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Calcium Chloride *Market Reviews*

Industrial Uses

14 Wastewater / Water Treatment

Calcium chloride ($CaCl_2$) is an inexpensive source of calcium ions and pH adjustment in wastewater treatment. Specific uses include treatment of oily wastes and the removal of various inorganic compounds, including fluorides, phosphates and heavy metals. Industries using $CaCl_2$ in wastewater treatment include aluminum, steel, metal finishing and electroplating, glass and ceramics, fertilizers, TV tubes, commercial laundries, and municipal wastewater.

DESCRIPTION - WASTEWATER TREATMENT

Calcium chloride is used in wastewater treatment to remove phosphates, fluorides, oily wastes and chromium. It functions as a coagulant or precipitant, often together with flocculation.

- Coagulation involves charge neutralization in which a cationic species (Ca^{++}) combines irreversibly with a negatively charged contaminant.
- Precipitation creates an insoluble material that settles out, e.g., $CaCl_2$ reacts with phosphates to form insoluble calcium phosphate.
- Flocculation agglomerates small charge-neutralized, coagulated and precipitated particles (1 to 500 milli- microns) to enhance settling and filtration. Calcium chloride is often used together with a flocculant.

Calcium chloride offers many benefits in wastewater and water treatment. For instance it:

- Is very soluble
- Is a ready source of calcium ions
- Does not elevate pH
- Produces a dense floc that is hard to break, which makes dewatering easier and creates a denser/dryer sludge cake for disposal
- Works well with pressure filters used in dewatering and can reduce downtime for filter cleaning
- Does not inherently add contaminants or sludge formation
- Enhances flocculation by anionic polymers, decreasing polymer dosage
- Is cost effective in fluoride treatment when added with lime
- Removes color from wastewaters at modest dosages (50 to 200 ppm as Ca^{++}) in the paper, food, tanning, laundry and textile industries
- Is available as a liquid and needs no special equipment

PHOSPHATE REMOVAL

Phosphate removal, the major application for $CaCl_2$ in wastewater treatment, is used in many industrial sectors, e.g., auto assembly, metal finishing, machining, heavy stamping, plating, coating, foundries, recycling, waste management, detergents and dairy.

Sources of phosphates in industrial wastewater include: phosphatizing (an anticorrosion coating for metal); phosphoric acid (cleaning plastic parts); various cleaners, polishes and metal finishers (basically phosphate-containing soaps); metal coating for better paint adherence (zinc phosphate); and soaps coated onto metal before heavy stamping to prevent friction fracture.

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Phosphates are removed from wastewater for two reasons. One, to limit phosphates in municipal sewage during microbial digestion (the secondary stage). An overabundance of phosphates fosters rapid microbial growth, which can cause overpopulation, microbial self-destruction and plant shutdown. And two, phosphates compete with hydroxides in steps that remove heavy metals. Since metal phosphates are more soluble than metal hydroxides, unacceptable metal residuals can appear in wastewater plant effluents.

The reaction between calcium and phosphate ions to create the precipitate calcium phosphate is most efficient at pH 9. This reaction also serves as a “polishing reagent” to reduce phosphates below 10 ppm. Calcium phosphate particles are usually flocculated by an anionic polymer to aid settling and filtration.

FLUORIDE REMOVAL

Calcium chloride provides calcium ions and pH adjustment in removing fluoride ions from wastewater generated by the aluminum, steel, metal finishing, electroplating, glass, ceramic, phosphate rock, fertilizer, TV tube, and fluoride chemical sectors.

Many users add lime to introduce calcium ions and adjust pH. Although lime costs less than $CaCl_2$, it is less soluble (1.85 gm/l) and must be used as a slurry, which slows precipitation and decreases settling. Lime is fully effective at a pH of 12, so an acid must be used to bring pH to 9 or less before discharge. Excess lime is generally needed for proper

fluoride removal, which yields large amounts of sludge and higher disposal costs.

Tests by General Chemical compared $CaCl_2$ and lime in this application. A lime dose of about 600 PPM at pH 12 reduced fluoride 81% to 16 mg/l. A $CaCl_2$ dose of 3,000 PPM with no pH adjustment reduced fluoride by 93% to 6.6

PPM, and a 1,500 PPM $CaCl_2$ dose removed 88%. The 1500 PPM $CaCl_2$ dose had less sludge, needed no pH adjustment before discharge, and gave somewhat better turbidity that the 600 PPM lime dose.

Lime-based fluoride removal can be improved by using a $CaCl_2$-lime mixture. The highly soluble $CaCl_2$ provides more calcium ions than lime without increasing pH. Fluoride removal by lime and $CaCl_2$-lime cost about the same. Use of $CaCl_2$-lime can lower dewatering and scavenging costs while decreasing sludge as much as 50%. Use of $CaCl_2$- lime requires just enough lime to raise pH to between 8.0 and 8.5, so neutralization is usually not needed.

OILY WASTES

Calcium chloride is an emulsion-breaking agent for oily wastes. (An emulsion has a dispersed liquid phase and a medium that do not mix.) Many industries generate oily-waste emulsions, i.e., oil dispersed in the water phase:

- Petroleum – light and heavy oils from producing, refining, storage, transporting and retailing
- Metals – grinding, lubricating and cutting oils used in metalworking operations and rinsed from metal parts in clean-up processes
- Food – natural fats and oils, both animal and plant processing, including slaughtering, cleaning and by-products
- Textiles – oils and grease from scouring of natural fibers (e.g., wool and cotton)
- Cooling and heating – dilute oil-containing cooling water and oil leaked from pumps, condensers, heat exchangers, etc.

Oil droplets in such emulsions are hydrophobic and carry a negative charge, which stabilizes the emulsion. To cause destabilization, a cationic emulsion breaker is added to neutralize the charge and allow the droplets to coalesce. Treatment of oily-waste emulsions occurs in two stages:

- A primary stage that removes floatable (free) oils from the water and emulsified oils through gravity separation and skimming.
- A secondary stage that demulsifies the oil-water emulsion and separates the oil and water. Chemicals are most often used to accomplish this. One widely accepted method involves acid cracking or breaking with sulfuric acid, which lowers secondary wastewater pH to 2 to 3 for 6 to 12 hours. After acid digestion, sodium hydroxide raises the pH and $CaCl_2$ adds polyvalent cations that coagulate oil droplets via charge neutralization. The coagulated oil floats and is skimmed. The process has efficiencies to 99% and can reduce oil concentration to about 6 mg/l.

CHROMIUM REMOVAL

Removal of chromium from wastewater involves reduction, neutralization and clarification. Industries using this application include plating, coating, automotive assembly, machining, stamping, foundry, and recycling of batteries and radiators.

The process involves reduction in which an acid changes soluble hexavalent chromium (Cr^{6+}) to trivalent chromium (Cr^{3+}). The effluent from this step joins other waste streams in a neutralization tank, where a base raises pH to about 8.5 to create metal hydroxides. The neutralized wastewater contains fine, suspended metal hydroxide solids with a density close to that of water. Since these do not settle out efficiently, $CaCl_2$ adds critical water hardness (calcium ions) to enable settling during clarification. Polymer flocculants are also used at this stage.

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