BARIUM COMPOUNDS

1. Introduction

The first report concerning barium compounds occurred in the early part of the seventeenth century when it was noted that the ignition of heavy spar gave a peculiar green light. A century later, Scheele reported that a precipitate formed when sulfuric acid was added to a solution of barium salts. The presence of natural barium carbonate, witherite [14941-39-0], $BaCO_3$, was noted in Scotland by Withering.

In its natural form, barium [7440-39-3], Ba, never occurs as the metal but is almost always found as the ore barite [13462-86-7], $BaSO_4$. More than 90% of all barium is actually used as the ore, albeit after preliminary beneficiation. In the U.S., nearly 95% of the barite sold in 2001 was used for oil- and gas-well drilling fluids (muds). The other 5% was used as filler and/or for extender uses and the manufacture of all other barium chemicals (1). Witherite, the only other significant natural barium ore, is not mined commercially.

Barium is a member of the alkaline-earth group of elements in Group 2 (IIA) of the period table. Calcium [7440-70-2], Ca, strontium [7440-24-6], Sr, and

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barium form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing size, the ionic and electropositive nature being greatest for barium (see CALCIUM AND CALCIUM ALLOYS; CALCIUM COMPOUNDS; STRONTIUM AND STRONTIUM COMPOUNDS). As size increases, hydration tendencies of the crystalline salts increase; solubilities of sulfates, nitrates, chlorides, etc, decrease (except fluorides); solubilities of halides in ethanol decrease; thermal stabilities of carbonates, nitrates, and peroxides increase; and the rates of reaction of the metals with hydrogen increase.

In metallic form, barium is very reactive, reacting readily with water to release hydrogen. In aqueous solution it is present as an ion with a +2 charge. Barium acetate, chloride, hydroxide, and nitrate are water-soluble, whereas barium arsenate, chromate, fluoride, oxalate, and sulfate are not. Most water-insoluble barium salts dissolve in dilute acids; barium sulfate, however, requires strong sulfuric acid.

Compared to the hydroxides of calcium and strontiuim, barium hydroxide is the most water-soluble and also the strongest base. Additionally, barium hydroxide is more difficult to convert to the oxide by heating than are the corresponding hydroxides of calcium and strontium. Barium oxide is more readily converted to the peroxide than are the oxides of the other alkaline earths.

The large size, ionic radius = 0.143 nm, and electronic configuration [Xe] $6s^2$, of the barium(II) ion [22541-12-4], Ba^{2+}, makes isomorphous substitution possible only with strontium, Sr^{2+}, 0.127 nm, and generally not with other members of Group IIA such as Ca^{2+}, 0.106 nm, and Mg^{2+}, 0.078 nm. Among the other elements that occur with barium in nature, substitution is common only for potassium, K^+, 0.144 nm, but not for the smaller ions of Na, Fe, Mn, Al, and Si (2). For a discussion of barium bromate [13967-90-3], $Ba(BrO_3)_2$, see BROMINE COMPOUNDS; for barium chlorate [13477-000-4], $Ba(ClO_3)_2{\cdot}H_2O$, see CHLORINE OXYGEN ACIDS AND SALTS, CHLORIC ACID AND CHLORATES; for barium chromate [10294-40-3], $BaCrO_4$, see CHROMIUM COMPOUNDS; and for barium cyanide [542-62-1], $Ba(CN)_2$, see CYANIDES. For a discussion of barium ferrite [11138-11-7] and [12409-27-7] ($BaFe_{12}O_{13}$), see FERRITES; and for barium hydride [13477-09-3], BaH_2, see HYDRIDES.

2. Barite

Barite [13462-86-7], natural barium sulfate, $BaSO_4$, commonly known as barytes, and sometimes as heavy spar, till, or cawk, occurs in many geological environments in sedimentary, igneous, and metamorphic rocks. Commercial deposits are of three types: vein and cavity filling deposits; residual deposits; and bedded deposits. Most commercial sources are replacement deposits in limestone, dolomitic sandstone, and shales, or residual deposits caused by differential weathering that result in lumps of barite enclosed in clay. Barite is widely distributed and has minable deposits in many countries.

Mineralogically, barite crystallizes in the dipyramidal class of the orthorhombic system. Although the barite of many deposits fractures unevenly or has an apparent cleavage along planes because of separation between successively deposited layers, well-formed crystals are mostly tabular and cleave along three different planes. The barite in most deposits occurs in irregular masses, nodules, rosettelike aggregates, and in laminated to massive beds of fine crystallinity. Barite is most commonly associated with quartz [14808-60-7], chert, jasperoid, calcite [13397-26-7], dolomite [17069-72-6], siderite [14476-16-5], rhodochrosite [14476-12-1], celestite [14291-02-2], gluorite, various sulfide minerals, and their oxidation products. In most mines, barite is the primary material being mined, yet barite is also a common gangue mineral in many types of ore deposits including those for lead, zinc, gold, silver, fluorite, and rare-earth minerals (3).

Barite is a moderately soft crystalline mineral, Mohs' hardness 3–3.5; sp gr 4.3–4.6; n_D 1.64. The ore is white opaque to transparent, but impurities can produce pale shades of yellow, green, blue, brown, red, or gray-black. The most important impurities are Fe_2O_3, Al_2O_3, SiO_2, and $SrSO_4$, all of which are undesirable in chemical-grade barite. When the barite is used for drilling mud, the iron content can be permitted to be much higher than for other uses.

Residual barite is usually mined by open-pit methods. Bedded and vein deposits may be mined by either open-pit or underground methods, depending on the characteristics of each deposit. Some barite is sufficiently high, up to 96% $BaSO_4$, grade that it can be shipped without beneficiation. Many deposits require concentration and beneficiation can involve any one or a combination of gravity separations. "Primary barite," the first marketable product, includes crude run-of-mine barite, flotation concentrates, and material concentrated by other beneficiated processing such as washing, jigging, or magnetic separation. Chemical and glass manufacturers prefer coarser material; for chemicals, ca 4760–840 μm (4–20 mesh) is preferred, and for glass, ca 590–105 μm (30–140 mesh). Barite to be used in well drilling is ground dry to 44 μm (−325 mesh).

2.1. Production and Consumption. About 80% of the world's barite production is used as a weighting agent for the muds circulated in rotary drilling of oil and gas wells (see PETROLEUM, DRILLING FLUIDS AND OTHER OIL RECOVERY CHEMICALS). Table 1 shows the U.S. production–consumption balance. The 2001 demand for barite increased nearly 17% over that recorded in 2000 (4).

Technological developments such as 3D-seismic surveying and new drilling techniques resulted in more production from fewer wells. The use of oil-based and synthetic drilling fluids based on water also resulted in a reduction of demand for barites. However, improved market conditions could see a significant increase in the number of active rigs, which could have a positive effect on barite demand (5). At present the natural gas industry appears to be the main market for barite consumption (4).

World mine production, reserves, and reserve base are listed in Table 2.

2.2. Uses. Drilling muds are aqueous suspensions of clay and barite used in the petroleum industry. During drilling operations, the muds are pumped into a well through the hollow drill stem, passing through the tip of the bit, and back up the space between the stem and the walls of the hole. The mud is effective in lubricating and cooling the drill bit, in sealing the walls to prevent the caving of the hole, in suspending the drill cuttings and carrying them to the surface, and, by establishing a hydrostatic column head of weighted fluid, helps to restrain high gas and oil pressures, reducing the tendency for blowouts. For this last reason, muds having a specific gravity as great as 2.5 are used and barite is the material of choice because of its high density, chemical inertness, relative nonabrasiveness, and widespread availability at reasonable cost.

Table 1. **U.S. Barite Production–Consumption Balance**[a]

Statistics	1997	1998	1999	2000	2001[b]
sold or used, mine	692	476	434	392	400
imports for consumption:					
crude barite	2210	1850	836	2070	2670
ground barite	31	20	17	16	20
other	12	13	18	15	10
exports	22	15	22	36	40
consumption, apparent[c] (crude barite)	2920	2340	1280	2460	2960
consumption[d] (ground and crushed)	2180	1890	1370	2100	2600
price, average value, dollars per ton, mine	22.45	22.70	25.60	25.10	25.00
employment, mine and mill, number[b]	380	410	300	330	340
net import reliance[e] as a percentage of apparent consumption	76	80	66	84	87

[a] From Ref. 1.

[b] Estimated.

[c] Sold or used by domestic mines - exports + imports.

[d] Domestic and imported crude barite sold or used by domestic grinding establishments.

[e] Defined as imports - exports + adjustments for government and industry stock changes.

Finely ground barite which may be bleached, usually by sulfuric acid, or unbleached, is used as a filler or extender in paints (qv), especially in automotive undercoats, where its low oil absorption, easy wettability in oils, and good sanding properties are advantageous (see FILLERS). It is also used as a filler in plastics

Table 2. **World Mine Production, Reserves, and Reserve Base of Barite**[a]

	Mine production			
Country	2000	2001[b]	Reserves[c]	Reserve base[c]
United States	392	400	6,000	60,000
Algeria	50	50	9,000	15,000
Bulgaria	120	120	10,000	20,000
China	3,500	3,800	30,000	150,000
France	75	75	2,000	2,500
Germany	120	120	1,000	1,500
India	550	650	53,000	80,000
Iran	185	190	NA	NA
Korea, North	70	70	NA	NA
Mexico	127	120	7,000	8,500
Morocco	350	320	10,000	11,000
Russia	60	60	2,000	3,000
Thailand	50	50	9,000	15,000
Turkey	130	120	4,000	20,000
United Kingdom	70	70	100	600
Other countries	350	250	12,000	160,000
World total (rounded)	*6,200*	*6,600*	*160,000*	*550,000*

[a] From Ref. 1

[b] Estimated

[c] NA = not available

and rubber products. In nonasbestos brake linings, the barite filler acts as a heat sink (see BRAKE LININGS AND CLUTCH FACINGS). In floor mats and carpet backings made of polyurethane foam, barite imparts sound-deadening characteristics and improves processing qualities (see URETHANE POLYMERS). In furniture manufacture where polyurethane foam is used for recoil and density properties, the unique chemical inertness of barite in combination with its high density plays a primary role.

In the glass (qv) and ceramic industry (see CERAMICS), barite can be used both as a flux, to promote melting at a lower temperature or to increase the production rate, and as an additive to increase the refractive index of glass. The viscosity of barite-containing glass often needs to be raised. Alumina in the form of feldspar is sometimes used. To offset any color produced by iron from the barite addition, more decolorizer may be needed. When properly used, barytes help reduce seed, increase toughness and brilliancy, and reduce annealing time. Barite is also a raw material for the manufacture of other barium chemicals.

3. Barium Acetate

Barium acetate [543-80-6], $Ba(C_2H_3O_2)_2$, crystallizes from an aqueous solution of acetic acid and barium carbonate or barium hydroxide. The level of hydration depends on crystallization temperature. At <24.7°C the trihydrate, density 2.02 g/mL is formed; from 24.7 to 41°C barium acetate monohydrate [5908-64-5], density 2.19 g/mL precipitates; and above 41°C the anhydrous salt, density 2.47 g/mL results. The monohydrate becomes anhydrous at 110°C. At 20°C, 76 g of the monohydrate dissolves in 100 g of water. Barium acetate is used in printing fabrics, lubricating grease, and as a catalyst for organic reactions.

4. Barium Bromide

Barium bromide [10553-31-8], $BaBr_2$, mp 854°C, density 4.781 g/mL, also exists as barium bromide dihydrate [7791-28-8], $BaBr_2{\cdot}2H_2O$, dehydration temperature 120°C, density 3.58 g/mL. The solubility, wt %, of $BaBr_2$ in water is

Temperature, °C	−20	0	20	40	60	80
Solubility, wt % $BaBr_2$	45.6	49.5	51.0	53.2	55.1	57.4

Barium bromide is very soluble in methanol, yet almost insoluble in ethanol. Reported uses of barium bromide include: fabrication of phosphors, for example from BaF_2, $BaBr_2{\cdot}2H_2O$ and $EuBr_3$ (6); as a crystallization nucleating agent to control supercooling of $CaBr_2$ solutions (7); and in the production of halide glasses having ir transmission properties (8). Glass-transition temperature is sometimes influenced by $BaBr_2$ content.

5. Barium Carbonate

Most barium compounds are prepared from reactions of barium carbonate [513-77-9], $BaCO_3$, which is commercially manufactured by the "black ash" process from barite and coke in a process identical to that for strontium carbonate production. Depending on the co-product, soda ash and/or carbon dioxide are also consumed.

Precipitated or synthetic barium carbonate is the most commercially important of all the barium chemicals except for barite. Barium carbonate is an unusually dense material, that is almost insoluble in water and only slightly soluble in carbonated water. It does dissolve in dilute hydrochloric, nitric, and acetic acids and is also soluble in ammonium nitrate and ammonium chloride solutions.

5.1. Manufacture. An outline of the black ash process for $BaCO_3$ manufacture is shown in Figure 1. It is from the appearance of the product exiting the thermal reduction step that the process derives its name.

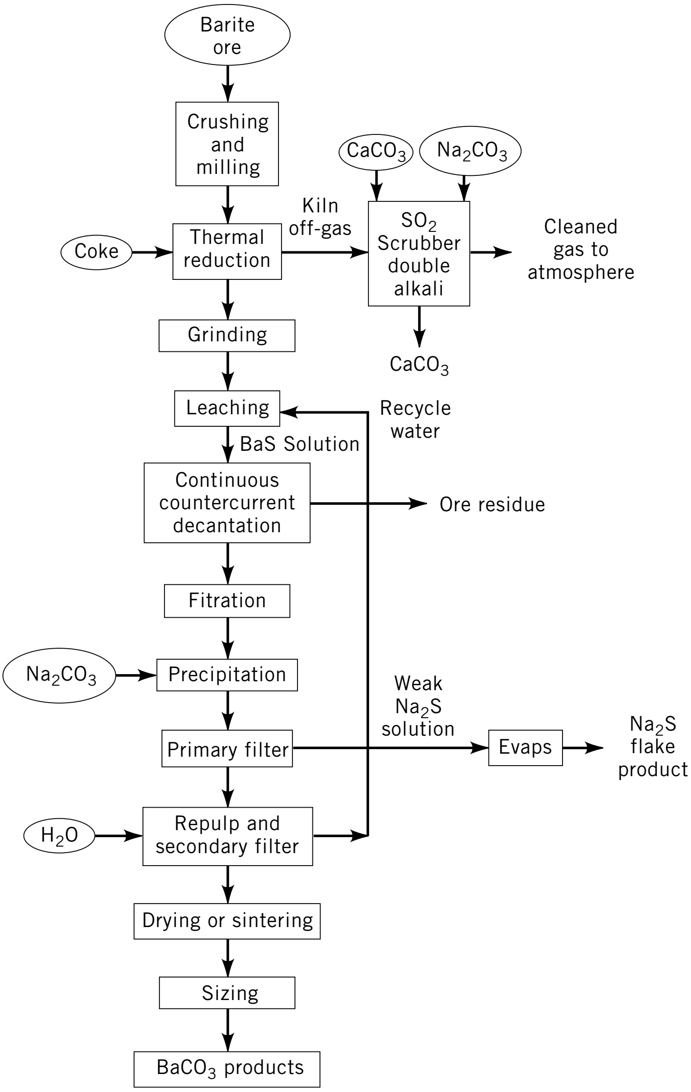

Fig. 1. Flow diagram for the black ash process.

Barite ore is reduced in size to between 20 and 200 mesh (840 to 74 μm). Sizing represents a compromise between increases in reaction rate and dust loss. Coke is fed to the kiln at a coke to ore ratio of about 0.20:0.25.

Thermal Reduction. Thermal reduction is usually accomplished in a high temperature countercurrent rotary kiln. "Hot zone," a region near the kiln spill, temperature is usually controlled at 1100–1200°C. The reaction rate has been shown to be only slightly lower at 1050°C than at 1130°C (9). About 6% of the feed $BaSO_4$ remains unreacted after 30 min at 1050°C. Reaction completion is approached in less than 10 min at 1100°C (10).

The chief reduction reaction in the kiln is

$$BaSO_4 + 4\,CO \rightleftharpoons BaS + 4\,CO_2 \tag{1a}$$

BaS is leached from the black ash by hot water. The resulting solution is filtered and then treated with soda ash or carbon dioxide or a combination of the two to precipitate fine $BaCO_3$ crystals, which in turn are filtered and dried. Sulfide values can be recovered as H_2S, NaHS, Na_2S, or elemental sulfur.

Carbon dioxide, detrimental to high BaS yields, is repressed according to the Boudouard equilibrium

$$C + CO_2 \rightleftharpoons 2CO \tag{1b}$$

Side reactions of barium with silicate impurities in the ore have been noted (1,11–13). These reactions can cause appreciable loss of barium values by forming water-insoluble barium compounds (14). For example, barium sulfate can form the orthosilicate

$$2\,BaSO_4 + SiO_2 \longrightarrow Ba_2SiO_4 + 2\,SO_3 \tag{2}$$

whereas if carbon is not present, this reaction does not occur below 1100°C. In the presence of carbon the reaction initiates at 1005°C.

Any $BaCO_3$ formed in the kiln can undergo the following reactions at temperatures below 1100°C to form the metasilicate (13)

$$BaCO_3 + SiO_2 \longrightarrow BaSiO_3 + CO_2 \tag{3}$$

and subsequently the orthosilicate

$$BaSiO_3 + BaCO_3 \longrightarrow Ba_2SiO_4 + CO_2 \tag{4}$$

In the hot leaching step, barium metasilicate is insoluble, and the orthosilicate yields only one-half of its barium value to give barium hydroxide

$$Ba_2SiO_4 + H_2O \longrightarrow BaSiO_3 + Ba(OH)_2 \tag{5}$$

If coke is not present in sufficient quantity, more silicates are formed, presumably because of increased CO_2 concentration which leads to greater amounts of $BaCO_3$ being formed (1).

Barium is reported in the kiln spill in three different forms: water-soluble, eg, BaS, BaO; acid-soluble, eg, $BaCO_3$, aluminate, silicate, ferrate; and insoluble, eg, unreduced barite.

Reduction of $BaSO_4$ appears to begin about 900°C (15). The presence of iron or iron oxide can catalyze the barium (9) and also strontium reduction reaction rates. However, iron impurity can also increase the acid-soluble content of the black ash (9).

Calcareous minerals such as gypsum [13397-24-5], when added in stoichiometric amounts relative to the barite impurities, reduce acid-soluble barium losses (16).

Off-gases from the kiln are scrubbed for SO_2, SO_3, dust, and organic volatiles. In addition to equation 2, reactions which can generate SO_x are

$$BaS + 3\,CO_2 \longrightarrow BaO + 3\,CO + SO_2 \tag{6}$$

and

$$BaSO_4 + CO \longrightarrow BaO + CO_2 + SO_2 \tag{7}$$

Black ash wt % composition is typically BaS, 65–72, SiO_2, 10, $BaSO_4$, 3, metal oxides, 0.5, $BaSiO_3$, 16, and carbon, 5.5. The amount of black ash produced is about 65% by weight of the total ore and coke fed.

Significant waste heat may be recovered from the high (about 600°C) kiln off-gas. Pre-heating combustion air or feed ore improves the energy efficiency of the process. Reduction of barite in a fluid bed with CO and/or hydrogen has been performed on an experimental scale.

Leaching. Details of a typical countercurrent decantation system used in the leaching of barium black ash are shown in Figure 2. Black ash from the ball milling step is fed to a series of staged make-up tanks in which the dissolution of BaS begins. The dissolving media is an aqueous solution of 6–7% BaS from the overflow of the second of three clarifiers. Barium sulfide on contact with water

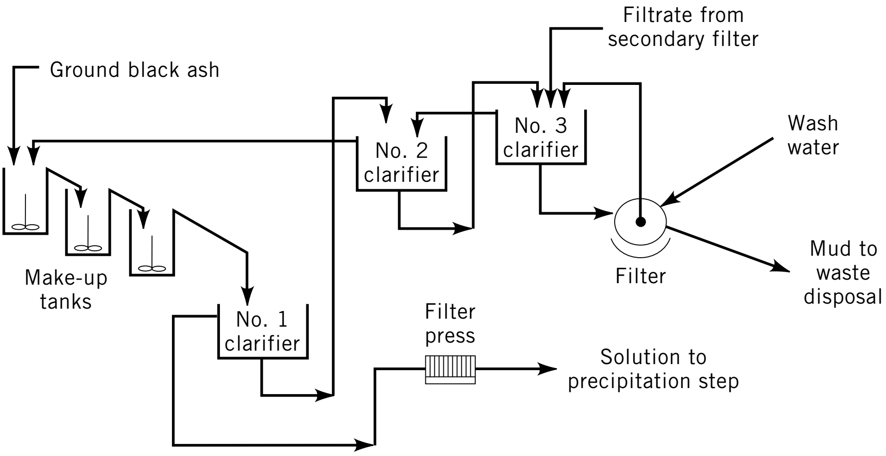

Fig. 2. Schematic of leaching circuit.

hydrolyzes to the hydroxide and hydrosulfide according to

$$2\,BaS + 2\,H_2O \longrightarrow Ba(OH)_2 + Ba(SH)_2 \tag{8}$$

Leaching is 90–95% complete as the solids exit in the underflow of the first clarifier. Final washing of the solids (mud) using fresh water takes place in a rotary filter from whence the mud, consisting of 65% H_2O, 10–15% $BaSO_4$ and silicates, and 10–15% coke, is delivered to landfill at an approved site.

Overflow from the first clarifier, typically a 20% BaS solution, is filtered and sent on to the precipitation department. Settling of solids in the clarifiers can be enhanced by various flocculating agents (qv), preferably weakly anionic polyacrylamides (17).

The net percentage of solids in the clarifier underflows increases in going from the first to the second to the third clarifier. Typical values are 11, 15, and 21% solids, respectively. Clarifier operations have been investigated by computer simulation studies (17).

Precipitation. Filtered overflow from the first clarifier, 20% BaS solution, is fed to an agitated tank where, on tight control, carbonate values are added in slight excess of stoichiometric requirements. The excess carbonate suppresses soluble barium which would otherwise later precipitate in equipment.

Carbonate values are usually supplied from soda ash or carbon dioxide or an equimolar mix. Possible reactions are

$$BaS + Na_2CO_3 \longrightarrow BaCO_3 + Na_2S \tag{9}$$

or

$$BaS + 0.5\,Na_2CO_3 + 0.5\,CO_2 + 0.5\,H_2O \longrightarrow BaCO_3 + NaHS \tag{10}$$

or

$$BaS + CO_2 + H_2O \longrightarrow BaCO_3 + H_2S \tag{11}$$

An additional possibility is

$$BaS + NaHCO_3 \longrightarrow BaCO_3 + NaHS \tag{12}$$

The H_2S in equation 11 can, if desired, be converted into elemental sulfur in a Claus furnace.

A photomicrograph of barium carbonate formed by precipitation using pure soda ash (eq. 9), is shown in Figure 3. The average particle size is 1.2 μm. The exclusive use of soda ash results in a barium carbonate having included sodium that cannot be reduced below a certain level by repeated washings. The sodium can be detrimental if the $BaCO_3$ is to be used for barium titanate production.

Filtration. The slurry resulting from the precipitation step is filtered in a primary stage on rotary filters separating the product, $BaCO_3$, from the coproduct, eg, Na_2S or NaHS in solution. The $BaCO_3$ wet cake is repulped in fresh water and filtered on a second-stage rotary filter. The aqueous stream

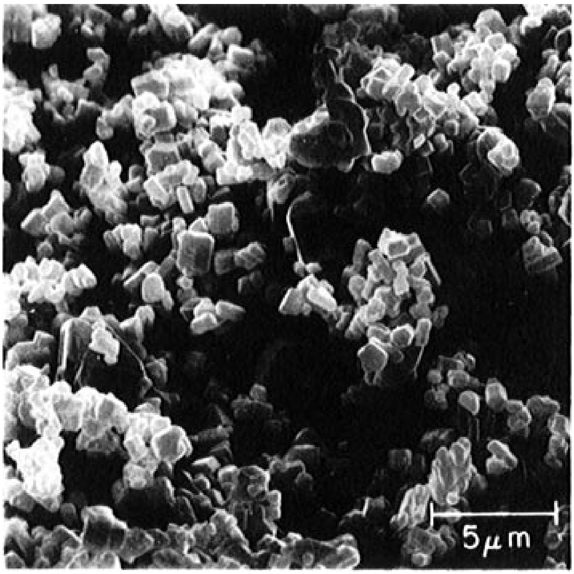

Fig. 3. Photomicrograph of precipitated $BaCO_3$.

from this separation, carrying some sulfide values, is then used in the third clarifier of the leaching step (see Figs. 1 and 2).

Drying and Calcining. A rotary dryer operating at a 600–800°C spill temperature may be used to form a hard, sintered, granular barium carbonate product. This form finds favor in glass manufacture. More powdery products can be produced at rotary dryer spill temperatures of less than 400°C (14). Spray-dried barium carbonate, including added dispersants (qv), provides a finer pigment-grade material which is used in ferrite production (see FERRITES).

Sulfide Solution Concentration. The by-product of the black ash process has considerable bearing on the ultimate economic viability of barium production. It is desirable to be able to vary by-products to maximize earnings. Sodium sulfide [1313-82-2], Na_2S, sold as 60% flake, and sodium bisulfide [16721-80-5], NaHS, sold as 45% solution or as 70% flake, are typically co-produced.

When solid soda ash is used to supply all the carbonate values in the precipitation step (eq. 9), a ca 10% Na_2S solution results from the primary filtration step which can be concentrated to 40% Na_2S in a three-effect evaporator train. Final concentration to 60% Na_2S occurs in a high vacuum single-effect evaporator. This concentrated solution can then be fed to a flaker to produce a 60% sodium sulfide flake which is sold as co-product.

Both sodium sulfide and the bisulfide are used in the flotation process for copper minerals and as a depilatory for animal hides (see COPPER; COPPER ALLOYS; LEATHER). Also, sodium polysulfide can be produced from Na_2S, and elemental sulfur can be produced if H_2S is generated as an intermediate.

5.2. Supply and Demand. The U.S. imported 18,600 t of barium carbonate in 2001, down from 26,200 t in 2000. The value in 2001 was $\$ 9.2 \times 10^6$ (4).

5.3. Uses. There are several different grades of barium carbonate manufactured to fit the specific needs of a wide variety of applications: very fine, highly reactive grades are made for the chemical industry; coarser and more readily handleable grades are mainly supplied to the glass industry.

The main use for barium carbonate is in the manufacture of glass. This is the most important use for a barium compound after well drilling fluids (5).

In 2000, 50% of the barium carbonate produced was used in glass manufacturing. Other uses include manufacturing of brick and clay products, barium chemicals, barium ferrites, and in the production of photographic papers.

Barium carbonate acts as a flux for silica. It is added to textile fiber glass, crown and flint optical glass, laboratory glassware, decorative glass, and frits for ceramic material. Barium carbonate has the lowest melting point of all the alkaline earths, and, in the presence of sodium carbonate, glass melting reactions may begin at less than 400°C. Barium oxide from the carbonate becomes part of the silicate structure and imparts many useful properties. It increases the glass durability, adds weight and density, increases the refractive index imparting a brilliance to the glass, and perhaps most significantly, absorbs x rays. Hence, barium carbonate is used in television glass manufacturing as an x-ray screening agent. Barium carbonate is used especially in black and white television face plates, and in small quantities in color face plates, where strontium carbonate is the principal screening agent.

Glass-grade barium carbonate has a high bulk density so that it does not become airborne when charged to the furnace. It also has a particle size distribution which has less tendency to segregate from other materials in the glass mixture.

Barium carbonate prevents formation of scum and efflorescence in brick, tile, masonry cement, terra cotta, and sewer pipe by insolubilizing the soluble sulfates contained in many of the otherwise unsuitable clays. At the same time, it aids other deflocculants by precipitating calcium and magnesium as the carbonates. This reaction is relatively slow and normally requires several days to mature even when very fine powder is used. Consequently, often a barium carbonate emulsion in water is prepared with carbonic acid to further increase the solubility and speed the reaction.

In the oil-well drilling industry, the barite suspension used as drilling mud can be destabilized by the presence of soluble materials such as gypsum. Addition of barium carbonate precipitates the gypsum, inhibits coagulation, and thus permits the mud to retain the desired consistency and dispersion.

Barium carbonate of finely controlled particle size reacts in the solid state when heated with iron oxide to form barium ferrites. Magnetically aligned barium ferrite [11138-11-7] powder can be pressed and sintered into a hard-core permanent magnet which is used in many types of small motors. Alternatively, ground up magnetic powder can be compounded into plastic strips which are used in a variety of appliances as part of the closure mechanism.

Barium carbonate also reacts with titania to form barium titanate [12047-27-7], $BaTiO_3$, a ferroelectric material with a very high dielectric constant (see FERROELECTRICS). Barium titanate is best manufactured as a single-phase composition by a solid-state sintering technique. The asymmetrical perovskite structure of the titanate develops a potential difference when compressed in specific crystallographic directions, and vice versa. This material is most widely used for its strong piezoelectric characteristics in transducers for ultrasonic technical applications such as the emulsification of liquids, mixing of powders and paints, and homogenization of milk, or in sonar devices.

Barium carbonate is also used in the manufacture of photographic paper to generate barium sulfate which imparts a flat white appearance (see PHOTOGRAPHY).

6. Barium Chloride

Both anhydrous barium chloride [10361-37-2], $BaCl_2$, mol wt 208.25, density 3.856 g/mL, and barium chloride dihydrate [10326-27-9], $BaCl_2{\cdot}2H_2O$, mol wt 244.28, density 3.097 g/mL, are produced from a filtered aqueous solution formed by the reaction of hydrochloric acid and $BaCO_3$ or BaS. If BaS is used, the H_2S generated must be appropriately handled.

The solubility of $BaCl_2$ in water is

Temperature, °C	0	20	40	60	80	100
Solubility, wt % $BaCl_2$	24.0	26.3	28.9	31.7	34.4	26.2

Anhydrous $BaCl_2$ exists as monoclinic or cubic crystals. The transition to cubic occurs at 925°C. Barium chloride melts at 962°C; the dihydrate, which has monoclinic crystals, loses water at 113°C. Barium chloride, which is very hygroscopic, is sold in moisture-proof bags and steel or fiber drums.

Barium chloride finds use in the production of barium colors, such as the diazo dyes barium lithol red [50867-36-2] and barium salt of Red Lake C [5160-02-1], a mordant for acid dyes and dying of textiles. Other uses include aluminum refining and boiler water treatment.

$BaCl_2$ is used in heat treating baths because of the eutectic mixtures it readily forms with other chlorides. The melting points of some eutectic mixtures are: $BaCl_2{\cdot}2KCl$, 672–680°C; $BaCl_2$–NaCl, 39 mol % $BaCl_2$, 654°C; $BaCl_2$–$CaCl_2$, 631°C. $BaCl_2$ is also used to set up porcelain enamels for sheet steel (see ENAMELS, PORCELAIN OR VITREOUS; STEEL), and it is used to produce blanc fixe [7727-43-7].

The U.S. imported 341 t of barium chloride in 2001 and was valued at $ 291,000. This figure is down from the 2000 demand of 1,240 t valued at $ 752,000 (4).

7. Barium 2-Ethylhexanoate

Barium 2-ethylhexanoate [4696-54-2], $Ba(C_8H_{16}O_2)_2$, also known as barium octanoate or barium octoate is usually used in synergistic combination with cadmium or zinc organic salts as a thermal stabilizer for PVC (18,19). It is often available preformulated with other additives such as the cadmium or zinc salts. Owing to cadmium's toxicity, the development of noncadmium stabilizers is growing, and use of barium octanoate is declining. Barium ethylhexanoate is a liquid; barium stearate [6865-35-6], $Ba(C_{18}H_{36}O_2)_2$, is a powder that also serves as a thermostabilizer for PVC. Organophosphites are often added to barium–zinc stabilizers to improve stabilizing effectiveness.

8. Barium Fluoride

Barium fluoride [7782-32-8], BaF_2, is a white crystal or powder. Under the microscope crystals may be clear and colorless. Reported melting points vary from 1290 (20) to 1355°C (21), including values of 1301 (22) and 1353°C (23). Differences may result from impurities, reaction with containers, or inaccurate temperature measurements. The heat of fusion is 28 kJ/mol (6.8 kcal/mol) (24), the boiling point 2260°C (25), and the density 4.9 g/cm^3. The solubility in water is about 1.6 g/L at 25°C and 5.6 g/100 g (26) in anhydrous hydrogen fluoride. Several preparations for barium fluoride have been reported (27–29).

High purity BaF_2 can be prepared from the reaction of barium acetate and aqueous HF (30), by dissolving the impure material in 2–12*N* HCl and recrystallizing at −40°C (31), by vaccum distillation of the metal fluoride impurities from BaF_2 melt (32), by purification of the aqueous acetate solution by ion exchange followed by fluorination (33), by solvent extraction using dithiocarbamate and CCl_4 (34–36), and by solvent extraction using acetonitrile (37).

A typical analysis of the commercial product is 99% with a loss on ignition of 0.9%; sulfates as SO_4, 0.2%; hexafluorosilicate as SiF_4, 0.02%; heavy metals as lead, 0.02%; and iron, 0.005%.

Barium fluoride is used commercially in combination with other fluorides for arc welding (qv) electrode fluxes. However, this usage is limited because of the availability of the much less expensive naturally occurring calcium fluoride.

Other reported uses of barium fluoride include the manufacture of fluorophosphate glass (38); stable fluoride glass (39); fluoroaluminate glass (40); fluorozirconate glass (41); infared transmitting glass (42); in oxidation-resistant ceramic coatings (43); in the manufacture of electric resistors (44); as a superconductor with copper oxide (45); as a fluoride optical fiber (46) (see FIBER OPTICS; GLASS); and in a high repetition rate uv excimer laser (47).

9. Barium Hydrosulfide

Barium hydrosulfide [25417-81-6], $Ba(HS)_2$, is formed by absorption of hydrogen sulfide into barium sulfide solution. On addition of alcohol, barium hydrosulfide tetrahydrate [12230-74-9], $Ba(HS)_2 \cdot 4H_2O$, crystallizes as yellow rhombic crystals that decompose at 50°C. Solid barium hydrosulfide is very unstable. Its solubility in water is

Temperature, °C	0	20	40	60	80	100
Solubility, wt % $Ba(HS)_2$	32.6	32.8	34.5	36.2	39.0	43.7

10. Barium Hydroxide

Barium hydroxide is the strongest base and has the greatest water-solubility of the alkaline-earth elements. Barium hydroxide (barium hydrate, caustic baryta) exists as the octahydrate [12230-71-6], $Ba(OH)_2{\cdot}8H_2O$, the monohydrate [22326-55-2], $Ba(OH)_2{\cdot}H_2O$, or as the anhydrous[17194-00-2] material, $Ba(OH)_2$. The octahydrate and monohydrate have sp gr 2.18 and 3.74, respectively. The mp of the octahydrate and anhydrous are 77.9°C and 407°C, respectively.

Solubility of $Ba(OH)_2$ in water is strongly temperature dependent in the range >40°C.

Temperature, °C	0	20	40	60	80
Solubility, wt % $Ba(OH)_2$	1.65	3.74	7.60	17.32	50.35

These solutions are highly alkaline and can effectively remove CO_2 or other acidic gases from ambient atmosphere. The octahydrate is also soluble in methanol, but only slightly soluble in ethanol.

The octahydrate is prepared by dissolving BaO in hot water for several hours, filtering off undissolved impurities, then cooling the solution to effect crystallization. Vapor pressure data for the octahydrate (48) is

Temperature, °C	17.6	32.1	40.7	50.7	57.8	64.8
Pressure, kPa	0.48	1.32	2.36	5.08	8.01	12.56

The monohydrate can be produced by vacuum drying of the octahydrate (49).

Barium hydroxide is used in the manufacture of barium greases and plastic stabilizers such as barium 2-ethylhexanoate, in papermaking, in sealing compositions (see SEALANTS), vulcanization accelerators, water purification, pigment dispersion, in a formula for self-extinguishing polyurethane foams, and in the protection of objects made of limestone from deterioration (see FINE ART EXAMINATION AND CONSERVATION; LIME AND LIMESTONE). Uses of the octahydrate include: use as a low temperature latent heat storage material in combination with Na or KNO_3 or NaOAc (50); use as a nucleating agent to reduce supercooling of $CaBr_2$ solution and removal of CO_2 and $^{14}CO_2$ by passing through a bed of solid mono- or octahydrate.

The U.S. imported 3,780 t of barium oxide, hydroxide, and peroxide valued at \$ 3.3×10^6 in 2001. In 2000, the U.S. imported 5,290 t valued at \$ 4.8×10^6 (4).

11. Barium Iodide

Barium iodide dihydrate [7787-33-9], $BaI_2{\cdot}2H_2O$, crystallizes from hot aqueous solution. Below 30°C, barium iodide hexahydrate [13477-15-1], $BaI_2{\cdot}6H_2O$, crystallizes. The dihydrate, sp gr 5.15, loses water to form anhydrous barium iodide [13718-50-8], BaI_2, at 150°C, mp 740°C. Barium iodide discolors on exposure to air containing carbon dioxide, and decomposes to barium carbonate and iodine. BaI_2 is soluble in water.

Temperature, °C	−20	0	25	60	120
Solubility, wt % BaI_2	58.60	62.5	68.8	70.70	74.30

BaI_2 is also soluble in alcohol and acetone. BaI_2 is useful in making other iodides. BaI_2 has been cited for producing ir transparent glasses that are useful in power transmission from CO and CO_2 lasers (qv) from the ZnI_2–CsI–BaI_2 system (51); as a catalyst promoter, for such catalysts as rhodium(III) chloride, in carbonylation reactions (52,53); as being useful in chemical vapor depositionas a precursor in forming the superconducting composition$YBa_2Cu_3O_{7-x}$; as a sintering aid for aluminum nitride (54), and in phosphor formulations for cathode-ray tubes.

12. Barium Metaborate

Barium metaborate monohydrate [23436-05-7], $Ba(BO_2)_2{\cdot}H_2O$, has a sp gr of 3.25–3.35, a fusion pt of 900–1050°C, n_D of 1.55–1.60, solubility of 0.3% in water at 21°C, and pH 9.8–10.3 for the saturated solution. It can be prepared from the reaction of a solution of BaS and sodium tetraborate.

$Ba(BO_2)_2{\cdot}H_2O$, used in flame retardant plastic formulations as a synergist for phosphorus or halogen compounds and as a partial or complete replacement for antimony oxide (see FLAME RETARDANTS), is excellent as an afterglow suppressant. The low refractive index of $Ba(BO_2)_2$ results in greater transparency and brighter colors in formulated plastics (55). Barium metaborate has been reported in paint formulations to convey insecticidal properties (56) (see INSECT CONTROL TECHNOLOGY). Barium metaborate crystals (the low temperature beta form) have been grown by Czocharski techniques (57,58) and are used in nonlinear optics for high power uv lasers and can be applied to uv photolithography (see LITHOGRAPHY; NONLINEAR OPTICAL MATERIALS). $Ba(BO_2)_2$ has been reported to be used in antibacterial coatings for aluminum heat exchanger surfaces of air conditioners (59). Use of the metaborate as a sintering aid for $BaTiO_3$ has been studied (60).

The barium oxide borate [12007-55-5], $BaO{\cdot}2B_2O_3$, and dibarium oxide triborate [13840-10-3], $2BaO{\cdot}3B_2O_3$, have also been reported.

13. Barium Nitrate

Barium nitrate [10022-31-8], $Ba(NO_3)_2$, occurs as colorless crystals; mp 592°C; sp gr 3.24. Its solubility in water is

Temperature, °C	0	25	40	60	80	100	135
Solubility, wt % $Ba(NO_3)_2$	4.72	9.27	12.35	16.9	21.4	25.6	32.0

Barium nitrate is prepared by reaction of $BaCO_3$ and nitric acid, filtration and evaporative crystallization, or by dissolving sodium nitrate in a saturated solution of barium chloride, with subsequent precipitation of barium nitrate. The precipitate is centrifuged, washed, and dried. Barium nitrate is used in pyrotechnic green flares, tracer bullets, primers, and in detonators. These make use of its property of easy decomposition as well as its characteristic green flame. A small amount is used as a source of barium oxide in enamels.

The U.S. imported 5,010 t of barium nitrate in 2001. Value of this quantity was \$ 6.10×10^6. The U.S. imported 4,930 t in 2000, valued at \$ 4.5×10^6 (14).

14. Barium Nitrite

Barium nitrite [13465-94-6], $Ba(NO_2)_2$, crystallizes from aqueous solution as barium nitrite monohydrate [7787-38-4], $Ba(NO_2)_2 \cdot H_2O$, which has yellowish hexagonal crystals, sp gr 3.173, solubility 54.8 g $Ba(NO_2)_2$/100 g H_2O at 0°C, 319 g at 100°C. The monohydrate loses its water of crystallization at 116°C. Anhydrous barium nitrite, sp gr 3.234, melts at 267°C and decomposes at 270°C into BaO, NO, and N_2. Barium nitrite may be prepared by crystallization from a solution of equivalent quantities of barium chloride and sodium nitrite, by thermal decomposition of barium nitrate in an atmosphere of NO, or by treating barium hydroxide or barium carbonate with the gaseous oxidiation products of ammonia. It has been used in diazotization reactions.

15. Barium Oxide and Peroxide

Barium oxide [1304-28-5], BaO, occurs as colorless cubic or hexagonal crystals; mp 1923°C; sublimation ca 2000°C; bp ca 3088°C; sp gr (cubic) 5.72, (hexagonal) 5.32. Barium oxide is highly reactive toward carbon dioxide in the presence of water vapor, and is converted to the hydroxide and carbonate when exposed to air. Upon additions of small amounts of water, or in a carbon dioxide atmosphere, absorption is so rapid that large amounts of heat are liberated, raising the temperature to a red heat. The heat of formation of barium hydroxide from barium oxide and water is 102 kJ/mol (24.4 kcal/mol) and that of barium carbonate from barium oxide and carbon dioxide is 264 kJ/mol (63.1 kcal/mol). Consequently, accumulation of barium oxide and the peroxide, dust, and dirt presents a fire hazard. When a fire occurs, large concentrations of carbon dioxide from burning organic matter cause further incandescence because the carbon dioxide is absorbed by the barium oxide. Such fires spread rapidly and are difficult to extinguish.

Of the alkaline-earth carbonates, $BaCO_3$ requires the greatest amount of heat to undergo decomposition to the oxide. Thus carbon in the form of coke, tar, or carbon black, is added to the carbonate to lower reaction temperature from about 1300°C in the absence of carbon to about 1050°C. The potential for the reverse reaction is decreased by removing the CO_2 as shown in equation 1b.

Barium oxide, which can react directly with oxygen to give the peroxide (61), is soluble in methanol and ethanol forming the alkoxides (see ALKOXIDES, METAL).

BaO is used to impart improved strength to porcelain (62), as a solid base catalyst, in specialty cements, and for drying gases.

The U.S. imported 3,780 t of barium oxide, hydroxide, and peroxide in 2001, valued at \$ 3.3×10^6. In 2000, the U.S. imported 5,290 t valued at \$ 4.8×10^6 (4).

When heated in air or oxygen to 500°C, barium oxide is converted readily to barium peroxide [1304-29-6], BaO_2. Upon further heating to 700°C, the peroxide decomposes to BaO and oxygen. This reaction was used for many years to make pure oxygen via the Brin process. Other preparations for the peroxide such as the reaction between $BaCl_2$ and H_2O_2 in alkaline solution, or between BaO and H_2O_2 have been reported.

Reported uses of BaO_2 include in the cathodes of fluorescent lamps, formation of $YBa_2Cu_3O_{7-x}$ superconducting phase from CuN_3, BaO_2, and Y_2O_3 (52), and as a drying agent forlithographic inks.

16. Barium Sodium Niobium Oxide

Barium sodium niobium oxide [12323-03-4], $Ba_2NaNb_5O_{15}$, finds application for its dielectric, piezoelectric, nonlinear crystal and electro-optic properties (63, 64). It has been used in conjunction with lasers for second harmonic generation and frequency doubling. The crystalline material can be grown at high temperature, mp ca 1450°C (65).

17. Barium Sulfate

Barium sulfate [7727-43-7], $BaSO_4$, occurs as colorless rhombic crystals, mp 1580°C (dec); sp gr 4.50; solubility 0.000285 g/100 g H_2O at 30°C and 0.00118 at 100°C. It is soluble in concentrated sulfuric acid, forming an acid sulfate; dilution with water reprecipitates barium sulfate. Precipitated $BaSO_4$ is known as blanc fixe, prepared from the reaction of aqueous solutions of barium sulfide and sodium sulfate.

Because of its extreme insolubility, barium sulfate is not toxic; the usual antidote for poisonous barium compounds is to convert them to barium sulfate by administering sodium or magnesium sulfate. In medicine, barium sulfate is widely used as an x-ray contrast medium (see IMAGING TECHNOLOGY; X-RAY TECHNOLOGY). It is also used in photographic papers, filler for plastics, and in concrete as a radiation shield. Commercially, barium sulfate is sold both as natural barite ore and as a precipitated product. Blanc fixe is also used in making white sidewall rubber tires or in other rubber applications.

18. Barium Sulfide

Impure barium sulfide with 20–35% contaminants is produced in large volume by the black ash kiln. Pure barium sulfide [21109-95-5], BaS, occurs as colorless cubic crystals, sp gr 4.25 and as hexagonal plates of barium sulfide hexahydrate [66104-39-0], $BaS{\cdot}6H_2O$. BaS melts at 2227°C. Solubility in water is reported (49) as

Temperature, °C	0	20	40	60	80	90	100
Solubility, wt % BaS	2.8	7.3	13.0	21.7	33.3	40.2	37.6

BaS hydrolyzes to $Ba(OH)_2$ and barium hydrosulfide. Cooling of an aqueous BaS solution can precipitate the double salt barium hydroxide sulfide hydrate [42821-46-5], $Ba(OH)_2 \cdot Ba(SH)_2 \cdot xH_2O$.

Barium sulfide solutions undergo slow oxidation in air, forming elemental sulfur and a family of oxidized sulfur species including the sulfite, thiosulfate, polythionates, and sulfate. The elemental sulfur is retained in the dissolved liquor in the form of polysulfide ions, which are responsible for the yellow color of most BaS solutions. Some of the more highly oxidized sulfur species also enter the solution. Sulfur compound formation should be minimized to prevent the compounds made from BaS, such as barium carbonate, from becoming contaminated with sulfur.

BaS is used in the manufacture of lithophone[8006-32-4], useful as a white pigment in paints, according to

$$BaS + ZnSO_4 \longrightarrow BaSO_4\ (ppt) + ZnS\ (ppt)$$

BaS has been used in the production of thin-film electroluminescent phosphors, often activated with Eu^{2+} (66, 67). Similarly, infrared-triggered phosphors may be fabricated from Ba or Sr sulfide, a dopant such as EuO and a fusible salt such as LiF (68). BaS has also been mentioned as a nucleating agent in combination with $BaCl_2 \cdot 2H_2O$ for a $CaCl_2 \cdot 6H_2O$ heat storage system (69), and in vulcanization of carbon black-filled neoprene rubbers (70).

19. Barium Titanate

The basic crystal structure of barium titanate [12047-27-7], $BaTiO_3$, the so-called perovskite structure, after the mineral, $CaTiO_3$, leads to unique, outstanding dielectric properties. The barium and oxygen ions together form a face-centered cubic lattice, the titanium ions fitting into octahedral interstices. The minimum energy positions for the titanium ion are off-center and give rise to an ordered electrical dipole, which can be made permanent during production by the proper heating and cooling regime (see CERAMICS; FERROELECTRICS; TITANIUM COMPOUNDS).

Barium titanate has widespread use in the electronics industry. Its high dielectric constant and the ease with which its electrical properties can be modified by combination with other materials make it exceptionally suitable for a variety of items, ie, miniature capacitors (see CERAMICS AS ELECTRICAL MATERIALS). Several mentions of barium titanate for use as a semiconductive ceramic have appeared in the patent literature (71–73).

Barium titanate is usually produced by the solid-state reaction of barium carbonate and titanium dioxide. Dielectric and piezoelectric properties of $BaTiO_3$ can be affected by stoichiometry, microstructure, and additive ions that can enter into solid solution. In the perovskite lattice, substitutions of Pb^{2+}, Sr^{2+}, Ca^{2+}, and Cd^{2+} can be made for part of the barium ions, maintaining the ferroelectric characteristics. Similarly, the Ti^{4+} ion can partially be replaced with Sn^{4+}, Hf^{4+}, Zr^{4+}, Ce^{4+}, and Th^{4+}. The possibilities for forming solution alloys in all these structures offer a range of compositions, which present a wide range of dielectric, temperature dependence, and other characteristics. At the same time, impurities such as SiO_2, Al_2O_3, Na_2O, etc, or anything affecting the crystal lattice, can also alter the dielectric properties and must be carefully controlled, both in raw materials and within the production process itself. Nonstoichiometry originating from the $BaO{:}TiO_2$ ratio or additional impurities may result in semiconductive ceramics upon firing.

Barium titanate ceramic products are used for application in numerous sonic and ultrasonic devices, such as underwater sonar, guided missiles, acoustic mines, ultrasoniccleaning, measuring instruments, eg, for flaw detection, liquid-level sensing, and thickness gauges, sound reproduction, filters, and ultrasonic machining (see LIQUID-LEVEL MEASUREMENTS; NONDESTRUCTIVE TESTING; SURFACE AND INTERFACE ANALYSIS). Its most important application is for ceramic capacitors of disk, tube, and multilayer designs (74).

20. Yttrium–Barium–Copper Oxide

Yttrium–barium–copper oxide, $YBa_2Cu_3O_{7-x}$, is a high T_c material which has been found to be fully superconductive at temperatures above 90 K, a temperature that can be maintained during practical operation. The foremost challenge is to be able to fabricate these materials into a flexible form to prepare wires, fibers, and bulk shapes. Ultrapure powders of yttrium–barium–copper oxide that are sinterable into single-phase superconducting material at low temperatures are required, creating a worldwide interest in high purity barium chemicals.

A number of promising new routes to chemically synthesize ultrapure, ultrahomogeneous particles of controlled particle size and particle size distribution are currently under development. A modified sol–gel method has been developed to produce thermoplastic gels that are compatible with fiber spinning technology (see SOL–GEL TECHNOLOGY), as has a process which avoids the formation of barium carbonate, a troublesome impurity at the grain boundaries which seriously detracts from the critical current. In this latter process, hyponitrites and hydrated oxides derived from the hydrolysis of organometallic solutions are subjected to a series of thermal treatments involving decomposition, oxidation, and finally annealing. Materials which can be decomposed and converted to the orthorhombic superconducting form are produced (75,76).

21. Analytical Methods

The classical analytical method of determination of barium ion is gravimetric, by precipitating and weighing insoluble barium sulfate. Barium chromate, which is more insoluble than strontium chromate in a slightly acidic solution, gives a fairly good separation of the two elements.

Alkaline-earth metals are often determined volumetrically by complexometric titration at pH 10, using Eriochrome Black T as indicator. The most suitable complexing titrant for barium ion is a solution of diethylenetriaminepentaacetic acid (DTPA). Other alkaline earths, if present, are simultaneously titrated, and in the favored analytical procedure calcium and strontium are determined separately by atomic absorption spectrophotometry, and their values subtracted from the total to obtain the barium value.

Barium can also be determined by x-ray fluorescence (XRF) spectroscopy, atomic absorption spectroscopy, and flame emission spectroscopy. Prior separation is not necessary. XRF can be applied directly to samples of ore or products to yield analysis for barium and contaminants. All crystalline barium compounds can be analyzed by x-ray diffraction.

22. Health and Safety Aspects

The average adult human body contains 22 mg Ba, of which 93% is present in bone (77). The remainder is widely distributed throughout the soft tissues of the body in very low concentrations. Accumulation of barium also takes place in the pigmented parts of the eyes.

22.1. Environmental Levels and Exposures. Barium constitutes about 0.04% of the earth's crust (77). Agricultural soils contain Ba^{2+} in the range of several micrograms per gram. The Environmental Protection Agency, under the Safe Drinking Water Act, has set a limit for barium of 1 mg/L for municipal waters in the United States.

Generally, barium content of food parallels calcium content in a ratio from $1/10^2$ to $1/10^5$ (77). Milk contains about 45–136 micrograms Ba per gram Ca; wheat and oatmeal contain 1300 and 2320–8290 micrograms Ba per gram Ca, respectively. The average daily intake of barium may be as high as 1.33 mg in the diet of the general population. Dietary barium intake has been estimated to originate 25% from milk, 25% from flour, 25% from potatoes, and 25% from miscellaneous high barium foods, such as nuts, consumed in small quantities.

22.2. Toxicity. The toxicity of barium compounds depends on solubility (77–79). The free ion is readily absorbed from the lung and gastrointestinal tract. The mammalian intestinal mucosa is highly permeable to Ba^{2+} ions and is involved in the rapid flow of soluble barium salts into the blood. Barium is also deposited in the muscles where it remains for the first 30 h and then is slowly removed from the site (80). Very little is retained by the liver, kidneys, or spleen and practically none by the brain, heart, and hair.

22.3. Soluble Compounds. The mechanism of barium toxicity is related to its ability to substitute for calcium in muscle contraction. Toxicity results from stimulation of smooth muscles of the gastrointestinal tract, the cardiac muscle, and the voluntary muscles, resulting in paralysis (77). Skeletal, arterial, intestinal, and bronchial muscle all seem to be affected by barium.

22.4. Oral Exposure. Following oral exposure to high doses of barium compounds, symptoms of nausea, vomiting, colic, and diarrhea result. Other symptoms include excessive salivation, hypertension, tremors, tingling of the extremities, twitching of facial muscles, and paralysis of the tongue and pharynx with loss or impairment of speech (79,81). Barium stimulation of arterial muscles causes an elevation in blood pressure resulting from vasoconstriction. Severe cases of poisoning cause loss of tendon reflexes, heart fibrillation, and general muscular paralysis, including the respiratory muscles, leading to death (77). Acute barium toxicity results in low serum potassium levels and leukocytosis in both experimental animals and humans (79,82). Symptoms of chronic barium poisoning are similar, but of lesser severity.

The more soluble forms of barium such as the carbonate, chloride, acetate, sulfide, oxide, and nitrate, tend to be more acutely toxic (80). Mean lethal doses for ingested barium chloride were 300–500 mg/kg in rats and 7–29 mg/kg in mice (77).

Administration of 5 ppm barium, the acetate, to mice in the drinking water in a life-time study had no observable effects on longevity, mortality, and body weights, or on the incidence of tumors (83). Longterm studies in rats exposed to Ba^{2+} in drinking water containing 5 mg/L, as acetate, or 10–250 mg/L, as chloride, resulted in no measurable toxic effects (77).

Water-insoluble barium salts are poorly absorbed. In fact, barium sulfate is used as a contrast material for x-ray examination of the gastrointestinal tract based on its limited solubility and low toxicity (82). Barium sulfate fed to mice at various levels up to 8 ppm dietary Ba ($\sim$1.14 mg/kg·d as Ba^{2+}) for three generations had no significant effects on growth, mortality, morbidity, or reproductive performance (83).

22.5. Inhalation Exposure. Workers exposed to barium carbonate dust for 7–27 years did not reveal any specific chronic poisoning (49). The American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) have recommended a threshold limit value (TLV) of 0.5 mg/m^3 as Ba, as a time weighted average, for soluble compounds of barium. This time weighted average is an average airborne exposure in any 8-h work shift of a 40-h work week which should not be exceeded.

The OSHA limit for barium sulfate dust in air is 10 mg/m^3. NIOSH currently recommends that a level of 50 mg/m^3 be considered immediately dangerous to health (84).

In humans, inhaled insoluble barium salts are retained in the lung (77,79). Inhalation of high concentrations of the fine dusts of barium sulfate can result in the formation of harmless nodular granules in the lungs, a condition called baritosis (79). Baritosis produces no specific symptoms and no changes in pulmonary function. The nodulates disappear upon cessation of exposure to the barium salt. However, it is possible that barium sulfate may produce benign pneumoconiosis because, unlike barium carbonate, barium sulfate is poorly absorbed (49).

The threshold of a toxic dose in adult humans is about 0.2–0.5 g Ba; the lethal dose in untreated cases is 3–4 g Ba, LD_{50} about 66 mg/kg (77). The fatal-dose of barium chloride for humans is reported to be between 0.8 and 0.9 g (0.55–0.60 g of Ba) (80). However, for most of the acid-soluble salts of barium, doses greater than 1 g have been tolerated (81). Lethal doses are summarized in Table 3. Dusts of barium oxide are considered potential dermal and nasal irritants (82).

22.6. Treatment. Treatment of poisoning from soluble barium salts may be preventive or curative (77,81). Preventive treatment involves inhibition of intestinal absorption by administering such soluble sulfates as magnesium or sodium, causing precipitation of barium sulfate in the alimentary tract. Curative treatment involves counteracting the paralytic effect of the Ba^{2+} ion on the muscle by intravenous infusion of a potassium salt.

Table 3. **Acute Lethal Doses of Soluble Barium Compounds**[a]

Compound	Route of exposure	Species	Toxicity, LD_{50}, mg/kg
$BaCO_3$	oral	rat	418
	oral	mouse	200
	oral	human	11[b] 29[b]
	oral	human	57[c]
$BaNO_3$	oral	rat	355
	intravenous	mouse	8.5
$BaCl_2$	oral	rat	118
	oral	human	11.4[c]
BaO	subcutaneous	mouse	50
BaF_2	oral	rat	250

[a] Ref. 85.

[b] Value is toxic dose low. TD_{LO}, the lowest dose of a substance introduced by any route other than inhalation, over any given period of time to which humans or animals have been exposed and reported to produce any nonsignificant toxic effect in humans or to produce nonsignificant tumorigenic or reproductive effects in animals or humans.

[c] Value is lethal dose low, LD_{LO}, the lowest dose of a substance introduced by any other route other than inhalation, over any given period of time and reported to have caused death in humans or animals.

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