SODIUM NITRATE AND NITRITE

1. Sodium Nitrate

1.1. Introduction. Sodium nitrate [7631-99-4], $NaNO_3$, is found in naturally occurring deposits associated with sodium chloride, sodium sulfate, potassium chloride, potassium nitrate, magnesium chloride, and other salts. Accumulations of sodium nitrate have been reported in several countries, but the only ones being commercially exploited are the unique nitrate-rich deposits in Chile, South America. Natural sodium nitrate is also referred to as Chilean saltpeter or Chilean nitrate.

The annual world production of sodium nitrate was steady throughout the early 1990s. About 85% is supplied by the natural product. The maximum world production of sodium nitrate occurred around 1930, at 3,000,000 t/yr, but the highest production levels attained by the Chilean nitrate industry (ca 2,900,000 t/yr) occurred in the late 1920s. Synthetic sodium nitrate production peaked in the mid-1930s at 730,000 t/yr. During that period, the Chilean industry production decreased to 1,360,000 t/yr.

Sodium nitrate is used as a fertilizer and in a number of industrial processes. In the period from 1880–1910 it accounted for 60% of the world fertilizer nitrogen production. In the 1990s sodium nitrate accounted for 0.1% of the world fertilizer nitrogen production, and was used for some specific crops and soil conditions. This decline resulted from an enormous growth in fertilizer manufacture and an increased use of less expensive nitrogen fertilizers (qv) produced from synthetic ammonia (qv), such as urea (qv), ammonium nitrate, ammonium phosphates, ammonium sulfate, and ammonia itself (see Ammonium compounds). The commercial production of synthetic ammonia began in 1921, soon after the end of World War I. The main industrial market for sodium nitrate was at first the manufacture of nitric acid (qv) and explosives (see Explosives and propellants). Sodium nitrate has been used in the production of some explosives and in a number of industrial areas.

1.2. Deposits. The Chilean nitrate deposits are located in the north of Chile, in a plateau between the coastal range and the Andes mountains, in the Atacama desert. These deposits are scattered across an area extending some 700 km in length, and ranging in width from a few kilometers to about 50 km. Most deposits are in areas of low relief, about 1200 m above sea level. The nitrate ore, caliche, is a conglomerate of insoluble and barren material such as breccia, sands, and clays (qv), firmly cemented by soluble oxidized salts that are predominantly sulfates, nitrates, and chlorides of sodium, potassium, and magnesium. Caliche also contains significant quantities of borates, chromates, chlorates, perchlorates, and iodates.

The nitrate deposits are made up of several layers (Fig. 1). The ore bodies are very heterogeneous and variable in size, thickness, composition, and hardness. The overburden may include *chuca*, a layer of unconsolidated sand, silt, and clay, and *panqueque*, a layer of semiconsolidated and porous material poorly cemented by salts over poorly cemented gravel. The ore composition has degraded considerably since the early days of the industry, when it was reported

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that ores of up to 50% sodium nitrate were mined. There are still reserves that can be commercially mined well into the twenty-first century (1).

Numerous theories exist as to how the Chilean deposits formed and survived. It has been postulated that the unique nitrate-rich caliche deposits of northern Chile owe their existence to an environment favorable to accumulation and preservation of the deposits, rather than to any unusual source of the saline materials (2). The essential conditions are an extremely arid climate similar to that of the Atacama desert in the 1990s, slow accumulation during the late Tertiary and Quaternary periods, and a paucity of nitrate-utilizing plants and soil microorganisms.

1.3. Properties. Selected physical and chemical properties of sodium nitrate are listed in Table 1. At room temperature, sodium nitrate is an odorless and colorless solid, moderately hygroscopic, saline in taste, and very soluble in water, ammonia, and glycerol. Detailed physical and chemical properties are also available (3,4).

1.4. Manufacture and Processing

Natural Sodium Nitrate. The manufacture of natural sodium nitrate is carried out by its extraction from the ore by leaching with a brine, followed by fractional crystallization. Historically the Shanks process was utilized, but the last plant closed in 1977. In the Shanks process, the ore was crushed and leached in large steel vats using a solution consisting of water and a mother liquor brine having ca 450 g/L sodium nitrate. During leaching, carried out at a temperature of 70°C, the brine was concentrated to 700–750 g/L sodium nitrate and then pumped to a preliminary cooling pan where temperature was allowed to drop to ca 25°C. Sodium chloride then crystallized and the slimes were allowed to settle after the addition of a coagulant, eg, wheat flour. The clear liquor, added to $NaNO_3$-crystallizing pans, was allowed to cool overnight to ambient temperature. The brine or mother liquor was then pumped and sent to the last stages of the leaching cycle. The Shanks process made possible the recovery of ca 60% of the sodium nitrate in the ore. Fuel consumption was ca 0.154 metric tons of fuel per metric ton of $NaNO_3$.

The Guggenheim process was introduced in the late 1920s, after been developed by Guggenheim Bros., a firm engaged in developing a Chile copper company in northern Chile. The process was developed based on leaching of caliche at 40°C, which yields a fairly good extraction. Also, the sodium nitrate concentration can be as high as 450 g/L, which is more than 50% of the total dissolved solids, and it can be easily removed through crystallization. If the leaching solution contains a certain level of protective salts, eg, $MgSO_4$ and $CaSO_4$, the sparingly soluble double salt darapskite, $NaNO_3 \cdot Na_2SO_4 \cdot H_2O$, present in the caliche is broken up by magnesium action, thereby increasing $NaNO_3$ extraction. In the Guggenheim process, astrakanite, $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, precipitates instead of darapskite.

The Guggenheim process was developed to permit the treatment of low grade caliche ores, making it possible to mine by mechanical methods instead of by hand. Furthermore, this lower grade ore could be leached with only slightly warm solutions, as opposed to the boiling solutions required for high grade ore, and the nitrate was precipitated by refrigeration, replacing the process of evaporation and cooling in open tanks. In order to provide low cost heat to warm the leach solutions and make subsequent mechanical refrigeration economical, a carefully balanced system of power-plant heat recovery was put into operation (5). The utilization of the Guggenheim process has made it possible commercially to exploit reserves having as low as 7% $NaNO_3$ ore. The process used in the mid-1990s is basically the same as the original one. Only a few modifications had been made, eg, those that permit obtaining anhydrous sodium sulfate and iodine as by-products.

A flow sheet of the processing operations for sodium nitrate production in Chile is shown in Figure 2.

Because the ore quality is variable, large open-pit mining areas are first identified by general exploration; specific mining strips are later identified by further exploration and testing. Surface mining methods are used. The overburden is drilled, blasted, and removed, and the waste from a given strip is dumped into a previously worked-out strip. After removal of the overburden, the exposed caliche is drilled, blasted, and loaded into 80-metric ton trucks that deliver the ore to a transfer rail station for transportation to the plants.

At the plant, the ore cars pass through a rotary-car dumper, and the ore is dumped into crushing units. The mineral brought from the mine varies in size from fine particles to chunks of 3–5 metric tons. Crushing is carried out in three stages by means of jaw and cone-type crushers. Before crushing, a selecting screen rejects material smaller than 0.42 mm. About 80% of the crushed material, ie, that having diameter >0.42 mm, is sent to the leaching plant. The remaining 20% is sent to the fines treatment ponds. These two fractions have to be leached separately because clay present in the fine fraction swells when in contact with rich brines, occurrence of which would retard the rate of leaching of the coarser fraction.

Once the coarser fraction is transferred to the leaching plant (see Fig. 2), leaching takes place in a series of 10,000-m^3 leaching vats built of reinforced concrete. The process consists of countercurrent leaching, with one cycle involving 10 vats, one of which is being loaded with crushed ore while another one is being unloaded. Leaching time is 20 h per vat; one total cycle takes 120 h. The leaching is carried out at a temperature of 40°C, using a mother liquor entering the process at a concentration of 320 g/L of sodium nitrate and ending at a concentration of 440–450 g/L. The leaching process terminates with a final washing with water, where Glauber's salt, $Na_2SO_4{\cdot}10H_2O$, is obtained by crystallization (qv). The depleted ores, containing ca 1% sodium nitrate, are removed by means of electromechanical dredgers into trucks that haul them to tailing disposal areas.

The strong solution from the leaching process is cooled to crystallize sodium nitrate in a series of shell-and-tube heat exchangers. Cooling is produced first by using the already cold spent solution. Further cooling is obtained by ammonia refrigeration. The final temperature is 8–12°C. The slurry containing sodium nitrate crystals is sent to thickening tanks and the resulting sludge is pumped to continuous centrifuges. The centrifuged product is rinsed to displace entrained brines, and crystallized sodium nitrate having 4–6% moisture is obtained. The crystallized sodium nitrate can be dried and prilled to produce fertilizer-grade sodium nitrate, or recrystallized to remove impurities and obtain technical grades of sodium nitrate for industrial uses. Otherwise, crystallized sodium nitrate can be sent to the potassium nitrate plant, where potassium nitrate is produced through a direct reaction of sodium nitrate and potassium chloride (see Potassium compounds). Crystallized sodium nitrate can also be combined with existing potassium nitrate to obtain a potassium sodium nitrate.

The sodium nitrate crystals are carried by conveyor belt to granulation plants where they are melted at 315–325°C. The melting system consists of reverberatory furnaces and indirect warming boilers. The melted salt is pumped to granulation (prilling) towers 30 or 70 m high and sprayed. The droplets solidify while falling against an upward air current, forming spherical granules (prills). The granules are collected and screened, then cooled to 35°C by means of shell-and-tube exchangers. The final product is transported by railway cars and stored in silos in the SQM Nitratos facilities at the seaport of Tocopilla.

Synthetic Sodium Nitrate. Sodium nitrate can be synthetically obtained by absorption of nitrous gases or by neutralization of nitric acid (qv). Whereas low NO_x content in waste gases from nitric acid plants makes these gases useless for producing nitric acid, one way to avoid emission of nitrous gases to the atmosphere consists of using an alkaline solution of NaOH or Na_2CO_3 to absorb them. Products are mainly sodium nitrite or sodium nitrate. The general reactions involved are as follows

$$NO_2 + NO + 2\,NaOH \longrightarrow 2\,NaNO_2 + H_2O$$

$$2\,NO_2 + 2\,NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

$$NO_2 + NO + Na_2CO_3 \longrightarrow 2\,NaNO_2 + CO_2$$

$$2\,NO_2 + Na_2CO_3 \longrightarrow NaNO_2 + NaNO_3 + CO_2$$

The kinetics of these reactions markedly favor sodium nitrite production. If some sodium nitrate is formed, it can be easily separated by differential crystallization. Otherwise, sodium nitrate can be formed by treating sodium nitrite with nitric acid:

$$3\,NaNO_2 + 2\,HNO_3 \longrightarrow 3\,NaNO_3 + 2\,NO + H_2O$$

The resulting nitrous oxide can be recirculated to the nitric acid plant or be used for other purposes. Free acid remaining in the impregnation water of sodium nitrate crystals is neutralized by adding some NaOH to the washing water. Whereas several nitric acid plants utilize absorption of nitrous gases to treat tail gases, almost all of these plants produce small volumes of sodium nitrate.

Sodium nitrate can also be produced by neutralizing nitric acid with sodium hydroxide or sodium carbonate:

$$2\,HNO_3 + 2\,NaOH \longrightarrow 2\,NaNO_3 + 2\,H_2O$$

$$2\,HNO_3 + Na_2CO_3 \longrightarrow 2\,NaNO_3 + CO_2$$

In the United States, Olin Corporation had a plant using this method that closed in 1988.

1.5. Economic Aspects. In 2004, world production of sodium nitrate was about 63,000 metric tons. Of this quantity, some 62,000 t were produced in Chile from natural deposits. The remainder was manufactured in Germany and Mexico, generally as a by-product of nitric acid production. Additionally, China is known to manufacture some unknown but significant volumes of sodium nitrate for domestic use.

See Table 2 for recent production statistics (6).

The product is offered in two main grades: technical and agricultural, the former being of somewhat higher purity.

1.6. Standards and Specifications. Typical analyses of some commercial grades of sodium nitrate are given in Table 3. Chilean sodium nitrate is a prilled product having a bulk density of 1.22 g/cm^3, a mp of 301°C, and a water solubility of 91 g/100 mL of water at 25°C. The specifications for reagent-grade sodium nitrate are given in Table 4, *Food Chemicals Codex* specifications are given in Table 5; U.S. Federal chemical specifications are listed in Table 6. U.S. Federal specifications for particle size refer to U.S. standard sieves and are as follows: minimum 98.0% to pass through sieve No. 60 for class 1 sodium nitrate; minimum 98.0% to pass through sieve No. 100 for class 2 sodium nitrate, and minimum 80.0% retained sieve No. 20 for class 3 sodium nitrate (8).

1.7. Health and Safety Factors. The acceptable daily intake by human adults for nitrates suggested by the World Health Organization (WHO) is 5 mg/kg body wt per day (expressed as sodium nitrate). Some studies have suggested that this figure might be increased to 25 mg/kg. High doses of nitrates are lethal. Accidental ingestion of ca 8–15 g or more of sodium or potassium nitrate causes severe abdominal pain, bloody stools and urine, weakness, and collapse. Victims of sodium nitrate or potassium nitrate poisoning contract severe gastroenteritis. Outbreaks of poisoning from the ingestion of meats containing sodium nitrate and sodium nitrite have occurred from the accidental incorporation of excessive amounts of nitrate–nitrite mixtures, ie, 0.5 wt % nitrite as compared to maximum ingredient specifications of 0.05 and 0.02 wt % of nitrates and nitrites, respectively. The health hazards associated with nitrates result mainly from the bacterial conversion of ingested nitrates to nitrites. Infants in the first 3 months of life are particularly susceptible to nitrite-induced methemoglobinemia. In most cases of illness and death, well water has been used to add to powdered milk. WHO has recommended a maximum permissible concentration of nitrates of 45 mg/L in drinking water. The U.S. Public Health Service standard for nitrates is 10 mg/L. Nitrate toxicity in ruminants is considered to depend on the ability of nitrate to reduce to nitrite, because nitrites are considerably more toxic. Maximum safe levels of nitrate in water for livestock consumption are $<$100 ppm, although levels in excess of 500 ppm nitrate are required to produce acute poisoning. Levels in feeds should not exceed 5,000 ppm nitrate, and death may result from 15,000 ppm nitrate in the total diet. For further information, see References 9,10.

Sodium nitrate appears on the following federal regulatory lists: hazardous substances; registered pesticide; Federal Insecticide, Fungicides, and Rodenticide Toxic Release Inventory Chemicals (11).

1.8. Uses

Fertilizers. Sodium nitrate is used as a fertilizer as well as in a number of industrial applications. As a fertilizer, it provides nitrogen, needed in large quantities by plants and commonly in shortage in soils. Sodium nitrate is a special fertilizer because all the nitrogen is in the most highly oxidized form and thus different from fertilizers providing ammonium nitrogen. Nitrate nitrogen, in contrast to the ammonium form, acts more quickly, has a neutralizing effect on soil and subsoil acidity, does not volatilize to the atmosphere in the form of ammonia, and does not interfere with absorption of potassium, magnesium, and calcium by plants. Nitrate nitrogen acts quickly even in cold weather, under low rainfall conditions, and in acid soils promoting better-quality vegetable and fruit crops and tobacco. Nitrate nitrogen is well suited to supply nitrogen to growing crops at the right time, and to replenish nitrogen promptly when it is lost by leaching from sandy soils.

Sodium is an indispensable element for some crops (notably sugar beet), can partially substitute for potassium in several crops, contributes to neutralizing soil and subsoil acidity, and has a positive effect on soil phosphorus solubility. Sodium is an essential nutrient for cattle, and sodium application to soil increases its content in pastures. Sodium nitrate is particularly effective as a nitrogen source for sugar beet, vegetable crops, tobacco, and cotton (qv), and for any crop in acid soils.

Industrial Uses. Sodium nitrate is used in a number of industrial processes, in most of them acting primarily as an oxidizing agent. A primary use is in the manufacture of medium and high quality glass (qv), such as optical and artistic glass, television and computer screens, and fiber glass. Sodium nitrate has a role in the elimination of bubbles, in the oxidation of organic matter, and in the oxidation of ferrous oxide and of arsenic or antimony trioxide. Additionally, it is a source of sodium oxide and a fluidizing agent. The amount of sodium nitrate added in the glass manufacture process is up to 2 wt % of the total raw material.

Explosives. In the manufacture of explosives, sodium nitrate is used mainly in blasting agents. In slurries and emulsions, sodium nitrate improves stability and sensitivity. It also improves the energy balance because sodium nitrate replaces water, so that more fuel can be added to the formulation. Sodium nitrate reduces crystal size of slurries, which in turn increases detonating speed. In dynamites sodium nitrate is used as an energy modifier. Typical content of sodium nitrate is 20–50 wt % in dynamites, 5–30 wt % in slurries, and 5–15 wt % in emulsions. Sodium nitrate is used also in permissible dynamites, a special type of dynamite for coal (qv) mining.

Charcoal Briquettes. Another large application is as an ingredient in the production of charcoal briquettes. The amount of sodium nitrate used in charcoal briquette manufacture depends on the type and amount of wood and coal used.

Typically charcoal briquettes contain up to almost 3% sodium nitrate. Sodium nitrate is also used in the manufacture of enamels and porcelain as an oxidizing and fluxing agent. In porcelain–enamel frits used for metal coating, the amount of sodium nitrate in a batch varies with the various metal bases to be coated, typically from about 3.8 to 7.8 wt %.

Other. Sodium nitrate is also used in formulations of heat-transfer salts for heat-treatment baths for alloys and metals, rubber vulcanization, and petrochemical industries. A mixture of sodium nitrate and potassium nitrate is used to capture solar energy (qv) to transform it into electrical energy. The potential of sodium nitrate in the field of solar salts depends on the commercial development of this process. Other uses of sodium nitrate include water (qv) treatment, ice melting, adhesives (qv), cleaning compounds, pyrotechnics, curing bacons and meats (see Food additives), organics nitration, certain types of pharmaceutical production, refining of some alloys, recovery of lead, production of uranium, and leaching of copper ore (12).

2. Sodium Nitrite

2.1. Introduction. Sodium nitrite [7362-00-0], $NaNO_2$, a stable, odorless, pale yellow or straw-colored compound of molecular weight 69.00, is the sodium salt of nitrous acid [7782-77-6], HNO_2. Sodium nitrite has been produced commercially in the United States since the 1920s, and is available in dry granular or flake forms, as well as in water solutions. Most of the common package types are offered, from bags to drums to bulk. Sodium nitrite is used in dye, rubber chemicals and pharmaceuticals manufacture, as a corrosion inhibitor, in heat treating and heat-transfer salts, in meat curing, and several other applications. Production is by absorption of oxides of nitrogen into sodium carbonate or sodium hydroxide solutions. Sodium nitrite is an oxidizer and is toxic; as such, it requires care in its handling, storage, and use.

2.2. Properties. Pure anhydrous crystalline sodium nitrite has a specific gravity of 2.168 at 0°C/0°C (13). The crystal structure is body-centered orthorhombic, having the unit cell dimensions $a = 0.355$ nm, $b = 0.556$ nm, and $c = 0.557$ nm (14). Sodium nitrite melts at ~284°C and decomposition begins above 320°C, yielding N_2, O_2, NO, and Na_2O. The heat of formation is −362.3 kJ/mol (−86.6 kcal/mol) at 25°C (15). Sodium nitrite has a transition point at 158–165°C and displays significant changes in physical properties within this temperature range. The specific heat increases gradually from ~980 J/(kg·K) (0.234 cal/(g·°C)) at 60°C to ~1160 J/(kg·K) (0.277 cal/(g·°C)) at 200°C, but exhibits a peak value of ~2290 J/(kg·K) (0.547 cal/(g·°C)) at 161°C corresponding to this transition temperature (13).

Sodium nitrite is hygroscopic and very soluble in water. Dissolution of sodium nitrite in water results in the absorption of heat in the amount of 15.1 kJ/mol (3.6 kcal/mol) at 18°C (15). Water solubility characteristics are displayed in Figure 3. Sodium nitrite has limited solubility in most organic solvents (Table 7). The pH of a 1% solution of sodium nitrite is ~9. A hemihydrate, $NaNO_2 \cdot 1/2H_2O$ [82010-95-5], reported at temperatures below −5.1°C, is of no known commercial significance. The eutectic composition is 28.1% $NaNO_2$, although some supercooling of solutions up to ~38% may occur.

Sodium nitrite is stable in alkaline solutions. Acidification liberates nitrous acid which is unstable. The decomposition of nitrous acid yields nitric acid [7697-37-2], HNO_3, according to the following reaction:

$$3\,HNO_2(aq) \longrightarrow HNO_3(aq) + 2\,NO(g) + H_2O$$

Colorless nitric oxide [10102-43-9], NO, spontaneously oxidizes, in the presence of atmospheric oxygen, to brown-colored nitrogen dioxide [10102-44-0], NO_2. The resulting mixture of NO and NO_2, commonly referred to as NO_x gases, is corrosive and toxic and its generation should be avoided. Nitrous acid is not an article of commerce owing to its inherent instability. Sodium nitrite serves as the primary industrial source for nitrous acid in organic syntheses, for instance in the diatozation and nitrosation of aromatic amines. Under controlled conditions of acidification, the nitrous acid generated can react before excessive decomposition occurs.

As an oxidizer, sodium nitrite can convert ammonium ion to nitrogen, urea to carbon dioxide and nitrogen, and sulfamate to sulfate and nitrogen. The oxidizing properties of sodium nitrite contribute to its application as a corrosion inhibitor (see Corrosion and corrosion control), in detinning of scrap tinplate, and phosphating of metal surfaces. Because it is a strong oxidizer, sodium nitrite is capable of supplying oxygen and thus accelerating the combustion of organic matter. It can undergo vigorous, perhaps violent reactions with certain inorganic compounds such as ammonium salts, acidic materials, thiocyanates, and thiosulfates. It functions as a reducing agent to more powerful oxidizers such as dichromate, permanganate, chlorate, and chlorine. At ambient temperatures, sodium nitrite is stable; it slowly oxidizes to sodium nitrate at elevated temperatures (see Sodium compounds, sodium nitrate). References (13) and (14) provide comprehensive data on the physical and chemical properties of sodium nitrite.

2.3. Manufacturing. Sodium nitrite has been synthesized by a number of chemical reactions involving the reduction of sodium nitrate [7631-99-4], $NaNO_3$. These include exposure to heat, light, and ionizing radiation (14), addition of lead metal to fused sodium nitrate at 400–450°C (14), reaction of the nitrate in the presence of sodium ferrate and nitric oxide at ~400°C (14), contacting molten sodium nitrate with hydrogen (19), and electrolytic reduction of sodium nitrate in a cell having a cation-exchange membrane, rhodium-plated titanium anode, and lead cathode (20).

Industrial production of sodium nitrite is by absorption of nitrogen oxides (NO_x) into aqueous sodium carbonate or sodium hydroxide. NO_x gases originate from catalytic air oxidation of anhydrous ammonia, a practice common to nitric acid plants:

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$

Gas contact is typically carried out in absorption towers over which the alkaline solutions are recirculated. Strict control over the conditions of absorption are required to efficiently capture the NO_x and convert it predominantly to sodium nitrite according to the following reaction, thereby minimizing the formation of by-product sodium nitrate. Excessive amounts of nitrate can impede the separation of pure sodium nitrite from the process.

$$2\,NaOH + NO + NO_2 \longrightarrow 2\,NaNO_2 + H_2O$$

Solutions of sodium nitrite thus produced are concentrated and a slurry of crystals obtained in conventional evaporation (qv) and crystallization (qv) equipment. Much of this equipment can be of mild steel construction because sodium nitrite functions as a corrosion inhibitor toward most ferrous metals. The crystals are typically separated from the mother liquor by centrifugation and subsequently dried. Because of its tendency to lump and cake rapidly in storage, dry sodium nitrite products are frequently treated with an anticaking agent to keep them free-flowing. Alternatively, larger flakes or pellets are prepared from the granular material through a compaction process. The limited surface contact between these larger particles allows them to remain uncaked for extended periods. Technical solutions for commerce can be obtained directly from the process; higher purity solution products are prepared by dissolving crystals.

2.4. Shipment and Storage. Dry products of sodium nitrite are most commonly packaged into 22.7 kg (50 lb) or 45.4 kg (100 lb) multiply paper bags which contain a polyethylene moisture barrier. Fiber drums and semibulk sacks are also utilized. Bulk shipments are limited to flake material in specially designed sparger cars which allow the material to be unloaded as a solution. Dry sodium nitrite is regulated by the U.S. Department of Transportation (DOT) and classified as an Oxidizer, Hazard Class 5.1, UN1500, UN Packaging Group III (21). Containers must bear the Class 5.1 Oxidizer label, and bulk shipments must be placarded appropriately.

Liquid sodium nitrite products are typically 40–42% $NaNO_2$ and can be shipped in tank cars or tank trucks when volume and freight considerations allow. Sodium nitrite solutions are also regulated by the DOT and classified as Nitrites, Inorganic, Aqueous Solution, NOS, Hazard Class 5.1 Oxidizer, UN3219, UN Packaging Group III (21). Liquid product must also carry the Oxidizer label. Lesser quantities of liquid product may also be available in drums from local chemical distributors. Solution products are often preferred because of more convenient, efficient, and cost-effective handling versus bagged material and compatibility with inexpensive mild steel equipment.

Care must be exercised in using sodium nitrite near other chemicals. It is incompatible with ammonium salts, thiocyanates, thiosulfates, and strong reducing agents. In acid solutions, sodium nitrite evolves toxic NO_x; in the presence of secondary amines it can form nitrosamines which are suspected carcinogens.

Sodium nitrite exhibits good shelf-life characteristics if stored in secure containers in a cool, dry place, segregated from combustible and incompatible materials. Sodium nitrite does not burn, but its decomposition in fire promotes burning by furnishing additional oxygen. In the case of fire, water flooding should be used and the runoff kept away from streams and sewers to the extent possible. If spilled, care should be exercised to avoid contact with any acidic materials, as toxic NO_x could evolve. Under current regulations, spills in excess of 45.4 kg (100 lb) of dry sodium nitrite equivalent are reportable to the U.S. EPA (22). Additional state and/or local regulations may also apply.

2.5. Specifications, Analysis, and Quality. Dry sodium nitrite is offered in several grades: technical, drug (*U.S. Pharmacopeia* (USP)), food (*Food Chemicals Codex* (FCC)), and reagent (American Chemical Society (ACS)). Granular product has a tendency to lump and cake into an unmanageable mass during storage. Flake or treated granular types overcome this caking tendency and exhibit excellent shelf life. The most commonly used anticake is sodium mono- and dimethyl naphthalene sulfonates at a typical dosage of $\leq 0.1\%$. This is the only such agent allowed in the food-grade product in the United States (23). The USP and reagent ACS grades contain no anticake, and in granular form harden within weeks. Dry products typically contain $>99\%$ sodium nitrite and $<1\%$ sodium nitrate; a small amount of residual alkalinity is also present. The specifications for technical, USP, food, and ACS reagent grades are given in Table 8. Typically liquid products are of a technical or purified grade containing between 35 and 45% sodium nitrite and varying levels of nitrate.

Sodium nitrite products can be analyzed using methods that accompany specifications for the particular grade of product used. Assay methods are typically based on oxidation of the sample by a known excess of standard potassium permanganate solution, which is in turn reduced with a known excess of standard oxalic acid or ferrous ammonium sulfate solution. The excess is then titrated to a pink color end point and calculation gives the percent sodium nitrite in the sample. Standard laboratory analytical equipment such as hot plates, glassware, reagents, and analytical balances are required to run the tests. Careful attention to the standardization of reagents is important in obtaining reliable results. In contaminated or process samples, other substances present, which may be oxidized by potassium permanganate, give positive interferences. The analysis should be carried out in a proper fume hood to avoid the introduction of toxic gases into the workplace. The same safety precautions apply to handling sodium nitrite in the laboratory as previously described for the production area. Complete details on assay procedures and impurities testing are available (16,24–27).

Nitrite can be estimated in the field by using one of the many available test kits offered by a number of companies specializing in this area. These kits are designed for specific concentration ranges, involve simple procedures, and provide accuracy reasonable for field work by using color comparators or by counting drops of titrant to a color-change end point. Facilities producing the drug and food grades must follow a rigid set of guidelines for cleanliness and product reliability known as Good Manufacturing Practices (GMPs) and avail their plants to inspections by the U.S. FDA. Accurate and thorough recordkeeping is also required in the production of these grades.

2.6. Health and Safety Factors. Sodium nitrite is poisonous and prolonged contact with dry sodium nitrite or its solutions can cause irritation to the skin, eyes, and mucous membranes. The LD_{50} (oral, rat) is 85 mg per kg body weight (29). Inhalation or ingestion of significant quantities of dust or mist may result in acute toxic effects such as nausea, cyanosis, and low blood pressure, which can lead to possible collapse, coma, and even death.

Sodium nitrite is one of the chemicals listed in the EPA Inventory Update Rule Amendments. This rule requires the fertilizer industry to report on details on the use of and information on chemicals *in re* downstream worker exposure and consumer use. The Fertilizer industry was to discuss the impact of these rules with the EPA (29).

Persons responsible for the procurement, use, or disposal of sodium nitrite products should become familiar with safety information contained in the manufacturer's Product Safety Data Sheet (PSDS) (30). For handling dry products, a hard hat, safety glasses, impervious gloves, and long sleeves should be worn as a minimum. Where dusty or misty conditions prevail or when handling solutions, a NIOSH-approved respirator, chemical goggles, and full impervious clothing may be required. Contact lenses should not be worn. Persons should wash thoroughly after handling sodium nitrite. Eating or smoking in areas where sodium nitrite is being handled should be prohibited.

In case of skin contact, the area should be washed thoroughly with water and examined by a physician if irritation persists. If exposed, the eyes should be flushed with water for at least 15 minutes. Remove inhalation victims to fresh air and administer artificial respiration if the victim is not breathing. If ingested, vomiting should be induced. All incidents should be followed by prompt medical attention.

2.7. Uses. The many industrial uses for sodium nitrite primarily are based on its oxidizing properties or its liberation of nitrous acid in acidic solutions.

Dyes. Sodium nitrite is a convenient source of nitrous acid in the nitrosation and diatozation of aromatic amines. When primary aromatic amines react with nitrous acid, the intermediate diamine salts are produced which, on coupling to amines, phenols, naphthols, and other compounds, form the important azo dyes (qv). The color center of the dye or pigment is the $-N{=}N-$ group and attached groups modify the color. Many dyes and pigments (qv) have been manufactured with shades of the entire color spectrum.

Rubber Chemicals. Sodium nitrite is an important raw material in the manufacture of rubber processing chemicals. Accelerators, retarders, antioxidants (qv), and antiozonants (qv) are the types of compounds made using sodium nitrite. Accelerators, eg, thiuram [137-26-8], greatly increase the rate of vulcanization and lead to marked improvement in rubber quality. Retarders, on the other hand (eg, *N*-nitrosodiphenylamine [156-10-5]), delay the onset of vulcanization but do not inhibit the subsequent process rate. Antioxidants and antiozonants, sometimes referred to as antidegradants, serve to slow the rate of oxidation by acting as chain stoppers, transfer agents, and peroxide decomposers. A commonly used antioxidant is *N*,*N*′-disubstituted *p*-phenylenediamine which can employ sodium nitrite in its manufacture (see Rubber chemicals).

Heat Treatment and Heat-Transfer Salts. Mixtures of sodium nitrite, sodium nitrate, and potassium nitrate are used to prepare molten salt baths and heat-transfer media. One of the most widely used eutectic mixtures uses 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3 [7757-79-1] to give a melting point of 143°C. Its advantages are low melting point, high heat-transfer rate, thermal stability to 538°C, and a noncorrosive effect on steel (qv) at high temperature. The salts can be used for indirect heating or cooling or as quenching baths in the annealing of iron and steel.

Corrosion Inhibition. Sodium nitrite acts as an anodic inhibitor toward ferrous metals by forming a tightly adhering oxide film over the steel, preventing the dissolution of metal at anodic areas. When used in mixed metal systems that may include, for instance, copper, brass, or aluminum (as in automobile cooling systems), synergistic additives may be required for complete system protection. Some renewed interest in furthering nitrite use has been spawned from reduction in widespread use of carcinogenic hexavalent chromium-based inhibitors. Loss of protection owing to biological consumption of nitrite has been addressed by the use of higher initial concentrations (31). Sodium nitrite is used in boiler water treatment, as a dip or spray for protection of metals in process and storage, and in concrete. The EPA has ruled that sodium nitrite should not be used as a corrosion inhibitor in amine-based metalworking fluids because of the formation of potentially carcinogenic nitrosamines (32).

Metal Finishing. In phosphating solutions, sodium nitrite performs as an accelerator and oxidizer, serving to reduce processing times and control buildup of ferrous ions in solution, respectively. Phosphate coatings are applied to steel as a base coating before painting. In gold–sulfite-plating baths, sodium nitrite functions in the formation a gold–sulfite–nitrite complex. $Na_4Au(SO_3)_2NO_2$ [51846-25-4], from which the gold can be electrolytically deposited (33) (see Gold and gold compounds). This bath is considered to be safer than the poisonous cyanide baths traditionally used for gold plating. Sodium nitrite is also used in the recovery of tin from scrap tinplate (see Tin and tin alloys). It functions as an oxidizer in converting tin to sodium stannate with caustic soda; high purity tin can then be electroplated directly from the stannate solution.

Meat Curing. Sodium nitrite was used extensively in curing meat and meat products (qv), particularly pork products such as ham, bacon, frankfurters, etc. As an ingredient in curing brines, sodium nitrite acts as a color fixative and inhibits bacteria growth, including *Clostridium botulinum*, the source of the botulism toxin. Certain fish and poultry products are also cured with brines containing sodium nitrite. All food uses of sodium nitrite are strictly regulated by the FDA (34) and USDA.

Currently nitrite is not used for curing except for specialty meats. In the past, 200 ppm of nitrite was to be used in curing baths. Present use is now one tenth of regulation amounts. Industry uses ascorbate and erythrorbate in curing. These compounds are known to prevent the formation of *N*-nitrosamines (35).

Other Uses. Other applications for sodium nitrite include the syntheses of saccharin [81-07-2] (see Sweeteners), synthetic caffeine [58-08-2] (36), fluoroaromatics (37), and other pharmaceuticals (qv), pesticides (qv), and organic substances; as an inhibitor of polymerization (38); in the production of foam blowing agents (39); in removing H_2S from natural gas (40); in textile dyeing (see Textiles); as an analytical reagent; and as an antidote for cyanide poisoning (see Cyanides).

Sodium nitrite has played a key role in the invention of the following: a freezing point depressant in a large steel thermal storage tank for a district cooling system (41), antifungal agent for treatment of skin diseases (42); vapor-phase corrosion inhibitor–desiccant material (43); method for estimating methyl anthranilate [134-20-3] (44); process for preparing optically active benzoic acid (qv) derivatives (45); process for dewaxing oil-producing formations (46); method for treating chelated metal wastewaters (47); method of sewage sludge treatment (48); and preparation of iron nitrosyl carbonyl catalysts (49).

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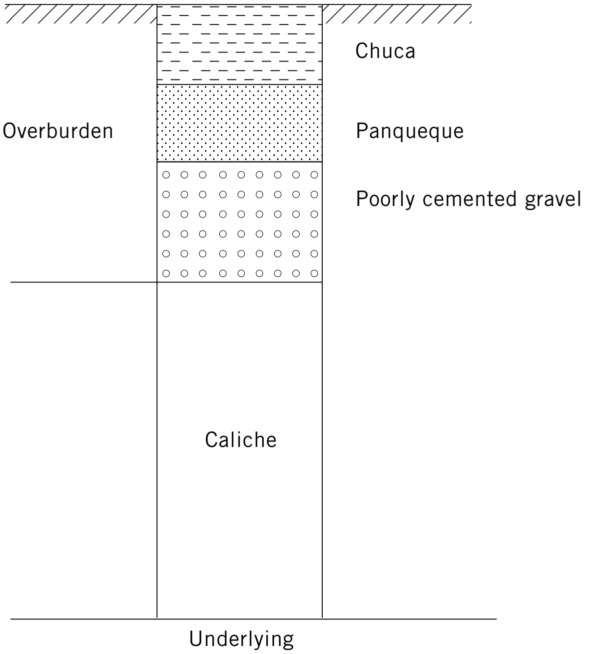

Fig. 1. Schematic of a nitrate ore bed, detailing the various overburden layers. The overburden thickness can vary from 0 to 2.5 m, where chuca = 0.1–0.5 m, panqueque = 0.1–0.4 m, and poorly cemented gravel = 1.5–2.5 m. Caliche ranges from 0.8 to 8 m.

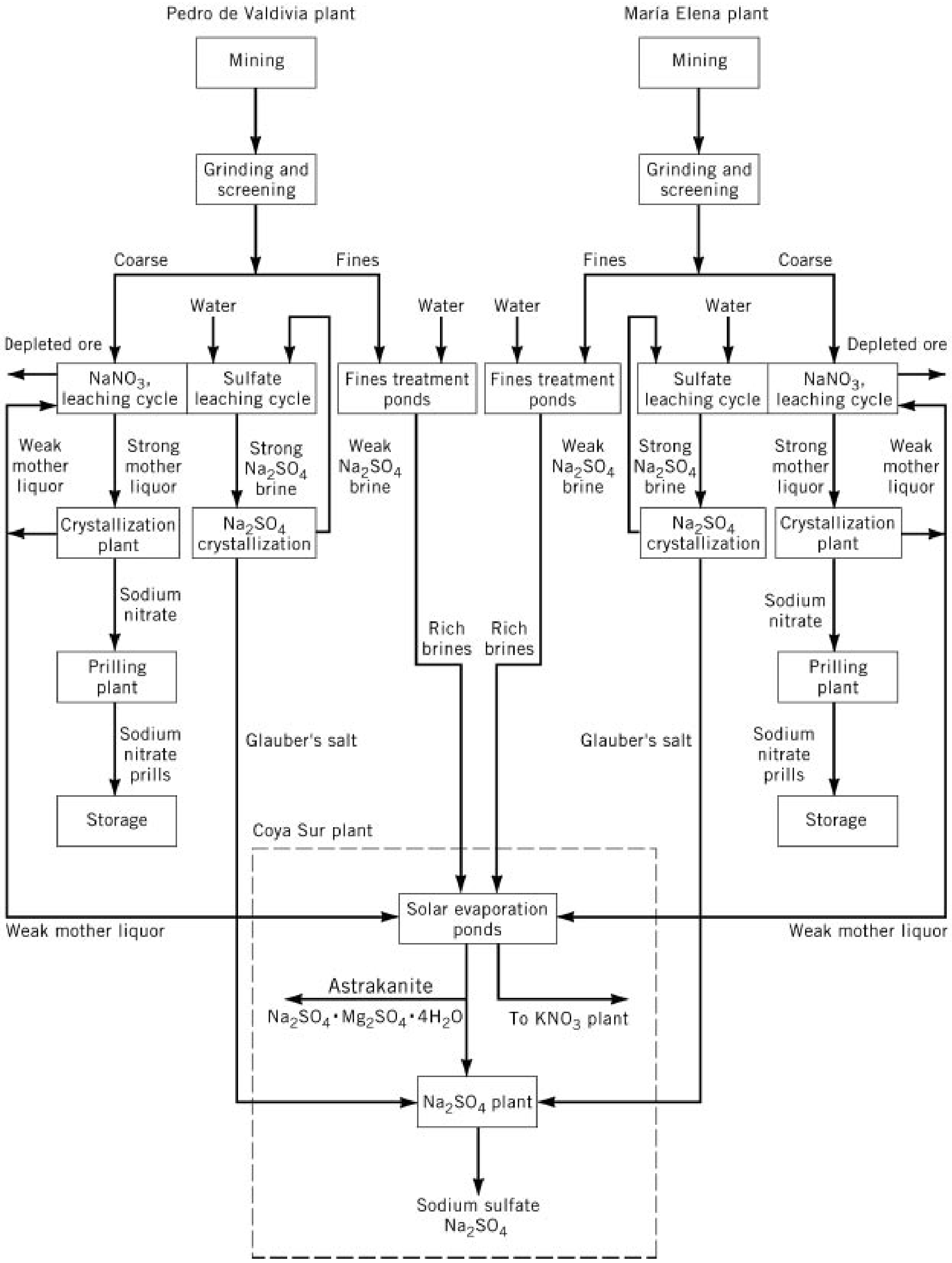

Fig. 2. Processing operations flow sheet of Chilean plants.

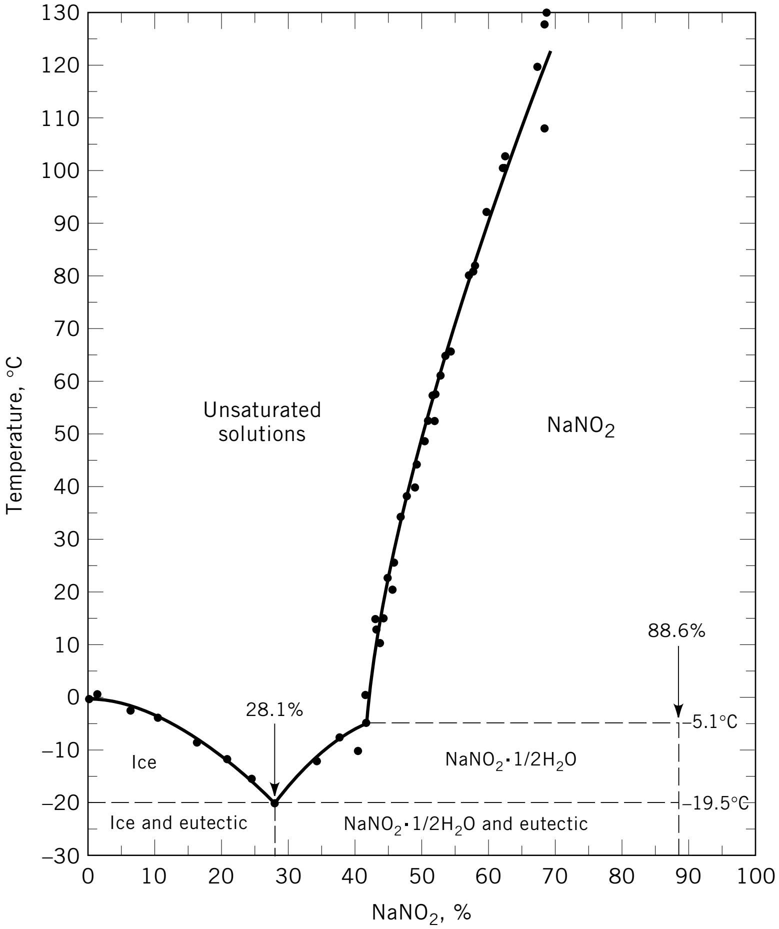

Fig. 3. Sodium nitrite solubility in water where (–) represents solid-phase boundaries (13,14,16,17).

Table 1. **Selected Properties of Sodium Nitrate**

Property	Value
mol wt	84.99
crystal system	trigonal, rhombohedral
mp, °C	308
refractive index, n_D	
trigonal	1.587
rhombohedral	1.336
density, solid, g/cm^3	2.257
solubility in H_2O, molality (±2%)	
at −17.5°C	7.4
0°C	8.62
40°C	12.39
80°C	17.42
120°C	24.80
specific conductivity, at 300°C, S/cm	0.95
viscosity[a], η, mPa·s(=cP)	
at 590 K	2.85
730 K	1.53
heat of fusion, J/g[b]	189.5
heat capacity, J/g[b]	
solid	
at 0°C	1.035 ± 0.005
100°C	1.23 ± 0.006
liquid at 350°C	1.80 ± 0.02
aqueous solution[c]	4.138 ± 3.045

[a] Measurement method: capillary; $\eta = 25.0987 - 6.0544 \times 10^{-2}\ T + 3.8709 \times 10^{-5}\ T^2$. Precision = ca 0.6%; uncertainty = ca 3%.

[b] To convert J to cal, divide by 4.184.

[c] $C_p = 4.175 - 37.42 \times 10^{-3}\ P + 216.6 \times 10^{-6}\ P^2$, where P = wt% solute can range from 1–39%.

Table 2. **World Producers of Sodium Nitrate**[a]

	2003		2004	
Country	Production, t	Value, $	Production, t	Value, $
Chile	84,689	13,827,814	61,511	12,851,771
Germany	538	130,391	1125	255,841
Mexico	298	26,400	262	28,600
Poland	22	6,482		
Canada	20	2,925		

[a] Ref. 6.

Table 3. **Analyses of Commercial Grades of Sodium Nitrate[a], wt %[b]**

Parameter	Agricultural	Industrial	Technical	Refined (Niterox)
		Components		
sodium nitrate	96.8–97.9	98.0[c]	99.2[c]	99.6[c]
nitrogen	16[c]	na	na	na
sodium	26	na	na	na
potassium, as K_2O	0.4–1.2	na	na	na
magnesium, as MgO	0.10	na	na	na
sulfur	0.10	na	na	na
sodium sulfate	na	0.35	0.10	0.10
chlorine	1	na	na	na
sodium chloride	na	0.8	0.30	0.13
sodium nitrite	na	0.05	0.005	0.005
boron	0.35	0.025	na	na
sodium tetraborate	na	na	0.03	0.03
insolubles	0.15	0.15	0.02	0.02
moisture	0.15	0.15	0.15	0.15
		Screen analysis		
screen size, mm (Tyler mesh)				
on 2.38 (8)	10	8	5	5
on 1.68 (10)	70	65	45	45
on 1.19 (14)	96	96	90	90
through 0.841 (20)	1.5	2	8	8

[a] Data correspond to Chilean sodium nitrate. Courtesy of SQM Nitratos (Chile).

[b] Value given is maximum unless otherwise noted.

[c] Value given is minimum.

Table 4. **ACS Specifications for Reagent-Grade Sodium Nitrate**

Specification	Value
insoluble matter, wt %	0.005
pH of 5 wt % solution at 25°C	5.5–8.3
total chlorine, wt %	0.001
iodate, IO_3^-, wt %	ca 0.0005
nitrite, NO_2^-, wt %	ca 0.001
phosphate, PO_4^{3-}, wt %	0.0005
sulfate, SO_4^{2-}, wt %	0.003
calcium, magnesium, and R_2O_3, wt %	0.005
precipitate, wt %	
heavy metals, as Pb	0.0005
iron, Fe	0.0003

Table 5. **Food Chemicals Codex Specifications for Sodium Nitrate**[a]

Specification	Value
$NaNO_3$ assay after drying, wt %	99.0
limits of impurities, wt %	
arsenic, as As	0.0003
heavy metals, as Pb	0.001
total chlorine	ca 0.2[b]

[a] Ref. 7.

[b] Passes the test.

Table 6. **U.S. Federal Government Chemical Specifications for Technical-Grade Sodium Nitrate**[a,b]

	Specification, wt %		
Parameter	Grade A	Grade B	Grade C
nitrates, as $NaNO_3$	97.0[c]	99.5[c]	97.0[c]
alkalinity, as Na_2O	0.05	none	0.06
chlorates, as $KClO_3$	0.06	none	0.06
calcium, as CaO	0.3	0.1	0.3
magnesium, as MgO	0.15	0.06	0.15
sulfates, as Na_2SO_4	0.5	0.2	0.45
chlorides, as NaCl	na	0.15	0.15

[a] Ref. 8.

[b] Values are maximum unless otherwise noted.

[c] Value is minimum.

Table 7. **Solubility of Sodium Nitrite in Nonaqueous Solvents**[a]

Solvent	g $NaNO_2$/100 g solvent	Temperature, °C
acetone	insoluble	
ammonia, anhydrous	very soluble	−77 to 172
ethanol		
absolute	0.31	19.5
94.9%	1.424	25
ethylenediamine	12.60	30
ethylene glycol	16.78	25
methanol, absolute	4.43	19.5
methyl ethyl ketone	insoluble	
monoethanolamine	8.74	30
propylene glycol	8.47	25
pryridine	0.34	25

[a] Refs. 16 and 18.

Table 8. **Specifications for Dry Grades of Sodium Nitrite**

Parameter[a]	Technical[b]	USP[c]	Food[d]	Reagent[e]
assay, as $NaNO_2$, wt %[f]	97.0	97.0–101.0	97.0	97.0
loss on drying, wt %		0.25	0.25	
heavy metals, as Pb, %		0.002	0.002	0.001
arsenic, as As, ppm			3	
lead, as Pb, ppm			10	
sodium sulfate, as Na_2SO_4, wt %	0.2			
sodium chloride, as NaCl, wt %	0.2			
insolubles, wt %	0.5			0.01
pH	8 ± 1			
chloride, as Cl, wt %				0.005
sulfate, as SO_4, wt %				0.01
calcium, as Ca, wt %				0.01
iron, as Fe, wt %				0.001
potassium, as K, wt %				0.005

[a] Value is maximum unless noted.
[b] Ref. 24.
[c] Ref. 25.
[d] Ref. 26.
[e] Ref. 27.
[f] Value is minimum.