

Product Recovery Through Ozone Oxidation Of Waste Liquor

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Abstract

The manufacturing of soda ash from Trona, a crystalline mineral composed of hydrate sodium bicarbonate carbonate, 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.

This paper reviews a chemical plant's pilot success at converting the waste stream from their soda ash processing facility into a marketable product, by reducing the liquor's total organic content (TOC) through ozone oxidation. The positive environmental impact and projected bottom line return on the investment in an ozone system are reviewed in detail.

Key Words: Ozone; Advanced oxidation; Trona; Soda ash; Sodium bicarbonate; Sodium Carbonate; Anhydrous sodium carbonate, Total organic carbon

Introduction

Soda Ash Manufacturing

Trona is a naturally occurring mineral deposit formed from non-marine evaporates. The clear to translucent crystals can be found in several regions of the US, including the counties of San Bernadino, Inyo and Mono counties in California and the Green River formation in Green River Wyoming. When mined and processed, this hydrated sodium bicarbonate carbonate, $\text{Na}_3(\text{HCO}_3)(\text{CO}_3) \cdot 2\text{H}_2\text{O}$, yields a pure sodium carbonate, commonly known as soda ash, which is utilized by a wide variety of industries.

Processing Trona into commercial soda ash is a multi-step process. It begins with crushing and screening to reduce the ore size to < 3/16 inch. The screened ore is then put in gas fired kilns and heated to drive off carbon dioxide and water, produce a raw sodium carbonate or soda ash, $2(\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}) \rightarrow 3\text{Na}_2\text{CO}_3 + \text{CO}_2 + 5\text{H}_2\text{O}$ (Figure 1).

Following the calcinations process, the ore is mixed with a dilute solution of soda ash and water to yield a saturated solution of sodium carbonate with a high total organic carbon (TOC) content. Insoluble suspended solids are settled out followed by filtration to remove the majority of organic impurities, primarily hydrocarbons from the oil shale associated with Trona ore formations.

The saturated sodium carbonate solution is then sent to evaporators where it is recirculated through steam driven heat exchangers, raising the temperature to 215 °F to boil off water, resulting in a supersaturated sodium carbonate solution 6 - 8 times its original concentration (Figure 2).



Figure 1. Kiln heating of crushed Trona ore courtesy OCI Chemical Corporation.

Following the evaporation process, the chemical solution is allowed to cool. It is during the cooling process that pure sodium carbonate monohydrate crystals, $2\text{Na} + \text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (monohydrate) are formed. Once crystal growth is completed, they are removed and sent into a gas fired kiln for additional drying, to produce an anhydrous sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (monohydrate) $\rightarrow \text{Na}_2\text{CO}_3$ (Anhydrous).

Waste Liquor By-Product

The concentration of hydrocarbons during the evaporation process results in foaming within the evaporator, which can carry over solids and damage the evaporator heat exchangers. Consequently, it is necessary to continuously waste some of the concentrated chemical liquor during the evaporation process to a outdoor pond. The outdoor pond uses natural evaporation to further reduce liquor volume. Analysis of the waste liquor shows that the plant is losing 6.5 tons of soda ash per day, which represents a revenue loss exceeding \$ 800.00 per day.

Over the past year, plant production has increased, resulting in a waste liquor discharge that exceeds 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 have had marginal success. The introduction of small amounts of the high solids, hydrocarbon rich waste liquor results in excessive foaming within the plant evaporators, resulting in excessive solids carryover to downstream processes and contamination of the crystalline Soda Ash.

Waste Liquor Chemical Oxidation

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 came 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 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 2. Evaporator for sodium carbonate monohydrate crystal growth, courtesy OCI.

Ozone Pilot Study

An internet search took the plant's process engineering team to the International Ozone Associations Pan American Group's (IOA) web site. Information provided by the IOA led the plant to contact several ozone generator manufacturers, resulting in the rental of a 760 g/hr ozone generator from ITT Water and Wastewater and the installation of a Mazzei ozone contacting system.

The on site pilot study of ozone oxidation for TOC reduction became an Advanced Oxidation Process (AOP) when it was discovered that the chemical liquor's pH averaged 11.5. The introduction of molecular ozone into the highly alkaline chemical liquor would result in a rapid formation of hydroxyl radicals according to the formula shown in Figure 3.

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 4).

A pump drives heated liquor through a venturi injector, which mixes a 760 g/hr, 10% wt ozone gas into the pressurized chemical stream. 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 pilot study continues during the writing of this white paper. Discussions with the project engineer indicates 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.

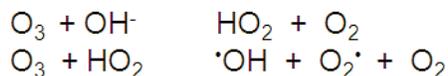


Figure 3. Hydroxyl Radical Formation under High pH Conditions.

Return on Investment

An accurate return on the investment in an ozone advanced oxidation process cannot be calculated until the completion of the pilot study, at which time an ozone bid specification will be written and sent to the various ozone manufacturers. However the savings derived from successfully rehabilitating the waste liquor into a useful product are significant and include:

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

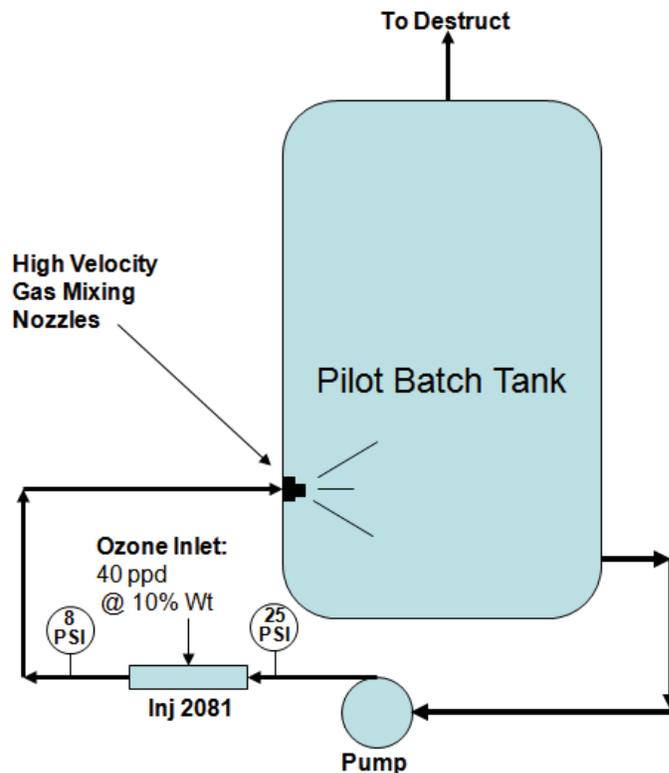


Figure 4. Batched Oxidation of Waste Liquor.

Summary

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.

The International Ozone Association (IOA) can be a valuable resource to those seeking further information on the efficacy of ozone oxidation for their industrial processes. In this particular instance, the process engineer, utilizing the resources of the IOA, 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 by the first quarter of 2009.

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