Explosion in a Water Treating Unit

Standard operating procedure has been modified to run rinse water through the cation regeneration section; units are not sealed on shutdown; copper sulfate has been discontinued as an algaecide

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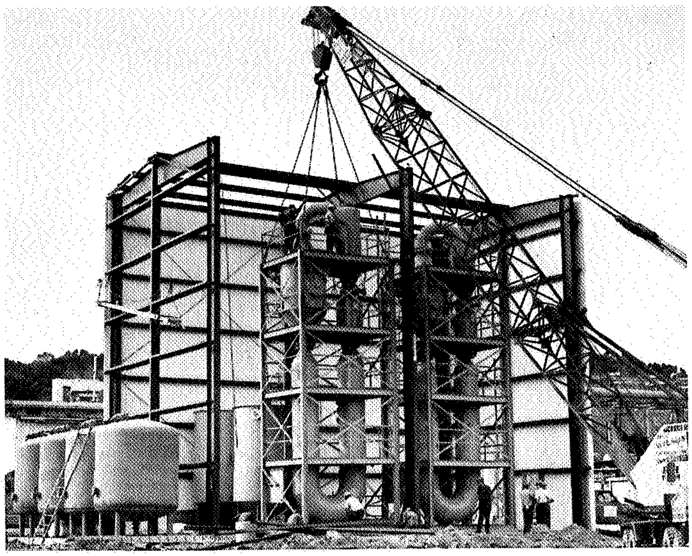

Figure 1. Water treating plant under construction.

A mixture containing nitric acid, ammonium nitrate, metal nitrates, algae, cation resin, and water was left sealed in an ion exchange vessel for several hours. A pressure buildup accompanied by ammonium nitrate decomposition and resin oxidation cracked an 18-in. diameter sealing valve and caused considerable deformation to the vessel.

The trend toward total recycle of plant water using ion exchange with ammonia and nitric acid as regeneration chemicals has not been researched for safety on the waste product side which could lead an operator to an unwanted disaster.

Process description

The production facilities of CF Industries, Inc., Chattanooga Nitrogen Complex, consist of a 500 ton/day ammonia plant, 550 ton/day nitric acid plant, acid neutralization, 650 ton/day AN prill plant, 120 ton/day urea plant for solutions and 400 ton/day ammoniated ammonium nitrate solutions plant. Process water, cooling tower blowdown and rainwater are collected in a 12 million gallon pond and then returned deionized to the cooling towers after passing thru strong base cation resin and weak base anion resin. A portion of the deionized water is purged to outside the plant limits to control the silica concentration. The ions removed by ion exchange are recovered as ammonium nitrate and added without evaporation to urea-ammonium nitrate solutions as dilution water.

The ion exchange units are of the Higgins moving bed contactor type. Resin moves periodically around two large pipe ring ovals. One ring contains cation resin, the other contains anion resin. Each pipe ring is divided into four sections by valves. Activities in each section approximate a fixed bed system in one stage of its operating cycle. One section of the ring is larger in diameter than the other three. Pond water flows thru this (load) section when the resin flow valves are closed. At the same time, rinse water and regenerant chemicals flow into the regen section of pipe preceding the load section. Before the regeneration section a pulsing section fills with resin, which has been backwashed in the section of pipe following the load vessel. On about a 10-minute cycle resin is pushed hydraulically for 30 seconds from the pulse section to the regen section. Regenerated resin is thereby forced into the load vessel. Spent resin from the load vessel is displaced into the backwash section. Once the resin movement has stopped the four ring valves seal the different sections and pond water, regeneration chemical, backwash water commence flowing for another 10 minute cycle.

Ammonia and metals removed in the cation load section are removed from the cation resin by 4N HNO_3 (22%) in the regeneration section producing ammonium nitrate, calcium nitrate, etc.

Nitrate and other anions are removed in the anion load section and are removed from the anion resin by 4N NH_4OH (7%) in the regeneration section producing ammonium nitrate, ammonium sulfate, etc. Silica or organics are not removed by the process.

Description of Failure

On April 16, 1972, the ion exchange units were shutdown due to an acid leak. All valves were closed as a normal operating procedure. After about 9 hours, the operator, who was in an adjoining building eating lunch, heard a noise similar to a steam hose being disconnected. As the operator traveled toward the ion exchange building, he saw yellow smoke coming from the door. Thinking there was a further acid leak he blocked the acid valve on the pipe rack outside the building. While closing this valve a much larger sound was heard. The sides of the building moved and the large garage type door closed by itself. Large amounts of yellow fumes came from every open hole in the building. No further reports were heard.

The Area Superintendent entered the building using a gas mask within 40 minutes. Acid and oxidized resin was dripping from the walls and the structure. The cation regeneration section was hot to the touch. A 2-in. rotometer bringing rinse water to the regen section was blown out. The 18-in. butterfly valve between the load and regen sections had failed. Oxidized resin escaped thru the failures and had sprayed on walls on both sides of the building. The vessel wall of the regen section had deformed noticeably.

Discussion

A resin manufacturer has information on a similar failure which had nothing to do with ammonium nitrate. Concentrated chromic acid was left in a sealed fixed bed type vessel. Destructive oxidation of the resin occurred with a violent exothermic reaction. Chromic acid is a strong oxidizing agent as nitric acid is. The resin manufacturer felt there would be no danger in confining resin with 4N acid but that there would be danger if the concentration were 8-10 normal. They also noted that certain metal ions such as copper, iron, and manganese act as catalysts for the degradation of the polymer matrix.

During the period before the units were shut down large amounts of algae were in the collection pond. Copper sulfate had been used in large amounts to kill the algae.

Attempts were made to duplicate the decomposition in the laboratory. Solutions containing resin, 3N ammonium nitrate, 8-10N nitric acid, 1000 ppm copper, and quite a bit of algae were held at temperatures ranging from 120°-180°F and at atmospheric pressure. No evidence of decomposition or resin oxidation was observed. At temperatures above 140°F the solution bubbled slightly. The gas leaving the solution was caught and analyzed as CO_2 and air.

Kjeldahl N, Nessler ammonia, and COD analysis run daily at the plant contain about 11 grams of mercury. Because of this, a solution similar to the above but containing about 1 ppm Hg was heated, but with negative results. A solution containing 1500 ppm Mg (magnesium nitrate is our prill additive) was heated with negative results. In all, 20 solutions were heated with no evidence of decomposition exhibited.

Although the lab results were negative all tests were run at atmospheric pressure. The regeneration section usually has about 10-15/lb./sq. in. gauge and could have had as much as 50-80/lb./sq. in gauge on it. The unit was shut down at night with cool ambient temperature. The unit failed around noon with warm ambient temperatures. A pressure rise could have accompanied the rise. The peak pressure at the time of the failure of the vessel was 260/lb./sq. in. gauge back-calculated from the vessel deformation.

Remarks

The standard operating procedure has been modifed to run rinse water through the cation regeneration section. The units are not sealed on shutdown. Copper sulfate has been discontinued as an algaecide. Algae concentration in the retention pond have been minimized but not eliminated. Possible water contamination from the TNT plant adjoining the plant boundary has been eliminated. Mercury from laboratory analysis is collected and precipitated to prevent its presence in the pond water. Acid concentration control has been improved to prevent high concentrations of acid from entering the cation regeneration section. A slightly higher crosslinked resin is being used.

Although there have been no failures of this type since the modifications were made, the cause of this decomposition has not been determined. Plant operators feel uneasy about the unit in times of trouble. With pollution control people tending to urge operators toward total water recycle it might be wise to warn other operators considering ion exchange that even this 20% ammonium nitrate solution decomposed destructively. The research on concentrated ion exchange products is not complete today.

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