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CHEMICAL INDUSTRY APPLICATIONS OF INDUSTRIAL MINERALS AND METALS

UNITED STATES DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

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By the Branch of Industrial Minerals
and Branch of Metals

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Foreword

Preparing a report on the use of minerals in the chemical industry requires the difficult task of defining the chemical industry itself. As a starting point, the category defined by the Standard Industrial Classification (SIC) code 28, Chemicals and Allied Products, was selected. Included are the raw materials used directly for chemical manufacture and also consumable mineral products such as filter media and catalysts. This paper does not attempt to define every chemical produced from every mineral, nor to address organic chemicals, but to provide a broad perspective of the large- to medium-sized minerals-consuming sectors of the chemical industry.

The U.S. Bureau of Mines commodity specialists were allowed considerable freedom in preparing the individual sections on their commodities, for which the depth of data collection and information available on chemical uses varies greatly. For many of the metals for which chemicals represent a small portion of the total U.S. demand, data on chemical uses are not broken down into individual components but simply reported as total chemical demand. For many industrial minerals used primarily by the chemical industry, demand data are readily available by individual component. Generally, if a large percentage of total U.S. demand is attributed to the chemical industry, greater detail on individual components is available.

This report was prepared under the direction of Donald G. Rogich, Chief, Division of Mineral Commodities, Dr. Aldo F. Barsotti, Chief, Branch of Industrial Minerals, and Harry V. Makar, Chief, Branch of Metals.

Introduction

The chemical industry, converts feedstocks from mined materials, crude petroleum, and natural gas into two major types of products: (1) basic or intermediate, used by other industries such as agriculture, manufacturing, construction, and the service sector; and (2) finished goods used by businesses and consumers. These chemical industry products are pervasive throughout modern industrial society in which very few goods or services would be conceivable otherwise.

Chemicals are divided into two basic groups—organic and inorganic. Organic chemicals, which by definition contain carbon as the main building block, are derived principally from crude petroleum, natural gas, and coal. From these energy materials intermediate organic hydrocarbons are produced; and subsequently processed into materials such as plastics, synthetic fibers, and synthetic rubber.

Mining, minerals, and metal products play a vital role in the synthesis of inorganic chemicals. Almost all minerals and metals are used by the chemical industry either as basic raw materials or catalysts used for chemical processing. Salt, for example, which can be either mined from underground deposits or recovered from salt water, can be used as salt or converted into chlorine and caustic soda. Caustic soda, an important intermediate that is processed into other chemicals, is also used in the pulp and paper, petroleum, and detergent sectors. Chlorine, an intermediate used as a building block in many other chemical products, is used also as an intermediate in producing consumer products such as plastics, dry cleaning solvents, and swimming pool chemicals. Table 1 shows the importance of mined materials to the inorganic chemical industry and their wide variety of applications.

The chemical industry is a significant contributor to the U.S. gross national product (GNP). In 1991, value added by the U.S. chemical industry was about 1.7% of the GNP, equivalent to about 8% of total U.S. manufacturing, according to the Chemical Manufacturers Association (CMA). Total chemical industry shipments for 1991 were $288 billion, including about 25% shipped back to the chemical industry itself *(table 2)*. Rubber, textiles, and petroleum refining were the principal manufacturing sectors that used chemicals *(fig. 1)*. The annual average growth rate for the value of chemical industry shipments was 4.4% for the 1981-91 period.

In 1991, the United States exported almost $43 billion worth of products produced by the chemical industry, including plastics. The European Community (EC) was the largest destination for these materials, accounting for about 26% of the total. Canada, 15%, and Japan, 12%, were the largest individual country destinations. Of the $24 billion in chemical products imported into the United States, the EC was the largest import source, accounting for 43% of total U.S. imports. As individual countries, Canada represented 18% and Japan 11% of total U.S. imports. Although the United States has maintained a trade surplus throughout the past 10 years *(fig. 2)*, a slight decrease occurred in 1985 and 1986 because of the strength of the U.S. dollar against other world currencies. This strength made the United States a more attractive market, while U.S. products became less competitive in world markets in terms of price.

Although Canada, Japan, and the EC are the major U.S. trading partners in chemicals, much of the trade surplus is due to the large ratio of exports to imports between the United States and developing countries *(fig. 3)*. This ratio is not unexpected because the designation "developing country" indicates that the industries operating in the country are not large enough to produce enough materials to satisfy domestic consumption and would therefore have no additional production available for export. Canada and China have shown significant increases in the percentages of total U.S. chemical trade surplus.

Both Federal and State agencies have enacted health, safety, and environmental regulations that have impacted the U.S. chemicals industry. Based on data compiled by the Bureau of Economic Analysis, the Bureau of the Census, and the Environmental Protection Agency (EPA), the CMA estimates the gross annual cost of pollution abatement in the chemical industry to be $4.45 billion in 1991, the average annual growth rate from 1981 to 1991 being 8.1%. Total U.S. pollution abatement spending was $112 billion in 1991, or about 2.0% of the GNP. EPA estimates that, based on programs existing before amendments to the Clean Air Act, total U.S. spending on pollution abatement will rise to about 2.83% of GNP by 2000.

The following list of Federal regulations and their statuses, although not comprehensive, gives some indication of the impact of Federal regulations on the chemical industry. Most of these regulations deal with pollution prevention, toxic use reduction, and hazardous wastes.

Toxic Substances Control Act (TSCA) of 1976—This legislation gives EPA comprehensive authority to regulate any chemical substance for which manufacture, processing, distribution in commerce, use, or disposal may present an unreasonable risk to health or the environment. TSCA remains in force through continuing resolutions.

Clean Air Act—This legislation, originally enacted in 1955, provides the EPA with authority to regulate air pollutants from a number of sources including chemical plants. Amendments to this act, passed in 1990, set limits for 41 pollutants from industrial sources by 1995 and for 148 other pollutants by 2003.

Clean Water Act—Originally passed in 1972, the Clean Water Act provides the EPA with authority to regulate effluents from chemical plants and other industrial sources. This act, amended in 1977 and 1987, has several proposals in Congress for reauthorization.

Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986 (SARA)—The 1980 CERCLA legislation imposed specific taxes on chemicals and petroleum to fund the cleanup for the Federal Superfund program. The SARA legislation extended these taxes for 5 years and adopted a broad-based corporate environmental tax. These taxes were extended for an additional 4 years in 1990.

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)—This legislation, enacted in 1947, provides the EPA with authority to assess the risks of agricultural pesticides, industrial biocides, and other nonagricultural pesticides. FIFRA, amended in 1988, was up for reauthorization in 1992.

Resource Conservation and Recovery Act of 1976 (RCRA)—RCRA provides the EPA with authority to establish standards and regulations for handling and disposing of hazardous wastes. This act also requires companies to establish programs to reduce the volume and toxicity of hazardous wastes. In 1984, RCRA was amended with tighter standards; reauthorization and amendment efforts began in 1990.

In addition to these regulations, through the Occupational Safety and Health Administration (OSHA), the Department of Labor has the authority to set comprehensive workplace health and safety standards, including permissible exposure limits for chemicals in the workplace. Other agencies such as the Food and Drug Administration, Department of Transportation, Drug Enforcement Agency, and Consumer Products Safety Commission have authority to regulate specific aspects of the chemical industry's products and practices. State governments, in addition to having an implementation role in Federal regulations, also have begun enacting legislation on issues that affect the chemical industry.

In addition to regulations such as those above that affect essentially the entire chemical industry, some regulations affect only specific sectors. In many cases, the specific sector regulations have an adverse impact on the mining industry that supplies the raw materials. In 1987, for example, the United States and 22 other nations signed the Montreal Protocol on Substances That Deplete the Ozone Layer. In essence, this agreement mandated a significant reduction in the use of chlorofluorocarbons (CFC's), which in turn affected the fluorspar industry, the raw material source of CFC's. In another example, regulations imposed on the oil and gas industry limiting sulfur emissions has encouraged oil and gas refining operations to capture sulfur as a byproduct. This additional supply of byproduct sulfur has reduced the need for mined sulfur.

Conversely, environmental regulations can play a part in creating new end-use markets for some chemicals. One example of this demand is the flue gas desulfurization market for lime. Under the Clean Air Act, increased regulation of sulfur dioxide emissions from large sources such as coal-fired powerplants has increased the usage of lime for flue gas desulfurization from zero to more than 1.5 million metric tons in 20 years. In other cases, more stringent industrial water regulations have increased the market for some chemicals used in water treatment.

Postconsumer recycling of chemicals has not been addressed on a large scale. Total demand for chemicals, however, has been affected by the recycling of products derived from chemicals. Some of the most common postconsumer recylables are plastics made from organic chemicals, glass made from soda ash, and paper made with a variety of chemicals including titanium dioxide, kaolin, and calcium carbonate. In essence, although the chemicals are not in their original form, increased recycling of materials such as these limits the demand for virgin chemicals; however, postconsumer recycling of chemicals is not a factor for consumables such as fertilizers and pharmaceuticals.

Spurred by signs of overall economic recovery, industry analysts think that the U.S. chemical industry also may begin to recover in 1993. Forecasts by Data Resources Inc. project a 5.5% increase in the value of chemical industry shipments from 1992 to 1993. Also projected is a 5.4-percent increase in the value of chemical exports and a 7.2% increase in the value of chemical imports over the same time period. Other chemical industry analysts think that a solid recovery for the chemical industry will occur in 1994.

Table 1.—Minerals demand by the chemical industry in 1990

Commodity	Units	Total U.S. demand	Chemicals demand (SIC 28)	Chemicals demand as a percent of total U.S. demand	Principal chemical end uses
Aluminum	Thousand metric tons . .	3,905	44	1.1	Intermediate aluminum chemicals.
Antimony	Metric tons	38,963	31,949	82.0	Flame retardants, plastics catalysts and stabilizers.
Arsenic	Metric tons As content . .	20,544	18,600	90.5	Wood preservatives, herbicides.
Barite	Thousand metric tons . .	NA	NA	98.9	Intermediate barium chemicals.
Bauxite	Thousand metric tons . .	12,042	212	1.8	Intermediate aluminum chemicals
Bismuth	Metric tons	1,274	577	45.3	Pharmaceuticals, industrial and cosmetic pigments.
Boron	Th. metric tons B_2O_3 content	319	33	10.3	Soaps and detergents.
Bromine	Million kilograms	178	92	51.7	Fire retardants in extinguishers and polymers, agricultural sanitizers.
Cadmium	Metric tons	3,107	1,554	50.0	Plating, pigments, plastic stabilizers.
Chromium	Th. metric tons Cr content	447	NA	NA	Intermediate chromium chemicals.
Clay	Thousand metric tons . .	42,904	1,221	2.8	Intermediate aluminum and silicon chemicals.
Cobalt	Metric tons	7,635	W	W	Catalysts, paint drying agents.
Copper sulfate . .	do	48,107	36,400	75.7	Fungicide.
Diatomite	Thousand metric tons . .	488	138	28.3	Fillers in paint, filtration.
Fluorspar	do	587	324	55.2	Hydrofluoric acid.
Gypsum	do	23,307	1,674	7.2	Soil conditioner.
Iodine	Thousand kilograms . . .	3,100	NA	NA	Catalysts, stabilizers, sanitary uses.
Lead	Thousand metric tons . .	1,297	57	4.4	Intermediate lead chemcials.
Lime	do	15,949	3,840	24.1	Flue gas desulfurization, water treatment.
Lithium	Metric tons Li content . .	[e]2,700	NA	NA	Intermediate lithium chemicals.
Magnesium	Thousand metric tons . .	557	175	31.4	Intermediate magnesium chemicals, agriculture.
Manganese	do	630	36	5.7	Intermediate manganese chemicals.
Mercury	Metric tons	720	334	46.4	Chlorine and caustic soda manufacture.
Mica	Thousand metric tons . .	105	86	81.9	Wallboard joint compound, paint.
Nickel	Metric tons Ni content . .	148,402	1,156	.8	Intermediate nickel chemicals.
Nitrogen	Thousand metric tons . .	14,974	14,974	100.0	Fertilizers.
Perlite	do	603	76	12.6	Filter media.
Phosphate	do	43,967	43,966	100.0	Fertilizer, detergents.
Platinum-Group .	Kilograms	77,487	36,373	46.9	Catalysts.
Potash	Thousand metric tons . .	9,176	9,176	100.0	Fertilizer.

Table 1.—Minerals demand by the chemical industry in 1990

Commodity	Units	Total U.S. demand	Chemicals demand (SIC 28)	Chemicals demand as a percent of total U.S. demand	Principal chemical end uses
Salt	do	40,619	20,767	51.1	Alkalies and chlorine.
Selenium	Metric tons	530	105	19.8	Pigments.
Silicon	Metric tons	198,635	98,000	49.3	Silicone-base chemicals.
Silver	do	3,475	NA	NA	Catalysts.
Soda ash	Thousand metric tons	6,844	2,706	39.5	Intermediate sodium chemicals.
Sodium sulfate	do	750	510	68.0	Soaps and detergents.
Strontium	Metric tons Sr content	NA	NA	NA	Intermediate strontium chemicals.
Sulfur	Thousand metric tons	13,056	10,864	83.2	Fertilizers and agricultural chemicals.
Talc	do	1,042	265	25.4	Filler in paint.
Thallium	Kilograms	700	10	1.4	Pharmaceuticals.
Tin	Metric tons	50,494	6,547	13.0	PVC stabilizers, wood preservatives.
Titanium	Th. metric tons Ti content	621	573	92.3	Pigment for paints, paper, plastics.
Tripoli	Metric tons	80,558	56,468	70.1	Filler and extender for paints.
Tungsten	Metric tons W content	8,147	352	4.3	Dyes, pigments.
Vanadium	Metric tons V content	4,098	8	.2	Catalysts.
Vermiculite	Thousand metric tons	142	57	40.1	Horticulture, soil conditioning, fertilizer.
Zinc	do	1,049	155	14.8	Pigments, rubber, intermediate zinc chemicals.
Zircon	Metric tons	NA	NA	NA	Pigments, glazes.

[e]Estimated. NA Not available. W Withheld to avoid disclosing individual company proprietary data.

Table 2.—Salient U.S. chemical industry statistics

	1981	1986	1991
Shipments, billion dollars	$186.9	$205.7	$288.0
Operating rate, percentage	78.3	78.9	79.0
Total employment, thousands	1,109.0	1,021.8	1,072.4
Exports, billion dollars	$21.2	$22.5	$43.0
Imports, billion dollars	$9.5	$15.3	$24.2
Trade surplus, billion dollars	$11.7	$7.2	$18.8

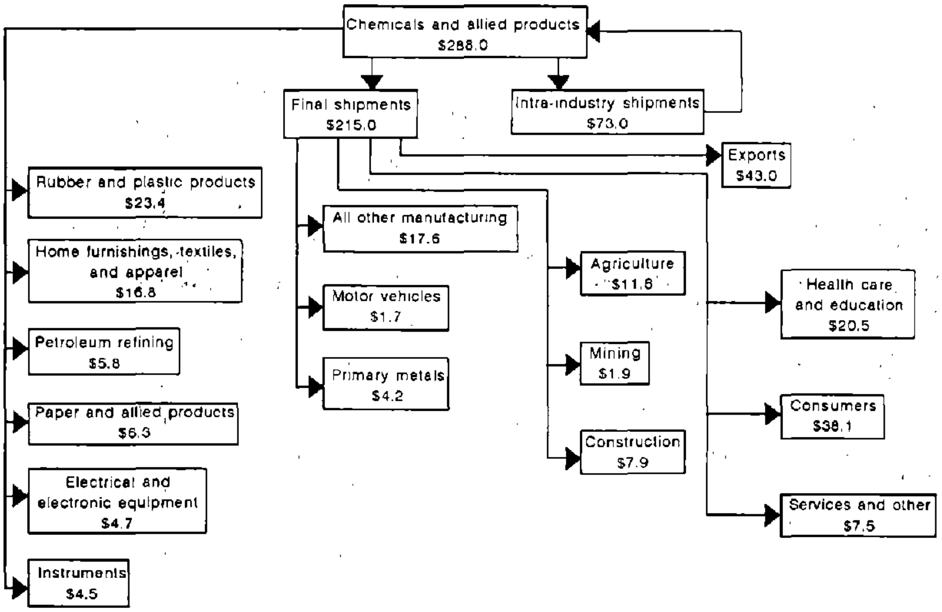
Table 3.—Top ten inorganic chemicals produced in the United States

(Thousand metric tons)

Chemical	1970	1980	1990
Sulfuric acid	26,785	40,059	39,956
Nitrogen	4,970	15,752	24,636
Ammonia, anhydrous	12,541	17,829	15,237
Phosphoric acid	5,156	9,841	10,917
Caustic soda	9,200	10,529	10,913
Chlorine	8,858	10,361	10,714
Soda ash	6,415	7,507	8,306
Urea	2,830	7,103	7,366
Nitric acid	6,897	8,375	7,257
Ammonium nitrate	5,857	8,280	6,424

Source: Chemical Manufacturers Association.

Figure 1.–U.S. chemical industry flow, 1991.
(Billion dollars)



Source: Chemcial Manufacturers Association

Figure 2.–U.S. chemical trade.

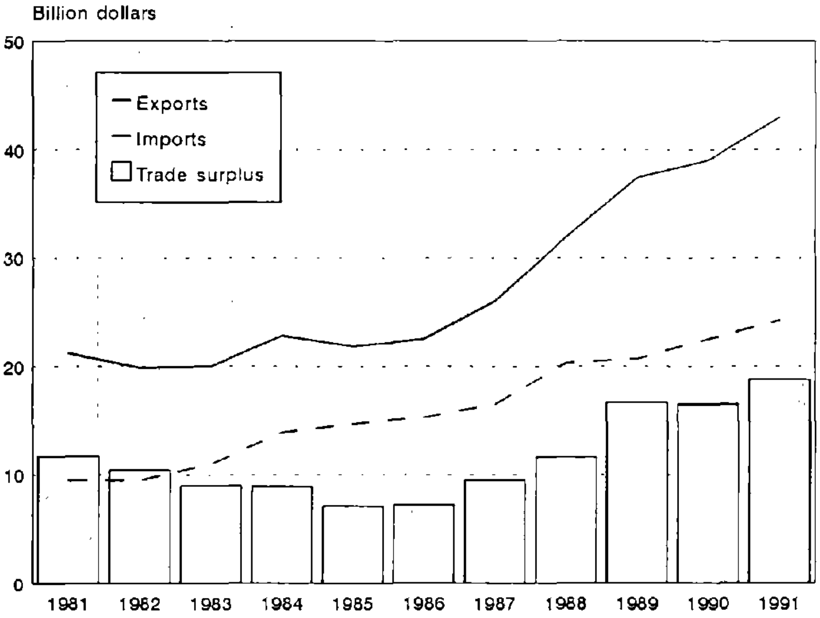
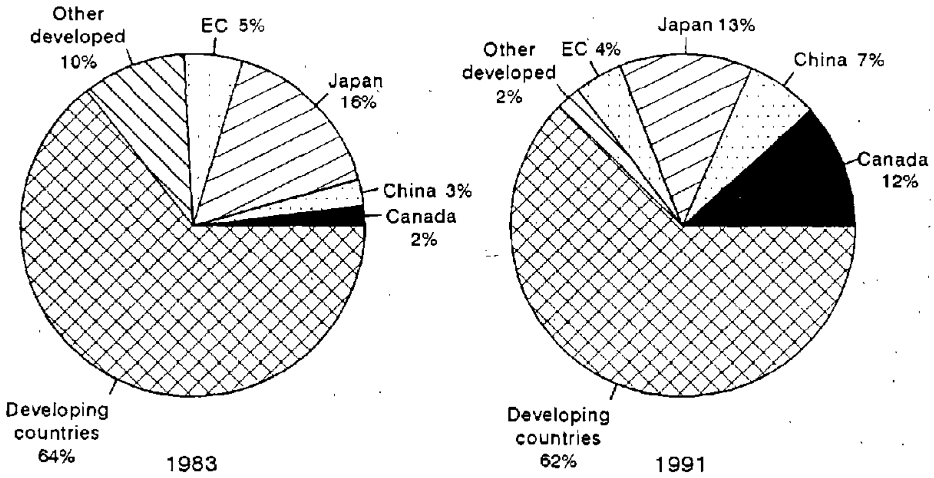


Figure 3.—Balance of U.S. trade in chemical materials.



Aluminum

By Patricia A. Plunkert

Background.—Aluminum metal powders, produced by a variety of techniques, have physical and metallurgical characteristics related to their method of manufacture and tailored to their end uses. The Aluminum Association Inc. classifies powders as granule, flake, or atomized; Granule powders are larger than about 74 micrometers; flake powders have one or two dimensions several hundred times larger than the third; atomized powders usually have all three dimensions of the same order of magnitude.

Aluminum powders are used in the fields of metallurgy, chemistry, commercial explosives, and other industries. The U.S. Department of Commerce, Bureau of the Census, publishes data on shipments of aluminum powders in their Current Industrial Report—Aluminum Ingot and Mill Products. According to 1990 Commerce data, shipments of aluminum powder accounted for less than 1% of aluminum ingot and mill product shipments, amounting to about 44,000 metric tons. These Commerce data include powder shipments for both metallurgical and chemical uses.

Chemical Industry Consumption.—The chemical industry consumes aluminum powders in the synthesis of organic-metallic compounds and as catalysts. The high surface areas of powders and the availability of a variety of particle sizes, which promote rapid and controllable reaction rates, make aluminum powders ideal for use by the chemical industry. Some aluminum compounds that may be manufactured using aluminum powders are aluminum alkyls, anhydrous aluminum chloride, and aluminum alkoxides. The aluminum compounds formed are used as process intermediates or final products in the manufacture of detergents, plasticizers, polymerization catalysts, and antiperspirants.

The addition of aluminum flakes to paint pigments utilizes the intrinsic advantages of this metal—high reflectance and durability, and low emissivity and moisture penetration. Aluminum flakes are used as pigments in industrial paints, roof coatings, paper coatings, and printing inks.

The plastics industries use powders in a variety of end products including fillers in adhesives, epoxy casting compounds, cold solders, and thermal conductors in thermosetting-type systems.

Aluminum powder continues to be one of the most important fuels in solid propellants used in missiles and rockets. These propellants essentially consist of mixtures containing an oxidizer (usually ammonium perchlorate), a binder (usually a polymer), controlling and stabilizing additives, and aluminum powders.[1]

Outlook.—The information available on the consumption levels of aluminum powders does not differentiate between metallurgical and chemical uses. The use of powders appears to have stabilized over the past 15 years. Over the next few years, the consumption of aluminum powders by the chemical industry should remain relatively stable.

Reference

[1] Lyle, J. P., W. S. Cebulak, P. Matthews, J. Pickens, O. R. Singleton, and W. Ullrich. Aluminum Powder and Powder Metallurgy Products. Ch. in Aluminum: Properties and Physical Metallurgy, ed. by J. E. Hatch. American Society for Metals, 1984, pp. 379-397.

Table 1.—Salient aluminum statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Production:					
Primary metal	3,607	3,519	4,654	3,500	4,048
Secondary (old scrap)	179	305	617	850	1,359
U.S. net shipments of aluminum wrought and cast products:[1]					
Total	3,865	3,993	5,453	6,042	6,393
Powder, flake, paste	93	45	53	49	44

[1] Source: Current Industrial Reports, Series M33, U.S. Dep. Commerce, Bureau of the Census.

Antimony

By Thomas O. Llewellyn

Background.—Antimony is seldom found in nature as a native metal because of its strong affinity for sulfur and the metallic elements such as copper, lead, and silver. Antimony in its elemental form is a silvery white, brittle, crystalline solid that exhibits poor electrical and heat conductivity properties.

The known domestic deposits of antimony ores have generally been small and uneconomical when compared with those of foreign producers, resulting in a dependence by the United States on foreign sources of supply. Although about 23 countries haved mined antimony, Bolivia, China, Mexico, and the Republic of South Africa have historically been the principal sources of supply. These four countries accounted for about 90% of the total world antimony production in 1990.

Antimony is included in the National Defense Stockpile (NDS) because of its strategic uses in flame retardant formulations, friction bearings, and batteries. In addition, the United States depends on imports for more than 60% of its requirements.

Currently, only one domestic company, Sunshine Mining Co., produces antimony as a byproduct of the treatment of tetrahedrite, a complex silver-copper-antimony sulfide ore from the Coeur d'Alene district of Idaho.

In 1990, primary antimony metal and oxides were produced by six companies operating six smelters utilizing both foreign and domestic materials. ASARCO Incorporated, Omaha, NE, recovered antimony as a byproduct of processing lead ores; while Sunshine Mining Co., Kellogg, ID, produced antimony as a byproduct of treatment of tetrahedrite. The other four companies produced antimony products mainly utilizing foreign feed materials: Amspec Chemical Corp, Gloucester City, NJ; Anzon America, Laredo, TX; Laurel Industries Inc., La Porte, TX: and U.S. Antimony Corp., Thompson Falls, MT.

Secondary antimony is a very important source of supply, the majority being recovered from spent lead-acid batteries. Historically, secondary antimony has accounted for about 50% of the total industrial demand for antimony.

Exports of antimony products, as shown in table 1, have been low compared to the amount of antimony imported; however, exports of antimony oxide increased dramatically in 1990 and reached their highest level since the Bureau of Mines began reporting these data 23 years ago. In 1985, about 800 metric tons of antimony oxide was exported, whereas in 1990 that figure was more than 7,000 tons.

Imports of antimony materials during the last two decades have changed in composition. In the early 1970's, the bulk of the imported material was in ores and concentrates; by 1975 antimony oxide was the major product; and since 1988 antimony metal has been the major imported material. The switch from using ores and concentrates to using antimony metal as raw material to produce antimony oxide was due strictly to economics. The price for metal had become so low that domestic antimony trioxide producers had started using metal instead of crude antimony oxide as feed material.

Chemical Industry Consumption.—The Bureau of Mines divides domestic consumption by enduse into seven categories as shown in table 1. In this table, the chemical category represents only the antimony materials used directly for chemical manufacture, being about 9% of the total 1990 consumption; however, if flame retardants were included in the domestic chemical applications of antimony, the consumption for domestic applications would be over 80%.

Flame retardants are generally divided into two groups—reactives and additives. Reactive fire retardants such as halogens and phosporus-containing organic compounds are part of the chemically reacting components of the system in which they are used. Additive flame retardants such as antimony oxide, hydrate aluminum oxide, and other compounds do not chemically react with the components of the system in which they are used.

The greatest consumption of primary antimony is in flame retardants, the three main compounds being antimony pentoxide, sodium antimonate, and the most widely used of the three, antimony trioxide. These antimony compounds are not flame retardants by themselves; but when they are combined with halogens such as chlorine or bromine, a synergistic reaction takes place that produces a flame retardant. These compounds are used to enhance the flammability resistance of plastics, paints, textiles, and rubber.

Antimony compounds are used in the manufacture of plastics as catalysts and stabilizers. Several antimony compounds (fluoride and chloride) are used in catalysts for chemical and petrochemical processes.

Antimony-bearing stabilizers prevent the degradation of polyvinyl chloride (PVC) exposed to heat and ultraviolet light rays, which can cause mechanical breakdown of the material. Because antimony-bearing stabilizers, compared to cadmium-bearing stabilizers, have the disadvantage of producing some discoloration of the PVC, the antimony compounds are mainly used in dark-colored pipes for sewage and in underground conduits.

Antimony oxides are used as white pigments in paints. Other antimony compounds such as trisulfide and pentasulfide produce black, vermilion, yellow, and orange pigments.

Environmental and ecological problems associated with the treatment of antimony metal and ores are minimal because emissions and effluents are controlled at the processing plants. A recent inhalation study sponsored by the Antimony Oxide Industry Association found no evidence of antimony trioxide as being carcinogenic.

Compounds of titanium, zinc, and tin can be substituted for antimony in paint and pigments. Selected organic compounds and hydrated aluminum oxide are widely accepted alternative materials in flame retardant formulations.

Growth in the antimony chemical industry from 1970 to 1990 resulted from the higher demand for fire retardant applications. The antimony oxide consumed for fire retardants was about 7% of total domestic consumption in 1970, but had reached about 73% of the total by 1990.

Outlook.—Consumption of antimony trioxide in flame retardants will continue to grow in the 1990's, but probably at a less dramatic lower rate. Industry sources indicate that the projected growth of antimony trioxide demand for the next three years will be in the range of 1% to 3% per year.

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Roskill Information Services Ltd. The Economics of Antimony 1990. London, England, 7th ed., Oct. 1990, 279 pp. and appendixes A and B.

Table 1.—Salient antimony statistics

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Mine production[1]	1,567	804	311	W	W
Byproduct antimonial lead[2]	542	243	16	W	W
Secondary (from old scrap)	19,436	14,533	15,602	12,561	19,202
Imports:					
In ore and concentrate	12,537	7,548	4,749	6,022	3,454
Metal	1,187	1,916	2,350	4,653	13,940
In oxide	3,204	7,461	9,206	7,997	12,009
In sulfide[3]	—	45	21	102	NA
Shipments of Government stockpile excesses	—	—	—	842	—
Industry stocks, Jan. 1	5,750	10,609	6,481	6,255	6,270
Total U.S. supply	44,223	43,159	38,736	38,432	54,875
Distribution of U.S. supply:					
Industry stocks, Dec. 31	8,026	13,569	7,630	5,479	8,185
Exports[4]	887	570	1,244	1,131	7,727
Industrial demand	35,310	29,020	29,863	31,821	38,963
U.S. demand pattern:					
Ceramics and glass	1,658	1,864	2,150	1,905	1,558
Chemicals	5,740	5,282	4,300	1,542	3,506
Flame retardants	2,395	4,661	6,759	12,701	28,443
Machinery	1,474	1,553	1,225	1,451	1,020
Rubber products	2,580	2,796	1,842	454	350
Transportation	19,049	11,884	12,247	12,792	3,506
Other	2,414	980	1,340	976	580
Total U.S. demand	35,310	29,020	29,863	31,821	38,963

NA Not available. W Withheld to avoid disclosing company proprietary data.

[1] Includes byproduct antimony from domestic ores, recovered as antimonial lead.

[2] Produced from domestic ores at primary lead refineries (antimony content).

[3] Includes needle or liquated antimony.

[4] Exports of metal and oxide (antimony content).

Arsenic

By J. Roger Loebenstein

Background.—The toxic effects of arsenic have been known for centuries. In general, inorganic arsenic compounds are condisered to be more toxic than organic compounds. Many of the uses of arsenic are based on its toxicity. The earth's crust contains about 3mg/kg arsenic, while coal can contain five times this amount.

All arsenic consumed in the United States has been derived from imported sources, the most important being arsenic trioxide, but also minor amounts of arsenic acid and arsenic sulfide.

Imported arsenic trioxide is converted to arsenic acid for use in the production of arsenical wood preservatives by three major companies-Hickson Corp., CSI, and Osmose Corp.

Hickson International PLC, Castleford, United Kingdom, the parent company of Hickson Corp., has wood preservative plants in Australia, New Zealand, the Republic of South Africa, and the United Kingdom, as well as in the United States.

LaPorte PLC, United Kingdom, is the parent company for CSI, Mineral Research and Development, and Rentokill. CSI manufactures wood preservatives in the United States, and Mineral Research and Development formulates arsenical pharmaceuticals for veterinary purposes in the United States. Rentokill produces wood preservatives in Liverpool, United Kingdom.

Only a few agricultural uses for arsenic remain. ISK Biotech (formerly Fermenta Corp.), Mentor, OH, produces the arsenical herbicide monosodium methanearsonate (MSMA) at a plant in Houston, TX. Atochem Corp., Bryan, TX, has been a major producer of arsenic acid for use by cotton growers and wood preservative companies. A company in Israel, Luxembourg Chemicals & Agriculture Ltd., produces sodium cacodylate, an arsenical used as a bait preparation against ants.

Minor amounts of arsenic acid have been used by Corning Glass as a decolorizer. Corning has purchased arsenic acid from wood preservative companies.

Chemical Industry Consumption.—Chromated copper arsenate (CCA) is the most common arsenic-based wood preservative. Others include ammoniacal copper arsenate (ACA) and fluorchrome arsenate phenol (FCAP). Arsenic trioxide is also used as a reagent in ore flotation.

During the 1930's and 1940, an estimated 45,000 metric tons of arsenic-based insecticides was used annually in the compound paris green (copper acetoarsenite) and the arsenates of calcium, chromium, lead, and sodium.[1] Only 15 years ago, agricultural chemicals were the most important end use for arsenic; but in the future, because of environmental problems, agricultural chemical use will probably decline to a negligible amount. The only two remaining major agricultural uses for arsenic are as a herbicide for control of weeds and as an aid for cotton production. Because arsenic acid is used as a desiccant to aid in the mechanical harvesting of cotton in Oklahoma and Texas; weather conditions during harvest determine the amount of arsenic acid used: an early frost tends to help dry cotton bolls and thus reduces arsenic acid consumption.

Arsenic has a long history of environmental problems because of its well-known toxicity and the more recent Government finding that inorganic arsenic is a human carcinogen. Most of the published literature on arsenic emissions dates back to the mid-1970's when the EPA studied the U.S. nonferrous smelting industry and the arsenic industry in depth. In 1978, OSHA promulgated the final standard on occupational exposure to inorganic arsenic based on the conclusion that inorganic arsenic was a carcinogen and that worker exposure had to be limited. In 1980, EPA listed inorganic arsenic as a hazardous air pollutant based on its findings that inorganic arsenic was carcinogenic to humans and that there was significant public exposure to the pollutant. In 1983, EPA estimated that over 85% of the 1,200 tons per year of atmospheric arsenic emissions came from copper smelters and glass manufacturing plants. EPA identified other source categories for which standards were not proposed-primary lead and zinc smelters, zinc oxide plants, arsenic chemical manufacturing plants, cotton gins, and secondary lead smelters.[2]

As a result of the necessity to comply with Federal and local regulations on atmospheric emissions of sulfur dioxide and arsenic, ASARCO Inc. closed its copper smelter and associated arsenic recovery plant at Tacoma, WA, in 1985. At that time, Asarco was the only producer of arsenic in the United States. Currently, no arsenic is recovered in the United States, and all arsenic consumed is derived from imported sources.

EPA regulates the uses of inorganic arsenic under provisions of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).[3] A pesticide product may be sold or distributed in the United States only if it is registered or exempt from registration under FIFRA. Before a product can be registered as a pesticide, it must be shown that it can be used without "unreasonable adverse effects on the environment", and without causing "any unreasonable risk to man and the environment taking into account the economic, social, and environmental costs and benefits of the use of the pesticide." The proponent of initial or continued registration must prove that the pesticide meets the risk and benefit standard of FIFRA above. If at any time EPA determines that a pesticide does not meet this standard for registration, EPA may cancel the registration under section 6 of FIFRA.

In 1986, EPA issued its final rules on arsenic emissions from copper smelters and glass manufacturing plants. In the following year, EPA issued its preliminary position to cancel most of the nonwood pesticide uses for inorganic arsenicals. Included in the list were lead arsenate, calcium arsenate, sodium arsenate, and arsenic trioxide.

Registrations for lead arsenate, calcium arsenate, and sodium arsenite have been voluntarily canceled: the sole registrant of the growth-regulator use of lead arsenate in 1987; the registrant of calcium arsenate in 1989; and the registrant of sodium arsenite in 1990.[4]

In 1991, EPA announced its preliminary decision to cancel the registration of products containing arsenic acid used as a desiccant on cotton. EPA provided for a period of hearings before making its final decision on arsenic acid.[4] EPA estimated that current usage of arsenic acid is 2 to 3 million pounds of arsenic acid per year, representing 5% to 10% of total U.S. acreage.[3] Using 2.5 million pounds as an estimate, this quantity represents a usage of about 1,100 tons of arsenic acid per year (containing about 580 tons of arsenic).

Outlook.—The major market for arsenic is in wood preservatives. The future for arsenic consumption is therefore tied to new housing, where wood decks containing arsenical preservatives have become almost standard items in recent years. Treated wood is also used in decks added to existing houses.

The use of arsenic acid as a desiccant on cotton is expected to disappear in the near future, leaving the arsenical herbicide MSMA as the only major agricultural use for arsenic.

References

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[2]Edelstein, D. Other Metals. Ch. in BuMines, v. 1, 7 pp., Minerals Yearbook 1983.

[3]U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Office of Pesticide Programs. Inorganic Arsenicals, Technical Support Document, Oct. 1991, 53 pp.

[4]Federal Register, U.S. Environmental Protection Agency. Inorganic Arsenicals; Preliminary Determination to Cancel Registration of Pesticides Containing Inorganic Arsenicals Registered for Non-Wood Preservative Use: Availability of Technical Support Document; Notice of Intent to Cancel. Oct. 7, 1991, pp. 50576-50585.

Table 1.—Salient arsenic statistics[1]

(Metric tons, arsenic content)[2]

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production	9,900	7,400	3,400	1,700	—
Imports, metal	500	400	300	400	796
Imports, compounds	13,100	8,200	8,800	13,600	19,897
Industry stocks, Jan. 1	5,800	2,300	—	3,300	100
Total	29,300	18,300	12,500	19,000	20,793
Distribution of U.S. supply:					
Industry stocks, Dec. 31	10,800	2,900	100	900	100
Exports[3]	—	—	—	—	149
Apparent demand	18,400	15,400	12,400	18,100	20,544
Estimated U.S. demand pattern:					
Agricultural chemicals	14,600	12,700	5,700	4,500	4,200
Glass	1,900	1,300	600	700	800
Industrial chemicals	900	700	5,400	12,100	14,400
Nonferrous alloys and electronics	500	450	400	400	800
Other	500	250	300	400	300
Total	18,400	15,400	12,400	18,100	20,500

[1] Figures prior to 1990 are rounded; some of the 1990 figures are rounded.

[2] Arsenic trioxide (As_2O_3) contains 75.7% arsenic by weight.

[3] Metal.

Barite

By James P. Searls

Background.—Barite, also known as barytes, heavy spar, and tiff, is a heavy, soft, and chemically inert mineral that contains 58.8% barium (Ba) and 41.2% sulfate (SO_4). U.S. consumption of barite ($BaSO_4$) is a direct result of the need for weighted muds in oil and gas well drilling, with over 90% of demand stemming from those activities. Barite is fine ground for use in well drilling muds, as a filler in rubber, paint, plastic, and paper, and is crushed and/or coarse ground for manufacture of barium chemicals and glass.

In the 1960's more than 20 firms were involved in producing a variety of basic, intermediate, and specialty barium compounds for sale and internal consumption. By 1993, only one "basic barite" producer remained in the barium chemical business, and an additional company remained in the intermediate and specialty barium compounds business.

The principal use for barite, as a weighing material in well drilling muds, accounted for more than 92% of total U.S. consumption. The use of barite as a filler or extender and other uses accounted for about 7% of total U.S. consumption in 1990. Barite has a high specific gravity, low oil absorption, easy wettability by oils, and good sanding qualities.

In painting automobiles, barite is used as a filler for the primer coats. Barite is also used as a filler or extender in some plastic and rubber products. Processors of polyurethane foam use barite in manufacturing such products as floormats and carpet-backings to add weight and improve processing qualities. Barite is used in white sidewalls for tires; sidewalls consist mainly of rubber, zinc oxide, and a small quantity of barite.

Other industries use small quantities of barite fillers. In the paper industry, the white and dense barite coatings serve as a base for the sensitized layers in photographic prints. In the printing industry, barite is used in inks.

In glassmaking, barite is added to the glass melt to reduce the heat-insulating froth that forms on the melt surface, thus saving fuel, and to act as an oxidizer and decolorizer, making the glass more workable and increasing its brilliance. Barium-base glass (using barium carbonate) is considered to be more brilliant than lime glass and more durable than lead glass.

Chemical Industry Consumption.—Barite is also a raw material for barium chemical manufacturing. A small amount of barite is converted into a soluble form before its use in the manufacture of lithopone or other chemicals. Crushed barite is roasted with coke in a kiln at about 1,200° C to reduce the barium sulfate to the more soluble compound, barium sulfide, commonly called black ash. The sulfide is leached from the clinker with hot water. By adding zinc sulfate to the leach liquor, an intimate mixture of barium sulfate and zinc sulfide called lithopone is precipitated.

The leach liquor is a precursor of a number of barium chemicals. Addition of sodium sulfate precipitates a pure barium sulfate (called blanc fixe). Barium carbonate is precipitated by either carbonating or adding sodium carbonate to the leach liquor. Hydrochloric acid added to the leach liquor produces a solution of barium chloride.

The most important barium chemical is precipitated barium carbonate, which is a raw material for production of many of the other compounds. It is also used in brick and tile manufacturing to control scum caused by gypsum or magnesium sulfate in the clay and to diminish porosity and prevent discoloration in brick. Other uses are in television picture tubes as a radiation barrier, optical glass, ceramic glazes, porcelain enamel, ferrites, and miscellaneous ceramic products. Roasting of barium carbonate and ferric oxide above 1000° C produces useful permanent magnets. Barium carbonate is used to manufacture barium titanate and barium niobate, which are extremely useful in modern electronic and solid state communication devices.

Blanc fixe, chemically precipitated barium sulfate, is used as a white filler in paints, rubber, inks, and other materials where a degree of purity higher than natural barite is required. Lithopone (a white pigment composed of a mixture of barium sulfate, zinc sulfide, and zinc oxide), formerly manufactured in large tonnages for use as a white pigment in paints, has been largely replaced by titanium dioxide.

Barium chloride is used in case-hardening and heat-treating baths, in leather and cloth, in making magnesium metal, in preventing scum on brick, in water treatment, and as a laboratory reagent. Fused barium chloride may be electrolyzed to produce barium metal.

Barium nitrate is used in green signal flares, tracer bullets, primers and detonators, and enamels. Barium oxide is used in electric furnace ferrous metallurgy to increase the life of acid furnace linings, to give a quieter

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and steadier arc, to reduce the sulfur content of the iron, and to lower the slag viscosity.

Barium hydroxide is used to make barium stearate for lubricating greases. Barium-based greases are excellent for load-bearing, water-resisting applications. It is also used as a rust preventative because it is extremely sticky and resistant to even steam cleaning.

Outlook.—The drilling mud demand reached its peak around 1980 in the United States. Since then, domestic demand for barite has fallen and risen with the price of oil and natural gas. In 1991, large domestic petroleum companies have been moving into joint ventures overseas and have restricted operations in the United States. The domestic demand for barite in drilling mud is likely to continue falling to some lower, stable level.

A longer term review of the barite data shows that demand for barium compounds, other than barite for drilling muds, reached a peak in the 1960s and has declined to about 100,000 tons. Many of the historic end-use-demand materials have been replaced by other materials or other technologies. There is little expectation that demand for barium compounds will increase significantly in the near future. Only the recent developments of barium titanate use in electronics and perhaps barium in superconducting materials may add some increase in demand for barium compounds.

Table 1.—Barite supply-demand relationships

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Sold or used by producers	775	1,196	2,037	670	430
Imports	640	575	1,678	1,865	988
Total	1,415	1,771	3,715	2,536	1,418
Distribution of supply:					
Exports	55	52	88	5	9
Apparent consumption	1,255	1,660	3,420	1,981	1,434
Apparent surplus (+) or deficit (-) of supply[1]	+106	+59	+207	+549	-25

[1] Sales + imports - exports - apparent consumption.

Table 2.—Barite demand pattern

(Thousand metric tons of barite)

End use	1970	1975	1980	1985	1990
Drilling mud	1,015	1,486	3,254	1,852	1,329
Barium chemicals	132	65	61	NA	NA
Paints and plastics	40	32	31	NA	NA
Glass	45	W	W	NA	NA
Other	22	77	74	NA	NA
Total[1]	239	174	166	129	105

NA Not available. W Withheld to avoid disclosing company prorietary data; included in "Other."
[1] Excludes barite used in drilling mud.

Bauxite and Alumina

By Errol D. Sehnke

Background.—Bauxite is a naturally occurring, heterogeneous material primarily composed of one or more aluminum hydroxide minerals and various mixtures of aluminum silicate (clay, etc.), iron oxide, silica, titania, and other impurities in minor or trace amounts. The principal aluminum hydroxide minerals found in varying proportions within bauxite are gibbsite, $Al(OH)_3$; boehmite, AlOOH; and diaspore, AlOOH.

Bauxite and its derivative alumina (Al_2O_3), the oxide of aluminum, are the principal feedstocks to the primary aluminum metal industry, but they also have significant applications within the chemicals industry. The nature of these specialty usages is outlined in figure 1, which traces the flow of aluminum oxide from its origin at the bauxite mine through various processing steps to an extraordinarily broad array of end uses and product applications. Some of the more significant aluminum chemicals and their associated uses are listed in table 1.

Chemical Industry Consumption.—The most direct application of bauxite within the chemicals industry is in the production of aluminum sulfate, which is used as a flocculating agent in water and effluent treatment. This compound is made by dissolving high-quality specialty grade bauxite in sulfuric acid. Because only certain bauxites are amenable to this treatment, just gibbsitic bauxites customarily are utilized for this application. Another direct utilization of bauxite by the chemicals industry is as activated bauxite, a drying agent for gases and organic liquids. Activated bauxite is produced by low-temperature roasting (400° C) of low-iron gibbsitic bauxite, which drives off two of the three hydroxyl groups from the gibbsite to leave an activated residue that readily recombines with water. This substance is also noted for its high surface area, which enhances its reactivity and results in its added use as an absorbent for sulfur- and fluorine-based compounds. As such, activated bauxite has a limited role as a catalyst and filtering agent within both the petrochemical and fertilizer industries.

Beyond the direct applications of bauxite in the chemicals industry, the point of origin for most aluminum-based chemicals is alumina trihydrate. This compound is produced by caustic digestion of raw bauxite followed by drying, and in some cases, calcination at 1,400° C is applied to the product to form calcined alumina (fig. 1). In addition to being used for the production of aluminum sulfate, alumina trihydrate has important applications in the pigments industry. Very finely ground and precipitated hydrate is also used as a paper filler and coating pigment with very excellent gloss characteristics. Alumina trihydrate may also be applied as a titanium dioxide extender in papermaking. By far, one of the more prominent chemical usages of alumina trihydrate is as a flame retardant and smoke suppressant within plastics and rubbers used in electrical insulation, polyester resins, and carpet-backing applications. The consumption of high-quality bauxite for use within the U.S. chemicals industry has remained at approximately the 200,000-metric-ton-per-year level since the mid-1970's (table 3). Specialty aluminas, and their precursor alumina trihydrate, used in nonmetallurgical applications, have accounted for some 600,000 to 655,000 tons of total U.S. alumina production within recent years.

Outlook.—The outlook for the specialty and chemical usages of alumina currently is very positive, and it is considered to be an area with a high potential for market expansion. Technological progress in the field of advanced materials and the growing use of environmentally friendly products such as nontoxic alumina trihydrate-based fire retardants and smoke suppressants are rapidly opening up new opportunities for growth in the application of bauxite-and-alumina-sourced chemical products within the U.S. economy.

Table 1.—Selected aluminum chemicals and their industrial applications

Chemical	Use
Aluminum chloride anhydrous [$AlCl_3$] hexahydrate [$AlCl_3 \cdot 6H_20$]	Catalyst in organic reactions. Metallurgical and metal-finishing applications.
Aluminum fluoride, [AlF_3]	Flux in remelting and refining aluminum and aluminum alloys. Opacifier aid in glass, enamels, and ceramics.
Aluminum nitrate, nonohydrate [$Al(NO_3)_3 \cdot 9H_2O$]	Salting-out agent in the extraction of actinides.
Aluminum sulfate, hydrate [$Al_2(SO_4)_3 \cdot 18H_2O$] anhydrous [$Al_2(SO_4)_3$]	Water and sewage treatment. Sizing in the paper industry.
Aluminum tristearate, [$Al(OOC(CH_2)16CH_3)_3$]	Textile finishing agent. Lubricating grease. Gelling agent.
Sodium aluminate, [$NaAlO_2$]	Industrial and municipal water treatment. Aid to sizing and filler retention in paper. Production of alumina-based catalysts.

Source: Kirk-Othmer Encyclopedia of Chemical Technology.

Table 2.—Salient bauxite statistics

(Thousand metric tons and thousand dollars)

	1970	1975	1980	1985	1990
United States:					
Production: crude ore (dry equivalent)	2,115	1,801	1,559	674	W
Value	\$30,070	\$25,083	\$22,353	\$12,855	W
Exports (as shipped)	3	20	21	56	53
Imports for consumption[1]	13,039	12,749	14,087	7,158	12,142
Consumption (dry equivalent)	15,925	12,587	15,962	8,206	12,042
World: Production	57,786	74,791	89,220	84,189	109,601

W Withheld to avoid disclosing company proprietary data.

[1] Excludes calcined bauxite. Includes bauxite imported to the U.S. Virgin Islands.

Table 3.—Bauxite consumption by the U.S. chemical industry

(Thousand metric tons, dry equivalent)

	1970	1975	1980	1985	1990
Chemical uses	312	221	211	219	212

Table 4.—Production and shipments of selected aluminum salts in the United States

Item	Number of producing plants	Production (thousand metric tons)	Total shipments, including interplant transfers		Number of producing plants	Production (thousand metric tons)	Total shipments, including interplant transfers	
			Quantity (thousand metric tons)	Value (thousands)			Quantity (thousand metric tons)	Value (thousands)
	1970				1975			
Aluminum sulfate:								
Commercial and municipal (17% Al_2O_3)	61	1,096	1,023	$46,662	65	1,056	XX	XX
Iron-free (17% Al_2O_3)	19	64	42	2,773	16	229	228	$7,938
Aluminum chloride:								
Liquid and crystal (32° Bé)	5	21	9	861	5	W	W	W
Anhydrous (100% $AlCl_3$)	5	28	29	8,890	5	24	24	18,245
Aluminum fluoride, technical	5	123	122	26,795	4	118	115	46,003
Aluminum hydroxide, trihydrate [100% $Al(OH)_3$]	7	330	299	26,936	6	382	363	W
Aluminates	XX	XX	XX	XX	XX	XX	XX	XX
Other aluminum compounds[1]	XX	XX	XX	23,122	XX	XX	XX	34,956
	1980				1985			
Aluminum sulfate:								
Commercial and municipal (17% Al_2O_3)	66	1,167	1,079	$123,985	81	1,092	1,014	$131,653
Iron-free (17% Al_2O_3)	17	106	79	8,006	20	93	91	12,229
Aluminum chloride:								
Liquid and crystal (32° Bé)[2]	5	19	3	844	3	6	W	W
Anhydrous (100% $AlCl_3$)	5	67	35	21,613	4	W	W	W
Aluminum fluoride, technical	5	135	133	90,331	4	W	W	W
Aluminum hydroxide, trihydrate [100% $Al(OH)_3$]	7	588	565	116,210	7	530	530	147,171
Aluminates	XX	XX	XX	XX	XX	XX	XX	XX
Other aluminum compounds[1]	XX	XX	XX	32,981	XX	XX	XX	69,943

See footnotes at end of table.

Table 4.—Production and shipments of selected aluminum salts in the United States—Continued

Item	Number of producing plants	Production (thousand metric tons)	Total shipments including interplant transfers	
			Quantity (thousand metric tons)	Value (thousands)
	1990			
Aluminum sulfate:				
Commercial and municipal (17% Al_2O_3)	75	1,113	1,054	$135,063
Iron-free (17% Al_2O_3)	21	115	110	14,467
Aluminum chloride:				
Liquid and crystal (32° Bé)	3	W	W	W
Anhydrous (100% $AlCl_3$)	3	W	W	W
Aluminum fluoride, technical	2	W	W	W
Aluminum hydroxide, trihydrate [100% $Al(OH)_3$]	9	725	701	234,198
Aluminates	17	95	89	29,033
Other aluminum compounds[1]	XX	XX	XX	147,366

W Withheld to avoid disclosing company proprietary data. XX Not applicable.

[1] Includes sodium aluminate, light aluminum hydroxide, cryolite, and alums.

[2] No crystal production or shipments in 1980.

Source: Data are based upon Bureau of the Census report Forms MA-28E.1 and MA-28A, Annual Report on Shipments and Production of Inorganic Chemicals.

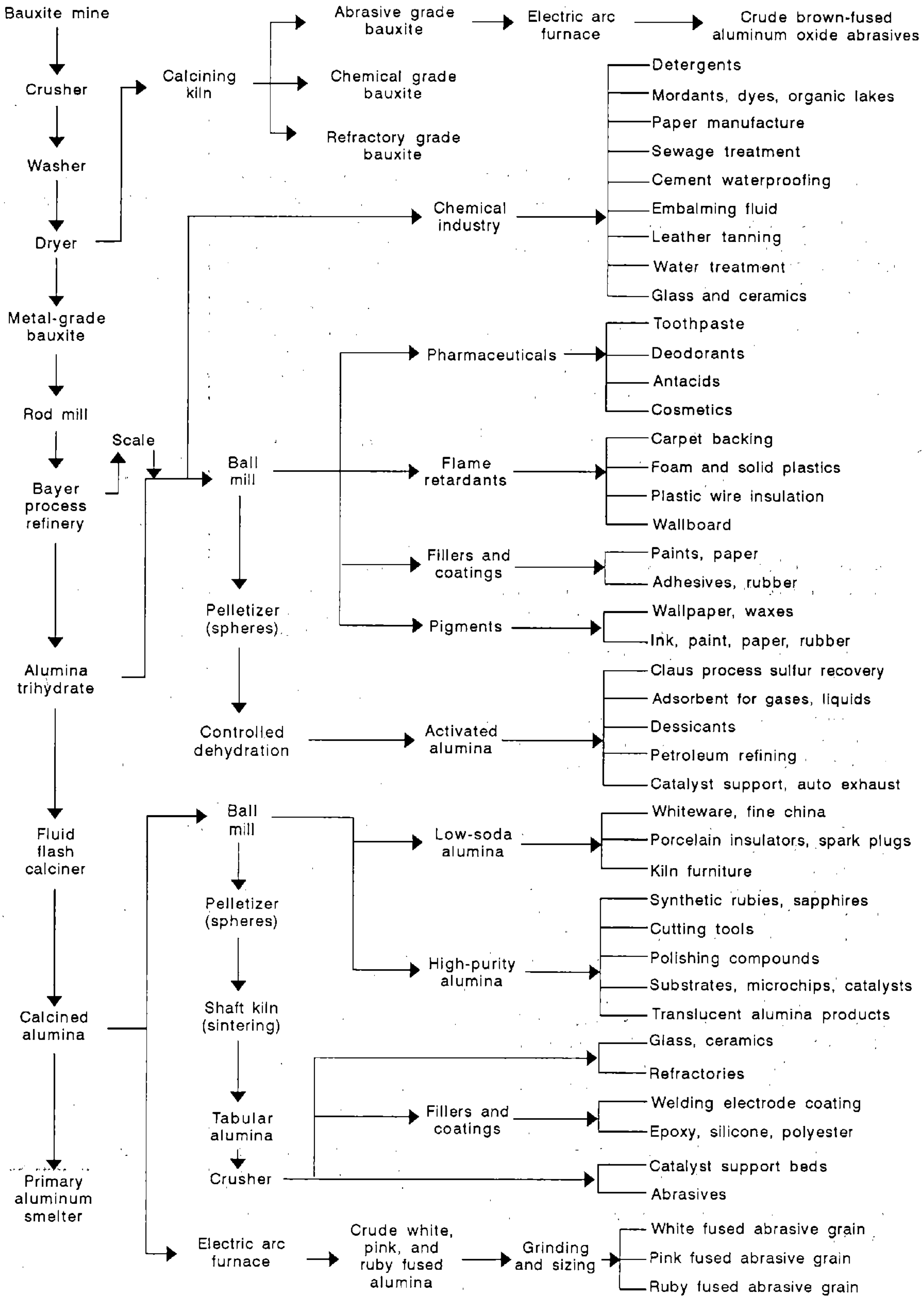

Figure 1.–Bauxite and alumina end uses.

Bismuth

By Stephen M. Jasinski

Background.—Bismuth is a soft, dense, coarsely crystalline metal having silvery color with a red or blue tinge. In addition to chemical compounds, it is also used in low-melting-point alloys, found in electrical fuses, fire sprinklers, and safety devices, and as a metallurgical additive to aluminum, iron, and steel.

Chemical Industry Consumption.—Chemical compounds have constituted the largest category of use for bismuth for centuries. Bismuth preparations were first described as a treatment for digestive ailments in the late 1500's and still account for the majority of bismuth consumed in chemicals. Other medicinal uses for bismuth have included preparations to treat syphilis, burns, and skin wounds. Several new bismuth-base medications for treating stomach ulcers are expected to become available by 1995.

Another large category of chemical consumption is for industrial and cosmetic pigments, which are found in everything from nail polish and shampoo to plastics and paint. Bismuth compounds also are used as radiopaque pigments to make plastic objects such as catheters appear on X-rays.

The amount of bismuth consumed in chemicals has been around 50% of total U.S. consumption since 1980. It is expected that growth of new pharmaceutical uses will help to keep chemical compounds a major use for bismuth.

Pharmaceutical uses.—The treatment of digestive disorders with bismuth compounds, which began in the 16th century, accounted for almost 90% of world consumption before 1930. For centuries, because the high density of bismuth compounds allows for better adherence to mucous surfaces, physicians have used bismuth compounds for many purposes such as a mild, nonirritating, antiseptic coating for the digestive tract for diarrhea and stomach ulcers, a treatment for syphilis before the development of penicillin, and in antiseptic dusting powder for skin wounds. Although certain burn dressings, antinausea preparations, hemorrhoid medications, and veterinary medications also still use bismuth compounds, many related uses are now obsolete. In the past 30 years, modern faster acting compounds such as aluminum hydroxide and magnesium hydroxide or antibiotics have replaced bismuth for internal use.

The following bismuth compounds are commonly used in medicine:

Bismuth subcarbonate-for treating stomach disturbances and as a radiopaque pigment to make catheters apparent on X-rays.

Bismuth subgallate-for anti-inflammatory skin medications and deodorizing stools in colostomy patients.

Bismuth subnitrate-for treating skin inflammation and stomach disorders.

Bismuth subsalicylate-for active ingredient in over-the-counter medications for indigestion, nausea, and diarrhea.

When properly administered, bismuth compounds are safe and nontoxic, but two incidents attributed to imprudent prescribing of bismuth in the 1970's contributed to a worldwide decline in pharmaceutical usage. In 1972, Australian health officials first reported ill effects from bismuth drugs used in large doses to deodorize stools of colostomized patients. After a 2-year investigation, the Australian Government restricted over-the-counter sales of certain preparations in 1974. Yet most medications remained available by prescription.

France banned orally administered medications containing bismuth in 1978 after 16 people died during 1974 and 1975 from the effects of ingesting abnormally large quantities of bismuth over uninterrupted long periods. Apparently overlooking well-documented warnings, some physicians allegedly prescribed massive doses of bismuth medications for use against constipation and other digestive ailments. The excess substance involved was absorbed into the bloodstream and tissues to cause serious but reversible neurological disorders, but in exceptional cases, death. The French Government lifted the ban in 1981 but classified bismuth as a suspended substance subject to review every 2 years. Bismuth medications remain available only by prescription. Before the restrictions, France was the leading consumer of bismuth for pharmaceutical uses, reaching 1,000 metric tons per year in 1975.

Bismuth compounds are being tested as a possible cure for stomach ulcers linked to the *Helicobacter pylori* bacterium, discovered to be associated with stomach ulcers in 1983. Proctor & Gamble Co. provided funding for a project at the University of Virginia to develop a medication to treat ulcers, and preliminary tests have shown encouraging results from using a combination of bismuth medications and antibiotics.

Pigments.—Bismuch oxychloride, the most widely used bismuth-base pigment, produces a pearlescent luster in plastics and cosmetics in place of natural pearl luster extracted from guanine, a component of certain fish scales, that is expensive and time consuming to produce. Although materials such as titanium-coated mica flakes, which can be costly to manufacture, and lead carbonate, a toxic material, have also been used as replacements; bismuth oxychloride provides a low-cost, nontoxic pigment for many applications. It produces the luster by crystallizing into thin plates having a high index of refraction. It is inert in most plastics, insoluble in most liquids, and nontoxic.

The pigment was first successfully tested in plastic materials in the 1950's. In the 1960's, the cosmetic industry became the first widespread consumer when bismuth-base pigments were introduced for use in lipstick and eye shadow. In the early 1970's, the development of a higher luster bismuth oxychloride pigment for nonsettling nail polishes (the pigment remains in suspension after drying) provided another big boost for bismuth in cosmetic pigment usage.

Also in the 1970's, button manufacturers became the first large plastic industry to switch to bismuth oxychloride pigments when the EPA classified as hazardous waste the dust generated from plastic buttons containing lead carbonate pigments. After 1980, the pigment was adapted for use in all types of polyester resins; and as a result, it became a commercially successful replacement for lead carbonate in the United States and Asia.. The only drawback was that bismuth pigments darkened when exposed to ultraviolet light, but the addition of ultraviolet-absorbing compounds corrected the problem. Bismuth compounds are used in various types of automobile and truck paint as pigments and drying agents. Bismuth oxychloride is used to produce the luster in metallic paint, and bismuth vanadate-molybdate yellow pigment is used for cars and school buses, primarily in Europe.

The addition of an organic bismuth compound, triphenylbismuth, makes plastic detectable to X-rays. It can be used to make medical devices such as catheters, implants, and dental restorations visible in X-ray diagnosis. This compound also would be helpful in making plastic gun parts detectable by airport security systems. In testing, triphenylbismuth has shown no deterioration from heat or moisture.

Other Uses.—Electronic ceramic materials are a growing use for bismuth chemicals. Small quantities of bismuth oxide are added to zinc oxide varistors that are used as lightning and surge protectors in high-voltage applications. Bismuth oxide increases the ability of the varistor to absorb voltage surges and lowers the temperature required to produce the ceramic. This use was developed in 1970 in Japan, the world leader in the use of bismuth in electronic materials. The electronic ceramics are often classified in the ferrite category, which includes magnetic materials, varistors, magnetic recording media, and other electronic applications. Bismuth oxide is also used as a sintering aid in the production of barium titanate capacitors.

Bismuth oxide has a variety of other applications. It is added to ceramic permanent magnets (ferrites) to increase their magnetic field and strengthen the ceramic, combined with silver to form a durable contact material in certain switches, and used for some video screens as a coating on the shadow mask, which is a thin perforated steel sheet located behind the screen that directs the electrons to the proper phosphors and absorbs excess electrons. Electronic glasses for radar and color video screens used in high technology or defense applications may contain varied amounts of bismuth oxide to increase the durability, specific gravity, and refractive index of the glass. Infrared detection systems often use lead or cadmium bismuthate glass windows. Other electronic uses include bismuth germanate crystals for radiation detectors.

Bismuth oxide has been tested as a flame retardant for plastics. Research has been sporadic due to periodic uncertainty of the supply, wide fluctuations in the price, and the abundance of other lower cost materials such as antimony oxide.

Chemical manufacturers usually purchase bismuth metal in the form of needles, which have a greater surface area than ingots and thus are easier to dissolve into solution.

Outlook.—The outlook for bismuth use in chemicals is optimistic. Because of tightening restrictions on the use of lead and cadmium in pigments, usage may increase as a substitute for those metals. As improved ultraviolet-absorbing compounds are developed, more bismuth oxychloride may be used in metallic automobile paint. Pharmaceutical uses have been rebounding since the late 1980's due to the discovery that bismuth medications are effective as a treatment for certain stomach and duodenal ulcers. The use of bismuth compounds in electronics should remain strong through the next decade.

Table 1.—Salient bismuth statistics

(Metric tons unless otherwise specified)

	1970	1975	1980	1985	1990
United States:					
Consumption	1,002	638	1,038	1,199	1,274
Exports[1]	413	58	59	122	122
Imports for consumption[2]	453	604	1,006	907	1,612
Price, average, domestic dealer, per pound[3]	$6.00	$7.72	$2.83	$5.18	$3.56
Stocks, Dec. 31, consumer	327	205	306	230	344

[1] Includes bismuth, bismuth alloys, and waste and scrap.

[2] General imports 1970, 1975, and 1980.

[3] Domestic producer price 1970 and 1975.

Table 2.—Bismuth consumption by the U.S. chemical industry
(Metric tons)

	1970	1975	1980	1985	1990
Chemical uses[1]	537	251	506	601	577
Total U.S. consumption	1,002	638	1,038	1,199	1,274

[1] Includes pharmaceutical uses, industrial chemicals, and cosmetic pigments. Categories are not listed separately to avoid disclosing company proprietary data.

Boron

By Phyllis A. Lyday

Background.—Over four-fifths of U.S. boron production comes from mineral deposits mined only for their boron content. The remainder is produced from lake brines, which also supply sodium carbonate, sodium sulfate, potassium sulfate, and potassium chloride.

Tincal and kernite ore and brines are the U.S. source of refined borate chemical compounds. The most common refined borates, borax pentahydrate and its derivative anhydrous borax, are marketed in technical and agricultural grades. Lesser quantities of borax decahydrate are produced in technical, United States Pharmacopeia, and special-quality grades.

Boric acid is a white, odorless, crystalline solid sold in technical, National Formulary, and special-quality grades as granules or powder. Boron oxide is a hard, brittle, colorless solid resembling glass that is ground and marketed most often under the name anhydrous boric acid.

The major use for boron is in various glass products that include textile-grade and insulation-grade glass fibers, borosilicate glass, enamels, frits, and glazes. Many of the boron compounds and ores can be interchanged in the glass process depending upon the price of the boron source.

United States Borax & Chemical Corp., a part of Borax Consolidated Ltd. of the RTZ Corp. PLC of London, United Kingdom, continued to be the primary domestic supplier of sodium borates. U.S. Borax mined and processed crude and refined sodium borates, their anhydrous derivatives, and anhydrous boric acid at Boron, in Kern County, CA. A second plant at Boron, CA, used a proprietary process to produce technical-grade boric acid from extensive kernite ore reserves. The boric acid was produced to compete with imported colemanite used in glass manufacture. In addition, colemanite was mined at Shoshone, in Inyo County, CA.

The majority of boron products was shipped to Wilmington, CA. Products made at a plant in Wilmington included ammonium borates, potassium borates, sodium metaborates, and zinc borate.

American Borate Co. continued sales of ulexite from storage at Dunn, CA. Mine plans for the closed Billie Mine were submitted to the Bureau of Land Management for approval. North American Chemical Co. operates the Trona and Westend plants at Searles Lake, in San Bernardino County, to produce refined sodium borate compounds and boric acid from the mineral-rich lake brines. At the Trona plant, a differential evaporative process produced borax with potash as a byproduct. Boric acid was produced by solvent extraction. The Westend plant continued production of sodium borates by a carbonation process.

The source of foreign competition to domestic boron has been Turkey, which became the world's leading producer of boron minerals and compounds in 1988. Development of boron deposits in Argentina, Chile, and Peru could make South America a primary supplier of boron material.

In 1990, the desert tortoise was designated an endangered species by the Fish and Wildlife Service (FWS) of the U.S. Department of the Interior. About 500 plants and animals are now protected by the 1973 Act. By law, FWS looks only at scientific facts as to whether further pressure will lead to extinction.

The FWS cited habitat deterioration and loss, disease, and varied human uses of the desert as some of the principal threats facing the tortoise. Energy and mineral development were listed as one of the land uses affecting the tortoise. The listing extends long-term protection to tortoises living north and west of the Colorado River, including eastern California, southern Nevada, northwestern Arizona, and southwestern Utah. The areas listed include boron areas being surface mined and a solution-mining project area. Any change in land use in these areas requires consultation with the FWS beforehand.

Chemical Industry Consumption.—Boron is used in three primary areas in chemicals and allied products as defined by the Standard Industrial Classification Manual: agriculture, soaps and detergents, and fabricated metal products. Boron is 1 of 16 nutrients essential for plant growth, just as nitrogen, phosphorus, and potassium are essential. Boron deficiency can manifest itself in a variety of symptoms. For example, deficiency in apples causes cork in the fruit, cessation of new growth, and rosetting of the leaves. Boron deficiency affects the connecting tissue that allows food products produced in the leaves to move into storage areas and causes deterioration in crop quality and reduced yield. A continuous supply of boron is required because boron is used and fixed in the cell rather than moved into new growth areas.

Borax reacts with a strong base or a strong acid to form a neutral or buffer solution that can be utilized in soaps and detergents. Because the buffering ability of a borate solution is used to remove stains by neutralizing acidic soil and protein, borate usually is added as a prewash along with soaps and detergents. Sodium perborate monohydrate is added as a bleaching agent in detergents and cleaning products. The perborate liberates hydrogen peroxide, a strong oxidizer, upon hydrolysis. The bleaching action is most effective above 131° F.

Boron, hydrogen, nitrogen, and carbon form interstitial solutions between metal atoms. Boron-alloy steels are solid solutions of two metals of approximately the same atomic radius with boron in the spaces, or interstices. Interstitial compounds can be harder and stronger than the parent metal(s), although an excess of the interstitial element can causes brittleness. Boron compounds and master alloys are used in aluminum smelting as grain refiners. An iron-boron-rare-earth compound is an alternative to cobalt magnets in stereo speakers, computer disk drives, and telecommunication printers. Boron is used to neutralize the residual acid from the pickle in the drawing of fine steel wire. Boric acid and borax are exceptional fluxes for metal welding. The fluxing action of the borates is due to the capacity of molten borates to dissolve metal oxides, thus cleaning the surface and permitting good metal-to-metal contact. Potassium perborate is used in metallurgy for welding and brazing stainless steel. Trimethyl borate is used in gas-welding fluxes.

Outlook.—The outlook for boron in usage in agriculture and fabricated metal products will remain constant at 1990 levels until 1996. The usage for soaps and detergents is expected to increase by approximately 10% by 1996.

Table 1.—Salient boron statistics

(Thousand metric tons boron oxide content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production[1]	505	547	710	577	608
Industry stocks, Jan. 1[e]	6	6	3	NA	NA
Imports	12	12	28	58	63
Total U.S. supply	523	565	741	635	671
Distribution of U.S. supply:					
Industry stocks, Dec. 31[e]	6	6	3	NA	NA
Exports	260	311	390	304	312
Demand	255	247	348	327	319
Apparent surplus (+) or deficit (-) of supply	+2	+1	—	+4	+40

[e] Estimated. NA Not available.

[1] Boron oxide sold as such or used in the preparation of boron compounds by primary producers.

Table 2.—Boron consumption by the U.S. chemical industry

(Thousand metric tons boron oxide content)

End use	1970	1975	1980	1985	1990
Agriculture	35	20	14	14	6
Soaps and detergents	41	44	24	22	24
Fabricated metal products	6	9	6	3	3
Total chemicals demand	115	73	44	39	33
Total other demand	140	174	304	288	286
Total U.S. primary demand	255	247	348	327	319

Bromine

By Phyllis A. Lyday

Background.—The U.S. portion of world bromine production has decreased steadily since 1973 when the United States produced 71% of the world supply. The quantity of bromine sold or used in the United States during 1990 was about 177 million kilograms valued at $173 million. Exports of elemental bromine and bromine contained in compounds was valued at $22 million. The price of elemental bromine in bulk was $1.24 per kilogram.

Bromine is widely distributed in the Earth's crust, but in small quantities. By far the largest potential source of bromine in the world exists in the oceans. At a concentration of only 65 parts per million large amounts of water are processed to obtain the bromine.

Arkansas brines contain about 5,000 ppm at depths of 7,500 feet in limestone of the Smackover Formation of Jurassic age. Three companies produce bromine at six plants in Arkansas. In Michigan, brines containing about 2,600 ppm of bromine occur in the Sylvania Sandstone Formation of the Detroit River Group of Devonian age. One producer produces bromine at one plant, that is recycled in another company's plant in Arkansas.

At the processing facility, bromine is separated from the brine by a steaming-out process. The brine is pumped into the top of a tower constructed of granite and filled with ceramic packing. As the brine falls through the packing material, it reacts with chlorine and steam that are injected at the bottom of the tower. The chlorine replaces the bromine in the brine, and the gaseous bromine rises with the steam out of the top of the tower; there it is condensed to a reddish-brown liquid. One kilogram of chlorine is required to produce 1 kilogram of bromine. About 95% of the bromine, or about 0.7 to 0.8 kilogram of bromine per barrel of brine, is recovered if the raw brine first is acidified to a pH of 3.5. Bromine is separated from gases because it is heavy and settles on the bottom. The bromine liquid can be further purified or reacted with other materials to form bromine compounds. Bromine vapor, a little chlorine, and water vapor are captured at the top of the tower. Hot bromine-free liquor emerges from the bottom of the tower. After neutralization with lime, the waste liquor is pumped through a heat exchanger to a waste pond. Brine from the pond is reinjected into the same producing zone to maintain hydrostatic pressure.

Chemical Industry Consumption.—Bromine consumption can be divided into five major end uses. Primary uses of bromine compounds were in flame retardants (28%), agriculture (20%), petroleum additives (14%), well drilling fluids (11%), and other (27%).

Approximately 73 million kilograms of bromine is used in halon fire extinguishers and as fire retardants in nylon, foams, and plastics used in textiles, carpets, upholstery, electronics, etc.

The second major end use for bromine is in metal bromides for use as drilling-completion-workover fluids. Domestic production increased from nearly zero to over 45 million kilograms between 1970 and 1990.

The use of bromine as a scavenger for lead in gasoline has decreased since concern over the toxic effects of lead surfaced in the 1970's. The EPA gasoline lead phasedown program that began in 1973 banned the use of leaded gasoline in automobiles equipped with catalytic converters. Ethylene dibromide (EDB) use as a combustion-exhaust lead scavenger has decline by roughly 25% between 1974 and 1979, resulting in a decrease of 27 million kilograms of bromine for EDB in 1979 compared to 1974. Presently about 23 million kilograms per year of bromine is still used in leaded gasoline. Bromine combines with the lead and is exhausted to the atmosphere.

Bromine that is used primarily as a sanitizer in agriculture has decreased in the last 10 years because of contamination of ground water supplies as a result of overusage. Bromine compounds are used to kill nematodes prior to planting certain crops and to sanitize grains and storage bins to decrease insect infestation and spoilage.

The last major use of bromine is as a catalyst in chemical processes. Bromine waste material is recycled. Because bromine is a toxic gas, it is contained in sealed vessels and processed in closed systems.

Because bromine is considered a hazardous material, persons who may be exposed to the fumes must wear respirators and protective clothing. Recycling of bromine used in intermediate products amounts to about 30% of domestic production. Some end products that are considered toxic must be incinerated or disposed of in hazardous waste sites. Recent tests that caused concerns over dioxins in Europe have caused a voluntary ban on usage of the fire retardant materials. The EPA studied the effects of bromine on the environment and determined that the greatest potential environmental hazard is not with bromine emissions, but rather with exposure to chemicals that are potentially carcinogenic or teratogenic such as EDB, certain fire retardants, methyl bromide, and vinyl bromide.

Because of changing market conditions, much of which is attributable to various environmental considerations, substantial alterations in existing production and consumption patterns of bromine compounds have occurred as follows: lead phasedown; dibromochlorpropane ban; EDB regulations; ban on the flame retardant "Tris;" polybrominated biphenyls contamination; and EDB replacement in some fumigation.

In 1958, the United States produced 92% of world bromine production; by 1988 the U.S. share of world bromine production had declined to 40%. The major change has been the beginning of bromine production as a byproduct of potash and magnesium compounds production in Israel, which has become the second largest producer of bromine and bromine compounds. Waste brines in Israel, used for bromine recovery, contain 14,000 ppm bromine, more than two-and-one-half times as concentrated as the U.S. source.

Besides causing increased competition for U.S. companies, imports are not required to pay the Superfund Tax on raw material production. The Superfund Tax is collected to reclaim abandoned toxic waste dump sites. During 1979, import reliance increased significantly, having approximately 99% of the accounted-for imports from Israel. The U.S. companies receive a double tax in that 1 kilogram of chlorine is needed to produce 2 kilograms of bromine. Both chlorine and bromine are taxed. Imported material is not subject to the environmental tax but contributes to the solid waste disposal problems.

Outlook.—The use of bromine in sanitary preparations and fire retardants is expected to increase by 5% by 1996.

Table 1.—Salient bromine statistics

(Million kilograms)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production[1]	159	185	172	145	175
Industry stocks, Jan. 1[e]	15	10	3	3	3
Imports	([2])	([2])	([2])	8	21
Total U.S. supply	174	195	175	156	199
Distribution of U.S. supply:					
Industry stocks, Dec. 31[e]	15	11	4	4	4
Exports	([2])	30	36	26	17
Demand	155	155	135	127	178
Apparent surplus (+) or deficit (-) of supply[3]	+4	-1	—	-1	—

[e] Estimated.

[1] Elemental bromine sold as such or used in the preparation of bromine compounds by primary producers.

[2] Estimated at less than 1/2 unit.

[3] The difference between total U.S. distribution of supply and total U.S. supply.

Table 2.—Bromine consumption by the U.S. chemical industry

(Million kilograms)

End use	1970	1975	1980	1985	1990
Sanitary preparations	22	17	21	19	18
Fire retardants	8	22	25	45	74
Total chemicals demand	30	39	46	64	92
Total other demand	126	116	89	63	85
Total U.S. primary demand[1]	155	155	135	127	178

[1] Data may not add to totals shown because of independent rounding.

Cadmium

By Thomas O. Llewellyn

Background.—Cadmium, a soft, malleable, ductile, bluish-white metal, was discovered in Germany in 1817. Germany, which produced the first commercial cadmium metal later in the 19th century, was the only important producer of cadmium until World War I, recovering the metal as a byproduct of the smelting of cadmium-bearing zinc ores of Upper Silesia. Because cadmium minerals are not found in commercially viable deposits, cadmium is usually produced as a byproduct in the recovery of primary zinc from zinc ores and also from some lead ores or complex copper-lead-zinc ores. Production in the United States began in 1907 when the Grosselli Chemical Co. of Cleveland, OH, recovered metallic cadmium as a byproduct of zinc smelting. By 1917, the United States became the world's leading producer of cadmium and held that position for over 50 years. Currently, the United States is the fourth largest producer of refined cadmium in the world.

Cadmium is included in the National Defense Stockpile (NDS) because of its importance in specialized military applications such as plating, where substitutes may be in short supply or unsatisfactory. In April 1980, the stockpile goal for cadmium was set at 5,307 metric tons. At the end of 1991, the NDS cadmium inventory was 2,871 tons, which represents 54% of the established goal, and has remained at this level for the last 12 years.

In 1990, primary cadmium was produced by ASARCO Incorporated, Denver, CO; Big Zinc Corp., Sauget, IL; Jersey Miniere Zinc Co., Clarksville, TN; and Zinc Corp. of America, Bartlesville, OK. The companies in Illinois, Oklahoma, and Tennessee recovered cadmium as a byproduct of smelting domestic and imported zinc concentrates. The company in Colorado recovered cadmium from other sources such as lead smelter baghouse dust.

Secondary sources of cadmium are small. Some domestic cadmium producers report as secondary production material that is actually a remelt of new scrap generated during primary production. Sources of secondary cadmium are remelting of cadmium-containing alloy scrap, spent nickel-cadmium batteries, and dust generated during the operation of electric arc furnaces (EAF) used in the steelmaking industries.

Statistics on the exports of cadmium before 1941 are not available, but it is known that domestic cadmium was exported during War World I as well as in other years after the war. The U.S. Department of Commerce, which had previously recorded data on cadmium exports in combination with other commodities, began to report them separately in 1941. Cadmium average exports per year during the 1970's were equivalent to about 7% of the total domestic production; however, in the 1980's, average exports reached 15% of the domestic production.

In the early 1900's, cadmium was imported from Germany as metallic sticks and as cadmium sulfide pigment; however, the annual amount of cadmium imported before 1927 was always less than 10 tons. Supplies from Germany were curtailed during World War I, and no cadmium was imported from 1916 to 1920. Imports were resumed in 1921 but on a much smaller scale, and none was imported in 1923, 1925, and 1926. For the last 15 years, over 60% of the domestic requirements for cadmium have been met by imported metal and metal contained in imported zinc ores and concentrates.

Chemical Industry Consumption.—For about 70 years after its discovery cadmium was used primarily in the sulfide form in small amounts in paint pigments. In the early part of this century, cadmium sulfide was used in this country mainly as pigment. Minor amounts of metallic cadmium were used in amalgam and other alloys. The common dental amalgam of those days consisted of 26% cadmium and 74% mercury. During World War I, cadmium was used mainly as a substitute for tin. Limited data are available on the amount of cadmium consumed in each particular application. Although cadmium is used by a great number of consumers in many industrial products, it is mainly used in small quantities. The Bureau of Mines makes annual consumption estimates for five major end uses in the United States-batteries, coating and plating, pigments, plastics and synthetic products, and alloys and other.

The adoption of cadmium electroplating for rustproofing parts and accessories by the automobile industry was an important factor in making plating the biggest end use for cadmium for many years. Manufacturing of storage batteries using cadmium-nickel cells started in the United States during World War II. For the period 1940-45, the estimated consumption of cadmium in batteries was less than 1%, while that of plating was about 70%, however, by 1990, the consumption of cadmium in batteries reached 40%, and plating had gone down to 25%.

Commercially most cadmium plating is made using an alkaline cyanide bath prepared by dissolving cadmium

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oxide in a sodium cyanide solution. Cadmium metal balls suspended in steel wire cages are used as the plating anodes. During this electrochemical process, the ratio of the total sodium cyanide to cadmium metal content is very important to maintain the desired operating characteristics of the bath system.

Batteries classified as being primary or secondary, are electrochemical devices that convert stored chemical energy into electrical energy. Cadmium is used in secondary batteries, and its use has grown in importance during the last two decades and now represents the major use for cadmium. Cadmium is used in the negative plates of nickel-cadmium, mercury-cadmium, and silver-cadmium batteries. The nickel-cadmium batteries are the most popular of the three, and production of mercury-cadmium batteries is being phased out.

Cadmium pigments are stable inorganic coloring agents having essential properties such as high temperature stability, high resistance to degradation by light, insolubility in organic solvents, and a wide range of excellent brilliant colors and opacity for applications such as ceramics, coatings, plastics, and artist's colors. The pigments are based upon the compound cadmium sulfide, which produces a golden yellow pigment. Partial substitution of cadmium by zinc or mercury and the substitution of sulfide by selenium in the crystal lattice forms a series of intercrystalline compounds making up the intermediate colors in the lemon-yellow-to-maroon range of cadmium colors. Their high heat stability makes them ideal for use in high-temperature plastic moldings.

Liquid cadmium-bearing stabilizers prevent the degradation of polyvinyl chloride (PVC) and related polymers by ultraviolet light rays, which may cause discoloration and/or mechanical breakdown of the material. Carboxylates of cadmium and barium are mixed to produce the most common stabilizer formulations. Cadmium-stabilized PVC is used mainly in window frames and other external profiles.

Cadmium has long been recognized as a toxic metal that must be handled with care to avoid prolonged exposure to cadmium fumes and/or dust. Cadmium poisoning can result from inhalation of cadmium dust and fumes or the ingestion of contaminated food and water. Chronic exposure to cadmium can lead to kidney dysfunction.

On August 31, 1992, OSHA, meeting a court-imposed deadline, issued its final decision on permissible 8-hour exposure limit (PEL) to airborne cadmium in the workplace. OSHA's final ruling requires that cadmium fumes or dust levels be lowered to an average of 5 micrograms per cubic meter of air over an 8-hour period. The previous allowable average PEL levels for an 8-hr period were 100 micrograms per cubic meter for cadmium fumes and 200 micrograms per cubic meter for cadmium dust.

OSHA has determined that some processes in six industries would be unable to achieve the PEL of 5 micrograms per cubic meter through engineering controls and work practice alone; therefore, OSHA established separate engineering control air of either 15 or 50 micrograms for those processes. The six industries were nickel-cadmium battery manufacturing, zinc and cadmium refining, pigments manufacturing, plastic stabilizer production, lead smelting, and plating. These final standards took effect 90 days from their publication in the Federal Register dated September 14, 1992.

Coatings of zinc or vapor-deposited aluminum substitute for some cadmium-coating applications, and tin can be used in place of cadmium pigments. The search for substitutes has been triggered by increasing environmental concerns.

In 1903, the apparent cadmium consumption was only about 4 tons; however, in 1969, the United States had a record-high apparent consumption of about 6,830 tons. For 1990, the total apparent consumption was calculated at about 3,100 tons—about one-half the quantity consumed during the peak year.

Outlook.—The short-term demand for cadmium in the United States is expected to fall below the level of 1990. This decline is expected to be the result of continuing lower demand for cadmium in coating and plating, pigments, and plastics products during the next 3 to 4 years as a consequence of stricter environmental and health regulations now under consideration.

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Table 1.—Salient cadmium statistics

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production	4,293	1,990	1,578	1,603	1,678
Imports, metal	1,130	2,375	2,617	1,988	1,741
Shipments from Government stockpile excesses	3	—	—	—	—
Industry stocks, Jan. 1	1,022	1,423	1,343	901	726
Total U.S. supply	6,448	5,788	5,538	4,492	4,145
Distribution of U.S. supply:					
Industry stocks, Dec. 31	2,148	2,577	1,768	686	653
Exports	169	180	236	86	385
Demand	4,131	3,031	3,534	3,720	3,107
U.S. demand pattern:[e]					
Batteries	400	490	940	1,000	1,243
Coating and plating	2,200	990	1,450	1,260	777
Pigments	700	650	550	600	404
Plastic stabilizers	600	600	470	560	373
Other	231	301	124	300	310
Total U.S. primary demand	4,131	3,031	3,534	3,720	3,107

[e]Estimated.

Chromium

By John F. Papp

Background.—Chromite, the ore mineral of chromium, is not currently produced in the United States. The Republic of South Africa and the Commonwealth of Independent States (CIS) are the two leading producers of chromite ore. The chromite ore producers may be categorized as major, significant, and minor based on quantity of production. The two major chromite producers, South Africa and the CIS, consistently produce more than 1 million metric tons per year each. Together they account for about two-thirds of world annual production. There are seven additional significant chromite producers—Albania, Brazil, Finland, India, the Philippines, Turkey, and Zimbabwe—having annual production consistently in the range of from 1,000 tons to 1 million tons. Together they account for about one-third of world annual production. The remaining producers account for about 3% of world annual production. Chromite is typically consumed by industries primarily located in the developed countries: steel, chemicals, and refractories.

Chromite is used in the metallurgical, chemical, and refractory industries. In the metallurgical industry, chromite is processed into ferrochromium or chromium metal, which are used as alloying metals to make a variety of ferrous and nonferrous alloys. The major end use is in stainless steel, a ferrous alloy made resistant to oxidation and corrosion by the addition of chromium. Chromite is used in the chemical industry to make sodium dichromate, which is both a chemical industry product and an intermediate product used to make other chromium chemicals. Chromium chemicals find a wide variety of end uses including pigments and plating and surface-finishing chemicals. Chromite is used in the refractory industry to produce refractory materials including shapes, plastics, and foundry sands. These refractory materials are then used in the production of ferrous and nonferrous alloys, glass, and cement. Chromite is useful in the refractory industry because it retains its physical properties at high temperatures and is chemically inert.

Based on the chromium contained in ore, chromium ferroalloy, metal, and chemicals, it is estimated that U.S. chromium demand averages about 410,000 tons per year (contained chromium). On average, about 70% of U.S. consumption goes into the metallurgical industry of which 70% goes into stainless steel. The remaining chromium consumed in the United States goes into the chemical industry (about 20%) and the refractory industry (about 10%). The allocation of chromium consumption in other market economies is similar to that in the United States.

Chemical industry chromite use increased slowly from 1940 through 1985. Over the time period in which the metallurgical, chemical, and refractory industry data were reported separately (i.e., 1940-85), the metallurgical industry accounted for 56% of reported chromite consumption; refractory industry, 27%; and chemical industry, 18%. More recently (from 1976 through 1985) metallurgical industry chromite use decreased to 51%, while refractory use declined to 18% and chemical use increased to 31%. Over the most recent 5 years (1986-90), refractory use has declined further to 11% of chromite use, while chemical and metallurgical use has been 89% of reported chromite consumption. The latter two categories have been combined to preserve confidentiality. (Chromium consumption differs from chromite consumption because chromium consumption includes chromium contained in chromite, alloys, and chemicals, while chromite consumption includes only chromite ore.)

Chemical Industry Consumption.—Chromium is used in the chemical industry to make a variety of products including biocides, catalysts, corrosion inhibitors, metal-plating and finishing chemicals, oil-field chemicals, pigments, printing chemicals, and tanning compounds. Chromium was first used in pigments and tanning compounds. Chromium plating, the electrodeposition of chromium from a solution of chromic acid, started in the early 1900's. A more recent use for chromium is in wood preservation. Chromium-copper-arsenate (CCA) impregnated wood is protected from weathering, insects, and rotting for 30 years.

The terms chromium and chrome are both in the chemical industry to and mean the same, the element chromium. Similarly, the terms bichromate and dichromate are used interchangeably in the chemical industry. Historically, the term chrome was used more commonly than chromium. Thus many chemical products, namely pigments, have chrome in their name. To be consistent with the chemists' convention for naming compounds, dichromate would be used instead of bichromate; however, in trade and commerce, the term bichromate is used.

Chromite is used in the chemical industry to produce sodium dichromate from which other chromium chemicals are manufactured. Chromite ore is pulverized and mixed with soda ash (sodium carbonate) and a diluent. The diluent could be lime (calcium oxide) or recycled material from the production processes. The mixture is roasted in a rotary kiln to produce a compound containing sodium chromate, which is leached out and treated with acid to produce sodium dichromate and then purified. Sodium chromate and dichromate are produced by this process in the United States. The major commercial product is sodium dichromate dihydrate. Several primary chromium chemicals produced by U.S. chemical companies that produce chromium chemicals from chromite include sodium dichromate anhydrous and sodium dichromate dihydrate; sodium chromate anhydrous and sodium chromate tetrahydrate; chromic acid; chromic oxide; and potassium bichromate. American Chrome & Chemicals Inc. and Occidental Chemical Corp. are the primary chromium chemical producers in the United States. Many other chromium chemicals are manufactured from sodium dichromate and these other primary chromium chemicals.

A chromium chemical end use with which many people are familiar is pigment. Medium yellow pigment, a lead-chromate base pigment, is used in traffic-marking yellow paint found on all major streets and highways. Copper-chrome pigment is used in the black coating found on outdoor grills and wood-burning stoves. An important use of chromium pigments is in anticorrosion coatings. Chromate metal primers are used extensively by the Federal Government, both in civilian and military applications. Chromium oxide green pigment is used in camouflage because it has desirable infrared reflectance properties.

Annual chromite ore consumption at the end of the 1940-85 time period was nearly double that of the beginning of the period, yielding an average annual growth rate of about 1.4% over the period. The United States has the world's largest chromium chemicals production capacity and is a major producer, consumer, and world supplier of chromium chemicals. Other major world producing countries include the Federal Republic of Germany, Japan, the CIS, and the United Kingdom. World production capacity in 1991 was about 250,000 tons contained chromium, or about 750,000 tons sodium dichromate dihydrate equivalent. Many small chromium chemical plants are located in chromite-producing countries, however, of the countries producing chromium chemicals, only the CIS is a significant chromite ore producer, with about one-third of world chromite production. The CIS republics are also a significant chromium chemical producers, having the world's estimated second largest production capacity. Japan produces chromite ore, but the quantities are insignificant compared to its industrial demand. Therefore, all of the major chromium chemical production, except that in the CIS, is located in industrialized countries that do not produce chromite. On average over the time period 1986-90, U.S. chromium chemical exports exceeded imports by about 41% in terms of weight and by about 7% in dollar value. Sodium dichromate and chromic acid accounted for the largest volume of exports and of imports.

Outlook.—The U.S. demand for sodium dichromate was reported to have been 130,200 tons in 1990 and projected to be 130,800 tons in 1991 and 133,400 tons in 1995. The domestic chromium chemicals market showed -0.7% growth from 1981 through 1990 and was expected to show a +1% growth from 1991 through 1995. Reported price for sodium dichromate crystals was $0.60 per pound of sodium dichromate dihydrate equivalent content (for pricing purposes sodium dichromate dihydrate equivalent content of crystals is 100%), and sodium dichromate liquor was $0.55 per pound of sodium dichromate dihydrate equivalent content (typically the sodium dichromate dihydrate equivalent content of liquor ranges from 69% to 70%). Sodium dichromate was used as follows: chromic acid, 55%; chromium oxide, 10%; leather tanning, 8%; pigments, 7%; wood preservatives, 2%; drilling mud additives, 2%; other uses (including metal finishing, water treatment, textiles, and catalysts), 3%; and export 13%. Environmental concerns were seen as driving the chromium chemicals markets because chromium markets were both created and limited by environmental restrictions.

Demand for chromic acid was expected to continue to grow at an annual rate of about 2% to 3% through 1995. Domestic chromic acid producers, American Chrome and Chemicals and Occidental Chemicals, increased their chromic acid production capacity to the current annual rate of 71,000 tons to meet increasing demand. Chromic acid prices were about $1.10 to $1.15 per pound in 400 per pound drums. Chromic acid was consumed for the production of wood preservatives, metal finishing, and chromium dioxide. Wood preservation currently accounts for about 70% of chromic acid demand and was expected to increase even though chromium chemicals account for about 70% of the U.S. wood treatment market. Environmental restrictions on the use of creosote (in marine pilings) and pentachlorophenol (in utility poles) were expected to result in greater use of chromic acid for wood preservation. The most widely used chromium-containing wood preservative is CCA. CCA-treated wood is resistant to decay and termite attack and is easier to paint than wood treated with oil-base formulations. CCA-treated wood thus finds use in roofing, outdoor decks, and house foundations. Metal finishing, which accounts for about 27% of chromium oxide demand, includes chromium plating, aluminum anodizing, and other metal treatments. No growth was anticipated for metal finishing. The remaining 3% of chromic acid consumption included the production of chromium dioxide, a growth market that included the production of magnetic particles for use in magnetic recording media (audio and video tapes and computer disks).

EPA regulation limiting chromium releases has encouraged recycling of chromium chemicals and the use of substitutes to reduce releases. As a result, demand is expected to be reduced for many end uses.

Table 1.—Salient chromium statistics

(Thousand metric tons, contained chromium)

	1970	1975	1980	1985	1990
World production:					
Chromite ore (mine)[1]	1,822	2,495	2,981	3,295	3,889
Ferrochromium (smelter)[2]	NA	1,065	1,879	1,947	1,965
Stainless steel, Western World[3]	NA	NA	1,171	1,346	1,830
Components of U.S. supply:					
Domestic mines	—	—	—	—	—
Secondary	NA	NA	58	85	90
Imports:					
Chromite ore	402	347	254	109	92
Chromium ferroalloy	24	180	160	173	244
Chromium metal	NA	1	4	4	7
Chromium chemicals	NA	NA	1	5	4
Chromium pigments	NA	NA	3	2	NA
Stocks, Jan. 1:					
Government	NA	NA	1,051	1,051	[4]1,097
Industry	NA	NA	288	114	139
Total U.S. supply	—	—	1,818	1,542	1,676
Distribution of U.S. supply:					
Exports:					
Chromite ore	38	11	2	27	2
Chromium ferroalloy	NA	NA	16	6	5
Chromium metal	NA	NA	([5])	([5])	([5])
Chromium chemicals	NA	NA	9	4	7
Stocks, Dec. 31:					
Government	NA	NA	1,051	1,080	1,099
Industry	NA	NA	219	106	118
Total U.S. distribution	—	—	1,297	1,223	1,231
Apparent industry demand	—	—	521	349	447

NA Not available.

[1] Calculated assuming chromite ore to average 44% Cr_2O_3 that is 68.42% chromium.

[2] Calculated assuming chromium content of ferrochromium to average 57%.

[3] Calculated from World Stainless Steel Statistics, 1991 ed., reported production, assuming chromium content of stainless steel to average 17%.

[4] Variation in stockpile quantity does not contribute to apparent industry demand because variation resulted from upgrading programs.

[5] Less than ½ unit.

Table 2.—Chromium consumption by the chemical industry

(Metric tons, gross weight)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Chemical production:					
Sodium bichromate	139,297	112,975	140,139	115,873	NA
Chromic acid	20,172	NA	NA	NA	NA
Pigment production:					
Lead chromate green	2,315	NA	NA	NA	NA
Chromic oxide green	6,124	5,087	5,157	NA	NA
Lead chromate yellow and orange	29,437	23,669	25,252	18,783	14,734
Chrome molybdate orange	10,002	8,672	8,895	5,585	NA
Zinc chromate yellow	5,216	NA	NA	2,005	NA
Other pigments	NA	NA	3,269	NA	NA
Total pigments	53,094	37,428	42,573	26,373	14,734
Imports:					
Chromium chemicals:					
Oxides and hydroxides:					
Chromic acid	NA	NA	39	4,450	1,677
Other	—	—	—	—	3,512
Sulfates	—	—	—	—	192
Salts and acids:					
Zinc or lead chromates	—	—	—	—	425
Sodium bichromate	—	—	—	—	1,661
Potassium bichromate	—	—	—	—	680
Other chromates	—	—	—	—	1,860
Potassium chromate and bichromate	NA	NA	137	660	—
Sodium chromate and dichromate	NA	NA	1,053	9,830	—
Carbides	NA	NA	204	112	123
Pigments:					
Chrome yellow	NA	NA	1,214	2,886	3,643
Molybdenum orange	—	—	—	977	916
Zinc yellow	—	—	—	1,570	436
Other pigments	—	—	—	—	657
Chrome green	NA	NA	(1)	183	—
Chrome oxide green	NA	NA	3,545	1,371	—
Hydrated chrome oxide green	NA	NA	—	12	—
Strontium chromate	NA	NA	—	391	—
Stocks, Jan. 1:					
Government	—	—	—	—	—
Industry	NA	NA	NA	NA	NA
Distribution of U.S. supply:					

Table 2.—Chromium consumption by the chemical industry

(Metric tons, gross weight)

	1970	1975	1980	1985	1990
Exports:					
Chromium oxides and hydroxides:					
Chromic acid	NA	NA	6,048	3,521	4,082
Other	—	—	—	—	1,226
Sulfates	—	—	—	—	44
Salts and acids:					
Zinc or lead chromates	—	—	—	—	209
Sodium bichromate	—	—	—	—	16,663
Potassium bichromate	—	—	—	—	48
Other chromates	—	—	—	—	228
Potassium chromate and dichromate	NA	NA	122	64	—
Sodium chromate and dichromate	NA	NA	21,642	8,823	—
Pigments	NA	NA	2,746	1,749	2,643
Stocks, Dec. 31:					
Government	—	—	—	—	—
Industry	NA	NA	NA	NA	NA

NA Not available.

[1] Less than ½ unit.

Source: Department of Commerce.

Clay

By Robert L. Virta

Background.—Clay is a rock term used to describe any naturally occurring fine grained material that becomes plastic when mixed with water. Clays are composed primarily of kaolin, montmorillonite, attapulgite, palygorskite, or halloysite, which are referred to as clay group minerals. These minerals are hydrous aluminous silicates although they may also contain significant amounts of iron, alkalies, and alkaline earth.

Over 300 firms operated 1,080 clay mines and mills in 44 States in 1990. A little under 43 million metric tons of clays, valued at $1.62 billion, were sold or used. In 1990, approximately 30,000 tons of clay was imported, and 4.12 million tons was exported. (table 1).

Chemical Industry Consumption.—Clay was used by the chemical industry in adhesives, agricultural products, chemical manufacturing, cosmetics, ink, paint, plastics, and rubber (table 2). Properties such as cost, whiteness, chemical inertness, low electrical and thermal conductivity, surface area, plasticity, and absorptive and refractory characteristics are important for these applications.

The clays serve as low-cost, inert carriers in fertilizers, insecticides, herbicides, and fungicides. Clays are similar to talc in that they dilute chemicals to prevent damage from concentrated dosages and act as anticaking agents for dry compounds. Fuller's earth is the most commonly used clay for agricultural applications.

Clays are used in chemical manufacture. In these applications, clays serve as a valuable source of aluminum for the production of aluminum sulfate, aluminum phosphate, and aluminum trichloride and the production of fiberglass. They are also used as a source of aluminum and silicon to synthesize zeolites used in petroleum production. Kaolin is the most commonly used clay in chemical manufacture.

Clays are used in cosmetics, pharmaceutical products, and medicinal tablets. In cosmetics, they improve the hiding power of a product, act as stabilizing agents in lotions and creams, adjust a lotion's viscosity, and suspend pigments. Clays act as carriers in pharmaceutical products and medicinal tablets and can be used to relieve intestinal disorders. Bentonite is the most commonly used clay in these applications.

Used in paints, clays do not react with paint components, reduce settling and separation, increase viscosity, opacity, and hiding power, and act as inexpensive extenders for more expensive white pigments. They also reinforce the dry paint film. Kaolin is the most commonly used clay in paint.

Clays are used as fillers and reinforcers in plastics. As bulk fillers, clays reduce the amount of expensive resin required. Clays also improve the plastic's impact and tensile strength, dimensional stability, and creep resistance. Clays are inert and will not react with the plastic compounds. Clays also may be used as antiblocking agents on plastic films. Kaolin is the most commonly used clay in plastics.

Clays are used by the rubber industry to reinforce and stiffen compounds and as low-cost fillers to reduce the amount of expensive resins used to produce rubber products. Clays also increase the abrasion resistance and tensile strength of some rubber products. Kaolin is the most commonly used clay in rubber.

Clays are used in the filtering and clarification of oils and fats to absorb impurities such as fatty acids, gums, and trace metals. Fuller's earth is the most commonly used clay for clarifying and filtering. Clays also are used in adhesives to reduce the amount of expensive resin used. The large surfaces of clay particles also makes them good carriers for the resins. Kaolin is the most commonly used clay in adhesives.

Outlook.—Overall consumption of clays by the chemical industry can be expected to remain unchanged in the near future. The use of clays in cosmetic, paint, and plastic applications probably will increase in response to demand. Despite the drop in consumption of clays for filtration and clarification applications in the 1970's, demand should increase slowly over the next few years. Consumption in the remaining markets should fluctuate around current consumption levels.

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Table 1.—Salient clay statistics

(Thousand metric tons and thousand dollars)

	1970	1975	1980	1985	1990
Sold or used by producers:					
Tonnage	49,762	44,495	44,262	40,800	42,904
Value	$267,912	$424,556	$898,947	$1,011,377	$1,619,824
Exports:					
Tonnage	1,883	2,100	2,916	2,522	4,123
Value	$66,116	$120,298	$263,147	$309,871	$584,404
Imports:					
Tonnage	87	34	31	37	30
Value	$1,802	$1,947	$6,688	$5,981	$11,988
Apparent consumption:					
Tonnage	49,762	44,495	44,262	40,800	42,904

Table 2.—Clay consumption by end use

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Adhesives . .	NA	85	73	98	65
Agriculture .	294	306	332	377	289
Chemicals . .	W	NA	NA	46	228
Cosmetics . .	NA	2	3	6	19
Filtering . . .	183	126	120	48	86
Paint	99	110	165	196	266
Plastic	W	41	55	48	61
Rubber	W	256	299	291	207

NA Not available. W Withheld to avoid disclosing individual company proprietary data.

Cobalt

By Kim B. Shedd

Background.—Cobalt is a metallic element with many diverse uses. In its metal form cobalt is used in superalloys for aircraft turbine engines; permanent magnets for electrical devices; high-speed steels for metal cutting and drilling; cemented carbides for cutting tools, metal-working, rock drilling and mining; and corrosion- and wear-resistant alloys. As a chemical, cobalt oxides, inorganic cobalt salts, and complex organic cobalt compounds have a wide range of applications.

World production of refined cobalt during the past 20 years has been between 18,000 and 31,000 metric tons per year. From 1989 to 1991, cobalt refiners produced roughly 24,000 to 25,000 tons of cobalt per year. As shown in table 1, the United States consumes a significant portion of the world cobalt supply but is not currently a cobalt producer. The last U.S. cobalt production from domestic ores was in 1971, and the last production of refined cobalt from imported feed was in 1985. Therefore, U.S. demand for cobalt is met primarily from imports, the exception being cobalt from recycling superalloy scrap and other cobalt-bearing materials and occasional releases of cobalt from the National Defense Stockpile.

Cobalt mine production and refinery production are limited to a few countries. In 1991, Zaire was the world's leading cobalt refiner, followed by Zambia, Russia, Canada, Norway, and Finland. These six countries produced 96% of the world cobalt refinery production, with Zaire and Zambia producing more than one-half of the total. Zairian and Zambian production was from domestic ores. Russia and Canada refined cobalt from both domestic and imported raw materials. All of the cobalt refined in Norway and most of the cobalt refined in Finland was from imported raw materials. Countries producing cobalt-containing ores or intermediate products that were exported to be refined included Australia, Botswana, Canada, Cuba, Morocco, New Caledonia, the Republic of South Africa, Russia, and Zimbabwe.

Cobalt is rarely produced as a primary product from a mining operation. Most of the Western world's cobalt supply is a byproduct of copper production in Zaire and Zambia. Cobalt production in most other countries is a byproduct of nickel production, with the exceptions of Morocco, where small amounts of cobalt are produced as a primary product, and the Republic of South Africa, where cobalt is produced as a byproduct of platinum mining and refining.

Cobalt chemicals, along with cobalt metal powders, are called "cobalt special products" by the industry. Cobalt special products can be made by either refiners or processors. Refiners and processors differ in the raw materials they use and the products they make, although some overlap exists. Refiners produce cobalt primarily from materials originating from mining or refining operations—ores, concentrates, mattes, or residues—although a few refiners supplement their feedstock with cobalt-bearing scrap. Processors begin with refined cobalt metal or scrap as feed materials. In terms of products, both refiners and processors can make cobalt metal powders, oxides, and salts (acetate, carbonate, chloride, hydroxide, nitrate, and sulfates); however, other metal forms such as cathodes and granules are made only by refiners, and organic cobalt compounds like cobalt carboxylates are made only by processors.

The products made at cobalt refineries depend on the feed materials used and the processes by which they are refined. Some refineries produce only one product, whereas others produce a mix of cobalt metal, oxides, and salts. Most of the cobalt produced by refiners is in the form of cobalt metal or metal powder. Only about 5% of the cobalt produced by refiners is in chemical form. Refineries in the following countries produce cobalt chemicals: Canada (Inco Ltd., oxide), Finland (Outokumpu Oy, oxide and various salts), France (Eramet-SLN, chloride), Japan (Sumitomo Metal Mining Co., oxide and various salts), and South Africa (Rustenberg Base Metal Refiners Pty. Ltd., sulfate).

An estimated 35% of the cobalt metal produced by refiners is sent to cobalt processors who then convert it to cobalt special products. The world's largest cobalt processor is Union Minière S.A. in Belgium, having a capacity to produce 8,700 tons per year of cobalt metal powders, oxides, and salts. Other cobalt processors are located in the United States, Europe, and Asia.

Chemical Industry Consumption.—The oldest uses of cobalt were as chemical compounds rather than metal. Cobalt blue pigments were used by Persian glassmakers more than 4,000 years ago and in ancient Egyptian glazes more than 3,000 years ago. Cobalt chemicals are now used in a wide variety of applications. In the United States, the top four chemical uses of cobalt are as catalysts; drying agents for paints, varnishes, and inks; ground coats for porcelain enamels; and inorganic pigments. Other chemical uses include feed additives to prevent anemia in animals; electroplating, aluminum anodizing, and other metal treatments; magnetic recording media (audio and video tapes and computer disks); therapeutic agents (as vitamin B_{12} for the treatment of pernicious anemias in humans and in other forms as an antidote for cyanide poisoning); sympathetic inks; electronic devices; additives to nickel battery electrodes; moisture indicators; and feedstock for producing other cobalt chemicals and cobalt metal powders.

Cobalt catalysts are used in several processes in the petroleum and chemical industries, but three main uses predominate. The largest use is in hydrotreating and desulfurization of oil and gas. As produced, these catalysts are composed of cobalt oxide and molybdenum trioxide on an alumina support. Before use the catalysts are activated by converting the oxides to sulfides. The second largest use of cobalt catalysts is for the manufacture of terephthalic acid (TPA) and dimethyl terephthalate (DMT). TPA is an intermediate material used in the production of polyester textile fibers and polyethylene terephthalate films and bottles. Cobalt acetates and/or cobalt bromides are used with manganese as cocatalysts in these reactions. The third largest use of cobalt catalysts is in the OXO (hydroformylation) and hydroesterification reactions. In these reactions cobalt can be introduced as freshly reduced metal, oxide, hydroxide, carboxylate, or carbonyl, but the active species in the reaction is a carbonyl. The products of these reactions are alcohols and aldehydes that are used in the production of detergents and plastics. Other processes use cobalt catalysts, but those applications use less cobalt than the three uses described above.

The drying of paints, varnishes, and inks is accelerated by cobalt salts of carboxylic acids, also known as "cobalt soaps." Cobalt ethylhexanoate, linoleate, naphthenate, octoate, oleate, resinate, and stearate are examples of cobalt carboxylates used as driers. Cobalt carboxylates are the most effective surface driers. Other metals often are added to slow down and control the rate of the drying reaction. Another important use of cobalt carboxylates is as rubber additives. Cobalt abietate, naphthenate, neodecanoate, and stearate have been used to promote the adhesion of rubber to the brass-coated steel in steel-belted radial tires. More recently, cobalt boroacylate complexes have been developed for use in radial tires. Cobalt carboxylates are also used as catalysts in the production of polyesters and adhesives.

Cobalt oxide, often with nickel oxide and manganese dioxide, is used to improve the adherence of porcelain enamel to sheet steel. The cobalt oxide is used in the ground coat enamel. Examples of porcelain enamel products include cookware, appliances, and bath tubs.

Inorganic cobalt pigments are used in porcelain enamels, ceramics, glass, paints, artists colors, polyester fibers, and solid plastics such as vinyl siding. These pigments are prepared by mixing oxides or decomposable salts of cobalt and other metals, calcining the mixtures, then regrinding them to a fine powder. Depending on the other metals present, cobalt pigments for glass and ceramics can be various blues, blue-greens, and blacks. Cobalt pigments for paints are in a wider range of colors-purples, blues, blue-greens, green, pink, brown, and yellow. Specific examples of cobalt-containing pigments include cobalt aluminate ("cobalt blue"), cobalt chrome aluminate blue, cobalt chromite green, and cobalt titanite green. Inorganic pigments such as these are important for their heat resistance, chemical stability, lightfastness, and weather resistance. A special use of cobalt pigments is in camouflage paints. Cobalt chromite green meets military requirements including specific spectral characteristics in the near-infrared range.

Cobalt oxide is also used in glass and ceramics as a decolorizer. Only small amounts are needed to neutralize the yellowish tint resulting from traces of iron present in the raw materials used to make glass and ceramics.

Outlook.—U.S. cobalt use in chemical applications as reported to the Bureau of Mines is presented in table 2. Following a low point in 1982, total U.S. cobalt consumption in chemical applications has increased fairly steadily. Reported cobalt consumption in animal feeds and decolorizers remained fairly constant during this period. Cobalt consumption has been more variable in pigments, enamel ground coats, catalysts, and paint driers but has generally trended upward in each of these uses. Future use of cobalt in ceramics and enamels is subject to fashion trends as well as general economic conditions. Cobalt use in catalysts is expected to continue growing. Demand for cobalt-molybdenum desulfurization catalysts is expected to increase with the passage of environmental regulations reducing allowable sulfur levels in fuels. Demand for cobalt catalysts used in the production of TPA is expected to grow with growing demand for polyethylene terephthalate food and drink packaging materials. Two additional cobalt applications where growth in demand is expected are rubber adhesives and magnetic recording media.

Cobalt availability and high price are concerns during periods of actual or perceived shortages. During these times, consideration is given to cobalt substitutes or reducing cobalt levels. In many chemical applications, cobalt is used regardless of price because cobalt substitution would cause a decrease in the final product's quality or performance and/or because the small quantities of cobalt in the final product do not contribute significantly to the product's total cost. In the long term, concerns over availability can impact materials choices in the development of new products.

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Table 1.—Salient U.S. cobalt statistics

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Mine production	316	—	—	—	—
Secondary[1]	31	155	537	407	[2]1,225
Industry stocks, Jan. 1	2,326	4,294	3,473	5,107	4,550
Imports	5,632	2,997	7,394	8,032	6,529
Shipments from National Defense Stockpile[3]	2,341	2,878	—	-721	-108
Total U.S. supply[4]	10,647	10,325	11,404	12,825	12,196
Distribution of U.S. supply:					
Industry stocks, Dec. 31	2,600	3,147	3,404	5,422	3,220
Exports	670	802	264	284	1,340
Demand[4] [5]	7,376	6,376	7,735	7,118	7,635
Demand by the chemical industry[6]	1,532	2,018	[2]1,754	1,564	W

W Withheld to avoid disclosing company proprietary data.

[1] Consumption from recycled scrap.

[2] Data not comparable with those of previous years because of a change in reporting.

[3] Negative numbers denote imports for the National Defense Stockpile.

[4] Data may not add to totals shown because of independent rounding.

[5] Production + cobalt from scrap + imports - exports + adjustments for Government and industry stock changes.

[6] Reported consumption for chemical end uses regardless of form.

Table 2.—Cobalt consumption by the U.S. chemical industry

(Metric tons)

End use	1970	1975	1980	1985	1990
Catalysts	182	504	[1]751	497	W
Drier in paints or related usage	(2)	(2)	[1]604	517	[1]751
Feed or nutritive additive	(2)	(2)	[1]34	21	W
Glass decolorizer	31	19	[1]18	19	W
Ground coat frit	59	38	[1]219	328	W
Pigments	70	59	[1]128	182	W
Miscellaneous chemical and ceramic uses[3]	1,190	1,398	—	—	—
Total U.S. chemical demand[4]	1,532	2,018	[1]1,754	1,564	W
Total U.S. demand[5]	7,376	6,376	7,735	7,118	7,635

W Withheld to avoid disclosing company proprietary data.

[1] Data not comparable with those of previous years because of a change in reporting.

[2] Included in "Miscellaneous chemical and ceramic uses."

[3] Driers in paint and related products, pigments, enamel ground coats, feed, electroplating, etc.

[4] Reported consumption for chemical end uses regardless of form.

[5] Production + cobalt from scrap + imports - exports + adjustments for Government and industry stock changes.

Copper

By Daniel L. Edelstein

Background.—The copper chemical market constitutes only a small percentage of the total domestic demand for copper. Most copper is consumed as copper metal or copper alloy metal. In 1990, copper chemicals accounted for less than 1% of the total demand for copper in the United States. Of the many known copper compounds, only a few were used on a large scale. Copper sulfate, from a tonnage aspect, was the most important and was a feedstock for producing many other copper chemicals. In 1990, five domestic companies reported production of copper sulfate. Although most copper sulfate is produced from secondary copper, either scrap or spent electroplating solutions, at least one producer recovered copper sulfate as part of its electrolyte regeneration circuits at its primary copper refinery, and a second used copper precipitates as its feed stock. Copper sulfate has also been produced from blister copper. This production represents a historical change; prior to 1970 most copper sulfate was produced at primary refineries. In 1990, domestic apparent demand for copper sulfate was about 48,000 mt, of which imports accounted for about 25%.

Chemical Industry Consumption.—Anhydrous copper sulfate ($CuSO_4$) is a white crystalline substance, but the usual commercial form is the blue crystalline pentahydrate ($CuSO_4{\cdot}5H_2O$), which contains about 25% copper. It is marketed in various crystalline sizes ranging from plus 3/4 inch to as fine as 250 mesh, depending on application. As much as 25% of domestically produced copper sulfate is sold as basic copper sulfate powder ($CuSO_4{\cdot}3Cu(OH)_2{\cdot}H_2O$) containing 53% copper.

Copper sulfate is used in agriculture as an algicide and fungicide and as a source of copper for plant and animal feed. Basic copper sulfate is used principally as a fungicide. Its principal remaining area of use is in the citrus industry, organic fungicides having largely replaced its use in other areas during the 1960's; however, greater concern for the environment has resulted in a return to increased use of copper. Copper hydroxide fungicides, first developed in the 1970's, have become favored for most fungicide applications. Copper carbonates are also used as fungicides. In recent years agricultural uses, including fungicides and animal feed, accounted for the growth in demand.

In industrial applications, copper sulfate is used in a variety of ways: for activation of zinc and other sulfide minerals in froth flotation; as a print toner in photography; as a stabilizer and blue and green pigment in dyes; in copper plating baths used for electronics, metal finishing and pickling; and numerous other chemical, pigment, and fungicidal applications. The estimated end-use distribution of shipments from domestic producers in 1990, which accounted for about 75% of demand, was 65% for agricultural uses, 28% for industrial uses, and 7% for water treatment. Large crystal copper sulfate has special application in water treatment where it is used as an algicide and water purifier in municipal water supplies and other applications.

Other copper chemicals of commercial significance include copper carbonate, once used widely for production of wood preservatives and now used primarily as a chemical intermediate, copper hydroxide, and copper oxide. Copper oxide has replaced carbonate and sulfate in wood preservatives, and zinc carbonate has replaced copper carbonate in drilling muds. Copper sulfate and, in some instances, copper chloride are used as starting materials to make hydroxide.

Following a decline in production and demand in the early 1970's, domestic production and consumption of copper sulfate remained relatively stable until the mid-1980's. While domestic production continued at the same level, beginning in 1987, demand for agricultural uses spurred a large increase in apparent demand. Thus, the market became increasingly import dependent, as shown by the quadrupling of U.S. imports of sulfate since 1985. Major import sources include Canada, Mexico, Peru, the countries of the former U.S.S.R., and Yugoslavia. Few data are available on world production and consumption of copper sulfate. Japan, one of the few countries to report production of copper sulfate, has more than doubled its production since the early 1950's to about 12,000 tons, but consumes most of it domestically. At the same time, the United Kingdom has reduced its production of copper sulfate from about 56,000 tons in 1950 (almost all was exported) to less than 10,000 tons (2,500 tons exported) in 1987. Trade data indicate that Western Europe comprises the largest import market for copper sulfate. The Federal Republic of Germany was one of the largest importers, importing an average of 10,000 tons per year between 1982 and 1987.

Outlook.—Domestic demand for copper sulfate has risen steadily since 1987 owing to a resurgence in demand for copper chemicals in agricultural usage. Demand is expected to remain stable or continue to grow in this area owing to environmental concern about the use of organic chemicals and to increasing usage in the feed industry. Imports are expected to decline, as at least one producer of copper sulfate greatly increased its capacity and shipments to the domestic market during the second half of 1990.

Table 1.—Salient copper sulfate statistics

(Metric tons, gross weight)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production	41,143	32,309	31,010	32,740	35,294
Industry stocks, Jan. 1	3,854	3,789	8,861	3,564	3,485
Imports	NA	325	974	2,958	12,254
Total U.S. supply	44,997	36,423	40,845	39,262	51,033
Distribution of U.S. supply:					
Industry stocks, Dec. 31	7,994	6,228	5,736	4,353	2,367
Exports	2,254	1,132	NA	NA	559
Apparent demand	34,749	29,063	35,109	34,909	48,107

NA Not available.

Table 2.—Distribution of copper sulfate shipments by producers

(Metric tons, gross weight)

	1970	1975	1980	1985	1990
Agricultural	13,100	14,700	14,100	14,700	23,700
Industrial	21,300	13,700	19,100	13,400	10,200
Water treatment[1]	NA	NA	NA	3,800	2,500
Other[2]	2,200	500	900	NA	NA
Total shipments	36,600	28,900	34,100	31,900	36,400

NA Not available.

[1] Water treatment not listed separately prior to 1985.

[2] Most of "Other" was believed to be exports.

Diatomite

By Lawrence L. Davis

Background.—Diatomite, or diatomaceous earth, is a siliceous, sedimentary rock consisting principally of the fossilized skeletal remains of diatoms, unicellular aquatic plants related to algae. Processed diatomite possesses characteristics such as unique particulate structure, chemical stability, low bulk density, high absorptive capacity, high surface area, and low abrasion that enable the material to be commercially applicable as a filter aid, functional filler, absorbent, anticaking agent, thermal insulator, catalyst carrier, polish and abrasive agent, and as an additive for numerous other uses.

Processing of diatomite involves a series of basic crushing and drying steps developed and refined over the years to preserve the diatom skeletal structure. The principal products produced are aggregates and powders of various sizes of uncalcined, straight-calcined, or flux-calcined grades.

The United States is the world's largest producer and consumer of diatomite. Production in 1990 was 631,000 metric tons valued at $138 million, from 7 companies with 11 processing facilities in 5 States-Arizona, California, Nevada, Washington and Oregon. The major producers are Celite Corp., a subsidiary of Alleghany Corp., having operations in Lompoc, CA, and Grant County, WA; Grefco Inc., having operations in Lompox and Burney, CA, and Mina, NV; and Eagle-Picher Minerals Inc., having operaitons in Nevada and Oregon.

The principal domestic and world markets for diatomite are in filtration and filler uses. About one-fourth of U.S. sales of diatomite in 1991 were exports, and of that, 85% to 90% was for filtration. About 50% of the quantity annually exported in recent years has gone to Australia, Canada, the Federal Republic of Germany, Japan, and the United Kingdom.

Owing to the commodity's high silica content (up to 94%), inertness to most chemical reactions, and high surface area, diatomite is a particularly suitable and reactive form of silica in combination with lime for the hydrothermal manufacture of lime-silicate insulations as well as highly absorptive calcium-silicate powders.

Chemical Industry Consumption.—The major use of diatomite in the chemical industry is as a filler, and the major filler use is in paint. Diatomite has a lower refractive index making it an ideal flatting agent. Diatomite also improves paint touch-up characteristics, burnish resistance, and ease of wetting.

Diatomite fillers are also used in plastics, agricultural chemicals, adhesives and sealants, and numerous other products, and as catalyst carriers in many industrial processes.

Outlook.—Diatomite consumption in the United States has increased gradually over the 1970 to 1990 period. Most of the growth, however, is in the filtration applications, most of which are not associated with the chemical industry. Chemical uses of diatomite nearly doubled from 1970 to 1980 but have decreased almost 25% between 1980 and 1990. Near future use of diatomite in the chemical industry is expected to remain steady or show very modest growth. Because a number of alternative minerals can be substituted for diatomite (calcined clay, talc, sand, limestone, mica, etc.), major increases in use ahead are unlikely.

Table 1.—Salient diatomite statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production[1]	542	520	625	576	631
Industry stocks Jan. 1[e]	34	33	33	33	33
Imports	—	4	([2])	5	1
Total U.S. supply	576	557	658	614	668
Distribution of U.S. supply:					
Industry stocks, Dec. 31[e]	34	33	33	33	36
Exports	140	133	157	109	144
Demand	402	391	468	472	488

[e] Estimated.

[1] Processed ore sold or used by producers.

[2] Less than ½ unit.

Table 2.—Diatomite consumption in the U.S. chemical industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Fillers	76	93	150	125	88
Filtration	24	21	29	28	45
Other	4	5	2	4	5
Total chemical demand	104	118	181	157	138
Total U.S. primary demand	402	391	468	422	488

Fluorspar

By M. Michael Miller

Background.—Technically, pure fluorspar, or the mineral fluorite, contains 51.1% calcium and 48.9% fluorine. Natural fluorite is commonly associated with other minerals such as quartz, barite, calcite, galena, siderite, celestite, sphalerite, chalcopyrite, other sulfides, and phosphates. It occurs in well-formed isometric crystals, in massive and earthy forms, and as crusts or globular aggregates with radial fibrous texture. In crystalline form, it can be colorless or may exhibit a wide range of colors. It has a hardness of 4 on the Mohs' scale, a specific gravity of 3.18, and a melting point of 1,378° C.

Three principal grades of fluorspar are available commercially: acid, ceramic, and metallurgical. Almost all chemical consumption of fluorspar consists of acid-grade fluorspar (or acidspar). Acidspar is produced by multistage froth flotation, where impurities are floated off or depressed by the addition of collectors or depressants to the ground fluorspar. In the United States, acidspar contains greater than 97% CaF_2. Some manufacturers of hydrofluoric acid in the United States and Europe can use 96% CaF_2 or a slightly lower grade if the remaining impurities are acceptable. User specifications may impose limits on silica, calcium carbonate, sulfide or free sulfur, calcite, beryllium, arsenic, lead, phosphates, and other constituents. Moisture content of the dried material is preferably 0.1% or less. Particle size and distribution are sometimes specified for proper control of the rate of chemical reaction and stack losses.

All U.S. production of acidspar comes from one producer in Illinois, Ozark-Mahoning Co., a subsidiary of Elf Atochem North America, which operates three mines and a flotation plant in Pope and Hardin Counties, IL.

The United States has been import reliant since World War II. Since the mid-1970's, imports have accounted for over 90% of consumption. In the last 20 years, the major import sources have been Mexico, the Republic of South Africa, Spain, Italy, and China. In the past decade, most imports have come from Mexico, the Republic of South Africa, and China, which has assumed an increasingly prominent position in the fluorspar trade. Total fluorspar consumption hit its peak in 1973 at about 1.368 million metric tons. Consumption has been decreasing in recent years as a result of the mandated phaseout of chlorofluorocarbon compounds. Consumption in 1990 was only 587,000 tons.

Chemical Industry Consumption.—The major use for acid-grade fluorspar is for the production of hydrofluoric acid (HF), or hydrogen fluoride. This is accomplished by reacting about 2.4 tons of finely ground acidspar with 2.7 tons of concentrated (96%-98%) sulfuric acid in a heated, rotating steel kiln to produce 1 ton of HF. In a commercial HF plant, the rate and yield is influenced by the purity and size of the fluorspar, the concentration of the sulfuric acid, the ratio of sulfuric acid to fluorspar (generally 5% to 10% excess sulfuric acid), the reaction mixture temperature, and the mixing of the reactants. The reaction is as follows:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

The anhydrous HF is collected as a gas and cleaned of solids and sulfuric acid mist before being condensed. The condensate is 99% HF material, which can be redistilled to greater than 99.9% purity.

HF is the key feedstock for the production of fluorine chemicals. In recent years over 60% of this production has been fluorocarbons, and the largest part of the fluorocarbon market has been for chlorofluorocarbons (CFC's) and hydrochlorofluorocarbons (HCFC's). These products are produced by the catalytic reaction of HF with chlorinated hydrocarbon compounds such as carbon tetrachloride, chloroform, and perchloroethylene. An international mandated phaseout of CFC's has required the development of additional HCFC's and a new class of fluorocarbons called hydrofluorocarbons (HFC's).

Fluorocarbon compounds are used widely as refrigerants, plastic foam blowing agents, solvents, cleansers for electronic components, and as feedstock for the production of fluoroplastics. Brominated chlorofluorocarbons are used as very efficient fireextinguishing agents.

Additional uses for HF are in the manufacture of inorganic fluorides, fluoroborates, and other fluorinated chemicals. It is used to produce aluminum fluoride and synthetic cryolite for use in the electrolytic production of aluminum. Other important uses are as a catalyst in producing high-octane alkylates to boost octane ratings in gasoline, in uranium processing to make uranium tetrafluoride and elemental fluorine necessary for further uranium processing, for etching and polishing glass, and for processing stainless steel.

Acid-grade fluorspar is consumed directly by the Aluminum Co. of America for the production of aluminum fluoride. In this process, HF is produced via the method discussed above but is then immediately transferred under vacuum to a fluid converter where it is reacted with activated alumina hydrate to produce aluminum fluoride. A fluid converter is a multibedded reactor where countercurrent streams of gas and solids mix in such a way that the resulting mixture acts like a fluid. The reaction is shown as follows:

$$6HF + Al_2O_3{\cdot}xH_2O \rightarrow 2AlF_3 + (x+3)H_2O$$

Other chemical uses of fluorspar involve the consumption of small amounts of ceramic-grade fluorspar for the manufacture of enamels and welding rod fluxes.

Consumption of fluorspar by the chemical industry has decreased substantially in the last 20 years. Most of the large decrease can be traced to lost CFC markets. In the late 1970's, the use of CFC's in aerosols was banned in the United States. In 1987, the United States and 22 other nations signed the Montreal Protocol on Substances That Deplete the Ozone Layer. The protocol, under the auspices of the United Nations Environmental Program, mandated a freeze on CFC production at the 1986 level by July 1989, followed by a 20% reduction by mid-1993, and an additional 30% reduction by mid-1998. New scientific data led to an accelerated Montreal Protocol phaseout schedule and the inclusion of a similar schedule in the stratospheric ozone protection section of the U.S. Clean Air Act Amendments of 1990 (CAAA). The CAAA also allowed for the further acceleration of the phaseout schedule if new scientific evidence warrants it, the availability of substitute compounds makes it practical, or the Montreal Protocol is modified to include a phaseout schedule more accelerated than the one under the law. As of the end of 1992, the phaseout schedule had been modified to bring forward the complete phaseout of CFC's to January 1, 1996.

Outlook.—The fluorocarbon industry has developed replacement HCFC and HFC compounds to replace the CFC's. These replacements are in varying stages of commercial readiness. Some compounds are already available in commercial quantities; others are in the pilot-plant stage or development and testing stage. Despite the availability of some replacement HCFC and HFC compounds, sales of the replacements have lagged. CFC production has dropped by over 50% since 1986, but this reduction has been due in large part to conservation, recycling, and not-in-kind replacements by consumers. Consuming industries have been slower than expected to develop and introduce design improvements that allow the use of the replacement compounds. At the end of 1991, production capacities for the replacement compounds were underutilized.

Many of the replacement compounds actually contain more fluorine than the CFC compounds. By the mid-1990's, it is expected that consuming industries such as the automobile and refrigeration industries will have introduced design improvements, and the demand for HF and fluorspar will increase accordingly. The only cloud on this horizon is the probability that the HCFC compounds will face an accelerated phaseout themselves due to the continued deterioration of stratospheric ozone.

Table 1.—Salient fluorspar statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production, mine (shipments)	244	127	84	60	64
Industry stocks, Jan. 1	239	391	205	109	79
Imports	991	953	816	502	514
Total U.S. supply	1,471	1,471	1,105	671	657
Distribution of U.S. supply:					
Industry stocks, Dec. 31	381	290	166	42	55
Exports	14	1	16	9	15
Demand	1,079	1,180	923	620	587

Table 2.—Fluorspar consumption by the U.S. chemical industry

(Thousand metric tons)

	1970	1975	1980	1985	1990
Hydrofluoric acid	681	611	533	371	324
Total chemical demand	681	611	533	371	324
Total U.S. demand	1,079	1,180	923	620	587

Gypsum

By Lawrence L. Davis

Background.—Gypsum, the most common of the naturally occurring sulfate minerals, is found in very extensive bedded sedimentary deposits all over the world and is associated with limestones, shales and sandstones, marls, and clays. High-purity deposits of gypsum are relatively common, and for most uses, little or no beneficiation is required.

Gypsum rock, crushed and screened to specifications, is marketed directly to cement plants to be used to retard the setting time of concrete. Finely ground gypsum rock is used in agriculture as a soil conditioner. Small amounts of very pure gypsum are used as fillers and in glassmaking, papermaking, and pharmaceutical applications.

In the United States, most gypsum rock is finely ground and partially calcined to drive off 75% of the chemically combined water, converting gypsum, $CaSO_4{\cdot}2H_2O$, to the hemihydrate product, $CaSO_4{\cdot}\frac{1}{2}H_2O$. Commonly called plaster of paris, this material quickly sets and hardens back to gypsum when mixed with the appropriate amount of water. The hemihydrate is used to make a variety of building and industrial plasters and to make gypsum wallboard products.

In 1990, the United States consumed about 27 million short tons of gypsum, of which about 64% was produced domestically and 36% was imported. About 21 million tons were calcined and consumed as plaster or wallboard, and 6 million tons were consumed in uncalcined form as a cement setting retarder or as a soil conditioner. Twenty-nine companies mined crude gypsum at 58 mines in 20 States. Leading States were, in decreasing order of production, Iowa, Oklahoma, Michigan, Texas, Nevada, California, and Indiana. These seven States accounted for about 76% of U.S. production. Thirteen companies calcined gypsum at 71 plants in 28 States.

This large domestic gypsum industry is dominated by a few large vertically integrated companies that mine and calcine gypsum and manufacture plaster and wallboard products. These companies also sell crude gypsum for use in cement and agriculture. The large domestic wallboard producers, through foreign subsidiaries, produced most of the crude gypsum that is imported to feed coastal wallboard plants. Plants on the east coast import mostly from Canada's Maritime Provinces, whereas plants on the west coast import gypsum from Mexico. Crude gypsum from Spain, the other major source of U.S. imports, is used mainly by cement plants.

Chemical Industry Consumption.—A relatively small percentage (5% to 10%) of the gypsum produced in the United States is used by the chemical industry. The major chemical industry use in agriculture is as a soil conditioner. Gypsum rock, finely ground, is called "land plaster." It is used in agriculture to neutralize alkaline and saline soils, improve the permeability of argillaceous materials, and provide sulfur and catalytic support for maximum fertilizer utilization and leguminous productivity.

Gypsum granules are used as a carrying medium for nutrients, pesticides, and herbicides. Finely ground, high-purity gypsum is also used as a filler or extender in plastic, paper, pills, pigments, and food products.

Outlook.—Consumption by the chemical industry has been relatively constant over the period from 1970 to 1990. No major issues affect the use of gypsum by the chemical industry, and the outlook is for continued use at about the same levels in the near future.

Table 1.—Salient gypsum statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production	8,560	8,846	11,227	13,359	14,883
Industry stocks, Jan. 1	3,344	3,629	3,538	2,473	3,472
Imports	5,559	4,942	6,681	9,001	7,916
Byproduct gypsum	NA	335	601	707	667
Total U.S. supply	17,463	17,752	22,048	25,540	26,938
Distribution of U.S. supply:					
Industry stocks, Dec. 31	3,783	1,814	2,906	2,756	1,796
Exports	37	68	80	75	117
Demand	12,892	14,141	17,685	22,393	23,307
Apparent surplus (+) or deficit (-) of supply	+751	+1,728	+1,378	+316	+1,718

NA Not available.

Table 2.—Gypsum consumption in the U.S. chemical industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Agriculture	729	1,349	1,504	1,070	1,500
Fillers and miscellaneous	87	161	122	120	173
Total chemical demand	816	1,510	1,627	1,190	1,674
Total U.S. primary demand	12,892	14,141	17,685	22,393	23,307

Iodine

By Phyllis A. Lyday

Background.—Three companies produce crude iodine from brines in Oklahoma, IoChem Corp., Dewey County, OK, being the largest. A major portion of production is shipped to Schering AG, Federal Republic of Germany, under a long-term contract. IoChem was reported to have nine production wells and four injection wells having a total production capacity of 1,200 kilograms. North American Brine Resources has operated a miniplant at Dover in Kingfisher County, OK, at an oilfield reinjection disposal site where iodine concentrations range up to 1,200 parts per million. The company has also operated a plant at the border of Woodward and Harper Counties. Woodward Iodine Corp., a subsidiary of Asahi Glass Co. of Japan, has operated a plant in Woodward County.

Because some export and import data are not separately identified, net import data are not easily compiled. Although the United States has increased iodine production significantly during the last 5 years, Japan supplies approximately 40% and Chile about 20% of domestic consumption. Iodine is used primarily in animal feed supplements, catalysts, inks and colorants, pharmaceuticals, photographic equipment, sanitary and industrial disinfectants, stabilizers, and radiopaque medium. Other smaller uses include production of batteries, high-purity metals, motor fuels, iodized salt, and lubricants.

Japan is the major producer of iodine in the world. Japanese brines contain 50 to 135 ppm of iodine in the Kiwada, Otadai, and Umegase Formations of the Kazusa Group of Pliocene age. The major iodine-producing area was the southern Kanto Gasfield, which extends over Chiba, Tokyo, and Kanagawa Prefectures. Iodine was produced in the Niigata and Nakojo Gasfields in Niigata Prefecture, on the Sea of Japan side of central Japan, and the Sadowara Gasfield in Miyazaki Prefecture, southern Kyushu.

Chile is the second largest producer of iodine in the world. Extensive iodine-bearing nitrate ores occur in caliche deposits in a belt several hundred kilometers long in the Atacama Desert of northern Chile. The ore layers are 1 to 3 meters thick, usually flat or gently dipping and near the surface. Evaporate minerals such as lautarite (CaI_2O_6) and dietzeite ($2CaO \cdot I_2O_5 \cdot CrO_3$) occur as cementing material in unconsolidated surface material or as veins and impregnations in bedrock. Iodine is recovered by leaching the ore.

The United States and the former U.S.S.R. are considered to be approximately equal in the production of iodine. Other producers are China and Indonesia.

Chemical Industry Consumption.—Commercial crude iodine normally has a minimum purity of 99.5%. Resublimed iodine is greater than 99.9% pure. Most iodine is converted for industrial use to potassium iodide, sodium iodide, and other inorganic compounds, as well as numerous organic compounds.

In Japan and the United States, iodine is removed from brines by two processes that separate the brines from any associated hydrocarbons. In the blowing-out process, brine is acidified and iodine is liberated by reducing the pH to about 3. A countercurrent stream of air transports the liberated iodine to a second tower in which the iodine is absorbed by a solution of hydriodic acid. The iodine settles, is filtered, and melted under concentrated acid. Brine stripped of iodine is treated and then reinjected into the subsurface formation of its origin.

In the absorption process, brine is passed through an absorber, and the waste brine is neutralized and sent to a disposal well. The absorbent, laden with iodine, is treated with an alkaline solution to regenerate the absorbent and elute iodine as sodium iodide. Iodine is precipitated under acid.

Iodine and silver are recycled from photographic processing solutions such as developer, fixer, bleach fixers, and washwaters. Photographic silver is commonly recovered by electrolytic methods if its concentration is greater than 500 ppm. Absorbents such as natural and synthetic zeolites, activated alumina, activated silica, Fuller's earth, and ion exchange resins are used to recover low concentrations of silver from a stream, thus leaving a high iodine solution that can be recycled. In addition, some catalytic uses of iodine leave a solution that can be recycled to produce crude iodine.

The reinjection of waste brine is a limiting factor to the production of iodine. During 1982, the EPA reclassified disposal wells for spent brine after halogen extraction as class 5 wells, thus separating the reinjection wells from toxic waste reinjection wells. All of the reinjection wells for iodine in Oklahoma were drilled for the reinjection of waste associated with brine production or oil and gas effluent.

Outlook.—The outlook for the demand for iodine in catalysts, pharmaceuticals, stabilizers, and sanitary uses is expected to remain at present levels through 1996.

Table 1.—Salient iodine statistics

(Thousand kilograms)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production	272	272	1,134	1,293	1,973
Industry stocks, Jan. 1[e]	441	1,082	NA	NA	NA
Imports	2,741	2,408	2,812	2,464	3,161
Net Government purchases (-) or sales (+)	—	—	—	—	5
Total U.S. supply	3,454	3,762	3,946	3,757	5,139
Distribution of U.S. supply:					
Industry stocks, Dec. 31[e]	538	904	NA	NA	NA
Exports	115	46	NA	NA	2,100
Demand	2,860	2,811	3,947	3,530	3,100
Apparent surplus (+) or deficit (-) of supply	-59	+1	-1	+227	-61

[e]Estimated. NA Not available.

Table 2.—Iodine consumption by the U.S. chemical industry

(Thousand kilograms)

End use	1970	1975	1980	1985	1990
Catalysts	454	544	862	815	NA
Pharmaceuticals	454	408	862	360	NA
Stabilizers	408	408	499	680	NA
Sanitary uses	272	272	91	545	NA
Total chemicals demand	1,588	1,632	2,314	2,400	NA
Total other demand	1,270	1,179	1,633	1,130	NA
Total U.S. primary demand	2,860	2,811	3,947	3,530	3,100

NA Not available.

Lead

By William D. Woodbury

Background.—About 80% of domestic and over 60% of world consumption of lead is for storage batteries. In the United States in 1989 and 1990, this usage amounted to over 1 million metric tons per year, all but 175,000 to 185,000 tons per year in starting-lighting-ignition (SLI) functions. SLI applications include those for buses, trucks, cars, marinecraft, aircraft, motorcycles, golf carts, and general utility (compressors, generators, drill rigs, etc). The combined industrial (stationary) and traction (motive) battery sectors consumed 170,000 to 175,000 tons per year in 1989 and 1990, and the emerging consumer battery sector (toys, lawnmowers, flashlights, power tools, etc.) consumed an estimated 5,000 to 10,000 tons per year and growing. The latter are totally sealed, unvented, "gel-cells," competing with many nickel-cadmium battery uses. The industrial battery sector consists first of uninterrupted power supply systems (UPS), that are continuously on-line for voltage regulation between external power and mainline or mini-networked computers in banks, hospitals, business, etc. In addition are standby power systems (SPBS) that are off-line in reserve for emergency power loss only, primarily in communication networks. Traction batteries are motive power for electric vehicles, including forklifts, mine locomotives, etc. The industrial-traction battery market has doubled since 1983 in terms of lead usage and promises ever greater growth when load leveling, especially "customer-side-of-the-meter," and general purpose electric vehicles become a greater reality over the next 10 to 20 years.

On the production side, during 1990 there were about 50 secondary producers of recycled lead metal, and 2 primary producers of lead metal that were both integrated with mining. There were about 30 lead-producing mines in 1990, but 8 in Missouri and 2 in Alaska accounted for over 90% of the total production. Recycled battery scrap at 23 plants accounted for 85% of secondary production. There are about 200 lead-consuming facilities in the United States. Table 1 portrays the total domestic supply-demand relationship from 1970 to 1990.

Chemical Industry Consumption.—Three distinct categories of lead oxide are the product bases for lead chemicals: lead monoxide (PbO) or litharge, lead dioxide (PbO_2), and trilead tetraoxide (Pb_3O_4), or red lead. A subcategory of litharge known as black or grey oxide (leady litharge) is the most widely utilized—430,000 tons of lead content in 1990, solely in storage batteries, the production of which are not considered to be a part of the chemical industry. Leady litharge is a mixture of lead monoxide and 20% to 35% metallic lead. Common litharge is the most important commercial chemical compound of lead today, from which most other lead chemicals are derived. (Leaded gasoline additives, which are produced from "pure" lead, are no longer domestically made). Litharge's spectrum of chemical, electrical, electronic, and optical properties offers a wide range of industrial applications, albeit restricted in volume today, and in many the physical properties dictate the method of processing for end use.

Lead oxides all can be prepared hydrometallurgically; but with the exception of PbO_2, they are prepared thermally by direct oxidation of lead metal in one of three ways: (1) below the melting point of lead; (2) between the melting point of lead and litharge; or (3) above the melting point of litharge. Leady litharge is produced autogenously in a ball mill by frictional heating and exothermy (method 1). Moderate-temperature oxidation (method 2) employs two types of reverberatory furnaces, conventional with rotating stirrer on a vertical shaft, or inclined rotary. Barton pots, although less common today, are also used in this range because they are more versatile operationally and can produce both leady and common litharge. High-temperature oxidation (method 3) is a fuming process utilizing a blast furnace-injector system. The result is a fine grain, high-purity orthorhombic litharge, highly desirable for further chemical processing to most pigments and salts.

Regulation against the use of lead interior house paint in the early 1970's and a simultaneous proliferation of television sets and subsequently computer video display terminals (VDT's), which utilize leaded glass, have altered drastically the end-use pattern for lead chemicals over the past 20 years (table 2). In the near term lead will probably also be outlawed in all external nonporcelain coatings, including that for construction steel undercoating, salts for pesticides (lead arsenates) or road markings (lead dichromate-chrome yellow), and possibly even in ceramic glazes and crystal glassware. Today, about 75% of the lead in the ceramics and glass category is for "TV glass" for optical purity and clarity. Leaded glazes and vitreous enamels in ceramics have higher indices of refraction, superior electrical characteristics, better melting qualities, greater density, higher chemical stability, and lower thermal conductivity, than unleaded ceramics. Litharge is also used in capacitors, electrophotographic plates, ferrimagnetic-ferroelectric materials such as lead zirconate-lead titanate and lead metaniobate. Because of its chemical properties, litharge is also used as an activator of accelerators in rubber, a curing agent in selected elastomers, a sulfur removal agent in the production of thioles and in oil refining, and as an oxidation catalyst in organic processes. Other lead salts are used as stabilizers for plastics, especially polyvinyl chloride. Leaded porcelain enamels are indispensable for some cast iron and aluminum applications, especially where acid resistance is critical. Such enamels applied to glass are essentially modified lead borosilicates containing 50% PbO. A potentially valuable future use for lead as a chemical, although highly controversial at this time but that could involve considerable tonnage, is as an antioxidant for asphalt in shingles, flat roofs, and highway pavings. Several test sites in Canada and the United States have indicated possible severalfold lifetime extensions in some instances using the lead diamyldithiocarbamate (LDAC) antioxidant additive.

Outlook.—Various forms of legislation and administrative regulations pending at this time indicate that any near-term growth in the total demand for lead chemicals is unlikely; however, the expected continual demand growth of VDT applications makes total usage in the next 5 years unlikely to decline significantly below 50,000 tons per year. Acceptance of LDAC, apparently unlikely in the near term, could create a slight growth market in the longer term, although lead in paints and nonceramic coatings will probably be phased out completely.

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Table 1.—Salient lead statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production:					
Domestic ore	489	483	509	423	386
Foreign ore	126	96	39	71	18
Old scrap	459	512	581	570	874
Imports—metal, excluding scrap	222	90	82	133	97
Industry stocks, Jan. 1, pigs and bars	138	185	199	142	98
Government stockpile releases	11	6	—	—	—
Total U.S. supply	1,445	1,372	1,410	1,339	1,473
Distribution of U.S. supply:					
Industry stocks, Dec. 31, pigs and bars	210	195	181	178	112
Exports—metal, excluding scrap	7	19	164	27	64
Industrial demand	1,228	1,158	1,065	1,134	1,297
U.S. demand pattern:					
Ammunition	66	68	49	50	58
Construction	90	63	37	39	34
Electricals	80	70	70	120	143
Gasoline additives[1]	253	189	128	46	21
Oxides and chemicals[2]	90	72	78	73	57
Transportation	560	625	640	760	950
Other	89	71	63	46	34
Total U.S. demand	1,228	1,158	1,065	1,134	1,297
Total U.S. primary demand (Industrial demand less old scrap)	769	646	484	564	423

[1] Domestic production ceased, mid-1991.

[2] Excludes litharge and black oxides in batteries.

Table 2.—Lead consumption by the U.S. chemical industry

(Thousand metric tons)

Chemical end use	1970	1975	1980	1985	1990
Paints and coatings (excluding varnish)[1]	24	18	21	14	—
Ceramics and glass	[2]22	[2]31	45	44	[3]43
Other pigments and salts	[4]44	[4]23	12	15	14
Total chemical demand	90	72	78	73	57

[1] Excludes basic lead sulfate for proprietary reasons; included with other pigments.

[2] From distribution of litharge shipments.

[3] Categories combined for concealment of proprietary data.

[4] From litharge shipped for use in insecticides, oil refining, rubber, varnish, chromates,and other lead salts. For proprietary concealment also includes red lead in batteries.

Lime

By M. Michael Miller

Background.—Lime is a manufactured chemical product made by calcining (burning) high-purity calcitic or dolomitic limestone at temperatures ranging from 980° C to 1,320° C. The calcination process drives off the carbon dioxide to form calcium oxide (quicklime). The subsequent addition of water creates calcium hydroxide (hydrated lime). The term "lime" refers primarily to five chemicals produced by the calcination process followed by hydration where necessary: (1) quicklime or calcium oxide (CaO); (2) hydrated lime or calcium hydroxide [$Ca(OH)_2$]; (3) dolomitic quicklime ($CaO \cdot MgO$); (4) type N dolomitic hydrate [$Ca(OH)_2 \cdot MgO$]; and (5) type S dolomitic hydrate [$Ca(OH)_2 \cdot Mg(OH)_2$].

Lime burning was one of the earliest chemical industries developed by man. Archaeologists have discovered primitive kilns that may have been used for making lime during the Stone Age. Its earliest use in ancient civilizations was in Egypt, where it has been found in some pyramids constructed over 4,500 years ago. In Egypt, as well as in subsequent civilizations, lime was used almost exclusively in plaster and mortar. Not until the rapid growth of the chemical process industries at the beginning of the 20th century did lime consumption begin to shift significantly toward its use as a chemical reagent. Today, well over 90% of lime consumption in the United States is as a chemical reagent.

As of 1990, there were 70 producers of lime in the United States, excluding industries that regenerate lime. Of these 70 companies, 51 were involved predominantly in commercial sales, and the remaining 19 were captive producers. The 10 largest companies operated 26 plants and accounted for 57% of total production. Lime production occurred in 32 States and Puerto Rico. Based on available data, the commercial sector of the lime industry operated at 79% of capacity in 1990.

Lime is a basic chemical that at 15.832 million metric tons ranked fifth in total production in the United States in 1990. Total consumption for the year was 15.949 million metric tons valued at more than $905 million. Commercial sales were at record-high levels of 14.040 million tons captive consumption was 1.818 million tons. The breakdown of consumption by major end uses was as follows: 32%, iron and steel production; 24%, environmental uses; 8%, construction uses; 7%, nonferrous metal production; 7%, paper and pulp processing; and 4%, sugar refining.

The import-export trade in lime is relatively insignificant. Imports of lime in 1990 were only 157,000 tons and exports were only 40,000 tons. Almost all trade is with Canada and Mexico. Net import reliance as a percentage of apparent consumption is 1%.

Chemical Industry Consumption.—Since lime is a manufactured chemical product produced by the pyroprocessing of calcium carbonate into calcium oxide, it could be argued that all its uses are chemical uses. Unfortunately, the U.S. Bureau of Mines does not collect end-use data for many of the chemical industry's uses. Using as a guideline the end-use categories from the Office of Management and Budget 1987 Standard Industrial Classification Manual, lime consumption by the chemical industry is shown in table 2 for the following uses: alkalies, aluminum and bauxite, calcium carbide, citric acid, fertilizers, flue gas desulfurization, insecticides, magnesium compounds, paint, rubber, sewage treatment chemicals, tanning, and water treatment chemicals.

The most visible decrease in consumption of lime by the chemical industry has been in the manufacture of sodium alkalies (sodium hydroxide, sodium carbonate, and sodium bicarbonate) by the Solvay process. In this process lime is used to regenerate the ammonia catalyst in the manufacture of sodium carbonate. In the early 1970's, this predominantly captive market consumed over 3 million tons of lime. Environmental regulation of effluent discharges and competition from natural soda ash mined in Wyoming eventually forced the closure of all Solvay plants in the United States, the last in early 1986.

In the manufacture on alumina via the Bayer process, bauxite is reacted with sodium hydroxide to produce a sodium aluminate liquor. The clarified sodium aluminate is reintroduced into the process and mixed with "seed" aluminum trihydrate. About 50% of the sodium aluminate decomposes into aluminum trihydrate, that is precipitated and removed. This precipitate is dewatered and calcined to produce concentrated anhydrous alumina. Lime is utilized to causticize sodium carbonate solutions to generate the sodium hydroxide necessary to digest the bauxite ore.

High-calcium quicklime is utilized in the manufacture of calcium carbide, which is used to manufacture acetylene and calcium cyanamide, an important nitrogen fertilizer. Quicklime is combined with coke and heated in an electric furnace at 2,000° C resulting in the following reaction:

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$$CaO + 3C \rightarrow CaC_2 + CO$$

The molten carbide is cooled, crushed, and shipped or reacted with water to produce acetylene gas:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

About 1 ton of lime is needed to produce 1 mt of calcium carbide. To manufacture calcium cyanamide, calcium carbide is heated and reacted with nitrogen:

$$CaC_2 + N_2 + \text{heat} \rightarrow CaCN_2 + C$$

In the environmental sector lime's largest market is as a chemical reagent for the removal of sulfur dioxide from smokestack gases. This process, generally known as flue gas desulfurization (FGD), is dominated by wet and dry SO_2 scrubbing systems, about 85% being wet systems. All wet scrubbers contain three basic components: a vertical spray tower, reaction or slurry tanks, and thickener tanks. Operation of the process involves pumping wet reagent from the reaction tanks to the top of the spray tower for discharge, where the spray reacts with stack gases entering from below. A reacted sulfite-sulfate slurry is collected at the bottom and directed back into the reaction tanks where settling takes place. That portion that settles, the underflow, is directed to the thickening tanks for separation of solids for disposal. A portion of the reacted slurry is recirculated with fresh slurry to the spray tower for reuse.

Some commercial manufacturing processes that have been developed to produce magnesium, magnesium chloride, magnesia, dead-burned magnesia, and certain other magnesium compounds either utilize a high-calcium lime in the process or utilize dolomitic lime as the raw material. Examples of these processes are the Dow seawater process, the seawater chemical magnesian process, and the ferrosilicon (Pidgeon) process. In the first two processes, magnesium chloride is obtained from seawater and reacted with hydrated lime to produce magnesium hydroxide, that then undergoes either further reaction and electrolysis to produce magnesium or thermal reduction to produce magnesia.

Lime is used in the biological sewage treatment process and in the more advanced biological-chemical treatment process. It is used for chemical precipitation of sewage, to maintain the proper pH for efficient biological oxidation of the sewage, and for conditioning sludge when dewatering. It is used as a coagulant to precipitate phosphorus and nitrogen compounds that occur as suspended and dissolved solids. When alum or ferric chloride is used as the coagulant, lime is used to adjust the pH for optimum nitrogen removal.

Lime remains the major bulk chemical used in the treatment of potable and industrial waters. In water purification, lime serves several purposes: (1) it helps clarify water through the coagulation of suspended solids by maintaining the proper pH; (2) it acts as a disinfectant, fungicide, and deodorizer; and (3) it removes temporary hardness caused by dissolved salts such as calcium and magnesium bicarbonate.

In 1970, the Clean Air Act was passed, setting limits on the emissions of SO_2 from large sources such as coal-fired powerplants. This low accelerated the development of FGD technology and the market for scrubbing reagents. The Clean Air Act, and subsequent amendments, has pushed the FGD market from zero to over 1.5 million tons of consumption per year over the last 20 years.

Outlook.—The largest change in demand over the short and long term is a result of the Clean Air Act Amendments of 1990. Title IV-Acid Deposition Control was amended to include a market-based system of SO_2 and nitrogen oxide emission reduction. The goal is to reduce SO_2 emissions by about 9 million metric tons from 1980 levels. Since one of the main compliance options currently available to utility powerplants is the use of FGD scrubbing systems, consumption of lime for FGD use is expected to grow dramatically during the 1990's. The utilities' compliance plans will have to be set prior to January 1, 1995, when phase I goes into effect; and for many, this regulation will mean FGD scrubbers. Consumption for FGD could easily double or triple in the next decade.

In addition to the FGD market, other environmental markets are also expected to display growth. The Safe Drinking Water Act regulations, requiring "corrosion control" by water companies to prevent lead from leaching into the water supply, may boost demand by the water purification market. Lime can be used as a "corrosion control" measure by raising the water's pH, thus lowering the rate at which lead dissolves and at the same time forming a protective film of calcium carbonate on the interior of pipes. Clean Water Act and Water Quality Act regulations should generate increased demand for lime for pH control of industrial and mine drainage waste waters, treatment and disposal of sewage sludge, and treatment of septic tank wastes.

Although the historically large alkali market disappeared when the last of the synthetic soda ash plants closed in the 1980's, potential exists for a new alkali market in Wyoming. Three Wyoming producers of natural soda ash have built facilities for the lime-soda production of caustic soda (known as chemical caustic). Most caustic soda is currently produced as a coproduct of chlorine in electrochemical cells; and since chlorine appeared to have a negative growth rate, it was believed there would be sufficient demand to justify construction of chemical caustic production facilities. The process simply involves reacting soda ash (or trona) with hydrated lime. This combination yields caustic soda and waste calcium carbonate. The impact on lime demand is uncertain, as large plants using this process would filter and recalcine the waste calcium carbonate to recycle much of the required lime. Unfortunately for the soda ash producers, the caustic soda supply-demand situation has changed dramatically, and the chemical caustic facilities may be shut down.

A major manufacturer of propylene oxide is considering switching from the use of caustic soda to hydrated lime for the dehydrochlorination stage of the process. If the switch is made, it would not take place until the mid-to-late 1990's. The substitution would increase demand for lime by an estimated 450,000 tons of lime annually.

Table 1.—Salient lime statistics

(Thousand metric tons unless otherwise specified)

	1970	1975	1980	1985	1990
United States:[1]					
Number of plants	194	171	153	115	113
Sold or used by producers:					
Quicklime	13,833	14,402	14,490	11,791	13,392
Hydrated lime	2,836	2,126	2,308	2,099	2,098
Dead-burned dolomite	1,246	829	448	343	342
Total	17,915	17,357	17,246	14,234	15,832
Industry stocks, Jan. 1	NA	NA	NA	NA	NA
Imports	183	235	435	176	157
Total U.S. supply	18,098	17,592	17,681	14,410	15,989
Distribution of U.S. supply:					
Industry stocks, Dec. 31	NA	NA	NA	NA	NA
Exports	49	49	38	17	40
Demand	18,049	17,543	17,643	14,393	15,949

NA Not available.

[1] Excludes regenerated lime. Excludes Puerto Rico.

Table 2.—Lime consumption by the U.S. chemical industry[1]

(Thousand metric tons)

	1970	1975	1980	1985	1990
Alkalies	2,831	1,905	1,064	585	96
Aluminum and bauxite	346	267	249	102	141
Calcium carbide	509	186	168	208	W
Citric acid	NA	NA	NA	W	W
Fertilizers	NA	6	5	5	NA
Flue gas desulfurization	W	3	674	1,195	1,590
Insecticides	31	9	3	W	NA
Magnesia from seawater	NA	NA	648	370	592
Paint	3	4	NA	1	NA
Rubber	NA	3	W	W	NA
Sewage treatment	286	618	780	769	424
Tanning	33	24	25	36	24
Water treatment	1,113	1,321	1,357	1,369	973
Total chemicals demand	5,152	4,346	4,973	4,640	3,840
Total U.S. demand	18,049	17,543	17,643	14,393	15,949

NA Not available. W Withheld to avoid disclosing individual company proprietary data.

[1] Includes Puerto Rico.

Lithium

By Joyce A. Ober

Background.—Lithium is more important in its various chemical forms than as metal. An estimated 90% of all lithium consumption is as compounds of some type, be they manufactured chemicals or easily beneficiated ore concentrates.

There are several hard rock lithium ores including spodumene, petalite, lepidolite, amblygonite, and others; but in all known cases, lithium chemicals are produced from geothermal brines or spodumene, a lithium aluminum silicate. Petalite is another commercially important lithium ore, but it is consumed as ore concentrate and is not treated in a chemical plant. In both cases, whether processing spodumene or brines, lithium carbonate is the initial product from which other lithium chemicals are derived.

The two largest lithium carbonate producers in the world are Cyprus Foote Mineral Co. and FMC Corp., Lithium Division, both of which are U.S. companies. Cyprus Foote produces lithium carbonate from brine deposits in Silver Peak, NV, and from the Salar de Atacama in the Chilean Andes. Concentrated brine from the Salar is treated at a lithium carbonate plant in Antofagasta, Chile. Cyprus Foote operates downstream chemical plants in Frazer, PA, Sunbright, VA, and New Johnsonville, TN. The company also owns a spodumene mine and chemical plant at Kings Mountain, NC. The plant has been on a care-and-maintenance status since 1986, and only small quantities of spodumene concentrate have been produced at the mine since that time.

FMC's Lithium Division mines spodumene from a pegmatite deposit in Bessemer City, NC, for processing into lithium carbonate and other lithium chemicals at its nearby chemical plants.

Because there are only two companies producing lithium carbonate in the United States, actual production and consumption information are withheld to avoid releasing company proprietary information. Any consumption information is estimated. Imports of lithium carbonate have increased dramatically since the Cyprus Foote operation in Chile began production in 1984 and the Kings Mountain plant was closed. But even with the growth in imports, the United States remains a net exporter of lithium chemicals.

Chemical Industry Consumption.—As stated above, lithium carbonate is the most important chemical produced from spodumene. The majority of lithium chemical consumption is lithium carbonate consumed directly in the production of primary aluminum, ceramics, and glass; but carbonate is also important as the basis for the production of other lithium chemicals. Aluminum production and the ceramics and glass industry in the United States are the leading lithium consumers with nearly equal quantities of consumption; but the ceramics and glass industry worldwide consumes the largest proportion of lithium compounds, both in the form of lithium carbonate and ore concentrates from spodumene and petalite.

Spodumene is transformed into lithium carbonate by undergoing a process through which the mineral's chemical structure is altered when the ore concentrate is heated to a very high temperature. This process makes it more reactive to sulfuric acid. The converted ore is heated with sulfuric acid, forming lithium sulfate, the sulfate solution is filtered and treated with soda ash, forming lithium carbonate that precipitates from the solution.

Lithium carbonate production from lithium brines is much less energy intensive. The lithium chloride enriched brines are pumped from the underground deposits into a series of evaporating ponds through which they progress over the course of about 18 months. During this time the lithium concentration increases from an average of about 300 parts per million to 6,000 parts per million through solar evaporation. When the brine reaches optimum lithium concentration, it is pumped to a recovery plant and treated with soda ash. This treatment causes the precipitation of lithium carbonate, which is then filtered and dried.

The next most important lithium chemical is lithium hydroxide, which is consumed in the multipurpose grease industry. Lithium hydroxide monohydrate is the crystallized reaction product of lithium carbonate and calcium hydroxide. When heated above 100° C, the water of crystallization is driven off, and the lithium hydroxide monohydrate is transformed to anhydrous lithium hydroxide. For use in the grease industry, lithium hydroxide is converted to lithium stearate, a lithium soap that is combined in a 1-to-9 ratio with lubricating oil.

Organic lithium chemicals, especially *n*-butyllithium, are important as catalysts in synthetic rubber production. The process by which these compounds are derived is more complicated than those of other lithium chemicals. Lithium carbonate is converted to lithium chloride through the reaction of lithium carbonate and hydrochloric acid.

This material is then used as the raw material in the production of lithium metal through molten-salt electrolysis. The organic lithium chemicals are then derived through the reaction of lithium metal with organic halides.

Lithium consumption patterns have not altered appreciably for the past 20 years. In the mid to late 1980's, there was much discussion of the development of aluminum-lithium alloys and lithium batteries creating a tremendous demand for lithium metal. The alloys were expected to replace more traditional aluminum alloys in aircraft because of the weight reduction that would result from their use. The batteries were to replace alkaline batteries with improved performance characteristics. No significant gains in these areas have occurred yet.

Production problems with the alloys, have delayed their use in most types of aircraft; and in the interval, composite materials have made significant inroads into that market, displacing aluminum-lithium before it had established itself. Sale of lithium batteries have not grown as much as was predicted. Lithium batteries last longer than alkaline batteries but also are more expensive. The first U.S. company to introduce a lithium battery for general consumer use discontinued production after a short period of time due to weak sales.

Outlook.—No significant growth in lithium consumption is expected in the near term. The use of organic lithium chemicals is expected to increase, and consumption in ceramics and glass will probably grow slowly; but as existing aluminum potlines are replaced with more modern, energy efficient devices, lithium carbonate consumption will diminish for that end use. Nuclear fusion reactors could represent a huge market for lithium metal, but the technology has not yet been proven. Fusion energy may eventually become a commercially sound source for electricity, but not in this century. No other new significant lithium end uses have been discovered.

Table 1.—Salient lithium statistics

(Metric tons of contained lithium)

	1970	1975	1980	1985	1990
United States:					
Production[1]	W	W	W	W	W
Producers' stock changes[1]	W	W	W	W	W
Imports[2]	5	82	82	370	790
Shipments of Government stockpile surplus[3]	—	55	—	1	—
Exports[4]	[5]102	816	2,270	2,300	2,600
Consumption:					
Apparent	W	W	W	W	W
Estimated	NA	3,200	2,700	2,300	2,700
Rest of world: Production[1]	1,620	1,800	2,540	3,400	[e]5,400

[e]Estimated. NA Not available. W Withheld to avoid disclosing company proprietary data.

[1] Mineral concentrate and carbonate.

[2] Compound, concentrate, ores, and metal.

[3] Lithium hydroxide monohydrate.

[4] Compounds.

[5] Data available for lithium hydroxide only.

Magnesium and Magnesium Compounds

By Deborah A. Kramer

Background.—Magnesium is the eighth most abundant element in the Earth's crust and the third most abundant element in seawater. Although many minerals contain magnesium, magnesite, dolomite, olivine, and brucite are the only minerals from which magnesium and magnesium compounds are recovered commercially; magnesite and dolomite are the largest sources. Seawater, brines, and bitterns represent vast sources of magnesium and magnesium compounds. In the United States, more than 60% of the magnesium compounds produced annually are recovered from seawater and brines, and 80% of the magnesium metal production capacity uses seawater or brines as a raw material.

Magnesium Metal.—Most metallic magnesium is used in applications outside of the chemical industry. Magnesium and its alloys are used as alloying additions to aluminum, as structural components in automobiles and machinery, and for iron and steel desulfurization. Small quantities of magnesium are used as Grignard reagents, formed by reacting an alkyl or aryl halide compound with magnesium granules or powder. Grignard processes are used in the manufacture of perfumes, pharmaceuticals, and organometallic compounds, such as tetraethyl lead.

Metallic magnesium use in the chemical industry has declined from about 19% of total annual consumption in 1970 to less than 1% in 1990. Phaseout of leaded gasolines in the United States curtailed the production of tetraethyl lead causing consumption of magnesium in this end use to disappear.

Magnesium Compounds.—Hundreds of magnesium compounds are used in the United States, but the compounds of largest commercial significance are magnesium oxide (magnesia), magnesium hydroxide, magnesium sulfate, magnesium carbonate, and magnesium chloride. On average, about 70% to 75% of the magnesium compounds produced in the United States are used in refractories; the remainder is used in the chemical and other industries.

From the early 1970's until the mid-1980's, 14 companies produced magnesium compounds from seawater or brines. By 1990, this number had dropped to 10, because of changes in the U.S. steel industry, the principal user of magnesia refractories, and because of competition from cheaper imports. Throughout this period, one company produced magnesia from magnesite.

Chemical Industry Consumption.—In other Bureau of Mines publications, such as the Minerals Yearbook chapters and Minerals Facts and Problems chapters, magnesium compounds demand has been broken into two categories—refractories and chemicals. Perhaps a better term for the chemical enduse categories would be nonrefractory because chemical uses include end uses not specifically classified under Standard Industrial Classification (SIC) code 28. These applications include animal feed supplements, pulp and paper processing, and construction industry products. These nonchemical applications use about one-half of caustic-calcined magnesia shipments annually. The same nonchemical applications for magnesia also are significant users of other magnesium compounds.

Magnesium oxide (magnesia).—Various magnesia products are made by calcining magnesium carbonate or magnesium hydroxide at different temperatures. Caustic-calcined magnesia, which is readily reactive with water and is used principally by the chemical industry, is calcined at temperatures up to 890° C. Dead-burned magnesia, also called refractory or sintered magnesia, is calcined at temperatures up to 1,450° C and is unreactive with water. Fused magnesia is produced at temperatures greater than 3,000° C. Magnesia produced from magnesite is generally called natural magnesia, and magnesia produced from seawater or brines is called synthetic magnesia.

To prepare caustic-calcined magnesia from magnesite, the magnesite is first crushed to a specific size, depending on the type of magnesia to be produced. After crushing, magnesite is beneficiated; the degree of beneficiation depend on the quality of the ore and its ultimate end use. Lower quality ore often requires heavy-media separation, magnetic separation, and flotation to remove impurities. High-quality ore may require only screening or hand sorting to produce a material of acceptable quality. Caustic-calcined magnesia is produced in shaft kilns, multiple-hearth furnaces, or rotary kilns.

In producing synthetic magnesia, seawater or brines are treated with either a small quantity of lime or sulfuric acid to remove dissolved carbon dioxide. Calcium hydroxide, in the form of lime or dolime, then is added to precipitate the dissolved magnesium as magnesium hydroxide. The resulting slurry is thickened and vacuum filtered to yield a filter cake containing about 50% magnesium hydroxide. The filter cake is calcined directly to produce caustic-calcined magnesia.

The largest use of magnesia is in agricultural applications—animal feed and fertilizer. Magnesium serves as a structural part of the chlorophyll molecule, a compound necessary for plant photosynthesis. Without sufficient magnesium, either from the soil or from fertilizer application, plants can die. Corn, potatoes, cotton, citrus, tobacco, and sugar beets are among the crops that are highly responsive to magnesium fertilization.

Pasture fertilization with magnesium-containing fertilizers also is important in animal nutrition. Without enough magnesium in their diet, cattle and sheep can develop an often-fatal disease called grass tetany. Two of the most popular methods of introducing magnesium in cattle diets are to incorporate the magnesium with molasses in a liquid lick or to add caustic-calcined magnesia to purchased feed. In 1990, agricultural applications (fertilizers and animal feed) accounted for 36% of U.S. shipments of caustic-calcined magnesia.

In the manufacturing industry, caustic-calcined magnesia is used in the production of rayon, fuel additives, and rubber. Caustic-calcined magnesia is used to produce magnesium acetate, which is used for neutralization purposes in producing rayon fiber. Caustic-calcined magnesia is a starting material for the production of magnesium overbased sulfonates, which are used as acid acceptors and sludge dispersants in crankcase lubricating oils and as a fuel additive. Magnesium oxide also may be injected into oil-fired utility boilers where it reacts with vanadium salts to form a magnesium vanadate, which alleviates slagging and corrosion problems caused when using high-vanadium fuels. In water-base oil well drilling muds, magnesia is used as a buffer, for viscosity control, and as a corrosion inhibitor. In the rubber industry caustic-calcined magnesia is used as a vulcanizing agent in the curing of rubbers and elastomers.

In water treatment, magnesia is used to remove silica and heavy metals from industrial wastewater. It also is used as a neutralizing agent for some wastewater streams. Caustic-calcined magnesia is used for removal of sulfur dioxide (SO_2) from industrial flue gases; the magnesium oxide reacts with the SO_2 to form magnesium sulfate. Magnesia competes with calcium compounds in this application.

Special grades of magnesium oxide are used in the pharmaceutical and food industries. In pharmaceuticals, magnesia is used in consumer products such as antacids, milk of magnesia, and toothpastes. In the food industry, magnesia is used for acid neutralization in sugar beet processing.

Magnesium hydroxide.—Production of magnesium hydroxide is similar to that of magnesium oxide recovery from seawater or brines. Although magnesium hydroxide occurs naturally as the mineral brucite, very little brucite is recovered in the United States. In magnesium hydroxide recovery, brines or seawater is treated with a small quantity of lime or dolime to precipitate the bicarbonate as calcium carbonate, which is separated. The seawater is seeded with magnesium hydroxide to promote crystal growth. The resulting slurry is thickened, washed, and filtered to produce a filter cake containing about 50% magnesium hydroxide.

Most of the magnesium hydroxide produced in the United Stated is calcined to produce dead-burned magnesia, but small quantities are used as flame retardants in polymers and elastomers. Magnesium hydroxide reduces the quantity of smoke generated while burning and also has been shown to promote char formation. Some of the polymers that incorporate magnesium hydroxide in processing are polyvinyl chloride, polypropylene, and polyethylene.

Magnesium sulfate.—Minerals containing magnesium sulfate are widespread, occurring either as a double salt or as a hydrate. The most common commercially used magnesium sulfate minerals are kieserite ($MgSO_4 \cdot H_2O$) and epsomite, or epsom salt, ($MgSO_4 \cdot 7H_2O$). In addition to being recovered from minerals, these materials also are produced synthetically. Technical-grade epsom salt is manufactured by dissolving magnesium oxide, hydroxide, or carbonate in sulfuric acid, followed by crystallization. Anhydrous magnesium sulfate is prepared from dehydration of a hydrate; it cannot be prepared by crystallization from an aqueous solution.

Magnesium sulfate is used primarily as a starting point for the manufacture of other magnesium chemicals and in the pharmaceutical industry as a cathartic and analgesic. It also is used as a source of magnesium in fertilizers.

Magnesium carbonate.—Magnesium carbonate, the essential mineral in magnesite, may be recovered from magnesite; however, precipitated magnesium carbonate is manufactured by combining solutions of magnesium sulfate and sodium carbonate followed by precipitation, filtration, and drying. A common commercial product is basic magnesium carbonate, $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$, which can be prepared by boiling a magnesium bicarbonate solution or by drying a magnesium carbonate trihydrate precipitate at 100° C.

Basic and precipitated magnesium carbonate are used primarily in pharmaceuticals and cosmetics. Magnesium carbonate also can be used as an additive to table salt and cleaning powders to keep them free flowing. In some rubbers, magnesium carbonate is used as a reinforcing agent. Like magnesium hydroxide, magnesium carbonate also is used as a flame retardant and smoke suppressant in some polymers and elastomers.

Magnesium chloride.—In the United States, most magnesium chloride that is used in the chemical industry is recovered from brines. Solar evaporation concentrates the brine, and as the water evaporates, sodium chloride precipitates. After removing most of the sodium chloride, several potassium salts are precipitated, leaving a brine enriched in magnesium chloride. At equilibrium, the brine contains 30% to 35% magnesium chloride. This brine can be used directly for applications such as mine road dust control, or it can be processed further to produce magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$).

Olivine.—Olivine, $Mg_2Fe_2SiO_4$, is used mainly as a foundry sand in the iron and steel industry. Small quantities of olivine are fused with phosphate and added to fertilizers as a source of magnesium. In the United States, production of olivine consists of open pit mining followed by crushing and drying to produce material with a specific particle size.

Outlook.—Consumption of magnesium metal in the chemical industry is likely to remain stable since its primary use, production of tetraethyl lead, already has been eliminated. The applications that continue to use metallic magnesium are specialized, and these uses are unlikely to experience significant swings in rates of consumption.

In the past 20 years, magnesium compound use by the chemical industry, as a percentage of total demand, has increased from about 10% to 30%. This change was not a result of a large increase in chemical demand but rather a decrease in demand for refractories, which affected total magnesium compounds demand. Considering the wide array of industries that consume magnesium compounds, large changes in one sector probably will not have a significant effect on the total demand for magnesium compounds. Because many of the industries that use magnesium compounds are fairly mature, growth rates are likely to be small.

Table 1.—Salient magnesium and magnesium compounds statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Production:					
Metal	102	[1]109	[1]154	136	139
Nonmetal	933	792	727	420	499
Total	1,035	901	881	556	638
Secondary (old scrap)	3	5	16	24	31
Government stockpile releases, metal	13	—	—	—	—
Industry stocks, metal, Jan. 1	12	W	40	31	26
Imports for consumption:					
Metal	3	7	3	8	27
Nonmetal	76	89	46	134	147
Total U.S. supply	1,142	1,002	986	753	869
Distribution of U.S. supply:					
Industry stocks, metal, Dec. 31	13	36	45	39	26
Exports:					
Metal	32	30	51	37	52
Nonmetal	54	50	59	25	59
Industrial demand:					
Metal	88	60	117	123	145
Nonmetal	955	831	714	529	587
U.S. demand pattern:					
Metal:					
Chemical	14	7	7	5	1
Other	74	53	110	120	144
Nonmetal:					
Chemical	97	79	85	127	174
Refractories	858	752	629	402	413

W Withheld to avoid disclosing company proprietary data.

[1] Derived from data published by the International Magnesium Association and the Canadian Department of Energy, Mines and Resources.

Table 2.—U.S. magnesium compounds shipped and used

(Metric tons)

	1970	1975	1980	1985	1990
Caustic-calcined and specified (USP and technical) magnesias[1]	111,054	108,455	142,703	90,280	134,727
Magnesium hydroxide [100% $Mg(OH)_2$]	78,971	54,743	447,538	237,916	366,016
Magnesium sulfate (anhydrous and hydrous)	NA	43,053	38,898	50,678	55,411
Magnesium chloride	465,413	NA	NA	NA	NA
Precipitated magnesium carbonate[1]	6,150	6,334	4,667	3,398	2,821

NA Not available.

[1] Excludes material produced as an intermediate step in the manufacture of other magnesium compounds.

Manganese

By Thomas S. Jones

Background.—Manganese units for chemical applications have essentially come from foreign sources due to the lack of domestic high-grade deposits. Because U.S. import statistics, since August 31, 1963, have differentiated manganese ore by manganese content rather than by use, import statistics currently do not give an indication of quantities of ore used in producing chemicals. Australia and Gabon appear to have been important sources of ore used domestically in producing manganese chemicals. The salient statistics data in table 1 indicate the relatively minor proportion of total domestic consumption represented by chemical uses of manganese. Some domestic low-grade or manganiferous ore has been used to color brick, an application not considered to fall within the present context.

Chemical Industry Consumption.—The most significant manganese compounds from a chemical standpoint are manganese dioxide (MnO_2), manganous oxide (MnO), manganese sulfate ($MnSO_4$), and potassium permanganate ($KMnO_4$). Stoichiometric manganese contents of these compounds are in percent, 63.2%, 77.4%, 36.4%, and 44.7%, respectively. The scale of use of both oxides and the sulfate is in the tens of thousands of tons, and for the permanganate in millions of kilograms. The value of domestic consumption of these materials in 1990 is estimated as roughly $100 million, of which the majority is accounted for by MnO_2. Steps involved in preparation of the more industrially significant manganese compounds are shown schematically in figure 1.

Various other manganese compounds are produced or used in lesser amounts. Manganese acetate and manganese (III) acetylacetonate are used to catalyze organic reactions. Manganese borate is a drying agent. Manganese carbonate and manganese nitrate are often used as intermediates in the preparation of other manganese compounds, especially oxides. Manganese phosphate is used in rust-proofing iron-base surfaces. Manganese fluoride is used to prepare fluorine-bearing organic compounds. Manganese hypophosphite is used to improve synthetic fibers. Manganese ethylenebis (dithiocarbamate) (Maneb) is an agricultural fungicide that is used but not made domestically. Methylcyclopentadienylmanganese tricarbonyl (MMT) is used as an antiknock compound in gasoline, particularly in Canada.[1]

Manganese Dioxide.—The three types of dioxide are commonly referred to as natural manganese dioxide (NMD), electrolytic manganese dioxide (EMD), and chemical manganese dioxide (CMD). Selected battery-active NMD's, virtually all EMD, and some CMD are used domestically to manufacture dry cell batteries. Non-battery-active NMD from certain sources has been used as an oxidant in chemical reactions. EMD and a small quantity of CMD are manufactured domestically, whereas NMD is imported. In 1990, manufacturers of EMD were Chemetals Inc. at New Johnsonville, TN; Kerr-McGee Chemical Corp. at Henderson, NV; Eveready Battery Co. at Marietta, OH; and RAYOVAC Corp. at Covington, TN, having a combined capacity in 1988 of about 36,000 tons.[2] Production by RAYOVAC was ended in 1991. The sole facility for CMD was that of Chemetals at Baltimore, MD, having a capacity of about 5,400 tons.

MnO_2 is used in battery mixes as a powder. Preparation of EMD generally involves the sequence of crushing and grinding ore, reducing the ore in a furnace operation to form sulfuric-acid soluble MnO, and digesting the reduced ore with sulfuric acid to form a $MnSO_4$ solution. This solution is purified and electrolyzed to deposit MnO_2, which is stripped from the anode plate as chips. After washing and neutralization, the chips are ground into powder. Precipitated CMD can be made by several chemical routes that begin with reduced ore, the same as for EMD; finishing is similar to EMD processing.

Industry sources indicate that during the latter part of the 1980's worldwide demand for synthetic dioxide grew at a rate of about 4%, and that the industry suffered from an excess of production capacity. Synthetic dioxide is used predominantly in alkaline batteries, although some is also used in carbon-zinc batteries. NMD finds use only in carbon-zinc batteries. The domestic market for alkaline batteries has been growing partly because of consumer preference for alkaline rather than carbon-zinc batteries, whereas the market for carbon-zinc batteries has been relatively static. In recent years, growth in demand for EMD has been below that of the alkaline battery market because of development of improved EMD's with higher performance per weight unit.

Little data on EMD are publicly available. Data submitted to the U.S. International Trade Commission indicated apparent U.S. consumption of EMD was about 37,600 tons in 1985, 41,200 tons in 1986, 40,200 tons in 1987, and 42,900 tons in 1988.[3] These data are from investigations of charges of dumping of EMD in the United States in the 1980's, primarily by Japanese producers. U.S. imports of EMD from Japan, the country with the largest EMD capacity, had grown from

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3,676 tons in 1978 to 17,141 tons in 1988, but then fell sharply to almost zero after a large antidumping duty was imposed on dioxide from Japan.

No data are available on domestic CMD demand and growth. The United States has been importing CMD regularly from Belgium, the location of the manganese chemicals plant of Sedema SA, sister company to Chemetals. During the 1980's, the annual level of these imports averaged about 1,000 tons within a range of about 360-1,800 tons. One particular long-standing use of CMD is in magnesium batteries for the military. CMD is also used for specialized chemical applications.

One of the current trends in battery manufacture that affects EMD and CMD usage is the environmentally driven objective of eliminating mercury. As of 1990, battery manufacturers had achieved freedom from mercury in batteries based on NMD and a particular battery that uses CMD and had lowered the mercury content of typical alkaline batteries to 0.025%. Other factors in the intensely competitive battery industry that bear on demand for MnO_2 are the growing usage of lithium cells (principally those with MnO_2) and sales promotion of such rechargeable batteries as the nickel-cadmium type.

Manganous Oxide.—MnO is used mostly as an impure material obtained by roasting manganese ore containing the dioxide to reduce its MnO_2 content to MnO. Domestic suppliers of MnO so obtained in 1990 included American Minerals (plant at Rosiclare, IL), Chemetals (plants at Baltimore, MD, and New Johnsonville, TN), and Prince Manufacturing (plant at Quincy, IL). Other manganese processors also similarly roasted ore, but mainly for internal purposes.

Naturally derived MnO is used as an intermediate in production of other manganese compounds, as already indicated for EMD. Other uses of naturally derived MnO are in agriculture as an ingredient of animal feed and plant fertilizer, for example, the application to citrus trees. Various figures published between the late 1970's and 1990 put domestic consumption of MnO for animal feed and fertilizer combined in the range of 18,000 to 36,000 tons per year. Specifics cannot be given for possible foreign trade involving MnO because of the lack of unambiguous data. Some sources state that the majority of use is as fertilizer and others say it is as animal feed. In fertilizer, use of MnO from roasted ore may be in competition with such lower cost manganese-bearing materials as ferromanganese fines.

In agricultural applications, MnO may be used with $MnSO_4$ in forms referred to as the oxysulfate. One type of product is obtained by physically mixing oxide and sulfate; another is obtained by acidulating MnO with sulfuric acid, which can be done so as to give, after granulation, a material containing approximately equal proportions of oxide and sulfate. Appreciable quantities of oxysulfate are being produced domestically by acidulation, in recent years principally by Frit Industries Inc. (plant at Walnut Ridge, AR), Royster Co. (plant at Chesapeake, VA), and Stoller Inc. (plant at Charleston, SC).

A relatively small amount of synthetic, high-purity MnO is produced for such uses as manufacture of high-purity manganese chemicals, ferrites, and welding rod fluxes. Manufacture of high-purity MnO by reduction of dioxide requires high-purity synthetic dioxide as feed material.

Manganese Sulfate.—$MnSO_4$ is available in solid form as granules and as the monohydrate, having manganese contents typically ranging from 27% to 32%. It is also available as a water solution containing about 8% manganese. In 1990, domestic producers of the solid sulfate were American MicroTrace Corp. (plant at Fairbury, NE) and Koch Industries (plant at Pittsburg, KS); capacity data are not available. The production process generally consists of dissolving roasted manganese ore in sulfuric acid, purifying the manganese-bearing solution, and crystallizing the sulfate. $MnSO_4$ in solution was produced by Elkem Metals at Marietta, OH, as an adjunct of manganese metal operations. A small amount of high-purity $MnSO_4$ was also produced by the specialty chemicals industry. Tennessee Eastman Co. at its Kingsport, TN, plant had been the predominant domestic producer of $MnSO_4$, as a byproduct of hydroquinone manufactured by a process utilizing manganese dioxide-type ore as oxidant; but this process was discontinued in 1986.

One of the major uses of $MnSO_4$, as an in-process solution, is manufacture of manganese metal and synthetic dioxide. The other main use is, like MnO, in animal feed and fertilizer, having perhaps twice as much sulfate being used in feed as in fertilizer. Because of its water solubility, the sulfate can be applied by spraying. Industry sources indicate that domestic demand for the sulfate may have exceeded 30,000 tons in 1975 but has since declined to perhaps 15,500 tons in 1990. One reason given for the decline is one company's transfer of manufacture of a manganese-bearing fungicide from a domestic to a foreign location, an operation in which the sulfate was a feed material. It also appears that a relatively low price for Tennessee Eastman's byproduct sulfate had favored greater usage. The citrus fruit industry has been a significant user of $MnSO_4$. The outlook for this application is for a relatively level demand.

Imports have replaced at least part of the supply formerly provided by Tennessee Eastman, as shown by trends over the period 1985-88: 151 tons in 1985, 599 tons in 1986, 2,102 tons in 1987, and 7,919 tons in 1988. Mexico has emerged as a significant new producer and import source of $MnSO_4$, only 2 tons were imported from Mexico in 1987, but 4,377 tons were imported in 1988. Because of changes in tariff classes upon adoption of the Harmonized Tariff Schedule, later data on imports of $MnSO_4$ have not been directly available. Beginning in 1989 they are included within a category of "other sulfates." Imports from Mexico in this category were 7,340 tons in 1989 and 10,026 tons in 1990. Belgium, by virtue of the plant at Tertre of Chemetals' sister company, is another source of U.S. imports of sulfate.

Potassium Permanganate.—$KMnO_4$ is sold commercially as a solid in three basic grades: free-flowing, technical, and pharmaceutical. The free flowing and technical grades are the most used and generally are interchangeable. In water and wastewater treatment, the freeflowing grade can be fed dry automatically, whereas the technical grade requires use of a solution feeding system.

Since 1915, Carus Chemical Co. has produced $KMnO_4$ at La Salle, IL, and for years has been the only domestic source. Carus' present manufacturing technology, after steady evolution, consists of oxidatively fusing ground manganese ore with alkali, after which the resultant manganate is anodically oxidized to permanganate in a continuous electrolyzing-crystallizing process. Carus expanded its annual capacity to about 13.6 million kilograms as of 1980, which the company estimates to have been about one-third of world capacity in 1990.[1] The expansion was in response to a demand of from 1.8 to 5.5 million kilograms of permanganate by the Chemagro Agricultural Div. of Mobay Chemical Corp. for use in making a soybean herbicide;[4] however, this requirement ended in 1981 after Chemagro changed its manufacturing process.

The strong oxidizing nature of $KMnO_4$ is the basis of its principal uses: purification of drinking water (37%), for which hydrogen peroxide is a competitor; wastewater treatment (24%); purification of industrial fumes (6%); oxidant in chemical processing (14%), especially for manufacture of organic compounds; fish farming (6%); and metal processing, for removal of oxides and other substances on external surfaces (6%). These percentages are estimates of total U.S. consumption in 1982 of about 6.4 million kilograms. Time-trend data on domestic consumption of $KMnO_4$ are not available, but demand is believed to have increased in the 1980's as Carus has been active in meeting competition and developing new markets. $KMnO_4$ is designated a controlled substance by the Drug Enforcement Agency because of the possibility of its use in making illegal drugs. Domestic production by Carus in the 1980's has been impacted not only by the loss of Chemagro but also by more or less steadily increasing imports of $KMnO_4$, particularly from China and Spain. Imports of about 0.6 million kilograms in 1980 had risen to about 1.9 million kilograms in 1990. Antidumping duties were assessed against imports from China in 1984 and against imports from Spain for a brief period in 1984 and then again in 1988.

Carus also produces sodium permanganate, the only other permanganate of industrial importance. Sodium permanganate, used for example in etching of printed circuit boards, is five or more times as expensive as $KmnO_4$.

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Table 1.—Salient manganese statistics

(Thousand metric tons, manganese content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Domestic production (shipments)[1]	60	17	21	2	1
Shipments of Government stockpile excesses	127	280	144	83	20
Imports	984	1,009	780	552	611
Industry stocks, Jan. 1	1,126	1,073	679	381	294
Total U.S. supply[2]	2,297	2,380	1,625	1,018	926
Distribution of U.S. supply:					
Industry stocks, Dec. 31	1,066	1,233	644	345	241
Exports	27	119	47	[3]40	[3]54
Industrial demand (apparent consumption)[2]	1,204	1,028	933	633	630
Of which, chemicals[4]	34	47	45	42	36

[1] Including manganiferous ore.

[2] Data may not calculate to quantities shown because of independent rounding.

[3] Adjusted for reexports.

[4] Including miscellaneous nonmetallurgical uses of ore.

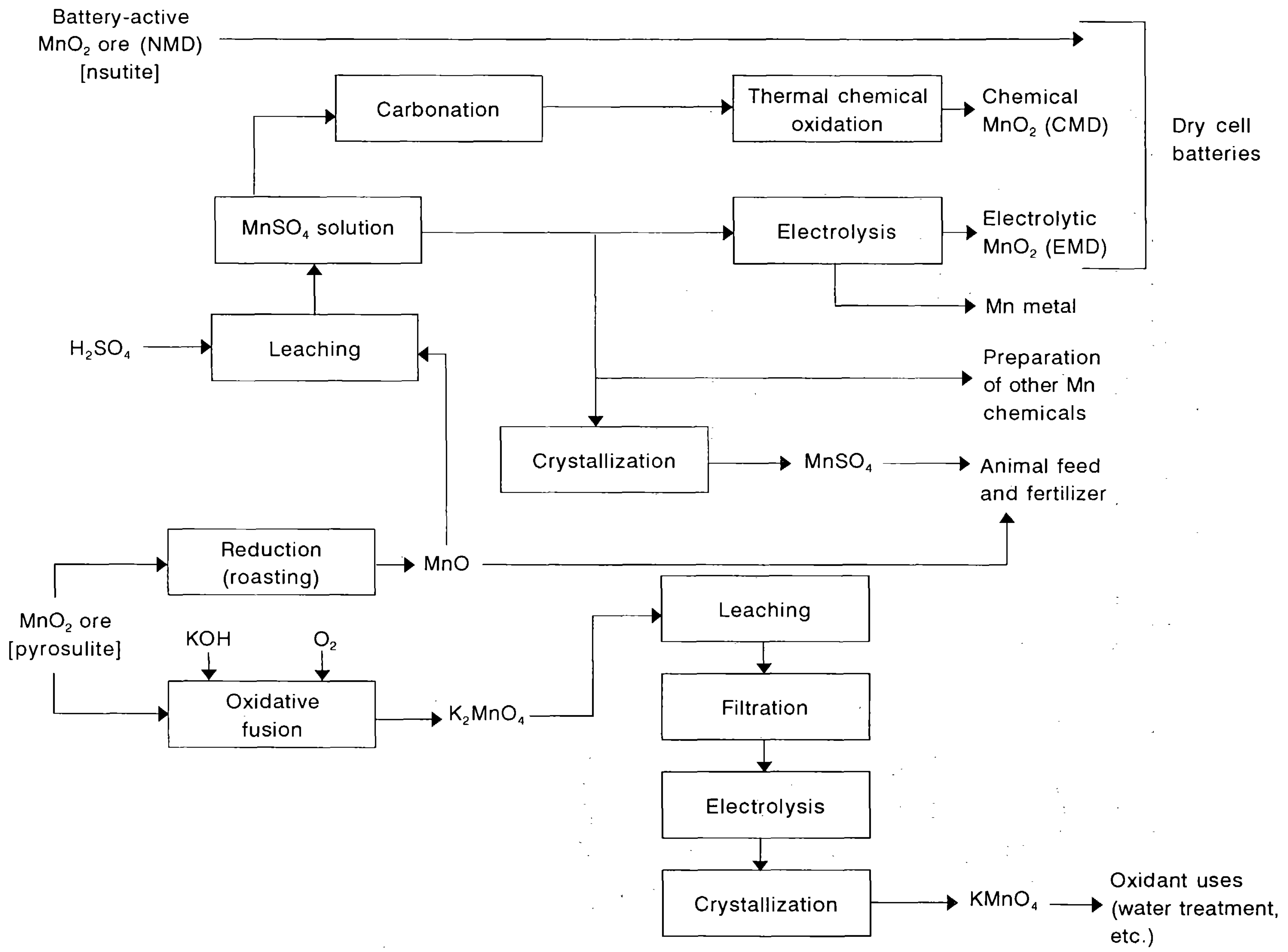

Figure 1.—Simplified diagram of processing and uses for key manganese chemicals.

Mercury

By Robert G. Reese, Jr.

Background.—Mercury has been recognized and used for more than 2,000 years. Initially, mercury was probably used in religious ceremonies and for medicinal and cosmetic purposes; however, its unique properties, such as the ability to alloy readily with most metals, liquidity at normal temperatures, and electrical conductivity, led to mercury's use in industrial applications. In the mid-16th century, development of the Patio amalgamation process for silver recovery was among the first commercial uses for mercury. Later, other uses such as in barometers, thermometers, and pigments were developed. Until the 20th century, however, the primary use of mercury was in the recovery of gold and silver.

Although mercury has been identified in many areas of the world, over the years, only a few countries have produced the metal. In general, other than in the United States, production within individual countries occurs only from a few mines. Following World War II, world mercury production steadily increased until the early 1970's; but since that time, world output has declined. Most mercury is recovered by processing cinnabar (mercury sulfide) ore; but some gold mines recover additional mercury as a byproduct of their gold operations. World mercury production in 1990 was estimated to be more than 6,000 metric tons from 11 countries. The largest productions were from the former U.S.S.R. (2,100 tons), Spain (1,500 tons), China (750 tons), Algeria (600 tons), and Mexico (345 tons). In earlier years, the United States was also a major mercury producer; however, the last primary mercury mine in the United States closed in late 1990.

Domestic mercury production began in California during the mid-19th century. Historically, California has been the largest mercury-producing State; however, for the past 17 years essentially all the newly mined mercury has come from Nevada. In 1990, mercury was produced as a principal product at one mine in Nevada, the McDermitt Mine, and as a byproduct at eight gold mines in Nevada, California, and Utah. The McDermitt Mine closed in late November 1990, reportedly in response to poor market conditions, a ban on the use of mercury in certain paints, and excessive sales from the Federal Government stockpiles.

Chemical Industry Consumption.—Historically, mercury's unique properties have resulted in its use in thousands of applications. In the chemicals industry, mercury and mercury compounds were used extensively in medicines to produce antibacterial and antifungal preparations, purgatives, and diuretics. Mercury also has been used as a pesticide and biocide to control agricultural diseases and pests and as a fungicide additive for paint. However, the recognition of the dangers associated with mercury usage in the early 1970's, curtailed or eliminated many applications.

As of 1990, the major domestic chemical industry use for mercury was in the production of chlorine and caustic soda. The mercury-cell chlor-alkali process, one of three processes used to produce chlorine and caustic soda, is the only one that uses mercury. In the process, a primary cell is connected to a denuder cell by a flowing mercury cathode. Also in the primary cell is a graphite-coated metal anode. Electrolysis of a purified brine in the primary cell results in the formation of chlorine gas at the anode and a sodium ion that amalgamates with the mercury cathode. As the cathode flows to the denuder cell, it is subjected to a stream of water. The sodium ion reacts with the water to produce hydrogen gas and caustic soda, leaving the mercury cathode for reuse in the primary cell.

Until 1990, the other important use for mercury in the chemical industry was as an additive to paints for mildew-proofing. Near mid-1990, the EPA reached an agreement with paint manufacturers eliminating mercury as an additive in interior latex paints. In 1991, the ban was expanded to exterior paints.

Outlook.—Total domestic mercury consumption has been in a downward trend since the early 1970's, and mercury consumption by the chemical industry has also declined during this period. Environmental concern and technological change have been the primary causes for the lower consumption. These trends are likely to continue in both the short and long terms. Continued use of mercury in the production of chlorine and caustic soda is expected; however, as existing mercury-cell chlor-alkali plants become noncompetitive, they are unlikely to be replaced.

Table 1.—Salient mercury statistics

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Domestic mines (primary)	941	254	1,057	570	W
Secondary production:					
Industry (from old scrap)	253	260	234	185	93
Government[1]	24	17	345	20	193
Shipments from the National Defense Stockpile	—	—	—	156	52
Imports for consumption	757	1,512	325	651	15
Industry stocks, Jan. 1	782	685	951	940	W
Total U.S. supply	2,757	2,728	2,912	2,522	W
Distribution of U.S. supply:					
Industry stocks, Dec. 31	571	881	1,140	965	W
Exports	160	12	NA	NA	311
Industrial demand	2,120	1,753	2,033	1,718	720
Apparent surplus (+) or deficit (-) of supply	-94	+82	NA	NA	W

NA Not available. W Withheld to avoid disclosing company proprietary data.

[1] Secondary mercury shipped from the U.S. Department of Energy stocks.

Table 2.—Mercury consumption by the U.S. chemical industry

(Metric tons)

	1970	1975	1980	1985	1990
Chemical and allied products:					
Chlorine and caustic soda manufacture	517	525	326	235	247
Pigments	NA	NA	W	(1)	(1)
Catalysts:					
Miscellaneous	NA	NA	26	17	(1)
For plastics	NA	NA	W	(1)	(1)
Total catalysts	77	29	W	(1)	(1)
Laboratory uses	62	12	13	14	32
Pharmaceuticals	24	15	—	(1)	(1)
Paint	357	239	297	169	22
Agriculture	62	21	W	—	—
Other	NA	NA	W	44	33
Total chemicals demand	1,100	840	663	479	334
Total U.S. demand	2,120	1,753	2,033	1,718	720

NA Not available. W Withheld to avoid disclosing company proprietary data; included in "Total chemicals demand."

[1] Pigments, pharmaceuticals, catalysts for plastics, and miscellaneous catalysts, shown previously as separate items, have been included in "Other."

Mica

By Lawrence L. Davis

Background.—Mica refers to a group of minerals having crystals that (1) exhibit a high degree of basal cleavage allowing them to be split into very thin sheets that are strong, flexible, chemically inert, and transparent; (2) possess useful electrical and thermal properties; and (3) can be cut or stamped into various shapes to very close tolerances. The two mica minerals of commercial importance are muscovite and phlogopite. Phlogopite remains stable at higher temperatures and finds applications where a combination of electrical properties and high heat stability is required. Both muscovite and phlogopite are used either in sheet form or ground.

Scrap and flake mica is mica that is unsuitable for use as sheet mica. It is ground to various sizes and used as a filler and/or extender in wallboard joint compounds, paints, and plastics; as an ingredient in well-drilling muds; as a lubricant; and for various other uses. In the United States, crude muscovite mica for grinding is recovered as a byproduct or coproduct from domestic feldspar, kaolin, and lithium beneficiation, from mica schists, or from scrap from sheet mica operations. Russia, the Republic of Korea, and India also produce significant quantities of scrap and flake muscovite mica. Phlogopite scrap and flake mica is produced in Canada and Madagascar.

In 1990, an estimated 109,000 metric tons of scrap and flake mica valued at about $5.8 million was produced in the United States. About 58% was mined in North Carolina, and the remainder came from Connecticut, Georgia, New Mexico, Pennsylvania, South Carolina, and South Dakota. The mica was processed to produce an estimated 97,000 tons of ground mica valued at $22 million.

Chemical Industry Consumption.—The largest use of ground mica by the chemical industry is in gypsum plasterboard joint compounds, where the mica acts as a filler and extender, provides a smooth consistency, improves the workability of the compound, and imparts resistance to cracking. In the paint industry, ground mica is used as a pigment extender that also facilitates suspension, reduces checking and chalking, prevents shrinking and shearing of the paint film, increases resistance of the paint film to water penetration and weathering, and brightens the tone of colored pigments. Ground mica is used in the well drilling industry as an additive to drilling muds. The coarsely ground mica flakes help prevent lost circulation by sealing porous sections of the drill hole. The plastics industry uses ground mica as an extender and also as a reinforcing agent. Small amounts of ground mica are used as an inert filler and as a mold lubricant in the manufacture of molded rubber products and as an ingredient in some special greases.

Outlook.—Consumption of ground mica generally follows activity in the construction industry because such a high percentage is used in construction. Over the 20-year period, use in joint compounds has grown, while other uses have stayed flat or decreased. The short-term outlook is for joint compounds to continue to be the major use for ground mica.

Table 1.—Salient mica statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production[1]	104	102	101	123	97
Industry stocks, Jan. 1[e]	9	6	6	6	6
Imports	3	5	8	9	13
Total U.S. supply	116	113	115	[2]139	116
Distribution of U.S. supply:					
Industry stocks, Dec. 31[e]	9	6	6	6	6
Exports	7	5	13	8	5
Demand	100	[2]103	96	[2]124	105

[e] Estimated.

[1] Ground mica sold or used by producing companies.

[2] Data do not add to total shown because of independent rounding.

Table 2.—Mica Consumption in the U.S. Chemical Industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Wallboard joint compound	29	37	42	62	60
Paint	22	19	15	18	16
Plastics	W	W	W	W	2
Well-drilling muds	W	W	W	W	8
Total chemical demand	60	67	69	97	86
Total U.S. primary demand	100	103	96	124	105

W Withheld to avoid disclosing individual company proprietary data.

Nickel

By William S. Kirk

Background.—Nickel is a silvery-gray metallic element, having an atomic number of 28, and an atomic weight of 58. The density of nickel is 8.9 grams per cubic centimer; one cubic foot of nickel weighs about 250 kilograms (550 pounds). Nickel melts at 1,453° C and is a ductile metal with excellent high-temperature strength.

More than 90% of nickel used is in the form of metal, chiefly in alloys. Within alloys, its chief use (more than 60%) is in stainless steel, where it imparts corrosion resistance and high-temperature strength. Other uses include superalloys, copper-nickel alloys, electroplating, and chemicals. The chemical properties of nickel led to its use in batteries and catalysts.

Nickel is the Earth's fifth most abundant element but occurs in the Earth's crust only in the range of 0.008% to 0.02% by weight. Nickel deposits generally originate from ultramafic rocks, igneous rocks that are low in quartz and feldspar and high in ferromagnesian silicates. The nickel content of ultramafic rocks, although relatively high compared with that of other rocks, seldom exceeds 0.3% by weight. These values are too low to make them economically minable as nickel ore. Moreover, nickel is less likely to be found in any significant degree of concentration than are some less abundant elements such as copper. To be rich enough to mine, some natural process must have concentrated the nickel. These processes result in the two very different types of nickel ore that can be mined economically.

The first deposit type, nickel laterites, is formed by the weathering of ultramafic rocks. As the rocks weather, nickel and sometimes cobalt are taken into solution by ground water and redeposited at greater depth, producing a zone of enrichment. At the base of the weathered rock, zones of enrichment may form that contain between 0.8% and 4% nickel, although the typical content is closer to 1%. The main ore mineral in this deposit type is Garnierite.

The second deposit type, nickel sulfides, is formed by the intrusion of molten ultramafic rocks or by replacement of the host rock by hydrothermal solutions. After the emplacement of a magmatic sulfide, the rock cools, and nickel and other metals combine with sulfur to form dense immiscible droplets that settle to the bottom of the magma chamber. These accumulations often form deposits rich in nickel as well as copper, cobalt, and the platinum-group metals. Pentlandite is the principal sulfide nickel ore mineral.

Chemical Industry Consumption.—Nickel chemical producers can be placed in two categories: those that are nickel producers and those that buy nickel from nickel producers to be processed into chemicals. Worldwide, five nickel producers also produce nickel chemicals; none is in the United States. The United States, has seven nickel chemical producers. There is one instance of overlap between the two groups. Outokumpu Metals & Resources, the Finnish nickel chemicals producer, merged with Mooney Chemicals Inc., Cleveland, OH, on September 30, 1991. The merger created a large, international, vertically integrated nickel chemical producer.

The major nickel chemicals are oxide, sulfate, nitrate, chloride, carbonate, hydroxide, acetate, phosphate, and sulfamate.

Nickel Oxide.—Nickel oxide (NiO) chemicals can be green or black. Green NiO is a crystalline compound that can be prepared by firing a mixture of water and pure nickel powder in air at 1,000° C or by firing a mixture of high purity nickel powder, nickel oxide, and water in air.[1] A sintered form of green NiO is made by smelting a purified nickel matte at 1,000° C. Green NiO is an inert and refractory mixture. Black NiO is a microcrystalline form resulting from the calcination of the carbonate or nitrate at 600° C. This incomplete calcination product typically has more oxygen than its formula indicates, i.e., 76-77 weight percent nickel compared to the green form, which has 78.5% nickel by weight.

Green and black NiO's are used in the ceramic industry for making frits, ferrites, and inorganic colors. Black NiO is also used for the manufacture of nickel salts and the specialty ceramics. Black and green NiO's are used for nickel catalyst manufacture by admixing, usually when wet, with a powdered ceramic support form. The mixture is formed into a suitable shape and then reduced with hydrogen to form the finished catalyst.

Nickel Sulfate.—Nickel sulfate hexahydrate, $NiSO_4 \cdot 6H_2O$, is an emerald-green crystalline salt. Much of it is produced commercially by adding nickel powder to hot dilute sulfuric acid. Some crude nickel sulfate is a byproduct of copper refining and recycling and is used as an intermediate product in nickel refining. The main use for nickel sulfate is as an electrolyte for nickel electroplating. It is also used as the electrolyte in electroless nickel plating and nickel electrowinning. Nickel sulfate is used as an intermediate in the manufacture of other nickel chemicals and as a catalyst intermediate.

Nickel Nitrate.—Nickel nitrate hexahydrate, $Ni(NO_3)_2 \cdot 6H_2O$, is a green deliquescent crystal. Nickel nitrate is made commercially by several methods, most of which include mixing nickel metal or black NiO powder with nitric acid. Nickel nitrate in as intermediate product used in the manufacture of nickel catalysts and nickel hydroxide.

Nickel Chloride.—Nickel chloride hexahydrate, $NiCl_2 \cdot 6H_2O$, is formed by the reaction of nickel powder or nickel oxide with a hot mixture of water and hydrochloric acid. Nickel chloride is used extensively in nickel electroplating and as an intermediate product in the manufacture of certain nickel catalysts. It is also used to absorb ammonia in industrial gas masks.

Nickel Carbonate.—Nickel carbonate, $NiCO_3$, is a light-green crystalline salt that can be prepared by the oxidation of nickel powder in ammonia and carbon dioxide. Boiling away the ammonia causes the precipitation of pure $NiCo_3$. It is used in the manufacture of catalysts, in the preparation of colored glass, in the manufacture of certain nickel pigments, and as a neutralizing compound in nickel electroplating solutions.

Nickel Hydroxide.—Nickel hydroxide, $Ni(OH)_2$, is a light-green microcrystalline powder that can be prepared by treating a solution of nickel sulfate with sodium hydroxide, which yields the gelatinous $Ni(OH)_2$. When neutralized, the gel forms a fine precipitate that can be filtered. Another industrial route for the manufacture of $Ni(OH)_2$ is by electrodeposition at an inert cathode using metallic nickel as the anode and nickel nitrate as the electrolyte. High purity $Ni(OH)_2$ can be made from nickel nitrate solution and potassium hydroxide by subsequently extracting the gelatinous precipitate with hot alcohol. The major use for $Ni(OH)_2$ is in the manufacture of nickel-cadmium batteries. Another use is as an intermediate product in the manufacture of nickel catalysts.

Nickel Acetate.—Nickel acetate, $Ni(C_2H_3O_2)4H_2O$, is a green powder used in manufacturing catalysts, and other nickel compounds and in aluminum anodizing and nickel electroplating.

Nickel Phosphate.—Trinickel phosphate orthophosphate, $Ni_3(PO_4)_2 \cdot 7H_2O$, is a green platy material which is prepared by the reaction of nickel carbonate with hot dilute phosphoric acid. Nickel phosphate is a component of a mixture used to coat steel prior to painting.

Nickel Sulfamate.—Nickel sulfamate, $Ni(SO_3NH_2)_2 \cdot 4H_2O$, is prepared by the reaction of fine nickel powder or black NiO with sulfamic acid in hot-water solution. It is used as an electrolyte in nickel electroforming systems.

The primary use of nickel in the chemical industry is in catalysts. Nickel is an important hydrogenation catalyst because of its ability to chemically absorb hydrogen. One important nickel catalyst is Raney Nickel, which is widely used in laboratory and industrial hydrogenation processes. It is the most active and least specific of the nickel catalysts. Nickel catalysts are used in the three major industries using catalysts, i.e., petroleum, chemical, and environmental (industrial and automotive) control. The second largest application for nickel chemicals is in electroplating.

Outlook.—There is potential for growth in the demand for nickel chemicals used in electroless plating. Researchers at the Department of Energy facility at Oak Ridge, TN, have developed a process for recycling chemicals used in electroless nickel plating. As the name implies, electroless nickel plating does not use electrodes or electricity; instead, parts are placed in a chemical bath, and chemical reactions cause the nickel to be plated onto the surface of the parts. As the plating progresses, however, the bath accumulates impurities that eventually render the bath ineffective. The new process removes these impurities by using a combination of ion exchange and selective chemical precipitation. The advantages of the process are (1) impurities that formerly had to be disposed of as hazardous material can be removed in a way that is environmentally safe (in fact, they could be used as fertilizers), (2) nickel and other valuable constituents can be returned to the bath, and (3) the amount of downtime for the bath is much reduced. The process is expected to be licensed for commercial development.

References

[1]Encyclopedia of Chemical Technology. John Wiley Interscience Publications, 3d ed., v. 15., pp. 801-819.

Table 1.—Nickel chemicals, imports and exports

(Metric tons, nickel content)

	1990			1991		
	Imports	Exports	Net imports	Imports	Exports	Net imports
Chlorides	364	70	294	218	39	179
Oxide and oxide hydroxides	2,569	236	2,333	372	227	145
Reaction initiators, catalysts, and compounds	7,516	1,344	6,172	1,014	1,224	-210
Sulfates	1,302	1,344	-42	744	92	652

Table 2.—Salient U.S. nickel statistics

(Metric tons, nickel content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production:					
Primary	14,114	13,012	10,183	4,730	3,701
Secondary	44,180	37,764	44,716	47,829	33,716
Industry stocks, Jan. 1[1]	15,036	37,748	43,561	52,738	13,581
Imports	141,750	145,610	171,629	143,054	131,116
Total U.S. supply	215,080	234,134	270,089	248,351	182,114
Distribution of U.S. supply:					
Industry stocks, Dec. 31[1]	22,415	32,191	68,248	33,118	17,816
Exports[1]	5,937	6,695	17,657	19,727	34,219
Demand	188,649	198,995	186,750	191,815	148,402
Apparent surplus (+) or deficit (-) of supply[2]	+1,921	-3,747	-2,566	+3,691	-18,323
Chemicals demand	885	2,253	1,338	1,863	1,156

[1] Includes scrap.

[2] The difference between total U.S. distribution of supply and total U.S. supply.

Nitrogen

By Raymond L. Cantrell

Background.—The United States is a leading domestic producer and global consumer of anhydrous ammonia. During the past 20 years, anhydrous ammonia containing 82.2% nitrogen (N) has provided the base for the production of a wide variety of nitrogen fertilizers and industrial nitrogen products consumed domestically and shipped to the international marketplace.

The U.S. ammonia supply peaked at 18.1 million metric tons N in 1980, representing 25% of the global market, at a value of $3.3 billion. In 1990, the U.S. ammonia supply was 16.3 million tons N, 13% of the global market, at a value of $2.1 billion. Global competitiveness is closely linked to natural gas feedstock prices.

During the early to mid-1980's, the U.S. ammonia industry adjusted to the pressures of increasing offshore competition and an extended downturn in domestic agriculture by rationalizing obsolete capacity and upgrading production facilities. In 1980, 56 firms were operating 81 ammonia facilities in 29 States having a combined annual capacity of 18.8 million product tons. By 1990, industry consolidation and restructuring had resulted in a 41 percent decline in the number of active producers, a 21-percent decline in the number of producing States, and a 16-percent drop in ammonia production capability. The U.S. ammonia trade deficit doubled during the decade, from 1.1 million tons N in 1980 to 2.2 million tons N by 1990. Significant quantities of ammonia were imported from Canada, the Soviet Union, Trinidad, and Mexico.

Following World War II, the United States entered into a sustained period of economic growth and industrial development that, in turn, gave birth to unprecedented growth in the U.S. fertilizer and farm sectors, known as the "Green Revolution." By 1970, the demand for fertilizers, farm commodities, and industrial goods at home and abroad generated by the Green Revolution had pushed the U.S. ammonia supply to 11.8 million tons N, representing about 31% of the global ammonia-N market. The United States also enjoyed a 0.4 million tons N trade surplus in 1970.

U.S. ammonia capacity and production continued to grow unabated during the 1970's in spite of our nation's increasing dependence on expensive imported foreign oil, double-digit inflation, and a nine-fold rise in domestic natural gas feedstock prices. Ammonia capacity increased by another 25% during the decade and peaked at a record 15.1 million tons N in 1980 but was outstripped by a production increase of 41% that also peaked at a record 14.7 million tons N. Although the ammonia trade deficit increased dramatically during the 1970's, from 0.2 million tons N in 1970 to 1.1 million tons N by 1980, a modest total nitrogen trade surplus was maintained because of the emergence of diammonium phosphate fertilizer as a major export commodity. Domestic nitrogen fertilizer consumption also peaked at a record 10.5 million tons N in 1980.

The energy crunch of the 1970's and resultant inflationary pressures resulted in a major global recession by mid-1981, throwing the U.S. fertilizer industry into an unprecedented downturn that would not improve significantly until 1987. The downturn was further exacerbated by an embargo of U.S. grain trade with the Soviet Union and the pressure of international competition. The Green Revolution in the developed regions-principally the United States, Canada, and Western Europe—came to an abrupt end; and U.S. ammonia production declined 12% between 1980 and 1985 to 13.0 million tons N, or 14% of the global supply.

Chemical Industry Consumption.—The domestic use of ammonia in the United States during the past 20 years has paralleled supply trends, characterized by dynamic growth during the 1970's, a decline in the early 1980's, and recovery toward the end of the decade. Approximately 80% of the U.S. ammonia supply is used by the domestic fertilizer industry for production, consumption, and trade; whereas about 20% is used for the production of synthetic plastics and resins, fibers, explosives, and a myriad of nitrogen-containing chemicals. The United States is a significant net importer of ammonia, urea, and ammonium nitrate used in the fertilizer and industrial sectors, and a significant net exporter of ammonium phosphate fertilizers.

The major downstream fertilizer nitrogen products produced from ammonia are urea (46% N), the ammoniated phosphates-diammonium phosphate (18% N) and monoammonium phosphate (11% N) ammonium nitrate (33.5% N), and ammonium sulfate (21% N), in order of importance. In 1990, 8.9 million tons N of the above materials was produced by the domestic ammonia industry, of which urea accounted for 38%; ammonium phosphates, 31%; ammonium nitrate, 25%; and ammonium sulfate, 6%. Anhydrous ammonia is also a popular source of direct application nitrogen fertilizer. Urea demand has grown dramatically during the past 20 years principally because of its high analysis and utility in bulk blending, and use in the popular urea-ammonium nitrate solutions (UAN) containing 28% to 32% N. U.S. ammoniated phosphate domestic demand and trade have also increased dramatically.

The anhydrous ammonia process is basically a catalytically driven high pressure-temperature process. Modern ammonia plants employ efficient centrifugal compressors for air and synthesis gas compression. A nickel catalyst is used in the reformer and associated front-end sections of the plant where hydrogen and nitrogen are produced in the proper ratio to effect ammonia (NH_3) synthesis, while an iron-promoted catalyst is used in the actual ammonia synthesis section. U.S. ammonia plants typically consume in excess of 30 million British thermal units (Btu) of natural gas per product ton, although new processes may approach 25 million Btu per ton, or a production efficiency of about 70%. Fertilizer-grade anhydrous ammonia assays 99.5% ammonia by weight, minimum; refrigeration grade, 99.98%; and metallurgical grade, 99.99%.

Urea is formed when ammonia is reacted with byproduct carbon dioxide generated during ammonia synthesis. The materials are reacted under high pressure and temperature in a two-step process to first form ammonium carbamate, that then decomposes to urea (NH_2CONH_2).

Nitric acid is formed when ammonia is passed over a platinum-rhodium catalyst under conditions of high temperature and pressure. The resulting nitric oxide is then converted to nitric acid by mixing with water in a countercurrent absorption tower. Ammonium nitrate (NH_4NO_3) is formed when ammonia is reacted with nitric acid.

The current ammonia supply-demand analysis indicates that approximately 20% of U.S. domestic ammonia disappearance goes into the industrial nitrogen sector, approximately 10% of which can be accounted for in the polymeric fibers, resins, plastics, and explosives materials. The accountable polymeric materials have grown at an average annual rate of about 8% during the 20 year period, while explosives have grown at a more moderate 3% per year.

A wide range of important polymeric materials are produced from ammonia, including the popular nylon diamide fibers and resins: nylon-6, produced from caprolactam monomer, and nylon-6,6, a condensation polymer resulting from the reaction of hexamethylenediamine and adipic acid. Acrylic fibers, resins, and elastomers are produced from acrylonitrile, an oxidation product of propylene and ammonia. Urea is used in the production of the popular urea-formaldehyde adhesive resins and in melamine plastics. Toluene 2,4-diisocyanate, an ammonia derivative, is employed in polyurethane foam; whereas hexamethylenetetramine, produced from ammonia and formaldehyde, is used in the manufacture of phenolic thermosetting resins. Ammonia is also used in a myriad of other industrial applications including urea protein supplements in ruminant animal feeds, refrigeration, the pulp and paper industry, the metal industry, and as a medium to reduce nitrogen oxides in stack gases, and for the production of sodium azide, a propellant in vehicular air bags.

The U.S. nitrogen fertilizer and farm industries have taken several steps to increase nitrogen efficiency, including the reduction of emissions, the production of slow-release fertilizers, and improved agronomic practices, including improved application methods and no-till cultivation practices. The Food, Agriculture, Conservation, and Trade Act of 1990, Public Law 101-624, commonly known as the "1990 Farm Bill" extended many of the innovative measures of the "1985 Farm Bill" designed to control crop production and inventories, firm grain prices, and improve the environment while reducing government subsidizes.

Environmental Issues.—Ammonia discharges to the environment (air, water, and land) are regulated by the EPA under Title III of the Superfund Amendments and Reauthorization Act (SARA), known as the "Emergency Planning and Community Right-to-Know Act." Under Title III of the Clean Air Act of 1990 (Public Law 101-549), a list of 190 hazardous chemicals and materials was established for regulation with the requirement that maximum achievable control technology (MACT) be achieved to reduce toxic air emissions by more than 75%. Several important industrial nitrogen chemicals were on the list, including acrylonitrile, aniline, caprolactam, ethyl carbamate (urethane), hydrazine, coke oven byproducts, and cyanides.

Ammonia and its downstream nitrogen fertilizer products have been subjected to intensive investigation relevant to nitrate pollution of groundwaters, coupled with the alleged inefficiencies of nitrogen fertilizer application methods. During the late 1980's, EPA conducted an extensive national Drinking Water Well Survey, which concluded that nitrate occurrence in U.S. waters is a limited, site-specific problem that results from many sources other than nitrogen fertilizers. The number of wells exceeding the EPA 10 parts per million nitrate drinking water limit was minor. The few records of methemoglobinemia (blue baby syndrome) on record involved nitrate levels significantly above EPA 10 parts per million limit.

Outlook.—The future security of the U.S. ammonia industry and agriculture will be critically dependent upon the price of energy and the continuation of reasonably priced domestic natural gas feedstock prices to counter increasing offshore competition from government subsidized plants and cheap natural gas. The passage of legislation for the phase out of U.S. natural gas price controls in the late 1970's and for its complete phase out in 1989 have been strategic to the increase in domestic natural gas supplies and a downward trend in prices. Still, there are threats of disrupting the U.S. energy equation as evidenced by the recent oil shock precipitated by the Persian Gulf Crisis and planned energy tax legislation for U.S. fossil fuels. Urea antidumping actions imposed against the former Soviet Union, Germany (Eastern States), and Romania by the International Trade Commission (ITC) in 1987 continue in force and are effective in preventing landed U.S. urea imports at below fair market values.

The future supply-demand environment in the U.S. ammonia industry will also be dependent upon (1) a favorable resolution of the ongoing Uruguay Round of General Agreement on Tariffs and Trade (GATT) negotiations that would liberalize trade opportunities for U.S. grain and fertilizers; (2) favorable U.S. implications for the proposed North American Free Trade Agreement; (3) the transition in democratic reforms in the former Soviet Union and Eastern Europe; (4) a resolution of the most favored nation (MFN) status with the China; and (5) new industrial outlets for U.S. agricultural crops.

Table 1.—U.S. ammonia supply[1]

(Thousand metric tons nitrogen)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production:					
Anhydrous ammonia	10,309	12,244	14,656	12,915	12,680
Coke oven byproduct[2]	133	102	85	50	50
Total	10,442	12,346	14,741	12,965	12,730
Inventories, Jan. 1	983	849	1,590	1,546	849
Imports[3]	361	601	1,743	2,092	2,674
Total U.S. supply	11,786	13,796	18,074	16,603	16,253
Distribution of U.S. supply:					
Inventories, Dec. 31	1,067	1,538	1,346	1,628	797
Exports[3]	735	264	620	916	482
Domestic use[4]	9,984	11,994	16,108	14,059	14,974
Total distribution	11,786	13,796	18,074	16,603	16,253

[1] Production and inventory data: Current Industrial Reports, MA28B and M28B, Bureau of the Census.

[2] Data for 1985 and 1990 are Bureau of Mines estimates.

[3] U.S. Bureau of the Census.

[4] Sum of gross ammonia production, and net trade (imports - exports) adjusted for changes in producer ammonia inventories.

Table 2.—U.S. domestic ammonia demand[1]

(Thousand metric tons nitrogen)

	1970	1975	1980	1985	1990
Fertilizer demand:					
Domestic consumption[2]	6,872	7,948	10,513	9,937	10,391
Net trade and miscellaneous[3]	192	630	1,427	749	999
Total	7,064	8,578	11,940	10,686	11,390
Industrial demand:					
Polymers and miscellaneous[4]	470	620	850	960	1,200
Explosives[5]	430	590	620	560	690
Total	900	1,210	1,470	1,520	1,890
Other disappearance[6]	2,020	2,206	2,698	1,853	1,694
Total demand[1]	9,984	11,994	16,108	14,059	14,974

[1] Sum of gross ammonia production and net trade (imports - exports) adjusted for changes in producer inventories; U.S. Bureau of the Census data.

[2] Commercial Fertilizers, Tennessee Valley Authority-U.S. Dep. of Agriculture, annual series.

[3] U.S. net exports and changes in producer inventories of ammonia conversion products.

[4] Based on Synthetic Organic Chemicals, United States Production and Sales, U.S. International Trade Commission, annual series.

[5] Apparent Consumption of Industrial Explosives and Blasting Agents in the United States, U.S. Bureau of Mines, annual series.

[6] Ammonia consumed in unidentified industrial applications, process and distribution losses, and swings in field inventories.

Perlite

By Wallace P. Bolen

Background.—Perlite is a rhyolitic volcanic rock that contains 2% to 6% water in its mineral composition. When perlite is subject to high temperatures, the water expands, creating great pressure throughout the rock, that causes the rock to expand in volume as the water is driven off as steam. The resultant product is expanded perlite, a very lightweight and porous mineral product. Because of its porosity and irregularly shaped particles, expanded perlite makes an excellent filter medium.

In 1991, crude perlite was produced at 10 locations and expanded at 62 plants throughout the United States. Imports of perlite from Greece in 1990 were about 54,000 metric tons. Imports, received mainly in the east and gulf coasts, are expanded primarily for use in building and construction products. Expanded perlite consumed for filter uses in 1991 totaled 69,000 tons in the United States. Total consumption of expanded perlite for all uses was 452,000 tons.

Chemical Industry Consumption.—Expanded perlite was used by breweries to filter out extremely fine solids such as algae and bacteria; by water companies to make water potable and safe; and by other industries in the processing of fruit juices, syrups, sugar, waxes, plastics, lacquers, antibiotics, and countless other products.

Outlook.—Use of expanded perlite for filter media has fluctuated from 1970 to 1990. Because of the many possible uses for filter-media grade perlite, future growth in consumption for this end use is hard to predict. Nonetheless, usage is expected to stay in the 70,000- to 100,000-ton-per-year range for about the next 10 years.

Diatomite is traditionally the major competing material for filter-media applications. Other materials, including silica sand and zeolites, compete on a limited basis.

Table 1.—Salient perlite statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
U.S. mine production[1]	414	464	579	470	576
Imports	—	—	—	54	59
Total U.S. supply	414	464	579	524	635
Distribution of U.S. supply:					
Exports[e]	15	20	32	27	32
Industrial demand	399	444	547	497	603

[e] Estimated.

[1] Processed ore sold or used by producers.

Table 2.—Expanded perlite consumption by the U.S. chemical industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Filter media	87	93	104	64	76
Total chemical demand	87	93	104	64	76
Total U.S. demand	399	444	547	497	603

Phosphate Rock

By David E. Morse

Background.—Sixteen companies mined phosphate rock in the United States in 1991, and phosphate rock from 25 mines was converted into phosphate fertilizer for agricultural uses and chemicals for industry. The mines have a nameplate capacity of about 62 million metric tons per year and an effective capacity of about 55 million tons per year.

Because the United States was a net exporter of phosphate rock, phosphate rock imports were normally confined to small tonnages of low-fluorine phosphate rock for animal feed products. Currently, high grade and quality phosphate rock is imported into one plant on the Mississippi River and an additional facility on the tidewater in Mississippi.

Phosphate rock consumption grew significantly during the 1970's and early 1980's; however, consumption fluctuated over a wide range between 29.4 million tons in 1982 to 42.8 million tons in 1984. Consumption from 1987 to 1991 has only varied from 41 million tons in 1987 to nearly 44 million tons in 1990. Phosphate rock exports, which accounted for 20% to 30% of U.S. output during the 1970's and early 1980's, have shown a declining trend in recent years. This decline expected to continue as phosphate rock will be converted into higher value products for the export market.

Chemical Industry Consumption.—Approximately 90% of the phosphate rock mined and beneficiated in the United States was used to produce phosphate fertilizers. Phosphate rock acidulated with sulfuric acid produces the intermediate chemical phosphoric acid and waste phosphogypsum. Controlled acidulation of phosphate rock with sulfuric acid produces single superphosphate, a low-analysis phosphate fertilizer. Controlled acidulation of phosphate rock with phosphoric acid produces triple superphosphate, a high-analysis phosphate fertilizer. Phosphoric acid reacted with anhydrous ammonia produces diammononium and monoammonium phosphate fertilizers, currently the most popular high-analysis fertilizer commodities.

The phosphate chemicals, containing phosphorus and nitrogen, are usually blended with potassium chloride and applied to the farmers' fields. Phosphorus, a primary plant nutrient, is responsible for processes in plant life where energy is stored and utilized. For cereal products, it promotes root growth, improves grain quality, and accelerates ripening of the grain.

Elemental phosphorous is produced in electric furnaces by smelting a mixture of agglomerated phosphate rock, lump coke, and silica. Phosphorus vapor is condensed to a liquid and stored under water. Most organophosphorus products are derivative of phosphorus trichloride, phosphorus pentasulfide, or phosphorus pentoxide. The chloride or sulfide is produced by direct reactions of elemental phosphorus with chlorine or sulfur. Sodium tripolyphosphate (STPP) is produced by calcining a mixture of monosodium and disodium phosphates. Disodium phosphate is produced by reacting phosphoric acid with soda ash. STPP is the single largest builder used in compounding detergents for consumer and industrial laundry detergents.

Fertilizer consumption will depend on the type of crops planted, acres cultivated, and fertilizer application rates. This consumption, in turn, will be influenced by weather, Government programs, U.S. and world economics, and of course, population changes. The phosphate fertilizer industry is recognized as being cyclical, fluctuating with the above listed factors affecting demand. The relationship with the phosphate rock mining industry is direct and immediate. The economic well-being of the farmer, or more directly, the farmer's ability to purchase phosphate fertilizer, influences the demand on the phosphate rock mining industry. The past decades were characterized as ones of oversupply of phosphate rock in both the world and the United States. Oversupply depressed prices and reduced profit margins for phosphate rock and phosphate chemicals producers. The recent closing of three mines in Florida and two in Tennessee from depletion of reserves and economics, respectively, focuses attention on the adequacy of supply. New mines can be opened in the eastern United States if capital formation is justified. New mines will not be developed unless profitability can be demonstrated.

During the past 30 years, a number of events have affected the phosphate rock mining industry. The 1969 National Environmental Policy Act required companies to prepare draft Environmental Inspect Statements prior to receiving preference right mining permits or leasing Federal land. In 1970, the Council on Environmental Quality established a moratorium on new mine developed on Federal land. Concerns over water consumption, land use, and reclamation caused the State of Florida to develop a comprehensive set of laws and regulations for the mining industry. State and Federal regulations were applicable in other areas mining phosphate rock in the

United States. In 1977, the Resource Conservation and Recovery Act was enacted; however, phosphate rock mining and processing wastes were not considered hazardous through 1990. In 1988, the EPA proposed removing phosphate wastes from the "Bevill Exclusion." In 1990, the processing wastes were removed from the "Bevill Exclusion" but were not assigned to be regulated under Subtitle C (i.e., hazardous wastes).

An embargo was placed on grain and phosphate exports to the Soviet Union in 1980, disrupting the markets for these commodities. The payment-in-kind (PIK) program was implemented in 1983 to reduce the supply of farm commodities, reduce storage costs, and raise prices. The drought in the United States and the PIK program reduced world stocks of coarse grains. The Food Security Act of 1985 was passed to encourage grain exports. The 1990 Farm Bill was implemented and emphasized reduced Government spending for agricultural programs.

Outlook.—The phosphate industry will be pressured to reduce water consumption, reclaim mined land, accelerate dewatering of stored waste colloidal clay, neutralize phosphoric acid plant wastewater, and safely store phosphogypsum. Remaining electric smelting furnaces will have to meet air quality standards and control all furnace solid and liquid wastes.

Increasing energy costs have influenced the closing of two elemental phosphorus furnace plants in the past several years. Lower cost purified wet-process phosphoric acid facilities replaced the electric furnaces. The future supply of phosphate rock may decline after 1995 as phosphate mines are mined out in Florida and replacement mines are deferred or canceled because of economics and environmental deterrents. The current oversupply capability of the industry, on a world basis, continues to affect planning for mines and processing facilities in the United States and overseas.

Restrictions on phosphorus levels in household detergents have been implemented by many States because increased phosphate levels in streams and lakes contribute to eutrophication. Projected changes in the detergent industry will probably mitigate any increase in the demand for STPP and other phosphate formulations. A negative growth rate of 1% to 2% per year is forecast for elemental phosphorus unless the bans on phosphate detergents are reversed.

Worldwide, the demand for phosphate fertilizers during the next 5 years is forecast to increase at a rate of about 1% per year. The demand, dependent on the various factors identified in prior sections, will continue to influence the future. Phosphate rock exports will likely decline, and exports of phosphate fertilizers will increase to meet the demand from Asian countries. Phosphate rock smelting furnaces will be replaced by lower cost purified wet-process phosphoric acid plants.

Table 1.—Salient phosphate rock statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
U.S. production	38,739	44,276	54,415	50,835	46,343
Industry stocks, Jan. 1	13,697	5,800	14,400	11,897	11,027
Imports	136	34	486	34	451
Total U.S. supply	52,572	50,110	69,301	62,766	57,821
Distribution of U.S. supply:					
Industry stocks, Dec. 31	14,566	9,900	13,700	15,534	8,912
Exports	11,738	10,141	13,873	10,284	6,238
Demand	27,163	31,022	41,194	37,532	43,967
Apparent surplus (+) or deficit (-) of supply[1]	-895	-953	+534	-584	-1,296

[1] The difference between total U.S. distribution of supply and total U.S. supply.

Table 2.—Phosphate rock consumption by the U.S. chemical industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Domestic fertilizer	NA	17,649	18,922	15,013	15,490
Domestic other chemicals	NA	5,673	4,273	2,278	1,720
Fertilizer exports	NA	6,906	17,228	19,875	26,184
Other chemical exports	NA	794	771	366	572
Total U.S. chemical demand	NA	31,022	41,194	37,532	43,966
Total U.S. demand	27,163	31,022	41,194	37,532	43,967

NA Not available.

Platinum-Group Metals

By J. Roger Loebenstein

Background.—The chemical industry uses platinum-group metals (PGM) to produce a variety of catalysts used to control emissions from automobiles; to produce inorganic, organic, and pharmaceutical chemicals; and to refine petroleum.

Chemical Industry Consumption.—For emissions control, platinum, palladium, and rhodium are the only metals of the platinum group that are used in autocatalysts, but all three metals are not always used in every autocatalyst produced. Platinum and palladium are used to oxidize carbon monoxide and hydrocarbons to less harmful constituents, whereas rhodium is used to reduce nitrous oxides. The term "three-way catalyst" refers to the ability of an autocatalyst to deal with all three pollutants in a single unit.

Beginning with the passage of the Clean Air Act of 1970 and continuing today, the use of PGM in autocatalysts has been driven by legislation, the usage of the metals generally increasing as emission limits are lowered in successive years. The pattern of industrial application for platinum and palladium changed significantly in 1974 with the introduction of autocatalysts for the 1975 model year. These early autocatalysts used from 1.6 to 3 grams of platinum-palladium, the two metals being present roughly in a 2-to-1 ratio.

In 1977, Congress amended the Clean Air Act and set progressively more stringent emission limits, particularly for the 1981 model year. In 1981, three-way catalysts came into use. These catalysts used about 1.6 grams of platinum, 0.62 grams palladium, and 0.16 grams rhodium.

In 1986, the EPA, which regulates the use of autocatalysts, required that used autocatalysts pass an emissions test before being sold for reuse on vehicles. Before this ruling, some of the used autocatalysts were ineffective. This ruling had the effect of increasing the number of autocatalysts available for recycling.

With the passage of the Clean Air Act of 1990, stricter standards on emissions of nonmethane hydrocarbons, carbon monoxide, and oxides of nitrogen were imposed beginning in 1994. In addition, the law requires that autocatalysts be guaranteed to operate for 100,000 miles, double the previous limit. A typical autocatalyst in 1990 contained a total of about 2.7 grams PGM (approximately 2.18 grams platinum, 0.31 grams palladium, and 0.31 grams rhodium).

It is interesting to note the increase in rhodium and platinum usage and the decrease in palladium usage since 1981. The increase in rhodium usage can be explained by the stricter nitrous oxide limits. Platinum has substituted somewhat for palladium in autocatalysts because of platinum's better durability and ability to withstand trace amounts of lead present in gasoline. Recently, however, the trend is for catalyst manufacturers to substitute palladium for platinum. In May of 1990, Nissan Motors announced it had developed a palladium-only autocatalyst. A month later, Isuzu Motors announced that it had developed a palladium autocatalyst for use on trucks to be sold in the United States. If palladium does eventually replace platinum in autocatalysts, the biggest obstacle will be how to increase the durability of the catalyst.

Another factor that might reduce platinum use in autocatalysts was an announcement by Atlantic Richfield Co. (ARCO) that it had developed a new fuel, called EC-X, aimed at reducing air pollution. The company said toxic emissions will be reduced by 47% and smog producing potential by 37%. Unless it becomes mandatory, ARCO will not produce EC-X. The fuel is expected to cost $0.16 per gallon more than conventional fuel.

In the chemical industry, PGM are used as catalysts in chemical manufacture, pharmaceutical production, and laboratory ware. PGM catalysts are used for inorganic and organic oxidation and hydrogenation.

For inorganic oxidation reactions, a platinum-rhodium gauze is used in the production of nitric acid and hydrogen cyanide. In a hydrogenation process, a supported palladium catalyst is used to produce hydrogen peroxide.

A number of organic hydrogenation catalysts use PGM. For example, cyclohexane is produced using an alumina supported platinum catalyst, and caprolactam nylon is made using a palladium hydrogenation catalyst on an activated carbon carrier.

Other organic chemicals produced include vinyl acetate using a palladium catalyst and acetic acid using a rhodium catalyst. Silicones are made by complex reactions using platinum or chloroplatinic acid, one of the few uses where the platinum catalyst remains in the product.

The demand for nitric acid is tied to the demand for fertilizer and explosives. Typically, the demand for new fertilizer plants in the United States has been highly cyclical in nature. In the United States, nitric acid production grew between 1970 and 1980, but since 1980, production has fallen due to depressed economic conditions in the agricultural and industrial sectors.

The growth of PGM use in chemical catalysts is related to the growth of the U.S. chemical industry and to the growth of the U.S. economy. Since 1970, the consumption of PGM has declined as a result of a downward trend in catalyst requirements per ton of output due to continual process improvements and to better recycling efforts. As a result, most new demand as a result of new chemical plant capacity and growth in coming years is expected to be negligible.

PGM are used in the petroleum refining industry for catalytic reforming, hydrocracking, and isomerization. Reforming processes are used for octane improvement of gasoline.

Palladium is used in hydrocracking catalysts to increase the yield of gasoline. Nonnoble metals of either nickel or nickel-tungsten are also used.

Isomerization processes rearrange the molecular form of feedstocks. Catalysts are usually platinum on alumina or zeolite carrier. Nickel is the major non noble metal used. The life of isomerization catalysts ranges from 7 to 9 years.

Older reforming processes used a monometallic platinum catalyst, whereas newer bimetallic catalysts consist of platinum-rhenium and platinum-iridium. By the early 1980's, bimetallic catalysts accounted for over 80% of total reforming catalysts used because of their much longer service life, averaging about 5 years. An additional benefit to using bimetallic catalysts was that they used about one-half the amount of platinum as monometallic catalysts.

Further reduction in the use of platinum was achieved with the technique of continuous catalytic reforming (CCR). Instead of removing a catalyst unit for regenerating, CCR allowed a refinery to regenerate the catalyst in a side stream and add it back in a continuous cycle. Less platinum was used in CCR than in older catalyst units.

Outlook.—Between 1970 and 1990, usage of PGM in petroleum refining has been relatively stable, between 3,000 and 5,000 kilograms annually. Future growth is limited by the high degree of recycling for PGM. Only about 5% of PGM is lost in petroleum refining. On the other hand, demand for high-octane, lead-free fuel is expected to gradually increase, which will cause refiners to expand reforming capacity. In 1985, the United States ended the practice of adding lead to gasoline, stimulating reforming catalyst sales and catalyst recycling.

Table 1.—Salient U.S. platinum-group metal statistics

(Kilograms)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Primary refined production	9,020	1,058	93	227	64
Imports, refined metal	46,593	52,378	96,701	106,928	120,631
Secondary refined	10,886	8,398	10,295	8,043	5,800
Industry stocks, Jan. 1	33,219	34,898	23,670	41,026	32,543
Shipments of Government stockpile excesses	93	—	—	—	—
Total U.S. supply	99,811	96,732	130,759	156,224	159,038
Distribution of U.S. supply:					
Industry stocks, Dec. 31	22,084	26,407	30,264	35,106	30,324
Government acquisitions	5,225	—	—	75	—
Exports	12,877	20,528	23,794	27,640	55,044
Demand	41,399	40,715	68,614	70,636	77,487
Apparent surplus (+), or deficit (-) of supply[1]	+18,226	+9,082	+8,087	+22,767	-3,817

[1] Total U.S. supply less total distribution of U.S. supply.

Table 2.—Platinum-group metal consumption by the U.S. chemical industry[1]

(Kilograms)

	1970	1975	1980	1985	1990
Catalytic uses:					
Automotive	—	11,508	22,747	27,039	26,957
Chemical	11,819	9,829	8,851	5,369	4,654
Petroleum	4,977	3,515	5,312	3,413	4,762
Total	16,796	24,852	36,910	35,821	36,373
Chemical use as a % of total demand	41	61	54	51	47

[1] Uses not considered to be chemical include dental and medical, electrical, glass, jewelry and decorative, and miscellaneous.

Potash

By James P. Searls

Background.—Potash is a generic term for several compounds that contain the potassium ion in a water-soluble form. A crude sodium-potassium alkali, derived from ashes of burned marsh plants, was used in Mesopotamia around 4000 B.C. to make glass beads. This crude alkali also was used to make soap. Later it was used for medicines, paints, photography, dyeing, washing, bleaching, and as a component of potassium nitrate for fireworks and gunpowder, matches, etc. The word "potash" originally referred to a mix of potassium carbonate and potassium hydroxide that came from wood ashes and was precipitated in iron pots. Over the past 50 years, the term, potash, has been used to denote a variety of potassium salts and includes potassium chloride (KCl), potassium sulfate (K_2SO_4), potassium nitrate (KNO_3), and potassium magnesium sulfate ($K_2SO_4 \bullet 2MgSO_4$).

In 1991, 10 companies in the United States mined potash at 11 sites. Production was centered in the Carlsbad, NM, area, where five companies operated six mines, the oldest of which has been in production since 1930. One operation, which has been in production since 1915 in southern California, produced two forms of potash, soda ash, salt cake, and bromine from shallow brines located under a dry lake bed. The three Utah producers, the oldest of which has been in operation since 1939, recovered potash from a variety of sources. One based recovery on a dry lake brine; another used brines from Great Salt Lake to produce potash, salt, and magnesium chloride by solar evaporation; the third solution mined a sedimentary deposit and employed solar evaporation and froth flotation in potash processing. One new potash mine, a pilot-plant, solution-mining facility in Michigan, commenced operations in 1991. Annual U.S. potash production capacity is about 3.6 million metric tons and about 35% of production is exported each year. Domestic consumption of potash in 1991 was about 8.93 million tons; imports were necessary to meet U.S. demand and were supplied from Canada (91%), Israel, Germany, and the former U.S.S.R.

Chemical Industry Consumption.—*Agriculture.*—Agriculture is the largest use of potash in the United States, representing between 90% and 96% of annual demand since 1970. Potassium, one of the three major plant nutrients, along with nitrogen and phosphorus, must be applied to a farmer's field to maintain high productivity because crops remove large amounts of nutrients from the soil. A mixed or blended fertilizer, containing measured quantities of the major nutrients, is typically applied by the farmer to produce an expected crop harvest per acre. Micronutrients such as sulfur, calcium, magnesium, boron, and zinc are added to the primary nutrients in quantities dependent on soil conditions and type of crop.

After 1885, when carnallite (a hydrated potassium-magnesium chloride) deposits were found in Germany, it became profitable to use on highly valued crops because potash was a mined product with a relatively lower price, compared to potash inefficiently manufactured from ashes. Between 1927 and 1960, large, high-grade potash ore reserves, primarily containing KCl, were discovered first in the United States, then in Russia, and later in Canada; low-cost potash from these deposits permitted profitable fertilizing of low-priced commodity crops, such as grains and fibers. At present, most of the potash produced and consumed in the world is as KCl, also known as muriate of potash.

Potash consumption in the United States increased from an estimated 500,000 tons in 1910 to a peak of 11.9 million tons in 1979. Potash consumption declined irregularly from 1979 to 1985 and started a fairly smooth annual increase of about 280,000 tons per year from 1985 through 1991.

Industrial Chemicals.—Historically, the industrial chemical end uses of potash have increased from about 4% of the total consumption of potash in the United States in the 1970's to about 8% in 1990.

An estimated one-half of nonagriculturally consumed potassium chloride is used in the production of potassium hydroxide. The next largest end use is for oil well drilling. About one-tenth is converted into potassium nitrate, and about one-tenth goes into metal recycling processes. The remainder is used in animal feed supplements, in steel heat-treating, to melt ice, in water softening, and in the production of synthetic styrene butadiene rubber.

Potassium hydroxide (KOH) is used directly in boiler water treatment, alkaline batteries, in many manufacturing processes, and even chocolate making. KOH as a chemical intermediate is the "doorway" into the production of a wide variety of potassium chemicals. Some of the potassium chemicals produced from KOH are potassium carbonate, potassium phosphates, potassium permanganate, potassium iodide, and potassium bromide.

Potassium sulfate (K_2SO_4) is used in the gypsum wallboard industry for initiating and accelerating the precipitation of gypsum. It is used in some pyrotechnical compositions.

Outlook.—The "green revolution" has has improved agricultural productivity in many parts of the world so that fewer countries need to import the excess agricultural productivity of North American soil and climate. Medical findings that discourage red meat consumption will tend to reduce the production of coarse grains that are used as feed for cattle. Farmers are apparently using fertilizers more efficiently, which reduces consumption while maintaining crop yields. Overall, there is reason to believe that potash consumption in fertilizers will grow slowly, if at all, in the foreseeable future.

In the short term, U.S industrial production will probably be level to slightly increasing as low-valued U.S. currency encourages exports of domestically produced goods. This should create a level demand for potash in food and chemicals.

Table 1.—Salient U.S. potash statistics

(Thousand metric tons of product)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production	4,403	4,152	4,315	2,569	3,360
Industry stocks, Jan. 1	656	357	568	677	618
Imports	3,994	5,689	8,193	7,571	6,952
Total U.S. supply	9,053	10,198	13,076	10,817	10,930
Distribution of U.S. supply:					
Industry stocks, Dec. 31	794	1,045	618	730	738
Exports	876	1,287	1,584	973	1,016
Apparent consumption	7,383	7,866	10,874	9,114	9,176

Table 2.—Potash consumption by the U.S. chemical industry

(Thousand metric tons of product)

End use	1970	1975	1980	1985	1990
Agricultural chemicals	7,074	7,463	10,290	8,516	8,436
Industrial chemicals	309	403	584	598	740
K_2SO_4	10	6	8	14	10
KCl	299	397	576	584	730
Apparent consumption	7,383	7,866	10,874	9,114	9,176

Source: U.S. Bureau of Mines and Potash & Phosphate Institute.

Salt

By Dennis S. Kostick

Background.—Salt, also known chemically as sodium chloride, is one of the most plentiful minerals in the world, yet at one time, it was so scarce that it was considered to be as precious as gold in certain areas. In terms of quantity produced, salt is the largest mineral commodity consumed by the chemical industry in the world, annual world output exceeding 190 million metric tons. Four types of salt are produced in the United States-rock salt, solar salt, vacuum pan salt, and salt brine. Solution mining of underground salt beds or salt domes yields salt brine, which is the dominant type of salt used by the chemical industry. Approximately 96% of total domestic salt brine is consumed by the chemical sector as feedstock.

Chemical Industry Consumption.—Of the approximately 14,000 different direct and indirect uses of salt, the chemical industry is the major end use, especially the chloralkali sector. About 51% of total domestic demand is consumed by the chemical industries listed in SIC 28. They include alkalies and chlorine, synthetic rubber, water treatment, and other chemicals.

Alkalies and Chlorine.—**Chlorine.**—About 97% of domestic chlorine and coproduct sodium hydroxide is obtained from the electrolysis of salt brine feedstock using three different cell technologies. The types of cells, and the percentage of chlorine produced, are diaphragm, 75%; mercury, 16%; and membrane, 6%. On the average, about 1.75 tons of salt are needed to produce 1.0 ton of chlorine and 1.1 mt of sodium hydroxide. The remaining 3% of U.S. chlorine production is as a byproduct from sodium and magnesium production, hydrochloric acid decomposition, or other processes. The electrolytic process disassociates into sodium and chlorine ions; the chlorine gas that forms at the anode is collected, while the sodium ions migrate through membranes toward the cathode where the sodium hydroxide forms and hydrogen gas evolves.

In 1990, 10.7 million tons of chlorine were produced in the United States by 24 U.S. companies that have a combined annual production capacity of 11.8 million tons. The end uses and percentage of distribution are as follows: vinyl chloride, 24%; pulp and paper, 14%; other organics, 12%; propylene oxide and inorganic chemicals, 8% each; chlorinated ethanes and chlorinated methanes, 7% each; epichlorohydrin and water treatment, 5% each; export, 4%; and titanium dioxide and other, 3% each. The largest sector, vinyl chloride, is used to make polyvinyl chloride plastics.

Sodium hydroxide (caustic soda).—Sodium hydroxide is produced with coproduct chlorine in electrolytic processes using salt brine. About 75% of domestic caustic soda production is from diaphragm cells. Hydrogen gas and aqueous sodium hydroxide form at the cathode in the cell. The cell liquor contains about 12% caustic soda and some dissolved salt. The liquor is concentrated to a 50-percent solution with all but approximately 1% of the salt removed. The majority of the liquid sodium hydroxide is sold as standard commercial grade, but some is further concentrated and dried into flakes and beads.

In 1990, about 11.3 million tons of sodium hydroxide were produced domestically. The industry had a combined annual production capacity of 12.3 million tons. The percentage distribution of the end uses are pulp and paper, 24%; other organics, 22%; inorganic chemicals, 12%; other, 10%; petroleum, water treatment, and soaps and detergents, 8% each; textiles, 5%; and alumina production, 3%.

Soda ash (synthetic).—Manufacturing synthetic soda ash had been the major method to obtain soda ash in the United States until 1971, when natural soda ash production exceeded that of synthetic. Rising energy costs, environmental pollution, and competition from less expensive natural soda ash forced the closure of all but one plant by 1979. Synthetic soda ash production ceased in 1986 with the closure of the last Solvay plant in the United States. The Solvay process, named after two Belgian brothers who invented the method in the early 1860's, continues to be the dominant method of soda ash production elsewhere in the world. This process is also known as the ammonia-soda process.

In the Solvay process, carbon dioxide gas is percolated through a carbonation tower containing nearly saturated salt brine to which ammonia has been added. Ammonium bicarbonate forms, which reacts with the brine to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate precipitate is collected, filtered, and calcined into soda ash. Some of the sodium bicarbonate is further processed and sold as such. The calcining liberates carbon dioxide that is recycled for future carbonation. Calcium hydroxide is added to the ammonium chloride and heated to recover the ammonia, which is also recycled. Although no synthetic soda ash is now produced, the distribution of U.S. soda ash (which includes imported synthetic soda ash) in 1990 was glass, 49%; chemicals, 24%; soap and detergents, 13%; distributors, 6%; flue gas desulfurization, 3%; pulp and paper, and miscellaneous, 2% each; and water treatment, 1%. Five companies in Wyoming and one in California compose the U.S. natural soda ash industry.

Industrial Inorganic Chemicals, Not Elsewhere Classified.—Although many downstream inorganic chemicals are derived by salt, only two are of significance: metallic sodium and sodium chlorate.

Metallic sodium.—Production of metallic sodium involves the electrolysis of fused sodium chloride that results in elemental sodium and chlorine gas. An electrolyte of 33.2% sodium chloride and 66.8% calcium chloride is introduced into a cell containing a carbon anode and iron cathode. A sodium-calcium mixture deposits on the cathode. As the temperature in the bath decreases, calcium settles out, permitting the sodium to be filtered out of the solution. The molten sodium is sent to storage tanks or nitrogen-filled tank rail cars where the sodium solidifies before shipment.

The U.S. metallic sodium industry consists of two companies with a combined annual production capacity of 76,000 tons. The uses include titanium metal reduction, 36%, and tetraethyl lead additives, 33%. The remaining miscellaneous uses accounting for 31% include pulp bleaching, agricultural chemicals, dyes, pharmaceuticals, catalysts, and exports.

Sodium chlorate.—Sodium chlorate is produced by the electrolysis of an acidified salt solution in electrolytic cells made of rubber-lined steel or ceramics. Dilute hydrochloric acid is added to a saturated sodium chloride brine to adjust the pH to about 6.5. The cell electrodes are made of a titanium or tantalum base coated with a platinum or platinum-base metal. The sodium chlorate that forms in the cell is treated to remove impurities during processing.

The chemical is further concentrated, crystallized, centrifuged, washed, dried, and screened. It is usually shipped in crystalline form or in 25% to 50% solutions. Because sodium chlorate is a strong oxidant, it is an extreme fire hazard when mixed with certain combustible compounds. Therefore because it is unstable, most sodium chlorate is made near pulp mills, the largest consumer of the chemical for pulp bleaching.

In 1990, total U.S. sodium chlorate production capacity of the nine producers was about 412,000 mt annually. Sodium chlorate is used to make chlorine dioxide for bleaching wood pulp. The uses of sodium chlorate are wood pulp bleaching, 94%; other chlorates, perchlorates, and chlorites, 3%; and miscellaneous (including herbicides, water treatment, and uranium mining), 3%.

Synthetic Rubber (Vulcanizable Elastomers).—Salt is consumed by the rubber industry in relatively minor quantities in making neoprene, white, or buna rubber. This type of rubber is made from an emulsified latex, which is manufactured from chlorinated butadiene. The salt brine and sulfuric acid are used to coagulate the latex.

Water Treatment.—Industrial and municipal water treatment involves processes to remove impurities before the water is used (e.g., filtration, ion exchange, etc.) and processes to remove impurities as the water is being used (e.g., boiler water treatment compounds). Salt is used to reduce the hardness (content of the soluble calcium and magnesium salts) of water by passing the hard water through a bed of ion exchange resin in which the calcium and magnesium ions are exchanged for sodium ions. The process is usually done in commercial cation-exchange water softening systems. Eventually the resin becomes depleted and must be recharged by running salt brine through the resin bed, thereby removing the calcium and magnesium ions and replacing them with sodium. The brine is made by adding salt, usually compressed pellets, to the water softening unit.

Outlook.—The environmental concerns regarding chlorine-base bleaching agents in the pulp and paper industry will reduce the quantity of salt consumed for chloralkali manufacture in the future. Although the use of salt for highway deicing will continue to be an environmental issue, no safe, effective, and less expensive alternate deicing agents are available to replace salt. Therefore, the demand for deicing salt should remain proportional to the severity of winter weather. Demand for salt is forecast to grow about 1.5%/yr for the next several years, primarily due to the growth in population.

Table 1.—Salient salt statistics

(Thousand metric tons and thousand dollars)

	1970	1975	1980	1985	1990
United States:					
Production[1]	42,424	37,839	37,633	35,577	36,794
Sold or used by producers[1]	41,636	37,222	36,607	36,348	36,916
Value	$304,759	$368,063	$656,164	$739,609	$826,659
Exports	384	1,208	754	820	2,266
Value	$3,657	$9,070	$12,829	$15,988	$32,944
Imports for consumption	3,208	2,917	4,775	5,631	5,969
Value	$13,329	$15,272	$44,071	$65,593	$88,419
Consumption, apparent[2]	44,460	38,930	40,627	41,159	40,619
World: Production	146,130	161,667	168,878	172,936	182,334

[1] Excludes Puerto Rico.

[2] Sold or used plus imports minus exports.

Table 2.—Salt consumption by the U.S. chemical industry

(Thousand metric tons)

	1970	1975	1980	1985	1990
Alkalies and chlorine	25,327	21,912	22,447	18,539	17,402
Other chemicals	1,278	926	925	697	1,856
Rubber	187	115	86	33	41
Water treatment	824	821	785	1,307	1,468
Total chemicals demand	27,616	23,774	24,243	20,576	20,767
Total U.S. primary demand	44,460	38,930	40,627	41,159	40,619

Selenium

By Daniel Edelstein

Background.—Selenium, a relatively rare element, is recovered as a byproduct from the processing of nonferrous ores, principally copper. Its economic recovery is dependant upon its concentration during the processing of the primary metal. In copper refining, selenium accumulates along with precious metals in the anode slimes generated in the electrolytic refining of copper. Worldwide, fewer than one-quarter of primary copper refineries recover selenium.

Primary selenium is recovered in the United States at three electrolytic copper refineries. Selenium-containing anode slimes or residues generated at other domestic copper refineries are exported for processing. Scrap selenium from photoreceptor manufacturing and used photoreceptor drums is also exported for processing.

As the world's largest consumer of selenium and its compounds, the United States depends on imports of selenium to meet about one-half of its demand. The United States is import dependent for all high-purity selenium used in electronics.

Selenium and its compounds are considered toxic in large doses. Although there are no clear indications of long-term systemic effects among industrial workers, selenium exposure is monitored and regulated; however, the occurrence and toxicity of selenium in the environment from nonindustrial sources has been reported in considerable detail. Agricultural irrigation practices in California and other arid regions of the western United States have leached selenium compounds from the soil, and they have accumulated in the evaporation ponds and catch basins. The resultant high selenium levels have had significant detrimental effect on waterfowl nesting in these areas.

Although selenium is toxic in high doses, it is an essential micronutrient in the diet of humans and livestock. Selenium is added to animal feed to compensate for feed grown in selenium deficient soils. Several selenium deficiency diseases have been identified in humans, and recent evidence suggests that selenium may be a cancer inhibiting agent.

Chemical Industry Consumption.—Selenium demand by end use can be divided broadly into five applications: electronics (including photoconductor uses), glass and ceramics manufacturing, pigments and chemicals, and other including metallurgical and agricultural uses. In recent years, growing agricultural demand has accounted for an increasing share of the "other" category. Domestic apparent demand for selenium metal in 1990 was about 530 metric tons, of which an estimated 20% (105 tons) was used for chemical and pigment applications, and about 80 tons was used for other uses. Excluded from 1990 demand estimates were 5 tons of selenium contained in imported selenium dioxide, and an undifferentiated quantity of sodium selenite and miscellaneous compounds. In 1988, the last year for which data on sodium selenite are available, 41 tons of selenium contained in selenite was imported, principally for use as an animal feed additive.

In pigment applications, selenium is used to produce color changes in cadmium sulfide-based pigments. Increasing substitution of selenium for sulfur causes the yellow cadmium pigment to become redder. Sulfoselenide red pigments, having good heat stability, are used in ceramics and plastics, as well as paints, inks, and enamels. Because of the relatively high cost and toxicity of cadmium-based pigments, their use is generally restricted to applications requiring long life, brilliance, and high thermal stability and chemical resistance.

In addition to pigment usage, chemical uses of selenium include industrial, pharmaceutical, agricultural, and biological applications. Agricultural uses are the largest component of the "other" category. Dietary supplements for livestock is the largest agricultural usage, although selenium may also be added to fertilizer, a practice that is more prevalent outside the United States. Small quantities of selenium are also used as human food supplements because selenium has been recognized as an essential nutrient for human health. The principal pharmaceutical use of selenium is in antidandruff hair shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounding, and catalysts.

Outlook.—Demand for selenium in pigment applications has already begun to show the impact of increased environmental concern over the use of cadmium-based pigments. At least one European country has banned the use of cadmium-based pigments, while other countries have sought to limit its use in applications associated with toys and foodstuffs. Increasing environmental concern has stimulated the development of alternative pigments and diminished the application of cadmium sulfoselenide pigments, their use being reserved for those applications for which they are uniquely suited. This trend is expected to continue or even accelerate.

Demand for selenium compounds in agricultural uses is expected to remain stable or even increase. In 1987, demand in this application increased significantly, including imports of sodium selenite, following new U.S. Food and Drug Administration regulations that increased, by a factor of three the maximum allowable selenium supplementation levels in animal feed.

Table 1.—Salient selenium statistics

(Metric tons selenium content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production:					
Primary	456	162	141	W	287
Secondary	5	9	45	—	—
Industry stocks, Jan. 1	109	36	284	139	W
Stockpile releases	—	3	—	—	—
Imports	206	403	284	401	[1]383
Total U.S. supply	776	613	754	W	W
Distribution of supply:					
Industry stocks, Dec. 31	86	69	284	W	W
Exports	171	54	82	123	195
Apparent demand[2]	520	490	390	[3]500	[4]530
U.S. demand pattern:					
Electronics	235	200	135	215	185
Glass manufactuing	175	140	115	100	160
Pigments and chemicals	70	90	100	100	105
Other (includes agricultural)	40	60	40	85	[5]80
Total U.S. demand	520	490	390	500	530

W Withheld to avoid disclosing individual company proprietary data.

[1] Metal and selenium dioxide only.

[2] Totals may be rounded.

[3] Excludes estimated exports of selenium scrap.

[4] Apparent demand of metal only. Calculated using reported shipments, imports of selenium metal, and estimated exports of selenium metal, excluding scrap.

[5] Excludes imports of sodium selenite.

Silicon

By Larry D. Cunningham

Background.—Silicon metal is produced by reducing quartz or quartzite in an electric arc furnace. In the United States, silicon metal production is distributed among seven companies in eight plants, the majority being located on the East Coast and obtaining most of their raw materials from Alabama, North Carolina, and West Virginia. Total U.S. production capacity for silicon metal is estimated to be 160,000 metric tons per year.

As late as 1975, the United States was completely independent of foreign imports; however, in 1990, the net import reliance for silicon metal was estimated to be 27% of consumption. The major sources from which silicon metal is imported to the United States include Argentina, Brazil, Canada, and China. Although a breakdown of imports by consuming industries is not available, most of the imported metal is believed to be consumed by the aluminum industry.

Chemical Industry Consumption.—Since 1970, consumption of silicon metal in the United States has doubled. The consumption of silicon metal is primarily divided between the aluminum and chemical industries; however, the electronic and photovoltaic industries constitute a small but important part of consumption, and miscellaneous other industries such as the iron and steel also contribute.

The addition of silicon to aluminum alloys improves processing and adds strength to both wrought and cast parts. Within the chemical industry, silicon metal is the basic raw ingredient in the manufacture of many silicone-base products and intermediates.

Silicone-base products are produced from a starting material of metallurgical grade silicon metal ground to a fine powder. Several different processes may be used to produce silicone-base materials; however, the predominant commercial process involves the production of a family of methylchlorosilanes from a reaction between silicon and methyl chloride within a fluid bed reactor. A distillation of the product stream separates methylchlorosilane, dimethylchlorosilane, trimethylchlorosilane, and any unreacted methyl chloride. The methylchlorosilanes produced are the intermediate forms of a variety of silicone-base products. To produce methyl silicones, dimethylchlorosilane is hydrolyzed. Several processes are used to tailor the resulting dimethylhydrolyzate into a multitude of products.

Like many chemical products, most silicon-base chemicals are used to improve an existing process or end product. Some of the major industries in which silicone-base chemicals and intermediates are used include automotive, construction, cosmetics, and electronics. In general, silicone chemicals can be grouped into the categories of elastomers, fluids, and resins.

The silicone elastomers sector of the silicone market is divided between room-temperature vulcanization (RTV), heat-cured rubber (HCR), and liquid-injection-moldable (LIM) applications. RTV silicon is utilized for caulking, bonding, and sealing and also for sealing and encapsulating electrical and electronic equipment. HCR silicones are used in wire and cable, especially spark plug wires, o-rings, gaskets and hoses, and are somewhat dependent upon the automotive market. LIM applications include a variety of molded and extruded parts including those used for medical use.

Silicone fluids are a major portion of the silicone market. The major end uses include antifoam agents, release agents, and lubricants. Silicone fluids are often used as noncorrosive hydraulic fluids in brake systems. Silicone oils are used as dielectric fluids for replacing polychlorinated biphenyls (PCB's) in electrical transformers.

Silicone resins constitute a small but important sector of the silicone market. They are often used in high-temperature paints and coatings or as binders for inorganic fibers. Resins are utilized in electrical insulating varnish, auto muffler-catalytic convertor coatings, gas turbine parts, and fiberglass. These products resist oxidation at high temperatures, exhibit a high dielectric strength, and are water repellant.

Since 1970, historical growth in the domestic silicone chemical industry is estimated to be about 7% annually. Annual consumption data show the growth rate is not constant. Fluctuations are caused by several factors. Surges in consumption have been caused by frequent expansions into new markets, and fluctuations in the rate of consumption are tied to price swings in the oil industry. The connection between these two industries lies in the fact that silicone products often compete with oil-base products. Although the performance of silicone products is usually superior, silicone products are more expensive than oil-base materials. Since oil-base products are often chosen because they are more economical, demand for silicone products increases as the price of oil-base products increases.

Some of the major issues with which silicone chemical manufacturers must contend relate to raw material and energy costs. In recent years, chemical manufacturers have been working closely with metal producers to lower costs and improve the quality of raw materials. Chemical manufacturers have made significant research and development investments to lower the energy requirements of silicon metal. As a result of these efforts, a newly developed direct current furnace was commissioned in late 1992. The new pilot process is expected to reduce energy and raw material costs significantly.

Outlook.—Because many of the existing silicon markets are mature, in the coming 5 years growth is expected to be somewhat slower than in the past owing to market saturation. This slower growth will be passed to the silicon metal market. The driving force behind silicone chemicals growth is expected to be expansion into new markets, and improved cost competitiveness will contribute to growth in existing markets. In the long term, silicon-base materials may penetrate the engineered plastics market. Fluorosilicon elastomers, used as sealants for alternate fuels, may also be an area for growth.

Table 1.—Salient silicon metal statistics

(Gross weight, metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production	98,893	93,473	117,595	111,391	145,744
Industry stocks, Jan. 1	3,559	7,590	7,820	9,464	8,716
Imports for consumption	430	3,545	19,812	46,993	66,383
Total U.S. supply	102,882	104,608	145,227	167,848	220,843
Distribution of U.S. supply:					
Industry stocks, Dec. 31	5,524	12,595	10,052	9,026	13,228
Exports	NA	NA	13,038	1,923	8,980
Total demand	97,358	92,013	122,137	156,899	198,635
Chemical demand[e]	29,000	34,000	58,000	72,000	98,000

[e]Estimated. NA Not available.

Table 2.—Estimated consumption of silicon metal by major end use

(Gross weight, metric tons)

End use	1970	1975	1980	1985	1990
Chemical products	29,000	34,000	58,000	72,000	98,000
Aluminum alloys	65,000	54,000	60,000	83,000	93,000
Other	3,000	4,000	4,000	5,000	6,000
Total	97,000	92,000	122,000	160,000	197,000

Silver

By Robert G. Reese, Jr.

Background.—Silver was one of the earliest metals identified and used by primitive societies. Like gold, silver was an esteemed and prized possession that could be used not only in the arts but also as a medium of exchange. As a result of its perceived value and availability, silver became the basis for many monetary systems. In the 19th century, silver's unique properties such as its photosensitivity and its electrical and thermal conductivity led to the development of new industrial uses. Subsequently, silver's use in monetary systems declined.

In general, world silver production has increased steadily since World War II. In 1946, 53 countries produced nearly 4,200 metric tons of silver; whereas in 1990, 55 countries produced 16,216 tons. Throughout the world, most silver is recovered as a byproduct of some other primary metal, generally, copper, gold, lead, zinc, or some combination of these metals. In 1990, the largest silver producing nations were Mexico (2,346 tons), the former U.S.S.R. (2,500 tons), the United States (2,121 tons), Canada (1,400 tons), and Australia (1,138 tons).

In the United States, silver was produced from precious-metal ores at 118 lode mines, from base metal ores at 19 lode mines, and at 16 placer operations. In 1990, 18 mines each produced more than 30 tons of silver; their aggregated production being nearly 78% of total domestic production. Most silver-producing mines are located west of the Mississippi River. For 1990, the largest silver-producing States were Nevada (646 tons), Idaho (442 tons), Montana (220 tons), Arizona (173 tons), and Utah (147 tons). Domestic silver production in 1990 was the largest annual production since 2,211 tons was produced in 1941.

Using data supplied by the Bureau of the Census, the Bureau of Mines follows four categories of U.S. silver imports and exports. Based on these data, the United States, despite being a leading silver-producing nation, has been a net silver importer from 1981 to 1990. During these 10 years, the United States has imported nearly 37,000 tons, of which nearly 85% has been refined bullion. Ores and concentrates, waste and scrap, and doré bullion account for the remainder. Based on cumulative shipments, the countries supplying the most silver to the U.S. market between 1981 and 1990 were Mexico and Canada, which supplied 33% and 31% of the cumulative imports, respectively. Other major sources of U.S. imports were Peru (11%) and the United Kingdom (10%). In addition to the types of material identified above, the United States also imports silver contained in semifabricated and fabricated products as well as silver compounds.

During the 10 years between 1981 and 1990, the United States exported nearly 10,000 tons of silver. In contrast to U.S. imports, only 43% of exported silver consisted of refined bullion. Cumulatively, 24% of U.S. silver exports went to Canada, 23% to Japan, 21% to the United Kingdom, and 11% to France.

Silver is consumed by numerous industries. Some, such as the electroplating industry, use pure silver metal. Others, such as the electronics and sterlingware industries, use alloyed silver. Manufacturers also use silver compounds. The most important silver chemical compound is silver nitrate, an important raw material for the photographic industry.

Chemical Industry Consumption.—Silver's use in the chemicals industry has primarily been as a catalyst. Silver and silver compounds are used for oxidation, reduction, and polymerization reactions. Probably the most important catalytic uses for silver are in oxidation reactions to produce ethylene oxide and formaldehyde. Ethylene oxide is used as a fumigant and sterilizing agent and to produce ethylene glycol. Ethylene glycol is used as an automotive antifreeze and as a raw material for the production of polyesters. Formaldehyde is used to produce a number of organic compounds including the glue used to manufacture various wood products, slow-release fertilizers, and chelating agents.

Ethylene oxide is produced by passing a feed material through a reactor vessel. The feed material consists of a mixture of purified air and ethylene, although oxygen can be substituted for the purified air. The reactor vessel contains several thousand small tubes, each of which is filled with the silver catalyst. As the feed material passes through the reactor, oxygen is adsorbed by the silver and subsequently reacts with ethylene to produce ethylene oxide, carbon dioxide, and water. The quantity of ethylene converted to ethylene oxide is probably less than 50% of the ethylene available. As a result, the feed gas is recycled and supplemented with new feed material. Following the reaction, the ethylene oxide is recovered and purified.

Formaldehyde can be produced by passing an air, heated methanol, and steam mixture over a shallow catalyst bed containing silver crystals or gauze. The reaction results in the formation of formaldehyde, carbon monoxide, carbon dioxide, methyl formate, and formic acid. As in the production of ethylene oxide, not all of the feed material is converted. Any remaining methanol is removed and purified before its reuse.

Outlook.—Data on silver consumption in catalysts was developed and published by the Bureau of Mines from 1966 to 1987. This data may be inaccurate, especially in the later years, owing in part to the nonparticipation of several companies in the voluntary survey used to obtain the data. Given growing concern about subjects such as plant emissions and work environments, it is reasonable to assume that the quantity of silver used in catalysts has declined since 1970. Forecasting demand for silver catalysts is equally difficult. In the short term, it is believed that demand will track the demand for consumer goods such as automobiles, clothing, and housing.

Table 1.—Silver supply-demand relationships

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production (primary)	2,531	1,869	1,224	1,674	1,611
Secondary (refined old scrap)	1,743	1,590	1,653	866	433
Imports, refined metal	920	1,917	2,017	4,244	2,698
Stocks, Jan. 1:					
Industry, future exchanges	6,183	4,247	4,638	4,941	8,339
Dept. of the Treasury	3,235	1,369	1,213	992	997
National Defense Stockpile	5,132	4,339	4,339	4,277	2,973
Total stocks	14,550	9,954	10,190	10,209	12,309
Total U.S. supply	19,744	15,330	15,084	16,993	17,051
Distribution of U.S. supply:					
Exports, refined metal	536	704	1,779	392	736
Stocks, Dec. 31:					
Industry, future exchanges	6,536	4,940	4,363	5,959	9,170
Dept. of the Treasury	778	1,275	1,213	1,015	840
National Defense Stockpile	5,132	4,339	4,339	4,277	2,830
Total stocks	12,446	10,554	9,914	11,251	12,840
Apparent demand	6,762	4,072	3,391	5,350	3,475

Table 2.—Silver consumption by the U.S. chemical industry

(Metric tons)

	1970	1975	1980	1985	1990
Chemical and allied products:					
Catalysts	62	273	94	75	NA
Total chemical demand	62	273	94	75	NA
Apparent demand	6,762	4,072	3,391	5,350	3,475
Total chemical demand as a % of apparent demand	0.92	6.71	2.78	1.40	NA

NA Not available.

Soda Ash

By Dennis S. Kostick

Background.—Soda ash, also known as sodium carbonate, may be produced from natural sodium carbonate-bearing brines or from processing trona ore. It also can be manufactured by one of a few synthetic processes; however, no synthetic soda ash has been made in the United States since 1986. One company in California at Searles Lake produces natural soda ash from underground brines and also various other sodium, potassium, and boron coproducts. In Wyoming, five companies produce soda ash from vast underground beds of trona ore using a combination of conventional, continuous, longwall, and solution mining techniques. The Green River trona deposit, the world's largest trona resource, is capable of supplying the U.S. and world soda ash demand for many centuries.

Aside from being the largest soda ash-producing Nation in the world, the United States also is the largest exporter of soda ash. In 1990, U.S. soda ash exports represented 26% of domestic production. Imports, mainly from Canada, usually are less than 150,000 metric tons annually. The sole Canadian producer is a subsidiary of a U.S. soda ash company; therefore, virtually all imports are under the control of the domestic producer. Although glass is the major end use sector, soda ash use by the chemical industry represents about 41% of total domestic demand.

Chemical Industry Consumption.—Technically, only synthetic soda ash is covered in SIC 28, under 2812, Alkalies and Chlorine; whereas natural soda ash is contained in SIC 1474, Potash, Soda, and Borate Minerals. The data in the accompanying tables includes both natural and synthetic soda ash for 1970 through 1985, but only natural in 1990. The chemical uses of soda ash, as defined in SIC 28, include (1) industrial inorganic chemicals, (2) soaps and detergents, (3) water treatment, and (4) flue gas desulfurization.

Industrial Inorganic Chemicals.—The inorganic chemical industry is the second largest user of soda ash, comprising 24% of total domestic demand. Although many sodium-based compounds are indirectly produced from soda ash, only six major chemicals are directly manufactured from soda ash feedstock, three classified as alkalies and chlorine and three others.

Alkalies and Chlorine.—*Sodium bicarbonate.*—Sodium bicarbonate, or baking soda, is manufactured by percolating carbon dioxide gas through a carbonation tower containing a saturated soda ash solution. The sodium bicarbonate precipitate is collected, filtered, centrifuged, dried, screened, and packaged. Approximately 0.68 tons of soda ash is required to make 1 ton of sodium bicarbonate. The major uses of sodium bicarbonate include household consumer products, 26%; animal feed, 21%; food, baking, and beverage, 16%; plastics and chemicals, 14%; exports, 9%; pharmaceuticals and personal care products, 6%; fire extinguishers, 2%; soaps and detergents, 25%; flue gas scrubbing, 2%; and other, 2%. Five producers operating six plants have a combined annual production capacity of about 470,000 tons. Three of the companies are also soda ash producers.

Sodium hydroxide (caustic soda).—Caustic soda is mainly produced as a coproduct with chlorine gas in the electrolysis of salt brine in either mercury, diaphragm, or membrane cells; however, nonelectrolytic caustic soda, also known as chemical caustic soda, is also presently being made from lime and soda ash. The lime-soda process had been the primary method of caustic soda manufacture at the beginning of the 20th century before the electrolytic process gained favor.

The lime is slaked (CaO converted to $Ca(OH)_2$) and added to 1.33 tons of dissolved soda ash to produce one ton of chemical caustic soda. Calcium carbonate is precipitated from the reaction, calcined back to lime, and recycled. Two Wyoming soda ash producers currently have a production capacity of about 127,000 metric tons of chemical caustic soda with a third company scheduled to come on-stream in late 1992 with 90,000 tons of capacity. One of the producers uses about one-half of its caustic soda to produce captive sodium cyanide for precious metal recovery at its gold operation. The balance of the chemical caustic is sold to various regional customers for different applications including pulp and paper, water treatment, and inorganic chemical preparation.

Sodium sesquicarbonate.—Sodium sesquicarbonate is a hydrated compound containing soda ash and sodium bicarbonate. Trona ore is first crushed and dissolved to separate the insoluble impurities. The sodium compounds in solution are then clarified, filtered, crystallized, centrifuged, calcined, and recovered as long needle-shaped monoclinic crystals of sodium sesquicarbonate. One Wyoming soda ash company has a 50,000-ton-per-year sodium sesquicarbonate facility that sells mainly to the detergent industry.

Industrial Inorganic Chemicals, Not Elsewhere Classified.—**Sodium chromates.**—Chrome ore is roasted with soda ash in a rotary kiln to produce sodium chromate or sodium bichromate that is used to produce other chromium compounds such as chromic acid and chromic sulfate. For every metric ton of sodium bichromate produced, 0.79 tons of soda ash is required. Two producers with a combined annual production capacity of 149,000 tons operated in 1990. The end use distribution of sodium bichromate is chromic acid, 55%; chromium oxide, 10%; leather tanning, 8%; pigments, 7%; wood preservatives, 2%; drilling mud additives, 2%; other (metal finishing, water treatment, textiles, catalysts), 3%; and exports, 13%.

Sodium phosphates.—Sodium phosphates are the largest soda ash-consuming sector of the industrial inorganic chemicals. The phosphate chemicals and the corresponding quantity of soda ash required to make 1 ton of the chemical are as follows: sodium tripolyphosphate ($Na_5P_3O_{10}$), 0.76 tons; monosodium phosphate (NaH_2PO_4), 0.45 tons; disodium phosphate (Na_2HPO_4), 0.747 tons; trisodium phosphate, 0.68 tons; sodium metaphosphate, 0.557 tons; sodium acid pyrophosphate, 0.478 tons; and tetrasodium pyrophosphate ($Na_4P_2O_7$), 0.84 tons. The sodium phosphates have exceptional cleaning properties, especially sodium tripolyphosphate, and are also used in baking powder, carbonated beverages, milk products, dental materials, fire-resistant products, metal surface treatment, and water treatment.

Sodium silicates.—Sodium silicate is produced from silica sand and soda ash in a process similar to glass manufacture except the sodium silicates are water soluble and glass is not. The two raw materials are melted at 2,450° C in an open-hearth furnace. The melt is withdrawn, cooled, crushed, and dissolved under pressure with steam. The three types of sodium silicates and the corresponding quantity of soda ash needed to produce 1 ton of the chemical are sodium orthosilicate (0.8 tons), sodium metasilicate pentahydrate (0.33 tons), and water glass (0.37 tons). Sodium silicates are used in soaps and detergents, 29%; silica-type catalysts and gels, 28%; pigments, 22%; paper adhesives, 8%; water, paper, and ore treatment, 6%; and other, 7%. Twelve companies operating 34 plants have an annual production capacity of 1.133 million metric tons of sodium silicates.

Other sodium chemicals.—There are many other sodium-based chemicals that are derived from soda ash. Sodium aluminate, sodium cyanide, sodium fluoride, and sodium sulfite are just a few examples.

Soaps and Detergents.—The third largest end use of soda ash is for soap and detergent manufacture, accounting for 13% of total domestic consumption. Soda ash is used directly and indirectly in this sector with different functions. First, soda ash is added directly to different detergent formulations to serve as an agglomerating aid, surfactant carrier, and as a source of alkalinity. Second, soda ash is the feedstock to make other sodium-based chemicals used as builders. Builders are agents that enhance the cleaning action in the liquid washload by tieing up the calcium and magnesium ions to improve surfactant activity. The builders include sodium tripolyphosphate (which is an excellent builder but contributes to the environmental problem of eutrophication), sodium silicates, and synthetic zeolites. A combination of one or all of these is used in various detergent formulations.

Soap and Other Detergents, Except Specialty Cleaners.—The end-use data presented pertain to the direct use of soda ash in soap and detergent manufacture; the quantity of soda ash used to produce other sodium chemicals used in formulations are included in the chemicals sector, which is the primary, first-tier consumer. Soda ash is used in powdered home and industrial detergents, but not in the newer liquid detergent formulations. Many States have legislation to restrict or ban the use of phosphatic detergents because of environmental considerations; therefore, detergent companies have modified product formulations to accommodate regional market restrictions. As a result, national sodium tripolyphosphate consumption has been decreasing, thereby reducing soda ash usage. To compensate for the decline, additional soda ash has been added to detergents as alternate medium-strength builders such as in synthetic zeolites and in sodium silicates. Despite the growth of liquid detergents, which represent about 40% of all home laundry detergents, the net effect is that soda ash consumption in the soap and detergent sector remains strong.

Water Treatment.—**Chemicals and Chemical Preparations, Not Elsewhere Classified.**—Soda ash is used to chemically alter the pH of municipal and industrial water supplies and as a precipitant to remove impurities in brine and industrial-process water. In the basic water treatment process, soda ash is added to adjust the acidity or alkalinity of water. Generally, it is added to acidic water to raise the pH and reduce the corrosivity of the water and the accumulation of mineral scale, thereby extending the life of metal pipes and equipment. One example of this application is in swimming pool chemicals where soda ash is added to adjust the pH of the water.

As a precipitant, it removes calcium and magnesium ions and other contaminants from water, which lessens hardness. Most chlorine and caustic soda manufacturers pretreat the sodium chloride-rich brine feedstock with soda ash to remove any calcium and magnesium impurities, thereby improving feedstock composition and product quality.

Since 1987, when the Bureau of Mines began collecting reported soda ash consumption data, a certain quantity of soda ash equivalent contained in purge liquors, soda liquors, and mine waters has been sold to coal-fired power plants for process-water treatment. These data are included under the water treatment category rather than under flue gas desulfurization.

Another unique soda ash application in water treatment involves the treatment of surface waters (e.g., lakes and rivers) contaminated from acid rain or natural causes. Although soda ash is a more expensive alkali compared with less expensive calcium-based reagents such as limestone, soda ash reportedly is more effective than lime in neutralizing the effects of acidification. The concept has been used in lakes in Sweden and New York with positive results; however, the practice has been criticized for merely treating the result of acid rain rather than attempting to prevent the spread of pollution from the source, which would involve flue gas desulfurization. The total quantity of soda ash used for all water treatment applications is only about 1% of total soda ash demand.

Flue Gas Desulfurization.—Flue gas desulfurization is a method used to reduce sulfur dioxide emissions in stack gases from the burning of fuel. Soda ash and other soda ash-based compounds such as sodium bicarbonate and sodium sesquicarbonate are very effective dry sorbents of sulfur and nitrogen compounds. Compared to calcium-based compounds such as lime and limestone, soda ash-based scrubbing reagents have been proven to be more effective scrubbers because of their greater surface area that enhances the reaction with sulfur and nitrogen; however, soda ash remains more expensive and geographically restrictive than calcium materials. Most of the power plants that burn high-sulfur coal are located east of the Mississippi River where plentiful limestone quarries can be mined more economically for shorter transport distances than soda ash produced in the West. Therefore, the quantity of soda ash sold for this end use is restrictive because of the economic advantages of lime and limestone. Some soda ash, however, is blended with lime for use in the dual-alkali process. The flue gas desulfurization market is 3% of total domestic soda ash sales.

Outlook.—Domestic soda ash consumption is forecast to decline slightly in the short term as more glass cullet is collected and recycled for reuse by the glass container manufacturers, the largest soda ash-consuming sector. Because many of the end uses are mature, soda ash consumption tends to parallel population and gross national product trends. In addition, many of the synthetic soda ash plants in the world will continue to encounter environmental problems that may force some of the antiquated facilities to close, thereby enabling the U.S. producers of natural soda ash to export additional quantities. Exports of U.S. soda ash are forecast to grow throughout the remainder of this century.

Table 1.—Salient soda ash statistics

(Thousand metric tons and thousand dollars)

	1970	1975	1980	1985	1990
United States:					
Production[1]	6,435	6,468	7,507	7,721	9,156
Value[e] [1]	$149,165	$300,886	$768,168	$622,253	$836,188
Production, Wyoming trona	—	7,101	11,708	10,726	14,665
Exports[2]	305	480	992	1,584	2,392
Value[2]	$12,007	$45,822	$121,945	$173,937	$346,693
Imports for consumption	—	2	16	51	146
Value	—	$341	$2,389	$8,089	$20,495
Stocks, Dec. 31, producers'	51	49	121	355	287
Consumption:					
Apparent[4]	6,137	5,974	6,472	6,125	6,844
Reported	NA	NA	NA	NA	6,527
World: Production	19,133	23,365	28,346	29,142	32,273

[e] Estimated. NA Not available.

[1] Includes natural and synthetic. Natural only, and soda liquors and mine water converted to soda ash equivalent in 1987 and thereafter: 63,469 tons in 1987; 73,365 tons in 1988; 95,027 tons in 1989; and 111,894 tons in 1990.

[2] Export data for 1986-1988 were adjusted by the Bureau of Mines to reconcile data discrepancies among the Bureau of the Census, the American Natural Soda Ash Corp., and Statistics Canada.

[3] Less than ½ unit.

[4] Defined as production - exports + imports plus or minus industry stock changes.

Table 2.—Soda ash consumption by the U.S. chemical industry

(Thousand metric tons)

	1970[e]	1975[e]	1980[e]	1985[e]	1990
Chemicals[1]	1,796	1,479	1,294	1,361	1,573
Soaps and detergents	172	299	453	544	835
Water treatment	181	181	227	272	91
Flue gas desulfurization	NA	NA	NA	159	207
Total chemicals demand	2,149	1,959	1,974	2,336	2,706
Total U.S. primary demand[2]	6,137	5,974	6,472	6,125	6,844

[e] Estimated. NA Not available; included in "Total."

[1] Includes primarily sodium bicarbonate, sodium chromate, sodium fluoride, sodium hydroxide, sodium phosphates, and sodium silicates.

[2] Also known as apparent consumption (production + imports - exports plus or minus stock changes.)

Sodium Sulfate

By Dennis S. Kostick

Background.—Sodium sulfate is obtained from natural underground brines and as a byproduct from various chemical and industrial manufacturing processes. These manufacturers include ascorbic acid, boric acid, cellulose, chromium chemicals, lithium carbonate, rayon, resorcinol, and silica pigments. The byproduct sodium sulfate is recovered as a waste product from these operations and sold at any price to ensure prompt sale. As a result, the natural sodium sulfate producers set their prices accordingly.

Approximately one-half of domestic sodium sulfate production is from natural sources. Three companies operating a total of three plants in California, Texas, and Utah compose the U.S. natural sodium sulfate industry that has a combined annual nameplate production capacity of 404,000 metric tons. Fifteen companies operating 16 plants recover byproduct sodium sulfate in 11 States. This industry has an aggregate annual nameplate capacity of about 432,000 tons.

The largest use of sodium sulfate is for soap and detergent manufacturing, which represents about 60% of total domestic consumption. Its use in the pulp and paper industry accounts for about 28%, and glass 4%. The remaining miscellaneous end uses include ceramics, feed supplements, printing inks, sulfonated oils, textile dyeing, veterinary medicines, and viscose sponges.

Chemical Industry Consumption.—Although sodium sulfate is used chemically in the kraft pulping process, in which sodium sulfate is converted to sodium sulfide that dissolves lignin binding cellulose fibers together, only the soap and detergent and other miscellaneous chemical uses compose the uses listed under SIC 28. These two sectors represent about 68% of total domestic sodium sulfate consumption.

Soaps and Detergents.—**Soap and Other Detergents, Except Specialty Cleaners.**—The soap and detergent industry consumes an estimated 60% of the domestic sodium sulfate supply. Anhydrous sodium sulfate sold to the soap and detergent industry is a high-quality, low-impurity, extremely white powder. Although it is reported that sodium sulfate improves detergency because of its effect on the colloidal properties of the cleansing formulation, sodium sulfate generally has been added as a filler in powdered home laundry detergents. Approximately 20% of the ingredients in a typical box of detergent is sodium sulfate. Because of its extreme whiteness, high-grade sodium sulfate provides an esthetic appearance to the detergent product. Its inertness and bulk density have a psychological effect on consumers, who believe that they have purchased more product for their money.

The pulp and paper industry traditionally had been the largest consumer of sodium sulfate, followed by detergent use as the second largest. The trend changed in the mid-1980's when environmental legislation forced most pulp mills to recover and recycle the sodium sulfate that historically had been discharged in waste effluent. In addition, the legislation forced the phosphatic detergent manufacturers to change their formulations because of environmental considerations. As a result, more inert sodium sulfate was added to many powdered home laundry products, thereby increasing sodium sulfate consumption.

The public concern regarding the growing volume of landfill waste in the late 1980's prompted most detergent manufacturers to modify formulations to reduce the quantity of detergent in the package as well as the size of the package itself. The strength of the detergent was concentrated to compensate for the reduced quantity. These new formulations required very little filler, thereby reducing sodium sulfate consumption. In addition, the liquid detergent sector, which composes about 40% of all home laundry detergents, uses no sodium sulfate at all.

Chemicals and Chemical Preparations, Not Elsewhere Classified.—Several miscellaneous industrial inorganic chemicals use sodium sulfate in their manufacture, including potassium sulfate, sodium hyposulfite, sodium sulfide, sodium silicate, and sodium aluminum sulfate, all of which have unique end uses. Specific data on sodium sulfate consumption in individual end uses is not available.

Other miscellaneous end uses of sodium sulfate are classified in other SIC chemical categories. Although the quantity of sodium sulfate used is undetermined, the uses and categories are textile dyeing pigments (SIC 2816, Inorganic Pigments), veterinary medicines (SIC 2834, Pharmaceutical Preparations), sulfonated oils (SIC 2869, Industrial Organic Chemicals, Not Elsewhere Classified), and printing ink (SIC 2893, Printing Ink).

Outlook.—Because of the environmental problems associated with pulp mill discharges and detergent reformulations requiring less sodium sulfate, the demand for sodium sulfate is forecast to remain stagnant or decline slightly in the short term. Some growth is expected in the textile industry, which historically has used salt in the dyeing process; but compared with salt, sodium sulfate is not as corrosive to textile manufacturing equipment, and thus preferred.

Table 1.—Salient sodium sulfate statistics

(Thousand metric tons and thousand dollars)

	1970	1975	1980	1985	1990
United States:					
Production[1]	1,246	1,113	1,033	736	713
Value[2]	$25,107	$50,886	$71,081	$74,792	$64,244
Exports	50	70	117	108	62
Value	$1,668	$6,144	$12,740	$11,899	$6,704
Imports for consumption	244	258	209	177	162
Value	$4,753	$12,624	$13,242	$14,492	$13,155
Stocks, Dec. 31, producers	31	28	30	28	39
Apparent consumption	1,452	1,297	1,121	831	798
World: Production	3,844	4,443	4,531	4,509	4,870

[1] Includes natural and synthetic. Total production data for synthetic sodium sulfate, obtained from the Bureau of the Census, was revised in Dec. 1990 M28A Inorganic Chemicals, Current Industrial Report.

[2] The value for synthetic sodium sulfate is based upon the average value for natural sodium sulfate.

Table 2.—Sodium sulfate[1] consumption by the U.S. chemical industry[2]

(Thousand metric tons)

	1970	1975	1980	1985	1990
Soaps and detergents	259	259	437	318	450
Other[3]	141	67	79	20	60
Total chemicals demand	400	326	516	338	510
Total U.S. primary demand	1,452	1,297	1,121	831	750

[1] Includes natural and synthetic sodium sulfate.

[2] Estimated using data from "Chemical Profile" issues on sodium sulfate by Chemical Marketing Reporter for 1971, 1975, 1978, 1980, 1986, and 1989.

[3] Includes ceramics, chemicals (potassium sulfate, sodium hyposulfite, sodium sulfide, sodium silicate, and sodium aluminum sulfate), feed supplements, printing inks, sulfonated oils, textile dyeing, veterinary medicines, and viscose sponges.

Strontium

By Joyce A. Ober

Background.—The majority of strontium is consumed as strontium chemicals are derived from celestite, an ore consisting primarily of strontium sulfate. Strontianite, another mineral that is mostly strontium carbonate, could be a more attractive source but generally does not occur in large, economic deposits.

Celestite is mined from sedimentary deposits located worldwide. Mexico is the largest producer; Iran, Spain, Turkey, and the United Kingdom also produce celestite. Strontium chemicals are produced by Germany, Japan, Mexico, the Republic of Korea, and the United States.

Chemical Products Corporation (CPC) is the only U.S. company that imports celestite as feedstock for its production of strontium chemicals. CPC produces strontium carbonate and strontium nitrate at its plant in Cartersville, GA. Other companies consume strontium carbonate as feed material in the production of additional strontium compounds. Mallinkrodt Inc., St. Louis, MO, produces strontium chloride, and Chemical Pigments Corp., Beltsville, MD, produces strontium chromate. A few other companies produce downstream chemicals, but on a small scale.

The United Kingdom was the world's main source of celestite until 1941, when World War II disrupted shipping lines. Subsequently, since deposits in Spain and Mexico were developed, the United Kingdom has lost its dominance in celestite trade. Imports of celestite are significantly less than they were 20 years ago. At that time FMC Corp., Modesto, CA, as well as CPC, produced strontium carbonate, and thus more celestite was required to meet production requirements. FMC quit producing strontium chemicals in 1984. Currently, the majority of celestite consumed in the United States comes from Mexico. Although Mexican reserves have not been precisely determined, they are believed to be vast.

Imports of strontium carbonate have risen steadily over the past 15 years. Mexico, fast becoming a leader in strontium carbonate trade; has recently replaced Germany as the primary source of U.S. strontium carbonate imports and is also the leading source of U.S. imports of strontium nitrate.

Exports of strontium chemicals, negligible until very recently, are about 10% of the volume of imports.

Chemical Industry Consumption.—Because so few companies are involved in the production of specific strontium chemicals, production and consumption information are withheld to avoid disclosing company proprietary data.

Strontium carbonate is by far the most important strontium chemical, followed by strontium nitrate. Strontium carbonate, the initial product recovered through processing celestite, is the raw material for all other strontium compounds. Celestite is converted to strontium carbonate using the black ash process in which crushed celestite is mixed with coal and heated in kilns to about 1,100° C to convert the insoluble strontium sulfate in the celestite to water-soluble strontium sulfide. Strontium sulfide is then dissolved in water, and the resulting water is filtered. Carbon dioxide is passed through the sulfide solution, or soda ash is introduced, to cause strontium carbonate to precipitate from solution. Strontium carbonate is then filtered, dried, ground, and packaged. The sulfur released through this process is recovered either as elemental sulfur or in other byproduct sulfur compounds.

Strontium nitrate is formed through the reaction of strontium carbonate with nitric acid. Strontium halides are also formed through the reaction of strontium carbonate with the appropriate mineral acids. A water-soluble chromate solution and strontium carbonate react to precipitate strontium chromate. The chromate may also be produced by reacting chromic acid with a strontium hydroxide solution.

The largest end use of strontium carbonate is in the production of color television picture tube faceplate glass. Strontium carbonate is added to the glass melt, where it is converted to strontium oxide and performs the function of blocking X-ray emissions from the energized tube. About 70% of all strontium consumption is for this use.

Another ceramic and glass application is in the production of permanent ceramic ferrite magnets. Strontium ferrites are produced through the sintering of strontium carbonate, iron oxide, and crystal growth inhibitors at 1,000° C to 1,300° C. The resulting material is ground, mixed with a binder, and pressed into rigid, semirigid, or flexible permanent magnets. Smaller quantities of strontium carbonate are used in the electrolytic production of zinc to remove lead impurities.

Strontium nitrate is used in pyrotechnic devices such as fireworks, distress signals, and tracer bullets because of the bright red flame it produces when burning. Strontium chromate is used in corrosion-resistant paints, and strontium chloride is used in temperature-sensitive toothpastes.

Although consumption has altered significantly since the invention of color television, pyrotechnics had been the most consistent and largest end use for strontium chemicals. The use of strontium nitrate in pyrotechnics continues, but the quantity of material consumed has been dwarfed by the tonnages required as color television has gained in popularity. Strontium requirements in other end uses remain relatively stable, while consumption in faceplate glass continues to grow as color television sales and the average size of television screens increase.

Outlook.—Continued growth in demand for strontium chemicals is expected over the short term; however, changes in television technology and particularly the development in flat-screen technology could have a negative impact on the demand for strontium carbonate. Consumer electronics companies have been working to perfect a large-screen flat display that would reduce the bulk of a television set. If and when this development reaches the market, demand for strontium carbonate from the television will diminish and possibly be totally eliminated. At that time pyrotechnics may once again be the largest consumer of strontium chemicals.

Table 1.—Salient strontium statistics

(Metric tons of contained strontium unless otherwise noted[1])

	1970	1975	1980	1985	1990
United States:					
Production, strontium minerals	—	—	—	—	—
Imports for consumption:					
Strontium minerals	33,800	19,600	15,400	15,000	21,500
Strontium compounds	NA	1,600	1,480	3,710	11,800
Exports[2] (compounds)	NA	NA	NA	NA	1,300
Shipment from Government stockpile excesses	4,050	—	—	—	—
Prices, average value of mineral imports at port of exportation, dollars per ton	$24	$42	$61	$97	$86
World production[3] (celestite)	59,900	53,100	95,000	163,000	235,000

NA Not available.

[1] The strontium content of celestite is estimated to be 43.88%, which is used for conversions.

[2] Export data were obtained from the Journal of Commerce Port Import/Export Reporting Service.

[3] Excludes China and the former U.S.S.R.

Sulfur

By Joyce A. Ober

Background.—Sulfur, through its major derivative sulfuric acid, ranks as one of the more important elements used as an industrial raw material. It is of prime importance to every sector of the world's industrial and fertilizer complexes. Sulfuric acid consumption has been regarded as one of the best indicators of a nation's industrial development.

The majority of all sulfur is produced from three sources: mining of elemental deposits; refining of crude oil & natural gas; and recovery of sulfuric acid from nonferrous metal smelters. The traditional primary source has been from native sulfur deposits occuring in elemental form that may be mined through conventional mining methods; however, the more important deposits usually use the Frasch process, by which molten sulfur is extracted through wells after being melted with super-heated water. Currently three companies in the United States produce sulfur by the Frasch method from four mines in Texas and in the Gulf of Mexico off the coast of Louisiana.

Other important sources of elemental sulfur are crude oil and natural gas, from which sulfur is recovered during the refining of these energy materials. As environmental controls have become more stringent and the consumption of lower quality crude oil and natural gas containing high percentages of sulfur has increased, the amount of sulfur recovered from these sources has increased tremendously since these statistics were first reported by the U.S. Bureau of Mines in 1938. Although recovered sulfur comes from different types of deposits, the processes through which it is recovered are essentially the same. Sulfur is driven off as hydrogen sulfide (H_2S) and passed through an absorbent solution that is then stripped to yield concentrated H_2S gas. The gas is then burned under controlled conditions that convert about one third of the H_2S to sulfur dioxide (SO_2), which reacts with the remaining H_2S to form elemental sulfur. In the United States, 58 companies recover sulfur at 151 refineries in 26 States and Puerto Rico.

Sulfur is recovered at nonferrous metal smelters in the form of sulfuric acid (H_2SO_4). Byproduct acid is recovered at eight copper smelters and at eight lead, molybdenum, and zinc smelters. Pyrites, H_2S, and SO_2 are also sources of sulfur in other forms.

Sulfur is an internationally traded commodity, and imports to the United States are an important source, comprising 18% to 20% of domestic production over the past 20 years. The major import sources have been Canada and Mexico. Exports have varied from 8% to 15% of domestic production over the same period.

Chemical Industry Consumption.—Ninety percent of all sulfur is consumed as H_2SO_4, the highest volume inorganic acid produced in the United States. H_2SO_4 primarily is produced through burning elemental sulfur to produce SO_2. This gas is subsequently passed over a catalyst where it is converted to sulfur trioxide (SO_3), which is then dissolved in water to form H_2SO_4. Because the gases released during the smelting of nonferrous ores have a high SO_2 concentration, it is possible to recover the sulfur as H_2SO_4 by essentially the same process. A myriad of other sulfur compounds are consumed in various chemical processes, but none comes close to H_2SO_4 and elemental sulfur in quantity or value.

Consumption of sulfur has trended upward practically from the beginning of time. Recent years have continued the trend, overcoming some setbacks from time to time, with recovery within a few years. The largest end use for sulfur and H_2SO_4 has long been in the production of phosphatic fertilizers. This trend has increased over the past 20 years, and in fact has increased from about 51% of total sulfur consumption in 1970 to about 67% in 1990. All agricultural chemicals, including phosphatic fertilizers, nitrogenous fertilizers, pesticides, animal feeds, and other agricultural chemicals, comprised about 71% of all sulfur consumption in 1990. The vast majority was consumed as H_2SO_4.

Other chemical uses for sulfur are listed in table 2, consumption trends varying with end use. Sulfur consumption has tended to increase in drugs and food products; soaps, detergents, and water treatment; and acid storage batteries. Consumption has trended downward in paints and explosives and remained about the same in plastics and synthetics.

Outlook.—Obviously the fortunes of the sulfur industry are closely tied to those of agricultural chemicals and the general health of the world economy. Decreases in the production and consumption of sulfur between 1980 and 1985 were due to a recession in the early 1980's. Production and consumption had recovered by the end of the decade but remain vulnerable to changes in the world economy.

Short-term outlook for sulfur consumption is not very positive. Because consumption of fertilizer and thus sulfur in the United States is not expected to experience much, if any, growth, any possible growth would be for the export fertilizer market. However, worldwide economic conditions are very unstable; and political and economic stability may not return to Eastern Europe and particularly the former U.S.S.R. until the end of the century.

New Government policies limiting fertilizer subsidies have been instituted in India and China, having the immediate effect of curtailing fertilizer consumption. These countries represent the largest markets for exported fertilizers, and the potential for growth in these markets is quite good; but significant growth will probably not resume at least until the mid-1990's.

Table 1.—Salient sulfur statistics

(Thousand metric tons, sulfur content, and thousand dollars unless otherwise specified)

	1970	1975	1980	1985	1990
United States:					
Production:					
Frasch	7,195	7,327	6,390	5,011	3,726
Recovered[1]	1,480	3,017	4,073	5,313	6,536
Other forms	1,034	1,096	1,403	1,285	1,298
Total	9,710	11,440	11,866	11,609	11,560
Shipments:					
Frasch	6,608	6,175	7,400	4,678	3,676
Recovered[1]	1,495	2,949	4,115	5,266	6,483
Other forms	1,034	1,096	1,403	1,285	1,298
Total	9,137	10,220	12,918	11,229	11,457
Exports, elemental[2]	1,456	1,316	1,673	1,365	972
Imports, elemental	1,694	1,927	2,523	2,104	2,571
Consumption, all forms	9,375	10,773	13,659	11,968	13,056
Stocks, Dec. 31: Producer: Frasch and recovered	3,890	5,208	3,094	2,799	1,423
Value:					
Shipments, f.o.b. mine or plant:					
Frasch	$153,809	$304,843	$720,511	$573,570	$335,189
Recovered[1]	$30,725	$104,886	$305,046	$485,084	$479,011
Other forms	$35,958	$50,053	$84,332	$123,937	$117,139
Total	$220,492	$459,782	$1,109,889	$1,182,591	$931,339
Exports, elemental[3]	$33,096	$71,801	$138,852	$189,248	$109,327
Imports, elemental[4]	$34,149	$70,848	$185,866	$199,240	$206,450
Price, elemental, dollars per metric ton, f.o.b. mine or plant	$23.14	$44.91	$89.06	$106.46	$80.14

[1] Includes Puerto Rico and the U.S. Virgin Islands.

[2] Includes exports from the U.S. Virgin Islands to foreign countries.

[3] Includes value of exports from the U.S. Virgin Islands to foreign countries.

[4] Declared customs valuation.

Table 2.—Sulfur consumption by the U.S. chemical industry

(Thousand metric tons)

	1970[1]	1975	1980	1985	1990
Agriculture	4,755	—	—	—	—
Phosphatic fertilizers	—	5,552	8,499	7,872	8,650
Other agricultural chemicals	—	425	634	686	550
Drugs and food products	—	44	36	56	50
Soaps, detergents, and water treatment compounds	—	196	228	215	230
Plastics and synthetic products	420	357	371	314	400
Paints	427	341	257	111	128
Explosives	259	42	13	31	56
Storage batteries (acid)	—	33	34	67	55
Other	1,735	2,192	1,426	906	745
Total chemical demand	7,596	9,182	11,498	10,258	10,864
Total U.S. primary demand	9,375	10,773	13,659	11,968	13,056

[1] Data in 1970 are not comparable to succeeding years.

Talc

By Robert L. Virta

Background.—The mineral talc, a soft, hydrous magnesium silicate, $Mg_6 Si_8O_{22}(OH)_4$, is formed through hydrothermal alteration of ultrabasic rocks and low-grade metamorphism of siliceous dolomites.[1] Talc deposits may contain minor to major amounts of talc as well as magnesite, quartz, chlorite, magnetite, serpentine, anthophyllite, tremolite, dolomite, and actinolite.[2]

Seventeen companies operated 23 mines and 30 mills in 10 States in 1990. Approximately 1.3 million metric tons of talc, valued at $30 million, were mined in 1990. Slightly more than 1.1 million tons of crude and processed talc were sold. Imports and exports of talc were 78,000 tons and 219,000 tons, respectively. Apparent domestic consumption of talc was 1.1 million tons, most being consumed by the ceramics, paint, and paper industries *(table 1).*

Chemical Industry Consumption.—Talc is used by the chemical industry in agricultural products, cosmetics, paint, pharmaceuticals, plastics, soaps, and rubber (table 2). Properties such as softness (1 on the Mohs scale), whiteness, luster, moisture content, oil and grease adsorption, chemical inertness, low electrical conductivity, high dielectric strength, and high thermal conductivity are important for these applications.[3]

Talc serves principally as a carrier to distribute fertilizers, insecticides, herbicides, and fungicides. It also dilutes chemicals to prevent damage from concentrated dosages and acts as an anticaking agent for dry compounds. Talc is used because it is absorbent, disperses in liquids, does not react with insecticides, will not clog equipment when finely ground, and will not abrade nozzles.[3, 4, 5]

Cosmetic-grade talc is used in face powders, body dusting powders, creams, soaps, pharmaceutical products, and medicinal tablets.[6] Talc constitutes over 50% of most cosmetics, the remainder being a combination of oxides, stearates, perfumes, and starch. Talc is used in cosmetics because it is soft, acts as a lubricant, improves the product's hiding power, and retains added perfumes.[4, 7] The paint category covers all varieties: water-base, oil-base, synthetic resins, and lacquers. Talc is used primarily in top coats, industrial paint, and industrial primers in the United States.[8] Talc, particularly when it contains prismatic tremolite, is an excellent reinforcer and greatly reduces cracking in the dry paint film.[3, 4, 9] Talc also reduces settling and separation of components, acts as a flatting agent, is an inexpensive extender for more expensive white pigments, and absorbs oil better than most minerals.[3, 4, 6, 9] Its softness minimizes abrasion of high-speed paint mixers and it disperses well in both oil- and water-based paint.[4, 9]

Talc is used as a filler and reinforcer in plastics, primarily in polypropylene.[4, 10, 11, 12, 13] As a bulk filler, it reduces the amount of resin required, and improves resistance to chemical attack and electrical resistivity. As a reinforcer, it improves a plastic's impact strength, dimensional stability, tensile strength, and creep resistance.[3, 4, 9, 10, 11, 12, 13] Because it is inert it will not react with plastic compounds.

Talc is used by the rubber industry in the production of tires, tubing, sheets, and valves and use in flooring products, backing for textiles, and electric cable insulation.[4] Its major use is as a dusting agent to prevent sticking of the rubber to the mold. As a filler, talc reduces the amount of expensive resins used to produce rubber products, increases the stiffness of uncured compounds, and reinforces the rubber product.[3, 4, 9]

The use of talc in cosmetics and paints has increased over the past 20 years, mainly due to increased production of these products. Its use as an insecticide carrier has decreased because of substitution of other less expensive minerals. Consumption by the rubber industry has declined considerably over the 20-year period, partially because of the controversy over asbestos in talc used for dusting molds. Consumption by the plastic industry has declined, caused partly by market losses to competing minerals such as calcium carbonate, clays, feldspar, mica, silica, and wollastonite.

Outlook.—The major market for talc in the chemical industry will continue to be in paints, although growth is not expected to be large. Demand for talc by the cosmetics industry should remain relatively constant. Although consumption of talc in plastics has declined over the past 20 years, the trend probably will not continue based on the increased demand for plastic products. The lowest potential for growth is in the agricultural and rubber markets.

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Table 1.—Salient talc statistics

(Thousand metric tons and thousand dollars)

	1970[1]	1975	1980	1985	1990
Mine production, crude:					
Tonnage	933	792	1,022	1,078	1,178
Value	$7,773	$7,454	$18,600	$27,768	$30,054
Sold by producers:					
Tonnage	860	767	1,064	968	1,025
Value	$25,980	$16,496	$84,523	$114,542	$121,287
Exports:					
Tonnage	95	143	249	215	209
Value	$5,739	$6,338	$14,963	$14,282	$13,883
Imports:					
Tonnage	27	21	19	43	73
Value	$1,294	$1,471	$3,720	$9,532	$16,182
Apparent consumption: Tonnage[2]	792	722	977	979	1,042

[1] Includes pyrophyllite.

[2] Includes pyrophyllite in apparent consumption.

Table 2.—Talc consumption by end use

(Metric tons)

End use	1970	1975[1]	1980	1985	1990
Agriculture	30,569	38,071	9,979	6,350	6,000
Cosmetics	12,447	28,341	53,524	41,731	36,000
Paint	139,947	127,616	178,712	130,634	155,000
Plastic	NA	NA	99,790	63,503	48,000
Rubber	25,717	14,301	33,659	24,494	20,000

NA Not available.

[1] Includes pyrophyllite.

Thallium

By Thomas O. Llewellyn

Background.—Thallium, a trace element having an estimated average abundance of 2.2 parts per million in zinc sulfide ores, is recovered as a byproduct from flue dust and residues collected in the smelting of zinc as well as copper and lead ores. A number of rare thallium minerals found in nature have no commercial importance as sources of thallium metal.

Prior to 1982, thallium metal and compounds were recovered in the United States by ASARCO Incorporated, Denver, CO, from zinc residues obtained from various sources. ASARCO, the sole domestic refiner of thallium, has not sold thallium metal or thallium compounds since 1981.

The U.S. demand for thallium during the last decade has been met by imports. In 1990, thallium materials were imported only from Belgium.

Chemical Industry Consumption.—Although for many years the major use for thallium was in insecticides and rodenticides, in 1965 the U.S. Department of Agriculture restricted the use of thallium compounds for these products; and apparently all foreign countries have also stopped using thallium sulfate as an ingredient in rodenticides because of its high toxicity to humans. Thallium compounds have limited industrial applications: thallium sulfide in producing photoelectric cells; thallous oxide in the manufacture of glass with high coefficient of refraction; and thallium formate-malonate aqueous solutions (Clerici's solution) in laboratory separation of precious stones from ores by sink and float process. Currently, research and development in the use of thallium-based superconductor formulations represent about 50% of annual thallium consumption.

Thallium metal and its compounds are highly toxic materials that are strictly controlled to prevent a threat to humans and the environment. Thallium and its compounds can be absorbed into the human body by skin contact, ingestion, or inhalation of dust or fumes.

Total thallium consumption for 1990 was 700 kilograms, or about 75% less than in 1970.

Outlook.—The short-term demand for thallium in the United States is expected to fall below the level of 1990. Domestic consumers will continue to depend on foreign sources for the supply of thallium as no U.S. resumption of thallium refinery production is foreseen for the near future.

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Table 1.—Salient thallium statistics

(Kilograms)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Refinery production	W	W	W	W	—
Imports:					
Metal	570	420	24	400	450
Compounds[1]	750	140	44	640	NA
Industry stocks, Jan. 1	W	W	W	W	W
Total U.S. supply	W	W	W	W	W
Distribution of U.S. supply:					
Industry stocks, Dec. 31	W	W	W	W	W
Exports	NA	NA	NA	NA	NA
Demand[e]	2,810	810	1,900	1,040	700
U.S. demand pattern:					
Agriculture	900	—	—	—	—
Eclectrical	1,500	450	1,310	730	430
Pharmaceuticals	90	90	90	40	10
Other	320	270	500	270	260
Total U.S. primary demand	2,810	810	1,900	1,040	700

[e] Estimated. NA Not available. W Withheld to avoid disclosing company proprietary data.

[1] Estimated thallium content.

Tin

By James F. Carlin, Jr.

Background.—Domestic tin mine production has generally been minuscule, accounting for less than 1% of U.S. demand. The United States must rely on imports of refined tin metal for virtually all of its needs. The approximately 35 countries that mine tin are well distributed among most of the world's continents, the greatest concentration of mine activity being in Southeast Asia and South America.

An estimated 200 tin mines in the world use mining methods varying from hand-panning in streams to gravel pump mining to huge dredging operations in lake and ocean beds. Although most of the world's tin mines are located in free enterprise economy countries, a fair number are in countries with centrally planned economies. Many of the world's tin mines are in countries with socialist governments, and are government owned. World tin reserves and resources are deemed adequate to meet the anticipated world demand in the next few decades.

From the mine stage, tin concentrates are usually smelted in the same country, but are shipped around the world to be smelted at particular smelters with special capabilities. These particular capabilities may include the ability to make high-purity tin or to treat low-grade concentrates. In the past two decades a significant world overcapacity of tin smelters relative to tin mines, has created competition for tin smelters to obtain tin concentrate feedstock.

Domestically, the United States has only two or three intermittently active small tin mines. One tin smelter, in Texas City, TX, for decades had treated tin concentrates mostly of foreign (especially Bolivian) origin but closed tin smelting operations in 1989. Consequently, the United States is almost totally dependent on imports to meet requirements, primarily from Bolivia, Brazil, China, and Indonesia.

The huge U.S. Government strategic stockpile has also been a source of tin metal during the past 30 years. From the start of this stockpile in the 1940's, tin has almost continuously been the largest dollar-volume holding of all minerals and metals. Starting in 1960, the sale of excess stockpiles has continued rather steadily and is expected to continue for decades to come, to add to the U.S. tin supply.

Secondary, or scrap tin, an important contributor to supplies, accounts for an estimated 20% of the total tin consumed. Scrap tin is generated partly by detinning new tinplate scrap and used tin cans but mostly from the recycling of tin alloys.

Chemical Industry Consumption.—Tin chemicals, comprising the third major category of tin usage, well behind solder and tinplate, use mostly primary tin, but some secondary tin. Fewer than 10 companies, produce tin chemicals, the top firm being Atochem North America Co.

The major tin chemicals are used for stabilizers for making polyvinylchloride (PVC), for wood preservatives, for fluoridated toothpaste, for antifouling marine paints, and as an anti-abrasion coating for glass bottles.

Typically, the tin ingot is made molten and undergoes a variety of additions and reactions of a proprietary nature to produce a variety of mostly organic and some inorganic tin chemicals in either the stannous or the stannic valence states. These chemicals are then utilized in a variety of ways, in which the tin chemical usually comprises a very small component of the final product. For example, colorless tin tetrachloride is sprayed on glass bottles, in extremely thin coating to prevent abrasion.

Since the 1950's, when research efforts resulted in several new tin chemical applications, the tin chemical field has been growing gradually. From 1970 to 1985, tin usage in this category almost tripled, although by 1990 the general economic slowdown had caused a moderate decline. The growth largely resulted from new applications developed by the International Tin Research Institute in the United Kingdom, a laboratory funded since the 1930's by the major tin-producing countries.

Generally speaking, tin has been unfettered by environmental or OSHA-type restrictions as almost none of its applications has been found to be harmful. However, a tin chemical was partially banned in the late 1980's for leaching out and killing shellfish when used for painting boat hulls to prevent barnacles from forming in certain shallow water conditions. Consequently, this antifoulant tin chemical paint was banned only from use on small boats, a small fraction of total tin chemical usage.

Domestically, the tin chemical industry is dominated by Atochem North America, a French-owned firm that often uses more than 80% of domestic tin chemicals. Although substitutes are possible, especially for lead, in some chemical applications they sometimes lack the same quality. Foreign competition seems modest, although Germany and Japan have especially strong tin chemical industries.

Outlook.—Continued moderate growth in tin chemicals is expected when the current economic slowdown is reversed. Tin chemical research is active in many countries, but no single project seems ready to gain major commercial acceptance soon.

Table 1.—Salient tin statistics

(Metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Smelter production	4,742	6,500	3,000	4,302	—
Government sales	3,123	594	25	3,005	2,145
Secondary (old scrap)	12,083	9,130	1,703	10,037	13,200
Imports for consumption (metal)	51,366	44,366	45,982	33,830	33,810
Industry stocks, Jan. 1	31,086	26,151	10,704	9,679	14,668
Total U.S. supply	102,400	86,741	61,414	60,853	68,823
Distribution of U.S. supply:					
Industry stocks, Dec. 31	26,732	25,684	12,101	12,359	17,671
Exports, metal	4,253	3,596	595	1,429	658
Industrial demand	66,783	53,693	46,718	45,934	50,494
U.S. demand pattern:					
Cans and containers	23,811	19,230	13,940	8,805	11,115
Transportation	8,015	6,530	5,770	6,372	7,610
Machinery	7,436	6,260	4,930	5,044	6,728
Electrical products	11,250	7,970	7,800	9,311	9,133
Construction	10,485	7,430	6,140	6,290	7,210
Chemicals	3,196	4,390	5,810	7,980	6,547
Other	2,590	1,883	2,328	2,132	2,151
Total U.S. industrial demand	66,783	53,693	46,718	45,934	50,494

Titanium

By Joseph M. Gambogi

Background.—Titanium comprises about 0.6% of the earth crust and occurs primarily in the minerals anatase, brookite, ilmenite, leucoxene, perovskite, rutile, and sphene. Titanium metal is well known for its use in commercial and military aerospace because titanium alloys exhibit excellent corrosion resistance and have high strength-to-weight ratios. Although titanium is best known for its use as a metal, over 90% of titanium is consumed in pigment form as titanium dioxide (TiO_2). TiO_2 pigments are typically white in color and have a very high refractive index. In the chemical industry, the largest applications for TiO_2 pigments are in paints, paper, and plastics. Minor uses of titanium minerals and pigments include ceramics, coated fabrics and textiles, floor coverings, printing inks, roofing granules, rubber, specialty glass, and welding-rod coatings.

Titanium-bearing minerals are located throughout the world; however, the largest commercial deposits are currently found in Australia, Canada, Norway, and the Republic of South Africa. The leading producers of titanium ores and concentrates are Richards Bay Minerals in South Africa; QIT-Fer et Titane Inc. in Canada and South Africa; Renison Consolidated Ltd. in Australia; and Titania A/S in Norway. There are three domestic producers of titanium ores: E.I. du Pont de Nemours & Co., Inc. (Du Pont), RGC (USA) Mineral Sands, Inc. and P.W. Gillibrand. Du Pont and RGC operate heavy mineral sands operations in Florida; Gillibrand operates a sand and gravel operation in California to produce a titanium mineral concentrate byproduct.

The world's five largest TiO_2 pigment producers are the following: Du Pont, having plants in the United States and Mexico; Tioxide, having two U.S. plants and facilities in Australia, Canada, France, Italy, Spain, the United Kingdom, and the Republic of South Africa; SCM Chemicals, having plants in the United States, the United Kingdom, and Australia; Kronos Inc., having producing plants in the United States, Belgium, Canada, Germany, and Norway; and Kemira, having facilities in the United States and Finland.

U.S. companies, mainly Du Pont, SCM, Kronos, and Kerr-McGee, own or control about one-half of world productive capacity for TiO_2 pigments. The remaining portion is owned principally by large chemical firms or groups such as Bayer AG of Germany, Ishihara Sangyo Kaisha Ltd. (ISK) of Japan, and Kemira Oy of Finland. The top five producers in the world hold almost two-thirds of global capacity.

Historically, the demand for titanium in the chemical industry has closely followed the economy. In the recessionary period of the late 1970's and early 1980's, demand for titanium pigments was depressed; but the growth in the economy during the 1980's caused increased demand. World demand growth has been estimated at 6% per year from 1982 to 1989. The global demand rate was twice the predicted rate, causing shortages of titanium feedstocks and titanium pigments in the late 1980's. Many producers began expansion programs during the late 1980's; however, the completions of these expansions were delayed as the economy had once again slowed. Subsequently, the current situation is one of depressed demand and surplus capacity. TiO_2 pigment output in 1991 came from about 60 separate facilities ranging in annual capacity from a few thousand metric tons to nearly 300,000 tons. In 1991, the United States accounted for about 40% of the world's TiO_2 pigment capacity.

Chemical Industry Consumption.—TiO_2 pigment is characterized by its purity, refractive index, surface properties, and particle size, which is critical and controlled within the range of about 0.2 to 0.4 micrometer to develop optimum pigment properties. The superiority of TiO_2 as a white pigment is due mainly to its high refractive index and resulting light-scattering ability, which impart excellent hiding power and brightness. TiO_2 pigments are produced as two major types—rutile and anatase. These pigment types are not related to the minerals rutile and anatase. Rutile and anatase pigments are chemically similar but differ in crystal form. Rutile-type pigment, which is less reactive with paint vehicles in sunlight than the anatase type, is preferred for use in outdoor paints. Anatase pigment, which has a bluer tone than the rutile type and is somewhat softer, is used mainly in indoor paints and paper manufacturing. Depending on the manner in which titanium pigment is produced and subsequently finished, titanium pigments can exhibit a range of functional properties including opacity, durability, dispersion, and tinting.

Ilmenite is by far the most abundant ore, the most commercially viable deposits being placer (sand) deposits. To a lesser degree, titanium ore is available from hard-rock deposits in massive ore bodies, and open-pit mining is normally practiced. The mining of sand deposits of titanium minerals, is usually done by a dredge that floats in its own pond, digging forward and stacking tailings aft. Rough concentration, the separation of heavy minerals from the lighter quartz-feldspar-mica fraction, is usually accomplished by wet-gravity methods.

The final wet-mill concentrate is dried, usually in a rotary kiln, prior to further treatment. Ilmenite and rutile are usually removed together by electrostatic separation. The ilmenite-rutile conductor fraction of dried wet-mill concentrate is then subjected to high-intensity magnetic separation, yielding a final ilmenite product.

Depending on the nature of the deposit and the method of processing, an ilmenite concentrate may be upgraded to form a higher grade TiO_2 feedstock. In one method, ilmenite is smelted in an electric furnace to produce a slag containing 75% to 85% TiO_2 and a pig iron byproduct that is suitable for use by the iron and steel industry. Another method produces a material referred to as synthetic rutile that is produced through the chemical separation of TiO_2 from ilmenite.

TiO_2 pigment is generally produced commercially by two methods that sometimes require different raw materials. The two methods are referred to as the chloride process and the sulfate process. The decision to use one process over the other is based on a number of factors including raw material availability, freight, and waste disposal costs. Recoveries of TiO_2 in pigment are approximately 90% for chloride and 80% to 85% for sulfate process plants. The crude form of the pigment is milled to produce a controlled distribution of particle size and surface-treated or coated to improve its functional behavior in different media. Some typical treatments include alumina, silica, and organic treatments.

In the sulfate process, ilmenite or titanium slag is reacted with sulfuric acid, and a portion of the iron sulfate formed may be crystallized and removed. Titanium hydroxide is precipitated by hydrolysis, filtered, and calcined.

In the chloride process, rutile is converted to titanium tetrachloride ($TiCl_4$) by chlorination at 850° to 950° C in the presence of petroleum coke. $TiCl_4$ can be used either in making pigment or, with additional purification, for reduction to metal. In making pigment, the $TiCl_4$ is oxidized with air or oxygen at about 1,000° C, and the resulting fine-size TiO_2 is calcined at 500° to 600° C to remove residual chlorine and any hydrochloric acid that may have formed in the reaction. Aluminum chloride is added to the $TiCl_4$ to assure that virtually all of the titanium is oxidized in the rutile crystalline form.

TiO_2 pigments account for over 95% of all prime white pigments. The largest end uses for TiO_2 pigments in the United States are paints and coatings (46.6%), paper (26.4%), and plastics (16.8%). Rubber, printing ink, cosmetics, and miscellaneous other end uses make up the remainder of domestic demand.

Paints and Coatings.—In the paints and coatings industry, TiO_2 is used in both white and color formulations. The coatings market is made up of original equipment manufacturers (OEM), architectural coatings, and special-purpose applications. The OEM portion of the market includes the automotive (transportation), appliances, containers, and wood. Automotive applications require haze-free high gloss, high durability, and brightness. Industrial applications seek good heat resistance, gloss, and chemical and abrasion resistance. Architectural applications include interior and exterior coatings, including lacquers and stains, which focus on high durability, gloss, and hiding power. Special purpose coatings include marine, traffic, refinish, and aerosol coatings.

Plastics.—The plastics industry primarily consumes rutile grades of pigment, TiO_2 pigments represent the majority of all inorganic pigments used. Although in comparison to mineral fillers and extenders their volume is relatively small, TiO_2 pigments have a much higher unit value. Titanium dioxide pigments are used in the polyolefins industry in a variety of applications. They serve to provide opacity and act as barriers against ultraviolet light degradation. Most TiO_2 pigments are introduced as pelletized concentrates containing up to 50% TiO_2 in a carrier resin; however, liquid and dry concentrates also are used by the industry. The final TiO_2 content is normally 3% to 25% of the finished product.

The plastics market is often broken down by process type, including film, blow molding, injection molding, fiber, and extrusion. Films, which contain 2% to 12.5% TiO_2, have some familiar end-use applications including diaper liners, frozen food packaging, shrink wrap, and plastic bags. Blow-molded products, which normally contain 1.5% to 2.0% TiO_2, have typical end uses as plastic containers for bleaches, shampoos, motor oils, etc. Injection-molded products include, for example, housewares, appliances, and furniture. The fiber category consists of tapes and filaments. Extrusions, which are characterized by long product runs of single profiles, include automotive and appliance applications.

Paper.—The paper industry consumes TiO_2 pigments as fillers and in coatings, and anatase-grade pigment is often used because it is less abrasive to paper-making machinery. Paper products contain a high percentage of minerals as filler material; however, TiO_2 is estimated to be less than 5% of the total by weight. Titanium pigments are used in paper products to give opacity and brightness, and typical TiO_2 content is estimated to be 1% to 3% of the dry weight of paper. Titanium pigment content is highest in coated products, for example, laminates used in furniture and construction applications and coatings for paperboard. Recycled paper fibers are coated with pigment to provide a printing surface for graphics; whereas coated paperboard is used to construct boxes for packaging merchandise such as grocery products, clothing, tools, etc.

Miscellaneous.—In addition to its use in the pigment industry, $TiCl_4$ is used to produce a number of organic titanium compounds and titanium metal.

Titanium dioxide is well known for its ability to absorb ultraviolet radiation. A recent development in the pigment market is micronized TiO_2, which has a particle size of less than 1 micrometer and can be used to block ultraviolet radiation, but may be transparent to visible light. Several producers are marketing this type of product for use in cosmetics and sunscreens.

Most countries have in place, or are in the process of implementing, stringent controls on the discharge from both sulfate- and chloride-base TiO_2 production facilities. The cost of conforming to the regulations has resulted in the closure of several facilities. Currently, these facilities have included only sulfate-process plants, but in the future may include chloride-process plants. Sulfate pigment producers have met the increased regulation through a variety of means including acid recycling, neutralization, and conversion to the chloride process. Effluent wastes generated in the sulfate process include iron sulfate and both strong and weak acids. Acid produced in the sulfate process can be concentrated and recycled or, as an alternative, neutralized to produce gypsum suitable for use in wallboard and cement applications. Some of the iron sulfate generated in the sulfate process can be beneficiated for use in water treatment and in the production of iron oxide pigments. The treatment or recycling of wastes increases both capital costs and operating costs.

Wastes generated in the chloride process are primarily iron chlorides as well as other metal chlorides. Some iron chloride is suitable for use by the water treatment industry, but a substantial portion is unusable and must be disposed. One method of disposal, deep-welling, has raised environmental concerns and is being phased out. Another alternative is to neutralize the iron and minor metal chlorides to form nonhazardous insoluble metal hydroxides. Some hydrochloric acids produced in the chloride process can be recycled, neutralized, or sold as commercial products.

An important issue affecting TiO_2 pigment consumption is substitution. Although there are no absolute substitutes for TiO_2, some applications will permit a reduction in the amount of TiO_2 pigment by the addition of mineral extenders, the most common being calcium carbonate, kaolin, and talc.

Outlook.—Ore resources will continue to be readily available for some time. Although natural rutile will continue to decline in importance as a feedstock, competition will increase between titanium slag and synthetic rutile as feedstocks. In the short term, the domestic demand growth has been estimated to be about 3% per year.

The short term outlook for titanium pigments is largely dependent on the world's economy. Several industry estimates of demand growth are between 2% and 3%; however, significantly higher growth is forecast for Asia and Latin America. Although environmental restrictions may force the closure of some existing capacity, recent expansions should inhibit the development of additional capacity. Within the next few years, supply and demand are expected to come into balance.

Table 1.—Salient titanium statistics

(Thousand metric tons of titanium content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Nonmetal:					
Mine production[1]	250	227	179	W	W
Imports:					
Concentrates	193	219	311	355	459
For metal production	(14)	(15)	(21)	(21)	(25)
Pigment	31	14	51	99	83
Industry stocks, Jan. 1	456	300	377	193	251
Shipments of Government stockpile excesses	—	—	—	—	—
Total nonmetal supply	931	759	918	W	W
Total U.S. supply	957	787	958	W	W
Distribution of U.S. supply:					
Nonmetal:					
Exports	15	5	32	70	110
Industry stocks, Dec. 31	473	356	513	214	290
Government stockpile acquisitions	3	—	—	—	—
Apparent demand	440	399	374	562	621
U.S. demand pattern, nonmetal:					
Paints	250	234	169	302	304
Paper products	71	75	93	114	165
Plastics and synthetic products	39	29	40	91	103
Rubber products	13	11	8	9	9
Ceramics and glass	9	8	8	4	3
Fluxes	10	9	6	5	6
Other	48	33	49	37	31
Total nonmetal demand	440	399	373	562	621

W Withheld to avoid disclosing individual company proprietary data.

[1] Contains a mixed product containing ilmenite, leucoxene, and rutile.

Tripoli

By Gordon T. Austin

Background.—Tripoli, as broadly defined, is composed of extremely fine-grained crystalline quartz in various stages of aggregation. The particle sizes usually range from 1 to 10 micrometers, but particles as small as 0.1 to 0.2 micrometers are common. Commercial tripoli contains 98% to 99% silica and minor amounts of alumina (as clay) and iron oxide. Tripoli may be white or shades of yellow, brown, or red, depending on the percentage of iron oxide. One company markets a pure black tripoli that is actually novaculite.

In the United States three firms produce tripoli in three States. Malvern Minerals Co., Garland County, AR, produces crude and finished materials. American Tripoli Co. produces crude material in Ottawa County, OK, and finished material in Newton County, MO; and Unimin Specialty Minerals Inc. operates the Alco and Tams plants, in Alexander County, IL; which produce both crude and finished products. Additionally, Keystone Filler and Manufacturing Co. in Northumberland County, PA, processes rottenstone, a decomposed fine-grained siliceous shale, produced by B.J. Ulrick & Sons, also in Northumberland County, PA.

Historically, tripoli has had unique uses as an abrasive because its hardness and its grains lack distinct edges and corners. As a mild abrasive, it is suitable for use in toothpaste and tooth polishing compounds, industrial soaps, and metal and jewelry polishing compounds. The automobile industry uses it in buffing and polishing compounds in lacquer finishing.

The end-use pattern for tripoli has changed significantly in the past 20 years. In 1970 nearly 70% of the processed tripoli was used as an abrasive; whereas today 70% is used as a filler and extender in paint, plastic, rubber, caulking compounds, and enamel. Additionally, annual consumption of tripoli has declined each year since 1985, consumption in 1990 being only 74% of that in 1985. The consumption of processed tripoli is shown in table 1.

Chemical Industry Consumption.—Tripoli is processed in mills that are jasper lined using flint or jasper pebbled in closed circuit with banks of mechanical classifiers. Material from the mechanical classifiers is fed to micronizing mills in which it is ground and sized at the same time. Material that is 100% minus 10 micrometers and 96% minus 5 micrometers is the smallest particle size sold. Even this very fine particle material is not the results of fragmentation of crystalline particles, but the breaking apart of clusters of quartz crystals, many less than 1 micrometer in size, that are joined at their points. The ultra fine-grained tripoli is a collection of clusters and individual quartz crystals.

The largest use of tripoli in the chemical industry is as a filler and extender in paints, estimated to account for as much as 85% of the tripoli used as filler and extender. Its use in exterior latex paints is as a low-micrometer grade micronized product. In these paints tripoli aids in tint retention, durability, leveling, and flowability. In enamels it permits higher loading with no appreciable increase in vehicle demand and improves sheen. Because of its controlled grain or particle size, paints containing tripoli disperse more easily and results in an uniform film. Additionally, because of its abrasive qualities the paints are more resistive to wear and chemicals than those in which water-ground whitings and other reactive fillers are used.

Plastics, rubbers, and resins each use about 5% of total annual tripoli filler and extender production. It is used extensively in plastics for electrical uses because of its dielectric properties and its effects on flexural and compressive strengths. Its chemical resistance, weatherability, and resistance to salt spray also are important to its use in plastics. Its physical properties allow high loading in most compounds, but its abrasiveness results in high wear in extruding nozzles and molds. The same properties that make tripoli useful as a filler and extender in plastics make it valuable to the rubber and resin industries.

After 5 consecutive years of growth, from 1982 to 1987, the amount of tripoli used as filler and extender in 1990 declined for the third consecutive year. The 10% decline in 1990 followed an 8% decrease in 1989 and an additional 4% decrease in 1988. The average annual consumption of filler-grade tripoli for the past 10 years was 60,953 tons, having a high of 71,160 tons in 1987 and a low of 50,180 tons in 1982.

Because tripoli, which contains essentially 100% crystalline silica, can cause silicosis, it falls under the jurisdiction of the OSHA Hazard Communication Standard. In 1987, the International Agency for Research on Cancer (IARC) determined that crystalline silica is a probable carcinogen for humans. As a result, OSHA is required to regulate materials containing more than 0.1% crystalline silica. To date, these regulations have had no apparent adverse effect on the use of tripoli, but all tripoli must be labeled in compliance with OSHA regulations.

In the filler and extender uses listed, substitutions can be made using ground calcium carbonate, ground silica sand, pyrogenic and precipitated silica, calcined kaolin, and talc.

Outlook.—The use of tripoli as a filler and extender declined an additional 7% in 1991. The use of tripoli in the chemical industry is expected to decline to a level of about 50,000 tons per year and then to stabilize at this level. The decline will be the result of a combination of factors including the concern for possible health risks and economic conditions.

Table 1.—Processed tripoli sold by U.S. producers, by use

Uses	1970	1975	1980	1985	1990
Abrasives:					
Quantity (metric tons)	41,703	38,815	38,352	40,022	24,090
Percentage of total	68	57	39	37	30
Value (thousands)	$1,583	$1,518	$2,253	$3,670	$3,083
Filler:					
Quantity (metric tons)	18,093	27,630	59,909	68,800	56,468
Percentage of total	32	43	61	63	70
Value (thousands)	$545	$1,205	$4,025	$6,452	$11,041
Total:					
Quantity (metric tons)	60,930	68,184	99,261	108,822	80,558
Value (thousands)	$2,156	$2,783	$6,277	$10,122	$14,124

Tungsten

By Gerald R. Smith

Background.—Tungsten metal and its alloys possess high melting points, high density, good corrosion-resistance properties and good thermal and electrical conductivity. In addition, the tungsten carbides are extremely hard and wear-resistant. As a result, most tungsten is consumed in end-use sectors that use these properties effectively. Table 1 illustrates the U.S. tungsten supply-demand patterns, in 5-year increments, for the period 1970-90. As shown, the demand for tungsten in the chemical industry represented an average of about 4% of total demand.

Most of the tungsten chemicals consumed in the United States each year are produced by about five U.S. companies. Exports of tungsten compounds generally ranged from 3% to 5% of total exports of tungsten-bearing materials.

Chemical Industry Consumption.—Tungsten chemicals are used in a variety of ways. Probably the most widely used chemical is sodium tungstate (Na_2WO_4), which is produced commercially from tungsten concentrates as either a crystal or a liquor during the extractive metallurgy process. Na_2WO_4 is employed in the production of phosphotungsten and phosphotungstomolybdic acids for the manufacture of organic dyes and pigments. These brilliant dyes and pigments are important color ingredients in oil- and water-based paints, printing inks, plastics, rubber, waxes, glass, and paper. Their luminescent qualities are particularly useful in the manufacture of phosphors for X-ray screens and television picture tubes. A minor application for Na_2WO_4 is in the manufacture of fire-proofing textiles.

Calcium tungstate ($CaWO_4$), like Na_2WO_4, is also used to produce phosphorescent materials and is more frequently found in these end-use chemicals than is Na_2WO_4. Its strong fluorescence when exposed to ultraviolet radiation can be used advantageously in its detection and separation as the major constituent in the natural mineral scheelite. Pure $CaWO_4$ salt crystals can be produced by extractive metallurgy processing of most tungsten ore deposits. Phosphors produced from $CaWO_4$ are employed in color television tubes, lasers, fluorescent lights, tubes for high-voltage signs, and oscilloscopes.

In addition to phosphor-related industries, tungsten chemicals also are used in the catalyst industry. Ammonium paratungstate (APT), ammonium metatungstate (AMT), isopolytungstate chemicals (those having an anion containing only tungsten with hydrogen and oxygen), and Na_2WO_4 are all used to produce petroleum refining catalysts for hydrocracking procedures. Typically in hydrocracking processes, catalysts in the form of nickel-tungsten are located on a zeolite or alumina base. APT is produced as a major intermediate material in the processing of tungsten ore concentrates to the important downstream tungsten metal powder and tungsten carbide powder materials. AMT is produced from APT by adjusting the ammonia to tungsten ratio.

The other major use of tungsten chemicals is in the metal coating industry. Using vapor deposition techniques, tungsten hexachloride (WCl_6) is chemically reduced to deposit thin films of metallic tungsten on ceramics and graphite, as well as onto metal bearings, dies, rolls, and gauges. The resulting coating effectively utilizes tungsten's superior properties of high-temperature strength, resistance to corrosion and wear, and good electrical conductivity. WCl_6 is generally synthesized from the individual elements but can be prepared by the reaction of tungsten oxide (WO_3) with phosphorus pentachloride (P_2O_5).

High-purity tungsten hexafluoride (WF_6) has become useful as a medium for vapor-depositing thin films of tungsten on semiconductor devices. Such coatings provide some of the electrical wiring circuitry on these devices. The hexafluoride is prepared in a manner similar to that described for the preparation of the hexachloride.

Environmental regulations governing the production of chemicals such as Na_2WO_4, $CaWO_4$, APT, and AMT are generally covered under those regulations affecting primary tungsten processors. The tungsten halide chemicals are regulated according to those specified for halogen compounds.

Outlook.—From 1970 to 1990 no events or issues occurred that appeared to have a significant impact on tungsten chemical consumption trends. In the short term, some marginal increases in consumption are likely to occur as the use of tungsten coatings in semiconductor devices increases.

Table 1.—Salient tungsten statistics

(Metric tons tungsten content)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production:					
Domestic mine shipments	4,224	2,490	2,738	983	W
Secondary	680	945	1,920	1,622	1,961
Shipments of Government stockpile excesses	13,013	1,347	1,703	902	
Total	17,917	4,782	6,361	3,507	1,961
Industry stocks, Jan. 1	2,829	4,094	3,785	5,586	4,509
Imports, all forms	690	3,780	6,200	7,117	8,832
Total U.S. supply	21,436	12,656	16,346	16,210	15,302
Distribution of U.S. supply:					
Industry stocks, Dec. 31	3,962	4,713	3,702	5,307	4,221
Exports, all forms	9,280	1,615	2,705	2,692	2,934
Industrial demand	8,194	6,328	9,939	8,211	8,147
Chemicals demand	245	190	395	346	352

W Withheld to avoid disclosing company proprietary data.

Vanadium

By Henry E. Hilliard

Background.—Vanadium, chemical symbol V, is often considered to be an uncommon element, but actually its abundance in the Earth's crust is comparable with or greater than that of nickel, zinc, and copper. It is found in many parts of the world, usually in association with uranium, iron, and other minerals. Although vanadium is plentiful, there are few ores from which it can be economically extracted as a single product; it is one of the most expensive elements to recover. In most cases, whether vanadium occurs as a primary ore (vanadiferous clays), co-ore (titaniferous magnetite and carnotite), or in petroleum, the vanadium content of the material is usually less than 1.5% V as vanadium pentoxide (V_2O_5). Vanadium pentoxide is the starting material for most vanadium products.

The United States imports mainly vanadium raw materials such as vanadium-bearing iron slag, petroleum residues, boiler residues, fly ash, and spent catalysts. Vanadium pentoxide is extracted from these materials and converted to high-value vanadium products, most of which are consumed domestically, but some are exported. The Republic of South Africa is the world's largest supplier of vanadium ore and slag, the other major producers being China and the Russia. Japan, Western Europe, and North America are heavily dependent on imports of vanadium-bearing slag and V_2O_5 from the Republic of South Africa.

Although more than 100 vanadium-bearing minerals have been identified, probably less than 20 are primary, about 80% of the total being secondary. The minerals were formed in zones of weathering and oxidation, or by metamorphic processes. Primary vanadium minerals include the following: titanomagnetite [$Fe(Ti, V)_3O_4$]; patronite ($V_2S_5+Sn+C+Fe$); roscolite [$(Al, V)_2(Al, Si)_3(K, Na)O_{10}(OH, F)_2$]; and vanadium-bearing chromite [$(Cr, Al, V)_2O_3$]. The secondary minerals include the following: carnotite [$K_2(UO_2)_2\ (VO_4)_2{\cdot}3H_2O$]; clay (hydrous V, Al silicate); descloizite [$4(Zn, Cu, Pb)O\ V_2O_5\ H_2O$]; vanadinite [$Pb_4(VO_4)_3\ PbCl$]; and vanadium-bearing chlorite [hydrous V, Al silicate].

The first stage in the processing of a vanadium mineral or vanadium-bearing material is the production of an oxide concentrate. The material is crushed, ground, screened, and mixed with a sodium salt and then roasted at about 850° C to convert the oxides to water-soluble sodium metavanadate. Next, the metavanadate is leached with water, and the vanadium is precipitated at pH 3 as sodium hexavanadate (red cake) by the addition of sulfuric acid. The red cake is fused at 700° C to yield a dense black product that is sold as technical-grade V_2O_5, having a minimum 86 weight-percent V_2O_5 and a maximum 8 weight-percent sodium oxide. The red cake may be further purified by dissolving it in an aqueous solution of sodium carbonate. Aluminum, iron, and silicate impurities precipitate from solution upon pH adjustment. Ammonium metavanadate is then precipitated by the addition of ammonium chloride. The precipitate is calcined to give a V_2O_5 product of greater than 99.8% purity.

Vanadium is extracted as a coproduct with uranium from carnotite by direct leaching of the ore with sulfuric acid. An alternative method is roasting the ore followed by countercurrent leaching with dilute sulfuric acid. In some cases, the first leach may be with a sodium carbonate solution. The uranium and vanadium are then separated from the pregnant liquor by liquid-liquid extraction techniques.

Five companies are producing V_2O_5 in the United States. Of these, one is a totally integrated company producing vanadium chemicals, ferrovanadium, vanadium pentoxide, and other vanadium alloys. The others produce mainly vanadium pentoxide from a variety of raw materials.

The principal commercial use of vanadium, about 85% of U.S. consumption, is as an alloying agent in steel. Another 12% to 13% is consumed in the production of aluminum-vanadium master alloys used in the production of aerospace titanium alloys and other specialty alloys. About 2% is consumed in the production of vanadium oxide catalysts, ceramics, pigments, and other vanadium compounds.

Many chemical reactions are influenced by the presence of substances called catalysts that possess the ability to accelerate or decelerate the rates of reaction. These chemical reactions are designated as catalyzed reactions. Catalysts are classified as being either homogeneous or heterogeneous. A catalyst is said to be heterogeneous if a phase boundary exists between the catalyst and the reacting substances. If the catalyzed reaction takes place in one phase only, the catalyst is said to be homogeneous.

Chemical Industry Consumption.—The single dominant use of vanadium in the chemical industry is in the production of catalysts. Much less is consumed in ceramics, pigments, and electronics (batteries). U.S. consumption of vanadium in catalysts and other chemicals from 1970 to 1990 is listed in table 2. The data show a sharp decline after 1975 from 217 metric tons to only 8 tons in 1990. Part of the decline appears to have been caused by unfavorable economic conditions and conservation efforts, but a major part of the apparent decline can be attributed to incomplete collection of data.

By far the largest use of vanadium catalysts is as a heterogeneous oxidation catalyst in the production of sulfuric acid. The first effective vanadium catalyst for sulfuric acid production was developed in Germany by Badische Anilin und Soda Fabrik (BASF). This type of catalyst later was employed in the United States starting in 1926 and gradually replaced platinum-based catalysts. Perhaps the second largest consumption of vanadium catalysts is in the production of maleic and phthalic anhydrides. The predominant commercial route to maleic anhydride is the vapor-phase oxidation of hydrocarbons over catalysts of vanadium oxides. Maleic and phthalic anhydrides are used in the manufacture of unsaturated polyester resins. Phthalic anhydride may also be used as a plasticizer in synthetic resins.

Catalytic uses result in little loss or consumption of vanadium; however, under normal operating conditions, vanadium catalysts slowly lose catalytic activity over time and must be replaced. Typical sulfuric acid plant operations require that first-pass catalyst beds be replaced completely about every 5 to 10 years. Catalyst beds subsequent to the first pass usually operate for many years if not abused.[1] The need to increase conversion efficiency for pollution control at sulfuric acid plants and the need to expand capacity of these plants and build new plants were factors in the growth of demand for vanadium catalysts in the mid-1970's. The use was about evenly divided between initial charges to new plants and replacements or additions to existing plants. Since that time, improvements in catalysts and catalytic processes have held down growth in both value and volume of catalysts. Oxidation catalysts, e.g. vanadium oxides, are second to polymerization catalysts in terms of volume and value. Growth in demand for these types of catalysts is forecast to be slow.[2] During the period from 1980 to 1990 demand for sulfuric acid, the largest market for vanadium oxide catalysts, was flat.[3] During the same period of time, demand for maleic and phthalic anhydride grew at the rate of 3% and 1%, respectively.

Monsanto Enviro-Chem Systems, Inc. a subsidiary of Monsanto Co., St. Louis, MO, is the world's largest single producer of sulfuric acid catalysts. Monsanto is thought to have a 70% share of the U.S. market and more than 50% of the market in market economy countries. BASF, Ludwigshafen, Germany, is Monsanto's major competitor. Scientific Design Co., Little Ferry, NJ, is the largest manufacturer of maleic anhydride catalysts having a world market share of about 65%. Germany's BASF is the dominant producer of phthalic anhydride catalysts. Several other companies produce homogeneous and heterogeneous vanadium catalysts solely for internal use or for use by wholly owned subsidiaries. Vanadium consumed by these catalyst producers is thought to be insignificant when compared to consumption by Monsanto and BASF.

Outlook.—Oxidation catalysts represent the largest segment of chemical uses of vanadium. Improvements continue to be made in sulfuric acid catalysts aimed at reducing resistance to gas flow without loss of properties, such as activity, durability and life. Also, newer technologies for the production of phthalic anhydride from oxylene use fixed-bed catalysts· systems that reduce catalyst losses from levels that occur in older fluid-bed technologies. Growth in demand for thse catalysts is forecast to be slow.

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[1]Encyclopedia of Chemical Technology. Vanadium Compounds. John Wiley Interscience Publications, 3d ed., v. 23, p. 702.

[2]Greek, Bruce F. Process Catalysts Enjoy Surging Market. Chem. & Eng. News, v. 67, No. 22, May 24, 1989, pp. 29-56.

[3]Chemical & Engineering News. Facts & Figures for the Chemical Industry. V. 69, No. 25, June 21, 1991, pp. 28-67.

Table 1.—U.S. vanadium pentoxide producers

Producer	Plant location	Capacity (metric tons pentoxide per year)
AMAX Metals Recovery Corp	Braithwaite, LA	1,800
Gulf Chemical & Metallurgical Corp	Freeport, TX	1,400
Kerr McGee Chemical Corp	Soda Springs, ID	2,000
UMETCO Minerals Corp	Blanding, UT	6,800
U.S. Vanadium Corp	Hot Springs, AR	6,800

Source: U.S. Bureau of Mines 1990 Vanadium Annual Report.

Table 2.—Salient vanadium statistics

(Metric tons of contained vanadium unless otherwise specified)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production:					
Ore and concentrate:					
Shipments of Government stockpile excesses	1,779	90	—	—	—
Recoverable vanadium[1]	4,825	4,307	4,360	W	W
Vanadium oxide recovered from ore[2]	5,075	4,408	4,995	W	W
Vanadium recovered from petroleum residue[3]	—	—	—	2,445	2,308
Total all forms	5,075	4,408	4,995	W	W
Industry stocks, Jan. 1	3,517	3,542	10,060	W	W
Imports	1,836	3,843	3,818	991	4,153
Total U.S. supply	12,207	11,883	18,873	W	W
Distribution of U.S. supply:					
Industry stocks, Dec. 31	3,639	4,097	10,120	W	W
Exports	1,861	657	1,023	1,276	2,709
Demand	6,410	7,129	7,730	W	W
Apparent surplus (+) or deficit (-) of supply[4]	+297	—	—	W	W
Consumption by end use:					
Catalyst	113	217	54	13	8
Pigments, ceramic, and electrical	10	W	W	W	W
Total U.S. consumption	3,908	4,221	4,834	4,646	4,081

W Withheld to avoid disclosing proprietary data.

[1] Recoverable vanadium contained in uranium and vanadium ores and concentrates received at mills, plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock.

[2] Produced directly from all domestic ores and ferrophosphorus slag; includes metavandates.

[3] Includes vanadium recovered from fly ash, residues, and spent catalysts.

[4] The difference between total U.S. distribution of supply and total U.S. supply.

Source: U.S. Bureau of Mines Minerals Yearbooks.

Vermiculite

By Michael J. Potter

Background.—Vermiculite is a mica like mineral that rapidly expands upon heating to produce a low-density material. The expanded (exfoliated) vermiculite is used as a lightweight aggregate and thermal insulation in construction applications, as a fertilizer carrier and soil conditioner in agriculture, and as a filler and texturizer for plastics and rubber, among many other uses.

In 1990, four companies produced vermiculite concentrate at five operations and sold material from a stockpile at a sixth operation, four operations being in South Carolina. Exfoliated vermiculite was sold or used by 13 companies from 33 plants in 20 States. Twenty plants in 16 States were operated by the largest producer.

In 1990, U.S. imports of vermiculite concentrate were approximately 45,000 metric tons, largely from the Republic of South Africa; while U.S. exports were estimated to be 18,000 tons, primarily to Canada. Total U.S. consumption of exfoliated vermiculite was 142,000 tons.

Chemical Industry Consumption.—Chemical end uses of exfoliated vermiculite include agricultural products for horticulture and soil conditioning as a fertilizer carrier, etc. Exfoliated vermiculite is usually produced from crude ore by first beneficiating the ore with washing, crushing, flotation, screening, and drying. The vermiculite concentrate is exfoliated by dropping concentrate continuously through a gas- or oil-fired vertical furnace at a controlled rate. Exfoliation occurs over a temperature range of 870° C to 1,090° C and is completed in 4 to 8 seconds. Part of the water of hydration is converted to steam, and the vermiculite expands 8 to 12 times in volume. The product is in the form of accordion-shaped granules and has a density of 4 to 11 pounds per cubic foot.

In horticulture, vermiculite improves soil aeration while retaining moisture and nutrients to feed roots, cuttings, and seeds for faster maximum growth. As a soil conditioner, vermiculite breaks up heavy clay soil and permits sandy soil to retain moisture. Vermiculite is used as an anticaking agent for fertilizers and as a carrier and extender for pesticides and herbicides to ensure more even distribution in applications.

The consumption of vermiculite in horticulture and soil conditioning appeared to follow the general cycle of the economy from the early 1970's to 1980. In the 1980's, the level of consumption decreased and remained flat through 1990, possibly because of competition from other materials such as perlite. The estimated consumption of vermiculite as a fertilizer carrier went up abruptly after 1975, which appeared to result from new producer canvass data becoming available. Fertilizer carrier data have been largely estimated since the mid-1970's.

Outlook.—The demand for vermiculite in agricultural uses in the near future should remain steady or show moderate growth, reflecting new potting soils, lawn-care products, etc., and continuing interest in gardening and horticulture.

Table 1.—Salient vermiculite statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Production: Concentrate	259	299	306	285	[e]209
Industry stocks, Jan. 1	NA	NA	NA	NA	NA
Imports	11	30	[e]24	[e]34	[e]45
Total U.S. supply	270	329	330	319	[e]254
Distribution of U.S. supply:					
Industry stocks, Dec. 31	NA	NA	NA	NA	NA
Exports	20	41	27	[e]21	[e]18
Demand (exfoliated)	200	213	255	234	142
Apparent surplus, plus losses and waste material from exfoliation (by difference)	50	75	48	64	[e]94

[e]Estimated. NA Not available.

Table 2.—Vermiculite consumption (exfoliated) by the U.S. chemical industry

(Thousand metric tons)

End use	1970	1975	1980	1985	1990
Agriculture:					
Horticulture and soil conditioning	NA	28	41	28	26
Fertilizer carrier	NA	6	[e]41	[e]26	[e]32
Total chemicals demand	28	34	[e]82	[e]54	[e]58
Total U.S. primary demand	200	213	255	234	142

[e]Estimated. NA Not available.

Zinc

By James H. Jolly

Background.—Zinc, the fourth most widely used metal after iron, aluminum, and copper, is one of the major nonferrous metals required in the modern industrial economy. It is consumed primarily in the form of metal slabs and ingots for metallurgical applications, but important quantities are also consumed in the form of metal, dust, and compounds for a myriad of chemical applications in many industrial sectors. Major uses of zinc metal include the following: galvanizing iron and steel products; brass alloy production; zinc-base metals for diecasting; and rolled-metal sheets and plates for uses ranging from zinc-carbon battery cans to U.S. pennies.

Galvanizing is the principal use of zinc and, in a sense, is a type of chemical use in that zinc protects iron and steel from corrosion both cathodically and by barrier protection. Being electromotively more anodic than iron, zinc protects iron electrochemically by sacrificing itself first under corrosion conditions; and the tight bonding between the iron and zinc coating forms a barrier that prevents corrosive elements from directly attacking the substrate iron. In a somewhat similar manner, sacrificial zinc anodes are widely used to cathodically protect iron and steel in water heaters, offshore drilling platforms, buried metal pipelines, and ship bottoms.

Chemical Industry Consumption.—Numerous zinc compounds are made for chemical uses; however, three basic compounds—zinc oxide, zinc chloride, and zinc sulfate—are the most widely used based on tonnage. Except for some trade data (see tables 3 and 4), these three basic compounds are the only ones that have been monitored for production and, partially, for quantities consumed by end use.

Zinc oxide, the principal zinc compound used, is often the source material for the production of many other zinc chemicals. Zinc oxide was instrumental in the early development of ready-mix paint, heavy-duty tires, photocopying, and television. It is largely made from melted metal, that is vaporized and oxidized (burned in air) and then collected in a bag house. Large amounts of zinc oxide have also been made directly from ore, especially in the United States, by this same process, but with a reduction step using coke or coal before vaporization. Production from ores ceased in 1987 in the United States and is little used today elsewhere. High-quality zinc oxide for face powders, artist's paints, and pharmaceuticals is sometimes prepared by calcining high-purity zinc hydroxide or carbonate.

In paints, rubber, and plastics, zinc oxide imparts whiteness, hiding power, tinting strength, and resistance to ultraviolet light damage. Use of zinc oxide and lithophone, another extensively used white pigment composed of zinc sulfide and barium sulfate, in paint has steadily declined since the 1930's when titanium dioxide became the dominant paint pigment. Most zinc oxide currently is used in exterior house paints to inhibit mold and mildew formation.

The rubber industry, largely the automobile tire sector, accounts for about one-half of the zinc oxide consumption. It is primarily used as an activator of accelerators in the vulcanization process but is also used for foam control and improved heat conductivity and as a reinforcement filler and pigment in white rubber. In the past decade zinc oxide consumption for tires has generally trended downward owing to development of radials and smaller, longer-lasting tires and to increases in tire imports.

The photoconductive properties of zinc oxide were first commercially utilized in 1956 for development of the first successful photocopying process not employing silver salts or chemical reactions. In the process, conventional-type paper thinly coated with light-sensitive, electrostatically charged zinc oxide is exposed to light passing through overlying print to be copied. Where the light passes through to the charged paper, the charge is partially or fully discharged depending on the light intensity; pigmented resin powder that adheres to still-charged areas provides the resulting duplicate image. Until the mid-1970's, photocopying was the fastest growing new market outlet for zinc oxide; however, competition from the plain-paper photocopying process (xerography) has since reduced consumption in this area to one-fourth its former levels. This use sector is likely to continue to decline.

After World War II, ferrites, containing varying amounts of zinc oxide, were discovered and became essential components for ferromagnetic applications for television, radio, and telecommunication equipment. Ferrites remain a growth area for zinc oxide.

Included among the many other chemical-use areas of zinc oxide are adhesives, sealants, agricultural and animal feed nutrients, catalysts, ceramics and glass, food packaging, fungicides, lubricants, phosphors, plastic stabilizers, and electroplating baths.

Zinc sulfate is the most widely used zinc salt of any inorganic acid. It is generally produced by leaching roasted zinc concentrate or galvanizer's waste and scrap products with sulfuric acid. Zinc sulfate is typically marketed in one of its solid hydrated forms or in aqueous solutions in various concentrations. Since the mid-1960's, its major use has been to correct zinc deficiencies in soil. Formerly, zinc sulfate was largely consumed in viscose rayon fiber manufacture, in which viscose filaments are ejected from the spinnerets, into a sulfuric acid bath to regenerate in fiber form. Zinc sulfate is added to the bath to promote coagulation and crenelation. In the past two decades, however, rayon production has fallen precipitously owing to substitution of other man-made fibers, leading to a sharp reduction in zinc sulfate use in this sector.

Other uses of zinc sulfate include water treatment, froth flotation, electrogalvanizing, fire proofing, and starting material for the production of zinc stearate, zinc bacitracin, and many other chemicals.

All zinc chloride produced in the United States is prepared from secondary materials or waste streams from chemical operations. Most zinc chloride is marketed in solutions of various concentrations, although crystallized and fused solid forms also are sold. Zinc chloride is commonly used in wood preservation, in dry cell batteries as an electrolyte, in the petroleum industry as an effective packer fluid and corrosion inhibitor for oil and gas wells, in agriculture to form solutions of zinc that are biologically available to plants and animals, and in metal plating and joining to act as a flux for galvanizing, soldering, and tinning. In addition, zinc chloride is used as a preferred starting material in the manufacture of some zinc rubber accelerators and for the production of zineb, a commonly used agricultural fungicide.

Other important zinc chemicals are arsenate, borate, bromide, chromate, cyanide, silicate, sulfide, and numerous organic compositions. These and others are used in a range of applications including pharmaceuticals, cosmetics, dyeing, lubricants, poisons, toothpastes, mouthwashes, phosphors, pigments, varnishes, inks, and dyes.

Zinc metal dust is an important reducing, condensing, and dehalogenating agent in the chemical industry. It is made by distillation of primary metal or metal scrap. Particle size, usually below 10 microns, is controlled by the cooling rate. Coarser-grained zinc dust, also called powder, is made by atomizing a stream of molten zinc by blasting with inert gas, followed by collection of particles in a closed cooling chamber. The major market for zinc dust is in primers and paints mainly for the protection of iron and steel. It is used to improve the properties of plastics and epoxy resins, to produce porosity in concrete, to promote antiseizing properties in thread compounds, specialty lubricants, and sealants, and to precipitate noble metals from solution. Other applications include use in match heads, in alkaline and zinc-air batteries, and in the production of chemicals necessary for the paper and textile industries.

Outlook.—World zinc metal consumption is expected to continue upward, rising to about 8.5 million tons by the year 2000 from the 7 million tons consumed in 1991. No new major uses for zinc are expected. Traditional zinc uses, in meeting the needs of a rapidly growing and more affluent world population, are expected to be the driving force for increased zinc consumption in the next decade. However, growth is likely to be less in the early years of the decade because of monetary and restructuring problems associated with former Eastern European nations.

Many other compounds and/or uses of zinc chemicals can be found in the references listed in the bibliography.

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Table 1.—Salient zinc statistics

(Thousand metric tons)

	1970	1975	1980	1985	1990
Components of U.S. supply:					
Primary production, domestic mines (recoverable)	485	426	317	227	515
Old scrap	65	70	66	69	109
Imports:					
Ore and concentrate	409	389	182	90	47
Metal	236	345	414	611	632
Compounds and scrap	16	46	35	54	91
Government transactions, shipments of Government stockpile excesses	1	5	—	—	—
Industry stocks, Jan. 1	152	228	152	138	91
Total	1,364	1,509	1,166	1,189	1,485
Distribution of U.S. supply:					
Industry stocks, Dec. 31	197	165	126	120	88
Exports:					
Metal	—	6	5	1	1
Ores and concentrates	NA	NA	54	23	220
Compounds and scrap	8	7	30	46	127
Industrial demand	1,159	[1]1,331	951	999	1,049

NA Not available.

[1] Calculated demand using same basis as other years listed. Ore and concentrate imports in 1975 were exceptionally and unrealistically high owing to changes in the tariff rate. Demand based on consumption data was 968,000 tons and is the quantity used in table 2 for 1975.

Table 2.—U.S. demand pattern

(Thousand metric tons, zinc content)

Form and sector of use	1970	1975	1980	1985	1990
Metal:					
Construction	350	355	380	380	410
Transportation	245	220	140	165	180
Electricall	145	95	115	90	100
Machinery	75	44	60	85	100
Other	160	126	105	125	105
Total metal	975	840	800	845	895
Nonmetal:					
Zinc oxide:					
Rubber	85	65	60	65	74
Paint	25	11	10	9	6
Chemicals	19	22	40	38	28
Photocopying	23	17	8	7	W
Ceramics	7	4	5	7	3
Other	2	2	5	4	17
Zinc chloride[1]	9	4	9	7	8
Zinc sulfate:[1]					
Agriculture	5	1	11	14	13
Other	9	2	3	3	2
Total nonmetal	184	128	151	154	155
Total U.S. demand	1,159	968	951	999	1,050

W Withheld to avoid disclosing individual company proprietary data; included in "Other."

[1] Includes all forms of zinc chloride or sulfate compounds.

Table 3.—Imports of zinc chemicals, quantity and value, 1970-90

	1970		1975		1980		1985		1990[1]	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Zinc arsenate	—	—	—	—	—	—	18	$14	—	—
Zinc chloride	1,044	$228	696	$518	1,008	$726	2,386	1,668	2,833	$2,595
Zinc cyanide	130	96	9	15	20	37	160	254	NA	NA
Zinc hydrosulfite	—	—	—	—	337	371	142	227	NA	NA
Zinc sulfate	5.713	651	2.894	1,065	3,871	1,350	3,615	2,049	4,204	2,234
Other zinc compounds, n.s.p.f	612	239	861	766	513	804	1,458	2,625	NA	NA
Zinc formaldehyde, sulfoxylate . . .	99	67	31	38	—	—	219	440	NA	NA
Zinc salts, other	141	88	38	34	183	262	1,825	2,521	NA	NA
Zinc yellow pigment	1,227	559	552	672	1,255	1,786	1,570	2,121	NA	NA
Lithopone pigment, under 30% zinc sulfide	25	3	5	2	1,143	563	1,058	594	2,487	2,189
Lithopone pigment, over 30% zinc sulfide	53	16	9	4	46	35	49	27	NA	NA
Zinc oxide, dry	10,948	2,763	11.963	8,162	29,806	23,696	38,992	34,317	49,454	71,998
Zinc oxide, other	5	1	—	—	37	31	383	805	NA	NA
Zinc sulfide	317	109	298	214	409	401	672	1,037	1,525	3,256

NA Not available.

[1] Because of implementation of the Harmonized Tariff System in Jan. 1989, import categories for 1990 are not necessarily comparable to those in prior years.

Source: Bureau of the Census.

Table 4.—Exports of zinc chemicals, quantity and value, 1970-90

	1970		1975		1980		1985		1990[1]	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Zinc oxide	5,739	$2,343	2,816	$2,363	302	NA	362	NA	7,141	$10,032
Zinc chloride	NA	NA	NA	NA	NA	NA	NA	NA	2,267	2,275
Zinc sulfate	NA	NA	NA	NA	NA	NA	NA	NA	3,200	6,180
Zinc sulfide	NA	NA	NA	NA	NA	NA	NA	NA	47	251
Zinc compounds, n.s.p.f	NA	NA	NA	NA	NA	NA	NA	NA	2,205	29,935
Lithopone	1,398	523	832	1,060	NA	NA	NA	NA	370	541

NA Not available.

[1] Because of implementation of the Harmonized Tariff System in Jan. 1989, import categories for 1990 are not necessarily comparable to those in prior years.

Source: Bureau of the Census.

Zircon

By David Templeton

Background.—Zircon is a heavy mineral sand that accounts for virtually all of the zirconium minerals mined in the world. Predominant producing countries, in decreasing order, are Australia, the Republic of South Africa, and the United States. The bulk of zirconium minerals is consumed by basic industries such as foundries (mold sand, facings, and investment castings), glass and steel manufacturing (refractories), alumina-zirconia abrasives, and ceramic wares (opacifiers, colors, and glazes). Excluding small specialty uses, the balance goes into the production of metal, oxide, and chemicals. Most zirconium chemicals consumed domestically are produced in the United States from zircon ore mined both here and abroad.

Baddeleyite is another zirconium mineral that is produced in relatively small quantities as a byproduct of other mineral production in the Republic of South Africa (Phalaborwa Complex) and the Commonwealth of Independent States (Kola Peninsula). The South African ore is mostly converted to acid zirconium sulfate tetrahydrate (AZST) and accounts for three-quarters of zirconium-related U.S. imports from that country. It typically is consumed by the leather tanning industry but also finds uses as a primary chemical for specialty producers.

Chemical Industry Consumption.—A plethora of commonly used zirconium-based chemicals are used in such consumer products as antiperspirants, poison ivy ointments, and fingernail polishes. Inks, paints, adhesives, and specific coatings on food packaging also rely on zirconium chemicals to infuse better quality and/or performance. Leather tanning, fabric treatments, and kidney dialysis filters are also reliant on zirconium chemicals.

Until recently, the zirconium chemical market was supplied primarily by one domestic company and its United Kingdom parent. By using a process referred to as caustic fusion (details below), zirconium ores are broken down to produce an assortment of chemicals to be distributed to end users and intermediate or secondary chemical producers; but the decline in zirconium metal consumption has forced metal producers faced with declining revenues to begin to participate in the nonmetal markets—zirconium oxide and chemicals.

Zirconium metal is produced in the United States by the Bureau-developed Kroll process, whereby zircon sand is converted into zirconium tetrachloride ($ZrCl_4$). This chlorination method, begins by digesting zircon in a fluidized bed of chlorine gas. The resulting $ZrCl_4$ can be taken off and used as a primary, precursor chemical, or it can proceed through the plant process and be taken off later as zirconium oxide or other mainstream chemicals such as basic carbonate and basic sulfate. Zirconium tetrachloride may be further reacted with magnesium to produce zirconium metal by the following exothermic reaction:

$$ZrCl_4 + 2Mg \quad Zr + 2MgCl_2$$

By far the world's largest producer of zirconium chemicals, Magnesium Elektron Ltd. in the United Kingdom and Inc. in the United States (Manchester, England, and Flemington, respectively) has been in the zirconium chemical business since the 1940's when new magnesium-zirconium alloys it produced required additions of zirconium in the form of a salt. The company produces a plethora of chemicals, all from the simple digestion of zircon sand in sodium hydroxide, i.e., caustic-soda fusion. The reaction produces sodium zirconate and sodium silicate, the latter being water soluble. Following a water wash, the zirconate is reacted with hydrochloric acid and cooled to produce zirconium oxychloride crystals, a major commercial chemical.

Over the past 50 years an extensive list of zirconium chemicals have come to be used in myriad applications has led to an increase in the number of companies involved in manufacturing specialty chemicals. Domestically, about one dozen secondary producers further refine basic zirconium chemicals (e.g., tetrachloride, oxychloride, carbonate, and sulfate) into specialty chemicals. Basic chemicals are those produced in the first stages of processing subsequent to the digestion of zircon sand, whether by chlorination caustic-soda or fusion. Besides Magnesium Elektron and the two metal producers, Teledyne Wah Chang Albany and Western Zirconium, only one other domestic company is considered a primary producer, the KBI Division of the Cabot Corporation, which captively produces a zirconium salt for the production of aluminum master alloys.

Inorganic pigments of zirconium are not related to the mainstream chemical industry but are significant enough to warrant mention (and are included in SIC 28). Many different colors can be obtained for staining ceramic glazes by combining zirconium with other elements. Those currently used include ZrV and ZrPrSi (both yellow), ZrVSi (turquoise), ZrFeSi (pink), and ZrCoNiSi (gray). Many other combinations and colors are available. Some of these include a variety of ZrFe stains (peach, plum, and tan) that are stabilized with zircon opacifiers to bring out stronger, brighter colors. Zirconium oxide (zirconia) is an excellent white pigment that is used only in special applications. Zirconium orthosulfate is used to coat special purpose titanium dioxide, which is the world's leading white pigment. The end result is a zirconia coating that imparts better ultraviolet durability and chalking resistance in paints and coatings.

Because the metal and chemical industries have too few producers both separately and combined, the mineral consumption data of these sectors is proprietary. At present only three companies consume zircon to produce primary zirconium chemicals. The Bureau estimates that the three consumers of zircon for commercial and captive chemical production consume about 7,500 metric tons of zircon per year.

Outlook.—The use of zirconium chemicals in their broad spectrum of applications seems most likely to experience greater growth than that of the general economy. Events justifying this forecast include the recent expansion of Magnesium Elektron in both the United States and the United Kingdom; a metal producer's entrance into the market; and recently added capacity in Japan. The underlying reason is that these chemicals are being found to improve many old processes and products. Furthermore, as other elements such as lead and cadmium experience increasing environmental scrutiny, replacements for them will grow in use. Zirconium colors have already been developed and employed to meet the new, strict requirements for the lead and cadmium levels permissible in tableware glazes.