Kirk-Othmer Encyclopedia of Chemical Technology.

POLYALUMINUM CHLORIDES

Aluminum chloride hydroxide [1327-41-9], [10284-64-7], $AlCl(OH)_2$ [14215-15-7], $AlCl_2(OH)$, products, commonly known as polyaluminum chlorides (PAC), are used for a wide variety of industrial applications. Other names for PAC are basic aluminum chloride, polybasic aluminum chloride, aluminum hydroxychloride, aluminum oxychloride, and aluminum chlorohydrate. The presence of polymeric, aluminum-containing cations, the distribution of which can differ greatly, typifies PAC products. Although the formation of polynuclear aluminum species in solution has been studied for over a century, there is still much controversy concerning aluminum polymerization reactions and the resulting product compositions.

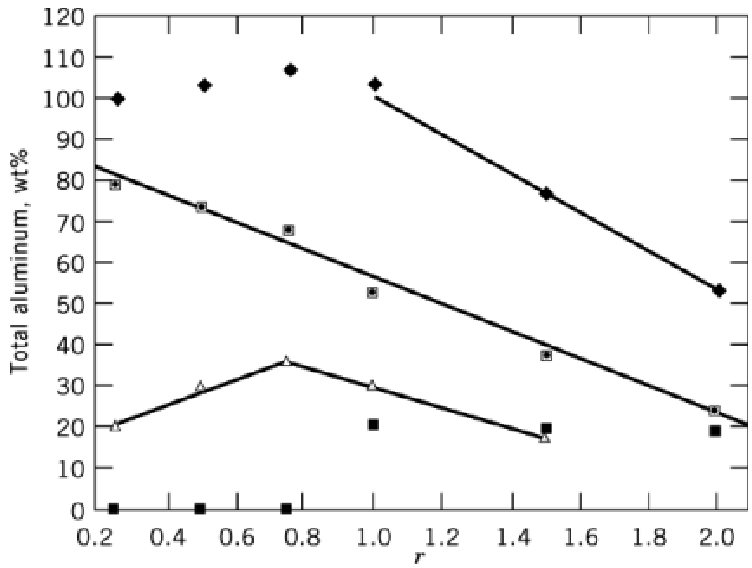
Commercially, PAC has been used in water (qv) and wastewater treatment in Japan, the USSR, and Europe since about 1970, and in the United States since the early 1980s (1). Aluminum chlorohydrate [12042-91-0], $Al_2Cl(OH)_5$, a specialty PAC product, has been utilized as an antiperspirant for over 50 years (see Cosmetics) (2). Other PAC uses include preparation of pillared clay catalysts (3), stabilization of formation clays (see Clays) (4), paper (qv) sizing in papermaking (5), catalysts in durable-press finishing of fabrics (6), and preparation of alumina-coated silica sols (7).

1. Properties

Physical and chemical properties of the numerous PAC products can vary considerably. PAC products are usually aqueous solutions, although solid products are also sold. Solutions range from colorless to amber and from clear to hazy in appearance; specific gravities at 25°C vary from about 1.2 to 1.35. Product viscosities, as measured by a Brookfield viscometer at 25°C, are generally about $10 - 50$ mPa·s(= cP), but can be much greater than $10,000$ mPa·s(= cP) for certain aged compositions.

An empirical formula, $Al_n(OH)_mCl_{(3n-m)}$, where $0 < m < 3n$ can be written to describe overall PAC composition. The degree of neutralization of hydrated Al(III), or basicity, is expressed as the mole ratio of OH/Al (m/n). This ratio is often called the ligand or hydroxyl number *r:* aluminum chloride has $r = 0$; aluminum hydroxide, $r = 3$; and PAC products have r values ranging from about 0.5 to 2.5. PAC solution products are always acidic. The pH ranges from <1 to ca 4.0. The total aluminum concentration, conventionally expressed as Al_2O_3 or alumina content, is important to product composition and activity. Total Al content of PAC products as Al_2O_3 ranges from about 6 to 24% by weight in aqueous solutions. PAC products can also contain other inorganic salts, such as sodium, potassium, calcium, or magnesium chlorides and/or bromides, and these salts can affect PAC properties.

Whereas the nature of the Al species in PAC products is not fully understood, it appears that there are three or four species or molecular weight categories: monomers, a dimer, an Al_{13} polymer, and several higher Al polymers. ^{27}Al-nmr spectroscopy has been useful in the identification and quantification of these cations (8–14). Using an aluminum salt standard, the monomeric species hexaaquaaluminum ion [15453-67-5], $Al(H_2O)^{3+}{}_6$, pentaaquahydroxyaluminum (+2) ion [18499-02-0], $Al(OH)(H_2O)^{2+}{}_5$, and $Al(OH)_2(H_2O)^{+}{}_4$ exhibit a sharp peak at 0 ppm; the dimer, octaaquadi-μ-hydroxydialuminum ion [46130-83-0] (Al_2), $Al_2(OH)_2(H_2O)^{4+}{}_8$, gives a



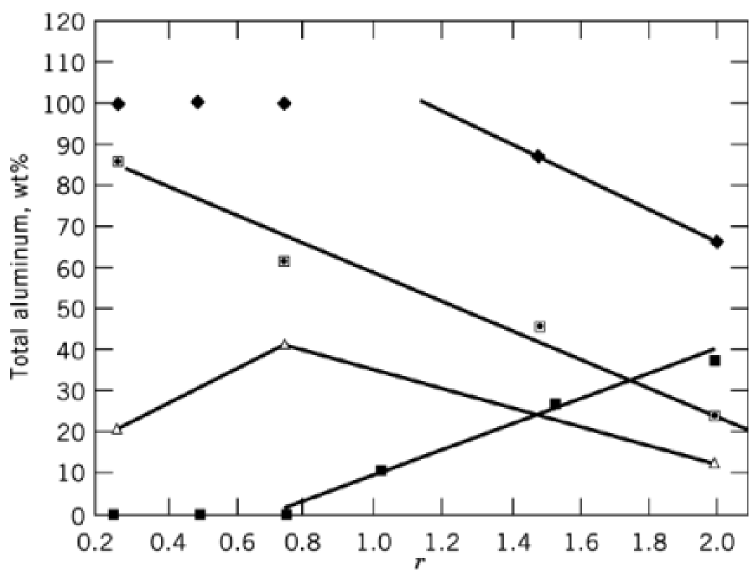


Fig. 1. Al species as a function of *r*, the OH/Al ratio. ⊡, Monomers; △, dimer; ■, Al_{13} polymer; ♦, the sum of the Al species for PACs prepared from 27% $AlCl_3$ (aq) and (**a**) $Ca(OH)_2$ and (**b**) Na_2CO_3.

broad, less readily discernible band at 3 ppm; and the polymeric species dodecaaquatetracosa-μ-hydroxy-tetra-μ_4-oxotridecaaluminum ion [12703-68-3] (Al_{13}), $Al_{13}O_4(OH)_{24}(H_2O)^{7+}{}_{12}$, exhibits a sharp resonance indicating a tetrahedrally coordinated Al, such as in $AlO^{-}{}_4$, at 62.5 ppm. The fraction of PAC products not identifiable by nmr may be polymeric and/or colloidal Al hydroxide precipitates (14). The distribution of Al species for two series of PACs was found to be a function of the ligand number *r*, as shown in Figure 1 (15).

The structure proposed for Al_{13} is a central Al in a tetrahedral configuration having four oxygens surrounded by 12 AlO_6 octahedra (16). The existence of the tetrahedral Al has been explained by assuming that aluminate ion, $AlO^{-}{}_4$, is the Al_{13} precursor. Whereas $AlO^{-}{}_4$ is not stable in solutions below pH 10, localized, high concentrations of hydroxide have been postulated to occur during aluminum chloride base neutralization, forming an aluminate ion (12). In processes utilizing Al metal, the oxidation of Al is accompanied by reduction of water to hydrogen gas creating a high hydroxide concentration on the metal surface (17). The resultant aluminate ion then rapidly reacts with octahedrally coordinated Al in the bulk solution, forming Al_{13} which is sometimes written as an aluminate and a dodecamer, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$.

The Al_{13} polymer, readily recognizable and often predominant in PAC solutions, is probably the most stable, highly charged cation in PAC. Al_{13} has an overall charge of +7 corresponding to a charge density of +0.54/Al as compared to Al monomers with +3 charge and charge density. In applications where charge neutralization is an important mechanism for PAC activity, cations of highest charge may be most effective (18). Therefore, there is some indication that Al_{13} content in PAC should be maximized (19). In a patented use of PAC chemistry in clarifying certain natural waters, however, it was found that maximizing the concentration of the dimer was most effective (15), even though Al_2 has an overall charge of +4 and a charge density of +2/Al.

2. Aluminum Chlorohydrate

Aluminum chlorohydrate [12359-72-7], $Al_2(OH)_5Cl{\cdot}2H_2O$ is a PAC product of specific composition, having $r = 2.5$. Aluminum chlorohydrate is used in antiperspirants regulated by the U.S. Food and Drug Administration (FDA). Solutions sold for FDA-approved use are colorless in appearance, have 23–24% Al as Al_2O_3, and low levels of iron (<50 ppm), sulfate (<0.025 %), metals (Ca, Mg, Na <10 ppm), and heavy metals (as Pb <10 ppm). The pH of these solutions at 25°C is about 3.8–4.0. Typically, solutions at 25°C have specific gravities from 1.33 to 1.35 and viscosities from 40 to 60 mPa·s(= cps). Aluminum chlorohydrate [12042-91-0] is also available in dry form with different particle-size distributions.

Characterization of aluminum chlorohydrate has revealed a predominance (about 88%) of Al_{13} polymer with the balance being monomers and smaller polycations (20). The highly charged $Al^{7+}{}_{13}$ surrounded by Cl^- counterions is self-stabilized by repulsion forces, preventing association and subsequent aluminum hydroxide precipitation (21). Thus, aluminum chlorohydrate solutions remain clear and free of precipitate after years of storage at room temperature. Aqueous dilution or an increase in pH to 5–6, however, results in rapid degradation and formation of gibbsite [14762-49-3], an insoluble aluminum hydroxide polymorph (8).

3. Manufacture

A generic manufacturing process for PAC involves the addition of base to aluminum chloride solution

$$n\mathrm{AlCl_3} + m\mathrm{OH^-} \longrightarrow \mathrm{Al}_n(\mathrm{OH})_m\mathrm{Cl}_{3n-m} + m\mathrm{Cl^-}$$

Typical values for m/n are 0.5 to 2.5. Commercially used bases include sodium hydroxide, potassium hydroxide, calcium hydroxide (lime), magnesium hydroxide, sodium carbonate, sodium aluminate, calcium carbonate, or various mixtures. For certain applications, PAC can be made from waste grades of aluminum chloride [7446-70-0] such as spent catalyst solutions from Friedel-Crafts synthesis (see Friedel-crafts reaction).

The OH/Al mole ratio or ligand number r is an important factor in the speciation of Al cations in the PAC product. Product composition also depends upon initial aluminum concentration, base addition rate, mixing intensity, and temperature (14). Al content of products from processes utilizing aluminum chloride as the Al source are less than 10% as Al_2O_3 because the maximum solubility of aluminum chloride in water is about 30% at 25°C.

Aluminum sulfate [7784-31-8] solutions can also be used for all or part of the PAC Al source. In one process, a mixture of alum and aluminum chloride is neutralized using calcium carbonate, and solid calcium sulfate [7778-18-9] is removed by filtration (22). In another process alum is mixed with calcium chloride and calcium hydroxide (23):

$$0.5\ Al_2(SO_4)_3 + 0.62\ CaCl_2 + 0.78\ Ca(OH)_2 \longrightarrow Al(OH)_{1.56}(SO_4)_{0.093}Cl_{1.25} + 1.40\ CaSO_4$$

This PAC contains 1–2% sulfate as soluble calcium sulfate. Sulfate has been found to make PAC products unstable: precipitate forms in less than one week at 50°C. Sulfate, however, has also been seen to increase PAC activity in water clarification and is thus intentionally added in one preparation (24). Precipitated calcium sulfate creates a sludge disposal problem. Typical Al content as Al_2O_3 of PAC products made from alum is 6–8%.

Aluminum oxide solids can be utilized to manufacture PAC by the addition of acid (15). Alumina trihydrate [12252-70-9], $Al_2O_3{\cdot}3H_2O$, a reactive intermediate from bauxite beneficiation, is first slurried with water, and the slurry is gradually added to concentrated hydrochloric acid. PAC forms when the HCl/Al_2O_3 mole ratio is less than 6; typical ratios in commercial processes are 3 to 4.5.

$$Al_2O_3{\cdot}3\ H_2O + 4.5\ HCl + xH_2O \longrightarrow 2\ Al(OH)_{0.75}Cl_{2.25} + xH_2O$$

The reaction is facilitated by elevated temperature necessitating pressure-capable, glass-lined reactors and exotic metallurgy for fittings to withstand the severely corrosive conditions. PAC product having 10–12% Al as Al_2O_3 can be produced.

3.1. Aluminum Chlorohydrate

A common process for the manufacture of aluminum chlorohydrate involves the addition of metallic Al to aluminum chloride

$$AlCl_3 + 5Al + 21H_2O \longrightarrow 3Al_2(OH)_5Cl{\cdot}H_2O + \frac{15}{2}H_2$$

The reaction proceeds spontaneously, but can be accelerated by the use of an electrode more noble than Al, such as Fe, Sn, Ni, Pb, or graphite (25). Heavy metal salt catalysts, such as copper chloride and silver nitrate, have also been used to avoid heating (26). Hydrogen gas is generated by the reaction, so explosion hazards must be managed. Aluminum powder, turnings, cuttings, bars, and ingots have been used as the metal source. PAC product having 23–24% Al as Al_2O_3 can be produced.

The electrolysis of aluminum chloride solutions may also be used to produce PAC having 23–24% Al as Al_2O_3.

$$2\ AlCl_3(aq) + 7\ H_2O \longrightarrow Al_2(OH)_5Cl{\cdot}2\ H_2O + \frac{5}{2}Cl_2 + \frac{5}{2}H_2$$

An electrolytic cell, preferably having anode and cathode compartments separated by a porous membrane to prevent formation of explosive gas mixtures, is required (27).

4. Shipping and Handling

Liquid polyaluminum chloride is acidic and corrosive to common metals. Suitable materials for construction of storage and handling facilities include synthetic rubber-lined steel, corrosion resistant fiber glass reinforced plastics (FRP), ceramics, tetrafluoroethylene polymer (PTFE), poly(vinylidene fluoride) (PVDF), polyethylene, polypropylene, and poly(vinyl chloride) (PVC). Suitable shipping containers include rubber-lined tank trucks and rail cars for bulk shipment and plastic-lined or all-plastic drums and tote bins for smaller quantities. Except for aluminum chlorohydrates, PAC products are shipped as hazardous substances because of their acidity.

5. Economic Aspects

Production figures for polyaluminum chlorides are not released by manufacturers. However, total U.S. production of PAC excluding aluminum chlorohydrate was estimated at 30,000 metric tons in 1989 from Nalco Chemical Company (Naperville, Ill.) and General Chemical Corporation (Parsippany, NY) and retail prices for polyaluminum chloride solutions were approximately $0.30–$0.70/kg. Three U.S. manufacturers of aluminum chlorohydrate, Reheis Chemical Company (Berkeley Heights, N.J.), Courtney Industries (Baltimore, Md.) and Westwood Chemical Corporation (Middletown, N.Y.) are estimated to produce 25,000 metric tons per year. There are other manufacturing companies that utilize all of their aluminum chlorohydrate internally in antiperspirant products; no estimate of this capacity can be made. The wholesale price of aluminum chlorohydrate in 1989 was about $1.00/kg.

6. Specifications and Safety

Polyaluminum chloride products used in the treatment of potable (drinking) water must be approved by the National Sanitation Foundation (NSF). NSF certification has superseded EPA approval. Aluminum chlorohydrate for topical use as an antiperspirant is regulated by FDA.

Contact with polyaluminum chloride products may cause burns or irritation to the eyes or skin; thus, protective clothing and eye protections are recommended.

7. Uses

7.1. Water and Waste Water Treatment

PAC products are used in water treatment for removal of suspended solids (turbidity) and other contaminants such as natural organic matter from surface waters. Microorganisms and colloidal particles of silt and clay are stabilized by surface electrostatic charges preventing the particles from coalescing. Historically, alum (aluminum sulfate hydrate) was used to neutralize these charges by surface adsorption of Al cations formed upon hydrolysis of the alum. Since 1983 PAC has been sold as an alum replacement in the treatment of natural water for U.S. municipal and industrial use.

Alum and PAC usage have been compared (1, 28, 29), and PAC is advantageous in waters of low to moderate turbidity, possibly because of the greater charge-neutralizing capacity relative to alum (1). PAC, typically applied at much lower total Al dosages than alum, results in less aluminum hydroxide sludge to be dewatered (qv) and trucked out. Consumption of water alkalinity is significantly lower using PAC because of partial neutralization of Al, and savings are realized in treating low (less than 20 mg/L as $CaCO_3$) alkalinity waters when caustic, lime, or soda ash are conserved. Finally, the use of PAC in cold water treatment provides greater removal of turbidity than using alum because of the higher reactivity of PAC's preformed polymers at low temperatures (29). PAC products are similarly used in removal of suspended solids or dispersed oil (30) from waste waters, and for precipitation of fluoride and phosphates (31).

7.2. Antiperspirants

Aluminum chlorohydrate, widely used as an antiperspirant (32), came into usage in the early 1940s (2). The mechanism for antiperspirant activity is the formation of an obstructive aluminum hydroxide plug within the sweat gland duct (17). When aluminum chlorohydrate at body temperature is simultaneously diluted with sweat and exposed to the higher pH on the skin, insoluble aluminum hydroxide rapidly forms.

7.3. Preparation of Pillared Clay Catalysts

PAC products are used for the preparation of zeolite-like catalysts by intercalation, the insertion of Al polycations molecules between the aluminosilicate sheets of clay (3, 33). Aqueous clay suspensions are slowly added to vigorously stirred PAC solutions, and the reaction mixture is aged for several hours. The clay is separated from the PAC solution and washed free of chloride ion. The treated clay is first dried at low temperature and then calcined in air at 450–500°C, producing a high surface area material having a regular-sized pore opening of about 0.6 to 1.0 nm. These pores openings are shape selective for molecules, allowing pillared clays to be used for hydrocarbon cracking. Selectivities are similar to zeolitic catalysts (see Molecular sieves) (33).

7.4. Catalysts for Finishing of Durapress Fabrics

PAC products are used as catalysts in the textile finishing industry (see Textiles) (6, 34). Fabric is impregnated with a finishing agent such as dimethylol methyl carbamate and a catalyst in aqueous solution, dried, and heat cured. Whereas various types of aluminum salts can be used as catalysts, PAC is preferred because PAC use avoids fabric degradation and discoloration.

7.5. Papermaking Use

PAC is widely used in Europe in papermaking processes. The gradual changeover from acid to alkaline systems in U.S. paper mills is expected to be accompanied by an increase in the use of PAC as an alum replacement (35).

BIBLIOGRAPHY

Cited Publications

1. B. A. Demsey, H. Sheu, T. M. Tanzeer Ahmed, and J. Mentink, *J. Am. Water Works Assoc.* **77**(3), 74–80 (1985).
2. T. Govett and M. G. de Navarre, *Am. Perfum.* **49**, 365–368 (1947).
3. T. J. Pinnavaia, M. Tzou, S. D. Landau, and R. H. Raythatha, *J. Mol. Catal.* **27**, 195–212 (1984).
4. M. G. Reed, *J. Pet. Technol.* **24**, 860 (1972).
5. J. C. Ginocchio, *Sulzer Tech. Rev.* **65**(3), 12 (1983); *Chem. Abstr.* **100**(2), 8841d.
6. R. M. Reinhardt, N. A. Cashen, and W. A. Reeves, *Text. Chem. Color* **4**, 241 (1972).
7. U.S. Pat. 4,451,388 (May 29, 1984), C. C. Payne (to Nalco Chemical Co.).

8. D. L. Teagarden, J. F. Kozlowski, J. L. White, and S. L. Hem, *J. Pharm. Sci.* **70**(7), 758 (1981).
9. J. W. Akitt, N. N. Greenwood, B. L. Khandelwal, and G. D. Lester, *J. Chem. Soc. Dalton Trans.* **1972**, 604 (1972).
10. J. W. Akitt and A. Farthing, *J. Chem. Soc. Dalton Trans.* **1981**, 1606 (1981).
11. Ref. 10, p. 1609.
12. Ref. 10, p. 1617.
13. Ref. 10, p. 1624.
14. P. M. Bertsch, G. W. Thomas, and R. I. Barnhisel, *Soil Sci. Soc. Am. J.* **50**, 825 (1986).
15. U.S. Pat. 4,655,934 (Apr. 7, 1987), G. R. Rose and J. R. Hurlock (to Nalco Chemical Company).
16. G. Johansson, G. Lundgren, L. G. Sillen, and R. Soderquist, *Acta Chem. Scand.* **14**, 769 (1960).
17. D. L. Teagarden and S. L. Hem, *J. Soc. Cosmet. Chem.* **33**, 281–295 (1982).
18. W. Stumm and J. J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley & Sons, Inc., New York, 1970, pp. 474, 502–503.
19. N. Parthasarathy and J. Buffle, *Water Res.* **19**(1), 25–36 (1983).
20. D. L. Teagarden, J. F. Radavich, J. L. White, and S. L. Hem, *J. Pharm. Sci.* **70**(7), 762 (1981).
21. D. L. Teagarden, J. L. White, and S. L. Hem, *J. Pharm. Sci.* **70**(7), 808 (1981); P. M. Bertsch, *Soil Sci. Soc. Am. J.* **51**, 825 (1987).
22. Jpn. Pat. 53 77899 (July 10, 1978), I. Miyanohara, H. Miyazaki, and H. Kawamura (to Toyo Soda Mfg. Co., Ltd.).
23. Jpn. Pat. 48 50998 (July 18, 1973), Kanamasa, M. Takeo, and S. Hiroshi (to Central Glass Co., Ltd.).
24. U.S. Pat. 3,929,666 (Dec. 30, 1975), Y. Aiba, T. Furumori, S. Shinpo, and K. Funabiki (to Taki Fertilizer Manufacturing Co., Ltd.).
25. Jpn. Pat. 49 47639 (Dec. 17, 1974), S. Anpo (to Nikkei Kako Co., Ltd.).
26. USSR Pat. 833516 (May 30, 1981), A. P. Shut'ko, S. L. Oleinikov, and P. A. Samandasyuk (to Kiev Polytechnic Institute).
27. Rom. Pat. 63835 (Apr. 20, 1979), L. Rivola, M. Piro, M. Tolomei, and B. Notari (to SNAM Progetti S.p.A.).
28. C. R. O'Melia and B. A. Dempsey, *Proc. 24th Annual Public Water Conference,* Baltimore, Md., (1982).
29. B. A. Demsey and L. Willnow, *Proc. 47th International Water Conference,* Pittsburgh, Pa. (1986).
30. A. P. Shut'ko, O. N. Dubchak, Ya. B. Kozlikovskii, Yu. Ya. Bogatchuk, *Neftepererab. Neftekhim.* **8**, 5 (1986); *Chem. Abstr.* **105**(18), 158243c.
31. J. Buffle, N. Parthasarathy, and W. Haerdi, *Water Res.* **19**(1), 7–23 (1985).
32. E. S. Bretschneider, A. M. Rubino, and J. J. Margres, *J. Soc. Cosmet. Chem.* **28**, 441–446 (1977).
33. T. J. Pinnavaia, V. Rainey, M. Tzou, and J. W. White, *J. Mol. Catal.* **27**, 213 (1984).
34. R. M. H. Kullman and R. M. Reinhardt, *Text. Res. J.* **48**, 320 (1978).
35. B. Worley, Paper Management Association, 45–47 (1990).

General Reference

36. P. M. Bertsch, "Aqueous Polynuclear Aluminum Species," in G. Sposito, ed., *The Environmental Chemistry of Aluminum*, CRC Press, Boca Raton, Fla., 1989, Chapt. 4. (This is an excellent review of the literature on this chemistry.)

KRISTINE S. SIEFERT
Nalco Chemical Company

Related Articles

Molecular sieves; Water, industrial water treatment; Water, municipal water treatment