ALUMINATES

1. Introduction

Sodium aluminate [1302-42-7], $NaAlO_2$, has been used as a commercial product since about 1925 when it was introduced as an effective water treatment chemical. Among industrial users of sodium aluminate are producers of paper (qv), paint pigments (qv), silica–alumina or alumina-based catalysts, dishwasher detergents (qv), molecular sieves (qv), concrete, antacids, and others. Sodium aluminate is used in removal of phosphates from municipal and industrial waste waters and for clarification of industrial process and potable water. Commercial sodium aluminate products are available as liquids, and to a lesser degree, in solid form. The formula of anhydrous sodium aluminate is variously given as $NaAlO_2$ (aluminum sodium oxide [1302-42-7]), $Na_2O{\cdot}Al_2O_3$, or $Na_2Al_2O_4$. Commercial sodium aluminates are not accurately represented by these formulas because the products contain more than the stoichiometric amount of sodium oxide [1313-59-3], Na_2O. The amount of excess caustic in commercial products is indicated by ratios of Na_2O/Al_2O_3 that are typically between 1.05 and 1.15 for dry products, and 1.26 and 1.5 for liquids.

2. Physical and Chemical Properties

Commercial grades of sodium aluminate contain both waters of hydration and excess sodium hydroxide. In solution, a high pH retards the reversion of sodium aluminate to insoluble aluminum hydroxide. The chemical identity of the soluble species in sodium aluminate solutions has been the focus of much work (1). Solutions of sodium aluminate appear to be totally ionic. The aluminate ion is monovalent and the predominant species present is determined by the Na_2O concentration. The tetrahydroxyaluminate ion [14485-39-3], $Al(OH)^-_4$, exists in lower concentrations of caustic; dehydration of $Al(OH)^-_4$, to the *meta*-aluminate ion [20653-98-9], AlO^-_2, is postulated at concentrations of Na_2O above 25%. The

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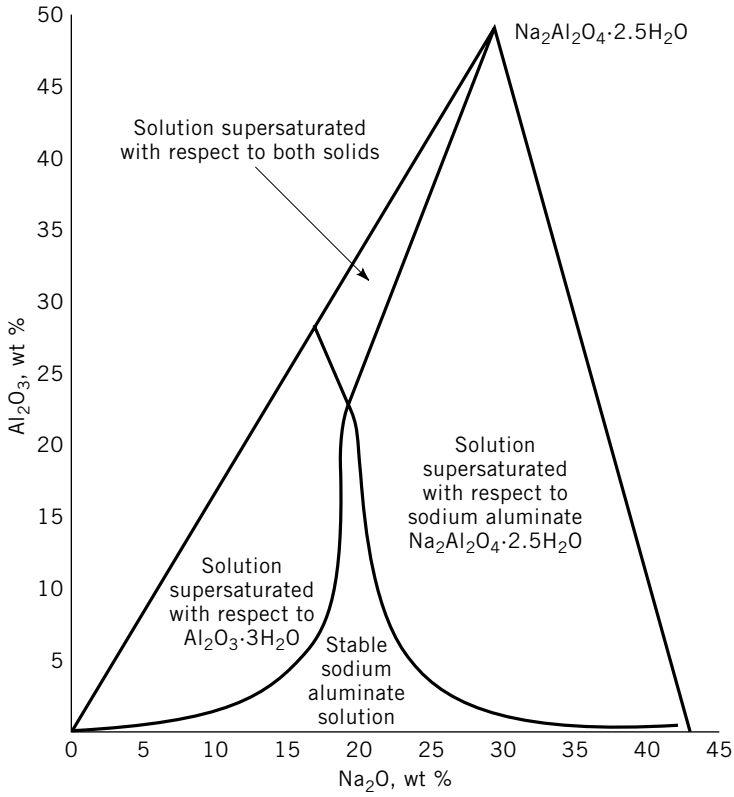

Fig. 1. Equilibrium diagram for the Na_2O–Al_2O_3–H_2O system at 30°C (3).

formation of polymeric aluminate ions similar to the positively charged polymeric ions formed by hydrolysis of aluminum at low pH does not seem to occur. $Al(OH)^-_4$ has been identified as the predominant ion in dilute aluminate solutions (2).

Figure 1 shows a phase equilibrium diagram for soda–alumina–water (3). The point of maximum solubility at 30°C for alumina trihydrate [12252-70-9], $Al_2O_3 \cdot 3H_2O$, and sodium aluminate is near 23% Al_2O_3 and 20% Na_2O. At higher Na_2O concentrations, the solutions are supersaturated with respect to sodium aluminate; at lower concentrations of Na_2O, the solutions are supersaturated with respect to the trihydrate. At concentrations greater than 23% Al_2O_3 and 20% Na_2O, the solution is supersaturated with respect to both solids. Most commercial solutions are supersaturated with regard to one or both of the solids.

3. Manufacture

Small amounts of sodium aluminate are prepared in the laboratory by fusion of equimolar quantities of sodium carbonate [497-19-8] and aluminum acetate [139-12-8], $Al(C_2H_3O_2)_3$, at 800°C (4). Other methods involve reaction of sodium hydroxide with amorphous alumina or aluminum [7429-90-5] metal. Commercial

quantities of sodium aluminate are made from hydrated alumina, in the form of aluminum hydroxy oxide [24623-77-6],AlO(OH), or aluminum hydroxide [21645-51-2], $Al(OH)_3$, a product of the Bayer process (5,6) which is used to refine bauxite [1318-16-7], the principal aluminum ore.

Commercial grades of sodium aluminate are obtained by digestion of aluminum trihydroxide in aqueous caustic at atmospheric pressure and near the boiling temperature (7). Digestion of the aluminum hydroxy oxide in aqueous sodium hydroxide requires pressures of up to 1.38 MPa (13.6 atm) and temperatures of about 200°C. Dry sodium aluminate is obtained by evaporation of water. Several processes for the production of sodium aluminate are known that do not require the addition of water. In one process, bauxite reacts with molten sodium hydroxide at approximately 400°C (8); in another, aluminum trihydroxide reacts with solid sodium hydroxide (9); additionally, sodium carbonate has been treated with alumina or bauxite in rotary kilns at about 1000°C (10, 11). Other similar methods have also been described.

The form of sodium aluminate produced depends upon the manufacturing process. In high temperature, nonaqueous processes, the sodium aluminate product normally contains less than 1% moisture. If a dry product is desired from aqueous digestion processes, some sort of drying operation is required. In practice about half of the digestion liquor is sold as liquid sodium aluminate after filtration and dilution or concentration to conform with product specifications. Some products contain small amounts of powdered insoluble solids that act as precipitation or coagulation aids in water-treatment processes (12). Concentrated solutions of sodium aluminate tend to decompose by precipitation of alumina. Such decomposition is controlled in commercial products by addition of excess caustic and small quantities of certain organic compounds, or stabilizers (7,13–15).

Liquid sodium aluminate is available in steel drums having an approximate capacity of 210 L and bulk shipments are available in either tank trucks or railroad tank cars. The density of liquid sodium aluminate is usually from 1450 to 1510 kg/m^3. Solid products are available in moisture-proof paper bags or fiber drums containing approximately 23 and 150 kg, respectively.

4. Economic Aspects

Demand for aluminates for the treatment of industrial water should grow annually at the rate of 9% to $\$40 \times 10^6$ or 84×10^6 kg (185×10^6 lb) in 2004 and 110×10^6 kg (242×10^6 lb) in 2009 (16).

The primary U. S. producers of aluminates for water treatment are General Chemical, Geo Speciality Chemicals, and Kemwater North America.

Price range history 1989–2000 was \$0.07–0.10/kg (\$0.15–0.22/lb). Expected price in 2004 should be \$0.11/kg (\$0.25/lb) (16).

5. Analytical Methods

Commercial liquid sodium aluminates are normally analyzed for total alumina and for sodium oxide by titration with ethylene diaminetetraacetic acid

[60-00-4] (EDTA) or hydrochloric acid. Further analysis includes the determination of soluble alumina, soluble silica, total insoluble material, sodium oxide content, and carbon dioxide. Aluminum and sodium can also be determined by emission spectroscopy. The total insoluble material is determined by weighing the ignited residue after extraction of the soluble material with sodium hydroxide. The sodium oxide content is determined in a flame photometer by comparison to proper standards. Carbon dioxide is usually determined by the amount evolved, as in the Underwood method.

The determination of the soluble or available sodium aluminate presents difficulties because sodium aluminate begins to hydrolyze to the insoluble alumina trihydrate in water. The degree of hydrolysis depends on concentration, temperature, and time. It is therefore necessary to use a method of analysis that simultaneously affords control of the hydrolysis and gives the amount of available sodium aluminate encountered. This is best done by extracting the soluble alumina using sodium hydroxide solutions and subsequently determining the alumina content by gravimetric methods or titration with EDTA or hydrochloric acid (17).

6. Health and Safety Aspects

Sodium aluminate is highly alkaline and should be treated as a corrosive.

ACGIH has assigned a maximum concentration for TLV TWA OF 2.0 mg/m^3. It is considered a soluble salt of aluminum because of its relatively high solubility (18).

7. Uses

Sodium aluminate is used in the treatment of industrial and municipal water supplies and the use of sodium aluminate is approved in the clarification of drinking water (19). The FDA approves the use of sodium aluminate in steam generation systems where the steam contacts food. One early use of sodium aluminate was in lime softening processes, where it increases the precipitation of ions contributing to hardness and improves suspended solids removal from the treated water (20). Sodium aluminate reacts with silica to leave very low residual concentrations of silica in hot process water softeners. Sodium aluminate is often used with other chemicals such as alum, ferric salts, clays, and polyelectrolytes, as a coagulant aid (21,22).

Sodium aluminate is an effective precipitant for soluble phosphate in sewage and is especially useful in wastewater having low alkalinity (23,24). Sodium aluminate hydrolyzes in water to $Al(OH)_3$ and Al^{+3} which precipitate soluble phosphate as aluminum phosphate [7784-30-7], $AlPO_4$. Sodium aluminate has also been described as an effective aid for the removal of fluorides from some industrial waste waters (25). Combinations of sodium aluminate and other chemicals are being used to improve the detackification of paint particles in water from spray-painting operations (26).

Large quantities of sodium aluminate are used in papermaking where it improves sizing, filler retention, and pitch deposition (19,27–31). The addition

of sodium aluminate to titanium dioxide paint pigment improves the nonchalking performance of outdoor paints (19,32,33). The etching of glass (qv) and ceramics (qv) by alkaline washing solutions is inhibited by inclusion of sodium aluminate in the formulations (34,35). The use of sodium aluminate solutions in the processing of acrylic and polyester synthetic fibers improves drying, antipiling, and antistatic properties of the fibers (36,37).

The recovery of sand from foundry molds and cores is much easier when binders made water soluble by use of sodium aluminate are used in place of insoluble resin binders (38,39). Sodium aluminate acts as a setting accelerator for Portland cement (qv) (40). In similar application, addition to concrete provides a longer gel time before fully curing (41).

One application patented in 1989 is the injection of sodium aluminate into silica-containing formations for enhanced petroleum recovery (42). Additionally, the pharmaceutical industry uses sodium aluminate as an alkaline source of aluminum for the production of certain antacids (43).

Sodium aluminate is widely used in the preparation of alumina-based catalysts. Aluminosilicate [1327-36-2] can be prepared by impregnating silica gel with alumina obtained from sodium aluminate and aluminum sulfate (44,45). Reaction of sodium aluminate with silica or silicates has produced porous crystalline aluminosilicates which are useful as adsorbents and catalyst support materials, ie, molecular sieves (qv) (46,47).

One method for using sodium aluminate to desulfurize flue gas containing sulfur dioxide is described (48). This procedure led to a process where aluminum sulfate [10043-01-3] could be generated as a by-product of flue gas desulfurization (49).

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