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Water soluble polymers' role in improving the clarification of water

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Water must be clarified for many applications. This requirement encompasses potable water, industrial water supply, and the treatment of industrial and sewage effluents. All of these water clarification operations must meet measurable standards to suit their specific use.

In the last fifty years, much progress has been made in the changing types of treatment chemicals used for water clarification. New products have replaced older technologies such as cationic substituted starch, resulting in enhanced performance. The environmental impacts of processes have been improved to reduce the amount of waste solids generated and to allow the safe release of certain materials back into the environment.

Coagulation

Raw, potable water can be taken from a variety of sources such as rivers, reservoirs, underground aquifers or lakes. Depending on the turbidity, suspended solids, and colour, primary treatment entails coagulation (charge neutralisation) to provide a colourless water, free of suspended solids and suitable for secondary treatment by filtration and sanitisation. Higher valent coagulants, such as aluminium salts, are good coagulants and flocculants.

Raw water quality

Raw water quality is assessed by measuring:

- turbidity
- colour
- pH
- alkalinity; and
- temperature.

In the past, coagulation was achieved through the use of aluminium or ferric salts of sulfate or chloride. The trivalent metal ion neutralises the anionic charge associated with the dispersed material in suspension and solution. Once neutralisation is complete, the particles self-agglomerate after intimate mixing. This agglomeration produces very small, discrete flocs, which slowly settle to leave a clear, supernatant liquid. Flocs are nominally composed of the metal hydroxide $M(OH)_3$, along with the contaminant species from the raw water. This treatment generally works well. Nevertheless, complications arise when the process is scaled up.

Eco footprint

The coagulant demand of a water treatment system reflects how much cation M^+ is needed to remove the contaminants. This presupposes that there is enough alkalinity in the water to allow the hydrolysis of the metal salt, and that the final pH is within the range of maximum insolubility of the metal: around 6-8 for aluminium and 5+ for ferric ion. For some surface waters, such as moorland runoff or water from granite-like bedrock, sodium hydroxide or lime must be added to augment the low natural alkalinity. Trivalent metal salts are relatively acidic, and if the dose required adds more acid than the natural alkalinity of the water, the pH will drop below pH 5, whereupon no precipitation will occur.

The density of sludge produced during water treatment by coagulation is very high due to the retention of water by the metal hydroxides, even after treatment. Usually no more than 35% dry matter is attainable under ideal conditions of pressure and time. However, the performance of most mechanical dehydration systems normally returns sludge with somewhere between 10% and 28% dry matter. Originally, the water treatment industry used drying beds where sludge was fed into a lagoon and solids sank to the bottom before excess water was decanted off. The remaining sludge concentrate would then be disposed of to landfill. The amount of sludge produced was large by any standard and represented a major disposal problem. However, with the introduction of stricter laws on waste disposal, the chemical industry developed new polymeric technologies to tackle these inherent problems.

Polymer solutions to sludge management

Potable water treatment is somewhat of an anomaly. Although synthetic coagulants were available for use in potable water, concerns about residual product in water were expressed by potential users. At the same time, aluminium levels in treated water became a major health concern with aluminium linked to Alzheimer's disease. The water companies responded by increasing the quality of process and analytical control of product water to ensure absolute minimum amounts of aluminium. Alternatively, they changed to ferric based coagulation.

The net result was that little product technology change has been in the industry. In the UK, metal salts are predominately used for drinking water clarification, and polymers tend to only be used for sludge dewatering. There may be extra solids removed from these wastewaters, thus adding to the amount of sludge produced. Here, organic polymers have reduced the need for, or replaced, the large volumes of metal salts otherwise required for coagulation, whilst other polymers are used to improve floc size and strength, making sludge dewatering more rapid and simple.

Coagulants

Synthetic organic coagulant systems were introduced approximately 50 years ago with the advent of polyamine-type compounds, of which there are two types: condensation polymers of organic secondary amines with epichlorohydrin to produce relatively low molecular weight polymers, usually sold as liquid products with a solid content of up to about 50%; and polyDAMAC (poly(diallyldimethylammonium chloride), a free radical polymerisation product of relatively low molecular weight, a liquid product sold in varying concentrations. These polymers have a very high cationic charge, often referred to as having '100% charge density'. This charge density is provided by pendant quaternary ammonium groups on the backbone. They act as coagulants, but remain in solution without precipitation as a salt. They are adsorbed strongly onto the contaminants. The polymers do not require alkalinity to function; nevertheless, pH usually needs to be maintained between 5 and 10 for optimum performance. The polymers do not add significantly to the solids burden and they structure the flocs to optimise efficient draining. They are also ultimately biodegradable, and are permitted for use in potable water within certain dose rate limits.

The primary sludge produced by these coagulants is still slow to dewater without further treatment. For rapid dewatering and high ultimate dryness by mechanical means (pressing or centrifuging), another type of synthetic polymer is needed to enhance drainage. The products that became commonplace to resolve this issue are known as flocculants.

Flocculants

Flocculants are used to rapidly dewater sludges, act as process drainage aids in the paper industry, and generally improve clarification to such an extent that the size and capital cost of high throughput water treatment plants is significantly reduced.

Many flocculants are polyacrylamides ("polys") produced from the copolymerisation of acrylamide with a substituted acrylamide, usually with a pendant quaternary amine group, to make a random linear copolymer with a specified cationicity. Anionic copolymers can be similarly made using acrylic acid as the co-monomer.

Anionic and cationic polymers have different uses. Cationic polymers produce stronger flocs to facilitate subsequent handling. Anionic polymers flocculate mineral solids where large flocs are produced at low dose rates. The various products that can be made have distinctive flocculation characteristics dependent upon cationicity, molecular weight and structure. By introducing chain branching and cross-linking monomers, complex structures can be synthesised which provide beneficial effects such floc shear resistance, useful for centrifuge applications.

The products now available cover a massive range of processing properties. For example, 100% polyacrylamide powder product is slow to dissolve and makes low concentration solutions requiring large dissolving systems. This meant that smaller users had to spend capital on equipment to use the products. The introduction of emulsion products was a timely innovation which allowed much greater market penetration. The polymer is formed in a solvent oil carrier liquid, which contains the reactants. The oil is emulsified with dispersants to form a very stable emulsion. After an initiator is added under inert atmosphere, the polymer is formed and contained in the oil droplets. The product contains up to 40% active product and is stable for extended periods of time. Higher concentrations may be achieved by evaporating some of the water as an azeotrope to leave 50% solids. The main benefit is that this product can be pumped and dosed. It may be inverted so that the active material is released from the oil into water. This lowers the ageing time and the ease of handling.

Summary and Conclusions

Without the introduction of polymeric coagulants and flocculants, water clarification and sludge dewatering would be very problematic both economically and environmentally. The environmental impact has been enormous, from sewage sludges to be dewatered or dried for incineration to industrial wastes that need volume reduction prior to landfill. Such is the ubiquitousness of these chemistries that they are now regarded as commodities. Many people, including chemists, are unaware of their existence, let alone their contribution to modern society. To the customers, they are a 'black box' product with an air of alchemy. However, high level of understanding of the mechanisms by which they work is nearly always needed for actual applications of this technology to obtain optimum results.