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Product Recovery Through Ozone Oxidation Of Waste Liquor

Chemical Plant's Pilot—Waste Liquor from Trona Mining/Processing
Green River, Wyoming, USA

The Problem: Trona, a hydrated sodium bicarbonate carbonate, is a naturally occurring mineral that forms in non-marine evaporite deposits. When mined and processed it yields a pure sodium carbonate, commonly known as “soda ash,” which is utilized by a wide variety of industries.

The manufacturing of soda ash from Trona is a multi-step process that results in the production of a waste liquor that contains significant levels of organic contamination. US Environment Protection Agency (USEPA) regulations do not allow for disposal of this chemically rich liquor without extensive processing; consequently, manufacturers of soda ash must collect the waste liquor and store it in an environmentally acceptable manner.

During the process of making soda ash, the saturated sodium carbonate solution is sent to evaporators resulting in a supersaturated sodium carbonate solution 6 – 8 times its original concentration. During this evaporation process, the concentration of hydrocarbons foam within the evaporator which can damage the evaporator heat exchangers (FIGURE 1). Consequently, it is necessary to continuously waste some of the concentrated chemical liquor during the evaporation process to an outdoor pond.

The outdoor pond uses natural evaporation to further reduce liquor volume. Analysis of this waste liquor showed that the plant was discharging 6.5 tons of soda ash per day.

When plant production increased, the waste liquor discharge exceeded the holding capacity and evaporation rate of the outdoor pond. Attempts to recover lost product by introducing small amounts of the concentrated pond liquor into the plant evaporators had marginal success. The introduction of small amounts of the high solids, hydrocarbon rich waste liquor resulted in excessive foaming within the plant evaporators, causing excessive solids to carryover to the downstream processes and contaminate the crystalline soda ash.

The need to “do something” became more urgent when a crack was found in the waste storage pond's containment. Costs to repair and enlarge the containment pond approached 3 million dollars, prompting the plant to seek methods to minimize or utilize the waste liquor.

Process testing showed that hydrogen peroxide (peroxide) could oxidize the waste liquor's total organic content (TOC) sufficiently to utilize the liquor as a seed solution for the production of an industrial grade soda ash. However, the required batch detention time as well as plant safety concerns over the storing and handling of peroxide made chemical oxidation an unattractive option.



FIGURE 1: Evaporator for sodium carbonate monohydrate crystal growth

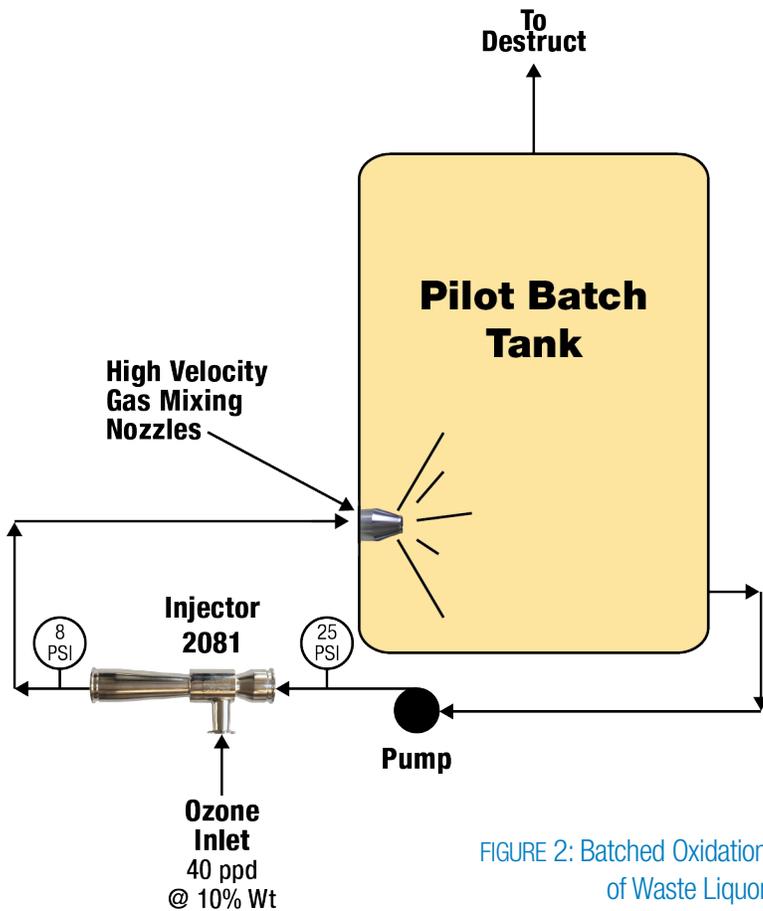


FIGURE 2: Batched Oxidation of Waste Liquor

The Solution:

The plant's process engineering team contacted the International Ozone Association Pan American Group (IOA PAG) for guidance. The decision was made to rent an ozone generator and install a Mazzei ozone contacting system. The introduction of molecular ozone into the highly alkaline chemical liquor to oxidize the total organic content would result in a rapid formation of hydroxyl radicals (an advanced oxidation process (AOP)). Based on the amount of hydrogen peroxide required to oxidize the waste liquor's TOC during laboratory process testing, it was estimated that ozone demand could be as high as 3,000 mg/L, consequently the pilot study was set up as a batch oxidation (FIGURE 2).

The system included a pump to drive heated liquor through a Venturi injector, mixing a 760 g/hr, 10% wt ozone gas into the pressurized chemical stream. Then the two phase flow is rapidly mixed into a fixed volume of liquor contained in a vented, atmospheric vessel through a high velocity mixing nozzle. Contact time and ozone dosages were varied by changing the duration of each batch oxidation, beginning with a timed oxidation that applied a 3,000 mg/L dosage to the fixed liquor volume. The absence of an ozone off gas monitor prevented the determination of the transferred ozone dosages.

The Results: Discussions with the project engineer indicated that the advanced oxidation process is reducing the liquor's TOC, producing a clear liquor with a blue-green color at a third of the estimated ozone dosage. Cost per ton of recovered soda ash using ozone driven advanced oxidation has been calculated to be less than 50% of the cost of TOC oxidation using hydrogen peroxide. The savings derived from successfully rehabilitating the waste liquor into a useful product are significant and include:

- Cost avoidance of almost 3 million dollars, needed to repair and expand the waste liquor containment pond;
- The recovery of lost product from the waste liquor, valued in excess of \$ 300,000 per year; and
- Cost effective advanced oxidation of waste liquor organics at less than half the cost of chemical oxidation.

The industrial use of ozone in the United States continues to expand thanks to a growing awareness by process engineers that ozone oxidation can be a safe and economical alternative to chemical oxidation. In this particular instance, the process engineer, utilizing the resources of the International Ozone Association, was able to contact the manufacturers of large ozone systems, discuss the feasibility and protocol of their ozone pilot study, and obtain pilot ozone equipment with on site assistance in a matter of weeks. The successful conclusion of their pilot study will lead to a new ozone installation.