. SITE SELECTION**

Surface Water  
Soil Type  
Vegetation  
Access  
Land Use (Zoning)

## **7. DESIGN**

Environmental Considerations

Storm Water Management  
Leachate Controls

## **8. CONSTRUCTION AND OPERATION**

Operation of Various Types of Landfills  
Sludge-Only Area  
Runoff Control  
Environmental Control Practices  
Management Responsibility

## **9. MONITORING**

Groundwater Monitoring  
Gas Monitoring

## **10. LANDFILL APPLICATION TO SPECIFIC INDUSTRY WASTES**

Pulp and Paper Industry Wastes  
Iron & Steel Industry Wastes  
Descriptions of Selected Steel Industry  
Dump Sites  
Impact of Section 4004 RCRA Criteria  
Pesticide Industry Wastes  
Oil Spill Cleanup Debris

## **11. ECONOMIC ASPECTS**

Cost Accounting  
Typical Costs  
Hauling Costs  
Site Costs  
Overall Costs  
Cost of Landfill Monitoring for Enforcement of Groundwater Standards  
Financing  
General Obligation Borrowing  
Revenue Bonds  
Sewer Rate Increases and Special Assessments  
Grants or Subsidies  
Loans  
User Fees

## **12. FINAL LAND USE**

Procedures for Site Closure  
Characteristics of Completed Site  
Settlement  
Bearing Capacity  
Final Grade  
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Vegetation  
Considerations Relating to Hazardous Waste Landfills  
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and it is preferred that the specific surface area be reasonably high, though this did not appear to be critical but is a preference for maximum activity. Preferred is a silica with a specific surface area ranging from such as about 10 to 100 m<sup>2</sup>/g, more preferably from about 50 to 100 m<sup>2</sup>/g.

While the silica supported catalyst can be prepared in any convenient fashion, one effective method is to impregnate the silica with a solution containing one or more rare earth metal salts which are convertible to the oxide on calcination in a molecular oxygen atmosphere. Typical and suitable of such rare earth metal salts are the bromates, halides, nitrates, sulfates, various organic complexes such as those derived from ethylenediaminetetraacetic acid, and the like, preferred being the nitrates for ease and convenience of dissolving and handling.

After impregnation of the support, the composite is dried, and calcined in a molecular oxygen-containing atmosphere, such as air, at a suitable calcining temperature, such as about 600° to 1500°F (315° to 816°C), suitably and preferably from 800° to 1200°F (about 426° to 649°C), for a time suitable to effectuate the conversion of the rare earth metal salt to the oxide, typically for such as about 1 to 20 hours.

After calcining, the catalysts can be activated at elevated temperatures in gases such as air, hydrogen and nitrogen and mixtures thereof. The choice of gas appears to be related to the catalyst. Praseodymium-containing catalysts are preferably activated in air, whereas cerium-containing supported catalysts are preferably activated in hydrogen, for example.

**Example:** A catalyst was prepared by impregnating 10 to 20 mesh (U.S. Sieve Series) catalytic grade silica having a specific surface area of about 88 m<sup>2</sup>/g with an aqueous solution of praseodymium nitrate, drying the composite, and calcining the dried material at 900°F in air for two hours. The final catalyst was calculated to contain 10 wt % praseodymium oxide calculated as the metal and 90 wt % silica.

A tubular reactor was charged with 20 cc of the catalyst, the reactor was heated to 900°F and air was passed through it for two hours and then nitrogen overnight (about fifteen hours). The reactor was cooled to 705°F (374°C) and hexene-1 passed through it at atmospheric pressure for 0.7 hour at the rate of 0.5 LHSV. The effluent was cooled and the liquid portion collected in a wet ice trap and analyzed by gas-liquid chromatography.

The results showed the liquid product contained 10.8 wt % olefins lower in molecular weight than hexene and 19.6 wt % olefins higher in molecular weight than hexene. In terms of hexene converted, olefins lower in molecular weight than hexene constituted 35.5 wt % of the products and olefin higher in molecular weight than hexene constituted 64.5 wt % of the products.

### Rare Earth Metal Phosphates

*W.L. Kehl and R.J. Rennard, Jr.; U.S. Patent 3,752,878; August 14, 1973; assigned to Gulf Research & Development Company* have found that aryl halides, such as chloroxylene, are hydrolyzed to the corresponding ring hydroxylated aryl compounds, such as xylenol, by contacting the aryl halides and steam with a rare earth metal phosphate catalyst, such as lanthanum phosphate, cerium phosphate and neodymium phosphate.